BRITISH STANDARD

BS 5050:1974

Methods of test for

Cryolite

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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*

Department of Trade and Industry — Laboratory of the Government Chemist*

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 Government departments and 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

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 August 1974

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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 natural and artificial cryolite.

In the drafting of this standard, account has been taken of methods 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 addenda to this standard, as the work of Technical Committee 47 — Chemistry, and, in particular, ISO/TC 47 Sub-committee 7 — Alumina and related compounds, advances.

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 5050.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 14, 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 British Standard describes methods of test for natural and artificial cryolite having a NaF : AlF_3 ratio of between 3 and 1.7.

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

2 Preparation and storage of test samples

2.1 Introduction. This clause is based on ISO/R 1619, modified to take into account the comments made by the United Kingdom during its development.

The method described is intended for the preparation of two test samples from a laboratory sample which shall be representative of the material under test, the two samples being:

a) a crude sample for moisture determination and certain physical tests, and

b) a ground and dried analytical sample for other tests.

2.2 Preparation of crude sample. Thoroughly mix 3 kg of the laboratory sample and place approximately 300 g of it in an airtight container of such a capacity that it is nearly filled by the sample.

2.3 Preparation of analytical sample

2.3.1 *Principle.* The sample is ground, sieved until the whole passes through a 0.125 mm aperture sieve, well mixed and dried at 110 °C.

2.3.2 *Procedure.* Sieve approximately 100 g of the laboratory sample using a 0.125 mm aperture sieve, complying with the requirements of BS 410 and constructed of a material that cannot cause introduction of the impurities that are being determined. Select the sieve material in relation to the nature of the impurities to be determined. Grind the material remaining on the sieve in a corundum mortar and sieve again. Add the sieved part previously obtained and mix carefully. Repeat the crushing, sieving and mixing operations until none of the material remains on the sieve.

Place the sample thus prepared in a platinum dish and dry for 2 h in an electric oven, ventilated by convection and controlled at 110 ± 2 °C. Then allow to cool in a desiccator containing fresh phosphorus pentoxide and keep the dried sample in an airtight container of a capacity such that it is nearly filled by the sample.

3 Determination of silica content

3.1 Introduction. This clause is based on ISO/R 1620, modified to take into account the comments made by the United Kingdom during its development.

3.2 Principle. The sample is fused with a mixture of sodium carbonate and boric acid. The fused mass is dissolved in excess nitric acid so that the pH of the resultant solution is between 0.3 and 0.5 after dilution to 250 ml. The silicon is complexed with sodium molybdate in acid solution and the complex reduced. The absorbance of the reduced silicomolybdate complex is measured at a wavelength of about 815 nm.

The method is applicable provided that the P_2O_5[1)] content does not exceed 0.02 %.

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

NOTE Water produced by ion-exchange may not be suitable, because it may have too high a silica content.

3.3.1 *Sodium carbonate,* anhydrous.

3.3.2 *Boric acid*

3.3.3 *Ascorbic acid,* 20 g/l solution, freshly prepared.

3.3.4 *Tartaric acid,* 100 g/l solution.

3.3.5 *Nitric acid,* approximately 8N solution.

Dilute 540 ml of nitric acid solution, ρ approximately 1.40 g/ml, about 68 % (*m*/*m*) solution, with water to 1 000 ml.

3.3.6 *Sulphuric acid,* approximately 16N solution.

Carefully add 450 ml of sulphuric acid solution, ρ approximately 1.84 g/ml, about 96 % (*m*/*m*) solution, to about 500 ml of water. Cool and dilute to 1 000 ml.

3.3.7 *Sodium molybdate,* 195 g/l solution.

Dissolve 19.5 g of sodium molybdate dihydrate, $Na_2MoO_4.2H_2O$, in hot water, cool, dilute with water to 100 ml and mix. Store in a polyethylene bottle. If necessary, filter before use.

3.3.8 *Stock silica solution,* corresponding to 0.5 g of SiO_2 per litre.

1) The preparation of a method for the determination of phosphorus is being undertaken, and will be included in an addendum to this standard.

Into a platinum crucible weigh, to the nearest 0.001 g, 0.500 g of finely ground quartz, previously heated at 1 000 °C for 1 h and cooled in a desiccator. Add 5 g of the anhydrous sodium carbonate (**3.3.1**) to the crucible, mix thoroughly and heat until its contents are completely fused. Allow to cool, add hot water to the crucible and use gentle heat to complete solution of the contents. Transfer to a polyethylene beaker and allow to cool. Transfer to a 1 000 ml one-mark volumetric flask (BS 1792), dilute with water to the mark and mix. Transfer without delay to a polyethylene bottle.

3.3.9 *Standard silica solution,* corresponding to 5 mg of SiO_2 per litre.

Pipette 50.0 ml of the stock silica solution (**3.3.8**) into a 1 000 ml one-mark volumetric flask (BS 1792), dilute with water to the mark and mix. Pipette 50.0 ml of this solution into a 250 ml one-mark volumetric flask (BS 1792), dilute with water to the mark and mix. This solution shall be freshly prepared.

1 ml of this diluted solution ≡ 5 μg of SiO_2.

3.4 Apparatus. Ordinary laboratory apparatus and the following are required.

3.4.1 *pH meter,* with glass and calomel electrode assembly. Essential performance requirements are given in BS 2586, BS 3145 and BS 3422.

3.4.2 *Photoelectric absorptiometer or spectrophotometer,* with 1 cm and 4 cm cells.

3.4.3 *One-mark volumetric flask,* 250 ml capacity, complying with the requirements of BS 1792.

3.4.4 Eight *one-mark volumetric flasks*, 100 ml capacity, complying with the requirements of BS 1792.

3.4.5 *Platinum dish,* approximately 100 mm diameter and 45 mm depth, fitted with a platinum lid.

3.5 Procedure

3.5.1 ***Preparation of calibration graph***

3.5.1.1 *Preparation of the blank solution.* Weigh 30 g of the sodium carbonate (**3.3.1**) and 10 g of the boric acid (**3.3.2**) into the platinum dish (**3.4.5**) and mix thoroughly. Cover the dish with its lid, place in an electric furnace, controlled at 550 ± 25 °C, and allow it to remain at this temperature until the reaction has ended. Transfer the dish to an electric furnace, controlled at 750 ± 25 °C, making sure that this temperature is maintained for 5 min.

Remove the dish and allow it to cool in air. Add about 125 ml of boiling water to the dish, heating gently until the material is dissolved. After cooling slightly, transfer the contents of the dish to a polyethylene beaker, of suitable capacity, containing 50 ml of the nitric acid solution (**3.3.5**), and carefully wash the dish and lid, first with 45 ml of the nitric acid solution and then with water, transferring the washings to the polyethylene beaker. Carefully transfer the contents of the beaker, by washing, to a glass beaker. Simmer gently for several minutes. Cool and transfer to the 250 ml one-mark volumetric flask (**3.4.3**) and dilute to the mark.

3.5.1.2 *Colour development.* Transfer 20 ml of the blank solution (**3.5.1.1**) into a beaker and add 15 ml of water, 15 ml of the standard silica solution (**3.3.9**) and 5 ml of the sodium molybdate solution (**3.3.7**). Mix thoroughly and, using the pH meter (**3.4.1**), adjust the pH of the solution to between 0.85 and 0.90 by the addition of the nitric acid solution (**3.3.5**). This pH value should relate to a solution volume of 65 ml. Note the volume of nitric acid solution added to adjust the pH value. Discard this solution.

Into a series of six of the 100 ml one-mark volumetric flasks (**3.4.4**), transfer 20 ml of the blank solution (**3.5.1.1**) and the volume of nitric acid solution determined above. Transfer amounts of the standard silica solution (**3.3.9**) equivalent to 0 μg (reagent blank) to 125 μg of silica, increasing by stages of 25 μg, and treat each solution in the following manner.

Dilute to 60 ml with water and then add 5 ml of the sodium molybdate solution (**3.3.7**). Mix thoroughly and allow to stand for 15 min to 25 min at 20 °C to 25 °C. Then add 5 ml of the tartaric acid solution (**3.3.4**), 11 ml of the sulphuric acid solution (**3.3.6**) and finally 2 ml of the ascorbic acid solution (**3.3.3**). Mix, dilute to the mark with water and mix again.

3.5.1.3 *Photometric measurements.* After an interval of 10 min to 40 min, measure the absorbance of each solution against water at the wavelength of maximum absorption (approximately 815 nm), using 4 cm cells, and prepare a calibration graph.

NOTE For samples of higher silica content, where it is necessary to use 1 cm cells in the determination, a calibration graph covering the appropriate range should be prepared using 1 cm cells.

3.5.2 ***Determination***

3.5.2.1 *Preparation of the test solution.* Weigh 12 g of the sodium carbonate (**3.3.1**) and 4 g of the boric acid (**3.3.2**) into a platinum dish similar to that used for the preparation of the blank solution (**3.5.1.1**). Add 1.000 ± 0.001 g of the analytical sample (see **2.3**) and mix thoroughly. Cover the dish with its lid, place in an electric furnace, controlled at 550 ± 25 °C, and allow it to remain at this temperature until the reaction subsides (about 30 min). Transfer the dish to an electric furnace, controlled at 750 ± 25 °C, making sure that this temperature is maintained for 20 min.

Remove the dish and allow it to cool in air. Add about 50 ml of boiling water to the dish, heating gently until the solid is dissolved. After cooling slightly, transfer the contents of the dish to a polyethylene beaker, of suitable capacity, containing 20 ml of the nitric acid solution (**3.3.5**).

Dissolve any residue adhering to the walls of the dish with a further 18 ml of the nitric acid solution and carefully wash the dish and lid with hot water, transferring the washings to the polyethylene beaker. Carefully transfer the contents of the beaker, by washing, to a glass beaker. Simmer gently for several minutes. Cool and transfer to the 250 ml one-mark volumetric flask (**3.4.3**) and dilute to the mark.

Transfer the solution without delay to a polyethylene bottle.

3.5.2.2 *Colour development.* Transfer 50.0 ml of the test solution (**3.5.2.1**) into a beaker, add 5 ml of the sodium molybdate solution (**3.3.7**) and mix.

Using the pH meter, adjust the pH value of the solution to between 0.85 and 0.90 by the addition of the nitric acid solution (**3.3.5**). Note the volume of nitric acid solution added to adjust the pH value. Discard this solution.

Transfer 50.0 ml of the test solution (**3.5.2.1**) to one of the 100 ml one-mark volumetric flasks (**3.4.4**). Add the volume of the nitric acid solution determined above and 5 ml of the sodium molybdate solution (**3.3.7**). Mix thoroughly and allow to stand for 15 min to 25 min at 20 °C to 25 °C. Then add 5 ml of the tartaric acid solution (**3.3.4**), 11 ml of the sulphuric acid solution (**3.3.6**) and finally 2 ml of the ascorbic acid solution (**3.3.3**). Mix, dilute to the mark with water and mix again.

At the same time, carry out a blank test using 20.0 ml of the blank solution (**3.5.1.1**) and dilute to a final volume of 100 ml.

3.5.2.3 *Photometric measurements.* After an interval of 10 min to 40 min, measure the absorbance of each solution against water, at the wavelength used in the calibration, using 4 cm cells, and read the amount of silica present, expressed as SiO_2, from the calibration graph. If the absorbance is too great for the 4 cm cells, use 1 cm cells and the appropriate calibration graph.

3.5 Calculation. Silica content, expressed as a percentage by mass of SiO_2, is given by the formula:

$$0.5 \times (m_1 - m_2)$$

where

m_1 is the mass of silica (SiO_2) contained in the aliquot portion of the sample solution taken (mg), and

m_2 is the mass of silica (SiO_2) contained in the aliquot portion of the blank solution taken (mg).

4 Determination of fluorine content

4.1 Introduction. This clause is based on ISO/R 1693, modified to take into account the comments made by the United Kingdom during its development, in particular in omitting the alternatives of spectrophotometric titration and distillation using perchloric acid.

4.2 Principle. The sample is fused with sodium carbonate, the fluorine present is separated as fluorosilicic acid by distillation with sulphuric acid and determined by titration with thorium nitrate solution using either sodium alizarinsulphonate, with or without methylene blue as masking agent, or methylthymol blue as indicator.

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

4.3.1 *Sodium carbonate,* anhydrous.

4.3.2 *Sodium fluoride.* (See **4.5.1**).

4.3.3 *Hydrochloric acid,* approximately 0.06N solution.

4.3.4 *Sodium hydroxide,* 0.5N solution.

4.3.5 *Sulphuric acid,* approximately 24N solution.

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

4.3.6 *Buffer solution,* pH 2.7.

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

4.3.7 *Buffer solution,* pH 3.4.

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.

4.3.8 *Thorium nitrate,* approximately 0.067N solution.

Dissolve 10.01 g of thorium nitrate hexahydrate (Th $(NO_3)_4$. $6H_2O$) in water and dilute to 1 000 ml.

1 ml of this solution = approximately 1.3 mg of fluorine.

4.3.9 *Sodium alizarinsulphonate,* 0.5 g/l solution.

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

4.3.10 *Methylene blue,* 0.5 g/l solution.

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

4.3.11 *Methylthymol blue,* 0.5 g/l solution.

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

4.3.12 *Perchloric acid,* N solution.

NOTE Instead of using the two indicators **4.3.9** and **4.3.10**, sodium alizarinsulphonate solution may be used alone. Alternatively methylthymol blue **4.3.11**, or any other indicator that gives equivalent results with the appropriate buffer and within the specified pH range, may be used.

4.4 Apparatus. All glassware used shall be carefully rinsed with a hot chromic/sulphuric acid mixture, then rinsed well with tap water and finally with water complying with the requirements of BS 3978.

4.4.1 *Steam generator,* such as a flask, capacity about 3 000 ml, fitted with a stopper into which are inserted three glass tubes, each of internal diameter 6 mm, as follows.

a) *Vertical recovery bend tube,* for introducing the steam into the distillation flask [**4.4.2** a)], and with one limb dipping into the distillation flask.

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

c) *Safety tube,* about 1 m long.

4.4.2 *Steam distillation apparatus,* with ground glass joints, comprising the following (a typical form of the apparatus is shown assembled in Figure 1).

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

distance between side neck and central neck: 65 mm

diameter of side neck: 20 mm.

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

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

11 groups of 3 indentations, spaced at 120° on the circumference, at 12 mm separation

c) *Thermometer sheath.*

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

e) *Walter dropping funnel,* capacity about 100 ml, to fit the *Vigreux column* [**4.4.2** b)].

f) *Graham condenser,* effective length about 400 mm, complying with the requirements of BS 3787.

4.4.3 *Electric heater,* for heating the distillation flask [**4.4.2** a)].

4.4.4 *pH meter,* with glass and calomel electrode assembly. Essential performance requirements are given in BS 2586, BS 3145 and BS 3422.

4.4.5 *Magnetic stirrer*

4.5 Procedure

4.5.1 *Standardization of the thorium nitrate solution.* Weigh, to the nearest 0.1 mg, about 200 mg of the sodium fluoride (**4.3.2**), previously heated at 600 °C in a platinum dish and allowed to cool in a desiccator. If analytical reagent grade sodium fluoride is not available, it may be prepared as follows.

Dissolve approximately 40 g of pure sodium fluoride in 1 000 ml of water and, when it is completely dissolved, filter the solution under vacuum through a small Buchner funnel. Evaporate the solution down to approximately 500 ml in a platinum dish, cool and separate the sodium fluoride crystals by centrifuging. Transfer the product to a platinum dish and dry in an electric oven, ventilated by convection and controlled at 110 °C. Remove the dish from the oven, cool in a desiccator and grind the crystals in an agate mortar to pass through a 0.355 mm aperture sieve, complying with the requirements of BS 410. Place the sieved sodium fluoride in a platinum dish and heat for 2 h at 600 °C and then cool in a desiccator.

Transfer the weighed sodium fluoride into the distillation flask [**4.4.2** a)], containing several soda-lime glass beads of 2 mm to 3 mm diameter, using 20 ml to 30 ml of water. Place a 500 ml one-mark volumetric flask (BS 1792) under the condenser [**4.4.2** f)], to collect the distillate. Connect the distillation flask to the condenser and start the circulation of the cooling water. Stopper the distillation flask and add, through the dropping funnel [**4.4.2** e)], 50 ml of the sulphuric acid solution (**4.3.5**).

Carry out the distillation procedure and titration as described in **4.5.3**.

At the same time carry out a blank test following exactly the same procedure and omitting only the sodium fluoride.

Calculate the mass, in milligrams, of fluorine corresponding to 1 ml of the thorium nitrate solution from the formula:

$$\frac{0.4525 \times M_3}{V_1 - V_2}$$

where

M_3 is the mass of sodium fluoride in the aliquot portion of the distillate solution taken for titration (mg),

V_1 is the volume of the thorium nitrate solution used for titration of the aliquot portion of the distillate solution (ml), and

V_2 is the volume of the thorium nitrate solution used for the blank test (ml).

4.5.2 *Blank test.* Carry out a blank test at the same time as the determination using the same procedure and with the same quantities of all reagents.

4.5.3 ***Determination***

4.5.3.1 *Preparation of the test solution.* Weigh, to the nearest 0.1 mg, approximately 200 mg of the analytical sample (see **2.3**) into a flat bottom platinum crucible of approximately 30 mm diameter at the top, 15 mm diameter at the bottom and 30 mm depth, fitted with a platinum lid. Add 2 g of the sodium carbonate (**4.3.1**) and mix thoroughly. Cover the crucible with its lid and place in an electric furnace at about 200 °C. Increase the temperature progressively to 800 ± 20 °C, and keep the crucible and contents at this temperature until evolution of carbon dioxide ceases and the sample is completely melted (about 20 min).

Remove the crucible from the furnace and cool rapidly by plunging the bottom of the crucible into a bath of cold water. Transfer the fused mass directly to the distillation flask [**4.4.2** a)] containing several soda-lime glass beads of 2 mm to 3 mm diameter; wash the crucible carefully with 20 ml to 30 ml of hot water to dissolve any of the melt adhering to the crucible and collect the washings in the distillation flask.

4.5.3.2 *Distillation.* Place a 500 ml one-mark volumetric flask (BS 1792) under the condenser [**4.4.2** f)] to collect the distillate. Connect the distillation flask to the condenser and start the circulation of cooling water. Stopper the distillation flask and add, through the dropping funnel [**4.4.2** e)], 50 ml of the sulphuric acid solution (**4.3.5**).

Using the electric heater (**4.4.3**), heat the distillation flask until the solution reaches 150 °C. Pass steam from the generator (**4.4.1**) into the distillation flask so as to maintain the solution at 150 ± 1 °C and collect about 400 ml of distillate over a period of about 90 min.

Disconnect the distillation flask from the steam generator, allow the steam to escape to air and remove the heater. Wash the condenser with a jet of water. Dilute the distillate to the mark in the collecting flask and mix.

4.5.3.3 *Titration.* Transfer a 50.0 ml aliquot portion of the contents of the collecting flask to a 250 ml tall form beaker, add about 50 ml of water, 0.50 ml of the sodium alizarin sulphonate solution (**4.3.9**) and then the sodium hydroxide solution (**4.3.4**) until a pink coloration appears (pH of the colour change 6.6 to 6.8). Using the pH meter (**4.4.4**), adjust the pH value of the solution to between 4.9 and 5.2 by addition of the hydrochloric acid solution (**4.3.3**) (yellow colour of the solution).

Add 1.5 ml of the sodium alizarin sulphonate solution and then adjust the pH value of the solution to 3.4 ± 0.1 by addition of the buffer solution (**4.3.6**) (about 1 ml is required). Add 0.50 ml of the methylene blue solution (**4.3.10**) (green colour of the solution). Place a small glass-enclosed iron bar in the solution and stir vigorously, using the magnetic stirrer (**4.4.5**).

Titrate the solution with the thorium nitrate solution (**4.3.8**) from a 10 ml burette (BS 846), graduated in 0.02 ml, until a blue-violet colour is developed. Ensure that the same lighting conditions are used for the determination and for the standardization of the thorium nitrate solution.

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 (**4.3.11**) is used as indicator, the pH 3.4 buffer solution (**4.3.7**) should be used instead of the pH 2.7 buffer solution (**4.3.6**) and pH adjustments carried out with N perchloric acid solution (**4.3.12**) instead of hydrochloric acid.

4.6 Calculation. Fluorine content, calculated as a percentage by mass of fluorine (F), is given by the formula:

$$\frac{(V_3 - V_4) \times M_4}{M_5}$$

where

V_3 is the volume of thorium nitrate solution used for the titration of the aliquot portion of the distillate solution (ml),

V_4 is the volume of thorium nitrate solution used for the blank test (ml),

M_4 is the mass of fluorine corresponding to 1 ml of the thorium nitrate solution (see **4.5.1**) (mg), and

M_5 is the mass of sample taken (g).

5 Determination of iron content

5.1 Introduction. This clause is based on ISO/R 1694, modified to take into account the comments made by the United Kingdom during its development.

5.2 Principle. A sample is fused either with sodium carbonate and boric acid or with potassium pyrosulphate. Trivalent iron is reduced by means of hydroxylammonium chloride and a complex is formed between divalent iron and 1,10-phenanthroline in a buffered medium of pH value between 3.5 and 4.2. The absorbance of the coloured complex is measured at a wavelength of about 510 nm.

The method may be used for iron contents greater than 0.020 %, expressed as Fe_2O_3.

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

5.3.1 *Sodium carbonate,* anhydrous.

5.3.2 *Boric acid*

5.3.3 *Potassium pyrosulphate,* finely crushed.

5.3.4 *Nitric acid,* approximately 8N solution.

Dilute 540 ml of nitric acid, ρ approximately 1.40 g/ml, about 68 % (*m*/*m*) solution, with water and dilute to 1 000 ml.

5.3.5 *Hydrochloric acid,* approximately 6N solution.

Dilute 515 ml of hydrochloric acid, ρ approximately 1.18 g/ml, about 38 % (*m*/*m*) solution, with water and dilute to 1 000 ml.

5.3.6 *Acetic acid,* approximately 8N solution.

Dilute 500 ml of glacial acetic acid, approximately 17.4N, with water and dilute to 1 000 ml.

5.3.7 *Hydroxylammonium chloride,* 10 g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH.HCl$) in water and dilute to 1 000 ml.

5.3.8 *1,10-Phenanthroline hydrate,* 2.5 g/l solution.

Dissolve 2.5 g of 1,10-phenanthroline hydrate ($C_{12}H_8N_2H_2O$) in water and dilute to 1 000 ml.

5.3.9 *Buffer solution*

Dissolve 272 g of sodium acetate trihydrate, $CH_3COONa.3H_2O$, in approximately 500 ml of water and filter. Add 240 ml of glacial acetic acid (17M) and dilute with water to 1 000 ml.

5.3.10 *Sodium acetate,* trihydrate, 300 g/l solution. Filter before use.

5.3.11 *Stock iron solution,* corresponding to 0.20 g of Fe_2O_3 per litre.

Dissolve a weighed quantity of high purity iron, of known iron content, in 20 ml of sulphuric acid, diluted 1 + 3, the mass of iron being such as will give 0.200 g of iron (III) oxide (Fe_2O_3). Cool the solution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (BS 1792), dilute to the mark and mix.

5.3.12 *Standard iron solution,* corresponding to 10 mg of Fe_2O_3 per litre.

Dilute 50.0 ml of the stock iron solution (**5.3.11**) with water to the mark in a 1 000 ml one-mark volumetric flask (BS 1792) immediately before use.

1 ml of this diluted solution ≡ 10 μg of Fe_2O_3.

5.3.13 *Narrow range indicator papers,* covering the range pH 3.5 to 4.2.

5.4 Apparatus. Ordinary laboratory apparatus and the following are required.

5.4.1 *pH meter,* with glass and calomel electrode assembly. Essential performance requirements of the apparatus are given in BS 2586, BS 3145 and BS 3422. Alternatively the narrow range indicator papers (**5.3.13**) may be used.

5.4.2 *Photoelectric absorptiometer* or *spectrophotometer,* with 4 cm cells. When a filter photometer with two balanced photo-cells is used, the filter combination should conform as closely as possible to the required wavelength. The following combination has been found suitable:

Mercury vapour lamp

Ilford 603 or equivalent filter.

5.4.3 Two *one-mark volumetric flasks*, 1 000 ml capacity, complying with the requirements of BS 1792.

5.4.4 Two *one-mark volumetric flasks*, 250 ml or 500 ml capacity, as required by **5.5.3.1.1** or **5.5.3.1.2**, complying with the requirements of BS 1792.

5.4.5 Eight *one-mark volumetric flasks*, 100 ml capacity, complying with the requirements of BS 1792.

5.5 Procedure

5.5.1 *Preparation of calibration graph.* Into six of the 100 ml one-mark volumetric flasks (**5.4.5**) transfer amounts of the standard iron solution (**5.3.12**) equivalent to 0 µg (reagent blank) to 250 µg of iron (III) oxide (Fe_2O_3), increasing by stages of 50 µg, and treat each solution in the following manner.

Dilute to approximately 50 ml, then add 5 ml of the hydroxylammonium chloride solution (**5.3.7**), 5 ml of the 1,10-phenanthroline solution (**5.3.8**) and 25 ml of the buffer solution (**5.3.9**). Dilute with water to the mark and mix.

After 10 min, measure the absorbance of each solution against water at the wavelength of maximum absorption (approximately 510 nm) and prepare a calibration graph.

5.5.2 *Preparation of the blank solution.* Prepare a blank solution as described below, by the same fusion technique as is used for the preparation of the test solution.

5.5.2.1 *Alkaline fusion.* Weigh into a flat bottom platinum dish, approximately 75 mm in diameter and approximately 30 mm deep and with a platinum lid, 12 g of the sodium carbonate (**5.3.1**) and 4 g of the boric acid (**5.3.2**) and mix thoroughly. Cover the dish with its lid and place in an electric furnace, controlled at 550 ± 25 °C, and allow it to remain at this temperature until the reaction has ended. Transfer the dish to an electric furnace, controlled at 750 ± 25 °C, making sure that this temperature is maintained for 5 min. Remove the dish and allow it to cool in air.

Add about 50 ml of boiling water to the dish, heating gently until the material is dissolved. After cooling slightly, transfer the contents of the dish to a beaker of suitable capacity containing 20 ml of the nitric acid solution (**5.3.4**) and carefully wash the dish and lid, first with 18 ml of the nitric acid solution and then with hot water, carefully transferring the washings to the beaker. Simmer gently for several minutes.

Cool and transfer to a one-mark volumetric flask of the same capacity as that used for the preparation of the test solution (see **5.5.3.1.1**) Dilute to the mark and mix.

5.5.2.2 *Acid fusion.* Weigh into a flat bottom platinum dish, approximately 75 mm in diameter and approximately 30 mm deep and with a platinum lid, 10 g of the potassium pyrosulphate (**5.3.3**). Cover the dish with its lid and place in an electric furnace, controlled at 700 ± 20 °C, and allow to remain at this temperature for not more than 10 min. Remove the dish and allow it to cool in air. Add about 10 ml of water and 10 ml of the hydrochloric acid solution (**5.3.5**) to the dish, heating gently until the material is dissolved. After cooling slightly, transfer the contents of the dish to a one-mark volumetric flask of the same capacity as that used for the preparation of the test solution (see **5.5.3.1.2**). Carefully wash the dish and lid with hot water, collecting the washings in the volumetric flask. Dilute to the mark and mix.

5.5.3 *Determination*

5.5.3.1 *Preparation of the test solution*

5.5.3.1.1 *Alkaline fusion.* Weigh into a platinum dish similar to that used for the preparation of the blank solution (**5.5.2.1**), 12 g of the sodium carbonate (**5.3.1**) and 4 g of the boric acid (**5.3.2**). Weigh, to the nearest 0.001 g, about 1 g of the analytical sample (see **2.3**) into the dish and mix thoroughly. Cover the dish with its lid and place in an electric furnace, controlled at 550 ± 25 °C, and allow it to remain at this temperature until the reaction has ended. Transfer the dish to an electric furnace, controlled at 750 ± 25 °C, making sure that this temperature is maintained for 5 min.

Remove the dish, and allow it to cool in air. Add about 50 ml of boiling water to the dish, heating gently until the material is dissolved. After cooling slightly, transfer the contents of the dish to a beaker of suitable capacity containing 20 ml of the nitric acid solution (**5.3.4**) and carefully wash the dish and lid, first with 18 ml of the nitric acid solution and then with hot water, carefully transferring the washings to the beaker. Simmer gently for several minutes. Cool and transfer to a 250 ml or 500 ml one-mark volumetric flask, according to the iron content to be determined. Dilute to the mark and mix.

5.5.3.1.2 *Acid fusion.* Weigh into a platinum dish similar to that used for the preparation of the blank solution (**5.5.2.2**), 10 g of the potassium pyrosulphate (**5.3.3**). Weigh, to the nearest 0.001 g, about 1 g of the analytical sample (see **2.3**) into the dish and mix thoroughly. Cover the dish with its lid and place in an electric furnace, controlled at 700 ± 20 °C, and allow to remain at this temperature for 30 min.

Remove the dish and allow it to cool in air. Add about 10 ml of water and 10 ml of the hydrochloric acid solution (**5.3.5**) to the dish, heating gently until the material is dissolved. After cooling slightly, transfer the contents of the dish to a 250 ml or 500 ml one-mark volumetric flask (**5.4.4**), according to the iron content to be determined. Carefully wash the dish and lid with hot water, collecting the washings in the volumetric flask. Dilute to the mark and mix.

5.5.3.2 *Colour development.* Take an aliquot portion of the test solution containing between 50 µg and 250 µg of Fe_2O_3. Dilute this aliquot portion to 60 ml, add 1 ml of the hydroxylammonium chloride solution (**5.3.7**), 5 ml of the 1,10-phenanthroline solution (**5.3.8**) and 25 ml of the buffer solution (**5.3.9**). Verify the pH value using a narrow range indicator paper (**5.3.13**) externally or the pH meter (**5.4.1**); this value should be between 3.5 and 4.2. If necessary, adjust the pH by adding slowly either the sodium acetate solution (**5.3.10**) or the acetic acid solution (**5.3.6**), stirring after each addition. Transfer to a 100 ml one-mark volumetric flask (**5.4.5**), dilute with water to the mark and mix.

At the same time develop the colour in the blank solution (**5.5.2**), taking a similar aliquot portion as used for the test solution.

5.5.3.3 *Photometric measurements.* After 10 min, measure the absorbance of each solution against water at the wavelength used in the calibration and read the amount of iron present, expressed as Fe_2O_3, from the calibration graph.

5.6 Calculation. Iron content, calculated as a percentage by mass of iron (III) oxide, Fe_2O_3, is given by the formula:

$$\frac{(M_6 - M_7)}{M_8} \times D \times 0.1$$

where

M_6 is the mass of iron (III) oxide (Fe_2O_3) contained in the aliquot portion of the test solution taken (mg),

M_7 is the mass of iron (III) oxide (Fe_2O_3) contained in the corresponding aliquot portion of the blank solution (mg),

D is the ratio of volume of test solution prepared to volume of aliquot portion taken, and

M_8 is the mass of sample taken (g).

6 Determination of sodium content

6.1 Introduction. This clause is based on ISO 2366, modified to take into account the comments made by the United Kingdom during its development, in particular in omitting the atomic absorption alternative.

6.2 Principle. A sample solution is prepared by attack with concentrated sulphuric acid and recovery in hydrochloric acid. The solution is atomized in a flame and the sodium content is determined by photometric measurement of the light emitted at a wavelength of 589 nm.

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

6.3.1 *Sulphuric acid,* concentrated, 98 % (*m*/*m*) (36N), diluted (1 + 1).

6.3.2 *Hydrochloric acid,* concentrated, 36 % (*m*/*m*) (11N).

6.3.3 *Stock sodium solution,* corresponding to 2.00 g of Na per litre.

Weigh, to the nearest 0.001 g, 5.084 g of sodium chloride, previously dried for approximately 12 h at 110 °C and cooled in a desiccator, and dissolve in water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix. Transfer the solution without delay to a polyethylene bottle.

6.3.4 *Standard sodium solution,* corresponding to 0.20 g of Na per litre.

Dilute 50.0 ml of the stock sodium solution (**6.3.3**) to the mark in a 500 ml one-mark volumetric flask (BS 1792) immediately before use and transfer to a polyethylene bottle.

1 ml of this solution = 0.200 mg of Na.

6.4 Apparatus. Ordinary laboratory apparatus and the following are required.

6.4.1 *Flame spectrophotometer,* provided with an atomizer-burner suitably fed to excite the emission of the 589 nm sodium line.

6.4.2 Sixteen *one-mark volumetric flasks*, 1 000 ml capacity, complying with the requirements of BS 1792.

6.4.3 *One-mark volumetric flask,* 250 ml capacity, complying with the requirements of BS 1792.

6.4.4 Two *one-mark volumetric flasks*, 100 ml capacity, complying with the requirements of BS 1792.

6.5 Procedure

6.5.1 *Preparation of calibration graph*

6.5.1.1 *Preparation of reference solutions.* Into eleven of the 1 000 ml one-mark volumetric flasks (**6.4.2**), transfer amounts of the standard sodium solution (**6.3.4**) equivalent to 0 mg (reagent blank) to 20 mg of Na, increasing by stages of 2 mg, and treat each solution in the following manner.

Add 20 ml of the sulphuric acid solution (**6.3.1**) and 10 ml of the hydrochloric acid (**6.3.2**). Dilute to the mark with water and mix. Transfer the solution without delay to a polyethylene bottle.

NOTE Bearing in mind the difference in sensitivity between flame photometric instruments, the concentrations of the reference solutions, of the test solution, and of the blank test solution may be modified to enable the measurement to be made in the range of greatest sensitivity of the equipment used.

6.5.1.2 *Spectrophotometric measurements.* Switch on the current to the apparatus (**6.4.1**) a sufficient time in advance to ensure its stabilization. Adjust the sensitivity of the apparatus and the slit aperture in accordance with the characteristics of the apparatus used, providing a band pass of not greater than 6 nm centred on the emission maximum (theoretical value 589 nm).

Atomize the series of reference solutions (**6.5.1.1**) in the centre of the flame and, for each, measure the intensity of the radiation emitted, after having adjusted the zero on the transmission scale to the reagent blank and the 100 mark to the 20 mg/l Na solution. Ensure that the rate of atomization of the solutions into the flame is kept constant throughout the calibration.

Prepare a calibration graph showing the sodium concentrations against the values of the measured intensities (reduced by the measured value for the reagent blank used in the preparation of the calibration graph) on a logarithmic scale.

6.5.2 *Determination*

6.5.2.1 *Preparation of test solution.* Weigh, to the nearest 0.1 mg, approximately 500 mg of the dry analytical sample (see **2.3**) into a flat bottom platinum dish of approximately 75 mm diameter and 30 mm depth and with a platinum lid. Add 5 ml of the sulphuric acid (**6.3.1**) and cautiously heat on a sand bath or hot plate to complete removal of hydrogen fluoride.

Then raise the temperature and evaporate the excess sulphuric acid. Add 3 ml of the hydrochloric acid (**6.3.2**) and then 30 ml of water to the dish and heat to complete solution. Leave to cool, transfer quantitatively to the 250 ml one-mark volumetric flask (**6.4.3**), dilute to the mark with water and mix. Transfer 10.0 ml of this solution to a 100 ml one-mark volumetric flask (**6.4.4**.). Add 20 ml of the sulphuric acid solution (**6.3.1**), 5 ml of the hydrochloric acid (**6.3.2**), dilute to the mark with water and mix. Transfer the solution immediately to a polyethylene bottle.

6.5.2.2 *Spectrophotometric measurements.* Carry out an initial photometric measurement, as described in **6.5.1.2**, at the same time as the photometric measurements on the reference solutions.

Carry out a second measurement on the sample solution by bracketing it between two reference solutions, differing only by 2 g of Na (referred to 100 g of cryolite). Prepare these bracketing solutions as described in **6.5.1.1** with the addition of the appropriate volumes of the standard sodium solution (**6.3.4**); these quantities should not differ from each other by more than 5 ml.

6.5.3 *Blank test.* At the same time carry out a blank test following exactly the same procedure and using the same quantities of all reagents, but without bracketing.

6.6 Calculation. Sodium concentration, C, expressed in grams per litre, of the solution actually submitted to the spectrophotometer, is given by the formula:

$$\left[C_1 + (C_2 - C_1)\frac{E - E_1}{E_2 - E_1}\right] - C_o$$

where

C_1 is the concentration of the weaker bracketing solution used in the determination (g/l),

E_1 is the value of the corresponding measurement,

C_2 is the concentration of the stronger bracketing solution used in the determination (g/l),

E_2 is the value of the corresponding measurement,

E is the value corresponding to the determination, and

C_o is the concentration of the blank test solution, as determined from the calibration graph (**6.5.1.2**) (g/l).

Sodium content, expressed as a percentage by mass of Na, is given by the formula:

$$\frac{C \times 100 \times 10}{M_9}$$

where

M_9 is the mass of sample taken (g).

7 Determination of aluminium content (gravimetric method)

7.1 Introduction. This clause is based on ISO 2367, modified to take into account the comments made by the United Kingdom during its development.

7.2 Principle. A sample solution is prepared by acid fusion using potassium pyrosulphate and recovery in hydrochloric acid. Aluminium is separated from interfering elements by precipitation with ammonium benzoate in an acetic acid/reducing medium. The precipitate is dissolved and the aluminium reprecipitated as aluminium 8-quinolinoxide in an acetic acid buffer medium. The precipitate is then filtered, washed, dried at 130 °C and weighed.

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

7.3.1 *Potassium pyrosulphate,* finely crushed.

7.3.2 *Sodium sulphite,* heptahydrate.

7.3.3 *Sulphuric acid,*
concentrated, 98 % (*m*/*m*) (36N).

7.3.4 *Hydrochloric acid,*
concentrated, 36 % (*m*/*m*) (11N).

7.3.5 *Ammonia solution,*
approximately 6.7 % (*m*/*m*).

Dilute the concentrated solution (**7.3.11**) with water (1 + 3).

7.3.6 *Buffer solution*

Dissolve 50 g of hydroxylammonium chloride and 50 g of ammonium chloride in a little water, add 50 ml of glacial acetic acid (17M), dilute to 1 000 ml with water and mix.

7.3.7 *Ammonium benzoate,* 100 g/l solution.

Dissolve 100 g of ammonium benzoate in tepid water, add 0.001 g of thymol and, after cooling, dilute to 1 000 ml with water and mix.

7.3.8 *Ammonium benzoate/acetic acid washing solution*

Dilute 100 ml of the ammonium benzoate solution (**7.3.7**) with 900 ml of water and add 20 ml of glacial acetic acid (17M).

7.3.9 *Hydrochloric acid,*
approximately 10.5 % (*m*/*m*) solution.

7.3.10 *Tartaric acid,* 500 g/l solution.

7.3.11 *Ammonia solution,* ρ
approximately 0.91 g/ml, about 25 % (*m*/*m*).

7.3.12 *Acetic acid,* 1.7N solution.

7.3.13 *8-hydroxyquinoline,* 20 g/l solution in acetic acid.

Dissolve 20 g of 8-hydroxyquinoline in 80 ml of glacial acetic acid (17M), dilute to 1 000 ml with water and mix. Store the solution in a dark glass bottle.

7.3.14 *Ammonium acetate,* 600 g/l solution.

7.3.15 *Bromophenol blue indicator solution,* 2 g/l ethanolic solution.

Dissolve 0.2 g of bromophenol blue in 95 % (*v*/*v*) ethanol and dilute to 100 ml with the same ethanol.

7.3.16 *Neutral red indicator solution,* 0.5 g/l ethanolic solution.

Dissolve 0.05 g of neutral red in 95 % (*v*/*v*) ethanol and dilute to 100 ml with the same ethanol.

7.4 Apparatus. Ordinary laboratory apparatus and the following are required.

7.4.1 *One-mark volumetric flask,* 250 ml capacity, complying with the requirements of BS 1792.

7.4.2 *Sintered glass crucible,* porosity grade No. 4 of BS 1752.

7.5 Procedure. Weigh, to the nearest 0.1 mg, about 500 mg of the dry analytical sample (see **2.3**) into a flat bottom platinum dish of approximately 75 mm diameter and 30 mm depth and with a platinum lid. Add 10 g of the potassium pyrosulphate (**7.3.1**) and carefully mix with a platinum spatula. Cover the dish with its lid and transfer the dish to an electric furnace, controlled at 750 ± 25 °C. Maintain the dish at this temperature for 30 min then withdraw it from the furnace and leave it to cool in air.

Add 5 ml of the sulphuric acid solution (**7.3.3**) directly to the dish and heat on a hot plate until white sulphuric acid fumes cease to be evolved. Then add 10 ml of the hydrochloric acid solution (**7.3.4**) to the dish. Heat at near to the boiling point until solution is complete, rinsing the lid and walls of the dish with warm water and collecting the washings in the dish. Leave to cool slightly and then transfer the solution quantitatively to the 250 ml one-mark volumetric flask (**7.4.1**). After cooling, dilute to the mark with water and mix.

Transfer 50.0 ml of this solution to a 250 ml beaker. Add 40 ml of water, 10 to 15 drops of the bromophenol blue indicator solution (**7.3.15**) and neutralize by addition of the ammonia solution (**7.3.5**) until the colour of the indicator changes to violet. Then add 20 ml of the buffer solution (**7.3.6**) and 20 ml of the ammonium benzoate solution (**7.3.7**). Heat the solution to boiling point, While stirring, and simmer for 5 min, then filter through a medium grade filter paper. Wash the beaker and the precipitate 8 to 10 times with the boiling washing solution (**7.3.8**) and discard the filtrate.

Dissolve the precipitate on the filter paper by means of a boiling solution, prepared by mixing 50 ml of the hydrochloric acid solution (**7.3.9**) and 10 ml of the tartaric acid solution (**7.3.10**), added in small portions. Wash the filter with warm water and collect the solution and washing water in the beaker used for the first precipitation.

Transfer the solution quantitatively to a 400 ml beaker, add 1 g of the sodium sulphite (**7.3.2**), a few drops of the neutral red indicator solution (**7.3.16**) and, slowly and cautiously, the ammonia solution (**7.3.11**) until the colour of the indicator changes to yellow. Dilute the solution to approximately 200 ml and then heat to about 70 °C. Add the acetic acid solution (**7.3.12**) until the colour of the indicator changes to red and then, whilst stirring, add 40 ml of the 8-hydroxyquinoline solution (**7.3.13**) and finally 50 ml of the ammonium acetate solution (**7.3.14**). Leave to precipitate at approximately 70 °C for 30 min.

Filter the precipitate on the sintered glass crucible (**7.4.2**), previously weighed after drying in an oven at 130 °C and cooling in a desiccator, applying slight suction. Wash six to eight times with 10 ml to 15 ml portions of tepid (60 °C to 70 °C) water. Dry for 2 h in an electric oven, ventilated by convection and controlled at 130 ± 2 °C. Remove the crucible from the oven, allow it to cool to room temperature in a desiccator and weigh it again. Repeat the operations of drying, cooling and weighing until the mass is constant.

7.6 Calculation. Aluminium content, expressed as a percentage by mass of Al, is given by the formula:

$$\frac{5.87 \times M_{10}}{M_{11}} \times D$$

where

M_{10} is the mass of weighed aluminium 8-quinolinoxide (g),

D is the ratio of volume of sample solution prepared to volume of aliquot portion taken, and

M_{11} is the mass of sample taken (g).

8 Determination of aluminium content (atomic absorption method)

8.1 Introduction. This clause is based on ISO 2830, modified to take into account the comments made by the United Kingdom during its development.

The method is applicable to the determination of aluminium in natural and artificial cryolite of normal composition for which the molar ratio NaF/AlF_3 is equal to about 3.

8.2 Principle. A test portion is dissolved in concentrated sulphuric acid and treated with hydrochloric acid and water. The solution is atomized into an acetylene nitrous oxide flame and the aluminium content determined by photometric measurement of the absorption of the 309.3 nm line emitted by an aluminium hollow cathode lamp.

8.3 Reagents. Water complying with the requirements of BS 3978, or water of equivalent purity, shall be used in the test.

8.3.1 *Sulphuric acid, ρ* approximately 1.84 g/ml, about 98 % (*m*/*m*) solution.

8.3.2 *Hydrochloric acid, ρ* approximately 1.18 g/ml, about 36 % (*m*/*m*) solution.

8.3.3 *Sodium chloride,* 4.067 g/l solution.

Weigh, to the nearest 0.1 mg, 406.7 mg of sodium chloride, previously dried at 105 °C and cooled in a desiccator, place in a 100 ml one-mark volumetric flask, complying with the requirements of BS 1792, dissolve in a little water, dilute to the mark and mix.

8.3.4 *Standard aluminium solution,* corresponding to 1 g of Al per litre.

Pickle 1.5 g of extra pure aluminium (99.999 % purity), in the form of shavings obtained by milling or drilling, in a little nitric acid, *ρ* approximately 1.40 g/ml, about 68 % (*m*/*m*) solution.

Wash the pickled shavings with water and then dry them by washing with acetone. Weigh, to the nearest 0.1 mg, 1 000 mg of the dried shavings, put them in a tall form beaker of suitable capacity (for example, 250 ml) and add about 100 ml of water, 10 ml of the sulphuric acid solution (**8.3.1**) and 5 ml of the hydrochloric acid solution (**8.3.2**). Wait until the reaction subsides, then place the beaker on a sand bath or hot plate and maintain a gentle heat until all the aluminium has dissolved. Leave to cool, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask (BS 1792), dilute to mark and mix.

1 ml of this standard solution contains 1 mg of aluminium (Al).

8.4 Apparatus. Ordinary laboratory apparatus and the following are required.

8.4.1 *Spectrophotometer,* atomic absorption type, fitted with a burner fed from cylinders of acetylene and nitrous oxide.

8.4.2 *Aluminium hollow cathode lamp*

8.5 Procedure

8.5.1 *Test portion.* Weigh, to the nearest 0.1 mg, 500 mg of the dry test sample, prepared according to the instructions in clause **2**.

8.5.2 ***Preparation of the calibration graph***

8.5.2.1 *Preparation of the standard matching solutions.* Into a series of eleven 100 ml one-mark volumetric flasks, complying with the requirements of BS 1792, place the volumes of the standard aluminium solution (**8.3.4**) shown in the following table.

Standard aluminium solution (8.3.4)	Corresponding mass of aluminium	Percentage of aluminium relative to 50 mg of cryolite
ml	mg	
0[a]	—	—
1.0	1.0	2
2.0	2.0	4
3.0	3.0	6
4.0	4.0	8
5.0	5.0	10
6.0	6.0	12
7.0	7.0	14
8.0	8.0	16

[a] Blank on the reagents used for the preparation of the calibration graph.

Add to each flask 1 ml of the hydrochloric acid solution (**8.3.2**), 1 ml of the sulphuric acid solution (**8.3.1**) and 10 ml of the sodium chloride solution (**8.3.3**) (corresponding mass of sodium 0.016 g: this mass corresponds on average to the sodium present in a test portion of 0.05 g of cryolite containing 32 % of sodium). Dilute to the mark, mix, and transfer to plastics bottles.

Use only freshly prepared standard matching solutions.

8.5.2.2 *Spectrophotometric measurements*

8.5.2.2.1 *Adjustment of the apparatus fitted with aluminium hollow cathode lamp* (**8.4.2**). Switch on the current to the apparatus (**8.4.1**) allowing sufficient time for its stabilization. Adjust the wavelength to 309.3 nm and the sensitivity and the aperture according to the characteristics of the apparatus. Adjust the pressures of the acetylene and the nitrous oxide according to the characteristics of the burner so as to obtain a clear, non-luminous, oxidizing flame.

8.5.2.2.2 *Spectrophotometric measurements.* Atomize the series of standard matching solutions (**8.5.2.1**) into the flame and measure the absorbance of each. Take care to keep the quantity of solutions atomized in the flame constant per unit of time throughout the preparation of the calibration graph. Carry out at least three measurements for each standard matching solution and calculate the mean value.

Pass water through the burner after each measurement.

8.5.2.3 *Preparation of the calibration graph.* Plot a graph having, for example, the number of milligrams of aluminium contained in 1 000 ml of the standard matching solutions as abcissae and the corresponding values of the measured absorbances, minus the absorbance of the reagent blank, as ordinates.

8.5.3 ***Determination***

8.5.3.1 *Preparation of the test solution.* Place the test portion (**8.5.1**) in a platinum dish, approximately 75 mm in diameter and approximately 30 mm deep, add 5 ml of the sulphuric acid solution (**8.3.1**) and heat carefully on a sand bath or hot plate in a well-ventilated fume cupboard until the hydrofluoric acid is completely eliminated (15 min to 20 min). Then raise the temperature and evaporate the excess sulphuric acid. Add 3 ml of the hydrochloric acid solution (**8.3.2**) and 30 ml of water to the dish and heat until solution is complete. Allow to cool, transfer quantitatively to a 100 ml one-mark volumetric flask (BS 1792), dilute to the mark and mix.

Place 10 ml of this solution in a 100 ml one-mark volumetric flask (BS 1792), add 1 ml of the hydrochloric acid solution (**8.3.2**) and 1 ml of the sulphuric acid solution (**8.3.1**), dilute to the mark and mix.

Transfer the solution to a plastics bottle.

8.5.3.2 *Spectrophotometric measurements*

8.5.3.2.1 *Approximate measurement.* Carry out a first measurement of the test solution (**8.5.3.1**), following the procedure described in **8.5.2.2**, at the same time as the spectrophotometric measurements are made on the standard matching solutions (**8.5.2.1**).

8.5.3.2.2 *Bracketing measurement.* Carry out a second measurement on the test solution (**8.5.3.1**) by bracketing between two standard matching solutions varying in aluminium content by only 1 mg of aluminium per 100 ml, one at a concentration above, and one at a concentration below, that of the test solution. For the preparation of these standard matching solutions, follow the procedure given in **8.5.2.1**, using suitable quantities of the aluminium standard solution (**8.3.4**).

8.5.4 ***Blank test***

8.5.4.1 *Preparation of the blank test solution.* 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.

Transfer the blank test solution to a plastics bottle.

8.5.4.2 *Spectrophotometric measurement.* Carry out measurement following the procedure given in **8.5.2.2**, at the same time as the spectrophotometric measurements are made on the standard matching solutions (**8.5.2.1**), but without bracketing.

8.6 Expression of results. The aluminium concentration C, expressed as milligrams per litre, of the solution measured by the spectrophotometer, is given by the formula:

$$C = \left[C_1 + (C_2 - C_1)\frac{E - E_1}{E_2 - E_1}\right] - C_o$$

where

C_1 is the concentration of the weaker bracketing solution used during the determination (mg/l);

E_1 is the value of the corresponding measurement;

C_2 is the concentration of the stronger bracketing solution used during the determination (mg/l);

E_2 is the value of the corresponding measurement;

E is the value of the measurement corresponding to the test solution;

C_o is the concentration (mg/l) corresponding to the reading for the blank test, obtained from the calibration graph.

The aluminium (Al) content, expressed as a percentage by mass, is given by the formula:

$$\frac{C}{M_{12} \times 10}$$

where

M_2 is the mass of the test portion (g).

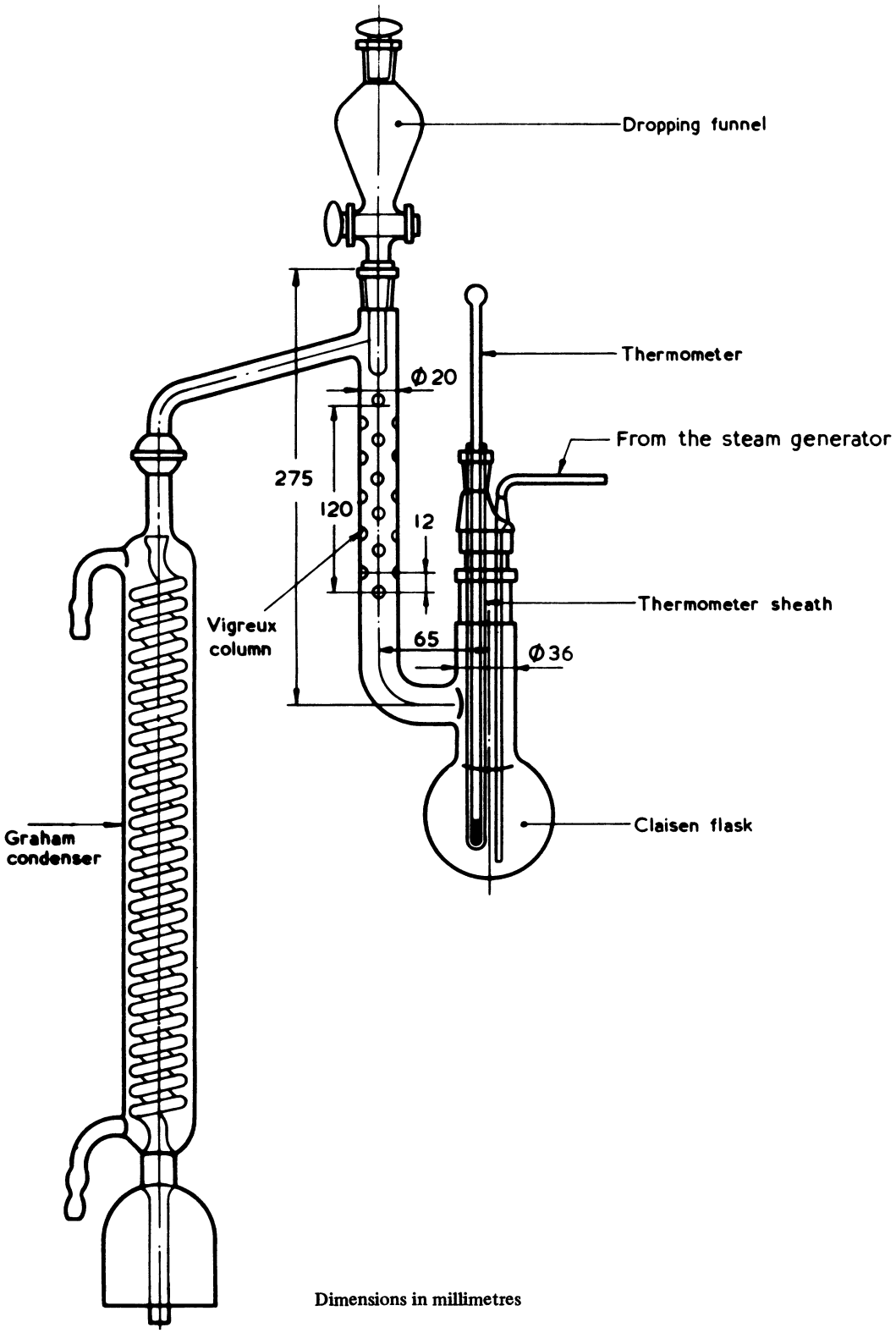

Figure 1 — Typical form of steam distillation apparatus for use in determination of fluorine content

Publications referred to

This standard makes reference to the following British Standards and International publications:

BS 410, *Test sieves.*

BS 846, *Burettes and bulb burettes.*

BS 1647, *pH scale.*

BS 1752, *Laboratory sintered or fritted filters.*

BS 1792, *One-mark volumetric flasks.*

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

BS 3145, *Laboratory potentiometric pH meters.*

BS 3422, *Laboratory deflection pH meters.*

BS 3787, *Glass condensers with standard joints.*

BS 3978, *Water for laboratory use.*

BS 4123, *Schedule of preferred chemical indicators.*

ISO/R 1619, *Cryolite (natural and artificial). Preparation and storage of test samples.*

ISO/R 1620, *Cryolite (natural and artificial). Determination of silica content. Spectrophotometric method using the reduced silicomolybdic complex.*

ISO/R 1693, *Cryolite (natural and artificial). Determination of fluorine content.*

ISO/R 1694, *Cryolite (natural and artificial). Determination of iron content. 1,10-phenanthroline photometric method.*

ISO 2366, *Cryolite (natural and artificial). Determination of sodium content. Flame emission spectrophotometric and atomic absorption methods.*

ISO 2367, *Cryolite (natural and artificial). Determination of aluminium content. 8-hydroxyquinoline gravimetric method.*

ISO 2830, *Cryolite (natural and artificial). Determination of aluminium content. Atomic absorption method.*

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