BRITISH STANDARD

**BS 4258-4:
1975**

Methods of test for

Phosphoric acid (orthophosphoric acid) for industrial use —

Part 4: Determination of fluorine content

UDC 661.634.2:546.185 – 325:543.4.062:546:16

Co-operating organizations

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

Association of Fatty Acid Distillers
British Steel Industry
Chemical Industries Association
Department of Health and Social Security
Department of Industry, Chemicals and Textiles Division
Department of 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
Soap and Detergent Industry Association
Society of Analytical Chemistry

The Government department and industrial 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:

British Pharmacopoeia Commission
Campden Food Preservation Research Association
Flour Milling and Baking Research Association
Institute of Metal Finishing
National Association of Soft Drink Manufacturers
Textile Institute

This British Standard, having been approved by the Chemicals Industry Standards Committee, was published under the authority of the Executive Board on 30 January 1976

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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 phosphoric acid.

For some years the United Kingdom has participated in the work of preparing methods of test applicable to phosphoric acid, sodium tripolyphosphate and sodium pyrophosphate for industrial use, organized by Sub-committee 6 (formerly Working Group 7) “Phosphoric Acid and Condensed Phosphates” 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 3360 but has been considerably modified to take into account comments made by the United Kingdom during its development, in particular regarding the use of lanthanum nitrate instead of cerium nitrate in the combined colour reagent. The same method is being published as Part 9 of BS 4427 “*Methods of test for sodium triphosphate (pentasodium triphosphate) and sodium pyrophosphate (tetrasodium pyrophosphate) for industrial use*”.

This standard specifies 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 comply with the requirements of BS 4258.

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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 and field of application

This Part of BS 4258 specifies an alizarin complexone and lanthanum (III) nitrate photometric method for the determination of the fluorine content of orthophosphoric acid for industrial and food uses.

The method is applicable to products whose fluorine (F) content is equal to or greater than 10 mg/kg.

2 References

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

3 Principle

The fluorine from a test portion is separated by steam distillation in a phosphoric acid medium. A blue-coloured complex is formed, at a controlled pH, between the fluorine and the combined reagent alizarin complexone-lanthanum nitrate. Acetone is added to increase the stability of the complex and the sensitivity of the method.

The complex is photometrically measured at a wavelength of about 600 nm.

4 Reagents

Water complying with the requirements of BS 3978 shall be used in the test. All reagents shall be of analytical grade and of as low a fluorine content as possible.

4.1 *Phosphoric acid*, ρ approximately 1.70 g/ml, about 85 % (*m*/*m*) solution. The same batch of this acid shall be used for the calibration, determination and blank test.

4.2 *Silica*, powdered, washed with hot 10 % hydrochloric, sulphuric or nitric acid, rinsed with water and then with ethanol 95 % (*v*/*v*), and dried in an oven at 150 °C for 2 h.

4.3 *Acetone*

4.4 *Sulphuric acid or nitric acid*, approximately 0.02N solution.

4.5 *Sodium hydroxide*, approximately 0.2N solution.

4.6 *Combined colour reagent*

4.6.1 *Buffer solution*, pH **4.6**. Dissolve 5.9 g of succinic acid in approximately 300 ml of water and adjust the pH to 4.6 with 0.5N sodium hydroxide solution, using a pH meter. Dilute to 500 ml with water.

4.6.2 *Alizarin complexone*, 0.88 g/l solution. Suspend 0.44 g of alizarin complexone in 200 ml of water and add 0.5N sodium hydroxide solution, in small portions, until the solid has just dissolved. Add 50 ml of the buffer solution (**4.6.1**). Check the pH of the solution using a pH meter and adjust, if necessary, to between **4.5** and **4.8**. Dilute to 500 ml and store between 0 °C and 50 °C.

NOTE This solution has a slightly higher equivalency than the lanthanum nitrate solution (**4.6.3**) in order to ensure that the trivalent lanthanum ions are fully complexed in the test.

4.6.3 *Lanthanum nitrate*, 0.86 g/l solution. Dissolve 0.43 g of lanthanum (III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$) in 500 ml of water.

4.6.4 Mix equal volumes of the alizarin complexone solution (**4.6.2**) and the lanthanum nitrate solution (**4.6.3**) when required for use.

4.7 *Standard fluorine solution*, corresponding to 0.100 g of F per litre.

Weigh, to the nearest 0.0001 g, 0.2210 g of sodium fluoride, previously dried for 2 h at 105 °C and cooled in a desiccator. Place in a 250 ml beaker containing about 100 ml of water. After dissolution, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask complying with the requirements of BS 1792, dilute to the mark and mix.

1 ml of this standard solution contains 0.100 mg of F.

4.8 *Standard fluorine solution*, corresponding to 1.00 mg of F per litre.

Place 10.0 ml of the standard fluorine solution (**4.7**) in a 1 000 ml one-mark volumetric flask complying with the requirements of BS 1792, dilute to the mark and mix.

1 ml of this standard solution contains 1 µg of F.

Prepare this solution at the time of use.

4.9 *Phenolphthalein*, 1 g/l ethanolic solution.

4.10 *Sodium hydroxide*, approximately 2N solution.

5 Apparatus

Ordinary laboratory apparatus is required in addition to the following.

5.1 *Glass steam-distillation apparatus*, capable of ensuring complete distillation and recovery of the fluorine.

The efficiency of the apparatus used shall be previously checked by testing with known quantities of the standard fluorine solution (**4.7**).

It is necessary, especially when low levels of fluorine are to be determined, to condition a new apparatus or a new component of an apparatus by carrying out about 12 distillations with fluoride samples so as to bring the glass surfaces into a state of equilibrium with fluorine. For example, these distillations can be carried out with a mixture of 30 ml of the phosphoric acid (**4.1**), 0.75 g of the silica (**4.2**) and 1 g of a natural fluor-apatite (Moroccan phosphate).

Before using an apparatus so treated for a determination, ensure, by means of two blank distillations in succession, that the assembly is in good condition. The quantity of fluorine found shall not be greater than that from a normal blank test, using an apparatus known to be in good condition.

An example of suitable apparatus is illustrated in Figure 1 and comprises the following.

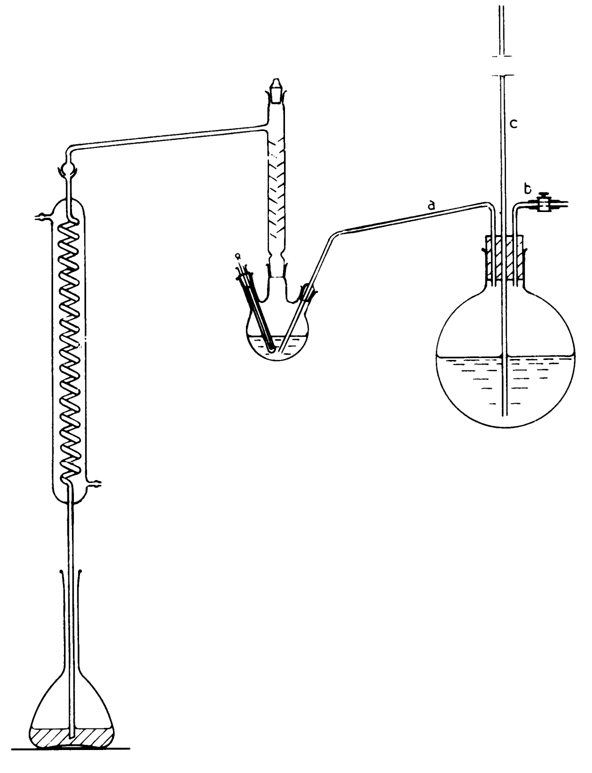

Figure 1 — Suitable distillation apparatus

5.1.1 *Steam generator*, for example a wide-neck flask of approximately 3 000 ml capacity, fitted with a stopper into which are inserted three glass tubes, a), b), and c), of internal diameter about 6 mm:

a) vertical recovery bend tube for introducing the steam into the distillation flask (**5.1.2.1**) (one limb dipping into the liquid in the distillation flask);

b) tube for regulating the flow of the steam to the distillation flask, fitted at its outer end with a rubber tube fitted with a screw clip;

c) safety tube about 1 m long.

5.1.2 *Apparatus of borosilicate glass* for steam distillation, with ground glass joints, consisting of the following.

5.1.2.1 *Distillation flask*, 250 ml nominal capacity, round-bottomed with a 19/26 central neck and two 14/23 side necks.

5.1.2.2 *Distillation column*, Vigreux, column length between the first and last of the series of points 120 mm, with a 19/26 cone, 14/23 socket (stoppered) and S13 male joint on the side-arm. The internal diameter of the side-arm shall be about 6 mm.

5.1.2.3 *Condenser*, Graham, with an effective length of about 400 mm and with an S13 female joint at the top.

5.1.2.4 *Thermometer pocket*, with a 14/23 cone, for introduction of the thermometer (glycerol in the pocket ensures thermal exchange).

5.1.3 *Thermometer*, including the range 0 °C to 200 °C.

5.1.4 *Receiver*, a 500 ml one-mark volumetric flask complying with the requirements of BS 1792.

5.2 *Spectrophotometer*, or

5.3 *Photoelectric absorptiometer*

6 Procedure

6.1 Test portion. Weigh, to the nearest 1 % a mass of the test sample containing not more than 10 mg of F. The mass of the test portion shall not exceed 50 g.

NOTE To avoid having to take too small an aliquot portion of the distillate for colour development (see **6.5.1**), the test portion can be diluted with water in an appropriately sized one-mark volumetric flask and an aliquot portion taken for the distillation.

6.2 Blank test. Carry out a blank test at the same time as the determination, under the same conditions, using the same quantities of all the reagents used for the determination and taking the same aliquot portion of the distillate for colour development.

6.3 Fluorine distillation. Place the test portion (**6.1**) in the distillation flask (**5.1.2.1**) and 20 ml of the sodium hydroxide solution (**4.10**) in the distillation receiver. Add about 0.75 g of the silica (**4.2**) and a volume of the phosphoric acid (**4.1**) such that the total quantity of phosphoric acid present is equal to 45 g of orthophosphoric acid (H_3PO_4).

Rinse with about 5 ml of water to collect all the test portion (**6.1**) and the silica (**4.2**) in the bottom of the distillation flask (**5.1.2.1**). Place a few millilitres of glycerine in the thermometer pocket, put the thermometer (**5.1.3**) in place, assemble the glass steam-distillation apparatus (**5.1**) and start the water circulation in the condenser (**5.1.2.3**). Heat the distillation flask (**5.1.2.1**) and, if the apparatus described is used, the steam generation flask (**5.1.1**).

Do not pass steam into the distillation flask (**5.1.2.1**) until the temperature of the solution in the flask reaches 138 °C to 139 °C.

Distil about 400 ml, collecting the distillate in the 500 ml one-mark volumetric flask (**5.1.4**), dilute to the mark and mix.

NOTE It has been shown that the presence of aluminium, which can complex the fluorine, does not interfere if the test portion contains up to 0.5 g of Al.

6.4 Preparation of the calibration graph

6.4.1 *Preparation of the standard matching solutions for photometric measurements with 4 cm cells*. Into a series of five 50 ml one-mark volumetric flasks complying with the requirements of BS 1792, place the volumes of the standard fluorine solution (**4.8**) indicated in the following table.

Standard fluorine solution (4.8)	Corresponding mass of fluorine
ml	µg
0[a]	0
5.0	5.0
10.0	10.0
15.0	15.0
20.0	20.0

[a] Compensation solution.

Add to each flask the quantity of water necessary to bring the volume to 20 ml and then add 0.1 ml of the phenolphthalein solution (**4.9**). Adjust the colour of the solution to pink by the addition of the sodium hydroxide solution (**4.5**) and then to colourless by the addition of the sulphuric or nitric acid solution (**4.4**). Add 5 ml of the buffer solution (**4.6.1**), 10 ml of the combined colour reagent (**4.6**) and 10 ml of the acetone (**4.3**), dilute to the mark and mix.

6.4.2 *Photometric measurements*. After allowing the solution (**6.4.1**) to stand for 20 min, carry out the photometric measurements with the spectrophotometer (**5.2**), at the wavelength of maximum absorption (about 600 nm), or with the photoelectric absorptiometer (**5.3**), fitted with appropriate filters, after having adjusted the apparatus to zero absorbance against the compensation solution.

6.4.3 *Plotting the calibration graph*. Plot a graph having, for example, the numbers of micrograms of F contained in 50 ml of the standard matching solutions as abscissae and the corresponding values of absorbance as ordinates.

6.5 Determination

6.5.1 *Colour development*. Place an accurately measured volume of the solution obtained by the procedure specified in **6.3**, containing not more than 20 µg of F and having a volume not greater than 20 ml, in a 50 ml one-mark volumetric flask. Add, if necessary, the quantity of water necessary to bring the volume to 20 ml and then add 0.1 ml of the phenolphthalein solution (**4.9**). Adjust the colour of the solution to pink by addition of the sodium hydroxide solution (**4.5**) and then to colourless by addition of the sulphuric or nitric acid solution (**4.4**).

Add 25.0 ml of the combined colour reagent (**4.6**), dilute to the mark and mix.

6.5.2 *Photometric measurement*. Carry out the photometric measurement by the procedure specified in **6.4.2**, after having adjusted the instrument to zero absorbance against the compensation solution (**6.4.2**).

7 Expression of results

By means of the calibration graph (**6.4.3**), determine the masses of fluorine (F) corresponding to the values of the photometric measurements on the test solution (**6.5.2**) and on the blank test solution.

The fluorine (F) content, expressed as milligrams per kilogram, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times \frac{500}{v}$$

where

m_0 is the mass of the test portion (**6.1**) (g);

m_1 is the mass of fluorine (F) found in the aliquot portion of the test solution taken for the colour development (µg);

m_2 is the mass of fluorine (F) found in the aliquot portion of the blank test solution taken for the colour development (µg);

v is the volume of the aliquot portion of the test and blank solutions taken for the colour development (ml).

8 Test report

The test report shall include the following particulars:

a) the reference of the method used, i.e. BS 4258-4;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this British Standard or any operation regarded as optional.

Publications referred to

This standard makes reference to the following British Standards:
BS 1792, *One-mark volumetric flasks*.
BS 3978, *Water for laboratory use*.

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W4 4AL