BRITISH STANDARD

**BS 4258-13:
1990**

Methods of test for

Phosphoric acid (orthophosphoric acid) for industrial use —

Part 13: Determination of soluble sulphate content (potentiometric method)

UDC 661.634:543.4.062:546.226:543.257.3:620.1

Committees responsible for this British Standard

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Association of Public Analysts
British Coal Corporation
Chemical Industries Association
Department of Trade and Industry (Laboratory of the Government Chemist)
Fertiliser Manufacturers' Association Limited
Institute of Trading Standards Administration
Ministry of Agriculture, Fisheries and Food
Ministry of Defence

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Contents

Foreword

This Part of BS 4258 has been prepared under the direction of the Chemicals Standards Policy Committee. It describes a method of test for phosphoric acid (orthophosphoric acid) derived by the "wet process", in which sulphate contents are generally higher than in phosphoric acid (orthophosphoric acid) derived by the "thermal process". For products having sulphate contents below 0.4 % (*m*/*m*), the method described in BS 4258-3, by which the total sulphate content is determined, is applicable.

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 4258 describes a potentiometric method for the determination of the soluble sulphate content of phosphoric acid (orthophosphoric acid) for industrial use. The method is applicable to products having sulphate contents, expressed as SO_4, not lower than 0.4 % (*m*/*m*).

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

2 Principle

Removal of phosphate from the sample by a controlled precipitation titration with lithium hydroxide solution, followed by filtration to remove the precipitate. Titration of the sulphate remaining in the filtrate with a solution of barium perchlorate, the end point being determined by potentiometry.

3 Reagents

Use reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

3.1 *Orthophosphoric acid solution*, ρ 1.75 g/mL, approximately [about 88 % (*m*/*m*)].

3.2 *Lithium hydroxide solution,* $c(Li(OH)_2)$ = 100 g/L.

3.3 *Hydrochloric acid solution,* $c(HCl)$ = 20 g/L, approximately.

3.4 *Sodium hydroxide solution,* $c(NaOH)$ = 20 g/L, approximately.

3.5 *Propan-2-ol*

3.6 *Sodium sulphate solution*, corresponding to 1.0 g of sulphate per litre.

Dry sodium sulphate for 2 h at 105 ± 2 °C. Weigh 1.4786 g into a 1 000 mL one-mark volumetric flask, dissolve in water and dilute to the mark. Mix thoroughly.

NOTE 1 mL of this solution contains 1 mg of sulphate.

3.7 *Barium perchlorate solution,* $c(Ba(ClO)_4)_2)$ = 0.02 mol/L, approximately.

Weigh 7.0 g of $Ba(ClO_4)_2.3H_2$ O into a 1 000 mL one-mark volumetric flask. Add 50 mL of water and mix. Once dissolved, dilute to the mark with water.

Standardize this solution by following the procedure described in **5.3**, using 10.0 mL of the sodium sulphate solution (**3.6**) in place of the test solution and determine the titrant volume, *V* (see clause **6**).

3.8 *Phenolphthalein indicator,* 10 g/L solution in ethanol.

NOTE For the purposes of **3.8**, the ethanol may be replaced by industrial methylated spirits 95 % (*V*/*V*) complying with BS 3591. It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations, 1983 (S.I. 1983 No. 252). It is not permissible to use duty-free ethanol, received under the provisions of the Alcoholic Liquors Duties Act 1972, Section 10, for purposes for which industrial methylated spirits is an acceptable alternative.

4 Apparatus

4.1 *Ordinary laboratory apparatus*

4.2 *Magnetic stirrer*, fitted with a hot plate and a PTFE-coated stirrer bar 40 mm long.

4.3 *Ion activity/pH meter*, with glass and reference electrodes.

4.4 *Two platinum electrodes*

NOTE To avoid any electrode drift, the electrodes should have been lightly polished using a proprietary abrasive strip.

4.5 *Büchner funnel*, 60 mm in diameter.

4.6 *Glass microfibre filter pads*, 60 mm in diameter.

4.7 *Two one-mark volumetric flasks*, 250 mL, complying with BS 1792, class B.

5 Procedure

5.1 Test portion

Weigh, to the nearest 0.001 g, a test portion containing between 100 mg and 200 mg of sulphate and not more than 15 g of *di*phosphorus pentaoxide.

5.2 Preparation of the test solution

Place the test portion (**5.1**) into a 250 mL beaker and dilute to approximately 50 mL with water. Add several drops of the phenolphthalein indicator solution (**3.8**). Place the beaker on the magnetic stirrer (**4.2**), insert the stirrer bar and commence stirring.

Add, from a burette, the lithium hydroxide solution (**3.2**) at a rate of 10 mL to 15 mL/min until the solution is just pink. Place the pH electrodes (**4.3**) into the solution and continue to add the lithium hydroxide solution until the pH reaches 11.6 ± 0.1.

Note the volume, V_1, in millilitres, of lithium hydroxide solution added. Remove the pH electrodes and rinse them into the beaker with a little water. Continue the stirring and warm the solution to 80 ± 5 °C on a hotplate.

Cool the beaker and solution to room temperature in a stream of water. Filter the solution under suction through three of the filter pads (**4.6**) contained in the Büchner funnel (**4.5**).

Wash the beaker and the filter with water without exceeding a total volume of 200 mL.

Transfer the filtrate quantitatively to the 250 mL one-mark volumetric flask (**4.7**), dilute to the mark with water and mix thoroughly.

5.3 Preparation of the blank solution

Follow the procedure described in **5.2**, replacing the test portion with between 2.5 g and 3.0 g of the orthophosphoric acid (**3.1**) and recording the volume, V_2 in millilitres, of lithium hydroxide solution (**3.2**) added.

5.4 Determination of the test solution

5.4.1 *Measurement solution*

Take an aliquot portion of the test solution (**5.2**) containing approximately 10 mg of sulphate and place this in a 100 mL beaker. Dilute to 25 mL if necessary and add 50 mL of the propan-2-ol (**3.5**). Place the beaker on the magnetic stirrer, insert the magnetic stirrer bar, commence stirring and introduce the pH electrodes.

Adjust the pH of the solution to 3.5 ± 0.1 using the hydrochloric acid solution (**3.3**) or the sodium hydroxide solution (**3.4**). Remove the pH electrodes and rinse them into the beaker with about 5 mL of water.

5.4.2 *Titration*

Introduce the platinum electrodes (**4.4**) into the measurement solution (see **5.4.1**).

Set the meter (**4.3**) for potentiometric titration, referring to the operating manual as necessary.

While continuing the stirring, add the barium perchlorate solution (**3.7**), in 1 mL portions, from the burette, noting the meter reading after each addition. Towards the expected end-point reduce the portions added to 0.1 mL, continuing to note the meter readings. Continue this procedure until the differences, $\Delta_1 E$, in millivolts, between successive readings remain essentially constant.

Record the volume of barium perchlorate solution added and the corresponding millivolt readings and construct a table as shown in Table 1. Calculate the successive differences, $\Delta_1 E$, and record these. The end-point of the titration is given by the largest increase, $\Delta_2 E$, between the values of Δ_1E.

Table 1 — Example of table used for determination of end-point and titre

Titrant volume	Meter reading	$\Delta_1 E$	$\Delta_2 E$
mL	mV	mV	mV
0	620	9	
1.0	629	6	– 3
2.0	635	5	– 1
3.0	640	8	3
4.0	648	7	– 1
5.0	655	8	1
5.1	663	7	– 1
5.2	670	15	8
5.3	685	9	– 6
5.4	694	6	– 3
5.5	700	5	– 1
5.6	705		

In this example V_3 is evaluated as follows.

$$V_3 = 5.2 + \left(0.1 \times \frac{8}{8 - (-6)}\right)$$

From the table prepared, determine the volume, V_3, in millilitres, of titrant added, at the exact end-point of the titration, from the following expression:

$$D + \left(C \times \frac{a}{a - b}\right)$$

where

- a is the largest positive value of $\Delta_2 E$ (in mV);
- b is the first value of $\Delta_2 E$ following a (in mV);
- C is the increment of barium perchlorate solution (**3.7**) added which gave rise to the largest value of $\Delta_1 E$ (in mL);
- D is the volume of barium perchlorate solution (**3.7**) which had been added prior to addition of the increment C (in mL).

NOTE The titration procedure may be simplified by the use of an automatic titration apparatus fitted with a recorder, to give adirect indication of the end-point.

5.5 Determination of the blank solution

5.5.1 *Blank measurement solution*

Follow the procedure described in **5.4.1** taking 10.0 mL of the standard sodium sulphate solution (**3.6**), and adding a 15.0 mL aliquot portion of the blank solution (**5.3**) in place of the test solution (**5.2**).

5.5.2 *Titration*

Follow the procedure described in **5.4.2**, using the blank solution (see **5.5.1**). Determine the titre, V_4 in millilitres, at the exact end-point of the titration.

Calculate the blank value, V_O, (in mL) as the volume of barium perchlorate solution (**3.7**) corresponding to 1 mL of lithium hydroxide solution (**3.2**) from the following expression:

$$\frac{V_4 - V}{V_2} \times \frac{V_a}{V_b}$$

where

V is the volume of barium perchlorate solution corresponding to 10.0 mL of sodium sulphate solution (see **3.7**) (in mL);

V_2 is the volume of lithium hydroxide solution (**3.3**) used in the preparation of the blank solution (**5.3**) (in mL);

V_4 is the volume of barium perchlorate solution (**3.7**) used in the blank determination (in mL);

V_a is the volume of the blank solution (in mL), i.e. 250 mL;

V_b is the volume of the aliquot portion taken from the blank solution (in mL), i.e. 15 mL

6 Expression of results

The sulphate content of the orthophosphoric acid, expressed as a percentage by mass of SO_4, is given by the following expression:

$$\frac{1}{10 \times m} \times \frac{m_s}{V} \times \frac{V_6}{V_5}\left[V_3 - \left(\{V_1 \times V_O\} \times \frac{V_5}{V_6}\right)\right]$$

where

m is the mass of the test portion (in g) (see **5.1**);

m_s is the mass of the SO_4 in 10.0 mL of sodium sulphate solution (**3.6**) (in mg), i.e. 10 mg;

V is the volume of the barium perchlorate solution corresponding to 10.0 mL of the sodium sulphate solution (in mL) (see **3.7**);

V_O is the blank value corresponding to 1 mL of lithium hydroxide solution (in mL) (see **5.5.2**);

V_1 is the volume of lithium hydroxide solution used in the preparation of the test solution (in mL) (see **5.2**);

V_3 is the volume of the barium perchlorate solution used in the actual determination (in mL) (see **5.4.2**);

V_5 is the volume of the aliquot of the test solution taken for the actual determination (in mL) (see **5.4.2**);

V_6 is the volume of the test solution (in mL) (see **5.2**), i.e. 250 mL.

Inserting the values for m_s and V_6, this simplifies to

$$\frac{1}{m \cdot V} \times \left[\left(\frac{V_3 \times 250}{V_5}\right) - (V_1 \times V_O)\right]$$

7 Test report

The test report shall include the following information:

a) a complete identification of the test sample;

b) a reference to this Part of this British Standard, i.e. BS 4258-13:1990;

c) the results expressed in accordance with clause **6**;

d) any unusual features noted during the determination;

e) any operation not included in this Part of this British Standard or regarded as optional.

blank

Publications referred to

BS 1792, *Specification for one-mark volumetric flasks.*
BS 3591, *Specification for industrial methylated spirits.*
BS 3978, *Specification for water for laboratory use.*
BS 4258, *Methods of test for phosphoric acid (orthophosphoric acid) for industrial use.*
BS 4258-3, *Determination of sulphate content.*

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