BRITISH STANDARD

BS 4427-11: 1983

Methods of test for

Sodium tripolyphosphate (*penta*sodium triphosphate) and sodium pyrophosphate (*tetra*sodium pyrophosphate) for industrial use —

Part 11: Separation by column chromatography and determination of the different phosphate forms

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Cooperating organizations

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

Association of Fatty Acid Distillers
British Tar Industry Association
Chemical Industries Association*
Chemical Society, Analytical Division
Consumer Standards Advisory Committee of BSI
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Contents

Foreword

This British Standard has been prepared under the direction of the Chemicals Standards Committee in order to provide methods for the analysis of sodium tripolyphosphate and sodium pyrophosphate.

For some years the UK has participated in the work of preparing methods of test applicable to sodium tripolyphosphate and sodium pyrophosphate for industrial use, organized by subcommittee 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 of BS 4427 is based on ISO 3358:1979 "*Sodium tripolyphosphate and sodium pyrophosphate for industrial use — Separation by column chromatography and determination of the different phosphate forms*". It is a revision of the 1979 edition of BS 4427-11, which was identical with the first (1976) edition of ISO 3358. BS 4427-11:1979 is now withdrawn. Experimental work carried out since the first edition of ISO 3358 has shown that the method described therein was specific only for ortho-, pyro- and tripolyphosphates, and that trimetaphosphate was not eluted quantitatively in all cases with the 0.75M potassium chloride solution specified for that purpose, although it was eluted together with all other higher condensed phosphates by the final elution with 2M hydrochloric acid solution. The revision of the 1979 edition of ISO 3358 reflects this fact and also replaces the non-SI "unit" molarity used for expressing the concentrations of reagents by mass concentrations, although the corresponding concentrations in terms of molarities are given in footnotes.

This revision of BS 4427-11 differs from ISO 3358:1979 in the following respects which remove features of the International Standard that were unacceptable to the UK (although it was approved by the UK):

a) deletion of a suction device to introduce the solutions into the chromatographic column;

b) substitution of a revised typical diagram (Figure 3) obtained during determination of the elution conditions, that corrects the misleading implication that the higher condensed phosphates are eluted by 5 mL of hydrochloric acid solution.

In addition, some errors in the text of the International Standard have been corrected. These changes and corrections have been notified to ISO for consideration in a future revision of ISO 3358.

This standard describes methods of test only and should not be used or quoted as a specification defining limits of purity. References to the standard should indicate that the methods of test used conform to the requirements of BS 4427.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 8, 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 4427 describes a method for the separation and the determination of the different phosphate forms in sodium tripolyphosphate (*penta*sodium triphosphate) and sodium pyrophosphate (*tetra*sodium diphosphate) for industrial use.

The procedure specified allows the selective determinations of orthophosphate (Na_2HPO_4), of pyrophosphate ($Na_4P_2O_7$) and of tripolyphosphate ($Na_5P_3O_{10}$), and also the evaluation of the total content of more condensed forms of phosphates in the absence of *tetra*metaphosphates and *penta*metaphosphates.

NOTE 1 In practice, *tetra*metaphosphates and *penta*metaphosphates are not usually present in commercial tripolyphosphates and pyrophosphates.

NOTE 2 Although the procedure can separate orthophosphate, its determination is not possible if the content is lower than 0.1 % (*m*/*m*); in this case its determination should be carried out by the method specified in BS 4427-8.

NOTE 3 The titles of the publications referred to in this Part of this British Standard are listed on the inside back cover.

2 Principle

The phosphate anions in a test portion are absorbed on to an anionic ion-exchange resin and eluted with potassium chloride solutions of increasing concentrations and finally with hydrochloric acid solution. The contents of P_2O_5 in the different eluate volumes (containing the different phosphate forms) are then determined.

3 Reagents

3.1 *General.* During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity complying with the requirements of BS 3978, free from silica.

3.2 *Ion-exchange resin*, strongly basic anionic type, in the chloride form, particle size between 0.07 mm and 0.16 mm.

NOTE The resins commercially available as Biorad AG 1 × 8 or Dowex 1 × 8, purified and graded, meet these requirements and have given satisfactory results.

3.3 *Hydrochloric acid*, approximately 73 g/L[1)] solution of HCl.

3.4 *Buffer solution, pH 4.3*. Dissolve 51 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$) and 46 mL of glacial acetic acid, ρ approximately 1.05 g/mL, in water.

Add several milligrams of phenylmercury(II) acetate ($C_6H_5HgOOCCH_3$) and dilute to 1 000 mL.

3.5 *Potassium chloride*, approximately 18.5 g/L[2)] solution of KCl. Dissolve 18.5 g of KCl in water, add 10 mL of the buffer solution (**3.4**) and several milligrams of polymercury (II) acetate to 1 L.

3.6 *Potassium chloride,* approximately 37 g/L[3)] solution of KCl. Dissolve 37 g of KCl in water, add 10 mL of the buffer solution (**3.4**) and several milligrams of polymercury (II) acetate and dilute to 1 L.

4 Apparatus

Ordinary laboratory apparatus is required together with the following.

4.1 *Ion-exchange column* consisting of a glass tube 300 mm long and with an internal diameter of 12 mm. The top of the tube is fitted with a ground glass socket enabling a 100 mL graduated cylindrical dropping funnel to be fitted (see Figure 1). The bottom of the tube is extended by a narrower glass tube approximately 90 mm long and 8 mm in diameter, fitted at its middle with a stopcock, the end of which is drawn out to a jet. The bottom of the ion-exchange column is fitted with a silica wool pad about 10 mm thick or, preferably, a fritted glass disk of porosity P 100 (pore diameter of between 40 µm and 100 µm).

NOTE The solutions can also be introduced into the column using a syphon as illustrated in Figure 2.

5 Procedure

5.1 Preparation of the ion-exchange column. Wash approximately 20 g of the resin (**3.2**) with a jet of water on a 63 µm sieve (see BS 410) to remove fine particles. Transfer the residue on the sieve to a ground-glass filter, porosity P 40 (pore diameter between 16 µm and 40 µm) and remove most of the water by suction. After this preliminary preparation, allow the resin to stand for about 12 h in 100 mL of the hydrochloric acid solution (**3.3**); 18 g of the resin are required.

Introduce the resin into the ion-exchange column (**3.2**) (18 g occupies a height of approximately 240 mm) and wash with water until the pH of the effluent is between 4.5 and 5.

During the analysis, maintain the liquid level at all times several millimetres above the top of the column of resin.

[1)] Previously 2M.

[2)] Previously 0.25M.

[3)] Previously 0.50M.

5.2 Test portion and preparation of the test solution. Place 0.500 g, weighed to the nearest 0.000 1 g, of the test sample in a 250 mL one-mark volumetric flask. Dissolve it in water, add 5 mL of the buffer solution (**3.4**), dilute to the mark and mix. Filter the solution if it is turbid.

5.3 Preliminary test

5.3.1 *General*. The conditions under which the elution of phosphates is carried out depend on the particle size distribution of the ion-exchange resin. The separation can, moreover, be influenced by the presence of foreign salts in the product examined. For this reason it is recommended that a preliminary test be carried out on the test solution (**5.2**) to determine the conditions to be observed during the chromatographic separation. In addition, this test provides confirmation that the product is "normal" and that it can be analysed by the procedure described in this British Standard.

5.3.2 *Determination of the elution conditions*. Immediately after preparation, place 10.0 mL of the test solution (**5.2**) in the upper part of the column, on top of the ion-exchange resin. Apply a slight air pressure, controlled by means of the pressure regulator, and open the stopcock so as to allow the solution to penetrate into the resin. Close the stopcock before the solution has completely run through so that several millimetres of solution remain above the resin surface.

Carefully wash the inner walls of the column above the resin surface with about 5 mL of water and re-open the stopcock to allow the washings to enter the resin.

Close the stopcock before all the liquid has penetrated into the resin. Pass through the column, from the graduated cylindrical dropping funnel, about 110 mL of the potassium chloride solution (**3.5**), controlling the flow at a constant rate of about 2.5 mL/min to 3 mL/min (obtained by application of pressure, controlled by the regulator), and collect the eluate in fractions of 5 mL.

Determine the P_2O_5 content of each fraction (see **5.6** and Appendix A) so as to establish which contain orthophosphate and pyrophosphate respectively, when eluted in that order.

Then carry out the same procedure, running about 80 mL of the potassium chloride solution (**3.6**) through the column, to elute the tripolyphosphate.

Plot a graph (see Figure 3 for a typical graph) having the successive 5 mL fractions as absciassae and the corresponding contents of P_2O_5 as ordinates.

Determine from this graph the minimum volumes of the potassium chloride solutions which should be used to effect the separation.

5.4 Regeneration of the column. At the end of the preliminary test, check that several millimetres of potassium chloride solution remain above the resin surface, pass about 200 mL of the hydrochloric acid solution (**3.3**) through the column and allow the column to stand under acid conditions for about 12 h. Wash the column, first by running through about 50 mL of the hydrochloric acid solution (**3.3**) and then by running through 50 mL of water. Add more water so as to fill the column completely. Stopper the column and invert it to suspend the resin in the water. Return the column to the upright position, allow the resin to settle and pass water through the resin until the pH of the effluent is between 4.5 and 5.

5.5 Separation procedure. Carry out the procedure described in **5.3.2**, using 10.0 mL of the test solution (**5.2**) prepared immediately beforehand and using the volumes of the different potassium chloride solutions determined as in **5.3.2**. Collect separately the three eluate volumes corresponding to each of the three phosphate forms (orthopolyphosphates, pyropolyphosphates and tripolyphosphates). Before changing from one eluate volume to the next, collect two or three 5 mL fractions and check the P_2O_5 content according to the method described in Appendix A to verify that the separation is satisfactory. The intermediate fractions should contain only negligible quantities of P_2O_5. Otherwise the test should be repeated. After collection of the last eluate volume, regenerate the column, following the procedure specified in **5.4**, retaining the eluate obtained by passing the 200 mL of the hydrochloric acid solution (**3.3**). This will contain any higher condensed forms of phosphate that may be present.

5.6 Determination of phosphorus(V) oxide in the eluates

5.6.1 *For the analysis of the* 5 mL *fractions collected during the preliminary test*. Use the reduced molybdophosphate photometric method specified in Appendix A.

5.6.2 *For the analysis of sodium tripolyphosphate*. Determine the phosphorus(V) oxide in the eluate volume corresponding to the orthophosphate and in that corresponding to the pyrophosphate using the reduced molybdophosphate photometric method specified in Appendix A. Use the same method to determine the phosphorus(V) oxide content in the eluate volume corresponding to higher condensed forms of phosphate after having previously evaporated the hydrochloric acid.

Determine the phosphorus(V) oxide in the eluate volume corresponding to the tripolyphosphate by the following method.

Quantitatively transfer the eluate volume to a 600 mL beaker. Add 10 mL of nitric acid solution, ρ approximately 1.42 g/mL, cover the beaker with a clock glass and boil the solution for 20 min. Cool to room temperature, add 100 mL of the citromolybdate reagent (**3.2** of BS 4427-10:1976) and proceed as described in **5.3.2** of BS 4427-10:1976, omitting paragraph 1.

5.6.3 *For the analysis of sodium pyrophosphate.* Determine the phosphorus(V) oxide in the eluate volume corresponding to the orthophosphate and in that corresponding to the tripolyphosphate, using the reduced molybdophosphate photometric method specified in Appendix A. Use the same method to determine the phosphorus(V) oxide in the eluate volume corresponding to higher condensed phosphate forms after having previously evaporated the hydrochloric acid.

Determine the phosphorus(V) oxide in the eluate volumes corresponding to pyrophosphate by the following method.

Quantitatively transfer the total quantity of the eluate volume to a 600 mL beaker. Add 10 mL of nitric acid solution, ρ approximately 1.42 g/mL, cover the beaker with a clock glass and boil the solution for 20 min. Cool to room temperature, add 100 mL of the citromolybdate reagent (**3.2** of BS 4427-10:1976) and proceed as specified in **5.3.2** of BS 4427-10:1976, omitting paragraph 1.

5.6.4 *Phosphorus(V) oxide contents.* The sum of the phosphorus(V) oxide contents obtained by the procedures described in **5.6.2** and **5.6.3** should not differ by more than 1 % from the phosphorus(V) oxide content determined on 10.0 mL of the test solution (**5.2**) by the method specified in BS 4427-10. Otherwise, repeat the test.

6 Expression of results

Using the quantities, in milligrams, of the phosphorus(V) oxide found in each eluate volume, calculate the corresponding contents of phosphate and express them as percentages by mass, using the general formula

$$m_i \times F_i \times \frac{100}{m_o} \times \frac{250}{10} = \frac{2500}{m_o} \times m_i \times F_i$$

where

m_o is the mass of the test portion (in mg) (see **5.2**);

m_i is the mass of P_2O_5 found in the eluate volume concerned (in mg);

F_i is the conversion factor from P_2O_5 to the corresponding phosphate form, which takes the following values:

for the eluate volume corresponding to Na_2HPO_4, $F_i = 2.000$

for the eluate volume corresponding to $Na_4P_2O_7$, $F_i = 1.873$

for the eluate volume corresponding to $Na_5P_3O_{10}$, $F_i = 1.728$

for the eluate volume corresponding to the total higher condensed phosphates, expressed as $NaPO_3$, $F_i = 1.437$.

7 Test report

The test report shall include the following particulars:

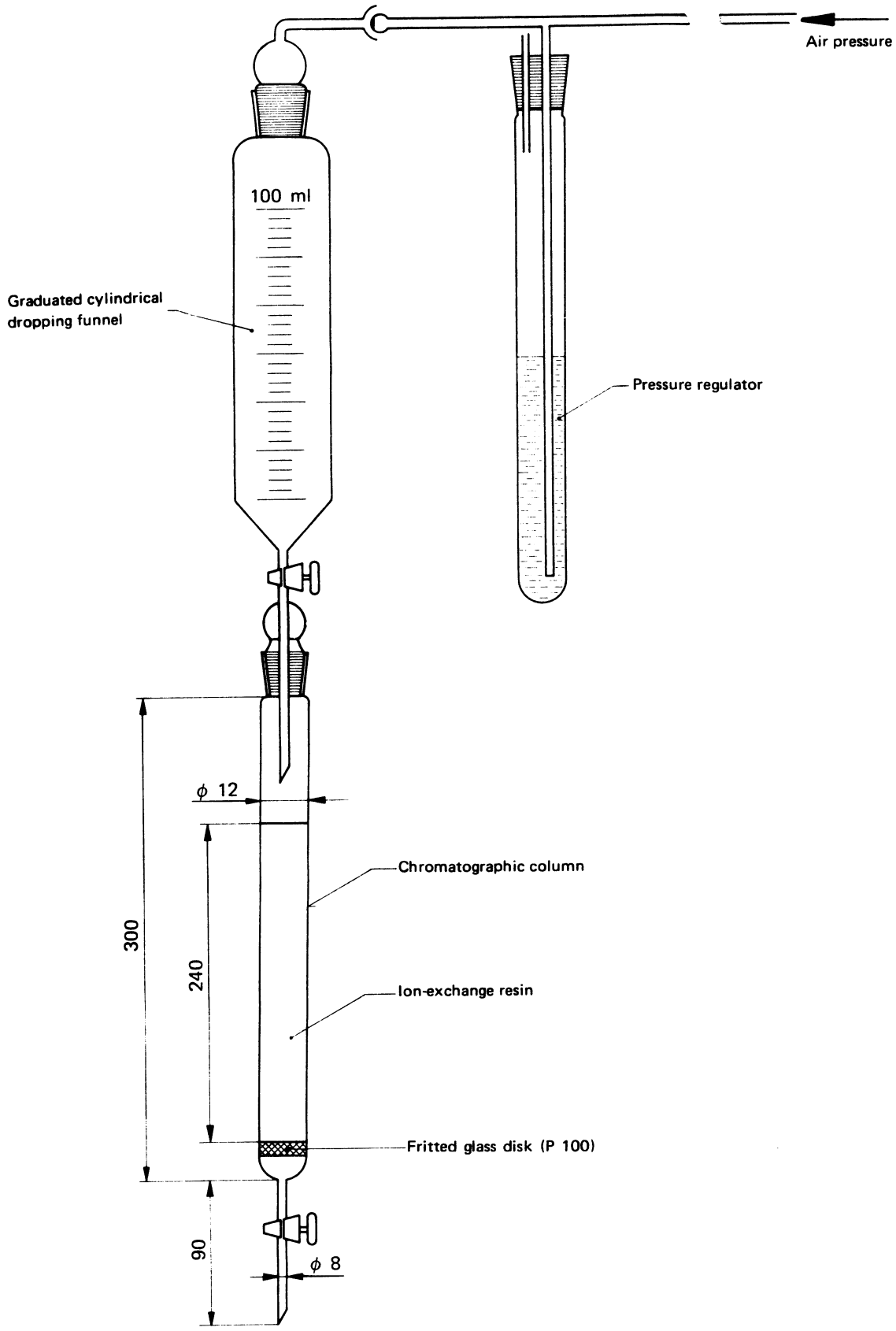
a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

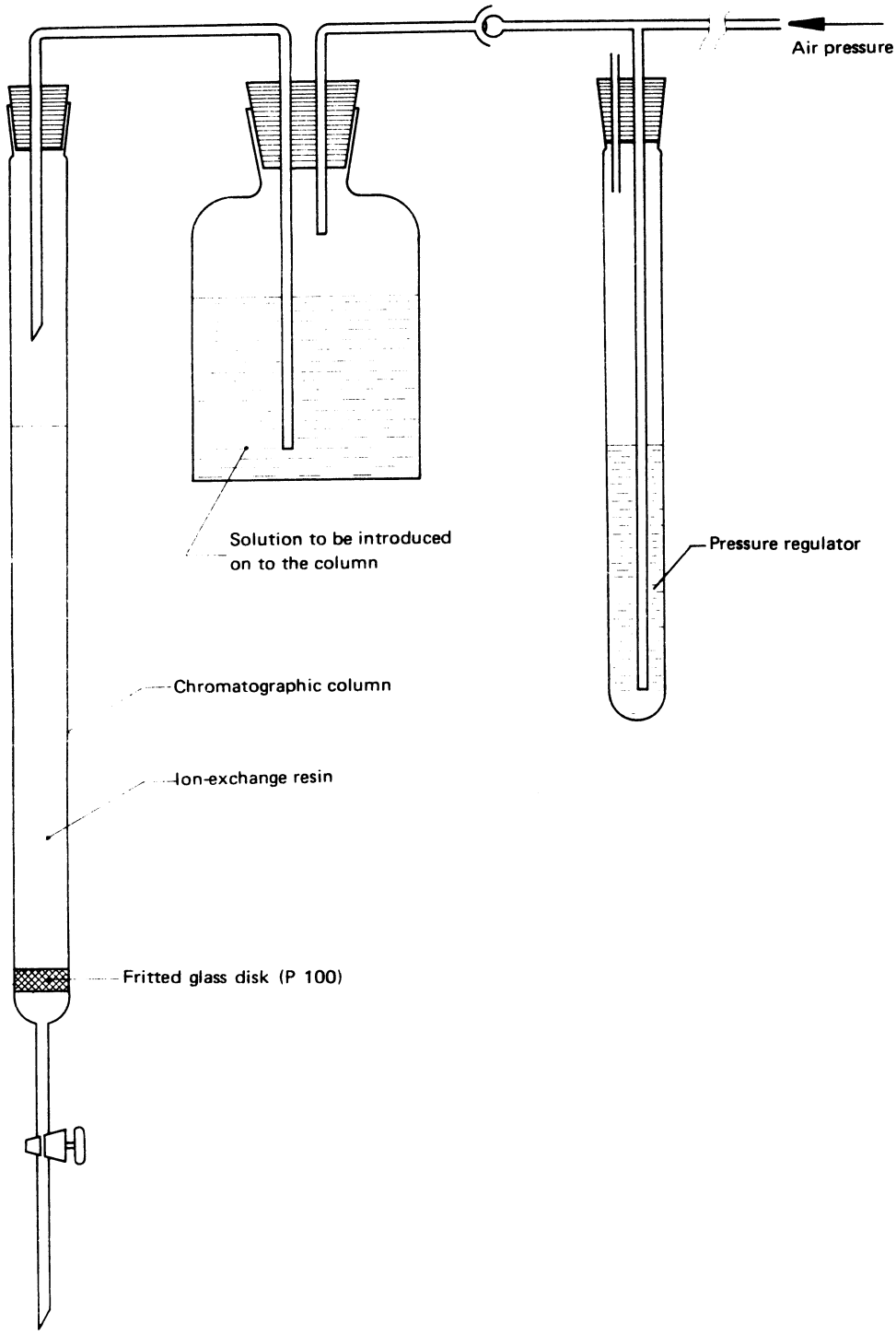
d) any unusual features noted during the determination;

e) any operation not included in this Part of BS 4427 or in the British Standards to which reference is made or regarded as optional.



All dimensions are in millimetres.

Figure 1 — Ion-exchange column with dropping funnel



NOTE The dimensions of the column are given in Figure 1.

Figure 2 — Ion-exchange column with typical syphon device

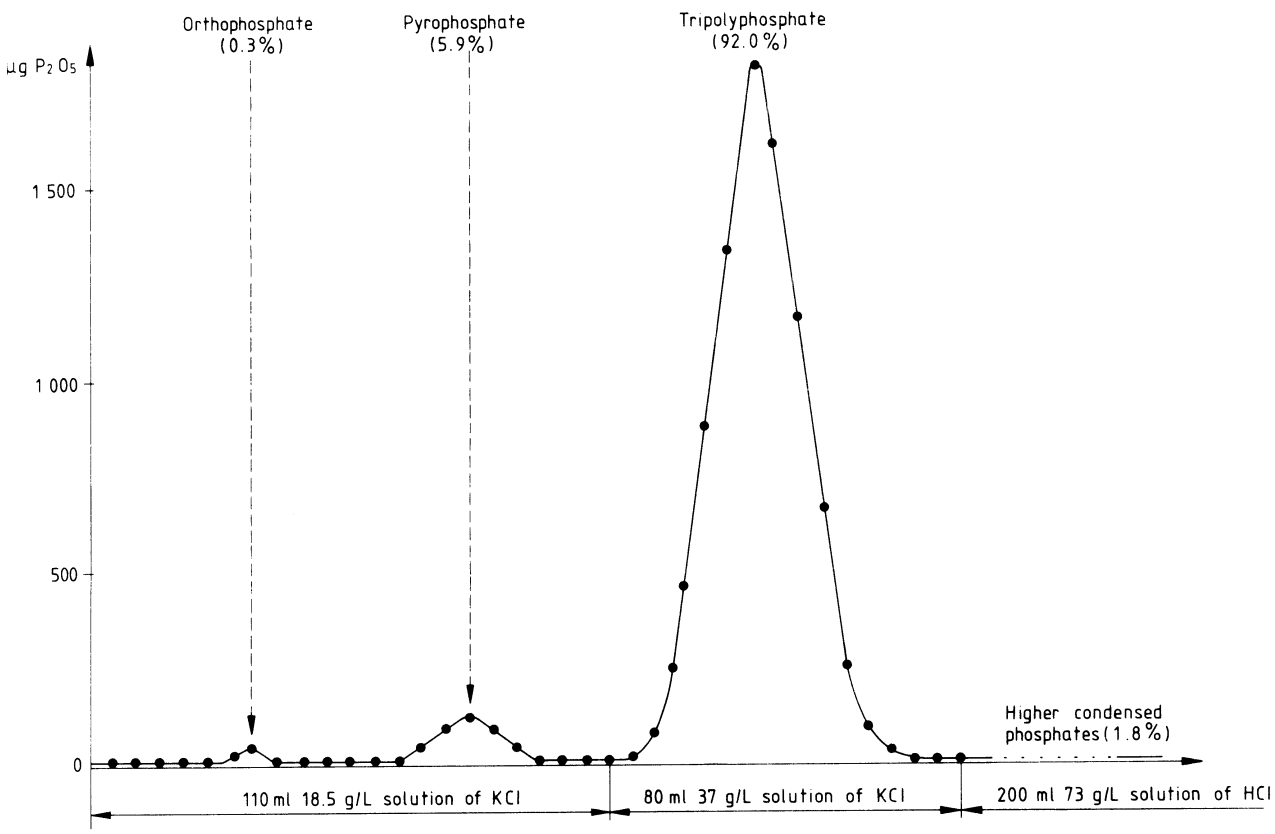


Figure 3 — Typical graph obtained during the determination of the elution conditions

Appendix A Determination of phosphorus(V) oxide in the eluates obtained by chromatographic separation on a column

A.1 General

This appendix describes a photometric method for the determination of phosphorus(V) oxide in the eluates obtained by chromatographic separation on a column of the different phosphate forms.

A.2 Principle

Formation of molybdophosphate in a dilute sulphuric acid medium and reduction with ascorbic acid. Photometric measurement of the reduced complex at a wavelength of about 650 nm.

A.3 Reagents

A.3.1 *General*. During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity complying with BS 3978.

A.3.2 *Ascorbic acid*, 25 g/L solution.

NOTE This solution should be renewed every 2 or 3 days.

A.3.3 *Ammonium molybdate*, 7.2 g/L solution in sulphuric acid.

Dissolve 7.2 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in 400 mL of approximately 490 g/L[4)] sulphuric acid solution and dilute to 1 000 mL. This solution contains about 6 g of MoO_3 per litre in approximately 196 g/L[5)] sulphuric acid solution.

A.3.4 *Phosphorus(V) oxide*, standard solution corresponding to 1.00 g of P_2O_5 per litre.

Weigh, to the nearest 0.001 g, 1.917 g of potassium dihydrogen phosphate (KH_2PO_4), previously dried at 110 °C and cooled in a desiccator. Place in a 1 000 mL one-mark volumetric flask, dissolve in water, dilute to the mark and mix.

1 mL of this standard solution contains 1.00 mg of P_2O_5.

A.3.5 *Phosphorus(V) oxide*, standard solution corresponding to 0.010 g of P_2O_5 per litre.

Place 10.0 mL of the standard solution (**A.3.4**) in a 1 000 mL one-mark volumetric flask, dilute to the mark and mix.

1 mL of this standard solution contains 10 µg of P_2O_5.

A.4 Apparatus

Ordinary laboratory apparatus is required together with the following.

A.4.1 *Spectrophotometer*, or **A.4.2**.

A.4.2 *Photoelectric absorptiometer*.

A.5 Procedure

A.5.1 *Test portion*. For the determination on the 5 mL fractions collected during the preliminary test (see **5.3**), analyse each fraction directly.

For the determination on the eluate volumes collected during the actual separation (see **5.5**), start by adjusting, in a one-mark volumetric flask, the solution to a volume (V) of which a 5 mL aliquot portion will contain, at the most, 0.25 mg of P_2O_5.

A.5.2 *Blank test*. 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 in the determination.

A.5.3 ***Preparation of the calibration curve***

A.5.3.1 Preparation of the standard matching solutions, relating to photometric measurements carried out with 1 cm or 4 cm or 5 cm optical path length cells (see Table 1).

Into a series of nine 250 mL conical flasks, introduce the volumes of the standard phosphorus(V) oxide solution (**A.3.5**) indicated in Table 1.

Table 1 — Concentrations of standard matching solutions and corresponding optical path lengths of cells

Standard phosphorus(V) oxide solution (A.3.4)	Corresponding mass of P_2O_5	Optical path length of cells
mL	µg	cm
0[a]	0	1 or 4 or 5
2.0	20	
4.0	40	
6.0	60	4 or 5
8.0	80	
10.0	100	1 or 4 or 5
15.0	150	
20.0	200	1
25.0	250	

[a] Compensation solution.

Add to each flask the quantity of water necessary to adjust the volume to 25 mL and then 10 mL of the ammonium molybdate solution (**A.3.3**) and 2 mL of the ascorbic acid solution (**A.3.2**).

[4)] Previously 10N or 5M.

[5)] Previously 4N or 2M.

Warm the flasks on a boiling water bath for about 30 min. Allow the solutions to cool to ambient temperature and transfer them quantitatively to 100 mL one-mark volumetric flasks. Dilute to the mark and mix.

A.5.3.2 *Photometric measurements*. Measure the absorbances of the standard matching solutions (**A.5.3.1**) using the spectrophotometer (**A.4.1**), adjusted to a wavelength in the region of 650 nm, or the photoelectric absorptiometer (**A.4.2**), fitted with appropriate filters, after having adjusted the instrument to zero absorbance against the compensation solution.

A.5.3.3 *Preparation of calibration graph*. Plot a graph having, for example, the number of micrograms of phosphorus(V) oxide (P_2O_5) contained in 100 mL of standard matching solution as abscissae and the corresponding values of the absorbance, corrected to a path length of 1 cm, as ordinates.

A.5.4 ***Determination***

A.5.4.1 *Colour development*. Place the 5.00 mL of solution constituting the test portion (**A.5.1**) in a 250 mL conical flask and add the quantity of water necessary to bring the volume to 25 mL; then add 10 mL of the ammonium molybdate solution (**A.3.3**) and 2 mL of the ascorbic acid solution (**A.3.2**). Warm the flask on a boiling water bath for about 30 min. Allow the solution to cool to ambient temperature and then transfer quantitatively to a 100 mL one-mark volumetric flask. Dilute to the mark and mix.

A.5.4.2 *Photometric measurement*. Measure the absorbance of the solution (**A.5.4.1**), following the procedure specified in **A.5.3.2** but after having adjusted the instrument to zero absorbance against the blank test solution (**A.5.2**).

A.6 Expression of results

By means of the calibration curve (**A.5.3.3**) determine the mass of phosphorus(V) oxide corresponding to the photometric measurement (**A.5.4.2**).

The phosphorus(V) oxide (P_2O_5) content in the eluate volume (in mg) is given by the formula

$$\frac{m \times V}{5}$$

where

m is the mass of P_2O_5 found in the test portion (in mg);

V is the volume to which the eluate volume has been adjusted (in the case of the preliminary test, $V = 5$) (in mL).

Publications referred to

BS 410, *Specification for test sieves.*

BS 3978, *Water for laboratory use.*

BS 4427, *Methods of test for sodium tripolyphosphate (pentasodium triphosphate) and sodium pyrophosphate (tetrasodium pyrophosphate) for industrial use.*

BS 4427-8, *Determination of orthophosphate content.*

BS 4427-10, *Determination of total phosphorus(V) oxide content; quinoline phosphomolybdate gravimetric method.*

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