



G-92-52

Published 1979-11-15

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

**Sodium tripolyphosphate and sodium pyrophosphate for industrial use —
Separation by column chromatography and determination of the different
phosphate forms**

ERRATUM

Page 3

Sub-clause 7.6.3, first paragraph, second and third lines, should read as follows :

"volume corresponding to the ortho- and to the tripolyphosphate using . . ."

Page 7

Insert the following legend under the figure

**"FIGURE 4 — Typical diagram obtained during the
determination of elution conditions"**





Sodium tripolyphosphate and sodium pyrophosphate for industrial use — Separation by column chromatography and determination of the different phosphate forms

Tripolyphosphate et pyrophosphate de sodium à usage industriel — Séparation par chromatographie sur colonne et dosage des différentes formes de phosphates

Second edition — 1979-05-01

UDC 661.833.456/.458 : 546.185 : 543.544

Ref. No. ISO 3358-1979 (E)

Descriptors : sodium tripolyphosphates, sodium pyrophosphates, chemical analysis, determination of content, orthophosphates, phosphorus oxides, column chromatographic analysis.

Price based on 10 pages

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3358 was developed by Technical Committee ISO/TC 47, *Chemistry*.

This second edition was submitted directly to the ISO Council, in accordance with clause 6.13.1 of the Directives for the technical work of ISO. It cancels and replaces the first edition (i.e. ISO 3358-1976), which had been approved by the member bodies of the following countries :

Belgium	Hungary	South Africa, Rep. of
Bulgaria	India	Spain
Chile	Israel	Switzerland
Czechoslovakia	Italy	Thailand
Egypt, Arab Rep. of	Netherlands	Turkey
France	New Zealand	United Kingdom
Germany, F. R.	Poland	Yugoslavia

No member body had expressed disapproval of the document.

Sodium tripolyphosphate and sodium pyrophosphate for industrial use — Separation by column chromatography and determination of the different phosphate forms

1 SCOPE

This International Standard specifies a method for the separation and the determination of the different phosphate forms in sodium tripolyphosphate (pentasodium triphosphate) and sodium pyrophosphate (tetrasodium diphosphate) for industrial use.

2 FIELD OF APPLICATION

The procedure specified allows the selective determinations of orthophosphate (Na_2HPO_4), of pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) and of tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), and also the evaluation of the total content of more condensed forms of phosphates in the absence of tetrameta- and pentametaphosphates.

NOTES

1 In practice, tetrametaphosphates and pentametaphosphates are not usually present in commercial tripolyphosphates and pyrophosphates.

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 shall be carried out by the method specified in ISO 2998.

3 REFERENCES

ISO 2998 — *Sodium tripolyphosphate and sodium pyrophosphate for industrial use — Determination of orthophosphate content — Photometric method using the reduced molybdophosphate.*

ISO 3357, *Sodium tripolyphosphate and sodium pyrophosphate for industrial use — Determination of total phosphorus(V) oxide content — Quinoline phosphomolybdate gravimetric method.*

4 PRINCIPLE

Absorption of the phosphate anions on an anionic ion-exchange resin. Elution with potassium chloride solutions of increasing concentrations. Determination of P_2O_5 in the different eluate volumes.

5 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, free from silica.

5.1 Ion-exchange resin, strongly basic anionic type, in the chloride form, particle size between 0,07 and 0,16 mm.

NOTE — The resins commercially available as Biorad AG 1 X8 or Dowex 1 X8, purified and graded, meet these requirements and have given satisfactory results.

5.2 Hydrochloric acid, approximately 73 g/l solution.

5.3 Buffer solution, pH 4,3.

Dissolve 51 g of sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) and 46 ml of glacial acetic acid, ρ approximately 1,05 g/ml, in water. Add several milligrams of phenylmercury(II) acetate ($\text{C}_6\text{H}_5\text{HgOOCCH}_3$) and dilute to 1 000 ml.

5.4 Potassium chloride, approximately 18,5 g/l solution.

5.5 Potassium chloride, approximately 37 g/l solution.

Prepare solutions 5.4 and 5.5 and then add to each solution 10 ml of the buffer solution (5.3) and several milligrams of phenylmercury(II) acetate per litre.

6 APPARATUS

Ordinary laboratory apparatus and

6.1 Ion-exchange column consisting of a glass tube 300 mm long and internal diameter 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 about 90 mm long and 8 mm 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 between 40 and 100 μm).

NOTE — The solutions can also be introduced into the column using either a syphon, as illustrated in figure 2, or a suction device, as illustrated in figure 3.

7 PROCEDURE

7.1 Preparation of the ion-exchange column

Wash about 20 g of the resin (5.1) with a jet of water on a 63 μm sieve (see ISO 565) to remove fine particles. Transfer the residue on the sieve to a ground-glass filter, porosity P 40 (pore diameter between 16 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 (5.2); 18 g of the resin are required.

Introduce the resin into the ion-exchange column (6.1) — 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.

7.2 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 in water, add 5 ml of the buffer solution (5.3), dilute to the mark and mix. Filter the solution if it is turbid.

7.3 Preliminary test

7.3.1 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 (7.2) 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 specified in this International Standard.

7.3.2 Determination of the elution conditions

Immediately after preparation, place 10,0 ml of the test solution (7.2) 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 (5.4), controlling the rate at a constant

value of about 2,5 to 3 ml/min (obtained by application of pressure, controlled by the pressure regulator), and collect the eluate in fractions of 5 ml.

Determine the P_2O_5 content of each fraction (see 7.6 and annex A) so as to determine which contain orthophosphate and pyrophosphate respectively, eluted in that order.

Then carry out the same procedure passing about 80 ml of the potassium chloride solution (5.5) through the column to elute the tripolyphosphate.

Draw a diagram (see figure 4 for a typical diagram) having the successive 5 ml fractions as abscissae and the corresponding contents of P_2O_5 as ordinates.

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

7.4 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 (5.2) through the column and allow the column to stand under acid conditions for about 12 h. Wash the column, first by passing about 50 ml of the hydrochloric acid solution (5.2) and then by passing about 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.

7.5 Separation procedure

Proceed as in 7.3.2, using 10,0 ml of the test solution (7.2) prepared immediately beforehand and using the volumes of the different potassium chloride solutions determined as in 7.3.2. Collect separately, but in one portion each, the three eluate volumes corresponding to each of the three phosphate forms (ortho-, pyro- and tripolyphosphates). Before changing from one eluate volume to the next, collect two or three 5 ml fractions to verify that the separation is satisfactory. (The intermediate fractions should contain only negligible quantities of P_2O_5 . Otherwise, repeat the test.) After collection of the last eluate volume, regenerate the column, following the procedure specified in 7.4, retaining the eluate obtained by passing the 200 ml of the hydrochloric acid solution (5.2). This will contain any higher condensed forms of phosphate which may be present.

7.6 Determination of phosphorus(V) oxide in the eluates

7.6.1 For the analysis of the 5 ml fractions collected during the preliminary test, use the reduced molybdo-phosphate photometric method specified in annex A.

7.6.2 For the analysis of sodium tripolyphosphate :

– Determine the phosphorus(V) oxide in the eluate volumes corresponding to the ortho- and to the pyrophosphate using the reduced molybdophosphate photometric method specified in annex 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 tripolyphosphate by the gravimetric method specified in ISO 3357 as follows. Quantitatively transfer the eluate volume to a 600 ml beaker. Add 10 ml of nitric acid solution, ρ approximately 1,40 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 ISO 3357) and proceed as described in 5.3.2 of ISO 3357, starting from paragraph 2.

7.6.3 For the analysis of sodium pyrophosphate :

– Determine the phosphorus(V) oxide in the eluate volume corresponding to pyrophosphate by the phosphate using the reduced molybdophosphate photometric method specified in annex 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 gravimetric method specified in ISO 3357 as follows. Quantitatively transfer the total quantity of the eluate volume to a 600 ml beaker. Add 10 ml of nitric acid solution, ρ approximately 1,40 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 ISO 3357) and proceed as specified in 5.3.2 of ISO 3357, starting from paragraph 2.

7.6.4 The sum of the phosphorus(V) oxide contents obtained by the procedures specified in 7.6.2 and 7.6.3 should not differ by more than 1 % from the phosphorus(V)

oxide content determined on 10,0 ml of the test solution (7.2) by the method specified in ISO 3357. Otherwise, repeat the test.

8 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

$$m_i \times F_i \times \frac{100}{m_o} \times \frac{250}{10} = \frac{2\,500}{m_o} \times m_i \times F_i$$

where

m_o is the mass, in milligrams, of the test portion (7.2);

m_i is the mass, in milligrams, of P_2O_5 found in the eluate volume concerned;

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 $NaPO_3$	$F_i = 1,437$

9 TEST REPORT

The test report shall include the following particulars :

- an identification of the sample;
- the reference of the method used;
- the results and the method of expression used;
- any unusual features noted during the determination;
- any operation not included in this International Standard or in the International Standards to which reference is made or regarded as optional.

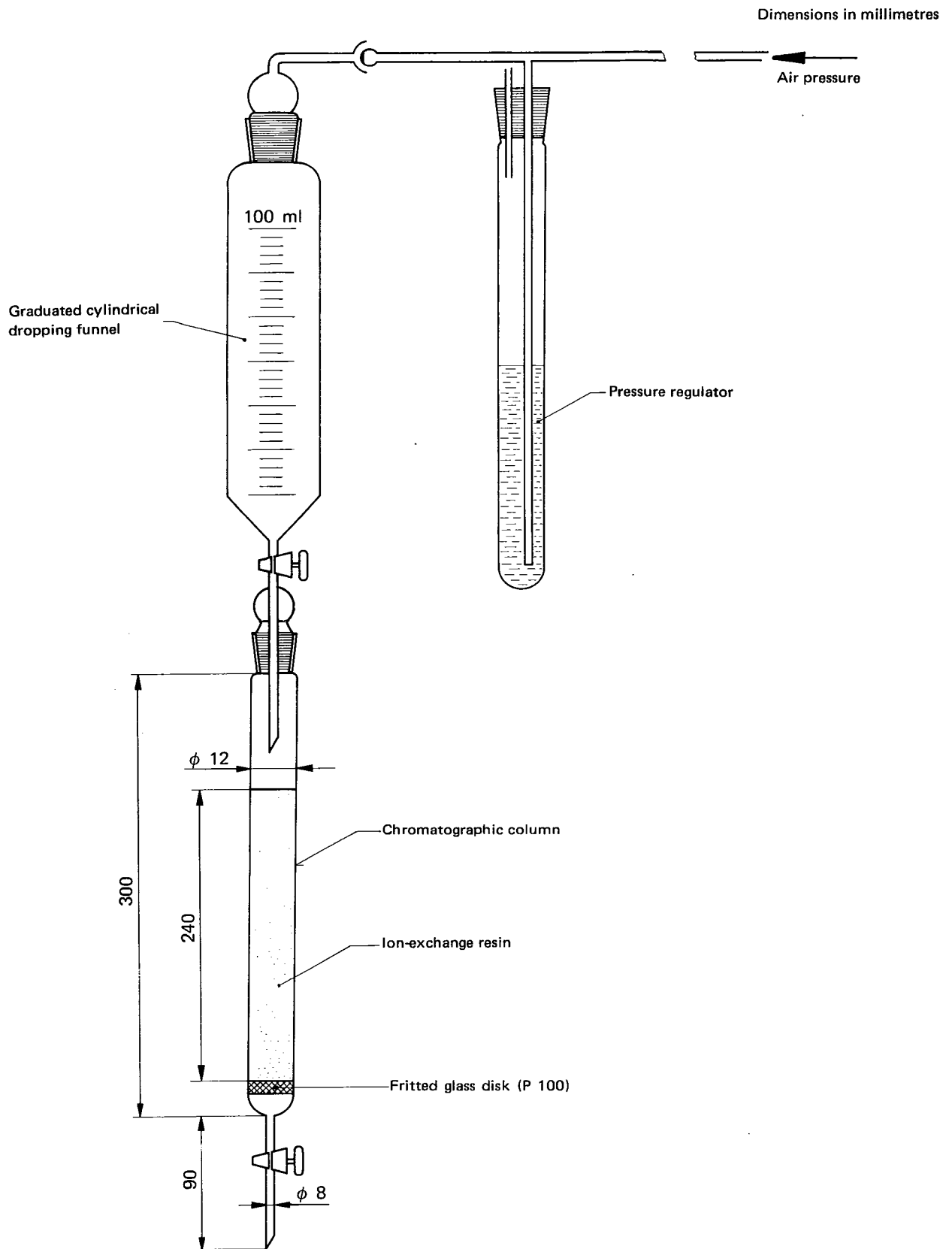


FIGURE 1 – Ion-exchange column with dropping funnel

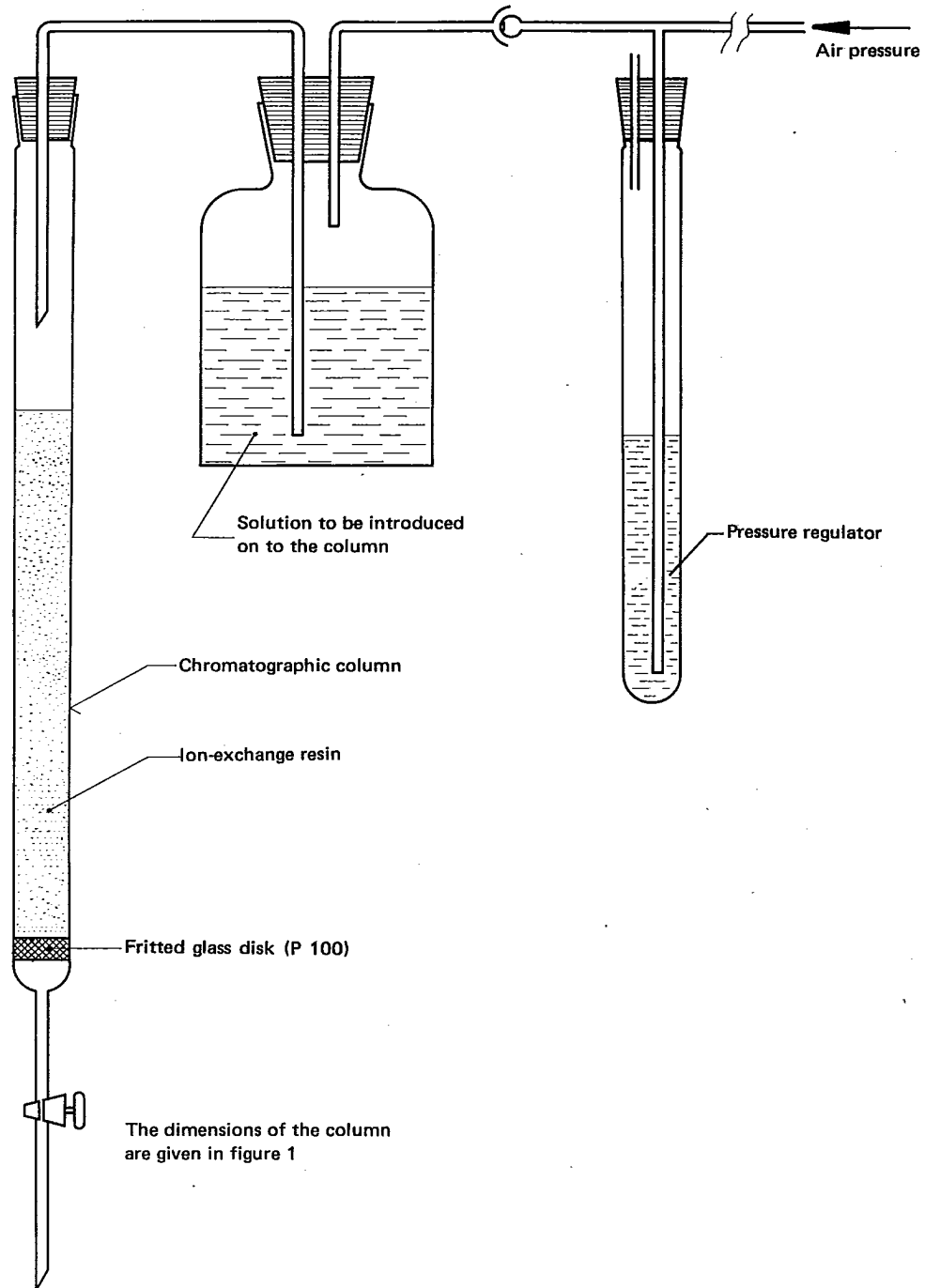


FIGURE 2 – Ion-exchange column with typical syphon device

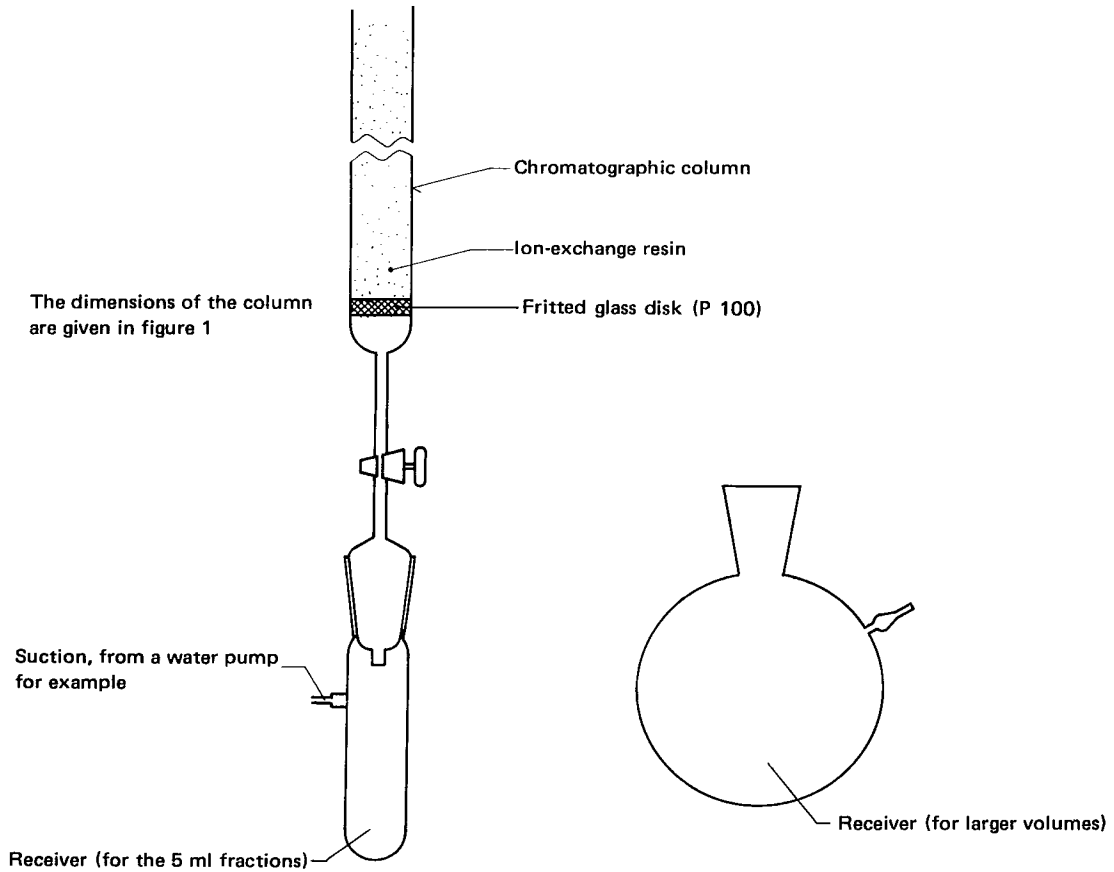
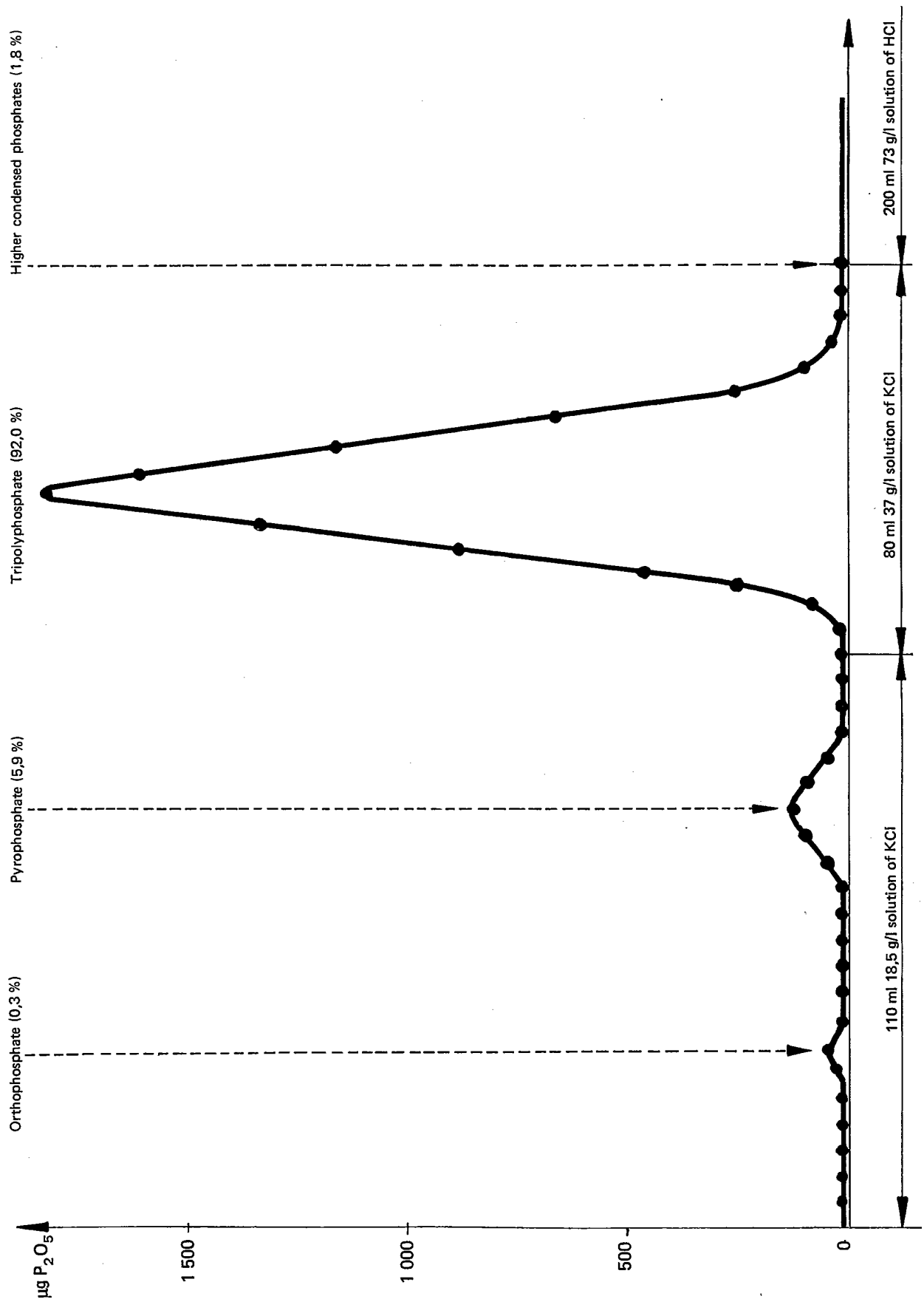


FIGURE 3 — Ion-exchange column with typical suction device



ANNEX A

**DETERMINATION OF PHOSPHORUS(V) OXIDE IN THE ELUATES OBTAINED BY
CHROMATOGRAPHIC SEPARATION ON A COLUMN**

A.1 SCOPE AND FIELD OF APPLICATION

This annex specifies 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

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

A.3.1 Ascorbic acid, 25 g/l solution.

Renew this solution every 2 or 3 days.

A.3.2 Ammonium molybdate, 7,2 g/l solution in sulphuric acid.

Dissolve 7,2 g of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in 400 ml of approximately 490 g/l 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 sulphuric acid solution.

A.3.3 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.3.4 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.3.3) 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 and

A.4.1 Spectrophotometer, or**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, analyse each fraction directly.

For the determination on the eluate volumes collected during the actual separation, 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 or 4 or 5 cm optical path length cells (see table)

Into a series of nine 250 ml conical flasks, introduce the volumes of the standard phosphorus(V) oxide solution (A.3.4) indicated in the following table.

Standard phosphorus(V) oxide solution (A.3.4)	Corresponding mass of P_2O_5	Optical path length of cell
ml	µg	cm
0*	0	1 or 4 or 5
2,0 4,0 6,0 8,0	20 40 60 80	4 or 5
10,0	100	1 or 4 or 5
15,0 20,0 25,0	150 200 250	1

* 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.3.2) and 2 ml of the ascorbic acid solution (A.3.1).

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.3.2) and 2 ml of the ascorbic acid solution (A.3.1). 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 is given, in milligrams, by the formula

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

where

m is the mass, in milligrams, of P_2O_5 found in the test portion;

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

ANNEX B

ISO PUBLICATIONS RELATING TO CONDENSED SODIUM PHOSPHATES
FOR INDUSTRIAL USE**SODIUM PYROPHOSPHATE** (*tetrasodium diphosphate*)

ISO 2999 – Estimation of pyrophosphate content – Potentiometric method.

SODIUM TRIPOLYPHOSPHATE (*pentasodium triphosphate*)

ISO 850 – Determination of matter insoluble in water.

ISO 851 – Measurement of pH – Potentiometric method.

ISO 3000 – Estimation of tripolyphosphate content – Tris(ethylenediamine) cobalt(III) chloride gravimetric method.

SODIUM PYROPHOSPHATE AND SODIUM TRIPOLYPHOSPHATE (*tetrasodium diphosphate and pentasodium triphosphate*)

ISO 852 – Determination of iron content – 2,2'-Bipyridyl photometric method.

ISO 853 – Determination of loss on ignition.

ISO 2996 – Determination of particle size distribution by mechanical sieving.

ISO 2998 – Determination of orthophosphate content – Photometric method using the reduced molybdophosphate.

ISO 3357 – Determination of total phosphorus(V) oxide content – Quinoline phosphomolybdate gravimetric method.

ISO 3358 – Separation by column chromatography and determination of the different phosphate forms.