151. *The Composition of the " Strong " Phosphoric Acids.*

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A study of the composition of the " strong " phosphoric acids between the range 67·4—89·4% of phosphoric oxide has largely confirmed Parks and Van Wazer's reorganisation theory (based on a flexible chain model).[1] The ion-exchange chromatographic method used permitted separation of linear phosphoric acid polymers containing up to 14 phosphorus atoms in the chain, and some evidence for the formation of ring polymers was found in the solutions containing more than 86·1% of phosphoric oxide. The present results also indicate no essential change in the composition at the concentration of phosphoric oxide equivalent to $(HPO_3)_n$, *i.e.*, at 88·7%, and it is thus possible that the small-ring polymers found are only formed from more complicated ring and branched-chain polymers by hydrolysis during the preparation of the sample for analysis.

EQUILIBRIUM mixtures of phosphoric oxide and water containing more than 72·4% of phosphoric oxide, the so-called " strong " phosphoric acids,* have been shown by earlier workers[2] to be equilibrium mixtures of various linear polymeric species of the form $H_{n+2}P_nO_{3n+1}$. The first important attempt to analyse the mixtures was by Bell,[3] who used wet-chemical methods, but these methods are limited to very short chain-length polymers, up to the triphosphate. Paper chromatography has been employed by several workers,

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* The term " strong phosphoric acids " used in this Paper has a special significance in that it refers to those mixtures of phosphoric oxide and water that contain more phosphoric oxide than is required for the formation of orthophosphoric acid, and does not refer to the concentration of hydrogen ion.

[1] Parks and Van Wazer, *J. Amer. Chem. Soc.*, 1957, **79**, 4890.

[2] Thilo, *Chem. Tech.* (*Berlin*), 1956, **8**, 251, and references therein.

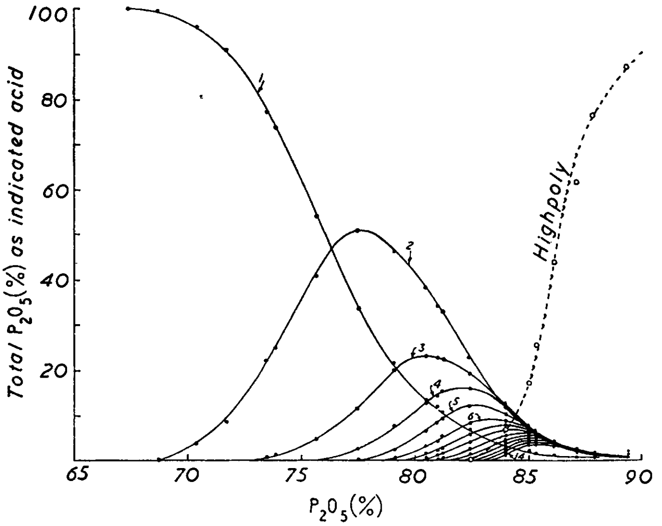
[3] Bell, *Ind. Eng. Chem.*, 1948, **40**, 1464.

and a complete analysis by this method was given by Huhti and Gartaganis [4] covering the series up to nonaphosphoric acid.

Anion-exchange was developed by Beukenkamp, Rieman III, and Lindenbaum [5] and by Higgins and Baldwin,[6] and data for the system were also given by Ohashi and Sugatani.[7] The method has also been developed by Busch, Ebel, and Blanck [8] as a means of preparing samples of the free acids up to the octaphosphoric acid. The present work was carried out by using a gradient-elution technique, first proposed by Grande and Beukenkamp,[9] supplemented by ascending one- and two-dimensional paper chromatography.

Other methods that have been suggested include pH titration,[10] infrared spectroscopy,[11] *X*-ray diffraction,[12] and nuclear magnetic resonance,[13] the last three methods having the advantage that the sample is not broken down before analysis, but at present they are relatively insensitive.

FIG. 1. *The composition of the strong phosphoric acids.*



——●—— 1 = Ortho-; 2 = pyro-; 3 = tri-, etc.

– – – ○ – – – Highpoly. = highly polymeric material hydrolysed from column.

During the course of this work, Parks and Van Wazer,[1] using a flexible-chain model, calculated from theoretical considerations the distribution of polymers in the strong phosphoric acids. They assumed the polymers to be entirely of the linear type, and their results are in very close agreement with the present work, except that this work suggests the presence of more complicated structures above *ca.* 81% of phosphoric oxide.

Results.—The results of a series of analyses of the strong phosphoric acids are shown in Table 1 and Fig. 1. A typical elution curve is given in Fig. 2 in order that the degree of separation achieved and the method of estimating the 13th and 14th members of the series can be illustrated. Occasionally a 15th peak in the elution series of straight-chain

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[4] Huhti and Gartaganis, *Canad. J. Chem.*, 1956, **34**, 785, and references therein.

[5] Beukenkamp, Rieman III, and Lindenbaum, *Analyt. Chem.*, 1954, **26**, 505; also Lindenbaum, Peters, and Rieman III, *Analyt. Chim. Acta*, 1954, **11**, 530, and Peters and Rieman III, *ibid.*, 1956, **14**, 131.

[6] Higgins and Baldwin, *Analyt. Chem.*, 1955, **27**, 1780.

[7] Ohashi and Sugatani, *Bull. Chem. Soc. Japan*, 1957, **30**, 864.

[8] Busch, Ebel, and Blanck, *Bull. Soc. chim. France*, 1957, 486.

[9] Grande and Beukenkamp, *Analyt. Chem.*, 1956, **28**, 1497.

[10] Van Wazer, Griffith, and McCullough, *ibid.*, 1954, **26**, 1755.

[11] Corbridge and Lowe, *ibid.*, 1955, **27**, 1383.

[12] Mabis and Quimby, *ibid.*, 1953, **25**, 1814.

[13] Callis, Van Wazer, and Shoolery, *ibid.*, 1956, **28**, 269.

TABLE 1. *Composition of the strong phosphoric acids.*

Total P_2O_5 (%) *	$[P_2O_5]/[H_2O]$	Percentage composition in terms of the constituent polyphosphoric acids.† 1	2	3	4	5	6	7	8	9	10	11	12	13	14	High-poly.	Tri-meta-	Tetra-meta-
67·4 [a]	0·263	100·0																
68·7 [a]	0·279	99·7	0·33															
70·4 [a]	0·302	96·2	3·85															
71·7 [a]	0·321	91·0	8·86	tr.														
73·5 [a]	0·352	77·1	22·1	0·79														
73·9 [b]	0·360	73·6	25·1	1·34														
75·7 [b]	0·394	53·9	40·7	4·86	0·46													
77·5 [a]	0·438	33·5	50·6	11·5	2·68	0·74	tr.											
79·1 [a]	0·481	22·1	46·3	20·3	7·82	2·26	1·02	0·34										
80·5 [b]	0·523	13·8	38·2	23·0	13·0	6·86	3·38	1·67	1·03	0·22								
81·0 [b]	0·542	12·2	34·0	22·7	14·6	8·42	4·36	2·27	1·41	0·56	tr.							
81·2 [b]	0·549	10·9	32·9	22·3	15·0	9·36	5·41	2·85	1·75	0·97	0·36	0·05						
82·4 [a]	0·594	7·32	23·0	19·3	15·9	12·3	8·21	5·73	3·89	2·52	1·36	0·91	0·14			tr.		
84·0 [a]	0·667	3·92	11·8	12·7	12·0	10·5	8·97	7·99	6·62	5·63	4·54	3·72	3·03	2·46	1·68	6·63		
85·0 [b]	0·717	2·28	6·36	7·32	8·01	8·17	7·67	7·22	6·93	6·42	5·89	5·27	4·69	3·99	3·83	16·9		
85·3 [a]	0·736	1·87	4·73	6·33	6·58	6·66	6·71	6·36	6·11	5·88	5·46	5·07	4·90	4·64	4·38	25·6		
86·1 [b]	0·787	1·46	2·81	3·74	4·43	4·52	4·77	4·79	4·93	4·67	4·54	4·67	4·63	4·38	4·17	43·5	0·17	
87·1 [b]	0·860	0·83	1·81	2·17	2·53	3·09	3·39	3·46	3·33	3·55	3·47	3·45	3·52	3·26	3·24	61·1	tr.	
87·9 [b]	0·920	0·50	0·82	1·56	1·76	1·72	2·03	2·13	2·26	2·07	2·26	2·06	2·20	1·99	2·30	76·4	0·42	0·11
89·4 [b]	1·066	1·88	1·52	0·77	0·61	0·62	0·68	0·54	0·71	0·86	1·03	0·98	1·16	1·23	1·37	86·8	1·17	0·41

* [a] Prepared by dehydration of orthophosphoric acid; [b] prepared by dissolving phosphoric oxide in orthophosphoric acid.

† 1 = Ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-phosphate, etc.; highpoly. = material retained by resin and includes the 15-phosphoric acid when this was separated.

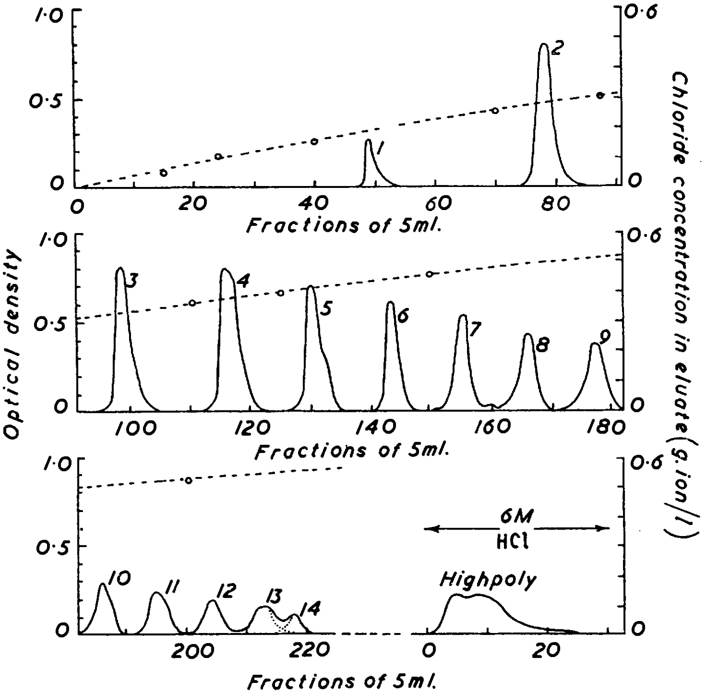
TABLE 2. *Composition of the hydrolysis products of the highly polymeric phosphates retained by the resin, analysed by paper chromatography.*

Total P_2O_5 (%)	Constituent acids (%) Ortho-	Pyro-	Trimeta-	Tetrameta-
84·0	95·2	4·8	—	—
85·0	86·8	12·8	0·4	tr.
85·3	93·7	6·3	tr.	—
86·1	82·2	17·2	0·5	0·1
87·1	84·3	15·3	0·4	tr.
87·9	86·4	12·6	0·9	0·1
89·4	80·7	16·6	2·3	0·4

TABLE 3. *Eluting solutions (quantities for* 1 *l. of solution).*

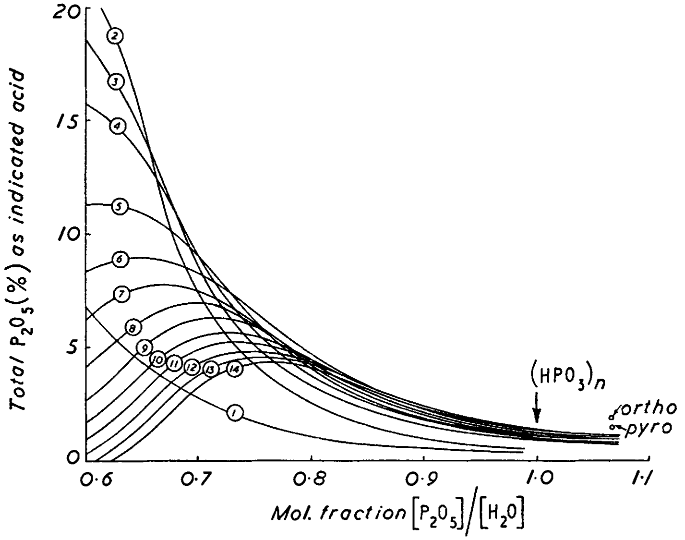
Solution	Potassium chloride (g.)	Potassium formate (g.)	Formic acid (ml.)	25% Aqueous ammonia
(i)	74·5	6·3	2·5	Until the pH = 5·5
(ii)	63·4	5·5	2·0	
(iii)	55·8	4·2	2·0	

FIG. 2. *A typical elution curve.*



1 = Ortho-; 2 = pyro-; 3 = tri-, etc.
———— % of P_2O_5 in terms of optical density (molybdenum blue; 830 mμ).
---○--- chloride content of eluate (g.-ion/l.), theoretical curve and experimental points.

FIG. 3. *Variation of the composition of the strong phosphoric acids with the mol. fraction* $[P_2O_5]/[H_2O]$.



1 = Ortho-; 2 = pyro-; 3 = tri-, etc.
Experimental points omitted for clarity.

polymers was obtained, but in general, a sharp cut-off in the series occurred at a chain length of 12—14 phosphate units according to the resin used. Higher polymers required hydrolysis on the column with 6M-hydrochloric acid before they could be eluted.

The result indicated by Huhti and Gartaganis,[4] namely, that the concentration of all the lower polymers tend to zero at the composition representing $(HPO_3)_n$, *i.e.*, 88·7% of phosphoric oxide, is not supported. In fact, the results show no discontinuity at this point, as is illustrated in Fig. 3. However, the possibility that the lower chains indicated at these high concentrations of phosphoric oxide are only produced during the preparation of the sample for analysis or on the column by hydrolysis cannot be ruled out.

Occasionally the ring polymer trimetaphosphoric acid (I) appeared in the elution series, and sometimes a trace of tetrametaphosphoric acid (II) was indicated (Table 1). Since, however, hydrolysis on the column of the highly polymeric material obtained above about 82·4% of phosphoric oxide led to the formation of these compounds (paper chromatography of the eluate, Table 2) it is probable that they are not present in the form of simple compounds, but are the hydrolysis products of more complex compounds. The relatively high concentration of ortho- and pyro-phosphoric acids found in the solution containing 89·4% of phosphoric oxide also suggests fairly extensive hydrolysis of this material (Table 1).

DISCUSSION

Nature of the Elution Curves.—The sharp cut-off in the elution series at the 12—15th member is almost certainly a molecular-sieve effect as suggested by Van Wazer.[14] The gradient-elution technique used in this work would be expected to enhance any such effect, as it causes continual shrinkage of the resin as the run proceeds and also cuts the amount of " tailing " of each fraction. Further support is also obtained from the fact that the cut-off varies with the type of resin used, and this probably explains why Ohashi and Sugatani [7] failed to find evidence for more than the tetraphosphoric acid in their work.

Nature of the Strong Phosphoric Acids.—The present results support the conclusions of earlier workers [2-4] in indicating that the composition of the strong phosphoric acids is a function of the phosphoric oxide concentration and not of the method of formation, the solutions having been prepared both by concentrating orthophosphoric acid by evaporation and by dissolving anhydrous phosphoric oxide in syrupy phosphoric acid. Contrary to the work of Huhti and Gartaganis,[4] the present work suggests that the formula $(HPO_3)_n$ has no physical or chemical significance. The former authors show that the concentration of the lower members of the series, up to the nonaphosphoric acid, tends to zero at 88·7% of phosphoric oxide, whereas the results shown in Table 1 and Figs. 1 and 3 suggest a persistence of these polymers beyond this point. Thus the formula $(HPO_3)_n$ cannot represent the presence of only extremely long polymers of the type $H_{n+2}P_nO_{3n+1}$ where $n \longrightarrow \infty$, but must be a mixture that also contains more complex structures. Also the presence of tri- and tetra-metaphosphoric acids in the solutions of high phosphoric oxide content and in the hydrolysis products of the highly polymeric species retained by the resin suggests that these complex materials are based on ring-containing compounds. Thilo and Sauer,[15] using paper chromatography, have also shown that materials containing more than 90% of phosphoric oxide give rise to substantial quantities of trimetaphosphoric acid and traces of tetrametaphosphoric acid. Further evidence for the continuity of the system is found in the work of Tarbutton and Deming,[16] who show that the system phosphoric oxide–water is azeotropic with a maximum in the boiling point occurring at a concentration of 92% of phosphoric oxide.

The complex ring compounds could arise *via* two main mechanisms: either by the partial hydrolysis of the P_4O_{10} molecule, perhaps by long-chain acids instead of by water, or by extensive cross-linking of the linear and branched chain polymers.

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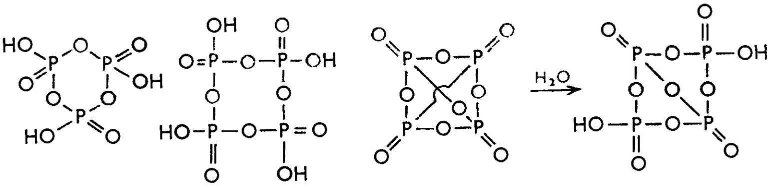
[14] Van Wazer, personal communication.
[15] Thilo and Sauer, *J. prakt. Chem.*, 1957, **4**, 324.
[16] Tarbutton and Deming, *J. Amer. Chem. Soc.*, 1950, **72**, 2086.

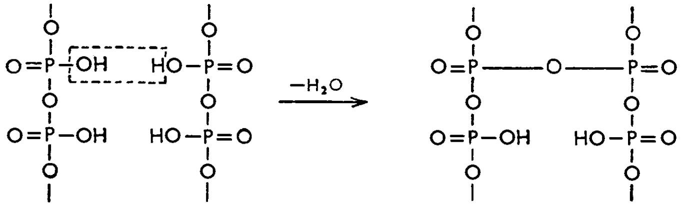
The hydrolysis of phosphoric oxide probably follows the scheme:



(I), $(HPO_3)_3$ (II), $(HPO_3)_4$ (P_4O_{10}) ($H_2P_4O_{11}$)

the next stage resulting in the formation of either a six-membered trimetaphosphate ring or an eight-membered tetrametaphosphate ring, according to which P–O–P link is next to be broken (of the five P–O–P links, four of them are identical, and any one of these will give the trimetaphosphate ring on hydrolysis, whereas the fifth and more anhydrous link will give the tetrametaphosphate product). The actual ratio of tri- to tetra-metaphosphate produced in such a reaction would be difficult to obtain as the greater stability of the trimetaphosphate ring makes its detection easier. The amount of " free water " in the concentrated solutions is very low (Parks and Van Wazer,[1] Huhti and Gartaganis,[4] and Ohashi and Sugatani [7]) and it could thus well be that the hydrolysis is effected by long-chain phosphoric acids instead of by water, leading to the formation of even more complex compounds. The first stages of the hydrolysis would thus give rise to extremely unstable compounds containing more phosphoric oxide than is permitted by the formula $(HPO_3)_n$, although their presence cannot be demonstrated by any method that involves dilution of the original material. That they exist is suggested, however, by the presence of their hydrolysis products and by the work of Brown and Whitt [17] on the vapour phase. These authors concluded that the vapour above the strong phosphoric acids consists mainly of P_4O_{10} molecules with some water vapour, basing their conclusions on vapour-density measurements made at 1020°, but the relatively high temperature employed could have led to considerable dissociation. It seems highly improbable that the P_4O_{10} molecules would dissolve unchanged, especially in the more dilute solutions.

It has been suggested by Thilo and Sauer [15] that cross-linking of the long-chain polymers can take place as follows:



this reaction leading to the formation of compounds in the form of a large three-dimensional network, and with the required high phosphoric oxide content. It is believed that any side-chain polymers that might be formed in this way would defy detection by methods such as have been employed here (Van Wazer and Holst [18]), but extensive cross-linking might well lead to the formation of the more stable tri- and tetra-metaphosphate rings, which could be detected. However, as Thilo and Sauer [15] have pointed out, hydrolysis of such materials would also give rise to high results for linear polymers of intermediate chain-length, and this effect has not been noted either in this work or in that of Huhti and Gartaganis.[4] This mechanism would also seem less likely to lead to a system in which the vapour had only a very low concentration of polymeric acids, but a

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[17] Brown and Whitt, *Ind. Eng. Chem.*, 1952, **44**, 615.

[18] Van Wazer and Holst, *J. Amer. Chem. Soc.*, 1950, **72**, 639.

high concentration of unchanged P_4O_{10} molecules (Brown and Whitt[17]), although extrapolation of these data (at 1020°) to room temperature may not be justified.

In the lower concentration range, Parks and Van Wazer's theoretical calculations[1] would appear to be confirmed, in many cases better than has been shown previously by paper chromatography.[4,7] In the higher range the inherent experimental error makes the deviation insignificant, although a certain amount of discrepancy is to be expected on the basis of the ideas discussed above.

EXPERIMENTAL

Preparation of the Acids.—Two methods were used to prepare the strong phosphoric acids: (*a*) Samples of " AnalaR " orthophosphoric acid were dehydrated by heating to temperatures up to 400° in a platinum crucible and then allowed to cool in a vacuum-desiccator (without desiccant) and left for 5—10 days before analysis, and (*b*) anhydrous phosphoric oxide was dissolved in " AnalaR " phosphoric acid to give the required mixture and heated in order to obtain a uniform melt, the sample then being allowed to cool as in (*a*).

The higher acids became opaque and crystallised when kept for longer periods, but only the one-phase syrups or glasses were analysed in order to circumvent any complications that may have arisen when more than one phase was present. The method used for each sample is indicated in Table 1.

Preparation of the Solutions for Analysis.—The acid was first cooled to −5° and then, by means of a glass rod, a small quantity was removed and dissolved in about 10 ml. of ice-cold 0·5M-sodium hydroxide solution. The final mixture was alkaline to phenolphthalein. A further weighed quantity of the acid was hydrolysed to orthophosphoric acid by boiling with 0·3M-perchloric acid, and the total phosphate (in terms of phosphoric oxide, P_2O_5) estimated by titration of a suitable aliquot portion with bismuthyl perchlorate (see below).

Paper Chromatography.—Ebel's two-dimensional technique[20] and Huhti and Gartaganis's ascending method[4] were employed. The solvents were those described by Ebel[20] and specially treated Whatman No. 1 chromatographic paper was used. The paper had first been washed with a 3% solution of EDTA (disodium salt) and then several times with distilled water and dried. This treatment was necessary in order to remove traces of alkaline-earth metals from the paper as these cause serious streaking of the chromatogram by forming complexes with the polyphosphoric acids and with the paper.

Preparation of Resins.—The resins used in the chromatographic analyses were of the strongly basic, quaternary ammonium type and two main varieties were used: (*a*) De-Acidite FF with a water regain of 1·36 g. per g. of the chloride form, and (*b*) De-Acidite FF with a water regain of 1·66. Both resins were of 100—200 mesh and were specially supplied by the Permutit Company Ltd. Resin (*b*) gave the best results except for the very concentrated acids, as these required a stronger eluting solution (see below) which caused too pronounced a shrinking of the resin. Resins with higher water-regains were also tried but the extensive shrinkage and tendency to break up into finer particles during a run made them impracticable. Another resin, Amberlite C.G. 400-I, was also used, but was not so efficient in separating the higher members, and the elution series usually terminated at about the 11th member.

The resins were first washed with 6M-hydrochloric acid and then with distilled water. The column was then filled with a slurry of the resin in water, and a 1 m. long extension tube of the same diameter as the column was fitted. The column was then back-washed with distilled water at such a rate as to allow the " fines " to be run off the top of the tube. After removal of the " fines," the back-washing was discontinued, and the resin allowed to settle. The extension tube was then removed and the water-level adjusted so as to be just above the resin; the column was then ready for use. This treatment was repeated after every run, since the resin shrank considerably as the run progressed, and the 6M-hydrochloric acid used to complete each separation caused the resin to break up a little.

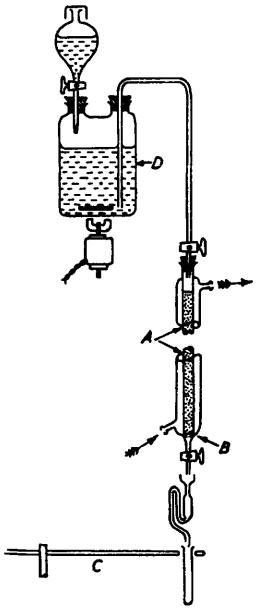
Ion-exchange Chromatography.—The apparatus employed is illustrated in Fig. 4. The columns (*A*) were 75 cm. long and 12 mm. in diameter and fitted with a water-jacket, the resin being supported on a sintered-glass disc (*B*). The fraction collector (*C*) was of the conventional siphon-pipette type, and fractions of 5 or 10 ml. were collected and analysed as outlined below.

A sample of the alkaline test solution, prepared as described above, was introduced by means of a weight-burette to the top of the column, the total phosphate thus added being estimated by analysing another weight-fraction by the colorimetric method described below—not more than 5 mg. of phosphoric oxide were added for each run. The level of the liquid in the column was lowered to the level of the resin, 2 ml. of water added, and the level again adjusted, this procedure being carried out three times. It was necessary to keep the column at about 15° in order to get the best separation, and this was conveniently achieved by circulating tap-water around it. Temperatures of above 30° caused rapid hydrolysis, and below 15° the rate of flow through the column became too low. Lack of temperature control resulted in uneven heating (*e.g.*, by sunlight) and consequent poor separation of the bands.

The run was then commenced with 1 l. of water in the mixing-chamber (*D*) (stirring by means of a magnetic stirrer) and one of the three solutions given in Table 3 in the reservoir: solution (i) for mixtures initially containing more than 84% of phosphoric oxide, solution (ii) for those containing 80—84% of phosphoric oxide, and solution (iii) for those containing less than 80% of phosphoric oxide. Thus, as the run proceeded, so the strength of the elution solution increased (Fig. 2). There was no necessity to collect the first 150 ml. of eluate (see Fig. 2).

The elution was completed in each case with 6M-hydrochloric acid which was kept overnight in the column before the run was completed, thus enabling any highly polymeric material to be hydrolysed (mainly to ortho- and pyro-phosphoric acids, but some ring compounds survived this low-temperature hydrolysis, see Table 2) and removed from the column. Heating the column during this stage was disadvantageous as it caused complete hydrolysis to orthophosphate, thus preventing any information regarding the structure of the highly polymeric acids being obtained, and also increased the extent of the decomposition of the resin, and so was abandoned. About 0·1 ml. samples of the hydrolysate were examined by means of paper chromatography, and the amounts of the component phosphates recorded in Table 2.

FIG. 4. *Apparatus.*



Analysis.—Each fraction was hydrolysed by boiling dilute sulphuric acid, and the phosphoric oxide content estimated by Bolz and Mellon's method,[21] based on the hydrazine reduction of phosphomolybdate, optical densities being measured in 1-cm. glass cells at 830 $m\mu$ in a "Unicam" spectrophotometer and converted into mg. of phosphoric oxide by means of a calibration graph.

Paper chromatograms were first sprayed with a molybdate solution of the type recommended by Hanes and Isherwood,[22] and the spots then brought up by exposure to ultraviolet light. For quantitative work, the spots were then cut out and the phosphate leached out with ammonia solution and estimated as above; other portions of the same sheet were used in order to obtain a blank correction.

The phosphoric oxide contents of the original polyphosphoric acid mixtures were estimated, after hydrolysis with perchloric acid (see above), by the method of Salmon and Terrey [19] (titration with bismuthyl perchlorate with thiourea as indicator).

Occasional checks on the chloride content of the eluate were made and compared with the calculated values (Fig. 2).

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[19] Salmon and Terrey, *J.*, 1950, 2813.
[20] Ebel, *Bull. Soc. chim. France*, 1953, 998, 1085, 1089.
[21] Bolz and Mellon, *Ind. Eng. Chem. Anal.*, 1947, **19**, 873.
[22] Hanes and Isherwood, *Nature*, 1949, **164**, 1107.