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Ion-exchange Chromatographic Analysis on the Chain Length of Polyphosphate Products

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The ion-exchange chromatographic technique was used in order to find the average chain number of a polyphosphate product. For the assignment of the *n*th polymer in the obtained chromatogram, the dependence of the distribution coefficient, K_d, on the eluent concentration examined by the use of both 20-cm and 60-cm resin columns. A lower series of polyphosphate was included in a relatively large amount in order that the average chain number based on the chromatographic analysis could be duly appreciated only for the case of basic polymers with lower molecular weights. For a product "Graham Salt" with a number of phosphate links, the higher series of polyphosphate could not be desorbed entirely from the resin column; the accurate estimation of the average number was, then, improbable. The viscosity method is also not advisable to use the computation of a mean polymerization number in the polyphosphate with a low molecular weight. An attempt was made to improve the data on the average chain number by the viscosity measurements together with the chromatographic analysis of the polymer constituent.

Among the wide range of industrial applications of the condensed polyphosphate[1,2] its use as an inorganic high polymer, soluble in water and inert to redox chemical reagents, is of great interest for promise and it holds of a possible improvement in the natural products in both the solid and dispersion phases. In order to have a correct understanding of its polymer structure, the knowledge of the chemical composition of a polyphosphate product is indispensable for physical and chemical research into the characteristic properties of this material. Paper chromatographic analysis is a convenient tool for the detection of the constituent members in a polyphosphate product;[3-5] nevertheless, the obtained result offers only a perspective on qualitative or semi-quantitative analysis. In this work, a microamount of an ingredient in the polyphosphate was examined in the presence of an excess of a major component by the ion-exchange chromatographic technique, which makes it possible to treat several hundred milligrams of the sample in order to obtain more detailed information on the chemical composition.[6] A large number

1) S. Ueda, *Denki Kagaku*, **30**, 798 (1962).

2) Van Wazer, "Phosphorus and Its Compounds, Vol. 1, Interscience Pub., New York, (1958).

3) H. Hettler, *J. Chromatogr.*, **1**, 389 (1956).

4) H. Huhti and P. A. Gartagams, *Can. J. Chem.*, **34**, 785 (1956).

5) S. Ohashi, "Handbook of Inorganic Chem. (Muki Kagaku Zensho)," Maruzen Pub., Tokyo (1965); *Kagaku to Kogyo*, **22**, 878 (1969).

of works have been published on the analytical procedure, studying the conditions to be used in separating the constituent members of polyphosphate by means of ion-exchange chromatography;[5-10] however, few of them have dealt with the distribution of the constituent species. The conventional degree of polymerization in a polyphosphate product is evaluated as a mean value on the basis of the molar ratio in a mixture of the monobasic salt of $M^{I}H_2PO_4$ and the dibasic salt of $M^{I}_2HPO_4$ taken as starting materials, although the true degree of polymerization is far different, depending on the conditions of the synthesis, particularly on the temperature and the time of dehydration.

In the course of our studies of the hot atom and the radiation chemistry of polyphosphate in the aqueous phase and in the solid glassy state,[11] a hundred various samples were dealt with. The data resulting from the analysis of the phosphates, detected as resolved constituent members, will be summarized; they subtantiate, from the analytical point of view, the polymer structure of the condensed phosphate, using its molecular weight and polymerization number as an average.

Experimental

Reagent and Materials. For the purification of sodium triphosphate, a commercial anhydrate product which was 80% pure was used as the starting material. Purification by recrystallization[2] was carried out from an aqueous solution consisting of 20% ethyl alcohol; the procedure was repeated five times. The anhydrate polyphosphates were prepared from a mixture of monophosphates, dibasic sodium dihydrate salt, and monobasic sodium decahydrate salt by pyrosynthesis with a temperature-controlled electric-muffle furnace. A chelate triphosphate of the divalent metallic cation was obtained by the precipitation method. A hot clear solution containing one equivalent of the metallic ion and two equivalents of the triphosphate ion separates out when a chelate salt with the composition of $Na_6M^{II}(H_2P_3O_{10})_2$ is cooled. The ammonium triphosphate was obtained by the cation-exchange method through a column of ammonium-form resin, while the ammonium salt was precipitated by the addition of alcohol, as was in the precipitation of sodium salt. All the other chemical reagents used were of an analytical grade.

Chemical Analysis. For the chemical analysis, from 20 to 1000 mg of the sample were dissolved in 5 to 25 m*l* of distilled water, out of which 1 or 2 m*l* was adsorbed on a Dowex 1×8 anion-exchange resin column. The gradient elution technique described in a published paper[6] was used in the chromatographic development of polyphosphate species. Each 5- or 10-m*l* fraction of the eluates from the resin column was subjected to the colorimetry of the phosphate by the molybdenum blue method using a red filter (Madzuda VR-1 filter). A fractionated aliquot sample should be diluted for color development when the fraction is too concentrated with phosphate.

Viscosity Measurements. An Ubellohde-type viscosimeter of 1 to 5 centi-Stokes was used for the viscosity measurements. The temperature was controlled by a thermostat at 25.00 ± 0.05°C for all the measurements. In order to obtain reproducible data, the hydrolysis of the unstable branch-points in the polyphosphate glass should be completed before the measurements by keeping the sample solution for 12 hr. According to our preliminary examination,[12] the anion species of a supporting electrolyte little affected the reduced viscosity of a sample solution. In the present work, 0.035 N sodium chloride was, therefore, employed in place of bromide. In the medium containing 0.035 N NaCl or NaBr, the reduced viscosity is regarded as constant no matter what the concentration of the phosphate is, and the intrinsic viscosity was determined by the standard of 1 g/100 m*l* phosphate solution according to this equation:

$$[\eta] = K \cdot M$$

where K is a constant based on the light scattering data given by 1.76×10^{-5} M^{-1},[13] and where M is the average molecular weight to be computed.

Results

1. Analysis of Short-chain Members. The chromatographic development of orthophosphate, pyrophosphate, and triphosphate can be effcted in an excellent resolution by using as the eluent a potassium chloride solution whose concentration is raised in an exponential-gradient form. At a certain stage of elution the effluent has a concentration of KCl, C being given by (1).[14]

$$C = C_0 + (C_r - C_0)(1 - \exp[-V_f/V_0]) \quad (1)$$

In Eq. (1) C_0 is the starting concentration of KCl in the mixing bottle of V_0 m*l* and C_r is the concentration of KCl in the reservoir joined to the mixing bottle for the supply of a concentrated eluent solution. For the purpose of the impurity analysis of a purified triphosphate hexahydrate sample, the parameters in Eq. (1) were 2×10^{-3}M HCl for C_0 and 0.6 M KCl for C_r; 500 m*l* was the volume for V_0,[6] and as the sample as much as 100 mg of $NaPO_3$ was taken for the adsorption on

6) N. Matsuura and K. Kyokawa, *Bunseki Kagaku*, **16**, 612 (1967).
7) F. H. Pollard, G. N. Nickless and M. T. Rothwell, *J. Chromatogr.*, **27**, 214 (1967).
8) F. H. Pollard and R. F. Jameson, *J. Chem. Soc.*, **1959**, 752.
9) M. Kobayashi, *Kogyo Kagaku Zashi*, **69**, 2071 (1966); **70**, 1097 (1967).
10) N. Shiraishi and T. Iba, *Bunseki Kagaku*, **13**, 883 (1964).
11) N. Matsuura, N. Shinohara and C. K. Lin, *J. Inorg. Nucl. Chem.*, **24**, 1252 (1969).
12) R. C. Mehrotra and V. S. Gupta, *J. Polym. Sci.*, **55**, 81 (1961).
13) U. P. Strauss, E. H. Smith and P. L. Wineman, *J. Amer. Chem. Soc.*, **75**, 3935 (1953).
14) L. E. Netherton, A. R. Wheath and D. N. Berhart, *Anal. Chem.*, **27**, 214 (1955).

a 20-cm resin column. The developed pattern, as is illustrated in Fig. 1, demonstrates that three peaks are located about equidistantly apart, even though the highest peak of the major component (triphosphate) is present thousand times in excess. In the analysis of a commercial product of triphosphate, a very small amount of the sample is required; for example, two mg or less is sufficient for an accurate analysis. However, for assaying the impurities of polyphosphate present in an orthophosphate sample, the tailing of the precedent peak interferes with the accurate computation of the nearest neighbor, as is shown in Fig. 2. The results of the impurity analysis of

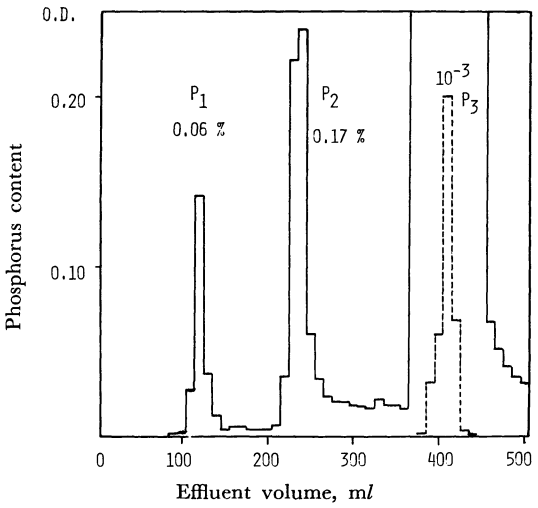

Fig. 1. Impurities in $Na_5P_3O_{10}\cdot 6H_2O$. Chromatogram developed through 20 cm resin column of Dowex 1×8 by KCl solution in exponential gradient concentration of 2×10^{-3} M to 0.6 M Each fraction: 10 ml, sample taken: 53.2 mg.

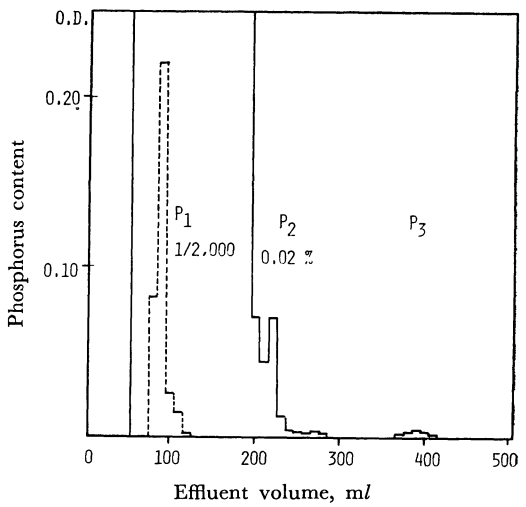

Fig. 2. Ion-exchange chromatogram of $NaHPO_4\cdot 12H_2O$ developed under the same condition as Fig. 1, sample taken: 42 mg.

triphosphate products are summarized in Table 1. A considerable amount of monophosphate is included as an impurity in a variety of triphosphate products, probably because the chemical treatment of repeated dissolutions and precipitations brings about a partial degradation of the triphosphate products.

2. Standardization of Polyphosphate Analysis. The separation of polyphosphates into their components can be achieved by anion-exchange chromatography according to their step-by-step rising negative charge on the $H_2P_nO_{3n+1}^{n-}$ ion. The resolution among them depends on the partition of polyphosphate between the resin and liquid phases, and its distribution coefficient, K_d, is defined by Eq. (2):[15]

TABLE 1. COMPOSITION ANALYSIS OF TRIPOLYPHOSPHATE AND PYROPHOSPHATE PRODUCTS IN P% UNIT

Sample	Phosphate species				
	P_1, %	P_2, %	P_3, %	$P_{4,5}$, %	$P_{6,}$ *etc.*
$Na_5P_3O_{10}\cdot 6H_2O$	0.035	0.163	99.8	0.026	0.011
$Na_5P_3O_{10}$	0.50	8.07	87.25	0.95	3.23
Commercial triphosphate	3.60	47.61	41.77	7.02	0.0
$(NH_4)_5P_3O_{10}$*	0.06	0.19	99.6	0.15	0.02
$Na_8Mn(P_3O_{10})_2$**	0.77	1.05	97.7	0.38	0.08
$Na_8Co(P_3O_{10})_2$**	1.56	5.11	93.0	0.30	0.0
Commercial metaphosphoric acid	13.5	17.4	13.8	24.6	30.7
$Na_4P_2O_7\cdot 10H_2O$	0.10	99.8	0.05	0.03	0.01
$Na_4P_2O_7$	0.20	96.75	1.69	1.36	—

* Prepared by substitution of sodium ion with ammonium ion on the ammonium ion form cation exchange-resin.

** Precipitated from the solution containing 1 mol of manganese chloride and and 2 mol of sodium triphosphate hexahydrate with 20% alcohol and crystallized from hot water.

15) S. Ohashi, K. Koguchi and H. Waki, *J. Chromatogr.*, **25**, 398 (1968).

$$K_d = (V_f - V_m)/(V_b - V_m) \quad (2)$$

The effluent volume, V_f, at a break-through point was determined from the appearance of a concentration peak, while the holding-up volume, V_m, in the column was measured by pouring 2 N hydrochloric acid through the column until the indicator added to the recipient changed color. Since the total resin-bed volume, V_b, is given by our experimental conditions, the net volume of the charged resin is, then found to be $(V_b - V_m)$ by measuring the difference. In our routine work, both 20 cm- and 60-cm columns were employed in comparing the results in detail, assuming $V_m =$ 10 ml for the first and 30 ml for the second.

As Beukenkampf *et al*,[16] have pointed out, the K_d value of a polyphosphate ion species, $H_2P_nO_{3n+1}^{n-}$, obeys the rule of n-power inverse proportionality with regard to the chloride concentration, [Cl⁻], in the exchange reaction (3):

$$R_n(H_2P_nO_{3n+1}) + Cl^- = n \cdot RCl + H_2P_nO_{3n+1}^{n-} \quad (3)$$

This rule is a valuable guide for determining the polymerization number, $\bar{n}$ of the species found in a chromatogram, particularly in the analysis of a polyphosphate sample lacking several members of an unknown $\bar{n}$. To the first approximation, the activity of the chloride in the resin, [RCl], can be regarded as unity, because a greater part of the resin phase is in the form of RCl; therefore:

$$K_d = [R_n(H_2P_nO_{3n+1})]/[H_2P_nO_{3n+1}^{n-}]$$
$$= [RCl]^n/K \cdot [Cl^-]^n = 1/K \cdot [Cl^-]^n$$

or

$$\log K_d = -\log K - n \cdot \log [Cl^-] \quad (4)$$

where K denotes the ion-exchange selectivity coefficient. In accord with this rule, K_d values were obtained from the data on the gradient elution of a polyphosphate sample with the mean-chain number of ten, as is shown in Table 2. The agreement is surprisingly good; a constant value of 0.15 ± 0.03 was obtained for the sum $(\log K_d + n \cdot \log[Cl^-])$ if a non-integer number of polymerization is allowed to serve for the assignment of the nth polymer of a suspicious peak, very close to a distinct maximum, as is shown in Fig. 3.

However, a negative deviation of the calculated n in Eq. (4) was observed in the data by the use of a 60-cm column charged with Dowex 1×4, especially for higher members of polyphosphate, even though the agreement is quite excellent for the first three members, ortho-, pyro-, and triphosphates. A picture of the chromatogram pattern of the same sample developed through the use of a 60-cm resin column is shown in Fig. 4. In so far as we have observed, it is likely that the unfavored conditions are related to the incomplete attainment of the exchange equilibrium, involving a shift of the K_d value to the negative side by the use of the 60-cm column.

By taking the polyphosphate sample with a mean chain number of ten as the standard reference, two products of polyphosphate with six and twenty links of phosphate were tested in order to find if the mean chain number coincides with the average composition of polyphosphate obtained from the chromatographic data. As is shown in Figs. 5—7, the largest peak lies at nearly the effluent volume corresponding to its mean chain number, while the distribution of the members is

Table 2. Distribution coefficient, $K_d = (V_f - V_m)/(V_b - V_m)$, of polyphosphates on 20-cm anion exchange resin column Dowex 1×8

Peak number (assumed chain no.)	Retention volume V_f ml	K_d	[Cl⁻] M	$\log K_d + n \cdot \log [Cl^-]$ (calculated for assumed chain number)
1	90	8.0	0.17	0.13
2	150	14.0	0.26	0.10
3	245	23.5	0.39	0.14
4	310	30.0	0.46	0.13
5	325	31.5	0.46_2	0.14
6 (5.5)*	345	33.5	0.50	0.27 (0.13)**
7 (6.5)*	380	37.0	0.53	0.07 (0.14)**
8 (7)	395	38.5	0.54_5	0.39 (0.18)
9 (7)	405	39.5	0.55_5	0.70 (0.19)
10 (9)	480	47.0	0.62	0.37 (0.17)
11 (10)	510	50.0	0.64	0.39 (0.20)
12 (10)	535	52.5	0.64	0.38 (0.13)
				mean $(0.15_4 \pm 0.03)$**

* No distinct peaks.

** Calculated for well unresolved peaks under assumption of a half-integer polymer chain number.

16) J. Beukenkampf, W. Rieman and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954).

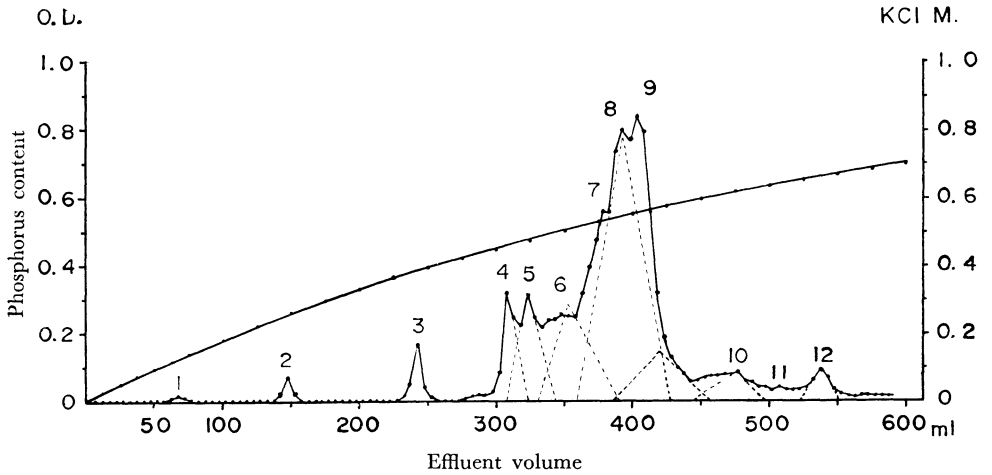

Fig. 3. Chromatogram of sodium polyphosphate with stoichiometric mean chain number of ten, developed through 20 cm resin column of Dowex 1×8.
The peaks, including several inconspicuous ones, are numbered in the order of their appearance and the corresponding nth polymer was assigned to a peak on the basis of of K_d value (see Table 2).
Sample under heat treatment at 800°C for 12 hr.

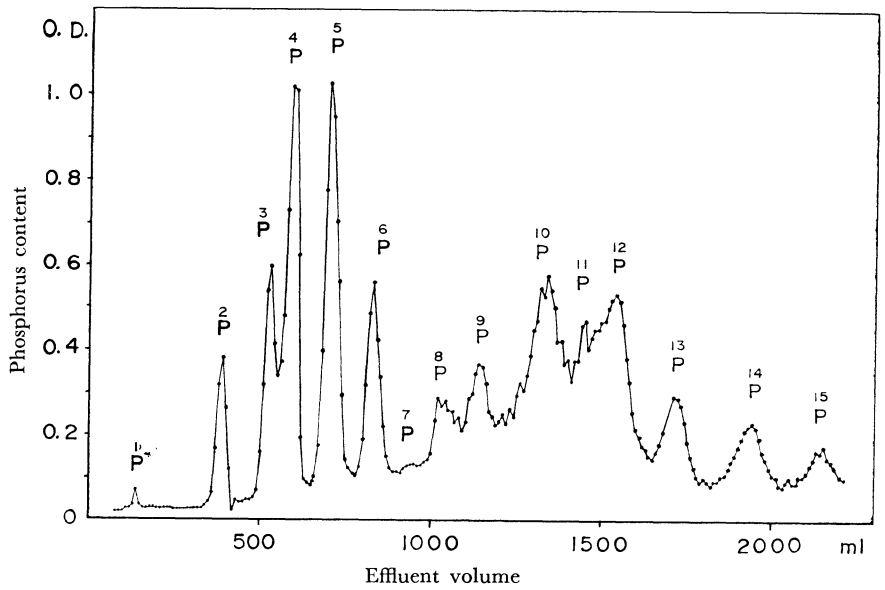

Fig. 4. Chromatogram of sodium polyphosphate with stoichiometric mean chain number of ten, developed through 60 cm column of Dowex 1×4.
Sample prepared under heat at 650°C for 12 hr

not of a Gaussian type. They contained, on the one hand, a considerable amount of low polymers with three to six links and, on the other hand, very high polymers. It should be emphasized here that preparing a polyphosphate with a normalized distribution of polymer components around its mean chain number is very hard, even for a lower polyphosphate product with six to twenty chains which has a melting point lower than long-chain Graham salt.

3. Calculation of the Mean Chain Number from the Chemical Composition. The mean chain number of a polyphosphate product is determined by end-group titration or by the viscosity measurement of its solution as a function of the molecular weight. More directly, the mean $\bar{n}$ can be calculated from the data of chemical analysis. The amount of the constituent members present in a given mean $\bar{n}$ product is evaluated by the colorimetry of Molybdenum-blue in optical-

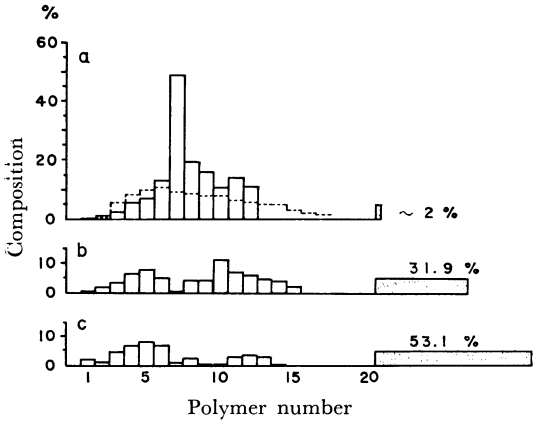

Fig. 5. Comparison of polymer ingredients in polyphosphate products of stoichiometric $\bar{n}=10$, prepared (a) commercial product (b) at 650°C for 12 hr, (c) at 650°C for 1 hr, by chromatographic analysis.

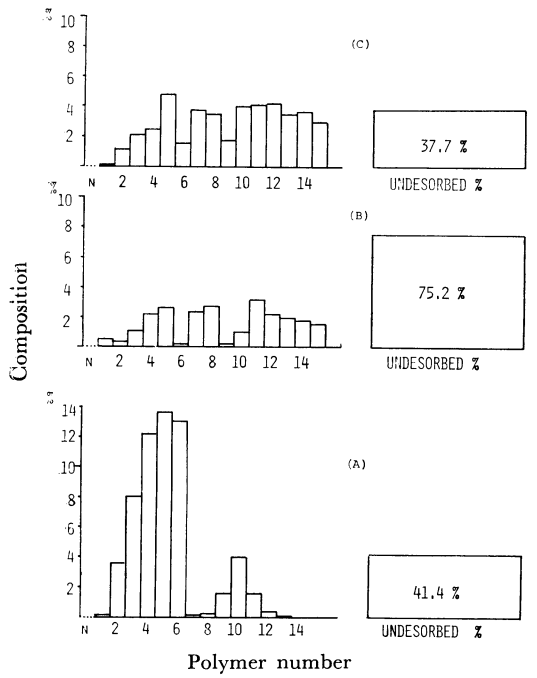

Fig. 6. Composition of polymers in polyphosphate products of $\bar{n}=6$ (A), 20 (B and C), prepared (A) 650°C, 12 hr, (B) 650°C, 1 hr, (C) 650°C 12 hr.

Chromatographic analysis under the same condition as Fig. 5.

density units, denoted here by x_n, which is proportional to the phosphorus content in the resolved nth polymer. The molar abundunce is, then, (x_n/n) for each nth polymer, while the mean value of n for a polyphosphate mixture is described by (5):

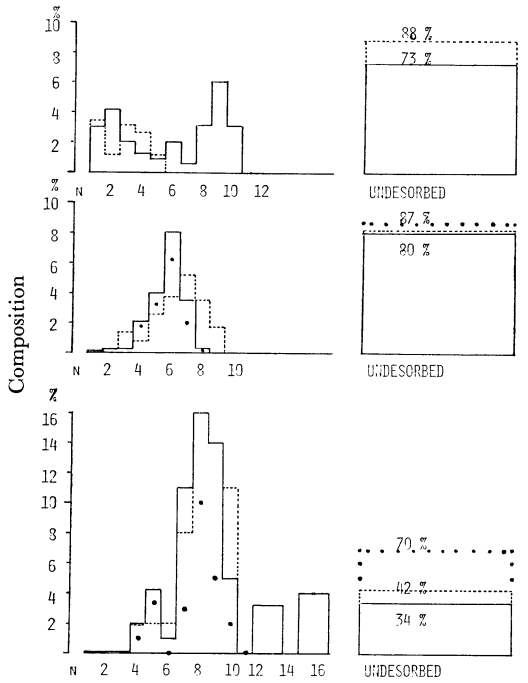

Fig. 7. Composition of polymers in Graham salt, prepared at (A) 800°C 3 hr (B) 850°C 12 hr (C) the sample as (B) irradiated in 2 MW reactor for 20 to 40 min.

Chromatographic analysis under the same condition as Fig. 5 and Fig. 6.

$$\bar{n} = \sum_1^\infty x_n / \sum_1^\infty (x_n/n) = 1/\sum_1^\infty (x_n/n) \qquad (5)$$

In practice, the greater the number of n in (5), the smaller the (x_n/n) value, and the latter value can be ignored in the calculation of the mean $\bar{n}$ value from (5) for uneluted fractions of a very high polymer. This approximation is valid in our case so long as the polyphosphate product has a mean chain length not greater than twenty. However, more than half of the higher members are left uneluted in the analysis of Graham salt. Accordingly, the mean $\bar{n}$ computed from the analysis of a developed chromatogram is surely underestimated, although a lower limit for $\bar{n}$ can be decided by means of the equation expressed in (6), where the suffix below $\bar{n}_l$ indicates the last number of n so far eluted throughout the resin column:

$$\bar{n}_l = \sum_1^l x_n / \sum_1^l (x_n/n) \qquad (6)$$

The calculated $\bar{n}$ values are displayed in Table 3, along with the lower limit, $\bar{n}_l$, as determined by (6), which must serve as a reference for the validity of the estimated $\bar{n}$ values. The difference between the values of $\bar{n}$ estimated under the above assumption and the lower limit, $\bar{n}_l$, is of no problem for a polyphosphate of a small $\bar{n}$, but the disagree-

Table 3. Mean chain number of polyphosphate products

Mixing of (NaH_2PO_4/Na_2HPO_4) molar ratio	Stoichiometric mean no.	Heat °C	Treatment hr	Observed mean number $\bar{n}_c$ chromatography	Observed mean number $\bar{n}$ chromatography	Observed mean number $\bar{n}_v$ viscosity	Uneluted fraction x_f	Mean $\bar{n}$ calculated by (7)
1/2	3	650	12	2.90	(2.90)	u.m.		
2	6	650	12	7.4	(4.4)	u.m.	0.41	
4	10			6.4	(6.3)	18	0.02	6.5
		650	12	9.6	(8.8)	20	0.32	11.5
		650	1	10	(4.7)		0.53	
9	20	650	12	15.4	(10.2)	26	0.38	18.7
		650	1	20	(9.6)		0.52	
Metaphosphoric acid		800	0.5	9.5	(5.0)	58	0.48	15.8
Graham Salt		800	3	11.2	(7.7)	110	0.31	15.6
		800	3	12.7	(7.2)	98	0.42	20.4
		800	3	15.5	(6.5)	89	0.70	37
		850	12	30.5	(6.0)	100	0.82	82
		850	12	62	(4.5)	100	0.93	96
		750	24	40	(5.5)	100	0.86	83
		750	24	65	(4.5)	100	0.93	96

Table 4. Comparison of K_d of phosphorus oxy-acids on anion-exchange resin, Dowex 1×8 (by column method)

Oxidation state phosphorus oxy-acid (Blaser notation[21])	Acetate method: Retention volume V_f, ml	Acetate method: [Ac^-] M	Acetate method: K_d	Acetate method: $K_d \times [Ac^-]$	Chroride method: Retention volume V_f, ml	Chroride method: [Cl^-] M	Chroride method: K_d	Chroride method: $K_d \times [Cl^-]$	Selectivity coefficient ($K_d \times [Ac^-]/K_d \times [Cl^-]$)
$\overset{1}{P}$	100±5*	0.28	19	5.3	60±10*	0.10	5.0	0.50	10.1
$\overset{5}{P}$	180±10*	0.36	35	12.6	80±10*	0.12	7.0	0.84	15
$\overset{3}{P}$	230±10*	0.40	45	18.0	90±10*	0.16	9.0	1.45	12.4
$\overset{4}{P}$-$\overset{4}{P}$	355±10*	0.48	70	33.6	123±5*	0.19	11.3	2.09	16
$\overset{2}{P}$-$\overset{4}{P}$	420±20*	0.52	83	43.2	160±5*	0.23	15	3.45	12.4
									mean 13

* Average deviation of V_f for ten experiments.

ment is conceivable for the Graham salt. For the sake of comparison, the mean chain number, $\bar{n}$, of polyphosphate was computed by means of viscosity measurements; the results are represented in the middle column of Table 3. These data indicate that the viscosity measurements are liable to evaluate too highly the mean $\bar{n}$ number for the lower homologue of polyphosphate. This is probably because the viscosity method is based on the interaction between long-chain polymer molecules and because the contribution of lower polymers to the viscosity is disregarded.

4. Analysis of Oxyphosphorus Acid in a Lower Oxidation State. By the use of a Molybdenum(V)+(VI) reagent[17] incorporated with acid sulfite[18] to facilitate the colorimetry of phosphorus, many oxyphosphorus acids with low oxidation numbers can be observed in a chromatogram developed by the usual method described above. The elution order of the lower oxidation species is: hypophosphite($\overset{1}{P}$), phosphite($\overset{3}{P}$), hypophosphate ($\overset{4}{P}_2$) and diphosphite($\overset{2\ 4}{P\text{-}P}$), and other polymerized oxyphosphorus acids with low oxidation numbers. all these non-polymerized species without bridged oxygen (P–O–P) behave like a monomer species in the chromatography, as is evidenced by the effluent volumes of hypophosphate and diphosphite, which are located very close to that of orthophosphate in the developed chromatographic pattern.

The distribution coefficients, K_d, of this series are shown in Table 4; they have been obtained from the data obtained both on the 20-cm resin column in the chloride form and on the 10-cm column in the acetate form. As may be seen in Table 4, the K_d values on the acetate resin are found to be several times larger than those on the chloride resin. A favorable condition is anticipated by the use of a resin bed in the acetate form from the point of view of mutual separation; however, the ammonium acetate reagent used for elution proved to cause an unadvisable contamination of phosphorus, which increased the reagent blank in our chromatogram. The radiometric technique used as this occasion has, though, caused no trouble, and has provided good results for computing the phosphorus content by means of the radioactivity of ^{32}P. The difference in K_d values between the ammonium acetate and potassium chloride methods can be interpreted in terms of their selectivity coefficients. The results of the comparison of these two methods, shown in Table 4, indicate that the two K_d values differ by the factor, of 13, which is in good agreement with the selectivity coefficient of the acetate ion to the chloride-form resin of Dowex 1×8.[19]

Discussion

As may be seen in Table 1, the commercial products named metaphosphate and metaphosphoric acid and formulated as MPO_3 and HPO_3 respectively, contain polyphosphate in a diverse composition. No PO_3^- ion is substantiated as a stable anion, taking part in the hydrolysis and condensation reactions, although such an ion is frequently assumed to be a transient intermediate in interpreting the kinetic behavior of phosphate derivatives. In general, the polyphosphate anion, $H_2P_nO_{3n+1}^-$, is characterized as a PO_3^- donor in an aqueous medium, while orthophosphate and lower members of polyphosphate behave like PO_3^- acceptors under limited conditions of a strongly dehydrated and acid medium. The identity of the lower polymers of phosphate with three to six links, appearing in considerable yields throughout the hydrolysis process of Graham salt, has been established by several authors.[11,12] It appears likely that there exists a polymer unit with chain or ring numbers of three to six in the intermediate stage of the alkaline hydrolysis of a long-chain polymer, and that a similarity exists in the dehydration of a single phosphate into a polymer. The quite high yields of the lower members in contrast to the low yields of the middle members of polyphosphate, as established in this work, reflect the important role played by the lower polymer in the condensation process. This means that the growth of the chain length needs a certain amount of phosphates with a low polymerization, one of them three to six. This coincides with the fact that the eutectic mixture has a composition corresponding to hexapolyphosphate, with a (NaH_2PO_4/Na_2HPO_4) ratio around two and with a melting point of 550°C. The contribution of the low-members of polyphosphate to the chemical composition was, thus, emphasized in correctly com puting the average number of links in polyphosphate in relation to the structure and the kinetic behavior of polyphosphate. The viscosity data, on the other hand, underestimate this contribution, since the viscosity is mostly decided by the long-chain polymers alone and is little affected by the presence of a solute with a low molecular weight. In view of the above points, and by a combination of two complimentary contributions, a more accurate evaluation of the mean chain number, $\bar{n}$, is possible on the basis of the data of

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the chromatographic analysis as well as those of the viscosity measurement, by the following relation (7):

$$1/n = (1-x_f)/\bar{n}_c + x_f/\bar{n}_v \qquad (7)$$

Equation (7) can be interpreted in terms of $\bar{n}_c$, the mean chain number as computed by chromatographic analysis, and $\bar{n}_v$, that based on the visocity data, where x_f is the fraction of phosphorus content belonging to the high-polymer group that could not be desorbed by our chromatographic technique. The assumption previously introduced for computing a mean $\bar{n}$ from the chromatographic data was that x_f, the high-polymer fraction, was considered to be. On this assumption, the $\bar{n}$ in (7) is exactly equal to $\bar{n}_c$. The results of the computation of $\bar{n}$, represented in the last column of Table 3, provide a reasonable way to correct the discrepancy in the data between those obtained by chromatographic analysis and those obtained by viscosity measurements.