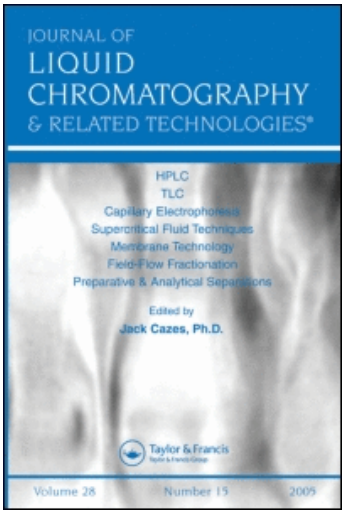

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FRACTIONATION AND CHARACTERIZATION OF INORGANIC LONG-CHAIN POLYPHOSPHATE BY GEL CHROMATOGRAPHY

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ABSTRACT

Inorganic long-chain polyphosphates were fractionated by Sephadex G-100 and G-50 columns. Fractions whose average chain lengths, $\bar{n}$, were 20 - 150 and 10 - 50 were obtained by the G-100 and G-50 columns, respectively. By rechromatography of these fractions, linear relationship was found for the plots of the elution volumes vs. logarithms of the $\bar{n}$ values. By the use of this relationship, chain length distribution analysis could be performed.

INTRODUCTION

Among condensed phosphates, linear phosphates whose chain length, n, range from 2 to several ten thousands form one family. Since these materials contain polyanions which bind metal cations such as calcium ions, they have found widespread applications in industry. The binding characteristic of these anions is dependent on the n value of a sample phosphate. The study of the interaction between these polyphosphate anions and metal cations (1) is expected to give clear insight to polyelectrolyte solution chemistry,

because these anions bear quite crowded negative charges on their molecules. Samples which have various n values will help the understanding of the transition from simple electrolyte to polyelectrolyte.

Preparation of pure samples of tri- and tetraphosphates has been reported (2,3). In order to prepare linear phosphates whose n value is higher than 4, sodium phosphate glass which has a broad chain length distribution has been used as a crude material (4). For a separation purpose, ion-exchange chromatography has been applied to yield pure samples whose n value is up to about 10 (5). Since it is quite difficult to prepare the pure samples whose n value is higher than 10, mixture samples whose chain length distribution is as narrow as possible should be prepared.

Gel chromatography has been applied to fractionations of water-soluble polymers (6). The aim of the present work is to examine the applicability of gel chromatography to fractionation of long-chain polyphosphates. The fractions obtained were analyzed for their $\bar{n}$ values and chain length distributions.

EXPERIMENTAL

Materials

Sodium phosphate glasses were prepared according to the literature (4). The $\bar{n}$ values of these crude materials determined by end group titration method (7) were 113 and 19 for Sephadex G-100 and G-50 systems, respectively. Other reagents were of analytical grade.

Fractionation Procedure

Sephadex G-100 and G-50 columns whose size was ϕ2.6x95 cm were used for the preparative purpose. 0.1 M sodium chloride solution was used as an eluent. Elution flow rate was 0.65 ml/min. Each 0.5 g of sodium phosphate glass sample dissolved in 10 ml of the eluent was applied to the gel column and was eluted. The effluent was divided successively into 18-ml fractions and an $\bar{n}$ value of each fraction was determined by the end group titration method.

Gel Chromatographic Analysis

Sephadex G-100 and G-50 columns whose size was ϕ1.5x30 cm were used for the analytical purpose. Eluent contained 0.1 M sodium chloride, 0.01 M sodium acetate and $5x10^{-4}$ M acetic acid (pH 6). 0.5 ml portions of the fraction samples obtained by the preparative columns were applied to the analytical columns and were eluted. An AutoAnalyzer detector (8,9) was used in order to detect continuously total phosphate concentration in an effluent. It has been reported that the plots of the peak area vs. the amount of polyphosphate give a good linearity (9). Furthermore, it was found that the slopes of the calibration curves are almost equal to each other for the linear phosphate samples whose $\bar{n}$ value is higher than 10 (9).

RESULTS AND DISCUSSTION

Since it took about a half day to accomplish the fractionation with each preparative column, hydrolysis of the sample during elution was examined prior to the fractionation. 0.01 M sample ($\bar{n}$ = 113) solution was allowed to stand at 50°C, and at dayly intervals, a portion of the sample solution was withdrawn to be analyzed by the gel column (Sephadex G-100, ϕ1.5x30 cm). No detectable change in elution profile was observed for three days, which ensured the stability of the samples to hydrolysis during fractionation.

In Fig. 1, representative elution profiles of the sodium phosphate glasses obtained with the preparative Sephadex columns are shown. It can be seen that these samples have a broad distribution. Small peaks appeared at approximately totally permeable volume of the columns may correspond to the cyclic phosphates (mainly trimeta- and tetrametaphosphates). An $\bar{n}$ value of each fraction was determined and some of the fractions were chromatographed with the analytical columns. The elution profiles of the fractions are shown in Figs. 2 and 3. The data of elution volumes, V_e, which were determined from the peak positions of these samples

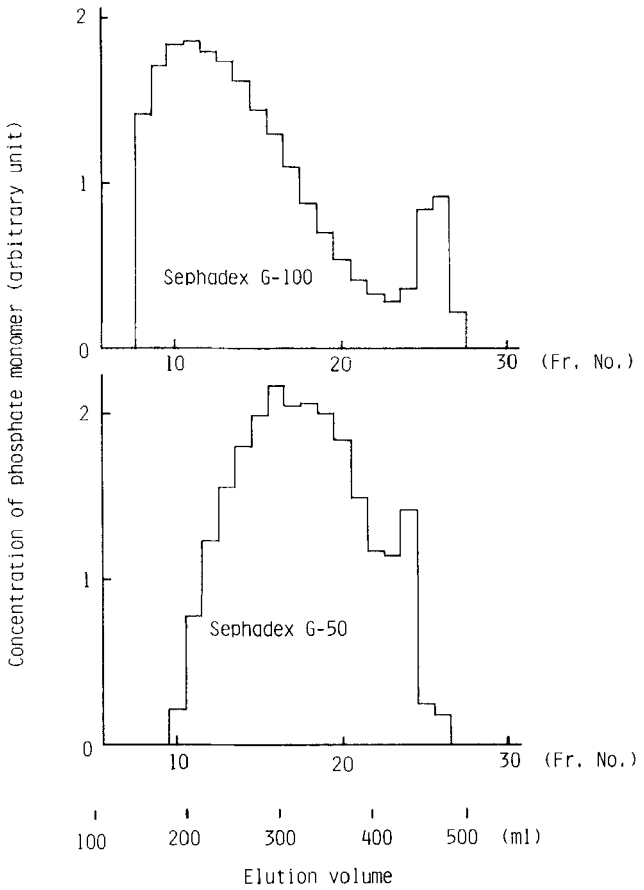

FIGURE 1.

Elution profiles of sodium phosphate glasses.

are given in Tables 1 and 2. It can be seen that linear phosphate mixture whose $\bar{n}$ value is from ca. 10 to ca. 150 can be prepared by the use of the Sephadex G-100 and G-50 columns with 0.1 M sodium chloride solution.

V_e values were plotted against log $\bar{n}$ values (Fig. 4). Good linearity was obtained for both the Sephadex G-100 and G-50 columns.

TABLE 1.

Fractionation of Sodium Phosphate Glass
($\bar{n}$ =113) by the Sephadex G-100 Column.

Fr. No.	$\bar{n}$	V_e (ml)	$\bar{n}$*	$\bar{M}_w/\bar{M}_n$
10	157	17.7		
11	128			
12	118	20.8	93	1.1_1
13	101			
14	83	24.9	67	1.1_2
15	65			
16	53	28.6	47	1.1_2
17	41	31.5	36	1.1_4
18	26**	32.8		
19	30	35.5		
20	24	37.2	21	1.1_2
21	19			
22	17	40.5	15	1.1_4
23	16			

** Since this value is considered to be too low, this plot is omitted in Fig. 4.

TABLE 2.

Fractionation of Sodium Phosphate Glass
(n = 19) by the Sephadex G-50 Column.

Fr. No.	$\bar{n}$	V_e (ml)	Fr. No.	$\bar{n}$	V_e (ml)
11	57		18	20	29.3
12	52	22.4	19	17	
13	45		20	14	33.5
14	37	24.9	21	11	
15	34	25.9	22	9	37.1
16	29	27.9	24*	12	41.2
17	24				

* This fraction contains cyclic phosphates.

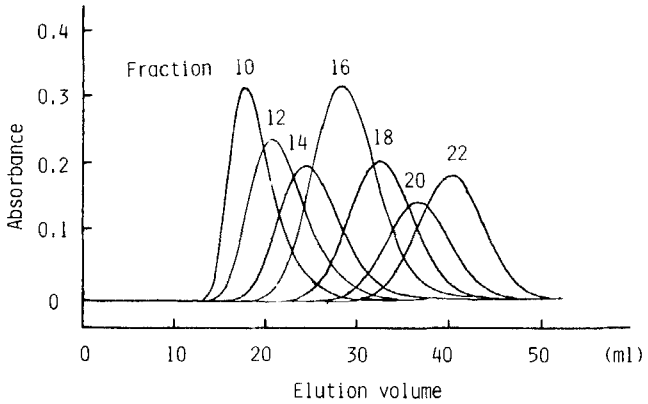

FIGURE 2.

Elution profiles obtained by the Sephadex G-100 analytical column. Each sample fraction was obtained by the Sephadex G-100 preparative column. Fraction numbers are the same as those in Table 1.

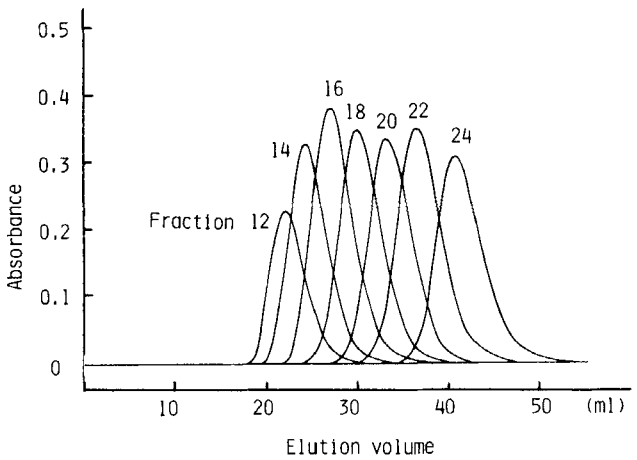

FIGURE 3.

Elution profiles obtained by the Sephadex G-50 analytical column. Each sample fraction was obtained by the Sephadex G-50 preparative column. Fraction numbers are the same as those in Table 2.

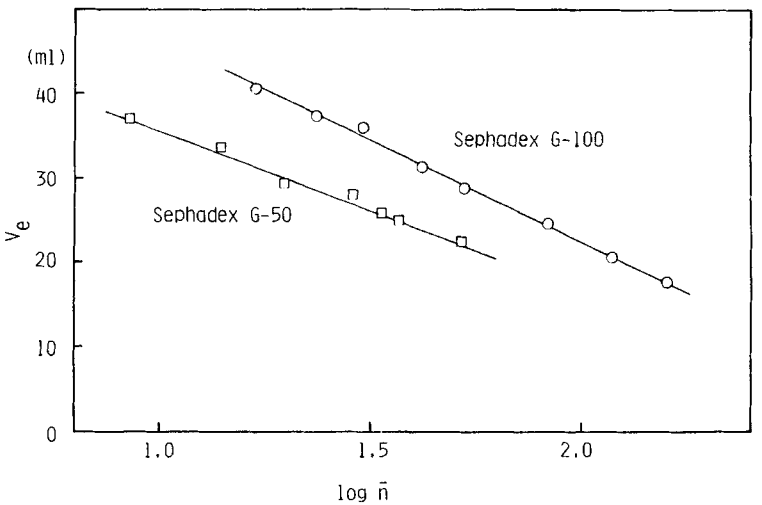

FIGURE 4.

Plots of V_e vs. log $\bar{n}$.

Since a similar phenomenon has been observed for a Sephadex G-25 system (10), it seems worthwhile to correlate the molecular structures of phosphate polymers in solution to their gel chromatographic behavior. Consideration on this point will be discussed elsewhere.

Practically, this relationship between V_e and log $\bar{n}$ is useful to determine chain length distribution of a phosphate mixture. The chain length distribution analysis of a phosphate mixture was carried out by the Sephadex G-100 column using the same procedure as has been applied to the analysis of dextrans (11). In Fig. 5, a representative chain length distribution analysis for fraction 14 in Table 1 is shown. In Table 1, chain lengths calculated from the gel chromatographic analysis, $\bar{n}$*, are presented. The $\bar{n}$* values calculated from the chromatographic analysis are not always consistent with the values determined directly by the end group titration method. This discrepancy may be attributed to small dispersion of the sample phosphate zone in tubes of the detector due to the wall effect (12). Elimination of this effect in the detector seems

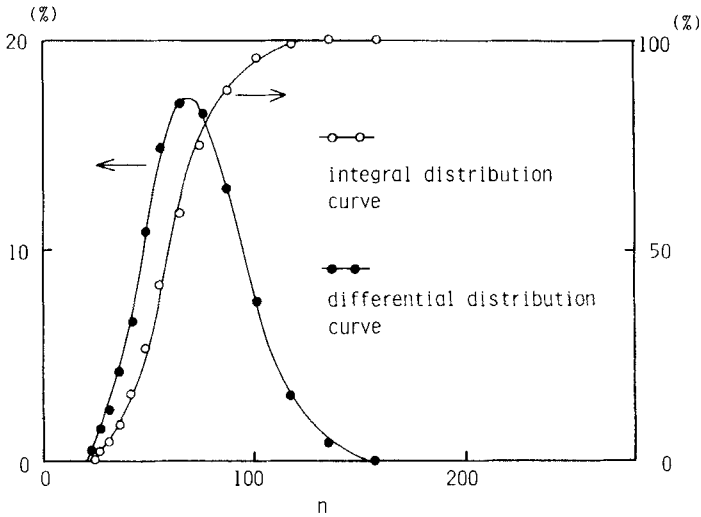

FIGURE 5.

Representative chain length distribution analysis. Sample: Fraction 14 in Table 1.

necessary to precise determination of the chain length distribution. Though there remains some problems to be solved in the detector, the gel chromatography-AutoAnalyzer system is quite useful for the present purpose, because only a small amount of sample is necessary for this analysis and the time needed for the analysis is relatively short. Both the weight average molecular weight, $\bar{M}_w$, and the number average molecular weight, $\bar{M}_n$, have been calculated from the gel chromatographic elution curves. The heterogeneity ratio, $\bar{M}_w/\bar{M}_n$, gives an indication of the efficiency of the fractionation. These values were calculated to be about 1.1 for all the fractions obtained (Table 1).

In order to obtain solid samples of phosphates, each fraction was freeze-dried. Since the elution profiles of the samples obtained after the freeze-drying procedure were quite the same as those obtained before the procedure, it was concluded no hydrolysis occured during the treatment.

ACKNOWLEDGMENTS

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