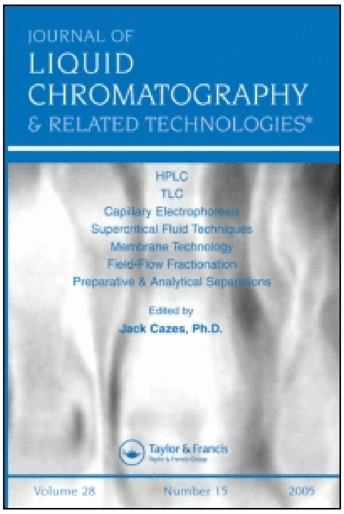

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Characterization of Water Soluble Polymers by Ion Chromatography. I. Poly(Acrylamide-co-Sodium Acrylate)

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CHARACTERIZATION OF WATER SOLUBLE POLYMERS BY ION CHROMATOGRAPHY.
I. POLY(ACRYLAMIDE-co-SODIUM ACRYLATE)

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ABSTRACT

The sodium counterion contents of a series of poly(acrylamide-co-sodium acrylate) copolymers of varying composition have been investigated by Ion Chromatography (IC). Sodium ion contents obtained by IC are comparable with values based on either elemental analysis or titration techniques. Therefore, IC results can be used to determine the degree of polymer hydrolysis. Since sodium ion can be quantified at ppm levels, this analysis is possible with solutions containing ≈20 ppm polymer. At such concentrations, there is no evidence for column plugging or excessive system backpressure. Ionic contamination from glass storage vessels can be significant at these dilutions, however. The results of polymer dialysis and sonication studies are included.

INTRODUCTION

Ion chromatography (IC) is rapidly becoming the technique of choice for quantitative determination of the ionic compositions of a variety of aqueous solutions containing relatively low molecular weight compounds (1). Application of IC for the analysis of organic polymers on the other hand has received much less attention. We have been investigating IC to determine its potential for the characterization of water soluble polymers. The polymer system selected for this study was poly(acrylamide-co-sodium acrylate). These polymers are derived from the controlled hydrolysis of polyacrylamide (PAM), and are therefore referred to as HPAM's.

Conventional methods for determining HPAM composition are generally lengthy and/or subject to uncertainties relating to water content, etc. (2,3) The specific question to be addressed here is whether compositional information relevant to these copolymers can be more readily obtained via IC. In this paper we will examine: (a) the effect of IC and polymer variables on HPAM compositional analysis via the sodium ion, and (b) the correlation of compositional properties determined by IC with those based on sodium analysis, or treatment with ion exchange resins followed by titration.

EXPERIMENTAL

The sodium ion analyses were performed on diluted samples (0.5-20 ppm Na^+) using a Dionex 2020i ion chromatograph operating at ambient temperature. Analyses were performed in an isocratic mode with 0.005 N HCl eluent (2.0 mL/min) and a 200 mm x 4 mm ID Dionex HPIC-CS1 cation separator column. A standard cation fiber suppressor system which was continuously regenerated with 0.04 N tetramethylammonium hydroxide solution (3.0 mL/min) was used. Ion detection was by conductivity (nominal 8 µS background). Aqueous samples were charged to the injection loop after passage through a 0.4 micron filter.

Polymer solutions were prepared by stirring the polymer in distilled water for about 16 hours at about 23°C. Polymer concentration was determined gravimetrically after drying a sample in a vacuum oven for 16 hours at 93°C. Sonication of polymer solutions was accomplished with a Heat Systems-Ultrasonic Inc. unit (model W-375). Sonication conditions were chosen to ensure extensive polymer molecular weight degradation. Dialysis of polymer solutions was performed using Spectrapor® Membrane Tubing #2 which had been preconditioned by boiling in 2% $NaHCO_3$ solution for two hours, followed by washing extensively with distilled water. Polymer solution (0.1-0.2 wt%; 0.04 Liter) contained in this membrane was dialyzed in 4 L of distilled water for 48 hours. The solution outside the membrane was replaced with fresh distilled water after 8, 24 and 32 hours.

Compositional data for a series of HPAM reference polymers are provided in Table I. The polymers were prepared from PAM via base catalyzed hydrolysis using conventional synthesis procedures. Sodium analyses, determined by Galbraith Laboratories by Atomic Absorption Spectrometry, are expressed on a dry weight basis. The degree of hydrolysis of the polymers was determined by (a) conversion of the acrylate groups to carboxylic acid groups via treatment with cation (Dow 50W-X4)- and anion (Dowex 1-X8)-exchange resins, followed by (b) titration of the carboxylic acid functionalities. Good agreement is noted between the measured and calculated sodium contents. This suggests that all of the sodium in the sample is present as the HPAM counterions. Any extraneous salts would have been removed by the cation- and anion-exchange resins.

RESULTS AND DISCUSSION

During the analysis of typical inorganic salts by IC, both the anion and the cation are able to pass readily through the guard and separator columns. In the present case, the sodium ions are associated with a relatively high molecular weight, polyanionic, organic species. Although not yet established with certainty, it is currently assumed that, due to its relatively high molecular weight and lower mobility, the polyanion HPAM component will be substantially retained in the guard column. Possible mechanisms for such retention include filtration and/or adsorption. The sodium counterions, however, apparently exchange in a

Table I

Composition of Poly(acrylamide-co-Na acrylate) Samples

	mole % Hydrolysis		weight % Sodium	
Polymer Code	Titration Method*	(calc'd.)‡	Elemental Analysis*	(calc'd.)§
A	18.60	18.22	5.55	5.68
B	26.93	25.18	7.54	8.03
C	41.65	43.10	12.25	11.91
D	56.38	55.72	15.29	15.46
E	22.20	--	--	6.78

* Direct measurement

‡ Based on Elemental Analysis

§ Based on Titration

facile manner with the H$^+$ ions in the HCl eluent, and subsequently proceed through the separator and detection subsystems in the usual manner.

Two observations suggest that the presence of the high molecular weight polyanion does not cause major problems in the analysis of the Na$^+$ counterion by IC. First, no significant increase in the operating pressure of the analytical pump system was noted for sonicated (i.e. fragmented) vs. non-sonicated polymer solutions. Sonication also had no effect on the measured sodium ion content and hence might be useful as a precautionary measure to guard against column plugging. Secondly, the presence of charged (HPAM) or uncharged (PAM) polymer did not interfere with determination of sodium ion when added to such solutions as NaCl (cf. Fig.1). Furthermore, additivity of Na$^+$ ion from HPAM and NaCl is clearly indicated by the linearity of these data. Also, the charge density, or degree of hydrolysis, of the particular HPAM sample does not appear to be a source of interference.

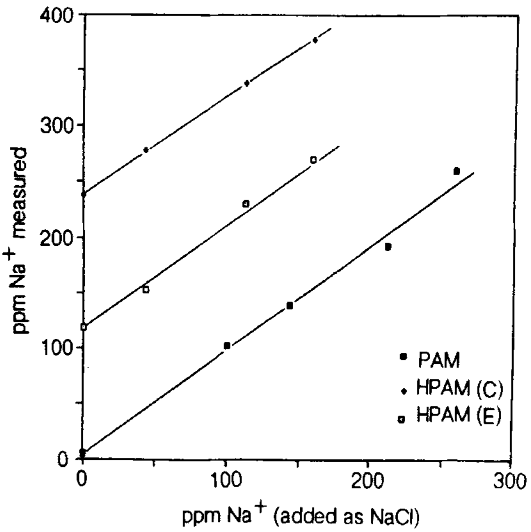

Fig. 1

IC Analysis for Na^+ in PAM and HPAM Solutions

The repeatability of the Na^+ ion determination in HPAM solutions has been examined for dialyzed vs. non-dialyzed solutions as shown in Tables II and III. This study also shows that significant errors can arise due to the contamination of samples with trace sodium which is extracted from glass containers used to prepare and/or store the HPAM solutions. For this reason, our major focus in this paper will be on polymer solutions which have been prepared, dialyzed and/or stored in plastic containers.

The observed vs. the theoretical sodium ion concentrations in solutions of the reference HPAMs are presented in Fig 2. Throughout this paper(except where specifically indicated) Na^+ ion contents of solutions have been normalized to a concentration of 0.178 weight %. The data shown in Fig. 2 are the average of four replicate analyses on samples which have been diluted 100 fold, and duplicate analyses on samples which have been diluted 10 fold. Linear behavior is noted for

Table II

Reproducibility of Na$^+$ Ion Determinations by IC

Polymer Sample[§] #	type	Number of Replicates*	average ppm Na$^+$	Sample Std. D.
A	non-dialyzed	6	1.66	±0.14
B	" "	6	2.30	±0.23
C	" "	6	3.25	±0.29
D	" "	6	4.07	±0.50
A'	dialyzed	8	1.10	±0.10
B'	"	7	1.61	±0.18
C'	"	9	2.50	±0.28
D'	"	8	3.34	±0.47

[§] Data normalized to 0.178 wt % Polymer Sample

* Over 75 day period, 100 fold dilutions stored in plastic

Table III

Effect of Container on Determinations of Na$^+$ in HPAM Solutions

Polymer Sample*		ppm Na$^+$ found[§] after storage			
		2 days		42 days	
#	type	**glass**	Δ	**Pyrex**	Δ
A	non-dialyzed	3.63	(+1.97)	--	--
B	" "	4.77	(+2.47)	--	--
C	" "	4.63	(+1.38)	--	--
D	" "	5.67	(+1.60)	--	--
		(average +1.86)			
A'	dialyzed	--	--	2.49	(+1.38)
B'	"	--	--	3.39	(+1.78)
C'	"	--	--	5.54	(+3.04)
D'	"	--	--	5.86	(+2.52)
					(average +2.18)

[§] Single determinations, 100 fold dilutions

* Concentrations normalized to 0.178 wt %

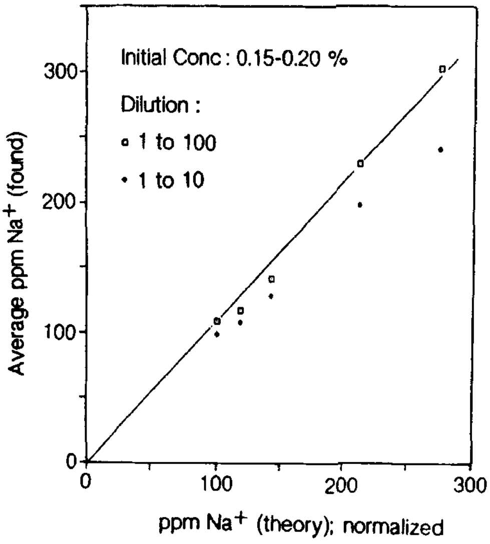

Fig. 2

Effect of Polymer Concentration on Na^+ Analysis

the 1 to 100 dilution data set. This dilution level, which results in a polymer concentration of < ca. 0.002 %, was used in most of this investigation.

At the 1 to 10 level of dilution (i.e higher polymer concentration) the observed Na^+ values appear lower than expected and the data appear to be non-linear. Significant resistance to liquid flow was noted during sample injection in the case of the more concentrated polyelectrolyte solutions. The above observations suggest the possibility of incomplete delivery of the polymer solution to the analytical system in the case of the 1 to 10 dilutions. Work is in progress to determine whether this results from polymer retention on a 0.4 micron prefilter used between the sample syringe and the injection loop.

The correlation between sodium ion content, as determined by IC, and the degree of hydrolysis of the reference polymers is shown in Fig. 3. These data

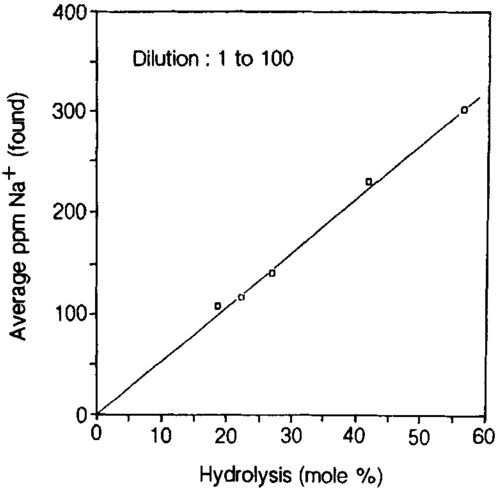

Fig. 3

Na^+ Ion Analysis vs. HPAM Composition

indicate the feasibility of determining the degree of hydrolysis of an HPAM sample as a function of the sodium ion content of the polymer.

The final topic to be addressed in this paper concerns the influence of dialysis on the sodium ion content of HPAM solutions. Our original intent was to utilize dialysis as a technique to check for the possible presence of extraneous inorganic salt in the water soluble polymers. Some commercial HPAMs reportedly contain excess salts as a result of the particular process employed during manufacture (4).

As shown in Fig. 4, which is based on four replicates of each dialyzed polymer solution, sodium ion content was generally lower in the dialyzed vs. the non-dialyzed polymer solutions. This result was unexpected since there appears to be good agreement between Na^+ ion values determined by elemental analysis vs. those based on titration of solutions which had been previously treated with

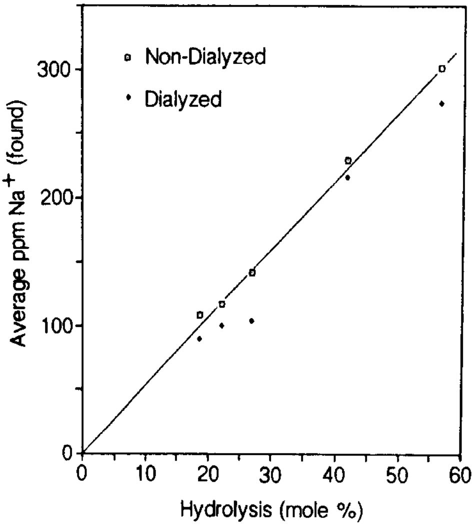

Fig. 4

Effect of Dialysis on Polymer Na^+ Content

cation and anion exchange resins (cf. Table I). This latter treatment should remove any extraneous salt from these polymer solutions. The data presented in Table I suggest that there is no significant quantity of extraneous salt in the HPAM reference polymers.

Assuming that this is correct, another mechanism must be found to explain the reduced sodium ion content in the dialyzed vs. the non-dialyzed HPAM solutions. The data suggest that either (a) there is some non-dialyzable impurity in the polymer which loses sodium ion and converts to a titratable acid form during dialysis, and/or (b) that some fraction of the carboxylate groups in the polymer undergo such a process. It is assumed that the lower sodium content found in the dialyzed solutions does not reflect loss of any significant amount of the lower molecular weight oligomers (< 10,000 Daltons) from the total polymer sample. Material in this molecular weight range would more likely have been removed during the precipitation process used to isolate the polymer.

Table IV

Influence of Dialysis on Composition of HPAM Solutions

mole % Hydrolysis of indicated solutions based on:

	Na^+ Ion Analysis*			Titration*
Polymer	Original	Dialyzed	Δ	(Dialyzed)
B	27	19	8	13
C	42	39	3	12
D	56	47	9	13
E	22	17	5	7

* Average of three replicates

The effect of dialysis is examined further in Table IV which contains data taken on four replicates of each respective solution. Based on the relationship of Fig. 3, the observed sodium ion contents of the dialyzed solutions indicate a lower degree of hydrolysis in comparison with the original non-dialyzed solutions. Further, titration of the dialyzed solutions indicates a significant level of acidity in these solutions. This would be consistent with the previous speculation regarding the polymer and/or an "impurity".

As shown in Table IV, this level of titratable acidity corresponds to a somewhat larger mole % hydrolysis than that suggested by the observed sodium ion content. Additional work will be needed to determine the precise reason for this discrepancy. At this point, however, the data suggest that dialysis of these HPAM solutions leads to changes in sodium ion content which are not related to removal of extraneous salt or other impurities from the system.

SUMMARY AND CONCLUSIONS

This study has explored the effects of key polymer and IC variables on the determination of Na^+ ion content of aqueous HPAM solutions. Good agreement with the results based on elemental analysis or an ion-exchange/titration technique was established. A good correlation was also obtained between the sodium ion content of replicated samples of HPAMs versus the degree of hydrolysis of these polymers. Thus the feasibility of using IC for compositional analyses of these water soluble polymers has been demonstrated. Refinement of the method should lead to improved precision and several useful applications.

Based on the inherent attributes of ion chromatography (e.g. small sample size requirements, high precision, quick analysis times, etc.) IC should have wide applicability in studies of ionic water soluble polymer systems. Potential applications include investigation of polymer composition, polymer concentration, polymer adsorption, and effects of processes such as dialysis.

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