

CHROM. 16,760

COATED ANION-EXCHANGE RESINS FOR ION CHROMATOGRAPHY*

DEAN L. DUVAL and JAMES S. FRITZ*

Ames Laboratory, U.S.D.O.E. and Department of Chemistry, Iowa State University, Ames, IA (U.S.A.)

(First received February 24th, 1984; revised manuscript received March 20th, 1984)

SUMMARY

Ion-exchange resins suitable for use in anion chromatography can be easily prepared by statically coating a porous, neutral resin with an appropriate quaternary ammonium salt. Anion exchangers formed by coating a polystyrene resin with large pores (XAD-1) or a porous polyacrylate resin are more easily wetted than coated PRP-1 resins previously reported and are more stable than dynamically coated silica resins. The chemical composition of the resin that is coated is shown to have a major effect on the relative affinity of the anion exchanger for certain anions. The chemical structure of the quaternary ammonium salt used as a coating also affects the affinity of the resin for different anions. Actual separations are included to demonstrate the convenience, flexibility and practical use of these anion exchangers.

INTRODUCTION

Since its introduction in 1975¹, ion chromatography has become the dominant analytical method for determining inorganic anions (and some organic anions). The original dual-column system which uses a conductivity detector has undergone numerous modifications and changes, such as substitution of a hollow-fiber reactor for the ion-exchange suppressor column. The invention of a single column system in 1979^{2,3} that uses a conductivity detector but requires no suppressor unit has been a major development in ion chromatography. Several detector systems besides conductivity have been used for single-column ion chromatography, including direct UV⁴, indirect UV⁵, amperometric⁶ and refractive index⁷.

The success and popularity of ion chromatography underlines the need to obtain a better understanding of the factors that influence ion-exchange selectivity and to use this knowledge to obtain better separations for certain samples. Basic studies on ion-exchange selectivities have not progressed nearly as fast as the technique of ion chromatography. Dionex Corp. markets anion-exchange columns in which nitrate is eluted before sulfate, and a 'brine' column in which this elution order is reversed. The reasons for this changed selectivity remains proprietary, although

* This paper was presented at the Minnesota Chromatography Forum in April, 1984.

other researchers^{8,9} have stated that it is due to different types of functional groups on the columns.

Iskandarini and Pietrzyk¹⁰ used a form of ion-pair chromatography to study some variations in selectivity. Their system uses commercial reversed-phase columns with a sorbed hydrophobic ionic modifier on the resin to retain ionic species in a charged double layer¹¹.

The only systematic study of selectivity variations caused by different functional groups on low-capacity ion-exchange resins in the scientific literature was recently done by Barron and Fritz^{9,12}. Recently Fritz *et al.*¹³ also published a study of selectivity variations caused by different eluents. These studies showed that a number of things can be done to vary the relative selectivities of different anions. However, studies in classical ion-exchange selectivities^{14,15} indicate that variations in the resin matrix should also have a large effect on the relative selectivities of different ions. Unfortunately, there is no set of commercially available, chromatographic resins with a single, smoothly varying set of characteristics. Resins with totally different backbone structures also cannot be tested unless the functionalization reaction is tested and characterized first.

Coating a porous, granular material with a liquid ion exchanger offers a convenient way to prepare exchangers for ion-exchange chromatography. In classical systems a neutral support was coated with a liquid ion exchanger or with a solution of the ion exchanger in a water-immiscible organic solvent. Such methods have been reviewed by Cerrai¹⁶ and by Braun and Ghersini¹⁷. More recently Cassidy and Elchuk^{18,19} prepared ion exchangers suitable for modern ion chromatography by coating a commercial LC column with a quaternary ammonium salt. This salt is sufficiently hydrophobic that it will not come off the support in an aqueous eluent. These coating methods offer a way to test different supports for selectivity variations without having to functionalize the support by chemical reactions.

The present work has two major goals. One is to demonstrate that anion-exchange resins of low and varying exchange capacity can be easily prepared by a static coating technique. These resins are economical and are satisfactory for practical ion chromatography. The second goal is to study how the selectivities of the coated exchangers for different anions change with the chemical nature of the resins coated and with the structures of the coating chemicals.

EXPERIMENTAL

Equipment

A home-built high-performance liquid chromatograph was used to measure retention times of various anions on the coated columns and to perform the separations included in this paper. The chromatograph was comprised of the following components: a Milton Roy Mini-Pump manufactured by Laboratory Data Control (Riviera Beach, FL, U.S.A.), a Mark III high pressure pulse dampener from Alltech (Deerfield, IL, U.S.A.), a Rheodyne (Berkeley, CA, U.S.A.) Model 7010 injection valve with a 50- μ l sample loop and a Model 213A conductivity detector made by Wescan Instruments (Santa Clara, CA, U.S.A.) with a measured cell constant of 33 cm^{-1} . Eluent flow-rate was 1.0 ml/min except where otherwise noted, detector output was 10 mV and recorder input was 1–10 mV full scale. Injector, column, detector and connecting tubing were all insulated to prevent excessive baseline drift.

Solutions were prepared from reagent grade salts and distilled, deionized water. Eluents were also prepared in distilled, deionized water using reagent grade acids. The pH of the eluent was adjusted using a sodium hydroxide solution. Before using, the eluent was filtered through a 0.45- μm membrane filter and stirred under vacuum to remove dissolved carbon dioxide.

Procedure

The statically coated resins were prepared using 30–37- μm , Soxhlet-extracted XAD-1 and XAD-8 resins from Rohm and Haas (Philadelphia, PA, U.S.A.). About 0.75 gram of dried resin was weighed out into a 50-ml glass beaker. Then 3–10 ml of 0.01 *M* quaternary salt in acetonitrile was added to the beaker. Additional acetonitrile was added to the solution until the total amount of liquid added to the resin was 10 ml. The beaker was then placed in a sonic bath for 10 min. After sonication, the mixture was transferred to a 400-ml glass beaker and diluted to 350 ml with deionized water. The solution was allowed to settle for about 15 min. Then the resin was filtered off and packed into 500 \times 2 mm glass columns using a slurry packing method.

Chemically bonded resins were prepared from XAD-1 using a formaldehyde-hydrochloric acid procedure²⁰ to chloromethylate, and trimethylamine to quaternize the resin so that the final capacity was 0.027 mequiv./g.

Dynamically coated columns were prepared using commercial reversed-phase columns from EM Reagents (Gibbstown, NJ, U.S.A.) and from Hamilton (Reno, NV, U.S.A.). The coating procedure was similar to the one Cassidy and Elchuk^{18,19} used for their PRP-1 and C₁₈ columns. The PRP-1 column was conditioned with 200 ml of HPLC grade acetonitrile, coated with 1 l of $5 \cdot 10^{-4}$ *M* cetylpyridinium chloride in 7% acetonitrile, and then conditioned with 1 liter of $5 \cdot 10^{-4}$ *M* sodium phthalate (pH 6.1) before testing. The C₁₈-, C₈- and C₂-columns were conditioned with 200 ml of acetonitrile, then coated with 250 ml of $1 \cdot 10^{-3}$ *M* cetylpyridinium chloride in 7% acetonitrile, followed by 500 ml of the phthalate eluent to condition and equilibrate the column. The amino- and cyano-phase columns were conditioned with 200 ml of acetonitrile, coated with 250 ml of $5 \cdot 10^{-3}$ *M* cetylpyridinium chloride in 7% acetonitrile, and then equilibrated with 500 ml of the phthalate eluent. A Model 980A solvent programmer from Tracor Instruments (Austin, TX, U.S.A.) was used to provide a gradual change from one solution to the next.

DISCUSSION

Static coating of resins

Initial experiments showed that anion-exchange resins suitable for ion chromatography can be produced by coating a porous resin, such as an XAD polystyrene or polyacrylate, with an appropriate quaternary ammonium salt, such as cetylpyridinium chloride. Static coating of the resins gave better results than when a dynamic coating of the resin in a packed column was attempted. Of several static coating procedures tried, the most successful was to add a solution of the quaternary ammonium salt to a weighed amount of resin. The solution was then diluted with water causing the quaternary ammonium salt to be taken up by the resin. (See Experimental for complete details.)

The reproducibility of this procedure was demonstrated by packing three dif-

ferent columns with chemically bonded anion-exchange resin from the same batch and measuring the retention times of several anions by single-column ion chromatography. Comparison of the retention times for the three columns showed good agreement with a coefficient of variation of 4.5%. This is largely an indication of the reproducibility of packing the three columns. A similar experiment was performed in which each of the three columns was packed with a different batch of coated resin. In this case the coefficient of variation of retention times was 5.7%, indicating that the reproducibility of coating the resins was quite good.

Figs. 1 and 2 show plots of adjusted retention times against the capacities of coated anion-exchange resins. Both plots show a linear increase in adjusted retention times with coating thickness. This behavior can be predicted with the aid of eqn. 1, which can be readily derived from the fundamental ion-exchange equilibrium

$$(t')^x = \text{Constant} \cdot \frac{(\text{Capacity})^y}{[\text{Eluent}]^y} \quad (1)$$

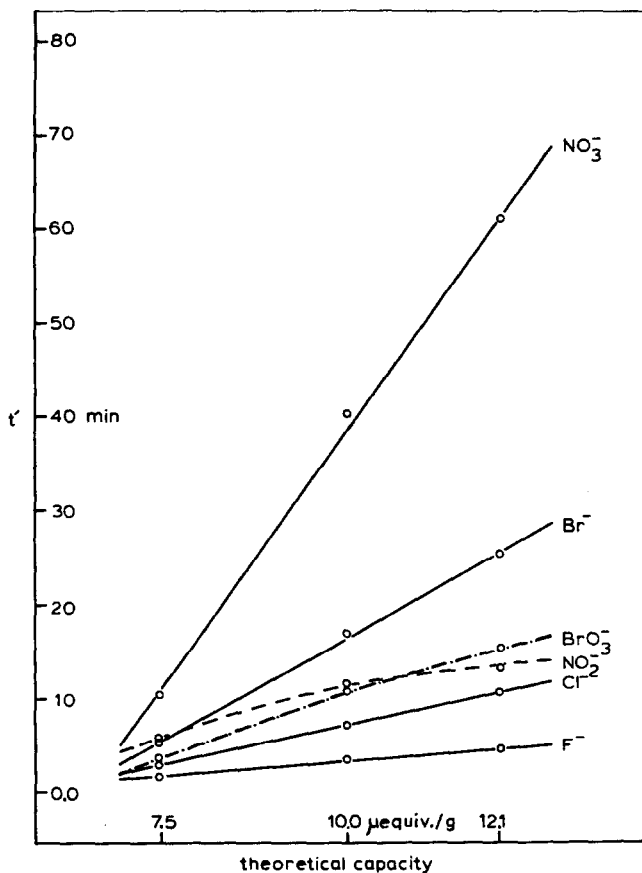


Fig. 1. Plot of adjusted retention times of F^- , Cl^- , NO_2^- , BrO_3^- , Br^- , and NO_3^- versus theoretical capacity of coated XAD-8 resin. Experimental conditions: 30-37 μm neutral XAD-8; cetylpyridinium exchanger coated onto the resin; eluent, 1 mM succinic acid; flow-rate, 1.0 ml/min.

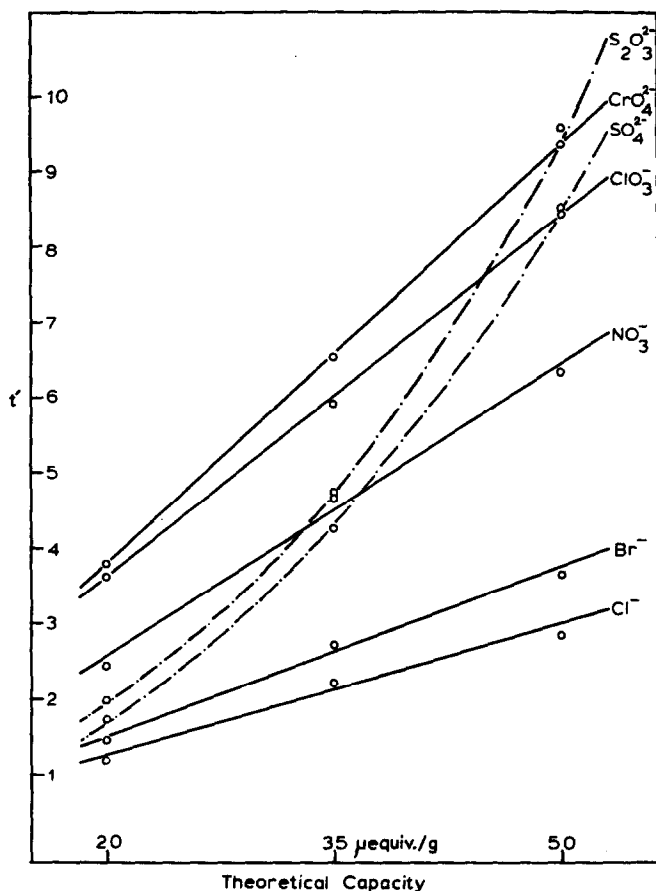


Fig. 2. Plot of adjusted retention times of Cl^- , Br^- , NO_3^- , ClO_3^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, and CrO_4^{2-} versus theoretical capacity of coated XAD-8 resin. Experimental conditions: 30–37 μm neutral XAD-8; cetylpyridinium exchanger coated onto the resin; eluent, 0.1 mM sodium phthalate, pH 4.5; flow-rate, 1.0 ml/min.

where t' is the adjusted retention time of a sample anion of charge y^- and $[\text{Eluent}]$ is the concentration of the eluent anion which has a charge x^- . If both x and y are 1 and the eluent concentration is kept constant, the adjusted retention time is a linear function of resin capacity (and hence of coating thickness).

Fluoride, chloride, bromide, and nitrate all show linear plots in Fig. 1. However, bromate and nitrite plots are not linear. This is because their selectivity coefficients vary with capacity in relationship to the other anions plotted. Selectivity variations with capacity are not uncommon and have been studied in great detail on resins of high capacity^{14,15}. Fig. 2 again shows a linear increase in retention times with column capacity with the stronger eluent system for monovalent anions, chloride, bromide and nitrate. The nonlinearity of the sulfate and thiosulfate plots was expected because of the 2- charge. It is not surprising that chromate acts like a monovalent anion instead of a divalent because its second $\text{p}K_a$ is 6.5 and the eluent

pH is only 4.5. Thus, these two figures show that capacity, and hence retention times, can be varied quite easily by varying the coating thickness.

Although the coating procedure used gives reproducible results, it was found that only about 25% of the quaternary ammonium salt in solution is coated onto XAD-8 and about 37% is coated onto XAD-1. The percent of exchanger coated onto the resin will vary if the ratio of resin weight to the volume of acetonitrile is not the same in each coating attempt. The exchange capacity of coated resins was measured by ion chromatography using a nitrate displacement procedure described by Barron and Fritz²⁰.

No significant degradation of the coated columns was noticed during chromatographic testing. The capacities of coated resins were also tested in gravity columns after passing 100 ml and then a second 100 ml of 0.5 *M* nitric acid with no significant change in capacities. The total ionic concentration in the 200 ml of nitric acid is larger than that normally passed through a chromatographic column during the lifetime of the column.

Properties of coated organic resins

Poly(styrene-divinylbenzene) resins such as XAD-2 and XAD-4 can be easily coated with cetylpyridinium chloride and they appear to retain the coating material tenaciously. These resins, when thinly coated, are hydrophobic and tend to agglomerate once they are slurried in an aqueous solution. However, the wettability of XAD-1 was reasonably good, and this resin was selected for further comparison. Chemically bonded anion-exchange resins based on XAD-1 have been well characterized and widely used in ion chromatography, and so are convenient to compare with coated XAD-1 anion exchangers.

Polyacrylic resins (XAD-7 and XAD-8) are also easy to coat. These resins are more polar and the coated resins are easily wettable by aqueous solutions. The XAD-8 resin was found to have better performance and coating characteristics, and was selected for further study. An amide resin, XAD-11, was studied briefly but did not have very good coatability.

Comparison of XAD-1 and XAD-8, coated with cetylpyridinium chloride, confirmed that the latter is much better wetted by aqueous solutions. However, both are acceptable for use in anion chromatography using aqueous eluents. There are noticeable differences between these two resins in selectivity for certain anions. Cetylpyridinium chloride on XAD-1 has a slightly higher selectivity for the more polarizable anions than trimethylamine chemically bonded to XAD-1, as shown by columns one and three in Table I. The same trend between the adsorbed exchanger and the chemically bonded exchanger is more evident in columns one and two in Table II. The slight increase in selectivity follows nicely with studies done by Barron and Fritz^{9,12} on chemically bonded ion exchangers which showed that the more hydrophobic the exchanger, the greater its affinity for certain large monovalent anions.

The most interesting points of Tables I and II are the differences in selectivity between cetylpyridinium chloride coated on XAD-1 and XAD-8 (columns three and four in Table I and columns two and three in Table II). Both tables show that there is a much higher affinity for some of the more polarizable monovalent anions on the more polar XAD-8 resin. This trend also agrees well with studies on high capacity

TABLE I

ADJUSTED RETENTION TIMES FOR EARLY ELUTING ANIONS RELATIVE TO THAT OF CHLORIDE (t'_A/t'_{Cl})

Conditions: eluent, 1 mM succinic acid; flow-rate, 1.0 ml/min, pH 3.54. Capacity of chemically bonded resins was 0.027 mequiv./g. Theoretical capacity of coated exchangers was 0.050 mequiv./g.

CPCI = cetylpyridinium chloride; TOACl = tetraoctyl ammonium chloride, TDACl = tetra-dodecylammonium chloride.

Anion	Chemically-bonded exchanger		Coated exchanger				
	Trimethyl amine, XAD-1	Pyridine, XAD-1	CPCI, XAD-1	CPCI, XAD-8	TOACl, XAD-1	TOACl, XAD-8	TDACl, XAD-8
Acetate	0.12	0.13	0.09	0.15	0.10	0.10	0.04
Azide	0.28		0.23	0.55	0.38		
Formate	0.42	0.45	0.48	0.42	0.45	0.31	
Bicarbonate	0.40	0.39	0.36	0.41	0.39	0.31	0.05
Fluoride	0.51	0.54	0.48	0.41	0.59	0.24	0.14
Phosphate	0.69	0.68	0.59	0.47	0.82		0.15
Iodate	0.72	0.69	0.59	0.49	0.81	0.31	0.19
Nitrite	0.97	1.06	0.93	1.49	0.96	2.80	2.94
Chloride	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Methylsulfonate	1.15	1.15	1.11	1.00	1.31	0.91	0.92
Bromate	1.26	1.19	1.27	1.44	1.34	1.76	3.38
Bromide	1.57	1.49	1.90	2.40	1.30	3.11	
Chloroacetate	1.63	1.61	1.77	1.92	1.68	2.26	2.11
Nitrate	1.85	1.73	2.30	5.13	1.82	8.61	
t'_{Cl} (min)	8.91	7.41	13.7	6.75	14.4	12.1	21.6

polystyrene resins^{14,15} which show that the less hydrophobic a resin is (less cross-linking), the greater its affinity for the more polarizable monovalents. Column two of Table I is of a chemically bonded resin using pyridine as the tertiary amine chemically bonded to XAD-1. The purpose here is to show that the selectivity changes that have been noted using cetylpyridinium chloride are not due to pyridinium quaternary structure, but rather to the overall hydrophobicity of the exchange group.

The remaining columns in Tables I and II compare the selectivities of XAD-1 and XAD-8 resins coated with large tetraalkylammonium chlorides. Tetraoctylammonium chloride (TOACl) and tetradodecylammonium chloride (TDACl) show an even greater affinity than cetylpyridinium chloride for some of the large monovalent anions. This is to be expected because of the increasing hydrophobic nature of these bulky quaternary ammonium salts. However, the differences in support polarity still have a large effect on the selectivity of these coated exchangers.

These large tetraalkylammonium anion exchangers have some drawbacks for practical ion chromatography. They give broader peaks, probably because of slower exchange kinetics, and they increase the back-pressure of the column.

Properties of coated silica resins

Cassidy and Elchuk prepared viable columns for ion chromatography by coat-

TABLE II

ADJUSTED RETENTION TIMES FOR LATE ELUTING ANIONS RELATIVE TO THAT OF CHLORIDE (t'_A/t'_{Cl})

Conditions: eluent, 0.1 mM tetrabutylammonium phthalate, pH 6.5. Other conditions and abbreviations are the same as in Table I.

Anion	Chemically-bonded exchanger Trimethyl amine, XAD-1	Coated exchanger					
		CPCI, XAD-1	CPCI, XAD-8	TOACI, XAD-1	TOACI, XAD-8	TDACI, XAD-1	TDACI, XAD-8
Chloride	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Nitrite	1.18	1.11	1.49	1.12	1.83	1.37	3.14
Methylsulfonate	1.18	1.01	1.03	1.13	0.99	1.00	0.83
Bromate	1.23	1.45	1.23	1.29	1.55	1.10	2.40
Bromide	1.38	1.49	2.05	1.30	3.85	2.31	5.22
Nitrate	1.54	2.37	3.67	1.44	10.2	4.31	
Chloroacetate	1.54	1.58	1.33	1.45	2.76	1.56	1.98
Chlorate	2.10	3.20	5.08	1.84			
Iodide	3.49	4.35	12.7	2.12			
Chromate	7.00	6.42	5.44	7.72	14.0	9.67	
Thiocyanate	8.95		9.72				
Sulfate	10.3	9.00	3.79	8.06	2.34	7.63	2.11
Thiosulfate		17.8	6.03	10.7	4.69	13.0	3.22
t'_{Cl} (min)	1.17	2.73	1.17	4.62	2.17	4.2	3.89

ing commercial C_{18} reversed-phase silica columns¹⁸ and PRP-1 (organic phase) columns¹⁹ with a quaternary salt such as cetylpyridinium chloride. They used a dynamic coating procedure in which a solution of the quaternary salt in acetonitrile-water or in methanol-water is pumped through the column. The PRP-1 column coated in this manner is so hydrophobic that an organic modifier (such as acetonitrile) must be added to the eluent in order to obtain sharp peaks. The organic modifier suppresses the signal of the conductivity detector somewhat. A more polar anion exchanger would be more desirable.

In this study we hoped to find out if a more polar commercial column might be used instead of the C_{18} or PRP-1 columns. The more polar column would eliminate the need for the organic modifier in the eluent. It possibly would provide a different set of selectivity ratios and yet allow the use of a high efficiency commercial column.

Table III lists the results of our study of dynamically coated commercial columns. The results seem to contradict the results in the static coating study. The affinity for the more polarizable ions increases when going from the PRP-1 to the C_{18} and then the C_8 column. This agrees with the batch coatings which showed that as the polarity of the resin increases, its affinity for the more polarizable anions also increases. However, when going from the C_8 to the C_2 and the cyano-phase columns, the affinity for the monovalent anions like nitrate and bromide decreases. This trend is the opposite of what would be expected because the polarity of the columns is increasing. However, the coating thickness is smaller on these columns, causing a

TABLE III

SELECTIVITY RATIOS OF PERMANENTLY COATED COMMERCIAL COLUMNS (t'/t'_{Cl})

Anion	PRP-1*	C ₁₈ *	C ₈ *	C ₂ **	CN**
Fluoride***	0.53	0.47	0.54	0.68	
Iodate	0.56	0.43	0.47	0.52	
Acetate	0.65	0.47	0.86	0.91	
Nitrite	0.89	1.70	1.90	1.67	1.53
Chloride	1.00	1.00	1.00	1.00	1.00
Methylsulfonate	1.04	0.73	0.97	0.86	
Bromate	1.45	1.15	1.34	1.21	1.36
Bromide	2.01	2.23	2.58	2.04	2.26
Nitrate	3.17	3.49	3.63	2.69	3.82
Iodide	—	13.4	15.4	11.2	15.0
Chlorate	6.43	7.15	7.45	4.94	5.66
Sulfite	5.10	4.79	5.58	6.10	4.27
Sulfate	4.90	5.63	5.71	5.43	4.34
Tartrate	9.90	5.16	6.30	5.94	
Thiosulfate	13.4	17.0	19.5	9.58	15.0
t'_{Cl^-} (min)	7.68	3.10	3.68	4.08	1.92

* Eluent was $5 \cdot 10^{-4}$ M sodium phthalate, pH 6.1.** Eluent was $2.5 \cdot 10^{-4}$ M sodium phthalate, pH 6.1.

*** Fluoride losses were observed on all silica columns which prevents quantitation.

decrease in their affinity for the later eluting monovalents. When the support becomes more polar, the coating thickness of the column decreases if the concentration of the exchanger is held constant in the coating solution. Increasing the concentration of the cetylpyridinium chloride in the coating solution by a factor of five for the C₂ and cyano-phase columns was not large enough to offset the reduced capacity. However, the results do show that the more polar commercial columns can be coated and that their selectivity variations follow the same general trend as seen before on the XAD resins.

In order to compare the relative selectivities of the coated silica columns for various anions, each column had to be coated, stripped and recoated several times. This was necessary to determine the correct solvent composition so that each column would have the same capacity. However, Cassidy and Elchuk^{18,19} stated that the performance of the column deteriorates with each coating and can only be coated several times. The same problem was encountered in this study, and the columns were worn out before the proper coating conditions were found. Therefore, the coating conditions for all columns were kept as similar as possible so that information on both selectivity and coating thickness under a given set of conditions could be gathered.

A silica precolumn was always placed before the commercial silica based columns during coating and testing, but the longevity of these columns is considerably less than the poly(styrene-divinylbenzene) or acrylic ester resins. Another problem that was encountered was eluent dips with the more polar silica based columns. The baseline perturbations are especially severe on the cyano-phase column. This was

unexpected because the acrylic ester resin (XAD-8) gave no problems with eluent dips. Several attempts were also made to coat an amino-phase column but they were unsuccessful. Apparently the column is too polar to permanently retain cetylpyridinium chloride on its surface.

Ion chromatographic separations using coated resins

The usefulness in having resins with different selectivities for anions is illustrated by the separation in Fig. 3. Under normal conditions, a chemically bonded trimethylamine XAD-1 resin column will not separate chloride and nitrite or bromide and nitrate very well. However, Fig. 3 shows both pairs of anions to be well resolved on a coated XAD-8 column.

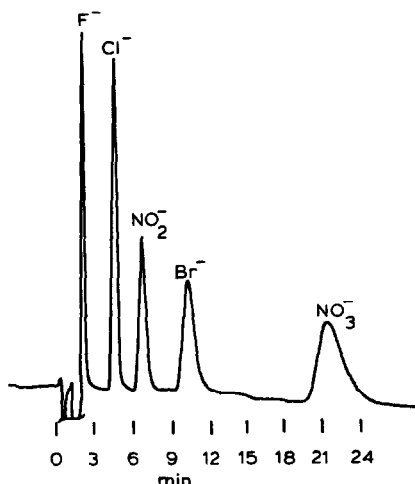


Fig. 3. Chromatogram of F⁻, Cl⁻, NO₂⁻, Br⁻, and NO₃⁻ to show usefulness of XAD-8 coated resins for separating common ions. Experimental conditions: 30-37 μ m neutral XAD-8; cetylpyridinium exchanger coated onto the resin so that the theoretical capacity was 0.050 mequiv./g; eluent, 1 mM succinic acid; flow-rate, 1.0 ml/min.

With coated columns it is easy to vary the exchange capacity as well as the chemical nature of the coating chemical. This is demonstrated in Fig. 4 where the separation of several anions is improved by increasing the resin capacity. However, faster separation of some anions can be achieved by using a resin of lower exchange capacity.

Fig. 5 demonstrates the ease with which a 'brine' column can be made. Sulfate is eluted before nitrate using tetraoctyl ammonium chloride on XAD-8. The broadness of the nitrate peak is characteristic of later eluting monovalents when using large symmetric ion exchangers.

Concern about iodide in foods has increased recently. Fig. 6 shows how the more polar XAD-8 columns can be used to determine late eluting ions like iodide in the presences of larger concentrations of common anions like chloride and sulfate. The eluent conditions in this experiment were chosen so that chloride and sulfate are eluted in the pseudo peak.

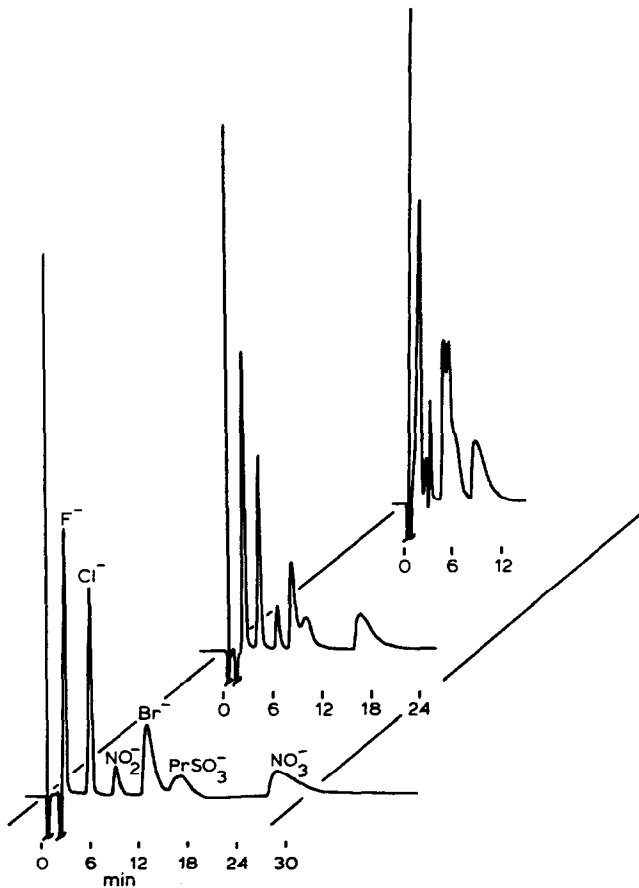


Fig. 4. Chromatograms of F^- , Cl^- , NO_2^- , Br^- , propylsulfonate ($PrSO_3^-$), and NO_3^- to show how the capacity of the resin can be increased to resolve various anions. Experimental conditions: 30–37 μm neutral XAD-8; cetylpyridinium exchanger coated onto the resin so that the theoretical capacity is 0.0121 mequiv./g, 0.010 mequiv./g, and 0.0075 mequiv./g, respectively from the bottom to top chromatogram. Eluent, 1 mM succinic acid; flow-rates were 1.88 ml/min.

CONCLUSIONS

The instability of silica-based columns in aqueous media makes them undesirable as ion exchange columns for routine use in ion chromatography. Although the PRP-1 column is very stable under the conditions commonly used in ion chromatography, the hydrophobicity of the column necessitates the use of organic modifiers in the eluent, which reduces the sensitivity of the conductivity detector. However, in some specialized cases, these columns might be very useful for specific separations.

The batch coating method is a simple method of preparing ion-exchange columns and would be useful for laboratories that would like to customize their columns to specific separations. The batch coating method is also an excellent method of screening supports for possible use as ion exchangers before devoting a lot of time to functionalizing the resins.

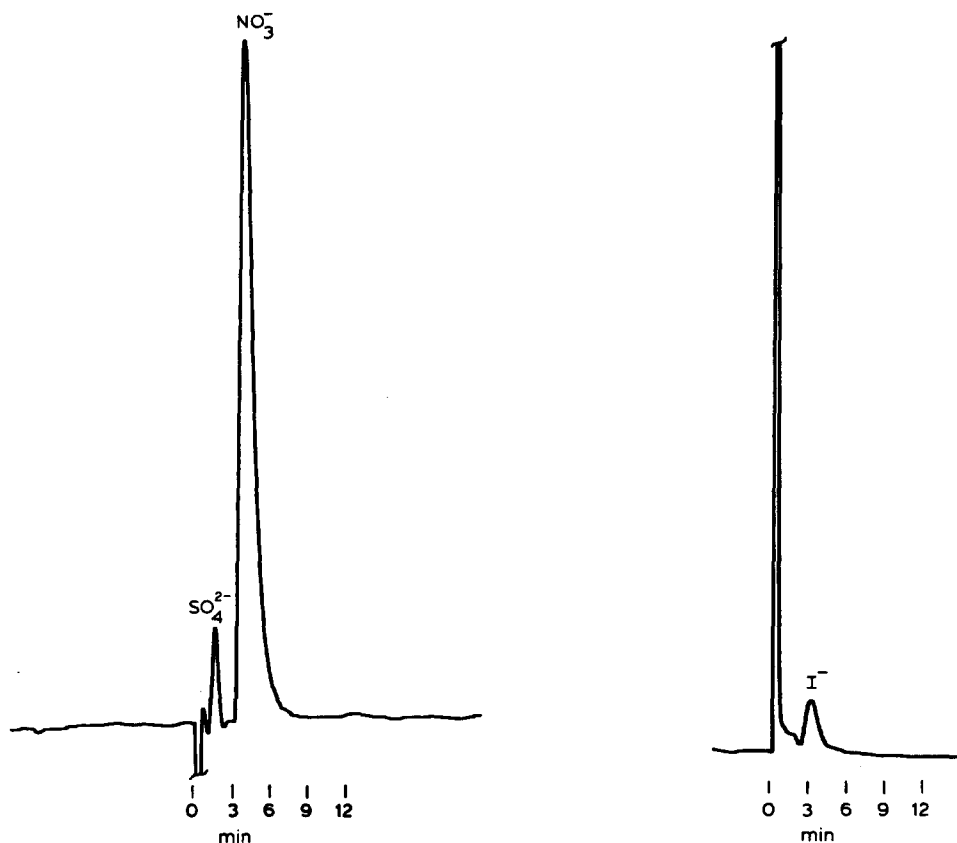


Fig. 5. Chromatogram of 5 ppm SO_4^{2-} and 100 ppm NO_3^- to demonstrate 'brine' column using XAD-8 and tetraoctylammonium chloride. Experimental conditions: 30-37 μm neutral XAD-8; tetraoctyl-ammonium chloride coated onto the resin so that the theoretical capacity of the resin is 0.06 mequiv./g; 250×2 mm glass column; eluent, $1 \cdot 10^{-4}$ M sodium phthalate, pH 6.0; flow-rate, 2.09 ml/min.

Fig. 6. Chromatogram of 20 ppm I^- in the presences of 100 ppm Cl^- and 100 ppm SO_4^{2-} using XAD-8 coated with tetraoctylammonium chloride. Experimental conditions: 30-37 μm neutral XAD-8; tetraoctyl-ammonium chloride coated onto the resin so that the theoretical capacity of the resin is 0.06 mequiv./g; 240×2 mm glass column; eluent, $1.25 \cdot 10^{-3}$ M, sodium phthalate, pH 5.55; flow-rate, 2.09 ml/min.

The type of support the ion-exchange group is bonded to or coated onto has a large effect on ion-exchange selectivities. This study also indicates that an acrylic ester resin or some other polar resin might be more useful for separating both major groups of anions (monovalents and divalents) in a single run. It should be pointed out that concurrent to this study, a low-capacity acrylic anion-exchange column has become commercially available.

ACKNOWLEDGEMENTS

Operated for the U. S. Department of Energy by Iowa State University under contract No. W-7405-Eng-84. This research was supported by the Director of Energy Research, Office of Basic Energy Sciences.

REFERENCES

- 1 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 2 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.
- 3 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 4 R. N. Reeve, *J. Chromatogr.*, 177 (1979) 393.
- 5 M. Dreux, M. Lafosse and M. Pequignot, *Chromatographia*, 15 (1982) 653.
- 6 J. E. Girard, *Anal. Chem.*, 51 (1979) 836.
- 7 J. P. du Kleijn, *Analyst (London)*, 107 (1982) 223.
- 8 D. A. Clifford and W. J. Weber, Jr., *Reactive Polymers*, 1 (1983) 77.
- 9 R. E. Barron, *Ph. D. Dissertation*, Iowa State University, Ames, IA, 1983.
- 10 Z. Iskandarani and D. J. Pietrzyk, *Anal. Chem.*, 54 (1982) 1065.
- 11 B. A. Bidlingmeyer, S. N. Deming, W. P. Price, Jr., B. Sachok and M. Petrussek, *J. Chromatogr.*, 186 (1979) 419.
- 12 R. E. Barron and J. S. Fritz, *J. Chromatogr.*, 284 (1984) 13.
- 13 J. S. Fritz, D. L. DuVal and R. E. Barron, *Anal. Chem.*, in press.
- 14 R. M. Diamond and D. C. Whitney, in J. A. Marinsky (Editor), *Ion Exchange: A Series of Advances*, Vol. 1, Marcel Dekker, New York, 1962, Ch. 8.
- 15 F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962, Ch. 5.
- 16 E. Cerrai, *Chromatographic Reviews*, 6 (1964) 129.
- 17 T. Braun and G. Ghersini, *Extraction Chromatography*, Elsevier, Amsterdam, 1975.
- 18 R. M. Cassidy and S. Elchuk, *Anal. Chem.*, 54 (1982) 1631.
- 19 R. M. Cassidy and S. Elchuk, *J. Chromatogr.*, 262 (1983) 311.
- 20 R. E. Barron and J. S. Fritz, *Reactive Polymers*, 1 (1983) 215.