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# New stationary phases for efficient separations and selectivity studies in anion chromatography

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# New stationary phases for efficient separations and selectivity studies in anion chromatography

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# New stationary phases for efficient separations and selectivity studies in anion chromatography

by

Linda M. Warth

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# GENERAL INTRODUCTION

Traditionally, common anions like sulfate, chloride, bromide or iodide were determined using one or more of the following techniques: spectrophotometry, fluorometry, titrimetry, potentiometry, amperometry, gravimetry or ion exchange (1-3). These methods were valuable in many instances but had numerous drawbacks including long analysis times, lack of selectivity or sensitivity, multi-step procedures or matrix interferences.

Of the classical methods, only ion-exchange chromatography is capable of analyzing mixtures of anions or removing ions that interfere with a quantitative analytical procedure (4-7). In ion-exchange chromatography, anions are separated by their different rates of migration down an anion-exchange column. The exchange column contains a high-capacity, gellular resin (2 to 5 meq/g) that is of a fairly large particle size (75 to 200 μm). The columns are usually 1 to 2 cm in diameter and 10 to 50 cm long. Large sample sizes (several milliliters) are used to ensure detectability and high eluent concentrations are necessary to elute the sample down the high-capacity column. The technique uses gravity-flow columns, fraction collecting and manual methods for quantifying the anions in the fractions.

During the 1960s and 1970s, advancements made in gas chromatography (GC) and high-performance liquid chromatography (HPLC) greatly improved the speed and analytical capabilities of these techniques. In 1975, classical ion-exchange chromatography was also up-dated to a high-performance technique known simply as ion chromatography. The major improvement made was the use of an automatic conductivity detector. This detector is desirable because it responds universally to ions in solution. More efficient resins, smaller columns, smaller sample sizes and modern chromatographic components were also used in this new version of ion-exchange chromatography. For the first time, many common anions could be determined at ppm levels in just 10 to 20 minutes. The invention of suppressed ion chromatography (SIC), or dual-column ion chromatography, by Small, Stevens and Bauman (8) was the important turning point which suddenly made ion chromatography the dominant method of inorganic anion analysis.

The original SIC invention consists of a low-capacity anion-exchange column to separate the anions. The anions are eluted using a sodium carbonate/sodium bicarbonate or sodium hydroxide eluent, which leaves the sample and eluent anions in the highly-conducting sodium form. The anions then travel through a "suppressor" column, which is a high-capacity cation-exchange column in the hydrogen form. In the suppressor column, the sample and eluent anions are converted to the hydrogen form, leaving the eluent in the form of weakly-conducting carbonic acid (or water). Sample anions of strong acids like chloride and sulfate are in the hydrogen form and are, therefore, completely dissociated. When this sample and eluent mixture passes through the conductivity detector, the highly-conducting sample anions can be sensitively detected in the presence of the suppressed eluent background signal.

At the same time, an analogous SIC system was invented for the determination of ammonium, alkali metal and alkaline earth cations (8). The separator column in this system is a low-capacity cation-exchange column and the suppressor column contains a high-capacity anion-exchange resin in the hydroxide form. Transition metals cannot be determined by this method because of precipitation in the hydroxide-form suppressor column.

A drawback of the original SIC method is that anions of weak acids are not ionized at the detector and cannot be sensitively detected. In addition, the suppressor column creates significant peak broadening because of extra dead volume (9). Further, the entire system must be shut down when suppressor column regeneration is necessary.

Later, the suppressor column was replaced with a system of hollow fibers made of a sulfonated polymer (10). This suppressor unit reportedly creates no extra-column band broadening and is self-regenerating. This hollow fiber system was later improved so that even higher eluent concentrations could be effectively suppressed. Then, gradient elution ion chromatography could be used to separate a mixture of 36 anions in just 30 minutes (11).

In 1979, Gjerde, Fritz and Schmuckler greatly simplified SIC by inventing single-column ion chromatography (SCIC), or nonsuppressed ion chromatography (12). By using very low-capacity (5 to 200 $\mu$eq/g) separator columns, dilute eluents with very low conductivities can be used so that eluent suppression is not necessary.

Ammonium and alkali metal cations can also be determined in SCIC (13) using a very low capacity (5 $\mu$eq/g) cation-exchange column and a dilute nitric acid eluent. Alkaline earth metals are separated and determined in SCIC using a divalent or weakly-complexing eluent like an ethylenediammonium salt.

Eluents originally used in SCIC for anion separations were benzoate or phthalate salts (12). Eluent studies performed later by Gjerde and Fritz (14) and Fritz, DuVal and Barron (15) used weak-acid eluents such as benzoic, succinic or nicotinic acid. These organic acid eluents have low background conductivities that give detection limits in the low ppb range for common inorganic anions.

The non-suppressed ion chromatographic system requires less hardware, cost and maintenance because of the absence of the suppressor unit. SCIC can also sensitively determine concentrations of weak acids, which are difficult to determine using conductivity detection in SIC. The disadvantage of the single-column method is the poorer detection limits as compared on an equivalent basis to those of the dual-column method. This difference in detection limits is due to slightly higher background conductivity levels obtained with the single-column method.

Several books and review articles describe the modifications and applications in ion chromatography over the last 13 years (9,16-18). Instrumental improvements have been directed at extending ion chromatography for use with other detectors. These include direct or indirect spectrophotometry (19-22), indirect fluorescence (23), electrochemical (24,25), refractive index measurements (26) and spectrophotometry using a post-column reactor (27).

Another major research thrust has been to develop an IC system which is capable of performing eluent, or solvent, programming to resolve complex mixtures. This has been successfully accomplished using the improved Dionex hollow fiber system and conductivity detection (11,28). Gradient elution can also be used with direct detection methods.

These methods include direct potentiometric detection of halides and pseudohalides (29) and the spectrophotometric detection of metal complexes after reaction with a post-column color-forming reagent (30). A clever technique was used by researchers at Waters (Millipore Corp., Milford, MA, USA) to perform gradient elution in SCIC with a conductivity detector (31). Using two eluents which have the same conductivities, the eluent composition can be programmed with minimal baseline disturbances because the background conductivity remains constant.

Another recent development in ion chromatography regards the simultaneous determination of anions and cations (32-34). For example, Iskandarani and Miller separated anions and cations in a single chromatogram using an anion- and cation-exchange column in series, a copper o-sulfobenzoate eluent and indirect spectrophotometric detection at 240 and 270 nm (32).

In other studies, new stationary phases for more efficient separations in ion chromatography have also been developed. The stationary phases used for SIC are agglomerated resins (35) with exchange capacities about 10 times greater than resins used in SCIC. SCIC stationary phases are usually chemically-functionalized or coated resins (36,37). In general, separation efficiencies obtained in ion chromatography are quite good. For example, Lee (38) reported 40,000 plates/m for nitrate using a macroporous strong-base anion exchanger (10 μm particles). However, peak efficiencies obtained in reversed-phase liquid chromatography are still greater than efficiencies obtained in ion chromatography. More efficient resins are still needed in ion chromatography to resolve more complex anion mixtures.

Factors affecting selectivity in anion chromatography have not been studied extensively. Selectivity theories formulated using classical ion-exchange resins do not necessarily apply to the selectivity effects observed in IC, which uses resins of very low exchange capacities. Selectivity effects caused by changing functional groups or resin matrices in SCIC have been investigated (37,39), but these studies by no means cover all of the factors which could influence anion selectivity.

Following this introduction, a brief literature review on resins and selectivity in anion chromatography is presented to provide the necessary background information on the topic of this dissertation. The rest of this dissertation is divided into three sections. Each section describes the use and preparation of a new stationary phase for anion chromatography. These new stationary phases are then used to separate anions more efficiently or to study selectivity effects in anion chromatography.

The goal of the first 2 sections was to study selectivity variations caused by altering the structure of a typical trimethylammonium ion-exchange resin. The first section describes the preparation and use of low-capacity spacer arm anion-exchange resins. These resins are different because spacers of varying lengths are inserted between the benzene rings of an XAD resin and the quaternary ammonium functional groups. The second section describes the use and preparation of a low-capacity quaternary phosphonium resin. The selectivity of the phosphonium resin is compared to that of quaternary ammonium ion-exchange resins. Information in each of the first 2 sections has been submitted for publication.

The goal of the third section was to quickly and easily prepare the most efficient anion-exchange resins ever used in our laboratories. A patent has been filed and a manuscript has been submitted for publication concerning the topic of this section.

# LITERATURE REVIEW

## Stationary Phases

### Anion-exchange chromatography

The first synthetic anion-exchange resin was prepared by Adams and Holmes in 1935 (40). This condensation polymer had primary amine groups which took up sulfuric acid in solution. Since this original work, several other "weak-base" resins (prepared from primary or secondary amines) have been synthesized. "Strong-base" quaternary ammonium resins (prepared from tertiary amines) have also been synthesized and are used most often. In addition, strong-base quaternary phosphonium and tertiary sulfonium anion exchangers have been reported (41).

As mentioned in the introduction, resins used for anion-exchange chromatography are typically gellular resins with high exchange capacities (2 to 5 meq/g) and large particle sizes (75 to 200 μm). The resin particles shrink and swell with electrolyte changes and are easily wetted by water.

Several excellent books describe the history of preparation, characteristics and use of classical anion-exchange resins (42,43,44).

## Anion chromatography

Anion-exchange resins used for ion chromatography can be placed into 3 categories according to their method of preparation: agglomerated, chemically-bonded and coated resins. These resins have very low exchange capacities compared to classical ion-exchange resins, so that dilute eluents and conductivity detection can be used in ion chromatography.

The first resins used in anion chromatography were agglomerated resins prepared by Small, Stevens and Bauman in 1975 for SIC (8). These stationary phases are made by "agglomerating" resin microparticles onto the surface of a sulfonated polymeric resin. The microparticles are highly functionalized with quaternary ammonium groups. They permanently adhere to the sulfonated resin because of electrostatic attractions. The resins and microparticles used are 5 to 100 $\mu$m and 0.1 to 5.0 $\mu$m in size, respectively. The result is a pellicular stationary phase which can be used to separate anions with good efficiency.

Anion-exchange latexes and much smaller sulfonated resins were used in 1982 to make agglomerated stationary phases, and much greater separation efficiencies were obtained (45,46). With the improved resins, the theoretical plate count is typically 2000 (for a bromide peak eluting in 5.5 minutes from a 100 X 8.0 mm i.d. column) using a 15 $\mu$m sulfonated resin and latex particles that are 0.02 to 0.10 μm in size. These agglomerated resins are still used and sold today in conjunction with the suppressed ion chromatographic systems made by the Dionex Corporation (Sunnyvale, CA, USA).

Other researchers have prepared similar agglomerated resins (47,48), some of which reportedly obtain even higher theoretical plate counts. A patent by Japanese workers describes the preparation of an agglomerated stationary phase that yields theoretical plate counts twice that obtained with a Dionex column of similar length (47).

Rokushika and coworkers (49) reported using an agglomerated resin packed in a microcolumn that is only 0.19 mm i.d. This is different because these resins are usually packed in "conventional" columns ranging from 2.0 to 4.6 mm i.d. Separation efficiency using this column is slightly lower than that obtained with conventional columns, but the miniaturized column requires only small amounts of packing material, sample and eluent.

Recently, Japanese researchers patented an interesting variation of the agglomerated method of resin preparation (50). Instead of electrostatically holding a latex onto the resin, the latex is "glued", or physically bound, onto the support. The glue is an insoluble binder that attaches a quaternized latex onto an unfunctionalized (meth)acrylate support. A wider variety of resin supports can be used to make these stationary phases because prior resin sulfonation is not necessary.

Chemically-bonded resins were synthesized by Fritz and coworkers in 1979 for SCIC (12). The resin used was XAD-1, which is a polystyrene-divinylbenzene polymer obtained from Rohm & Haas (Philadelphia, PA, USA). The polymer is obtained in spherical, 1 mm diameter particles and is first ground, sieved, cleaned and "defined". The functionalization process is a two-step procedure. The chloromethylation reaction uses a $ZnCl_2$ catalyst with chloromethyl methyl ether in methylene chloride and nitromethane. The chloromethylated beads are then aminated with trimethylamine to obtain a quaternary ammonium anion exchanger. The capacity of these resins ranges from 7 to 70 $\mu$eq/g and the columns give good separations of common inorganic anions. Rather low column efficiencies are obtained because of the large particle size of the resin particles (approximately 100 $\mu$m). A disadvantage of this procedure is that the chloromethylation reaction is very difficult to control, yielding widely varying resin capacities.

A better method of resin functionalization was published by Barron and Fritz (36). In this synthesis, a very reproducible chloromethylation reaction is used so that exchange capacities can be accurately predicted. This procedure differs from the previous method because an aqueous paraformaldehyde/hydrochloric acid solution is used for the chloromethylation reaction. Supposedly, this reaction promotes strictly surface functionalization because the aqueous solution does not swell the resin. A surface-functionalized resin should be more efficient for anion exchange. Anion separations obtained with this resin are more efficient than those previously obtained by Gjerde et al. (12). However, higher separation efficiencies are still obtained using SIC columns. This is due primarily to the particle size of the irregularly-shaped XAD-1 resins, which is still considered large at 28 to 37 $\mu$m.

Although early work in SIC and SCIC used polymeric-based resins as stationary phases, many of the first commercially-manufactured stationary phases for SCIC were silica-based. Silica is a desirable stationary phase because of its high mechanical stability. Silica-based ion chromatographic columns are similar to reversed-phase columns except that a quaternary ammonium group has been incorporated into the organic layer. Major manufacturers of silica-based ion-exchange columns are Vydac (Hesperia, CA, USA), Wescan (Santa Clara, CA, USA) and Toya Soda (Shin-nanyo, Yamaguchi, Japan).

An important drawback of the silica-based columns for ion chromatography is that they are unstable in aqueous media, especially above pH 7.0 (16,17). Because of this, the choice of eluents for these columns is limited and column lifetime is not long. However, column efficiencies on the silica-based columns are quite good. For example, efficiencies on columns manufactured by Toya Soda reach 25,000 N/m (theoretical plates/meter) (51).

One advantage of silica-based columns for IC is that longer columns may be used because of the greater mechanical strength of silica. Although the mechanical stability of the cross-linked polymers has improved, lower eluent flow rates and shorter column lengths are sometimes necessary because of resin pressure limits.

Many other chemically-functionalized stationary phases for IC have been prepared. For example, weak-base ion-exchange columns (with tertiary amine groups) have been synthesized and used as multifunctional columns (52,53). The amine group is protonated at low pH's and can act as an anion exchanger. Above the pH of the amine's $pK_a$, the amine group is deprotonated and can no longer exchange anions. By varying the ionic character (exchange capacity) of these weak-base resins, selectivity can be altered to better separate mixtures of anionic and neutral compounds.

The best chemically-functionalized polymeric stationary phase used for SCIC was reported by Lee (38). This polystyrene-divinylbenzene resin is a strong-base anion exchanger with quaternary ammonium functional groups. The resin is spherical in shape and can be either 5 or 10 μm in size. The column is designated PRP-X100 and is sold commerically by the Hamilton Company (Reno, Nevada, USA). Excellent separation efficiencies have been obtained with this column and a value of 40,000 N/m has been reported.

A rather different inorganic stationary phase for ion chromatography was reported in 1985 by Schmitt and Pietrzyk (54). A column containing 5 μm, spherical alumina obtained from Phase Separations (Norwalk, CT, USA) was used to separate common inorganic anions.

Recently, statically- or dynamically-coated resins have been used by many researchers in anion chromatography. These stationary phases are prepared by adding a long chain quaternary ammonium compound to the eluent or to the resin coating solution. This hydrophobic compound coats the neutral support and turns the resin into an anion exchanger.

Cassidy and Elchuk (55,56) were among the first to separate anions using a column containing a dynamically-modified polymeric support. DuVal and Fritz (37) successfully demonstrated the use of both dynamically- and statically-coated polymeric and reversed-phase columns for anion chromatography.

In the majority of cases, polymeric supports are used to prepare coated resins because the support needs to be hydrophobic in order to obtain a coating heavy enough so that anion exchange can occur. However, some studies have shown coated stationary phases made from silica and reversed-phase supports (57,58). Pfeffer, Takeuchi and Yeung also recently showed that a reversed-phase open tubular column can be coated and used as an anion-exchange column (59).

Coated resins as stationary phases are very popular today because they can be quickly and easily prepared using a variety of coating agents and resin matrices. Many other recent studies have used coated resins for anion separations (60-63), largely because the coated resins can be "custom-made" to suit the user. The last section of this dissertation describes the use and preparation of a new type of coated resin for anion chromatography which is used to obtain highly efficient anion separations.

## Resin Selectivity

### Anion-exchange chromatography

Initial work on ion-exchange selectivity was published in the 1950s and early 1960s. These studies focused primarily on the selectivity of cation-exchange resins because of the high interest in metal ion separations at that time. Beginning as an extension of work on cation exchangers, studies involving anion-exchange resins occurred because of the important applications of anion exchange to water treatment. Several excellent reviews and dissertations have outlined many of the factors affecting the selectivity of anion exchangers (6,7,64,65).

In ion-exchange chromatography, strong-base Type I or II resins are most often used for anion selectivity studies. Type I resins contain the benzyltrimethylammonium cation. Type II resins contain the same functional group with one of the methyl groups replaced by a hydroxyethyl group. These resins are commercially available under tradenames such as Amberlite, Dowex, Duolite and Ionac. The selectivity of weak-base (primary, secondary or tertiary amine functionalities) anion exchangers have also been compared to that of the strong-base quaternary ammonium exchangers.

Early work by Slough (66) concluded that resin selectivity is highly dependent on the polymeric matrix containing aromatic nuclei. Using strong-base anion exchangers, results from this study indicated that charge-transfer interactions occur between halide ions and the aromatic rings of a polymer. Supposedly, increasing amounts of charge-transfer in the series chloride < bromide < iodide are responsible for the elution order of these halides by an anion-exchange resin.

The selectivity of both strong- and weak-base resins was compared in 1967 by Boyd and Schwarz (67). Although no conclusive evidence was obtained, these researchers commented that anion selectivity is largely governed by the size and structure of the exchange group.

Type I and II strong-base resins were compared by Gregory and Dhond in 1972 (68) to determine their applicability in the removal of phosphate from wastewaters. They concluded that the more polar functional group in Type II resins has a higher affinity for sulfate as compared to Type I resins.

Boari et al. determined selectivity coefficients for sulfate and chloride on over 30 commercially-available strong- and weak-base anion exchangers (69). The main conclusion was that selectivity for sulfate is strongest with weak base (especially primary amine) resins.

Bartoli et al. synthesized a series of weak-base anion-exchange resins based on N-(dialkylaminomethyl)acrylamide-co-divinylbenzene polymers (70). They found that affinity for large, monovalent anions increases as the number of carbon atoms in the amino functional group increases.

In 1980, Gozdz and Kolarz (71) synthesized several strong- and weak-base anion exchangers using the same batch of macroporous polystyrene. Selectivity coefficients for anions like bromide, iodide and perchlorate were compared to that of chloride. Results showed that anion-exchange resins with more hydrophobic exchange sites have greater affinities for more hydrophobic anions. These trends were explained using the classical theory of water-structure induced ion pairing, which will be discussed later.

Interesting work by Guter (72) studied the selectivity of nitrate and sulfate on several strong-base resins. All resins were made from one batch of chloromethylated resin. This study showed that a triethylamine resin has a higher affinity for nitrate (as compared to chloride) than a trimethylamine resin.

Recently, factors affecting the selectivity of anions like chloride, nitrate and sulfate were studied by Clifford and Weber (73,74) and Walpole and Myers (75) using 30 commercially available anion-exchange resins. The resin matrix and functional group identity were considered two of the most important variables in determining the selectivity of mono- and divalent anions. Similar to conclusions drawn by Gregory and Dhond (68), results from this study showed that Type II resins have a greater affinity for sulfate as compared to Type I resins. Apparently, the more hydrophilic exchange group of Type II resins has a greater affinity for more hydrated anions.

Many of the selectivity studies performed in ion-exchange chromatography compared resins obtained from several commercial sources. These resins have widely different polymeric matrixes and the conditions of preparation are not known. Therefore, generalizations regarding the relation of resin structure and selectivity are difficult to substantiate. In spite of this, similar trends exist in several of the selectivity studies mentioned earlier. Generally, these studies indicate that resins with more hydrophobic exchange groups have greater affinities for larger, hydrophobic anions. Resins with more hydrophilic exchange groups have greater affinities for more hydrophilic anions like sulfate.

The best theoretical explanation of the selectivity of anion-exchange resins was first given by Chu, Whitney and Diamond in 1962 (76). Diamond (77) and Diamond and Whitney (78) later expanded this explanation and used the term "water-structure induced ion pairing" to describe this theory. The theory suggests that ion-water (hydration) and water-water (water structure) interactions in the resin and external solution phases are the most important selectivity-controlling factors.

According to the theory, ion hydration is the most important effect for anions of weak acids. These anions prefer the external solution phase to a greater extent because of strong interactions with the hydrogen atoms in water molecules. Small, highly hydrated anions like fluoride also prefer the solution phase because of their favorable water interactions.

The selectivity of large anions and anions of strong acids can be explained by their disruption of the hydrogen-bonded water structure. In the resin phase, the exchange group extends out into the external solution and can cause a water disturbance. Since the large anion also causes a water disturbance, the water structure forces the large anion and the resin ion into the same cavity to reduce their combined disturbance of the water structure. A tightening of the water structure surrounding the cavity helps hold the ion pair together. Thus, larger anions and larger exchange sites increase the effects of this "water-structure induced ion pairing" and cause greater anion retentions.

## Anion chromatography

Very little work has been published on altering the stationary phase to induce selectivity changes in anion chromatography. The reason for this is partly due to the proprietary nature of commercially-made resins.

The original resin used in SIC was a pellicular resin containing a Type I functional group. Anions elute from this column in an order typical of most anion-exchange resins: chloride < bromide < nitrite < nitrate < sulfate < thiosulfate. Another Dionex column, HPIC-AS2, shows rather different selectivity and has a very low affinity for sulfate. Clifford and Weber (74) reported that a benzyltriethylammonium functional group is responsible for this selectivity variation.

A comprehensive study by Barron (64) investigated the effect on selectivity of different quaternary R group lengths. Thirteen strong-base resins were prepared from tertiary amines like trimethylamine, tributylamine, trioctylamine, triethanolamine and methyldiethanolamine. All resins were prepared from XAD-1, and were synthesized to have very similar, low exchange capacities. The main conclusion of this work was that the size and hydrophobicity of the exchange site have a major effect on anion selectivities. Using a trioctylamine resin, the relative affinity for large monovalent anions like nitrate and iodide increases. At the same time, the relative affinity for divalent anions decreases. These results were supported by a recent study which investigated this effect using modified hydroxyethyl methacrylate copolymers (79). Barron and Fritz explained their results using the classical concept of water-structure induced ion pairing (76-78).

Since the resins used in ion chromatography have very low exchange capacities, the large amount of unfunctionalized resin surface area should influence anion selectivity. The first work in SCIC by Gjerde, Fritz and

Schmuckler (12) used Type I resins made from macroporous XAD-1 resin. A higher affinity for large, polarizable monovalent anions like iodide and thiocyanate was reported on this resin as compared to conventional gel resins. This increased affinity was attributed to the hydrophobic interactions caused by the resin matrix.

Afrashtehfar and Cantwell (80) also reported that the resin matrix of a low-capacity resin seemed to have an influence on the retention of ions. In this study, a low-capacity XAD-2 resin showed both ion exchange and surface adsorption. Related to this, Cantwell and Puon (81) mentioned the possibility of the adsorption of large monovalent anions like bromide and nitrate on an unfunctionalized XAD-2 surface.

The effect of the resin matrix on anion selectivity was studied using ion interaction chromatography by Iskandarani and Pietrzyk (62). DuVal and Fritz (37,65) also used coated resins to study this effect. In this work, various resin matrices were dynamically- or statically-coated with long chain quaternary ammonium compounds. The performance of the coated resins was then evaluated in ion chromatography. This study concluded that large, monovalent anions like nitrate and iodide are more highly retained on polar resin matrices, like polyacrylate, as compared to more nonpolar polystyrene-divinylbenzene. This effect was attributed to greater water-structure induced ion pairing at the exchange site caused by the more polar resin surface.

Schmitt and Pietrzyk (54) recently introduced the use and unique selectivity properties of an alumina stationary phase for SCIC. Using an acetate eluent at a pH of 4.5 to 5.5, halide anions are separated on the alumina column according to the following order of elution: fluoride >> chloride > bromide > iodide. This is the exact reversal of the elution order obtained with any other stationary phase. This strikingly-different anion selectivity is consistent with the magnitude of the aluminum-halide complex formation constants.

Many of the selectivity effects observed thus far in anion chromatography can be explained by the classical theory of water-structure induced ion pairing. However, many more experiments can be performed to fully understand how the structure of an anion exchanger affects selectivity in anion chromatography. The first two sections of this dissertation will investigate the effects on selectivity in SCIC of two new types of strong-base anion exchangers: spacer arm and phosphonium resins.

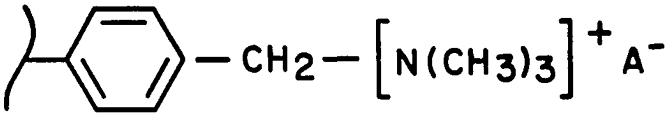
# SECTION I. LOW-CAPACITY SPACER ARM RESINS FOR SELECTIVITY STUDIES IN ANION CHROMATOGRAPHY

# INTRODUCTION

With the growing popularity of single-column ion chromatography (SCIC) and its applications, there is a need to better understand ion selectivity. A basic understanding of the factors that influence ion-exchange selectivity will allow better separations for certain samples to be obtained.

Basic studies of ion-exchange selectivities have not progressed nearly as fast as the technique of ion chromatography. For anion-exchange resins of a fairly low capacity, very little work has been published on altering the stationary phase to induce anion selectivity changes.

The anion-exchange resin most often used in our laboratories is a chemically-functionalized XAD resin:



XAD-1 resin

Previous work used a resin of this type to systematically study the effects on selectivity of different quaternary ammonium R groups (1). The results of this study were supplemented by a recent investigation (2) which studied the influence of functional groups on sorbent selectivity using modified hydroxyethyl methacrylate copolymers.

DuVal and Fritz (3) used resins coated with long chain quaternary amines to study the effects on anion selectivity of different resin matrices. Similar to this, Iskandarani and Pietrzyk (4) used ion interaction chromatography to study the effects on selectivity of several sorbed quaternary ammonium ions.

There are additional ways the structure of the resin shown above could be altered to induce selectivity variations in anion chromatography. In this investigation, we present results on the effects of inserting spacers of varying length between the benzene rings of an XAD resin and the quaternary ammonium functional groups. Explanations for the selectivity variations of anions on these spacer arm resins are presented.

# EXPERIMENTAL

## Materials and Equipment

The XAD-1 resin was obtained from Rohm & Haas (Philadelphia, PA, USA). The bromoalkenes were obtained from Aldrich (Milwaukee, WI, USA) or Fairfield Chemical (Blythewood, S.C., USA) and were at least 98% pure. The triflic acid and 99% 1,2-dichloropropane were obtained from Aldrich. A 25% solution of trimethylamine in methanol from Eastman (Rochester, NY, USA) was used for amination. All solvents used for extracting and rinsing resin were of reagent grade and were obtained from a number of sources. All reagents except XAD-1 were used as received.

Ion chromatography was carried out on an instrument built from several components. An LKB 2150 HPLC pump provided eluent flow. A Rheodyne (Berkeley, CA, USA) Model 7010 injection valve fitted with a 20-$\mu$l loop was used for sample introduction. The resins were packed in glass-lined stainless steel columns (250 X 2.0 mm i.d.) which were obtained from Scientific Glass Engineering (Austin, TX, USA). An Eldex (Menlo Park, CA, USA) column heater was used to insulate the column and prevent baseline drift. The detector used was a Model 213A conductivity detector manufactured by Wescan Instruments (Santa Clara, CA, USA). A strip-chart recorder manufactured by Curken Scientific (Danbury, CT, USA) was used to record chromatograms.

## Procedures

The XAD resin was prepared by first grinding the resin in a shear mill and then passing it through U.S. Standard Mesh sieves to obtain sized fractions of the copolymer. The small-sized resin fractions were then passed through 26 μm mesh cloth obtained from Hach Chemical Company (Ames, IA, USA). The fractions were then Soxhlet extracted for 24 hours each with methanol, acetonitrile and ether. The sized fractions were then slurried in methanol and allowed to settle. The supernatant liquid was poured off to remove suspended "fine" resin particles. This slurry process was repeated until the supernatant liquid was visually free of particles after settling.

Preliminary reactions were carried out using resin beads approximately 38 to 44 μm in size. The resin beads used for chromatography were approximately 15 to 26 μm in size. The 250 mm long columns typically had a back pressure of 200 psi with an eluent flow of 1.0 ml/min.

The spacer arm synthesis chosen was the one-pot procedure developed by Japanese workers (5). XAD-1 is reacted to give ω-bromoalkylated polystyrene-divinylbenzene. This intermediate is then aminated to give a strong-base quaternary ammonium resin for anion chromatography.

The reactions were carried out in a 2-neck 250-ml round-bottom flask equipped with a nitrogen inlet tube and an addition funnel. The sized XAD-1 resin (0.2 to 1.0 g) was placed into the flask, followed by the appropriate amount of 1,2-dichloropropane. The flask contents were magnetically stirred and the flask was filled with nitrogen. The triflic acid catalyst was added to the mixture. An ω-bromoalkene in 1,2-dichloropropane was added dropwise to the mixture over a 5 minute time period. The mixture was stirred for a total of 3 hours at room temperature under nitrogen. The resin beads were then filtered and washed with dioxane, acetone, methanol, tetrahydrofuran and methanol.

The ω-bromoalkylated resin was then aminated using 25% trimethylamine in methanol. This mixture was refluxed at least 10 hours to insure a complete reaction. The resin beads were again filtered and washed with 2 M hydrochloric acid, water, 2-propanol, water and methanol. The functionalized resin was then air dried.

The strong-base ion-exchange capacities of the resins were determined by rinsing a weighed portion of resin with methanol, water, 0.5 M potassium nitrate and then again with water to remove any excess nitrate. The resin was then transferred to a gravity column and the bound nitrate was eluted with 0.005 M potassium sulfate. The collected nitrate was then determined spectrophotometrically at 225 nm.

All solutions were made up in distilled, deionized water and were prepared from reagent grade salts. Eluents were prepared by dissolving the acid in distilled, deionized water and, if necessary, adjusting the pH by adding sodium hydroxide. The eluents were then filtered through a 0.2 μm membrane filter after which a vacuum was applied while stirring to remove dissolved gases.

Columns were packed using an upward packing, stirred slurry technique with 40% ethylene glycol and 1% sodium chloride in water as the packing solvent. The packing pressure was approximately 2000 psi. The instrument used to pack the columns was either a home-built apparatus or a Shandon H.P.L.C. Packing Pump (Phenomenex, Rancho Palos Verdes, CA, USA).

# RESULTS AND DISCUSSION

## Preparation of Resins

Several methods have been published which describe the synthesis of anion-exchange resins suitable for single-column ion chromatography (SCIC). Gjerde et al. (6) and Barron and Fritz (7) used chloromethylation and then amination of XAD resins to obtain a quaternary ammonium anion-exchange resin. It was possible to obtain resins with reproducible and very low capacities by careful control of the chloromethylation step. Both procedures either used or produced chloromethyl methyl ether (CMME) which contains small amounts of bis-(chloromethyl) ether. The latter compound is mutagenic and carcinogenic.

Static or dynamic resin coating procedures have also been reported, which convert almost any resin into an anion-exchange resin (3,8,9).

None of the reported methods has provided a convenient way to synthesize anion-exchange resins with a varying spacer length between the resin surface and the quaternary ammonium functional groups.

The procedure utilized in this work consists of a two-step synthesis. The first step is a slight modification of the procedure developed by Tomoi et al. (5) for synthesizing highly-functionalized (38%) gel phase-transfer catalysts.

Modifications of this synthesis were made to control the reaction of an ω-bromoalkene with a macroporous XAD-1 resin to obtain approximately a 1% degree of functionalization. The resins were then aminated with trimethylamine. (See Figure 1.)

The degree of bromoalkylation (which determined the final resin capacity) was controlled by varying both reactant concentrations or by varying the acid catalyst concentration. For the first resins synthesized, the studies performed were aimed at characterizing the extent of the bromoalkylation reaction while varying reaction parameters. Figure 2 shows the capacities obtained using allyl bromide when varying both reactant concentrations in a constant volume reaction. Several other spacer arm resins were synthesized with very little preliminary characterization of reaction yield.

Five different resins were synthesized where the number of carbons in the spacer arm (n) was 1, 2, 3, 4 or 6. The resins were packed in columns and designated C1, C2, C3, C4 or C6 according to the length of the spacer arm. The exchange capacities of the 5 resins are listed in Table I along with conditions for the synthesis of each resin.

Unlike the syntheses previously described, this synthesis does not involve the use or formation of the potentially dangerous bis-(chloromethyl) ether. In

Figure 1. Reaction scheme for the synthesis of spacer arm resins

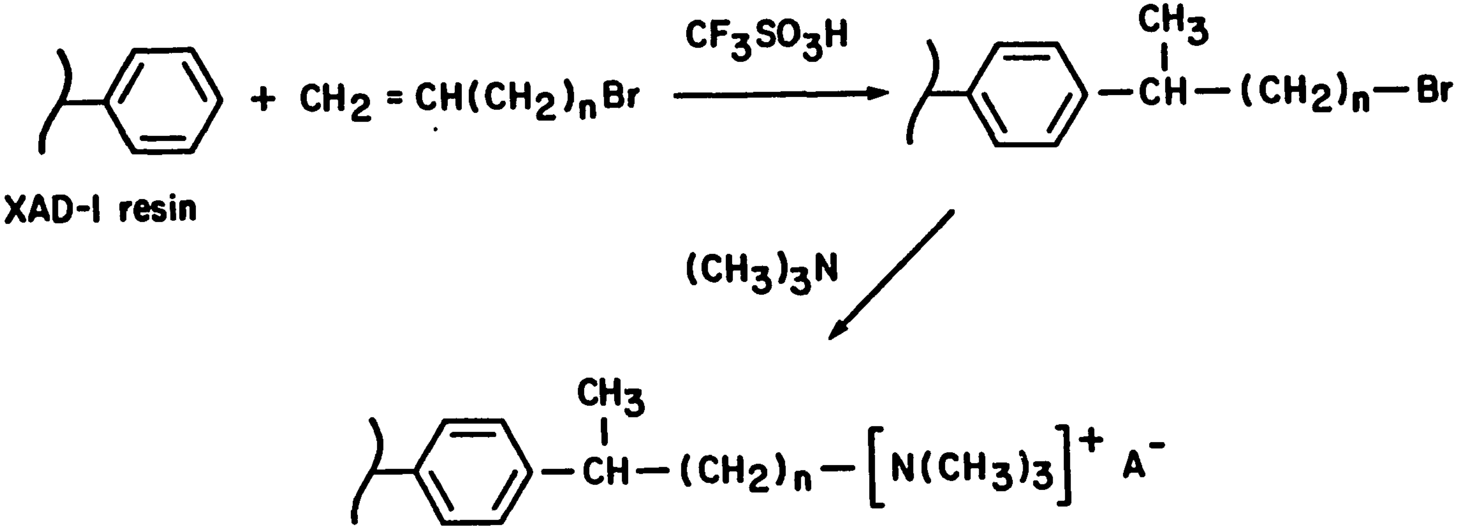

+ CH2 = CH(CH2)nBr
CF3SO3H
XAD-1 resin
CH3
—CH—(CH2)n—Br
(CH3)3N
CH3
—CH—(CH2)n—[N(CH3)3]+ A-

Figure 2. Exchange capacities vs. reactant concentrations obtained with C3 resins. *1 = 1.86 mmoles triflic acid and 9.42 mmoles allyl bromide (25-ml total reaction volume, 1,2-dichloropropane solvent)

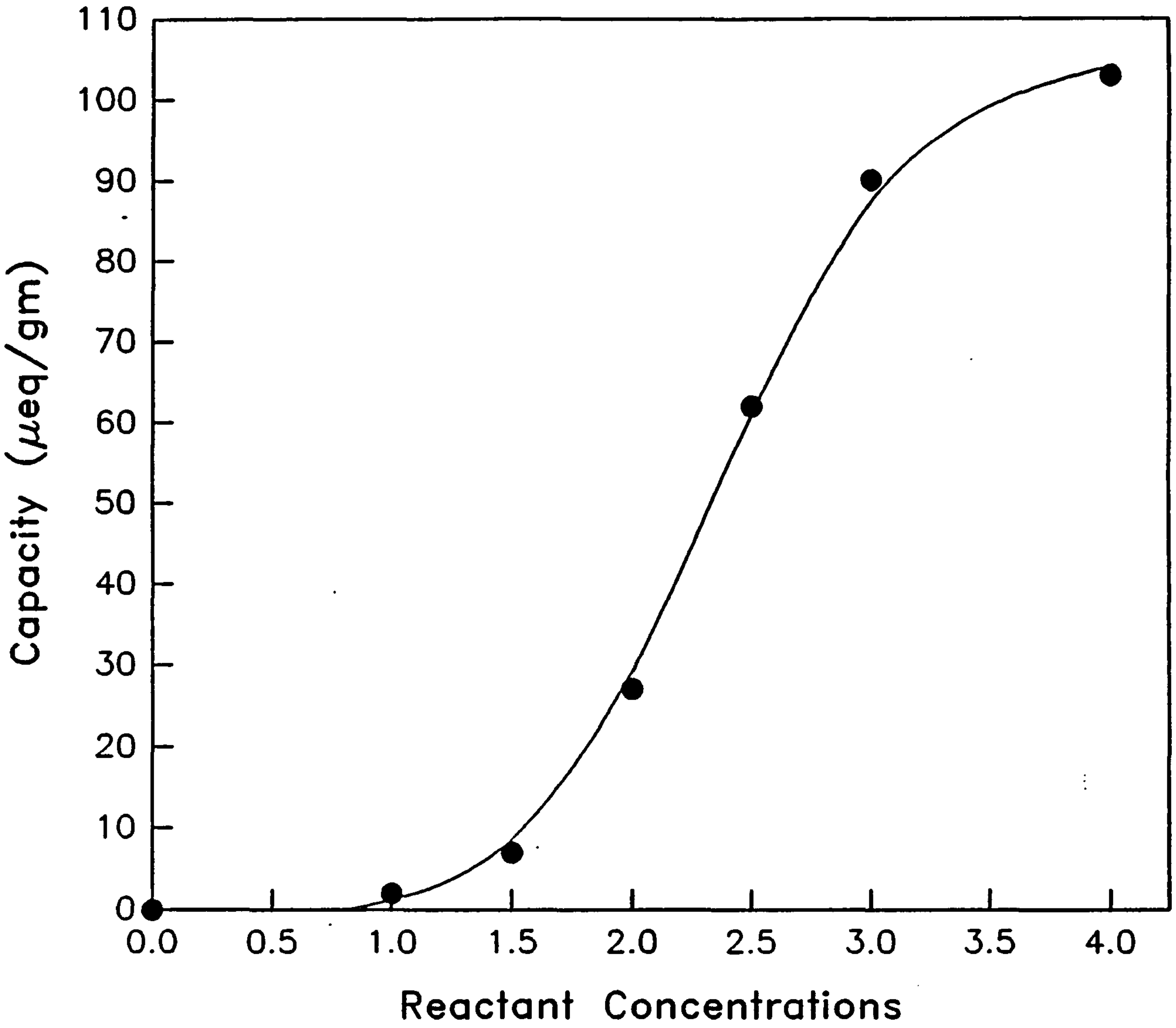

Capacity (μeq/gm)
110
100
90
80
70
60
50
40
30
20
10
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Reactant Concentrations

Table I. Preparation of Spacer Arm Anion-exchange Resins[a]

| Spacer Arm Resin (Cn) | $CH_2=CH(CH_2)_nBr$ (mmoles) | $CF_3SO_3H$ (mmoles) | Capacity (μeq/g) |
|---|---|---|---|
| C1 | 28.26 | 5.58 | 49 (±1) |
| C2 | 28.26 | 12.12 | 52 (±2) |
| C3 | 30.14 | 2.42 | 50 (±4) |
| C4 | 7.46 | 4.09 | 47 (±1) |
| C6 | 5.96 | 7.89 | 61 (±1) |

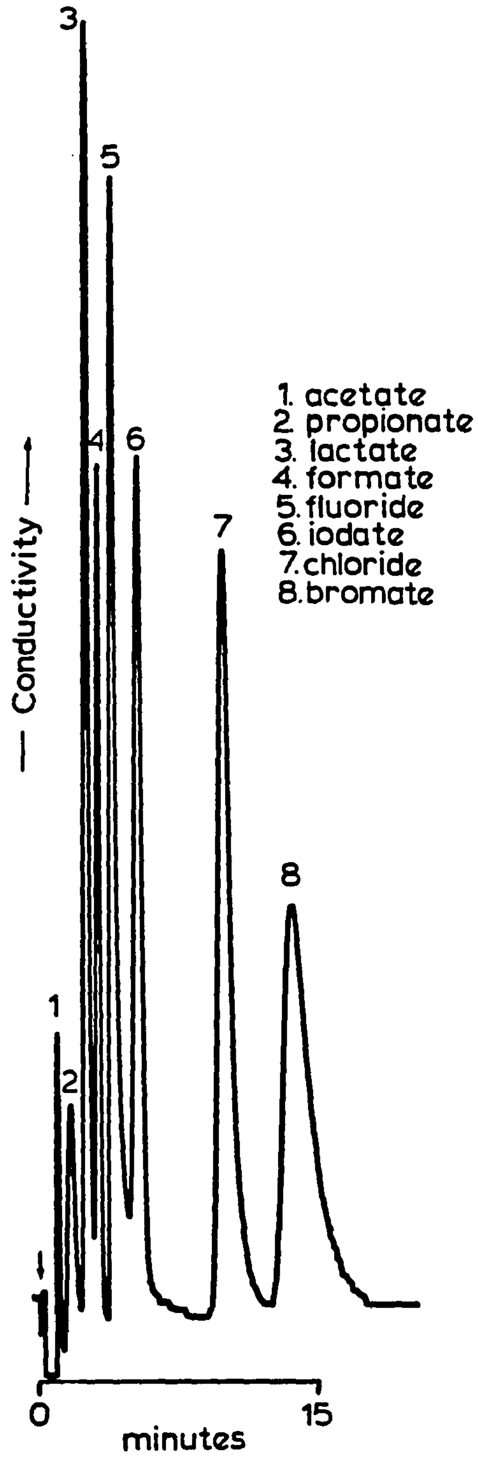
[a] All reactions were run at room temperature for 3 hours on 1 gram of 28 to 36 μm XAD-1 resin. Dilution with 1,2-dichloropropane was used to obtain a total reaction volume of 25 ml. All capacity determinations were performed in triplicate.

addition, the synthesis step producing the bromoalkylated intermediate is a one-step reaction. Other spacer arm synthetic routes are multi-step or difficult procedures which have been used to obtain phase-transfer catalysts (10 - 15), affinity chromatography supports (16,17,18), supports for solid phase peptide synthesis (19) or solid phase catalysts for asymmetric syntheses (20,21).

The spacer arm anion-exchange resins synthesized in this work were found to be very useful resins for anion chromatography. Figure 3 shows a good separation of several organic and inorganic anions using a C4 resin with a nicotinic acid eluent. The quality of this separation is comparable to the same separation obtained with a typical trimethylammonium XAD resin (of a similar capacity) synthesized by the Barron and Fritz method (7).

The purpose of this study was to determine the effects on selectivity of inserting spacers of varying length between the benzene rings of the resin polymer and the quaternary ammonium functional groups. To study these effects, several other selectivity-controlling factors were kept constant. For example, the resins were all prepared from the same resin lot and were synthesized to have similar capacities so that identical eluent conditions could be used for each resin.

Figure 3. Chromatogram showing usefulness of spacer arm anion-exchange resins. A C4 resin was used with a 6 mM nicotinic acid eluent and conductivity detection. The flow rate is 1.0 ml/min


1. acetate
2. propionate
3. lactate
4. formate
5. fluoride
6. iodate
7. chloride
8. bromate
Conductivity
1
2
3
4
5
6
7
8
0
15
minutes

## Evaluation of Resin Selectivity

A dynamic method was used to obtain selectivity data on the spacer arm resins. This method involved packing each resin in a chromatographic column and determining the retention times of various anions under identical eluent conditions for each column. The eluents used in this study were 6 mM nicotinic acid, 0.2 mM sodium phthalate at pH 6.0 and 0.8 mM sodium phthalate at pH 5.0. Relative retention times were determined by dividing the adjusted retention time of each ion by the adjusted retention time of the chloride ion. This calculation corrects for small flow rate or eluent concentration changes and also for slight differences in resin capacity.

Table II shows the relative retention times for 16 monovalent anions using 6 mM nicotinic acid as the eluent. The data show that the relative retention times for many of the anions are not affected by the length of the spacer arm. However, nitrate does show a lower relative retention time as the spacer arm length is increased. Nitrite, bromate and bromide show a similar trend, but to a lesser extent. In addition, some of the anions have broader peaks on the C1 resin than on the resins with longer spacer arms. This is shown for lactate in Figure 4.

Table III shows retention data for many typical inorganic anions using a 0.2 mM sodium phthalate eluent at

Table II. Adjusted Retention Time Ratios of Monovalent Anions on $C_1$, $C_2$, $C_3$, $C_4$ and $C_6$ Spacer Arm Anion-Exchange Resins[a]

| | $t_R'/t_{R,Cl}'$ | | | | |
|---|---|---|---|---|---|
| Anion | $C_1$ Resin | $C_2$ Resin | $C_3$ Resin | $C_4$ Resin | $C_6$ Resin |
| Acetate | 0.09 | 0.08 | 0.08 | 0.10 | 0.07 |
| Propionate | 0.24 | 0.18 | 0.13 | 0.18 | 0.13 |
| Glycolate | 0.24 | 0.24 | 0.23 | 0.26 | 0.24 |
| Lactate | 0.27 | 0.25 | 0.23 | 0.27 | 0.24 |
| Formate | 0.31 | 0.32 | 0.28 | 0.35 | 0.32 |
| Fluoride | 0.38 | 0.41 | 0.40 | 0.45 | 0.42 |
| Azide | 0.39 | 0.32 | 0.28 | 0.31 | 0.31 |
| Iodate | 0.50 | 0.57 | 0.51 | 0.58 | 0.57 |
| Dihydrogen Phosphate | 0.53 | 0.61 | 0.58 | 0.62 | 0.61 |
| Methylsulfonate | 0.90 | 0.95 | 0.91 | 0.93 | 0.93 |
| Chloride | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Ethylsulfonate | 1.23 | 1.31 | 1.23 | 1.27 | 1.29 |
| Nitrite | 1.29 | 1.11 | 1.05 | 1.07 | 1.13 |
| Bromate | 1.51 | 1.34 | 1.17 | 1.21 | 1.31 |
| Bromide | 2.55 | 2.34 | 2.26 | 2.07 | 2.16 |
| Nitrate | 4.14 | 3.27 | 3.01 | 2.76 | 3.00 |
| $t_R'$,$Cl^-$ (min) | 16.57 | 14.95 | 20.29 | 15.26 | 17.91 |

[a] Conditions: 6 mM nicotinic acid; 1.0 ml./min.; 0.2 μSFS conductivity detection.

Figure 4. Chromatogram of 7.5 ppm lactate on a.) C1 and b.) C6 columns. Conditions are listed in Figure 3

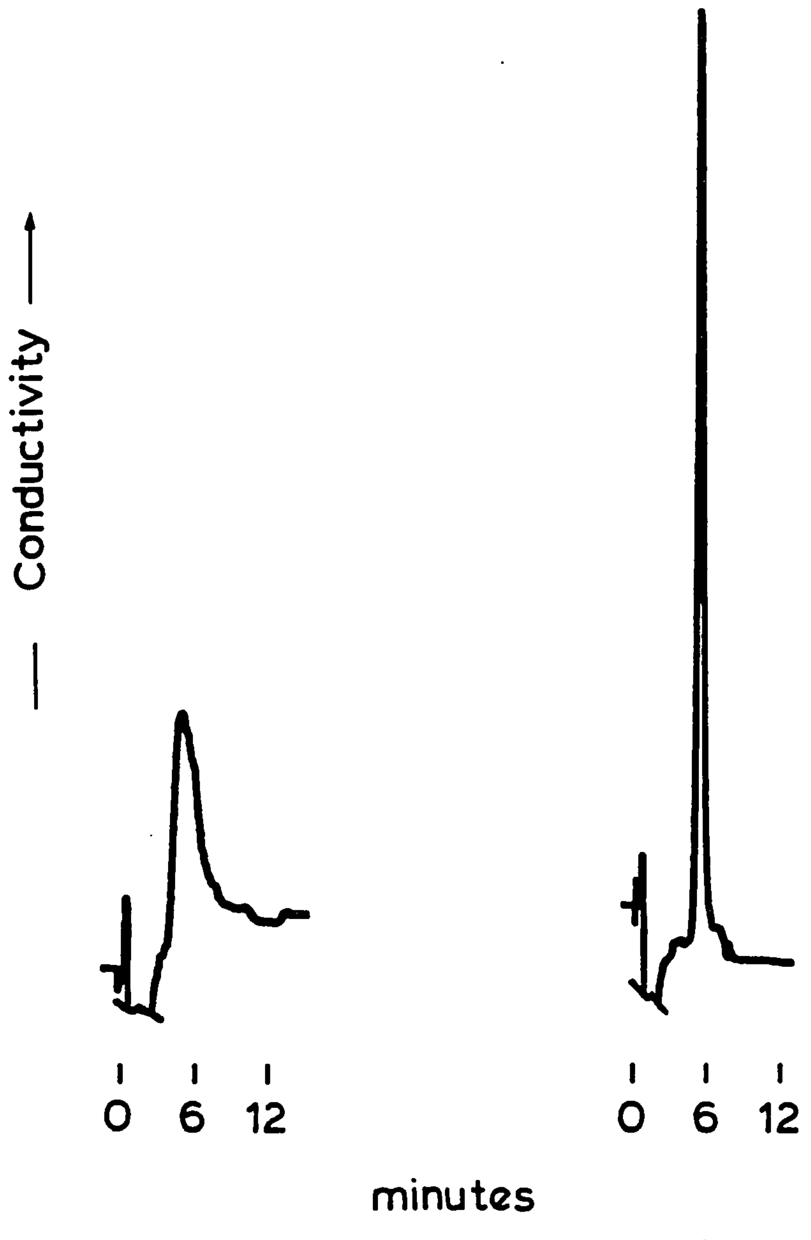

Conductivity
0
6
12
0
6
12
minutes
a.)
b.)

Table III. Adjusted Retention Time Ratios of Mono- and Divalent Anions on $C_1$, $C_2$, $C_3$, $C_4$ and $C_6$ Spacer Arm Anion-Exchange Resins[a]

| | $t_R'/t_{R,Cl}'$ | | | | |
|---|---|---|---|---|---|
| Anion | $C_1$ Resin | $C_2$ Resin | $C_3$ Resin | $C_4$ Resin | $C_6$ Resin |
| Chloride | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Methylsulfonate | 1.09 | 1.00 | 1.07 | 1.14 | 1.06 |
| Ethylsulfonate | 1.55 | 1.40 | 1.50 | 1.57 | 1.35 |
| Nitrite | 1.78 | 1.47 | 1.50 | 1.36 | 1.32 |
| Bromide | 2.53 | 2.13 | 2.00 | 1.79 | 1.88 |
| Nitrate | 3.62 | 3.07 | 2.46 | 2.43 | 2.65 |
| Propylsulfonate | 3.79 | 3.40 | 3.29 | 3.36 | 3.06 |
| Chlorate | 7.13 | 4.47 | 3.86 | 3.71 | 4.12 |
| Sulfate | 7.36 | 8.27 | 8.53 | 8.50 | 8.50 |
| Thiosulfate | 16.21 | 16.67 | 18.43 | 15.36 | 18.29 |
| Iodide | 17.59 | 12.20 | 8.86 | 8.57 | 11.24 |
| $t_R'$, $Cl^-$ (min) | 1.66 | 1.43 | 1.33 | 1.33 | 1.62 |

[a] Conditions: 0.2 mM sodium phthalate, pH 6.0; 1.0 ml/min; 0.2 μSFS conductivity detection.

pH 6.0. The trend seen in the previous table is again observed for the larger, more polarizable monovalent anions. This trend is graphically illustrated for several anions in Figure 5. As Figure 5 displays, these anions show lower relative retentions as the spacer arm length is increased. The minimum relative retentions occur with the C4 spacer arm column. Figure 6 shows chromatograms of the same 3 anions separated on 3 of the spacer arm columns. As seen in this figure, better peak shapes and much shorter separation times are obtained using the longer spacer arm columns.

Some additional divalent anions (chromate, oxalate, molybdate) were studied using a more concentrated eluent (0.8 mM sodium phthalate) at pH 5.0. Figure 7 plots the relative retention times of iodide and several divalent anions vs. the number of carbons in the spacer arm resin which was tested. The divalent anions showed little change in relative retention as the length of the spacer arm was changed. However, iodide showed a very pronounced drop in relative retention going from $n = 1$ to $n = 4$.

Figure 8 shows chromatograms of mono- and divalent anions on three of the spacer arm columns. Sulfate and thiosulfate have retention times of 14 and 27 minutes, respectively, in each chromatogram. It can easily be seen, however, that the retention times and peak shapes of the monovalent anions in these separations change according to trends described earlier.

Figure 5. Relative retention times versus spacer arm length for bromide, nitrate, chlorate and iodide using a 0.2 mM sodium phthalate eluent at pH 6.0 run at a flow rate of 1.0 ml/min and conductivity detection

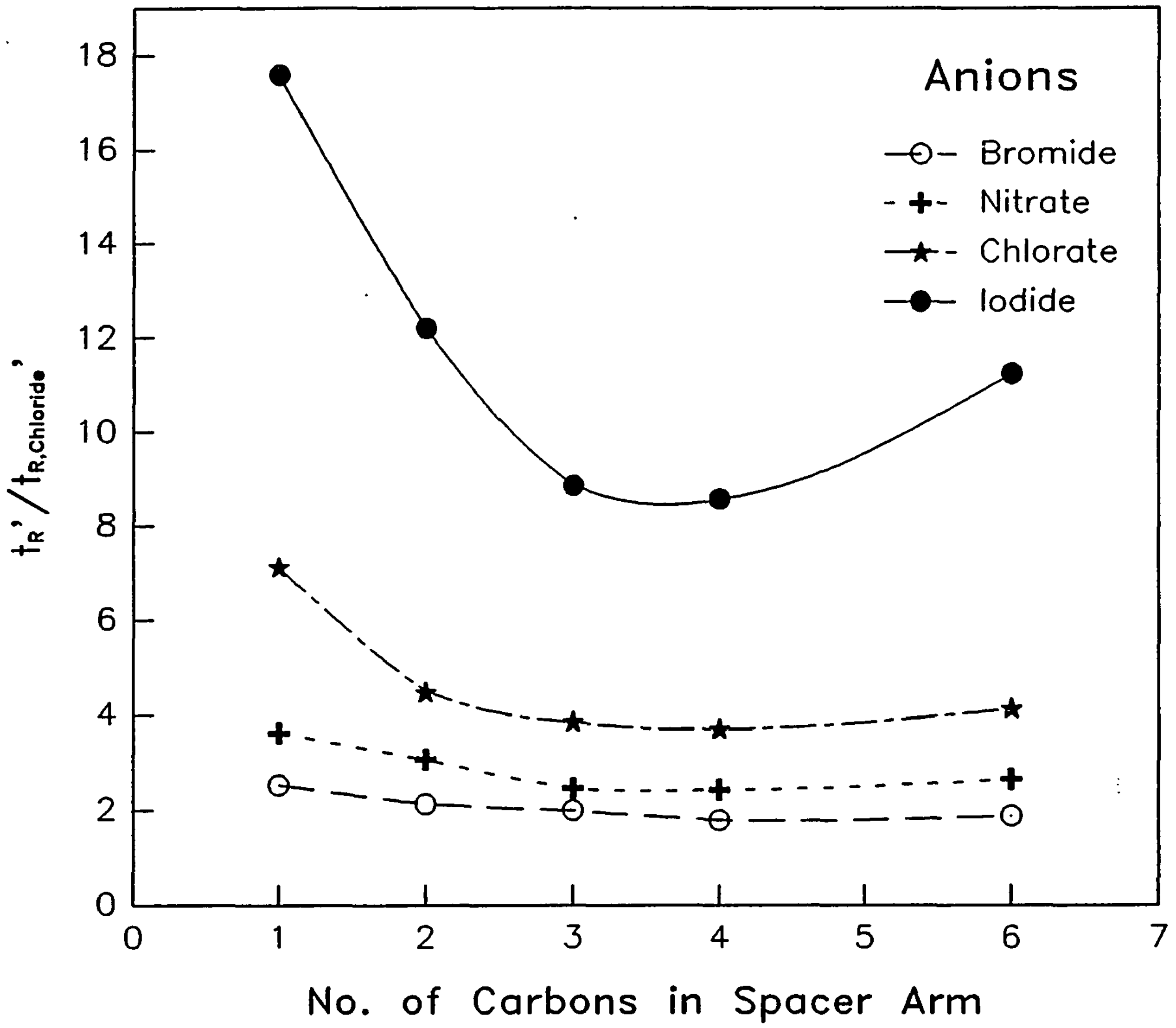

Anions
Bromide
Nitrate
Chlorate
Iodide
$t_R' / t_{R,Chloride}'$
0
2
4
6
8
10
12
14
16
18
0
1
2
3
4
5
6
7
No. of Carbons in Spacer Arm

Figure 6. Separation of 25 ppm nitrate, 75 ppm chlorate and 150 ppm iodide on the C1, C2 and C4 resins using conditions listed in Figure 5

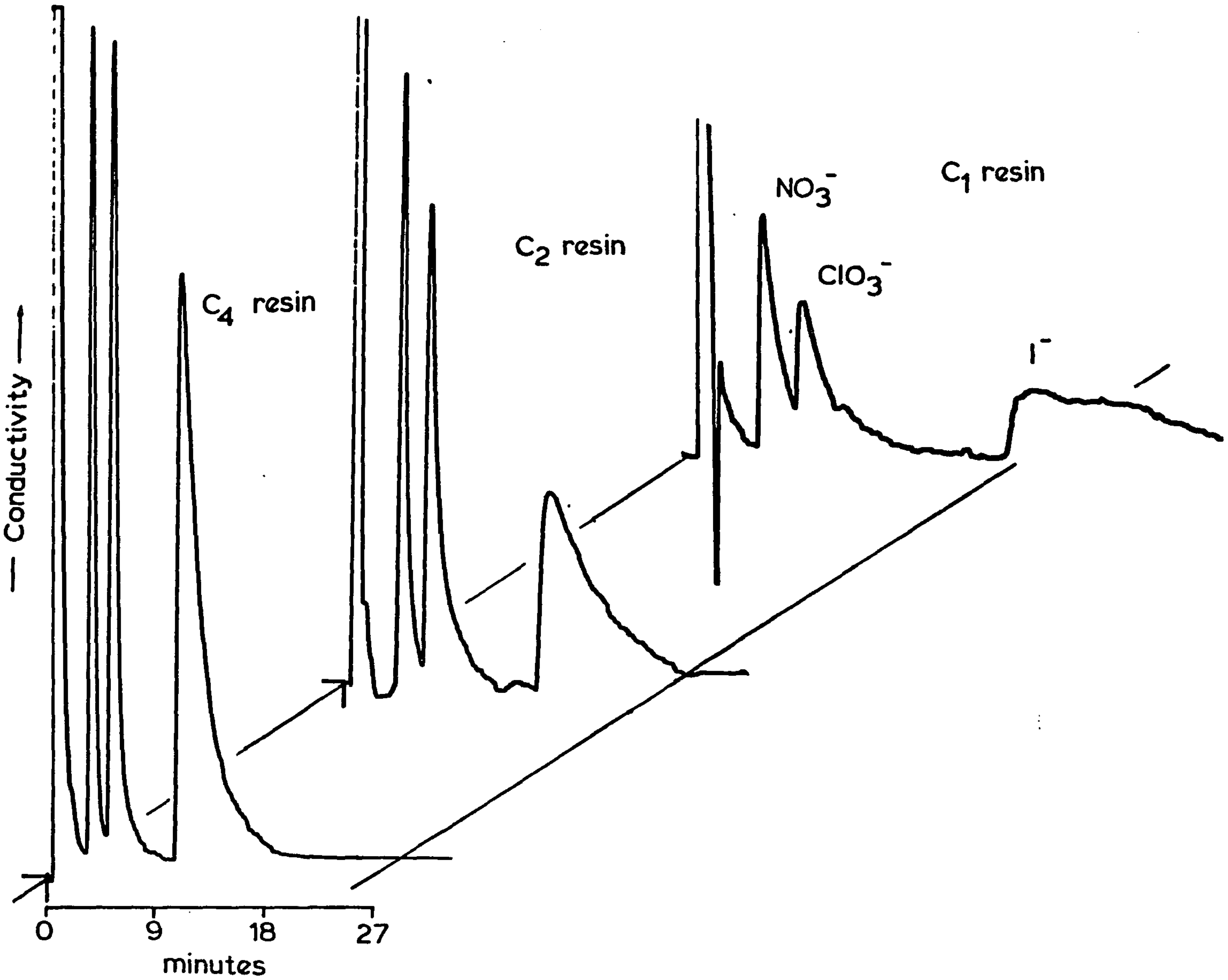

— Conductivity —
C4 resin
C2 resin
C1 resin
NO3⁻
ClO3⁻
I⁻
0
9
18
27
minutes

Figure 7. Relative retention times versus spacer arm length for divalent anions and iodide using a 0.8 mM sodium phthalate eluent at pH 5.0. The flow rate was 1.0 ml/min and detection was by conductivity

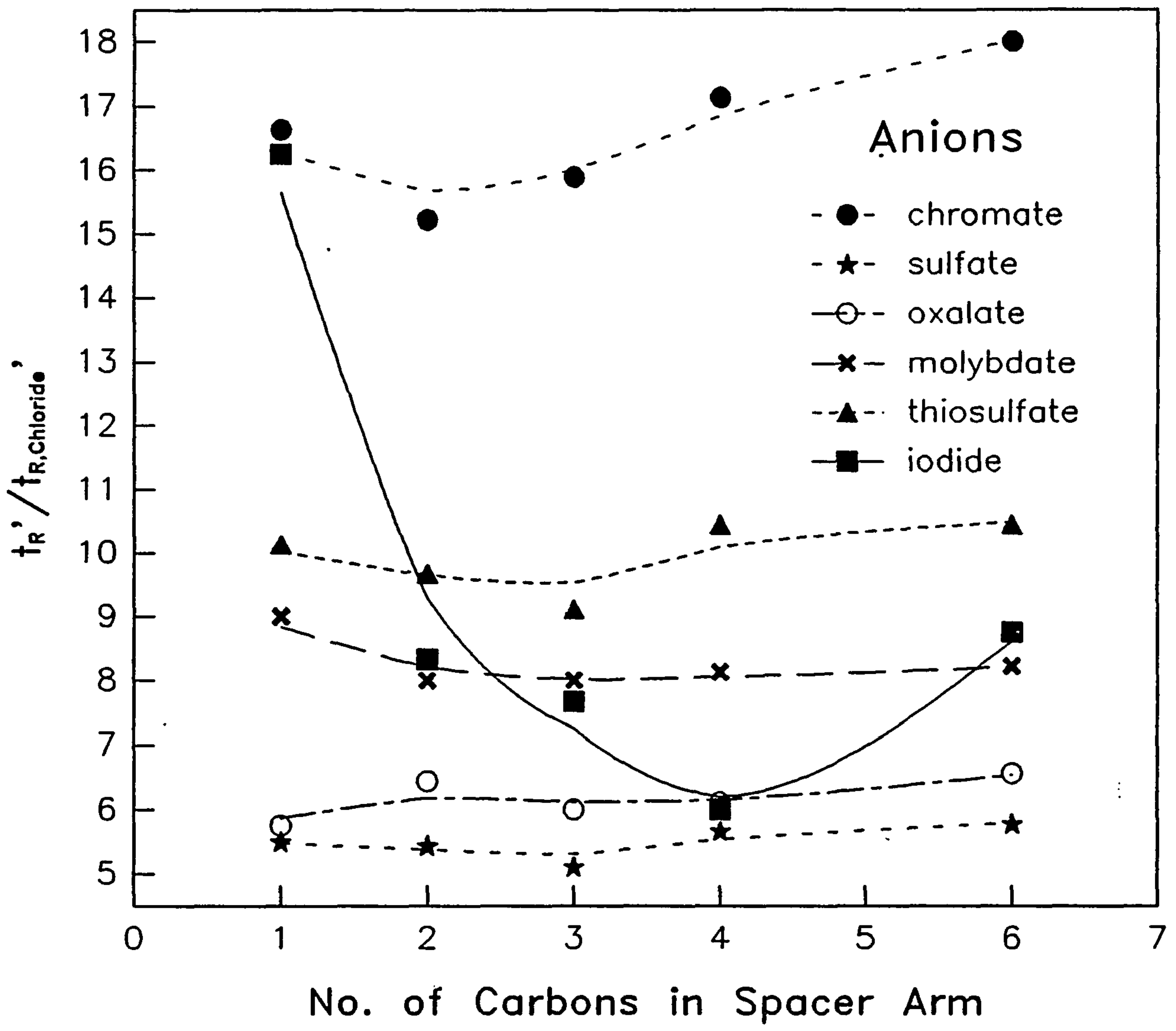
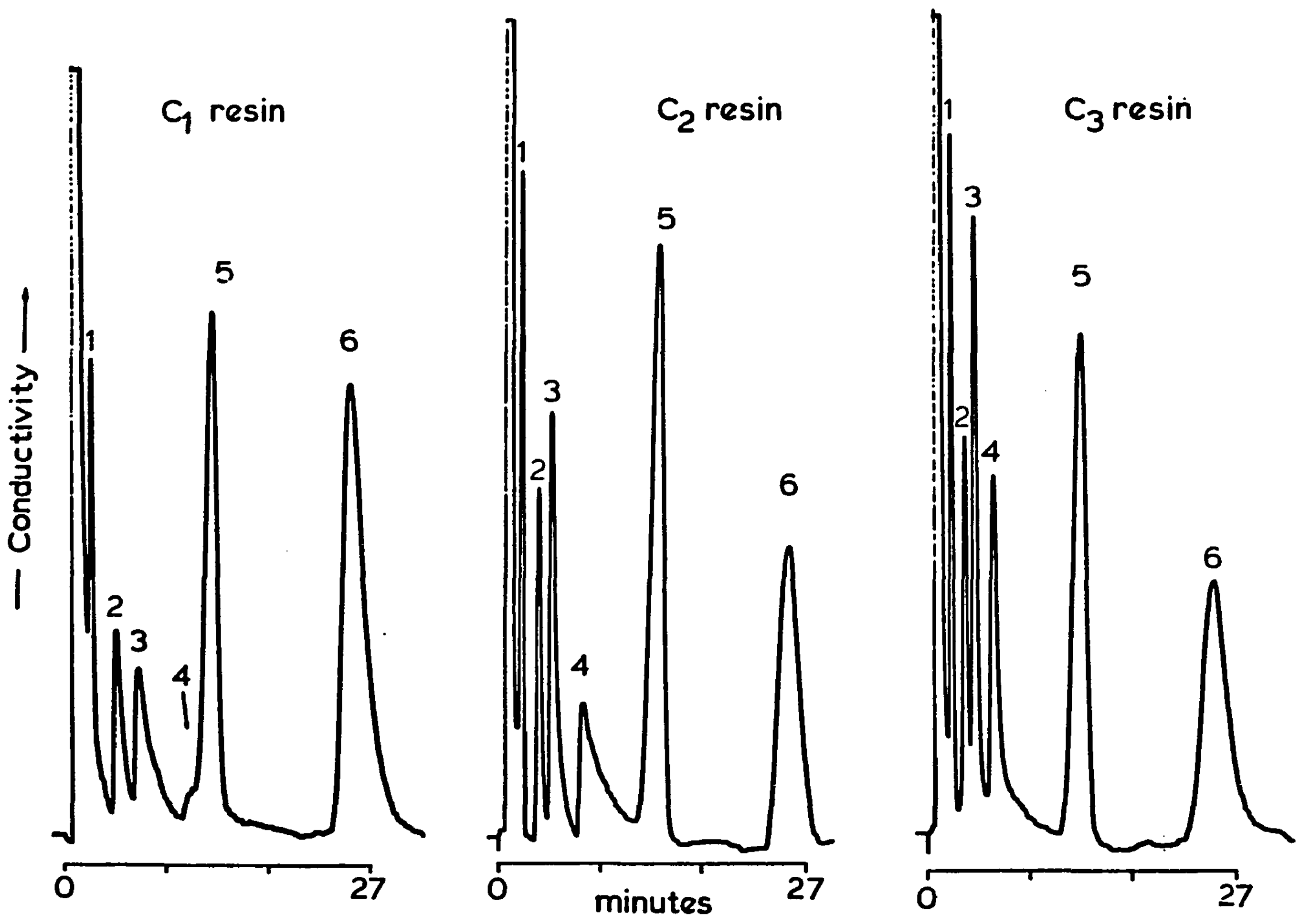

Anions
chromate
sulfate
oxalate
molybdate
thiosulfate
iodide
$t_R'/t_{R,Chloride}'$
No. of Carbons in Spacer Arm
18
17
16
15
14
13
12
11
10
9
8
7
6
5
0
1
2
3
4
5
6
7

Figure 8. Chromatograms showing anion separation on a.) C1, b.) C2, and c.) C3 resins. 1 = chloride, 2 = bromide, 3 = nitrate, 4 = chlorate, 5 = sulfate and 6 = thiosulfate. All conditions are listed in Figure 7



a.)   b.)   c.)

In order to realize the effect of resin capacity on anion selectivity, several C3 resins of different capacities were synthesized and tested. The results are shown in Figure 9. This graph explains at least partially why the previous tables and graphs show minimum relative retentions with the C4 spacer arm column followed by increased times with the C6 column. The capacities of the C1, C2, C3 and C4 resins were 0.047 to 0.052 meq/g. Figure 9 shows fairly constant relative retention values in this capacity range. The C6 resin, however, has a capacity of 0.061 meq/g. According to Figure 9, the higher capacity of this resin would cause it to retain ions like nitrate and iodide for a longer period of time. Due to capacity differences alone, the increased relative retentions seen for monovalent anions on the C6 column is expected. Figure 10 shows the data in Table III graphed with corrected C6 values. Using the data shown in Figure 9, the C6 relative retentions in Figure 10 were calculated assuming a column capacity of 0.050 meq/g. This capacity-corrected graph now shows gradually decreasing relative retentions for these anions as the spacer arm length is increased from C1 to C6.

## Resin Selectivity

The data presented show that the relative retentions of weak acid and divalent anions are virtually independent of

Figure 9. Relative retention times vs. exchange capacity using several C3 resins. All conditions are listed in Figure 7

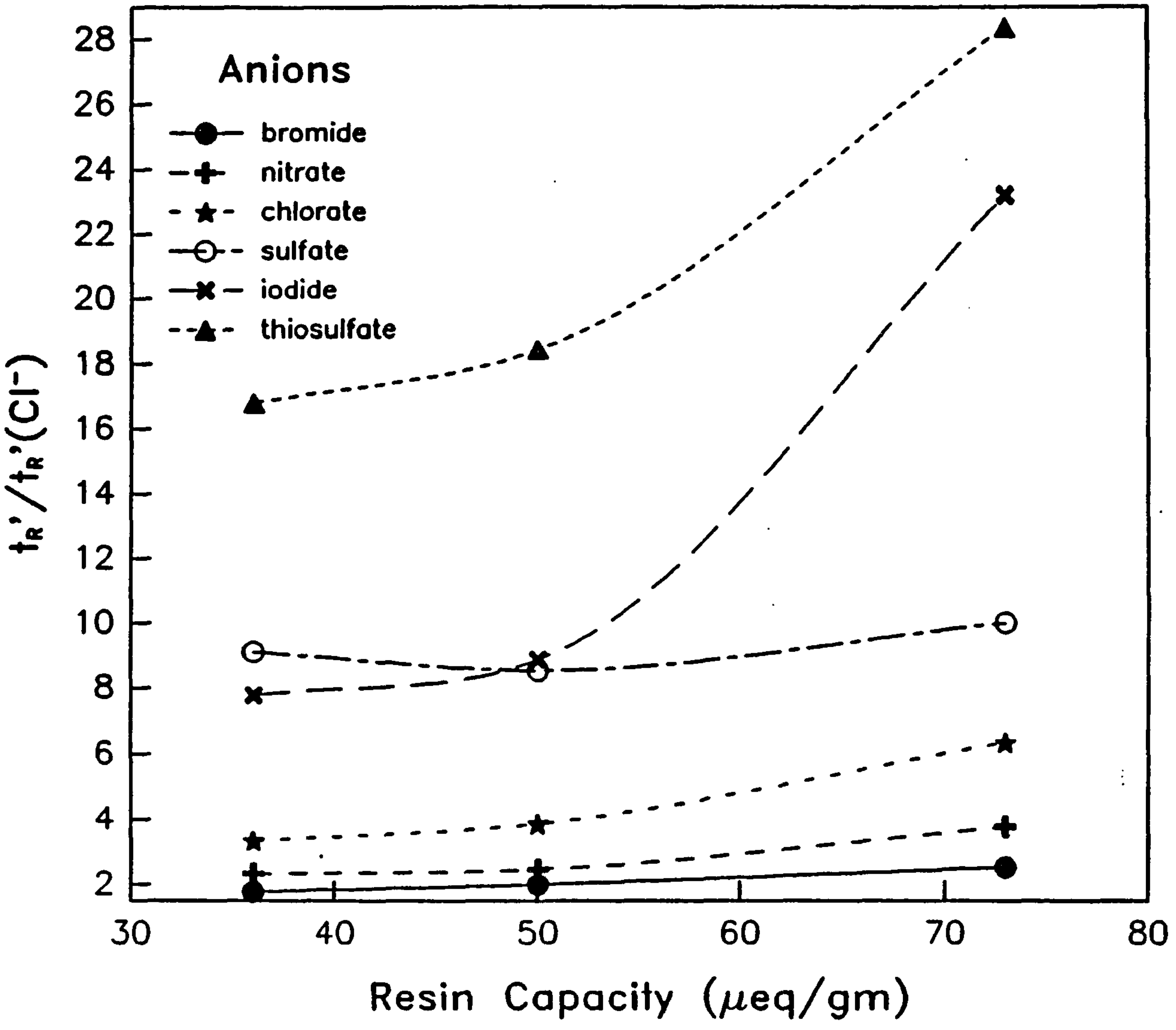
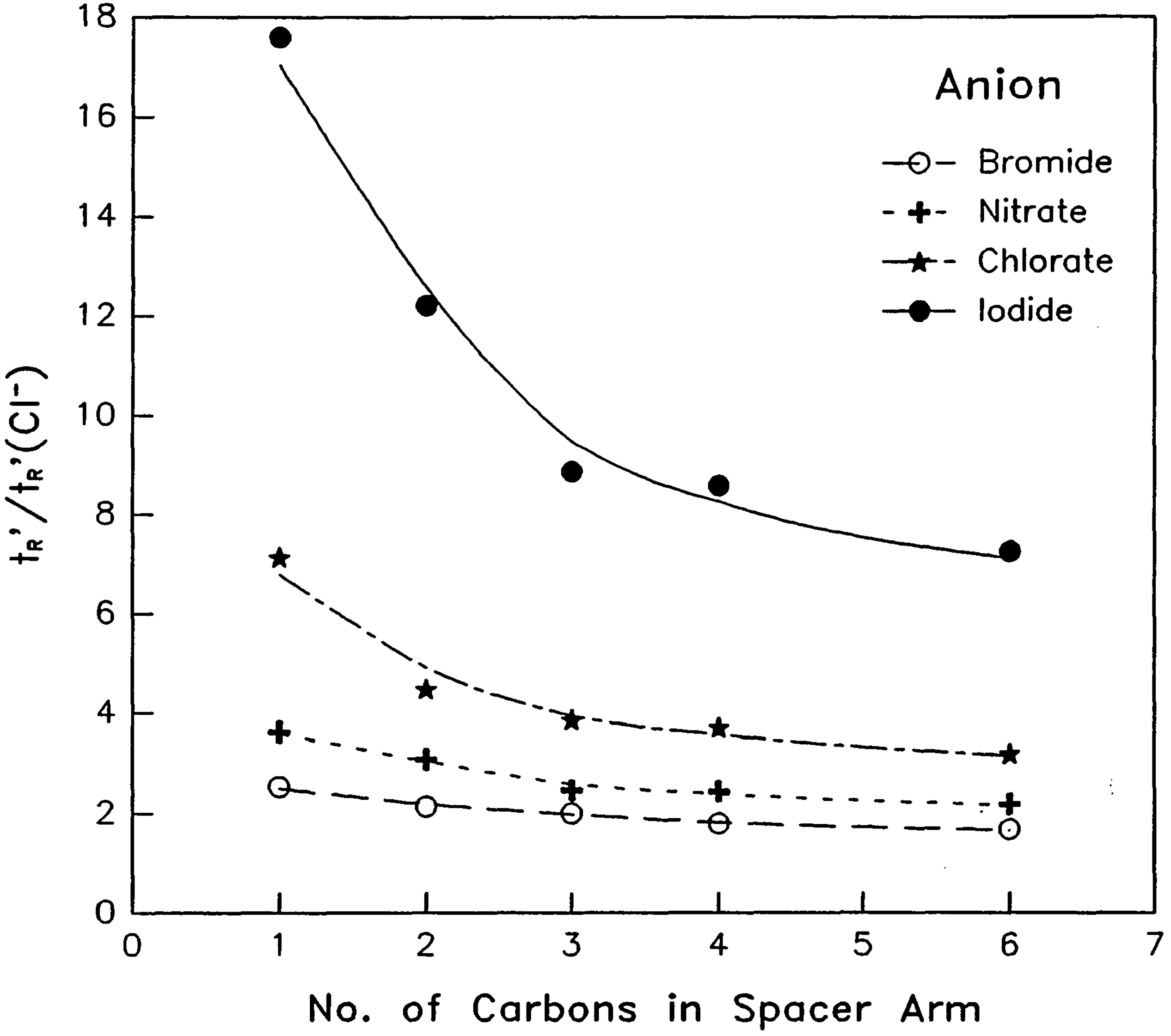

Anions
bromide
nitrate
chlorate
sulfate
iodide
thiosulfate
$t_R'/t_R'(Cl^-)$
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
40
50
60
70
80
Resin Capacity (μeq/gm)

Figure 10. Capacity-corrected graph showing relative retention times vs. spacer arm length for bromide, nitrate, chlorate and iodide using a 0.2 mM sodium phthalate eluent at pH 6.0. All conditions are listed in Figure 5


Anion
Bromide
Nitrate
Chlorate
Iodide
$t_R'/t_R'(Cl^-)$
0
2
4
6
8
10
12
14
16
18
0
1
2
3
4
5
6
7
No. of Carbons in Spacer Arm

the resin spacer arm length. However, the peak shapes of anions like lactate improve and the relative retentions of more polarizable anions (nitrate, chlorate, iodide) decrease as the length of the spacer arm increases.

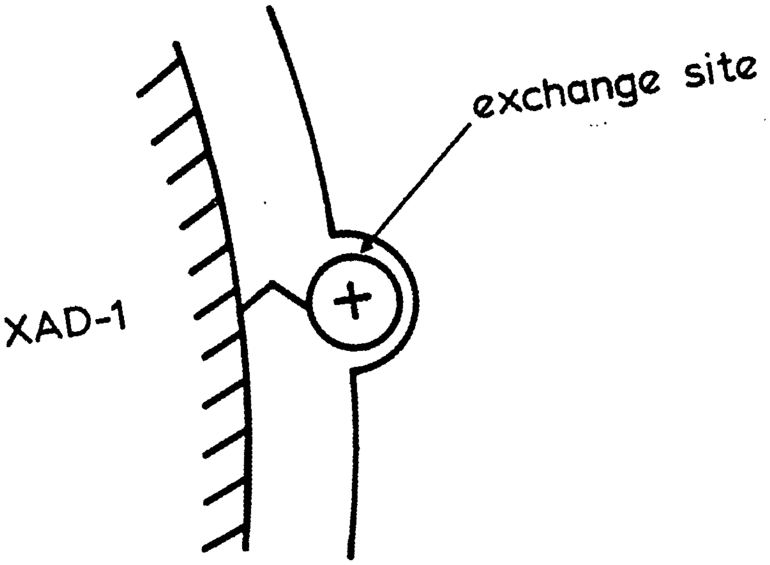
In simple terms, these phenomena can be explained by a spacer arm shielding effect. There may be competing interactions that partially interfere with the ion-exchange processes occurring on these polymeric resins. Large, polarizable anions may be slightly interacting with or adsorbing onto the polystyrene-divinylbenzene resin surface. The adsorption of large, polarizable anions on polystyrene-divinylbenzene resins has been reported previously (7,22,23). As the anions approach the quaternary ammonium groups to exchange, the longer spacer arms shield the anions more effectively from the resin surface and minimize any possible interactions. This shielding then results in better peak shapes and shorter relative retentions for anions like nitrate, chlorate and iodide on the longer spacer arm resins.

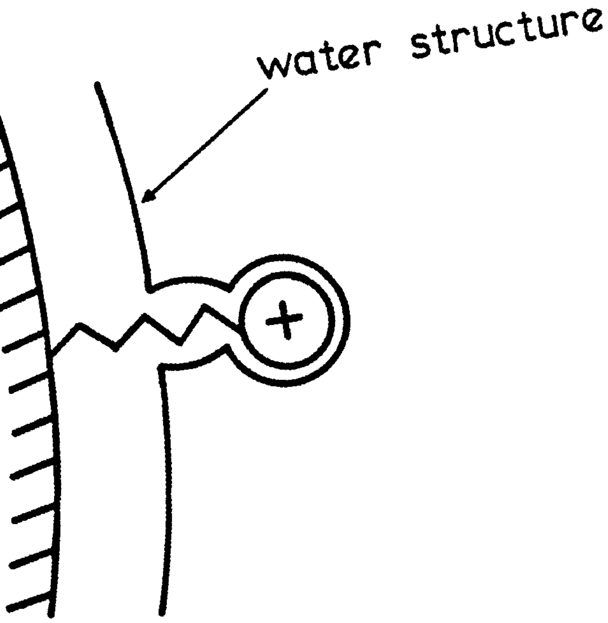
Previous work on polymeric anion-exchange resins has shown that greater selectivity for large, poorly hydrated anions (such as bromide, nitrate and iodide), compared to chloride, results when larger alkyl groups are present in the quaternary ammonium structure of the resin (1) and when a polyacrylate polymer is used instead of a polystyrene polymer (3).

The first of these effects has been explained by Barron and Fritz (1) using the theory of "water-structure induced ion pairing" that was suggested by Diamond (24) and by Diamond and Whitney (25). This theory suggests that water-structure induced ion pairing is stronger when the quaternary ammonium groups on the resin are large and when a large, polarizable sample anion is present. The prevailing, ordered water structure in the eluent is disrupted by the quaternary ammonium group and the sample anion, creating a force that brings these ions together to form an ion pair. The ion pair creates a cavity in the water structure; a tightening of the water structure surrounding the cavity helps hold the ion pair together.

Figure 11 helps visualize how this water-structure theory explains selectivity differences with spacer arm anion-exchange resins. In conventional anion-exchange resins, the quaternary ammonium functional groups are fairly close to the benzene rings of the polystyrene polymeric surface. This proximity might enhance the water structure effects that cause a strong ion pairing. However, as the spacer arms between the benzene rings and the quaternary ammonium groups become longer, any surface contribution to water-structure induced ion pairing would become weaker because the mobility of the longer spacer arm allows the exchange site to protrude farther into the aqueous eluent.

Figure 11. Diagram showing how different spacer arm lengths affect the size of the water cavity near the exchange site


exchange site
XAD-1


water structure

This is supported by the experimental evidence which shows a weaker relative retention of large polarizable anions, such as nitrate and iodide, as the spacer arm becomes longer.

# CONCLUSIONS

It has been demonstrated in this work that the synthetic route used to obtain spacer arm anion-exchange resins yields very practical resins for anion chromatography.

It has also been shown that the length of the spacer arm in quaternary ammonium ion exchangers has an influence on selectivity, especially for large polarizable anions. The observed behavior seems to fit the pattern outlined by the mechanism of water-structure induced ion pairing. Spacer arm shielding of the anions from the resin surface could also explain these effects.

The next section of this dissertation will examine changes in selectivity caused by using a new type of strong-base resin for SCIC. The selectivity of a quaternary phosphonium resin will be compared to that of quaternary ammonium resins.

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# SECTION II. LOW-CAPACITY QUATERNARY PHOSPHONIUM RESINS FOR ANION CHROMATOGRAPHY

# INTRODUCTION

Most stationary phases used in anion chromatography are "strong-base" quaternary ammonium resins. The strong-base resins most often used are referred to as Type I (benzyltrimethylammonium cation) and Type II (one methyl group replaced by a hydroxyethyl group) resins. A few other types of strong-base resins have also been used in anion chromatography. For example, Barron and Fritz (1,2) synthesized a series of new strong-base quaternary ammonium resins with varying R group lengths which were used to study the effect of functional group identity on anion selectivity.

Although classical ion-exchange work heavily used strong-base ammonium resins as stationary phases (3,4,5), strong-base phosphonium resins have also been synthesized (6,7). More recent work shows quaternary phosphonium resins used extensively as phase-transfer catalysts (8,9). In many cases, the quaternary phosphonium phase-transfer catalysts were more catalytically active than the analogous quaternary ammonium phase-transfer catalysts (10,11,12).

To our knowledge, low-capacity quaternary phosphonium ion-exchange resins have never been used in single-column ion chromatography. The goal of this work was to synthesize a quaternary phosphonium resin of a low capacity which is suitable for anion chromatography. The preparation, performance, and selectivity of this resin in anion chromatography is then evaluated and compared to that of two different quaternary ammonium ion-exchange resins.

# EXPERIMENTAL

## Materials and Equipment

The 7 to 12 μm, spherical polystyrene-divinylbenzene resin (PS-DVB) was obtained courtesy of Dr. Douglas Gjerde at the Benson Company (Reno, Nevada, USA). The 25% trimethylamine (in methanol) and tributylamine were obtained from Aldrich (Milwaukee, WI, USA). The tributylphosphine was obtained from Aldrich or Sigma Chemical Company (St. Louis, MO, USA). The paraformaldehyde and concentrated hydrochloric acid used for the chloromethylation reactions were obtained from Mallinckrodt, Inc. (Paris, KT, USA). All solvents used for rinsing resin were of reagent grade and were obtained from a number of sources. All reagents were used as received.

Ion chromatography was carried out on one of two instruments, both built from similar components. An LKB 2150 HPLC pump (Pharmacia LKB Biotechnology, Piscataway, NJ, USA) or a Milton Roy Mini-pump manufactured by Laboratory Data Control (Riviera Beach, FL, USA) equipped with a high-pressure pulse dampener provided eluent flow. Rheodyne (Berkeley, CA, USA) Model 7010 injection valves fitted with 50-μl sample loops were used for sample introduction. The resins were packed in glass-lined stainless steel columns (250 X 2.0 mm i.d.) that were obtained from Scientific Glass Engineering (Austin, TX, USA). An Eldex (Menlo Park, CA, USA) column heater or home-made insulation was used to insulate the column and prevent baseline drift. Detectors used were Model 213A conductivity detectors manufactured by Wescan Instruments (Santa Clara, CA, USA). Strip-chart recorders manufactured by Curken Scientific (Danbury, CT, USA) were used to record chromatograms.

## Procedures

Chemically-bonded resins were prepared using a two-step procedure. First, a formaldehyde-hydrochloric acid procedure (13) was used to chloromethylate the resin. Standard conditions for the chloromethylation reactions employed 1.0 g of resin and 2.2 M paraformaldehyde in 25-ml of 10 or 12 M hydrochloric acid at room temperature. Then, 40 ml of a 2.0 M or greater solution of trimethylamine (TMA), tributylamine (TBA) or tributylphosphine (TBP) in methanol or 1,2-dichloropropane (1,2-DCP) was reacted with the chloromethylated resin at 60 to 70 °C for at least 24 hours to obtain quaternary ammonium or phosphonium resins. The amination and phosphination procedures are similar to those in previously-published works (12,13).

The control quaternization experiment was performed by first chloromethylating 1.0 gram of resin using 2.2 M paraformaldehyde in 12 M hydrochloric acid for 18.5 minutes. The chloromethylated batch of resin was then divided into equal parts and aminated or phosphinated using exactly 2 M concentrations of the reagent in 40 ml of either methanol or 1,2-DCP.

After amination, the resin was filtered and washed thoroughly with 2.0 M hydrochloric acid, water, 2-propanol, water and methanol. The functionalized resin was then air dried.

The strong-base ion-exchange capacities of the resins were determined by rinsing a weighed portion of resin with methanol, water, 0.5 M potassium nitrate and then again with water to remove any excess nitrate. The resin was then transferred to a gravity column and the bound nitrate was eluted with 0.005 M potassium sulfate. The collected nitrate was then determined spectrophotometrically at 225 nm.

All solutions were made up in distilled, deionized water and were prepared from reagent grade salts. Eluents were prepared by dissolving the acid in distilled, deionized water and, if necessary, adjusting the pH by adding sodium hydroxide. The eluents were then filtered through a 0.2 μm membrane filter after which a vacuum was applied while stirring to remove dissolved gases.

Columns were packed using an upward packing, stirred slurry technique with 40% ethylene glycol and 1% sodium chloride in water as the packing solvent. The packing pressure was approximately 4500 psi. The instrument used to pack the columns was a Shandon H.P.L.C. Packing Pump (Phenomenex, Rancho Palos Verdes, CA, USA).

# RESULTS AND DISCUSSION

## Preparation of Resins

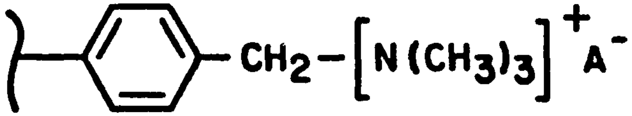
The purpose of this study was to evaluate and compare the selectivity and performance of low-capacity quaternary phosphonium and ammonium resins in anion chromatography. Three types of resins were prepared; the structures are shown in Figure 1. All factors other than the structure of the functional group were held constant. For example, the resins were all prepared from the same resin lot and were synthesized to obtain similar exchange capacities so that identical elution conditions could be used.

The anion-exchange resins were prepared by chloromethylating a cross-linked polystyrene resin, followed by reaction with a tertiary amine (TMA or TBA) or a tertiary phosphine (TBP). It became apparent immediately that the reactivities of the TMA, TBA and TBP were greatly different.

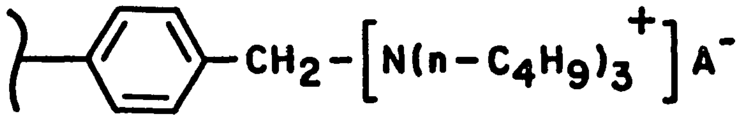
Preliminary reactions were performed so that reaction yields could be evaluated and the different resins could be prepared with similar capacities. Two factors determined the exchange capacity obtained after resin chloromethylation and quaternization: the length of chloromethylation time and the extent of the quaternization reaction.

The extent of quaternization using TMA, TBA and TBP in methanol or 1,2-DCP solvents was first determined by

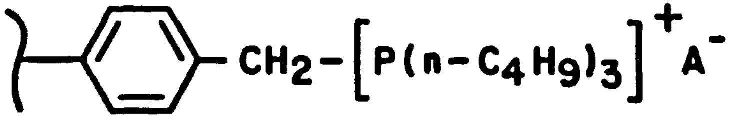
Figure 1. Structures of the 3 resins synthesized and compared chromatographically: trimethylammonium resin (TMA), tributylammonium resin (TBA) and tributylphosphonium resin (TBP)



TMA resin



TBA resin



TBP resin

performing a control experiment. Table I shows capacity results obtained when a chloromethylated batch of resin is divided into 4 parts and then aminated or phosphinated. Reaction conditions are described in the Experimental Section. As Table I shows, the TMA resin gave the highest reaction yield, or exchange capacity, of 219.1 μeq/g. This capacity is considered the maximum theoretical capacity of the resin. The TBP resin showed the next highest capacity of 93.5 μeq/g, although this is still less than 50% of the capacity of the TMA resin. The TBA resin, however, obtained only 4% or 24% (9.7 or 53.1 μeq/g) of the TMA resin's capacity using a 1,2-DCP or methanol solvent for the reactions, respectively. Low quaternization reaction yields for TBA resins are not unusual and have been reported by Molinari et al (14).

It was possible, however, to prepare resins of almost the same exchange capacity by varying the extent of chloromethylation. The major synthetic conditions and properties of the quaternary ammonium and phosphonium resins used in this study are summarized in Table II. Note that the times used for chloromethylation were varied considerably to compensate for the differences in reactivity of the amines and phosphine.

Table I. Trial Syntheses to Compare Amination and Phosphination Reaction Yields[a]

| Resin | Amination Solvent | Capacity ($\mu$eq/g) |
|---|---|---|
| Trimethylammonium | methanol | 219.1 |
| Tributylammonium | methanol | 53.1 |
| Tributylammonium | 1,2-dichloropropane[b] | 9.7 |
| Tributylphosphonium | 1,2-dichloropropane[b] | 93.5 |

[a] Conditions: One gram of 7 - 12 $\mu$m PS-DVB was chloromethylated and split into 4 parts for amination or phosphination. The chloromethylation reaction was performed using 2.2 M paraformaldehyde in 25 milliliters of concentrated hydrochloric acid at room temperature for 18.5 minutes. The aminations and phosphinations were performed using 2 M concentrations of the reagent in 40 ml of the appropriate solvent, at 60 - 70 °C overnight.

[b] Amination or phosphination was performed under a nitrogen atmosphere.

Table II. Preparation of Chromatographic Resins[a]

| Resin | Designation | Chloromethylation Time (min) | HCl (M) | Amination Solvent | Capacity ($\mu$eq/g) |
|---|---|---|---|---|---|
| Trimethylammonium | TMA | 2, 2.6, 2.5[b] | 10 | methanol | 90.2 |
| Tributylammonium | TBA | 125 | 12 | methanol | 93.3 |
| Tributylphosphonium | TBP | 18.5 | 12 | 1,2-DCP | 96.9 |

[a] Reaction conditions are listed in the Experimental Section.

[b] Three separate chloromethylation and amination reactions were used to obtain a 90.2 $\mu$eq/g TMA capacity.

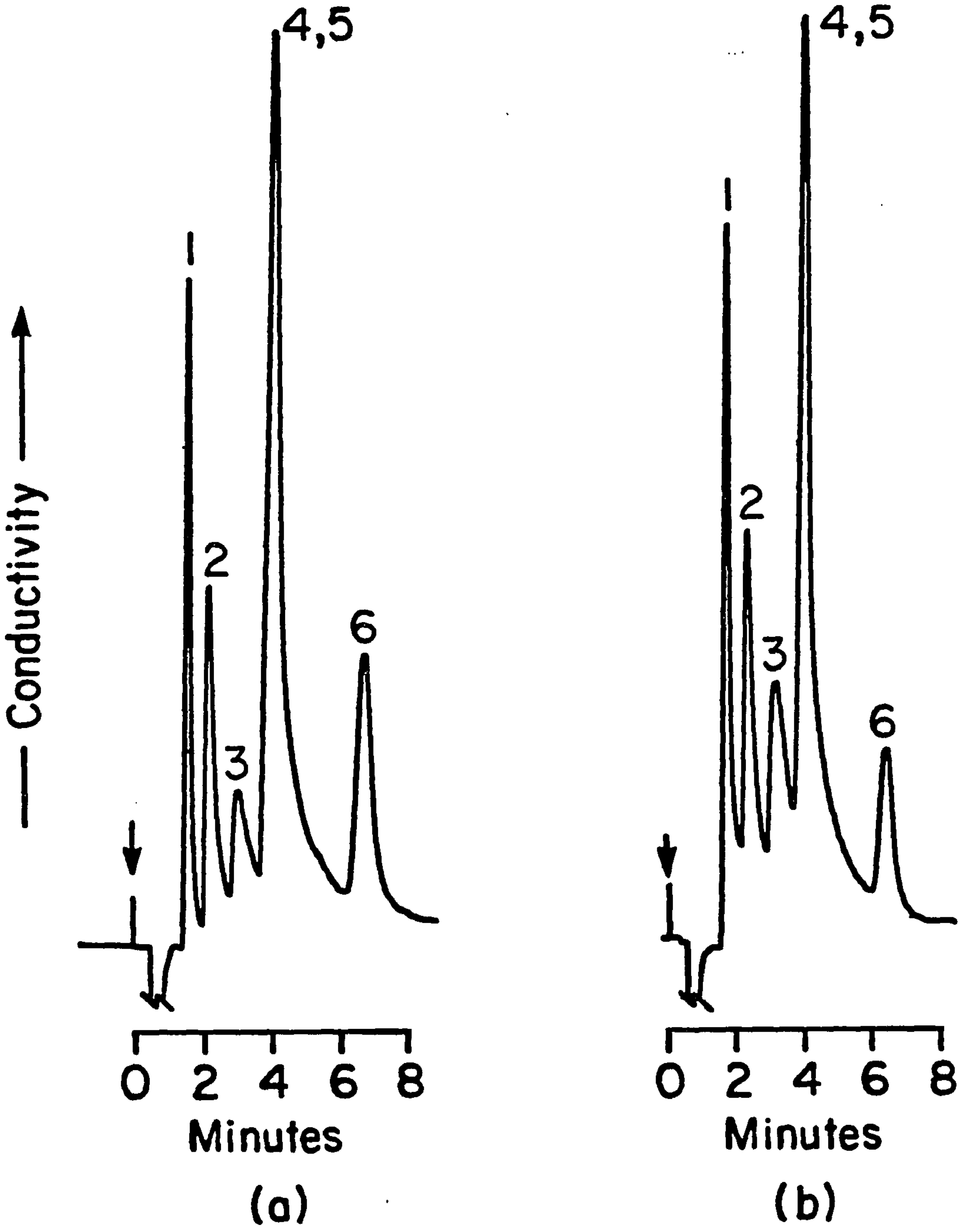
## Evaluation of Resin Selectivity

Although the exchange capacities of the three resins in Table II are similar, there will be a considerable difference in the amounts of unreacted chloromethyl groups. The presence of excess chloromethyl groups has been noted previously (15). However, the effect of these groups on anion selectivity has not been studied.

Figure 2 shows chromatograms of identical sample mixtures obtained on the same batch of TMA resin. The separation shown in Figure 2a was obtained with a resin that was first chloromethylated and then aminated using TMA to obtain an exchange capacity of 70.1 $\mu$eq/g. This column was then unpacked, chloromethylated again, repacked and tested. Figure 2b shows a separation using the TMA resin (70.1 $\mu$eq/g) with excess chloromethyl groups. Identical eluent conditions and sample mixtures were used in both cases in Figure 2. A portion of the resin was again aminated with TMA and a capacity of 191 $\mu$eq/g was obtained. Because of the similarity of these chromatograms, it can be concluded that the presence of excess chloromethyl groups (at a level of 121 $\mu$eq/g) on an anion-exchange resin has virtually no effect on the selectivity of the anions tested in this study.

Columns were packed with TMA, TBA and TBP resins and retention times for a number of anions were measured using

Figure 2. Separation on TMA resins of 1.) chloride, 2.) nitrite, 3.) bromide, 4.) sulfate, 5.) nitrate and 6.) thiosulfate using 1 mM sodium phthalate at pH 6.5 as the eluent at a flow rate of 0.75 ml/min. Anion concentrations were 6 to 50 ppm each. a.) TMA resin with a capacity of 70.1 μeq/g. b.) TMA resin with a capacity of 70.1 μeq/g and 121 μeq/g excess chloromethyl groups


Conductivity
1
2
3
4,5
6
0 2 4 6 8
Minutes
(a)
1
2
3
4,5
6
0 2 4 6 8
Minutes
(b)

identical elution conditions for each column. Relative retention times were then calculated by dividing the adjusted retention time of each anion by the adjusted retention time of chloride. This corrects for the small differences in resin capacity and for any other slight differences in elution conditions.

The relative retention times of various anions are given in Table III using two different eluents. Many of the anions tested show very little change in relative retention on the three columns. However, large polarizable anions, such as bromide, nitrate and iodide, show higher relative retention times on TBA compared to TMA and still higher relative retention times on the TBP column. For example, the relative retention of iodide is 29.08 on the TBP column, 17.88 on the TBA column and 9.60 on the TMA column. Chlorate shows almost the same retention times on the quaternary ammonium columns but a distinctly higher relative retention time on the quaternary phosphonium column. Because the TBP column retains the monovalent anions to a greater extent, more pronounced selectivity reversals occur as compared to those obtained using the TBA and TMA columns (shown later in chromatographic separations).

A previous study (1) noted that quaternary ammonium resins with larger R groups show longer relative retentions for poorly hydrated anions like nitrate and iodide.

Table III. Selectivity Data for Quaternary Ammonium and Phosphonium Ion-exchange Resins[a]

| | $t_R'/t_{R,\text{Chloride}}'$ | | | | | |
|---|---|---|---|---|---|---|
| | 30 mM nicotinic acid | | | 2.2 mM sodium phthalate, pH 6.0 | | |
| Anion | TMA Column | TBA Column | TBP Column | TMA Column | TBA Column | TBP Column |
| acetate | -- | -- | -- | -- | 0.73 | 0.67 |
| glycolate | -- | 0.22 | 0.20 | -- | -- | -- |
| lactate | 0.30 | 0.25 | 0.25 | -- | -- | -- |
| formate | 0.34 | 0.33 | 0.29 | -- | -- | -- |
| fluoride | 0.39 | 0.35 | 0.32 | -- | -- | 0.50 |
| dihydrogen phosphate | 0.46 | 0.44 | 0.43 | 0.63 | 0.71 | 0.62 |
| iodate | 0.50 | 0.47 | 0.44 | -- | -- | 0.49 |
| azide | 0.54 | 0.49 | 0.50 | -- | -- | -- |
| methylsulfonate | 0.95 | 0.89 | 0.86 | 0.95 | 0.98 | 0.94 |
| propionate | 0.96 | 0.42 | 0.46 | -- | -- | -- |
| chloride | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| bromate | 1.51 | 1.22 | 1.26 | 1.25 | 1.15 | 1.22 |
| ethylsulfonate | 1.61 | 1.18 | 1.20 | 1.49 | 1.33 | 1.35 |
| nitrite | 1.33 | 1.34 | 1.46 | 1.49 | 1.59 | 1.60 |
| bromide | 2.38 | 2.65 | 3.02 | 1.91 | 2.30 | 2.69 |
| malonate | -- | -- | -- | 2.09 | 2.72 | 2.53 |
| sulfate | -- | -- | -- | 2.09 | 2.42 | 2.32 |
| nitrate | 3.08 | 4.53 | 5.20 | 2.49 | 3.68 | 4.31 |
| thiosulfate | -- | -- | -- | 3.57 | 3.77 | 3.66 |
| chlorate | -- | -- | -- | 4.32 | 4.34 | 5.28 |
| propylsulfonate | -- | -- | -- | 4.92 | 3.20 | 3.38 |
| iodide | -- | -- | -- | 9.60 | 17.88 | 29.08 |
| $t_R'$,$Cl^-$(min) | 1.19 | 6.95 | 12.39 | 11.63 | 0.85 | 1.11 |

[a] Conditions: The TMA column is a trimethylammonium resin with a capacity of 90.2 μeq/g. The TBA column is a tributylammonium resin with a capacity of 93.3 μeq/g. The TBP column is a tributylphosphonium resin with a capacity of 96.9 μeq/g. All flow rates were 0.75 ml/min and detection was by conductivity.

This effect has been attributed to stronger ion pairing that results from disruption of the water structure by these anions and from a tightening of the water structure surrounding the ion pair caused by the larger R groups. These effects appear to be enhanced further by going from a quaternary ammonium to a quaternary phosphonium resin. The phosphonium group is larger and more hydrophobic than the ammonium exchange site. This causes a greater tightening of the water structure around the ion pair and results in longer relative retention times for ions like bromide, nitrate and iodide.

### Eluent pH

Chromatograms of a number of anions were compared on TBA and TBP resin columns using 1.5 mM sodium phthalate at several pH values. Results for a few of the anions are shown in Figures 3 and 4. At higher eluent pH values the relative retention times of divalent anions decrease, as expected, because the eluent is present primarily as the 2- anion. However, the relative retention times of monovalent anions increase as the eluent pH becomes higher. This effect is especially pronounced for nitrate and chlorate.

The longer retention of anions such as nitrate and chlorate at higher eluent pH values is rather puzzling, because a 2- eluent anion should elute monovalent sample

Figure 3. Relative retentions versus eluent pH using the TBA column (93.3 μeq/g) and a 1.5 mM sodium phthalate eluent. Detection was by conductivity

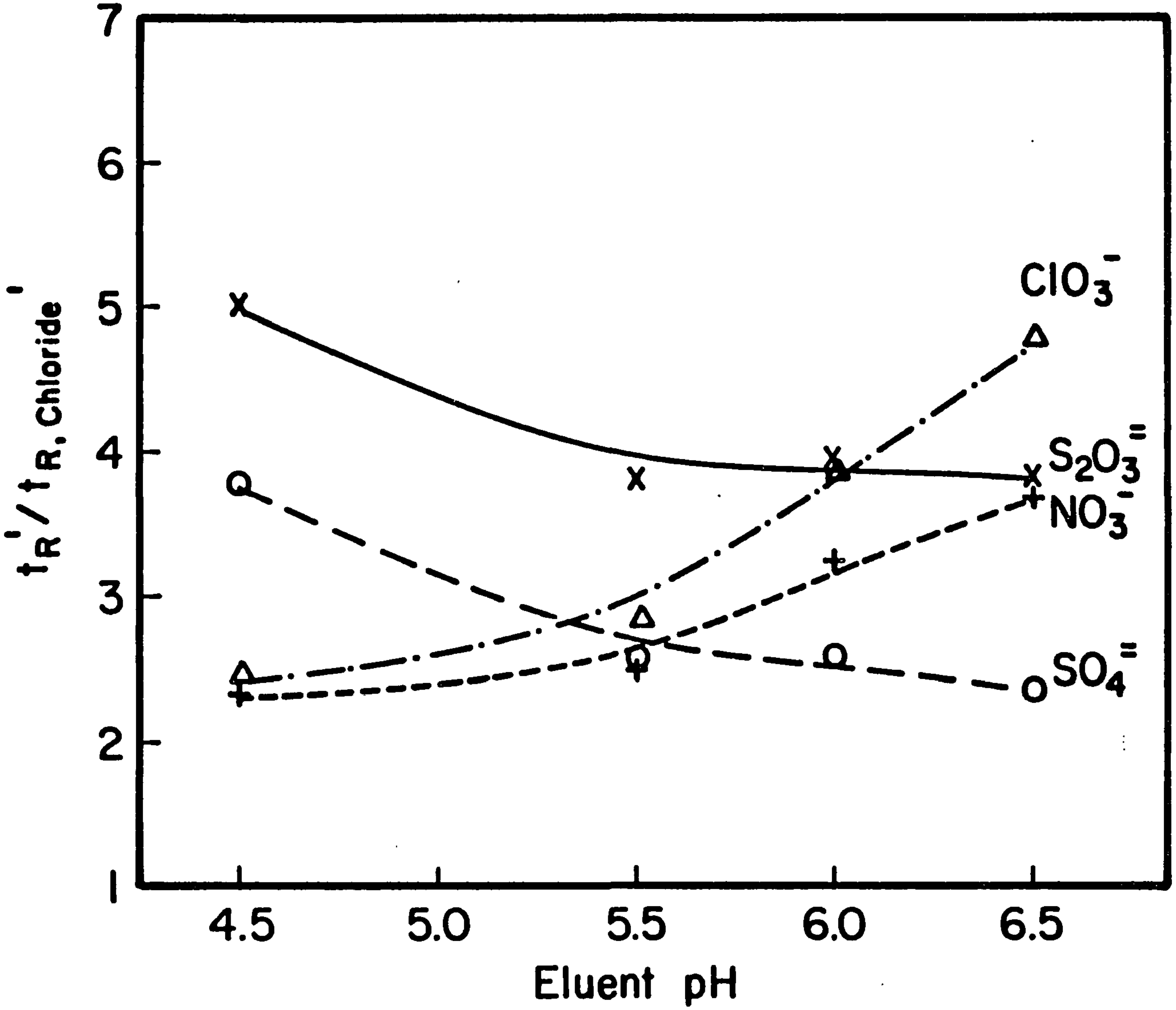
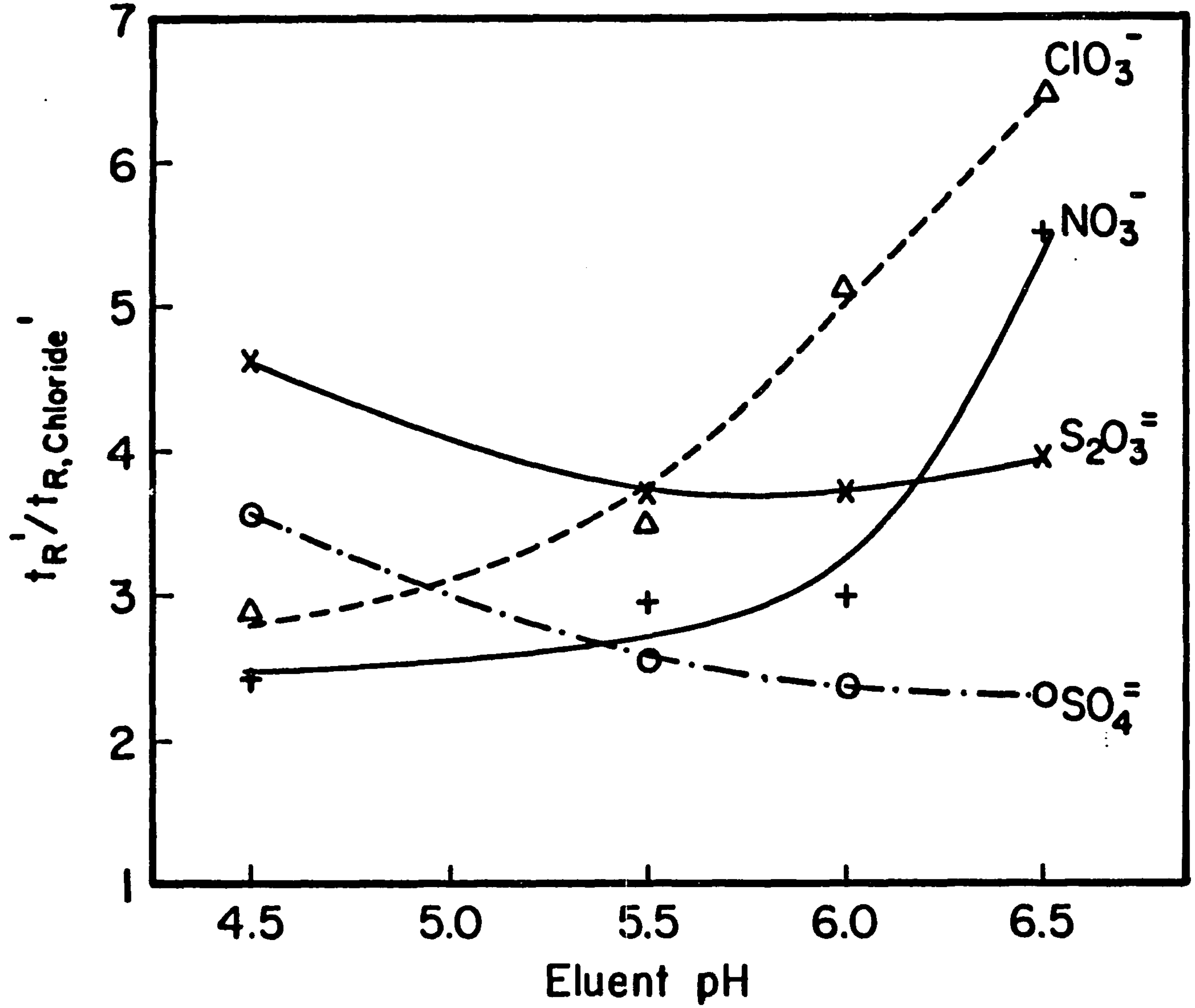

7
6
5
4
3
2
1
$t_R' / t_{R,\,Chloride}'$
4.5
5.0
5.5
6.0
6.5
Eluent pH
$ClO_3^-$
$S_2O_3^=$
$NO_3^-$
$SO_4^=$

Figure 4. Relative retentions versus eluent pH using the TBP column (96.9 μeq/g) and a 1.5 mM sodium phthalate eluent. Detection was by conductivity


7
6
5
4
3
2
1
$t_R'/t_{R,\text{Chloride}}'$
$ClO_3^-$
$NO_3^-$
$S_2O_3^=$
$SO_4^=$
4.5
5.0
5.5
6.0
6.5
Eluent pH

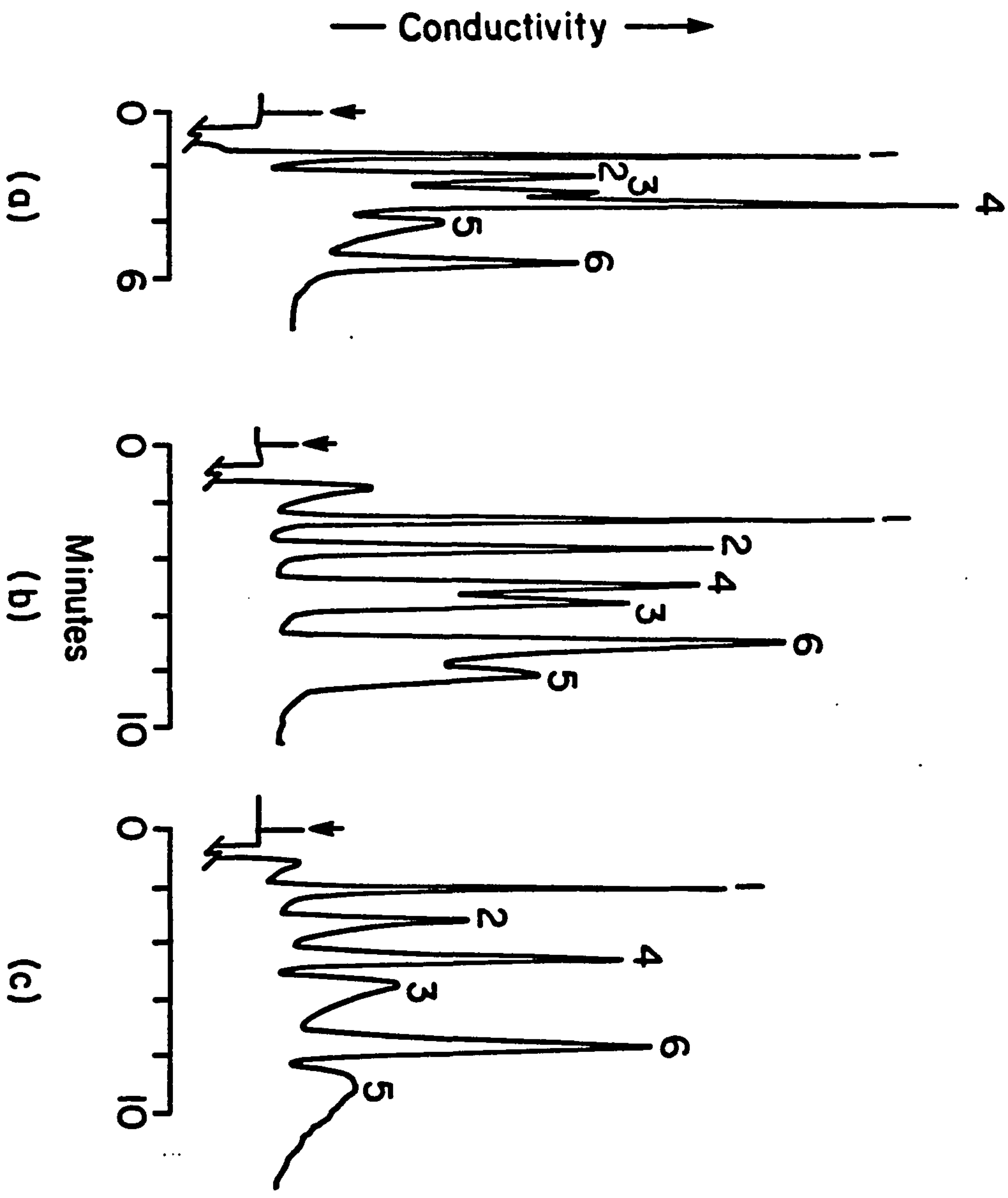
anions more quickly than a 1- eluent anion. One possible explanation is that more phthalate is adsorbed on the resin surface at pH 4.5 than at pH 6.5 (16). This adsorbed phthalate could partially relax the water structure surrounding the exchange site and lessen the effects of water-induced ion pairing on nitrate and chlorate. At pH 6.5, much less phthalate is adsorbed and the stronger water-structure induced ion pairing results in longer retention times for anions like nitrate and chlorate.

It is also possible that slight anion adsorption occurs on the exposed resin surface at pH 6.5. The possibility of adsorption of larger, more polarizable monovalent anions on polystyrene-divinylbenzene resins has been reported previously (17,18,19). If these anions adsorb even slightly on the XAD-1 matrix at higher eluent pH's (where less phthalate adsorbs on the surface), increased relative retentions would result, which is exactly the effect seen in this study.

## Chromatographic Separations

Figure 5 shows chromatograms comparing separations of several inorganic anions on all three columns. The eluent used was 1.5 mM sodium phthalate (pH 6.5) operated at a flow rate of 0.75 ml/min. Using these conditions, the TBP separation shows much greater resolution of the peaks

Figure 5. Separation of common inorganic anions on a.) TMA, b.) TBA and c.) TBP columns. Resin capacities are 90.2, 93.3 and 96.9 μeq/g, respectively. The eluent was 1.5 mM sodium phthalate (pH 6.5) at a flow rate of 0.75 ml/min. Detection was by conductivity. Anions are 1.) chloride, 2.) nitrite, 3.) bromide, 4.) sulfate, 5.) nitrate and 6.) thiosulfate at concentration levels of 6 to 30 ppm each anion


Conductivity
(a)
(b)
(c)
Minutes
0
6
0
10
0
10
1
2
3
4
5
6
1
2
4
3
6
5
1
2
4
3
6
5

separated. This is caused primarily by the greater retention of the monovalent bromide and nitrate anions obtained on TBP column.

Figures 6 and 7 show additional examples of separations obtained with the TBP column. Figure 6 shows a separation of chloride and several divalent anions (sulfate, oxalate, tungstate, thiosulfate and chromate). Conductivity detection is used and the eluent is 2.2 mM sodium phthalate at pH 6.5. The higher capacity of this column and high pH of this eluent allow chloride and the divalent anions that are normally late-eluting to be separated in just 10 minutes.

Figure 7 shows a separation of low levels of chloride (2.5 ppm) and sulfate (2.5 ppm) in the presence of a 200-fold excess of nitrate. The eluent used is again 2.2 mM sodium phthalate at pH 6.5. Because the TBP column is very selective for nitrate, the determination of low levels of other early-eluting anions is possible. With most columns, this determination would not be possible because the nitrate would elute too early in the chromatogram. A useful application for this type of determination is in the analysis of nitric acid digests.

Figure 6. Separation of chloride and late-eluting anions on the TBP column (96.9 μeq/g). The eluent was 2.2 mM sodium phthalate (pH 6.5) at a flow rate of 0.75 ml/min. Detection was by conductivity. Anions are 1.) 6 ppm chloride, 2.) 7.5 ppm sulfate, 3.) 10 ppm oxalate, 4.) 20 ppm tungstate, 5.) 12.5 ppm thiosulfate and 6.) 40 ppm chromate

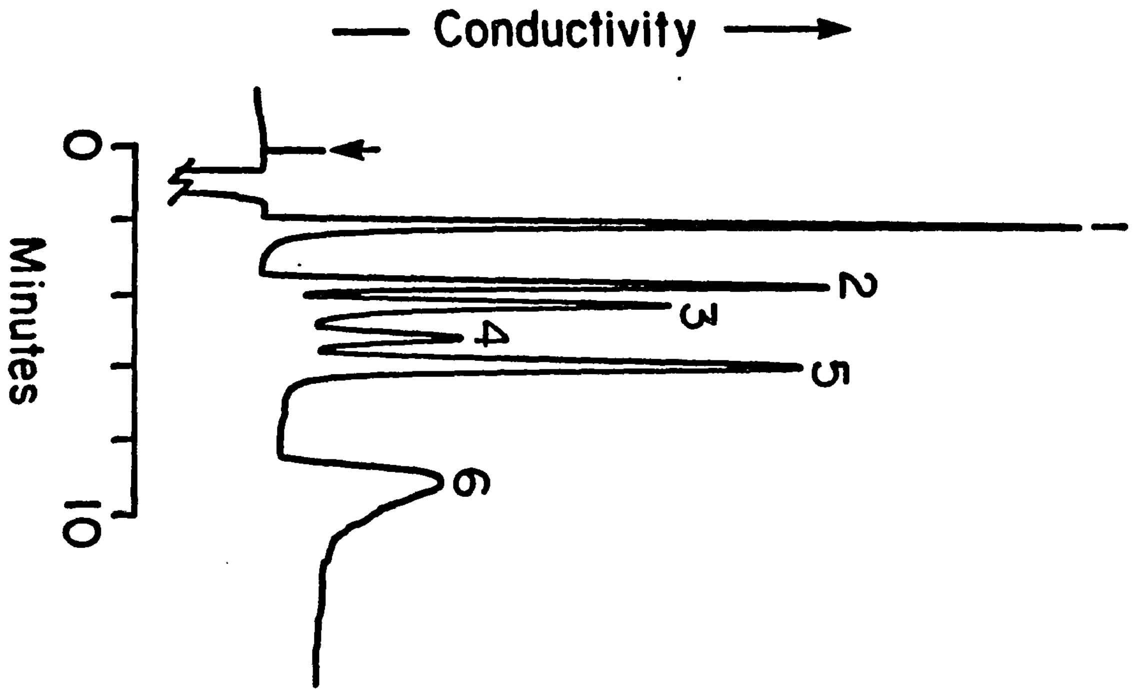
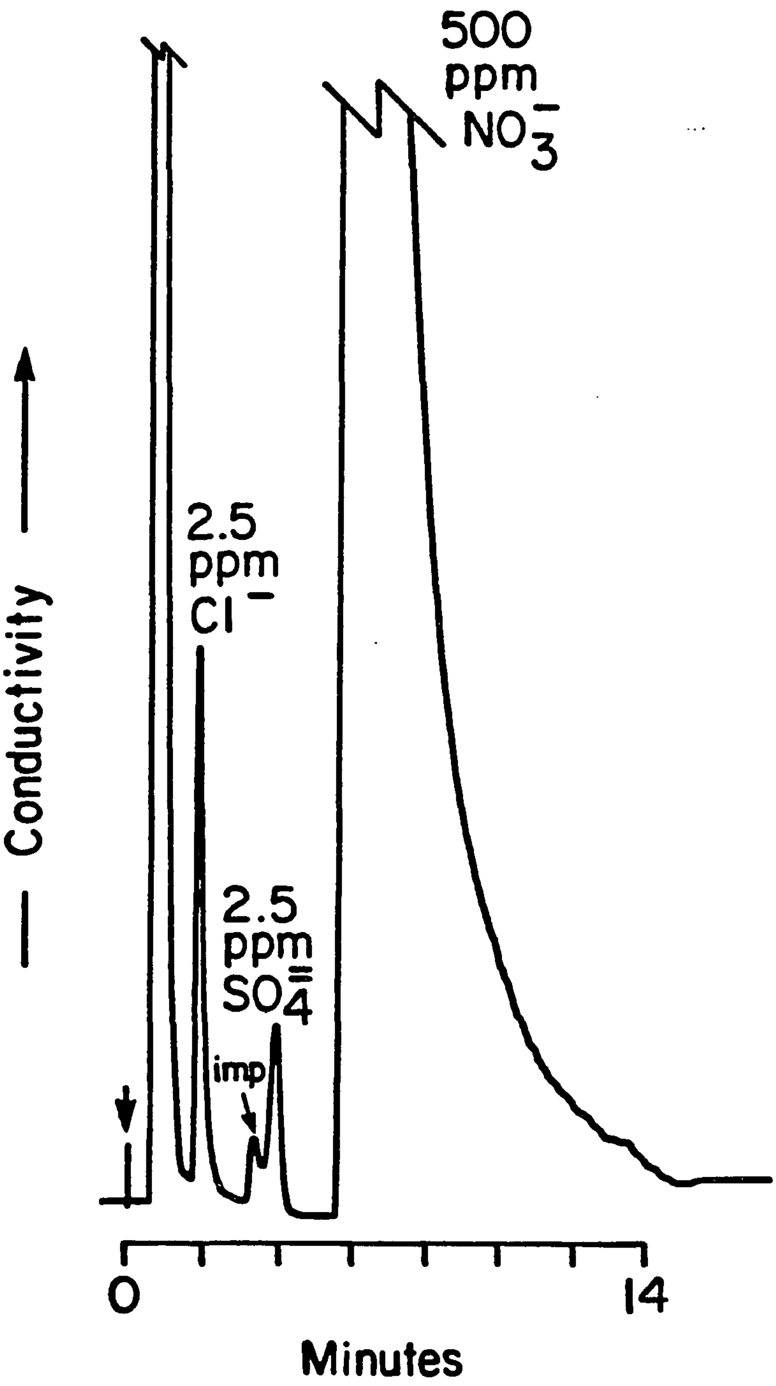

Conductivity
Minutes
0
10
2
3
4
5
6

Figure 7. Separation of low levels of chloride and sulfate in the presence of large amounts of nitrate using the TBP column (96.9 μeq/g). Separation conditions are listed in Figure 7


500
ppm
NO$_3^-$
2.5
ppm
Cl$^-$
2.5
ppm
SO$_4^=$
imp
Conductivity
0
14
Minutes

## CONCLUSIONS

The quaternary phosphonium resin prepared in this study was easier to prepare at high capacities (<90 μeq/g) as compared to the analogous quaternary ammonium resin (TBP compared to TBA). This is because of the low reaction yield of the quaternization reaction obtained when using the tributylamine reagent.

Because the TBP resin has some unique selectivity properties, useful and different anion separations are possible. This resin is especially useful for applications requiring high nitrate selectivity.

By varying eluent pH, using fairly high exchange capacities, varying group R length and by using quaternary phosphonium resins, the normal elution order obtained with strong-base resins is altered and mono- and divalent anion inversions occur.

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# SECTION III. PREPARATION AND USE OF LATEX-COATED RESINS FOR ANION CHROMATOGRAPHY

# INTRODUCTION

Since 1975, many improvements in stationary phase technology have been made, especially in anion chromatography. The anion-exchange resins originally used in dual-column ion chromatography were agglomerated resins (1). These polystyrene-based resins are sulfonated and then made into anion-exchange resins by agglomerating anion-exchange microparticles onto the resin surface (2). The microparticles are held onto the resin surface by electrostatic attractions. Later, more efficient separations were obtained by agglomerating anion-exchange latexes onto small-sized resins (3).

The first work in single-column ion chromatography (SCIC) used low capacity anion-exchange resins synthesized by reacting XAD-2 resin with chloromethyl methyl ether (CMME) in the presence of a zinc chloride catalyst (4). A similar procedure described by Barron and Fritz (5) chloromethylates the resin by reacting XAD-1 with aqueous hydrochloric acid and paraformaldehyde. This reaction has been found to be very useful for functionalizing porous substrates with comparatively low surface areas. Both syntheses previously mentioned for SCIC are rather lengthy and require reaction times over 24 hours. Theoretical plate counts for anions separated on these resins are only 800 to 4000 plates/m.

Recently, many researchers have favored using statically- or dynamically-coated resins for anion separations in SCIC (6,7). In most cases, a long chain quaternary ammonium compound is added to a coating solution or to the eluent. This hydrophobic compound then coats the resin and allows anion exchange to occur. Coated resins could be prepared very quickly and easily using a variety of coating agents and resin matrices.

In the present work it is shown that highly efficient resins for anion chromatography can be produced by a simple method of coating quaternized latex particles onto the surface of unsulfonated polymeric resins. A nonporous polystyrene resin of very uniform particle size is described that serves as an excellent substrate for the coated resins. These latex-coated resins are used to obtain highly efficient anion separations.

# EXPERIMENTAL

## Materials and Equipment

All latexes and resins were made by and obtained from Rohm & Haas (Spring House, PA, USA). All solvents and salts used were reagent grade and were obtained from a number of sources.

The latexes used in this study were strong- or weak-base anion-exchangers composed of either polystyrene or acrylic. The latexes varied between 0.08 and 0.60 μm in size and were made by emulsion polymerization followed by chemical functionalization to obtain the appropriate anion-exchange functionality (8).

The XAD-1 used chromatographically was 20 to 26 μm or 30 to 37 μm in size. Preliminary experiments were carried out using 38 to 44 μm XAD-1. The polystyrene used in this study was prepared by Rohm & Haas, and is 4.2 μm in size, essentially monodisperse and totally nonporous. Four different anion-exchanging latexes were used in this study. Physical characteristics and designations of the latexes and resins used are listed in Table I.

Scanning electron microscopy (SEM) of the uncoated polystyrene was performed by Fran Laabs of Ames Laboratory (Ames, IA, USA) using a JEOL 100CX analytical microscope. The samples were prepared in water, dropped onto a slide and

Table I. Characteristics of Latexes and Resins Used

| Description | Designation | Size | Characteristics |
|---|---|---|---|
| polystyrene-DVB | XAD-1 | variable | irregularly-shaped, 0.01 μm pore dia. |
| polystyrene | PS | 4.2 μm[a] | monodisperse, non-porous, spherical |
| strong-base anion-exchange latex, 75.6% functionalized | AL | 0.09 μm[a] | spherical, acrylate-based |
| weak-base anion-exchange latex | AL-WB | 0.08 μm[a] | spherical, acrylate-based |
| strong-base anion-exchange latex, 100% functionalized | PL-100 | 0.20 μm[a] | spherical, polystyrene-based |
| strong-base anion-exchange latex, 75.6% functionalized | PL-76 | 0.60 μm[b] | spherical, polystyrene-based |

[a] Sizes were determined by Coulter Counter (by Rohm & Haas).

[b] Size was determined by electron micrograph estimation.

air-dried before SEM examination. SEM of the uncoated polystyrene was performed by Rohm & Haas using an AMRAY 1200C analytical microscope. Samples were prepared by dropping dilute solutions of each onto aluminum SEM support stubs. The samples were allowed to air-dry and were then gold-coated before SEM examination.

All size estimations were performed by Coulter Counter (by Rohm & Haas) except for the sizes of the PL-76 latex and XAD-1 resin, which were determined by estimations from electron micrographs.

Ion chromatography was carried out on a home-built HPLC system previously described (9).

## Procedures

The XAD resin was prepared according to a previously published method (9).

To prepare a resin sample for coating, a portion of resin is wetted with acetonitrile, filtered and then rinsed with water to displace the acetonitrile. The resin is then filtered to remove excess water.

To coat the resin, a 25-ml volume of latex/sodium chloride solution is added to the wetted resin. The mixture is stirred and sonicated to remove resin clumps. After allowing time for the latex/resin solution to reach equilibrium conditions, the samples are filtered and rinsed with deionized, distilled water. The strong-base ion-exchange capacities were determined by a method previously published (9).

All solutions were made in distilled, deionized water and were prepared from reagent grade salts. Eluents were prepared by dissolving the acid in distilled, deionized water and sodium hydroxide was added, where necessary, to adjust the pH. The eluents were then filtered through a 0.2 μm membrane filter and a vacuum was applied while stirring to remove dissolved gases.

Columns were packed using an upward packed, stirred slurry technique with either a water or a 40% ethylene glycol/1% sodium chloride/water packing solvent. The packing pressure was approximately 2000 psi for the XAD resin. For the coated polystyrene resin, a pressure of no more than 3000 psi was used to pack the columns and obtain the most efficient anion separations. The coated XAD and polystyrene resins were packed in glass-lined stainless steel columns (Scientific Glass Engineering, Austin, TX, USA). Typical operating pressures for the packed columns using a 0.5 ml/min flow rate were 100 psi for the XAD columns and 2000 psi for the 4.2 μm polystyrene columns.

# RESULTS AND DISCUSSION

## Resin Preparation

A series of experiments were performed in order to determine how well the quaternized latexes coat onto various resins, how to vary the exchange capacity of the coated resins and which coated resins are the most suitable for anion separations by SCIC.

Initial experiments were performed to determine what type of unfunctionalized resins could be coated with the highly-charged latexes. Table II shows the exchange capacities obtained after coating several different Rohm and Haas resins with the strong-base anion-exchanging polystyrene and acrylic latexes. Table III also shows the capacities obtained after coating several TSK resins (Toya Soda Company., Japan) with the strong-base exchanging acrylic latex. After coating, all of the resins shown in Tables II and III had low capacities which would allow the resins to be used in SCIC. (A typical working capacity range in our laboratories is 5 to 100 μeq/g.) It is interesting to note that the latex particles are too large to fit into the pores of any of the resins listed in Table II. It is also important to recognize that unlike the electrostatically-coated latex resins (2,3), this procedure does not require the use of a sulfonated resin. Virtually any resin which is

Table II. Capacity Obtained on Various Latex-coated Resins[a]

| Resin | Functionality | Surface Area ($m^2$/gram) | Avg. Pore Diameter (Å) | AL Capacity (µeq/gram) | PL-100 Capacity (µeq/gram) | PL-76 Capacity (µeq/gram) |
|---|---|---|---|---|---|---|
| XAD-1 | styrene-DVB | 100 | 205 | 31 ± 2 | 46 ± 6 | ____ |
| XAD-2 | styrene-DVB | 300 | 90 | 29 ± 3 | 85 ± 7 | ____ |
| XAD-4 | styrene-DVB | 784 | 50 | 16 ± 2 | 26 ± 4 | ____ |
| XAD-7 | acrylic ester | 450 | 90 | 25 ± 2 | 62 ± 9 | ____ |
| XAD-8 | acrylic ester | 140 | 235 | 14 ± 2 | 31 ± 6 | ____ |
| XAD-11 | amide | 69 | 352 | 15 ± 2 | 45 ± 2 | ____ |
| XAD-1 | styrene-DVB | 100 | 205 | ____ | 36 ± 2[b] | 457 ± 2[b] |

[a] Conditions: 0.25 grams of 30 - 37 µm resin, 1 ml acetonitrile, 1 ml latex solution, diluted to 30 ml with 0.1 M sodium chloride; AL = strong-base anion-exchange acrylic latex (75% functionalized); PL-100 = strong-base anion-exchange polystyrene latex (100% functionalized); PL-76 + strong-base anion-exchange polystyrene latex (76% functionalized).

[b] Conditions: 0.15 grams of 30 - 37 µm resin, 0.6 ml acetonitrile, 0.31 ml PL-100 or 0.6 ml PL-76 (to add identical grams of latex), diluted to 10 ml with 0.05 M sodium chloride.

Table III. Capacities Obtained After Coating AL on Various Commercial TSK (Toya Soda Company, Japan) Resins[a]

| Resin | Mean Particle Diameter (μm) | Capacity[b] (μeq/g) |
|---|---|---|
| Polystyrene-divinylbenzene | 5 | 73 |
| Polyvinylacetate | 5 | 20 |
| Polyethylene glycol | 5 | 25 |

[a] Coating conditions were 0.25 g resin, acetonitrile wetted, 0.25 ml latex and 22 ml of 0.10 NaCl.

[b] Capacity determination was by the nitrate/sulfate displacement method.

sufficiently hydrophobic to allow latex adsorption can be coated and used for SCIC.

To determine the time required to coat the resins, an equilibration time study was performed. Figure 1 shows a graph of equilibration time (of the resin in the coating solution) versus the resin exchange capacity. As the graph shows, a 0.5 to 1.0 hour equilibration time is necessary to obtain 90% of the maximum amount of coating (using one set of coating conditions). This equilibration time can be reduced to 20 minutes by shaking or stirring the coating solution during the entire coating process. If reproducible capacities are desired, an equilibration time of just under 4 hours is needed to insure equilibration conditions are reached between the latex and resin (using coating conditions shown in Figure 1). It should be noted that the time required for the preparation of chemically-functionalized resins is at least 24 hours (4,5).

Latex-coated resins of varying capacities were prepared by altering the concentration of the inert electrolyte (sodium chloride) or the concentration of the latex slurry used to coat the resin. Figure 2 shows adsorption isotherms for coating latexes onto XAD-1. An increase in the salt or latex concentration resulted in an increase in exchange capacity. Using various resins and latexes, a capacity range of approximately 5 $\mu$eq/g to 400 $\mu$eq/g was possible.

Figure 1. Resin exchange capacity as a function of equilibration time for AL adsorption on 0.2 g of 38 - 44 μm XAD-1. Each trial used 25 ml of 0.8 ml latex in 0.1 M sodium chloride. The resin/latex solution was not stirred during the equilibration time periods

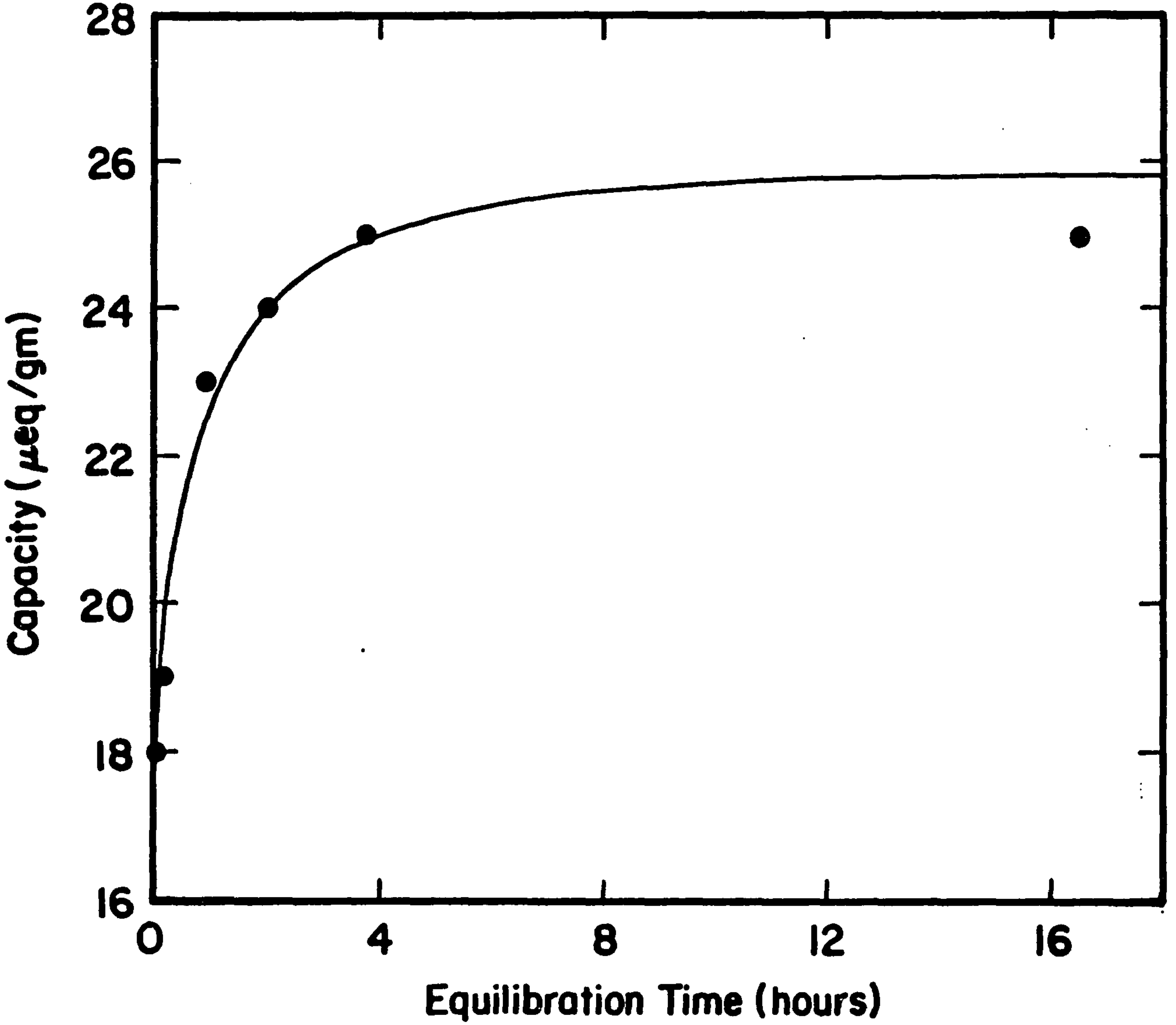
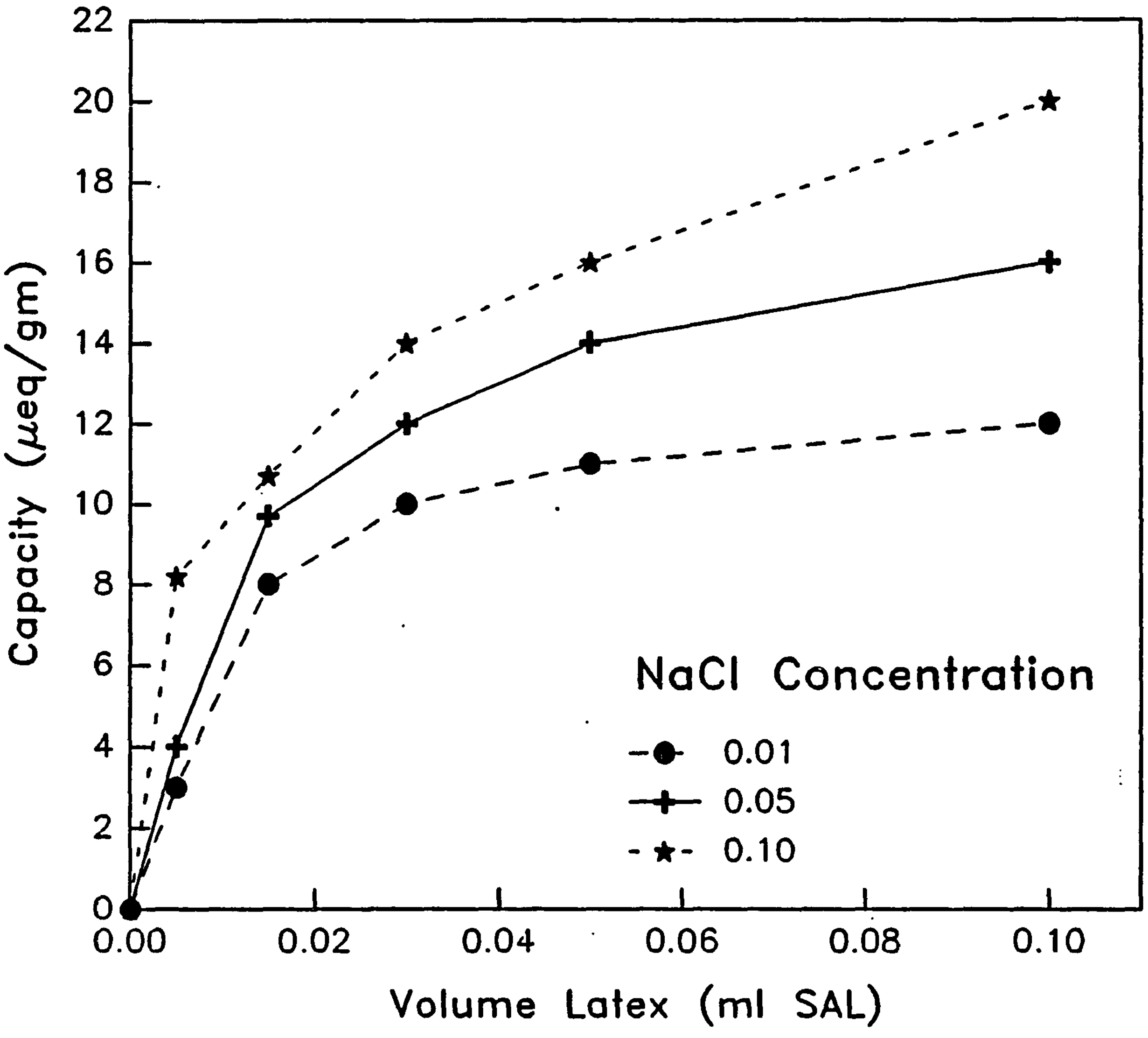

Capacity ( μeq/gm)
28
26
24
22
20
18
16
0
4
8
12
16
Equilibration Time (hours)

Figure 2. Adsorption isotherms for AL/X1 (strong-base anion-exchanging latex coated on 38 - 44 μm XAD-1)

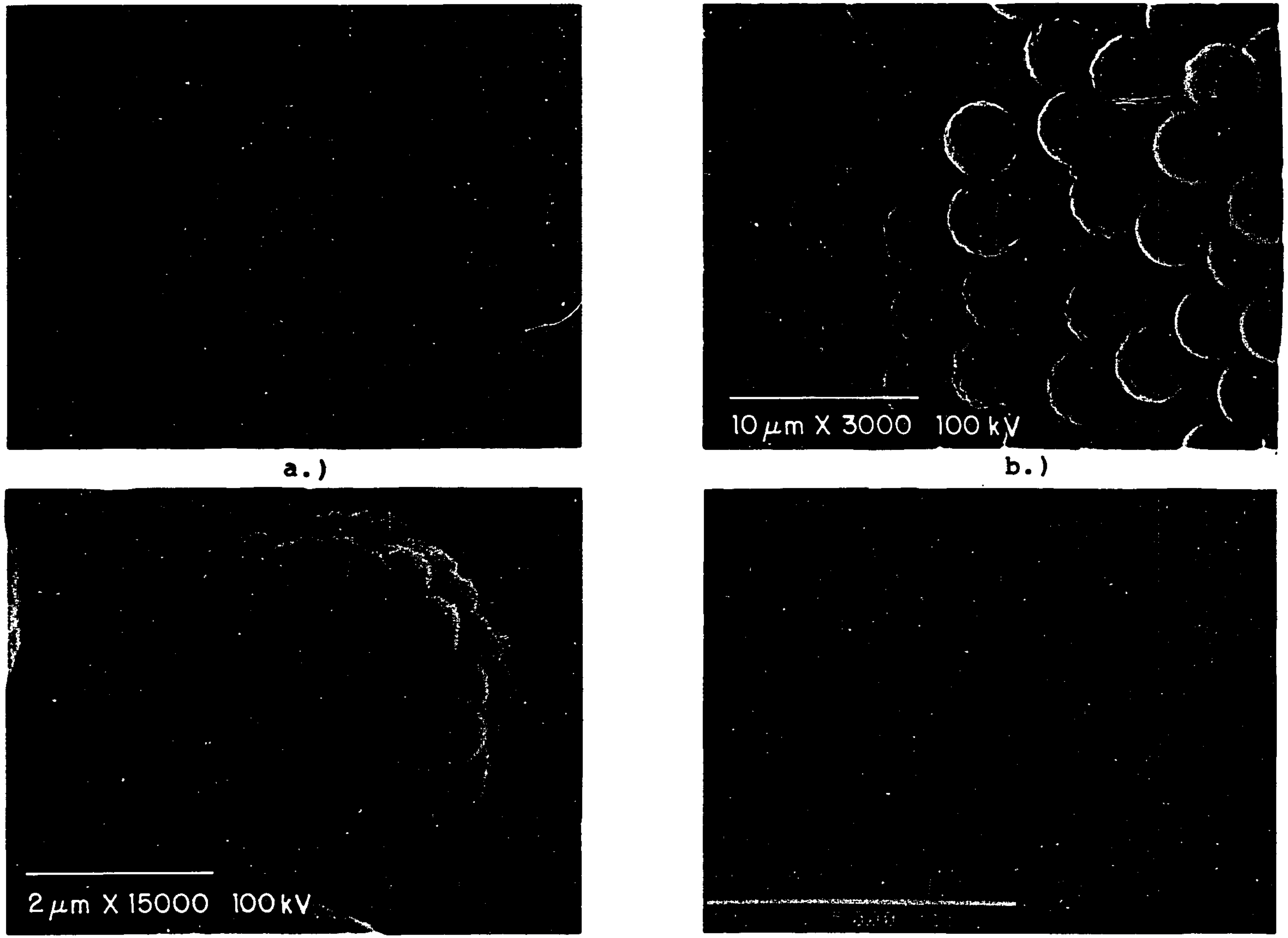

Capacity (μeq/gm)
22
20
18
16
14
12
10
8
6
4
2
0
0.00
0.02
0.04
0.06
0.08
0.10
Volume Latex (ml SAL)
NaCl Concentration
0.01
0.05
0.10

This broad capacity range is ideal for use in SCIC and makes available a wide range of anion separations and sensitivities.

A new polystyrene resin has been developed (10) that is greatly superior to the XAD resins for preparing latex-coated anion exchangers for use in anion chromatography. This resin is prepared in stages. The first is an emulsion polymerization performed with water-soluble initiators. The resin particles are <1 μm in diameter and are used as seed particles for the subsequent expansion stages. Although conditions can be adjusted to vary the particle size, the materials made available to us had a very uniform particle size of around 4.2 μm. For comparison purposes, Figures 3a and 3b show electron micrographs of irregularly-shaped 40 to 50 μm XAD-1 and 4.2 μm polystyrene. The polystyrene particles are approximately spherical but the method of polymerization gives them a somewhat billowy appearance, as show in Figure 3c. These resins, which will be designated as PS in this paper, have very little porosity.

Figure 3d shows some PS resin beads that have been coated with rather large 0.6 μm polystyrene latex 76% quaternized particles. The exchange capacity of this coated resin is fairly high (138 μeq/g) but the sparseness of the coating (Figure 3d) and the large size of the quaternized

Figure 3. Electron micrographs of a.) irregularly-shaped, 40 - 50 μm XAD-1, b.) many 4.2 μm polystyrene (PS) resin particles, c.) a higher magnification showing one PS resin particle and d.) PL-76/PS (strong-base anion-exchanging latex on PS)



a.) b.) c.) d.)

latex particles gave very inefficient separations when a column packed with this material was used for ion chromatography.

Polyacrylate latexes (AL) with 76% of the theoretical amount of quaternary ammonium groups were available in smaller particle sizes: 0.09 μm for strong-base acrylate latexes and 0.08 μm for the weak-base acrylate latexes. PS resins coated with these latexes produced columns with very high efficiencies for separating anions (see section on chromatographic separations). Stevens and Langhorst (3) reported that for electrostatically-coated latex resins the use of latexes smaller than 0.1 μm gave the most efficient anion separations.

Table IV lists the resins which were used chromatographically during the course of this study. The coated polystyrene gave more efficient separations than the coated XAD resins. Therefore, much of the chromatographic work done in this study was performed using the AL/PS columns. The AL/PS columns had linear pressure versus flow behavior up to a least 3500 psi. Flow rates of 0.5 to 1.0 ml/min were typically used, which gave column pressures of 1000 to 1900 psi.

## Mechanism of Latex Adsorption

Earlier work by Cantwell studied the mechanism of organic ion adsorption on a reversed phase resin,

Table IV. Characteristics and Designations of Coated Resins

| Designation | Latex[a] | Resin[b] | Capacity ($\mu$eq/g) | Column Size |
|---|---|---|---|---|
| AL/XAD-1 | AL | XAD-1 | variable | ---- |
| AL-WB/XAD-1 | AL-WB | XAD-1 | 18 | 250 mm X 2.0 mm i.d. |
| PL-76/PS | PL-76 | PS | 457 | 250 mm X 4.0 mm i.d. |
| AL/PS | AL | PS | 27 | 250 mm X 4.0 mm i.d. |
| AL/PS | AL | PS | 48[c] | 250 mm X 4.0 mm i.d. |

[a] See Table I for latex descriptions.

[b] XAD-1 resin is irregularly-shaped and 20 to 26 $\mu$m particle size. The polystyrene resin (PS) is spherical, nonporous and 4.2 $\mu$m in size.

[c] The AL/PS column of a higher capacity was prepared by increasing the latex and sodium chloride concentration in the coating solution.

unfunctionalized XAD-2 and sulfonated XAD-2 (11-13). Using adsorption isotherms, the mechanism was explained by the Stern-Guoy-Chapman (SGC) model of the electrical double layer. According to Cantwell, adsorption of an organic ion onto styrene-divinylbenzene copolymers is due to dispersion forces. As these ions are adsorbed, a resin surface charge is acquired due to the charged surface groupings on the adsorbed particle. Following the SGC electrical double layer model, addition of an electrolyte to the coating solution increases the number of counterions in the bulk solution. The surface potential remaining constant, more organic ions must adsorb onto the resin surface in order to maintain this potential, thus creating a heavier organic ion coating.

The adsorption isotherms shown in Figure 2 for latex-coated XAD seem to follow the trends shown in Cantwell's work. Addition of an electrolyte (NaCl) to the coating solution caused more latex particles to adsorb onto the support, giving a higher exchange capacity. This leads to the conclusion that a hydrophobic interaction is responsible for the coating of latex particles onto these resin matrices.

Table II also shows the capacities obtained by coating two latexes which differ in their degree of functionalization onto XAD-1. The latexes are 75.6% and

100% functionalized strong-base exchanger polystyrene. The 75.6% functionalized latex coated 13X heavier than the 100% functionalized latex. With a lower degree of ionic character in the 75.6% functionalized latex, the dispersive forces allow a larger amount of latex to be coated onto the support. This phenomenon also supports the mechanism of hydrophobic interaction between the latexes and the resin supports.

Latex particles held onto the resin surface by a hydrophobic attraction can be washed off by organic solvents. Passing acetonitrile or 2-propanol through a latex-coated column removed part of the latex coating and lowered the column capacity. This observation is similar to results by Iskandarani and Pietrzyk with alkylammonium-coated columns (14), where larger amounts of organic modifiers in the coating solution resulted in a lower degree of resin coating. The latex-coated resins, however, could tolerate low amounts of methanol without significantly affecting the exchange capacity.

The fact that organic solvents alter the column exchange capacity is not a great concern in SCIC. In most cases, aqueous eluents are used and aqueous samples are analyzed. In addition, our work has not found significant advantages from using organic modifiers in the eluents. However, organic solvents can be used to strip the latex off of a fouled or ruined latex-coated column so that the resin can be recoated and used again.

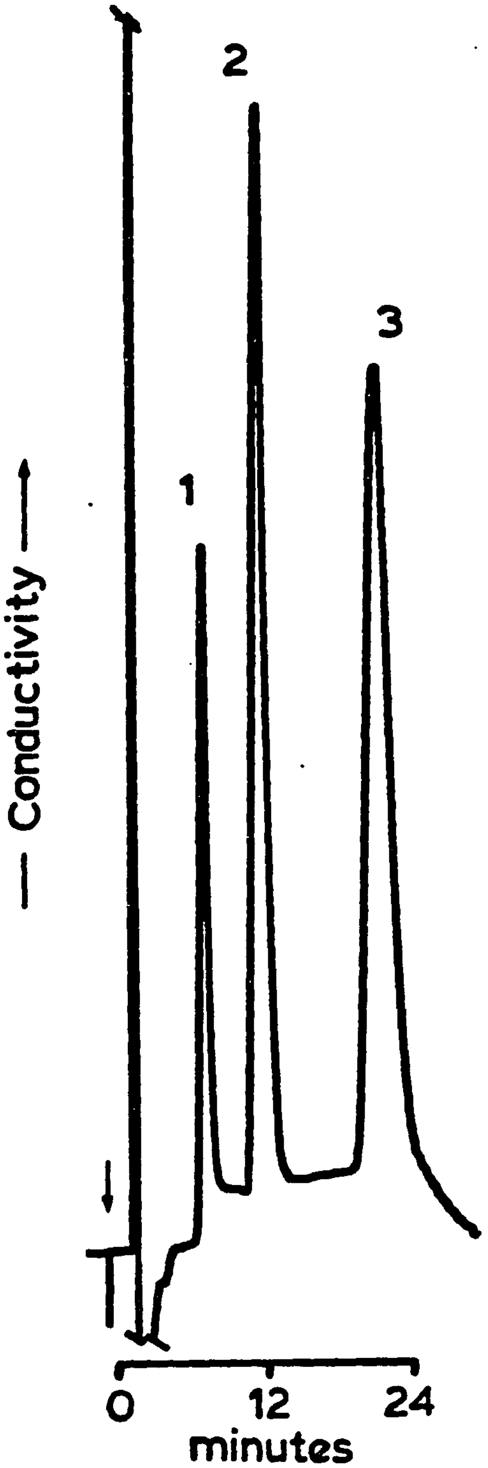
## Chromatographic Efficiency and Selectivity

Figure 4 shows chromatograms obtained both on a latex-coated XAD and on a latex-coated 4.2 μm polystyrene column (AL/XAD-1 and AL/PS). It can easily be seen that better column efficiencies are obtained with the AL/PS column. This is mainly due to the spherical, uniform, small-sized polystyrene resin substrate used with the AL/PS column.

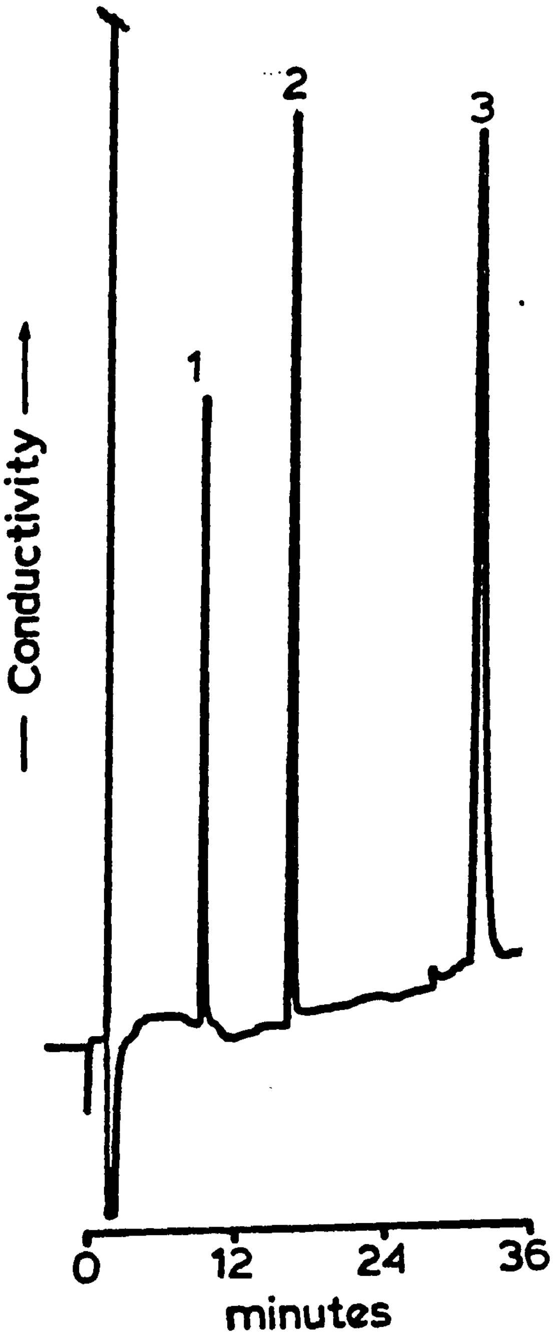
Figure 5 shows the relationship between the eluent linear velocity (or flow rate) and the height equivalent to a theoretical plate (HETP) for the AL/PS (48 μeq/g) column using a 4 mM molybdate eluent. The column efficiencies observed during the course of this work varied with different columns, eluents and test analytes. A typical 4.0 mm i.d. X 250 mm column yielded 12,000 to 72,000 N/m between flow rates of 0.23 and 1.05 ml/min. The maximum plate number of 72,000 N/m for sulfate was obtained at a flow rate of 0.23 ml/min.

The selectivity of the AL/PS (48 μeq/g) column for a series of anions using 3 different eluents is shown in Table V. The selectivity of this column for these anions is very similar to the selectivity obtained with previously-used

Figure 4. Separation of 25 ppm iodate, 25 ppm methylsulfonate and 10 ppm chloride on a.) AL/XAD-1 and b.) AL/PS (27 μeq/g) columns. (See Table II for column designations.) For a.) the eluent was 35 mM nicotinic acid at a flow rate of 1.0 ml/min. The column pressure was 14 bar. For b.), the eluent was 70 mM nicotinic acid at a flow rate of 0.75 ml/min. The column pressure was > 140 bar


— Conductivity →
1
2
3
0
12
24
minutes

a.)


— Conductivity →
1
2
3
0
12
24
36
minutes

b.)

Figure 5. Plot of HETP versus linear velocity (or flow rate) using the 250 mm X 4.0 mm i.d. AL/PS (48 $\mu$eq/g) column. The eluent was 4 mM sodium molybdate

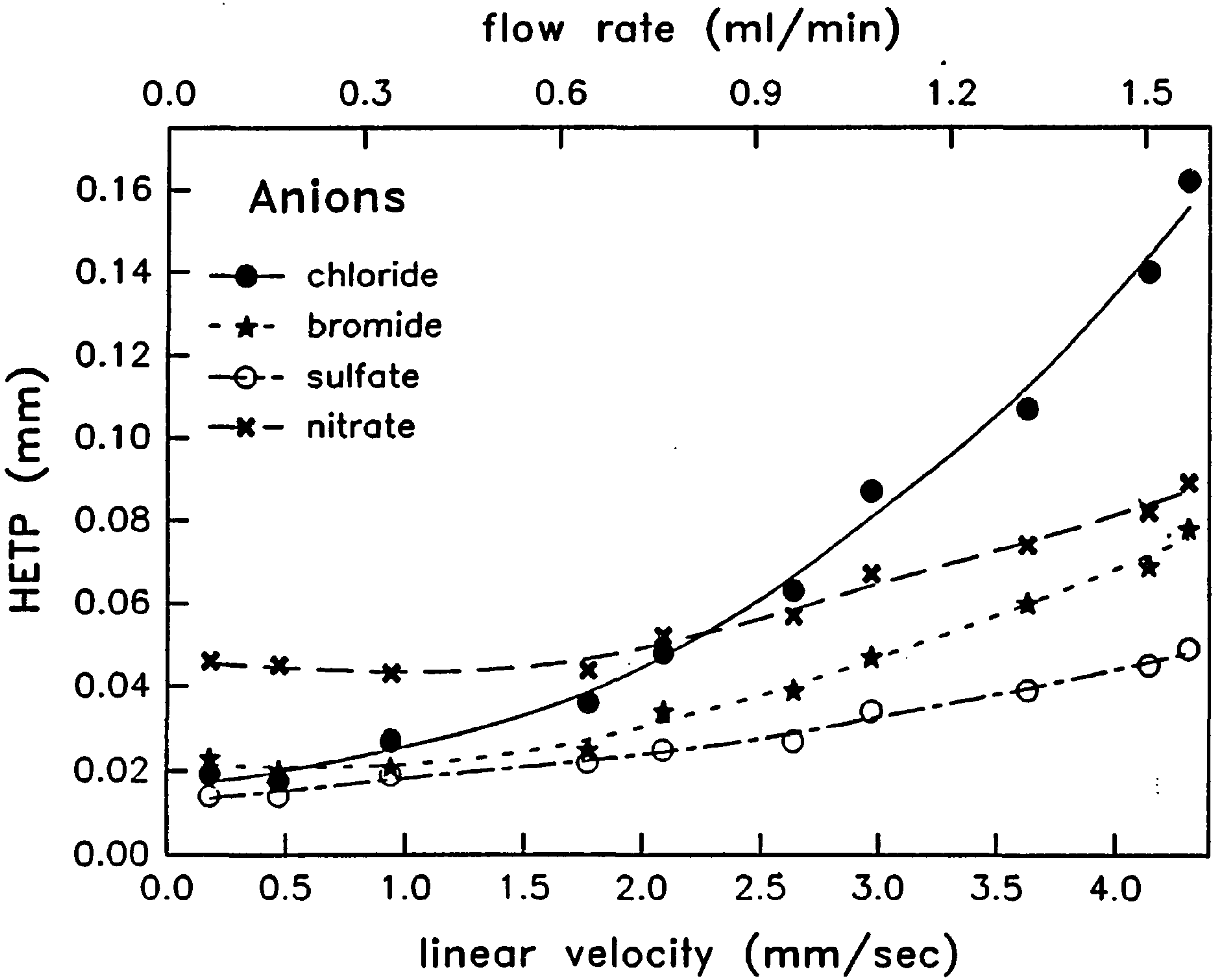

flow rate (ml/min)
0.0
0.3
0.6
0.9
1.2
1.5
Anions
chloride
bromide
sulfate
nitrate
HETP (mm)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
linear velocity (mm/sec)

Table V. Selectivity Data for AL/PS column[a]

| | k' | | |
|---|---|---|---|
| Anion | 90 mM nicotinic acid | 2.4 mM sodium phthalate, pH 6.0 | 4.0 sodium molybdate |
| methyl acrylate | 1.30 | - | - |
| lactate | 1.85 | - | - |
| formate | 3.45 | - | - |
| fluoride | 3.70 | 0.36 | 0.21 |
| acetate | - | - | 0.25 |
| iodate | 6.40 | 0.36 | 0.21 |
| dihydrogen phosphate | 8.25 | - | - |
| monochloroacetate | 12.25 | - | - |
| methylsulfonate | 13.50 | 0.73 | 0.54 |
| ethylsulfonate | 13.60 | 0.73 | 0.54 |
| sulfamate | 15.40 | - | - |
| propylsulfonate | 16.95 | 0.91 | 0.75 |
| bromate | 27.20 | 1.27 | 0.92 |
| chloride | 28.90 | 1.45 | 0.96 |
| nitrite | 31.65 | 2.04 | 1.42 |
| malonate | - | 4.27 | 2.21 |
| bromide | 48.90 | 5.00 | 3.13 |
| nitrate | - | 6.73 | 4.17 |
| chlorate | - | 6.91 | 4.71 |
| sulfate | - | 7.45 | 3.17 |
| thiosulfate | - | 32.27 | 13.58 |
| $t_R'$ for $Cl^-$ (min) | 55.00 | 3.00 | 2.19 |

[a] Conditions: AL/PS column is 4.2 μm spherical, nonporous, polystyrene coated with a strong-base anion-exchange acrylic latex (48 μeq/g capacity); 4.0 mm i.d. X 250 mm column; 1.0 ml/min flow rate; conductivity detection.

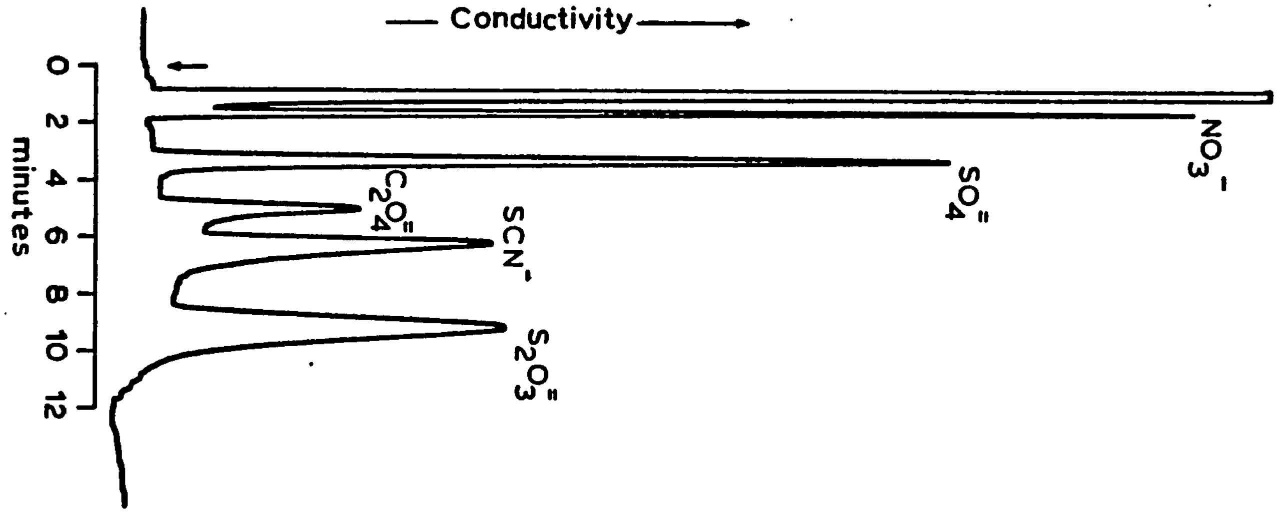
coated or chemically-functionalized resins (7,15), although a few differences can be noted. For example, ethyl- and propylsulfonate elute much earlier than chloride from the AL/PS column. This is unusual because all XAD-based and commercial columns used in our laboratories elute the sulfonates either simultaneously with or later than chloride.

The AL/PS column also does not retain fluoride or phosphate to a significant extent compared to chloride. The separations shown in this paper do not include these anions because of their elution in the column void volume. Most commercial and home-made columns used in our laboratories retain these ions to a greater extent.

## Chromatographic Separations

Figures 6 to 9 show typical examples of separations that can be achieved with the AL/PS and AL-WB/XAD-1 columns. Figure 6 shows a good separation of several normally late-eluting anions on a coated XAD column of very low capacity (AL-WB/XAD-1). These latex-coated columns can very easily be prepared with very low capacities so that low eluent concentrations can be used to obtain very sensitive anion determinations. For example, using an AL-XAD-1 column with a capacity of 0.005 meq/g and an eluent concentration of 3.7 X $10^{-5}$ M sodium phthalate (pH 6.0), a 0.4 ng detection limit

Figure 6. Separation of late-eluting anions on AL-WB/XAD-1 column using 9 X $10^{-4}$ M sodium phthalate at pH 5.10 as the eluent. The flow rate was 1.3 ml/min. and 13 to 17 ppm each of anion was injected


Conductivity
minutes
0
2
4
6
8
10
12
$NO_3^-$
$SO_4^=$
$C_2O_4^=$
$SCN^-$
$S_2O_3^=$

for sulfate was obtained using indirect spectrophotometric detection.

Figure 7 shows an excellent separation of 7 common anions using the AL/PS (27 μeq/g) column. Baseline resolution was achieved between every peak and the total analysis time was less than 7 minutes. The molybdate eluent used here serves to elute sulfate immediately after nitrate, and proved to be an excellent eluent for the separation of these anions with these latex-coated columns. Since conductivity detection is not suitable with this eluent, indirect spectrophotometric detection at 250 nm was used.

Figure 8 shows an excellent separation of 12 anions using the AL/PS (27 μeq/g) column and a nicotinic acid eluent. Again, baseline resolution was achieved with every peak. The organic acid eluents such as nicotinic acid are very useful for separating large series of weakly-retained monovalent anions with these latex-coated columns.

Figure 9 shows a separation using a AL/PS resin of a slightly higher capacity (48 compared to 27 μeq/g). In this separation, sulfate was eluted before nitrate, an inversion which is rarely seen. Dionex has marketed a proprietary column, HPIC-AS2, which also shows this inversion. This column is useful for determining early-eluting anions in nitric acid digests. Supposedly, the nitrate/sulfate

Figure 7. Separation of 7 common anion on AL/PS (27 μeq/g) column using a sodium molybdate eluent run at 0.75 ml/min. Indirect spectrophotometric detection was used at 250 nm with 0.05 AUFS. 1 = ethylsulfonate, 2 = propylsulfonate, 3 = chloride, 4 = nitrite, 5 = bromide, 6 = nitrate, 7 = sulfate (10 - 20 ppm each anion)

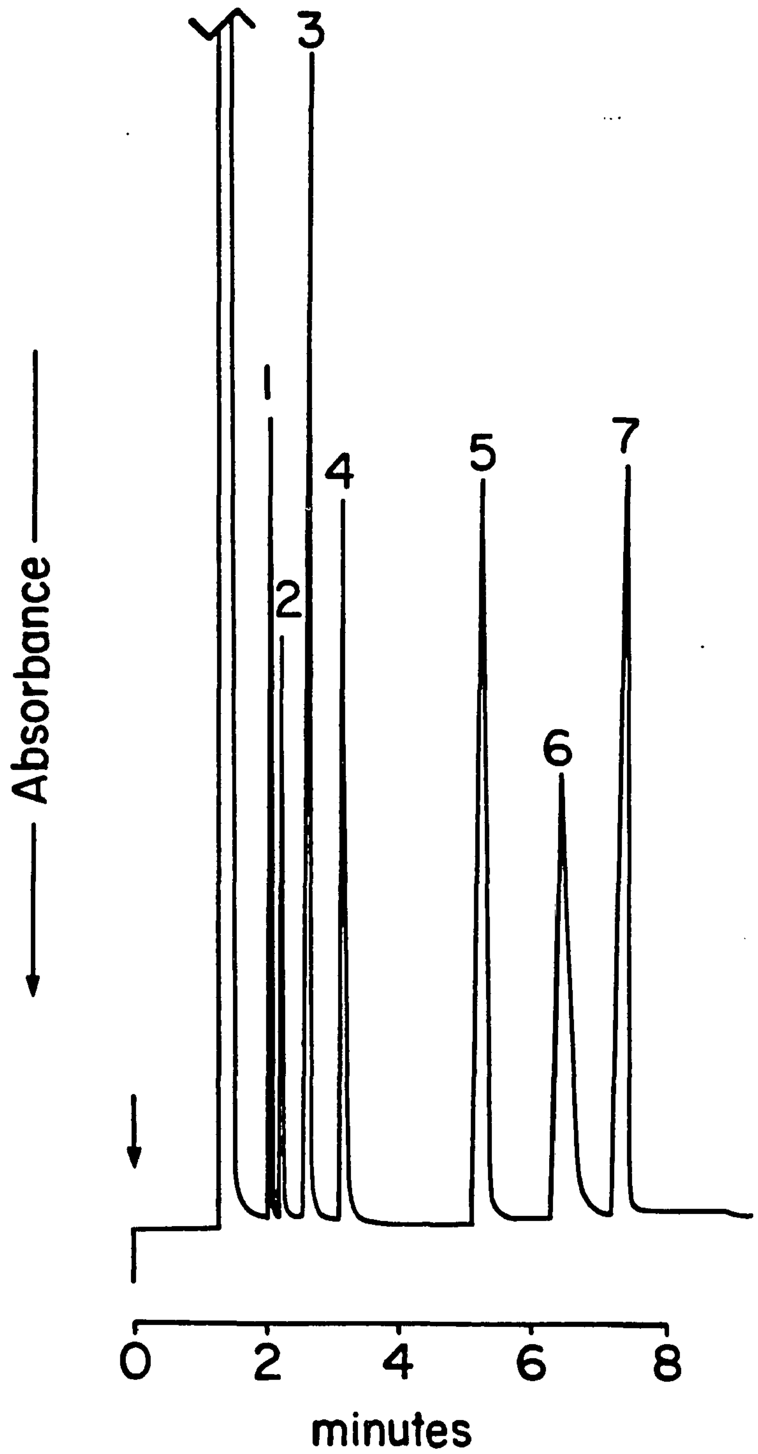

Absorbance
3
1
2
4
5
6
7
0
2
4
6
8
minutes

Figure 8. Separation of 12 monovalent anions on AL/PS (27 μeq/g) using 70 mM nicotinic acid (pH 3.5) as the eluent. The column pressure was 115 bar at a flow rate of 0.75 ml/min. Conductivity detection was used with 0.1 μSFS. 1 = methyl acrylate, 2 = lactate, 3 = formate, 4 = fluoride, 5 = iodate, 6 = dihydrogen phosphate, 7 = monochloroacetate, 8 = ethylsulfonate, 9 = sulfamate, 10 = n-propylsulfonate, 11 = bromate, 12 = chloride (25 - 100 ppm each)

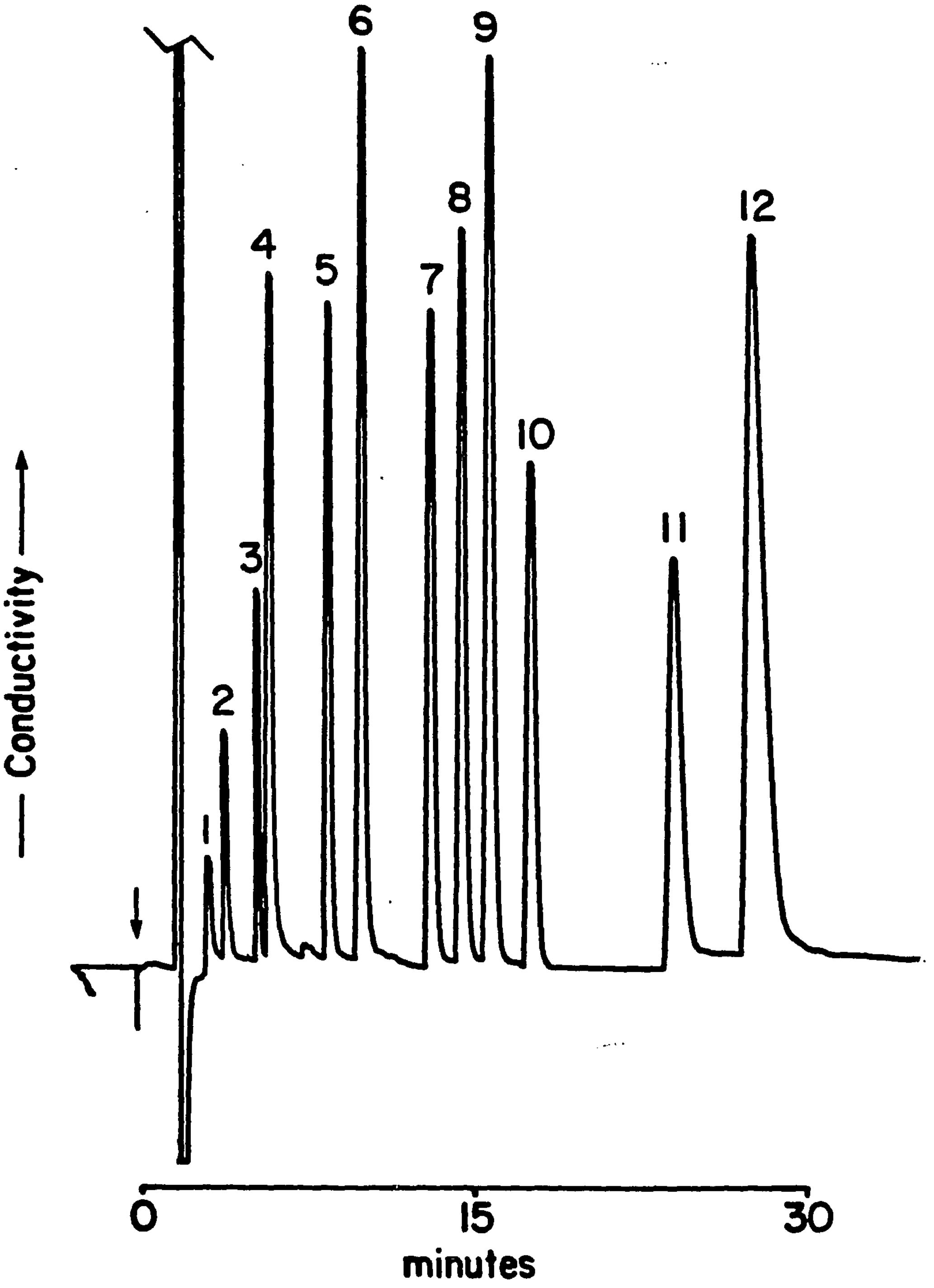
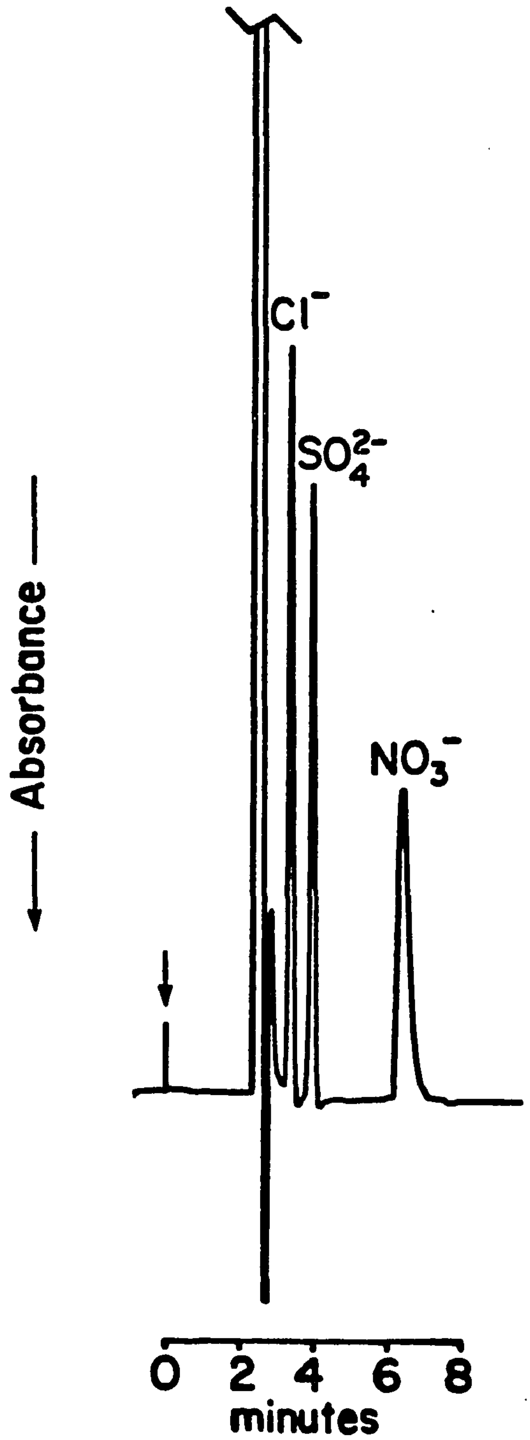

Conductivity
1
2
3
4
5
6
7
8
9
10
11
12
0
15
30
minutes

Figure 9. Separation on AL/PS (48 μeq/g) showing inversion of nitrate and sulfate (25 - 50 ppm each anion). The eluent is 16 mM sodium molybdate at a flow rate of 0.75 ml/min. Indirect spectrophotometric detection is used at 271 nm with 0.01 AUFS


Cl⁻
SO₄²⁻
NO₃⁻
Absorbance
0
2
4
6
8
minutes

inversion on the Dionex resin is brought about because of different resin functional groups. DuVal and Fritz (7) demonstrated this same inversion using tetraoctylammonium chloride coated on XAD-8 as the anion-exchanging resin.

The "nitrate-selective" column utilized in this work is a strong-base anion-exchanging acrylic latex coated on polystyrene. The exchange site is a typical trimethylammonium functional group. The higher capacity of this resin (as compared to the resin used in Figure 8) along with the molybdate eluent created the nitrate/sulfate inversion. Very good efficiency is again displayed in this chromatogram. The retention times of chloride, sulfate and nitrate were 3.3, 3.8 and 6.4 minutes, with a 2.6 minute separation between sulfate and nitrate.

# CONCLUSIONS

It has been demonstrated in this work that anion-exchanging latexes can be hydrophobically coated onto several different neutral resins. Since no prior resin sulfonation is necessary, the anion-exchanging latexes can be coated on virtually any porous or nonporous resin which is sufficiently hydrophobic. Because of the simple coating procedure, the latex-coated resins can be prepared very quickly and easily. These coated resins can then be used to separate anions in single-column ion chromatography.

Using various resins and latexes, the concentration of latex and/or electrolyte can be varied in the coating solution, and a capacity range of 5 to over 400 $\mu$eq/g is accessible. This wide capacity range allows a greater amount of flexibility when separating complex mixtures of anions. For example, by increasing the capacity of the AL/PS resins, nitrate/sulfate inversions can be obtained.

Using a latex-coated 4.2 $\mu$m polystyrene resin, highly efficient anion separations can be obtained. Anion efficiencies on this resin range from 12,000 to 72,000 N/m below a flow rate of 1.05 ml/min.

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# GENERAL CONCLUSIONS

In this work, selectivity variations caused by altering the stationary phase were investigated using spacer arm and quaternary phosphonium anion-exchange resins. It was shown that both of these new types of resins can be used to obtain useful anion separations. The unique selectivities obtained with these resins can be explained using the theory of water-structure induced ion pairing.

Although selectivity in anion chromatography appears straightforward, many variables should actually be considered when attempting to alter anion selectivity. A general understanding about the factors that affect selectivity is necessary so that separations can be fully optimized. Many more experiments could be performed, but the results of this work combined with results of previous investigations (64,65) provide a fairly complete selectivity study of anions with these types of low-capacity resins.

The last section of this dissertation describes a very quick procedure for preparing another new type of resin for SCIC. The stationary phase is prepared by hydrophobically coating an anion-exchanging latex onto a 4.2 μm, nonporous, monodisperse resin. Highly efficient separations are obtained with this resin so that more complex anion mixtures can be resolved.

# FUTURE WORK

## Spacer Arm Resins

To complete the spacer arm resin work, an organic modifier study should be performed. The hydrophobic spacer arms probably coil or lay down on the polymeric resin surface when an aqueous eluent is used. If an organic solvent is added to the eluent, the spacer arm should not adhere to the resin and these resins should show different selectivity trends.

Future work should be aimed at synthesizing new types of spacer arm resins. Water-structure induced ion pairing and spacer arm shielding seem to explain the observed selectivity trends on polymeric spacer arm resins. Selectivity information obtained on silica-based spacer arm resins might provide information to support one or both of these theories. For example, if the spacer arms are preventing the anions from interacting with the polystyrene surface, a totally different selectivity trend might occur using the silica support since identical anion interactions with silica would not exist.

A different type of spacer arm resin was recently synthesized by Sugii and coworkers (82). These macroporous polystyrene-based resins have carbonylalkylammonium exchange groups and were used as solid-phase reagents. This procedure could be modified so that low-capacity resins of this type could be synthesized and used for anion chromatography. It would be interesting to determine the effect on selectivity of the spacer arm carbonyl group and to compare these results to trends obtained previously.

## Phosphonium Resins

The studies of phosphonium resins have provided useful information which is leading to very interesting future work. Our study determined that tributylphosphonium resins can be prepared with capacities that are approximately double that of tributylammonium resins. The phosphonium resins also are more selective than tributyl- or trimethylammonium resins for large, polarizable monovalent anions like nitrate. Utilizing this information, work has already begun in our laboratories using phosphonium resins for applications in ion-exchange chromatography.

As suggested by Dr. Robert E. Barron several years ago, sulfides and stibines could also be used to prepare the corresponding sulfonium and stibonium anion-exchange resins. These new strong-base resins would certainly yield selectivities different from phosphonium or ammonium resins.

## Latex-Coated Resins

An important goal of our research is to obtain highly efficient resins for ion chromatography. The latex-coated polystyrene resins (4.2 μm) have given the best anion separations ever obtained in our laboratories. More research can be performed to further increase the separation efficiency obtained with these columns.

Our studies showed that the latex coatings on these resins are very sparse and rather nonuniform. Column efficiency should increase if a heavier and more uniform coating is obtained while still retaining a rather low exchange capacity. Our research has shown that latexes under 0.1 μm in size give higher column efficiencies, and that latexes which are not fully functionalized give heavier resin coatings. Therefore, a much higher and more uniform resin coating should be obtained by coating the 4.2 μm resin with a small-sized latex (under 0.1 μm) that is $\leq$ 75% functionalized. This should result in column efficiencies which are considerably higher than efficiencies previously obtained.

It would also be desirable to obtain a resin similar to the 4.2 μm polystyrene resin that would not swell or dissolve in organic solvents. This resin would be useful for other forms of chromatography, such as reversed-phase chromatography. The original polystyrene (no cross-linking) cannot be chemically-functionalized because it dissolves in solvents such as ether, THF and 1,2-dichloropropane. Work should be done to synthesize a monodisperse, small-sized polystyrene resin which is similar to macroreticular XAD-1 so that it does not swell in organic solvents.

Using a chelating latex, latex-coated resins could also be used to separate metal ions. This idea was originally suggested several years ago by the research group of Dr. James Fritz. This is a promising area because many researchers now desire inexpensive methods for metal determinations to compliment and verify spectroscopic methods of analysis. The only chelating stationary phases which have been synthesized up to this point are silica-based phases which give rather inefficient metal ion separations (83-85). Latex-coated polymeric resins should give very efficient separations because of the small-sized, nonporous resin and because the metal interactions would occur strictly on the outer surface of the resin. Another advantage of this polymeric, chelating phase would be that a very wide eluent pH range could be tolerated.

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