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New selective anion-exchange resins for nitrate removal from contaminated drinking water and studies on analytical anion-exchange chromatography

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Iowa State University

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from contaminated drinking water and studies on analytical
anion-exchange chromatography**

Lockridge, James Edward, Ph.D.

Iowa State University, 1989

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**New selective anion-exchange resins
for nitrate removal from contaminated drinking water
and studies on analytical anion-exchange chromatography**

by

James Edward Lockridge

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

**Department: Chemistry
Major: Analytical Chemistry**

Approved:

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**Iowa State University
Ames, Iowa**

1989

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DEDICATION

This work is dedicated to my wife, Rochelle.

**Without her unconditional love and support,
this examined life would surely not be livable.**

GENERAL INTRODUCTION

The contamination of drinking water supplies by nitrate is a growing concern. Most communities draw on ground water as their principal source of drinking water. In the past, ground water supplies have been relatively pure, thereby supplying water which requires very little treatment. With this generation's intense farming practices, however, ground water supplies are gradually becoming contaminated with nitrates. The application of nitrogen fertilizers is considered to be the major contributor. It is estimated that barely 50% of all applied nitrogen is actually used in crop growth. A large percentage of that unused nitrogen is converted to nitrates which begin a slow journey towards the ground water. Even if farming practices were drastically altered today, the effects of past application of nitrogen fertilizers would still be felt in 20 years time. Section I is a study on one solution to the nitrate problem.

Ion chromatography has become a vital technique for the determination of anions. A vast array of ion chromatographic methods exist which employ numerous variations on detection, separation and sample preparation. Most detectors used for ion chromatography are of a universal type. These types of detectors leave differentiation of sample components to the other system components and detect all ion which cross their paths. Presented in Section II is an anion specific detector

which solves or aids in the solution of many problems often encountered in anion chromatography.

The chromatographic determination of aluminum(III), being a positively charged ion, is most often done by cation chromatography. Unfortunately, aluminum is often found in a matrix where many other metal cations are also present. The limitation to cation chromatography, imposed by this situation, is due to cluttering of a separation. Often a determination is literally obscured by the presence of other metal cations. Furthermore, the presence of cations much more strongly retained than aluminum(III) require long analysis times. The determination of aluminum by anion chromatography is presented in Section III. The serendipitous combination of eluent and anion separator column gives this technique advantages unprecedented in the world of cation chromatography.

**SECTION I. SELECTIVE ANION-EXCHANGE RESINS FOR
NITRATE REMOVAL FROM CONTAMINATED
DRINKING WATER**

LITERATURE SURVEY

The biological hazard of nitrates in drinking water supplies is largely due to a disease called nitrate cyanosis, methemoglobinemia, or blue-baby syndrome. The disease reduces the oxygen carrying capabilities of the blood similar to that which occurs in cyanide poisoning. Certain enzymes must be present in the body to prevent the oxidation of hemoglobin to methemoglobin by nitrate. These enzymes are not yet formed in young infants. Hence, nitrate poisoning is predominantly associated with infants under 3 months of age and can be fatal if not treated properly (1).

The maximum contaminant level (MCL) for nitrate in drinking water in the U.S. is set by the Environmental Protection Agency (EPA) at 44 mg/L (ppm). The level for Europe, set by the European Economic Community (EEC), is 50 mg/L. As of 1984, 6% of all U.S. wells were above 44 ppm. A 1985 study estimates that 8% of all Danish wells and 7% of all Hungarian wells were above 50 ppm (2).

Most nitrates found in ground water supplies originate as some form of soil nitrogen. Typical examples of soil nitrogen are animal feces (from animal feed lots), crop residues, human wastes and agricultural fertilizers. The work of soil microorganisms causes these nitrogenous materials to be converted to nitrate. Contamination of a water supply results from the slow percolation of this nitrate into the ground water. Hence with this generation of intensive farming practices,

i.e., the application of mega-doses of nitrogen fertilizers, a virtual time bomb of nitrate contamination can be envisioned. One study estimates that "even if the use of artificial fertilizers could be stopped...past application would still be felt in 20 years time" (3).

A number of processes are capable of removing nitrate from contaminated waters. In evaluating a method for drinking water purification, an important factor to consider is economy. Processes which may be quite effective in the laboratory can quickly become cost prohibitive on a larger scale. A study by Clifford *et al.* (4) compared three popular techniques: reverse osmosis, electrodialysis and ion exchange. Their results showed ion-exchange processes as giving at least a 65% cost savings over that of the other two methods.

Some work has been done on nitrate removal by anion-exchange, the majority of which involves the use of typical weak-base or strong-base ion exchangers. Such commercially available resins usually lack the selectivity for nitrate, resulting in a lower net exchange capacity for nitrate removal. The above study by Clifford *et al.* (4) used a non-nitrate-selective resin and hence inherited the disadvantages of concentration effects for nitrate at the end of a run (see Results and Discussion section) and decreased capacity due to sulfate. Other investigators have found similar disadvantages when attempting nitrate removal using resins which are not nitrate-selective (4,5,6).

Another study by Clifford and Weber (5) investigated 30 commercially

available anion-exchange resins and related selectivity to a number of resin properties. Among the strong-base type I (trimethylammonium) resins, increased crosslinking had a positive effect on nitrate selectivity. The use of a gel or macroreticular resin base, as opposed to an isoporous resin, was also found to increase nitrate selectivity. Their work involved the use of only commercially available strong-base resins of the trimethylammonium or pyridinium type. The effect of the quaternary ammonium site on nitrate selectivity was not investigated by Clifford and Weber. Work by Guter (7), however, found some striking evidence for the effects of alkyl chain length on the fixed quaternary ammonium sites. As the number of carbons in the R groups increased from three (trimethyl) to nine (tripropyl), the nitrate to sulfate selectivity coefficient (K_S^N) increased 10 fold. A patent by Guter (8) demonstrates an increase in K_S^N of 100 fold on increasing the R groups from methyl to butyl.

Several investigators have explored the use of weak-base anion-exchangers for nitrate removal. Selneczi (9) and Andrejewski (10) removed nitrate from drinking water by weak-base resins, following acidification of the water with CO_2 . In each case, however, sulfate had to be removed completely before the resin could retain nitrate. Rolke *et al.* (11) used weak-base exchange to remove chloride, sulfate and nitrate from coal gasification waste waters. A study by Higgins (12) used weak-base anion-exchange to recover nitrate from a fertilizer plant waste water. Regeneration of the spent resin with ammonium hydroxide yielded ammonium nitrate which could

be recovered as a usable fertilizer product.

The major disadvantage of nitrate removal by ion-exchange is the disposal or treatment of the spent regenerant. A study by Solt and Klapwijk (13) demonstrates a rather elegant solution to the problem. Strong-base anion-exchange resins are most economically regenerated with concentrated sodium chloride solutions. Because regeneration is not 100% efficient, a nitrate contaminated brine waste results. In the above study, this brine solution was treated with anaerobic bacteria to reduce the nitrate to diatomic nitrogen (N_2). After removal of sulfate ion by precipitation as calcium sulfate, the brine could be reused in the next regeneration. Schemes using anaerobic bacteria to remove nitrate directly from drinking water have been proposed. A serious limitation to such methods is that reduction of nitrate can sometimes be incomplete, yielding nitrite. Furthermore, anaerobic bacteria require the addition of an electron donor, usually methanol. Hence, the possibility of introducing nitrite, a known carcinogen and methanol, a toxic substance, into a water supply make this method highly prohibitive. The combination of ion-exchange with anaerobic bacteria is a way to avoid the primary objections of each method.

In addition to this work, and the works of Guter (7,8), other studies have centered around the development of a nitrate-selective ion-exchange resin. Hauptmann et al. (14) attached 3-amino-1,2,4-triazole to a polystyrene-divinylbenzene (PS-DVB) resin. Triazole is a simpler analog to a well known

nitrate precipitating reagent, Nitron. They reported capacities of 2.3 meq/g and separation factors of 2-3 for $\text{NO}_3^-/\text{SO}_4^{=}$ and of 5-10 for $\text{NO}_3^-/\text{Cl}^-$. Such a high preference for nitrate over sulfate is good for reducing the amount of sulfate retained, thereby increasing the nitrate capacity of the resin. The high preference for nitrate over chloride, however, implies that such a resin could not be efficiently regenerated with sodium chloride. This is a typical paradox for resins which are highly selective for nitrate. While a large $\text{NO}_3^-/\text{SO}_4^{=}$ selectivity is desirable, it is often accompanied by an increase in the $\text{NO}_3^-/\text{Cl}^-$ selectivity, making the resin more resistive to regeneration by sodium chloride.

Grinstead and Jones (6) adsorbed long-chain amidines or guanines onto PS-DVB resins for removal of nitrates from waste waters. The amidines and guanines were hydrophobic enough to coat a resin yet some leaching into the effluent was still observed. While very favorable $\text{NO}_3^-/\text{SO}_4^{=}$ selectivity was observed ($K_S^N = 10^6$), this leaching of the stationary phase not only decreases the capacity of the resin but, more importantly, renders the technique unacceptable for drinking water applications. In a related patent by Roubinek (15), long-chain amidines were covalently bound to a resin matrix. While the leaching problem was obviated, the trade off of nitrate selectivity vs. regeneration efficiency remained. Roubinek reports that as the length of R in the amidine is increased, nitrate selectivity also increased while regeneration efficiency decreased.

This study employs phosphonium based anion-exchangers. While the existence of quaternary phosphonium resins is not new, their use as high capacity anion exchangers in water purification is unprecedented. Cinquini *et al.* (16) first used phosphonium based ion exchange resins in phase-transfer catalysis. Since that time, several studies have involved the ion exchange activity of phosphonium resins as heterogeneous phase-transfer catalysts (17-23). The present study was inspired by the work of Warth *et al.* (24) who used a low capacity tributylphosphonium resin in single-column ion chromatography.

One final aspect of nitrate removal is illustrated by the work of Prunac and Baur (25). During regeneration with sodium chloride, the chloride in the brine solution exchanges with nitrate, resulting in a regenerated column and a sodium chloride solution contaminated with sodium nitrate. Since the sodium ions in the regenerant are not consumed, it is possible to reuse this brine solution for regeneration of spent cation-exchangers from water softening. More conveniently, as in the work of Prunac and Baur, softening and nitrate removal, followed by regeneration with brine, can take place in a single mixed-bed column. Concomitantly, the spent regenerant is contaminated with calcium and nitrate ions. However, if the anion-exchange resin is not selective for nitrate, and enough sulfate is retained, calcium from the cation-exchanger may combine with sulfate from the anion-exchanger, resulting in precipitation of calcium sulfate during regeneration.

Both non-selective and selective anion-exchange resins were used by Prunac and Baur (25) and precipitates were observed for the non-nitrate-selective resin.

EXPERIMENTAL

Capacities

Capacities were measured by first converting the resin to the nitrate form, then quantitatively exchanging the nitrate with chloride ion. The nitrate level in the effluent NaCl solution was determined by absorption spectroscopy at 220 nm.

Approximately 40 mg of vacuum dried resin was placed in the capillary portion of a pasture pipet with a glass wool plug as bed support. This transfer was most easily accomplished using a piece of weighing paper shaped into a funnel and the resin dry. The resin was then wetted with deionized water and air channels removed by applying pressure with a large pipet bulb. The bed was converted to the nitrate form by passing 200 ml of 1 M NaNO_3 through the column at a rate of 0.2 ml/min. Residual nitrate was removed by passing 200 ml of deionized water. Bound nitrate was then removed and measured by passing 100 ml of 2 M NaCl through the column, collected in a 100-ml volumetric flask, and the eluted nitrate determined spectrophotometrically at 220 nm.

Resin Functionalization

For all of the anion-exchange materials in this study, functionalization began with a chloromethylated resin supplied by Rohm and Haas Co. The majority of this work used a chloromethylated XE-505 resin.

Approximately 1 g of chloromethylated resin was mixed with 30 ml of methanol

in a 100-ml round-bottom flask. A five-fold excess of nucleophile (amine or phosphine) was then added to the mixture and the reaction was allowed to proceed at room temperature for 7 days. Stirring was applied for only 30 min. each day as continual stirring for the entire period resulted in severe fragmentation of the resin beads. A reaction period of 7 days at room temperature, as in reference (26), was adopted to ensure complete reaction without the possibility of decomposing ion-exchange sites inherent with high reaction temperatures. On completion of the reaction period, the resin was filtered and washed 3 times with methanol, then water and acetone and, finally, air dried.

Phosphine Synthesis

The procedure for the synthesis of tripropyl and tripentylphosphine was adapted from work by Maier *et al.* (27a) and Kaesz and Stone (27b). Under a nitrogen atmosphere, 1.04 moles of propyl (128 g) or pentyl bromide (157 g) was added in 5 ml increments to 1.04 moles of magnesium turnings (25.4 g) in 1 L of THF solvent. Initiation of the Grignard reaction was aided by heating the reaction flask and crushing the magnesium turnings to expose fresh magnesium surface. Following the complete addition of the alkyl bromide, the THF mixture was refluxed for 20 minutes, cooled to -78°C and 23 ml of phosphorous trichloride (0.26 moles), diluted with 350 ml of pentane, was added drop-wise over a period of 2 h. The mixture, quite heavy with solids, was then allowed to warm to room temperature and heated to reflux for 1 h. Ammonium chloride and 40 mg of

hydroquinone (0.1 mole %), an oxidation inhibitor, were added and the solution was allowed to cool overnight. The solids were then filtered and washed with THF, the THF washings combined, and the solution concentrated by distillation on which more solids precipitated. Approximately 100 ml of ether was then added and the solids were filtered, washed and the filtrates combined. The ether was removed by distillation and the trialkylphosphine product distilled under 8 torr at 78-82^o C. The yield for the preparation of tripropylphosphine was 52%.

Nitrate Removal

The procedure for determining the ability of a resin to remove nitrate from drinking water was done in as direct a manner as possible. Tap water was placed in a plastic 55 gallon reservoir and sodium nitrate added to give a level of about 90 ppm NO₃⁻. The contaminated tap water was pumped, via a peristaltic pump, through a small column containing the anion-exchange resin. The bed dimensions were approximately 2.6 x 0.54 cm with a bed volume of 0.6 ml. Prior to the experiment, all resins were placed entirely in the chloride form by shaking, overnight, with several changes of 2 M NaCl. The column effluent was passed through a uv-vis detector and then to a fraction collector. Fractions were analyzed for chloride, nitrate and sulfate by anion chromatography and the results plotted against the number of bed volumes passed through the column. On line uv-vis detection of nitrate ($\lambda=220\text{nm}$) facilitated the selection of fractions for

chromatographic analysis and indicated the complete exhaustion of a resin.

Ion Chromatography

Anion determinations for all curves and selectivity coefficients in this study were done by single column anion chromatography. The system consisted of the following components: an Eldex model AA-94 dual channel pump, a Li-Chroma-Damp III pulse dampener, a Hitachi model 655A-40 autosampler, a Wescan model 269-029 anion-exchange column and model 213A conductivity detector and a Hitachi D-2000 integrator. The eluent used for most anions was 2.0 mM potassium acid phthalate at a pH of 6.5. For the determinations of fluoride and acetate, a 3 mM sodium benzoate eluent was used.

Selectivity Coefficients

Selectivity coefficients were measured by a batch method similar to that used by Clifford and Weber (5). A given resin was first converted to the nitrate form. This consisted of passing 200 ml of a 2 M solution of NaNO_3 through a column of 0.5 g of resin at 0.2 ml/min. The resin was then placed in a 50-ml plastic bottle and shaken overnight with several changes of the same salt solution. Such an elaborate procedure was found to be necessary for 100% conversion of a resin into the nitrate form. The resin was washed with deionized water followed by acetone then vacuum dried at room temperature and stored in a desiccator. Batch equilibrations were done by placing 150 mg of the resin in 100-ml plastic bottles, adding 50mL of a 5 mM sulfate solution and shaking for 3 days. The supernatant solutions were

removed and filtered with 0.2 μm filters. As recommended by Bagchi and Haddad (28), the filters were first conditioned with 20 ml of supernatant before collection of a sample. Determinations of anions in the equilibrated solutions were done by ion chromatography.

The selectivity coefficients for the chloride systems were calculated in slightly different manner. About 10 grams of resin was converted to the chloride form by shaking overnight with 2 M sodium chloride. The resins were then washed and shaken overnight with deionized water. The solution anions were equilibrated and determined in the same manner as for the nitrate system above. After equilibration, the total anion equivalents in solution were consistently higher than the amount of anion equivalents added. It was later discovered that this extra anion concentration was due to residual sodium chloride incompletely washed from the resin matrix. A sample of each resin was then shaken with 50 ml of deionized water for three days and the average amounts of sodium chloride in the matrix calculated. This extra chloride ion was taken into consideration in the selectivity coefficient calculations.

Regeneration Studies

Regeneration efficiency was evaluated by passing a 1 or 2 M solution of sodium chloride through a column of the resin. A peristaltic pump was used to pump the regenerant at a rate of 0.2 ml/min and fractions of the spent regenerant were collected with a fraction collector. The fractions were then diluted 1:10 and their nitrate and sulfate concentrations determined by anion chromatography.

Mixed-bed

The efficacy of water softening and nitrate removal with a single mixed-bed of resins was evaluated. The apparatus used is shown in Figure 1. A 110-gallon stainless-steel tank served as the sample water reservoir. The tank was filled with tap water and spiked to 90 ppm NO_3^- , 250 ppm $\text{SO}_4^{=}$ and 350 ppm Ca^{+2} . The bed consisted of 39 ml (3 inches) of the anion-exchanger and 52 ml (4 inches) of Dowex 50 cation-exchange resin. A homogeneous mix of the resins was obtained by wetting the bed, mixing vigorously by inverting several times followed immediately by a fast flow of distilled water. Mixed in this way, the usual settling and stratification of the bed was avoided, allowing the resin to be "frozen" as randomly as possible. Influent and regenerate solution was applied by separate peristaltic pumps (Masterflex model 7520-35). The pumps were connected to a Dayton 24 h timer and control of the pumps was such that the influent pump was off while the regenerant pump was on and vice versa. The outlet of each pump was connected to the column inlet by a T-connector. Monitoring of the breakthrough was done by on line detection of calcium by a calcium ion selective electrode and nitrate by uv-vis detection at 220 nm. The calcium detector was an Orion model 93-20 electrode and a Corning model 12 pH/millivolt meter. Nitrate was detected by uv-vis absorption with a Tracor model 980 detector fitted with a 4-mm-diameter quartz tube as a flow cell. The output from each detector was connected to a Fisher series 5000 dual-pen strip-

chart recorder. Electronic smoothing of the outputs was done by an R-C filter with a time constant of 10 seconds. The detectors were protected from high concentrations of brine solution by employing a 3-way solenoid valve between the column and detector bank. A second timer was used to switch the column effluent to waste during, and for 1 h following, regeneration to ensure that all brine was flushed from the system prior to switching the detectors on line. The strip-chart recorder was connected to the same circuit as the influent pump so that recording of breakthrough volumes would start at the beginning of each cycle. Such an elaborate system enabled the unattended automation of data collection and high reproducibility of column recycling over a long period of time.

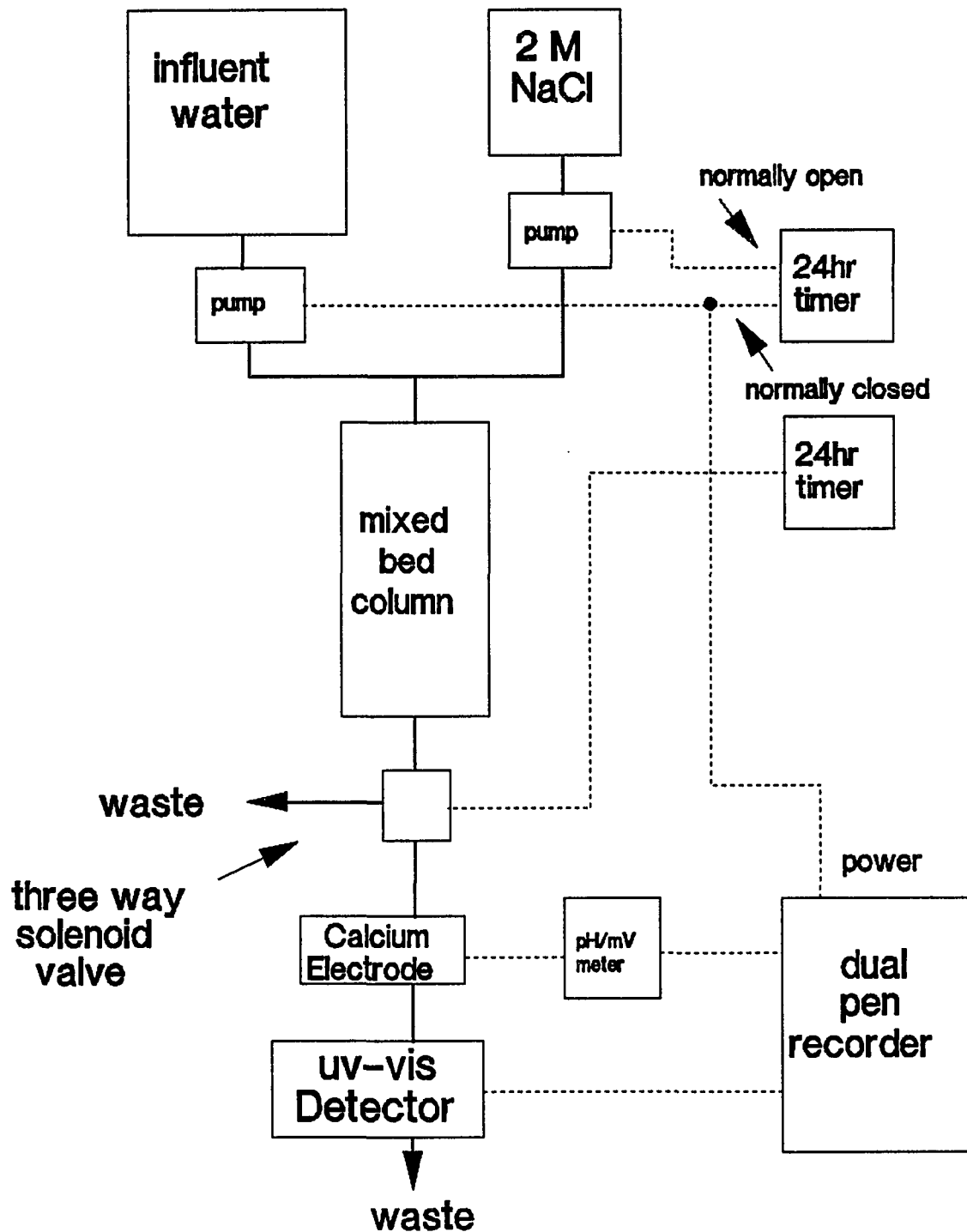


Figure 1. Schematic diagram of the mixed bed apparatus.

RESULTS AND DISCUSSION

Resin Functionalization

The basis of this work is the synthesis of an anion exchange resin with high exchange capacity and high selectivity for nitrate ion. This section primarily deals with reaction conditions which will optimize the capacity of such a resin.

In this study, the functionalization of a chloromethylated resin involves the reaction of a bound electrophile with a neutral nucleophile (tertiary amine or phosphine) and is shown in Figure 2a. Considerations similar to those used for solution chemistry involving nucleophilic reactions with a neutral nucleophile were also applied to resin functionalization. The yield of a nucleophilic reaction can be increased by the stabilization of the transition state and the destabilization of reactants (29). In the case of resin functionalization, the reactants are neutral and the transition state involves a large degree of charge separation. Selection of a highly polar solvent would therefore decrease solvation of the reactants and increase their potential energy. Fortunately, the polar transition state would be well solvated by a polar solvent and thereby show a decrease in potential energy. Hence, the overall result of using a polar solvent is to decrease the activation barrier resulting in increased capacity.

For this work, methanol was the solvent of choice. Although water is more

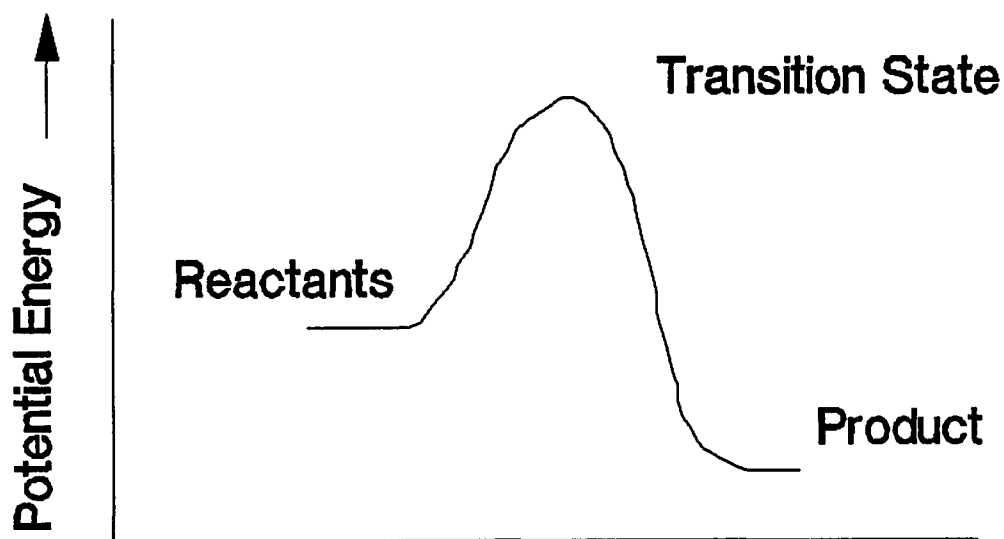
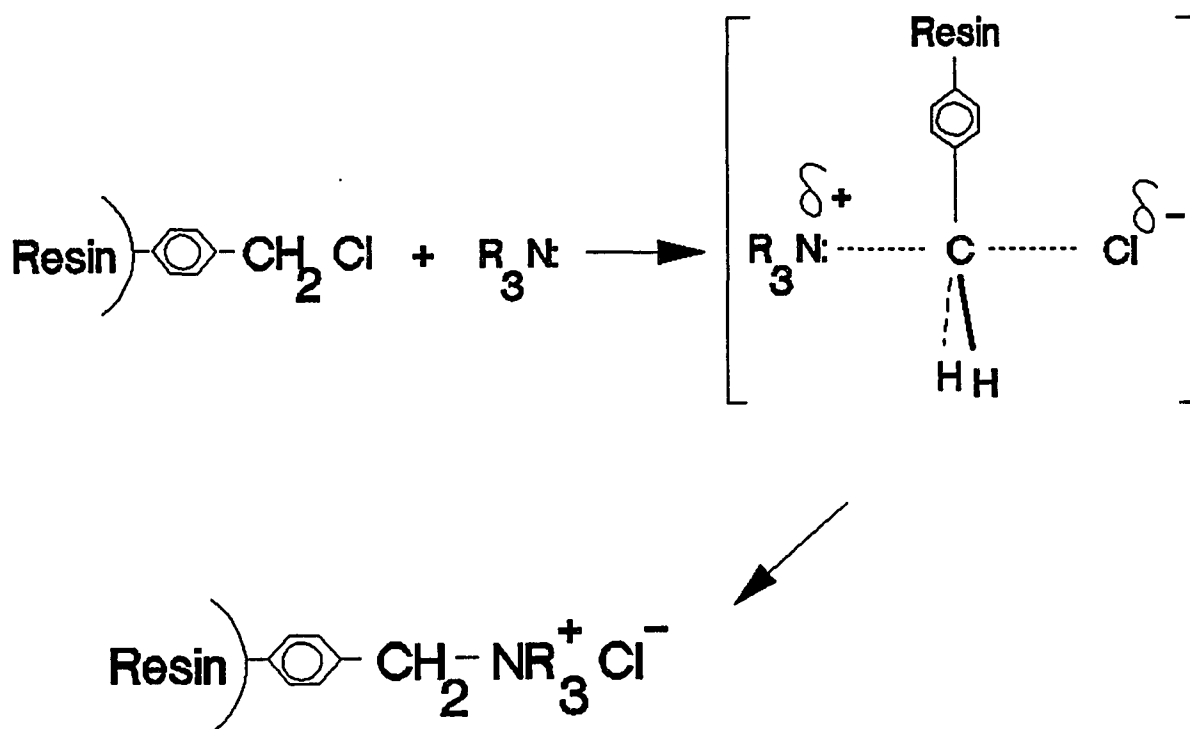


Figure 2a. Functionalization of a chloromethylated resin with a trialkylamine.

polar, it does not wet the PS-DVB matrix adequately and so may restrict access to part of the resin surface. A non-polar solvent, dichloromethane, was evaluated. This solvent would serve to increase the activation barrier and, as expected, was found to significantly reduce the yield of the functionalization procedure.

Another approach to increasing capacity is to improve the strength or nucleophilicity of the attacking group. Charged or highly polarizable nucleophiles are generally more reactive than neutral, tertiary amines. The higher polarizability and larger size of a tertiary phosphine enabled the preparation of anion exchangers with higher capacity while retaining high nitrate selectivity.

Selectivity Coefficients

Table I is a compilation of selectivity coefficients and capacities for the homologous series of quaternary ammonium and phosphonium resins. Comparison of the tripropyl and tributyl analogs in each series demonstrates a 5 to 6-fold increase in selectivity coefficient (K_S^N) for the phosphonium resin. This increase in selectivity is also concurrent with a 27% increase in capacity.

Within each series, as the number of carbons on the exchange site is increased, selectivity for nitrate is also increased. Figure 2b is a graphical demonstration of the trends shown in Table I. The tributyl and tripropylphosphonium resins are particularly phenomenal with K_S^N as high as 840,000. This trend in selectivity appears to be due to steric hindrance about the anion exchange site. While increased bulk in the exchange site is advantageous for high nitrate selectivity, a

Table I. Selectivity coefficients for quaternary ammonium and phosphonium exchangers on XE-505 resin matrix

<u>Resin</u>	<u>Selectivity Coefficient^a</u>	<u>Capacity^b</u>
Trimethylamine	600	3.61
Triethylamine	9,000	2.39
Tripropylamine	26,700	1.52
Tributylamine	102,000	1.23
Trimethylphosphine	2,000	2.22
Triethylphosphine	19,500	2.71
Tripropylphosphine	120,000	1.99
Tributylphosphine	660,000	1.68
Tripentylphosphine	840,000	1.27

^a K_S^N from units of mM/g and mM/mL.

^bmEq/g.

Selectivity Coefficients vs. Number of Carbons

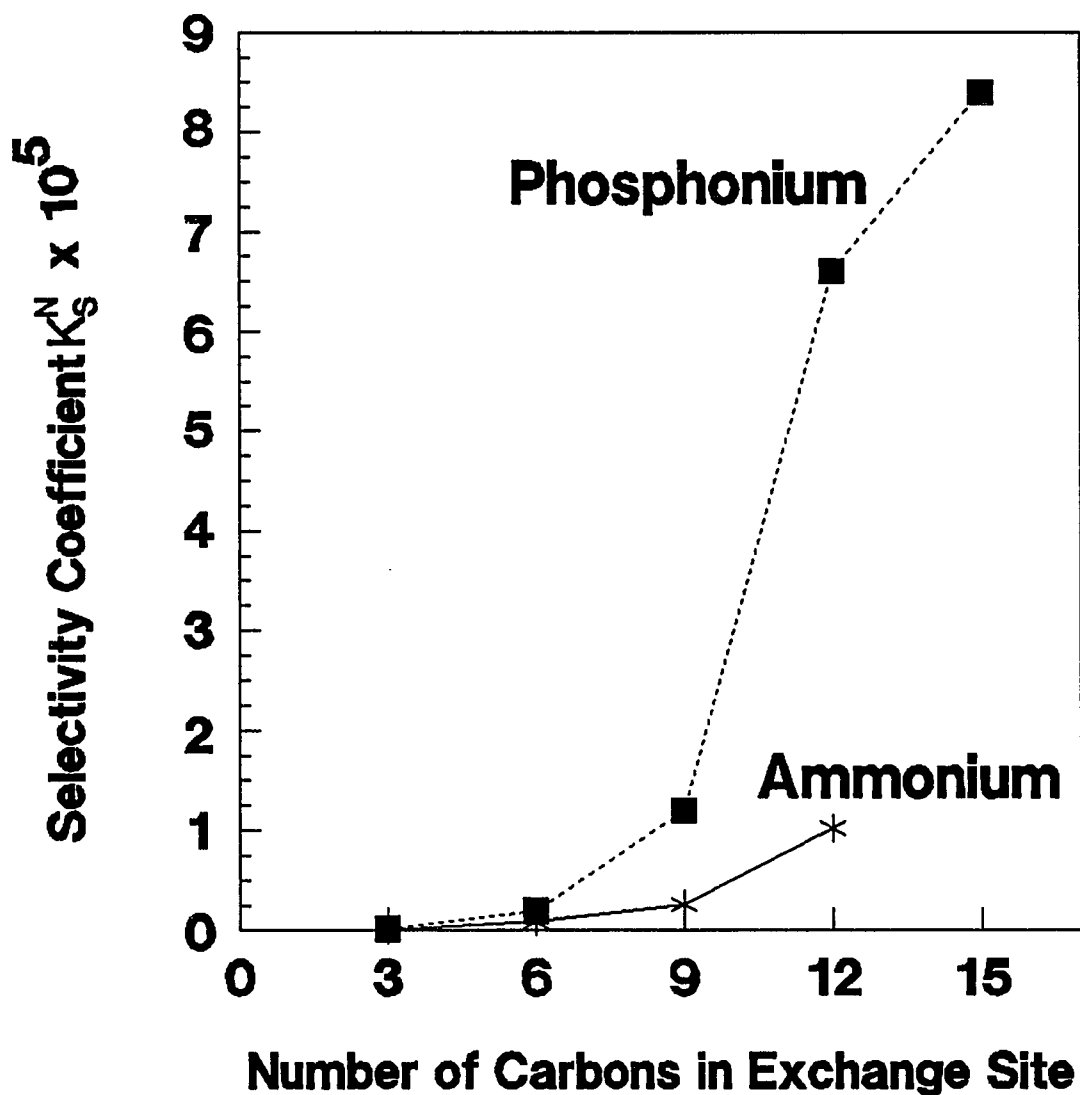


Figure 2b. Plot of selectivity coefficients vs. number of carbons in exchanger group.

trend of decreasing capacity is also clearly demonstrated.

The fact that capacity decreases for larger, more hindered exchange sites is due to steric hindrance during the functionalization process. For covalent attachment to occur, the nucleophilic center must approach the electrophilic carbon of the chloromethylated resin. As the length of R increases, it physically restricts the approach of the nucleophile and so decreases the yield (or capacity) of the functionalization step. The reactivity of a nucleophile depends on a number of factors but in this case a balance between steric factors and nucleophilicity of the amine center appears to be prevalent.

The trends in selectivity coefficients make clear the need for large R groups in the ion exchange sites. This requirement, however, is directly contradictory to increasing the yield of the functionalization process. One possible solution to this problem is to separate the two steps. The synthesis a molecule in which the nucleophile is unhindered and separated from a pre-formed, hindered ion exchange site is one approach. This molecule could then be used to functionalize a resin in high yield while retaining high selectivity. All attempts at the preparation of such a dynamic molecule were, however, unsuccessful.

A second approach, which was used in this study, was to change the identity of the attacking group from tertiary amine to tertiary phosphine. In contrast to the amines, phosphines are more polarizable nucleophiles making them better able to compensate for the build up of electron density in the transition state. The net

effect is a lowering of the transition state potential energy which translates into better nucleophilicity. As can be seen in Table I, the result of this improved nucleophilicity is the ability to retain increased bulk about the anion exchange site while increasing capacity.

While the effect of large R groups on nitrate selectivity is clearly demonstrated, a fundamental explanation for this phenomenon is not certain. The effects of fixed exchange site separation, as proposed by Clifford and Weber (5) were considered. It seems logical to envision a larger steric requirement for placement of the bulky exchange sites. This need for space would tend to spread out exchange sites, possibly resulting in nearest neighbors too far away for a divalent ion, such as sulfate, to occupy two sites at once. In this case, electroselectivity rules (30) may become less important and sulfate selectivity might then fall under the accepted mechanism for monovalent ions (31). In that event, the high degree of hydration on sulfate would cause it to be preferred far less than nitrate and chloride ions. The result of this type of binding mechanism would be a 1:1 molar exchange ratio for sulfate and nitrate ions (i.e., one divalent sulfate ion would exchange for one monovalent nitrate ion).

Table II presents some contrary evidence to the notion of sulfate binding to a single ion exchange site. In each coefficient measurement, the initial solution concentration was 5 mM (10 mN) of sulfate ion. Depending on the mechanism of the exchange process, total solution ions after equilibration will be either 5 mM or

Table II. Solution equivalents following batch equilibrations for quaternaryammonium and phosphonium exchangers on XE-505 resin matrix

<u>Resin</u>	<u>Solution Normalities</u>	<u>Solution Molarities</u>	<u>Selectivity Coefficient^a</u>
Trimethylamine	10.2	6.20	600
Triethylamine	10.1	4.06	9,000
Tripropylamine	10.0	3.72	26,700
Tributylamine	10.1	3.02	102,000
Trimethylphosphine	7.46	2.09	2,000
Triethylphosphine	10.1	3.49	19,500
Tripropylphosphine	10.0	3.10	120,000
Tributylphosphine	10.1	2.93	660,000
Tripenylphosphine	9.88	2.98	840,000

^a K_S^N from units of mM/g and mM/mL.

10 mN. Given the above theory, unhindered exchangers (low K_S^N) will exchange on a 1:1 equivalent basis (i.e., 1 sulfate ion exchanges for 2 nitrate ions) yielding a 10 mN solution after equilibration. Hindered exchanger sites (high K_S^N), on the other hand, would exchange on a 1:1 molar ratio (i.e., 1 sulfate ion exchanges for 1 nitrate ion). This would predict a correlation with solution molarities. More simply stated; initial concentration was 5 mM and so the final, equilibrated solution concentration should be 5 mM. What was found in every case, however, was a solution concentration of 10 mN after equilibration and in no case did solution concentrations add up to 5 mM. This implies that no matter what the size of the R group in the exchange site, sulfate always occupies two sites.

While exchange sites may be farther apart in the more hindered exchangers, sulfate ion is still able to bind two exchange sites simultaneously. The question may then be one of electrostatic bond strength. As the sulfate-resin bonds must become longer due to steric hindrance, the sacrifice may be in the strength of those bonds resulting in a decrease in sulfate affinity. This would explain the large increase in K_S^N as well as the 2:1 nitrate to sulfate exchange ratio.

Table III presents some evidence for the contribution of decreasing sulfate affinity to K_S^N . Selectivity coefficients of several anions for the trimethylammonium and the tributylphosphonium resins were determined against chloride ion. The table shows a 9-fold decrease in the coefficient for sulfate, and a 6-fold decrease for thiosulfate, for the phosphonium resin. Such a decrease in the selectivity for

Table III. Selectivity coefficients of trimethylammonium and tributylphosphonium on XE-505 resin for various anions vs. chloride

Anion	K_{Cl}^i		
	Me ₃ N resin	Bu ₃ P resin	Dowex1-8x resin
Fluoride	0.047	0.019	-
Acetate	0.08	0.63	-
Bromide	4.57	19.5	-
Nitrate	4.8	19.1	4.25
Thiosulfate	0.22	0.038	-
Sulfate	0.029	0.0033	0.26

divalent ions is expected if the distance between exchange sites is a valid consideration. Of the monovalent anions tested, only fluoride showed a decrease in the coefficient, while acetate, bromide and nitrate all demonstrated increases in selectivity coefficient for the phosphonium resin.

Some concern is felt over the selectivity coefficients for sulfate in Tables II and III. It is well known, in the realm of ion chromatography, that sulfate is retained much more strongly than nitrate or chloride. In spite of this, K_{Cl}^S and K_N^S , for all resins, are below 1. This indicates that sulfate is the least preferred ion in every case. Some consolation is found in a study by Boari *et al.* (30), where K_{Cl}^S for various resins were reported in the range of 0.017 to 1.13. Furthermore, separation factors in ion chromatography are heavily influenced by the choice of eluent. Monovalent eluents tend to elute monovalent anions most efficiently. The use of a divalent or trivalent eluent will often show reversals of retention behavior. Since the most common eluents in ion chromatography are monovalent (i.e., hydroxide, salicylate, bicarbonate, phthalate at low pH), comparison of batch selectivity coefficients to ion chromatographic retention data may not be valid.

Table III also includes selectivity coefficients for Dowex1-8x resin as a control. Note that the coefficient for nitrate did not differ from the Me_3N resin, but that the coefficient for sulfate increased by a factor of 10. Since the Dowex resin is also

functionalized with trimethylamine, this behavior is believed to be due to a difference in crosslinking. The study by Clifford and Weber (5) explained these effects in terms of site proximity. According to that study, increased rigidity in a resin, due to higher crosslinking, restricts the exchange sites from conforming to the bonding requirements of a divalent ion. The result of this hindrance is expressed in the selectivity coefficient.

The present work does not prove or disprove the significance of site proximity on the selectivity of a resin. A more definitive study would be to spectroscopically examine the exchange sites with a fluorescent probe, similar to the work of Lochmuller *et al.* (32). When pyrene molecules are within 2-8 angstroms from each other, a characteristic emission band due to the formation of excited state dimers is observed. When pyrene molecules are separated by more than 8 angstroms, only emission due to the monomers is observed. In the above study by Lochmuller *et al.*, pyrene was covalently bound to the surface of silica gel. By observing the ratios of monomer to dimer emissions, the intermolecular distances of species bound to the silica surface were inferred.

A similar study could be applied to the anion exchange sites of a resin. Pyrene can be easily converted to its sulfonate anion (33) and electrostatically bound to the

exchange sites of a resin. The analysis of the fluorescent spectrum of a resin, charged into the pyrene sulfonate form, might then demonstrate the distribution of anion exchange sites.

Nitrate Removal

The efficiency of a resin to remove nitrate is the result of a combination of selectivity and overall exchange capacity. While a resin may have a very high capacity, a low selectivity for nitrate will cause most of that capacity to be "wasted" on the most preferred ion (usually sulfate). Hence, the overall capacity of a resin does not directly translate into nitrate capacity. Evaluation of nitrate removal for a given resin was therefore done in as direct a manner as possible

The breakthrough profile of Dowex 1-8x is shown in Figure 3. Initially, the concentrations of nitrate and sulfate are low, as those ions are exchanged for chloride on the resin. Correspondingly, the concentration of chloride in the effluent represents the total ion equivalents entering the column. In this case chloride effluent equals the sulfate plus nitrate plus influent chloride equivalents. Dowex 1-8x is an example of a resin where K_S^N is less than one. The resin prefers sulfate over nitrate and the resultant curve demonstrates a concentration effect where nitrate levels rise well above the influent nitrate concentration.

The reason for this phenomena is illustrated in Figure 4. During exhaustion of

Dowex 1-8x

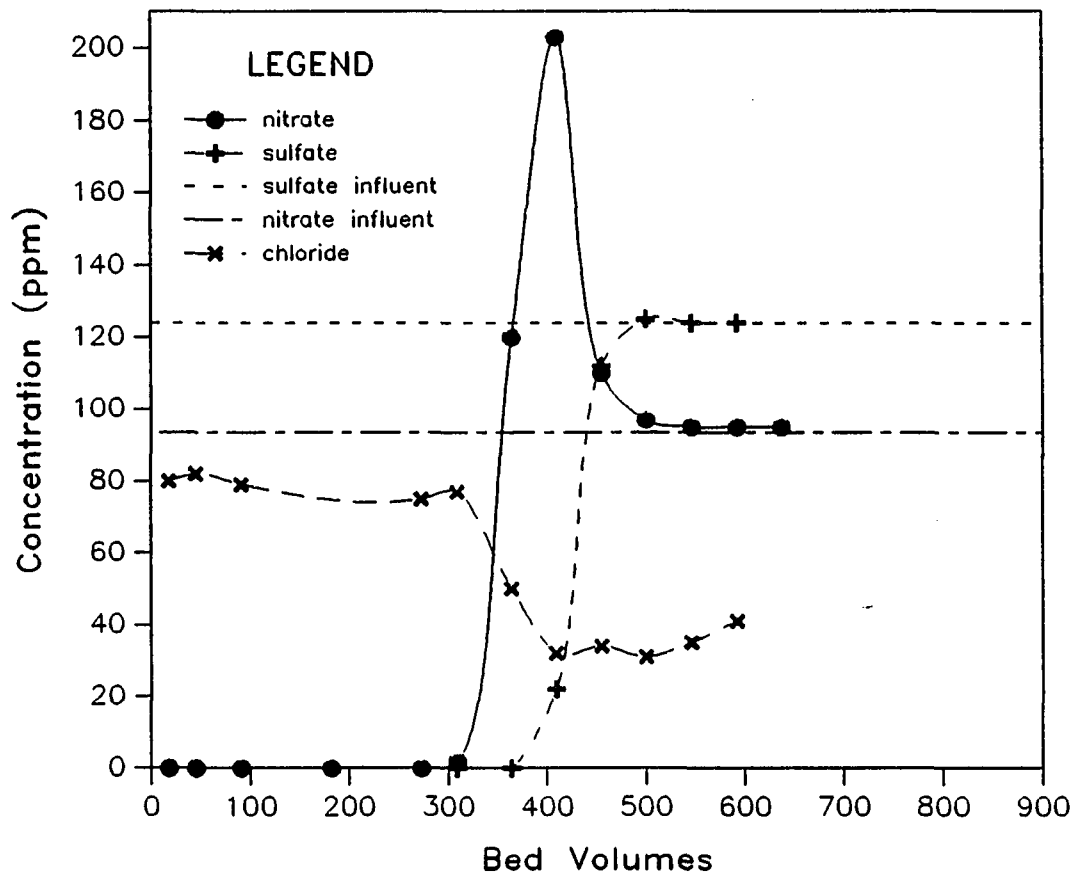


Figure 3. Breakthrough profile for Dowex 1-8X resin, 200-400 mesh. Bed volume, 0.8 ml; flow rate, 1.7 ml/min.

Dowex 1 (figure 4a), sulfate and nitrate exchange with chloride. Since the resin greatly prefers sulfate, it is the first anion to exchange. Influent nitrate passes by the bound sulfate and exchanges for chloride further down the column. As new sulfate enters the column, it pushes off bound nitrate, which in turn pushes off bound chloride. This chain of events continues until the chloride form of the resin is exhausted.

Figure 4b is the composition of the column just prior to nitrate breakthrough. All chloride form of the resin has been exhausted and so influent nitrate, finding no available sites to exchange with, must exit the column. Additionally, influent sulfate continues to exchange for sites occupied by nitrate at the top of the nitrate band. The nitrate concentration exiting the column consists of influent nitrate plus a concentration equivalent to the influent sulfate. Hence, at the end of a run, the level of nitrate in the effluent rises well above the influent nitrate concentration. Once the nitrate form of the resin is exhausted, the sulfate and nitrate effluent levels will equal the influent levels.

Figure 5 shows the breakthrough profile for a resin where K_S^N is relatively small but above unity. In this case, the resin only slightly prefers nitrate and so both sulfate and nitrate exhaust the column on an equal basis. Sulfate breaks through first but is closely followed by the nitrate breakthrough and no concentration effect is observed.

The trimethyl, triethyl and tributylammonium resins in Figures 5, 6 and 7

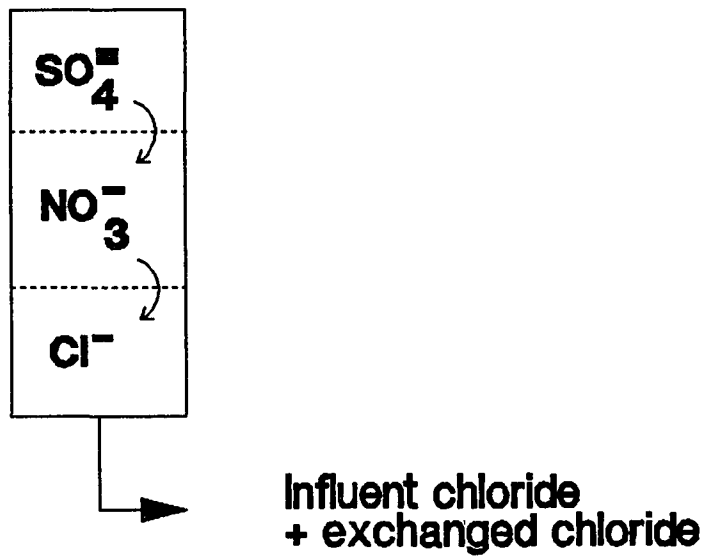


Figure 4a. Bed composition of Dowex 1-8x during exhaustion.

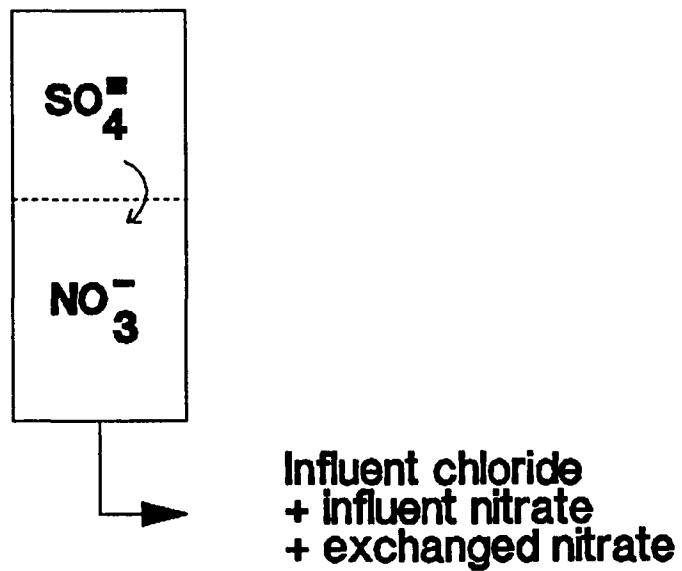


Figure 4b. Bed composition of Dowex 1-8x during nitrate breakthrough.

Trimethylammonium-505 Resin

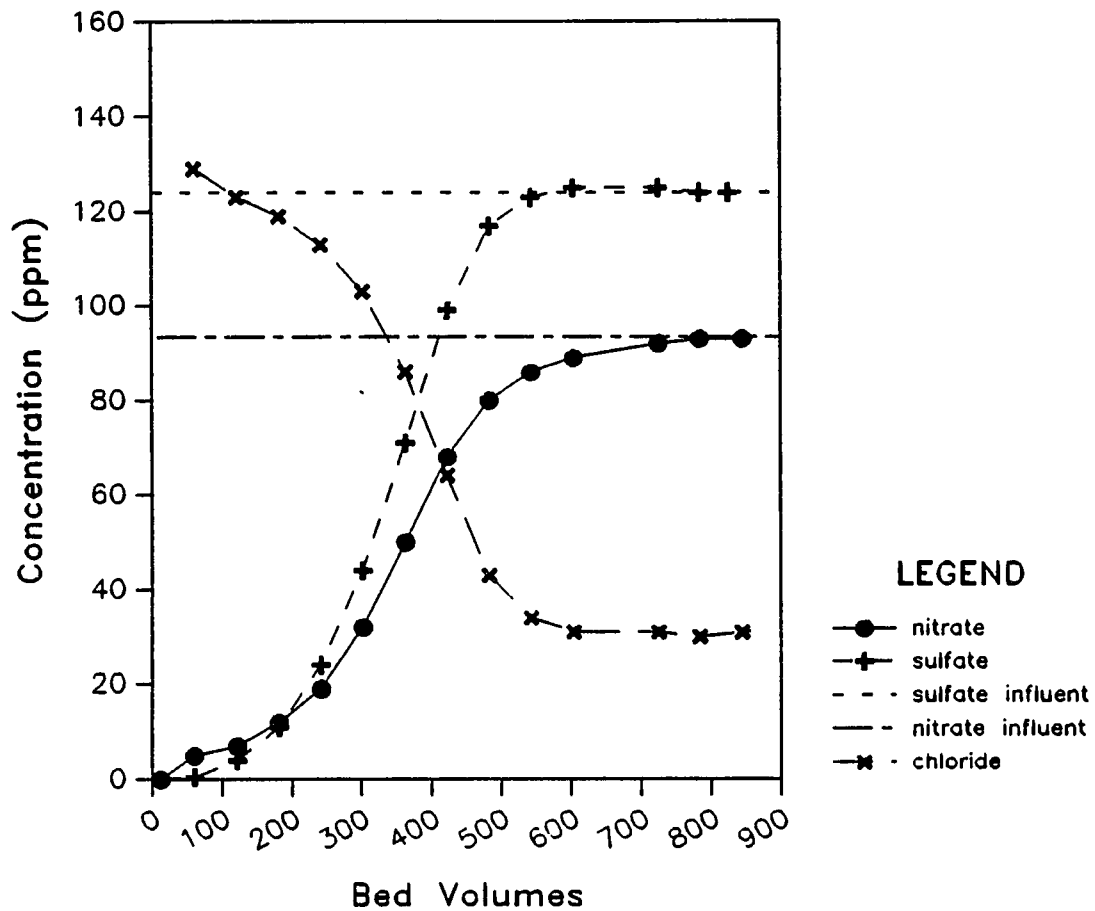


Figure 5. Breakthrough profile for trimethylammonium group on XE-505 resin. Conditions as in Figure 2.

demonstrate a trend of higher nitrate selectivity for larger R groups in the anion-exchange site. Initial chloride concentrations in these curves tend towards lower and lower values as sulfate becomes less preferred, exchanging for less chloride ions. The increase in nitrate selectivity enables a larger portion of the resins capacity to be used for nitrate ions. Unfortunately, a concurrent decrease in overall capacity was also observed. In the case of the quaternary ammonium series, a larger decrease in capacity than could be overcome by selectivity increases resulted in lower net nitrate removal capacities.

Figures 8, 9 and 10 are the breakthrough profiles of a homologous series of phosphonium resins. In contrast to the tributylammonium curve in Figure 7, the tributylphosphonium resin (figure 8) has retained a high capacity to remove nitrate with even greater nitrate selectivity.

The resins in Figures 9 and 10 were functionalized with a crude, undistilled phosphine preparation. The trends in the sulfate curves are as expected. However, the net capacity for nitrate may be less due to impurities interfering with functionalization. The previous work on selectivity coefficients was done with resins made from distilled tripropyl- and tripropylphosphine as described in the experimental section.

Nitrate Removal from Natural Waters

The ability to remove nitrate from a naturally contaminated water sample was evaluated. Several gallons of well water were obtained from George, Iowa, a small

Triethylammonium-505 Resin

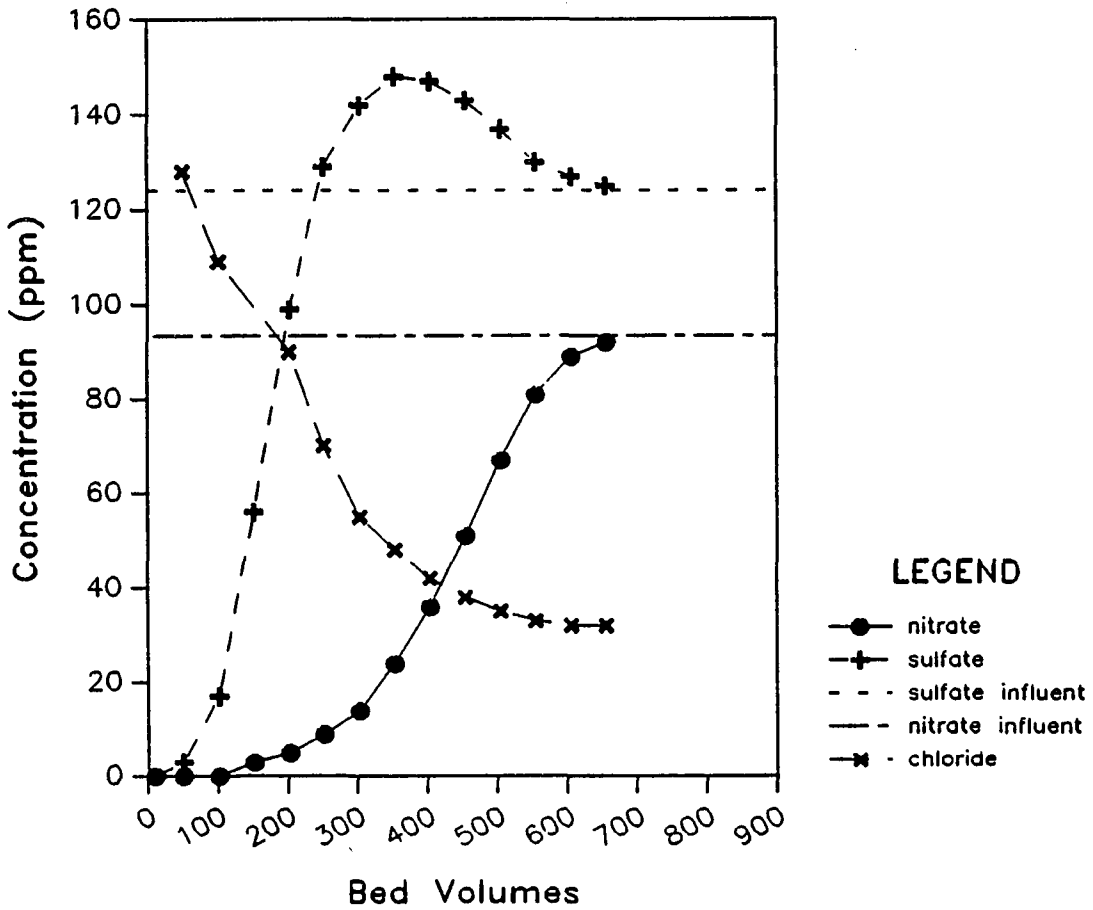


Figure 6. Breakthrough profile for triethylammonium group on XE-505 resin. Conditions as in Figure 2.

Tributylammonium-505 Resin

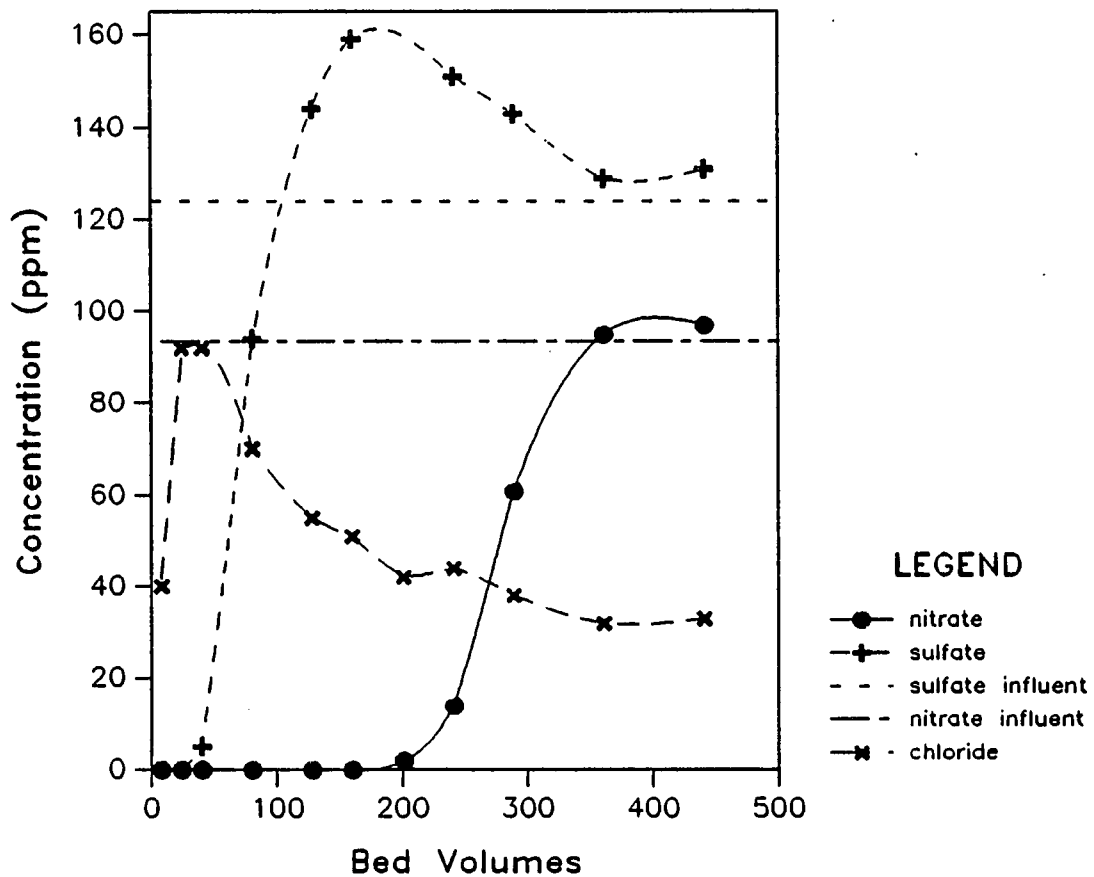


Figure 7. Breakthrough profile for tributylammonium group on XE-505 resin. Bed volume, 0.6 ml; flow rate, 0.63 ml/min.

Tributylphosphonium-505 Resin

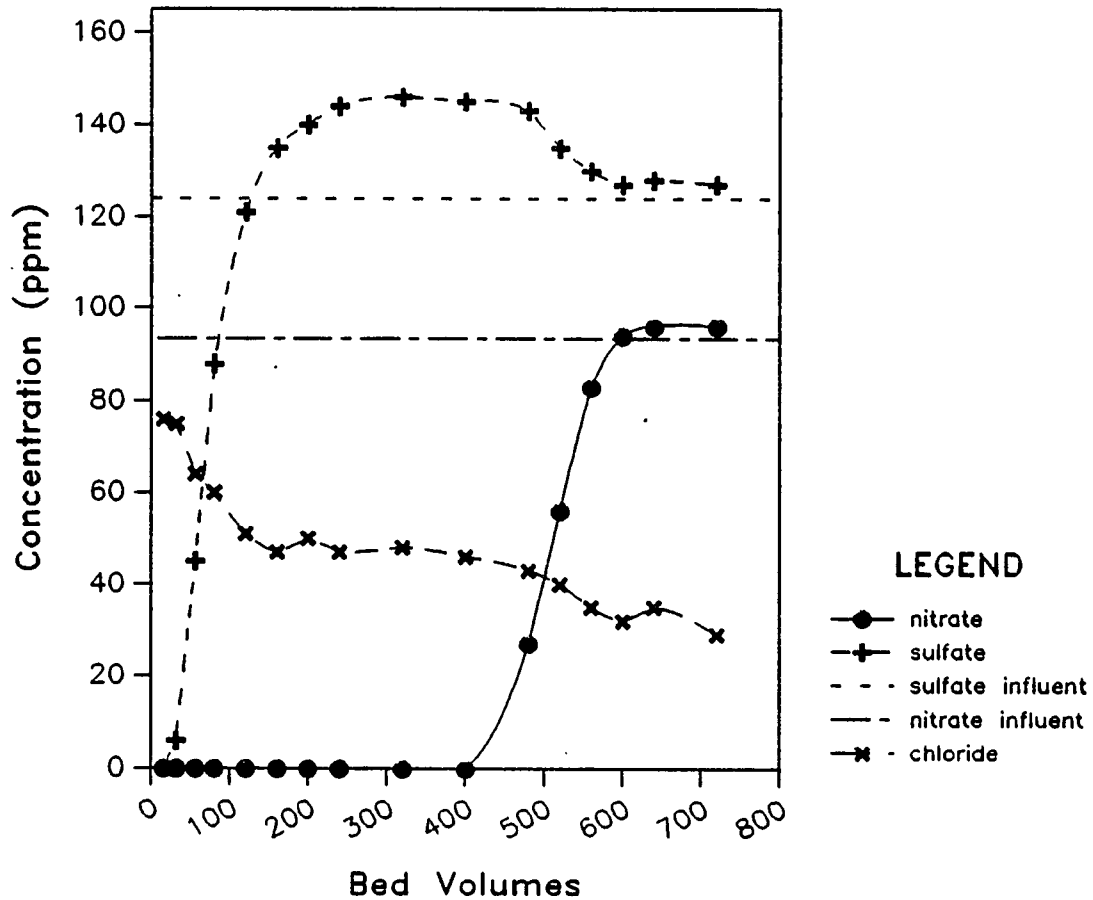


Figure 8. Breakthrough profile for tributylphosphonium group on XE-505 resin. Conditions as in Figure 6.

Tripropylphosphonium-505 Resin

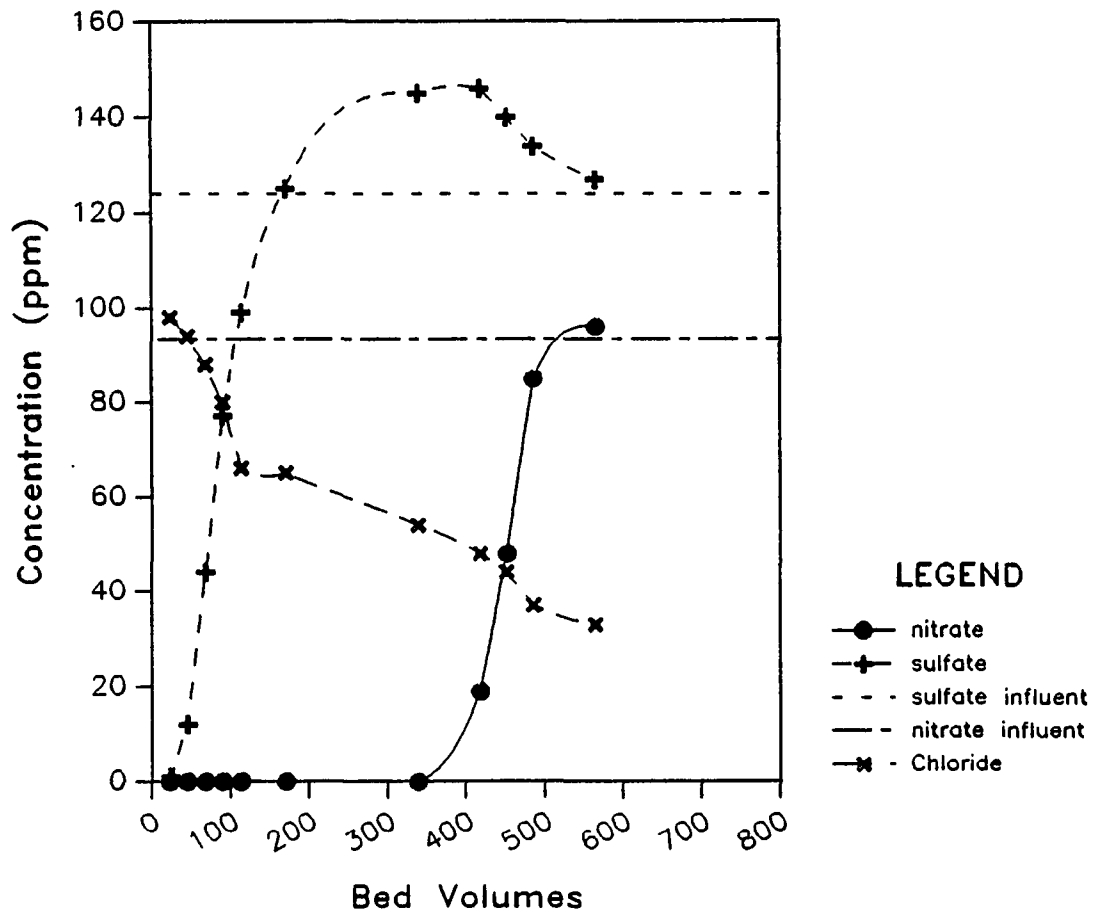


Figure 9. Breakthrough profile for tripropylphosphonium group on XE-505 resin. Conditions as in Figure 6.

Tripentylphosphonium-505 Resin

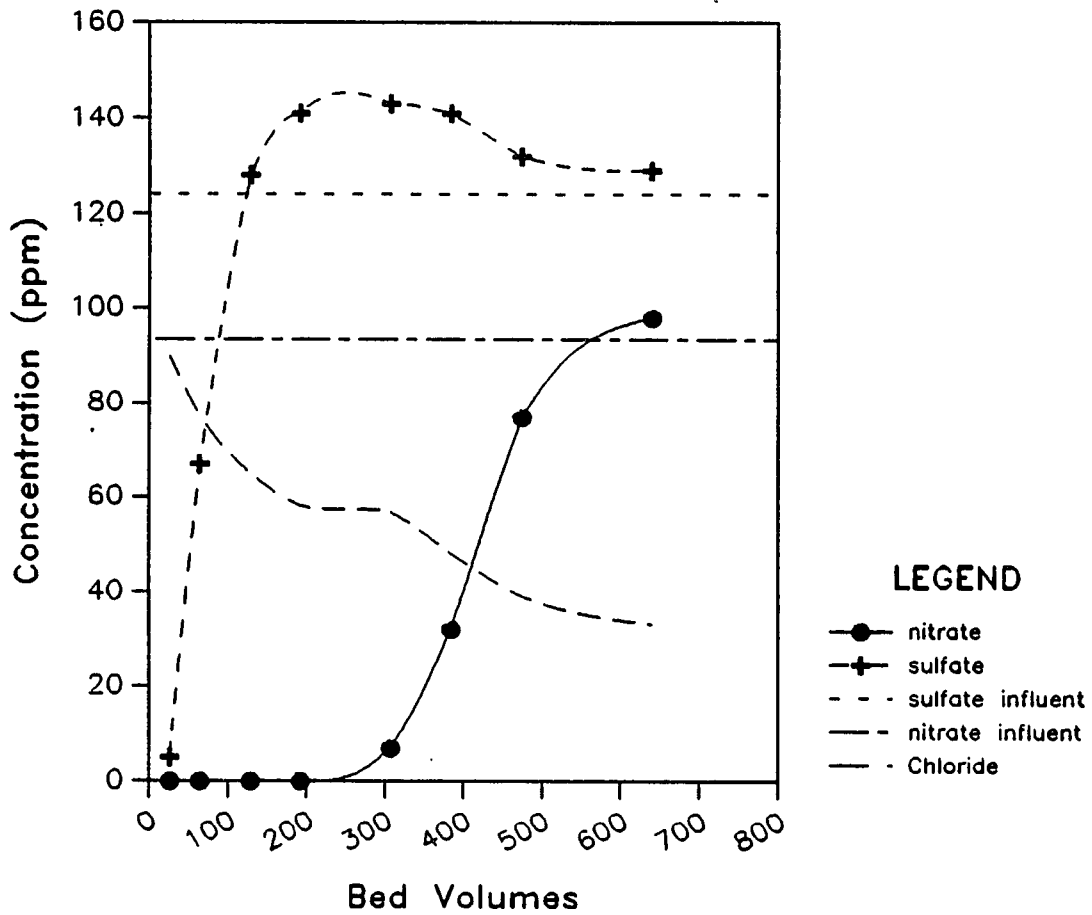


Figure 10. Breakthrough profile for tripentylphosphonium group on XE-505 resin. Conditions as in Figure 6.

town in northwest Iowa. The water supply used by George is drawn from an aquifer which extends up through North and South Dakota. This aquifer contains about 49 ppm nitrate from natural sources and so is over the EPA recommended level of 44 ppm nitrate.

Figure 11 shows the breakthrough curve for the tributylphosphonium resin. Note that very little sulfate is retained and the nitrate level rises above 45 ppm at about 1200 bed volumes. Figure 12 shows the breakthrough curve for a commercially available nitrate-selective resin, IRA 996. It has triethylammonium sites and is bound to a matrix different than that of the resin in Figure 11. Comparison of the sulfate breakthrough curves of Figures 11 and 12 indicates that the tributylphosphonium resin has much less selectivity for sulfate. The nitrate capacity of the IRA 996 resin in Figure 12 is about 700 bed volumes, much less than that of the tributylphosphonium resin.

For both of the resins in Figures 11 and 12, the K_S^N is well above unity and a concentration effect for sulfate is observed. During sulfate breakthrough, influent nitrate exchanges with the sulfate on the resin creating the observed concentration effect. By the logic presented in Figure 4, the effect on nitrate capacity by increased sulfate concentrations might be presumed to be negligible. Figures 13 and 14 are a comparison of the tributylphosphonium and IRA 996 resins when the sulfate content is increased to 260 ppm. Figure 13 shows a breakthrough almost identical to that of a water with low sulfate (figure 11). The IRA 996 resin in Figure 14

Tributylphosphonium-505; George Water

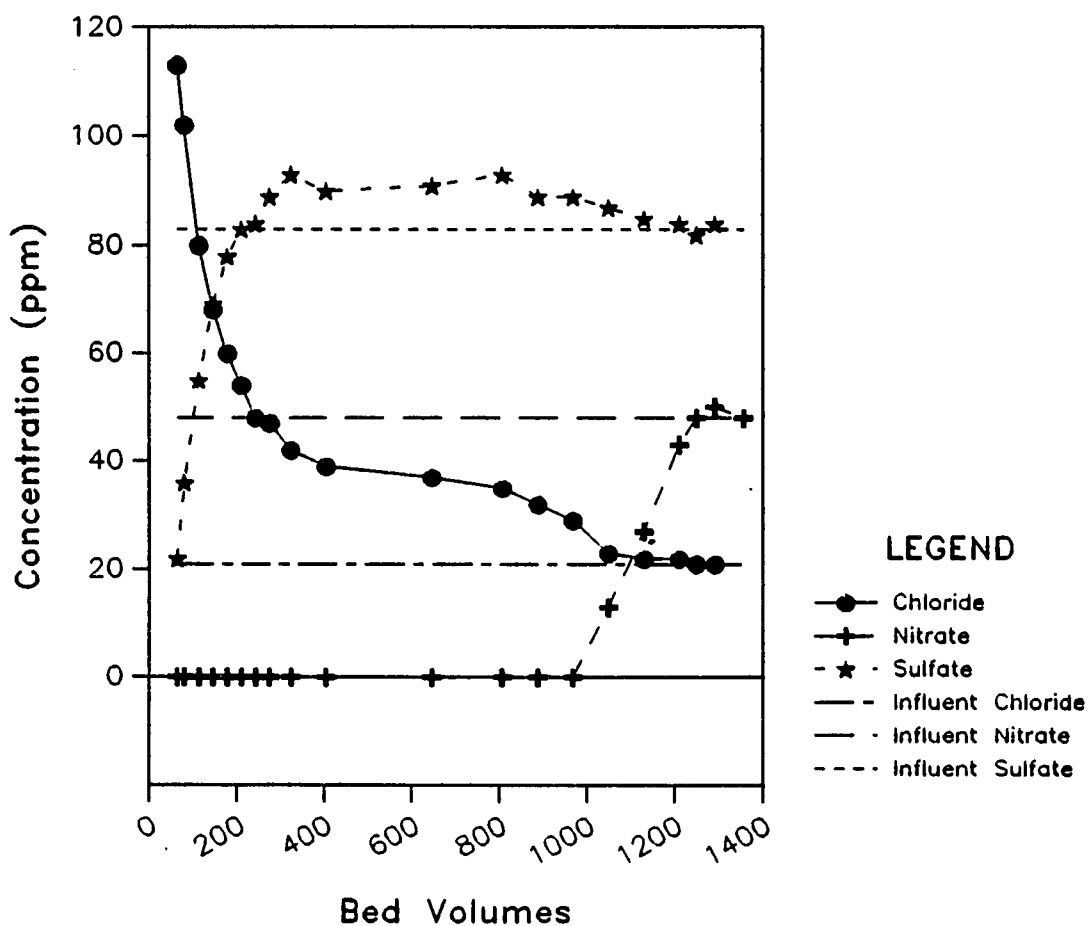


Figure 11. Decontamination profile for tributylphosphonium group on XE-505 resin for George, Iowa tap water. Bed volume, 0.5 ml; flow rate 0.5 ml/min.

IRA 996; George Water

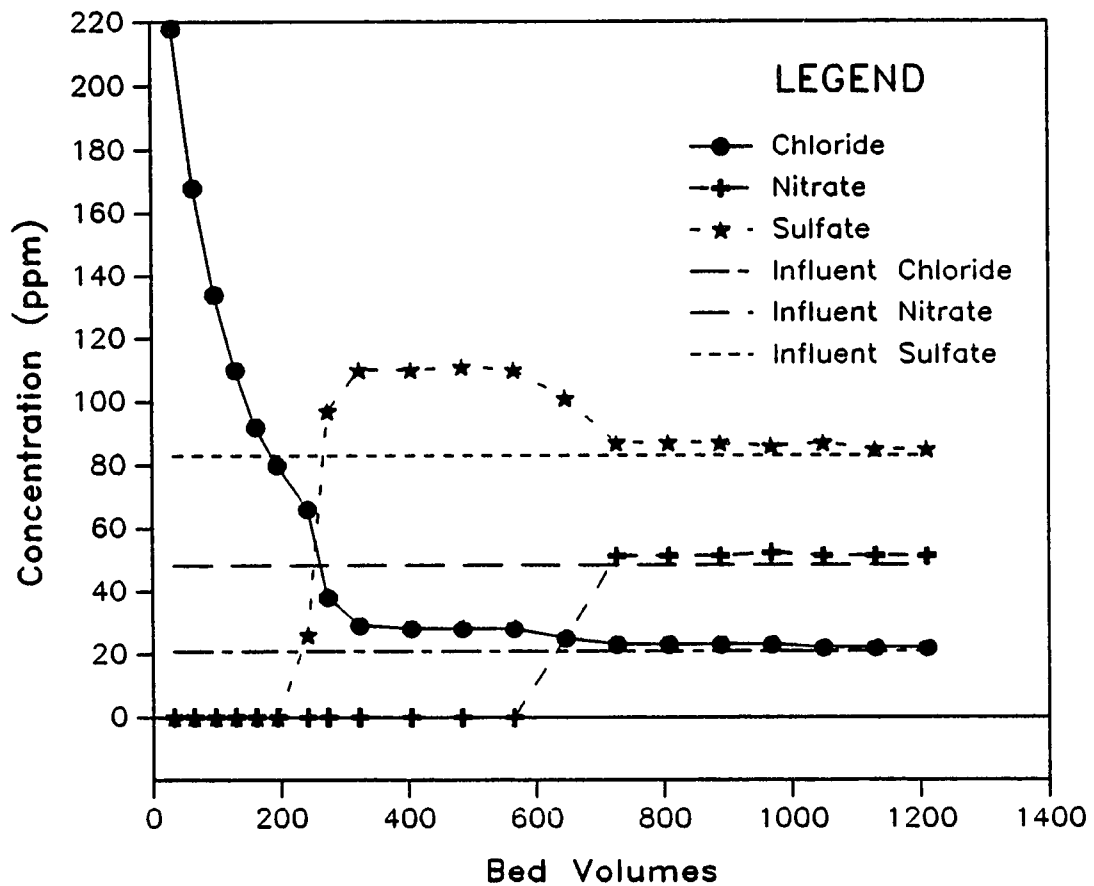


Figure 12. Decontamination profile for IRA 996 for George, Iowa tap water. Conditions as in Figure 10.

Tributylphosphonium-505; George Water + Sulfate

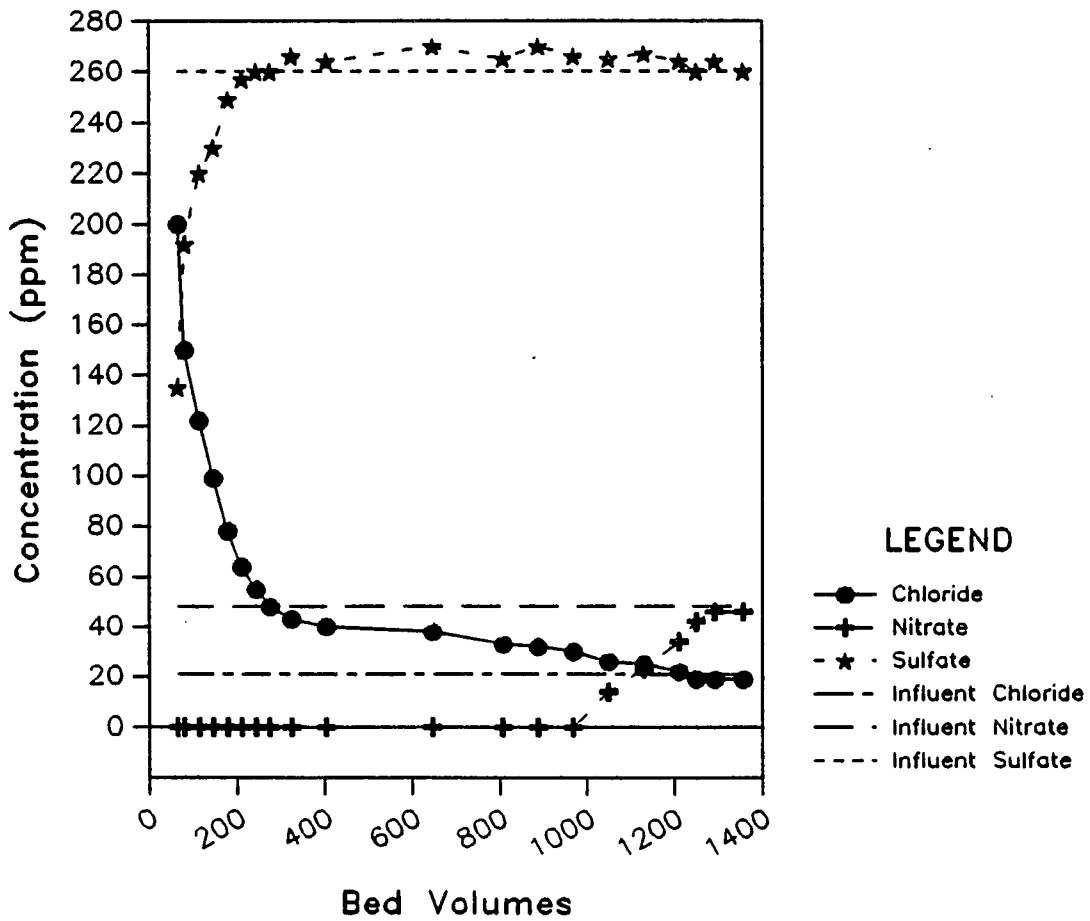


Figure 13. Decontamination profile for tributylphosphonium group on XE-505 resin for George, Iowa tap water with added sulfate. Bed volume, 0.5 ml; flow rate 0.5 ml/min.

IRA 996; George Water + Sulfate

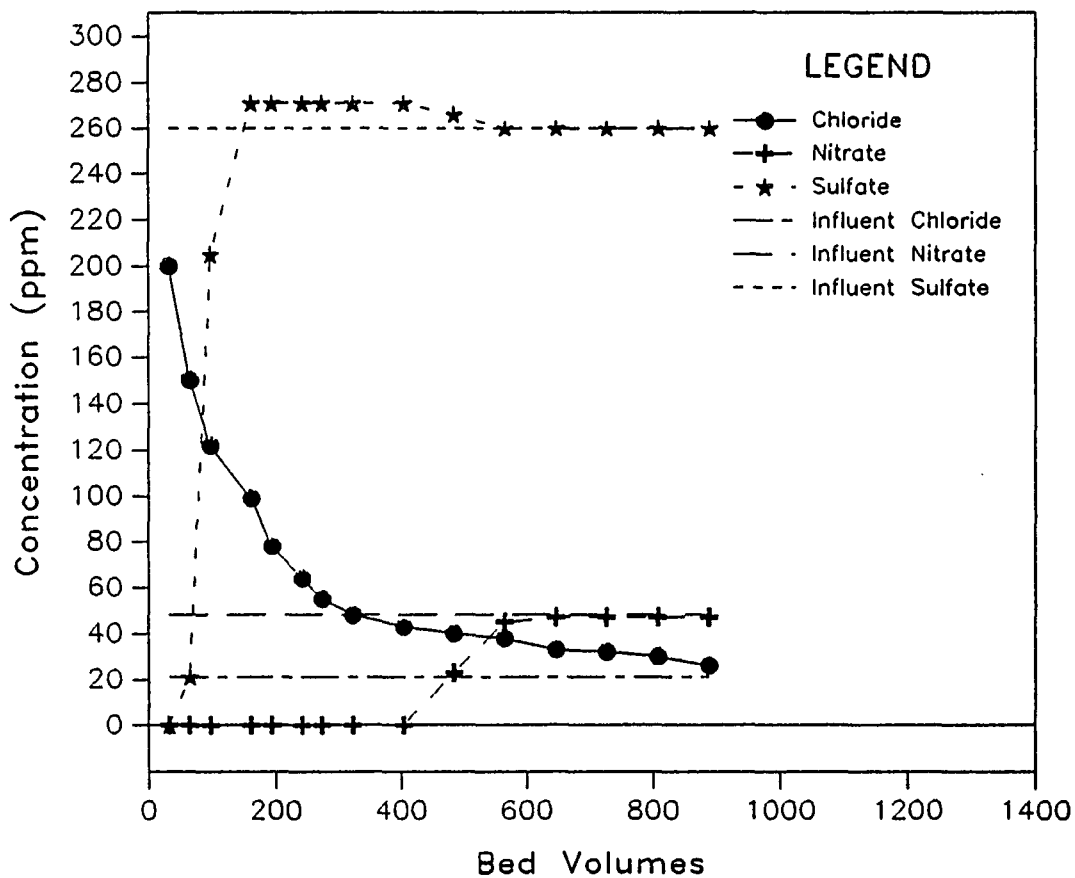


Figure 14. Decontamination profile for IRA 996 for George, Iowa tap water with added sulfate. Conditions as in Figure 12.

however, shows a decrease in nitrate capacity of nearly 200 bed volumes. It is apparent that although a resin may be nitrate-selective, it is the degree of nitrate selectivity which makes it immune to sulfate interference.

Regeneration

The above results for the George water are quite phenomenal. However, the resins used were completely in the chloride form. From a scientific basis, it is important to have a well defined starting point (such as 100% chloride form resins), however, in practice, an exchange material is never completely regenerated. The cost of regenerant and the resultant volume of waste makes such a practice highly prohibitive.

Figures 15 and 16 are a comparison of nitrate capacity for IRA 996 and tributylphosphonium resins after a partial regeneration of only 7 bed volumes. The IRA 996 resin still shows sensitivity to sulfate content but its nitrate capacity is very similar to that of the tributylphosphonium resin. The conclusion is that although the IRA 996 resin has a lower net capacity for nitrate on complete regeneration, its sites are far more efficiently regenerated with sodium chloride during partial regeneration. Hence, the same trade off is observed here as was seen by other authors (4,5,6); that is as K_S^N increases, regeneration efficiency decreases.

The regeneration profiles for nitrate and sulfate of exhausted IRA 996 and tributylphosphonium resins are shown in Figures 17 and 18. Comparison of Figures

Nitrate Removal after Partial Regeneration

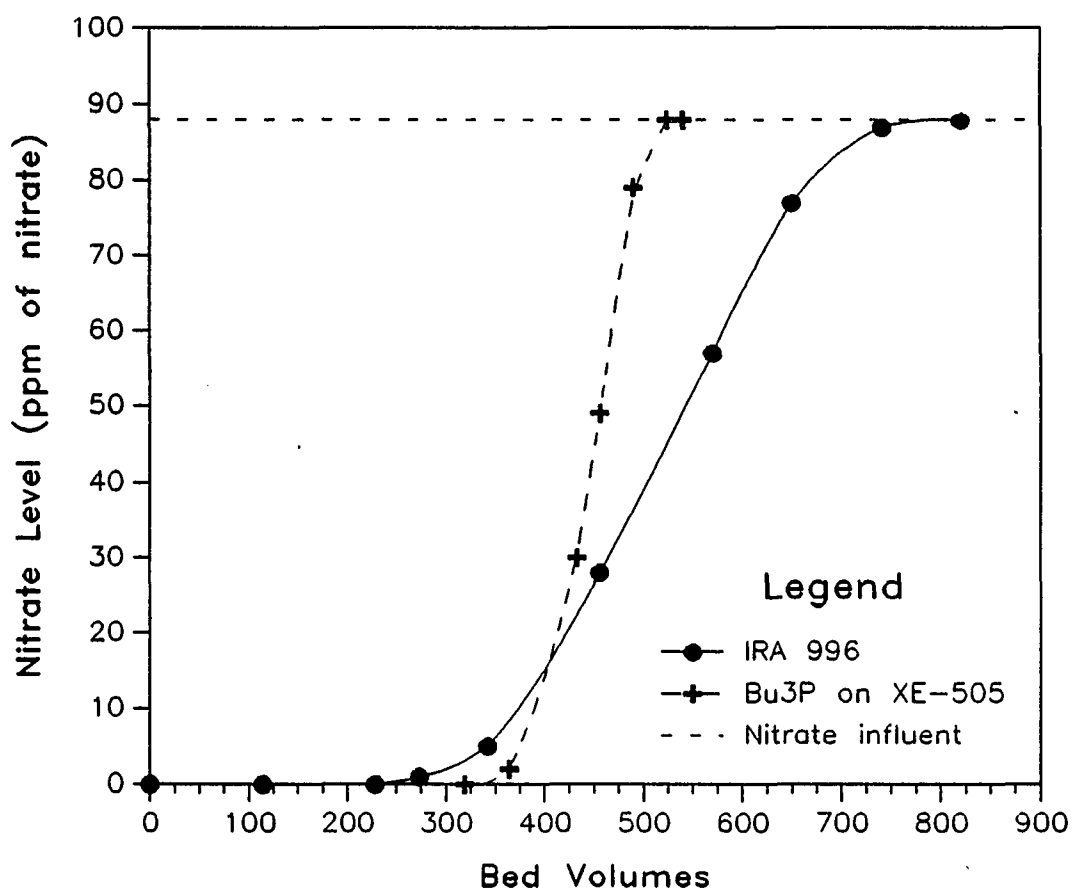


Figure 15. Nitrate removal for IRA 996 and tributylphosphonium resins after partial regeneration with 7 bed volumes of 2 M brine solution. Bed volume, 8.0 ml; flow rate, 3.5 ml/min; 100 ppm sulfate; 31 ppm chloride.

Nitrate Removal after Partial Regeneration

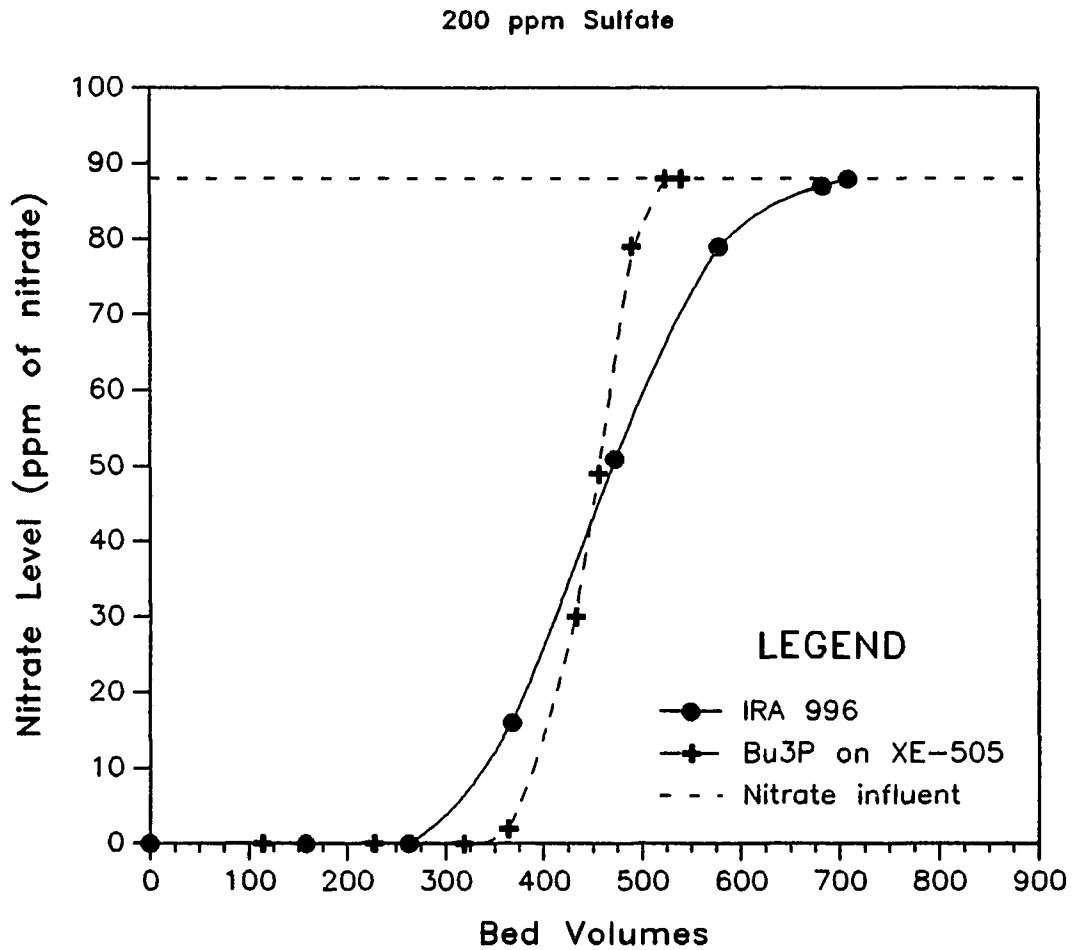


Figure 16. Nitrate removal for IRA 996 and tributylphosphonium resins after partial regeneration with 7 bed volumes of 2 M brine solution. Conditions same as Figure 14 but with 200 ppm sulfate.

17 and 18 indicates a much larger retention of sulfate for the IRA 996 resin. The nitrate levels for IRA 996 during regeneration, however, more quickly return to a lower level than for that of the tributylphosphonium resin. This behavior indicates that the bulk of the IRA 996 sites are efficiently regenerated while regeneration of the tributylphosphonium sites is initially efficient but that a large percentage of the sites are more difficult to regenerate.

Mixed-bed ion exchange

The concept of combining anion-exchange nitrate removal with cation-exchange water softening has the potential of being a very economical process. A column of cation-exchange resin and anion-exchange resin, intimately mixed, can effectively remove nitrates and calcium (hardness) at the same time. The economic advantages are observed during regeneration with sodium chloride. The cation-exchange regeneration process uses sodium ions to exchange with calcium and magnesium on the exhausted resin yielding a regenerated exchanger. In normal water softening, the chloride portion of a brine solution serves only as a counter ion in the process. In a mixed-bed, this chloride is used for regeneration of the anion-exchange resin as well. During regeneration of a mixed-bed, one is literally getting two regenerations for the price of one.

A potential problem with a mixed-bed process lies in the fact that anion-exchangers also retain sulfate. During regeneration, high concentrations of calcium and sulfate ions exist which may form precipitates of calcium sulfate. Calcium

Regeneration of Tributylphosphonium Resin

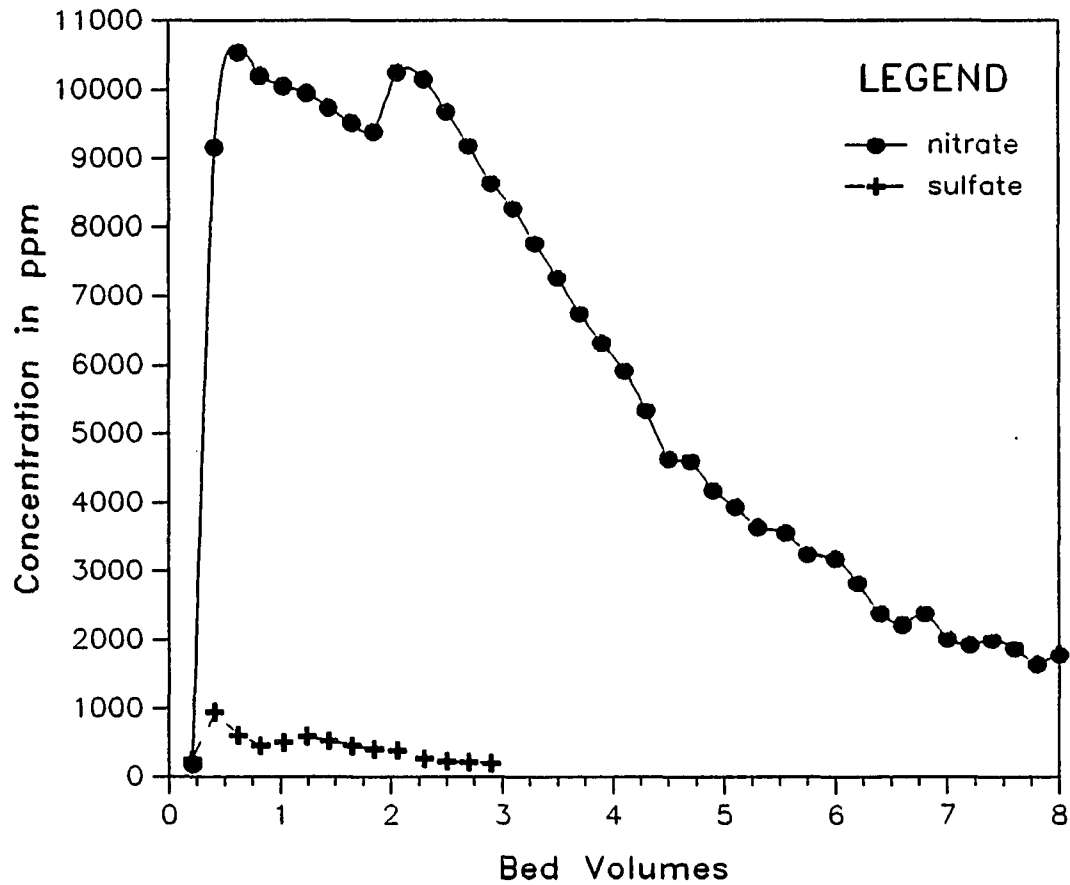


Figure 17. Regeneration profile for tributylphosphonium on XE-505 resin exhausted with 88 ppm nitrate, 124 ppm sulfate. Bed volume, 8.0 ml; flow rate, 0.2 ml/min; regenerant, 2M sodium chloride.

Regeneration of IRA 996

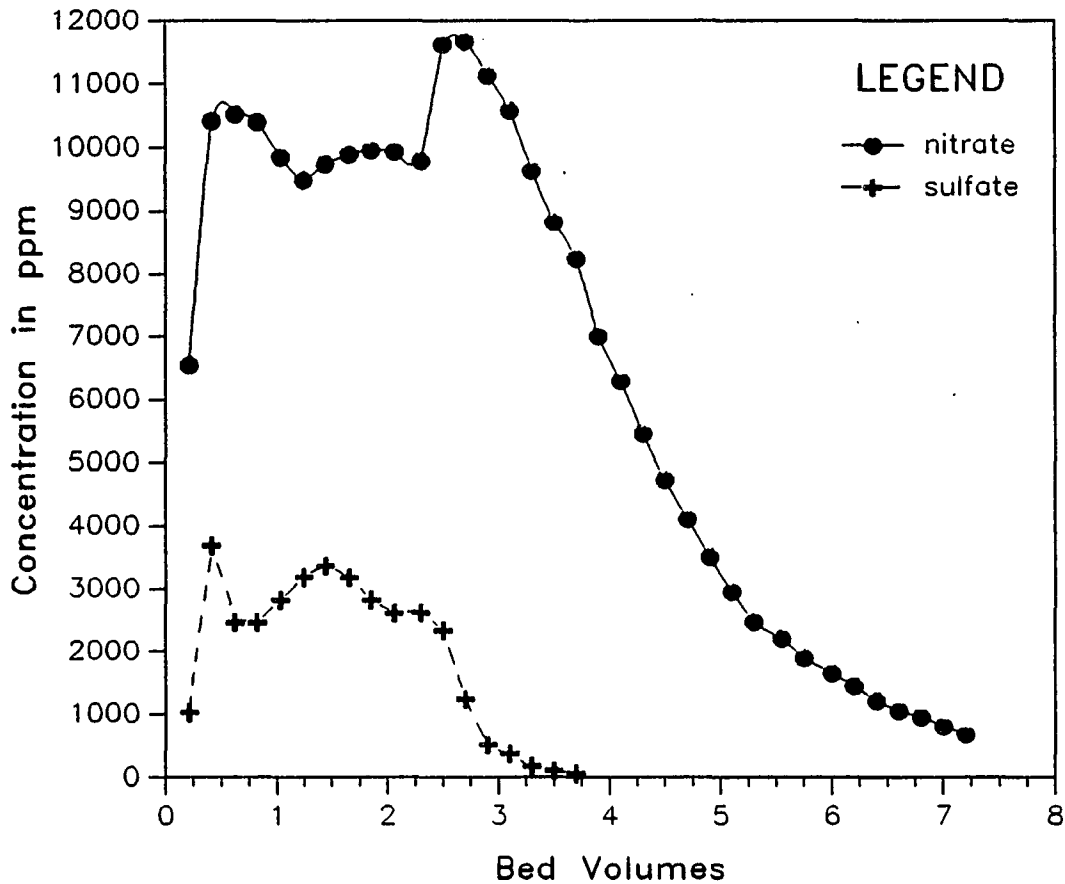


Figure 18. Regeneration profile for IRA 996 resin. Conditions as in figure 17.

Mixed Bed Water Treatment

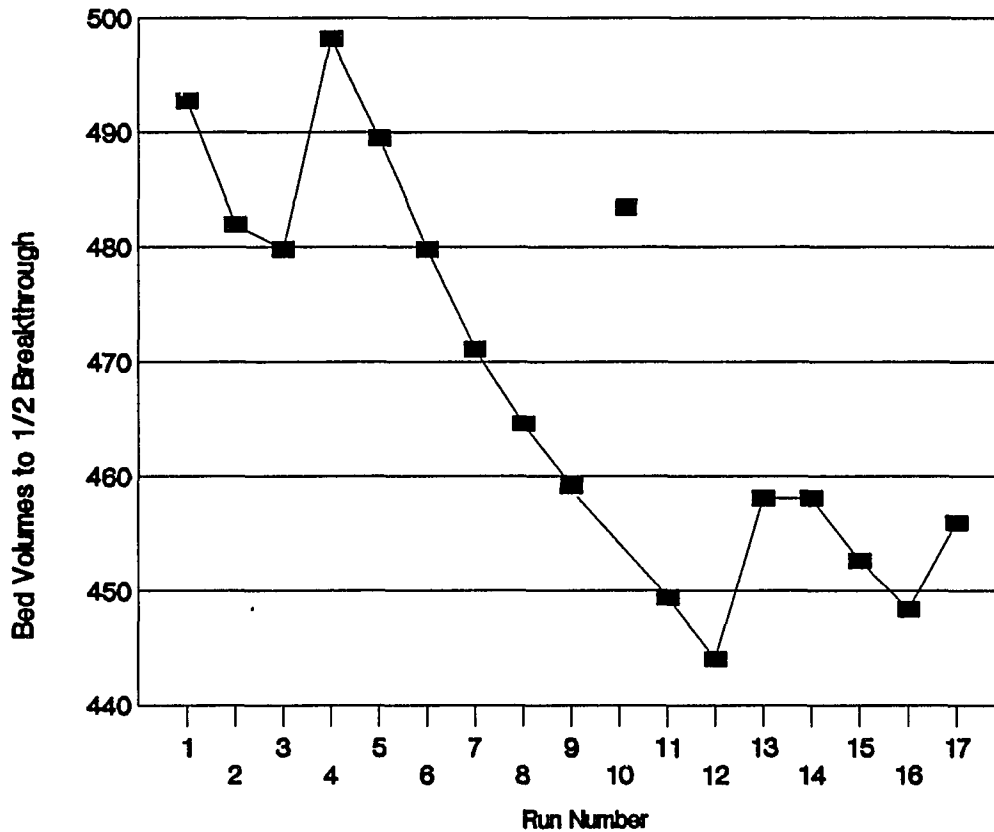


Figure 19. Breakthrough volumes vs. number of regeneration-exhaustion cycles for the mixed bed ion exchange process. Influent water: 90 ppm nitrate, 250 ppm sulfate and 350 ppm calcium; regenerant: 2M sodium chloride. Resins used were Dowex 50w-8x cation exchange and IRA 996 anion exchange.

sulfate precipitation or gypsum fouling, has been shown to exist in at least one study (25). The amount of sulfate retained by the anion-exchange resins can play a significant role in gypsum fouling. Obviously, a nitrate-selective resin which holds little sulfate, has a major advantage in mixed-bed ion exchange.

Figure 19 gives the half-height breakthrough volumes of seventeen exhaustion-regeneration cycles for a mixed-bed of IRA 996 and Dowex 50w-8x resins. Column back pressure or head pressure was also monitored for possible blockage of the column due to gypsum but no increase over the entire course of the experiment was observed. Gypsum fouling may explain the initial drop in capacity, but the lack of an increase in system back pressure or observation of calcium sulfate precipitate, makes this theory highly unlikely. A more reasonable explanation lies with the difference between a fully regenerated (100%) and a partially regenerated resin. As demonstrated earlier in Figures 11, 12 and 15, a drastic difference in capacity exists between a fully regenerated resin and a partially regenerated resin. The IRA 996 resin used in this mixed bed evaluation was initially 100% in the chloride form. Since the resin is only partially regenerated thereafter, a drop off from the initial capacity is expected. What is surprising is the large number of cycles required for this leveling off of capacity to be observed.

CONCLUSION

Phosphonium resins show great promise in nitrate removal from contaminated drinking water due to their extremely high nitrate/sulfate selectivity and higher capacity. Higher nitrate/sulfate selectivity has been shown to translate into nitrate removal capacities immune to the sulfate content of a water supply. Although the phosphonium resins regenerate less efficiently, they retain less sulfate than their amine counterparts. A major concern with nitrate removal by ion exchange is the disposal or decontamination of the nitrate laden brine wastes. A more efficiently regenerated resin yields smaller amounts of brine to be disposed. Decontamination of a brine by anaerobic bacteria as in reference (13), however, places more importance on sulfate-free regenerant waste and less importance on regeneration efficiency.

REFERENCES

1. Hanway, J. J.; Herrick, J. B.; Willrich, T. L.; Bennett, P. C.; McCall, J. T. Iowa State University, Cooperative Extension Service, Special Report No. 34 (Aug, 1963).
2. Water Quality Institute editorial, "Nitrates: A question of time?" 1987, 1, 24.
3. Hallberg, G. R. Agricultural Chemicals and Groundwater Quality in Iowa; Status Report 1985, Iowa State University, Cooperative Extension Service, CE-2158q (Dec, 1985).
4. Clifford, D.; Chieh-Chien, L.; Liou-Liang, H.; Boigel, J. U.S EPA 600-S2-86-107, March, 1987.
5. Clifford, D.; Weber, W.J. Reactive Polymers 1983, 1, 77-89.
6. Grinstead, R. R.; Jones, K. C. U.S. EPA, 17010, Jan, 1971.
7. Guter, G. A. U.S. EPA, 600/S2-82-042, Aug, 1982.
8. Guter, G. A. U.S. Patent 4,479,877, 1984.
9. Selneczi, J. G. U.S. Patent, 4,671,879, 1987.
10. Andrejewski, W.; Honke, I. M.; Masch, K. G. German Patent 3,301,054, 1982.
11. Rolke, D.; Hitzel, H.; Brink, A. U.S. Patent 4,483,772, 1984.
12. Higgins, I. R. U.S. Patent, 3,775,088, 1973.

13. Solt, G. S.; Klapwijk, A. U.S. Patent, 4,671,879, 1987.
14. Houptmann, R.; Froelich, P.; Weber, H. German (east) Patent DD 217,528, Jan, 1985; Chem. Abstr. 103 124434j.
15. Roubinek, L. U.S. Patent, 4,134,861, 1979.
16. Cinquini, M.; Colonna, S.; Molinari, H.; Montanari, F.; Tundo, P. J. Chem. Soc. Chem. Commun. 1976, 394.
17. Tundo, P. Synthesis 1978, 315.
18. Molinari, H.; Montanari, F.; Tundo, P. J. Chem. Soc. Chem. Commun. 1977, 639.
19. Tundo, P. J. Chem. Soc. Chem. Commun. 1977, 641.
20. Regen, S. L. Angew. Chem., Int. Ed. Engl. 1979, 18, 421.
21. Tomoi, M.; Shiiki, S.; Kakiuchi, H. Makromol. Chem. 1986, 187, 357.
22. Tomoi, M.; Kori, N.; Kakiuchi, H. Reactive Polym. 1985, 3, 341.
23. Tomoi, M.; Hosokawa, Y.; Kakiuchi, H. Makromol. Chem., Rapid Commun. 1983, 4, 227.
24. Warth, L.; Cooper, R.; Fritz, J. J. Chromatogr. 1988, submitted.
25. Prunac, A. D. L.; Baur, D. M. European Patent 86309491.8, 1987.
26. Gozdz, A. S.; Kolarz, B. N. Makromol. Chem. 1980, 181, 349-57.
- 27a. Maier, L. D.; Seyferth, F. G. A.; Rochow, E. G. J. Am. Chem. Soc. 1957, 79, 5884.
- 27b. Kaesx, H. D.; Stone, F. G. A. J. Org. Chem. 1959, 24, 635.

28. Bagchi, R.; Haddad, P. R. J. Chromatogr. 1986, 351, 541-47.
29. Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd edition, Harper and Row: New York, 1981, pp 291-365.
30. Boari, G.; Liberti, C.; Merli, C.; Passino, R. Desalination 1974, 15, 145-66.
31. Chu, B.; Whitney, D. C.; Diamond, R. M. J. Inorg. Nucl. Chem. 1962, 24, 1405-15.
32. Lochmuller, C. H.; Colborn, A. S.; Hunnicutt, M. L. Harris, J. M. Anal. Chem. 1983, 55, 1344-48.
33. Yoshito, A.; Pei-Chin, H. Yuki Gosei Kagaku Kyokai Shi 1975, 33, 277; Chem. Abstr. 1975, 83, 58514a.

**SECTION II. POTENTIOMETRIC DETECTION OF HALIDES
AND PSEUDOHALIDES
IN ANION CHROMATOGRAPHY**

LITERATURE SURVEY

Ion chromatography is the leading analytical method for determining anions in aqueous samples. Most frequently, detection of eluted anions is by conductivity or spectrophotometry. In a few cases, potentiometric detection of eluted anions has been employed. Franks and Pullen (1) used a small silver-silver chloride indicator electrode for the selective potentiometric detection of halides in anion-exchange chromatography. Deguchi *et al.* (2) used a similar detection system for gel chromatography. In both papers, the detectors worked well, but the speed and quality of the chromatographic separations were distinctly inferior to that now attainable.

Trojanowicz and Matuszewski (3) obtained good results in the potentiometric determination of chloride by flow-injection analysis. Hershcovitz, Yarnitsky and Schmuckler (4) used a silver wire coated with silver salicylate for potentiometric detection of halides and thiocyanate in ion chromatography. Alexander *et al.* (5,6) in Australia, and Loscombe *et al.* in England (7) have successfully used a copper electrode for the potentiometric detection of a number of anions and cations in ion chromatography.

In the present work, several types of silver electrodes, coated with an insoluble silver salt, are evaluated for potentiometric detection of anions in modern chromatography. The surface characteristics of the most promising are studied by

electron microscopy. The practical advantages of these as detectors in chromatography are demonstrated using both isocratic and gradient elution.

EXPERIMENTAL

Equipment

The HPLC equipment consisted of a Model AA-94 Eldex dual-channel pump, a Model 7000 Rheodyne injection valve with a 20 μ L sample loop, and a Li-Chroma-Damp III pulse dampener. The leads from the potentiometric cell (see below) were connected to a Model 12 Corning pH meter. The recorder output of the pH meter was connected to a Model 5000 Fisher chart recorder. For gradient work, a Tracor model 980A, low-pressure solvent programmer was used.

Column

The anion-exchange column used in this work was either a 4.6 x 50 mM TSK Gel or an XAD-1 column functionalized and packed in this laboratory. Neutral XAD-1 particles (20-26 μ m) were functionalized via chloromethylation followed by amination with trimethylamine as in Barron and Fritz (8). Conditions were chosen such that a final capacity of 84 μ eq/g would be obtained. A 400- x 2-mm glass column was packed using a 40% ethylene glycol diluent.

Potentiometric Cell

The potentiometric cell was made from two polypropylene tube fittings, a coupler and a teflon spacer as in Figure 1. One fitting held the column effluent

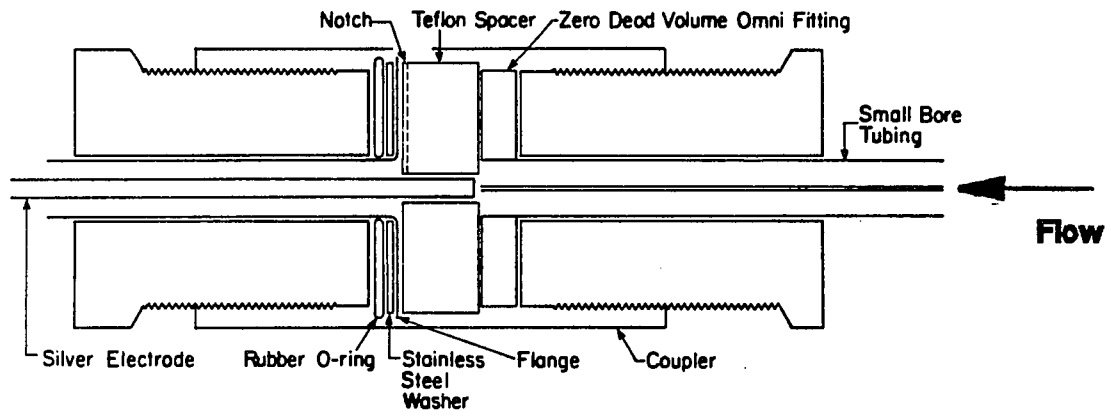


Figure 1. Potentiometric Cell.

delivery tube. The other held a larger bore polypropylene tube which tightly surrounded the silver wire electrode. The column effluent passed through one fitting, around the Ag/AgCl electrode, and out through a hole drilled into the center of the coupler. The fittings were tightened against the Teflon spacer and effluent was allowed to exit the electrode compartment via a notch in the electrode side of the spacer. The salt bridge of the reference electrode was placed in the hole in the coupler where electrical contact with the effluent could be maintained.

Electron Microscopy

A JEOL JSM-35 scanning electron microscope (SEM) in the secondary electron mode, with an accelerating voltage of 20 kV and a beam current of 65 microamps, was used to obtain the micrographs. Specimens were mounted on brass discs with double-stick tape and coated with approximately a 15 nm thickness of Au/Pd in a Polaron E5100 Sputter Coater. Images were recorded on Polaroid Type 665 film.

RESULTS AND DISCUSSION

Preparation and Preliminary Evaluation of Electrodes

Electrodes coated with a thin layer of a silver anion precipitate were prepared by electrical oxidation of a silver wire in an aqueous solution of the selected anion for a period of 3 to 7 min. In some cases, a silver chloride precipitate layer was formed by immersing a silver wire in a solution of the iron(III) chloride.

Silver wire electrodes coated with AgCl, AgBr, AgI, Ag₃PO₄, Ag₂S, and AgSCN were evaluated for detection of various anions by flow-injection analysis. The flow-injection apparatus consisted of a single-piston pump, a six-port injection valve and the electrode arrangement in Figure 1. A 0.01 M solution of sodium perchlorate was pumped through the system at a flow rate of 4.5 mL/min and a small volume of test solution was injected. Figure 2 shows the response and repeatability for several different anions with a Ag/AgCl electrode. The response and repeatability were equally good with a Ag/AgSCN electrode.

The surface of several of the electrodes was examined by electron microscopy. Figure 3 shows portions of the surfaces at high magnification (Bar = 2 μm). Electrode coatings of smaller particle sizes are observed to have less band broadening and tailing of peaks in flow injection experiments. Ag₂S is an exception to this trend; it has small particles but still shows peak deformations when used as an electrode.

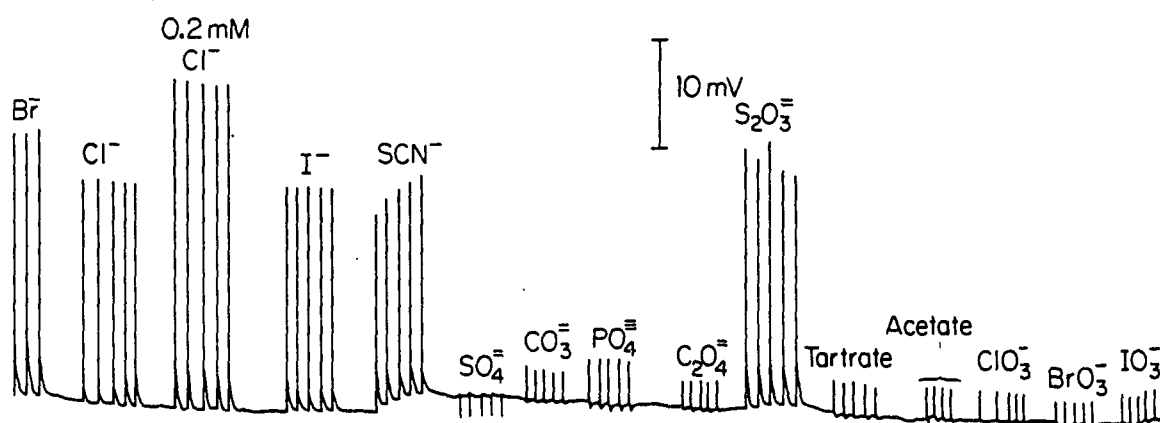
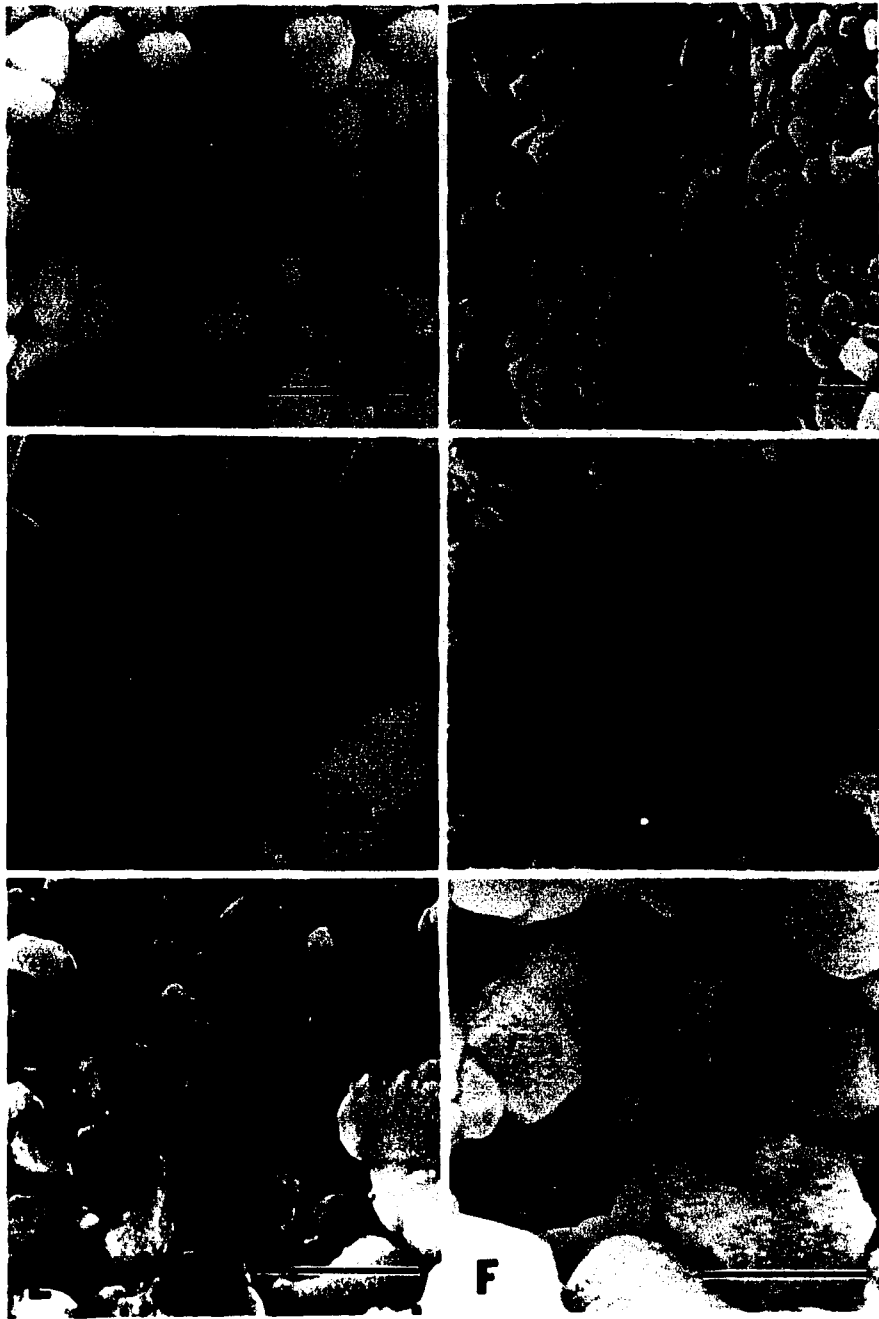


Figure 2. Flow injection analysis with a Ag/AgCl electrode. Carrier: 0.01 M sodium perchlorate, flow-rate, 4.5 mL/min . All samples are 0.1 mM unless indicated.

Figure 3. $\text{Ag}/\text{Ag}_n\text{x}$ electrode surfaces. Each was prepared by passing $100\mu\text{A}$ of current for 7 minutes through a solution containing the appropriate anion $\text{x}^{\text{n-}}$, a silver wire anode, and a platinum cathode. Bar = 2 microns. A. AgCl . B. AgSCN . C. AgI . D. Ag_2S . E. Ag_3PO_4 . F. AgBr .



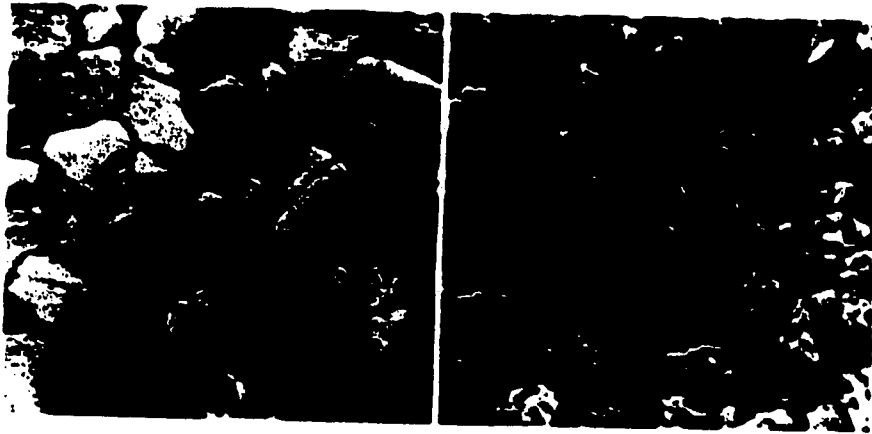
These preliminary evaluations indicated that either the Ag, AgCl or Ag, AgSCN should be a satisfactory detector electrode for flow-injection analysis or ion chromatography. Ag,AgBr may also be used, but some loss of resolution in chromatography is expected from the band broadening and peak tailing associated with this electrode.

Ion Chromatography with Isocratic Elution

A silver-silver chloride electrode in conjunction with a calomel reference electrode (see Figure 1) was used for detection of various anions separated by ion chromatography. A dilute aqueous solution of sodium perchlorate or sodium sulfate served as the eluent. The baseline was found to be unstable until several samples had been injected. However, it was found that a new silver-silver chloride electrode could be conditioned by dipping it into a solution of the analyte 3 or 4 times before installing it in the detector. Electrodes so treated quickly gave a steady baseline. Figure 4 shows an electron-micrograph of a conditioned silver-silver chloride electrode. Comparison with the photo in Figure 3d shows that the surface of the conditioned electrode appears to be a composite of many silver salts covering the underlying silver chloride precipitate.

Use of an ion-selective electrode as a detector in ion chromatography has the advantage that many anions are not detected (or are detected with very small response factors) and will not interfere in the determination of the detected anions.

Figure 4. Ag/AgCl electrode surfaces, prepared by dipping a silver wire into an aqueous FeCl_3 solution for 4 minutes. Bar = 2 microns. A. Fresh electrode. B. Electrode conditioned by dipping several times in a solution containing 10^{-3}M each of I^- , Br^- , Cl^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , PO_4^{3-} .



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Figure 5 shows the chromatographic separation and potentiometric detection of 1.0 mM chloride, bromide, iodide, thiocyanate and thiosulfate; the sample also contained equimolar concentrations of nitrate, phosphate, carbonate, sulfate and acetate which were not detected. A 4.5 mM solution of sodium perchlorate was employed as the eluent and injection volumes were 20 μ L.

Sodium sulfate eluents also give good separations of several inorganic anions when used in conjunction with the silver-silver chloride potentiometric detector. Table I compares the actual retention times of halide and pseudohalide ions with sulfate and perchlorate eluents. The retention times relative to chloride are also shown; these show perchlorate to be the more efficient eluent for iodide, chloride, bromide and thiocyanate. Thiosulfate is eluted more efficiently by the divalent sulfate eluent.

Calibration curves were prepared for peak area and peak height against anion concentration and against log of anion concentration. The calibration plots varied less from one anion to another when peak height was used. Figure 6 shows the curves obtained for peak height plotted against log concentration. While not linear, the curvature is sufficiently slight for use as practical calibration curves. The working range is approximately 0.05 mM to 2.0 mM. Two previous authors (1,2) noted linear calibration curves (detector response vs. concentration), but another work (4) found predominantly logarithmic curves. The combined influence of

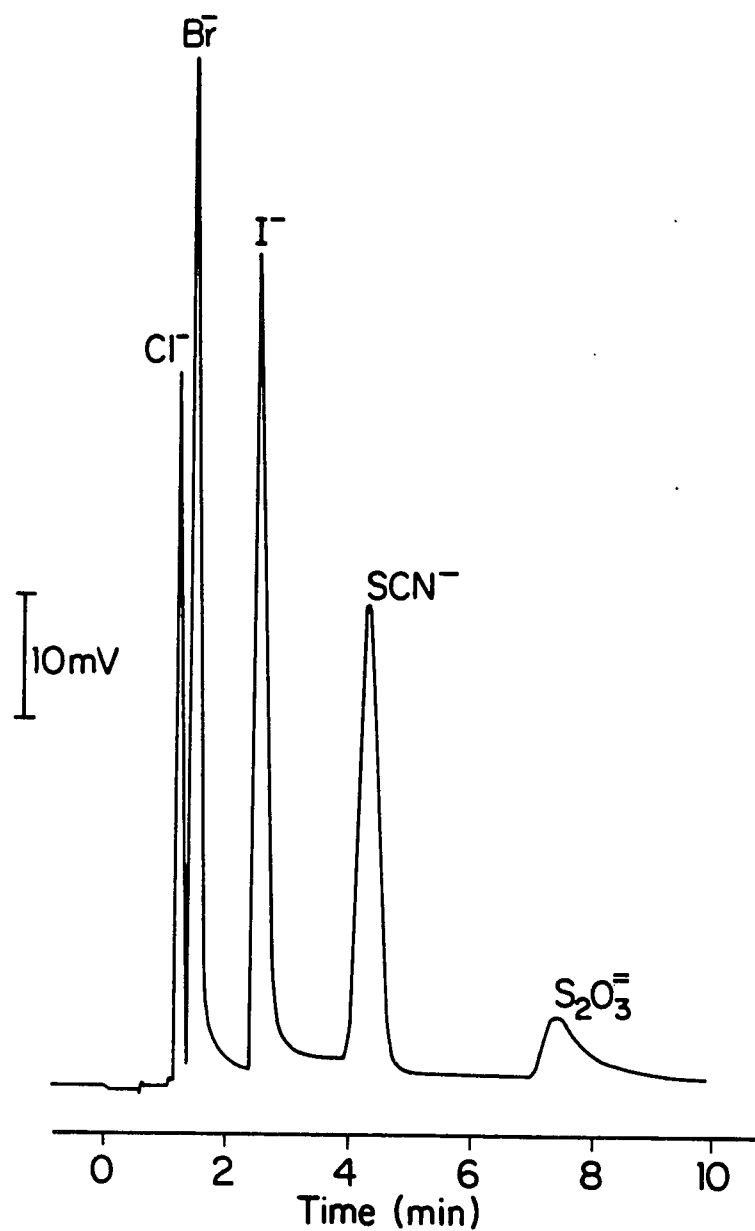


Figure 5. Typical chromatogram with potentiometric detection at a Ag/AgCl electrode. Eluent: 4.5 mM sodium perchlorate, flow-rate, 1.6 mL/min; injection volume, 20 μL ; analyte concentration, 1.0 mM.

Table I. Comparison of retention of anions with different eluents. TSK anion-exchange column; eluent flow rate 1.6 mL/min; Ag,AgCl detector electrode

Ion	Relative Retention, Cl ⁻ = 1.00		Actual Retention Time, min.	
	5.0mM	10.0mM	5.0mM	10.0mM
	ClO ₄ ⁻	SO ₄ ⁼	ClO ₄ ⁻	SO ₄ ⁼
Cl ⁻	1.00	1.00	2.08	1.41
Br ⁻	1.48	2.18	3.07	3.07
I ⁻	2.84	8.37	5.9	11.8
SCN ⁻	4.54	-	9.44	-
S ₂ O ₃ ⁼	7.83	3.01	16.28	4.25

concentration, solubility product, adsorption and rate effects determines the peak potentials (4).

Slopes for the calibration curves in Figure 6 were 30 mV/mM or less. The electrode response is a function of the total ionic strength of the solution in the detector cell as well as the activity. Thus, the slope of a calibration curve is expected to change with the concentration of eluent used. It may also change for samples containing a high concentration of non-detected anions.

The reproducibility of peak area of Cl^- , Br^- , I^- and SCN^- was checked by separating a sample containing these ions 10 times, and by separating a sample containing these anions plus equimolar amounts of phosphate, nitrate, sulfate, carbonate and acetate 10 times. The values of the mean (\bar{x}) and standard deviation (S) are given in Table II. The results show a negligible effect of the undetected anions at the concentrations used.

Ion Chromatography with Gradient Elution

The use of eluent concentration gradients in chromatography has been quite difficult using conductivity and spectrophotometric detectors. The large majority of papers published in ion chromatography have used isocratic elution. However, gradient elution would be advantageous for separation of samples containing both early- and late-eluting anions.

The fact that an ion-selective electrode gives little or no response to many ions suggests the possibility of programming the eluent concentration throughout the

chromatographic run. Figure 7 shows the separation and detection of five halides and pseudohalides using a gradient of 3.5 mM to 10.0 mM sodium perchlorate. Compared to the same separation in Figure 5, the peak shape for $S_2O_3^-$ is much improved and the time required for separation is significantly less.

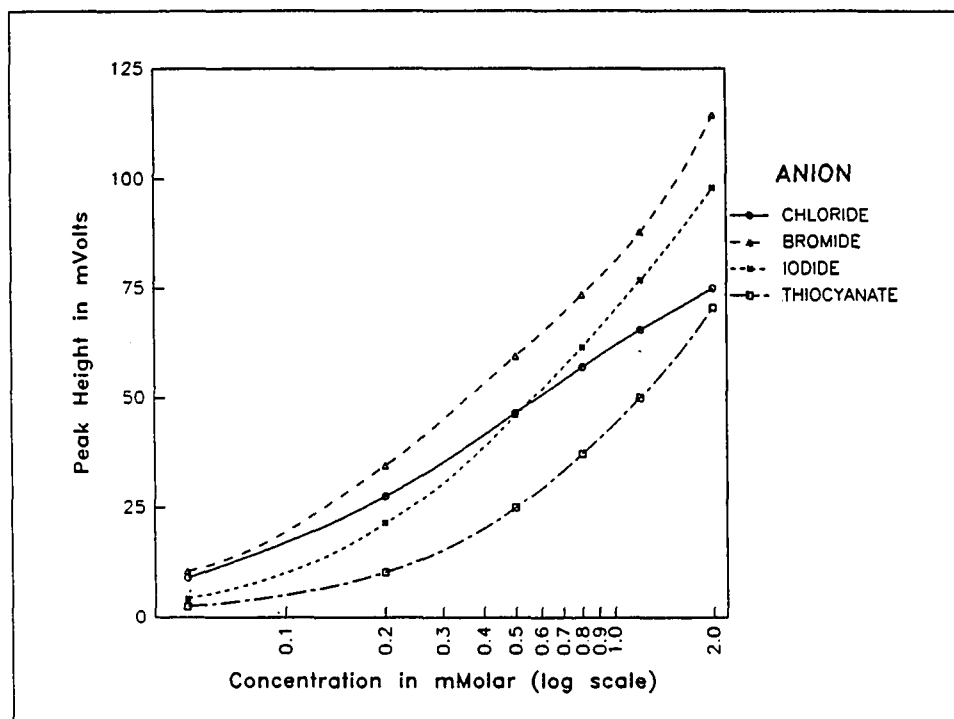


Figure 6. Calibration plot of peak height vs. log concentration. Eluent as in Fig. 5. Peak height in mvolts.

Table II. Reproducibility of peak areas. S and \bar{x} in each set are based on 10 runs

Ion ^a	No Foreign Ions		With Foreign ^b Ions	
	\bar{x}	S	\bar{x}	S
Cl ⁻	26.5	3.9	26.6	1.3
Br ⁻	51.2	2.5	53.1	1.5
I ⁻	68.1	2.4	66.0	1.1
SCN ⁻	74.3	3.0	72.5	2.3

^a1.0 mM concentration.

^bForeign ions are PO₄³⁻, NO₃⁻, SO₄⁼, CO₃⁼, AcO⁻ each 1.0mM.

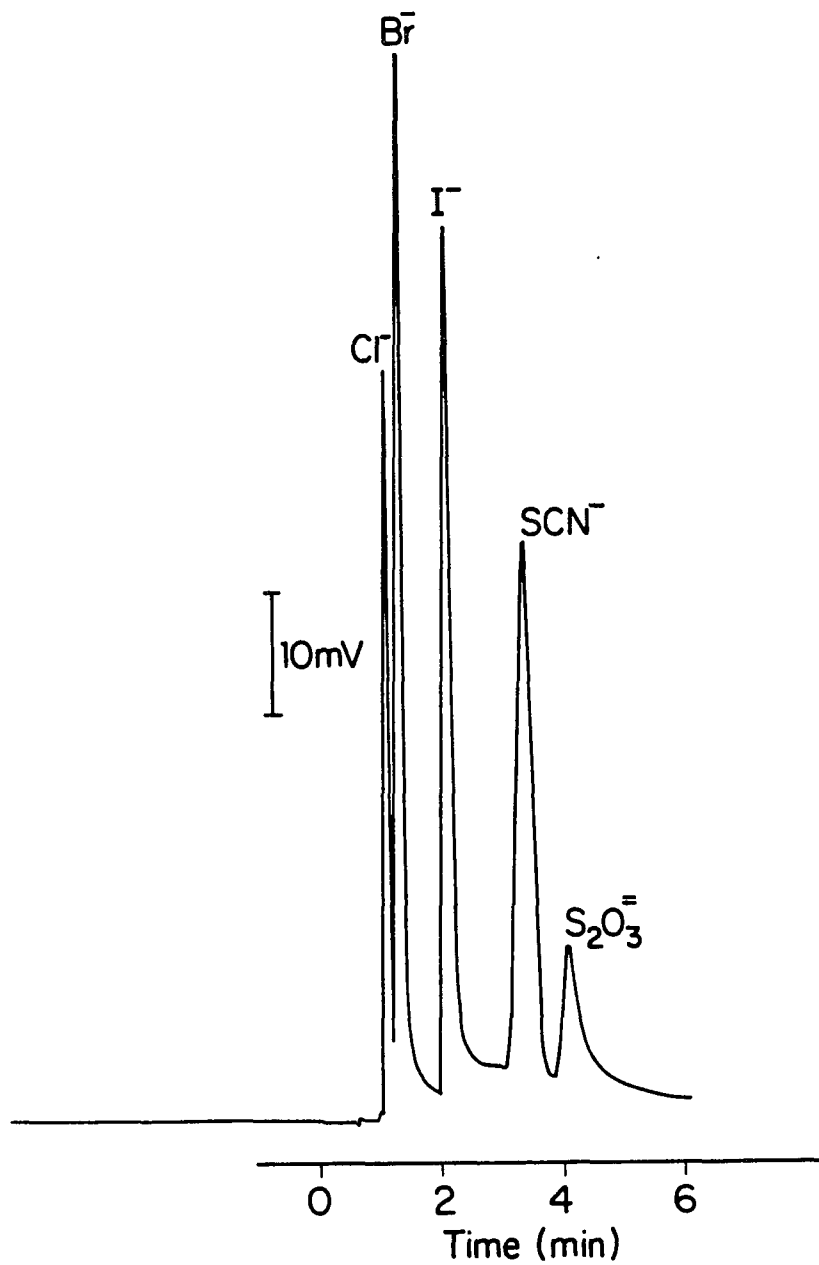


Figure 7. Gradient elution with potentiometric detection. Eluent: 3.5 - 10.0 mM sodium perchlorate; flow-rate, 1.6 mL/min; injection volume, 20 μ L; analyte concentration, 1.0 mM.

CONCLUSIONS

A small silver-silver chloride electrode rapidly attains a reproducible potential with varying concentrations of halide anions in a flowing system. This suggests the use of such an electrode for rapid determination of various halides by flow-injections analysis. However, individual halide and pseudohalide anions can be separated by ion chromatography and measured potentiometrically using a silver-silver chloride electrode. Gradient elution is also possible in the latter case.

REFERENCES

1. Franks, M. C. and Pullen, D. L. Analyst 1974, 99, 503-14.
2. Deguchi, T.; Kuna, T. and Nagai, H. J. Chromatogr. 1978, 152, 349-55.
3. Trajanowicz, M.; Matuszewski, W. Anal. Chim. Acta 1983, 151, 77-84.
4. Hershcovitz, H.; Yarnitzky, C.; Schmuckler, G. J. Chromatogr. 1982, 252, 113-19.
5. Alexander, P. W.; Haddad, P. R.; Trajanowicz, M. Anal. Chem. 1984, 56, 2417-22.
6. Alexander, P. W.; Haddad, P. R.; Trajanowicz, M. Chromatographia 1985, 20, 179-84.
7. Loscombe, P. W.; Cox, C. B.; Dalziel, J. A. W. J. Chromatogr. 1978, 166, 403-10.
8. Barron, R. E.; Fritz, J. S. Reactive Polymers 1983, 1, 215-26.
9. Electron microscopy in this work was performed by Dr. Nancy E. Fortier.

**SECTION III. DETERMINATION OF ALUMINUM BY
ANION CHROMATOGRAPHY**

INTRODUCTION

The chromatographic analysis of samples containing aluminum is most often done by cation-exchange chromatography. While in many instances this is a very excellent approach, some disadvantages are unavoidable. Bivalent and trivalent metal cations, which are often present in an aluminum sample, serve to clutter a chromatographic separation or necessitate long analysis times. High concentrations of these cations, as in the case of iron ore samples, intensify the problem by overloading a cation-exchange column and swamping the aluminum peak.

Two methods are presented for determining aluminum by anion chromatography. The first technique makes use of the strong formation constants between aluminum and fluoride ion. A standard fluoride solution will show a decrease in free fluoride from addition of Al(III) due to AlF_x complex formation. Fluoride complexed by Al(III) is then separated from free, excess fluoride and quantified. Al(III) in the original sample is then proportional to the depression of free fluoride peak height. The second method depends on the complexation of Al(III) by a phthalate eluent. The Al(III)-phthalate species are retained by an anion-exchange column while metal cations such as Ca^{2+} , Mg^{2+} , Cr^{3+} , Th^{4+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} and Fe^{3+} appear to elute in the injection peak. Al(III) can then be easily separated from metal cation interference and determined. The

method is applied to the determination of Al(III) in a synthetic iron ore sample consisting of 1 part Al^{3+} in 40 parts Fe^{3+} .

LITERATURE SURVEY

Typical analyses of aluminum-containing samples by chromatography have involved gravity separator columns and/or quantitation of Al(III) by atomic absorption spectroscopy (AAS), colorimetry or EDTA titrations of collected fractions (1-6). Such methods are often labor intensive, slow or inaccurate. Some colorimetric methods of aluminum analysis are also plagued with interference from Fe(III) and Mn(II) (7-9).

Fortier and Fritz (10) determined Al(III) by single-column cation-exchange chromatography with conductivity detection. Bertsch and Anderson (11) determined aluminum by separation with single-column cation chromatography and colorimetric detection by post-column reaction with the color-forming reagent, Tiron. A brief application note (12) also described a similar method for Al(III) using cation-exchange and Tiron. Sen Sarma and Majumdar (6) separated Al(III) from iron ore solutions by ion-exchange removal of anionic Fe(III) chloro-complexes in 9 M HCl. Al(III) was then extracted into methylene chloride as the oxinate complex and determined colorimetrically.

Retention of Al(III) in anion chromatography has been described, but only as an interference, not as an analytical method. Wimberley (13) described the retention of alkali and alkaline earth metals on an anion-exchange column made from anion-exchange latex agglomerated onto sulfonated resins. Retention was

shown to be due to a cation-exchange interaction with residual, unprotected sulfonic acid groups of the base resin. Jenke and Pagenkopf (14) and other studies (15-18) reported retention of metal ions on silica-based anion-exchange columns. This behavior was largely reported as being due to metal interactions with residual silanol groups on the silica gel surface.

EXPERIMENTAL

Equipment

The instrument used consisted of a model AA-94 Eldex dual channel pump, a model 7000 Rheodyne injection valve with a 20- or 100- μ l sample loop, a Li-Chroma-Damp III pulse dampener, a model 213 A Wescan conductivity meter and a model 5000 Fisher strip-chart recorder.

Column

The anion-exchange column used in this work was an XAD-1 column functionalized and packed in this laboratory. Neutral XAD-1 particles (20-26 μ m) were functionalized by chloromethylation followed by amination with trimethylamine as in Barron and Fritz (19). Conditions were chosen such that a final capacity of 84 μ eq/g would be obtained. A 400- X 2-mm glass column was packed by the balanced density method using a 40% ethylene glycol diluent (20).

Eluents and Sample Solutions

Analytical grade mono-potassium phthalate (KHP) was used for the eluent. An eluent pH of 4.0 was obtained on dilution of the appropriate amount of KHP and no further pH adjustment was required. Prior to use, eluents were filtered through 0.2-

μm membrane filters and degassed for 20 minutes. Sample solutions were made with the finest grade chemicals available from Fisher Chemical Inc. Tervalent cation solutions were made with an equimolar concentration of nitric acid to prevent flocculation.

RESULTS AND DISCUSSION

Indirect Determination of Aluminum

An indirect method for the determination of Al(III) was briefly investigated. The technique is based on the fact that aluminum(III) will form very strong complexes with fluoride ion. When a standard excess of fluoride ion is added to an aqueous aluminum sample, several AlF_x complexes are formed. Excess free fluoride can then be separated from the aluminum-fluoride complex by anion chromatography. A typical chromatogram for this separation is shown in Figure 1. The eluent used for this separation was 1.5 mM KHP at a pH of 4.0. Under these conditions, free fluoride is resolved from the pseudo peak followed by elution of sulfate. Increasing amounts of aluminum in a sample serve to decrease the peak height of the free fluoride. Aluminum can therefore be determined indirectly by noting the decrease in excess fluoride determined between the sample and a blank.

Figure 2 is a calibration curve for the fluoride peak height vs. the concentration of aluminum added. A standard fluoride concentration of 1.0 mM was used throughout, while aluminum concentrations were varied from 0.2 mM to 0.5 mM. The curve is linear when fluoride is in a 4-fold excess or greater. Extrapolation of the linear region to 0 fluoride peak height gives an intercept of 0.334 mM aluminum. Given that the fluoride concentration is 1 mM, a ratio of 3 F^- per 1 Al(III) is indicated. Confirmation of this AlF_3 stoichiometry is also shown by the

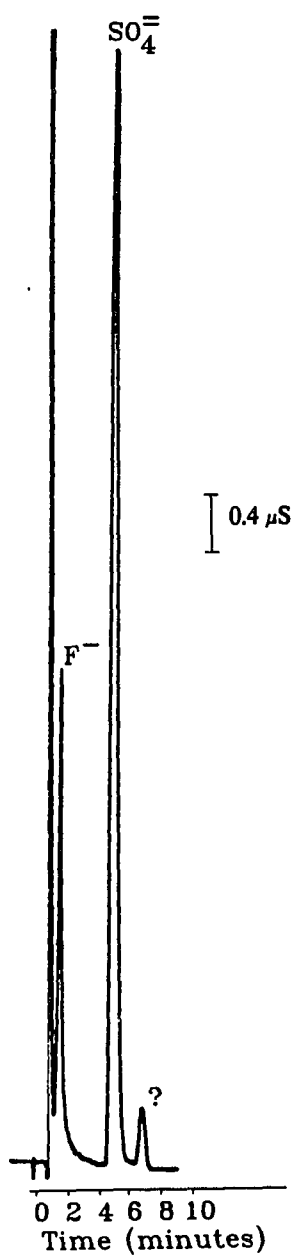


Figure 1. Separation of free fluoride from aluminum complexed fluoride. Eluent conditions; 1.5 mM KHP, pH 4.0. Flow rate; 1.6 mL/min. Sample; 0.1 mM $AlK(SO_4)_2$ in 1.0 mM F^- .

Indirect Aluminum Method

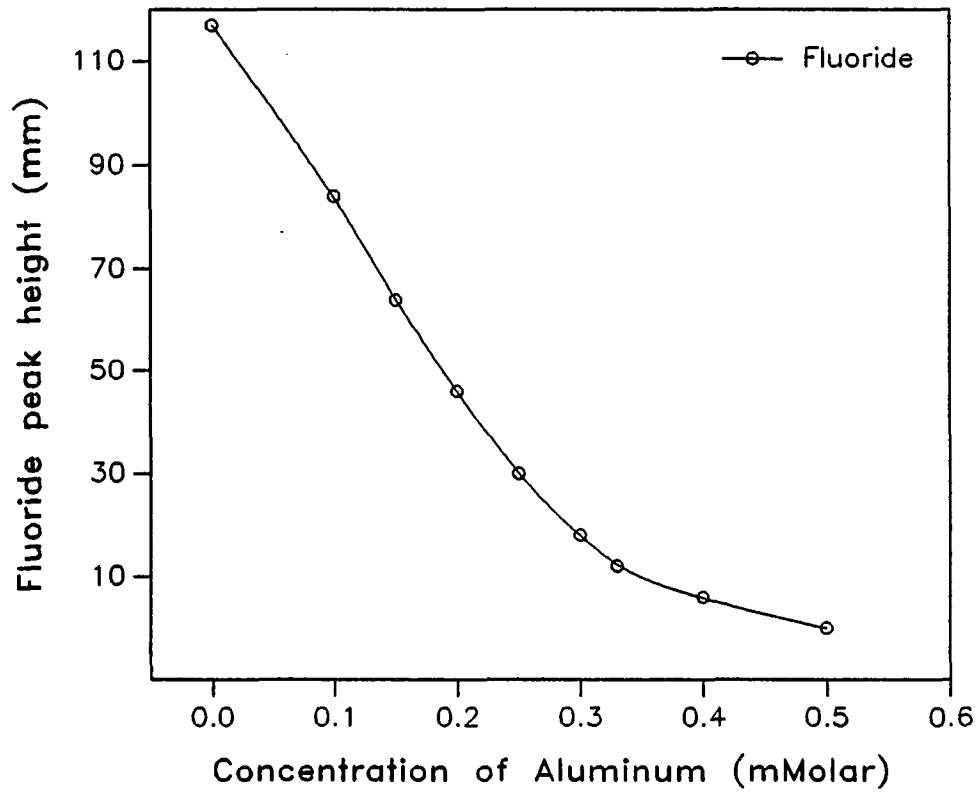


Figure 2. Calibration curve for the indirect aluminum method. Initial fluoride concentration is 1.0 mM.

slope of the linear region which gives a ratio of 3.25 F⁻ per Al³⁺. It follows that for every aluminum ion, three ions of fluoride are removed from the standard fluoride solution.

Interferences, Indirect Method

Interference due to metal cations was evaluated for Ca²⁺, Mg²⁺ and Fe³⁺. These metals were chosen because they are known to form complexes with fluoride ion (21). Concentrations of 0.3 and 3.0 mM of each metal ion were added to a solution containing 1 mM fluoride and 0.2 mM Al³⁺. Although Fe³⁺ has a very high formation constant with fluoride ion, interference was not observed at either concentration. Ca²⁺ and Mg²⁺, on the other hand, have relatively low formation constants but were found to interfere with the determination. The eluent pH of 4.0 may provide some explanation for the above results. Although Fe³⁺ has a stronger formation constant with F⁻, its value may fall off more sharply with pH. A further decrease in eluent pH may remove the interferences caused by Ca²⁺ and Mg²⁺.

Interferences by anions were mainly due to co-elution. Strongly retained ions such as sulfate also necessitated long analysis times and the situation was intensified by the mild eluent conditions necessary for resolution of fluoride from the pseudo peak.

Interferences due to other anions competing with the AlF₃ complex are expected. Since phosphate forms strong complexes with aluminum, interference due to phosphate competing with fluoride ion is expected. An indirect method using a

standard excess of phosphate instead of fluoride was also evaluated. The sensitivity of the phosphate method, however, was found to be far below that of the indirect method using fluoride and therefore was not further investigated.

Direct Determination of Aluminum

In the absence of free fluoride, Al(III) will give a chromatographic peak with the eluent conditions described in Figure 1. A chromatogram for this separation is shown in Figure 3. The peak labeled Al^{3+} is believed to be an anionic complex of aluminum phthalate and is retained slightly longer than fluoride ion (3 min for Al(III) vs. 1.8 min for F^-). The origin of the peak following sulfate in the chromatogram is not certain. Lower sample pH serves to increase this peak while addition of fluoride to complex Al(III) serves to decrease the peak.

The phenomenon of aluminum(III) retention by phthalate complexation was discovered while investigating the above indirect method using fluoride ion. As Al(III) began to exceed the amount of free fluoride in a sample, a new peak emerged while the peak for fluoride disappeared. The curve for this experiment is shown in Figure 4. A signal for the Al-phthalate complex was not observed until all free fluoride was consumed. Also shown in Figure 4 is the calibration curve for Al(III) in the absence of fluoride ion. The curve shows good linearity from 0.2 mM Al(III) to 1.4 mM Al(III).

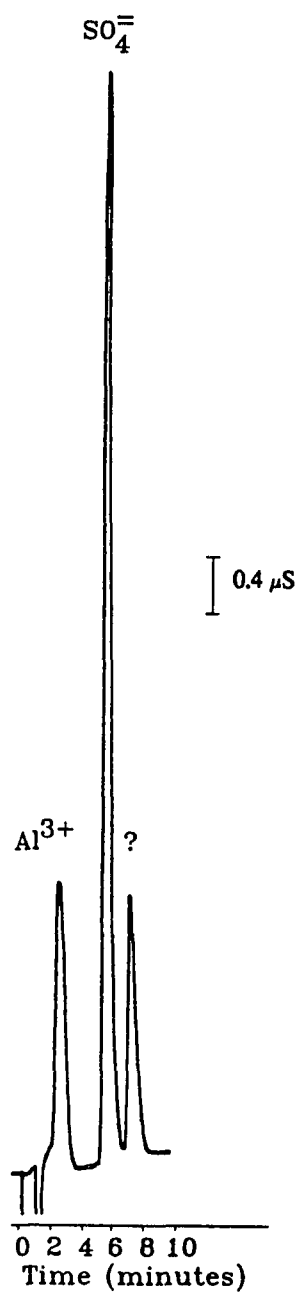


Figure 3. Separation of Al(III) as the Al(III)-phthalate complex. Eluent conditions were as in Figure 1. Sample; 0.2 mM $\text{AlK}(\text{SO}_4)_2$.

Direct Determination of Aluminum

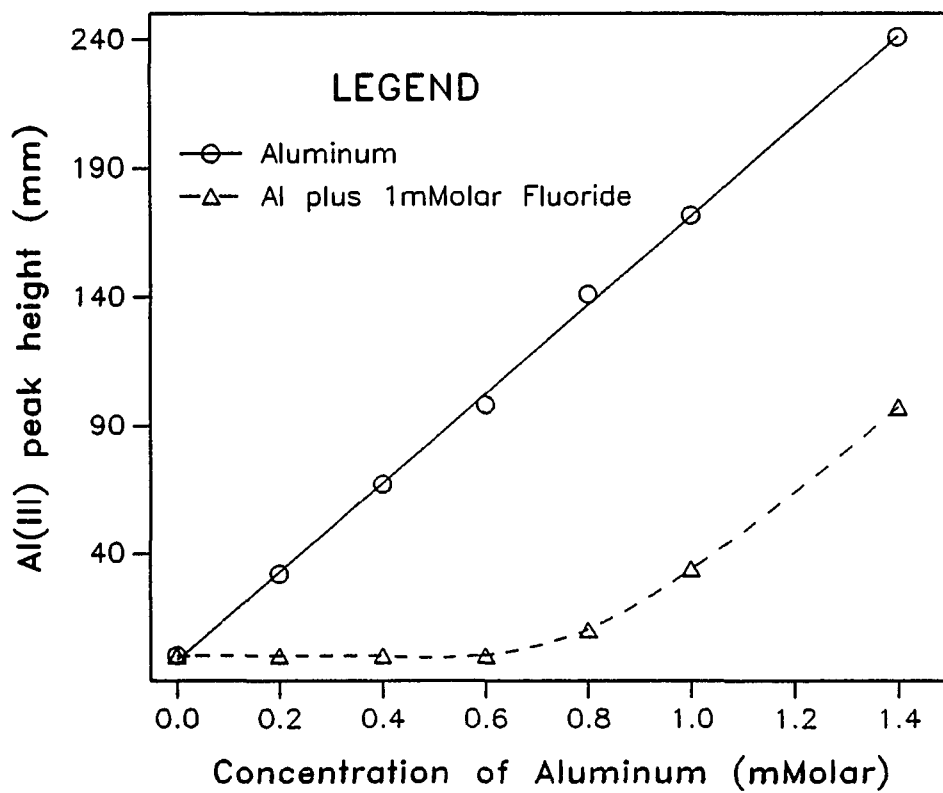


Figure 4. Calibration curve for the direct aluminum method. Also shown is the effect of 1.0 mM added fluoride.

Interferences, Direct Method

Interferences to the direct method naturally include fluoride and phosphate as they form stronger complexes than that of phthalate. Other species, which complex aluminum and prevent formation of the aluminum phthalate complex, are also presumed to interfere. Chloride and nitrate were not completely resolved from the aluminum peak and so interfered with its determination. Interferences due to chloride and nitrate were easily removed, however, by passage of the sample through a high capacity anion-exchange column in the sulfate or perchlorate form. In this case, all sample anions were exchanged for sulfate or perchlorate which elute later in the chromatogram and do not interfere with Al(III).

Interference due to metal ions was evaluated for 1.0 mM solutions of each of the following: Cr^{3+} , Cu^{2+} , Th^{4+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} . Interference was not observed for any metal cation except Cu^{2+} , which was unresolved from Al(III). Furthermore, Cu^{2+} gave a larger signal than an equal concentration of Al^{3+} .

Interference due to Cu(II) can be compensated by addition of fluoride to the Al(III) + Cu(II) sample. This procedure takes advantage of the fact that Al(III) will complex fluoride while Cu(II) will not. As shown in Table I, the peak height of 58 mm for Cu(II) is not affected by addition of 1.0 mM fluoride. The peak height for the Cu(II) + Al(III) sample is 84 mm. By addition of a 1.0 mM fluoride, the peak is reduced to the original peak height of 57 mm, that of 0.2 mM Cu(II) alone. Al(III)

could then be determined by the difference in peak height at the Al^{3+} - Cu^{2+} phthalate retention time or by the indirect method described above.

Table I. Removal of Al^{3+} from Cu^{2+} by complexation of Al^{3+} with F^-

Sample	Peak Height (mm)
0.2 mM Cu^{2+}	58
0.2 mM Cu^{2+} + 1.0 mM F^-	56
0.2 mM Cu^{2+} + 0.2 mM Al^{3+}	84
0.2 mM Cu^{2+} + 0.2 mM Al^{3+} + 1.0 mM F^-	57

Aluminum(III) in Excess Iron(III)

The direct method was successfully applied to the determination of Al^{3+} in a 40-fold molar excess of iron(III). Table II demonstrates the determination of 0.2 mM Al^{3+} and 0.2 mM Al^{3+} with 8.0 mM Fe^{3+} added. Each sample was made from the chloride salts and passed through a high capacity anion-exchange column in the sulfate form to remove Cl^- interference. During this exchange process the iron sulfate formed was found to precipitate on the column causing a significant

reduction in Fe^{3+} content. This reduction in Fe^{3+} was not required for this method as Fe^{3+} did not interfere, but may find utility in other methods where Fe^{3+} is an interferent. The last entry in Table II demonstrates the lack of interference in this method due to Fe^{3+} . In this case the Al^{3+} - Fe^{3+} sample was passed through a high capacity anion-exchange column in the perchlorate form. Iron perchlorate is a soluble salt, and so its precipitation was not observed. A reduction of Fe(III) content in the perchlorate system did not occur, yet the peak height due to Al(III) remained unchanged.

Table II. Determination of Al^{3+} in 40-fold excess Fe^{3+} .

Sample	Peak Height (mm)
0.2 mM $\text{AlK}(\text{SO}_4)_2$	44
0.2 mM $\text{AlK}(\text{SO}_4)_2$ + 8.0 mM Fe^{3+} (SO_4^-)	46
0.2 mM $\text{AlK}(\text{SO}_4)_2$ + 8.0 mM Fe^{3+} (ClO_4^-)	45

Mechanism of Retention

One possibility for the mechanism of retention is phthalate ion acting as an ion-pairing reagent. If this were the case, the retention of Al(III) and Cu(II) would still be observed on an unfunctionalized, neutral column of PS-DVB resin.

Furthermore, interferences due to the retention of anions would be removed.

To test the above theory, a column of the same dimensions as that of the anion exchange column was packed with neutral, unfunctionalized XAD-1 particles. Eluent conditions were exactly as described for the anion exchange column in Figure 3. Injection of Al(III) and Cu(II) solutions did not produce chromatographic peaks which were responsive to changes in analyte concentration. Eluent concentrations of 0.5 mM and 10 mM were also evaluated, but still no retention of Al(III) or Cu(II) was observed. The above experiment was also performed using a Polymer Labs PLRS, neutral PS-DVB column. Again, no retention of Al(III) or Cu(II) was observed.

To confirm the above results, fractions of effluent were collected and analyzed by flame atomic absorption spectroscopy (AA). In these experiments, Cu(II) was used because its limit of detection in flame AA was much higher than for Al(III). A strong signal for copper was observed only in the pseudo peak of the XAD-1 neutral column. AA analysis of fractions from the anion exchange column confirmed the retention of Cu(II) as labelled in Figure 3.

A study by Siriraks *et al.* (18) found retention for Zn^{2+} , Pb^{2+} and Cu^{2+} under conditions similar to this work. They concluded that retention was due to interaction of the metal-eluent complexes with the hydrophobic backbone of the resin and described retention on a neutral, PS-DVB column. A chromatographic

peak was observed on the XAD-1 neutral column after injection of Al(III) or Cu(II). The AA experiment, however, did not demonstrate retention of Cu(II). Furthermore, this peak was not responsive to varying Al(III) or Cu(II) concentrations.

CONCLUSION

Methods for the determination of aluminum by anion chromatography have been presented. An indirect method determines aluminum by its effect on free fluoride. The direct method is based on complex formation of aluminum with a phthalate eluent. While both methods contain certain limitations as individual techniques, used in conjunction, they become diverse and powerful tools for the determination of aluminum under a variety of circumstances.

REFERENCES

1. Maslowka, J., Pietek, W. Chromatographia 1983, 17, 693.
2. Brajter, K., Olbrych-Sleszynska, E. Talanta 1983, 30, 355.
3. Varshney, K. G., Khan, A. A., Varshney, S. S. Indian J. Chem. 1982, 21A, 398.
4. Phillips, J. R., Fritz, J. S. Anal. Chim. Acta 1982, 139, 237.
5. Varshney, K. G., Agrawal, S., Varshney, K. J. J. Liq. Chromatog. 1983, 6, 1535.
6. Sen Sarma, R., Majumdar, M. J. Indian Chem. Soc. 1982, 59, 790.
7. James, B. R., Clark, C. J., Riha, S. J. Soil Sci. Soc. Am. J. 1983, 47, 893.
8. Wright, R. J., Baligar, V. C., Wright, S. F. Soil Sci. 1987, 144, 224.
9. Strelow, F. W. E., Liebenberg, C. J., Toerien, F. Anal. Chem. 1969, 41, 2058.
10. Fortier, N., Fritz, J. Talanta 1985, 32, 1047.
11. Bertsch, P. M., Anderson, M. A. Anal. Chem. 1989, 61, 535.
12. Dionex Corporation, Application Note 42, 1983.
13. Wimberley, J. W. Anal. Chem. 1981, 53, 1709.
14. Jenke, D. R., Pagenkopf, G. K. Anal. Chem. 1983, 55, 1168.
15. Vydra, F. Anal. Chim. Acta 1967, 38, 201.
16. Schindler, P. W., Fuerst, B., Dick, R., Wolf, P. U. J. Colloid Interface Sci. 1976, 55, 469.
17. Strazhesko, D. N., Strelkp, V. B., Belyakov, V. N., Rabacik, S. C. J. Chromatogr. 1974, 102, 191.

18. Siriraks, A., Girard, J. E., Buell, P. E. Anal. Chem. 1987, 59, 2665.
19. Barron, R., Fritz, J. Reactive Polymers 1983, 1, 215.
20. Barron, R. Ph.D. Dissertation, Iowa State University, 1983, p. 49.
21. Siriraks, A., Girard, J. E., Buell, P. E. Anal. Chem. 1987, 59, 2665.

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