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SELECTIVITY VARIATIONS IN ANION CHROMATOGRAPHY

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Selectivity variations in anion chromatography

by

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PREFACE

Since its conception, ion chromatography has developed into a very useful analytical technique. The system has been improved through instrument design changes and its utility increased by extensive work in applications. Section I contains two studies that are intended to improve the eluents currently used and to help in finding better supports for anion chromatography.

In the rush to improve the efficiency and applicability of the system, no one has taken the time to study the basic interactions occurring in the system. If the mechanisms that cause selectivity in ion chromatography are understood, separations could be improved by systematically altering parts of the system that have a major affect on selectivity.

There have been a number of selectivity studies done with classical ion exchange chromatography and several theories have been formulated to explain the variations that were found. If one were to show that the same interactions occur in both systems, it would be quite useful to apply the selectivity theory derived from classical ion exchange chromatography to ion chromatography.

In the second section of this dissertation, theories

explaining selectivity variations found in classical ion exchange chromatography are reviewed. Variations in selectivities previously found in ion chromatography are discussed and current investigations into selectivities in ion chromatography are reported. Results are compared to those predicted by classical ion exchange theory and the utility of understanding the causes of selectivity variations are demonstrated.

The third section of the dissertation includes two applications of ion chromatography for the analysis of species that are not easily quantitated. Dr. Robert Barron, a former research associate, collaborated with the author on the acid eluent work presented in Section I; Margeret Rogers, a summer trainee from South Bend, Indiana helped with the aldehyde work presented in Section III; and Dr. Douglas Gjerde formulated the idea for the cyanide work presented in Section III.

GENERAL INTRODUCTION

Anionic species have been separated by classical ion exchange chromatography for quite some time. The major drawback to adding this class of compounds to the long list of compounds done by high performance liquid chromatography (HPLC) is the detector. A lot of anionic species are invisible to the most common detectors used in HPLC. There are examples of common anions being detected directly by ultraviolet/visible wavelength (1) and electrochemical (2) detectors as well as being detected indirectly with ultraviolet/visible wavelength (3), fluorescence (4), and refractive index (5) detectors. However, these detectors are not universal detectors for monitoring ionic species eluting from a chromatographic column. A conductivity detector would be very useful for monitoring these ionic species since they conduct electrical currents through an aqueous medium.

The only way to elute ionic species from an ion exchange column is by passing another ionic species of similar charge through the column. The second ionic species, commonly called an eluent, also conducts electricity in aqueous solutions. If the detector "sees" the eluent as well as the

analyte species, it is very hard to detect the analyte. In HPLC and ion exchange chromatography, the eluent is usually present in a concentration many times greater than the analyte species one is trying to detect. A conductivity detector would be required to monitor a very small change in signal on top of a very strong signal from the eluent. A good analogy to this problem would be trying to look at stars through a telescope during the daytime. The stars are still up there, but one cannot see them because their eyes (the detector) are overwhelmed by the light from the sun. While HPLC has been used extensively to analyze for a vast array of molecular species from low molecular weight steroids (6) and pesticides (7) to polymers (8) and proteins (9), common inorganic anions have been determined mainly by a variety of wet chemical methods (10).

In 1975, Hammish Small and coworkers (11) published a novel method for reducing the conductance of the eluent while increasing the conductance of the analyte. Their system involves placing a post column reactor (initially a suppressor column) after the analytical column to convert the eluent to a nonconducting molecular species while leaving the analyte species as a highly conducting ionic species. The suppression of the eluent signal allows the

conductivity detector to be used. The conductivity signal of the eluent is not reduced to zero, but it is reduced to a level where the detector can "see" the analyte species on top of the decreased eluent signal.

In Small and coworkers' system for detecting anions, the separator column is a low capacity, pellicular cation exchange resin coated with small anionic latex beads. The negatively charged sites on the resin electrostatically holds the latex onto the support and the positively charged sites on the latex act as immobile anion exchange sites. The salt of a weak acid is used as the eluent to exchange with the sample anions and force them down the analytical column (a mixture of sodium carbonate and sodium bicarbonate is the most commonly used eluent in this system). When the analyte species elutes from the column, the anions are in the sodium form and are also in the presence of a large excess of the eluent anions. The eluent anions are also in the sodium form which makes the eluent completely ionized and highly conductive.

Both the eluent and analyte anions then pass through the suppressor column containing a cation exchange resin in the hydrogen form. As analyte and eluent anions pass through the suppressor column, the anions are converted from the

sodium to hydrogen form. Analyte species emerging from the suppressor column are in the hydrogen form and completely dissociated, provided they are strong acid anions like chloride and sulfate. The eluent anions also emerge from suppressor column completely in the hydrogen form, but are only slightly dissociated. The eluent conductivity is greatly reduced because of the very slight dissociation of eluent anions. Meanwhile, the analyte signal is increased when the counter ion is changed from sodium to hydrogen. Both changes enhance the sensitivity of the system for strong acid anions.

An analogous system was designed for cations (11) but it only works for ammonium, alkali metal, and alkaline earth cations. Transition metals precipitate in the hydroxide-form suppressor column used for the cations. Applications of this dual-column system for anion analysis have been extremely widespread (12). Application of ion chromatography for cation analysis has not been as widespread because of competing spectroscopic methods like atomic absorption or emission spectroscopy for determining cations.

It should be pointed out that even though the dual-column system is a very useful instrument, it is not

without some drawbacks. One of the problems with the system is the suppressor column. The suppressor column broadens sample peaks, which decreases sensitivity (13), and also requires periodic regeneration. After a period of use, the suppressor column becomes loaded with sodium ions and depleted of hydrogen ions.

Regeneration of the suppressor column is accomplished by pumping an acid solution through the suppressor column which replaces the sodium ions with hydrogen ions. The major drawback with regeneration of the suppressor column is that the system must be shut down while the regeneration of the suppressor column is done. It has also been demonstrated that retentions times and peak heights of nitrite vary as the suppressor column capacity is consumed (14). These two problems were solved with the introduction of a hollow fiber suppressor (14).

The hollow fiber suppressor is essentially a short piece of tubing that is permeable to cations but not anions. Sodium ions from the eluent pass through the tubing wall to the outside while hydrogen ions in a solution surrounding the hollow fiber pass through the wall into the effluent stream. The hollow fiber accomplishes the same thing as the suppressor column but in a much smaller volume so that

analyte peaks are broadened to a lesser extent. Only a few early eluting ions such as fluoride, chloride, and nitrite are broadened appreciably by the hollow fiber suppressor (15). The down time associated with suppressor column regeneration is also eliminated.

It might appear that the dual-column system would be able to detect any ionic species since the system uses a conductivity detector, which is a universal detector for ionic species. However, any acid anion with a pK_a (log of the dissociation constant of the acid) equal to or above seven will be converted into an undissociated acid as it passes through the suppressor column. Therefore, even if the analytical column is able to separate very weak acid anions like cyanide and silicate, the conductivity detector will not detect them.

In 1979, Gjerde and coworkers (16,17) demonstrated that there was not an absolute need for a suppressor system. By lowering the ion exchange capacity of the resin by about a factor of ten, the eluent concentration could be lowered by a proportional amount and analyte signals could be detected on top of the eluent signal without the need for an eluent suppression system. This single-column system has advantages as well as drawbacks in comparison to the

dual-column system (18). The main advantages of this system are; one can analyze weak acid anions directly using a conductivity detector, analyte peaks are not broadened by the suppressor system, and extra equipment is not required for the suppressor system (regeneration pump, tubing, eluent, etc.). There are also some drawbacks to the single-column system. The most important drawback with the system is a lower sensitivity in comparison to the sensitivity of the dual-column system. In the dual-column system the eluent is only slightly dissociated after the suppressor column while the analyte species is completely dissociated. In the single-column system the eluent and analyte species are both completely dissociated. The higher sensitivity of the dual-column system is due to the differences in dissociation between the analyte and eluent anions.

Gjerde et al. (19) demonstrated that by lowering the pH of the eluent, one could increase the sensitivity of the single-column system. If a weak acid eluent is used so that the counter ion is the hydrogen ion for both the eluent and analyte anions, a very large increase in sensitivity can be obtained.

Throughout the development of ion chromatography there

has been a lot of work done on improving both systems, comparing the two systems (18,20,21), and in increasing the number of ionic species that can be analyzed by either system. However, an investigation of all of the factors affecting selectivity in the basic system has not been undertaken.

An extensive amount of work has been done studying selectivity in classical ion exchange chromatography (22,23). Interactions affecting selectivity in classical ion exchange chromatography might also affect selectivity in ion chromatography. However, there are several major differences between classical ion exchange chromatography and ion chromatography. The most important difference between the two systems is that high-capacity gel resins are used in classical ion exchange systems whereas low-capacity macroreticular resins are used in ion chromatography. The eluent concentration also differs greatly in the two systems.

There has been some work in ion chromatography which demonstrated selectivity can vary because of capacity (24), eluent concentration (24), and eluent pH (25). It should be pointed out that these variations are expected because of the ion exchange equilibrium involved in the retention of

the anions. Barron and Fritz (26,27) showed that the size and type of ion exchange group on the resin also has an affect on selectivity. However, these studies do not encompass all of the factors that could be involved in selectivity variations.

Throughout this dissertation, the term ion exchange chromatography will be used to describe the chromatographic system which utilizes gravity-flow columns, fraction collecting, and manual methods for analyte analysis. Ion or anion chromatography will refer to the newer chromatographic system which contains a high pressure pump, a high performance column, and an automatic detector.

The first section contains a study on acid eluents which demonstrates their usefulness and discusses factors that must be considered when choosing an acid eluent. This section also contains a study of adsorbed exchangers for use in anion chromatography. The goal of this study was to find a quick and reliable method for preparing and testing alternate supports for anion chromatography. Information in both parts of this section have been published previously in scientific journals (28,29).

The second section contains a literature review of the theories developed for classical ion-exchange

chromatography. The section also contains a discussion of what parameters of the system can be varied in single-column ion chromatography to affect selectivity according to classical ion exchange theory. Previous work in ion chromatography which investigated some of these parameters are described. Then, several investigations are presented which study the affect of changing other system parameters on the selectivity of the system. The results are then used to develop columns for specialized separations. Some of the information given in this section has also been published (28,29).

The last section of this dissertation contains methods for determining cyanide and aldehydes indirectly by first converting the species to be quantitated into species that are more readily detected by ion chromatography. The cyanide determination part of this section was published in 1982 (30).

SECTION I. SYSTEM MODIFICATIONS

ACID ELUENTS

Introduction

In single-column anion chromatography, the signal for an eluted anion arises from the higher equivalent conductance of that anion compared to the eluent anion. While this difference provides a detection sensitivity that is quite adequate for most purposes, the sensitivity is approximately 10 times lower than that typically obtained in dual-column methods. However, work (1) has demonstrated that a weak organic acid such as benzoic acid can be used with single-column anion chromatography. Benzoic acid provides the highly conductive hydrogen ion as the counter ion for the eluted sample anion, yet the background conductivity is still reasonably low because benzoic acid is only about 20% ionized. The detection sensitivity for sample anions is appreciably higher than with benzoate or phthalate salts and is almost as good as with systems that use a suppressor column.

Various organic acids are investigated for use as eluents in anion chromatography in this section. One objective was to find an eluent acid that is not adsorbed by

the resin matrix (as opposed to ion exchange) and that attains equilibrium faster than benzoic acid. It was also of interest to investigate the selectivity and sensitivity obtainable with different eluent acids.

Experimental

A single-column ion chromatograph was used with an insulated 500 x 2 mm glass column and a model 213A conductivity detector made by Wescan Instruments (Santa Clara, California) with a measured cell constant of 33 cm^{-1}. A Milton Roy Mini-Pump manufactured by Laboratory Data Control (Riviera Beach, Fl) was used to provide eluent flow. A Li Chroma Damp II pulse dampener manufactured by Handy and Harman Tube Co. (Norristown, PA) was used in an off-line mode to smooth pump-induced fluctuations in pressure. A Rheodyne (Berkeley, CA) Model 7010 injection value with 20, 50, and 100 µL sample loops was used for sample introduction. Insulation of the column and detector was necessary to prevent excess baseline drift. Eluent flow rate was 1.0 mL/min, detector output was 10 mV, and the recorder input was 1-10 mV full scale.

Anion exchange resins were prepared from Rohm and Haas (Philadelphia, PA.) XAD-1 using a formaldehyde-hydrochloric acid procedure (2) so that the final capacity was 0.026 meq/g. The anion exchange resins were strong-base type I resins prepared with trimethylamine.

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, filtering through a 0.45 micron membrane filter, and then applying a vacuum while stirring to remove dissolved carbon dioxide.

Results and Discussion

Eluent acids

Various organic acids were initially surveyed. The acids had to have a water solubility of 0.01 M or more and pK_a values between 2.75 and 4.25. Partial dissociation of the acid is needed to provide an anion concentration sufficient enough to push the analyte anions down the column, but some of the eluent must also remain in the molecular form to provide an enhanced conductivity signal, as discussed earlier.

After about 30 acids were found that fit these general conditions, a study was conducted of the retention of each of these acids on a 500 x 2 mm glass column filled with ordinary (unfunctionalized) XAD-1 resin. The column was equilibrated and tested with a 16 mM solution of aqueous phosphoric acid (pH 2.1), then the column was equilibrated and tested with a 5 mM solution of aqueous phosphate buffer (pH 6.7). The ionic strengths of both eluents were adjusted to 0.10 M with sodium chloride to prevent the distribution coefficients of the tested acids from reflecting differences in ionic strength between the two eluents. Each acid was injected and eluted with the phosphate eluents and the retention time of the acid measured.

A retention time significantly longer than the dead time of 0.85 minutes was taken to be a measure of the adsorption of that acid by the resin matrix. The term "adsorption" is used in a general way to avoid controversy. It is not intended to imply that adsorption of the acid molecules occurs at discrete sites on the resin or that the adsorption occurs in a layered fashion, but that some sort of interaction of the acid and resin takes place and causes retention of the solute. Earlier work by Cantwell gives a detailed explanation of the mechanism of adsorption of

organic anions on the poly(styrene-divinylbenzene) resin known as XAD-2 (3).

The results of the current study are listed in Table I. At pH 2.1 the acids are predominantly in the molecular form, while they are in an anionic form at pH 6.7. The results show that many of the acid anions are only slightly adsorbed, but that some of the acid anions with substituents on the benzene ring are appreciably adsorbed. Likewise, there is a large variation in the extent to which the molecular forms of the various acids are adsorbed. Variations in adsorption found with some of the nitrogen-containing acids in this study may be due to protonation of the nitrogen atom at the lower pH. Variations were noted and acids with favorable adsorption characteristics chosen for further study.

Table II lists several characteristics of six acids that were chosen for further study as eluents in ion chromatography. The first acid dissociation constant approximates the percentage of the acid that is dissociated at any given concentration (such as 1.0 mM). However, the second dissociation constant must also be taken into account with divalent acids that have dissociation constants that are fairly close to one another. The adsorption of each

Table I. Adsorption of acids on XAD-1 resin column

Acid	Retention Time[a,b] (min) pH 6.7	pH 2.1
benzoic acid	1.45	~21
phthalic acid	1.04	7.15
1,3,5-benzenetricarboxylic acid	0.98	4.60
pyromellittic acid	1.10	1.40
salicylic acid	2.75	>30
sulfosalicylic acid	1.05	1.20
3,5-dihydroxybenzoic acid	0.98	1.96
2,4-dihydroxybenzoic acid	1.40	4.46
D,L-mandelic acid	1.14	3.69
nicotinic acid	0.98	0.98
isonicotinic acid	0.95	0.89
quinolinic acid	1.00	1.10
dipicolinic acid	0.98	2.40
picolinic acid	1.00	1.00
benzenesulfonic acid	1.60	1.60
p-nitrobenzoic acid	2.65	>30
p-aminobenzoic acid	1.00	1.44
sulfanilic acid	1.09	0.90
succinic acid	0.98	1.06
fumaric acid	0.98	1.10
citric acid	0.86	1.04

[a]Greater-than signs indicate that the acid was not detected in the listed period of time.

[b]t_o was 0.85 minutes.

Table II. Characteristics of acids used as eluents

eluent	pK_{a1}	pK_{a2}	pK_{a3}	% dissociation[a]	adsorption	equil. time, h	retention time, min
nicotinic acid	4.87			11	weak	1-1.5	3.9[b]
benzoic acid	4.19			22	strong	4-5	8.1
succinic acid	4.16			25	weak	1-1.5	3.9
citric acid	3.14	4.77	6.39	58	weak	2	14.1
fumaric acid	3.03	4.44		62	weak	2	14.7
salicylic acid	2.97	13.4		63	strong	3-4	37.2

[a]At 1 mM concentrations.

[b]Using 2×10^{-4} M phthalate, pH 3.75, with a 500 x 2 mm glass column containing 0.027 mequivalents/g XAD-1 functionalized with trimethylamine.

acid is described qualitatively from the results in Table I. The equilibration time is based on the time needed to obtain a steady base line when the eluent acid is pumped continuously through an anion exchange column. Retention times listed in Table II indicate the relative affinity of the functionalized resin for the acid in question. The retention times were determined by injecting the acids into an ion chromatograph and eluting with 2×10^{-4} M sodium phthalate at pH 3.75. The effectiveness of an acid eluent for eluting various sample anions should depend on several factors. A higher percentage of ionization means that a higher concentration of the acid anion is available to move sample anions down the column. It will be demonstrated shortly that a greater interaction (adsorption) of the eluent anion with the resin structure also tends to increase the effectiveness of an eluent to elute sample anions. The selectivity coefficient of the ion-exchange resin for the eluent anion is also an important factor in determining the ability of an acid to elute sample anions.

Table III lists the relative retention times of selected sample anions using the acid eluents chosen for this study. First, note the adjusted retention times for chloride. The adjusted retention time of chloride decreases as the retention time for the eluent anion increases (column 8 in

Table III. Relative adjusted retention times of various anions with different acid eluents (Cl^- = 1.00)[a]

anion	$t'/t'_{(Cl)}$					
	succinic	nicotinic	benzoic	salicylic	fumaric	citric
$H_2PO_4^-$	0.73	0.87	0.81	0.82	0.67	0.68
IO_3^-	0.77	0.76	0.91	0.80	0.88	0.79
NO_2^-	0.91	1.00	0.89	0.79	0.87	1.04
Cl^-	1.00	1.00	1.00	1.00	1.00	1.00
BrO_3^-	1.14	1.11	1.05	1.00	1.29	1.28
$MeSO_3^-$	1.22	1.11	1.00	1.03	1.19	1.22
Br^-	1.41	1.42	1.21	1.03	2.27	2.08
$EtSO_3^-$	1.60	1.52	1.16	1.13	1.87	1.79
NO_3^-	1.62	1.57	1.29	1.13	1.70	1.76
ClO_3^-	2.31	2.14	1.56	1.29	2.65	2.45
$PrSO_3^-$	3.96	3.31	2.11	1.71	4.84	4.22
I^-	7.63	3.91	2.53	2.82	10.5	9.53
t' for Cl^- (min)	14.9	25.7	8.00	1.14	3.87	5.16

[a]Conditions: TMA-XAD-1, 0.027 mequiv./g, 30-37μm, 1mM acid eluent.

Table II) and it also decreases as the amount of ionization of the eluent increases (column 5 in Table II). The relative adjusted retention times of the anions listed in Table III (with chloride taken as 1.00) are interesting to compare. Ions such as iodate and nitrite show rather small changes in relative retention time from one eluent to another. However, iodide shows some large variations, changing from a relative retention time of 2.53 for benzoic acid to 10.48 for fumaric acid eluent. Most of the anions studied show significantly different relative retention times for at least some of the eluents. Thus, two anions that are difficult to separate with one eluent may be easily separated with another. A case in point is bromide which has an adjusted retention time only 1.03 times that of chloride with salicylic acid, but has an adjusted retention time 2.27 times that of chloride with fumaric acid as the eluent.

Even though only monovalent anions are included in this table, it is not implied that divalent anions cannot be eluted with weak-acid eluents. The stronger acids in this study will elute divalent anions in a reasonable amount of time; in fact, salicylic acid will elute sulfate and thiosulfate in 5.2 and 7.3 minutes, respectively, using the

same conditions as listed in Table III. However, the weaker acids like succinic or nicotinic acid take an excessive amount of time to elute divalent anions.

Sensitivity

In this dissertation, the term "sensitivity" is used in its technically correct context as the change in detector signal per unit concentration and should not be confused with detection limits which are dependent on base-line noise. During this study, it became apparent that the sensitivities of the anions varied with the acid eluents used as well as among the different anions. These variations can be explained, at least on a relative basis, with the aid of the equation

$$\Delta G = \frac{[(\lambda_{E^+} + \lambda_{A^-}) - (\lambda_{E^+} + \lambda_{A^-})]C_B}{10^3 \cdot K} \qquad (1)$$

where ΔG is the change in conductivity in μmhos, the λ terms are the limiting equivalent conductances of the eluent and sample ions, I_E is the fraction of the eluent that is ionized, I_S is the fraction of the sample anion acid that is

ionized, C_S is the concentration of the sample component (C_{HS} + C_{S^-}), and K is the cell constant of the detector.

This equation shows that sensitivity is dependent on the extent of ionization of the eluent as well as the difference in equivalent conductances between the analyte and eluent anions. Therefore, as the amount of dissociation decreases, the sensitivity of the system increases. However, decreased dissociation also decreases the eluting power of the eluent. There is a trade-off between sensitivity and elution power with this system. The easiest way around this problem is to increase the eluent concentration. The sensitivity will change slightly as the extent of dissociation changes, but the strength of the eluent can be greatly increased.

The pH of the eluent acid should also be expected to affect the detection sensitivity for various anions. The detection sensitivity should be excellent for anions of strong acids (chloride, bromide, nitrate, etc.,) because the sample anion and the highly mobile hydrogen counterion are completely ionized. However, with anions of weaker acids (acetate, fluoride, etc.), some of the anion will be present as the molecular acid and the detection sensitivity will consequently be less (see equation 1). Furthermore, the detection sensitivity will become progressively less

Table IV. Relative sensitivities of eluent acids (Cl^- = 1.00)[a]

anion	succinic (pH 3.56)	benzoic (3.66)	nicotinic (3.95)	fumaric (3.13)	salicylic (3.20)	citric (3.17)	rel equiv. conductance
Cl^-	1.00	1.00	1.00	1.00	1.00	1.00	1.00
F^-	0.37	0.41	0.34	0.04	0.26		0.71
Ac^-	0.15	0.09	0.03				0.53
$H_2PO_4^-$	0.60	0.75	0.47	0.62	0.59	0.54	0.74
NO_2^-	0.60	0.63	0.21	0.08	0.46	0.03	0.94

[a]Ratio of (peak area/unit concentration) of a specific anion to that of chloride.

favorable as the pH of the eluent acid becomes more acidic.

Table IV lists the relative sensitivities of four weak acid anions compared to chloride using the six acid eluents that were investigated. The relative sensitivities of each anion were determined by injecting known concentrations of the sample anions, measuring the areas of the detector signals, and calculating the signal area to concentrations ratios. These sensitivity ratios were then normalized by dividing by the chloride sensitivity ratios found with the same eluent. It was assumed that chloride remained completely ionized in all cases.

The results in Table IV confirm that a lower eluent pH reduces the sensitivity of the detector for the weak acid anions in relation to the strong acid anions. It also demonstrates that the higher the pK_a of the analyte anion, the more it is affected by eluent pH. There are a few irregular and unexpected changes in sensitivities, such as with nitrite using nicotinic acid. However, these variations are probably caused by specific interactions between the anion and eluent in question.

Variations in limiting equivalent ionic conductances of the anions also affect the sensitivity that can be obtained. The last column in Table IV lists the ratios of the limiting

equivalent conductances of each anion to that of chloride. These ratios alone do not account for the observed sensitivity reductions, thereby confirming that the ionization of the analyte acid anion also plays a major role in sensitivity variations.

While the much lower detection sensitivity of the anions of weaker acids is sometimes a drawback, it can also be used as an advantage. It should be possible to detect small amounts of strong-acid anions in the presence of much larger amounts of weak-acid anions. Another advantage of having eluent acids of different pH available is that the selectivity can be altered. Divalent anions such as tartrate and oxalate, which normally elute quite late, can be eluted quickly by converting them to the monovalent hydrogen anion with more acidic eluent acid .

Table V lists some common eluents used in single-column and dual-column anion chromatography and the relative sensitivities obtainable with each in terms of (x), the concentration of the analyte anion. The changes in conductance were calculated by using equation 1, the concentration of eluent given in column 2 of Table V, a cell constant of 33 cm^{-1}, and assuming that the analyte anion has a limiting equivalent ionic conductance of 70 $mho \cdot cm^2/equiv$.

Table V. Calculated sensitivity variations

eluent	concentration (M)	ΔG
potassium biphthalate	2×10^{-4}	$0.94 \times 10^{3}(x)$
sodium benzoate	2×10^{-4}	$1.15 \times 10^{3}(x)$
TBA benzoate	2×10^{-4}	$1.15 \times 10^{3}(x)$
citric acid	1×10^{-3}	$5.40 \times 10^{3}(x)$
salicylic acid	1×10^{-3}	$6.28 \times 10^{3}(x)$
succinic acid	1×10^{-3}	$10.0 \times 10^{3}(x)$
benzoic acid	1×10^{-3}	$10.1 \times 10^{3}(x)$
sodium (carbonate/bicarbonate)	$3 \times 10^{-3}/2.4 \times 10^{-3}$	$12.7 \times 10^{3}(x)$

The first two eluents listed in table V are commonly used in single-column ion chromatography. Table V shows that these eluents have about a 10-fold lower sensitivity than the last eluent, which is the most commonly used eluent in dual-column ion chromatography. This lower sensitivity has perhaps been the major drawback of single-column ion chromatography. However, Table V clearly shows that a suitable acid eluent (such as benzoic or succinic acid) gives single-column ion chromatography almost the same sensitivity as that normally obtained in the more complex dual-column system. The slightly larger sensitivity of the dual-column system could be lost in broadening caused by the suppressor column or hollow-fiber suppressor (4,5). Nicotinic and fumaric acid are not listed in Table V because literature values for the limiting equivalent ionic conductances of these two anions were not located.

Detection limits

Table VI lists detection limits for chloride, fluoride, and nitrite with two different eluent acids. These limits were calculated from experimental data using a 100 µL sample loop. The limit of detection was taken as two times the standard deviation of the short-term noise. Detection

Table VI. Limits of detection (ppb)[a]

anion	succinic acid	nicotinic acid
chloride	26	5
flouride	20	4
nitrite	35	9

[a]Eluents were 1 mM at natural pH, 500 x 2 mm glass column, 0.027 mequiv./g XAD-1, trimethylamine exchanger.

limits can also be estimated theoretically by use of equation 1 and experimentally determined short-term noise.

The results in Table VI show that extremely low detection limits can be obtained with succinic or nicotinic acid. It should be mentioned that strongly adsorbed eluents cannot be used with sample anion concentrations this low because their base line stability is very dependent on fluctuations in temperature of the surrounding environment.

Table VII lists the retention time and peak height of chloride from 1 to 50 ppm. The purpose of this table is to demonstrate that this eluent system has excellent linearity and reproducibility over a reasonably wide analyte concentration range. Table VII is also intended to show that strong-acid analyte anions do not suppress the dissociation of the eluent to any noticeable extent. If this phenomenon was occurring, there would be an increase in the retention of chloride as its concentration increased.

Applications

Figure 1 is a chromatogram of a painting bath solution from a major appliance manufacturer. The only preparation required was filtration and dilution before injecting the

Table VII. Retention times and peak heights of various concentrations of chloride[a]

concentration (ppm of Cl^-)	retention time (cm)	peak height (cm)
52.0	5.97	13.78
41.6	5.84	11.11
31.2	5.94	8.46
20.8	6.00	5.64
10.4	5.96	2.77
1.04	5.92	0.73

X = 5.94 cm corr = 0.9991 rel std dev = 0.93%

[a]Using 1 mM succinic acid, 500 x 2 mm glass column packed with TMA-XAD-1, 0.027 mequivalents/g, 30-37 μm.

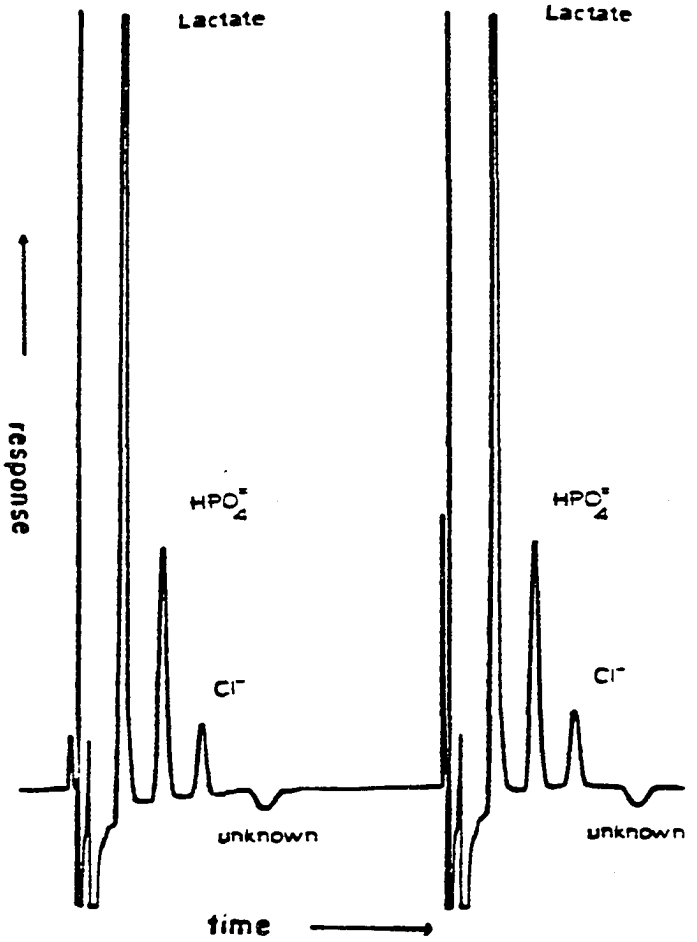

Figure 1. Chromatogram of a paint bath solution containing 6.91 ppm of phosphate with 1 mM succinic acid as the eluent

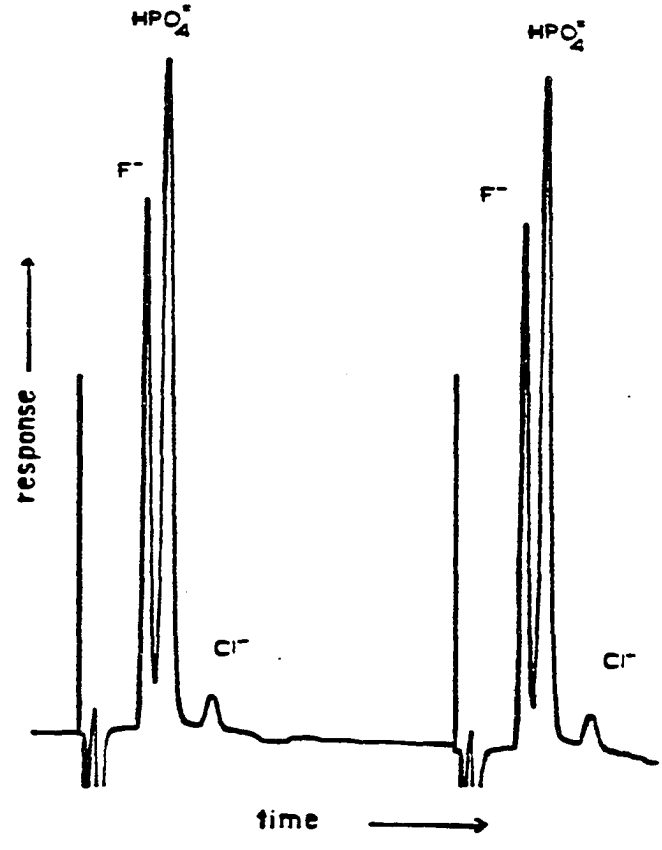

Figure 2. Chromatogram of a toothpaste solution containing 2.34 ppm of fluoride with 1 mM succinic acid as the eluent

sample into the chromatograph. The first peak is lactate, the second is phosphate, the third is chloride, and the last peak is unknown. The separation time was about 12 minutes and the phosphate concentration in the final sample was 6.91 ppm. The unkown peak is probably due to a polyphosphate but this assumption was not verified experimentally.

Figure 2 is a chromatogram of a toothpaste sample that was suspended in water, filtered, and then injected into the sample loop of the chromatograph through an XAD-4 (Rohm and Haas) precolumn to remove organics that tend to cause base line fluctuations. The first peak is fluoride (2.34 ppm), the second is phosphate, and the third is chloride. Total separation time is approximately 8 minutes using the conditions listed.

Figure 3 is a separation of 12 different anions using the weakest of the acid eluents that were tested. The chromatogram was included to show that early eluting anions could be separated from each other quite well simply by using a weaker eluent. The nicotinic acid concentration may also be increased enough to provide a separation of these anions in a much shorter time if desired.

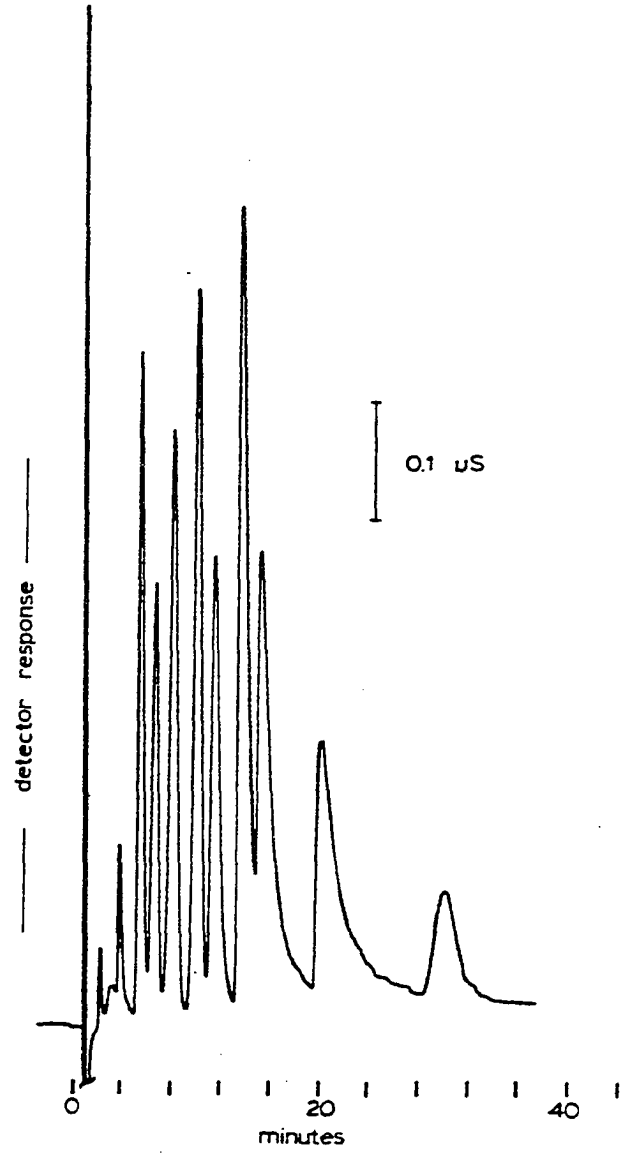

Figure 3. Separation of 12 early-eluting anions using a trimethyl amine exchanger chemically-bonded to XAD-1 (capacity; 0.027 meq/g). Eluent is 2mM nicotinic acid with a Wescan 213A conductivity detector. Peaks: acetate, propionate, azide, formate, fluoride, phosphate, chloride, bromate, bromide, nitrate, chlorate, and propylsulfonate

One difficulty involved with the use of an acid eluent is that an acid "dip" in the base line sometimes occurs during the chromatographic separation. Such a dip may be explained as follows. Some of the eluent acid is adsorbed during the column equilibration process. When a sample plug is injected that contains none of the eluent acid, some of the acid is apparently desorbed from the resin and is eluted with the first "pseudo" peak. After the sample plug has passed the portion of the column that lost some of the adsorbed eluent, some of the eluent acid is readsorbed onto the resin, thereby lowering the eluent concentration in the mobile phase. This causes a drop in the conductivity of the mobile phase and is detected as a "dip" in the base line conductivity. This dip can be avoided by making up the sample to contain the same concentration of the eluent acid as the eluent itself. However, a better answer to this problem is to select an eluent that is not adsorbed by the resin and therefore does not give any acid dip.

Another problem that arose during this work was that of base line fluctuations resulting from temperature-dependent equilibria. This tends to be more pronounced with eluents that are more strongly adsorbed. Fortunately, the problem is largely taken care of by proper insulation of the column and detector.

Conclusions

The advantages of single-column anion chromatography with acid eluents far outweigh the drawbacks mentioned. With a very simple system, numerous anions can be separated in a single chromatographic run. For most of the anions tested, the detection sensitivity is outstanding. Although the separations reported here were on columns containing polystyrene, acid eluents can be used on commercially available silica-based anion exchangers without excess column deterioration caused by the mobile phase pH.

Although salicylic acid is a reasonably powerful eluent, more work needs to be done to develop acid eluents more suitable for late-eluting anions.

SORBED EXCHANGERS

Introduction

Coating a porous, granular material with a liquid ion exchanger offers a convenient way to prepare exchangers for ion-exchange chromatography. In classical systems, a neutral support was coated with a liquid ion exchanger or with a solution of the ion exchanger in a water-immiscible organic solvent. Such methods have been reviewed by Cerrai (6) and by Braun and Ghersini (7). More recently Cassidy and Elchuk (5,8,9) published papers on permanently coating hydrophobic ionic modifiers onto commercial columns in a manner similar to the ion-pairing technique. The only difference is that with the method by Cassidy and Elchuk, the ionic modifier is sufficiently hydrophobic so that it will not come off the support in an aqueous solution. This permanent coating procedure offers a way of testing different supports for ion chromatography without having to functionalize the support first.

The present work has two major goals. One is to demonstrate that anion-exchange resins of low and varying

exchange capacity can be easily prepared by a static coating technique. The second goal is to demonstrate that these resins are economical and are satisfactory for practical ion chromatography.

Experimental

Equipment

A home-built HPLC chromatograph was used to measure retention times of various anions on the coated columns and to perform the separations included in this study. The chromatograph was comprised of the following components: a Milton Roy Mini-Pump manufactured by Laboratory Data Control (Riviera Beach, FL), a Mark III high pressure pulse dampener from Alltech Associates, Inc. (Deerfield, IL), a Rheodyne (Berkeley, CA) model 7010 injection valve with a 50 microliter sample loop, and a model 213A conductivity detector made by Wescan Instruments (Santa Clara, CA) with a measured cell constant of 33/cm. Other conditions are the same as described earlier.

Solutions were prepared from reagent grade salts and distilled, deionized water. Eluents were also prepared in distilled, deionized water using reagent grade acids. The

pH of the eluent was adjusted using a sodium hydroxide solution. Before using, the eluent was filtered through a 0.45µm membrane filter and stirred while under vacuum to remove dissolved gases.

Procedure

The statically coated resins were prepared using 30-37 micron, Soxhlet-extracted XAD-1 and XAD-8 resins from Rohm and Haas (Philadelphia, PA). About 0.75 grams of dried resin was weighed out into a 50ml glass beaker. Then, 3 to 10 ml of $1x10^{-2}$ M quaternary salt in acetonitrile was added to the beaker. Additional acetonitrile was added to the solution until the total amount of liquid added to the resin was 10 mL. The beaker was then placed in a sonic bath for 10 minutes. After sonication, the mixture was transferred to a 400 mL glass beaker and diluted to 350 mL with deionized water. The solution was allowed to settle for about 15 minutes; then the resin was filtered off and packed into 500x2 mm glass columns using a slurry packing method.

Chemically bonded resins were prepared from XAD-1 using a formaldehyde-hydrochloric acid procedure (2) to chloromethylate and trimethylamine or pyridine to quaternize the resin so that the final capacity was 0.027 meq/g.

Dynamically coated columns were prepared using commercial reverse phase columns from EM Reagents (Gibbstown, NJ) and from Hamilton Company (Reno, NV). The coating procedure was similar to the one Cassidy and Elchuk (5,8,9) used for their PRP-1 and C_{18} columns. The PRP-1 column was conditioned with 200 mL of HPLC grade acetonitrile, coated with 1 liter of $5x10^{-4}$ M cetylpyridinium chloride in 7% acetonitrile, and then conditioned with 1 liter of $5x10^{-4}$ M sodium phthalate (pH 6.1) before testing.

The C_{18}, C_8, and C_2 columns were conditioned with 200 mL of acetonitrile, then coated with 250 mL of $1x10^{-3}$ M cetylpyridinium chloride in 7% acetonitrile, followed by 500 mL of the phthalate eluent to condition and equilibrate the column. The amino and cyano-phase columns were conditioned with 200 mL of acetonitrile, coated with 250 mL of $5x10^{-3}$ M cetylpyridinium chloride in 7% acetonitrile, and then equilibrated with 500 mL of the phthalate eluent. A model 980A solvent programmer from Tracor Instruments (Austin, TX) was used to provide a gradual change from one solution to the next.

Results and Discussion

Static Coating of Resins

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

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

case, the coefficient of variation of retention times was 5.7%, indicating that the reproducibility of coating the resins was quite good.

Figures 4 and 5 show plots of adjusted retention times against the capacities of coated anion exchange resins. Both plots show a linear increase in adjusted retention times with coating thickness for most monovalent anions. This behavior can be predicted with the aid of equation 2, which can be readily derived from the fundamental ion exchange equilibrium

$$(t')^x = \frac{(\text{Capacity})^y(\text{Constant})}{[\text{Eluent}]^y} \qquad (2)$$

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

Fluoride, chloride, bromide, and nitrate all show nice linear plots in Figure 4. However, bromate and nitrite are not linear plots. This is because their selectivity

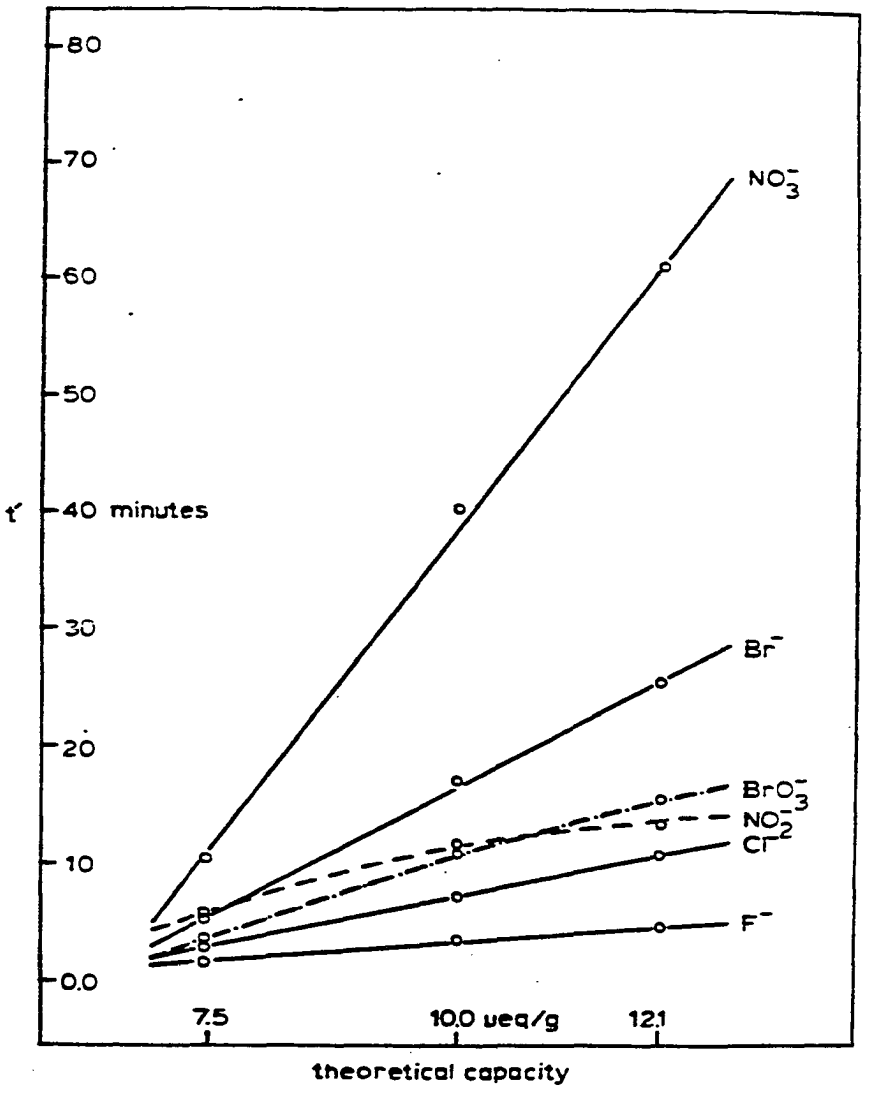

Figure 4. Plot of adjusted retention times of F^-, Cl^-, NO_2^-, BrO_3^-, Br^-, and NO_3^- versus theoretical capacity of coated XAD-8 resin. Experimental conditions: 30-37 µm neutral XAD-8; cetylpyridinium exchanger coated onto the resin; eluent, 1mM succinic acid; flow-rate, 1.0 mL/min

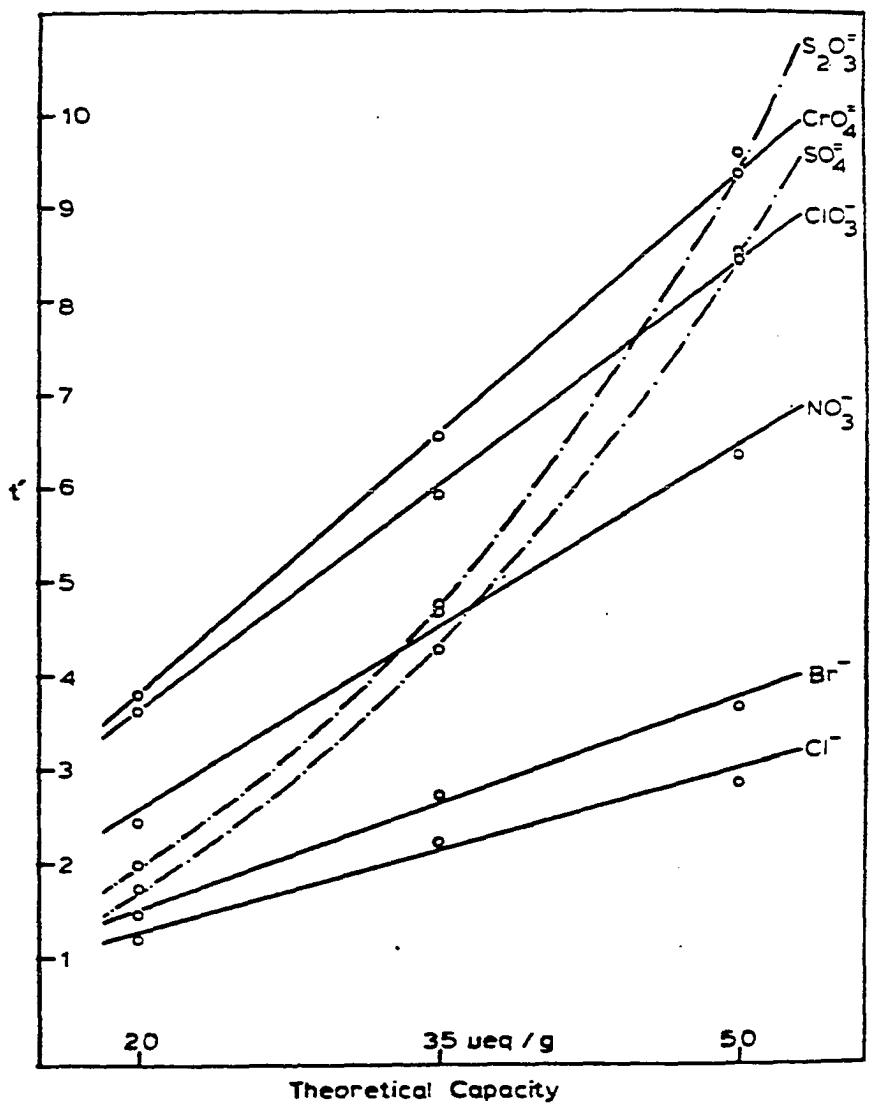

Figure 5. Plot of adjusted retention times of Cl^-, Br^-, NO_3^-, ClO_3^-, $SO_4^=$, $S_2O_3^=$, and $CrO_4^=$ versus theoretical capacity of coated XAD-8 resin. Experimental conditions: 30-37μm neutral XAD-8; cetylpyridinium exchanger coated onto the resin; eluent, 0.1 mM sodium phthalate, pH 4.5; flow-rate, 1.0 ml/min

coefficients vary with capacity in relationship to the other anions plotted. Selectivity variations with capacity are not uncommon and have been studied in great detail on resins of high capacity (10,11). Figure 5 again shows a linear increase in retention times with column capacity with the stronger eluent system for monovalent anions chloride, bromide, and nitrate; the nonlinearity of the sulfate and thiosulfate plots was expected because of the 2- charge. It is not surprising that chromate acts like a monovalent anion instead of a divalent because its second pK_a is 6.5 and the eluent pH is only 4.5. These two figures show that capacity, and hence retention times, can be varied quite easily by varying the coating thickness.

Although the coating procedure used gives reproducible results, it was found that only about 25% of the quaternary ammonium salt in solution is coated onto XAD-8 and about 37% is coated onto XAD-1. The percentage of exchanger coated onto the resin will vary if the ratio of resin weight to the volume of acetonitrile is not the same in each coating attempt. It was also determined that a maximum coating capacity of 0.090 meq/g and 0.078 meq/g could be obtained for XAD-8 and XAD-1, respectively. The exchange capacity of coated resins was measured by ion chromatography using a

nitrate displacement procedure described by Barron and Fritz (2).

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

Properties of Coated Organic Resins

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

Polyacrylic resins (XAD-7 and XAD-8) are also easy to coat. These resins are more polar and the coated resins remain wetted in aqueous solutions. The XAD-8 resin was found to have better performance and coating characteristics, and was selected for further study. An amide resin, XAD-11, was studied briefly but the various sorbed exchangers did not coat very well on this particular resin.

Comparison of XAD-1 and XAD-8, coated with cetylpyridinium chloride, confirmed that the former agglomerated in aqueous solutions to a greater extent. However, both are acceptable for use in anion chromatography using aqueous eluents. There are noticeable differences between these two resins in selectivity for certain anions. Cetylpyridinium chloride on XAD-1 has a slightly higher selectivity for the larger, more polarizable anions than trimethylamine chemically bonded to XAD-1, as shown by columns one and three in Table VIII. The same trend between the adsorbed exchanger and the chemically bonded exchanger is more evident in columns one and two in Table IX. The slight increase in selectivity follows nicely with studies done by Barron and Fritz (12,13) on chemically bonded ion exchangers which showed that the more hydrophobic the

exchanger, the greater its affinity for certain large monovalent anions.

The most interesting points of Tables VIII and IX are the differences in selectivity between cetylpyridinium chloride coated on XAD-1 and XAD-8 (columns three and four in Table VIII and columns two and three in Table IX). Both tables show that there is a much higher affinity for some of the larger monovalent anions on the more polar XAD-8 resin. This trend also agrees well with studies on high capacity polystyrene resins (10,11) which show that the less hydrophobic a resin is (less crosslinking), the greater its affinity for the larger monovalent anions. Column two of Table VIII is of XAD-1 with pyridine chemically bonded to the resin. The purpose here is to show that the selectivity changes that have been noted using cetylpyridinium chloride are not due to pyridinium quaternary structure, but rather to the overall hydrophobicity of the exchange group.

The remaining columns in Tables VIII and IX compare the selectivities of XAD-1 and XAD-8 resins coated with large tetraalkylammonium chlorides. Tetraoctylammonium chloride (TOACl) and tetradodecylammonium chloride (TDACl) show an even greater affinity than cetylpyridinium chloride for some of the large monovalent anions. This is to be expected

Table VIII. Adjusted retention times for early eluting anions relative to that of chloride (t'_A/t'_{Cl})[a]

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

[a]Conditions: eluent, 1mM succinic acid; flow-rate, 1.0mL/min, pH 3.54. Capacity of chemically-bonded resin was 0.027 mequivalents/g. Theoretical capacity of coated exchangers was 0.050 mequivalents/g. CPCl = cetylpuridinium chloride, TOACl = tetraoctylammonium chloride, TDACl = tetra-dodeclyammonium chloride.

Table IX. Adjusted retention times for late eluting anions relative to that of chloride (t'_A/t'_{Cl})

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

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

because of the increasing hydrophobic nature of these bulky quaternary ammonium salts. However, the differences in support polarity still have a large effect on the selectivity of these coated exchangers.

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

Properties of Coated Silica Resins

Cassidy and Elchuk (5,8,9) prepared viable columns for ion chromatography by coating commercial C_{18} reversed-phase silica columns and PRP-1 (organic phase) columns with a quaternary salt such as cetylpyridinium chloride. They used a dynamic coating procedure in which a solution of the quaternary salt in acetonitrile-water or in methanol-water is pumped through the column. The PRP-1 column coated in this manner is so hydrophobic that an organic modifier (such as acetonitrile) must be added to the eluent in order to obtain sharp peaks. The organic modifier suppresses the signal of the conductivity detector somewhat. A more polar anion exchanger would be more desirable.

The intent of this study was to find out if a more

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

Table X lists the results of the study of dynamically coated commercial columns. The results seem to contradict the results in the static coating study. The affinity for the more polarizable ions increases when going from the PRP-1 to the C_{18} and then the C_8 column. This agrees with the results on batch-coated resins which showed that as the polarity of the resin increases, its affinity for the more polarizable anions also increases.

When going from the C_8 to the C_2 and the cyano-phase columns, the affinity for the monovalent anions like nitrate and bromide decreases. This trend is the opposite of what would be expected because the polarity of the columns is increasing. However, the coating thickness is smaller on these columns, causing a decrease in their affinity for the later-eluting monovalent anions. When the support becomes more polar, the coating thickness of the column decreases if the concentration of the exchanger is held constant in the coating solution. Increasing the concentration of the

Table X. Selectivity ratios of permanently coated commercial columns (t'_A/t'_{Cl})

Anion	PRP-1[a]	C_{18}[a]	C_8[a]	C_2[b]	CN[b]
Fluoride[c]	0.53	0.47	0.54	0.68	
Iodate	0.56	0.43	0.47	0.52	
Acetate	0.65	0.47	0.86	0.91	
Nitrite	0.89	1.70	1.90	1.67	1.53
Chloride	1.00	1.00	1.00	1.00	1.00
Methylsulfonate	1.04	0.73	0.97	0.86	
Bromate	1.45	1.15	1.34	1.21	1.36
Bromide	2.01	2.23	2.58	2.04	2.26
Nitrate	3.17	3.49	3.63	2.69	3.82
Iodide		13.4	15.4	11.0	15.0
Chlorate	6.43	7.15	7.45	4.94	5.66
Sulfite	5.10	4.79	5.58	6.10	4.27
Sulfate	4.90	5.63	5.71	5.43	4.34
Tartrate	9.90	5.16	6.30	5.94	
Thiosulfate	13.4	17.0	19.5	9.58	15.0
t'_{Cl} (min)	7.68	3.10	3.68	4.08	1.92

[a]Eluent was 5×10^{-4} M sodium phthalate, pH 6.1.
[b]Eluent was 2.5×10^{-4} M sodium phthalate, PH 6.1.
[c]Fluoride loses were observed on all silica columns which prohibits quantitation of fluoride.

cetylpyridinium chloride in the coating solution by a factor of five for the C_2 and cyano-phase columns was not large enough to offset the reduced capacity. However, the results do show that the more polar commercial columns can be coated and that their selectivity variations follow the same general trend as seen before on the XAD resins.

In order to compare the relative selectivities of the coated silica columns for various anions, each column had to be coated, stripped and recoated several times. This was necessary to determine the correct solvent composition so that each column would have the same capacity. Cassidy and Elchuk (5,8,9) stated that the performance of the column deteriorates with each coating and can only be coated several times. The same problem was encountered in this study, and the columns were worn out before the proper coating conditions were found. Therefore, the coating conditions for all columns were kept as similar as possible so that information on both selectivity and coating thickness could be gathered under a given set of conditions.

A silica precolumn was always placed before the commercial silica based columns during coating and testing, but the longevity of these columns is considerably less than the poly(styrene-divinylbenzene) or acrylic ester resins.

Another problem that was encountered was eluent dips with the more polar silica based columns. The baseline perturbations are especially severe on the cyano-phase column. This was unexpected because the acrylic ester resin (XAD-8) gave no problems with eluent dips. Several attempts were also made to coat an amino-phase column but they were unsuccessful. Apparently, the column is too polar to permanently retain cetylpyridinium chloride on its surface.

Ion Chromatographic Separations Using Coated Resins

The usefulness in having resins with different selectivities for anions is illustrated by the separation in Figure 6. Under normal conditions, a chemically bonded trimethylamine XAD-1 resin column will not separate chloride and nitrite or bromide and nitrate very well. Figure 6 shows both pairs of anions to be well resolved on a coated XAD-8 column.

With coated columns it is easy to vary the exchange capacity as well as the chemical nature of the coating chemical. This is demonstrated in Figure 7 where the separation of several anions is improved by increasing the resin capacity. A faster separation of some anions can be achieved by using a resin of lower exchange capacity.

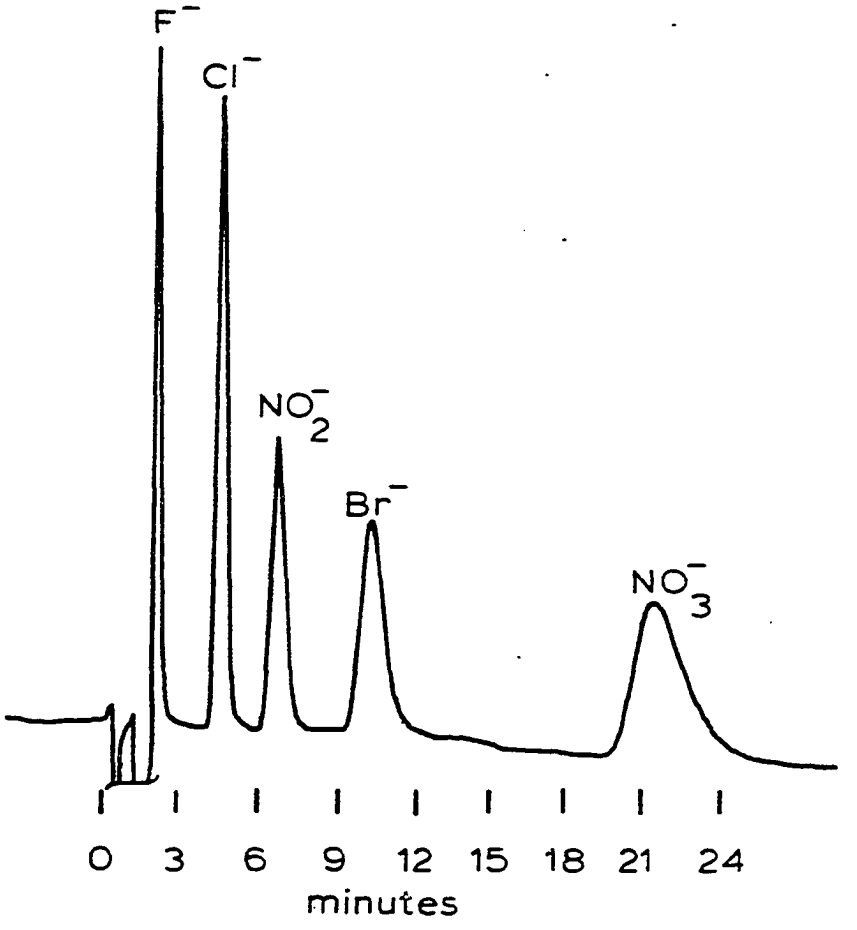

Figure 6. Chromatogram of F^-, Cl^-, NO_2^-, Br^-, and NO_3^- to show usefulness of XAD-8 coated resins for separating common ions. Experimental conditions: 30-37μm neutral XAD-8; cetylpyridinium exchanger coated onto the resin so that the theoretical capacity was 0.05 meq./g; eluent, 1 mM succinic acid; flow-rate, 1.0 ml/min

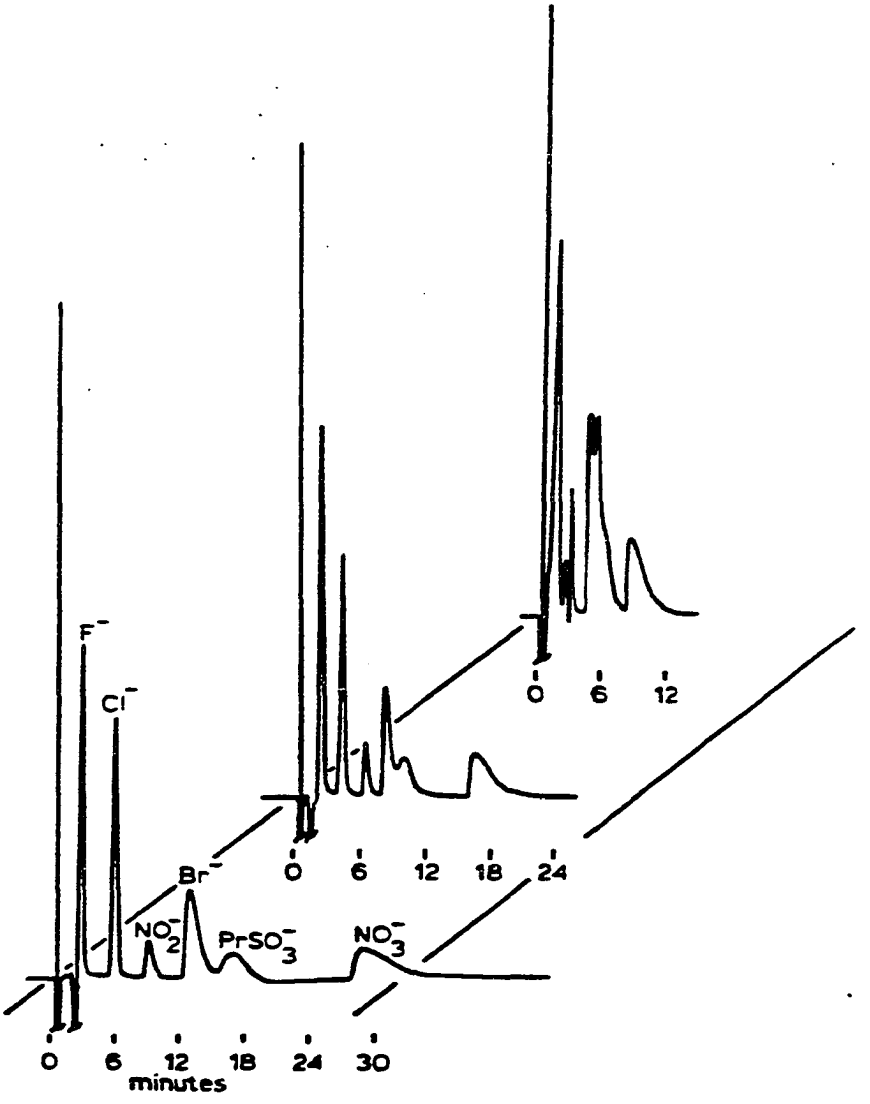

Figure 7. Chromatogram of F^-, Cl^-, NO_2^-, Br^-, propylsulfonate ($PrSO_3^-$), and NO_3^- to show how the capacity of the resin can be increased to resolve various anions. Experimental conditions: 30-37μm neutral XAD-8; cetylpyridinium exchanger coated onto the resin so that the theoretical capacity is 0.0121meq./g, 0.0100meq./g, and 0.0075meq./g, respectively from the bottom to top chromatogram. Eluent, 1 mM succinic acid; flow-rates were 1.88 mL/min

Conclusions

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

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

The type of support the ion exchange group is bonded to or coated onto has a large effect on ion exchange selectivities. This study also indicates that an acrylic ester resin or some other polar resin might be more useful for separating both major groups of anions (monovalent and divalent anions) in a single run.

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SECTION II. SELECTIVITY INVESTIGATIONS

SELECTIVITY THEORY

Classical Ion Exchange Theory

Theory

Since the invention of ion exchange chromatography, it has been noted that different ions have different affinities for the ion exchange resin. It has also been observed that these affinities can vary as experimental conditions are changed. The different models that have been formulated to explain these affinities and variations in affinities will be discussed in this section.

The ion exchange process is an equilibrium reaction that can be represented by the following equation;

$$x(R_y\text{-}E) + y(A^{-x}) \rightleftharpoons y(R_x\text{-}A) + x(E^{-y}) \qquad (3)$$

where E and A are the anions involved in the ion exchange process, x and y are the charges of the analyte anion, A, and eluent anion, E, respectively. R represents the exchange sites on the resin and R-A and R-E are notations indicating that the anions are in the stationary phase.

The ion exchange process can be defined using

thermodynamics. Unfortunately, the more rigorously the process is defined by thermodynamics, the more abstract the process becomes. A more useful understanding of the system can be obtained if the system is defined in terms that are easier to measure physically. Both approaches to understanding the exchange process will be discussed.

An equilibrium constant, $K_{A/E}$, called the selectivity coefficient can be used to define the equilibrium process according to equation 4,

$$K_{A/E} = \frac{[R_y\text{-}A]^y [E]^x}{[A]^y [R_y\text{-}E]^x} \qquad (4)$$

where $K_{A/E}$ is the selectivity coefficient and the other terms are the same as defined for equation 3.

In ion chromatography, the concentration of the eluent species, E, is much larger than the concentration of the analyte species, A, in both the stationary and mobile phases. Therefore, the relative fractions of each species remains constant in both phases. According to Dybczyński and Wódkiewicz (1), if the relative fractions of each species remains constant, a corrected selectivity coefficient, $K'_{A/E}$, can be related to the system's free energy change by equation 5 (corrected selectivity

coefficient means that the concentrations of the analyte and eluent ions have been replaced by activities in equation 4).

$$\Delta G = -RT\ln K'_{A/E} \qquad (5)$$

ΔG is the free energy change of the system, T is the absolute temperature of the system, and R is the ideal gas law constant. Equation 5 predicts that any change in the system that affects the free energy of the system will also affect the equilibrium of the exchange process and could cause changes in the selectivities of various ions.

If $K'_{A/E}$ is measured at different temperatures, enthalphy changes can be calculated using equation 6;

$$\Delta H = -2.303R \frac{d(\log K'_{A/E})}{d(1/T)} \qquad (6)$$

where ΔH is the enthalpy change of the system at the different temperatures, $d(\log K'_{A/E})$ and $d(1/T)$ signify the derivatives of the terms in parentheses, and R is the ideal gas law constant. If the free energy and enthalpy changes are calculated and combined, the entropy change in the system can be calculated using equation 7;

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (7)$$

where ΔS is the entropy change in the system. Equations 5, 6, and 7 demonstrate that the ion exchange process can be described in terms of free energy, enthalphy, and entropy changes. If one knows how these thermodynamic terms are affected when one ion is exchanged for another, they can develop a thermodynamic model to explain the relative affinities of the ions for the resin phase.

The major problem with this approach is that the specific mechanism or mechanisms that affect retention and selectivity are not described. If the individual components of the chromatographic system are analyzed in a systematic manner, a better understanding of the interactions that affect selectivity can be obtained.

The first step in this mechanistic approach is to modify equation 4 in a different manner. In chromatographic operations [E] is simply the eluent concentration and can be written as [eluent]. The ratio of $[R_y\text{-}A]$ to [A] is a distribution ratio, D, and $[R_y\text{-}E]$ is the column capacity which remains essentially constant. Substituting these changes into equation 4 gives equation 8.

$$K_{A/E} = D^{Y} \cdot \frac{[\text{eluent}]^{x}}{(\text{capacity})^{x}} \qquad (8)$$

The adjusted retention time of the ion, the weight of the resin in the column, and a constant can be substituted into equation 8 for the distribution ratio to give equation 9;

$$K_{A/E} = \frac{t'^{y}}{W^{y}} \cdot \frac{[\text{eluent}]^{x}}{(\text{capacity})^{x}} \cdot C_1 \qquad (9)$$

which can be rearranged to give equation 10.

$$\log(t') = -\frac{x}{y}\log[\text{eluent}] + \frac{x}{y}\log(\text{capacity}) - C_2 \qquad (10)$$

This equation predicts how the adjusted retention time of the various ions will change with eluent concentration, eluent charge (this would be pH dependent), and resin capacity. Equation 10 predicts how changes in the basic parameters of the system will alter selectivities. However, equation 10 does not explain what interactions actually cause selectivity.

Ion exchange models

The theoretical models used to explain ion exchange selectivity vary mainly in what components and reference states of the system are defined. Helfferich (2) points out that the components of the ion exchange system were originally defined as the salt of a macromolecular species (the support), a solid ion-exchange acid or base (the exchange site), the dissolved electrolyte (the eluent), and the solvent. Kielland (3), Gaines and Thomas (4), and Vanselow (5) used these components to develop theoretical models based on the thermodynamic properties of the system. Bauman also developed a theoretical model (6) based on thermodynamics but described the ion exchanger as a concentrated aqueous electrolyte containing one immobile species. These models do not point out the physical interactions affecting selectivity, they only help in visualizing the system.

Gregor (7) described the first semimechanistic model. In Gregor's model, the resin was pictured as a network of elastic springs (the crosslinking) and a polyelectrolyte (the exchange groups). The solvating effect of the surrounding water structure supposedly causes the resin to swell and exert a stress (swelling-pressure) on the

crosslinking of the resin. The resin continues to swell until further stretching of the crosslinking in the resin (the elastic springs) require more energy than is gained by increased solvation of the resin. The swelling pressure on the system affects the extent of swelling, the amount of sorption, and the position of the ion-exchange equilibrium.

Gregor's model considers the ion exchange sites, the solvent, and the various mobile ions (with their solvated shells) to be part of the system. In this model, selectivity arises from the effect the counter ion has on the swelling pressure of the resin. Any ion that causes the resin to shrink will reduce the swelling pressure and will be preferred by the resin. The resin will shrink when the internal water volume is reduced, and hence, when ions of smaller hydrated radii are exchanged for ions of larger hydrated radii. Gregor's model works at least qualitatively for alkali metals and other systems where the swelling pressure effect is not dominated by the effects of other forces. One of these other forces could be electrostatic attractions.

Lazare et al. (8) extended the original model proposed by Gregor to include electrostatic interactions. Including electrostatic interactions in the model allows consideration

of charge differences between two ions. The models introduced by Gregor (7) and Lazare et al. (8) are purely mechanical models and are on a macroscopic scale. They do not consider interactions that could be occurring on a molecular scale.

Katchalsky and Lifson (9) and Rice and Harris (10) introduced similar models that were developed originally for polyelectrolytes and later extended to include crosslinked gels. The major difference between these two theories and the previous models is that these models were developed on a microscopic scale. The elasticity of the matrix (and hence selectivity) was assumed to be caused by an increase in entropy which accompanies increased coiling of the polymer chains. Therefore, the selectivity is not caused by a mechanical effect, but rather an energetic effect.

Both models also include electrostatic effects to explain selectivity differences for solutions of linear polyelectrolytes. However, these models do not explain selectivity crossovers and reversals with changing experimental conditions. These changes in selectivity can be explained using Gregor's model (7). According to Gregor, if the amount of free water in the resin phase is reduced by changes in the system (such as high electrolyte

concentrations), some ions lose the outer layers of their hydration shell because the ions must compete with each other for the remaining water molecules to fill their hydration shells. As the hydration layers are removed from these ions, their sizes will change in comparison to other ionic species and their affinity for the resin will change.

There are several differences between the microscopic models proposed by Katchalsky and Lifson (9), and Rice and Harris (10). The two models differ in how electrostatic attractions are calculated. Rice and Harris's model also allows for ion-pair formation and can be extended to resins with a greater degree of crosslinking.

Eisenman (11,12) modified the mechanistic models mentioned previously in two respects. First, he considered the energetics of the hydration of ions to be of primary importance, not hydrated size. Hydration reduces the charge density of an ion and thereby reduces the electrostatic free energy of the ion. Second, electrostatic interactions are presumed to be the primary cause of selectivity changes, not changes in hydrated volumes.

Models explaining anion selectivity

It should be noted that the vast majority of the work

done in ion-exchange chromatography during this time (ca. 1940s and 1950s) was done with cation exchange resins and most of the ion exchange theories were developed mainly for cation exchange chromatography. The major problem with using ion-exchange theory developed from cation exchange chromatography and applying it to selectivities found in anion exchange chromatography is that the two systems are quite different. While anions have been shown to have a higher tendency to form hydration layers for ions of the same size, most anions are larger than most cations so they usually have a smaller number of hydration layers surrounding them. The selectivity of anions is therefore less dependent on the free energy change caused by hydration.

Another problem mentioned earlier about using theories developed for ion exchange chromatography for ion chromatography is the differences between the resin phases. Ion exchange chromatography uses high-capacity gel resins that have small pores, small surface areas, low amounts of crosslinking, and are considered hydrophilic. Ion chromatography uses low-capacity macroreticular resins that have large pores, large surface areas, a high amount of crosslinking, and are hydrophobic in nature. These

differences may prevent the use of theory developed for ion exchange chromatography in ion chromatography.

Chu et al. (13) qualitatively explained most anion selectivities as a result of hydration energy differences of the anion in the mobile phase in 1962. This model is similar to Eisenman's model for cations. However, Chu et al. (13) also mentions that the hydrocarbon matrix can affect the hydration shell of the anion. Chu and coworkers were the first researchers to mention a possible interaction between the ion and the resin itself.

The models based on pressure-volume changes (7,8,9,10) qualitatively predict the right selectivity order for cations, but fail qualitatively to predict the right selectivity order for most common anions (14) and even for large cations (15). Rice and Harris (10) explain the swelling of resins as a result of selectivity, not the cause of selectivity. However, using electrostatic ion-pairing (10) to explain selectivity also fails for anions. If electrostatic ion-pairing is a primary factor affecting selectivity, small ions with a high charge density should be preferred by the resin. With anion exchange resins, the opposite trend is observed.

It should be noted that liquid ion exchangers such as

the quaternary ammonium salts in organic solvents demonstrate selectivity orders similar to those found with resin-based exchangers. However, the liquid ion exchangers have no resin matrix and cannot have any pressure-volume effects.

Other researchers have suggested that anion exchange selectivity may also be affected by polarization (16). Large ions with a low charge density can be more easily polarized and would have a greater-than-expected drop in electrostatic free energy as the polarized ion get closer to the exchange site. The extra decrease in free energy caused by polarization might be used to explain the selectivity order for some ions like the halides ($F^- < Cl^- < Br^- < I^-$) but fails for other series of anions ($ClO_3^- > BrO_3^- > IO_3^-$ and $MnO_4^- > TcO_4^- > ReO_4^-$). There is also a conceptual problem with how the large resin ion (benzyltrimethylammonium cation) can polarize the large anions considering the low charge density of the resin ion. Usually, ions with a high change density are assumed to cause polarization of other ions.

Another selectivity sequence that hasn't been explained by any of the models mentioned so far is for the small carboxylic acid anions (acetate < propionate < formate < butyrate).

In 1962, Diamond and Whitney (17) proposed a mechanistic model that can be used to explain even the selectivity sequence found for the organic acid anions. They first considered the various possible interactions that could occur in the ion exchange system and then estimated which interactions would have the greatest effect on the relative selectivities of anions.

The four interactions considered by Diamond and Whitney to be possible in the ion exchange system are; water-water, ion-water, ion-ion, and ion-resin matrix interactions. After discussing results from other researchers and their own work, they concluded that water-water and ion-water interactions were the main cause of selectivity in anion exchange chromatography. Since Diamond and Whitney's model appears to explain variations in anion exchange chromatography better the models described earlier, it is described in more detail below.

Interactions

Water-water interactions could be of primary importance because water molecules at room temperature form a highly organized network of water molecules sometimes described as an elastic lattice structure. These intermolecular forces

are quite strong. The water structure tends to reject any other species unless it is hydrophilic or charged so that the species interacts more with the water molecules than the water molecules interact with each other. The water structure forces large ions of opposite charge together in the same water cavity to minimize their combined disturbance of water structure. This water-structure-enforced ion-pairing is different than the Bjerrum-type or electrostatic ion-pairing which occurs with small ions of high charge density.

Spectroscopic work reviewed by Barron (18) demonstrated that large cations and anions tend to cause a general tightening of the water structure around cavities formed by the ions. The work discussed also showed that the larger the ions are, the greater their disturbance of the water structure, and the greater their tendency to form water structure cavities. Theoretically, the tightening of the water structure could be viewed as causing a decrease in entropy. This means the ions that disturb the water structure the most (the larger ions), cause the greatest decrease in entropy, and are energetically less preferred by the mobile phase. Therefore, if water-water interactions affect affinities, the larger the ion, the more it should prefer the stationary phase.

Ion-water interactions are caused by the charge on the ion. The ions try to reduce their electrostatic free energy by reorienting water molecules around themselves. Diamond and Whitney (17) concluded that this interaction would be important mainly with cations and a few small anions like OH^-, F^-, and $CO_3^=$ because these ions are smaller and more hydrated. Anions should also be able to interact with the hydrogen atoms in water molecules because of their Bronsted base (proton acceptor) character. This interaction would be very dependent on the dissociation constant of the parent acid.

Ion-ion interactions result from ions trying to reduce their electrostatic free energy by associating with ions of opposite charge. The electrostatic free energy of two ions of opposite charge decreases as the ions get closer to each other. Besides these monopole-monopole (ion-ion) interactions, there can also be multi-pole interactions between ions caused by polarization and dispersion forces. If ion-ion interactions were the major factor influencing the selectivities, ions with the highest change density (small ions like fluoride) would have the largest affinity for the exchange site on the resin. The opposite selectivity trend is observed in both anion exchange

chromatography and anion chromatography so ion-ion interactions are not the main cause of anion selectivities.

The fourth posible interaction discussed by Diamond and Whitney (17) is ion-resin matrix interactions which are the result of dispersion forces acting between large anions and the aromatic rings in the support. It was pointed out earlier that Chu et al. (13) mentioned the possible interaction of the ion (or its hydration shell) with the resin matrix.

Relative importance of different interactions

From results in classical anion exchange chromatography, Diamond and Whitney concluded that the two interactions of primary importance are water-water interactions and ion-water interactions. It was mentioned earlier that water-water interactions would tend to force larger anions out of the water phase and onto the resin phase (to minimize the disturbance of the water structure caused by the anion). The ion exchange group on the resin is also a large bulky ion and can cause a disturbance of the water structure because the ion extends out from the resin surface into the water phase. The water structure will have a tendency to force the resin ion and the counter ion into the same cavity to reduce their overall disturbance of the water structure.

Since the resin ion is not completely enclosed by the water structure, the pairing of a large anion with the resin ion causes less disturbance of the water structure than if two ions of the same size were paired in the mobile phase. This would enhance the preference of a large anion for the resin.

Water-water interactions do not account for selectivity differences between anions of the same hydrated radii. Trimethylacetate, methyldichloroacetate, and trichloroacetate are very similar in size but trichloroacetate has a higher affinity for the resin than methyldichloroacetate or trimethylacetate. Methyldichloroacetate also has a higher affinity for the resin than trimethylacetate. Diamond and Whitney proposed that this difference is caused by ion-water interactions. These ions are not hydrated to any extent. However, they proposed that these completely dissociated anions can still have some interaction with hydrogen atoms in the water molecules. They also proposed that this interaction is directly related to the dissociation constant of the ion. The more acidic an anion is, the less it will interact with the water structure because the anion has a lower tendency to accept a proton from water in a hydrogen bond fashion. Therefore, the more acidic anions will have a higher

preference for the stationary phase. This effect correctly predicts the selectivity order of trichloroacetate > methyldichloroacetate > trimethylacetate.

In conjunction with water-water interactions, ion-water interactions correctly predicts the selectivity order of acetate < proprionate < formate < butyrate. When ion-water interactions are considered, formate is expected to be an abnormality because the pK_a of formate, (3.75), is much lower than the approximate pK_a values of the other anions in the sequence (4.8). The lower pK_a of formate indicates that the ion interacts less with the surrounding water molecules and should have a higher than expected affinity for the resin. When formate is excluded from the sequence, the selectivity order follows the size order predicted by the water-enforced ion-pairing model (the larger the anion, the more it prefers the stationary phase).

Weak-base anion exchange resins show an increased affinity for the smaller anions. Presumably, this is caused by the hydrogen atom in the exchange site interacting with the hydration layer of the small anions.

To summarize the effects of these two major interactions; as the hydrated ionic size of an anion increases, its affinity for the ion exchange resin

increases. The affinity of the ion exchange resin for the anion also increases as the pK_a of the anion decreases. Another effect of slightly less importance is that anions containing hydrophobic groups such as aromatic rings or aliphatic groups have an increased affinity for the ion exchange resin because of interactions with the resin.

Divalent anions are frequently cited as having a higher affinity for the resin phase in comparison to monovalent anions because of electrostatic attractions. This generalization is normally intended for cations but has also been applied to anions. If electrostatic interactions (Bjerrum-type ion-pairing) are the main interaction, there should be a increase in the resin affinity with increasing charge. Reference (19) demonstrates that for anions of the same size, the resin affinity decreases with increasing ion charge. Divalent anions appear to have a higher affinity for the resin than most monovalent anions presumably because of differences in size ($WO_4^{=}$, $CrO_4^{=}$, and $S_2O_3^{=}$ are rather large anions).

Clifford and Weber (20,21) recently investigated high capacity commercial resins for factors that affect the affinity of monovalent and divalent anions for the resin. Their study involved thirty commercial resins with a variety

of characteristics. The commercial resins did not have characteristics that were varied systematically so it was hard to draw conclusions from their results. However, Walpole and Myers (22) used analysis of variance to find statistically significant affinity trends and concluded that the resin matrix and functional group were the two most important factors affecting selectivity.

In classical ion exchange systems, three main parameters have been varied to study selectivities; resin crosslinking, resin exchange capacity, and functional group type. It has generally been found that as the amount of crosslinking is increased, the affinity of the resin for the larger monovalent anions increases. As the exchange capacity of the resin increases, the affinity of the resin for the larger monovalent anions also increases. Finally, the functional groups of strong-base anion-exchange resins are divided into two categories, Type I and Type II resins. Type I resins contain the benzyltrimethylammonium exchange site and usually demonstrates a higher affinity for the larger monovalent anions and lower affinity for divalent anions over the Type II resins which contain the benzylhydroxyethyldimethylammonium exchange site.

There have been some studies with cations where the

mobile phase of the chromatographic system was investigated, but the vast majority of selectivity work with anion exchange separations have involved only the stationary phase.

If Diamond and Whitney's views on anion exchange selectivity are valid, the major influence on selectivity is the mobile phase (the highly hydrogen-bonded water system) and how it interacts with ions and the resin phase. Therefore, two parameters of the chromatographic system that should have a large affect on selectivity are the exchange site and the resin matrix. These conclusions agree with the conclusions of Walpole and Myers (22) mentioned previously. Other parameters that should also affect the interactions predicted by Diamond and Whitney (17) are temperature, cosolvent composition, ionic strength of the mobile phase, anion structure, exchange site size, exchange site polarity, and resin structure.

Investigations in Ion Chromatography

In the following paragraphs, previous studies in ion chromatography that exhibited selectivity variations predicted by equation 10 are reviewed. Recent

investigations are also described which investigate selectivity variations which are not predicted by equation 10 but are predicted by Diamond and Whitney's ion exchange model. Equation 10 predicts logarithmic relationships between capacity and adjusted retention time and between eluent concentration and adjusted retention time. The equation also predicts how the charge on the eluent anion and analyte anion will affect the adjusted retention time of the anion. Research in single-column ion chromatography indicates that this equation is valid for the parameters that are included in the equation.

Capacity

In 1979, Gjerde and Fritz (23) published a method for preparing low-capacity anion-exchange resins for ion chromatography. They reported that log plots of capacity versus distribution ratios followed equation 10 (within experimental error) until a plateau was reached. The plateau at high capacity was explained as a result of the eluent anion, carbonate, being retained more efficiently by the resin as the capacity increased and the exchange sites became closer together.

Barron and Fritz (24) also investigated the effect of

capacity on retention times of monovalent and divalent anions. They reported that as the capacity of the resin increased, the retention times of the monovalent and divalent series of anions became closer in value except for thiosulfate. The thiosulfate abnormality is probably caused by the size of the anion. Even though thiosulfate is a divalent anion, it might be large enough to be affected by water-enforced ion-pairing like large monovalent anions.

DuVal and Fritz (25) investigated the effect capacity has on adjusted retention times using sorbed ion-exchangers instead of chemically bonded ion-exchangers. The results showed a linear increase in the retention of most monovalent anions as capacity increased. The divalent anions, $SO_4^{=}$ and $S_2O_3^{=}$, gave logarithmic plots that showed an increase in the relative retention times of both divalent anions in relation to monovalent anions as the capacity increased (predicted by equation 10). This trend is opposite of the trend reported by Barron and Fritz (24). It should be pointed out that the results reported by Barron and Fritz (24) were completed using a chemically bonded anion exchanger on XAD-1 (a macroreticular polystyrene-divinylbenzene) while the study by DuVal and Fritz (25) was done using a sorbed anion exchanger on XAD-8

(a macroreticular polymethacrylate). Therefore, the physical structure of the two systems are vastly different and a comparison of the results from the two studies should not be considered significant.

Eluent concentration

Work by Gjerde et al. (26) on single-column ion chromatography demonstrated that a logarithmic plot of adjusted retention times of analyte anions versus eluent concentration is linear. This relationship is predicted by equation 10. Later work reported by Glatz and Girard (27,28) reiterated the results reported by Gjerde et al. (26).

Eluent pH

Gjerde et al. (26) showed that eluent strength changed with pH and that as the pH increased and the eluent (sodium phthalate) became a divalent eluent anion, it reduced divalent analyte anion retention times to a greater extent than monovalent anions. These phenomena were also reported later by Glatz and Girard (27,28). Other work (29,30,31) demonstrated that eluent pH could be used to affect sensitivity. Japanese workers (29) showed that a very basic

eluent would increase sensitivity by a factor of three because the highly conductive hydroxide anion is the eluent anion. Acid eluents (30,31) increase sensitivity by a factor of 9 or 10 because the eluent is only partially dissociated. The pH extremes can also affect selectivity by changing the amount an analyte anion is dissociated. At low pH values, tartrate and succinate are monovalent anions and elute relatively early, while at higher pH values, tartrate and succinate are divalent anions and elute quite late. Cyanide and silicate are ionic species only at high pH values so they can be determined by ion chromatography only with alkaline eluents.

Eluent type

A large variety of eluents with inorganic, aliphatic, or aromatic anions have been investigated (31,32,33) for possible use as eluents in single-column ion chromatography. Fritz et al. (31) pointed out that selectivity changes occur when the eluent contains an aromatic acid anion rather than an aliphatic acid anion. They also pointed out that baseline stability and system dips were less of a problem with the aliphatic anion eluents. Both trends indicate that the aromatic acid anions interact more with the resin and

this interaction affects the elution ability of the eluent anion.

Cosolvents

Organic cosolvents have been avoided in ion chromatography because these solvents cause gel resins to swell and greatly increase column back-pressure. Organic cosolvents also suppress the ionization of the analyte species which decreases sensitivity when a conductivity detector is used. With the advent of macroreticular resins and silica-based supports, cosolvents have been used to some extent to improve peak shape and to prevent bacterial growth in some eluents.

Skelly (34) and Iskandarani and Pietrzyk (35) have done ion-pair chromatography of inorganic anions using reverse-phase HPLC columns. Both publications indicate that the amount of cosolvent (methanol or acetonitrile) in the aqueous phase has an effect on the retention times of various anions. However, the variations in retention times were explained to be the result of a change in the amount of ionic modifier (tetraalkylammonium cation) adsorbed on the resin surface as the cosolvent concentration change. Changes in the relative affinities of anions for the stationary phase were not reported.

Buechele and Reutter (36) demonstrated that methanol does effect relative affinities of various cations. In their study with methanol, the retention times of the alkali metal ions reached a minimum at 10 to 15% methanol and then increase dramatically as the methanol concentration was increased to 40%. The retention times of the larger alkali metal ions (which have the smallest hydration layers and the highest resin affinity) were affected the most.

Buechele and Reutter (36) also found that methanol has a different effect on larger monovalent cations like protonated amines. The larger cations do not form a significant hydration layer. The retention times of the protonated amines decrease quickly from 0 to 10% methanol. However, the retention times of the amines do not increase at higher concentrations of methanol like the smaller cations did. Instead, the retention times continued to decrease but at a more gradual rate as the methanol concentration was increased from 10% to 40%. They also reported a 33% drop in the analyte signal at 40% methanol. The background noise also drops by about 10% so the change in detection limits was not as drastic as the change in signal.

These changes in selectivity can be explained by

classical ion exchange theory. According to Diamond and Whitney (17), anything that disturbs or lowers the amount of water-water interaction should decrease the retention times of the larger ions. These results indicate that anion selectivities should also be affected by adding a cosolvent to the system.

Exchange group

There is a lot of work done with Type I and Type II resins in classical ion-exchange chromatography which has been reviewed by Barron (18). The primary conclusion from these studies was that the more hydrophobic Type I resin has an increased monovalent affinity and a decreased divalent affinity in comparison to the more hydrophilic Type II resins.

Skelly (34) and Iskandarani and Pietrzyk (35) optimized ion-pair separations of inorganic anions by varying the chain length of the ionic modifiers used in the separations. The chain length parameter of the tertiary amines and quaternary ammonium ions was used to speed up or slow down separations and was not used to vary relative affinities of the ions.

Barron and Fritz (24,37) showed that the size or

hydrophobicity of the ion exchange group has a major effect of relative selectivities. They found that for ion-exchange groups of the same size, the less polar ion-exchange group has a higher affinity for monovalent anions. It was also found that the larger the exchange group, the higher its affinity for the larger monovalent anions and the lower its affinity for divalent anions. DuVal and Fritz (25) found the same trends with sorbed exchangers. All three studies (24,25,37) found that ion exchange sites which contained ring structures with a heteroatom (pyridine, N-methyl morpholine, and N-methyl piperidine) had no unusual effect on relative selectivities. The relative selectivities of these ion exchangers were dependent mainly on the size and polarity of the exchange site.

Clifford and Weber (20,21) reported that the increased monovalent anion affinity and decreased divalent anion affinity characteristics of the commercial "brine column" sold by Dionex (Sunnyvale, CA) is caused by a triethylbenzylammonium ammonium exchange site instead of the normal triethylbenzylammonium exchange site. The phrase "brine column" means that the affinity of sulfate is reduced so that late eluting monovalent anions are eluted after sulfate and can be measured in solutions containing high concentrations of sulfate (brine solutions).

Resin type

The first paper on single-column ion chromatography by Gjerde et al. (38) indicated that XAD-1 anion exchangers appeared to have stronger hydrophobic interactions with large monovalent anions like I^- and SCN^- over conventional gel type resins. Afrashtehfar and Cantwell (39) reports evidence that the resin matrix has an influence on the retention of ionic species on low capacity resins. This points out that the resin support might indeed play a part in varying the relative affinities of the ion exchanger for different ions. Work by Cantwell and Puon (40) demonstrated that larger monovalent ions like Br^- and ClO_4^- that have essentially no hydration layer can indeed be adsorbed by the resin surface while smaller hydrated ions like Cl^- are not appreciably adsorbed. Skelly (34) also studied the effect of support polarity on ion-pair separations but was concerned mainly with efficiencies and total chromatographic time, not in relative affinities.

DuVal and Fritz (25) showed that support type and polarity had a dramatic effect on selectivity and could be used to improve specific separations in ion chromatography. Barron (18) also demonstrated in a brief study that if the support polarity was changed by derivatization (ca.

acetylation), relative affinities of different ions for the support could be changed. The interesting point about the effect of support polarity on the resin is that as the polarity of the support increases, the affinity of the resin for large monovalent anions increases while its affinity for divalent anions decreases. This trend is opposite of the trend with the exchange site hydrophobicity. An explanation for this discrepancy will be given in the results and discussion part of this section.

SELECTIVITY INVESTIGATIONS

Introduction

Previous work in ion chromatography demonstrates that capacity (20), exchange group type (24), eluent concentration (26), eluent charge (26), and eluent type (26) have an affect on the affinity of the ion exchange resin for various anions. These results contradict earlier work in ion exchange theory (7,8,9,10) which developed mechanistic ion exchange models. These models assumed that selectivity was the result of interactions occurring only in the resin phase (resin swelling and electrostatic interactions).

Later work by Diamond and Whitney (17) concluded that the affinity various anions had for the resin was the result of interactions of the surrounding water structure with the anions, the exchange sites, and the resin. Diamond and Whitney's model correctly predicts selectivity sequences found in anion chromatography as well as classical anion exchange chromatography. Previous models fail to predict some of the selectivity sequences found in both anion chromatography and anion exchange chromatography.

If one assumes that Diamond and Whitney's model for

anion exchange chromatography is valid for anion chromatography, it should be possible to use this model to predict selectivity trends that should be observed as other parameters of the system are varied. Results should also help explain some of the previously observed variations described in section II.

Eluent, exchange site, and support were shown in Section I to affect the selectivity that various anions have for the resin in a manner predicted by Diamond and Whitney's model. Cosolvents and temperature are the two main parameters that have not been previously investigated for their affect on selectivities. Temperature increases should help improve the chromatographic efficiency of the system by increasing the kinetics of the exchange reaction. Increasing the temperature should also decrease the amount of hydrogen bonding that occurs between water molecules. According to Diamond and Whitney's model, a decrease in the amount of hydrogen bonding would reduce the tendency of the water structure to force ions to form water-enforced ion-pairs. This trend would cause ions that are affected most by this interaction (large monovalent anions) to have a lower relative affinity for the stationary phase in comparison to other anions (small monovalent and divalent anions).

Cosolvents could have two possible effects on the system. The organic modifier would help the aqueous mobile phase interact more with the resin and allow a more efficient ion exchange to take place.

Hydrophobic surfaces (like XAD-1) are defined as surfaces that form high contact angles with water and have low heats of immersion (41). Both measurements indicate a low amount of interaction between the resin surface and the water structure. Adding cosolvent to the eluent would increase the amount of interaction occurring between the aqueous mobile phase and the hydrophobic stationary phase.

Improving the interaction of the resin and the water structure would improve the efficiency of the system and may also affect selectivities of ions for the resin. A cosolvent would reduce the tendency to form water-enforced ion-pairs on the resin surface because the organic modifier can disrupt the hydrogen-bonded network of the water structure to some extent and reduce the tendency of water to form water-enforced ion-pairs. The cosolvent might also reduce specific ion-water interactions which would have an effect on selectivity.

Selectivity variations caused by varying amounts of methanol, ethanol, and acetonitrile are reported and general

trends are explained. Variations in selectivity caused by elevated temperatures are also reported and conclusions are given for the results. General trends reported in previous work and contradictory trends are also discussed and related to interactions predicted by Diamond and Whitney's model of classical ion exchange chromatography.

Experimental

Equipment

A homebuilt HPLC was used with a Model 213A conductivity detector made by Wescan Instruments (Santa Clara, CA) with a measured cell constant of 33 cm^{-1}. The chromatograph contained a LKB/BROMMA Model 2150 dual-piston pump to provide eluent flow. A Rheodyne (Berkeley, CA) Model 7010 injection valve fitted with a 50 µL sample loop was used for sample introduction. Thermal stability of the system was maintained with an Eldex (San Carlos, CA) column oven and other appropriate insulation. The analytical column used in the temperature study was a resin based anion exchange column (269-029) from Wescan Instruments (Santa Clara, CA). A 25 x 4.6 mm steel column packed with 30-37µm XAD-1 (capacity of 0.030 meq/g) was used for the cosolvent studies.

Solutions

The eluent used in the temperature and cosolvent studies was 4 mM phthalic acid prepared from the reagent grade solid and distilled, deionized water. The cosolvents were added to the eluent before the pH of the eluent was adjusted to a pH of 6.20 using sodium hydroxide. All eluents were filtered through a 0.45 µm membrane filter and degassed under partial vacuum for twenty minutes to remove dissolved gasses. Analytical solutions were also prepared from the highest grade materials available and distilled, deionized water.

Results and Discussion

Effect of Temperature

According to Diamond and Whitney's model on anion exchange, the retention times of large monovalent anions like iodide should be affected most by changes in the amount of hydrogen bonding occurring in the water structure. The model predicts that as the amount of hydrogen bonding is decreased, the retention times of large monovalent anions should decrease in relation to the smaller anions.

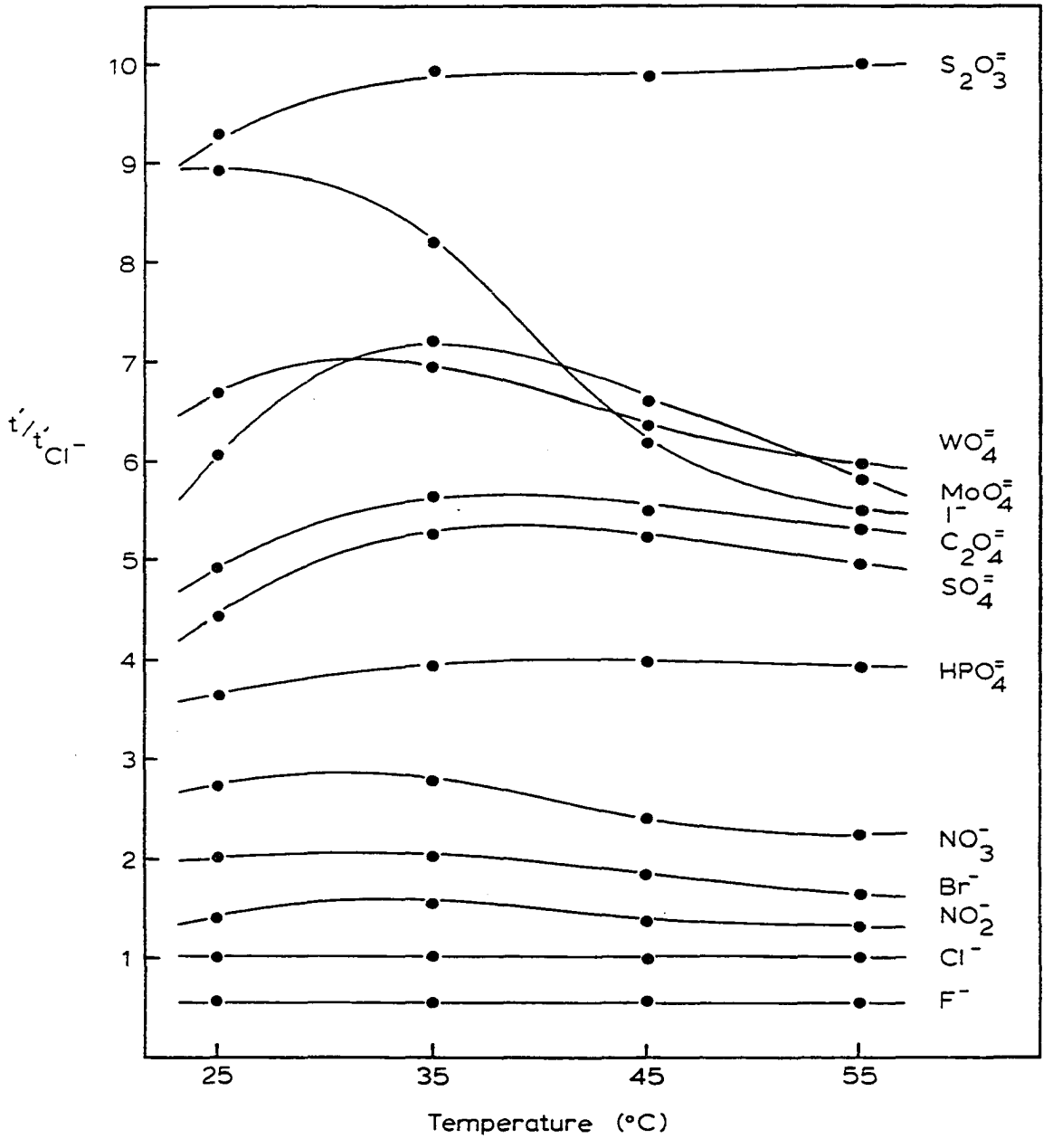
Increases in temperature should thus cause a decrease in the retention time of iodide in comparison to the retention time of anions like chloride. The retention times of divalent anions like sulfate should not be affected as much as the retention time of iodide because they have a much lower tendency to form water-enforced ion-pairs.

Figure 8 is a plot of the adjusted retention time ratios of twelve anions versus the temperature of the chromatographic system. Iodide shows a very dramatic decrease in retention time in comparison to the retention time of chloride. Smaller monovalent anions like fluoride, chloride, and nitrite are not affected to a large extent by ion pairing and their retention times do not change extensively.

The adjusted retention times of divalent anions are more confusing at first appearance. The increase in relative retention times from 25° to 35°C could indicate that the interaction of the divalent anions with water molecules in the mobile phase decreases over that temperature range. The decreased interaction may be related to changes in the hydration layers or specific ion-water type interactions, but no conclusions were made by the author.

It is interesting to note that the initial changes in

Figure 8. Plot of adjusted retention time ratios versus temperature. Conditions: eluent was 4mM Phthalate at pH 6.20, 1mL/min flowrate, and column was a resin based commercial anion exchange column (269-029) from Wescan Instruments


10
9
8
7
6
5
4
3
2
1
t'/t'Cl⁻
S2O3=
WO4=
MoO4=
I⁻
C2O4=
SO4=
HPO4=
NO3⁻
Br⁻
NO2⁻
Cl⁻
F⁻
25
35
45
55
Temperature (°C)

relative adjusted retention times appear to level out from 45° to 55°C for most anions. The most useful changes in relative retention times occurs between 25° and 35°C. It is also advantageous to operate the chromatographic system at the lower temperatures because the system's background noise is very dependent on temperature. In fact, with a conductivity detector, the system cannot be operated at temperatures much higher than 55°C because the background noise becomes too high. Temperature control of the system is more important for control of baseline drift rather than for alteration of the relative selectivities of the different anions. However, changes in the system's temperature can affect relative affinities and may be considered when the chromatographic system is being optimized, especially for late eluting anions.

Cosolvents

Cosolvents are used in anion chromatography to improve column efficiency and to preserve the eluent. Hydrophobic resins like XAD-1 and PRP-1 are poorly wetted by water (high contact angle at the interface) and their ion exchange characteristics are usually poorer than resins that are more easily wetted by water. Cassidy and Elchuk (42) found that

a small amount of a cosolvent like acetonitrile enhanced the efficiency of the column in ion-pair chromatographic systems. The improved column efficiency may be caused by the adsorption of the cosolvent onto the resin and making it appear less hydrophobic. If the resin appears less hydrophobic, the surrounding water molecules should interact more with the resin and allow faster exchange of an anion between the resin surface and the water phase. However, the cosolvent can also disrupt the water-water interactions in the mobile phase. This effect should cause the water structure to decrease its tendency to force large monovalent anions onto the resin surface in a water-enforced ion-pair cavity and would cause a decrease the affinity of late eluting monovalent anions for the resin.

The author has never had a problem with filtered sodium phthalate eluents becoming contaminated with microbiological material such as molds. However, molds can form in eluents and quickly plug a chromatographic column rendering it useless. Therefore, cosolvents are commonly used to prevent bacterial growth. These cosolvents can also disrupt the water-water interactions so a study of three cosolvents; methanol, ethanol, and acetonitrile was conducted to see if these cosolvents have an effect on the relative affinities

of different anions for the stationary phases. The results are listed in Tables XI, XII, and XIII.

Methanol can interact the most with water molecules by hydrogen bonding and therefore should have the least affect on hydrogen bonding in the aqueous phase. Methanol should therefore have the least effect on the selectivities of anions for the resin phase. Table XI shows very little change in selectivity ratios for the anions from 0% to 10% methanol. However, the sensitivity of the system dropped by about 40% as the methanol concentration was increased from 0% to 10%. It should be noted that the baseline noise is also lowered somewhat so that detection limits are not changed as much as the sensitivities are changed. The peak area reported is of 20.1 ppm of chloride using chromatographic conditions listed in the experimental section. These conditions were also used in Tables XII and XIII.

Table XII containing results for ethanol also show very little change in anion selectivities. The changes in relative retention times are more sensitive to changes in pH than cosolvent concentrations. Table XII does not contain a column for 0% ethanol like Tables XI and XIII because the ethanol study was done at a pH slightly higher than 6.20. The sensitivity of the system was also cut by about 40% with

Table XI. Relative adjusted retention time ratios of anions using varying concentrations of methanol as a cosolvent

Anion	$t`/t`_{Cl^-}$ 0%[a]	2%	4%	6%	8%	10%
Fluoride	0.67	0.75	0.78	0.78	0.80	0.79
Chloride	1.00	1.00	1.00	1.00	1.00	1.00
Bromide	1.13	1.23	1.32	1.34	1.42	1.35
Nitrate	1.21	1.47	1.59	1.56	1.60	1.50
Chlorate	2.10	2.09	2.02	1.98	1.92	1.90
Iodide	3.32	3.16	3.46	3.29	3.37	3.31
Sulfate	5.31	6.49	7.02	7.24	7.85	7.53
Tungstate	7.94	8.21	7.85	8.05	8.54	7.79
Molybdate	9.31	8.51	8.20	8.41	8.87	9.21
Thiosulfate	10.1	10.7	10.2	10.5	11.2	11.5
$t`$ (Cl^-) (cm)	2.39	2.25	2.05	2.05	2.12	2.15
peak area (mm^2)	603	429	406	416	416	370

[a]Concentration of methanol used in the eluent is listed as volume/volume percent.

Table XII. Relative adjusted retention time ratios of anions using varying concentrations of ethanol as a cosolvent

Anion	$t`/t`_{Cl^-}$ 2%	4%	6%	8%	10%
Fluoride	0.83	0.78	0.78	0.81	0.76
Chloride	1.00	1.00	1.00	1.00	1.00
Bromide	1.61	1.73	1.86	1.85	1.77
Nitrate	2.20	2.25	2.09	2.28	2.31
Chlorate	2.70	2.73	2.85	2.95	2.75
Iodide	4.40	5.74	5.61	5.22	5.00
Oxalate	5.10	5.00	4.59	4.87	4.72
Sulfate	4.87	4.23	4.15	4.35	4.16
Tungstate	5.09	5.06	4.68	5.08	4.89
Molybdate	5.30	5.48	4.85	5.09	5.06
Thiosulfate	6.02	5.69	5.80	6.02	5.37
$t`\ (Cl^-)$ (cm)	2.50	2.38	2.50	2.49	2.58
peak area (mm^2)	449	414	393	381	357

[a]Concentration of ethanol used in the eluent is listed as volume/volume percent.

Table XIII. Relative adjusted retention time ratios of anions using varying concentrations of acetonitrile as a cosolvent

Anion	$t`/t`_{Cl^-}$ 0%[a]	2%	4%	6%	8%	10%
Fluoride	0.67	0.83	0.73	0.77	0.75	0.78
Chloride	1.00	1.00	1.00	1.00	1.00	1.00
Bromide	1.13	1.30	1.38	1.45	1.57	1.59
Nitrate	1.21	1.58	1.79	1.80	2.18	2.43
Chlorate	2.10	2.18	2.35	2.41	2.72	2.98
Iodide	3.32	3.92	4.02	4.28	----	----
Sulfate	5.31	7.22	7.14	7.65	8.19	8.67
Tungstate	7.94	8.26	8.21	8.74	9.57	9.67
Molybdate	9.31	10.0	8.93	9.74	10.7	10.4
Thiosulfate	10.1	10.7	10.3	11.4	12.2	13.0
$t`$ (Cl^-) (cm)	2.39	2.16	2.34	2.3	2.32	2.41
peak area (mm^2)	603	472	(185)	320	----	----

[a]Concentration of acetonitrile used in the eluent is listed as volume/volume percent.

the ethanol cosolvent and the background noise decreased by an amount similar to the decrease in the methanol study. This indicates that either methanol or ethanol can be used as a cosolvent without a large increase in detection limits. The adjusted retention time of chloride was longer and its peak shape was broader in the ethanol study which was the last study completed. This indicates an increase in the void volume of the system because of column deterioration.

Acetonitrile does show a significant change in relative retention times in Table XIII. While all of the later eluting anions have an increased affinity for the resin. The later eluting monovalent anions, nitrate and chlorate in particular, have their retention time ratios increased by 100% and 42% respectively, while divalent anions like sulfate and thiosulfate have their retention time ratios increased by 63% and 29%, respectively.

It was pointed out that there is a larger drop in the sensitivity of chloride using acetonitrile as the cosolvent. An extra system peak was also observed when acetonitrile was used as the cosolvent. The retention time of the extra system peak varied with the amount of acetonitrile in the eluent but usually had a retention time similar to chloride. When sodium phthalate is used as the eluent, the extra

system peak and the large decrease in sensitivity caused by acetonitrile makes it an undesirable cosolvent.

Surface interactions

The contrasting trends in selectivity changes described in reference (25) and the sorbed exchanger part of section I are interesting. Barron (18) and others (35) explain the increase in retention times of the larger monovalent anions as the exchange site increases in size as a result of water-enforced ion-pairing described by Diamond and Whitney (17). In this model, as the exchange site increases in size or hydrophobicity, the exchange site causes a greater disturbance in the surrounding water structure. To minimize these disturbances, the water structure tries to force large anions into the cavity formed by the exchange site ion. As the exchange site increases in size and hydrophobicity, it becomes even more energetically preferable for the water structure to force larger anions like nitrate and iodide into the water structure cavity formed by the exchange site ion.

The interactions occurring at the water-resin interface have been investigated extensively. The results indicate that a hydrophobic interaction occurs at this interface

(43). When water contacts a hydrophobic surface, the first layer of water molecules has been found to be tighter or more compact than successive layers of water molecules (43,44). Gustafson et al. (45) also reported a positive entropy change when small organic molecules are adsorbed out of water onto XAD-2.

These results indicate that the polymer does affect the water structure and that it is energetically preferable for large ions and small molecules to be placed in the same cavity that is created by the hydrophobic resin. It is reasonable to expect that the larger these ions are, the more the the ions will affect the water structure and the more the ions will be preferred by the resin phase.

However, this model doesn't seem to explain why the affinity of the resin for the larger monovalent anions increases as the resin becomes more polar (see Selectivity Investigations, Section II). In fact, the trend seems contradictory to the interaction mechanism just described.

Kiselev (46) reports that the aromatic rings in hydrophobic resins like XAD-1 have electron donor properties which allows some hydrogen bonding to occur. Other work (41,46,47) indicates that the more hydrophobic resins like XAD-1 interact less with the surrounding water than the

hydrophilic resins like XAD-8. These results indicate that the hydrogen bonding that occurs with aromatic rings is not nearly as extensive as the hydrogen bonding that occurs with more polar groups found in hydrophylic resins (an example would be the carbonyl groups in polyacrylate resins). There will also be some hydrophilic impurities in a hydrophobic resin which can hydrogen bond but the amount of hydrogen bonding occurring with the impurities should be minimal. Therefore, the overall strength of the hydrogen bonding occurring between the resin and the water phase is lower with a hydrophobic resin.

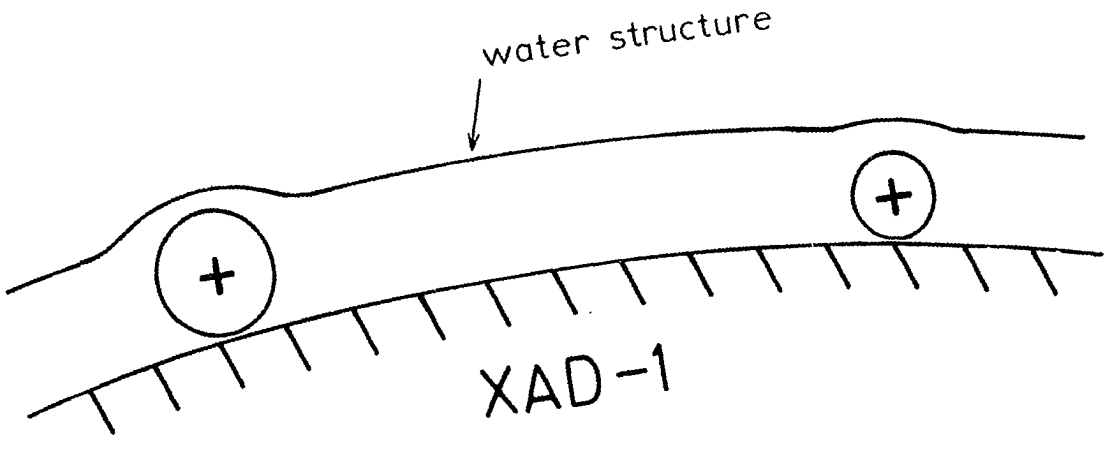
Researchers determine the extent of water structure interaction (or hydrogen bonding) with the resin surface as a function of water vapor adsorption on the resin surface (48). The greater the slope of the water vapor adsorption isotherm, the greater the interaction of the two phases. Various researchers have studied the adsorption isotherms of water vapor on a variety of supports (41,47,48). Results indicate that as the support becomes more apolar or hydrophobic, the tendency for the support to adsorb water vapor decreases. This indicates that the strength of the hydrogen bonding between the water structure and the hydrophobic support (or more specifically, the electron

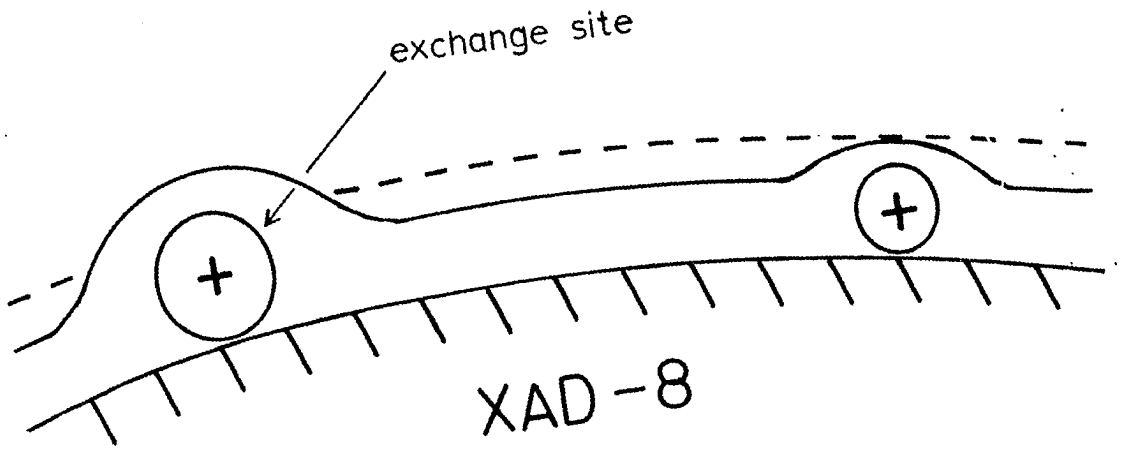
cloud of the styrene rings (46)) is lower than with a hydrophilic support.

Cotton and Wilkinson (49) mention that intermolecular distances decrease as the strength of the hydrogen bond increases. If the relative amounts of water vapor adsorbed on the resin surface is an indication of the strength of the hydrogen bonding between the resin surface and the water structure, it is also an indication of the distance between the water structure and the resin surface. This indicates that the water structure is closer to the more polar resin surface. Thus, the same exchange site ion would disrupt the water structure more on a hydrophilic resin than on a hydrophobic resin as indicated by Figure 9. Therefore, if one compares the retention times of a large monovalent anion on hydrophilic and hydrophobic resins containing the same ion exchange site, the large monovalent anion will have a higher affinity for the exchange site on the more polar resin.

It should be noted that the sorbed exchanger study (see section I) showed that even on the hydrophilic support, as the exchange site ion increased in size, its affinity for large monovalent ions increased. These experimental results and the explanation of the apparent abnormality confirm that

Figure 9. Diagram showing how changes in the distance between the water structure and resin phase can affect selectivities. XAD-8 represents a hydrophylic resin and XAD-1 represents a hydrophobic resin. Since the water structure is closer to the XAD-8 resin, exchange sites on XAD-8 should disturb the water structure to a greater extent than on XAD-1


water structure
+
+
XAD-1


exchange site
+
+
XAD-8

the water-enforced ion-pair model for classical ion exchange chromatography is valid for ion chromatography when specific ion-water interactions (relating to the dissociation constant of the parent acid) and ion-resin matrix interactions (see acid eluents, section I) are also considered.

The higher affinity of divalent anions over monovalent anions has been explained by electrostatic interactions in previous publications (18,33). Other studies indicate that divalent affinity increases as the mobile phase becomes more dilute and the stationary phase becomes more concentrated (24). However, ion extraction affinities indicate that divalent anions such as sulfate should have a lower resin affinity than chloride (50,51). It was mentioned earlier that Surls and Choppin (19) indicated that for anions of the same size, divalent anions actually have a lower affinity for the resin than monovalent anions. This trend (predicted by equation 3) indicates that a simple mass action law is the cause of the apparent high divalent anion affinity for the resin. As the mobile phase becomes more dilute, the monovalent ions have an increased preference for the mobile phase because they cause a greater increase in the concentration of ions in the mobile phase (entropy increases when monovalent anions are in the mobile phase).

Applications

The trends that have been observed indicate that support polarity and exchange group type and size are the two parameters of the system that have the greatest affect on selectivities. Figure 10 indicates that these two parameters can be used to make a "brine" column. A brine column (composed of a hydrophilic support and a hydrophobic exchange site) will retain large monovalent anions longer than a conventional ion chromatography column. This allows divalent anions to be eluted quickly so that these anions do not interfere with the determination of late eluting monovalent anions. In Figure 10, a small amount of sulfate is eluted before nitrate indicating that sulfate can be determined in brine solutions using this type of column.

Concern about iodide in foods has increased recently. Figure 11 shows how the more polar XAD-8 columns can be used to determine late eluting ions like iodide in the presences of larger concentrations of common anions like chloride and sulfate. The eluent conditions in this chromatogram were chosen so that chloride and sulfate are eluted in the pseudo peak.

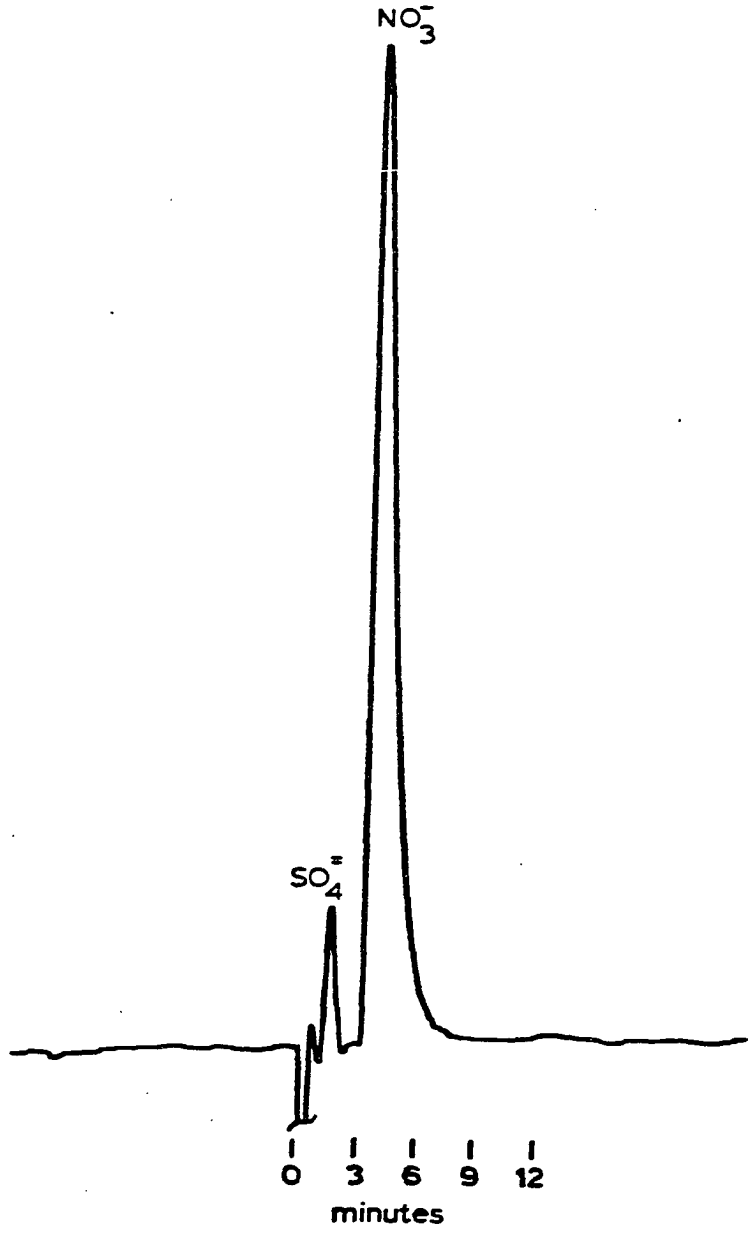


Figure 10. Chromatogram of 5 ppm sulfate and 100 ppm nitrate to demonstrate 'brine' column. Conditions include tetraoctylammonium chloride coated on XAD-8, 30-37µm XAD-8, 250 x 2mm glass column, theoretical capacity of 0.06 meq/g, 0.1mM sodium phthalate eluent at pH 6.0, flowrate of 2.09 mL/min

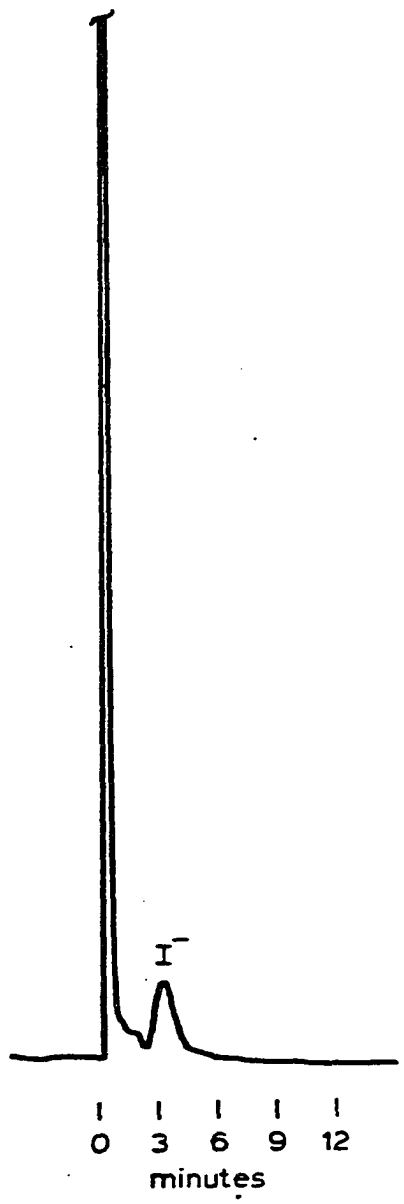


Figure 11. Chromatogram of 20 ppm I^- in the presences of 100 ppm Cl^- and 100 ppm $SO_4^=$ using 1.25mM sodium phthalate at pH 5.55 as eluent. Other chromatographic conditions are the same as listed in figure 10

Conclusions

Temperature and cosolvent do have some effect on the relative retention of anions in anion chromatography. However, these effects are much smaller than the effects caused by eluent anion charge, exchange group type, and support polarity. Therefore, temperature and cosolvent composition should be used mainly to improve the efficiency and stability of the chromatographic system. This study also indicates that the temperature of the system should be maintained constant between 25° and 35°C. Methanol or ethanol can both be used as cosolvents to preserve the eluent used in the system with less loss in sensitivity than with acetonitrile. The alcoholic cosolvents also cause less chromatographic problems than acetonitrile because they do not cause the formation of an extraneous system peak using the conditions used in this study. It should be pointed out that acetonitrile does improve the wettability of the very hydrophobic supports like XAD-1 to a greater extent than methanol or ethanol.

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SECTION III. APPLICATIONS

CYANIDE DETERMINATION

Introduction

There are several problems associated with determining cyanide directly by ion chromatography. It was previously mentioned that dual-column ion chromatography cannot determine cyanide with a conductivity detector because its parent acid, hydrocyanic acid, has a relatively high dissociation constant. The cyanide species is in its molecular form when it gets to the conductivity detector because of the suppressor column. The solution to this problem is an electrochemical detector (1) which can detect cyanide in its molecular form.

With single-column ion chromatography, a very basic eluent, such as sodium hydroxide, can be used so that cyanide is completely ionized. Then, cyanide can be separated by ion exchange and detected using a conductivity detector. Unfortunately, the cyanide peak is usually quite tailed and the sensitivity of the system for cyanide is poor. Therefore, it would be useful to determine cyanide indirectly by first converting it to another species.

There have been many methods developed over the years for determining cyanide. Most colorimetric methods form a cyanogen halide by reacting cyanide with a halogen. The product is then reacted with an aromatic amine and pyridine. The last reaction is called the König reaction (2) and most methods based on this reaction are sensitive from about 0.01 to 2 ppm of cyanide. A couple of titrimetric methods are also used to determine cyanide (2). These methods are based on the formation of a very stable silver cyanide complex. The major drawbacks of the titrimetric methods are that they require a cyanide concentration above 20 ppm and that the samples be free from interferences.

The chromatographic method described in this dissertation was developed by modifying a pneumatoamperometric method developed by Beran and Bruckenstein (3) that used the reaction of cyanide with iodine listed below.

$$I_2 + HCN \rightleftharpoons H^+ + I^- + ICN \qquad (11)$$

They describe the equilibrium as being well-known (the equilibrium constant is 0.73), pH dependent, and quantitative from a pH of 2 to 7. The final concentration

of iodide is proportional to the initial concentration of cyanide.

The new chromatographic method involves adding excess iodine to the original sample, allowing time for the reaction to occur, and then measuring the amount of iodide formed in the reaction by ion chromatography. Excess iodine in the solution is removed by adsorption onto a short precolumn containing unfunctionalized XAD-4 resin (Rohm and Haas). After a series of injections, the precolumn is removed from the chromatograph and the iodine is desorbed by flushing with a nitric acid-acetone mixture. The precolumn is then rinsed with deionized water and placed back in the injection line of the chromatograph to be reused.

Experimental

Chemicals

All chemicals were of reagent grade quality from Fisher Chemical Co. and were used as received. The 0.100 M iodine stock solution used in this work was prepared in a 95% ethanol solution because iodine is more soluble in ethanol than water. The container used to store the iodine solution

was wrapped in aluminum foil to slow the decomposition of iodine by UV and visible radiation.

Cyanide samples for calibration and for testing the procedure under various conditions were prepared from a stock solution of potassium cyanide. The cyanide stock solution was prepared fresh weekly and contained approximately 0.001 M sodium hydroxide. Cyanide samples of varying concentration were prepared by dilution of the stock solution just before analysis.

An acetate buffer solution (5×10^{-2} M, pH 4.75) was used to adjust the sample pH. This solution was prepared from glacial acetic acid and 0.1 M sodium hydroxide. The nitric acid solution (0.05 M) was prepared in acetone and the 100 ppm iodide stock solution used in these experiments was made from potassium iodide. Interferences were made from stock solutions of nitrate salts for the cations and sodium or potassium salts for the anions.

Apparatus

A single-column ion chromatograph described in Section I (acid eluents) was used with a Model 213A Wescan conductivity detector and cell. The chromatograph was modified by adding a glass precolumn as described below.

The precolumn was fitted with a female leur adapter on one end so that samples could be injected by hand directly into the precolumn using a syringe. The other end of the precolumn was connected to the injector valve, containing the sample loop, with a short length of Teflon tubing. This arrangement allows the operator to load the sample loop and remove the excess iodine from the sample at the same time.

The precolumn should be glass so that one can tell when the precolumn needs to be cleaned. The precolumn, 75 x 2 mm i.d., was packed with unfunctionalized XAD-4 resin (Rohm and Haas), 100 to 150 mesh particle size.

The analytical column, 500 x 2 mm i.d., was packed with anion exchange resin prepared from 325 to 400 mesh XAD-1 (Rohm and Haas). The resin had an anion exchange capacity of 0.025 meq/g (4). Other specific conditions were the same as mentioned in Section I (Acid eluents).

Procedure

If necessary, the samples should be diluted so that the expected cyanide concentration will be in the range of 0.5 to 10 ppm. Then, 40 mL of the sample is pipetted into a 50 mL volumetric flask which contains 1 mL of the 5×10^{-2} M acetate buffer (pH 4.75). After the sample and buffer are

mixed, 0.3 mL of 0.1 M iodine in 95% ethanol is added. A yellow color should remain after mixing, indicating that an excess of iodine has been added. The excess iodine is necessary for the reaction of cyanide and iodine to be quantitative. The solution is then diluted to 50 mL, mixed, and allowed to sit at least 5 minutes. Then, a 3 mL aliquot of the sample is slowly injected into the ion chromatograph through the XAD-4 precolumn. The slow injection time, approximately 5 to 10 seconds, through the precolumn allows the resin more time to adsorb the excess iodine. The iodide ion, resulting from reaction of cyanide with iodine, is separated chromatographically by elution with 2×10^{-4} M sodium or potassium phthalate, pH 6.25 and detected with a conductivity detector. The retention time for iodide on the column used was approximately 6 minutes. The height or the area of the iodide peak can be used to calculate the amount of cyanide in the original sample. Calibration plots were prepared by running several freshly made cyanide standards and plotting peak height (or area) against the micrograms of cyanide in the standards.

When the resin in the precolumn at the end closest to the injector valve starts to turn yellow, the iodine needs to flushed from the precolumn. This usually occurs after

four to six sample injections. The iodine is removed by flushing the precolumn with approximately 3 mL of 0.05 M nitric acid in acetone, followed by 3 to 6 mL of water. Flushing the precolumn of iodine is facilitated by removing the precolumn from the system to prevent any accidental contamination of the analytical column.

Results and Discussion

pH

The sample pH should be adjusted and buffered before adding iodine because side reactions involving iodine are likely at alkaline pH values. The results of the pH studies, summarized in table XIV, show that the iodide peak height is constant between pH 4.0 and 6.5 but that the peak height increases rapidly as the pH increases above pH 6.5. The pH range of 4.0 to 6.5 thus appears to be satisfactory for the quantitative cyanide determination. Because some actual samples are highly alkaline, some neutralization in addition to that obtained by adding the buffer may be required to place the sample in the desired pH range for analysis.

Table XIV. pH study

pH	Peak height,[a] (cm)	pH	Peak height,[a] (cm)
4.10	8.45	7.88	11.60
5.18	8.35	8.90	14.30
6.26	8.20		

[a]Done with 10 ppm cyanide.

The peak heights listed in Table XIV for 10 ppm CN^- (~8.3 cm) do not correspond with the calibration curve in Figure 12 (~15.5 cm) because different recorder attenuations were used for the two experiments.

Removal of unreacted iodine

Earlier studies by Jarosz and Fritz (5) showed that methylene chloride could be used to extract unreacted iodine before chromatographic separation of the iodide. However, the use of a small resin precolumn is convenient and is more time-efficient.

A preliminary separation of cyanide by distillation of hydrogen cyanide has been used (6) to avoid interferences in the determination of cyanide. Generally, a sodium hydroxide solution is used to trap the distilled HCN. The author tried an iodine trap that initially was unsuccessful but still appears to be a sound idea.

Calibration

It should be possible to base the cyanide calculation on the stoichiometric amount of iodide produced by the reaction listed in equation 11. Figure 12 shows two calibration plots, one based on iodide standards and the other based on

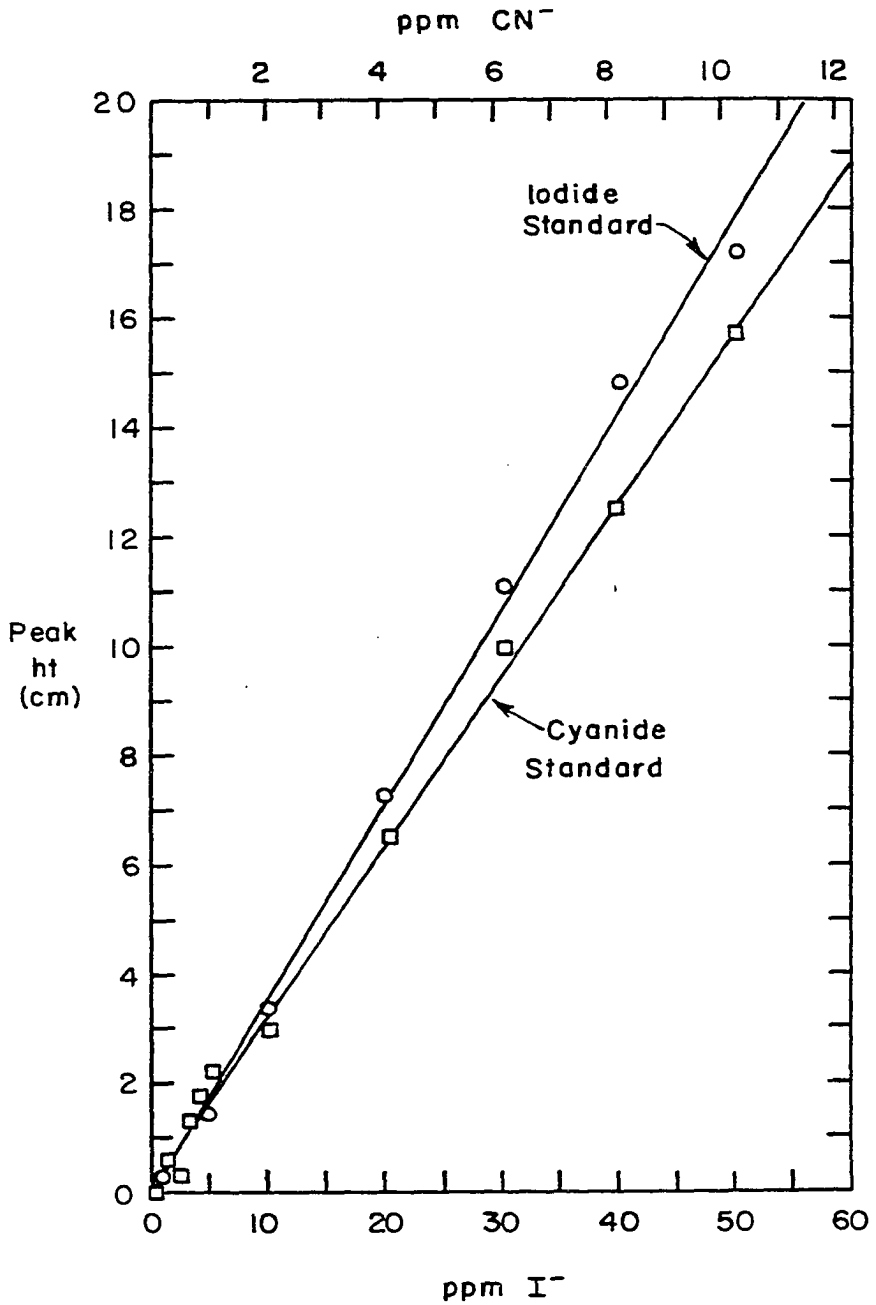


Figure 12. Calibration plots for cyanide based on iodide on cyanide standards

cyanide standards. Both of the plots are essentially linear and are similar enough to indicate that the iodine-cyanide reaction is approximately stoichiometric. However, the difference in slopes is large enough that quantitative results should be based on cyanide standards. The difference in slopes may be caused by the formation of I_3^-, but has not been verified. The calibration plot for cyanide standards is linear for points between 0.4 and 10 ppm cyanide with a correlation coefficient (for linear regression analysis) of 0.998.

Interference study

The effects of various metal ions and foreign anions on the results for cyanide were studied. The results for metal ions reported in Table XV show essentially no interference from nickel(II), magnesium(II), cadmium(II), or zinc(II). Mercury(II) and cobalt(II) form more stable complexes with cyanide and thus interfere with the new procedure for cyanide. The results in Table XVI indicate no interference from common anions such as chloride, nitrate, sulfate, perchlorate, chromate, and small amounts of sulfite. Thiosulfate and thiocyanate react readily with iodine and can interfere with the determination of cyanide.

Table XV. Cation interference study

Cation	Approximate molar ratio (CN^-/M^{n+})	Recovery[a], %	Relative dev., %
Ni^{2+}	10:1	98.5	2.1
Ni^{2+}	1:1	95.2	1.4
Mg^{2+}	10:1	98.2	2.2
Mg^{2+}	1:1	96.7	1.4
Co^{2+}	10:1	75.8	
Co^{2+}	1:1	0	
Hg^{2+}	10:1	74.0	
Hg^{2+}	1:1	0	
Cd^{2+}	10:1	100.2	4.9
Cd^{2+}	1:1	96.8	2.7
Zn^{2+}	10:1	96.4	3.1
Zn^{2+}	1:1	94.2	2.5
Cu^{2+}	10.1	103.6	4.0
Cu^{2+}	1:1	124.2	4.2

[a] Ni^{2+}, Mg^{2+}, Co^{2+}, and Cu^{2+} were measured by peak height, the other cations were measured by area because of increased broadening of peaks at higher interference concentration.

Table XVI. Anion interference study

Anions	Approximate ppm ratio (CN^-/A^{n-})	Recovery[a], %	Relative dev., %
Cl^-	1:10	101.8	2.9
Cl^-	1:1	99.6	0.8
$SO_4^=$	1:10	95.8	2.8
$SO_4^=$	1:1	99.1	3.3
$CrO_4^=$	1:10	96.1	2.9
$CrO_4^=$	1:1	101.4	4.1
NO_3^-	1:10	98.9	1.5
NO_3^-	1:1	99.2	1.9
ClO_4^-	1:10	102.5	2.0
ClO_4^-	1:1	100.9	0.5
$SO_3^=$	1:10	>400	
$SO_3^=$	1:1	101.0	1.7
$S_2O_3^=$	1:10	>500	
$S_2O_3^=$	1:1	>125	
SCN^-	1:10	>700	
SCN^-	1:1	>250	

[a] Cl^-, NO_3^-, and ClO_4^- were measured by peak height, the other anions were measured by area because of increased broadening of peaks at higher interference concentration.

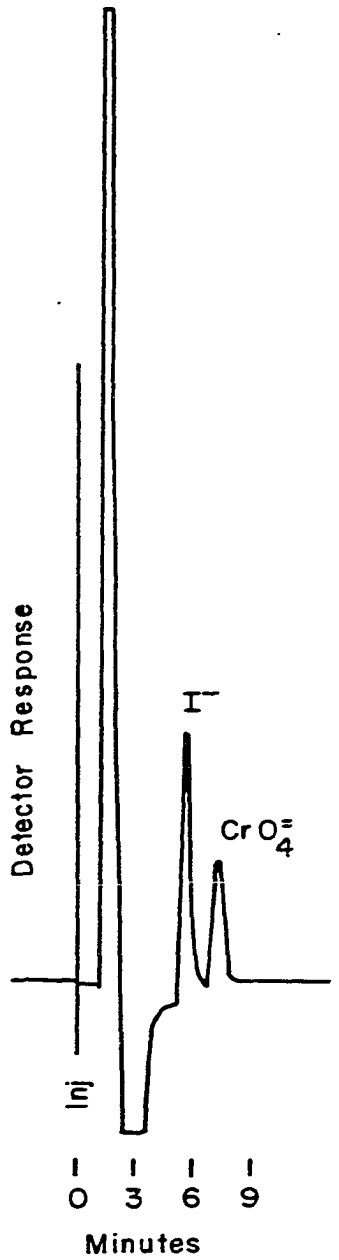


Figure 13. Chromatogram for a sample containing 4 ppm CN^- and 20 ppm $CrO_4^=$

An actual chromatogram of a sample containing both cyanide and chromate is shown in Figure 13. The initial positive peak is called the "pseudopeak" and is always encountered in single-column ion chromatography because of differences in the conductances of the sample and the eluent solutions. The negative peak immediately following the pseudopeak is caused by the buffer, sodium acetate. The next positive peak is iodide; the final positive peak is chromate.

Conclusions

The sensitivity of single-column ion chromatography for cyanide is improved by reacting cyanide to produce iodide, mainly because the chromatographic detection of iodide is several times more sensitive than it would be for the cyanide ion directly. There is less of a sensitivity loss due to peak tailing because the iodide peak is sharper than a cyanide peak. The study also shows that there are some problems involved with quantitating cyanide if the cyanide ion forms complexes with metal ions that are present in the sample. Total cyanide concentrations cannot be determined if these metal ions are present. However, this method would

be very useful for quantitating free cyanide (uncomplexed) in aqueous samples.

ALDEHYDE DETERMINATION

Introduction

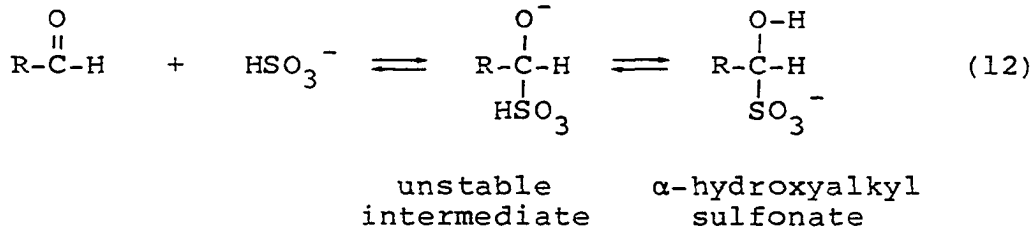
Aldehydes and ketones can be found in a wide variety of samples and are an environmental concern because of their adverse effect on health. This concern has caused several articles to be published concerning the determination of these species. Aldehydes and ketones can be removed from aqueous solutions using a resin-based concentrator column. These species can then be eluted from the concentrator column and into a gas chromatograph for analysis using thermal desorption (7). However, low molecular weight aldehydes and ketones (such as formaldehyde and acetone) have a high water solubility and are not completely retained by the resin. The high water solubility of low molecular weight aldehydes and ketones also prevents their complete recovery from water using a purge-and-trap procedure with gas chromatography.

Aldehydes and ketones can also be determined by high performance liquid chromatography, but usually preconcentration and derivatization steps are required. These steps are necessary to enhance the detection limits of

the UV/vis detector for these particular species. In the preconcentration step, the aldehydes are retained on a concentrator column as in gas chromatography and then eluted off the column with a small amount of an organic solvent (8). The sample is then derivatized with 2,4-dinitrodiphenylhydrazine and chromatographed (8,9). Unfortunately, preconcentrating low molecular weight aldehydes and ketones from aqueous solution for analysis by HPLC is also difficult because of the high water solubility of these species.

Low molecular weight aldehydes (formaldehyde and acetaldehyde) in aerosols have been determined by collection in a peroxide trap and then measured as formate and acetate by ion chromatography (10). The low concentration levels of formaldehyde and acetaldehyde in air can be measured because the peroxide trap concentrates the sample as the sample is collected and oxidized.

The reaction (equation 12) of bisulfite and the carbonyl group of various aldehydes and methyl ketones has been known for quite some time. The products formed are various α-hydroxyalkylsulfonates that have only a slight tendency to dissociate back into the original reactants.



(12)

unstable intermediate

α-hydroxyalkyl sulfonate

Work by Samuelson (11) showed that aldehydes and methyl ketones can be retained on an anion-exchange resin in the bisulfite form. The aldehydes and methyl ketones are converted to α-hydroxyalkylsulfonates on the resin and retained as an ionic species. One should be able to separate and quantitate these ionic species by ion chromatography. It should also be possible to preconcentrate aldehydes and methyl ketones on an anion-exchange concentrator column before analysis. Preconcentration would allow the determination of low molecular weight aldehydes and methyl ketones in the low ppb range.

In this study, calibration curves are given for the determination of formaldehyde, acetaldehyde, propionaldehyde, and acetone. The effects of reaction time, reaction interferences, and chromatographic interferences are investigated. Several chromatograms are also shown which demonstrate the utility of the method.

Experimental

Equipment

A homebuilt HPLC was used with a Model 213A conductivity detector made by Wescan Instruments (Santa Clara, CA) with a measured cell constant of 33 cm^{-1}. The chromatograph contained a LKB/BROMMA Model 2150 dual-piston pump to provide eluent flow. A Rheodyne (Berkeley, CA) Model 7010 injection valve fitted with a 50 µL sample loop was used for sample introduction. Thermal stability of the system was maintained with an Eldex (San Carlos, CA) column oven and other appropriate insulation. The analytical column used was a resin-based anion exchange column (269-029) from Wescan Instruments (Santa Clara, CA).

Solutions

The eluent used was 20 mM citric acid prepared from the reagent grade solid and distilled, deionized water. The pH of the eluent was not adjusted. All analytical solutions were also prepared from the highest grade materials available and distilled, deionized water. Aldehyde, ketone, and sodium bisulfite stock solutions were prepared weekly.

Mixtures of bisulfite and the aldehydes were allowed to

equilibrate for approximately three hours before injection except during the time-dependent studies on the formaldehyde-bisulfite reaction.

Procedure

Calibration curves were prepared by appropriate dilution of aldehyde or acetone stock solutions, adding a specific excess amount of bisulfite stock solution (five times the molar concentration of the most concentrated aldehyde or acetone sample), diluting, and mixing. After a given length of time (3 hours except for the timed reaction), the samples were injected into an ion chromatograph.

Reaction interference studies were done by adding the interferent (acetone) at the same time the formaldehyde and sodium bisulfite were added together in the volumetric flask. Chromatographic interference studies were done by adding the excess chloride to the aldehyde solutions before they were passed through an anion exchange column in the acetate form. The effluent was collected in a volumetric flask containing sodium bisulfite.

Results and Discussion

Formaldehyde has been used as a preservative for sulfite solutions in sulfite analysis procedures and ion chromatography (12). However, in ion chromatography, after preservation, one is no longer detecting the sulfite, but rather the α-hydroxymethylsulfonate. The retention time of the sulfonate is similar to the retention time of chloride rather than that of sulfate. Unpreserved sulfite has a retention time similar to sulfate (13). This indicates that a different species is being separated and detected. The preserved sulfite species also elutes very close to where methylsulfonate elutes, which supports the idea that α-hydroxyalkylsulfonate is being detected rather than sulfite.

Figure 14 is a chromatogram of 20 ppm formaldehyde with a two-fold molar excess of sodium bisulfite. This chromatogram demonstrates that the α-hydroxymethylsulfonate formed has a nicely shaped chromatographic peak which can be easily quantitated. The excess bisulfite in the sample elutes very late (at least three hours) and is not of major importance. However, as the amount of excess bisulfite in the sample is increased, the baseline disturbance later in

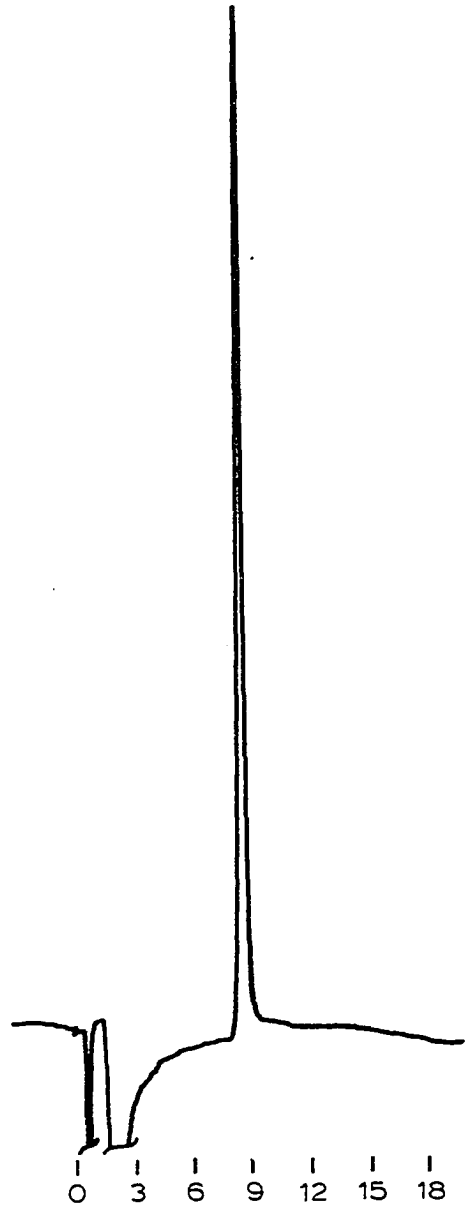


Figure 14. Chromatogram of 20 ppm formaldehyde with a 2 fold excess of bisulfite. Eluent was 20 mM citric acid and flowrate was 2.5 mL/min

chromatogram also increases. Figure 15 shows that the formaldehyde peak height does not change with bisulfite concentration provided a sufficient excess of the bisulfite is added.

Eluent

Previous work (14) demonstrated that the bisulfite addition product is most stable at a pH of about 3. Work by Gjerde and Fritz (15) and Fritz et al. (16) also demonstrate that an increased analyte sensitivity may be obtained at a lower eluent pH. Fritz et al. (16) demonstrated that citric acid is a strong eluent and is not adsorbed strongly by the resin. Strong adsorption of the eluent by the resin reduces baseline stability. It has also been shown (17) that the addition product is more stable when the eluent contains methanol (ca. 10%). However, a cosolvent also reduces the sensitivity of the conductivity detector so it was not included in the eluent (see section II).

Reaction time

The first study conducted was to find out how long a reaction time is necessary to obtain a constant peak height. Figure 16 is a plot of peak height versus reaction time

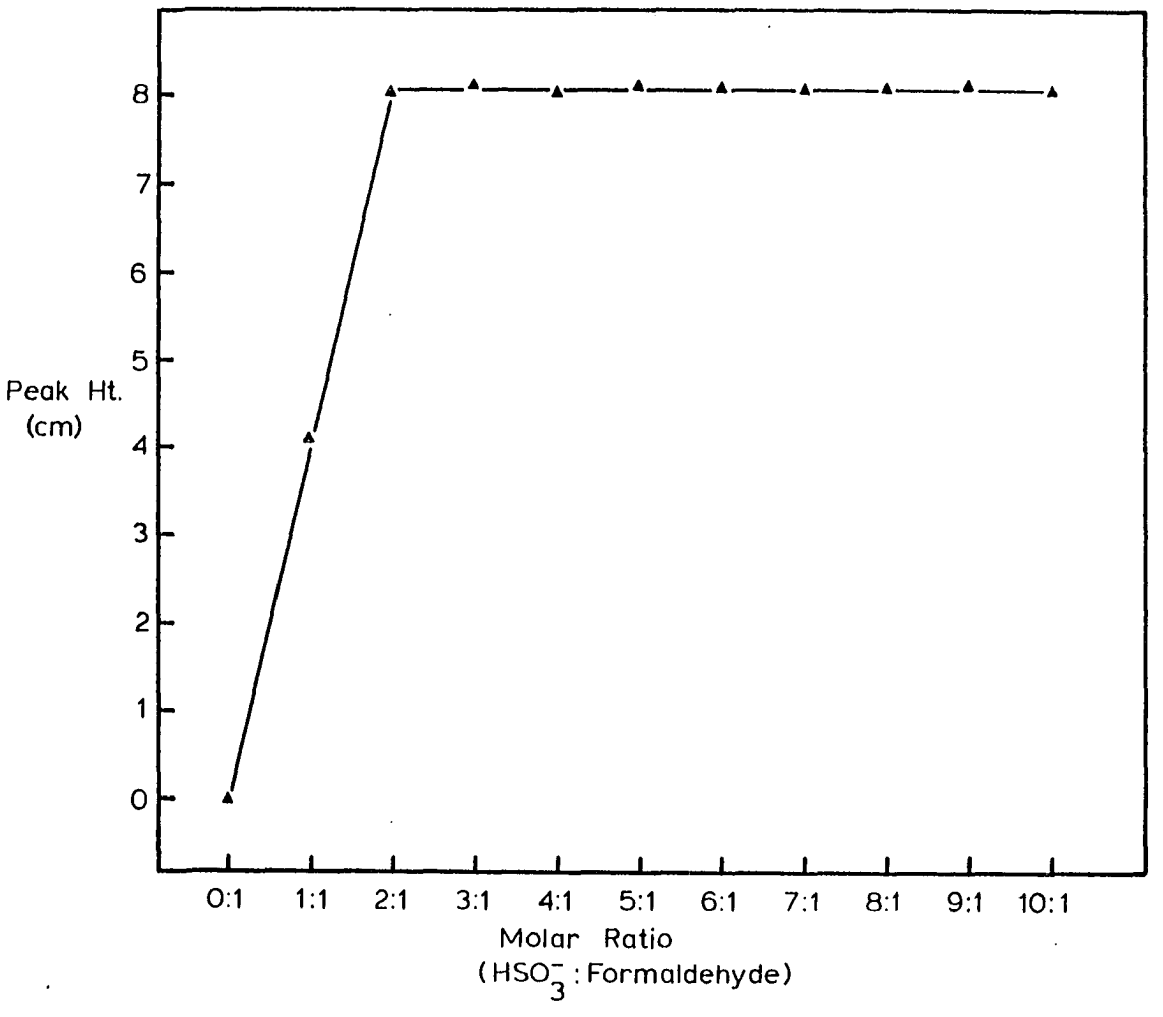


Figure 15. Plot of the peak height of 10 ppm formaldehyde versus the molar ratio of bisulfite to formaldehyde

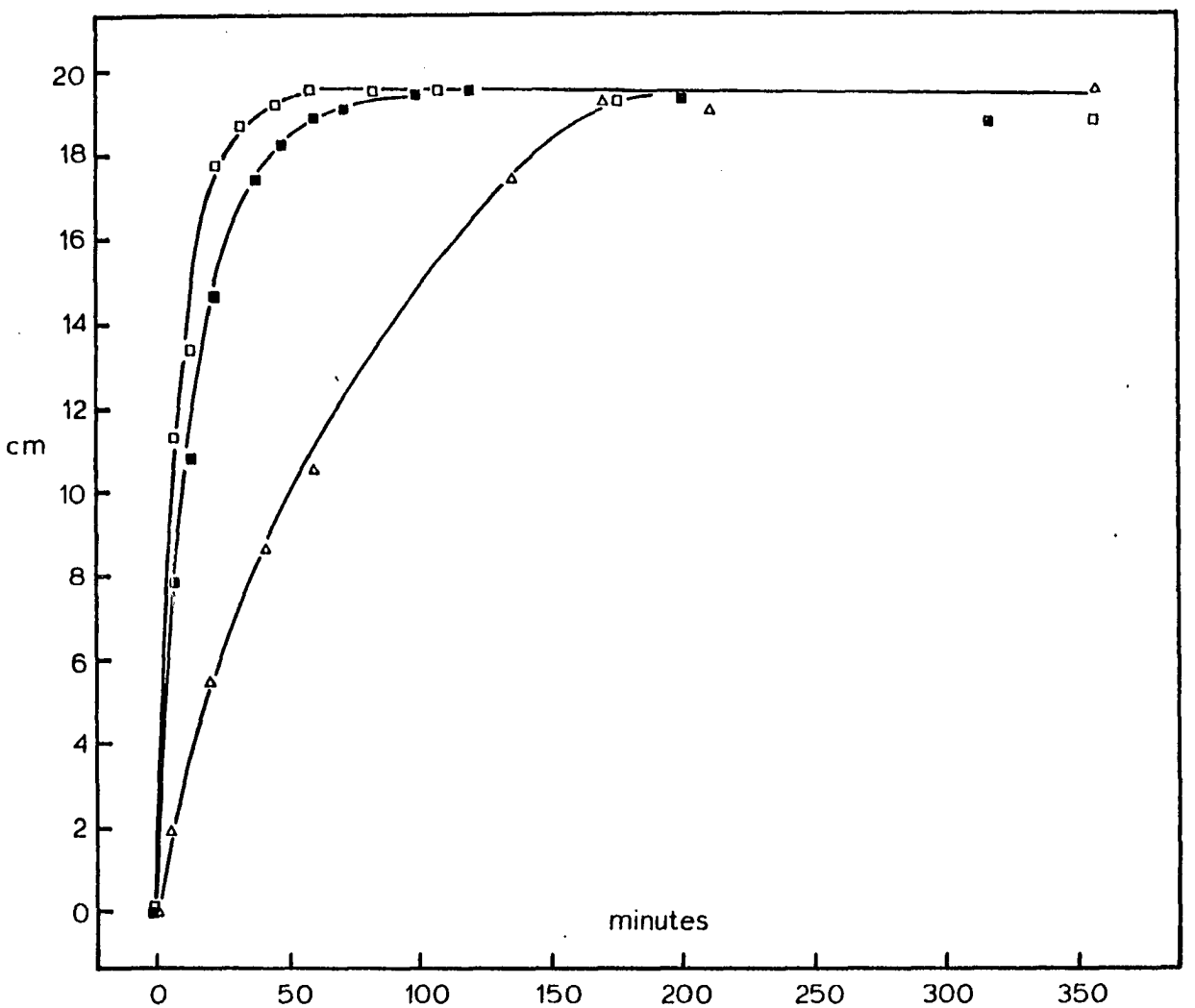


Figure 16. Plot of peak height of 20 ppm formaldehyde versus reaction time using 2, 5, and 10 fold molar excesses of sodium bisulfite. The 2 fold excess curve is plotted with triangles, the 5 fold excess is plotted with solid squares, and the 10 fold excess is plotted with open squares

using 2, 5, and 10 fold excesses of sodium bisulfite. The plot shows that a constant peak height is reached in about three hours with a two-fold excess of sodium bisulfite. Figure 16 also shows that maximum peak height is reached faster with a larger excess of sodium bisulfite. It was found that the peak height remains constant over a period of a week as long as the solution remains in a closed container.

Calibration Curve

Figure 17 is a plot of peak height versus formaldehyde concentration. This calibration curve was done twice. Once with no other species present and once with 250 ppm acetone in the sample. Since methyl ketones also react with bisulfite, it might be expected to affect the calibration curve. Acetone was found to have absolutely no effect on the peak height of formaldehyde although it did form its own peak later in the chromatogram. Both sets of standards gave identical calibration curves.

The appearance of a peak for acetone in the formaldehyde study also indicates that it might be feasible to separate a few other aldehydes and acetone using similar conditions.

Figure 18 is a chromatogram of methylsulfonate,

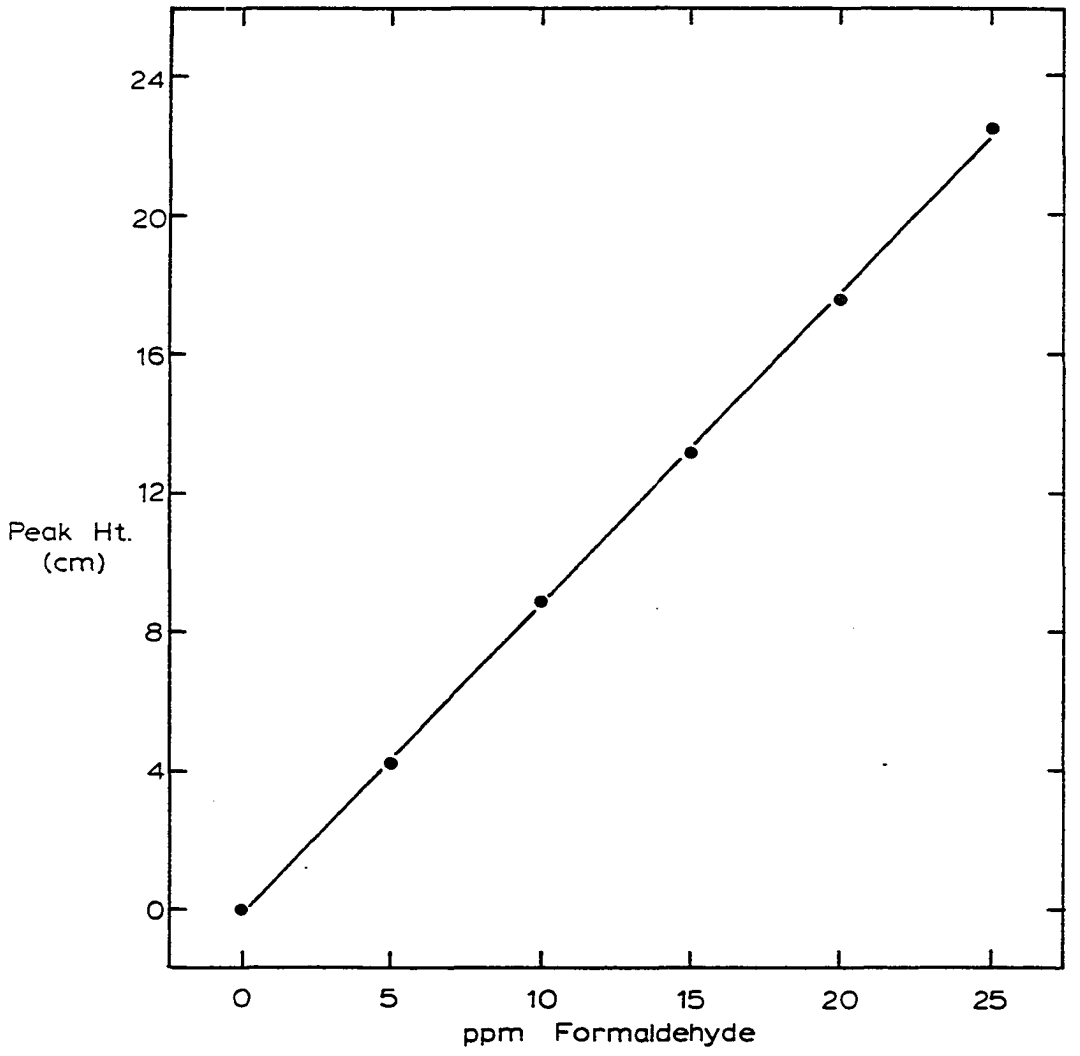


Figure 17. Calibration curve for formaldehyde with and without 250 ppm acetone in the standards. Conditions include 20 mM citric acid as eluent and 3.5 mL/min flow rate

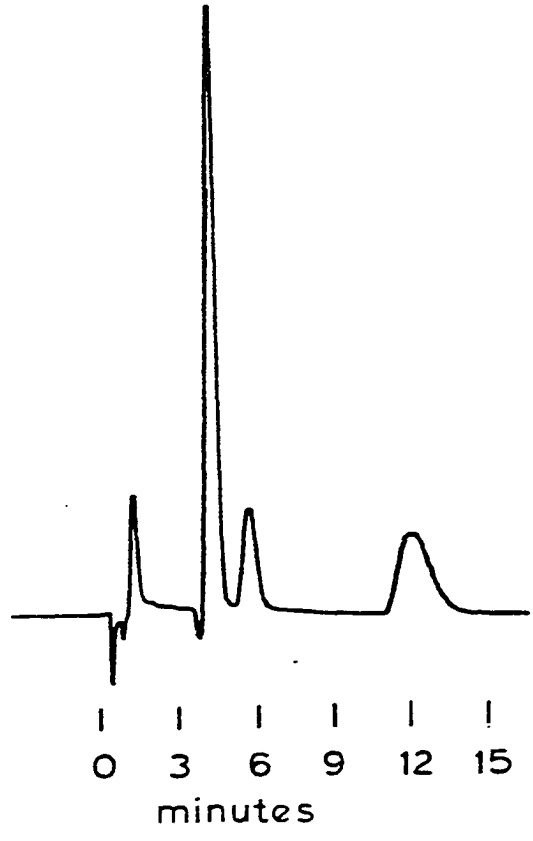


Figure 18. Chromatogram of methylsulfonate, ethylsulfonate, and propylsulfonate using 1 mM succinic acid and a 500 x 2 mm glass column containing 0.027 meq/g XAD-1

ethylsulfonate, and propylsulfonate which lends credence to the possibility of separating other aldehyde derivatives, since these derivatives are very similar to the alkylsulfonates. Figures 19, 20, and 21 are calibration curves for acetaldehyde, propionaldehyde, and acetone. The calibration curves show excellent linearity and indicate that these species can be determined by ion chromatography.

Figures 22 and 23 are chromatograms of the same solution containing α-hydroxyalkylsulfonate derivatives of formaldehyde, acetaldehyde, acetone, and propionaldehyde. The first chromatogram was done after the sample was prepared and allowed to equilibrate in a closed volumetric flask for about 3 hours. The second chromatogram was done after the solution was allowed to set in an open beaker for an additional four hours. There is little change in the relative peak heights of the formaldehyde, acetaldehyde, and propionaldehyde derivatives, but the peak height of the acetone derivative has decreased by a factor of about three. This is a reflection of the relative stabilites of the bisulfite addition products of these species. The dissociation constants of the reactions listed in Table XVII were obtained from Samuelson (11). Acetone forms a less stable product than aldehydes that are listed. A

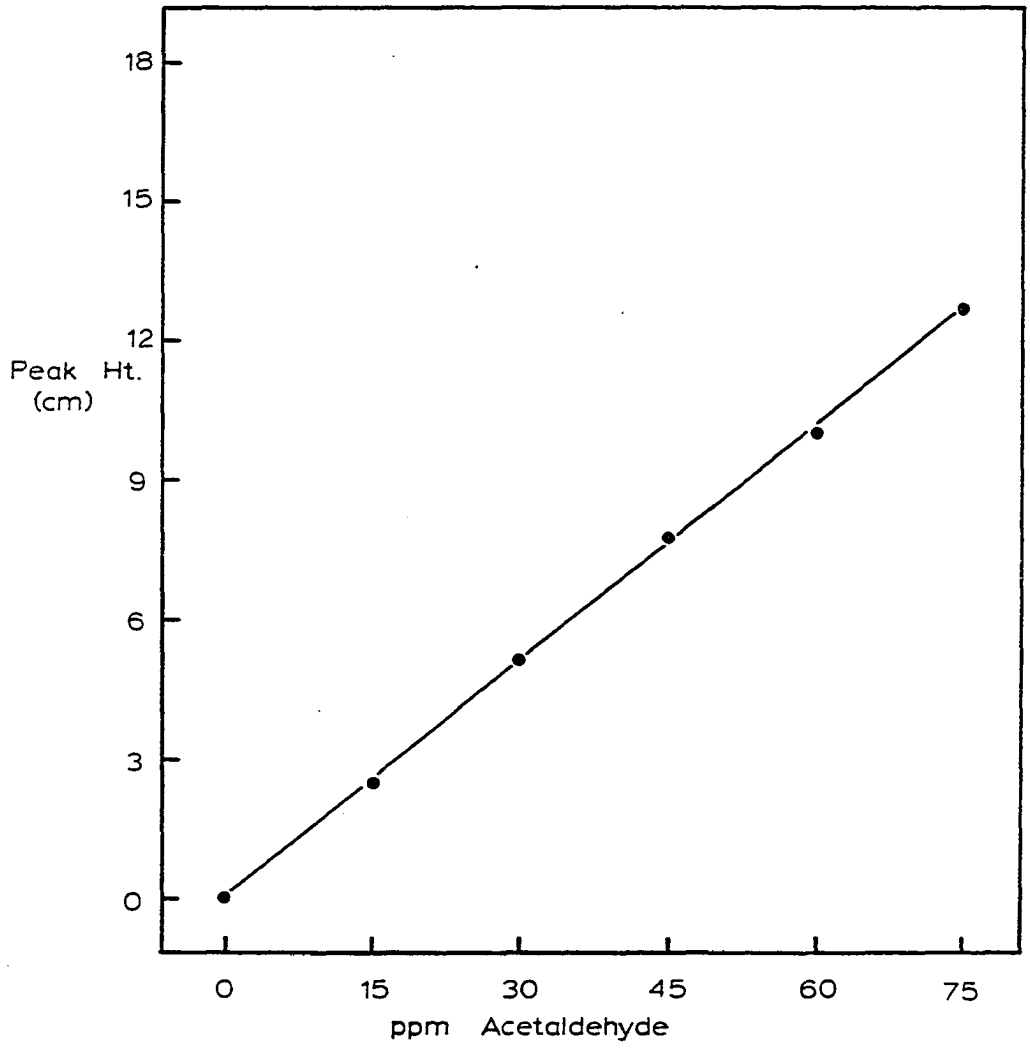


Figure 19. Calibration curve for acetaldehyde using conditions the same as Figure 16

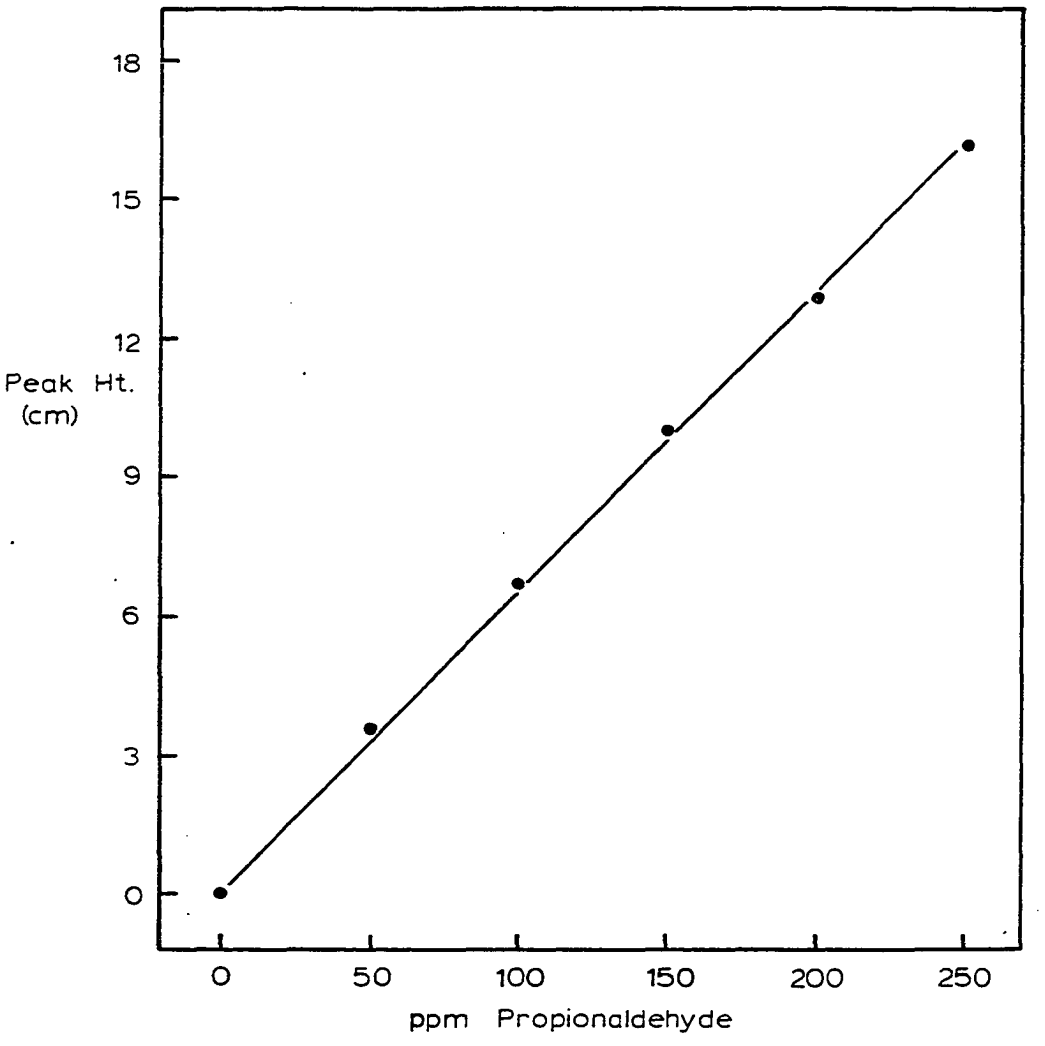


Figure 20. Calibration curve for propionaldehyde using conditions the same as in Figure 16

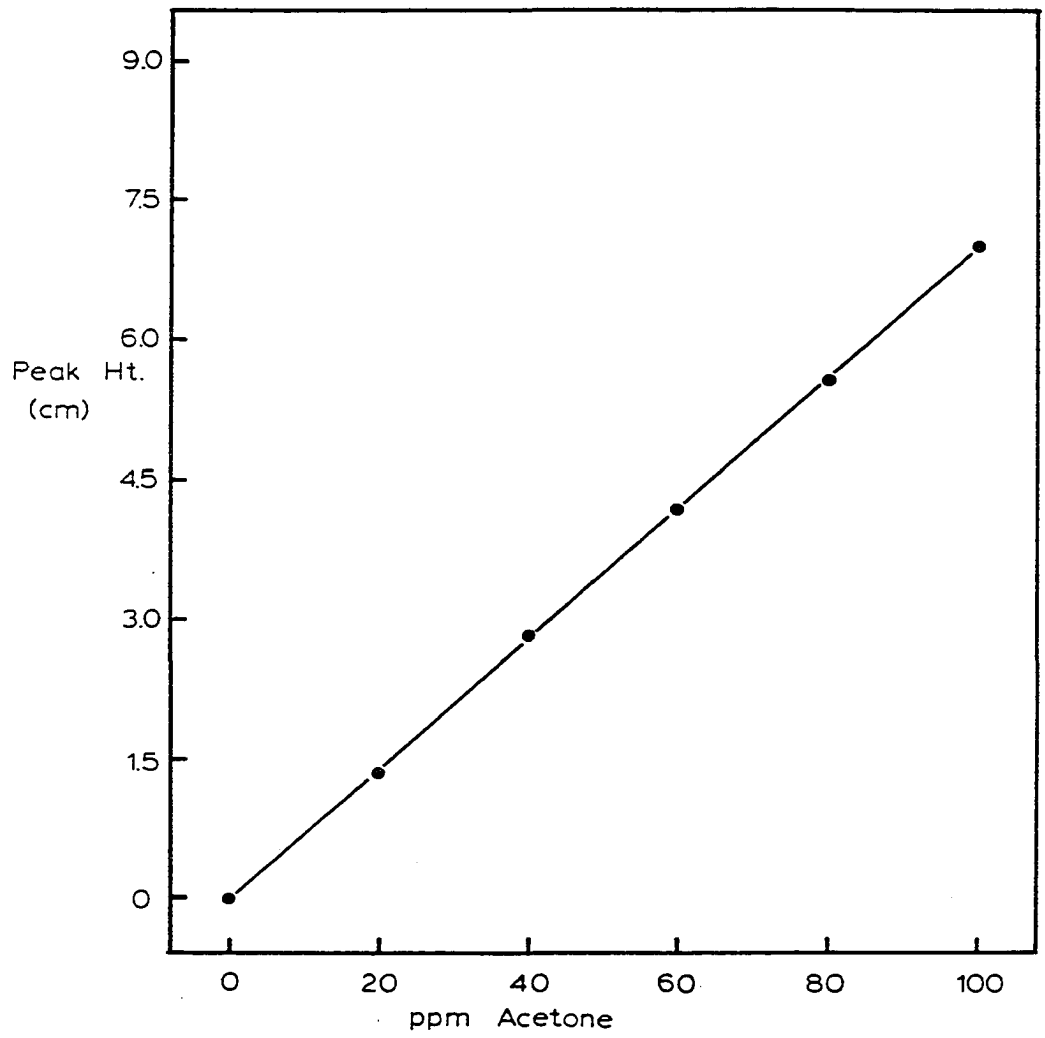


Figure 21. Calibration curve for acetone using the same conditions as in Figure 16

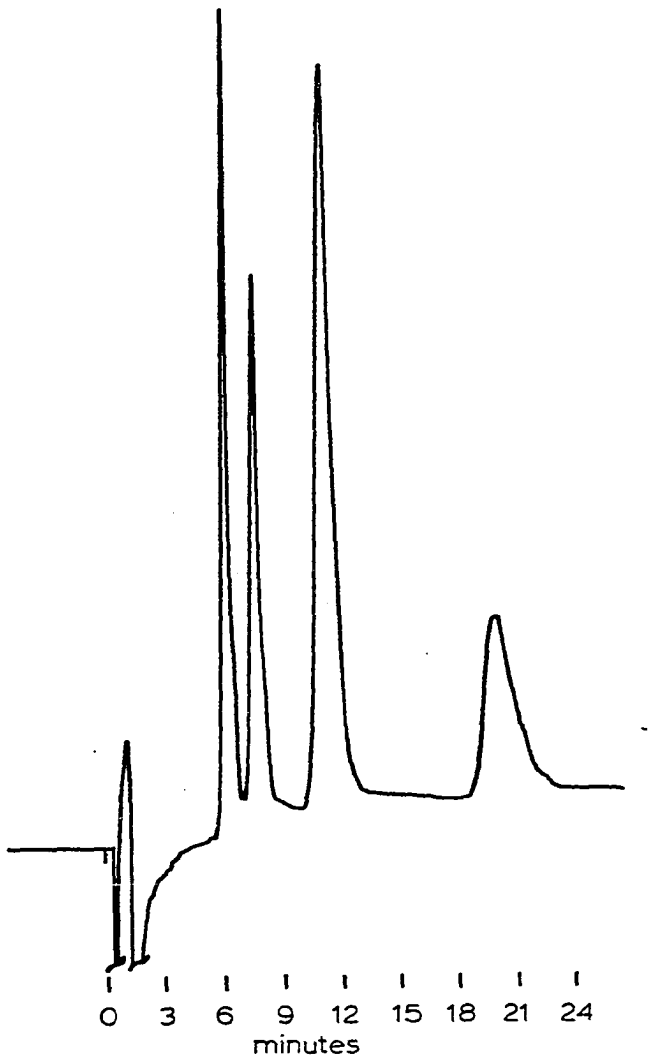


Figure 22. Chromatogram of 25 ppm formaldehyde, 50 ppm acetaldehyde, 100 ppm acetone, and 100 ppm propionaldehyde using the same conditions as in Figure 16

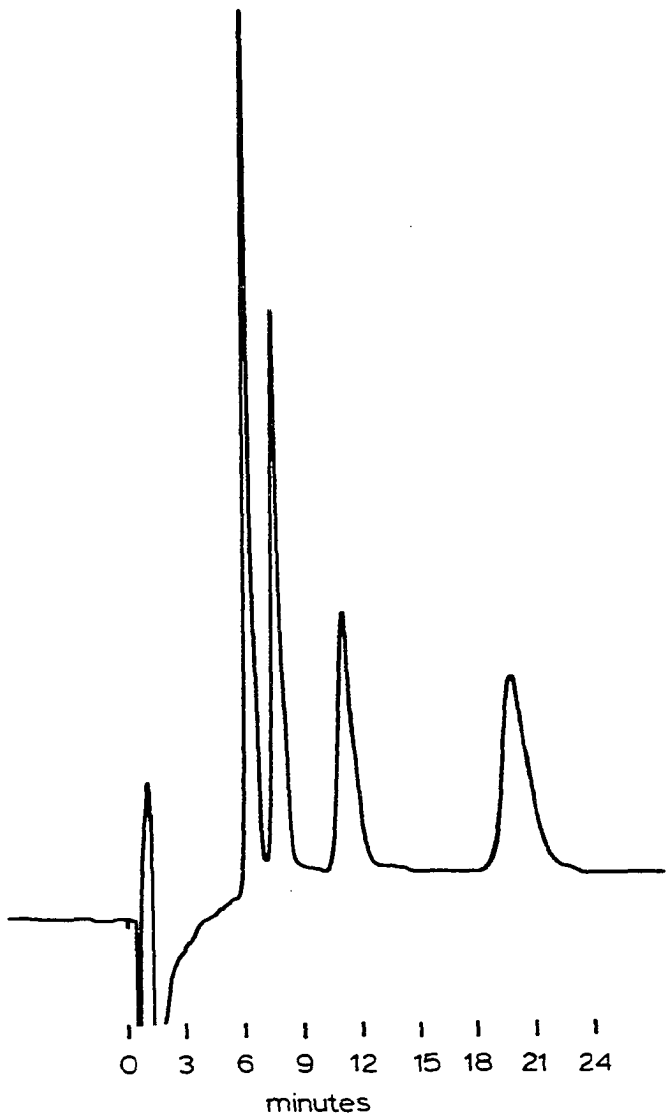


Figure 23. Chromatogram of 25 ppm formaldehyde, 50 ppm acetaldehyde, 100 ppm acetone, and 100 ppm propionaldehyde using the same conditions as in Figure 16

Table XVII. Dissociation constants of some aldehydes and methyl ketone derivatives of interest[a]

Compound	Dissociation Constant (at 25°C)
formaldehyde	1.2×10^{-7}
acetaldehyde	2.5×10^{-6}
benzaldehyde	1.0×10^{-4}
acetone	$3.5 - 4.0 \times 10^{-3}$
furfural	7.2×10^{-4}
chloral	3.5×10^{-2}

[a]Obtained from reference (11).

dissociation constant for propionaldehyde was not found in the literature.

Table XVIII lists retention times of the α-hydroxyalkylsulfonates investigated in this study as well as some other common ions. The only common ion that might interfere with a separation of low molecular weight aldehydes is chloride. Unfortunately, chloride is in just about any type of sample one might be interested in.

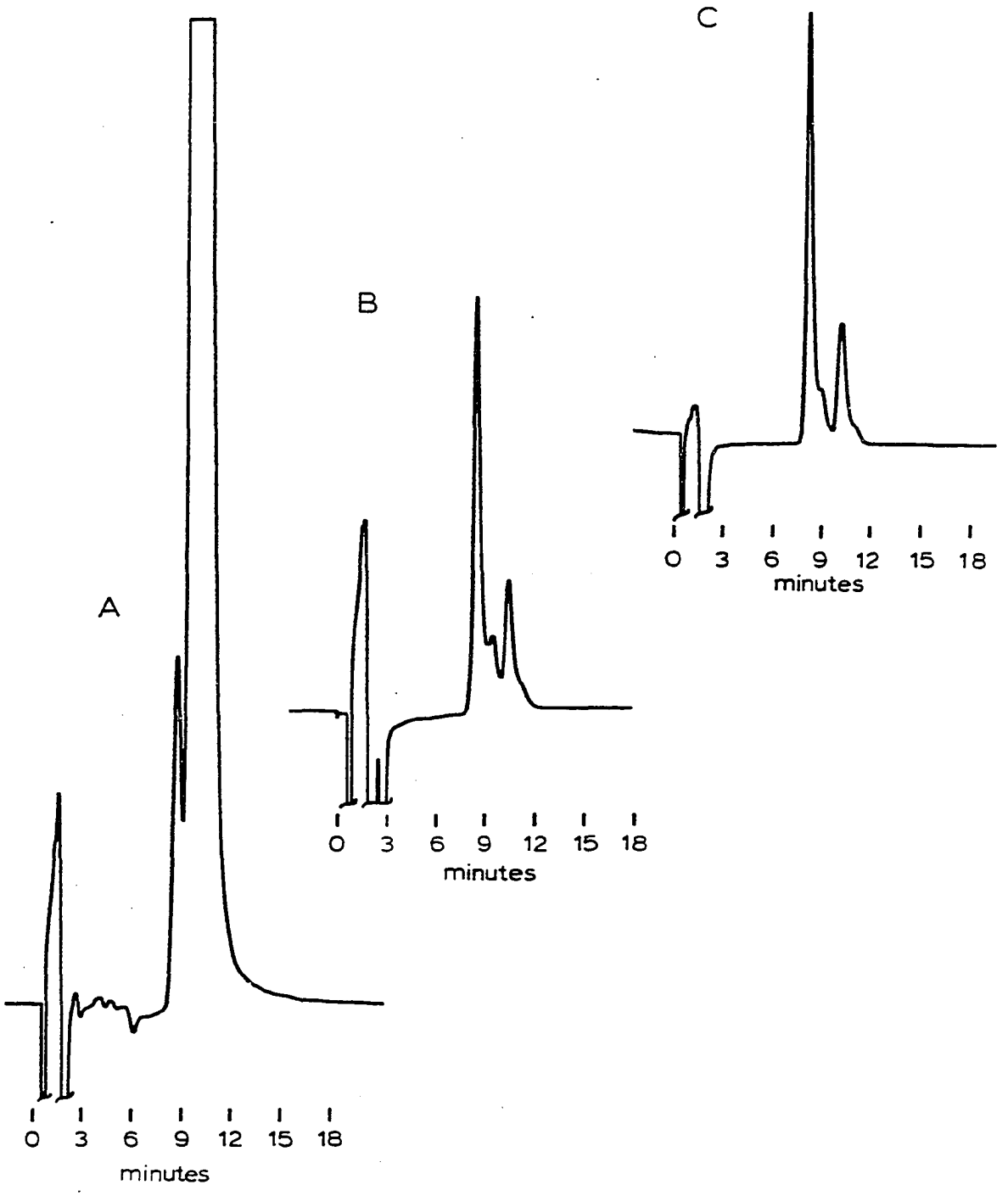
There are several ways of removing chloride from a sample. The aldehydes and methyl ketones are initially molecular species while any chromatographic interferences like chloride are ionic. The simplest way to remove the ionic interferences is by ion exchange before the aldehydes and methyl ketones are converted into α-hydroxyalkylsulfonates. Normally, one would exchange the chloride ions for hydroxide ions because the hydroxide ions are converted to water in the chromatographic system (the eluent has an acidic pH). The major problem with converting chloride to hydroxide is the instability of the α-hydroxyalkylsulfonates at a higher pH. In this study, instead of converting chloride to hydroxide, the chloride is converted to acetate so that the pH of the sample is not drastically changed. Acetate is converted into an

Table XVIII. Retention time of common anions and the aldehyde and methyl ketone derivatives[a]

Anion	Retention Time
Chloride	2.42 min
Phosphate	1.06 min
Nitrate	6.11 min
Methylsulfonate	2.86 min
Ethylsulfonate	5.27 min
Formaldehyde derivative	2.13 min
Acetaldehyde derivative	2.64 min
Proprionaldehyde derivative	6.50 min
Acetone derivative	2.13 min

[a]Conditions used were the same as in Figure 16.

Figure 24. Chromatograms of 25 ppm formaldehyde and 40 ppm acetaldehyde using conditions the same as in Figure 16. Chromatogram A also has 1000 ppm Cl^-; Chromatogram B had 1000 ppm Cl^- but was passed through an ion exchange column in the acetate form to remove the Cl^- before the aldehydes were derivatized; and C contains only the aldehydes


A
0 3 6 9 12 15 18
minutes
B
0 3 6 9 12 15 18
minutes
C
0 3 6 9 12 15 18
minutes

undissociated acid and is not retained by the anion exchange column because the pK_a of acetate, 4.76, is relatively high compared to the eluent pH (ca. 2.60). Figure 24 demonstrates that chloride and other ionic interferences can be removed from the sample without affecting the molecular species in the sample. The shoulder on the formaldehyde and acetaldehyde peaks are caused by column degradation.

Conclusions

The investigation demonstrates that low molecular weight aldehydes and methyl ketones can be successfully determined by ion chromatography. Chromatographic interferences can be successfully removed from the sample before the aldehydes are converted to α-hydroxyalkylsulfonates. Reaction time, amount of excess bisulfite, and sample handling (such as leaving solutions open for a period of time) can all have an affect on the chromatogram, but can be successfully controlled.

The results of this investigation indicate that the technique is worth further investigation. First, the technique should be applied to real samples, An analytical

technique is not worthwhile unless it can be applied to real samples. Second, preconcentration studies should be investigated to see if the useful analytical range of this method can be extended into the low ppb concentration levels.

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GENERAL CONCLUSIONS

In this work, selectivity variations in anion chromatography have been systematically investigated. The results indicate that these selectivity variations follow the same pattern as selectivity variations in classical ion exchange chromatography. It has been demonstrated that a general understanding of these selectivity variations is very useful in optimizing conditions for a specific separation.

This work also demonstrates that acid eluents are useful for improving the sensitivity of the single-column system. Acid eluents can also be used to reduce the signal of a matrix anion such as acetate or affect selectivities by reducing the amount of dissociation of an analyte anion.

A method for testing new supports in ion chromatography has been described and is useful for surveying a variety of supports as well as doing specific types of separations when a commercial column will not work.

The utility of single-column anion chromatography has been demonstrated by the analysis of real samples and expanded by the derivatization methods described in Section III.

FUTURE WORK

Very few research ideas are totally new concepts. Most ideas are a continuation or extension of ideas from other people. The work done in this dissertation is no exception to these generalizations either. The beautiful thing about research is that as ones solves a problem (or proves an idea), one usually creates at least two new problems (or ideas). The ideas expressed in this section are a few of the ideas generated by work described in this dissertation and extensions of work done by other people that relate to the work described. The ideas are discussed briefly so that another person might continue on with the current work and expand our scientific horizons.

Aldehydes

An expansion of the work done on aldehydes would be a worthwhile project. It should be realized that most of the current work is with concentration levels in the ppm level, whereas the aldehyde concentration levels in most natural samples are in the ppb level. Preconcentration of aldehydes on a bisulfite-loaded, anion-exchange concentrator column

would be the most likely solution to the problem. Samuelson (31) showed quite some time ago that aldehydes could be retained on a classical anion exchange column loaded with bisulfite. Using an HPLC concentrator column is a simple extension of both investigations.

Another extension of the aldehyde work would be to test the procedure on real samples. The matrices of real samples are much more complex than the matrices used in the current work. It would be essential to show that this work can be used on real samples before the scientific community accepts it as a practical method.

It would also be useful to determine detection limits for the various species detected in the aldehyde project. The eluent concentration and the background conductivity of the eluent are substantially higher than eluents commonly used in ion chromatography. According to Pohl and Johnson (32), the background noise increases as the eluent conductivity increases. Since the detection limit increases as the background signal increases, detection limits for the aldehydes would be higher than with the regular eluents. This information would be of fundamental importance if one is trying to decide whether to use direct injection or preconcentration methods for sample introduction.

Acetone should also be investigated in more detail. It is hard to analyze by any method and obtain useful results because of the high volatility and water solubility of acetone. The initial results in the aldehyde study indicate that extreme care must be taken in preparation and preservation of acetone samples when using this derivatization method.

Selectivity Theory

This dissertation has covered most of the parameters involved in selectivity theory and has shown that classical ion exchange theory can be applied to ion chromatography. However, the concept of the water structure lying closer to the surface of the more polar, hydrophilic support could use some additional experimental support.

There are two projects originally proposed by Barron (33) that would be useful studies in support of the concept of varying degrees of interactions or distances between the water layer and the support. The first project is an extender arm study. With type I resins, the exchange site is separated from the benzene ring by one methylene group. If the exchange site is separated from the benzene ring by

two or more methylene groups, it should disturb the water structure to a greater extent because the exchange site extends out further from the resin surface into the aqueous phase. Therefore, if the concept is right, a trimethylalkyl ammonium exchange group extended out from the resin by the extender arm might exhibit the same selectivity as a larger, more hydrophobic exchange site such as the tributylbenzyl ammonium ion which would be closer to the resin.

A second study proposed by Barron (33) that would support the work presented in this dissertation is an extensive derivatization study. If the unfunctionalized benzene rings on the surface of the resin were derivatized, (by acetylation, nitration, etc.), the water layer might interact more with the resin surface because the polarity of the surface would change. A change in selectivity following the pattern described in this dissertation would add support to the concept of water-resin surface interactions affecting selectivities.

Resin Work

An area of ion chromatography that could use more research is resin technology. Currently, there are three

types of anion exchange columns commercially available; silica, poly(styrene-divinylbenzene), and polymethacrylate based columns. All three types of columns could use improvement in terms of efficiency and selectivity. Gains in efficiency are necessary to improve the separating ability of the current resins. However, as pointed out by the sorbed exchanger study, varying the polarity or type of support might be very useful for ion chromatography and should be investigated in more detail.

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