STUDIES IN ION EXCHANGE CHROMATOGRAPHY

by

Lee Nicholas Polite

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

APPROVED:

H. M. McNair, Chairman

J. G. Dillard

G. L. Long

J. G. Mason

H. M. Bell

December, 1988
Blacksburg, Virginia

STUDIES IN ION EXCHANGE CHROMATOGRAPHY

by

Lee Nicholas Polite

(ABSTRACT)

This dissertation investigates three major problems in IC, ranging from the practical to the theoretical. The first is of interest to the field of quantitative analysis. Since ion chromatography is primarily a quantitative technique, the linear range of the detector is of particular interest. The linear range was determined to be nearly five orders of magnitude for several common ions. The probes used were fluoride, chloride, sulfate, sodium, and potassium with concentrations ranging from 10 ppb to 1000 ppm. This portion of the dissertation describes the first attempt made to elucidate the linear detection range in ion chromatography using micro-membrane suppression.

The linearity experiments demonstrate the versatility of ion chromatography with respect to quantifiable concentrations. However, a major problem is encountered when attempting to determine a trace ion concentration in the presence of a high concentration of a similarly charged ion (matrix ion). The second part of this dissertation offers a solution to this problem. In ion chromatography, the large excess of a matrix ion affects not only the ions expected in that region of the chromatogram, but also destroys the chromatographic exchange process. One objective of this study

was to develop a rapid quantitative method to determine 5 ppm chloride in the presence of 100,000 ppm sulfate. A standard anion exchange column will completely lose resolution between chloride and sulfate at a sulfate concentration of approximately 2500 ppm. The apparatus designed and built by the author uses two analytical ion-exchange columns coupled in series by a high pressure switching valve. In order to complete the system, the author designed and built a high pressure conductivity detector cell to monitor the conductivity of the effluent from the first column. The system works by overloading the first column and then allowing the effluent to pass onto the second column. When the trace chloride in on the second column, the first column is switched out of line. This process allows the trace chloride to be separated from the residual sulfate.

The column switching study brought to light several theoretical questions about the inner workings of the packing materials used in ion chromatography. These questions include the effects that flow rate and temperature have on capacity and efficiency in ion chromatography separations. Using chloride and sulfate as probes, the chromatographic efficiency was shown to decrease from 30° to 60° C. Even more surprising was the result that sulfate retention increased with increasing temperature while chloride retention decreased under the same conditions. Detailed studies as well as possible explanations are included in the third part of this dissertation.

ACKNOWLEDGMENTS

I would like to thank Dr. Harold M. McNair for giving me this opportunity to do graduate research under his direction. It is difficult for me to put into words the high level of respect that I have for Dr. McNair. Throughout my graduate career, he has served as my research director, my role model, and my friend. I would like to think that it was 100% forethought on my part when I decided to come to VPI in order to work for Dr. McNair, but I did not fully realize the great opportunity that I had stumbled onto until I joined the group. I will greatly miss being a part of Dr. McNair's research group.

I would also like to thank our secretary . Besides for serving as our secretary, was a mother and a friend to me. I hope that I will be lucky enough to encounter more people like her in my future.

A special thanks is in order to all my friends at Dionex. Thank you to the company for supporting my research and donating a great piece of equipment. Thank you to for acting as my "research director on the west coast" and for the numerous fruitful conversations. Thanks to , , and for their technical support and for all the equipment they sent at a moments notice.

I offer thanks to my friends , , and , each a great scientist in his own right. Thanks to for providing wisdom and

direction like a father. Thanks to sharing these years of common insanity. Thanks to for companionship and his unending knowledge of chemistry. And thanks to for his down-to-earth attitude and for answering the phone.

I am also grateful to my mentors (the best HPLC person I know), (the greatest GC person that ever was), (the best all around chromatographer), and (a great chromatographer and friend).

Finally, I owe the greatest thanks to my family. I offer thanks to my parents for providing financial support throughout the 21 years of my formal education. More importantly I thank them for the unending love that they have shown for me and instilled in me. I thank my siblings Dr. , Counselor , and Hipster (and future President) for their companionship and love over the years. They have put up with an awful lot. And a final thank you to someone who has put up with even more, my girl friend (especially in these last few months). I thank her for her companionship, friendship, and constant emotional support.

Table Of Contents

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Ion-exchange chromatography (IEC) was the first of the various liquid chromatography (LC) methods to be used widely under modern LC conditions.[1] Automated, high-resolution IEC dates from the early 1960's, with the introduction of routine amino acid analysis. IEC experienced moderate growth in the biological fields through the 1960's and into the early 1970's. In 1975 a renaissance began with the introduction of chemically suppressed conductivity detection by the Dow Chemical Company.[2] The use an ion-exchange separator followed by a chemical suppressor and a conductivity detector was renamed ion chromatography (IC) by its inventors. The use of conductivity detection made the new technique applicable to inorganic anions and cations. Since 1975 the list of potential analytes has continued to grow, making IC the fastest growing market in chromatography. Because of its extremely practical nature, most of the advancements in IC have been in expanding the list of applications, making the theory of IC almost neglected.

This dissertation investigates three major problems in IC, ranging from the practical to the theoretical. The first problem involves quantitative analysis. Since ion chromatography is primarily a quantitative technique, the linear range of the detector is of particular interest. The linear range is

defined as the difference in concentration between the minimum quantifiable value and the point where the calibration curve deviates by 10% from linearity. This portion of the dissertation describes the first attempt made to elucidate the linear detection range in ion chromatography using micromembrane suppression.

The linearity study demonstrates the concentration versatility of ion chromatography using chemically suppressed conductivity detection. However, difficulties were often encountered when trying to determine both high and low concentrations in a single injection. The second part of the dissertation addresses the problem of trying to determine a trace amount of a given ion in the presence of a large amount of a matrix ion of the same charge. This matrix ion interferes, not only due to the size of its peak, but also due to chromatographic behavior in the column. In other modes of HPLC, it is not uncommon to have a large peak "cover up" a portion of the chromatogram. For example, a peak which is five minutes wide would render those five minutes of the chromatogram useless, but the rest of the chromatogram should be unaffected. In ion chromatography, the large excess of a matrix ion affects not only the ions expected in that region of the chromatogram, but also destroys the chromatographic exchange process. This catastrophic effect is due to the matrix ion actually adding to the strength of the mobile phase and thereby displacing other ions into the void volume. Therefore, the injected sample acts as a plug of concentrated eluant passing through the column.

One objective of this study was to develop a rapid quantitative method to determine 5 ppm chloride in the presence of 100,000 ppm sulfate. This particular problem is of major concern to the computer chip making industry. In their electroplating process, the purity of the reagents is essential, since even a small amount of impurities (i.e. 1 ppm chloride) can ruin an entire batch of computer chips (worth about $100,000). The chip makers would, therefore, like to be able to check the purity of their reagents before they are added to the electroplating baths. One of the reagents used is sulfuric acid. Since a chloride free bath is so essential to the success of the process, they would like to be able to determine chloride at the 5 ppm level in the sulfuric acid reagent. The major problem is caused by the fact that sulfuric acid is a strong acid and therefore, completely dissociates into sulfate ions. This complete dissociation means that the analysts must determine 5 ppm chloride in a matrix of over 100,000 ppm sulfate. This type of analysis is not possible on a single analytical sized ion exchange column due to the interference problems discussed above. A standard anion exchange column will completely lose resolution between chloride and sulfate at a sulfate concentration of approximately 2000 ppm. These problems are even more dramatic in this particular case since sulfate is a divalent ion, making it an exceptionally strong eluant in anion chromatography. The solution to the problem of trace analysis in concentrated ionic solutions is presented in this part of the dissertation. The author designed and assembled a unique column switching system using two analytical

columns, a high pressure conductivity detector, and a high pressure switching valve. This column switching system allows the quantitation of 5 ppm chloride in a matrix of 100,000 ppm sulfate by overloading the first column with the matrix and then transferring the trace chloride and just some of the sulfate to the second column for further separation. In order to complete the column switching system, a high-pressure conductivity cell was needed in to monitor the effluent from the first column. Since no commercially available conductivity cell met the high pressure requirements of the system, the author designed and built a special conductivity detector cell for this system.

The use of the ion-exchange columns in an overload mode brought up many questions as to the actual mechanism of separation in ion chromatography. Sever questions arose regarding the temperature effects, and flow rate effects on capacity of ion-exchange materials. The third part of this dissertation includes theoretical studies which investigate the influences of temperature and flow rate on capacity, selectivity, and efficiency. The effect that temperature has on conductivity detection is well known, but very little work has been done to investigate the influence that temperature has on the separation in ion chromatography. This section of the dissertation shows some surprising data which indicates that selectivity and capacity increase with increasing temperature for certain ions. These experiments were conducted using chloride and sulfate ions to probe the influence that temperature has on retention times, selectivity, and the Van Deemter plots in ion chromatography.

CHAPTER II

HISTORICAL

The historical section includes some major landmarks in ion exchange theory and instrumentation which are necessary for the understanding of the current work. The second part discusses the actual instrumentation which is used in the dissertation work presented here. Therefore, it is meant to be a detailed description of the current state of instrumentation which is applicable to this project and not a complete review of all currently available instrumentation in the field of ion chromatography.

Ion chromatography (IC) is a powerful current technique with deep roots in the past. Scientific papers dealing with the process of ion-exchange date back as far as 1850 when two English agricultural chemists, Way and Thompson referred to it as "base exchange." Way's paper entitled "On the Power of Soils to Absorb Manure"[3] described how a solution of potassium chloride percolated through a bed of soil, giving up its potassium to the soil and receiving calcium and magnesium in its place. Way went on to show that the amount of calcium and magnesium displaced was equivalent to the amount of potassium adsorbed. Thompson reported similar results from a related experiment using ammonium sulfate as the displacement solvent.[4]

The noteworthy aspect of these two papers is that they appear nearly 40 years before Arrhenius proposed his theory of ionization, and over 55 years before Mikhail Tswett first coined the term "chromatography."[5] These may be considered the first scientific papers in ion-exchange, but use of ion exchange materials is documented as far back as 5,000 years ago when Moses placed a decomposed log (ion-exchange material) into a pool of brackish water at Marah in order to make the bitter water drinkable.[6]

The first attempt at ion-exchange chromatography was made in 1938 by Taylor and Urey using a 100-foot column of aluminosilicate exchanger mounted in the stairwell of the chemistry building of Columbia University[7]. They were able to achieve a partial separation of the isotopes of lithium and potassium (still considered to be a very difficult separation).

Ion exchange and ion chromatography have always been very practical subjects. The driving force behind most of the advances in the field has been necessity. The most productive time in the history of ion-exchange came about due to World War II. Only a handful of experiments had ever been done in ion-exchange by 1940, but within a few years, a new analytical technique was developed. The real groundwork in ion-exchange chromatography was done under the supervision of the Manhattan Project. Combined research efforts were begun concurrently at Ames, Iowa and Oak Ridge, Tennessee . Since the fission of uranium gave rise to most of the elements in the periodic table, and in particular to the members of the rare earth or

lanthanide series, ion-exchange was needed to separate the newly obtained elements. The Oak Ridge group was the first to achieve trace separations, while the Ames group was working on the purification of large amounts of these elements. Kettle and Boyd used the first polymerized resin called DOWEX-50 made by Dow Chemical[8]. It is a functionalized polystyrene-divinylbenzene copolymer which is quite similar to the resins used today.

One of the most remarkable papers in the history of nuclear chemistry involved the use of ion-exchange chromatography. In 1955 Choppin and his co-workers used cation-exchange chromatography to identify element 101 or mendelevium, from the spontaneous fission of only five atoms[9]. The mendelevium eluted in the expected place from a column of Dowex-50 cation-exchange resin.

These original separations of the rare earth metals did not rely on the affinity of the resins to differentiate between the various ions; instead, they relied on the selectivity of the eluant to move the ions at different rates. The resin based stationary phase acted simply as a charged surface to retain the ions while a citrate eluant formed complexes of differing stabilities with the various ions. Citrate forms the most stable complex with the smallest ion. Therefore, lutecium formed the most stable complex and eluted first, and lanthanum ,the largest ion, eluted last. Modern ion chromatography relies on the selectivity of the resin as well as the eluant to achieve today's high resolution results.

After World War II, research in ion-exchange dropped off considerably. It was seen as a tedious technique which lacked the reproducibility and ease of use necessary for an analytical technique. Cations were determined more easily by improving atomic spectroscopic techniques and inorganic anions were still quantitated by wet chemical procedures and ion selective electrodes. The overall lack of interest was due to the lack of a suitable on-line detector. Limited work was being done with certain photometric detectors (ultraviolet-visible, fluorescence, and refractive index) in the late 1960's and early 1970's, but these "borrowed" HPLC detectors lack the sensitivity and selectivity to detect most ions in the presence of the mobile phase.

What was needed was a universal and sensitive detector which could detect a variety of organic and inorganic ions. The obvious choice was the conductivity detector since all aqueous ions would produce a signal. The one major drawback was that the mobile phase would produce a very high background signal. The mechanism for separation in ion chromatography is competition for the charged sites on the exchange resin. The attraction between analyte ions and the exchange resin is due to coulombic forces which exist between charged species. Therefore, the analyte ion with the highest charge will be retained on the column the longest amount of time. In the case of ions with the same charge, the smaller ionic radii usually elute first since they are less polarizable. The competition for sites is only possible if the eluant or mobile phase contains ions to act as

"pushers". Almost by definition, anything which is ionic enough to be an adequate pusher must also be conductive, thereby producing a high conductivity background.

This dilemma prevented ion chromatography from being accepted as a useful analytical technique until Dr. William Bauman of Dow Chemical suggested the key idea behind suppressor-type ion chromatography.[10] His idea was to lower the background conductance of the eluant after the chromatography by using a second resin in series, thus, eliminating the problem of high background conductivity. He theorized that the second resin, which was opposite in charge to the separating resin, would selectively remove the counter ion of the eluant and replace it with a suitable ion.This process would render the eluting mobile phase non-conductive. The idea was to try cation chromatography using a standard cation exchange resin as the separator followed by a high capacity anion exchange resin to be used as the "suppressor resin." The separation would be accomplished by using a dilute inorganic acid as the eluant (ionic pusher). This acid would then be converted into water by exchanging its counter ion with an hydroxide ion from the suppressor resin. It was Bauman and his co-workers who first used the term "Ion Chromatography" (IC). They defined this term as "a device consisting of two ion exchange columns connected in series and followed by a conductivity detector."[11]

The first practical IC was initiated by Hamish Small ,a co-worker of William Bauman's, at the Dow Chemical company in 1974. Small

first packed a single mixed bed column using a conventional quaternary ammonium anion exchange resin in the hydroxide form as the "suppressor resin" in the bottom half of the column. The upper part of the column was packed with a low-capacity, surface-sulfonated styrene-divinylbenzene resin which acted as the separating resin. The remainder of this prototype ion chromatograph consisted of a standard HPLC injection valve, an unmodified HPLC reciprocating piston pump, and a homemade conductivity-measuring device. The mobile phase was 0.01 M HCl and the sample was a mixture of sodium and potassium ions. Therefore, when the mobile phase reached the suppressor resin at the bottom of the column, the chloride ions from the acid displaced an hydroxide ion due to chloride's greater affinity for the resin. The hydroxide ion then joined the leftover hydrogen ion to form water. The system successfully and repeatedly separated the two cations. However, the major drawback of the system was that the suppressor resin had a limited capacity for the hydroxide ions. This meant that when the capacity of the suppressor resin was reached, the system had to be shut down and the suppressor regenerated. This was accomplished by pumping sodium hydroxide over the column. Although Small had built in a valving arrangement to minimize the regeneration time, the column required a long time to re-equilibrate. It was then decided to use a separate column as the suppressor and simply connect it between the analytical column effluent and the detector inlet. This arrangement still required periodic regeneration of the suppressor,

but the analytical column remained equilibrated with the eluant. It was this arrangement which was subsequently patented by Dow and licensed exclusively to Dionex Corporation in early 1975.

When the chromatograms were further analyzed, an unexpected result was noticed: the resultant peaks were larger than they should have been based on theoretical calculations of conductivities. The eluting peaks were reproducibly larger than expected until the suppressor resin approached its capacity. After re-examining the system it was determined that the analyte ions were undergoing the same exchange process in the suppressor as the eluant anions thus producing a higher conducting species. In anion chromatography of chloride, for example, with sodium hydroxide as the mobile phase the chloride travels through the separator column associated with a sodium ion. When this pair reaches the suppressor column (a cation exchange material in the hydrogen form), the sodium will adhere to the resin and displace a hydrogen ion. The hydrogen ion will join the chloride and the pair will pass through the conductivity detector as HCl. Since the detector measures total conductivity, both the anions and cations contribute to the detector signal. The hydrogen ion has a much higher conductivity than the sodium ion due to its higher mobility (about 7 times faster than sodium). These combined effects result in larger signals and reduced background noise. This leads to greatly increased signal to noise ratios and lower detection limits. It is this instrumental arrangement

invented by Small, Stevens, and Bauman which is the direct forerunner to the modern ion chromatograph.

MODERN ION CHROMATOGRAPHY

Traditional IC analytes were limited to the standard inorganic anions and cations. Due to the 0 - 14 pH range of polymer based column resins, modern IC has greatly expanded this pool of potential analytes to include all species which can be put into an ionized form. This makes it possible to analyze a wide variety of organic compounds since many of them can be forced into an ionized form by chromatographing them at extreme pH's. These compounds include, but are not limited to, carboxylic acids, phenols, alcohols, sugars, and amines. The wide variety of potential analytes is a result of not only improved column technologies, but also a larger selection of detectors including conductometric, photometric, fluorometric, and electrochemical detectors. It is this versatility combined with Ion Chromatography's HPLC -like accuracy and precision which have led IC to replace many analyses previously done by ion selective electrodes and wet chemical techniques. Ion Chromatography has the major advantage over many of these techniques of being able to determine >30 ions in a single run, as well as speciate between the oxidation states of a single element.

COLUMNS

The anion chromatography included in this work was performed on a pellicular type of ion exchange packing material. Pellicular packings were commonly used in the early days of HPLC. These earlier packings gave high efficiencies but lacked the necessary capacity needed for adsorption type chromatography. Since the forces responsible for adsorption in HPLC are relatively weak, the surface active pellicular packings did not have enough surface area to adequately separate the desired compounds. It was this need for higher surface area packings which lead to the use of totally porous packing materials. In ion chromatography, however, the interactions between the analytes and the stationary phase is much stronger due to its coulombic nature. Therefore, Ion chromatography can take full advantage of the higher efficiencies of pellicular packings since only a relatively low surface area is required.

The most popular packings in use today are based on a core made of a polystyrene/divinylbenzene copolymer. The divinylbenzene (DVB) is copolymerized with the polystyrene to give the resin the necessary mechanical stability. The amount of DVB in the resin is denoted as "percent crosslinking" and ranges from 2% to 5% for the columns described below. The level of crosslinking is directly related to the amount the polystyrene/DVB will shrink or swell in varying solutions. Resins with levels of crosslinking <1% are

unacceptable for high efficiency work due to excessive shrinkage. If the resin shrinks, the column is left with a void at the top, which degrades the overall efficiency of the system. When the resin swells, it produces high backpressures at constant flow rates. Higher amounts of crosslinking (>5%) are also disadvantageous since they produce resins with decreased porosities. This tends to limit the mass transfer and, consequently, leads to a loss in column efficiency.[12]

Cation columns are based on this polystyrene/DVB copolymer with a diameter of 15 μm as a support material with a 2% crosslinking. Sulfonic acid groups are then covalently bound to this inert support material producing a totally porous sulfonated layer. It is this surface sulfonation which is responsible for the negative charge, thus producing a cation exchange stationary phase (See Figure 1). The hydrated ions will not interact beyond the surface sulfonated layer due to the high hydrophobicity of the support material. This means that the diffusion path in the stationary phase (d_f) is limited to the thickness of the sulfonated layer (~1μm). This thin film translates into a very efficient stationary phase.

The packing materials in anion chromatography columns are based on the same polystyrene/DVB with surface sulfonation support material as is described above. In fact, they were produced by first packing a cation exchange column, and then modifying it *in situ* with a technique known as latex agglomeration. In this technique, fully aminated latex spheres (~0.1 μm in diameter) are put into a slurry and pumped over the column. The presence of the quaternary

Surface Sulfonated Cation Exchange Particle

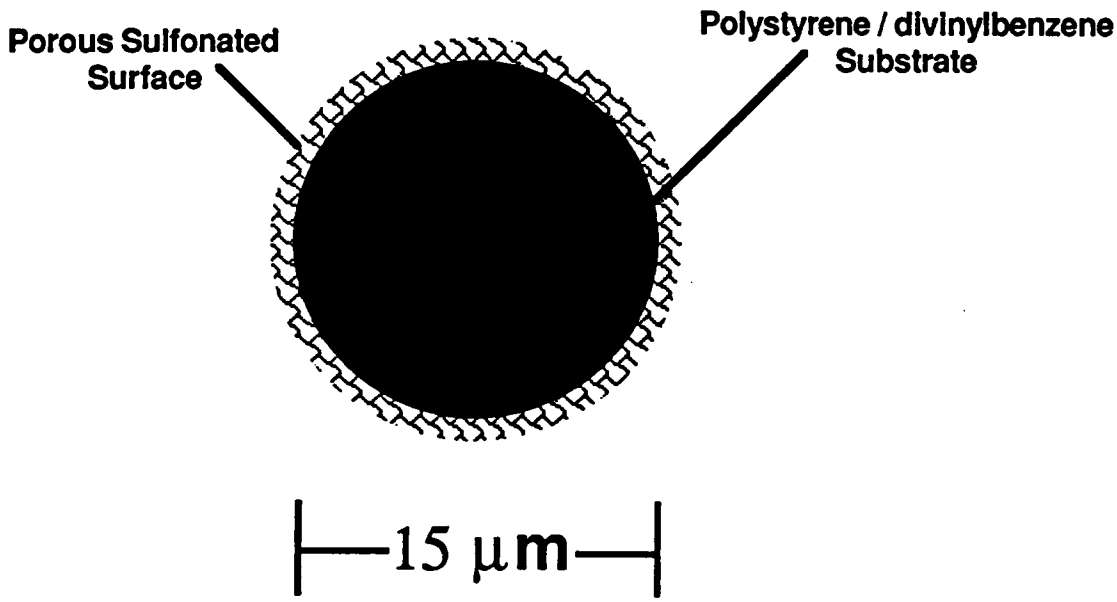


Figure 1 Sketch of a Cation Exchange Particle

ammonium groups throughout the latex imparts a high positive charge to the spheres. The positively-charged latex spheres are attracted to the negatively-charged sulfonated surface by coulombic forces and are held in place by this strong coulombic attraction. Van der Waals forces are also present due to the combined polystyrene/DVB matrix of the aminated beads and the PS/DVB resin of the support material (See Figure 2). This attachment is essentially irreversible under all but extreme operating conditions. This strong attachment is demonstrated by the fact that the column shows no appreciable loss of capacity even after washing with 4 M NaOH. The quaternary amines used to produce the positive charge on the latex beads can be changed to alter the selectivity. The R groups on the nitrogens will affect the selectivity by producing steric effects. Even though the charge density of the ion is the predominant factor in its retention, unique selectivities can be attained by altering these groups.

Latex-Anion Exchange Particle

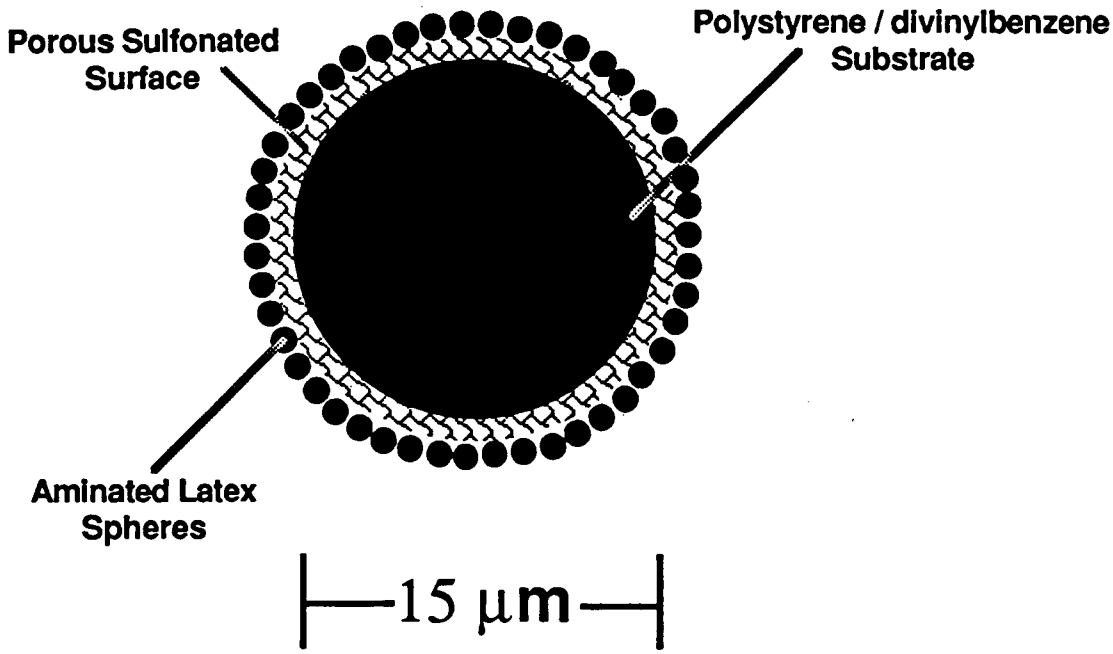


Figure 2 Sketch of an Anion Exchange Particle

SUPPRESSORS

Chemical suppression technology is primarily responsible for the improved sensitivity and versatility attainable by modern IC. The latest generation of suppressor is the micromembrane suppressor. This type of suppressor demonstrates several advantages over earlier generations of the suppressor. It is a continuously regenerating device(allowing analyses to continue uninterrupted for up to several months). Another important improvement is a decrease in the total "dead volume" of the system. This dead volume is about 45 µl, making very little contribution to extra-column band broadening. The first generation "packed bed" suppressors contributed over 1 ml of dead volume to the system; while the second generation "hollow fiber" suppressors contributed 200 µl to the total dead volume. Since the micro-membrane devices are continuously regenerating and have a high surface, they have a much higher capacity for suppression. As a result they can be used with higher concentration or higher flow rates of eluants. Also, since these suppressors are equilibrium driven ,i.e. their exchange rate is dependent upon the amount of exchangeable ions flowing through the membrane, gradients can be used for the first time in ion chromatography.

In anion chromatography, the chemical suppression device is a flow system consisting of a semi-permeable membrane sandwiched between two eluant screens (See figure 3). These screens become cation exchange membranes after being fully functionalized with

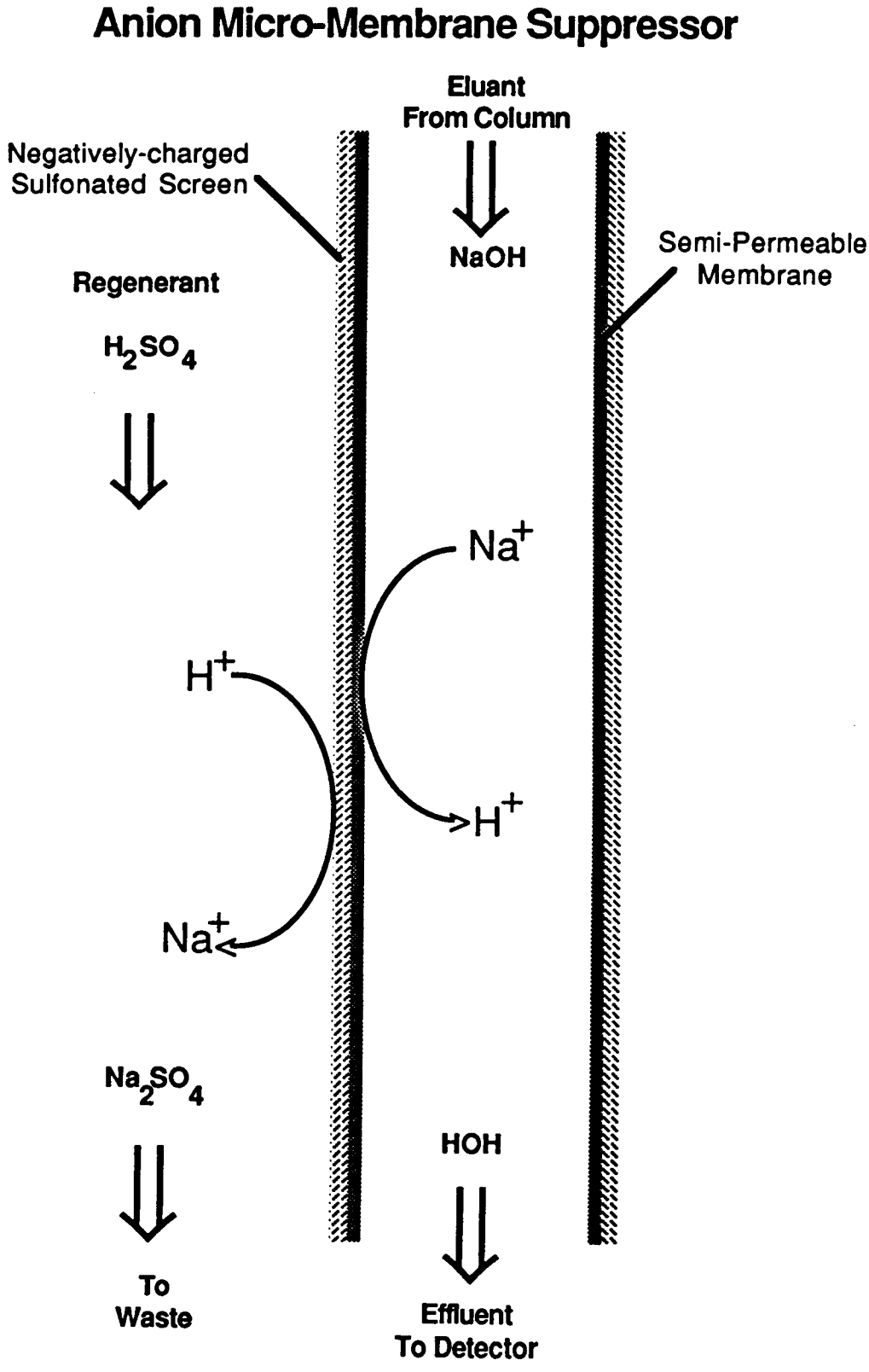


Figure 3 Schematic of Anion Micro-Membrane Suppressor

sulfonic acid groups. This assembly is surrounded by a flowing bath of dilute sulfuric acid ,the regenerant, which serves to replenish the hydrogen ions on the screens and to carry the exchanged cations to waste. The eluant, (e.g. NaOH), passes through the inside of the membrane where it encounters the negative charges of the sulfonic acid groups. The positive sodium ions are attracted to the negatively charged screens where they are exchanged for hydrogen ions. The free hydroxide ions combine with the displaced hydrogen ions to form water. The sodium ions, which have been adsorbed on the screens, diffuse into the flowing waste stream of sulfuric acid. This diffusion is a result of the concentration gradient of sodium ions between the screens and the waste stream. The concentration of sodium ions in the dilute sulfuric acid stream is much lower than the high concentration of sodium ions building up on the screens. The hydrogen ions from the sulfuric acid regenerant then pass through the screens to replenish the active sites. To further improve the efficiency of these suppressors, a counter current flow is used with the regenerant. Therefore, the freshest regenerant is used on the eluant immediately before it reaches the detector cell.

The sulfate ions from the regenerant do not pass through the permeable membrane due to repulsion forces established by the high negative charge of the screens. This repulsion is know as "Donnan exclusion."[13] It occurs whenever a high enough negative charge is established on the screen to effectively overpower the diffusion forces of ions with similar charge to the screen. It is this desirable Donnan

exclusion which places the upper limit on the regenerant concentration. Donnan exclusion breaks down when the concentration gradient of sulfate ions is extreme enough to force diffusion of the high concentration sulfate ions into the eluant stream. Complete Donnan exclusion can only be maintained at low concentrations of the sulfuric acid regenerant (< 0.01 M). A suppressor of this type can process an ion flux of up to 10 mEq/min with minimal loss of efficiency due to band broadening. It is the capacity of the suppressor which sets the upper eluant concentration limit, and consequently, the exchange capacity of the analytical column. Higher column capacities are desirable since they allow more sample to be placed on the column and result in longer column life times. The practical ion-exchange capacity of modern resins is in the range of 10 to 200 mEq/g.

The cation micromembrane suppressor is similar to the anion suppressor. The screens are functionalized with quaternary amines to impart a positive charge. The regenerant typically used is tetrabutyl ammonium hydroxide. The large counter ion is necessary to prevent its passage through the membrane and into the eluant flow.

INSTRUMENTATION USED

Figure 4 shows a detailed diagram of the Dionex series 4010i ion chromatograph used in these studies. Each component will now be described in more detail.

CONDUCTIVITY DETECTOR

The detector used in this work is a pulsed, bi-polar conductivity detector. The potential on the electrodes is pulsed and reversed continuously to avoid any charging current build up on the electrode surfaces. The flow through cell consists of two stainless steel electrodes housed in a polymethylmethacrylate block (See Figure 5). The active cell volume is about 2 µl, adding very little extra-column band broadening. A small potential difference is placed between the two electrodes causing ion migration to the electrodes.The resultant resistance of the flowing stream is measured and then converted to conductance with the units of Siemens. The conductivity of the flowing stream is proportional to the square root of the concentration of ons in the stream. The exact relationship is shown here in Kohlrousch's square root law:[14]

Modern Ion Chromatograph System

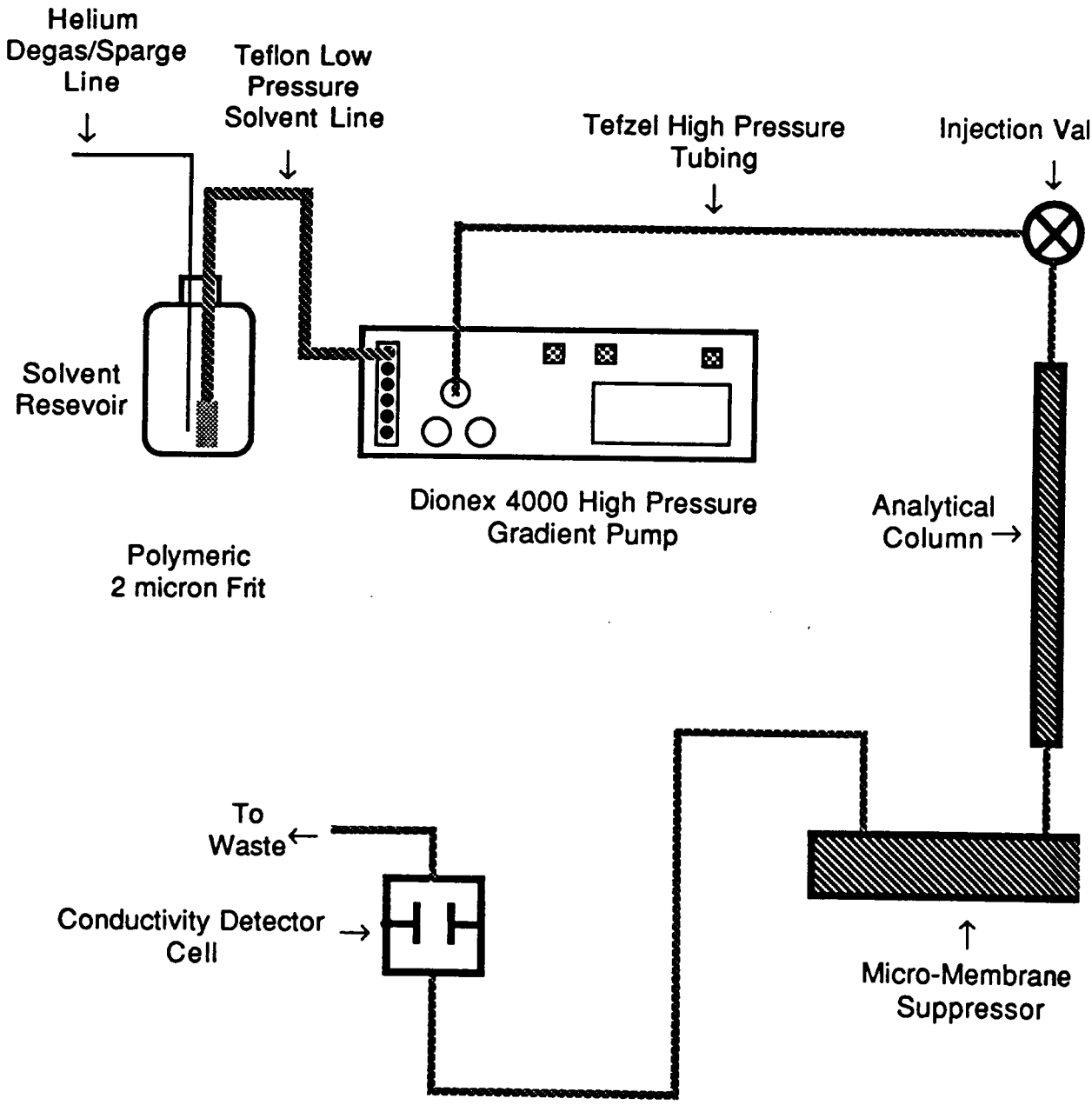


Figure 4 Diagram of Modern Ion Chromatograph

Conductivity Detector Cell

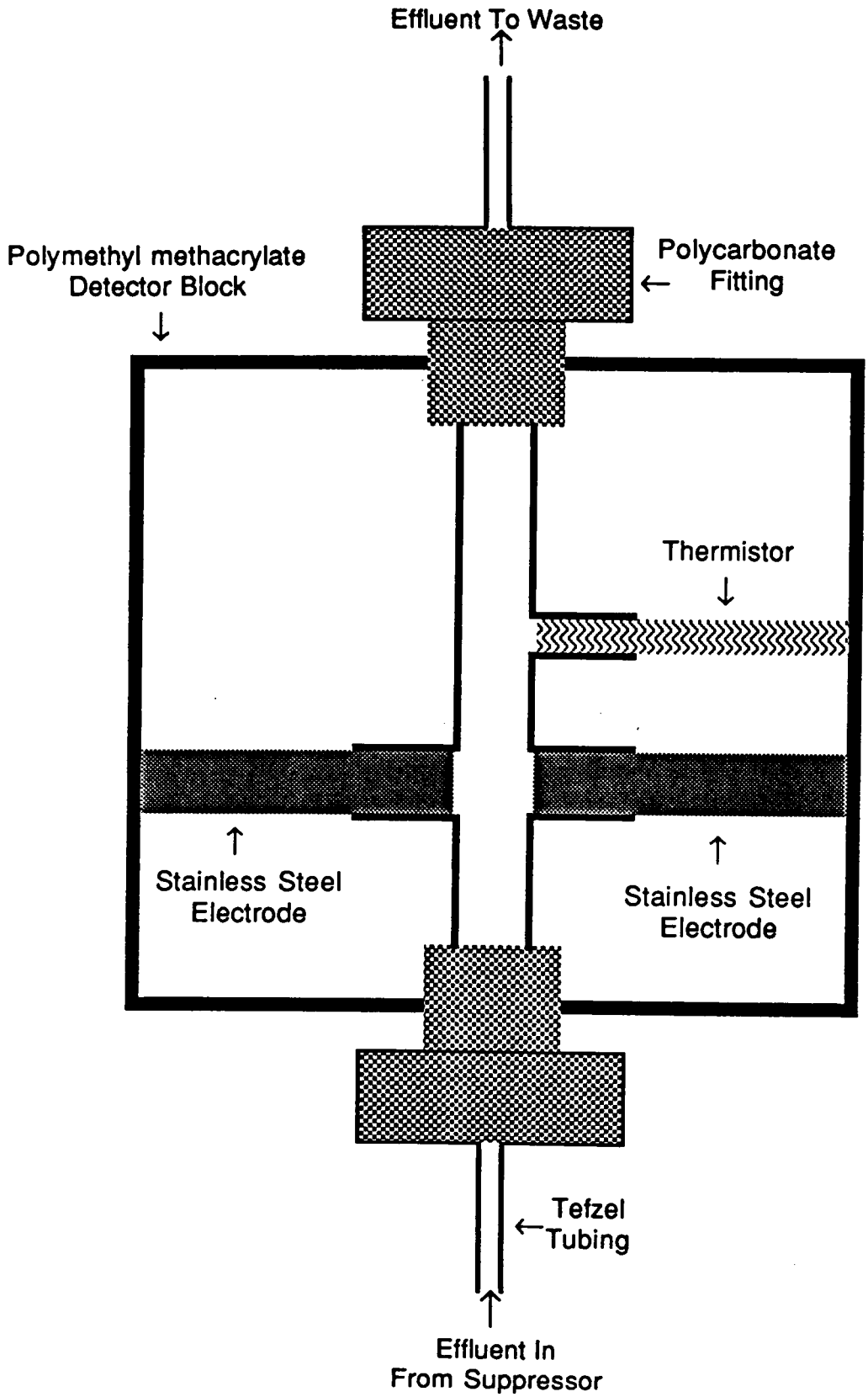


Figure 5 Schematic of Conductivity Detector Cell

$$\Lambda_m(c) = \Lambda_m^\circ - k\sqrt{c} \qquad \text{Equation 1}$$

where, Λ_m (c) is the molar conductance of the stream

Λ_m° is the molar conductance at infinite dilution

k is a coefficient which depends more on the nature of the ions than its specific identity.

and

c is the molar concentration

The major problem that has always plagued conductivity detection is the dependence of conductivity on temperature. The conductivity of a solution will increase by approximately 1.7% for every increase of 1° C. This temperature sensitivity requires that either the detector cell be thermally isolated, or the detector output must go through some compensation. Thermal isolation has been used in the past, but it tends to be the limiting factor in trace analyses. For example, a typical background in suppressed ion chromatography using carbonate / bicarbonate eluant is 20 μS. The conductivity drift due to a 1° C increase in temperature (0.34 μS) is approximately equal to the peak generated by a 200 ppb sulfate injection. Since the usual detection limits for sulfate is closer to 50 ppb, the temperature effects of the 1° C change decreases sensitivity 4 fold. Therefore, Dionex chose to try temperature compensation rather than thermal isolation. The detector electronics include an Intel 8088 microprocessor to accomplish this compensation. The cell

block has a thermistor mounted in the flow path immediately down stream of the electrodes. The microprocessor measures the temperature several times each second and uses this number to normalize the conductivity to 25° C with the following equation :

$$G_{normalized} = G_{measured} \times e^{k(25-T)} \qquad \text{Equation 2}$$

where,

k is the solution temperature coefficient (%/°C)

and

T is the solution temperature in °C

Temperature compensation circuitry allows the use of conductivity detection without thermal insulation. Ion chromatographs equipped with this circuitry can now routinely determine low part per billion levels of several ions by direct injection without interfering baseline instabilities that result from thermal drift.

HIGH PRESSURE PUMP

The pump used in this work is a dual reciprocating piston pump similar to those used in HPLC. The unique feature of this particular pump assembly is that its flow path is entirely metal-free. The solvent reservoirs are either glass or polypropylene with low pressure solvent delivery lines made of teflon. The synthetic sapphire piston rods are housed within pump heads which are made out of a proprietary polymeric material resembling poly-ether-etherketone. This material is able to withstand pressures up to 4000 psi while remaining chemically inert. The ball and seat check valves are housed in a similar material and contain synthetic ruby balls and Tefzel™ seats. Tefzel™ is also used for the high pressure outlet tubing connecting the pump to the injection valve.

The metal-free pumps were originally developed for trace metal analyses. The use of passivated stainless steel limits the minimum detectable quantity (MDQ) by producing unacceptable levels of metal contamination. In addition, these metal-free pumps have realized several other advantages over passivated stainless steel. They have less of a chance of destroying biologically active materials since their surface is less catalytic than metal. They also allow the use of metal chelating agents as mobile phase additives without destroying the pump, and they are more convenient due to their chemical inertness.

™-duPont

The entire flow path of the pump assembly is impervious to any solvent short of concentrated sulfuric acid. This allows the use of solvents which were previously avoided due to their incompatibility with stainless steel, such as sodium hydroxide, halogenated acids, phosphoric acid, buffers, and salts. These are the solvent systems which are of primary interest to the ion chromatographer. Other forms of HPLC can also be performed with this pump assembly using any organic solvent such as methanol, acetonitrile, hexane, methylene chloride, and THF.

INJECTION VALVE

The remainder of the system is also made of inert metal-free materials except for the detector cell electrodes which are made of passivated stainless steel. The high pressure injection valve is made of the proprietary polymer and has a function similar to standard HPLC injection valves. This particular design uses an internal slider to direct flow from the pump to the column, in the "load" mode. In the "inject" mode, the slider is moved by pneumatic actuation to direct flow from the pump, through the fixed volume sample loop, and then to the column (See Figure 6).

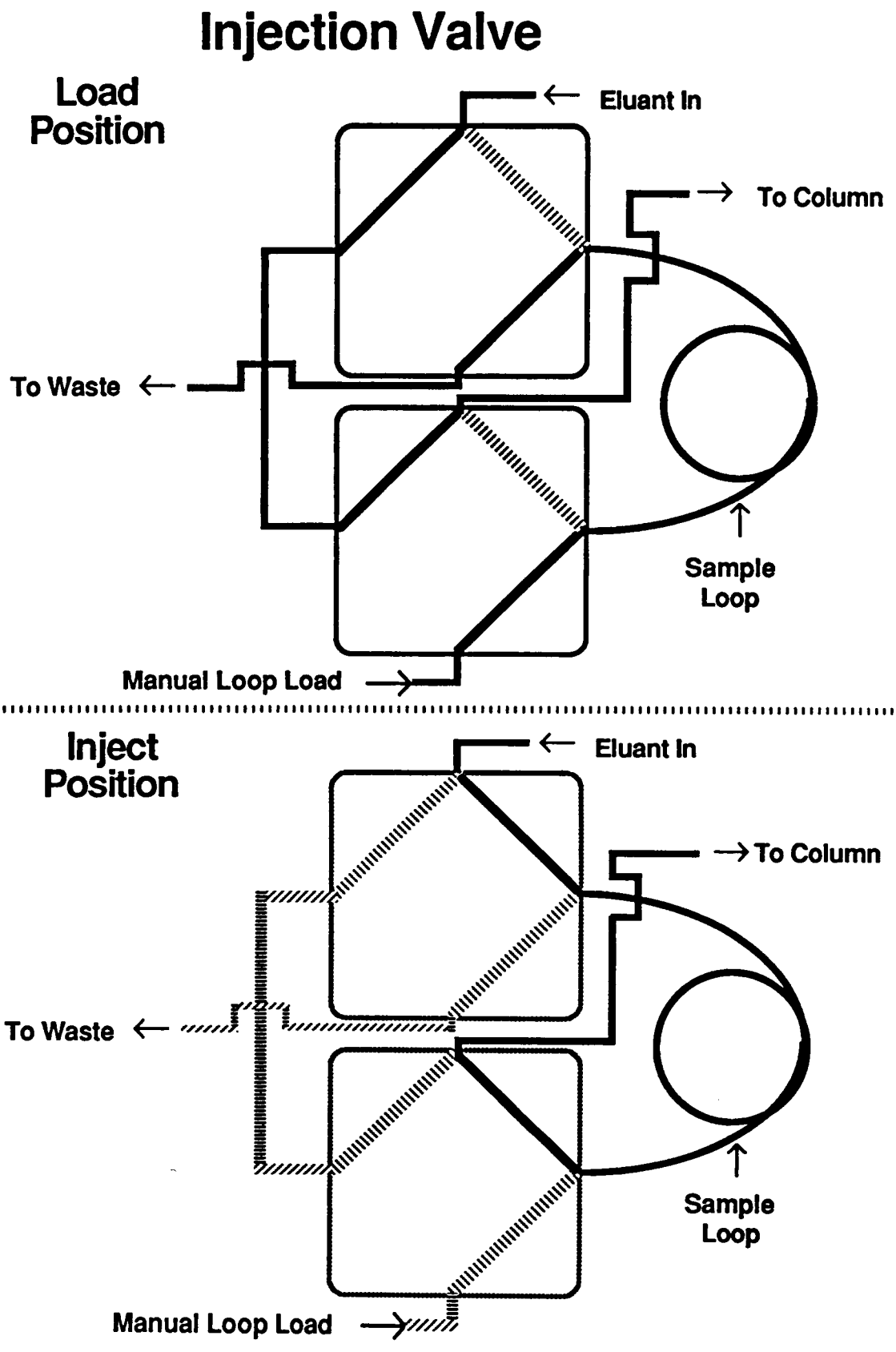


Figure 6 Schematic of Injection Valve

COLUMNS

The anion-exchange chromatography was done on Dionex AS4A columns. These are 25 cm long and have an internal diameter of 4 mm. They are packed with 15 μm pellicular packing material containing quaternary amine exchange sites. Their casings are made of a spun resin material giving them an upper pressure limit of 2000 psi.

The Dionex CS3 cation columns have the same dimensions as the AS4A columns described above. The packing material is a 15 μm pellicular packing which has been surface treated to give a porous, sulfonated surface.

DATA SYSTEM

The data system used was a Perkin-Elmer LSI-100 digital electronic integrator. The 1 volt analog outputs from the detector were fed into the 1 millivolt inputs of the integrator. The attenuation of the integrator was set at 1024, giving a full scale deflection with an approximate 1 volt input. All subsequent range changes were made on the detector. This configuration gives the highest resolution at all ranges since the detector uses digital circuitry for all of the conductivity manipulations. The detector output section has approximately 1024 steps of resolution, independent of its output

range. If the detector range were set at a constant 1000 μS, the best resolution obtainable would be 1 μS. With a 5 mS peak, the precision would be limited to 20%. However, if the range adjustments are made on the detector, the 10 μS range would give a resolution of 0.01 μS. Therefore, the precision of the technique would not be limited by the detector output electronics, but the analytical process.

CHAPTER III

LINEARITY IN CHEMICALLY SUPPRESSED ION CHROMATOGRAPHY [15]

Ion chromatography is now used to analyze a wide range of sample types, with analyte ion concentrations ranging from sub parts-per-billion to per-cent levels. Quantitative analysis is usually accomplished by preparing a multi-level calibration curve from the peak heights or peak areas of known standards and comparing the response of the analytes in the sample to the standard curve. Although the best-fit line through the calibration points is usually linear, a curve calculated from a quadratic equation should be used in the event of deviation from linearity. The calculation of the best-fit curve from a quadratic equation can be tedious, and is best performed by a computer. However, when computing equipment is not available and a strip chart recorder is used, linear calibration curves are used. A common practice in chemically suppressed ion chromatography is the use of a single calibration point, with the line drawn through the origin. This practice is especially popular when many analyses must be performed in a short time. It is obvious that in this case, accurate quantitative analyses will not result, if the detector response is not linear.

Some studies have been performed on linearity in ion chromatography, including studies by Pohl and Johnson[16] and by Doury-Berthod, et al[17]. In the latter report, the authors derived complex equations demonstrating that peak height response in anion exchange chromatography with suppressed conductivity detection is not linear. This prediction is in conflict with the results presented by Pohl and Johnson, and those in this study. Reported here are the results from calibration curves prepared for several anions and cations.

A. EXPERIMENTAL

The linearity experiments were performed on a Dionex Model 4010i ion chromatograph. Conditions for the chromatography were as follows:

Anion Determinations

Separator:	HPIC-AS4A Anion Exchange Column (15 µm particles with quaternery amine functionality)
Eluant:	0.75 mM sodium bicarbonate, and 2.2 mM sodium carbonate
Suppressor:	Anion Micromembrane
Regenerant:	25 mN sulfuric acid
Flow Rate:	1.0 ml/min
Samples:	serial dilutions of 1000 ppm stock solutions of fluoride, chloride, and sulfate as their Na salts
Injection Loop:	50 µl

Cation Determinations

Separator:	HPIC-CS3 Cation Exchange Column (surface sulfonated polystyrene/divinyl benzene)
Eluant:	12 mM HCl, and 0.5 mM diaminopropionic acid,
Suppressor:	Cation Micromembrane
Regenerant :	50 mM tetrabutylammonium hydroxide
Flow Rate:	1.0 ml/min
Samples :	Serial dilutions of 1000 ppm stock solutions of sodium and potassium as their chloride salts
Sample Loop:	50 µl

B. RESULTS AND DISCUSSION

Due to the extreme range of concentrations used to produce the calibration curves, plots of log (peak height or area) vs. log (concentration) were used. For log/log calibration plots, a slope of one will result from linear calibration curves of arithmetic plots, i.e. direct plots of peak height or area vs. analyte concentration. Log/log slopes of greater than one indicate upward curvature on arithmetic plots. Area and height calibration curves generated for Fluoride, Chloride, Sulfate, Sodium, and Potassium are shown in figures 7-16, respectively. The slopes and correlation coefficients from these plots are listed in tables 1-10.

TABLE 1

Fluoride Height Linearity Data

[Fluoride] ppm	Peak Height	Log([Fluoride])	Log (Peak Ht)
0.0100	72.08	-2.00	1.858
0.0100	71.27	-2.00	1.853
0.0100	71.54	-2.00	1.855
0.0200	138.6	-1.699	2.142
0.0200	139.6	-1.699	2.145
0.0200	138.1	-1.699	2.140
0.0500	340.2	-1.301	2.532
0.0500	338.7	-1.301	2.530
0.0500	338.1	-1.301	2.529
0.100	684.4	-1.000	2.835
0.100	687.0	-1.000	2.837
0.100	682.6	-1.000	2.834
0.200	1363	-0.699	3.134
0.200	1358	-0.699	3.133
0.200	1365	-0.699	3.135
0.500	2989	-0.301	3.476
0.500	2991	-0.301	3.476
0.500	2992	-0.301	3.476
1.00	5336	0.000	3.727
1.00	5319	0.000	3.726
1.00	5303	0.000	3.725
2.00	8742	0.301	3.942
2.00	8737	0.301	3.941
2.00	8747	0.301	3.942
5.00	15260	0.699	4.183
5.00	15240	0.699	4.183
5.00	15230	0.699	4.183
10.0	21660	1.000	4.336
10.0	21670	1.000	4.336
10.0	21650	1.000	4.335

Figure 7
Linearity of Fluoride
(Peak Height)

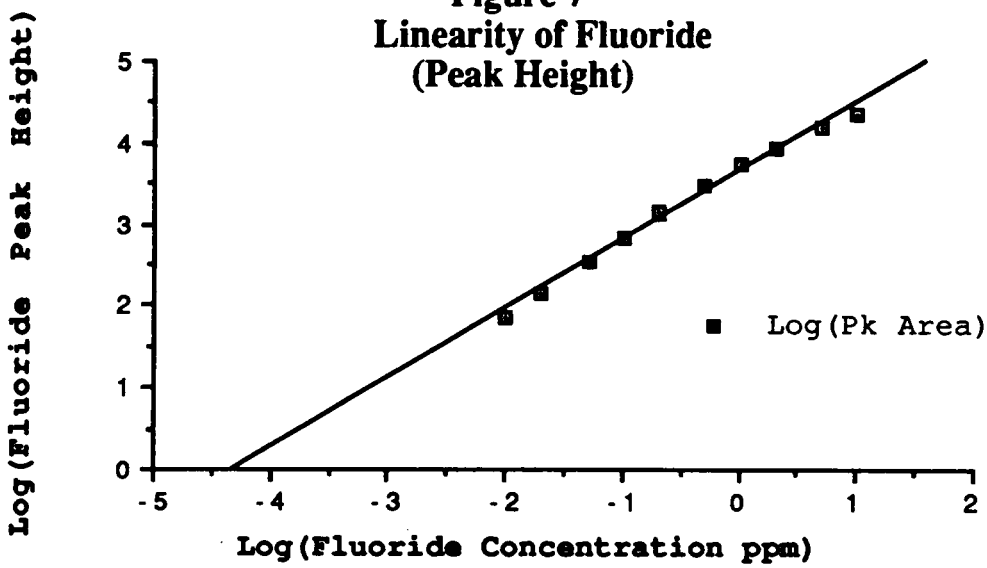


TABLE 2

Fluoride Area Linearity Data

[Fluoride] ppm	Peak Area	Log([Fluoride])	Log (Peak Area)
0.0100	1704	-2.00	3.231
0.0100	1662	-2.00	3.221
0.0100	1754	-2.00	3.244
0.0200	3504	-1.699	3.545
0.0200	3495	-1.699	3.543
0.0200	3467	-1.699	3.540
0.0500	8433	-1.301	3.926
0.0500	8374	-1.301	3.923
0.0500	8364	-1.301	3.922
0.100	16590	-1.000	4.220
0.100	16590	-1.000	4.220
0.100	16530	-1.000	4.218
0.200	33950	-0.699	4.531
0.200	32920	-0.699	4.517
0.200	32960	-0.699	4.518
0.500	83440	-0.301	4.921
0.500	82950	-0.301	4.919
0.500	83680	-0.301	4.923
1.00	162600	0.000	5.211
1.00	162700	0.000	5.211
1.00	162900	0.000	5.212
2.00	332800	0.301	5.522
2.00	333200	0.301	5.523
2.00	332300	0.301	5.522
5.00	807700	0.699	5.907
5.00	806200	0.699	5.906
5.00	808600	0.699	5.908
10.0	1584000	1.000	6.200
10.0	1605000	1.000	6.206
10.0	1603000	1.000	6.205

Figure 8
Linearity of Fluoride
(Peak Area)

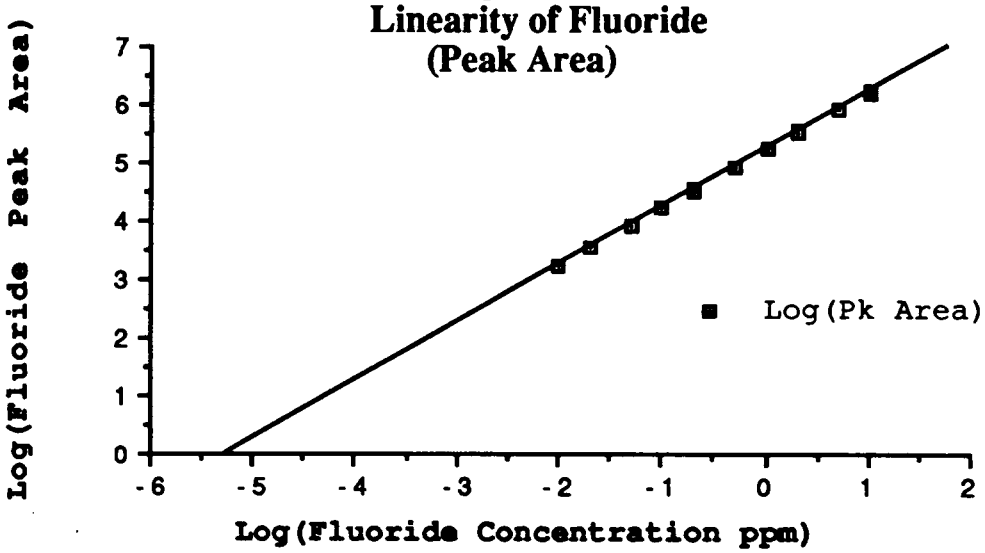


TABLE 3

Chloride Height Linearity Data

[Chloride] ppm	Peak Height	Log([Chloride])	Log (Peak Ht)
0.0200	41.31	-1.699	1.616
0.0200	42.06	-1.699	1.624
0.0200	41.70	-1.699	1.620
0.200	316.2	-0.699	2.500
0.200	313.0	-0.699	2.496
0.200	318.6	-0.699	2.503
2.00	3310	0.301	3.520
2.00	3317	0.301	3.521
2.00	3327	0.301	3.522
20.0	46150	1.301	4.664
20.0	16420	1.301	4.664
20.0	46400	1.301	4.667
200	342700	2.301	5.535
200	353500	2.301	5.548
200	351000	2.301	5.545
1000	760500	3.000	5.881
1000	760200	3.000	5.881
1000	761100	3.000	5.881

Figure 9
Linearity of Chloride
(Peak Height)

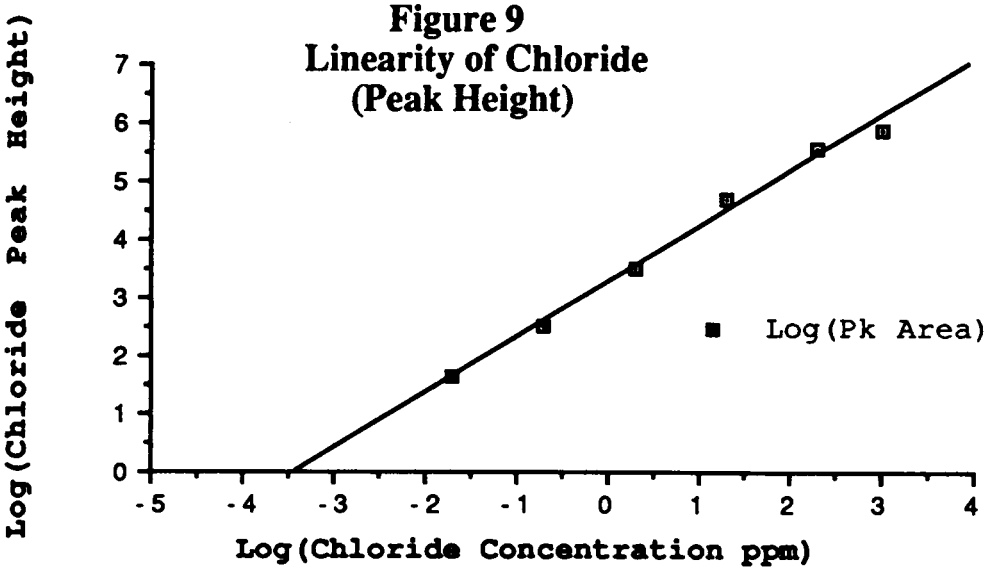


TABLE 4

Clhoride Area Linearity Data

[Chloride] ppm	Peak Area	Log([Chloride])	Log (Peak Area)
0.0200	1358	-1.699	3.133
0.0200	1258	-1.699	3.100
0.0200	1329	-1.699	3.123
0.200	8583	-0.699	3.934
0.200	9011	-0.699	3.955
0.200	8916	-0.699	3.950
2.00	64820	0.301	4.812
2.00	64910	0.301	4.812
2.00	62250	0.301	4.794
20.0	736300	1.301	5.867
20.0	739700	1.301	5.869
20.0	738700	1.301	5.868
200	9519000	2.301	6.979
200	9664000	2.301	6.985
200	9466000	2.301	6.976
1000	48640000	3.000	7.687
1000	48640000	3.000	7.687
1000	48720000	3.000	7.688

Figure 10
Chloride Linearity
(Peak Area)

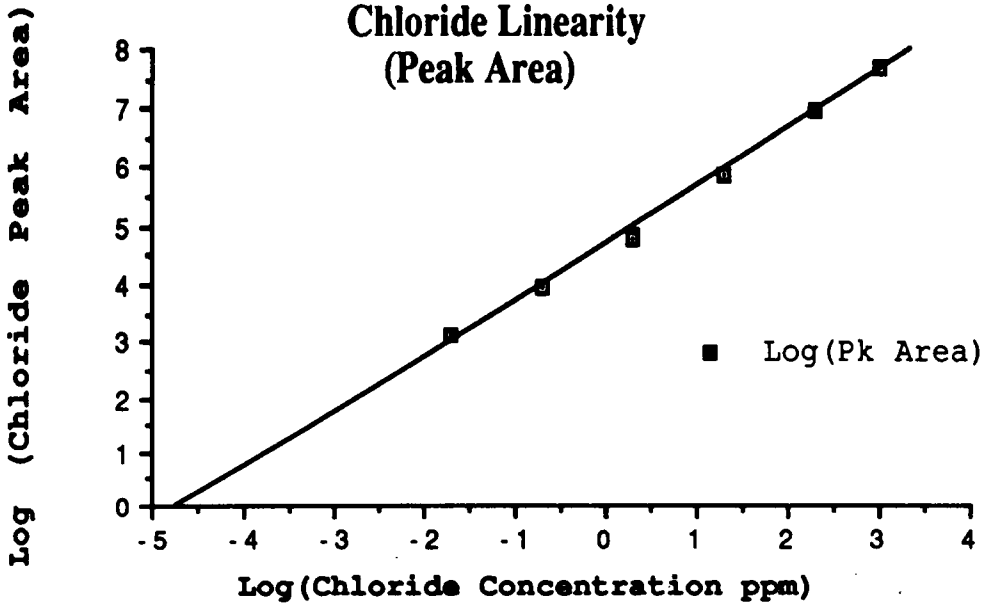


TABLE 5

Sulfate Height Linearity Data

[Sulfate] ppm	Peak Height	Log([Sulfate])	Log (Peak Ht)
0.0800	29.22	-1.097	1.466
0.0800	28.29	-1.097	1.452
0.0800	28.77	-1.097	1.459
0.800	292.9	-0.097	2.467
0.800	292.6	-0.097	2.466
0.800	294.4	-0.097	2.469
8.00	3192	0.903	3.504
8.00	3193	0.903	3.504
8.00	3197	0.903	3.505
80.0	42040	1.903	4.624
80.0	41990	1.903	4.623
80.0	41920	1.903	4.622
800	280200	2.903	5.447
800	281500	2.903	5.449
800	278200	2.903	5.444
1000	331200	3.000	5.520
1000	330900	3.000	5.520
1000	330300	3.000	5.519

Figure 11
Linearity of Sulfate
(Peak Height)

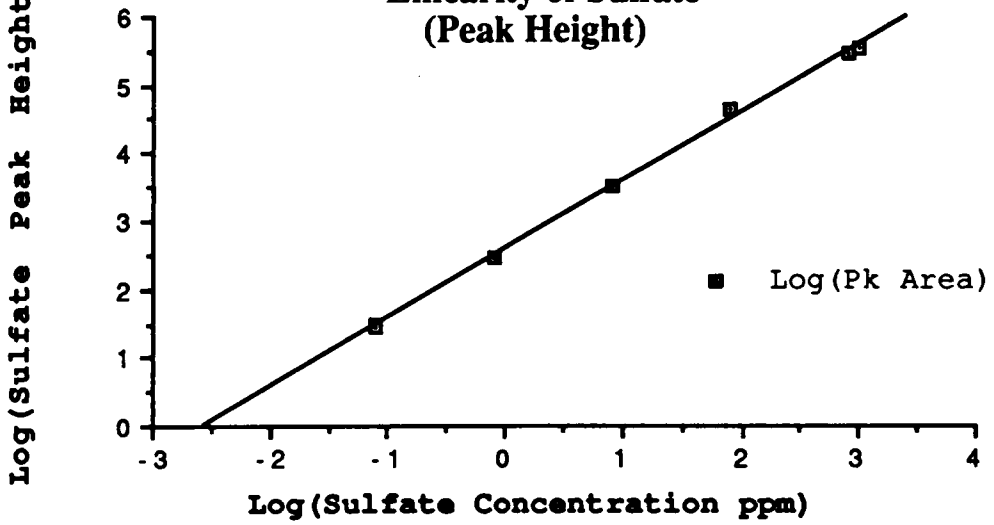


TABLE 6

Sulfate Area Linearity Data

[Sulfate] ppm	Peak Area	Log([Sulfate])	Log (Peak Area)
0.0800	2680	-1.097	3.428
0.0800	2509	-1.097	3.400
0.0800	2744	-1.097	3.438
0.800	18141	-0.097	4.259
0.800	17900	-0.097	4.253
0.800	18070	-0.097	4.257
8.00	215100	0.903	5.333
8.00	215400	0.903	5.333
8.00	207300	0.903	5.317
80.0	2455000	1.903	6.390
80.0	2453000	1.903	6.390
80.0	2449000	1.903	6.389
800	29840000	2.903	7.475
800	29950000	2.903	7.476
800	29630000	2.903	7.472
1000	36930000	3.000	7.567
1000	36840000	3.000	7.566
1000	36810000	3.000	7.566

Figure 12
Linearity of Sulfate
(Peak Area)

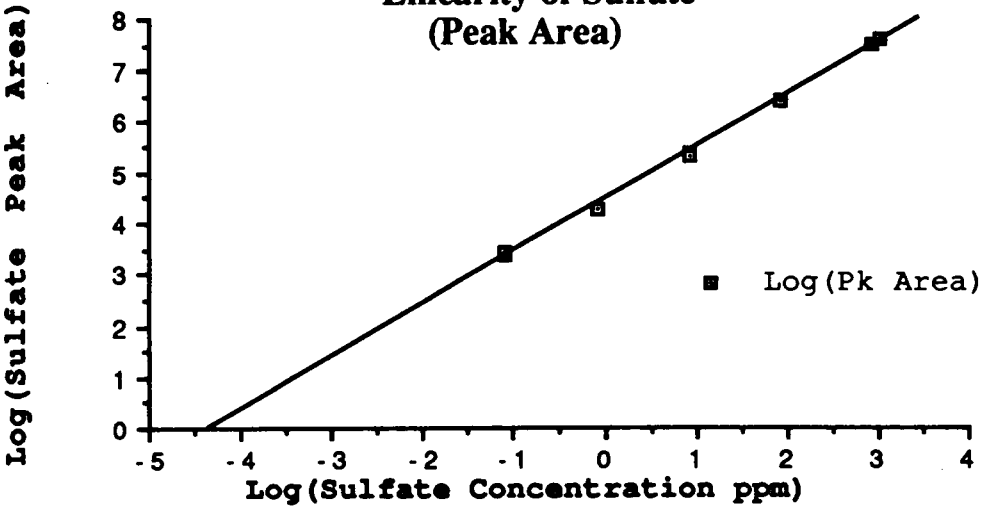


TABLE 7

Sodium Height Linearity Data

[Sodium] ppm	Peak Height	Log([Sodium])	Log (Peak Ht)
0.0500	166.1	-1.301	2.220
0.0500	162.9	-1.301	2.212
0.0500	164.5	-1.301	2.216
0.500	1036	-0.301	3.015
0.500	1061	-0.301	3.026
0.500	1048	-0.301	3.020
5.00	10400	0.699	4.017
5.00	10380	0.699	4.016
5.00	10450	0.699	4.019
50.0	103600	1.699	5.015
50.0	103600	1.699	5.016
50.0	103600	1.699	5.015
500	1029000	2.699	6.012
500	1028000	2.699	6.012
500	1029000	2.699	6.013
1000	12950000	3.000	6.112
1000	13040000	3.000	6.115
1000	12910000	3.000	6.111

Figure 13
Linearity of Sodium
(Peak Height)

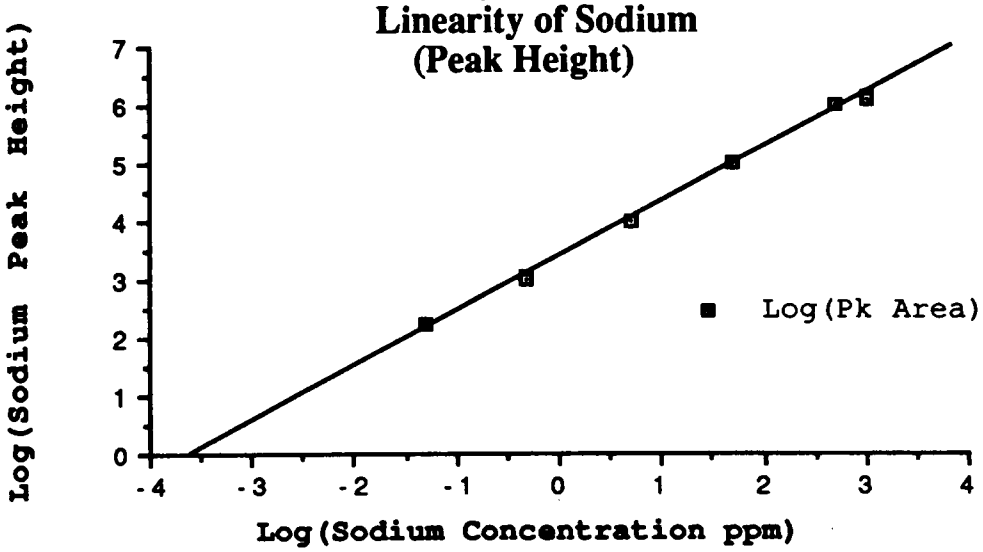


TABLE 8

Sodium Area Linearity Data

[Sodium] ppm	Peak Area	Log([Sodium])	Log (Peak Area)
0.0500	3654	-1.301	3.563
0.0500	3404	-1.301	3.532
0.0500	3529	-1.301	3.548
0.500	30690	-0.301	4.487
0.500	30870	-0.301	4.489
0.500	30780	-0.301	4.488
5.00	312300	0.699	5.495
5.00	310100	0.699	5.492
5.00	310100	0.699	5.491
50.0	3122000	1.699	6.494
50.0	3123000	1.699	6.495
50.0	3124000	1.699	6.495
500	30640000	2.699	7.486
500	30680000	2.699	7.487
500	30610000	2.699	7.486
1000	56090000	3.000	7.749
1000	55890000	3.000	7.747
1000	56240000	3.000	7.750

Figure 14
Linearity of Sodium
(Peak Area)

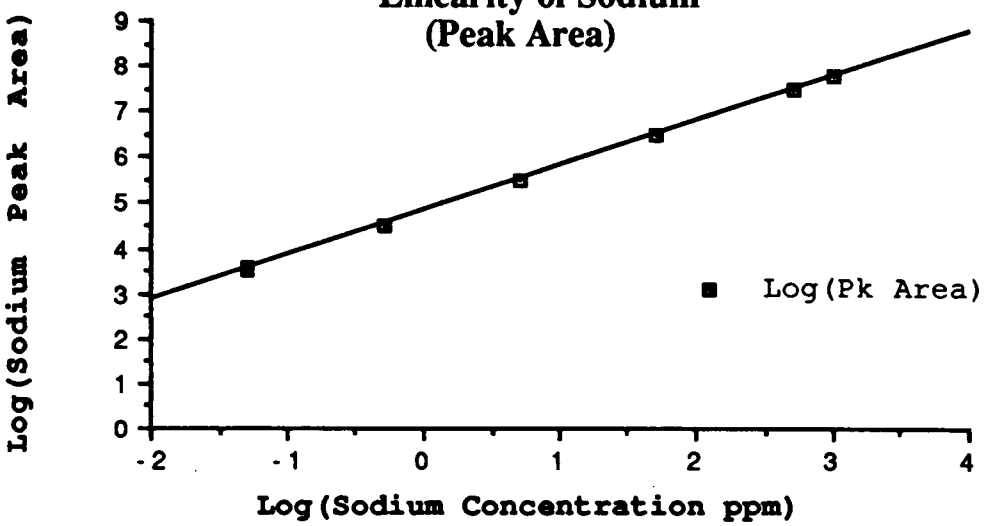


TABLE 9

Potassium Height Linearity Data

[K] ppm	Peak Height	Log([Potassium])	Log (Pk Height)
0.0500	86.64	-1.301	1.938
0.0500	89.67	-1.301	1.953
0.0500	88.17	-1.301	1.945
0.500	826.5	-0.301	2.917
0.500	842.5	-0.301	2.926
0.500	836.3	-0.301	2.922
5.00	8018	0.699	3.904
5.00	8008	0.699	3.904
5.00	8021	0.699	3.904
50.0	55860	1.699	4.747
50.0	55850	1.699	4.747
50.0	55760	1.699	4.746
500	279100	2.699	5.446
500	277300	2.699	5.443
500	280000	2.699	5.447
1000	446400	3.000	5.650
1000	442800	3.000	5.646
1000	440700	3.000	5.644

Figure 15
Linearity of Potassium
(Peak Height)

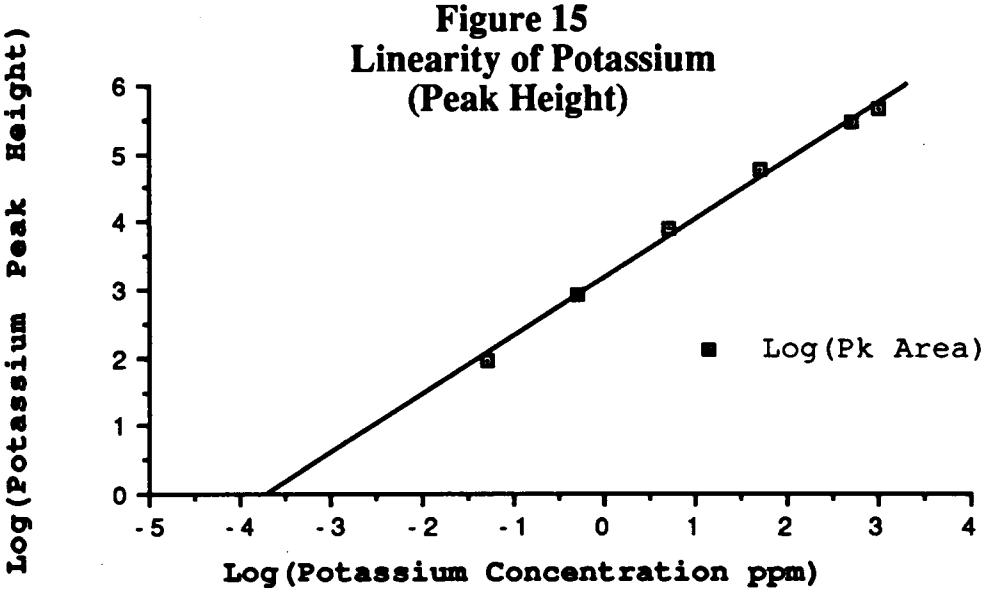
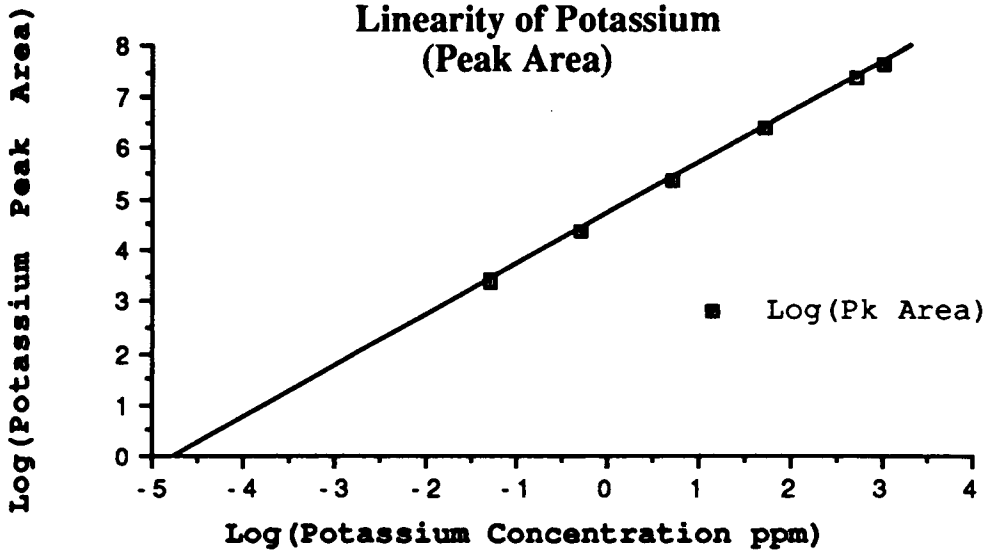


TABLE 10

Potassium Height Linearity Data

[K] ppm	Peak Area	Log([K])	Log (Peak Area)
0.0500	2300	-1.301	3.362
0.0500	2590	-1.301	3.413
0.0500	2445	-1.301	3.388
0.500	22890	-0.301	4.360
0.500	23080	-0.301	4.363
0.500	22990	-0.301	4.361
5.00	234000	0.699	5.369
5.00	234600	0.699	5.370
5.00	233400	0.699	5.368
50.0	2395000	1.699	6.379
50.0	2400000	1.699	6.380
50.0	2395000	1.699	6.379
500	23170000	2.699	7.365
500	23140000	2.699	7.364
500	23210000	2.699	7.366
1000	41750000	3.000	7.621
1000	41570000	3.000	7.619
1000	41890000	3.000	7.622

Figure 16
Linearity of Potassium
(Peak Area)



Calibration slopes from peak area are 0.99 for sodium and potassium 0.99 for fluoride, 1.01 for chloride, and 1.03 for sulfate. For each of these ions, the peak area calibration slopes are closer to one than the peak height plots. Correlation coefficients are also closer to one for the peak area plots. Both the slope and correlation coefficient results indicate that peak area determinations produce a better linear fit than peak height. For sulfate, the peak height slope is 1.00 and the peak area slope is 1.03. The correlation coefficients are roughly the same. As can be seen in the plots, both peak area and peak height plots are linear up to several hundred ppm. At higher concentrations, the ratio of peak height to area decreases as column overload broadens the peak (See Figure 17). This produces a downward curvature in the peak height calibration plot. When calibration plots indicate column overload, samples should be diluted or smaller injection volumes used where possible. Dilution is not possible if the ion of interest is already near the detection limits and there is another component in the sample matrix which is overloading the column. If column overload can not be avoided, peak area should be used for quantitative analyses.

The results presented here are in conflict with the theoretical plots generated by Doury-Bethod et al[18], who predict non-linear calibration curves. Their explanation for this prediction is as follows: There are two factors that determine the conductivity change during elution of a chromatographic peak. The first is the increase in

Overloaded Peak

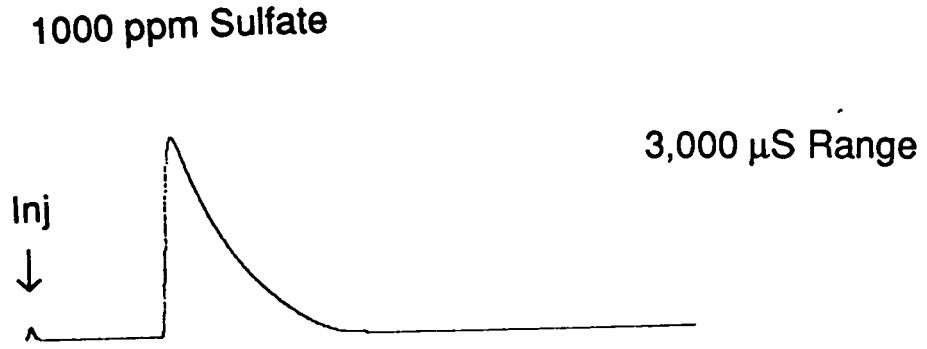


Figure 17

conductivity caused by the elution of analyte ions. The second is the decrease in conductivity caused by the decrease in eluant ion concentration during the elution of analyte ions. This is called the "vacancy peak" or "water dip". When the eluant consists of a carbonate, bicarbonate buffer, the conductivity change during the vacancy peak should be dependent on analyte concentration in a non-linear manner. Since the pK_a of carbonic acid is 6.37, there is some dissociation following suppression of the resulting carbonic acid, producing a significant background conductivity. The deviation from linearity predicted by Doury-Berthod should be caused by the effect of the increasing hydrogen ion concentration during the elution of the strong acid analytes suppressing the ionization of carbonic acid. The extent of this ionization suppression is dependent on the analyte ion's concentration. The sum of the conductivity changes from these factors should produce a non-linear calibration curve.

For the determination of cations, however, there should be very little deviation from linearity as the eluant largely consists of the strong acid HCl. The cation eluant is suppressed almost to zero background, so vacancy peaks following suppression are extremely small in comparison to the contribution of the analytes.

The different results for our anion calibration curves are probably caused by the use of different suppressors and by different eluant concentrations. The total carbonate concentration used by Doury-Bethod was 5 mM. The total carbonate concentration in the eluant used in this study is 2.95 mM. The lower eluant concentration

should minimize the effect of the vacancy peak, resulting in a more linear calibration curve. Also, Doury-Bethod used a packed bed suppressor, while this study was conducted with a continuously regenerated micromembrane suppressor. The effect of the water dip with packed bed suppressors has always been a problem, because the size and retention of the water dip change as the suppressor reaches exhaustion. The micromembrane suppressor produces background conductivities approximately 10% lower that those obtained with packed bed suppressors. There are several reasons for this decreased background conductivity. First, it is possible that some carbonic acid can decompose to carbon dioxide and water, and diffuse through the membrane to the regenerant solution. This could not occur in a packed bed suppressor. Second, the membrane suppressor might not be as efficient in removing sodium as the packed bed suppressor. Since the equivalent conductance of sodium is considerably lower than that of hydrogen, a small amount of sodium reaching the detector would result in lower background conductivity. For example, a 10% decrease in background conductivity for the anion eluant would result from a suppression efficiency of 99.8%. This effect is observed for packed bed suppressors immediately prior to suppressor exhaustion, as the baseline first dips slightly just before increasing off scale. Third, during operation of the anion micromembrane suppressor, a very small amount of sulfuric acid regenerant could leak through the membrane and reach the detector cell. Sulfate in the suppressor effluent has been detected by re-

injecting the effluent. This is of course not a problem for quantitative analysis, as the leakage occurs after separation, and cannot add or subtract from peak sizes. However, the leakage of sulfuric acid usually will suppress the ionization of carbonic acid, thus limiting the effect of the elution of the strong acid anions and causing an increase in background conductivity. It is possible that all three of the factors listed here may be occurring with the net conductivity change being negative.

When all of the factors listed above are considered, it is apparent that many simplifying assumptions must be made in order to derive an equation for conductivity detection. Whether or not an equation can be developed that accurately predicts the observed results, the important conclusion from the data presented here is that when ion chromatography is performed with micromembrane suppressors and calibration curves are prepared from peak areas, the curves are linear over a very wide range of analyte concentrations. In the case of the ions tested, the linear range is from the minimum detection limit, measured in parts-per-billion, to above 0.1%. This is a range of nearly five orders of magnitude.

A direct solution to the question of linearity is the use of sodium hydroxide as the eluant. Sodium hydroxide is converted to water following suppression, so there can be no effect from the vacancy peak. Also, membrane suppressors can suppress the high concentrations of sodium hydroxide required to elute polyvalent ions.

The analytical range of ion chromatography can easily be extended beyond the range reported here. More concentrated samples can be diluted so that the analyte concentrations will be within the linear range. For example, Rocklin used ion chromatography to determine per-cent level concentrations of ions in mixed acid etching solutions[19]. For trace analyses, analyte ions can be concentrated on short ion exchange columns by pumping the sample over the concentrator column. This method was introduced in a paper by Wetzel, et al in 1979.[20] In a recent report by Houskova and Chu[21], concentration techniques were used to determine anions in deionized water. Minimum detection limits were reported as low as 50 parts-per-trillion.

Depending on analyte concentrations, samples can be analyzed using either preconcentration, direct injection, or dilution followed by direct injection. With the use of these techniques, the analytical range of ion chromatography can extend from 50 parts-per-trillion to 50%, a range of ten orders of magnitude.

CHAPTER IV

TRACE ANALYSIS IN CONCENTRATED IONIC SOLUTIONS[22]

The linearity experiments demonstrate the concentration versatility of ion chromatography. In fact, the analysis of trace ions has become almost commonplace. However, a unique problem still exists when trying to determine a trace amount of an ion in a matrix which contains a high concentration of a similarly charged ion. The solution proposed here is to use two analytical columns in series, and to selectively switch the first column out of line when it has been saturated with sulfate (matrix ion).

The first step in this project was to determine the exact limitations of current ion chromatography systems with a single analytical column. The column chosen for this study was the Dionex AS4A anion separator, considered to be the work horse column of anion chromatography. The AS4A is a 25cm x 4mm column which contains the pellicular resin described in the historical section and pictured in figure 2. This column has a relatively high capacity for an analytical column while still maintaining good efficiency (2000-5000 theoretical plates). A series of standards containing 5 ppm chloride and varying amounts of sulfate were used for this investigation. Figure 18 shows the separation of 5 ppm chloride from 100 ppm sulfate. The peaks are well separated with no signs of peak distortion due to column overload. The

5 ppm Chloride + 100 ppm Sulfate on a Single Column

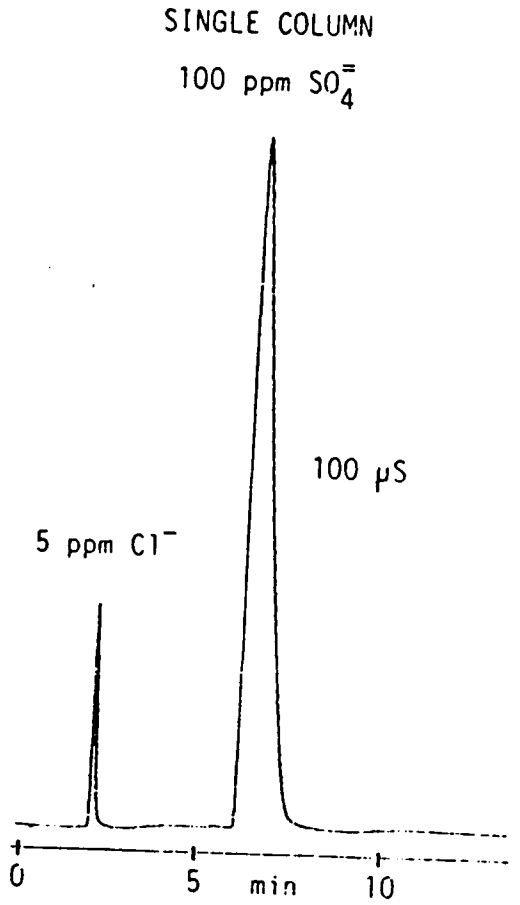


Figure 18

chloride peak has a retention of approximately 2 minutes with the sulfate peak beginning at approximately 6 minutes. This chromatogram was used as the "baseline" or comparison chromatogram. Figure 19 is a chromatogram of 5 ppm chloride in 1000 ppm sulfate. Although good resolution is still maintained under these conditions, several differences exist between this 1000 ppm chromatogram and the baseline chromatogram. For example, the sulfate peak on the 1000 ppm chromatogram begins at approximately 4.5 minutes instead of 6.0 minutes. Also, the sulfate peak on the 1000 ppm chromatogram has a width at base of approximately 4 minutes instead of 1.5 minutes. When the peak is examined under lower sensitivity conditions, it is also apparent that the peak is beginning to front, indicating column overload. When the concentration of sulfate is increased to 5000 ppm (Figure 20), the chloride peak is pushed into the void volume of the column and is entirely buried underneath the sulfate peak. Therefore, the column capacity of a single AS4A column is estimated to be approximately 2500 ppm for sulfate.

The theory behind the column switching is to use the first column as an initial separator with its effluent flowing into a second analytical column. When the void volume,which contains the chloride ion, passes from the first column, it is switched out of line and only the void volume passes to the second column for further separation. If the switching is done at the correct time, all of the chloride should pass onto the second column with a minimal amount of sulfate. The schematic of the system designed for this purpose is shown in Figure 21.

5 ppm Chloride + 1000 ppm Sulfate on a Single Column

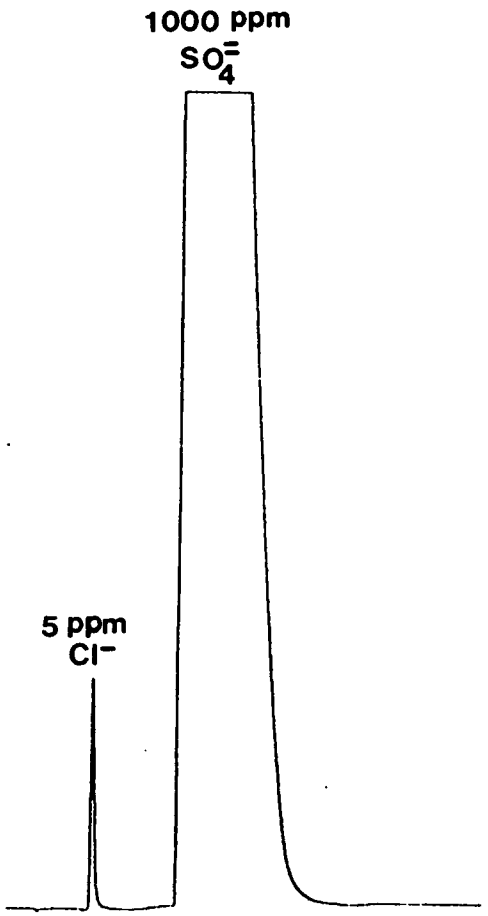


Figure 19

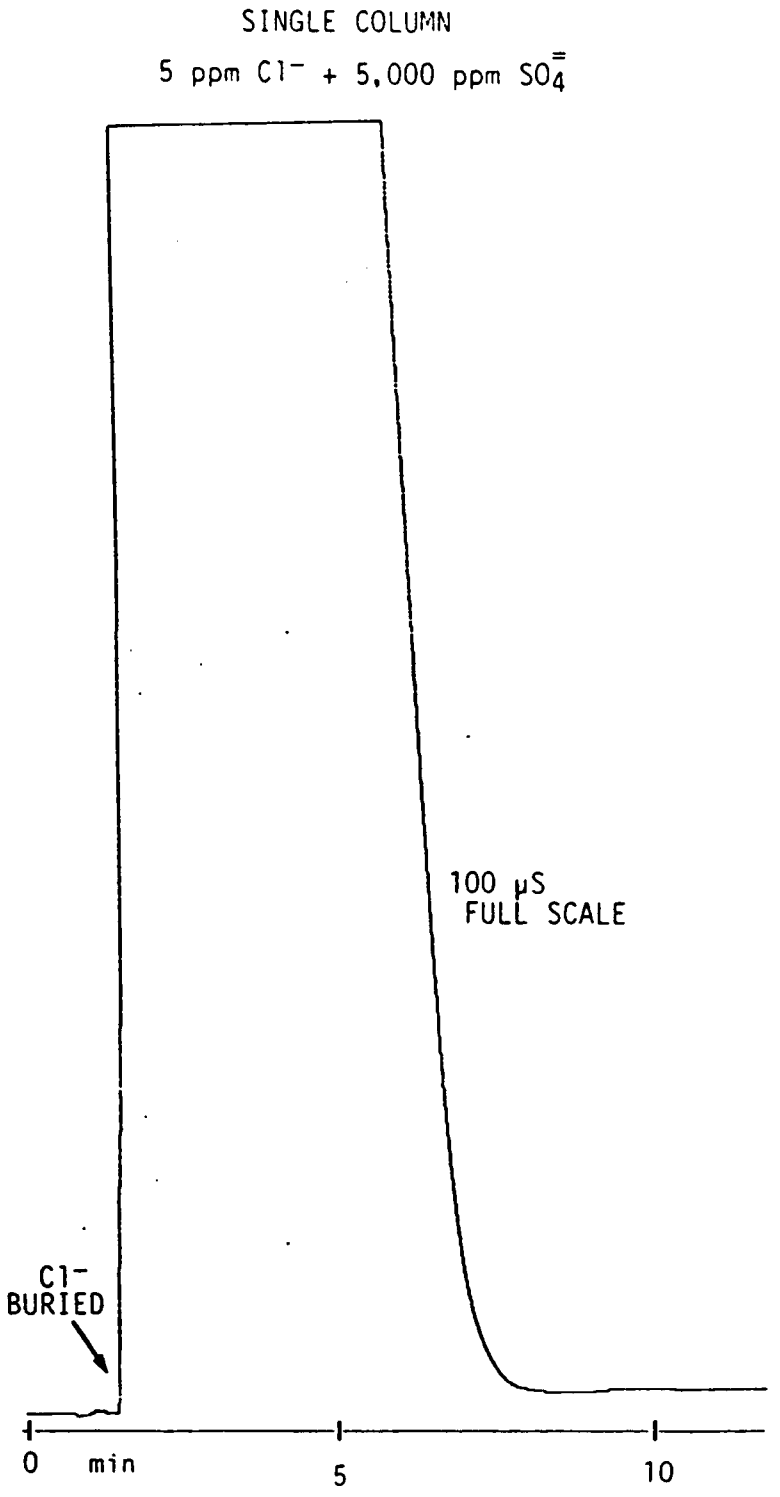

SINGLE COLUMN
5 ppm Cl⁻ + 5,000 ppm SO4=
100 µS
FULL SCALE
Cl⁻
BURIED
0 min
5
10

Figure 20

Column Switching Schematic

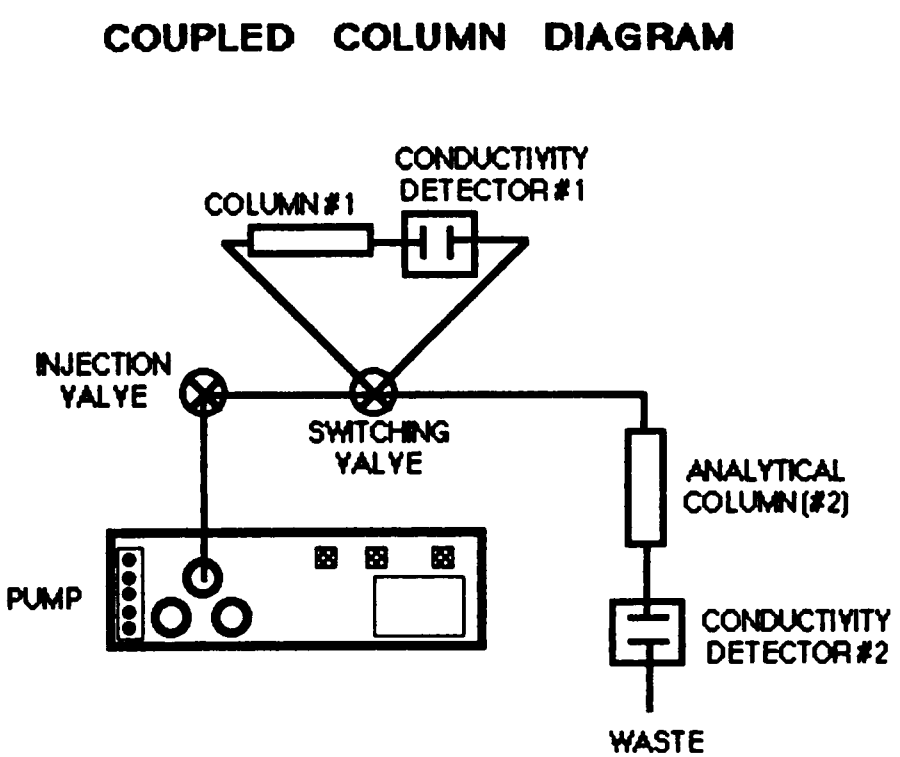


Figure 21

CHROMATOGRAPHIC CONDITIONS

COLUMNS : 2 Dionex AS4A Anion Exchange 250 mm x 4 mm ID

FLOW RATE : 1.0 ml/min

GRADIENT : 20 mM NaOH Hold for 0.8 min
Ramp to 35 mM NaOH in 1.0 min
Hold 35 mM NaOH for 3.2 min
Ramp to 50 mM NaOH in 1 min

DETECTOR #1 : Homemade High Pressure Conductivity Cell

DETECTOR #2 : Chemically Suppressed Conductivity

SUPPRESSOR : Dionex Anion Micro-Membrane

REGENERANT : 25 mN sulfuric acid

The rapidly changing gradient was used to sharpen up the broadened peaks. The chloride peak experiences extra band broadening due to the switching valve and the connecting tubing associated with it. The chloride peak hit the second column as a wide peak due to extra volumes noted above. The fast gradient ramp to 35 mM NaOH pushes the back of the peak faster than the 20 mM NaOH

is moving the front of the peak, thus making the peak sharper by the time it has reached the second detector. After the chloride peak passes through the second detector, the first column is switched back into the flow stream and the final gradient step to 50 mM NaOH is used to rapidly clean out the system.

The first detector cell is necessary to monitor what is eluting from column #1 and thereby determine when the first column should be switched out of line. Since detector #1 must be placed before column #2, a backpressure problem exists. Column #2 produces approximately 500 psi of backpressure. No commercially available conductivity detector cell is made to hold over 100 psi. This made it necessary for the author to design and build a high pressure conductivity cell consisting of two small platinum wires inserted into some high pressure Tefzel™ tubing. The extra-column volume was kept to a minimum by using 0.012 inch internal diameter tubing. The wires were placed in between the Tefzel™ tubing and the standard poly(carbonate) fittings. The tubing and wires were then forced through the stainless steel / polymeric grippers, and the excess wire was then fed through the center of the next piece of connecting tubing. This configuration formed a conductivity cell which was leak proof up to several thousand psi. The exposed ends of the wires were then connected to an ohm meter, and the resistance readings were taken manually from the analog meter. This configuration was not a highly sensitive conductivity detector, but it held the necessary pressure, added little to the band broadening, and was able to give an

adequate deflection when the void volume peak eluted from the column.

When the 5 ppm chloride and 5000 ppm sulfate solution was chromatographed using the column switching system, a quantifiable chloride peak was well resolved from the residual sulfate (See Figure 22). As long as the switch was made after the total elution of chloride, the time of the switch only affected the size of the residual sulfate peak. Therefore, the assumption that all of the injected chloride is pushed into the void volume is correct. This same switching process was used to chromatograph 5 ppm chloride in 10,000 ppm sulfate with similar quantifiable results (See Figure 23). The switching process was then applied to 5 ppm chloride solutions containing 20,000 ppm and finally 48,000 ppm sulfate (See Figures 24 and 25). In these latter two cases, however, it was noted that the chloride peak had a reduced height. This meant that the chloride was not being quantitatively recovered from the first column. Fortunately, the recovered chloride peak size was reproducible to 5% relative standard deviation (%RSD) for the 20,000 ppm sulfate solution and 9% RSD for the 48,000 ppm sulfate solution based on 5 replicate injections. Therefore, this column switching technique is amenable to quantitative analyses, provided matrix matched standards are used(i.e. the standards used to produce the calibration curve for quantitation must contain similar amounts of sulfate as the expected amounts in the samples). The 48,000 ppm sulfate solution seemed to be about as concentrated as the present set-up would allow, since there was barely baseline resolution between the chloride and sulfate

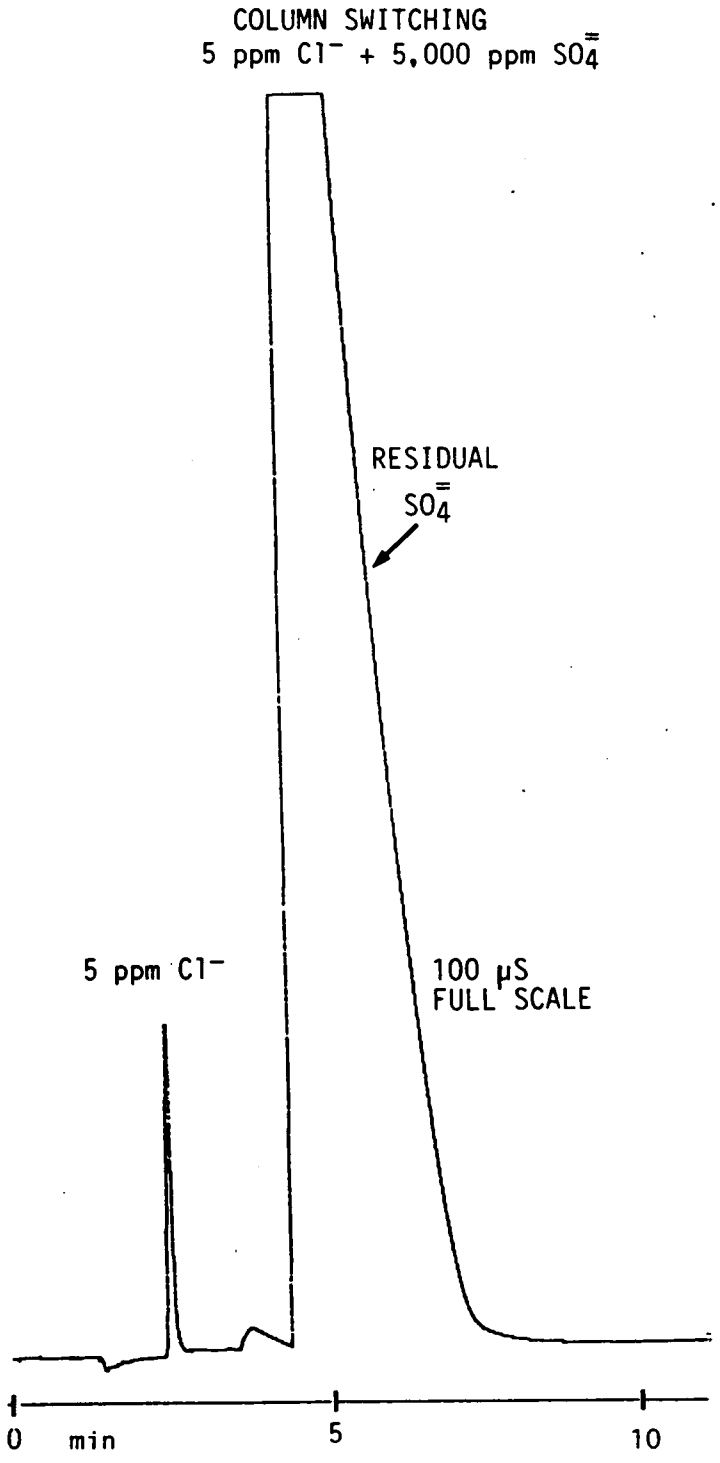

COLUMN SWITCHING
5 ppm Cl⁻ + 5,000 ppm SO4=
RESIDUAL
SO4=
5 ppm Cl⁻
100 µS
FULL SCALE
0 min
5
10

Figure 22

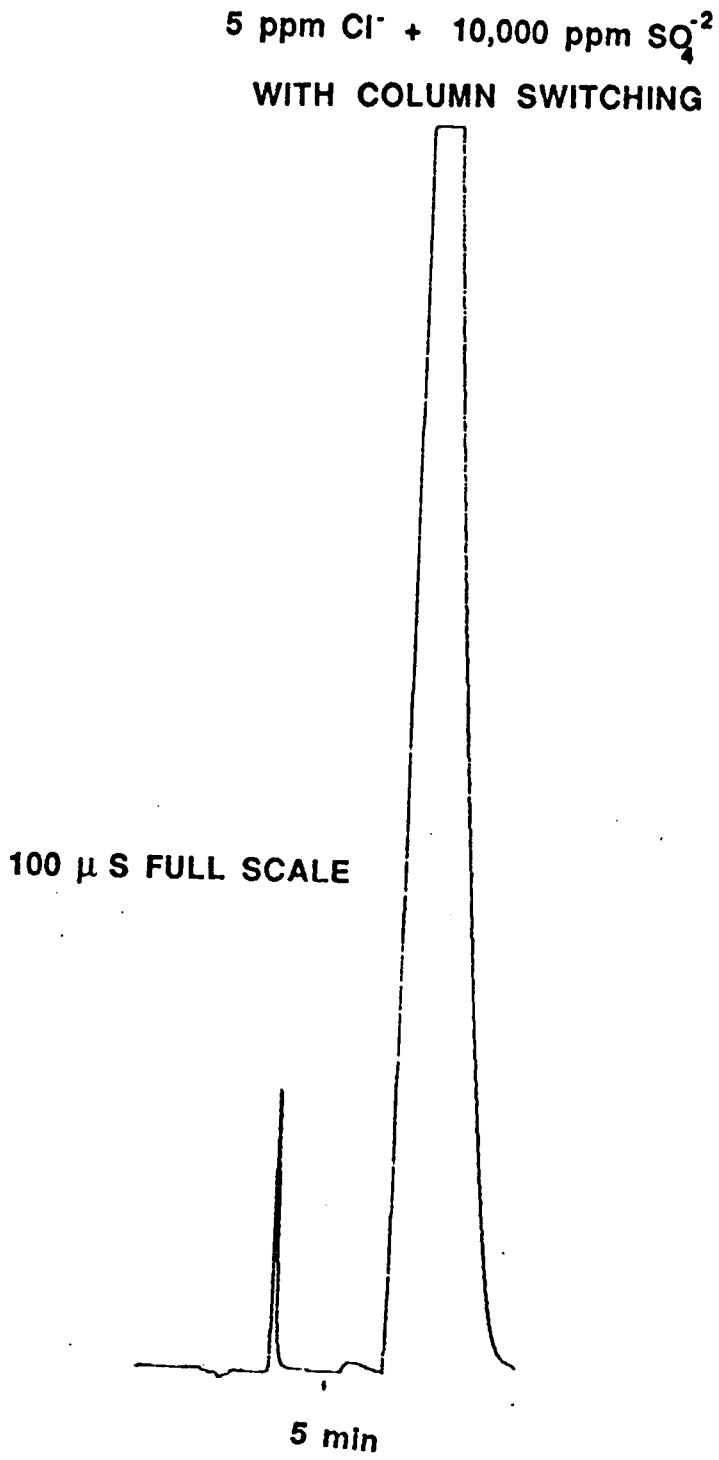

5 ppm Cl⁻ + 10,000 ppm SO4⁻²
WITH COLUMN SWITCHING
100 μ S FULL SCALE
5 min

Figure 23

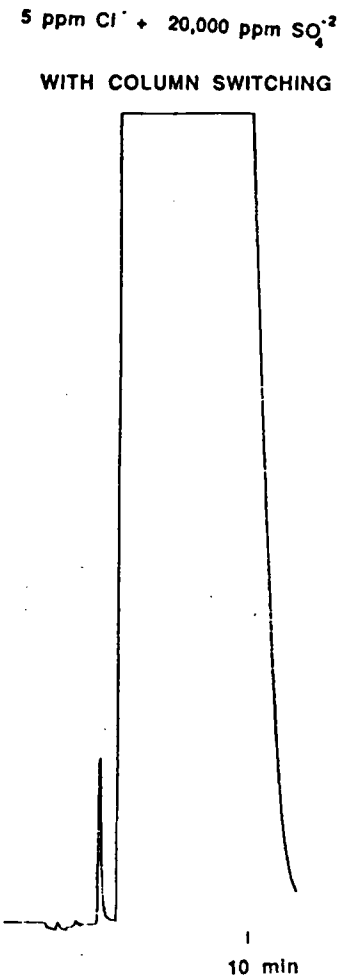


Figure 24

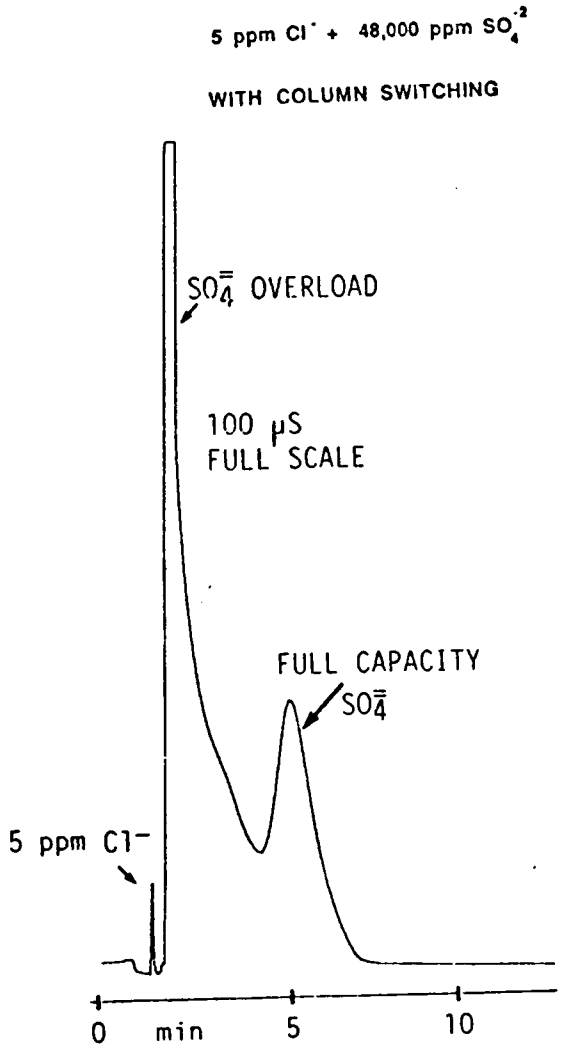

5 ppm Cl⁻ + 48,000 ppm SO₄⁻²
WITH COLUMN SWITCHING
SO₄⁼ OVERLOAD
100 μS
FULL SCALE
FULL CAPACITY
SO₄⁼
5 ppm Cl⁻
0
min
5
10

Figure 25

peaks. The switching time was also critical with this concentrated solution, probably accounting for the higher %RSD.

A final idea was implemented to increase the allowable concentration of sulfate. This idea was to combine the use of a very weak initial eluant and the column switching technique. The weak eluant would maximize the separation between the chloride and sulfate in both columns. The parameters used in this final attempt were as follows:

CHROMATOGRAPHIC CONDITIONS

COLUMNS : 2 Dionex AS4A Anion Exchange 250 mm x 4 mm ID

FLOW RATE : 1.0 ml/min

GRADIENT : 1 mM NaOH Hold for 1.0 min
Ramp to 25 mM NaOH in 1.0 min
Hold 25 mM NaOH for 3.2 min
Ramp to 50 mM NaOH in 1 min
Switch Column #1 in Line and Hold for Cleaning

DETECTOR #1 : Homemade High Pressure Conductivity Cell

DETECTOR #2 : Chemically Suppressed Conductivity

SUPPRESSOR : Dionex Anion Micro-Membrane

REGENERANT : 25 mN Sulfuric Acid

Under normal analytical conditions, sulfate will not migrate at all with the 1 mM NaOH (With a 1 mM isocratic eluant, fluoride, which is the most weakly retained anion, will have a retention time of about 7 minutes.) Of course the high concentration of sulfate still acts as a concentrated plug of eluant, but if the column is well equilibrated with the 1 mM NaOH, some increased retention should be expected. Figure 26 is a chromatogram of 5 ppm chloride and 100,000 ppm sulfate. The chloride peak appears to be well resolved, and the %RSD for the chloride peak height is 10%, again for 5 replicate injections. The baseline disturbance is probably due to the pressure change from the column switching and the ultra-high concentration of sulfate. This chromatogram was run at a much later date than the others, therefore the pressure feedback mechanism of the pump may have changed. The Dionex 4000 gradient pump is a pseudo constant pressure pump, equipped with a micro-processor and a pressure transducer to minimize pulsations. Unfortunately, when the column is switched out of line, the pump tries to maintain the original pressure by speeding up the flow rate of the pump. The system, therefore, takes 30 seconds to 1 minute to equilibrate to the new pressure. The column switching and gradient combination helps to solve the concentration problem by increasing the upper limit of sulfate concentration from about 3,000 ppm (maximum sulfate concentration for a 50 µl injection onto a single column) to at least 100,000 ppm.

5 ppm Chloride + 100,000 ppm Sulfate

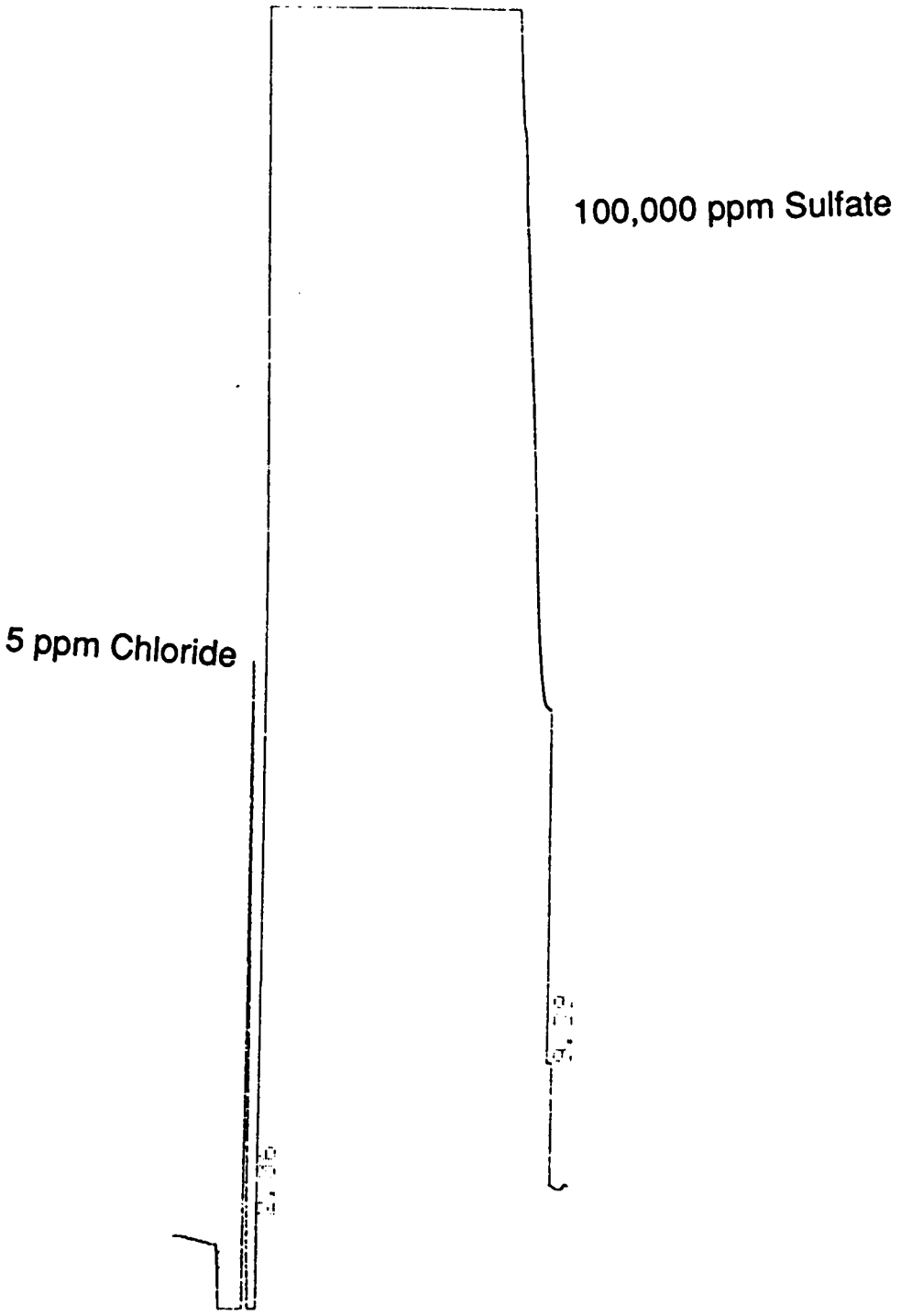


Figure 26

During these studies a previously unreported problem was encountered.

When the 10,000 ppm sulfate solution was chromatographed, an interesting phenomenon was observed; two very large peaks emerged from the chromatogram. This phenomenon was first noted by O'Bynum, et al in 1981.[23] The first peak elutes from the column near the void volume, while the second peak has a retention time similar to that expected for sulfate under the chromatographic conditions used. The existing explanation was that the first peak was chloride which was stripped from the column stationary phase. This conclusion was hastily reached since the retention time of the first peak was roughly equal to that of chloride under similar conditions. O'Bynum proposed that this chloride was an equilibrium build up on the chloride from chloride contamination in the eluant. This did not seem to be a viable explanation for several reasons. The extremely large size of the first peak could only have come from a concentration in excess of several thousand ppm. Also, the retention time was nearly the void volume, meaning that anything eluting at or near the void volume with such a high concentration would give the same retention time. The first experimental step was to run this high concentration of sulfate several times in a row and measure the size of this mysterious first peak. It was determined that the size of the first peak was not a function of how long the eluant was allowed to pump over the column. Therefore, the peak could not have been a result of contaminants in the mobile phase since one would expect the peak to get larger the longer the mobile phase flowed through the column.

Also, this high level of contamination would have taken quite a considerable time to build up on the column.

Since the existing theory was definitely incorrect, several other aspects of the system had to be carefully examined. The first possibility to eliminate was the extreme pH difference between the sample and the eluant. The source of sulfate for the sample was 1 N sulfuric acid and the eluant was 35 mM NaOH. In order to eliminate this pH difference as a possibility, two more 10,000 ppm sulfate solutions were made. The first was made by neutralizing the sulfuric acid with the appropriate amount of NaOH, while the second was made from high purity sodium sulfate. The results were identical to those obtained with the sulfuric acid as the eluant, thus eliminating the possibility of the pH differential causing the double peaks (See Figures 27 and 28).

The next step in explaining the problem was to qualitatively identify the two peaks. The peaks were collected as they eluted from the detector and analyzed. Ion chromatography was used to determine that both peaks were actually sulfate in the same SO_4^{2-} form. The proposed explanation for the existence of two well separated peaks for the same form of sulfate is as follows. The anion exchange column consists of a finite number of positive exchange sites. The sulfate ions are attracted to these sites by coulombic attraction. The sulfate ions begin to occupy these sites at the top of the column and slowly work their way down the column. If the number of sulfate ions is greater than the total number of accessible exchange sites, the unsorbed (excess) sulfate ions will pass rapidly

20,000 ppm Sulfate From H_2SO_4 + NaOH

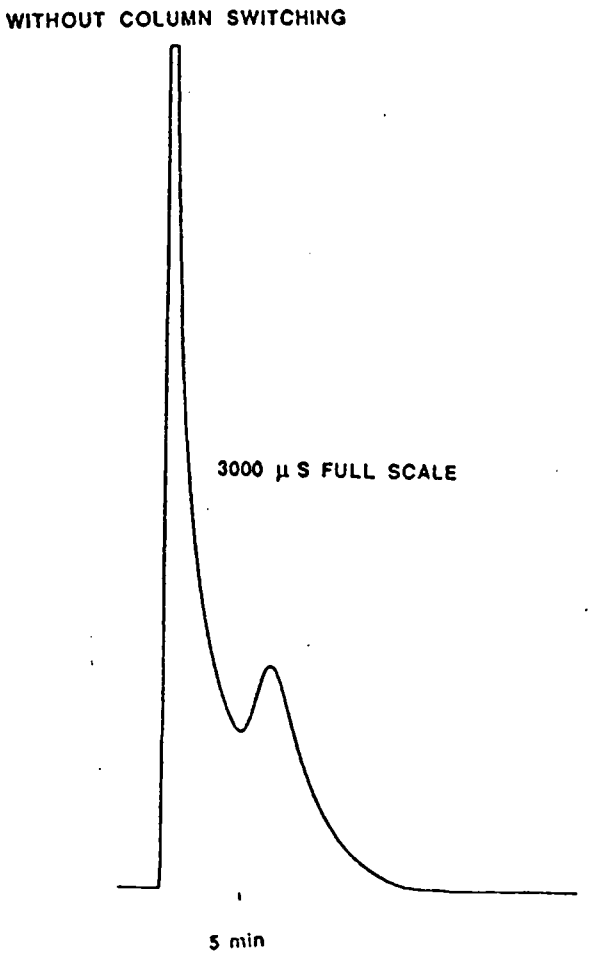


Figure 27

20,000 ppm Sulfate From Na_2SO_4

Figure 28

through the column traveling at the same speed as the mobile phase. They will necessarily be eluted in the void volume of the column, producing an extra peak. This is, therefore, the explanation for the sulfate in the void volume.

The sulfate ions remaining on the column will now undergo typical ion-exchange with the active sites on the column. These sulfate ions which remain on the column will then be eluted off by the mobile phase at the typical retention time expected for sulfate under the given chromatographic conditions. The fact that there are a fixed number of exchange sites on the column explains why the second peak does not increase in size with increasing amounts of sulfate. The first peak, however, does grow with increasing amounts of sulfate beyond this column limit. The column limit of the AS4A column was determined to be between 5000 and 7000 ppm sulfate with a 50 µl injection.

CHAPTER V

TEMPERATURE EFFECTS IN ION CHROMATOGRAPHY[24]

A standard ion chromatographic system was set up as follows :

Chromatographic Conditions

Column :	Dionex AS4A
Flow Rates :	0.3 to 3 ml/min depending on pressure limitations
Sample :	50 µL 1 ppm Chloride and 5 ppm Sulfate
Eluant:	75 mM NaOH, Isocratic
Detector :	Conductivity
Suppressor :	Anion Micro-Membrane
Regenerant :	25 mN Sulfuric Acid

In order to maintain constant temperature, the entire flow system was submerged in a constant temperature bath. This submerged system included eluant reservoirs, transfer tubing, static gradient mixer, injection valve, anion-exchange column, suppressor, regenerant bottle, and detector cell. The first Van Deemter study was done at 20° C with flow rates ranging

from 0.3 ml/min to 2.0 ml/min. The 2.0 ml/min upper limit was set by the pressure limitations and the suppression capacity at that temperature. The 0.3 ml/min lower limit was set by the pump limitations.

Figure 30 shows the curve resulting from the 20° data (See table 11). This plot is relatively flat and similar to those shown in the literature.[25] Figure 31 shows the curve resulting from the 30° C data (See Table 12). This plot reveals an increased efficiency over the 20° C data, a result that was expected based on a qualitative examination of the Van Deemter equation (Equation #3). This result suggested that if the system temperature were further increased, the overall efficiency would also increase. However, the plots obtained from the the 40°, 50°, and 60° C experiments reject this hypothesis (See Figures 32,33, and 34 and Tables 13,14, and 15).

The dependence of selectivity, α, on temperature was also investigated. Based on the reports in the literature, the selectivity was expected to decrease as temperature was increased.[26] In order to simplify the experimental portion of this study, a single flow rate was chosen and the system temperature was varied. The assumption was made that the capacity factors were independent of the flow rate used. This assumption was validated by measuring the capacity factors for chloride and sulfate from 0.3 ml/min to 2.5 ml/min at 50° C (See Figure 35). The capacity factors were shown to be independent, within experimental error, with respect to flow rate. The standard flow rate of 1.0 ml/min was chosen for the study.

VAN DEEMTER EQUATION

$$H = A + B/\mu + C\mu$$

WHERE :

H = Height Equivalent of a Theoretical Plate

$A = 2 * \lambda * (d_p)$ Peak broadening due to multipath effect

λ is a measure of the packing irregularity

d_p : Particle diameter of the packing material

$B = 2\gamma(D_m)$

$C = H_s + H_m$ Lateral diffusion and the delay in the mass transfer processes

$$H_s = \frac{f * p * (1-p) * d_f^2}{D_s} * \mu$$

f : Form factor for stationary phase

p : solute concentration in the stationary phase

(1-p) : Solute concentration in the mobile phase

d_f : Thickness of stationary phase

D_s : Diffusion coefficient of solute in the stationary phase

$$H_m = \frac{\omega * d_p^2}{D_m} * \mu$$

ω : Measure of the quality of the packing process

γ : Obstruction factor

TABLE 11

20°C Flow Rate vs HETP Data

Flow Rate (ml/min)	HETP (mm)
0.4	0.084
0.4	0.085
0.4	0.084
0.6	0.087
0.6	0.088
0.6	0.087
0.8	0.090
0.8	0.090
0.8	0.090
1.0	0.096
1.0	0.095
1.0	0.096
1.2	0.100
1.2	0.100
1.2	0.100
1.4	0.109
1.4	0.108
1.4	0.108
1.6	0.115
1.6	0.116
1.6	0.116
1.8	0.122
1.8	0.121
1.8	0.121
2.0	0.127
2.0	0.127
2.0	0.127

Figure 30

Van Deemter Curve for Sulfate at 20° C

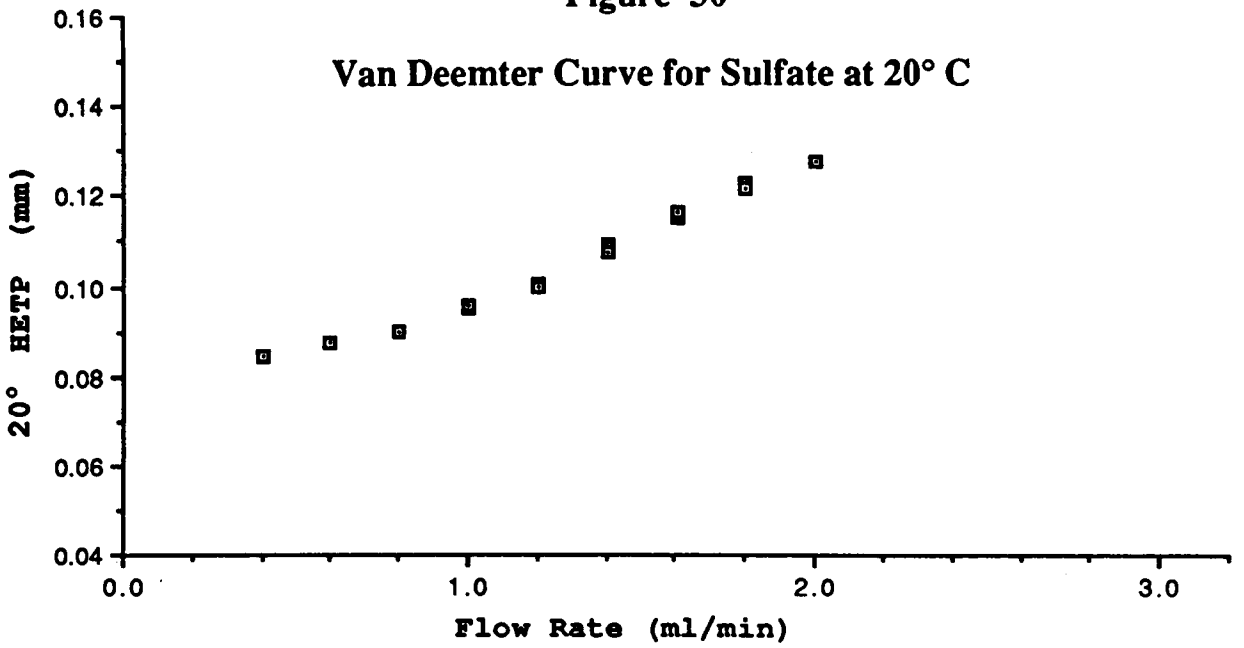


TABLE 12

30°C Flow Rate vs HETP Data

Flow Rate (ml/min)	HETP (mm)
0.3	0.052
0.3	0.052
0.3	0.052
0.4	0.059
0.4	0.058
0.4	0.058
0.6	0.064
0.6	0.064
0.6	0.063
0.8	0.070
0.8	0.071
0.8	0.070
1.0	0.078
1.0	0.078
1.0	0.078
1.2	0.083
1.2	0.083
1.2	0.083
1.4	0.087
1.4	0.088
1.4	0.087
1.6	0.092
1.6	0.094
1.6	0.093
1.8	0.093
1.8	0.092
1.8	0.094
2.0	0.099
2.0	0.100
2.0	0.101

Figure 31

Van Deemter Curve for Sulfate at 30° C

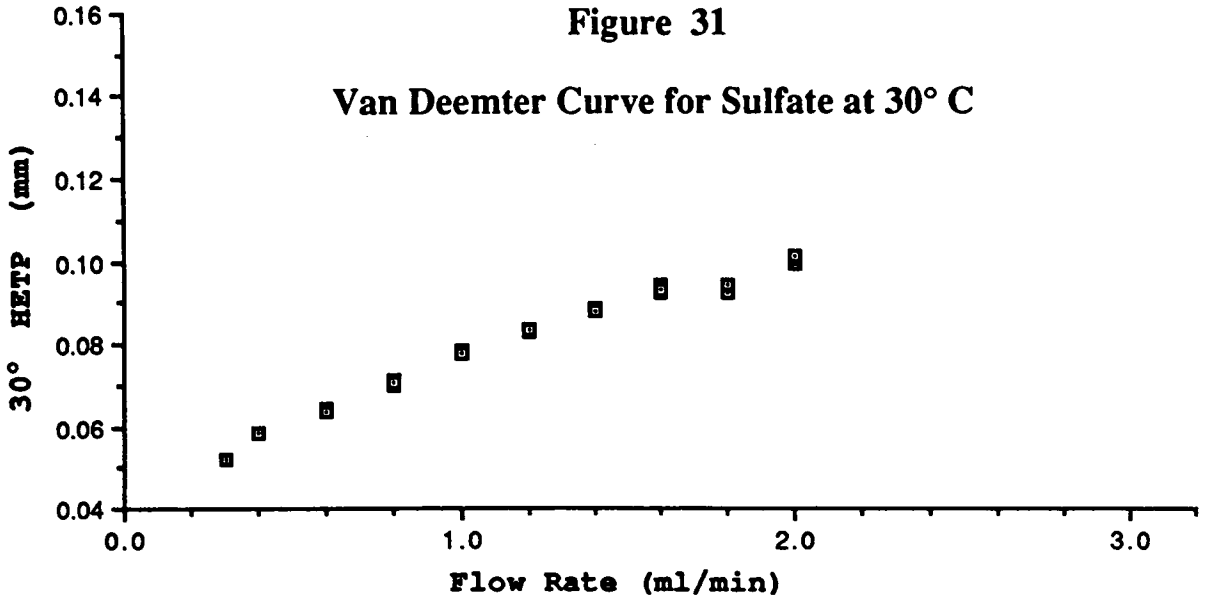


TABLE 13

40°C Flow Rate vs HETP Data

Flow (ml/min)	HETP (mm)	Flow (ml/min)	HETP (mm)
0.3	0.050	2.4	0.109
0.3	0.049	2.4	0.112
0.3	0.050	2.4	0.115
0.4	0.051	2.5	0.099
0.4	0.051	2.5	0.097
0.4	0.050	2.5	0.096
0.6	0.058		
0.6	0.057		
0.6	0.059		
0.8	0.065		
0.8	0.065		
0.8	0.065		
1.0	0.072		
1.0	0.072		
1.0	0.073		
1.2	0.085		
1.2	0.085		
1.2	0.084		
1.4	0.093		
1.4	0.094		
1.4	0.093		
1.6	0.098		
1.6	0.097		
1.6	0.098		
1.8	0.109		
1.8	0.109		
1.8	0.110		
2.0	0.118		
2.0	0.116		
2.0	0.117		
2.2	0.113		
2.2	0.116		

Figure 32

Van Deemter Curve for Sulfate at 40° C

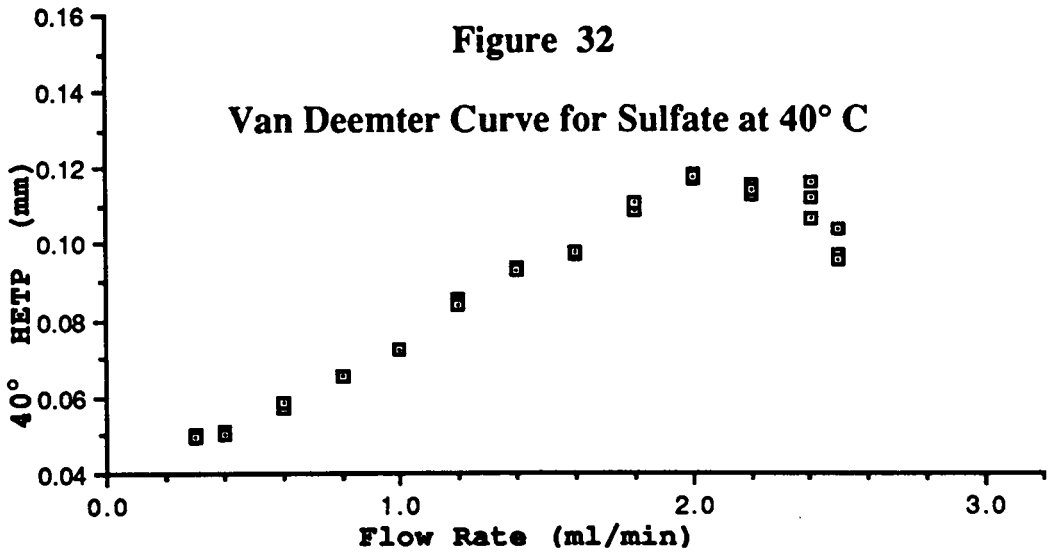


TABLE 14

50°C Flow Rate vs HETP Data

Flow Rate (ml/min)	HETP (mm)
0.3	0.069
0.3	0.070
0.3	0.070
0.4	0.073
0.4	0.073
0.4	0.073
0.6	0.079
0.6	0.080
0.6	0.079
0.8	0.085
0.8	0.085
0.8	0.086
1.0	0.100
1.0	0.100
1.0	0.100
1.2	0.115
1.2	0.115
1.2	0.115
1.4	0.122
1.4	0.122
1.4	0.124
1.6	0.121
1.6	0.123
1.6	0.121
1.8	0.123
1.8	0.123
1.8	0.125
2.0	0.131
2.0	0.131
2.0	0.129
2.5	0.128
2.5	0.129
2.5	0.129

Figure 33

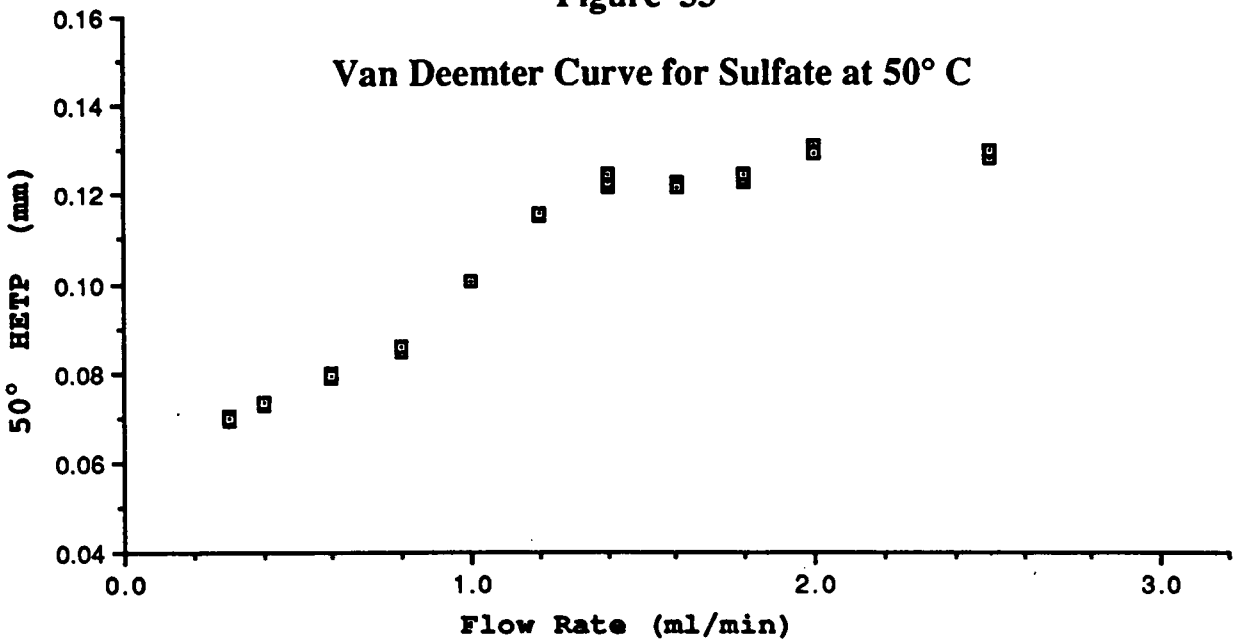

Van Deemter Curve for Sulfate at 50° C
50° HETP (mm)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.0
1.0
2.0
3.0
Flow Rate (ml/min)

TABLE 15

60°C Flow Rate vs HETP Data

Flow Rate (ml/min)	HETP (mm)
0.3	0.070
0.3	0.070
0.3	0.070
0.4	0.077
0.4	0.075
0.4	0.076
0.6	0.083
0.6	0.083
0.6	0.082
0.8	0.093
0.8	0.093
0.8	0.091
1.0	0.112
1.0	0.111
1.0	0.110
1.2	0.118
1.2	0.118
1.2	0.119
1.4	0.128
1.4	0.129
1.4	0.127
1.6	0.128
1.6	0.130
1.6	0.129
1.8	0.124
1.8	0.124
1.8	0.126
2.0	0.121
2.0	0.121
2.0	0.122
2.5	0.124
2.5	0.126
2.5	0.124
3.0	0.108
3.0	0.108
3.0	0.108

Figure 34

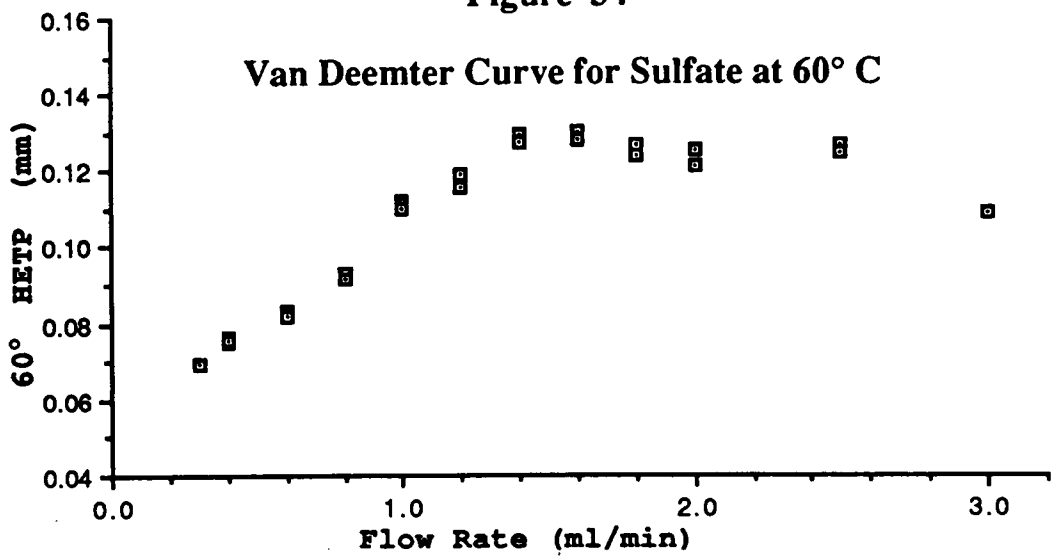

Van Deemter Curve for Sulfate at 60° C
60° HETP (mm)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.0
1.0
2.0
3.0
Flow Rate (ml/min)

TABLE 16

Selectivity vs Temperature Data

Temp (K)	k' Chloride	k' Sulfate	Selectivity
293	0.75	2.06	----
293	0.76	2.06	----
293	0.76	2.07	----
303	0.75	2.13	2.84
303	0.76	2.15	2.84
303	0.75	2.15	2.86
313	0.74	2.39	3.24
313	0.73	2.37	3.23
313	0.74	2.36	3.20
323	0.71	2.60	3.65
323	0.71	2.55	3.60
323	0.71	2.55	3.60
333	0.70	2.74	3.94
333	0.70	2.71	3.89
333	0.69	2.71	3.92

Figure 35
Capacity Factors (k') vs Flow Rate
For Chloride and Sulfate at 50° C

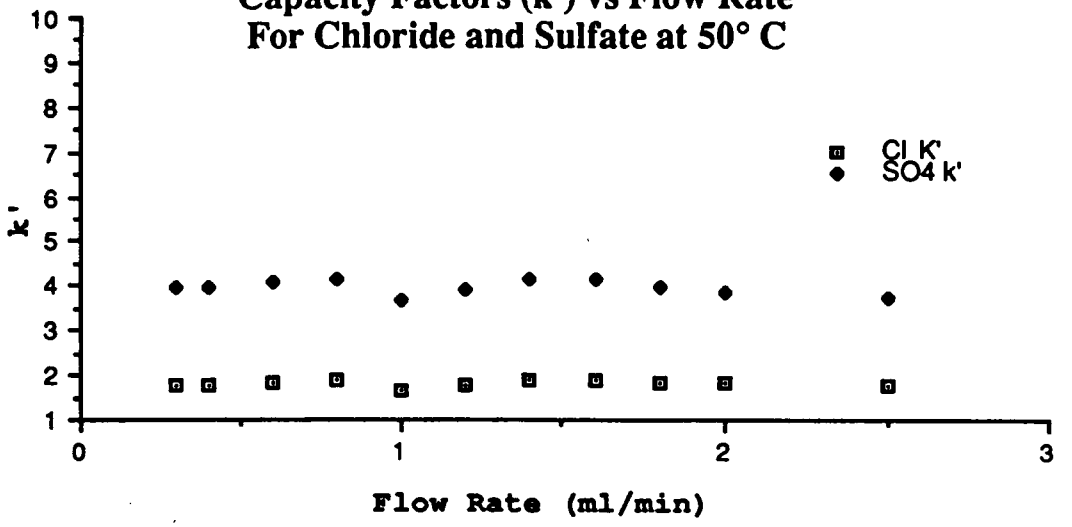
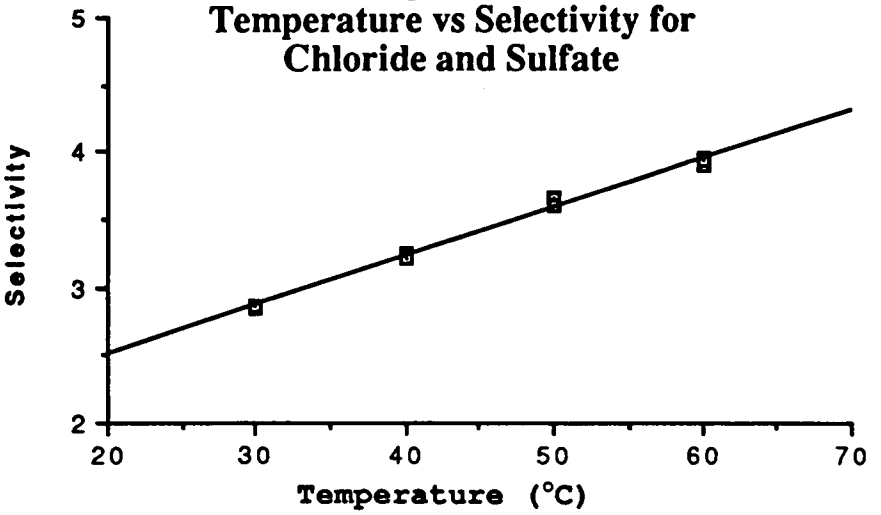


Figure 37
Temperature vs Selectivity for Chloride and Sulfate



The data obtained for the retention of chloride with respect to temperature was expected. The Van't Hoff plots are shown in figure 36. As expected, the capacity factors of chloride decreased with increasing temperature. The surprising result was the increasing capacity factors of sulfate with increasing temperature. This increased retention of sulfate with increasing temperature lead to the equally surprising result of increasing selectivities with increasing temperatures (See data in Table 16 and plot in Figure 37).

Results and Discussion

The increased efficiency from 20° to 30° C can be explained by the decreased diffusion coefficients in the radial diffusion or C term of the Van Deemter equation. As the temperature is increased, the viscosity of the stationary phase is decreased, resulting in a higher rate of diffusion. This increased diffusion in the stationary phase results in a higher diffusion coefficient for the solute in the stationary phase, D_S. This higher diffusion coefficient then results in a smaller contribution to H_S , the band broadening due to radial diffusion in the stationary phase. The contribution to this band broadening due to diffusion in the mobile phase, H_M, is also be reduced by increasing the temperature. This reduction is to the decreased viscosity of the mobile phase resulting from the increased temperature. Therefore, the combined effect of the increased temperature on H_S and H_M greatly reduces the C term of the Van Deemter, resulting in higher

Attention Patron:

Page 99 omitted from numbering

efficiency. These combined results explain the data obtained from the 20° and 30° C experiments, but not the loss of efficiency at higher temperatures. In order to explain these high temperature results, the longitudinal diffusion term or the B term in the Van Deemter equation must be considered. The longitudinal diffusion of solute molecules is usually considered to make negligible contributions to the overall band broadening of the system.[27] It is proposed here, however, that at the elevated temperatures used in this study, a significant contribution is made by the longitudinal diffusion of solute ions to the overall band broadening of the system. Therefore, the B term of the Van Deemter equation for ion chromatography must be considered when above ambient temperatures are used. In the B term, the D_M increases with increasing temperature, which leads to an overall decrease in efficiency. Therefore, it is concluded that at elevated temperatures, the longitudinal diffusion of solute ions becomes the predominant term of the Van Deemter equation, and thus explains the loss of efficiency at higher temperatures observed in this study.

The surprising and yet unexplained result obtained from this series of experiments was the increased retention of sulfate with increasing temperature. It is generally accepted that coulombic attractive forces decrease with increasing temperature. Therefore, some additional factors must have a greater influence on the retention of sulfate, than they do on the retention of chloride.

No single explanation can be offered to account for the increased retention of sulfate with increasing temperature. However,

some explanations can be eliminated. For example, the idea that the overall strength of the mobile phase decreases with increasing temperature is inconsistent with the experimental results, since the retention of chloride clearly decreased with increasing temperature. Also inconsistent is the idea that the overall attraction from the stationary phase increases with increasing temperature since, once again, the retention of chloride decreases.

One possible explanation is that the selectivity of the stationary phase is enhanced for sulfate at higher temperatures. The increased selectivity may be caused by some structural change offering some steric advantages to the sulfate ion. It has been shown that by changing the R groups on the quaternary amine of the anion-exchange resin, the selectivity can be changed for various ions. The enhanced selectivity of the stationary phase may also be caused by a change in size of the underlying sulfonated layer with increasing temperature, although this was deemed "possible, but not very likely" by some of the research staff at Dionex.[28]

A second possible explanation is that the hydrated structure of sulfate changes with temperature. A decrease in the sphere of hydration could result in an increased charge density of the hydrated ion. This increased charge density would then lead to increased retention. An increase in the sphere of hydration may also increase the retention of the hydrated ion. In anion chromatography, the retention is based on the charge of an ion and its overall size. The larger ions have more electrons and are therefore more polarizable.

The increased sphere of hydration could make the sulfate more polarizable and therefore increase its retention.

Chapter VI

CONCLUSIONS

This dissertation has addressed several problems in ion chromatography. The linear range in chemically suppressed ion chromatography was elucidated by producing linear calibration curves over nearly five orders of magnitude (from low ppb to 1000 ppm). This large linear range approaches that of the flame ionization detection (FID) in gas chromatography. The FID has a linear range of 6 orders of magnitude and is considered to the most linear detector in chromatography. It is most desirable to work within the linear range of a detector, since calibrations can only be guaranteed to be valid if they are produced within this linear range. Therefore, the larger the linear range, the larger the usable range of a particular analytical instrument. If the linear range is not known, the analyst must question the validity of the quantitative procedure. Therefore, the elucidation of the linear range for the conductivity detector has a real impact on quantitative analysis in IC. This impact is felt by analysts who are doing ion determinations in samples which differ greatly in concentration.

The linearity experiments elucidated the usable linear range for a modern ion chromatograph , but the range of concentrations allowed in a single analysis may be a more limiting factor. The second part of the thesis offers a simple and rapid method for the determination of trace ions in concentrated ionic solutions. This type of analysis is a growing problem in analytical chemistry. The determination of ppm levels of ions in samples which contain percent levels of other similarly charged ions cannot be accomplished with existing instrumentation. Without using the column switching technique described in Chapter 5, the concentration of sulfate in samples is limited to about 2500 ppm. The switching technique allows the analyst to exceed that limitation by a factor of 40. This technique uses two standard analytical columns coupled by a high pressure switching valve. The two columns are connected in series with the first column acting as a pre-separator for the two ions. When the trace chloride elutes from the first column, the first column is taken out of line. This switch leaves the bulk of the sulfate ion (matrix) on the first column, and allows the trace chloride along with some excess sulfate onto the second column for further separation. The factor of 40 noted above may be further increased by using a physically larger column as the first column.

The column switching experiments brought up some interesting questions about the inner workings of ion-exchange resins. When the columns were overloaded, they produced some previously unexplained results. These results prompted the author to further

study the packing materials used in ion chromatography. The final section of the dissertation investigates some interesting temperature and flow rate effects with theoretical implications. A series of Van Deemter plots were produced at temperatures ranging from 20° C to 60° C. The 20° to 30° transition showed an increase in efficiency with the increase in temperature. This efficiency increase was expected due to the higher diffusions at the higher temperature. The loss of efficiency above 30° C was a surprising result. The steady loss of efficiency from 30° to 60° C is theorized to be due to the increase in band broadening from higher longitudinal diffusions. Even more surprising was the retention time increase of sulfate with increasing temperature. It is very difficult to offer an explanation for this retention time increase. The coulombic interactions responsible for retention in ion chromatography are a form of adsorption. Adsorption is usually decreased at higher temperatures. The decreased retention of sulfate must be due to some particular interaction that sulfate has with the stationary phase since chloride retention is shown to decrease under the same conditions. The temperature data presented in chapter 6 brings to light several topics worth further study.

Overall, this dissertation has provided a deeper look into the workings of ion chromatography. It solved several existing problems and uncovered several additional problems. It is hoped that these studies will serve not only to provide answers to existing questions, but also provide a basis for new investigations.

CHAPTER VII

Literature Cited

1 Snyder, L.R., Kirkland, J.J., Introduction to Modern Liquid Chromatography **1979**, John Wiley & Sons, Inc., New York, NY. 410.

2 Small, H., Stevens, T.S., and Bauman, W.S., *Anal. Chem.* **1975**, 47, 1801.

3 Way, J.T. , *J. Royal Agricultural Soc. of England* **1850**, 11, 313.

4 Thompson, H.S., *J. Royal Agricultural Soc.of England* **1850**, 11, 68.

5 Tswett, M., *Ber. Deutsches Botan. Ges.*, **1906**, 24, 316, 384.

6 Exodus **15:** 22-25.

7 Taylor, I.T., and Urey, H.C., *J. Chem. Phys.*, **1938**, 6, 429.

8 Ketelle, B.H., and Boyd, G.E., *J. Amer. Chem. Soc.*, **1947**, 69, 2800.

9 Choppin, G.R., Harvey, B.G., and Thompson, S.G., *J. Inorg. Nucl. Chem.*, **1955**, 2, 66.

10 Smith, F.C., and Chang, R.C., *The Practice of Ion Chromatography*, **1983** John Wiley and Sons, New York, NY, 4.

11 Small, H., Stevens, T.S., and Bauman, W.S., *Anal. Chem.* **1975**, 47, 1801.

12 Weiss, J., *Handbook of Ion Chromatography*, **1986**, Dionex Corp., Sunnyvale, CA , 21.

13 Singhal, R.P., Cohn, W.E., **1972**, *Anal. Biochem.*, 45, 585.

14 Atkins, P.W., *Physical Chemistry*, **1982**, W.H. Freeman and Company, San Francisco,CA, 892.

15 Polite, L.N., McNair, H.M., and Rocklin, R.D. *J. Liq. Chromatography* **1987**, 10(5), 829.

16 Pohl, C.A., and Johnson, E.L. *J. Chromatographic Sci.* **1980**, 18, 442.

17 Doury-Bethod, M., Giampaoli, P., Pitsch, H., Sella, C., and Poitrenaud, C., *Anal. Chem.* **1985**, 57, 2257.

18 Ibid.

19 Rocklin, R.D., *Semiconductor Int.* May, **1986**.

20 Wetzel, R., Anderson, C., Schleicher, H., Crook, G. *Anal Chem.* **1979**, 51, 1532.

21 Houskova, J., Chu, T., *Solid State Tech.* **1986**, May, 205.

22 Polite, L.N., McNair, H.M., Pittsburgh Conference Paper, **1988**.

23 O'Bynum, M.O., Tyree, S., and Weiser, W.E., *Anal. Chem.* **1981**, 53, 1936 .

24 Polite, L.N., McNair, H.M., Paper Presented at Southeast Regional American Chemical Society Meeting, November **1988**.

25 Weiss, J., *Handbook of Ion Chromatography*, **1986**, Dionex Corp., Sunnyvale, Ca.,17.

26 Ibid.

27 Ibid.

28 Stillian, J., Personal Communication, November, **1988**.

The vita has been removed from the scanned document