ION CHROMATOGRAPHIC DETERMINATION OF ACIDITY

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ABSTRACT

The practice of acidity measurements by volumetric titration has remained unchanged for over two centuries. Though optochemical methods may exist for measuring H^+ concentrations, none of these methods are capable of measuring large concentration ranges or are able to determine the concentration of multiple cations, in addition to H^+ (i.e., K^+, NH_4^+, etc.), which may be of interest to the analytical chemist. The present work presents a new approach to acidity measurements based on cation exchange chromatography. A sulfonated styrene-divinylbenzene based stationary phase is used to separate hydrogen ion from other monovalent cations. In addition, several factors that govern the direct determination of strong and weak acids were examined.

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LIST OF ABBREVIATIONS

C_M	concentration of sample analyte
$-COO^-$	carboxyl functional group
ΔG	change in conductance
FIA	flow injection analysis
$[H^+]$	hydrogen ion concentration
HEtS	ethanesulfonic acid
HOAc	acetic acid
IC	ion chromatography
I.D.	internal diameter
k'	capacity factor
K_a	acid dissociation constant
K_c	partition/binding constant for H^+ and carboxyl groups
K_S	partition/binding constant for H^+ and sulfonate groups
λ	equivalent conductance
λ_{H^+}	equivalent conductance of H^+
λ_{Na^+}	equivalent conductance of Na^+
LOD	limit of detection
N	peak efficiency
$[Na^+]$	sodium ion concentration

NaEtS	sodium ethanesulfonate
$N(CH_3)_4^+$	tetramethylammonium ion
$N(C_2H_5)_4^+$	tetraethylammonium ion
O.D.	outer diameter
PCR	postcolumn reaction
PEEK	polyether ether ketone
$-SiO_3^-$	silanol functional group
$-SO_3$	sulfonic acid functional group
UV	ultraviolet

CHAPTER 1

INTRODUCTION TO ACIDITY DETERMINATION

1.1 Introduction

The determination of acidity (or basicity) has historically been one of the most fundamental and essential tasks ever performed in analytical chemistry. A volumetric approach to acid determination dates back nearly three centuries. As early as 1729, Geoffroy evaluated the quality of vinegar samples by noting the quantity of solid K_2CO_3 that could be added before effervescence ceased.[1] A similar approach was adopted by Neumann in 1732 and by Scheffer in 1751 for measuring the "strength" of nitric acid.[1] However, it was not until 1756 when the first clear instance of a volumetric approach was realized when the "value" of pearl ashes was measured by noting the number of teaspoons of dilute nitric acid required before effervescence ceased.[1]

The foundations of volumetric analysis, as it is presently known, was laid by Gay Lussac between 1824 and 1832.[1-3] In 1832, he published a paper describing a method for the determination of silver; the sample was dissolved in nitric acid followed by titration with a sodium chloride solution.[1] However, it is actually Mohr who is credited with making volumetric analysis popular, particularly through the publication in 1855 of his classic treatise on titrimetry,[4] and also through many innovations in the hardware for titrimetric analysis – Mohr's original designs[5] are in fact clearly recognizable in their present day counterparts.

Regarding the acidity (or basicity) of a sample, either an intensity parameter (pH, which was not introduced until the twentieth century by Sørenson[6]) or a capacity parameter (titratable acidity) is of interest. The pH of a sample is typically sensed and aside from potentiometric measurements, the mainstay, various alternatives such as optochemical sensing techniques have developed. However, the principle of the capacity determination, volumetric titration, has basically remained unaltered since its inception (with the possible exception of occasional use of coulometric titrant generation). Doubtless, the hardware and the methods of end-point detection have been vastly refined over the years but there are few other examples in measurement science where a given determination has been conducted in essentially the same manner for more than two centuries.

1.2 Optical Detection Methods

Aside from the historical volumetric approach to acid determination, other methods have developed for determining the amount of H^+ in a sample. Some of these approaches involve using flow injection analysis (FIA) systems with optochemical detection techniques. For example, Ruzicka and Hansen[7-9] used FIA titrations with an indicator based optical detection system to determine the end-point. In some of their experiments, H^+ samples were combined with a NaOH carrier solution containing bromothymol blue indicator in a flowing stream and then passed through a mixing chamber, followed by an optical detector, where the extent of light absorption was used to detect the end-point.

A unique experimental scheme was used by Mohan and Iyer[10] to determine the concentration of perchloric acid by using an organic dye, Rhodamine 6G, immobilized on a Nafion membrane. The method was based on the change in optical absorption of the dye at high acid concentrations. The Nafion membrane containing only Rhodamine 6G immersed in water absorbed at 525 nm, however, when the membrane was immersed in an acid solution, the maximum absorption of Rhodamine 6G shifted from 525 nm to 470 nm. The true acidity was determined by plotting the ratio of the intensities at 525 nm and 470 nm vs. the Hammett acidity function. The drawbacks of this method include the length of time (~10 min) required for the Nafion membrane to equilibrate with the acid and its ability to only measure concentrated solutions (1-5 M H^+).

Acid concentrations have also been determined with coulometric systems that do not use acid-base indicators. For example, Kamson[11] suggested the use of the iodate-iodide reaction (with photometric measurement of the I_3^- formed for the determination of mineral acids). However, the applicable range is very limited and such a technique will not be suitable for analyzing a wide range of concentrations.

Visualization of H^+ by postcolumn reaction (PCR) with an appropriate reagent/indicator is also possible and has been shown to be viable in ion exclusion chromatographic determination of weak acids.[12] However, not only do PCR detection approaches increase complexity, the detection of other ions of interest may be precluded. Also, the methods based on acid-base indicators are likely to have a very limited linear dynamic range.

1.3 Conductometric Acidity Measurements

Conductivity detection is an excellent detection method, since these types of detectors are highly sensitive and respond in direct proportion to concentration changes. Acidity may be measured either directly or indirectly via this detection scheme. For example, earlier from this laboratory, Ito and co-workers[13] devised a method for an indirect measurement of acidity in aerosols. The system contained two subsystems where the effluent was concentrated on a cation exchanger and an anion exchanger, respectively. This particular order may be of importance, since some anion exchange resins may contain a small number of cation exchange sites. The first system analyzed non-H^+ cations (primarily NH_4^+) as the corresponding hydroxide by elution with a strong acid (i.e., dilute HCl) eluent followed by suppression with a hydroxide-based anion exchanger. Therefore, in this case, NH_4^+ would pass through the conductivity detector, CD1, as NH_4OH. The non-H^+ equivalents could then be conductometrically determined based on the following equation

$$\Sigma\text{non-}H^+ \text{ equivalents} = K_1G_1/271.6 \qquad (1.1)$$

where K_1 is the calibration constant of the conductivity detector and G_1 represents the detector response in terms of peak area or height.

The second system analyzed the total (strong acid) anions present and was conductometrically determined with a carbonate/hydroxide-based eluent followed by suppression with a second conductivity detector, CD2. The choice of eluent for the second system essentially eliminated any CO_2 response. The

author's also noted that the presence of weak acid anions, such as acetate and formate, are not present in the aerosol to any significant extent. Therefore, the detector signal is mainly due to the presence of H_2SO_4, since the anions elute as their corresponding acids. However, smaller amounts of HNO_3 and HCl may be present in the aerosol. In any case, it can be seen from the following equivalent conductances (where the equivalent conductances are indicated in parentheses): H^+ (349.9), SO_4^{2-} (80.0), NO_3^- (71.4), and Cl^- (76.35), that the conductance is primarily dominated by H^+ and to a smaller extent by SO_4^{2-}. A similar equation to 1.1 can be shown for determining the anion equivalents:

$$\Sigma\text{anion equivalents} = K_2G_2/429.9 \qquad (1.2)$$

where K_2 and G_2 is the calibration constant and detector response for CD2, respectively. However, the presence of small amounts of other cations (non-NH_4^+ cations) or anions (non-SO_4^{2-} anions) will result in very small inaccuracies in the calculated equivalents for both analytes. In any case, these underestimates are fairly insignificant and should not cause any problems in over all quantitation. The H^+ equivalents can then be determined based on the difference between the calculated values from equations 1.1 and 1.2:

$$H^+ \text{ equivalents} = \Sigma\text{anion equivalents} - \Sigma\text{non-}H^+ \text{ equivalents} \qquad (1.3)$$

Another interesting application is the conductometric determination of acidity in rain samples.[14] Typically rainwater consists of a mixture of ions: Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, SO_4^{2-}, NO_3 , Cl^-, and H^+ or HCO_3 (but not both), including CO_2. Since these types of samples contain various amounts of salt, these ions

must be considered in measuring the acidity. The method presented by the author's evaluates a combination of titration (based on a Gran plot) and conductance measurements before and after sample treatment with an ion exchange resin to determine the total strong acids (acidity) present in the sample. Occasionally, rain samples may be alkaline, however for this discussion, only acidic samples will be considered. The author's determined the acidity or basicity of a sample by measurements with a pH meter or by conductance after sample treatment with a strong anion exchange resin in the bicarbonate form. In an acidic sample, the conductivity measurement is only based on the presence of the salt (measured as HCO_3^-), since the acid is removed as CO_2. However, in an alkaline sample, the conductance measurement is based on the presence of the salt and bicarbonate in which both are measured in the HCO_3 form. Obviously, an acidic sample would result in a lower conductance response.

For acidic rain samples, two conductance measurements are required. The first measurement (κ_1) is based on a single ionic solute, such as HCl. The second measurement (κ_2), containing two ionic solutes (i.e., HCl + NaCl) is based on the conductance response after ion exchange for H^+. These conductance measurements would then result in the following equations

$$\kappa_1 = \Lambda_a C_a + \Lambda_s C_s \qquad (1.4)$$

$$\kappa_2 = \Lambda_a C_a + \Lambda_a C_s \qquad (1.5)$$

where κ_1 and κ_2 are the measured conductances, Λ_a and Λ_s are the equivalent conductances of HCl and NaCl, and C_a and C_s are their corresponding concentrations, respectively.

Titration data revealed the concentration for the total strong acids (C_a) and cumulative concentration for the acids and salts ($C_a + C_s$) before and after ion exchange for H^+, respectively. Minor rearrangement of equations 1.4 and 1.5 results in the following

$$\kappa_2 = \Lambda_a (C_a + C_s) \tag{1.6}$$

$$\kappa_2 - \kappa_1 = (\Lambda_a - \Lambda_s) C_s \tag{1.7}$$

where κ_2 is plotted against $C_a + C_s$ (from titration results) and $\kappa_2 - \kappa_1$ is plotted against C_s. The slopes from these lines estimated Λ_a and Λ_s, respectively. In order to determine the acidity and salinity, the same data was fitted to equation 1.8, where $C(\kappa)$ is the concentration of the acid or salt (calculated from

$$C(\kappa) = a + bC(t) \tag{1.8}$$

conductance) and C(t) is the corresponding concentration from the titration data. The best fit line allowed the determination of a and b which represented the acidity or salinity concentration. However, this method resulted in very poor precision, about 15%, for determining these corresponding concentrations in rain samples. The next section discusses a direct conductometric determination of acidity based on ion chromatography.

1.4 Ion Chromatographic Determination of Acidity

Since its advent in the mid-70s by Small,[15] ion chromatography (IC), especially in its conductometric version, has become the dominant technique for ionic analysis. While the analysis of anions is the major application area, the determinations of alkali and alkaline earth metal ions have also become popular. Indeed, the selectivity of common sulfonate functionality cation exchangers typically follows the order $Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$, etc.[16] and individual cations in a mixture should therefore elute in the foregoing order. The fact that H^+ can be separated by standard cation exchange chromatography is rarely recognized because extant approaches do not allow ready visualization of H^+ as an eluite.

The fact that H^+ is not directly visible as an analyte in either suppressed (Figure 1.1a) or nonsuppressed (Figure 1.1b) cation chromatography as they are presently practiced, is obviously not due to the choice of conductometry as a detection method, as discussed in the previous section. However, in suppressed cation chromatography, acids or acidic eluents are used and therefore do not allow a direct measurement for H^+. For example, a typical suppressor reaction for HCl is as follows

$$\text{Resin-OH} + \text{HCl} \longrightarrow \text{Resin-Cl} + H_2O \qquad (1.9)$$

where H^+ is obligatorily removed by the suppressor. In nonsuppressed cation chromatography, acids or acidic eluents containing salts of protolyzable bases such as amines are used. It is not possible to determine the elution of H^+ in such systems either, especially in small amounts. However, with the correct choice of

an eluent, it should be readily possible to perform ion exchange separation and conductometric detection of H^+.

A second issue concerns whether the objective of interest is H^+ concentration or titratable H^+ (*total analytical concentration)*. In ion chromatography, while one typically refers to the determination of the concentration of an analyte, in reality, it is the total analytical concentration that is generally determined. Imagine that M^+ is to be determined and some of the M-species are present in solution not as M^+ but in some other form. As long as M^+ can be readily generated from this form in a labile fashion and such generation is thermodynamically favored, it is the total analytical concentration that is measured. Hence the sum of NH_3 and NH_4^+ is measured in the analytical peak appearing as NH_4^+ in cation chromatography and the sum of acetic acid and acetate appears as the acetate peak in anion chromatography. For strong acids, or in dilute solutions of weak acids where the H^+ is essentially fully dissociated, there is no difference between H^+ concentration and titratable acidity. In all other cases, the measured value must be more carefully interpreted. This thesis presents a direct conductometric strategy for the ion chromatographic determination of acidity.

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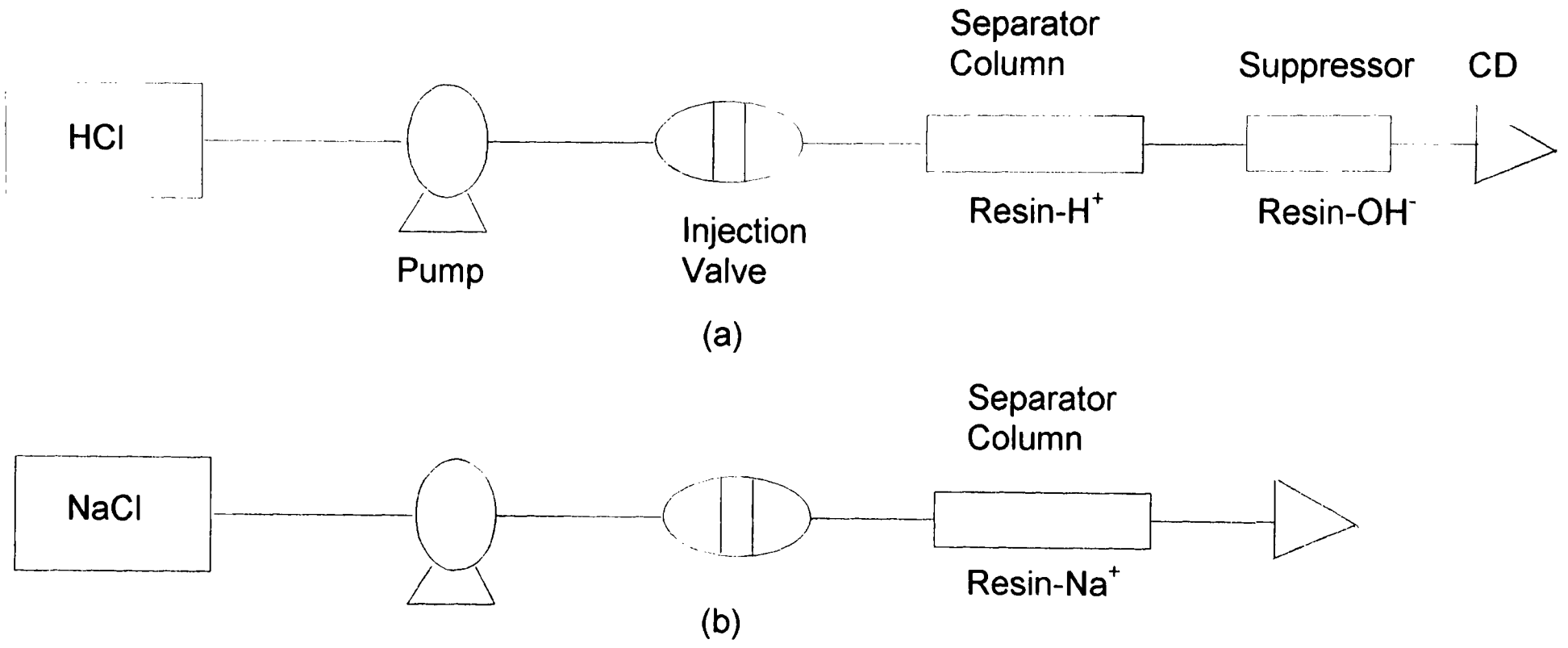

Figure 1.1. Schematic diagrams of typical cation chromatographs. CD = conductivity detector. (a) suppressed cation chromatograph, (b) nonsuppressed cation chromatograph

CHAPTER 2

ANALYTICAL SYSTEM

2.1 Introduction

Consider the simplest conductometric cation chromatography system, a solution of NaCl as an eluent followed by an injection valve, a cation exchanger separation column, and a conductivity detector. As a sample containing various cations are injected into the system, the cations are exchanged for Na^+ by the resin-Na sites and an equivalent amount of NaX is thus liberated (X being the anion(s) associated with the sample) and passes through the column to produce the first detector response. This peak is positive or negative depending on whether the total cation concentration in the sample (in eq/L) exceeds the eluent Na^+ concentration and also to a lesser extent on whether the equivalent conductance of X is greater or less than that of the eluent spectator ion (in our example, chloride). The injected cations then elute from the system (hopefully separated from each other) in the order of their affinity for the stationary phase. The magnitude of the signal associated with the analyte elution is directly proportional to the concentration of the analyte cation M^+ in the sample and the difference in equivalent conductance between the analyte cation and the eluent cation (in this case, $\lambda_{M^+} - \lambda_{Na^+}$) as shown in equation 2.1:

$$\Delta G = C_M(\lambda_{M^+} - \lambda_{E^+}) \qquad (2.1)$$

where ΔG is the change in conductance, C_M is the concentration of the sample analyte, λ_M^+ is the equivalent conductance of the analyte cation, and λ_E^+ is the equivalent conductance of the eluent cation (λ_{Na}^+ in this case). The equivalent conductances of common ions of interest in this context are shown in Table 2.1. As shown in this table, the equivalent conductance of H^+ (λ_H^+) is much greater than the equivalent conductance of any other cation. Therefore, such an ion chromatographic system is particularly sensitive to H^+ and is especially well suited for its measurement. Any eluent cation (in this case, Na^+) present is invisible to the detection system and cannot be measured.

In the present work, sodium was chosen as the eluent cation. Sodium can be measured in a simple manner by other means and it can also be present in many samples in large amounts. Because sodium is expected to elute immediately after H^+, making Na^+ invisible, its use in our system may therefore be advantageous. With a Na^+ eluent, alkali and alkaline earth metals, other than Li^+, produce positive peaks ($\lambda_{analyte} > \lambda_{Na}^+$). If it is desirable to measure [Na^+] (sodium ion concentration), another choice for an eluent cation can be made. A stable organic cation such as $N(C_2H_5)_4^+$ or $N(CH_3)_4^+$ may be a good choice because such an ion has a low equivalent conductance as well as reasonable retention on a cation exchanger. While Li^+ also has a low equivalent conductance, it has a very poor affinity for most conventional cation exchangers, and thus necessitates the use of inconveniently high eluent concentrations to elute strongly held cations making it a poor choice for an eluent cation. Lithium

ion is also expected to yield significant sensitivities and unidirectional signals for most other cations.

The role of the eluent anion is merely that of a spectator ion, as long as it is derived from a strong acid and is itself not protolyzed. It does however, contribute to the background conductance and it would be desirable to choose a strong acid anion of low equivalent conductance. In the present work, ethanesulfonate was chosen as the eluent anion.

2.2 System Requirements

2.2.1 Conventional-Scale System

In the conventional-scale system, either a Dionex DX-500 or DX-100 IC system was used. The DX-500 was equipped with a GP40 gradient pump, an LC30 chromatography oven (equipped with a 2 μL loop injector), and a CD20 Conductivity Detector. The DX-100 was equipped with an isocratic pι mp, a conductivity detector, and a 100 μL loop injector. The analytical columns (4 x 250 mm, except as stated), presented in Table 2.2, were based on poly(styrene-divinylbenzene) with 2-8% crosslinking and different degrees of sulfonation. The eluent flow rate was 1.00 mL/min except as stated.

2.2.2 Capillary-Scale System

The capillary-based IC system used in this work was built in-house. The basic components of the system included a pump, an injection valve, a pressure sensor, and a digital panel meter to monitor the pressure. The pump was a

48,000 step, motor driven syringe dispenser (Model 50300, Klohen, Reno, NV) equipped with a 500 μL syringe operated by WinPump software installed on an IBM Thinkpad laptop computer. A Kynar block was used to accommodate the pump head, a low leak dual ball and seat inlet check valve (P/N 44541, Dionex Corp., Sunnyvale, CA). An eluent reservoir was connected to the inlet check valve and was pressurized with N_2 gas. A Tygon tubing sleeve was placed around the glass syringe in case the syringe shattered due to high pressure. A pressure sensor (Model SP70-A3000, Senso-Metrics, Simi Valley, CA) was connected to the liquid output port of the Kynar block using a 250 μm I.D. (inner diameter) x 1500 μm O.D. (outer diameter) polyether ether ketone (PEEK) tubing. A 60 nL internal loop injector (Valco Instruments Co., Houston, TX) was connected to the pressure sensor and capillary column. A digital panel meter (Jewel Electrical Instruments, Manchester, NH) was used to continuously monitor the system pressure.

No suppressors were used in this work, and the conductivity cell was changed from that described.[2] The present cell design used two stainless steel electrodes (thin wall 30 gauge hypodermic tubing; P/N O-HTX-30, Small Parts, Miami Lakes, FL; 178 μm I.D. x 356 μm O.D., with both ends sanded flat; inserted into a tight fitting PEEK sleeve and epoxied in place with an ~7 mm separation between electrodes), similar to a previously described design (Figure 4a, ref. 3). The cell constant (~70) was determined by using 1 mM KCl as the

calibrant. Other cells of similar designs, but with different cell constants, were also used.

Capillary columns were 180 μm I.D. x 360 μm O.D. fused-silica tubes (Polymicro Technologies, Inc., Phoenix, AZ). Columns were ~50 cm long and packed in-house with glass wool frits using the same packing material as in the conventional-scale system. The conductivity cell was directly butt-joined with an elastomeric poly(vinyl chloride) sleeve to the exit end of the column.

2.2.3 Reagents

All solutions were prepared with house-distilled water deionized through a Barnstead Nanopure II system with a specific resistivity of ≥17.5 MΩ·cm. Acid solutions used as samples were standardized by volumetric titration with certified standard NaOH solutions. Ethanesulfonic acid (HEtS, 70% v/v) was purchased from Aldrich and standardized by titration. The acid was converted to the sodium form with standard NaOH, and the pH of the sodium ethanesulfonate (NaEtS) eluent was determined with a standard pH electrode on a Beckman Φ71 pH meter and adjusted with HEtS or NaOH, as necessary.

2.3 Role of the Stationary Phase

The affinity of the column resin for H^+ can be the limiting factor in its efficient determination. Most commercial columns for alkali metal separations are of the carboxylate type; H^+ cannot be eluted from any of these columns with

reasonable eluent concentrations (≤100 mM) or within a reasonable time (≤20 min). The pKa of an acidic functionality can be construed to be a direct measure of its affinity for H^+. If carboxyl ($-COO^-$) groups already exhibit too great a retention for H^+, silanol ($-SiO^-$) groups or other functionalities that are stronger conjugate bases than $-COO^-$ will have too great an affinity for H^+ relative to other cations. On the other hand, sulfonated ($-SO_3^-$) resins are strong acids and have a weak affinity for H^+. Therefore, these sulfonated resins should be ideal for chromatographically separating H^+ from other monovalent cations. During sulfonation of high surface area polymers, it is difficult, however, to avoid surface oxidation altogether; this can result in the presence of some carboxylate or phenolic exchange sites. In terms of overall exchange capacity, the contribution of the weak acid groups may be insignificant relative to that of the sulfonate groups. However, because their affinity for H^+ may be many orders of magnitude higher, their contribution to overall retention may still be very significant. It may nevertheless be possible to reduce the influence of the carboxylate groups by protonating them, via operating at a lower eluent pH.

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Table 2.1. Equivalent Conductance of Common Cations of Interest.[1]

Common Cations	Equivalent Conductance (λ, $S \cdot cm^2$/equivalent)
$N(n\text{-}C_3H_7)_4^+$	23.5
$N(C_2H_5)_4^+$	33.0
Li^+	38.7
$N(CH_3)_4^+$	45.3
Na^+	50.1
Mg^{2+}	53.1
Ca^{2+}	59.5
NH_4^+	73.5
K^+	73.5
Cs^+	77.3
Rb^+	77.8
H^+	350

Table 2.2. List of Analytical Columns Used in This Work.

Analytical Columns	Column Capacity (μequivalents)	Dimensions (I.D. x Length, mm)
47F#1[a]	7.5	2 x 250
A2-12297[b,c]	30	4 x 250
97-004-1045[c]	180	4 x 250
97-004-1065[d]	410	4 x 250
AS[b]	9500	4 x 250

[a]column used by D. Sherman
[b]columns used by C. M. Kinchin (*data presented in thesis)*
[c]columns used by the author (*data from A2-12297 was not presented in this thesis*)
[d]column used by T. K. Cook

CHAPTER 3

CHROMATOGRAPHIC DETERMINATION OF STRONG ACIDS

3.1 Introduction

This chapter discusses how cation exchange chromatography may be used to detect strong acids. The eluent used was a dilute solution of a neutral salt, sometimes containing a small concentration of the corresponding acid, e.g., sodium ethanesulfonate (NaEtS), pH adjusted with ethanesulfonic acid (HEtS). The high equivalent conductance (~350 $S \cdot cm^2$/equivalent) of H^+ and relatively low eluent concentrations allowed for the sensitive conductometric detection of H^+, down to the 50 μM level under favorable conditions. The conductometric response to H^+ can be linear over a wide range of H^+ concentrations, from sub-millimolar to several molar concentrations. The system allowed the quantitation of strong acids, which will be discussed further in this chapter. Chapter 4 will discuss the chromatographic determination of weak acids.

3.2 Effect of Eluent pH on Chromatographic Behavior

Consider the following model to illustrate the effect of the eluent pH on H^+ retention. The capacity factor, k', can be expressed as

$$k' = (t_R - t_0)/t_0 = AK_s + BK_c \qquad (3.1)$$

where t_R and t_0 is the retention time for the retained and unretained analyte, respectively. K_s and K_c are the partition/binding constants for H^+ and sulfonate groups and for H^+ and carboxylate groups, respectively, and A and B represent

constants related to the number of ionized sulfonate and carboxylate groups. Recognizing that B is a function of the original number of carboxylate groups (protonated and unprotonated) and the fraction that is ionized, equation 3.1 takes the form

$$t_R = a + bK_a/(K_a + [H^+]) \qquad (3.2)$$

where a and b are constants, $[H^+]$ is the concentration of H^+ in the eluent, and K_a is the dissociation constant of the carboxylate groups. Experimental data for a sulfonated column (97-004-1065, 410 μequivalent column capacity) operated with a 60 mM NaEtS eluent adjusted to pH 2-5 were obtained with HEtS flowing at a rate of 2.0 mL/min. In Figure 3.1, the experimental data are shown as points with ±1 standard deviations as error bars and the data are fitted to equation 3.2. Note that H^+ added to the eluent has a negligible effect on the eluting power of the eluent itself; there is relatively little or no effect of pH on alkali metal retention.

Above and beyond broadening caused by increased retention (retention decreased significantly at an eluent pH < 4), efficiency decreases dramatically due to the increased importance of mixed-mode retention as pH increases. On this particular column, peak efficiency (N), calculated as

$$N = 5.54\ (t_R/w_{0.5})^2 \qquad (3.3)$$

where t_R is the retention time of the retained ion and $w_{0.5}$ is the peak width at half the maximum height, decreased by more than a factor of 35 in going from pH 3 to 5. The observed results are consistent with the phenomenological model; best fit value for K_a is 3.5×10^{-5} (pK_a 4.45), quite characteristic of carboxylic acids.

Our experience indicates that the extent of carboxylate functionalities depends on the degree and conditions of the sulfonation. More extensive and aggressive sulfonation conditions also appear to lead to greater formation of carboxylate functionalities. For example, with a lower capacity column (97-004-1045, 180 μequivalent column capacity) containing a resin sulfonated under milder conditions, H^+ peaks could be discerned easily with a 20 mM NaEtS eluent at pH 5. However, peak tailing and general chromatographic performance improved significantly with a reduction of eluent pH to 3 (Figure 3.2). In general, there was no improvement in performance upon reducing the eluent pH below 3 with any of the columns examined, regardless of capacity. The maximum column efficiency was therefore observed at this eluent pH.

3.2.1 Separation of H^+ from Other Monovalent Cations

One of the attractive features of the present method is its ability to separate H^+ from other monovalent cations. This allows flexibility to the operator in determining the acidity of a sample, in addition to the salinity. If more "traditional" methods (as previously discussed in this thesis) are used to determine the H^+ content, other common cations must be measured in some other fashion and at least two separate techniques would be required. However, as presented here, this can be accomplished with a single technique, ion chromatography (IC).

The separation of a number of monovalent cations and H^+ on the 97-004-1045 column with a 50 mM NaEtS eluent, adjusted to a pH of 3 and operated at

a flow rate of 1.0 mL/min, is shown in Figure 3.3. The first peak is a positive displacement peak since the sample contains more ionic equivalents than the eluent. The selectivity of the column follows the expected order of $Li^+ < H^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$.[1] Note the negative signal for Li^+ ($\lambda_{Li}^+ < \lambda_{Na}^+$) and the substantial sensitivity of H^+ relative to any other cation. Obviously, a better separation can be achieved if the eluent concentration is decreased. It should also be emphasized that none of the other relative parameters, such as column capacity, particle size, packing techniques, etc. have been optimized in this initial study. It is clear that the determination of H^+, along with several other cations, is possible by this technique.

3.2.2 Limit of Detection

It is obvious, however, if the eluent itself contains 1 mM H^+ (pH 3), it will not be possible to detect H^+ concentrations below this level. A particularly attractive and unique application for the determination of sub-millimolar levels of H^+ along with comparably low levels of other cations involves the analysis of rain samples.[2] With a sufficiently low capacity column (47F#1, 7.5 μequivalent), it is possible to use a low concentration 1 mM NaEtS eluent to which virtually no acid has been added (pH 6-7). The inset in Figure 3.3 shows the response of 200 μM injected H^+ in this system; signals from 50 μM H^+ were above the limit of detection (LOD). Although, the chromatographic performance of the peak is

poor, due to higher eluent pH, the H^+ response is completely separated from NH_4^+, the next eluting peak under these conditions.

3.3 Effects of Flow Rate and Temperature

Compared to other types of liquid chromatographic separations, ion exchange separations often exhibit unique flow and temperature dependence on separation efficiencies since the ion exchange process can be intrinsically slower than adsorption/desorption processes. Figure 3.4 shows the plate counts for the 97-004-1065 column with a 50 mM NaEtS eluent over a flow rate range of 0.5-2.5 mL/min. The H^+ plate counts decreases exponentially from ~2,400 to ~1,100 plates over this flow rate range. At even higher flow rates, peak tailing becomes too large for meaningful chromatography.

Since the exchange kinetics should improve with temperature, the effect of temperature was studied on a 50 cm long capillary column packed with the same resin as the 97-004-1045 column, operating at a linear velocity corresponding to a flow rate of 1.0 mL/min for the conventional column, and using a 50 mM NaEtS eluent, adjusted to pH 3. The observed column efficiency increased from 5,400 plates/m at 30°C to over 15,000 plates/m at 60°C. In addition, the observed behavior followed an Arrhenius activation pattern (ln(number of plates (N) linearly related to 1/T with a linear r^2 of 0.96, n = 12) as shown from the Arrhenius equation

$$N = Ae^{-Ea/RT} \tag{3.4}$$

where A is a constant, E_a is the Arrhenius activation energy, R is the gas constant, and T is the temperature. A graph of the ln (number of plates) versus 1/T reveals a slope related to $-E_a/R$, where in this case the observed slope corresponded to an activation energy of 26.5 kJ/mol. The same experiment was done with the conventional-size column over a more limited temperature range of 28°C to 40°C with similar results; the mean activation energy was slightly higher, 31 kJ/mol, probably due to incomplete thermal equilibration in the larger column. In any case, the capillary column led to much better efficiencies overall. Obviously, it will be advantageous to conduct hydrogen ion chromatography for strong acids at an elevated temperature.

3.4 Applicable Range and Reproducibility

With very low capacity columns, as was shown in the inset in Figure 3.3, sub-millimolar concentrations at levels relevant to titratable strong acidity in acid rain samples can be determined. The low eluent concentrations that are used in conjunction with low capacity columns permit excellent sensitivity. The linear r^2 value for the response (all responses refer to peak area responses) to 0.05-1.00 mM H^+ was 0.9822 on the low capacity column 47F#1. The 97-004-1045 column of intermediate capacity provides a large linear working range. With a 2 μL sample volume, the system responded to injected H_2SO_4 over a 3 order of magnitude concentration range (5.0×10^{-4}-1.2 M H^+, Figure 3.5) with good linearity ($r^2 = 0.9987$). Peak efficiency was studied up to 100 mM H^+ injected, and no decrease was noted at least up to this concentration. With the highest

capacity fully sulfonated resin (AS column, 9.5 mequivalents capacity) and a 2 μL sample volume, good chromatographic determination of H^+ was possible with a 100 mM KEtS eluent, adjusted to pH 4. A high cell constant detector was used to keep the response within the working range of the detector electronics. This permitted determinations to unusually high ranges; we obtained an acceptably linear response (linear $r^2 = 0.9833$) for 0.5-8 M HCl. The response linearity may in fact be better than the linear r^2 value indicates because it is difficult to avoid HCl losses with the highest concentration samples.

The reproducibility of responses from individual injections at several molar concentrations was studied with a nonvolatile acid, H_2SO_4. The reproducibilities were within 0.1-0.3% relative standard deviation (generally the pumping precision of the pump is believed to be of this order). Using a quadratic fit, the r^2 value was 0.9999 for 0.1-10 M H_2SO_4. Therefore, it should be possible to assay the concentration of very small volumes of undiluted acids with good precision by direct injection into the system without sample preparation. This is presently not possible by any other technique.

The overall analytical method exhibited excellent reproducibility, even with the DX-100 system. The reproducibility for this system is shown in Figure 3.6 for 8 repeated sample injections containing 12.5 mM HNO_3 on the 97-004-1065 column with a pH 3, 50 mM NaEtS eluent. The DX-100 system produced peak height and retention time reproducibilities of <0.3% and <0.2%, respectively, in relative standard deviations. The relative standard deviations of retention times on the same system for a lower capacity column (A2-12297, 30 μequivalent)

ranged from 0.1% to 0.7% for samples containing 0.1 mM to 3 mM HNO_3 with a pH 5, 2 mM NaEtS eluent flowing at 2.0 mL/min. This data is summarized in Table 3.1 for each column indicated in the present study. Although the applicable range was not determined for the 97-004-1065, the range may be extrapolated from the available data and concentrations >>1.2 M H^+ should be easily obtained with excellent precision.

3.5 Effect of Coanalytes

Strong acid anions are fully ionized and have no effect on their determinations. The analysis of weak acids is discussed in the next chapter. Cations that elute on either side of H^+, e.g., Li^+ or NH_4^+ (or other cations that are further resolved), do not cause any problems in quantitation, unless they are present in such large amounts that the column is overloaded and peak overlap occurs. If the eluent cation (in most of our studies, this is Na^+) is present in significant amounts relative to the H^+ analyte, the H^+ signal can decrease. Overwhelming amounts of sodium or any other more retained cation may cause the H^+ signal to disappear altogether, since it was not retained from the matrix in the first place. Figures 3.7a and 3.7b shows the effects of adding various amounts of Na^+ to the matrix at lower (1-2.5 mM H^+) and higher (10-50 mM H^+) concentrations, respectively. As shown in these figures, the magnitude of this effect depends on the absolute amount of H^+ (being greater at low levels of H^+) and also the ratio of the eluent ion to analyte ion. Detailed data is also presented in Table 3.2. This problem is not unique and presents difficulties, for example, in

determining chloride in sulfuric acid. If the problem is significant for any sample matrix, as previously suggested, a less common cation such as a tetraalkylammonium ion can be chosen as the eluent ion.

Other cations, not associated with the eluent, may have substantial effects on the retention of H^+ from the matrix. For example, divalent cations, such as Mg^{2+} or Ca^{2+}, whose retention on the column is much greater than monovalent cations (e.g., Na^+, K^+, etc.), cause significant decreases in H^+ retention. On average, for a 30 mM HNO_3 solution containing equimolar amounts of Mg^{2+} or Ca^{2+}, the H^+ retention decreased nearly 65% in both cases. However, the effect observed from these ions should not create any problems in quantitation, since little to no deviation was observed in terms of H^+ peak areas.

3.6 References

1. D. T. Gjerde and J. S. Fritz, *Ion Chromatography*, 2nd ed., Hüthig, New York, (1987), 65.

2. R. A. Stairs and J. Semmler, *Anal. Chem.*, 57, (1985), 740-743.

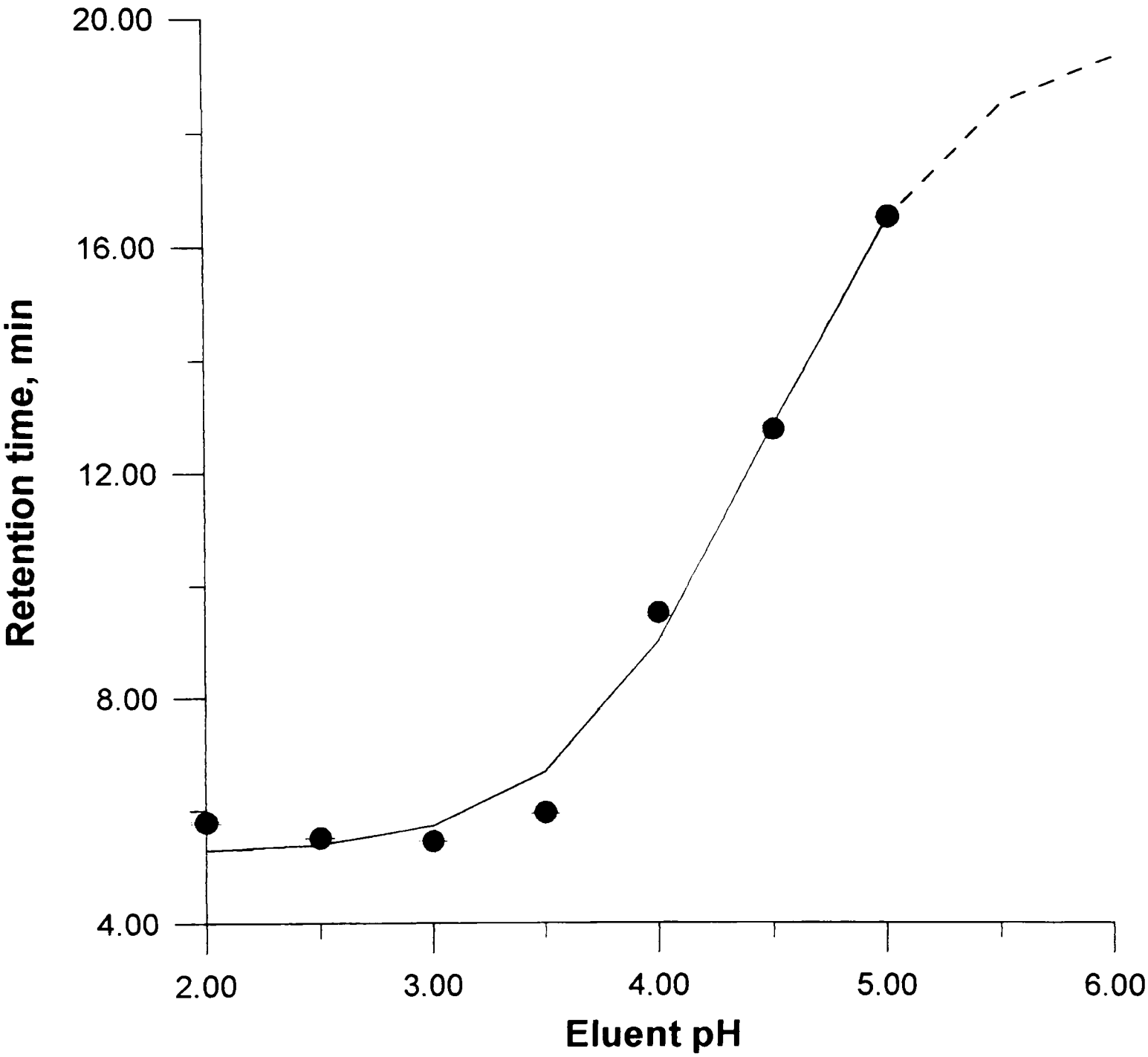

Figure 3.1. Experimental data for the retention time as a function of eluent pH (column 97-004-1065, 50 mM NaEtS, 2.0 mL/min). The solid line is the best fit to equation 3.2. The dashed line extrapolates the behavior expected according to equation 3.2 between pH 5 and 6 (experiments were not possible at this pH due to excessive peak broadening). *Data collected by T. K. Cook.*

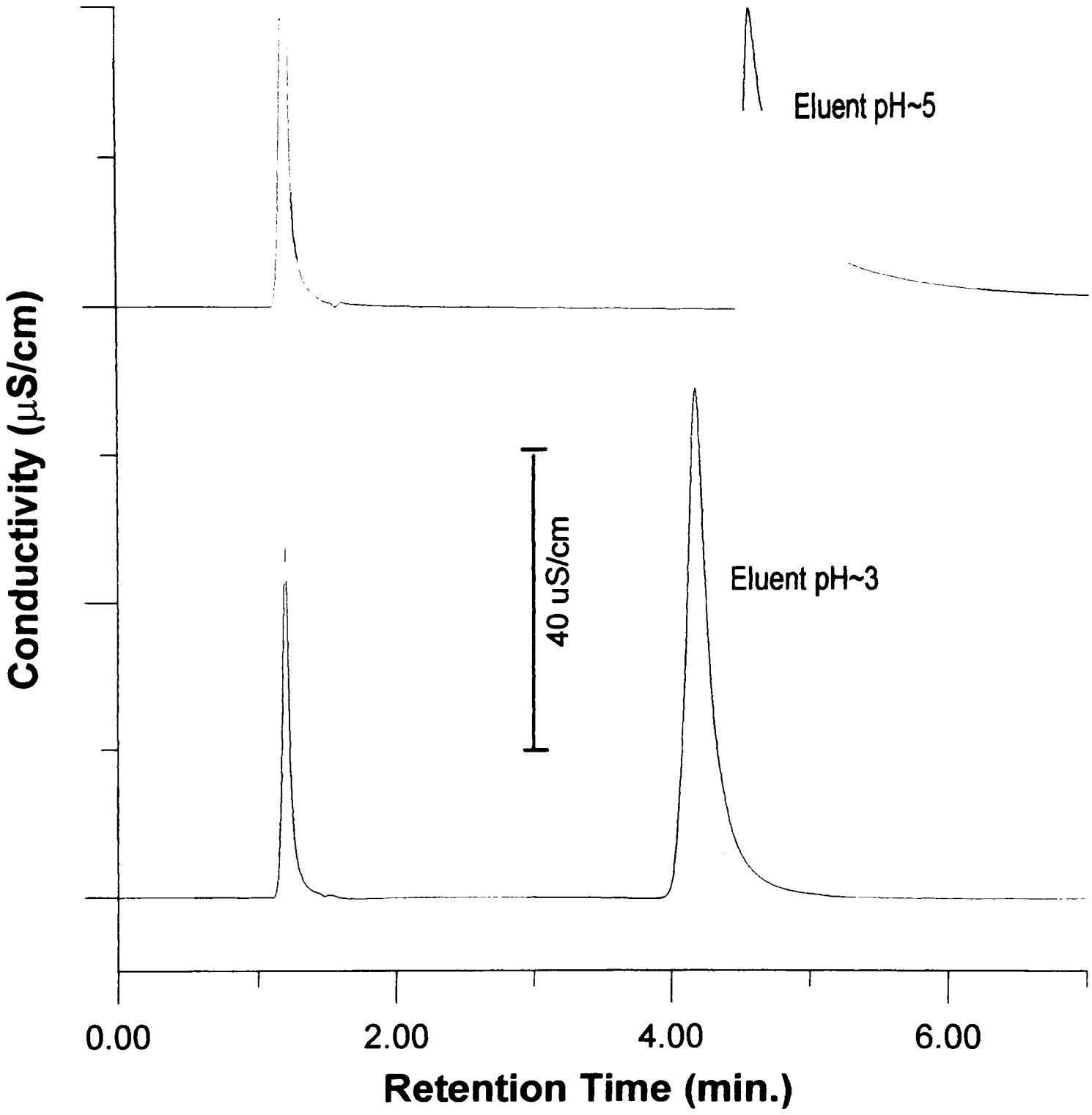

Figure 3.2. Broadening and change in retention time as a function of eluent pH (column 97-004-1045, 20 mM NaEtS, 1.0 mL/min).

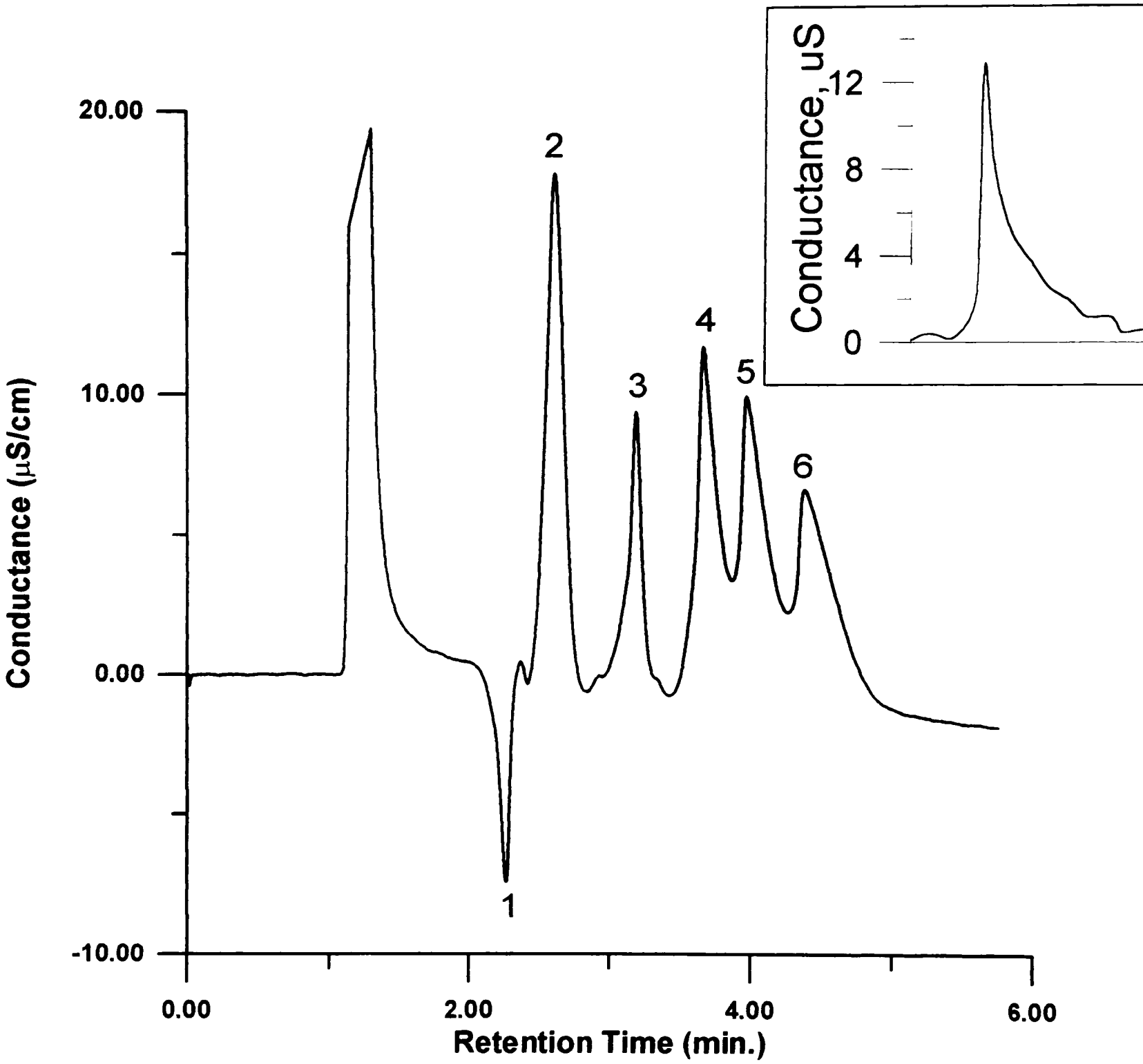

Figure 3.3. Separation of H^+ from other monovalent cations (column 97-004-1045, 50 mM NaEtS, pH 3, 1.0 mL/min, 2 μL sample, ambient temperature). Peaks: 1, 9 mM Li^+; 2, 2 mM H^+; 3, 15 mM NH_4^+; 4, 30 mM K^+; 5, 30 mM Rb^+; 6, 30 mM Cs^+. The inset *(data collected by D. Sherman)* shows the response from a 25 μL 200 μM H^+ sample on a low capacity 2 x 250 mM column (1 mM NaEtS, pH 6.5, 0.36 mL/min).

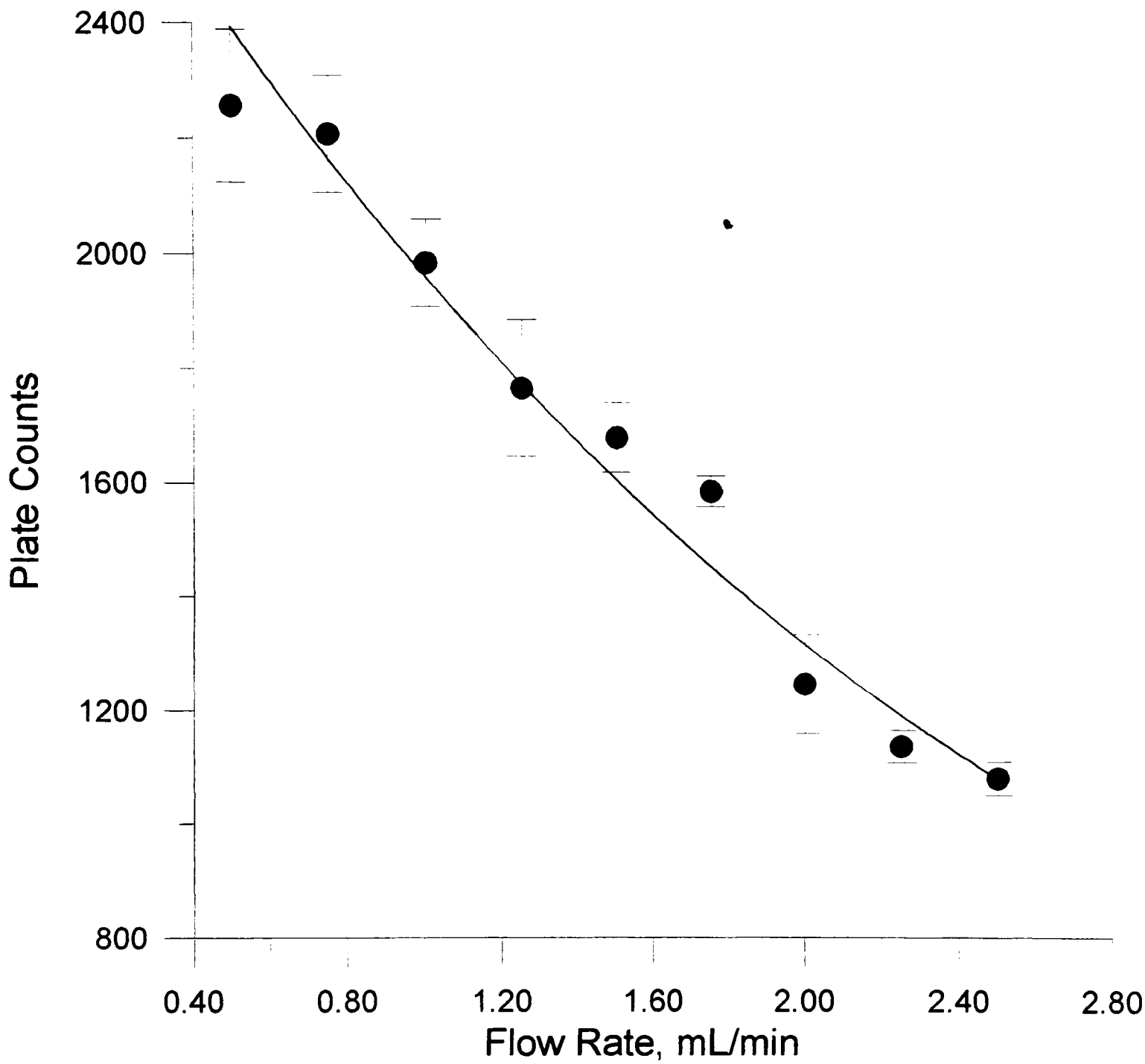

Figure 3.4. Plate counts for H^+ as a function of flow rate (column 97-004-1065, 50 mM NaEtS, pH 3, 2.0 mL/min). *Data collected by T. K. Cook.*

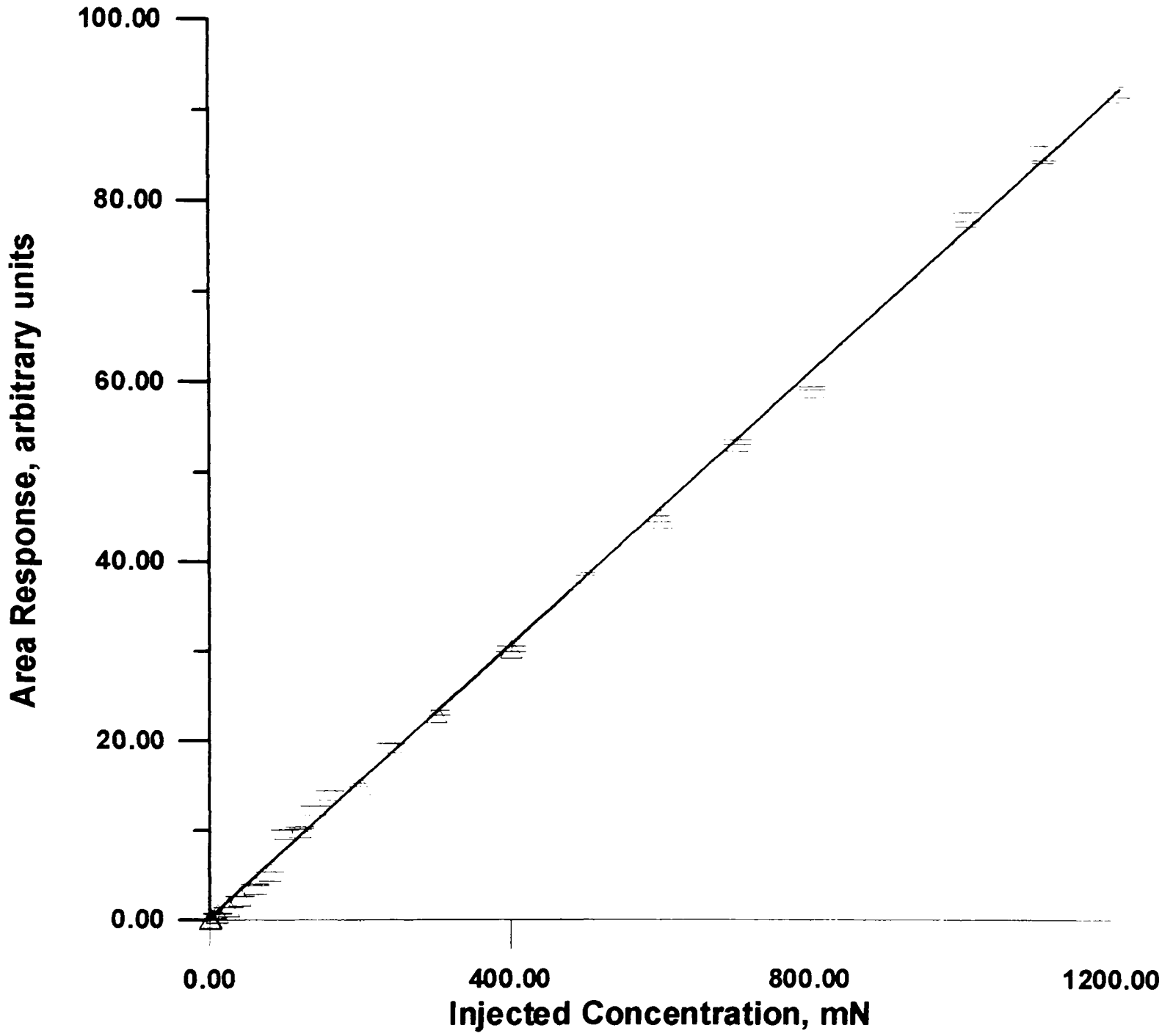

Figure 3.5. Calibration curve for H_2SO_4 over a three order of magnitude concentration range with an r^2 value of 0.9987(column 97-004-1045, 50 mM NaEtS, pH 3, 1.0 mL/min, 2 μL sample).

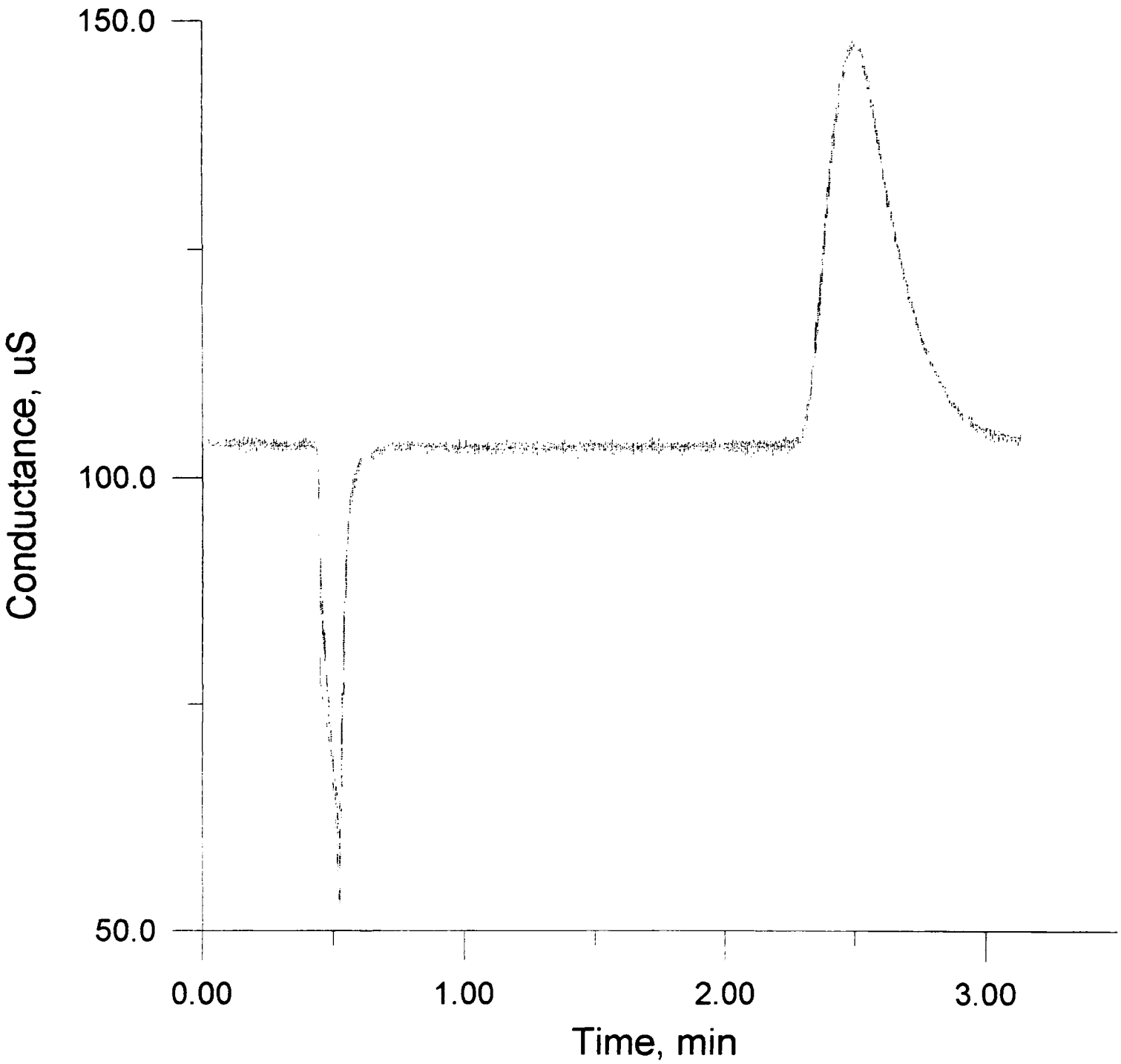

Figure 3.6. System reproducibility. Eight overlaid H^+ chromatograms (97-004-1065 column, 50 mM NaEtS, 2.0 mL/min). *Data collected by T. K. Cook.*

Table 3.1. Summary of Applicable Range for Selected Cation Exchange Columns in this Study.

Column	Column Capacity (μequivalents)	Eluent	Eluent pH	Applicable Range (mM)	r^2
47F#1[a]	7.5	1 mM NaEtS	6.5	0.05-1.00	0.9822
A2-12297[b]	30	1 mM NaEtS	5.0	0.3-100	-[c]
97-004-1045	180	50 mM NaEtS	3.0	1.0-1200	0.9987
AS[b]	9500	100 mM KEtS	4.0	0.1-10.0[d]	0.9999

[a]*data collected by D. Sherman*
[b]*data collected by C. M. Kinchin*
[c]calibration data was not available for this column
[d]concentration range refers to molar H^+

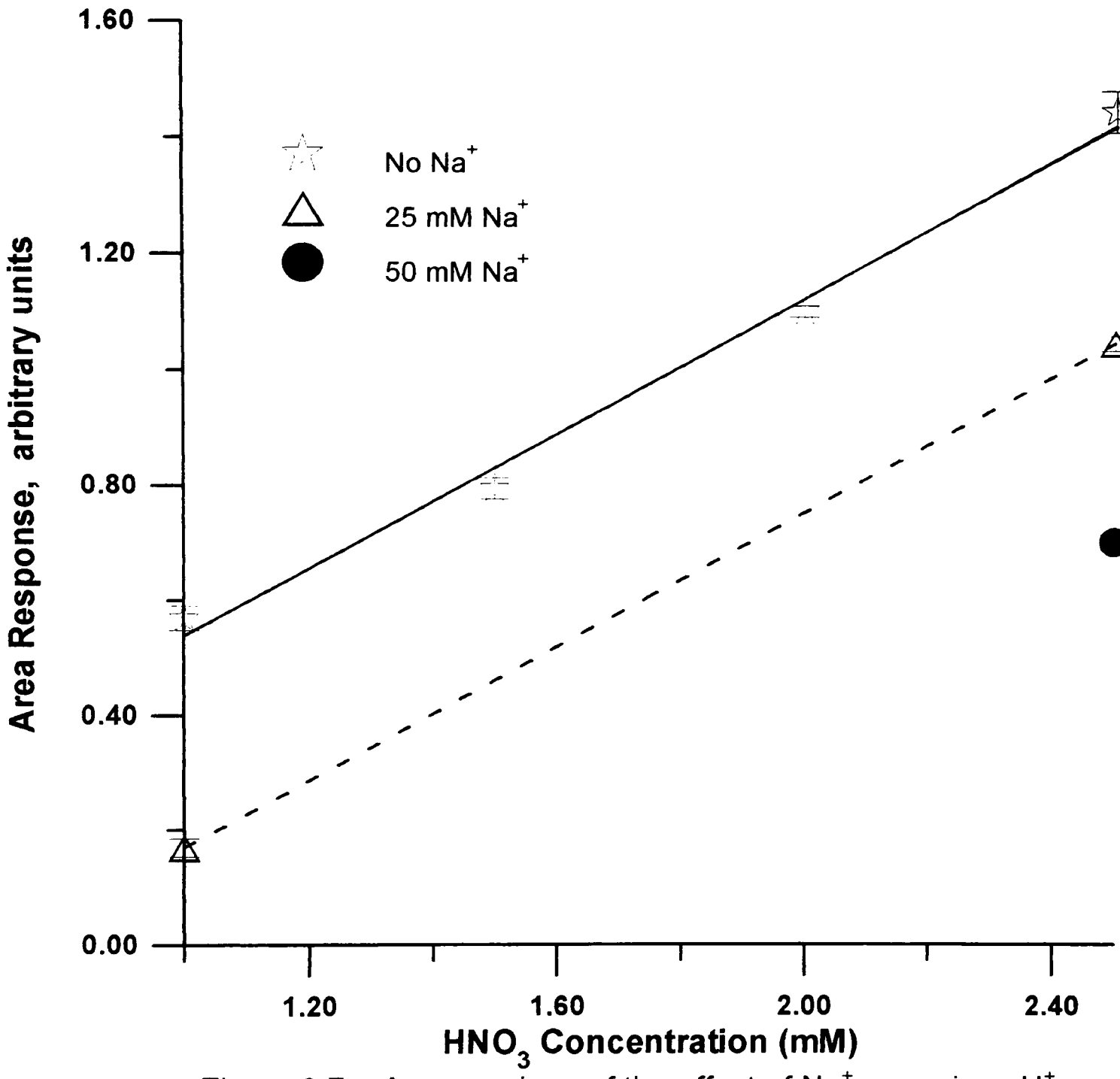

Figure 3.7. A comparison of the effect of Na^+ on various H^+ concentrations. (a) Effect of Na^+ on lower H^+ concentrations (column 97-004-1045, 50 mM NaEtS, pH 3, 1.0 mL/min).

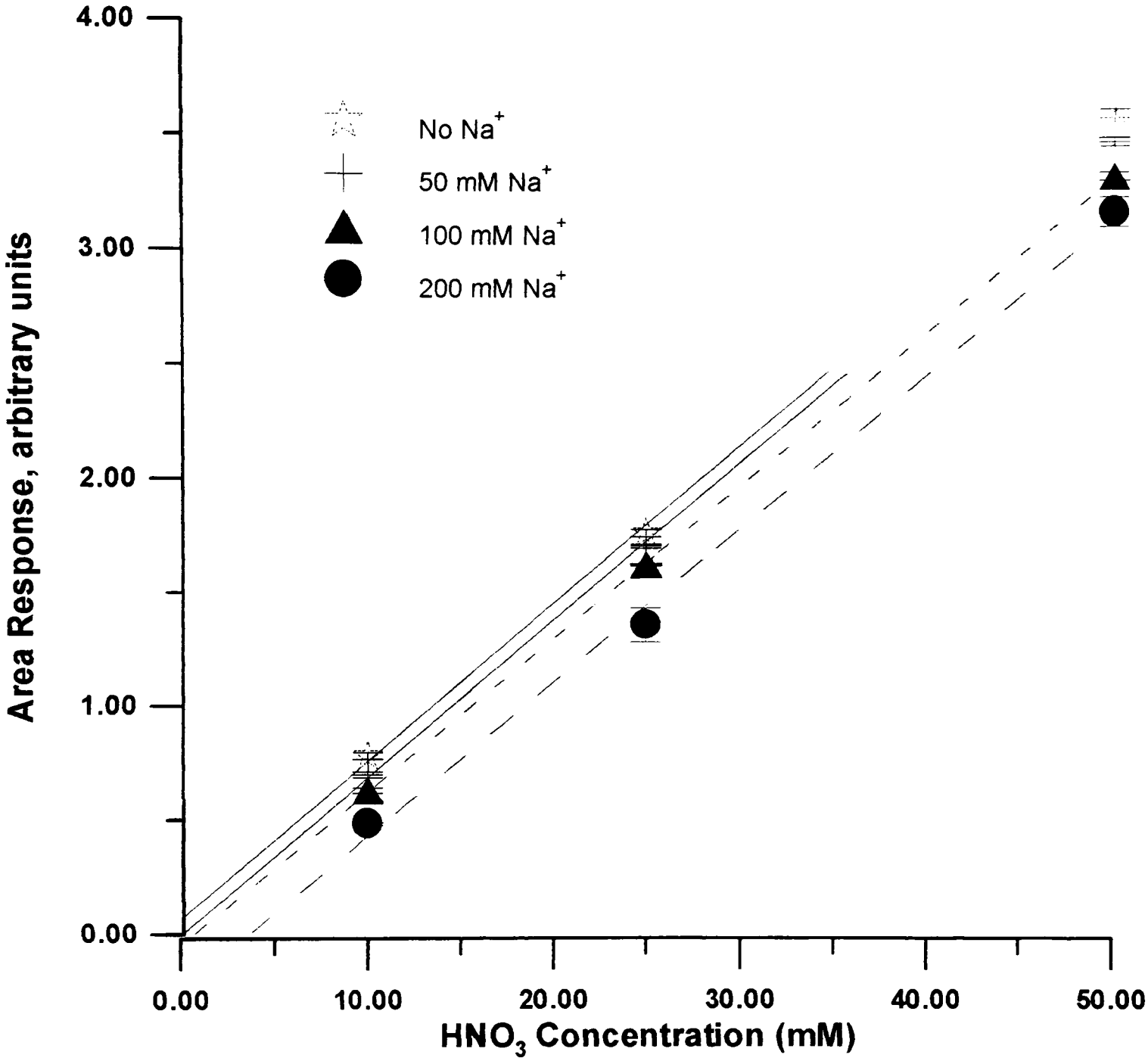

Figure 3.7. Continued. (b) Effect of Na^+ on higher H^+ concentrations (column 97-004-1045, 50 mM NaEtS, pH 3, 1.0 mL/min).

Table 3.2. Effect of additional salt added to various aqueous H^+ solutions (column 97-004-1045, 50 mM NaEtS, pH 3, 1.0 mL/min).

HNO_3 Conc. (mM)	Salt Added to Aqueous H^+ Solution	% Decrease in H^+ Peak Area Relative to No Salt Added
1.0	1 mM NaCl	5.90
	1 mM KCl	ND[a]
	25 mM NaCl	70.2
	50 mM NaCl	100
2.5	1 mM NaCl	1.98
	1 mM KCl	1.63
	25 mM NaCl	27.6
	50 mM NaCl	51.5
10	50 mM NaCl	10.6
	100 mM NaCl	19.4
	200 mM NaCl	38.3
25	50 mM NaCl	3.20
	100 mM NaCl	7.90
	200 mM NaCl	23.0
50	50 mM NaCl	2.30
	100 mM NaCl	6.50
	200 mM NaCl	10.8

[a]ND = no detectable change in H^+ peak area

CHAPTER 4

CHROMATOGRAPHIC DETERMINATION OF WEAK ACIDS

4.1 Introduction

The chromatographic analysis of weak acids is more complex than their strong acid counterparts. One complicating weak acid case is when they are present in the initial sample at such a concentration that they are substantially unionized. In addition, if a low eluent pH is used, dissociation of a weak acid is also inhibited. The ionization of a particular acid may be further inhibited by any tendency of the stationary phase to retain it in the unionized molecular form. On the other hand, chromatographic systems are multiplate equilibrium systems, and given a sufficient number of plates, there is still a potential that an accurate determination can be made. Consider an unionized acid HA enters the column and the following displacement reaction

$$\text{Resin-Na} + \text{HA} \longrightarrow \text{Resin-H} + \text{Na}^+ + \text{A}^- \qquad (4.1)$$

causes the uptake of H^+. H^+ and A^- are separated to the extent that the A^- formed is not reprotonated (the quantitative extent of this will depend on the pK_a of HA and the eluent pH) and continue with the next stage. While this results in peak tailing of both the initial displacement peak and the H^+ peak, it may still be possible to obtain good quantitation based on peak area.

4.2 Chromatographic Comparison Between Strong and Weak Acids

Moderately weak acids, up to *o*-phthalic acid (pK_{a1} 2.89) and an injected concentration of 100 mM (injected volume = 2 μL), produce nearly equivalent responses to an equal amount of a strong acid. The weak acids examined in this study included trichloroacetic, dichloroacetic, monochloroacetic, *o*-phthalic, *p*-chlorobenzoic, and acetic acids; the respective pK_a values are 0.70, 1.48, 2.87, 2.89 (pK_{a1}), 3.98, and 4.76. The responses of some of these acids in the analytical system consisting of the 97-004-1045 column and a 50 mM NaEtS eluent at pH 3 are shown in Figure 4.1, along with that of a strong acid, ethanesulfonic acid. The weakest acid, acetic acid, produces a far lower response compared to the others, but the responses of the other acids up to a concentration of 100 mM are similar to that of a strong acid. The response for *p*-chlorobenzoic acid could not be ascertained due its limited water solubility. However, although the data is not presented here, significant deviations occur at concentrations >100 mM H^+ as a function of pK_a.

4.3 Absorbance Studies

Peak tailing in the case of an acid as weak as acetic acid is thought to be caused by the retention of its molecular form. This can be proven experimentally if the anionic component can be uniquely detected by some other means, e.g., through its optical absorption. Acetate does not exhibit significant optical absorption, so such an experiment was conducted with *p*-chlorobenzoic and *o*-phthalic acids. An ultraviolet (UV) absorbance detector (set at a wavelength of

220 nm) was positioned after the conductivity detector in the DX-500 system. The conductance and absorbance signals for both *o*-phthalic acid and *p*-chlorobenzoic acid as analytes are shown in Figures 4.2 and 4.3, respectively. Due to its limited solubility, *p*-chlorobenzoic acid could only be measured at low concentrations. Considering the transit time between the two detectors, it is clear that while the phthalate anion is separated from H^+, the *p*-chlorobenzoate ion significantly overlaps the H^+ peak. From this data, it appears that a pK_a of 3 is the upper limit of applicability; with more efficient columns having a greater number of plates, as with capillaries, and containing even fewer carboxylate sites, it may be possible to extend this to weaker acids.

4.4 Effect of Coanalytes on Acetic Acid

The effect of coanalytes on the determination of strong acids was presented in the previous chapter (section 3.4). As demonstrated with strong acids, various amounts of Na^+ added to the sample matrix have significant effects on low H^+ concentrations ($[H^+]$), but negligible effects as the $[H^+]$ is increased. As discussed earlier in this chapter, acids with $pK_a > 3$ (such as acetic acid) are not completely ionized in aqueous solutions. This results in much lower signal responses than those observed with strong acids.

Equimolar amounts of K^+, whose retention is much greater than H^+, was added to the matrix of acetic acid (HOAc) solutions, ranging in concentration from 100 mM to 300 mM (Figure 4.4). As shown in this figure, the magnitude of the effect was greater as the amount of K^+ in the sample matrix was increased.

At this point, overwhelming amounts of K^+ present caused overloading of the column and thus peak overlapping between H^+ and K^+. Although not presented here, similar experiments with strong acids resulted in little to no effect on the quantitation of the H^+ peak. Obviously, the discrepancy between the differing results between strong and weak acids may simply be explained by the poor retention of the weak H^+ (as previously discussed in this chapter) in the first place. In addition, poor retention and the addition of a coanalyte (in large amounts) results in further suppression of the H^+ peak.

4.5 Effect of Temperature on Acetic Acid

The effect of temperature on the determination of strong acids was discussed in Chapter 3 (section 3.3). Unlike strong acids, temperature has a dramatically different effect on the determination of weak acids. In order to study this effect, a system was designed only to measure the conductivity detector response without any chromatographic column present. A very dilute sample of HOAC, 1 part per million (ppm), where the acid should be completely ionized in aqueous solution at this concentration was studied. A temperature range between 25°C to 100°C was examined. Results from this study indicated very little to no change in detector response relative to responses at ambient temperature. The dissociation constant (K_a) was calculated for HOAc at various temperatures. For example, at 100°C a pK_a value of 4.85 was calculated, greater than the pK_a at ambient temperature (pK_a 4.76 at 25°C). This confirms the conclusion that acetic acid becomes a slightly weaker acid at higher

temperatures. Therefore, unlike strong acids, it would not be advantageous to conduct chromatography experiments with weak acids at high temperatures.

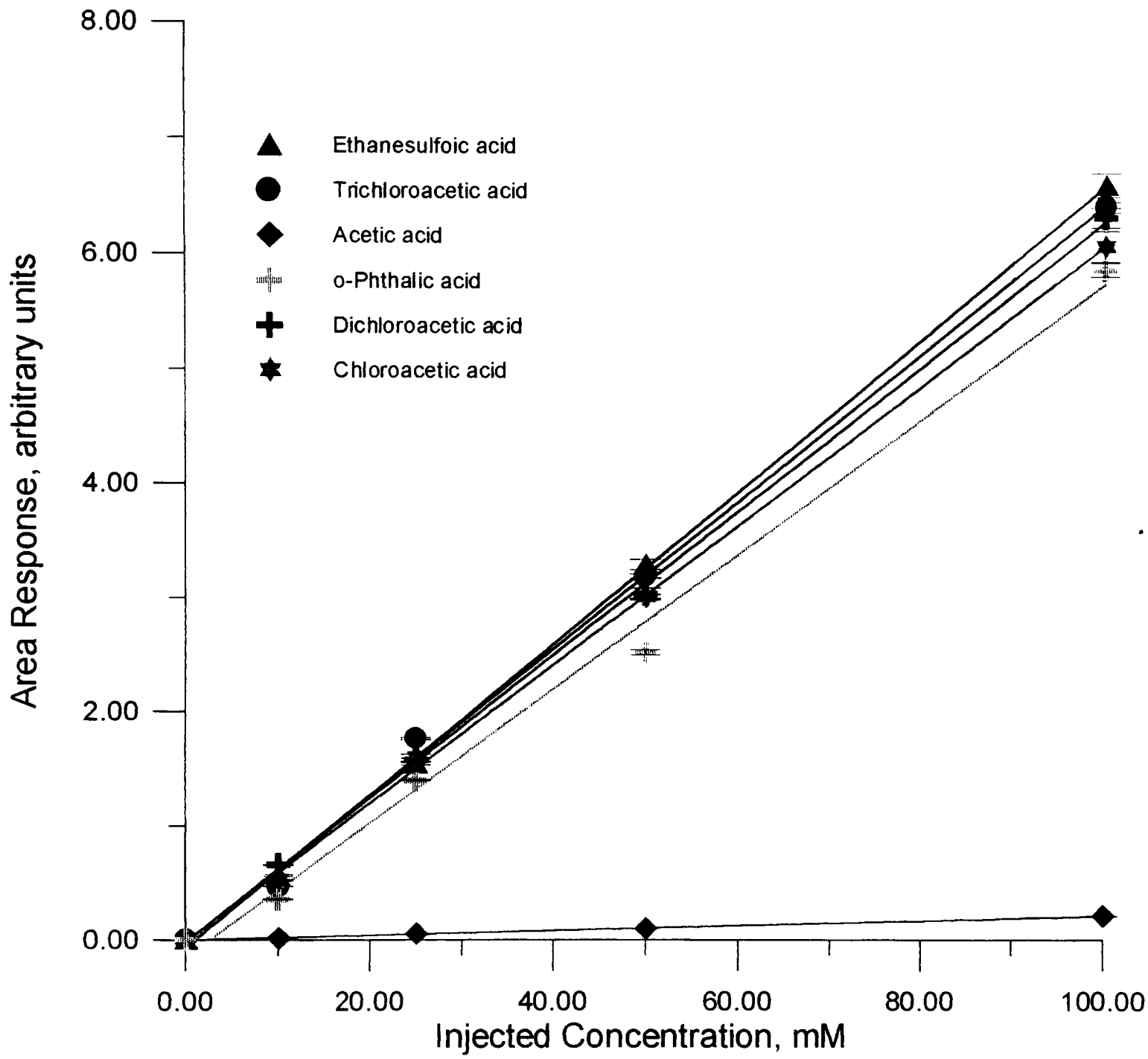

Figure 4.1. Calibration behavior of six acids (pK_a indicated in parentheses: ethanesulfonic acid (strong acid), trichloroacetic acid (0.70), dichloroacetic acid (1.48), monochloroacetic acid (2.87), *o*-phthalic acid (2.89, pK_{a1}), and acetic acid (4.76).

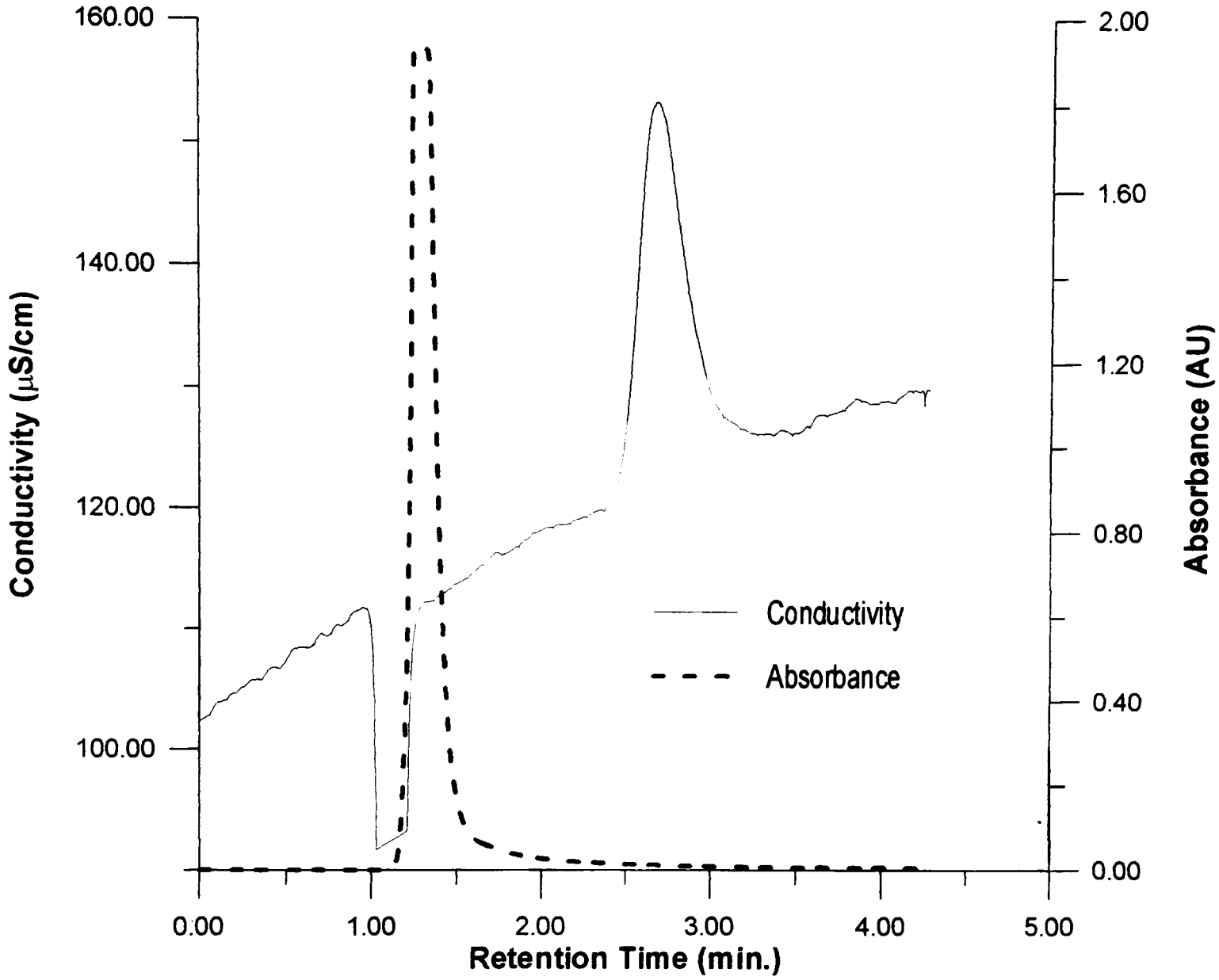

Figure 4.2. Sequential conductance and absorbance detection of *o*-phthalic acid. Conditions: 50 mM NaEtS eluent, pH 3, 97-004-1045 column.

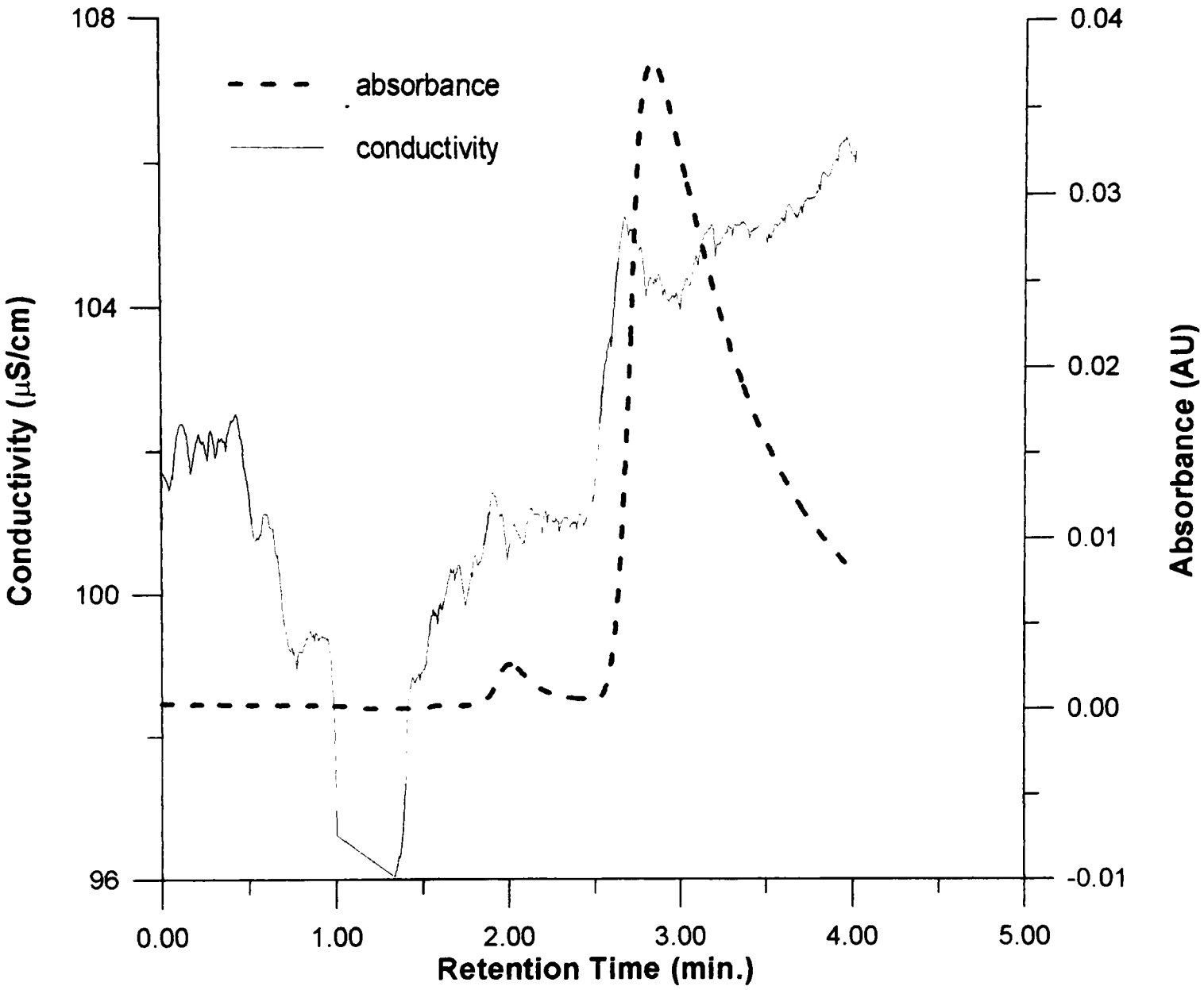

Figure 4.3. Sequential conductance and absorbance detection of *p*-chlorobenzoic acid. Same conditions as Figure 4.2. H^+ elutes at ~3 minutes.

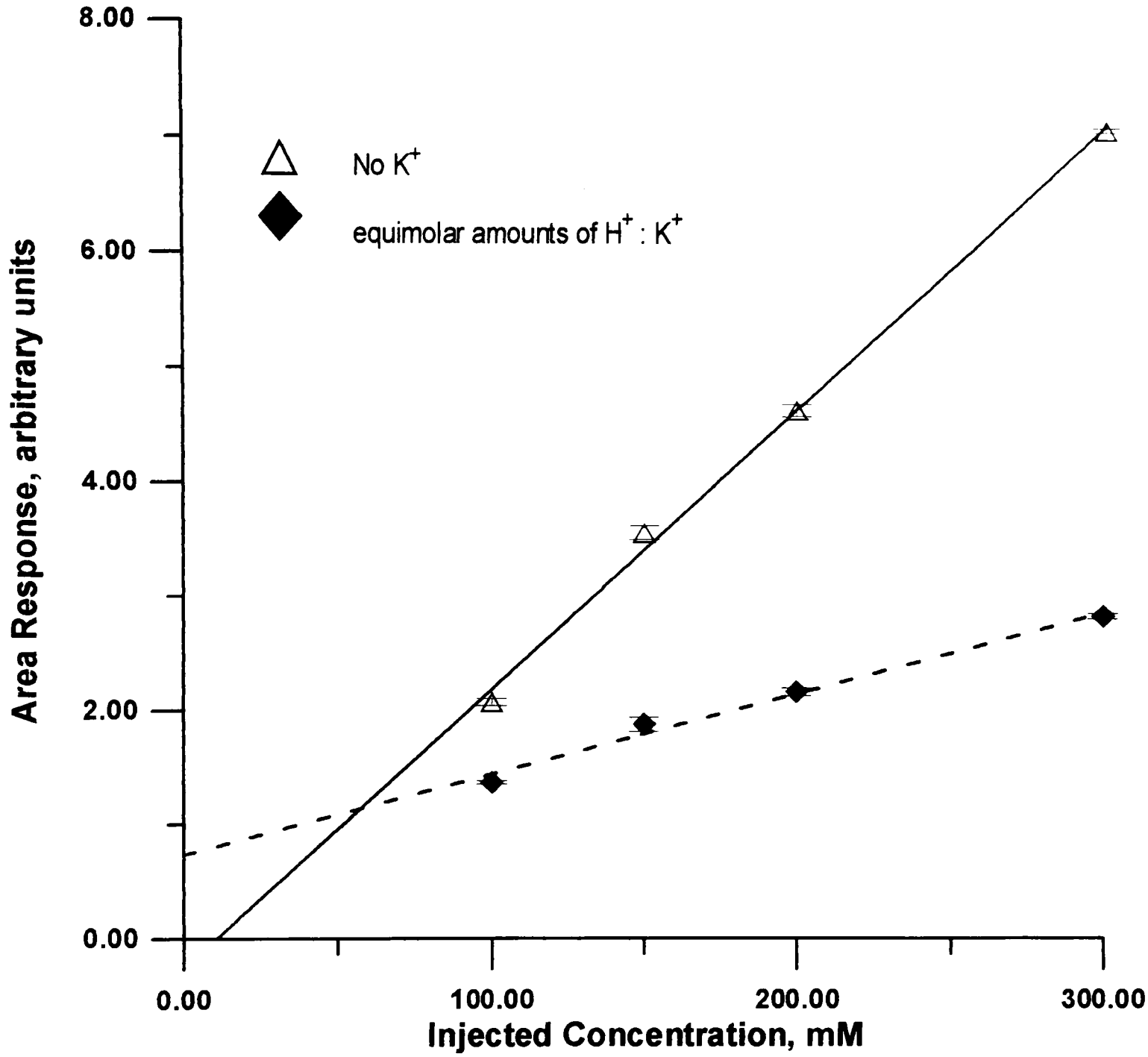

Figure 4.4. Effect of various amounts of K^+ added to the matrix of acetic acid solutions in a 1:1 ratio. Conditions: 50 mM NaEtS, pH 3, 097-004-1045 column.

CHAPTER 5

CONCLUSIONS

The performance of an ion chromatographic system to separate strong and weak acids on a sulfonated styrene-divinylbenzene based stationary phase was presented in this thesis. The system demonstrated the ability to measure H^+ concentrations over several orders of magnitude on the higher capacity columns and H^+ concentrations as low as 50 μM H^+ on the lowest capacity column. Also, several factors that affect the measurement of H^+ were examined, such as eluent pH, column temperature, flow rate, and the presence of coanalytes in the sample matrix. Since $-COO^-$ have a much greater affinity than $-SO_3$ groups for H^+, the optimum eluent pH in the current study was 3 (i.e., 1 mM H^+) to allow protonation of any residual carboxyl groups in a sulfonated resin and thus to efficiently measure H^+. However, in these studies, since the eluent was acidified with 1 mM H^+, hydrogen ion concentrations could not be measured below this level.

In addition to the measurement of strong acids, the chromatographic determination of weak acids was also examined. The examination of these types of acids presented a more complex situation, since they are not completely ionized in solution. However, as discussed in this thesis, moderately weak acids (up to a pK_a ~3) may produce similar responses to strong acids up to 100 mM H^+. At even higher pK_a values (i.e., acetic acid), a much different response is observed regardless of concentration. Optical detection studies demonstrated

that it is actually the molecular form of the acid that is retained on the column for acids of these pK_a values.

Conductometric ion exchange chromatography without the use of suppressors is a highly suitable technique for the determination of strong acids over a wide concentration range and for modestly weak acids over a low concentration range. The present technique represents a novel and different way of measuring titratable acidity that may have unique applications. Also, the use of smaller systems, such as capillaries, may increase its applicability in analytical measurements. Obviously, a similar method may be applied for the measurement of bases.

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