Ion Chromatographic Determination of Acidity

Brian M. De Borba, Christopher M. Kinchin, Diana Sherman, T. Kevin Cook, and Purnendu K. Dasgupta*

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061

Kannan Srinivasan and Christopher A. Pohl
Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086

The practice of determining acid concentrations by titrations has remained unchanged for more than a century. We introduce a new approach to the determination of acid concentrations based on cation exchange chromatography. We demonstrate the ability of sulfonated styrene–divinylbenzene based stationary phases to separate the hydrogen ion from other monovalent cations. The eluent is a dilute solution of a neutral salt, sometimes containing a small concentration of the corresponding acid, e.g., sodium ethanesulfonate, pH adjusted with ethanesulfonic acid. The high equivalent conductance (∼350 S·cm²/ equiv) of H⁺ and relatively low eluent concentration allows 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 allows the rapid quantitation of strong acids; weak acids can also be determined depending on pKₐ and injected concentration. The determinations of several strong and weak acids are presented along with factors that govern their chromatographic analysis.

The determination of acid or base content of a sample is one of the most essential tasks (and historically the most important task) ever performed in analytical chemistry. The foundation of volumetric analysis, as it is presently known, was laid by Gay Lussac between 1824 and 1832.1 However, it is Mohr who is credited with making volumetric analysis popular, particularly through the publication in 1855 of his classic treatise on titrimetry2 and also through many innovations in the hardware for titrimetric analysis—Mohr’s original designs3 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 by Sørensen4 until the 20th century) 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 been developed. In contrast, a sample must be analyzed to determine titratable acidity. The principle of this determination, volumetric titration, has basically remained unaltered since its inception; 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. Titrations can be carried out by flow injection analysis (FIA) with a large dynamic range, but the relationship between the measured parameter and the analyte concentration is logarithmic; this can lead to significant errors.5 Unlike that of other FIA measurements, the time for each analysis can also be significant.

Suppressed conductometric ion chromatography (IC)6 is now the dominant technique for ionic analysis. While anions are mostly determined, this technique is increasingly used for measuring alkali and alkaline earth metals. The selectivity of common sulfonate resins typically follows the order Li⁺ < H⁺ < Na⁺ < NH₄⁺ < K⁺ < Rb⁺ < Cs⁺;7 but the actual determination of H⁺ by chromatographic means has never been demonstrated. The fact that H⁺ can be separated from other cations by standard cation exchange chromatography is rarely recognized because extant approaches do not allow ready visualization of H⁺ as an eluite. Visualization of H⁺ by a postcolumn reaction (PCR) with an indicator is possible;8 however, this represents added complexity and other ions of interest cannot be measured. Further, unlike direct colorimetric indicator-based methods, conductometric detection, the mainstay of IC, displays a wide linear dynamic range. Presently, in suppressed IC for cations, H⁺ is obligatorily removed by the suppressor. In its nonsuppressed analogue, acids or acidic eluents containing amine salts are used. Consequently, small amounts of eluted H⁺ are invisible to a conductivity detector. We show in this work that H⁺ is readily determined by conductometric IC with the right choice of eluent.

EXPERIMENTAL SECTION

Equipment: Both conventional- and capillary-scale IC was used. In conventional scale, either a Dionex DX-500 ion chromato-
matograph equipped with a GP-40 gradient pump, an LC30 chromatography oven (equipped with a 2 μL loop injector), a CD20 conductivity detector, or a Dionex DX-100 chromatograph with a 100 μL loop injector was used. The analytical columns (4 × 250 mm, except as stated) 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.

The capillary-based IC system in this work was described previously. No suppressors were used in this work, and the conductivity cell was changed from that described. The present cell design used two tubular stainless steel electrodes (thin-wall 30 gauge hypodermic tubing; P/N O-HTX-30, Small Parts, Miami Lakes, FL; 178 μm i.d. × 356 μm o.d., with ends sanded flat; inserted into a tightly fitting PEEK sleeve and epoxied in place, similar to a previously described design (Figure 4a, ref 11). The cell constant (~70) was determined by using 1 mM KCl as the calibrator. Other cells of similar designs but different cell constants were also used.

Capillary column blanks were 180 μm i.d. × 342 μm o.d. fused-silica tubes (Polymicro Technologies Inc., Phoenix, AZ). Columns were ~50 cm long and were packed in house with glass wool frits using the same packing material as in the conventional system. The conductivity cell was directly butt-joined with an elastomeric poly(vinyl chloride) sleeve to the exit end of the column. A 60 nL internal loop injector (Valco Instruments) was used with the capillary columns.

Chromatographic data were acquired by using either a Dionex PeakNet chromatography workstation or a PC-based data acquisition system with a Keithley/Metrabyte A/D card and software written in house.

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 sodium hydroxide solutions. Ethanesulfonic acid (HES, 70% v/v) was purchased from Aldrich and standardized by titration. The acid was converted to the sodium form with standard sodium hydroxide solutions. Ethanesulfonic acid (HEtS, 50% v/v) was chosen by using 1 mM KCl as the calibrant. Other standard sodium hydroxide solutions. Ethanesulfonic acid (HEtS, 50% v/v) was chosen by using 1 mM KCl as the calibrant.

The equivalent conductances for common ions of interest in this context are as follows (S·cm2/equiv)23: Ni(C2H3)4+, 23.5; Ni(C2H3)43+, 33.0; Li+, 73.5; Na+, 77.8; K+, 73.5; Mg2+, 53.1; Ca2+, 59.5; NH4+, 73.5; K+, 73.5; Rb+, 77.8; Cs+, 77.3; H+, 350. Because of

RESULTS AND DISCUSSION

Principle of Determination. Consider a nonsuppressed conductometric IC system, with an NaCl eluent. Injected cations are exchanged for Na+, producing an NaX (being the anion(s) associated with the sample) system peak (or dip, depending on the relative cation equivalent concentrations in the sample vs the eluent). The sample cations then elute in the order of their affinity. The equivalent conductances for common ions of interest in this context are as follows (S·cm2/equiv): Ni(C2H3)4+, 23.5; Ni(C2H3)43+, 33.0; Li+, 73.5; Na+, 77.8; K+, 73.5; Mg2+, 53.1; Ca2+, 59.5; NH4+, 73.5; K+, 73.5; Rb+, 77.8; Cs+, 77.3; H+, 350. Because of

the very high value of $\lambda_{\text{Na}^+}$, the detection system is particularly sensitive to H+. Any eluent cation (in this case, Na+) present in the sample is invisible to the detection system and cannot be measured.

Sodium was chosen as the eluent cation because it can be measured in a simple manner by other means. Na+ can be present in some samples in large amounts; making Na+, which elutes immediately after H+, invisible may therefore be advantageous. With an Na+ eluent, alkali and alkaline earth metals other than Li+ produce positive peaks ($\lambda_{\text{analyte}} > \lambda_{\text{Na}^+}$). If it is desirable to measure Na+, another choice for an eluent cation can be made.

The eluent anion, as long as it is derived from a strong acid, plays no role. However, it contributes to the background conductance, and low equivalent conductance ethanesulfonate was chosen.

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 carboxylic acid type; H+ could not be eluted from any of these with reasonable eluent concentrations (≥100 mM) or within a reasonable time (<20 min). The $pK_a$ of an acidic functionality can be construed to be a direct measure of its affinity for H+. If −COO− groups already exhibit too great a retention for H+, SiO− groups or other functionalities that are stronger conjugate bases than −COO− will have too great an affinity for H+. On the other hand, sulfonated resins are strong acids and should be ideal for chromatographically separating H+ from other 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 carboxylic 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 carboxylic acid groups by already protonating them by operating at lowered eluent pH.

Effect of Eluent pH on Chromatographic Behavior. Consider the following simple model to illustrate the effect of eluent pH on H+ retention. The capacity factor $k'$ can be expressed as

$$k' = (t_e - t_0) / t_R = AK_s + BK_c$$

where $t_0$ and $t_e$ have their usual meanings, $K_s$ and $K_c$ are the partition/binding constants for H+ and sulfonate groups and for H+ and carboxylate groups, respectively, and A and B are 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, eq 1 takes the form

$$t_R = a + bK_s / (K_a + [H^+])$$

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, column capacity 410 µequiv) operated with a 60 mM NaEtS eluent adjusted to pH 2–5 were obtained with HES flowing at a rate of

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2 mL/min. In Figure 1, the experimental data are shown as points with ±1 standard deviations as error bars and the data are fitted to eq 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, efficiency decreases dramatically due to the increased importance of mixed-mode retention as pH increases. On this particular column, peak efficiency (calculated as $5.54(t_R/w_0)^{0.5}$) decreased by more than a factor of 35 in going from pH 3 to 5. The observed results are consistent with the phenomenological model; the best fit value for $K_a$ is $3.5 \times 10^{-5}$ ($pK_a 4.45$), quite characteristic of carboxylic acids.

Our experience shows 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 $\mu$equiv column capacity) containing a resin sulfonated under milder conditions, $H^+$ peaks could be discerned easily with a 20 mM NaEtS eluent at pH 5, although peak tailing and general chromatographic performance improved significantly with a reduction of eluent pH to 3 (Figure 2). In general, there was no improvement in performance upon reducing the eluent pH below 3 with any of the columns we have examined, regardless of capacity. The maximum column efficiency has been observed at this eluent pH.

The separation of a number of alkali metal cations and $H^+$ on the 97-004-1065 column with a 50 mM NaEtS eluent, adjusted to a pH of 3 and operated at a flow rate of 2 mL/min, is shown in Figure 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 $Li^+ < H^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$. Note the negative signal for $Li^+$ ($\lambda_{Li^+} < \lambda_{Na^+}$) and the very substantially greater sensitivity of $H^+$ relative to any other cation. It should be emphasized that none of the relevant parameters such as column capacity, particle size, packing techniques, eluent concentration, 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.

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. With a sufficiently low capacity column (47F #1, 7.5 $\mu$equiv), 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 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 that of NH₄⁺, the next eluting peak under these conditions.

**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. The H⁺ plate counts for the same column and eluent combination at 22 °C as in Figure 3 decrease exponentially from ~2400 to ~1100 for flow rates from 0.5 to 2.5 mL/min. At even higher flow rates, peak tailing becomes too large for meaningful chromatography.

Since 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 mL/min for the conventional column, and using a 50 mM NaEtS eluent, adjusted to pH 3. The observed column efficiency increased from 5400 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(no. of plates) linearly related to 1/T with a linear r² of 0.96, n = 12). The observed slope corresponded to an activation energy of 26.5 kJ/mol. The same experiment was done on the conventional-size column over a more limited temperature range of 28−40 °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 at an elevated temperature.

**Applicable Range.** With very low capacity columns, as was shown in the inset of Figure 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 r² 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 47F #1 column. 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 sulfuric acid over a 3 order of magnitude concentration range (5.0 × 10⁻⁴−1.2 M H⁺) with good linearity (r² = 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 (column capacity 9.5 mequiv) 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 r² = 0.9833) for 0.5−8 M HCl. The response linearity may in fact be better than the linear r² value indicates because it is difficult to avoid HCl losses with the highest concentration samples. The reproducibility of response from individual injections at several molar concentrations was studied with a nonvolatile analyte, H₂SO₄. The reproducibilities were within 0.1−0.3% relative standard deviation (generally the pumping precision of the system is believed to be of this order). Using a quadratic fit, the r² value was 0.9999 for 0.1−10 M H₂SO₄. It should thus 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. For an injected sample containing 12.5 mM HNO₃ 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 rsd.

**Effect of Coanalytes.** Strong acid anions are fully ionized and have no effects on the determination. The analysis of weak acids is discussed in a later section. Cations that elute on either side of H⁺, e.g., Li⁺ or NH₄⁺ (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 can consume all the available exchange sites such that the H⁺ ion is not retained and produces no response. This problem is not unique and presents difficulties, for example, in determining chloride in sulfuric acid. The magnitude of this effect depends both on the absolute amount of H⁺ (being greater at low levels of H⁺) and on the ratio of the eluent ion to the analyte ion. If this 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.

**Determination of Weak Acids.** When substantially un-ionized weak acids are injected as samples, the analytical situation is more complex. 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 un-ionized 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 that even when an un-ionized acid HA enters the column, the displacement reaction

\[
\text{resin–Na} + \text{HA} \rightarrow \text{resin–H} + \text{Na}^+ + \text{A}^- \quad (3)
\]

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 pKₐ of HA and the eluent pH) and can pass to the next stage. While this will lead to tailing of both the initial displacement peak and the H⁺ peak, it may still be possible to obtain good peak area based quantitation.

Aside from the behavior of strong acids, all of which show the same calibration curve up to a concentration of at least 0.1 M, we also examined the behavior of trichloroacetic, dichloroacetic, monochloroacetic, o-phthelic, p-chlorobenzoic, and acetic acids; the respective pKₐ values are 0.70, 1.48, 2.87, 2.89 (pKₐ), 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, 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 very close to that of a strong acid. However, although data are not shown here, at even higher concentrations, significant differences among the responses of the various acids begin to appear as a function of $pK_a$.

Figure 4. Calibration behavior of six acids ($pK_a$ indicated in parentheses): ethanesulfonic (strong acid), trichloroacetic (0.70), dichloroacetic (1.48), monochloroacetic (2.87), o-phthalic (2.89, $pK_{a1}$), and acetic (4.76).

Peak tailing in the case of an acid as weak as acetic acid is believed to be due to retention of the molecular acid. 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 acid. A UV absorbance detector (set at 220 nm) was connected after the conductivity detector. The conductance and absorbance signals for both o-phthalic acid and p-chlorobenzoic acid as analytes were followed. For phthalate, the phthalate anion eluted well before $H^+$, while the p-chlorobenzoate anion largely overlapped the $H^+$ peak. In effect then, a $pK_a$ of 3 appears to be the present upper limit of applicability; with more efficient columns having greater numbers of plates, as with capillaries, and containing even fewer carboxylate sites, it may be possible to extend this to weaker acids.

CONCLUSION

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 of modestly weak acids over a low concentration range. This technique represents a novel and different way of measuring titratable acidity that is likely to have unique applications. Obviously, a similar technique will be applicable to bases.

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