

Discovery and Early Development of Non-Suppressed Ion Chromatography

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Abstract

This year marks the 30th anniversary of the publication of *Non-Suppressed Ion Chromatography*, which is a method for the rapid separation of anions with on-line conductimetric detection. In this method, the separation column is connected directly to the conductimetric detector. This single-column method is a simpler technique than the original suppressed ion chromatography method, which requires a large suppressor column to reduce the background conductance. In the new method, the background signal is reduced to a manageable level simply by using an ion-exchange separation column of low exchange capacity that lowers the eluent concentration needed for separation. The eluent ion used for separation is chosen based on having large, bulky structure, which lowers the equivalent conductance and facilitates detection of the sample anions. This is a personal account of the initial discovery and early development of non-suppressed ion chromatography. The circumstances for the discovery are recounted by the two authors. Methods are described for determination of anions, cations with indirect detection, and techniques for increasing detection sensitivity. A fundamental equation for the prediction of ion chromatography detector response is given, and the development of several types of detection schemes for ion chromatography is discussed. Finally, the impact of non-suppressed ion chromatography is discussed together with comments on the discovery process.

Introduction

Ion-exchange chromatography actually has quite a long history. Displacement ion-exchange was used for some impressive preparative separations: of all the rare earth elements (1–4); of nitrogen 14 and 15 isotopes in ammonia (5,6); and of numerous metal ions as chloride, fluoride, nitrate, and sulfate complexes on anion-exchange columns (7–9).

In displacement chromatography, the various sample components are gradually resolved into separate zones that in tandem move down the column at the same speed once equilibrium has been reached. This occurs when the eluent ion is taken up very strongly by the ion-exchange column. The eluent pushes the sample ions like a chemical piston. There is some mixing of adjacent sample ions at the interface, but each zone is rather broad and most of each zone contains the pore material. This type of chromatography is used to separate or purify a comparatively large amount of material.

In elution chromatography, sample ions are gradually resolved into separate bands that move down the column at different rates. This type of separation is generally used for quantitative analytical work because much less sample is required, and there is no mixing at the boundaries between the bands provided the peaks are completely resolved.

Early investigators were able to obtain some ionic separations (mostly metal cations) by elution chromatography, but the separations were very slow and therefore not very popular.

The main drawback of these early investigations was that the separations required collection and subsequent analysis of numerous fractions with automatic on-line detectors. Clearly, some means of automatic on-line detection was required to make analytical ion-exchange chromatography a popular, widely-used technique.

Reversed-phase liquid chromatography (LC) of organic analytes went “high-performance” (HPLC) around 1970. This was made possible by the availability of small, efficient eluent pumps, more efficient packed columns, and on-line detectors (especially UV-vis).

Advances in HPLC soon began to influence metal ion separations. Cassidy in Canada pioneered the separation of metal cations by partial complexation with hydroxyl isobutyric acid (HIBA). The metal peaks were detected automatically by post-column addition of complexing reagent such as Arsenazo I or PAR. In 1974, a separation of all the lanthanides was obtained in 90 min. (10). A few years later, Elchuk and Cassidy obtained a more complete resolution of the 13 lanthanides in only 26 min (11).

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In some instances, collection of numerous fractions could be avoided by pre-determining the volume of column effluent that contained all of a desired sample ion. Then metal ions in the fraction could be quickly titrated with EDTA. Using this technique, cadmium II and zinc II were separated (12). Several metal ions could be eluted selectively from a cation-exchange column with dilute HF (13).

The Birth of Modern Ion Chromatography

A 1975 paper by Small, Stevens, and Bauman (14) working at Dow Chemical described "A novel ion exchange chromatographic method using conductometric detection." The authors noted that the conductivity from the species of interest is generally "swamped out" by that from the much more abundant eluting electrolyte. "This detection problem was solved by using a combination of resins which strips out the ions of the background electrolyte leaving only the species of interest as the major conducting species in the effluent."

An instrument based on this new technology was made available commercially by the newly organized Dionex (Sunnyvale, CA). The newfound ability to quickly separate and quantify complex mixtures of anions and alkali metal cations at low concentrations was an instant sensation. The powerful analytical technique facilitated scientific endeavors that were previously impractical, and its use expanded rapidly.

The success of Small, Bauman, and Stevens was due in a large part to their development of new ion-exchange resins of lower capacity. Based on the fact that sulfonation of polymeric gel beads proceeds from the outside in, low-capacity, surface sulfonated resins were prepared that were suitable for cation separations. Relatively low concentrations of an acidic eluent were used to separate alkali and alkaline earth metals.

Then some very clever chemistry was used to prepare anion-exchange resins. Their experience with ion-exchange resins showed that the positive charge on anion-exchange resins and the negative charge on cation-exchange materials caused a mixture of the resins to clump together. Using static charge, the surface-sulfonated beads were coated with a small thin-layer latex anion-exchange particles. This phenomenon was used to prepare an efficient column packing for chromatographic separation of anions.

Both Dionex cation- and anion-exchange analytical columns contained resins that were significantly lower exchange capacity than the older ion exchangers. For example, a carbonate-bicarbonate eluent of approximately 2.9 mM was commonly used for the separation of anions. Eluents of at least 100 mM and often much higher concentrations was required with columns packed with the earlier high-capacity ion exchangers. These ion exchangers had a significantly lower capacity than the conventional resins of that time.

The invention of suppressed ion chromatography has been one of the truly great developments in modern chemical analysis. The ability to rapidly determine low concentrations of anions and cations has permitted new lines of scientific investigations that were previously not feasible. However, the original ion chromatography system required the use of a bulky sup-

pressor column filled with a high-capacity ion exchanger. Frequent (often twice a day) regeneration of this suppressor column was needed. In addition, the extent of depletion of the suppressor affected the sample peak areas and therefore the quantitative results.

Working at Iowa State University, Gjerde, Fritz, and Schmuckler proposed a new method for a rapid separation of anions with on-line conductivity detection (15).

Subsequent papers described the separation of cations and covered the principles in greater detail (16,17).

The new method was called single-column ion chromatography (and later non-suppressed ion chromatography) because the separation chromatographic column connected directly to a conductivity detector. Through proper choice of column and eluent, no suppressor column or other suppression device was needed.

A non-suppressed ion chromatographic system was basically simpler than a suppressor ion chromatographic system. Later, it was found that either direct or indirect detection was possible. Direct detection non-suppressed ion chromatography was generally less sensitive than suppressed ion chromatography, although it was found to be adequate in many applications. Indirect detection non-suppressed ion chromatography for alkali metal cations was generally found to be more sensitive.

Scientific papers describe the final results of a scientific investigation but generally say little, if anything, regarding the inside story of how the investigation and discovery occurred. This paper is a personal account of the events that led to the discovery and early development of non-suppressed ion chromatography.

Setting the Stage for Discovery

Professor James Fritz arrived at Iowa State University as Assistant Professor in 1951. Initially, his major area of research was acid-base titrations in nonaqueous solvents. Several papers and a book were published on the subject, and the work found use in academic and industrial chemistry settings. Significant developments in chromatography don't just happen; they often occur after a series of seemingly unrelated preliminary events. The first step in the process was "a new direction for research" for Fritz.

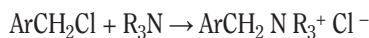
Jim Fritz relates: "Although my research on acid-base titrations in nonaqueous solvents was very successful and popular, my association with the Ames Laboratory of the U.S. Department of Energy required some effort in another area. After a few years, I was asked to undertake a project on separation of metal ion isotopes by ion-exchange chromatography. Although our goal was not attained, I learned a lot and became fascinated by the possibilities of ion exchange.

I learned about a series of new 'macroreticular' polystyrene and polyacrylate XAD resins from Rohm & Haas, Inc. The resins were porous and stable with a high surface area of around 300 m²/g and showed promise for extraction of organic solutes from aqueous solutions. I obtained samples from the company and found that a column packed with XAD particles effectively extracted phenol from water.

Two physical chemists at Iowa State (who wanted to do some “relevant” research) planned to identify trace organic pollutants in wells used for drinking water. They planned to separate and identify the pollutants by the using then-new technique of gas chromatography–mass spectrometry, but the pollutant concentration was too low. My group devised a successful concentration procedure that involved passing a 150-L water sample through an XAD column, followed by elution of the retained organics with ethyl ether and evaporating most of the ether. Over the next few years a large combined group identified for the first time many pollutants in water from a wide geographical area (18). This information enabled the sources of pollution to be located. This joint effort was a vivid demonstration of the value of collaboration.”

Although the XAD resins were neutral, it was postulated that selectivity could be improved for some of the pollutants by converting the resins to either cation exchangers or anion exchangers. The idea was to retain the adsorption power of the neutral aspect of the resins while imparting additional charge to the resins to enhance the ability to capture pollutants that had acidic or basic characteristics.

It was found that XAD resins could be easily derivatized to form ion exchangers. Cation exchangers of varying exchange capacity were produced by sulfonation with sulfuric acid for different time periods under mild conditions. The capacity of anion exchangers could be varied by chloromethylation using different temperatures and reaction times. Then the chloromethylated materials were converted into ion exchangers by reaction with a tertiary amine, usually trimethylamine:



Acidic pollutants were taken up by anion exchangers, and basic pollutants were taken up by cation exchangers.

The work with ion exchangers led to a study by Fritz and Story (19) on the effect of cation-exchange resin capacity on retention of ions in ion-exchange chromatography.

Later Gjerde and Fritz (20) studied the effect of anion-exchange capacity on anion retention. The adjusted retention times of several anions were shown to be approximately linear functions of resin exchange capacity (Figure 1). The slope of each plot is an indication of the ion's affinity for the resin.

Jim Fritz relates: “The work resulted in a better understanding on how ion-exchange resins work. The results demonstrated that resin capacity, as well as eluent concentration, is a useful parameter for adjusting ion retention times to a convenient range. Interestingly, we found that the selectivity coefficient of the sample versus the eluent remained more or less constant and independent of ion-exchange capacity. This allowed us to develop some interesting mathematical equations that predicted ion-exchange retention.”

Extrapolation of the plots to an adjusted retention time of zero occurs at a low but finite resin capacity. This implies that a resin must have a certain minimum

exchange capacity to function effectively. Resin capacity can also be used to control retention crossovers of monovalent and divalent sample ions. Retention crossovers are the point where a pair of anions reverses their relative elution times. Generally, lowering the capacity of an ion exchange column will reduce the retention of divalent ions faster than monovalent sample ions. Thus, there is a point at which a column of a certain resin capacity will cause a divalent anion (e.g., sulfate) to elute before monovalent anions (e.g., nitrate). But keeping everything else constant, a higher capacity column will cause the divalent anion to elute after the monovalent anion. Similar effects of crossovers can be obtained when using divalent eluent ions versus monovalent eluent ions.

The equilibrium equation for ion exchange was used to derive a new equation relating column capacity and eluent concentration to the column retention of monovalent and divalent sample ions. These key points can be summarized by the following equation:

$$\log t' = \log C - \log E + \log K \quad \text{Eq. 1}$$

where t' is the adjusted retention time of the sample ion eluting from the column, C is the resin ion exchange capacity, E is the eluent concentration, and K is the selectivity coefficient of the sample ion over the eluent ion.

Several useful resins were discovered that produced useful separations. In particular, it was found that low capacity cation resins (19) and low capacity anion-exchange resins (21) could be used to separate a variety of metals and metal complexes under relatively mild eluent conditions.

Shortly after the development of suppressed ion chromatography, our group was offered the loan of a Dionex Model 10 ion

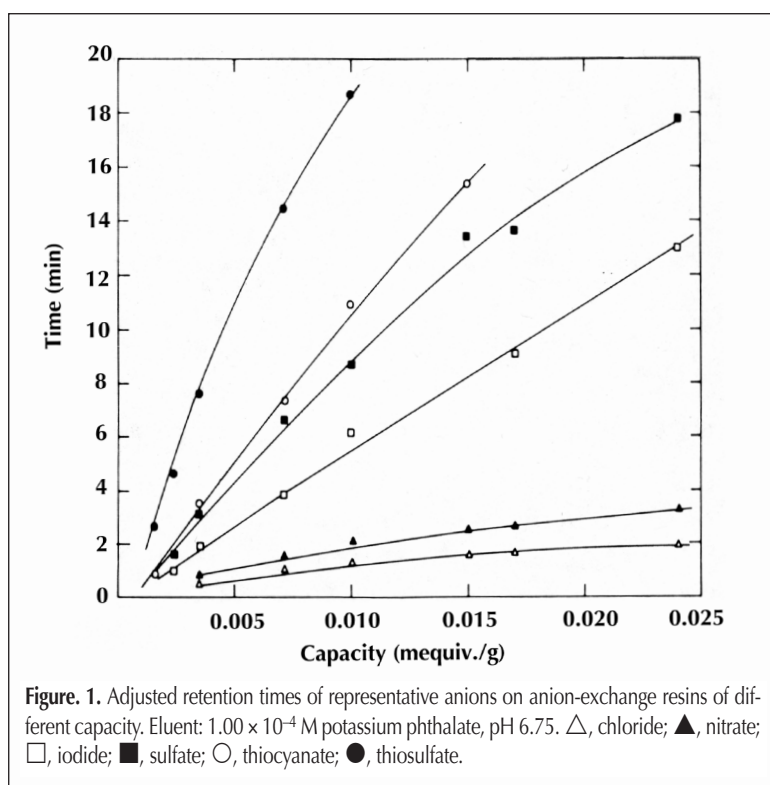


Figure 1. Adjusted retention times of representative anions on anion-exchange resins of different capacity. Eluent: 1.00×10^{-4} M potassium phthalate, pH 6.75. Δ , chloride; \blacktriangle , nitrate; \square , iodide; \blacksquare , sulfate; \circ , thiocyanate; \bullet , thiosulfate.

chromatograph to use for our research. We marveled at the ability of the new instrument to rapidly measure seven common anions in a matter of minutes. Bob Bachman's analytical service group at Ames Laboratory was also extremely interested in our research as a way to replace lengthy gravimetric methods for the routine determination of sulfate in metallurgical samples. But after opening the door panel and looking behind the columns, we also marveled at the array of spaghetti tubing that was used to accomplish the task. Adding a suppressor column to a chromatographic system seemed to add many meters of extra tubing.

Our first trials of the new instrument were performed with a low-capacity XAD-1 anion-exchange column (that we had made in our earlier anion-exchange capacity study.) This column replaced the analytical column in the Dionex instrument. After a little work, several anions were successfully separated on this instrument using the identical carbonate-bicarbonate eluent type and concentration recommended by Dionex. The selectivity was very similar to the Dionex column, but there were some differences, including the elution of fluoride away from the water dip. A few months later that year, Bill Rich, the Vice President of Marketing for Dionex, showed up for a visit to see how we were doing. When our results were shown to him, he remarked: "If you only knew how long it took us to get a separation this good." The final stage was set.

The Catalyst

In 1978 Professor Gabriella Schmuckler from Technion in Israel spent a year-long sabbatical with our research group at Iowa State. When she arrived, she made a tour with each graduate student giving presentation of his or her work. Schmuckler was shown the Dionex Model 10 ion chromatography and the next XAD-1 column that we had developed. She was quite curious about the flow paths and plumbing of the instrument, which was actually quite involved and had a huge dead volume by HPLC standards. This tubing was necessary because after 4 or 5 h of use, the system suppressor column was exhausted; the suppressor column could then be regenerated with the switching of valves in order to engage a separate and acid solution regenerate.

Finally, at the end of her first week with the group, Schmuckler gave a presentation to our entire research group where she described her work on the chromatographic separation of noble metal complex ions. She described using an eluent containing polyelectrolyte with conductivity detection. At the conclusion of the talk, she suggested the possibility of a new system of ion chromatography with a conductivity detector but no suppressor column, perhaps using a low conducting poly electrolyte eluent.

Jim Fritz relates: "We didn't think a polyelectrolyte eluent would work with anion exchange chromatography. Nevertheless, this idea excited me and my graduate student, Doug Gjerde. We designed some experiments using a dodecyl alkyl sulfate surfactant as the proposed eluent and the ion chromatography column developed in the capacity study. We were concerned about pumping a 'sudsy liquid' with the Model 10 ion chromatograph,

but being careful not to agitate the surfactant aqueous solution we were able to pump the liquid, condition the column, and get the conductivity detector to settle down. However, our experiments gave no separation of chloride and sulfate on our XAD 1 low capacity anion-exchange column. In fact, it appeared that nothing was retained on the column; only one large peak was obtained where the void volume eluted."

Experiments at a lower concentration of surfactant gave exactly the same result. Plumbing the suppressor back in line gave exactly the same result: just one huge peak eluting with the void volume. It was concluded that the column was poisoned by adsorption of the bulky surfactant anion by the resin. This poisoning was preventing uptake of the sample anions such as chloride and sulfate because they could not displace the surfactant anion from the column anion exchange sites. The selectivity of the surfactant anion for the column was just too high.

The Discovery

Doug Gjerde relates: "OK, I needed something that was large and bulky so that the background conductivity would be low. But it couldn't be too big – I didn't want to poison the column. I looked around the lab and spotted a bottle of potassium acid phthalate (KHP) and thought well, the phthalate anion is much bigger than chloride and sulfate so the conductance is lower. And also it is much smaller than a dodecyl alkyl sulfate anion so it shouldn't poison the column. I might as well give it a try. I guessed at 1×10^{-4} M as the concentration needed. Using a fresh XAD-1 anion-exchange column, I pumped the Dionex system until the conductivity detector settled down and then injected a

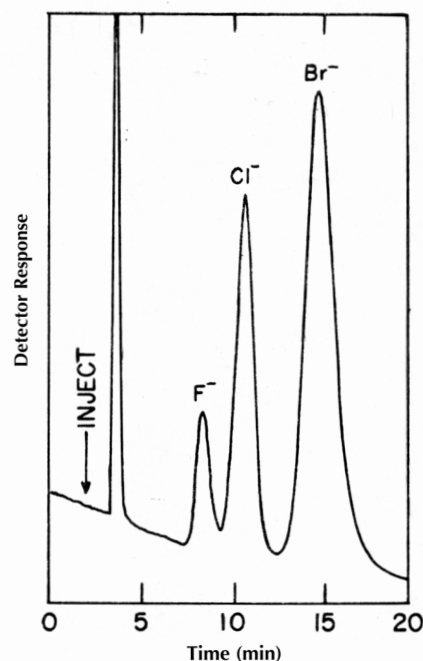


Figure 2. Separation of 4.8 ppm fluoride, 5.1 ppm chloride, and 26.0 ppm bromide. Resin: XAD-1 0.04 mequiv/g; eluent: 6.5×10^{-4} M potassium benzoate, pH 4.6.

tap water sample containing several inorganic anions within 10–15 min. I got a beautiful chromatogram. I was elated. By this time it was around midnight, so I shut down and went home. But I didn't get much sleep that night. As soon as I got home, I felt that I must not have by-passed the suppressor column. When morning came, I rushed to work and traced all of the plumbing. The suppressor was indeed by-passed as it had been last night. I made an injection of tap water and got another nice chromatogram. We had discovered single-column ion chromatography."

Our first paper entitled "Anion chromatography with low-conductivity eluents" was published in 1979 (15) with a follow-up paper in 1980 (17). An example chromatogram is shown in Figure 2, where fluoride is well-separated from the injection peak followed by chloride and bromide. In another example, Figure 3 shows several runs with increasing concentrations of sulfate with fixed concentrations of chloride and nitrate demonstrate the quantitative separation of 2.8–13.8 ppm sulfate. The separations were fast and had good detection sensitivity.

Increasing the Sensitivity of Separations

A significant improvement in the detection limit is obtained by lowering both resin capacity (C) and eluent concentration (E) approximately ten-fold. This is because a more sensitive setting of the conductivity detector can be used. However, the amount of sample must be reduced to avoid column overloading. Figure 4 shows the separation of 0.78 ppm chloride, 3.0 ppm iodide, 2.9 ppm thiocyanate, and 1.7 ppm sulfate. Conditions: C = 0.007 meq/g, E = 0.007 mM phthalate at pH 6.3.

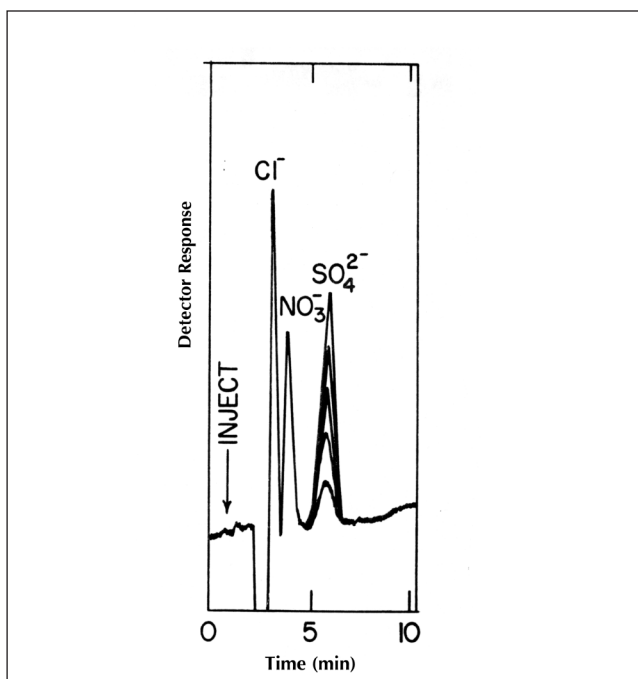


Figure 3. Separation of standard solutions of sulfate ranging in concentration of 2.75 ppm to 13.75 ppm in samples containing chloride and nitrate anions. Resin: XAD-1 0.04 mequiv./g; eluent: 5×10^{-4} M potassium phthalate, pH 6.2.

Another method of increasing sensitivity is to use a pre-concentration column in place of the injection valve sample loop (22). The maintenance of steam quality in power plants requires keeping the water clean from ions. Small amounts of anions such as chloride and sulfate can result in stress corrosion cracking of turbine blades. Ion chromatography provides a simple means of monitoring anions that cause corrosion at the low ppb concentration range. However, very low anion concentrations in very pure water samples require a pre-concentration step.

Anions in extremely dilute water samples are concentrated simply and effectively using a small anion-exchange column positioned on a sampling valve in the same way as a sample loop. With the valve in the load position, the sample water is pumped through the concentrator column. Sample anions displace the eluent anions and are captured on the concentrator column. After sample anions are collected, the sample valve is switched to the inject position, placing the concentration column in the eluent stream. The flow through the concentrator is reversed so that it is eluted directly from concentrator onto the separation column. At this point, the anion separation process proceeds as normal. Samples of condensed steam from the ISU power plant and from the Modderfontain factory in South Africa were found to contain 1 to 15 ppb sulfate and < 1 to 140 ppb chloride.

Prediction of Detector Response

By 1980, Schmuckler had left to resume her work at the Technion. The group had worked very hard on anion separation and had produced several applications. Around this time, we

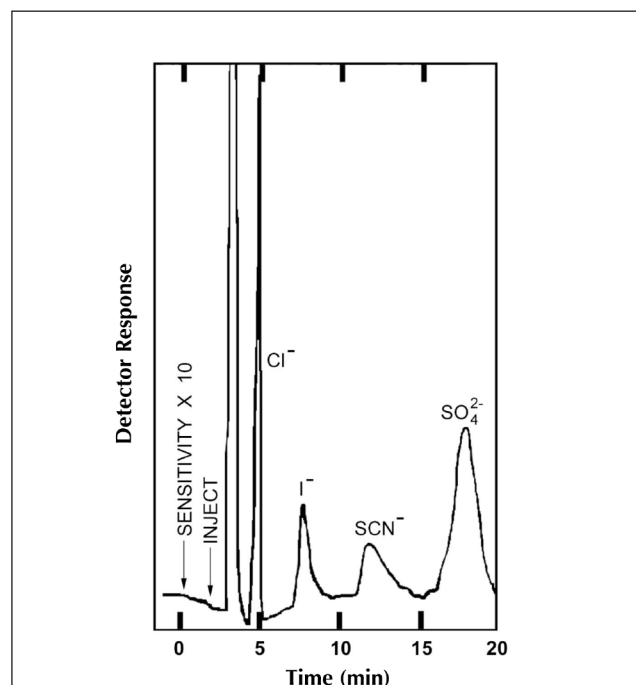


Figure 4. Separation of 0.77 ppm chloride, 2.95 ppm iodide, 2.85 ppm thiocyanate, and 1.65 ppm sulfate. Resin: XAD-1 0.007 mequiv./g; eluent: 5×10^{-5} M potassium phthalate, pH 6.25.

wondered if a non-suppressed ion chromatography system analogous to anion separations could be developed for cation-exchange separations.

A suitable cation-exchange resin was not available (macroporous resins gave too high of capacity), so a new resin had to be synthesized. While searching for a suitable substrate commercial source of gel resin to sulfonate, the authors considered how a single-column cation-exchange system might behave. The equivalent conductance of hydrogen ion is much higher than ammonium, alkali metal, and alkaline earth metal ions. In the anion system we relied on a large, bulky, low-conducting eluent ion. The obvious choice for a cation system was a very conductive hydronium ion. It was thought intuitively that cation-exchange sample peaks with this high conducting eluent would be of decreasing conductivity.

It seemed possible that an equation could be developed to predict detector response. The effect of varying resin capacity and eluent concentration on retention times was discussed earlier. Gjerde relates: "I was intrigued with the possibility of developing a general equation to predict chromatographic retention. My advisor, Jim Fritz, had described in our graduate chromatography course Chem 511 how you could take the general ion exchange equilibrium selectivity coefficient equation, make certain assumptions, and derive a new equation for the effect of resin capacity on eluent concentration or retention times. It was understood that ion exchange is a replacement process. If one anion comes off an ion exchange site, it is replaced by another anion. Once the injection peak clears through the column, the sum of eluent and sample anion concentration remains constant and is equal to the cation (counter ion) concentration."

Further study and derivation showed that the change in conductivity detector response (ΔG) is a function of the difference in

the equivalent conductance of the eluent anion and the sample anion: $\lambda_E - \lambda_S$. The sample cation is displaced (replaced) by the eluent cation (E^+), which is constant throughout a separation. The change in detector response is also proportional to the sample ion concentration (C_S). These factors were brought together to derive the Fritz-Gjerde equation:

$$\Delta G \approx (\lambda_E - \lambda_S) C_S \quad \text{Eq. 2}$$

The change in peak conductance is proportional to the differences in eluent and sample anion equivalent conductance and to sample anion concentration because factors such as the detector cell constant also affect detector response. Also, in some cases the ionic form of weaker acids will be less than one and is affected by the eluent pH.

Using essentially the same reasoning, the same equation should apply to cations as well as anions. The detection signal should be proportional to the difference in equivalent conductivity of the eluent and sample cations. Our plan for cation separation was to use dilute nitric acid as the eluent because the equivalent conductance of H^+ is much higher ($\lambda = 350$) than that of common cations ($\lambda = 50-80$). In this case, sample ion peaks of decreasing conductivity would be expected.

The terminology "direct detection" and "indirect detection" was used to describe the two cases:

$$\text{Direct detection} = \lambda_S > \lambda_E \quad \text{Eq. 3}$$

(Positive peak, as with KHP eluent)

$$\text{Indirection detection} = \lambda_S < \lambda_E \quad \text{Eq. 4}$$

(Negative peak, as with H^+ eluent)

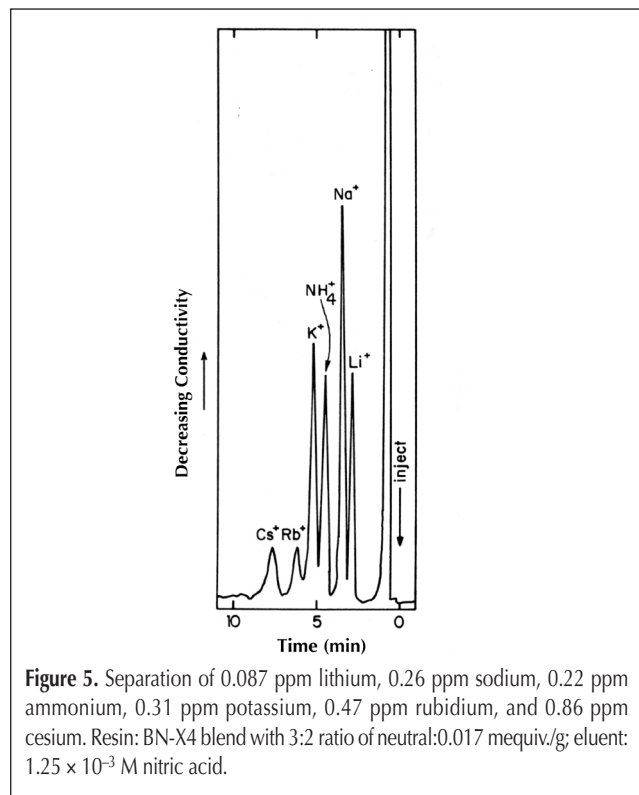
Experiments were performed to confirm the equations. Several separations were performed on a low capacity surface-sulfonated polystyrene gel resin using a dilute nitric acid eluent. Figure 5 shows complete resolution of all of the alkali metal cations plus ammonium < 10 min. The sensitivity obtained was outstanding (1 ppm each) owing to the large difference in equivalent conductances of the H^+ eluent and the sample ions, and as predicted, peaks are a measure of decreasing conductivity (16). The nitric acid eluent did not work well for divalent metal ions, but the alkaline earths metals were well-separated and detected with a divalent eluent, ethylenediammonium nitrate.

A Broader Fritz-Gjerde Equation

The Fritz-Gjerde equation can be written in different forms to be a general predictor of detector response in many types of chromatography (23). Rewriting Eq. 2 for conductivity to a general form becomes:

$$\Delta G_{\text{peak}} = (\text{Const}) (\lambda_S - \lambda_E) C_S \quad \text{Eq. 5}$$

where Const takes into account conversion factors and other



factors. The equation can be extended to UV-Vis detection:

$$\Delta A_{\text{peak}} = (\text{Const}) (\varepsilon_S - \varepsilon_E) C_S \quad \text{Eq. 6}$$

where ε is the absorptivity coefficient. The equation can be extended to Refractive index detection:

$$\Delta RI_{\text{peak}} = (\text{Const}) (RI_S - RI_E) C_S \quad \text{Eq. 7}$$

where RI is refractive index. And finally the equation is made into a general form of the equation (the Fritz Gjerde equation):

$$\text{Signal}_{\text{peak}} = (\text{Const}) (RF_S - RF_E) C_S \quad \text{Eq. 8}$$

in which Signal is the chromatographic peak signal, and RF is the detector response factor for sample and eluent species. The general form of the equation works not only for ion-exchange chromatography but ion pairing chromatography. It turns out that ion pairing is a replacement process so that detection prediction is analogous. This is interesting in its own right because of the many papers that have been published on mechanisms of ion pairing chromatography. Some forms of CE also conform to the detection equation, predicting both positive and negative detection peaks.

A Broader Definition of Ion Chromatography

The original definition of ion chromatography applied specifically to separations with a second suppressor column as used in early Dionex instruments. With the spreading popularity of non-suppressed ion chromatography and other developments, the need for a broader definition became apparent to us. Finally a book by Fritz, Gjerde, and Pohlandt published in 1982 by Heuthig Verlag (24) proposed that the name ion chromatography apply to the “efficient chromatographic separation of anions or cations with any form of automatic detection.”

Expanding the definition was not initially embraced by everyone in the early days. But over the next several years, the tide shifted and many papers by researchers all over the world were published using this new broader definition of ion chromatography. In particular, electrochemical detection and UV detection have found broad use in ion chromatography. Separation mechanism includes ion exchange, ion exclusion, and ion pairing chromatography. Even CE has shown that ion analysis can be done extraordinarily fast and with high sensitivity.

Over the years, books by a number of authors have played an important role in describing advances in the science and practice of ion chromatography (25–29).

Comments on the Discovery Process

We all derive considerable pleasure from solving a scientific problem or finding a better way to do something. Here are some of the ingredients that were found to contribute to the discovery process.

The freedom to experiment also includes freedom to fail without undue consequences. Persistence often pays off. An overly controlling management or sometimes overly controlling “group thinking” can stifle innovation.

A successful discovery doesn’t suddenly happen. A background of experience must be built up. One thing leads to another until, and with the right catalyst and good luck, the invention becomes a reality.

Collaboration is also needed. Collaboration is desirable and sometimes a necessity. Commercial companies can be helpful and sometimes necessary in academic research.

A little luck, if that is what it is called, can come in handy. But luck can be simply the ability to recognize the opportunity presented and to take advantage of it. Too many times new ideas are met with comments such as “dumb” or “someone must have already done that” or some other excuse. These negative attitudes can be discovery killers.

Analytical chemistry can be a demanding mistress. One measure of the quality of academic research is: Did anyone use it after it was published? Did any of the original or resulting publications eventually result in commercial products? A new invention will have only limited use unless the necessary columns and equipment are available commercially. In this case, commercial collaboration is useful in method development and can help eventual commercialization of the technology.

Summary

A suppressor column or other device to reduce background conductance is not essential. Background conductances are kept to a satisfactory level by use of an ion-exchange column of very low exchange capacity and dilute low conductivity eluent. Direct detection of sample ions is feasible when eluent ions are chosen with a significantly lower equivalent conductance from the sample ions. A fundamental equation supporting these principles was derived and verified experimentally. The equation also predicts that higher conducting eluents can be used with peaks eluting with decreasing conductivity peaks.

It is remarkable that the basic principles and practical separations were developed within a relatively short time span, starting with suppressed ion chromatography in 1975 and non-suppressed ion chromatography in 1979. Tremendous improvements in ion chromatography technology have occurred over the years. Today, ion chromatography remains a vibrant and growing analytical technique.

Dedication

The authors dedicate this paper to Professor Gabriella Schmuckler. Her camaraderie, talent, and enthusiasm helped lead us to discovery.

References

1. F.H. Spedding, A.J. Voigt, E.M. Gladrow, J.E. Powell, J.M. Wright, T.A. Butler, and P. Figard. The separation of rare earths by ion exchange. II. Neodymium and Praseodymium. *J. Am. Chem. Soc.* **69**: 2786–2792 (1947).

2. F.H. Spedding, E.I. Fulmer, T.A. Butler, E.M. Gladrow, M. Gobush, P.E. Porter, J.E. Powell, and J.M. Wright. The separation of rare earths by ion exchange. III. Pilot plant scale separations. *J. Am. Chem. Soc.* **69**: 2812–2818 (1947).
3. F.H. Spedding, E.I. Fulmer, B. Ayers, T.A. Butler, J. Powell, A.D. Tevebaugh, and R. Thompson. Improved ion exchange method for separating rare earths in macro quantities. *J. Am. Chem. Soc.* **70**: 1671–1672 (1948).
4. F.H. Spedding, E.I. Fulmer, J.E. Powell, and T.A. Butler. The separation of rare earths by ion exchange. V. Investigations with one-tenth per cent. citric acid-ammonium citrate solutions. *J. Am. Chem. Soc.* **72**: 2354–2361 (1950).
5. F.H. Spedding, J.E. Powell, and H. J. Svec. A laboratory method for separating nitrogen isotopes by ion exchange. *J. Am. Chem. Soc.* **77**: 1393 (1955).
6. F.H. Spedding, J.H. Powell, and H. J. Svec. A laboratory method for separating nitrogen isotopes by ion exchange. *J. Am. Chem. Soc.* **77**: 6125–6132 (1955).
7. J.S. Fritz and B.S. Garralda, and S.K. Karraker. *Anal. Chem.* **33**: 882 (1961).
8. J.S. Fritz and R.G. Greene. *Anal. Chem.* **35**: 811 (1963).
9. J.S. Fritz and J.E. Abbink. *Anal. Chem.* **34**: 1080 (1962).
10. J.N. Story and J. S. Fritz. Forced-flow chromatography of the lanthanides with continuous in-stream detection. *Talanta* **21**: 892–894 (1974).
11. S. Elchuk and R. M. Cassidy. Separation of the Lanthanides on high-efficiency bonded phases and conventional ion-exchange resins. *Anal. Chem.* **51**: 1434–1438 (1979).
12. Y. Yoshino and M. Kojima. Analyses with the aid of ion-exchange resins I. Determination of cadmium in copper and zinc, and of zinc and copper in cadmium. *Bunseki Kagaku* **4**: 311–315 (1955).
13. J.S. Fritz, B.B. Garralda, and S.K. Karraker. Cation exchange separation of metal ions by elution with hydrofluoric acid. *Anal. Chem.* **33**: 882–885 (1961).
14. H. Small, T.S. Stevens, and W.S. Bauman. Novel ion exchange chromatographic method using conductometric detection. *Anal. Chem.* **47**: 1801–1809 (1975).
15. D.T. Gjerde, J.S. Fritz, and G. Schmuckler. Anion chromatography with low-conductivity eluents. *J. Chromatogr.* **186**: 509–519 (1979).
16. J.S. Fritz, D.T. Gjerde, and R.M. Becker. Cation chromatography with a conductivity detector. *Anal. Chem.* **52**: 1519–1522 (1980).
17. D.T. Gjerde, G. Schmuckler, and J.S. Fritz. Anion chromatography with low-conductivity eluents II. *J. Chromatogr.* **187**: 35–45 (1980).
18. G.A. Junk, J.J. Richard, M.D. Grieser, D. Witiak, J.L. Witiak, M.D. Arguello, R. Vick, H.J. Svec, J.S. Fritz, and G.V. Calder. Use of macroreticular resins in the analysis of water for trace organic contaminants. *J. Chromatogr.* **99**: 745–762 (1974).
19. J.S. Fritz and J.N. Story. Chromatographic separation of metal ions on low capacity macroreticular resins. *Anal. Chem.* **46**: 825–829 (1974).
20. D.T. Gjerde and J.S. Fritz. Effect of capacity on the behavior of anion-exchange resins. *J. Chromatogr.* **176**: 199–206 (1979).
21. D.T. Gjerde and J.S. Fritz. Chromatographic separation of metal ions on macroreticular anion exchange resins of a low capacity. *J. Chromatogr.* **188**: 391–399 (1980).
22. K. Roberts, D.T. Gjerde, and J.S. Fritz. Single-column ion chromatography for the determination of chloride and sulfate in steam condensate and boiler feed water. *Anal. Chem.* **53**: 1691–1695 (1980).
23. D.T. Gjerde. Principles of detection in single-column ion chromatography. *Int. J. Environ. Anal. Chem.* **27**: 289–304 (1986).
24. J.S. Fritz and D.T. Gjerde. *Ion Chromatography*, 1st ed., Heuthig Verlag, Heidelberg, New York, 1982.
25. Frank Smith and Richard Chi-Cheng Chang. *Practice of Ion Chromatography*, Wiley, Hoboken, NJ, 1983.
26. Weiss, *Ion Chromatography*, 1st Ed 1984, 2nd Ed 1995, Wiley-VCH.
27. Hamish Small. *Ion Chromatography*, Plenum, New York, NY, 1989.
28. P.R. Haddad and P.E. Jackson. *Ion Chromatography, Principles and Practice*, Elsevier, Amsterdam, Netherlands, 1990.
29. J. Fritz and D. Gjerde. *Ion Chromatography*, 1st Ed. 1982, 2nd Ed. 1987 (Heuthig), 3rd Ed. 2000, 4th Ed. 2009, Wiley-VCH.

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