



Review

Early milestones in the development of ion-exchange
chromatography: a personal account

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Abstract

Ion chromatography as we know it today was built on a foundation of knowledge accumulated over a period of many years. Here, we review some of the outstanding earlier achievements in ion-exchange chromatography. Beginning about 1947, Spedding and Powell at Iowa State published a series of papers describing practical methods for preparative separation of the rare earths by displacement ion-exchange chromatography. The same group then demonstrated the ion-exchange separation of ^{14}N and ^{15}N isotopes in ammonia. Beginning in the 1950s, Kraus and Nelson at Oak Ridge published numerous analytical methods for metal ions based on separation of their chloride, fluoride, nitrate or sulfate complexes by anion chromatography. In the period from about 1960 to 1980 many clever chromatographic methods for metal ion separations were reported by researchers throughout the world and automatic in-line detection was gradually introduced. A truly innovative method by Small, Stevens and Bauman at Dow Chemical Co. marked the birth of modern ion chromatography. Anions, as well as cations, could now be separated quickly and conveniently by a system of suppressed conductivity detection. A method for anion chromatography with non-suppressed conductivity detection was published by Gjerde et al. in 1979. This was followed by a similar method for cation chromatography in 1980. Ion chromatography as we know it today did not just happen. It was built on a solid foundation of knowledge that has accumulated over a period of many years. Revisiting the older ion-exchange chromatography serves not only to pay tribute to some remarkable accomplishments, but it can also be a learning experience. Trends and ideas in science tend to run in repeating cycles. Thus, an awareness of older work may provide inspiration for new research using improved contemporary technology. Selection of milestones is a rather personal matter. I chose to write about subjects of which I came to have a firsthand knowledge during my career. The topics selected are in roughly chronological order and cover the period from about 1945 to 1980. An effort has been made to explain the chemical principles as well as to recount the major accomplishments of the various research projects.

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1. Separation of rare earths by displacement chromatography

The lanthanide elements, or the rare earths as they are commonly called, have very similar chemical properties in solution. In the mid-1940s even incomplete separation of individual rare earths could be accomplished only by a laborious series of fractionations. But in a series of publications beginning in 1947 Spedding and coworkers working at the Institute for Atomic Research at Ames, Iowa, described methods for separation of the rare earths by ion-exchange chromatography [1–4]. Not only were all of the rare earths separated from one another, but the quantities separated were substantial.

Today, the large bulk of ion-exchange separations are performed on an analytical scale by elution ion-exchange chromatography, which is commonly called ion chromatography. In this method a column filled with a cation-exchange resin is used to separate sample cations and a column containing an anion-exchange material is used to separate anions. The column is first equilibrated by pumping the eluent through. The eluent contains ions of a type and concentration to push sample ions through the column at different rates and thus be separated from one another. A detector is needed that will distinguish sample ions from the background ions in the eluent. Sample volume is generally small (10–25 μl is typical). Sharp peaks for sample ions are obtained at various points along the baseline.

A less common type of chromatography called displacement chromatography was developed by Spedding and Powell for the separation of rare earth ions. This type of chromatography is used for larger scale (preparative) separations. The column used has a high ion-exchange capacity. The column is not pre-equilibrated with eluent as in elution chromatography. Conditions must be selected so that:

- (1) The eluent ions are taken up much more strongly than the sample ions. The eluent may be thought of as a chemical piston that pushes sample ions along the column. Thus, there is a sharp boundary between the eluent and the top edge of the sample zone.
- (2) Movement of the lower (leading) edge of the sample zone is strongly constrained by a strong interaction of the sample ions with the ion exchanger so that a sharp lower boundary is formed.

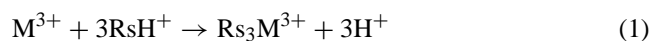
Separations by displacement chromatography require two steps.

- (i) *Loading*. A relatively large volume of sample solution is added to the column, forming a zone of mixed sample ions that extends for some distance along the column.
- (ii) *Displacement elution*. The eluent ion continuously displaces sample ions from exchange sites at the upper (back) edge of the sample zone. The displaced ions pass through the entire sample zone and are then set down at the lower (leading edge) boundary between the sample

zone and the rest of the ion-exchange column. By this process the entire sample zone moves along the column keeping its original volume. Continuous equilibration occurs between the displaced sample ions and the sample ions attached to exchange sites during the displacement elution process. After the sample zone has moved a sufficient distance along the column, a true equilibrium is reached in which the sample components are resolved into distinct zones containing the separated ions. Each pure sample ion fraction can then be collected as it is eluted from the column.

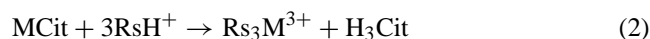
Displacement chromatography takes full use of the high exchange capacity of the ion-exchange resins and it uses a much lower volume of eluting solution than a preparative separation by elution chromatography. There is of course a small volume of eluate collected at the interface between the resolved sample ion zones that contains a mixture of the two ions. Careful column packing is needed so that the interfaces between sample ion zones on the column will be flat and not tilted.

In the original work by Spedding and coworkers a column packed with a sulfonated resin ion exchanger was used. A sample of mixed rare earth ions (M^{3+}) was added to the column. The sample ions were taken up as a compact zone 10 in. or more in length.



The acid was then washed from the column with distilled water.

A 0.1% solution of citric acid/ammonium citrate was used for the elution step. It was found necessary to also make the eluent 0.2% in phenol in order to prevent the growth of mold. The citrate complexed the rare earths at the upper edge of the sample ion zone and replaced the ion-exchange sites with an equivalent amount of ammonium cations, and possibly some H^+ . The citrate complexes of the mixed rare earths passed through the entire rare earth zone of the column and then reacted with the concentrated hydrogen ion section of the ion exchanger at the lower interface of the rare earth zone.



The entire rare earth zone moved down the column in this manner but the length of the zone remained essentially constant because of the chemical constraints at both the upper and lower boundaries of the zone. During the elution the individual rare earths are gradually arranged within the sample zone in the order of their complexation by citrate, with the more strongly complexed rare earths migrating faster. When a sufficient length of column has been traversed, an equilibrium is attained in which the individual rare earths are separated into sharp bands along the column. Fig. 1 shows the resolution obtained for a mixture of samarium(III), neodymium(III) and praseodymium(III) as a function of column length.

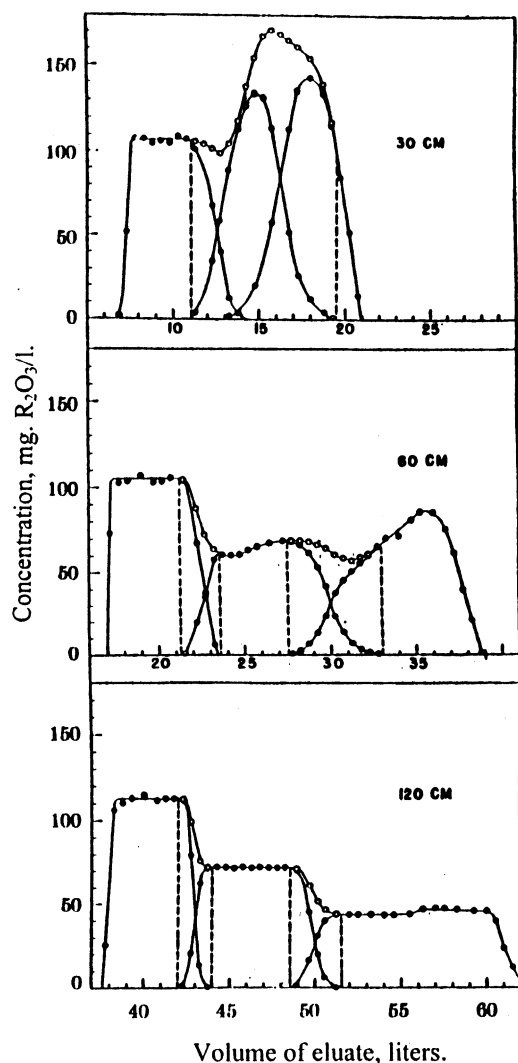


Fig. 1. Elution of mixtures of Sm^{3+} , Nd^{3+} and Pr^{3+} from Amberlite IR-100 beds, 22 mm in diameter and 30, 60 and 120 cm long with 0.1% citrate solution, pH 5.30. The open circles represent total rare earth (from [4] with permission).

In 1954, Spedding and Powell [5] published a detailed quantitative of the mechanism involved in elution of rare earths by dilute citrate solutions. They derived detailed equations to account for the effects of variables on the separation and came to the following conclusion:

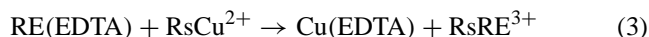
“It will be noted that once the ammonia in the eluant is fixed, all variables in the equilibrium eluate and on the column are determined for each individual rare earth present. As the equilibrium constants of the complexes change from rare earth to rare earth, the citrate concentration in the eluate changes. This means that the rare earths must separate into bands on the resin bed, each band having a specific citrate concentration, hydrogen-ion concentration and ionic strength associated with it. As a result of this, the bands develop autosharpening boundaries, and one band rides immediately on the tail of the preceding

band. If an ion of a given rare earth species gets ahead of or behind its own band for any reason, it will be subjected to an adverse citrate concentration and will either be accelerated or retarded in its movement down the column, so that it returns to its own band”.

During the Manhattan Project in the 1940s there was an urgent need to furnish pure rare earths to other members of the project. A pilot plant operation was set up in which rare earths were separated on a total of 24 columns connected in series. Each column was a Pyrex pipe 10 ft (308 cm) long and 4 in. (10.3 cm) in diameter [2]. Later, separations were performed on an even larger scale. Fig. 2 is a photo of the columns and equipment used in the separation of rare earths. In the original color photo separated rare earth bands of different pastel colors can be seen in the column at the right.

The relatively larger differences between the formation constants of adjacent rare earth complexes make EDTA attractive as an eluting agent. It was not feasible to use H^+ as a retaining ion because of the low solubility of the acidic forms of EDTA in water. However, converting the ion-exchange column to the Cu^{2+} form with subsequent elution by diammoniumdihydrogen-ethylenediamine tetraacetate (ammonium EDTA) was found to give excellent separations [6]. In the loading step the 3+ rare cations strongly displace 2+ cupric ions from the exchanger.

During the elution step the Cu^{2+} on the ion exchanger retains rare earth ions efficiently at the lower end of the sample bed according to the following reaction:



This equilibrium in this reaction lies well to the right because the copper-EDTA complexes are stronger than the rare earth-EDTA complexes, and also because the ion exchanger has a greater affinity for the Re^{3+} than for the Cu^{2+} . The rare earths were eluted by this method in descending order of their atomic numbers: lutetium first and lanthanum last. The separations achieved were considerably better than those obtained by eluting far greater distances with citrate as the eluent. Owing to its greater solubility in acidic solution, the ammonium salt of *N*-hydroxyethyl-ethylenediamine triacetic acid (HEDTA) was also used successfully for separations with H^+ as the restraining ion.

Ion exchange separations at Iowa State were carried out on a very large scale. For example, a substantial amount of yttrium was isolated from xenotime. When columns 30 in. (77 cm) in diameter were loaded with concentrate from 1000 lb (1 lb = 0.4536 kg) of ore, the absorbed band was 36 ft (11.1 m) long and the resolved band of yttrium was approximately 27 ft (8.3 m) in length. Years later, after production had been shut down, a considerable supply of pure rare earth oxides was stored in Mason fruit jars at Iowa State.

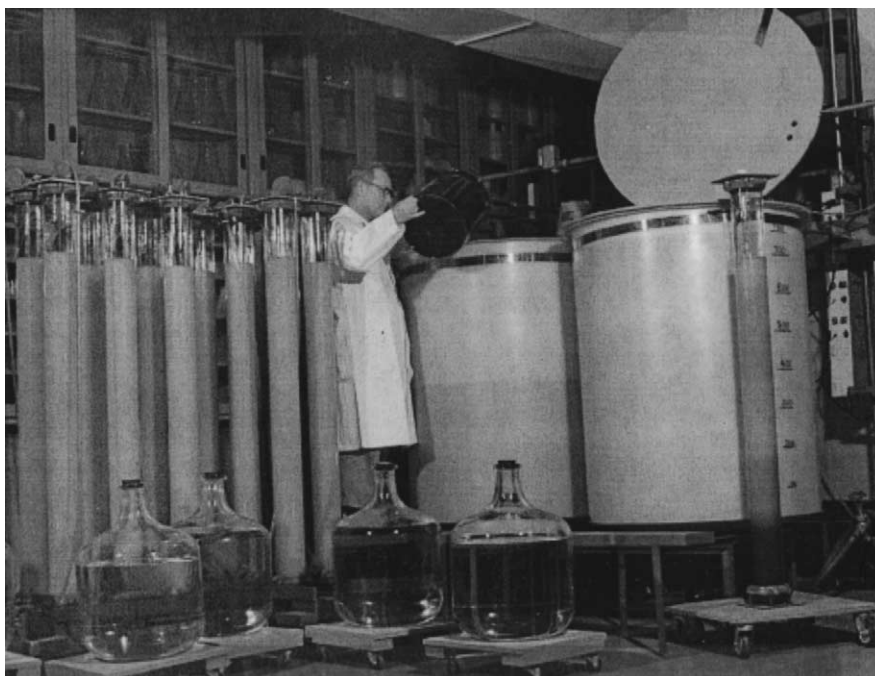


Fig. 2. Equipment used for ion-exchange separation of rare earths.

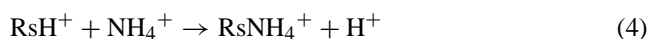
2. Separation of nitrogen isotopes in ammonia

The remarkable success achieved in separating adjacent rare earths in high purity suggested that isotopes might also be separated by a similar procedure. It was hoped that the slight differences in the exchange constants of various isotopes of an element might also cause the isotopes to be resolved into distinct zones within a chemically constrained band if the elution step was carried out under proper conditions. While the chemical constraints at the ends of a band cause the over-all band to attain equilibrium in a short distance of travel, the much smaller exchange constants of the isotopes would require that the band travel a much greater distance before complete isotopic equilibrium would be approached. In 1955, Spedding et al. did succeed in using nitrogen in the form of ammonium hydroxide (aqueous ammonia) to separate ^{15}N from ^{14}N [7].

To separate nitrogen isotopes the resin beds are first converted to the hydrogen cycle by passing a dilute mineral acid through the columns until the beds are saturated. The beds are then rinsed with water and a dilute solution of ammonium hydroxide is added until a band of ammonium ion of the desired length is obtained. When Dowex-50 resin is in the ammonium state it exhibits a somewhat different shade of brown than it does in the hydrogen cycle or the sodium cycle, so that the boundaries of the ammonium band can be seen distinctly.

If a boundary is to remain sharp, a chemical reaction which goes virtually to the completion must take place at the boundary. If ammonium ion from a salt solution such as ammonium chloride reacts with hydrogen resin the boundary

will not be very sharp, because the:



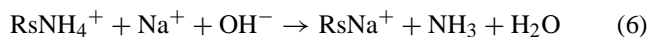
reaction has only a small equilibrium constant and therefore does not produce a sharp boundary at the upper edge of the loaded sample zone. However, when aqueous ammonia is loaded onto the ion-exchange column in the H^+ form, the reaction is:



For this reaction the equilibrium constant has a value on the order of 10^9 . Here the equilibrium is far to the right, resulting in an extremely sharp boundary.

It might be mentioned that considerable heat is liberated at the boundary by the above reaction and this limits the concentration of NH_4OH which can be used conveniently.

The adsorbed ammonium band is driven down the column with an eluting solution of sodium hydroxide. Here the reaction is:



This reaction also has a large equilibrium constant of about 10^5 and again a sharp boundary is produced.

The length of the adsorbed ammonium band is determined primarily by the amount of ammonia loaded onto the column and by the exchange capacity of the resin. Once the concentration of the sodium hydroxide eluent has been chosen, the length of the ammonium band remains constant as it is eluted down the resin bed.

If the aqueous ammonia solution in the pores of the resin bed is maintained for a sufficient time in contact with a

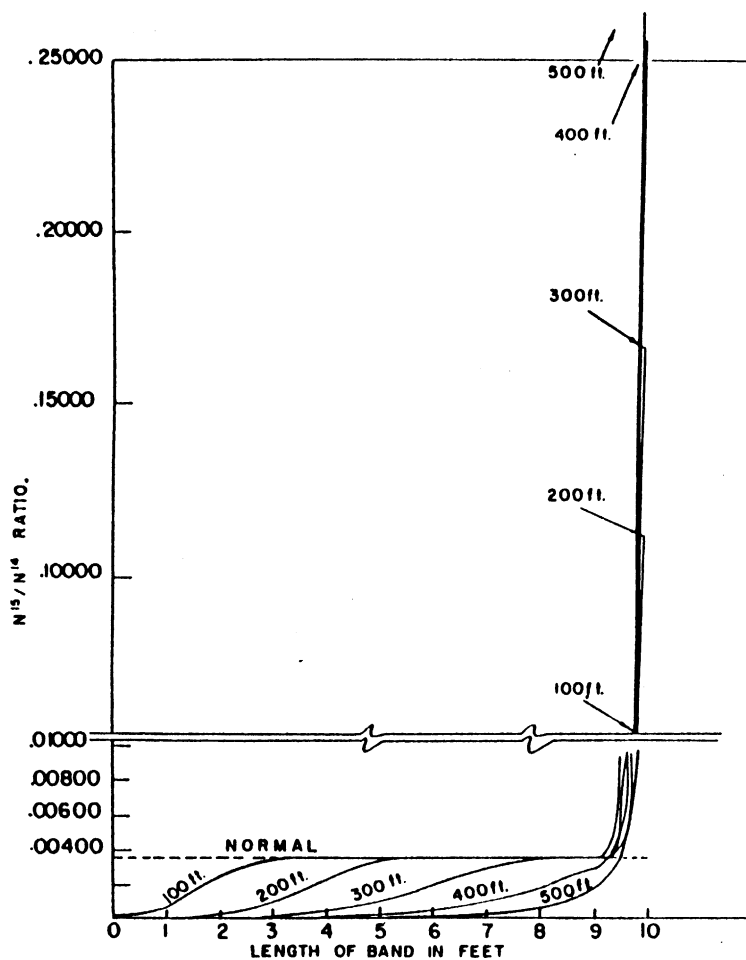
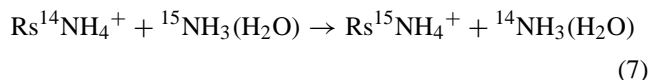


Fig. 3. Isotopic profiles of an adsorbed ammonium band after various distances of elution. The plateau region is magnified for greater clarity (from [7] with permission).

particular section of resin bed, the system will attain isotopic equilibrium according to the reaction.



The equilibrium constant for this reaction is 1.0257, which indicates that the ${}^{14}\text{N}$ isotope of ammonia will move down the column at a slightly greater rate than the ${}^{15}\text{N}$ form.

If the length of the ammonium band remains constant as the band is eluted down the resin bed, each time an equivalent of sodium ion is deposited at the rear edge of the band it displaces an equivalent of ammonium ion. The displaced ammonium ion comes to chemical equilibrium within the system very rapidly and isotopic equilibrium tends to be approached as the solution passes over the resin. When the ammonia in solution reaches the front edge of the ammonium band it is redeposited as ammonium ion in the resin bed. At all times, the ratio of ${}^{15}\text{N}$ to ${}^{14}\text{N}$ on the resin is greater than it is in the solution contacting it.

Fig. 3 shows a plot of how the isotopic ratio of ${}^{15}\text{N}/{}^{14}\text{N}$ varies across the band with different distances of travel. It

can be seen that the maximum isotope enrichment or depletion occurs at the ends of the band. In the plateau region the isotopic ratios in the resin phase and solution phase do not change, although they differ from each other by a small amount. Since the solution flowing past the resin in the plateau region is carrying ammonia richer in ${}^{14}\text{N}$ and leaner in ${}^{15}\text{N}$ than the resin it contacts, there is a net transfer of ${}^{14}\text{N}$ toward the leading edge of the band. If the plateau region is sufficiently long that isotopic equilibrium is attained within this region, the net transfer of ${}^{14}\text{N}$ per equivalent of ammonia passed over the plateau and redeposited is the same irrespective of the degree of equilibrium reached in the rest of band.

As the ammonia band is eluted along the series of ion-exchange columns connected in series, the plateau region in Fig. 3 gradually diminishes and virtually all of the ${}^{15}\text{N}$ is deposited at the back end of the band. In the work reported in 1955 [7] a 10 ft (3.08 m) long band was adsorbed onto a series of 10 columns connected in series, each column 58 in. (1.49 m) long and 4 in. (0.10 m) in diameter. It was necessary to move the ammonia band eight times along this series of ten columns filled with 100–200 mesh

Dowex-50 X12 resin in order to obtain a mole ratio of 0.20 for $^{15}\text{N}:^{14}\text{N}$ in the final eluate. By recycling the enriched ammonia a material containing >99% ^{15}N could be obtained. Unlike the ion-exchange separation of rare earths which was widely publicized, the large-scale separation of $^{15}\text{NH}_3$ by ion-exchange (approximately 1 kg of 99.7% $^{15}\text{NH}_3$ was eventually produced) was a tremendous accomplishment that has not received the recognition it deserves.

3. Separation of metal ions by anion- and cation-exchange chromatography

Since most metal ions are cationic, it may sound strange to discuss their separation by anion-exchange chromatography. However, in aqueous solutions containing a fairly high concentration of hydrochloric acid, many metal cations form anionic chloride complexes that are strongly taken up by anion-exchange column. Practical analytical separations are possible by stepwise elution with progressively lower concentrations of HCl. For example, cobalt(II) and iron(III) are strongly retained from 9 M HCl by an anion-exchange column as anionic complexes, CoCl_4^{2-} and FeCl_4^- . Nickel(II) does not form a chloride complex and passes quantitatively through the column. Cobalt(II) is then eluted from the column with 5 M HCl while iron(III) remains complexed. Finally, iron(III) is eluted by water alone.

The discovery of separations of this type by Kraus and Nelson at Oak Ridge (now ORNL) was an important milestone in chromatography. The extensive scope of their research is illustrated by a periodic table of the elements published in 1956 [8] in which the log of each distribu-

tion coefficient, D , on an anion-exchanger is plotted as a function of the HCl concentration of the solution (Fig. 4). A value for $\log D$ of 1–2 is needed for an element to be retained on the anion-exchange column.

Continuing studies at Oak Ridge demonstrated that a number of elements can also be taken up and separated as their anionic fluoride, bromide, nitrate or sulfate complexes. The extent of this work is illustrated by the publication entitled “anion-exchange studies XXVII” [9]. In this paper distribution coefficients were measured on Dowex 1 resin [10% divinylbenzene (DVB), 170–220 mesh] from aqueous solutions of 1 M HF and variable concentrations of HCl. Then a number of illustrative separations were shown. Thus, a mixture of arsenic, antimony and tin was separated by stepwise elution: As with 3 M HCl, Sb with 0.3 M HCl + 1 M HF, Bi with 1 M NH_4Cl + 1 M NH_4F . The chromatographic peaks were plotted manually after collecting and analyzing numerous fractions of the eluate. Radioactive tracers were used extensively to facilitate the analysis process.

Shortly after development of methods for separation of metal ions by the group at Oak Ridge, interest in the cation chromatography of metal ions began to pick up. Fritz and Karraker at Iowa State University published papers on chromatographic separation of metal cations using a 2+ protonated ethylenediammonium salt in the eluent [10,11]. Beginning in 1960, Strelow and coworkers in South Africa published extensive ion-exchange selectivity scales of cations in hydrochloric acid [12], nitric and sulfuric acid [13] and in perchloric acid [14] media. Although these selectivity scales were based on equilibrium distribution coefficients, numerous examples of specific separations were given. A Swedish author, Samuelson, published a book in

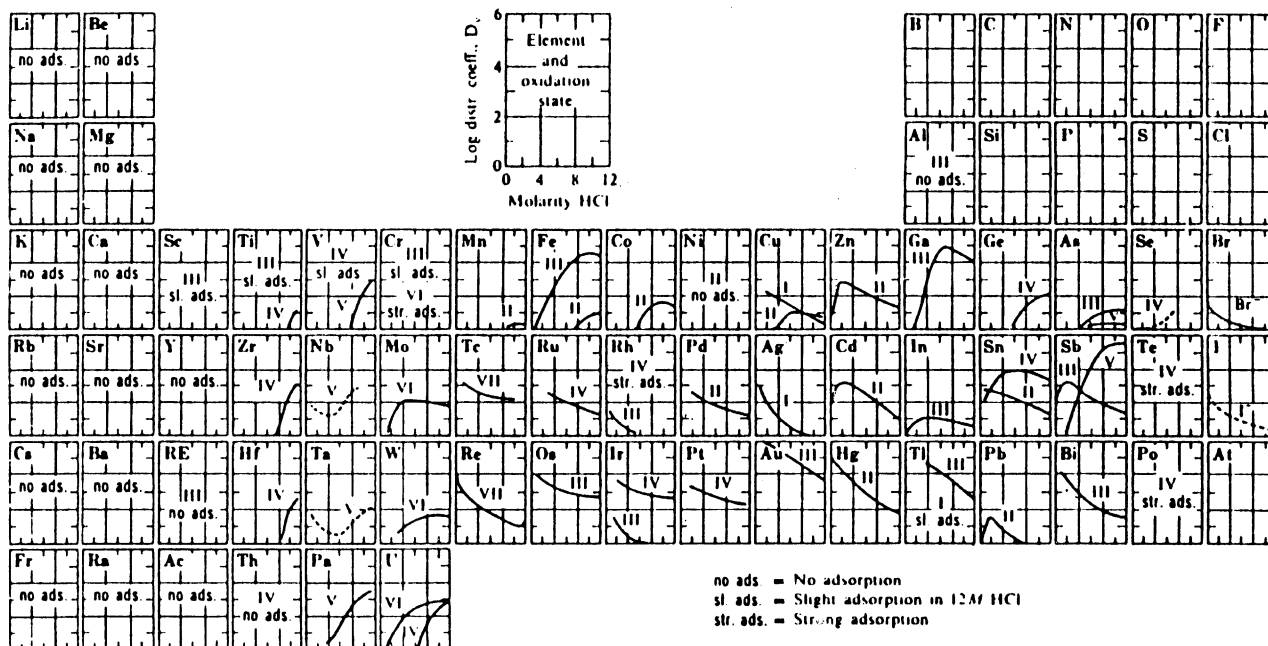


Fig. 4. Anion-exchange distribution coefficients (D_v) of the elements as a function of HCl concentration (from [8] with permission).

1963 that helped popularize the use of ion exchange in analytical chemistry [15].

In some instances selective complexation is a quick and practical way to separate metal ions. Metal ions that form fluoride complexes in 0.1 M HF Al(III), Mo(VI), Nb(V), Sn(IV), Ta(V), U(VI), W(VI) and Zr(IV) pass quickly through a short cation-exchange column while other metal cations are retained [16]. Lead(II) is selectively eluted from a cation-exchange column by 0.6 M HBr [17]. Vanadium(IV) or (V) is separated from most metal cations by elution with acidic 1% hydrogen peroxide [18]. Organic solvents were found to promote formation of metal–chloride complexes, even at very low concentrations of hydrochloric acid. A comprehensive study of cation-exchange separations in acetone–water–hydrochloric acid demonstrated that many practical separations are possible [19].

At this juncture in the development of ion-exchange chromatography, separations tended to be a slow and laborious process. Fractions of eluate were collected either manually or by automatic fraction collectors on a turntable. Then each fraction had to be analyzed to determine the concentration of analyte present. The chromatogram was a manually drawn plot of analyte concentration as a function of the fraction number. The situation was not quite as bad as might be imagined because once the volume of eluent required to elute an analyte had been established, future separations could be run by collecting the eluate containing each analyte in a single fraction. Analytical separations were often carried out by a series of step elutions in which each analyte was eluted with an eluent of a different composition. Conditions could often be selected so that one ion was eluted very quickly while the remaining sample ions remained strongly held by the stationary phase on the column. Nevertheless, it was becoming apparent that widespread use of ion-exchange chromatography as an analytical tool would require a system that gave fast separations and automatic recording of chromatograms.

In 1971 an apparatus for “forced-flow chromatography” was described in which the eluent was pushed through the analytical column by compressed nitrogen [20]. Detection of eluted ions was by UV-Vis spectrophotometry using a 30 mm × 2 mm flow cell. Iron(III) (10–90 μg) could be separated from most other metal ions and measured quantitatively in only 6 min. Forced-flow methods were soon

developed for the chromatographic separation of a number of other metal ions [21–24].

The chromatograph was modified in 1974 so that a complexing reagent such as PAR or Arsenazo could be added to the column effluent via a mixing tee [25]. This made it possible to detect virtually any metal ion that could form a highly-colored complex. A recorded chromatographic separation of all 30 rare earths was obtained in 1974 [26], with this apparatus (Fig. 5). This separation took 100 min. Five years later, Elchuk and Cassidy in Canada were able to obtain a better separation of earths in only 27 min using a similar but improved system [27].

4. The birth of modern ion chromatography

Liquid column chromatography went “high performance” around 1970 and is now commonly referred to as HPLC. Major improvements in speed and efficiency were obtained by using columns of relatively small bore packed with small spherical particles of uniform diameter, by using a pump to provide constant eluent flow, and by using automatic detection of the separated sample components. But application of this technology for the separation of ions lagged. It was mainly the lack of satisfactory detectors that held up the development of high-performance ion-exchange chromatography.

This situation changed dramatically with publication of a landmark paper in 1975 by Small et al., working at the Dow Chemical Co. [28]. As the authors put it: “It would be desirable to employ some form of conductimetric detection as a means of monitoring ionic species in a column effluent since conductivity is a universal property of ionic species in solution and since conductance shows a simple dependence on species concentration. However, the conductivity from the species of interest is generally “swamped out” by that from the much more abundant eluting electrolyte. We have solved this detection problem by using a combination of resins which strips out or neutralizes the ions of the background electrolyte leaving only the species of interest as the major conducting species in the effluent. This has enabled us to successfully apply a conductivity cell and meter as the detector system.”

This new system, which was given the name “ion chromatography,” enabled the analyst to quickly separate and measure quantitatively the cations or anions at low concentrations in fairly complex samples. A diagram of the system for cation analysis is shown in Fig. 6. The upper column, called the “separator column,” was packed with polystyrene–2% DVB particles, surface sulfonated to obtain an exchange capacity of approximately 0.02 mmol/g. The lower “suppressor column” was packed with anion-exchange resin of high exchange capacity in the hydroxide form.

A practical method for the separation of anions was described in the same paper [28]. Although some limited use

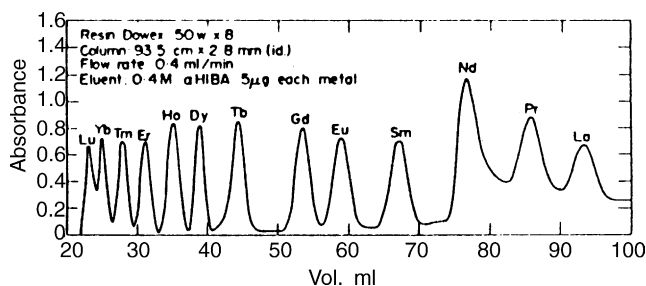


Fig. 5. Chromatographic separation of rare earths (from [26] with permission).

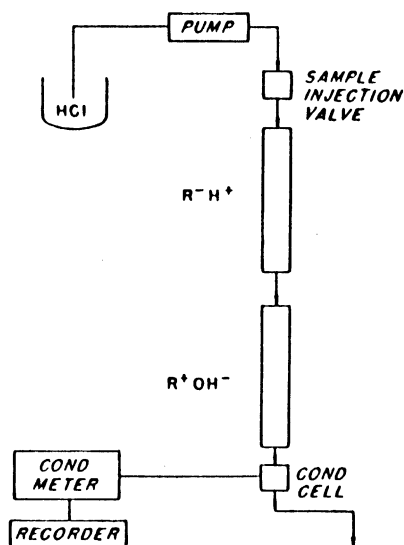


Fig. 6. System for cation analysis by conductimetric chromatography (from [28] with permission).

had been made of anion exchangers of low capacity, none were available commercially and so an alternate route to such a resin was devised. It had been known for some time that cation and anion exchangers have a marked tendency to clump together. This is a manifestation of the strong electrostatic interaction between polycationic and polyanionic materials in general. This clumping property was exploited to produce an effective anion exchanger of very low capacity that was suitable for chromatographic separations. A strong base anion exchanger was thoroughly ground in a rod mill and the larger particles removed by sedimentation. A very dilute suspension of the fine particles (ca. 0.5–2 μm) passed through a column packed with surface sulfonated particles similar to those used to separate cations. Eventually the column became saturated with a surface layer of the anion-exchange particles and the column was ready for use. In the original scheme for separation of anions a mixture of sodium hydroxide and sodium phenate was used in the eluent. The suppressor column was packed with a cation-exchange resin of high capacity. The suppressor column converted the eluent ions to water plus phenol, while the sample anions A^- were converted to the highly conducting pair H^+A^- .

An instrument called the “ion chromatograph” was offered commercially by the newly organized Dionex Co. and became an immediate success. The new technology made it possible to separate and determine both cations and most anions, but the ability to determine anions at low ppm concentrations had the greater impact. Many cations could already be determined by various spectral methods and by reasonably good chromatographic methods, but prior to the advent of ion chromatography there was no general analytical method for anions, especially at very low concentrations. Once the scientific world became aware that anions in fairly complex mixtures could be easily separated and quantified,

even at low ppm concentrations, the use of ion chromatography exploded. A powerful new analytical technique had again facilitated scientific endeavors that were previously impractical.

5. Non-suppressed ion chromatography

Any analytical method is apt to have some drawbacks and limitations. A major disadvantage of the original Ion Chromatograph was that it required use of a large suppressor column that contributed to peak broadening and required frequent regeneration. The eluent for anion separations had to be a base, and anions of very weak acids could not be detected because their acidic form after suppression was too weakly conducting.

In 1979 a synthetic method was described for producing anion-exchange resins of very low exchange capacity [29]. A porous polymeric resin such as Rohm and Haas XAD-1 was chloromethylated under mild conditions. Then the resins were alkylated with trimethylamine to form ionic quaternary ammonium groups. The exchange capacity could be varied from 0.17 to 1.46 meq./g by controlling the time and temperature of the chloromethylation reaction. It was firmly established that a resin of lower exchange capacity permits the use of a lower eluent concentration.

Working at Iowa State University, Fritz et al., devised a simple system for “anion chromatography with low-conductivity eluents” [30]. Anions were separated on a column containing macroporous anion-exchange particles of very low exchange capacity: 0.07, 0.04 or 0.007 mmol/g. The eluent was an aqueous solution of the sodium or potassium salt of an organic anion that had a significantly lower equivalent conductance than the anions to be separated. In this method some of the eluent anion is replaced by a sample anion of significantly higher conductance as the sample ion is eluted from the column and passes through the conductivity detector. Because of the low resin capacity, an eluent containing only ca. 10^{-4} M of an organic acid salt, such as benzoate or phthalate, could be used. The eluent conductance was sufficiently low that no suppressor column was needed, and the separated sample ions could be detected with a simple conductivity detector. Numerous anion separations were shown and in some instances detection limits below 1 ppm were obtained. This method was initially called “single-column ion chromatography” and later as “non-suppressed ion chromatography.” An additional paper on anion chromatography [31] was published in 1980.

The principles of non-suppressed anion chromatography may be explained as follows. In ion-exchange chromatography an equilibrium is attained in which the total anion concentration in solution is fixed by the eluent anion concentration. When a sample anion zone enters the detector cell, the eluent anion concentration is reduced by an amount equivalent to that of the sample anion. If the sample anion

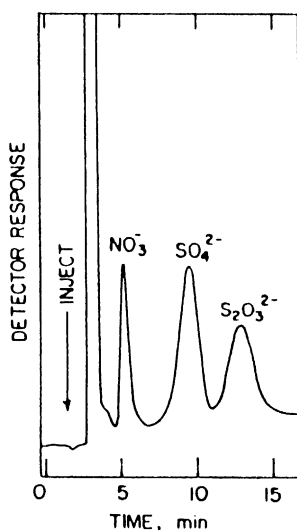


Fig. 7. Separation of 24.4 ppm of nitrate, 22.0 ppm of sulphate and 21.3 ppm of thiosulfate. Resin, XAD-1 0.04 meq./g; eluent, 5×10^{-4} M ammonium *o*-sulfobenzoate, pH 7.3 (from [30] with permission).

has a significantly higher equivalent conductance than the eluent anion, there will be an increase in conductance that is proportional to the sample anion concentration. For example, the limiting equivalent conductance for sodium benzoate is $50 \text{ S cm}^2/\text{eq.}$ (for Na^+) + $32 \text{ S cm}^2/\text{eq.}$ (for benzoate), or $82 \text{ S cm}^2/\text{eq.}$ The equivalent conductance of sodium chloride is $50 \text{ S cm}^2/\text{eq.}$ (Na) + $76 \text{ S cm}^2/\text{eq.}$ (Cl^-), or $126 \text{ S cm}^2/\text{eq.}$ Of course, not all of the benzoate in the solution is replaced by chloride. The percentage increase in conductance when chloride is eluted will depend on the ratio of eluent benzoate concentration to sample chloride concentration, as well as to the difference in equivalent conductance between benzoate and chloride. Thus, a key factor in the success of the new technique was the use of an ion exchanger of low exchange capacity, which in turn permitted the use of a very dilute eluent.

This new method for anion separation was very flexible. Ions such as fluoride, chloride, nitrate and bromide were separated with a potassium benzoate eluent, but iodide, thiocyanate and sulfate required a more powerful eluent such as potassium phthalate or ammonium *o*-sulfobenzoate for a rapid separation (see Fig. 7). More rapid separations with lower detection limits were possible by using an ion exchanger of 0.007 meq./g [31].

The use of indirect conductivity detection in non-suppressed cation chromatography was introduced in 1980 [32]. A 1×10^{-3} M solution of nitric acid was used as the eluent in conjunction with a sulfonated cation-exchange column of low exchange capacity. In this method, a baseline of relatively high conductance is established when the column is equilibrated with the acidic eluent. After introduction of a sample mixture, such as Na^+ and K^+ , and continued elution with the eluent, the sample cations are gradually resolved into zones in which some of the highly conducting H^+ (eq. conductance = $350 \text{ S cm}^2/\text{eq.}$) is exchanged for a sample

cation of much lower conductance. A sharp “peak” of lower conductance is obtained for each sample cation.

The practical utility of this new system was demonstrated by a chromatogram in which <1 ppm concentrations of each of the alkali metal cations plus ammonium were separated in under 10 min. Although separation of divalent cations was not practical with a nitric acid eluent, a fast separation of magnesium and calcium in tap water was obtained with a 1×10^{-3} M ethylenediammonium nitrate eluent.

6. Concluding remarks

This narrative covers selected milestones during the period from about 1945 to 1980. As would be expected, much has happened during the intervening years. Ion exchange production of rare earth salts persisted until about 1980. Today rare earths are separated more economically on a large scale by various liquid–liquid extraction techniques. Except for gadolinium and terbium, which are widely used in phosphates, the purity is not as high as that obtained by ion exchange.

After its initial introduction in 1975, modern ion chromatography has undergone continued growth and vigorous technical development. Enthusiastic acceptance by the scientific community has made ion chromatography the method of choice for the analytical determination of ions. Direct and indirect detection methods have been developed. Non-suppressed conductance occupies an important niche, but suppressed conductance is clearly the dominant detection method. “Reagentless” ion chromatography is now available in which both the eluent and the conductivity steps are performed with electrically generated chemicals.

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