Ion Exchange Chromatography

The separation and purification of various elements by ion exchange chromatography takes advantage of the variation of the electrostatic bond energies of ions in solution. Thus, the two main controlling factors in ion exchange chromatography are the ionic charge (z) and the ionic radius (r). These two are combined in the ionic potential – z/r – that can be used to compare relative electrostatic bond strengths. Ions of high charge (trivalent or greater) and small radius have high electrostatic bond strength, and therefore are likely to attach strongly to an oppositely charged solid surface, whereas ions of low charge and large radius form relatively weaker electrostatic bonds. By manipulating the chemistry of the solution, ions can be separated from each other using this contrast in bond strength.

In an ion exchange column, the stationary phase is a resin on which a usually organic coating provides a charged surface. The mobile phase is a solution with which the ions to be separated are introduced into the system; aqueous acid and base solutions, and organic, non-aqueous solutions can be used as the mobile phase. The resin typically consists of inert (commonly polystyrene), spherical beads; these are coated with any range of polar molecules, some of which provide negatively charged surfaces (for separation of cations), and others of which provide positively charged surfaces (for separation of anions). In our applications, the separation of Pb takes advantage of a very stable anionic Pb bromide complex ($PbBr_4^{2-}$), using "anion resin" (positively charged resin surfaces), whereas the separation of Sr (Sr^{2+}) uses a "cation resin" with negatively charged surfaces. The resin and mobile phase have to be chemically compatible, so that the only reactions that take place during chromatography are the adsorption – desorption reactions at the resin surface.

We can characterize the theoretical effectiveness of the separations in ion exchange chromatography by comparing the distribution coefficients (D) of various ions. The distribution coefficient is defined as the ratio of the concentration, at steady state, of an element or ion on the solid (resin) to the concentration in the liquid:

$D = C_s / C_l$

At high D (> 100), ions will remain attached to the stationary phase (resin), whereas at low D (< 0.1), ions will remain primarily in the mobile phase, the liquid. Obviously, the best separation of two ions occurs when they have contrasting D. In most ion exchange chromatographic procedures, the D of ions of interest is > 1000 during the stages when unwanted ions are being removed from the system, and is < 1 during stages when the ion of interest is being collected. It is obvious that ions that have similar z/r, and therefore broadly similar D, are difficult to separate. D for all ions varies as a function of the composition of the solution; for $PbBr_4^{2-}$, for example, D is > 100 for HBr concentrations below about 2 M HBr, but drops dramatically as the acid concentration is increased, and is < 1 for concentrated HBr solutions (8.3 M HBr).

The distribution coefficient can be defined thermodynamically (more detail than you need here). Consequently, it is affected by the factors that affect the thermodynamics of aqueous solutions – temperature, Eh, pH, solution composition, and ionic strength. It is less sensitive to variations in pressure because neither the stationary nor the mobile phase is very compressible. In most applications, conventional ion exchange chromatography is done at room temperature, but it is obvious that temperature has a pronounced effect on the kinetics of adsorption – desorption reactions. Eh is not directly controlled – most solutions are oxidizing because the procedures are conducted in an uncontrolled, oxidizing atmosphere. In exceptional applications, temperature and pressure can be controlled, and separations can be done in inert (low-oxygen) atmospheres. Solution composition and ionic strength are manipulated primarily by varying the amount of sample in relation to the amount of liquid initially loaded onto the column, and by varying the acid concentration of liquids that are added to the column. In the ideal case, sample solutions should be dilute enough to avoid ionic strength effects.

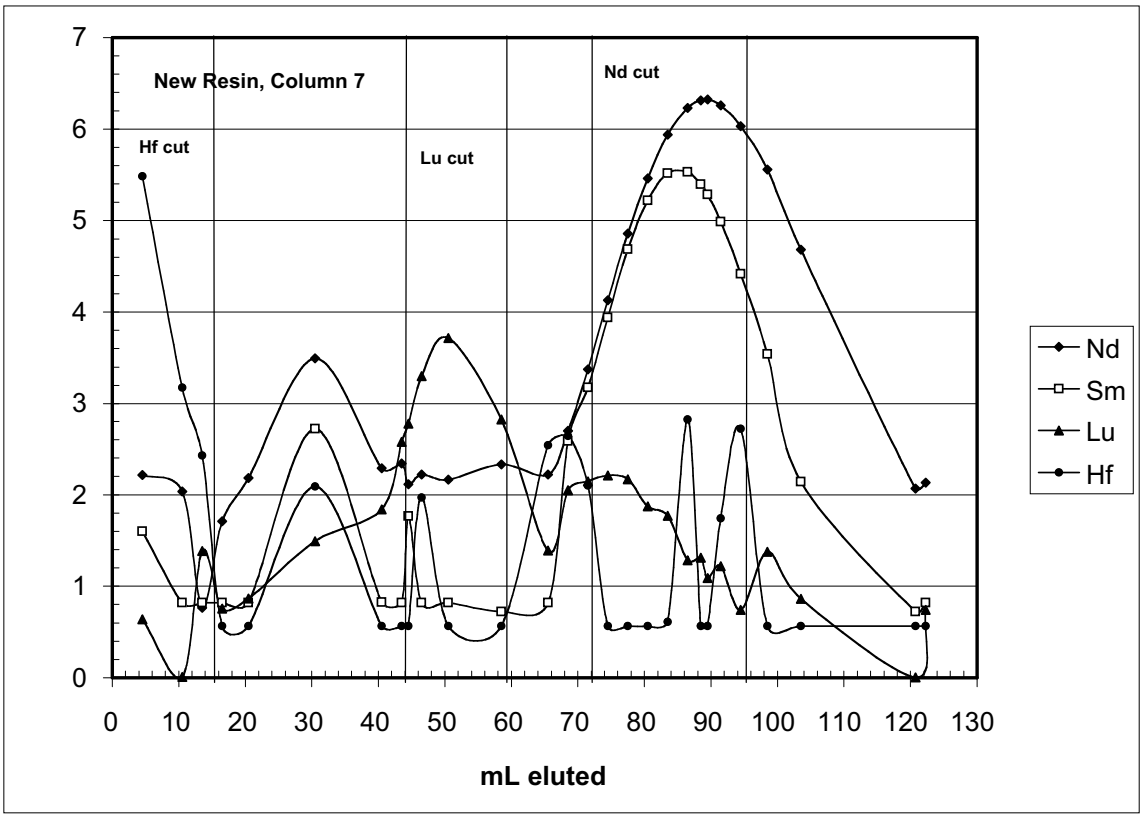
The factors that affect separation during ion exchange chromatography include the surface area of the stationary phase (resin bead size); the density of exchange sites on the stationary phase surface (cross-linkage); the flow rate of the mobile phase (resin bead size and column geometry; system pressure in high-pressure chromatography); and the chemistry of the mobile phase (ionic strength of the sample solution, concentration of mobile phase). As resin bead size decreases, the surface area per unit volume increases, so that finer-grained resins provide more numerous exchange sites and therefore usually better separations. The organic coating on the resin beads, during manufacture, can be altered to provide more or fewer exchange sites per unit area; this is called the cross-linkage of the resin. Higher cross-linkages (e.g., 12X) provide better separations but typically broader elution peaks. Newer resins may have organic coatings whose stereochemistry is custom-designed to fit specific ions; the crown ether family of organic molecules is particularly suited to this application. The combination of bead size and cross-linkage leads to a maximum exchange capacity per unit volume for each resin, and the sample size that is processed must be below this maximum exchange capacity for effective separations.

The flow rate of the mobile phase is determined in large part by the resin bead size; coarser resin beads have larger inter-bead spaces through which the fluid can move, and capillary effects are smaller, so that coarser resins have faster fluid flow. Faster flow usually leads to poorer separations. In our applications, fluid flow is controlled by gravity feed – the mobile phase moves as fast as gravity allows. At fine resin bead sizes, gravity is insufficient to induce flow (capillary forces and surface tension exceed gravity), and pressurized columns must be used.

Ultimately, the separation of elements on an ion exchange column is a statistical process. If all ions of a particular element were to behave identically, then the concentration peak of the element would move along the length of the column, from the injection site to the collection site, essentially as a step function that is identical along the length of the column. But because the behavior of ions in the adsorption – desorption reactions that produce the separation is statistical, there is a general broadening of the elution peak

along the length of the column. The adsorption front, where ions first encounter exchange sites that are available to them, is typically sharp, but the desorption front typically has a long tail. This asymmetry in the shape of the concentration curve means that most separations are not quantitative in the sense that, though > 99% of the ions of a specific element can be captured if a large enough volume of solution is collected, that solution will also contain a range of other ions with roughly similar z/r. The quality of the separation – the purity of the product – can be improved by decreasing the volume of solution collected, but this leads to loss of some fraction of the element of interest. In some cases, different isotopes of an element can have sufficiently different D to cause some fractionation of isotopes on the ion exchange column (this is likeliest with lighter elements that have a large mass range, e.g., calcium).

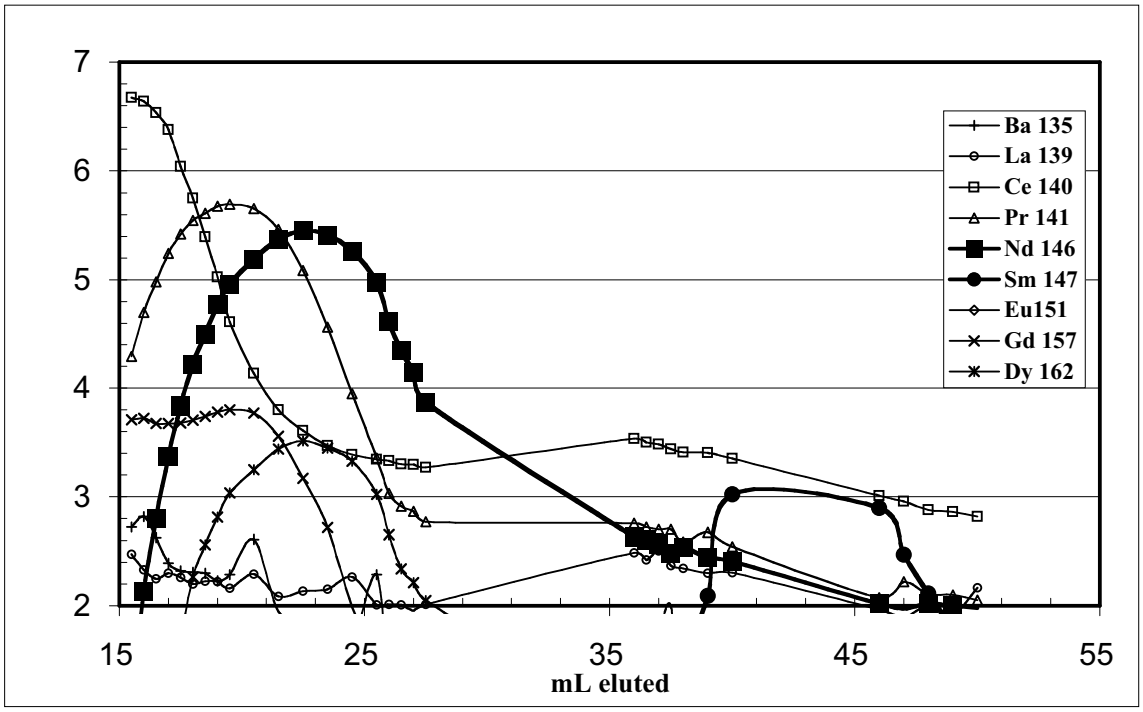
These general observations are illustrated by the chromatographic profiles of a couple of



different columns that we use for separation of Hf, Lu, Nd and Sm. The graph above shows the profile of an 8 cm^3 cation column, with solution volume on the abscissa and a rough measure of concentration as the ordinate. The sample (roughly 100 mg of rock that has been completely dissolved) is loaded onto the column in 3 mL of 1 M HCl. The first 15 mL of solution that is passed through the column is 1 M HCl, and results in virtually quantitative removal of Hf from the resin (this is counterintuitive, considering that Hf should form a small ion of high charge - +4; it is likely that Hf is present in solution as a large, low-charge cation complex, perhaps $HfCl_2^{2+}$). The 1 M HCl solution is followed by 45 mL of 3 M HCl, toward the end of which the heavy rare earth elements (Lu, for

example) begin to be released from the resin. After 60 mL have passed through the column, we change the mobile phase to 3 M HNO_3 and continue the elution to a total volume of about 125 mL. The reason for changing to HNO_3 is that barium remains on the column in HCl, and ultimately can interfere with the separation of the rare earths; in HNO_3, however, barium is mostly eluted before the rare earths of interest (Nd and Sm) are collected. Both Hf and Lu show small subsidiary peaks when the solution changes from HCl to HNO_3. During this separation procedure, essentially all of the major elements in the rock – Si, Al, Mg, Ca, Na, K, etc., - are removed in the mobile phase that we send to waste.

Our target is to separate Sm from Nd, so that each can be analyzed separately. Both Nd and Sm have an isotope at mass 144, and the interference of ^{144}Sm on ^{144}Nd is fatal to good Nd isotopic analyses. After collecting the volume between 70 and 95 mL from the column above, where there is complete overlap between Sm and Nd, we dry the solution down, and re-dissolve the sample in 100 µL of 0.3 M HCl. This solution we introduce onto a second column that contains a different type of cation resin. On this column, we



get good separation of Nd from Sm, but there is extensive overlap of Ce and Pr with Nd. ^{142}Ce is a low abundance isotope, and does not seriously impact on our analyses of $^{143}Nd/^{144}Nd$ (the ratio of interest); Pr has only one isotope, ^{141}Pr, that does not affect our Nd analyses. Note that there is a long tail on the Nd and Ce elution peaks on this second column. The rise in Ce content between 27 mL and 35 mL reflects a change in the mobile phase from 0.3 M HCl to 0.5 M HCl.

From these graphs, you should be able to imagine that the element concentration peaks are migrating down the length of the column as a function of time, gradually broadening

as some ions lag behind, whereas others rush ahead, potentially as fast as the mobile phase is flowing through the column. These graphs and column procedures also illustrate how solution concentrations and compositions are manipulated to effect separations.

For separation of Pb, we used anion resin in a column that has a total volume of 120 μL, compared with the 8 mL cation column illustrated above; the solution volumes were also much smaller, totaling only 2.5 mL for the Pb column, compared with 125 mL for the bulk cation column above. This gives you an idea of the variety of geometries and resin types that can be used. In our lab, the people who separate Pb from zircons use 50 μL columns with a total solution volume of only 8 drops (less than 0.5 mL).

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