Basic process of IC

The basic process of chromatography using ion exchange can be represented in 5 steps: eluent loading, sample injection, separation of sample, elution of analyte A, and elution of analyte B, shown and explained below. Elution is the process where the compound of interest is moved through the column. This happens because the eluent, the solution used as the solvent in chromatography, is constantly pumped through the column. The chemical reactions below are for an anion exchange process. (Eluent ion =

\[
\begin{align*}
&\text{Eluent ion } = \\
&\text{Ion A } = \\
&\text{Ion B } = \\
\end{align*}
\]

**Step 1:** The eluent loaded onto the column displaces any anions bonded to the resin and saturates the resin surface with the eluent anion.

This process of the eluent ion \((E^-)\) displacing an anion \((X^-)\) bonded to the resin can be expressed by the following chemical reaction:

\[
\text{Resin}^+ - X^- + E^- \leftrightarrow \text{Resin}^+ - E^- + X^-
\]

**Step 2:** A sample containing anion A and anion B are injected onto the column. This sample could contain many different ions, but for simplicity this example uses just two different ions ready to be injected onto the column.
Step 3: After the sample has been injected, the continued addition of eluent causes a flow through the column. As the sample elutes (or moves through the column), anion A and anion B adhere to the column surface differently. The sample zones move through the column as eluent gradually displaces the analytes.

Question to consider: How would you write the chemical reaction for elution process with respect to anion A and anion B. How would you write the $K_r$ expression for the two reactions? How would you sketch the elution process at this step using a figure similar to the figure in Step 1 if the $K_r$ for anion A is larger than the $K_r$ for anion B?

Step 3: The continued addition of the eluent causes a flow through the column. As sample elutes, anion A and anion B adhere to the column surface differently. The sample zones move through the column as eluent gradually displaces the analytes.

In reality not every eluent ion is removed from the surface of the column. It depends on the amount of analyte loaded. A better representation of the column can be seen by just looking at a slice of the column where the separation is occurring, as shown in the figure below.

Step 4: As the eluent continues to be added, the anion A moves through the column in a band and ultimately is eluted first.
This process can be represented by the chemical reaction showing the displacement of the bound anion ($A^-$) by the eluent anion ($E^-$).

$$Resin^+ - A^- + E^- \Leftrightarrow Resin^+ - E^- + A^-$$

**Question to consider:** If ion B had a very strong affinity for the resin, how would the elution time for ion B be affected? If it takes forever to come off, would this be useful in trying to determine the quantity of that ion present? When might this be useful? (Hint: go back to the introduction to the module and look at where ion-exchange is used...)

(Answer: As the affinity ion B has for the resin increases, the elution time would increase. If the affinity becomes large enough, in essence anion B will stay on the column. This phenomena is utilized in water filtration where ion exchange is used to remove particular ions from the sample.)

**Step 5:** The eluent displaces anion B, and anion B is eluted off the column.

$$Resin^+ - B^- + E^- \Leftrightarrow Resin^+ - E^- + B^-$$

The overall 5 step process can be represented pictorally:
Stationary phase (or resin) composition

There are a number of different resins or stationary phases that have been developed for use in IC. The main classes of substances used are: modified organic polymer resins, modified silica gels, inorganic salts, glasses, zeolites, metal oxides, and cellulose derivatives. The most commonly used resins are the silica gels and polymer resins. As the sample is injected onto the column, the two different analytes briefly displace the eluent as the counter-ion to the charged resin. The analyte is briefly retained at the fixed charge on the resin surface. The analytes are subsequently displaced by the eluent ions as the eluent is added to the column. The different affinities (see the chemical reactions in the basic process section) are the basis for the separation. The $K_f$ values of each reaction is also known as the selectivity coefficient. The greater the difference between the $K_f$ values for the two analytes, the more the two analytes will be separated during the ion chromatography process. In reality, the interaction between the solvent and the analyte can also have an impact on the order each analyte is eluted. For a more in-depth analysis of predicting the retention order see the material by Dr. Thomas Wenzel. (http://www.bates.edu/x65385.xml)

The common cation exchange resins are based on either polystyrenedivinylbenzene (PS-DVB) or methacrylate polymers. The surface of these polymers (Figure 1) is functionalized with a negatively charged sulfonated group (-SO$_3^-$). The cation in the eluent or the analyte of interest is the counter-ion in the vicinity of the charged functional group.

![Figure 1: cation exchange surface](image)

The surface of the polymer is functionalize with a quaternary amine (-N$^+$R$_3$) for anion exchange (see Figure 2). The quaternary amine provides a positive charge to the surface, attracting negatively charged anions in the liquid phase. Just like the cation exchange resin, the anion of the eluent or the analyte of interest exists as the counter-ion in the vicinity of the positive charge residing on the amine.

![Figure 2: anion exchange surface. The R stands for some organic (C and H) chain.](image)