

Quadrant II – Transcript and Related Materials

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Unit: 1

Module Name: Separation of lanthanides (ion exchange method)

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Notes

Chromatography

Chromatography is a technique used for separation of mixture. The mixture to be separated is dissolved in a suitable fluid (gas, solvent, water,....) called the mobile phase. The mobile phase carries the mixture through a material called stationary phase. This stationary phase could be packed in a column or a capillary, or supported on a plate or a sheet as a thin layer. Separation of constituents of the mixture takes place due to their differences in affinities for the stationary phase (refer figure 1).

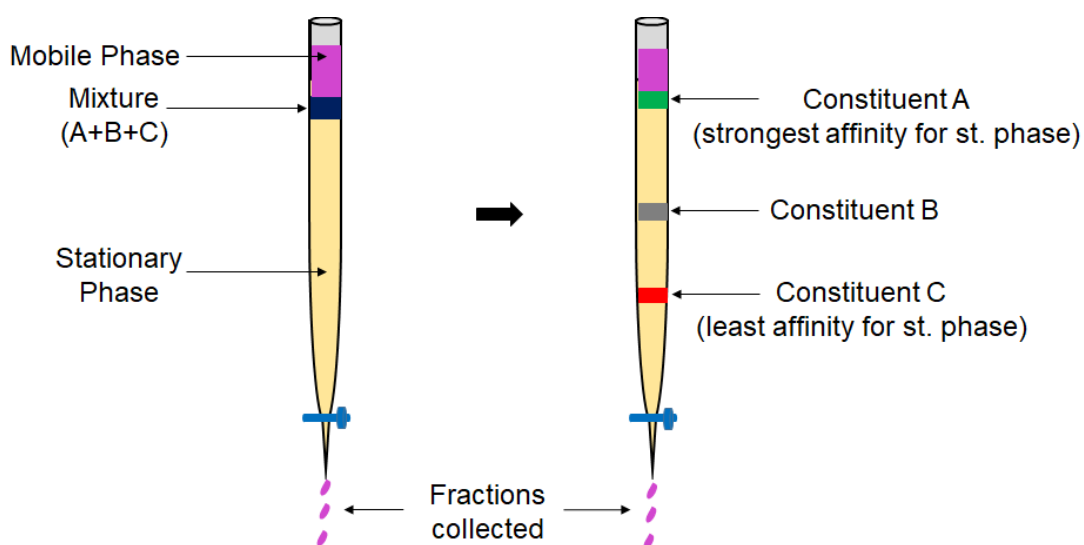


Figure 1: Illustration of a chromatography technique with stationary phase packed in a column, separating the mixture into its constituents (A, B and C) as the mobile phase runs through the stationary phase.

Ion exchange chromatography

Ion exchange chromatography is a type of chromatography technique. In this type of chromatography, the stationary phase (synthetic resin, an organic polymer with 3-dimensional network) contains covalently bonded anions or cations onto it with exchangeable counter ions. Solute ions of the opposite charge in the mobile liquid phase (electrolyte) are attracted to the resin by electrostatic forces, and then exchanged. Thus, solutes are separated due to the differences in the type and magnitude of their ionic charges. The separation is due to exchange of ions in the sample with the labile (exchangeable) ions onto the stationary phase (exchange resin).

Synthetic resin which has an exchangeable anion is called as anion exchanger and the technique utilising it is called anion exchange chromatography. On the other hand, the resin which has an exchangeable cation is called as cation exchanger the technique is called cation exchange chromatography; this technique is widely used for separation of lanthanides.

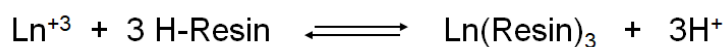
Separation of lanthanides

The properties of metal ions are determined by its charge and size. All the lanthanides carry same charge (typically +3), but their size decreases with increasing atomic number (lanthanide contraction). Thus, the properties of the lanthanides changes, and the separation techniques takes advantage of this change in properties for the separation of lanthanides. It is important to note that, although the size of lanthanides decreases due to lanthanide contraction, the decrease is not substantial, as a result of which the difference in properties of lanthanides is very slight. As a matter of fact, this inadequate slight difference in properties makes the separation of lanthanides very difficult. However, there are some techniques which can still successfully bring about the separation of lanthanides.

Separation of lanthanides by cation exchange chromatography

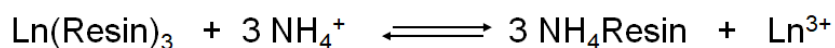
In this technique, a column is packed with cation exchanger resin containing groups like COOH , SO_3H , OH . The hydrogen ions of these groups in

the resin are exchangeable with other cations. Thus, when the solution containing a mixture of lanthanide ions (Ln^{+3}) is passed through the column, the lanthanide ions are exchanged with hydrogen ion on the cation exchanger resin.

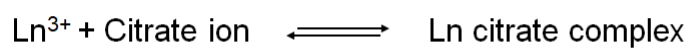


Bonding of Ln^{+3} with resin depends on its size. As Ln^{+3} are hydrated, the size of hydrated ions should be considered. Hydration of an ion depends on size of the ion, smaller the size, higher will be the degree of hydration. Since the size of lanthanides decreases from La^{+3} to Lu^{+3} , the Lu^{+3} will be most heavily hydrated. Larger the hydrated radius(Lu^{+3}), more loosely it is bound with resin, and vice versa. Thus, hydrated Lu^{+3} will be bonded most loosely and hydrated La^{+3} will be bonded most firmly with the resin. The lanthanides are then eluted from the column using a solution containing citric acid and ammonium citrate.

Firstly, ammonium ions elute the metal ions from the resin as:



Metal ions then forms complex with citrate ions:



Since Lu^{+3} is most loosely bound with the resin, the Lu citrate complex will be obtained first whereas La citrate complex will be obtained last from the bottom of the column.