Suppressed Ion Chromatography

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Chromatographic methods are recognized as the most powerful analytical separation techniques to date, for the identification and separation of complex mixtures of chemical compounds. The versatility comes from the separation ability, efficiency, sensitivity and low detection limits of advanced technologies. In chromatography, a mobile phase carries the analytes through a stationary phase. Mixture of analytes separates into individual compounds depending on the differences in migration rates of the analytes.

Chromatographic techniques are divided mainly into two, as column chromatography and planar chromatography depending on the physical method of separation. It is further classified into four categories as partition, adsorption, ion exchange and size exclusion. Adsorption chromatography is of two types as liquid-solid chromatography and gas-solid chromatography, where mobile phase is a liquid and a gas, respectively. In partition chromatography, stationary phase is a liquid supported on an inert solid. Partition chromatography is also further classified into two as liquid-liquid chromatography, when mobile phase is a liquid, and gas-liquid chromatography, when mobile phase is a gas. Ion exchange is a liquid chromatographic technique which is used to separate and quantify ions in a matrix.

The ions found in environmental matrices may get ingested to human body through food chains and drinking water. The World Health Organization has established threshold levels for ions in environmental matrices. If the ion concentration exceeds the threshold level, then it is identified as a system which may impose a threat to human health and the ecosystem. Therefore, ion levels in environmental compartments should be monitored regularly. Due to the high sensitivity and the separation ability, ion chromatography is preferred over most of the existing technologies to analyze ions in environmental matrices.

In an ion exchange chromatographic column, an ion exchange resin coated on a porous, insoluble solid functions as the stationary phase. Ion exchange resins are high molecular weight polymers which contains ionic functional groups. Cation exchange resins are mainly of two types. (Figure 1) Strong acid type exchangers which consist of sulfonic acid groups ($-SO_3^-H^+$), and weak acid type exchangers which consists of carboxylic acid groups. (-COOH).

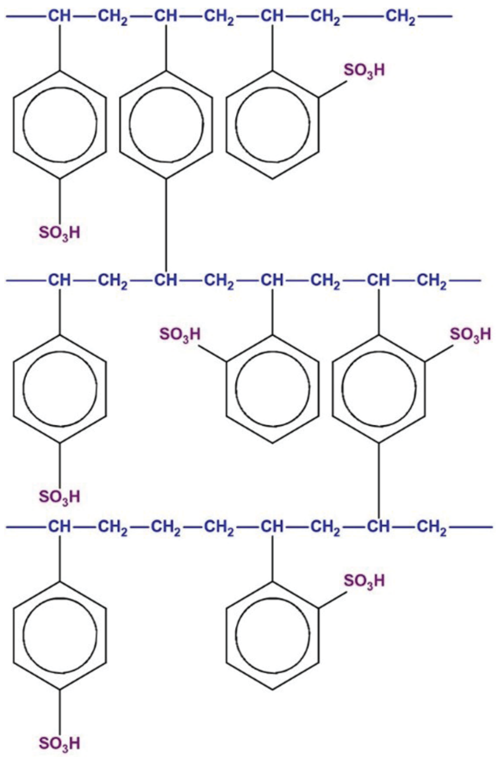

Figure 1: Sulphonated polystyrene cation exchange resin.

The chemical reaction for the exchange of cations can be given as below.

$$x\,RSO_3^-H^+ + M^{x+} \rightleftharpoons (RSO_3^-)_xM^{x+} + x\,H^+$$

Where, M^{X+} is the cation, and R is the part of a resin molecule containing one sulfonic acid group.

Anion exchange resins are also of two different types. Strong base anion exchangers have quaternary ammonium groups [$-N(CH3)^{3+}OH^-$] and weak base anion exchangers have secondary or tertiary amines. (Figure 2)

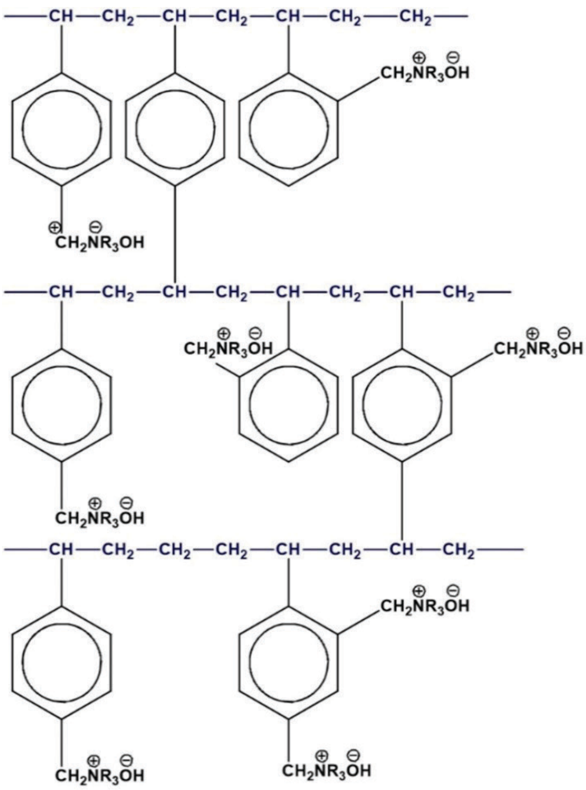

Figure 2: Polystyrene anion exchange resin with quaternary ammonium groups.

The chemical reaction for the exchange of anions can be given as below.

$$x\ RN(CH_3)_3^{+}OH^{-} + A^{X-} \rightleftharpoons [RN(CH_3)_3^{+}]_x A^{X-} + x\ OH^{-}$$

Where, A^{X-} is the anion, and R is the part of a resin molecule containing one quaternary ammonium group.

Conductivity detectors are used in ion exchange chromatography in order to detect charged ionic species. Conductivity detectors possesses several advantages in this technique such as high sensitivity, being universal for charged species, responding in a predictable way to concentration changes, simplicity, ease of miniaturization, low cost of maintenance and durability.

Ion exchange chromatographic technique can be classified into two as single column ion chromatography and suppressed ion chromatography. In single column ion chromatography, only a single analytical column is used for separations. However, in this technique, base line fluctuation is high. For example, in anion exchange chromatography, $NaHCO_3$ is usually used as the mobile phase. Due to the high conductivity of Na^+ ions, the detector produces a high signal corresponding to the Na^+ ions. Therefore, the baseline of the chromatogram shifts up. This causes the analyte peaks to appear smaller, incorporating a significant error in the peak integration. In order to avoid the above problem, the scientist Bauman introduced a suppressor column in 1971.

Suppressed ion exchange chromatography

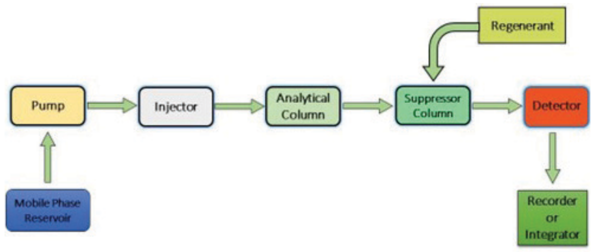

Figure 3: Block diagram of a suppressed ion exchange chromatography.

The suppressor column is used after the analytical column, and the mobile phase with analytes after eluting from the analytical column, enters the suppressor column. For the anion exchange discussed above, the reaction for the suppressor column can be given as follows.

$$Na^{+}_{(aq)} + HCO_3^{-}{}_{(aq)} + Resin^{-}H^{+}_{(s)} \longrightarrow Resin^{-}Na^{+}_{(s)} + H_2CO_{3\,(aq)}$$

In anion separations, the suppressor column uses a cation exchange resin. Sodium ions from the mobile phase bind to the resin. The protons in the resin get released to the mobile phase and combine with the HCO_{3-} liberating carbonic acid. Since carbonic acid is a very weakly dissociating species, the conductivity detector produces only a weak signal for carbonic acid. Therefore, the baseline does not shift to a significant height. Due to this reason, when the suppressor column is used, the base line noise is minimized and the signal to noise ratio is improved. The analyte peak is visible with a significant height with increased efficiency and the detection sensitivity of the system increases. The peak area integration includes less error than when a single analytical column is used. Therefore, the concentration determinations of the analytes are more accurate when a suppressor column is used.

However, the surface of the resin in the suppressor column can get saturated with Na^+ ions. At this moment the base line may shift up again. Therefore, the suppressor column is washed with an acid with suitable time intervals in order to regenerate the stationary phase surface of the suppressor column.

Problems:

1. Write down the existing methods for anion analysis.
2. State the advantages of ion chromatographic technique over other existing techniques for ion analysis.
3. Write down the chemical reactions relevant to the separations of cations using suppressed ion chromatographic technique.
4. Briefly describe how the micro membrane suppressors would operate in ion exchange chromatography.
5. Provide six applications of ion exchange chromatography.

Student Corner

Introduction to Organic Reaction Mechanisms

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Organic reactions are chemical processes that involve organic substances. The fundamental types of organic chemistry reactions include substitution reactions, elimination reactions, addition reactions, redox reactions, pericyclic reactions, and rearrangement reactions.

A reaction mechanism is a step-by-step series of simple reactions that allows for overall chemical change occurs. Every organic reaction involves both an Electrophile and a Nucleophile.

Let's find out what is a nucleophile?

A nucleophile is a substance that can donate an electron pair during a process. The word "nucleophile" means nucleus loving and denotes that it targets areas of the substrate molecule with low electron densities (positive centers). A nucleophile can be represented by a general symbol Nu. Nucleophile acts as electron source for arrows making new bonds in writing reaction mechanisms. These could be neutral molecules with unbound electron pairs or negative ions, such as carbanions and some example of nucleophiles are Cl^-, Br^-, I^-, CN^-, OH^-, RCH_2^-, NH_3, RNH_2, H_2O, ROH.

What is an Electrophile ?

An electrophile is a substance that can accept a pair of electrons during a reaction. The word "electrophile," which means to "**electrons-loving**," denotes that the substance reacts with areas of the molecule with a high density of electrons (negative centers). Electrophiles are deficient in electrons and the general symbol E+ can be used to denote an electrophile. Electrophile serve as **sinks** for these arrows in writing reaction mechanisms.

These could be neutral molecules with electron-poor centers or positive ions, such as carbonium ions and examples include H^+, Cl^+, Br^+, I^+, NO_2^+, R_3C^+, $^+SO_3H$, $AlCl_3$, and BF_3.

A molecule or portion of a molecule that acts as a source for such arrows is said to be nucleophilic, whereas a molecule or portion of a molecule that acts as a sink for such arrows is said to be electrophilic.

Success in organic chemistry classes depends on the student's ability to write an organic reaction mechanism properly. Arrow pushing is a method used by organic chemists to represent the flow or motion of electrons during chemical processes.

What Is an Arrow Pushing?

Arrow pushing demonstrates how to convert A into B while giving us a thorough understanding of how the products are made. **Arrow pushing** takes electrons from nucleophile to electrophile.

There are few important points to bear in mind when writing an organic reaction mechanism:

1: The movement of electrons is showed by using arrows.

There are two different types of arrows (double sided arrowhead and single sided arrowhead) used in writing