Ion Chromatography

Ion Exchange Chromatography

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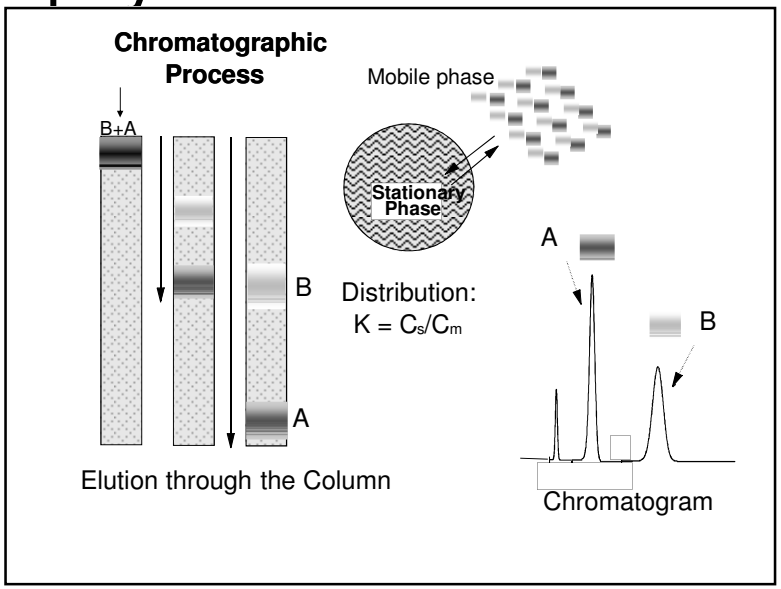
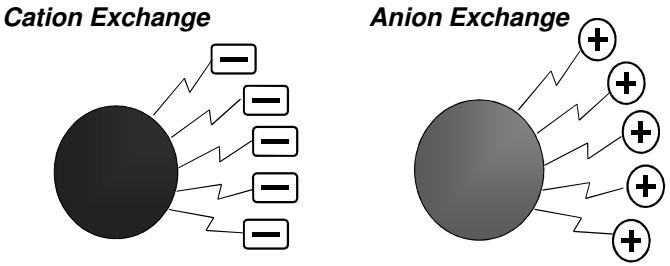
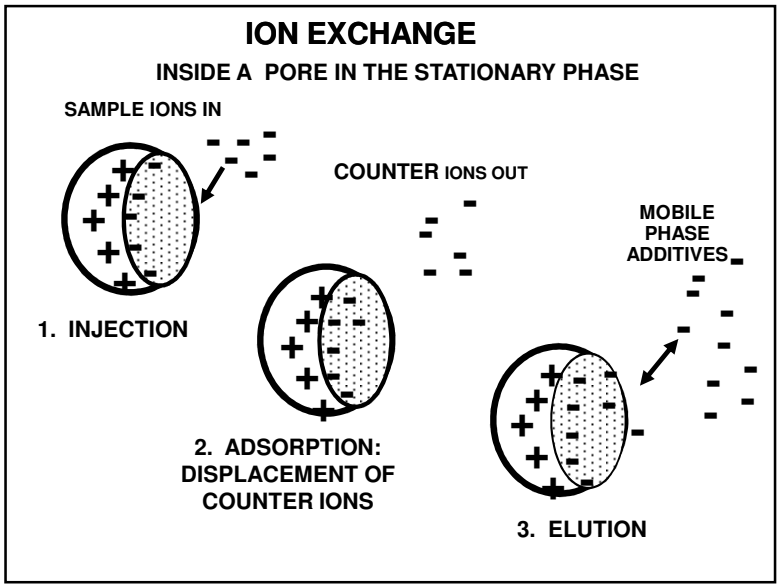


Ion Exchange Theory

Cation Exchange vs Anion Exchange

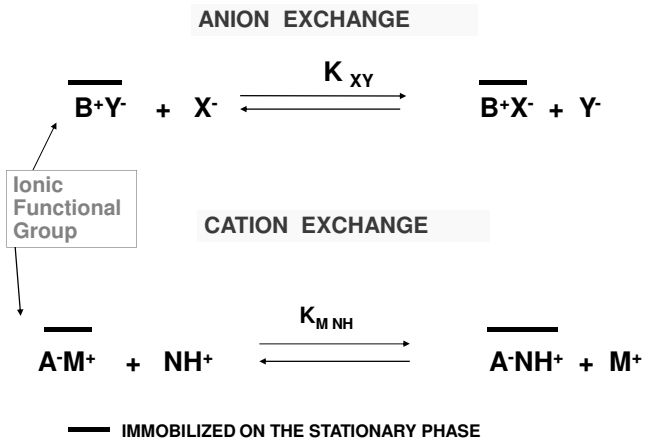


Cation exchange columns have a negative charge to attract cations.
Anion exchange columns have a positive charge to attract anions

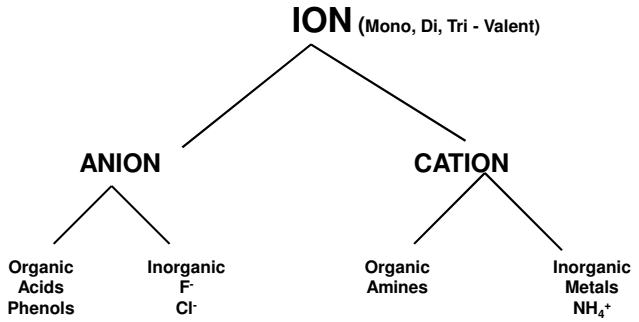


Ion Chromatography

ION EXCHANGER



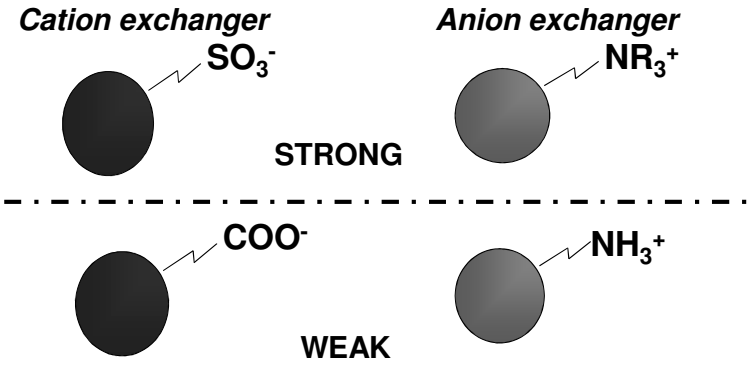
Analysis of Ions - Ion Chromatography



Ions can be characterized as:
organic or inorganic, anion or cation, mono or polyvalent.

Ion Exchange Theory

Strong vs. Weak Exchange Materials



Strong Exchangers stay ionized as pH varies between 2 and 12.
Weak exchangers can lose ionization as a functionof pH.

Ion Exchange - Bonded Functionalities

	Cation	Anion
WEAK	$\sim\sim COO^- Na^+$ Carboxylic Acid	$\sim\sim N^+(H)(R)\text{-}R\ Cl^-$ Primary, Secondary or Tertiary Amine
STRONG	$\sim\sim SO_3^- Na^+$ Sulfonic Acid	$\sim\sim N^+(R)(R)\text{-}R\ Cl^-$ Quaternary Amine

Typical chemical functionalities used for commercial exchangers.

Ion Chromatography

Columns' Matrices

- Silica-Based
- Polymer-based ion-exchangers
- Hydrous Oxide

$$\text{=M-O-H} \rightleftharpoons \text{=M-O}^- + \text{H}^+$$

$$\text{=M-O-H} \rightleftharpoons \text{=M}^+ + \text{OH}^-$$

Ion Exchange Theory

Packing Supports

Resin	Silica-Based

- **Capacity**
- **Swelling**
- **Mass Transfer**
- **Size Separation**
- **Reverse Phase**
- **Efficiency**
- **pH Range**
- **Equilibration**
- **Literature**

Both resin and silica based ion exchangers have advantages and disadvantages which are summarized here.

ION EXCHANGE

ANIONS

RETENTION ORDER: Charge/Size Ratio

$$A^- < A^{--} < A^{---}$$

When the charge is the same: charge/size determines the retention

$$F^- , OH^- > OAc^- > H_2PO_4^- > HCO_3^- > Cl^- > NO_2^- >$$

$$HSO_3^- > CN^- > Br^- > NO_3^- > I^-$$

ION EXCHANGE

CATIONS

Retention Order

MONO-VALENT

$$Li^+ > H^+ > Na^+ > NH_4^+ > K^+ > Rb^+ > Cs^+ > Ag^+$$

DI-VALENT

$$Be^{++} > Mn^{++} > Mg^{++} > Zn^{++} > Co^{++} > M^{++} > Ca^{++} > Sr^{++}$$

transition metals

TRI-VALENT

$$Al^{+++} > M^{+++} > Ce^{+++}$$

Transition metals

Ion Chromatography

Properties of Mobile phases

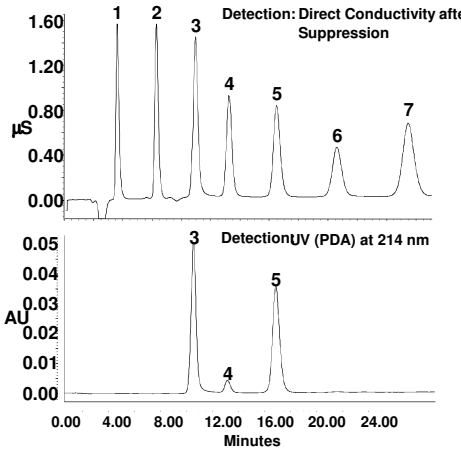
- Compatibility with the detection mode - Suppressed or Non-suppressed (Conductivity Detector).
- Nature of the competing ion
- Concentration of the competing ion
- Mobile phase's pH
- Buffering capacity of the mobile phase
- Ability to complex the ionic sample components
- Organic modifiers

Ion capacity

The number of functional groups per unit weight of the stationary phase.

A typical ion-exchange capacity in IC is 10-100 mequiv/g.

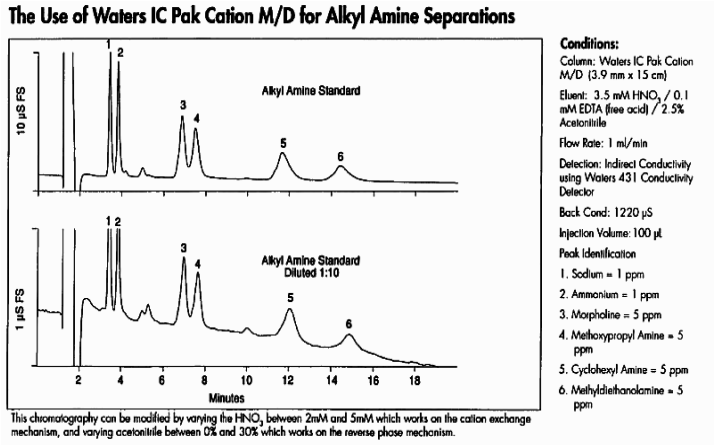
Conductivity and PDA Detectors in Series Anion Exchange



1. Fluoride 1 ppm
2. Chloride 2 ppm
3. Nitrite 4 ppm
4. Bromide 4 ppm
5. Nitrate 4 ppm
6. Phosphate 6 ppm
7. Sulfate 4 ppm

Column: Waters IC-Pak Anion HR
Eluent: 1.2 mM Sodium Carbonate/ 1.2 mM Sodium Bicarbonate
Flow rate: 1.0 mL/min
Injection vol. 50 µL

Cation Exchange



Ion Chromatography

IONIZATION and RETENTION

WEAK ACIDS

$HA \rightleftharpoons H^+ + A^-$

pKa~ 4-5

At pH >4-5 the main species is A^-

WEAK BASES

$HB^+ \rightleftharpoons H^+ + B$

pKa ~ 7-8

At pH < 7-8 the main species is BH^+

The Equilibrium Constant

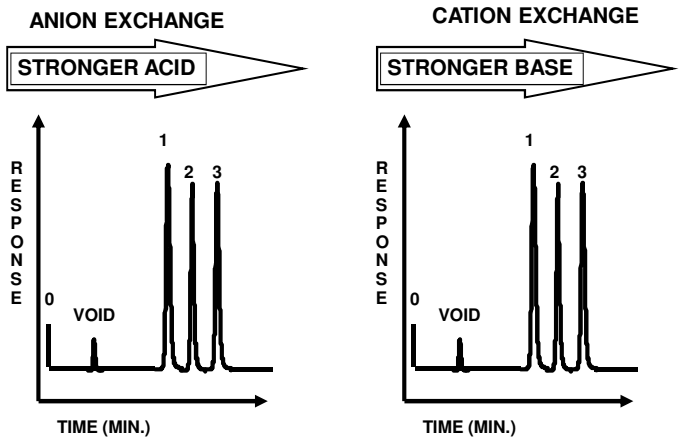
$$HAc \rightleftharpoons H^+ + Ac^- \qquad K_a = \frac{(H^+)\,(Ac)}{(HAc)}$$

pH and pK_a

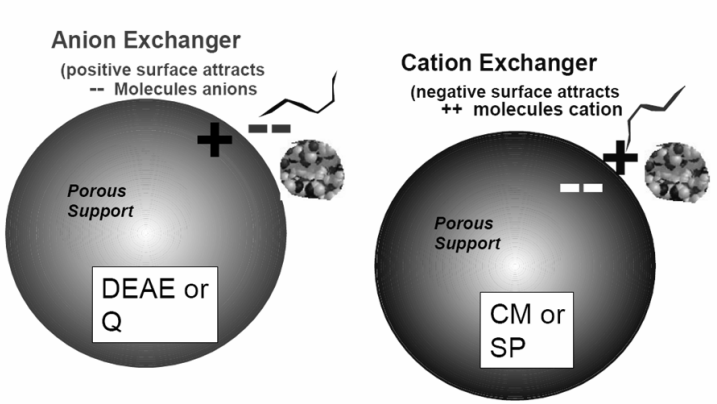
$$(H^+) = K_a \frac{(HAc)}{(Ac)} \qquad pH = pK_a - \log\frac{(HAc)}{(Ac^-)}$$

A general understanding of ionization constants, pH, and pK_a are useful in understanding ion exchange and buffer phenomena.

ELUTION ORDER IN ION EXCHANGE



Ion Exchange of Proteins



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