Ion Exchange Chromatography

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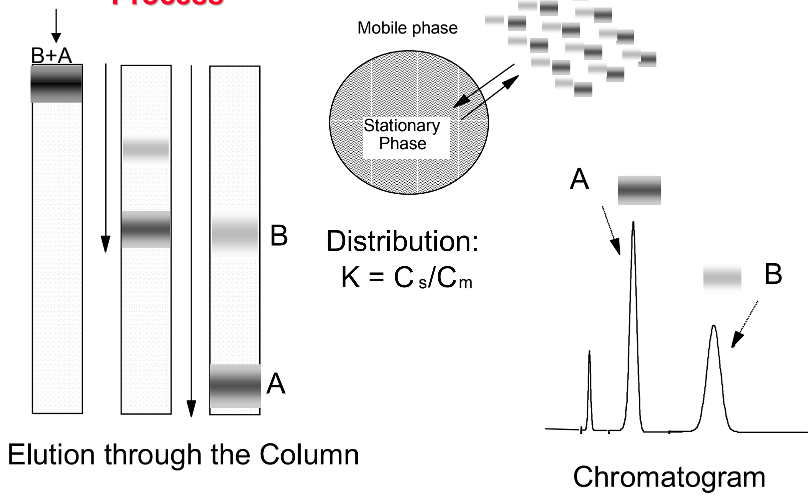
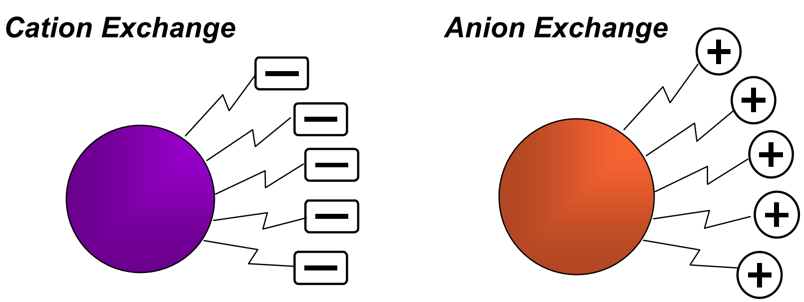
Chromatographic Process



Ion Exchange Theory

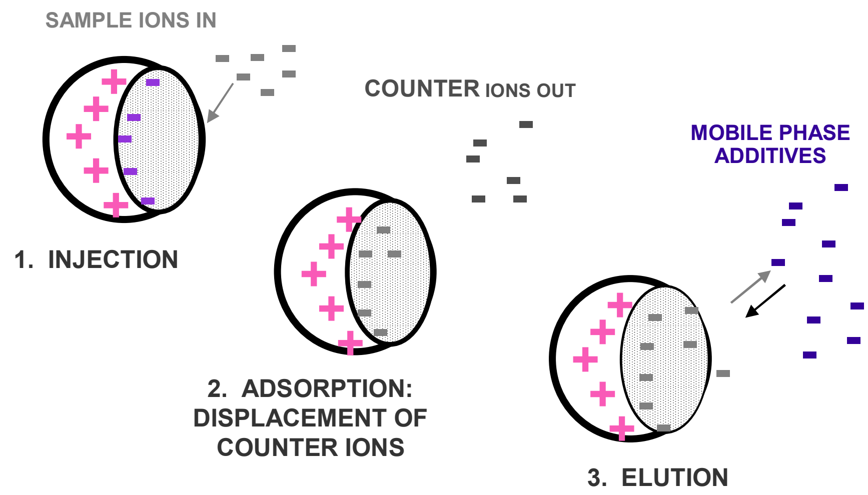
Cation Exchange vs Anion Exchange



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

ION EXCHANGE

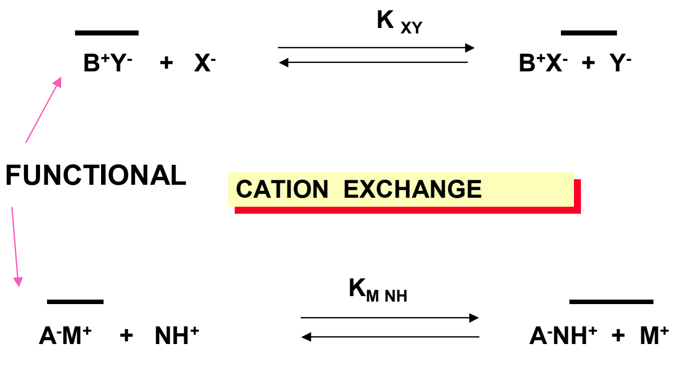
INSIDE A PORE IN THE STATIONARY PHASE



ION EXCHANGER

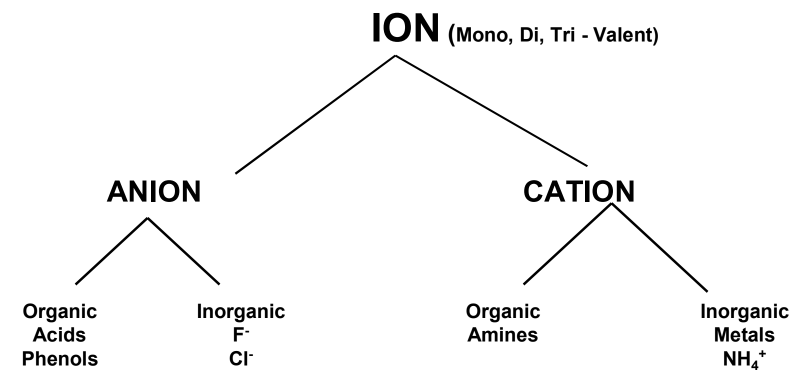
ANION EXCHANGE

CATION EXCHANGE



— IMMOBILIZED ON THE STATIONARY PHASE

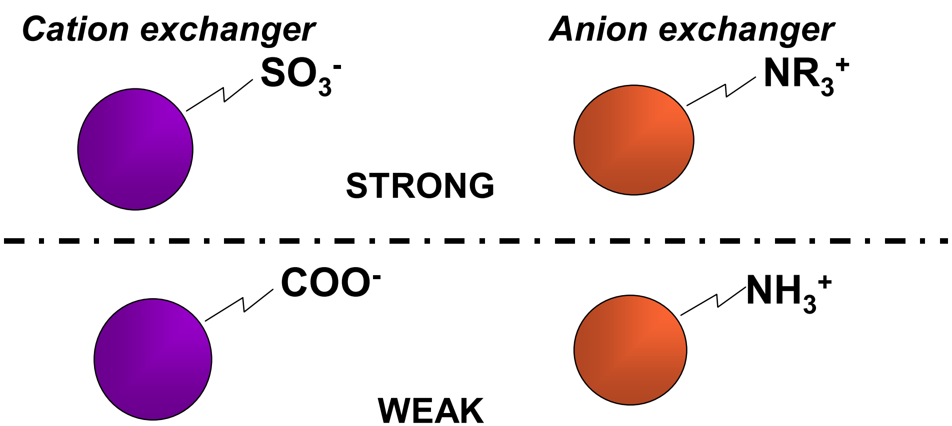
Analysis of Ions - Ion Chromatography



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	~~ COO^- Na^+ Carboxylic Acid	~~ N^+-R Cl^- (with R above, H below) Primary, Secondary or Tertiary Amine
STRONG	~~ SO_3^- Na^+ Sulfonic Acid	~~ N^+-R Cl^- (with R above, R below) Quaternary Amine

Typical chemical functionalities used for commercial exchangers.

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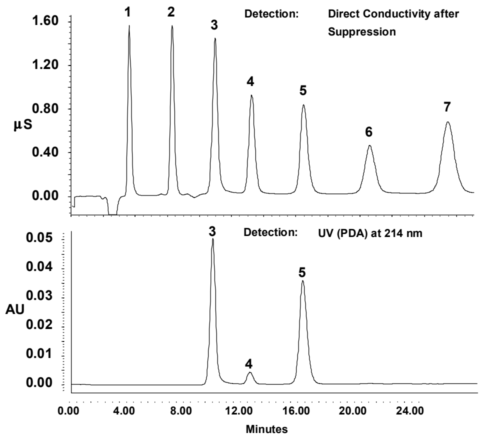
Conductivity and PDA Detectors in Series



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

Functional groups

CATION EXCHANGERS		ANION EXCHANGERS	
TYPE	FUNCTIONAL GROUP	TYPE	FUNCTIONAL GROUP
Sulfonic acid	$-SO_3^- H^+$	Quaternary amine	$-N(CH_3)_3^+ OH^-$
Carboxylic acid	$-COO^- H^+$	Quaternary amine	$-N(CH_3)_2(EtOH)^+$
Phosphonic acid	$PO_3^- H^+$	Tertiary amine	$-NH(CH_3)_2^+ OH^-$
phosphinic acid	$HPO_2^- H^+$	Secondary amine	$-NH_2(CH_3)_2^+ OH^-$
Phenolic	$-O^- H^+$	Primary amine	$-NH_3^+ OH^-$
Arsonic	$-HAsO_3^- H^+$		
Selenonic	$-SeO_3^- H^+$		

Columns' Matrices

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

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

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 & ELUTION STRENGTH

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

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

$$A^{---} > A^{--} > A^-$$

ION EXCHANGE

CATIONS

RETENTION & ELUTION STRENGTH

MONO-VALENT

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

DI-VALENT

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

transition metals

TRI-VALENT

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

Transition metals

Properties of Mobile phases

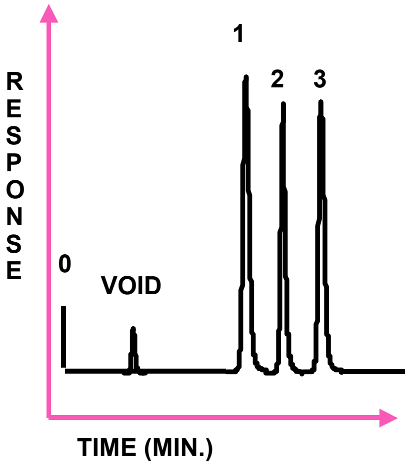
- Compatibility with the detection mode - Suppressed or Non-suppressed.
- Nature of the competing ion
- Concentration of the competing ion
- Mobile phase's pH
- Buffering capacity of the mobile phase
- Ability to complex the ionic sample components
- Organic modifiers

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.

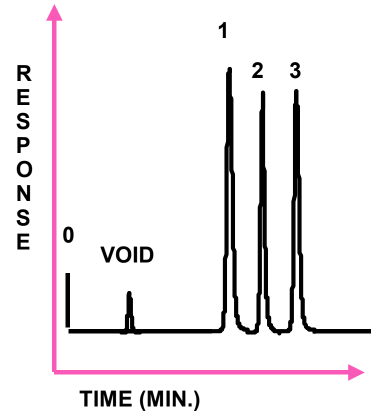
ELUTION ORDER IN ANION EXCHANGE



DENSITY OF CHARGE

1	2	3
OAc^-	OH^-	F^-
1	2	3
Cl^-	NO_3^-	NO_2^-
1	2	3
NO_3^-	SO_4^{2-}	SO_3^{2-}

ELUTION ORDER IN CATION EXCHANGE



DENSITY OF CHARGE

1	2	3
K^+	Na^+	Li^+
1	2	3
Ag^+	Zn^{++}	Al^{+++}

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

$$HAc \underset{k^2}{\overset{k^1}{\longleftrightarrow}} H^+ + Ac^- \qquad K_a = \frac{(H^+)\,(Ac)}{(HAc)}$$

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