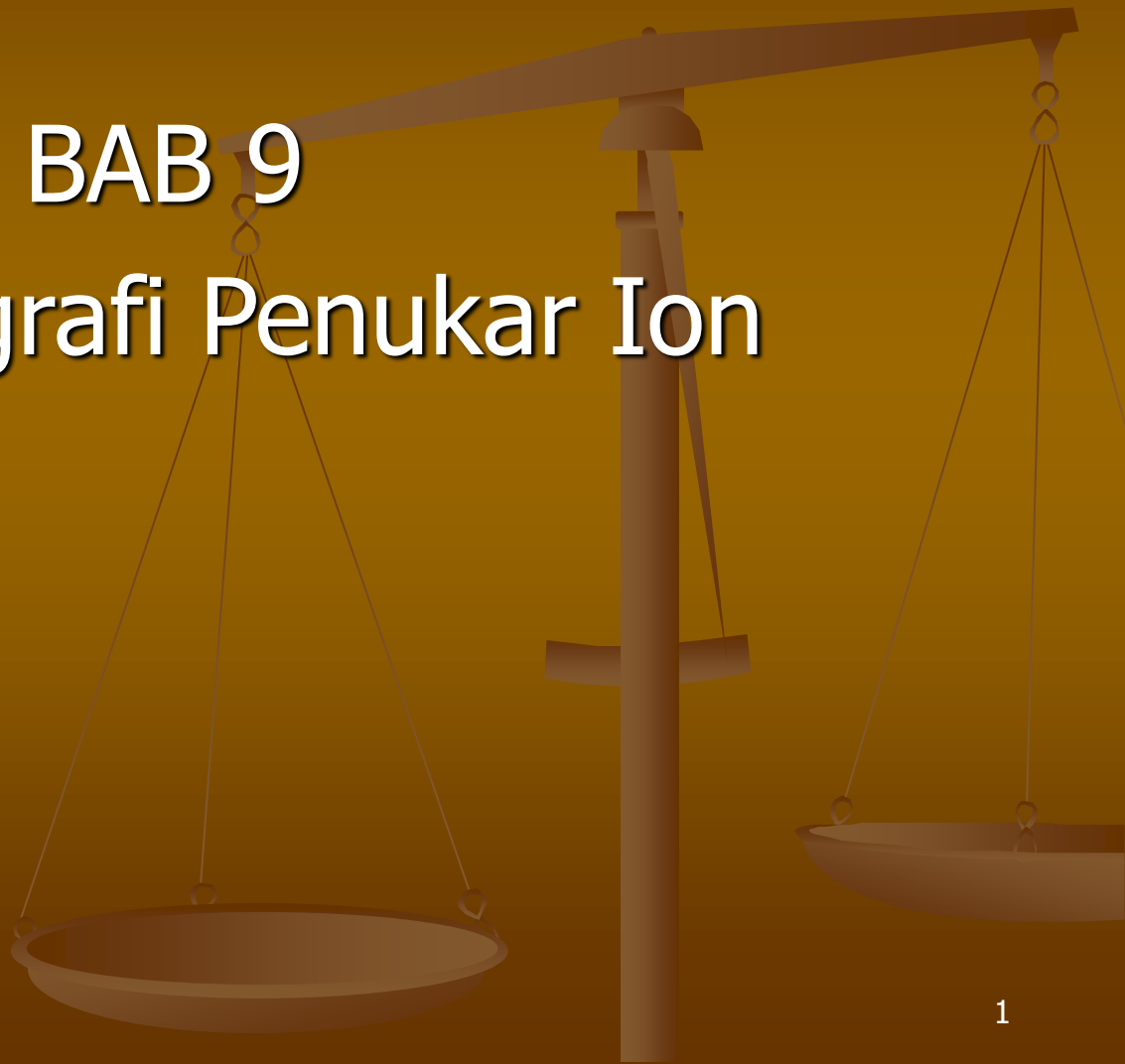
BAB 9
Kromatografi Penukar Ion



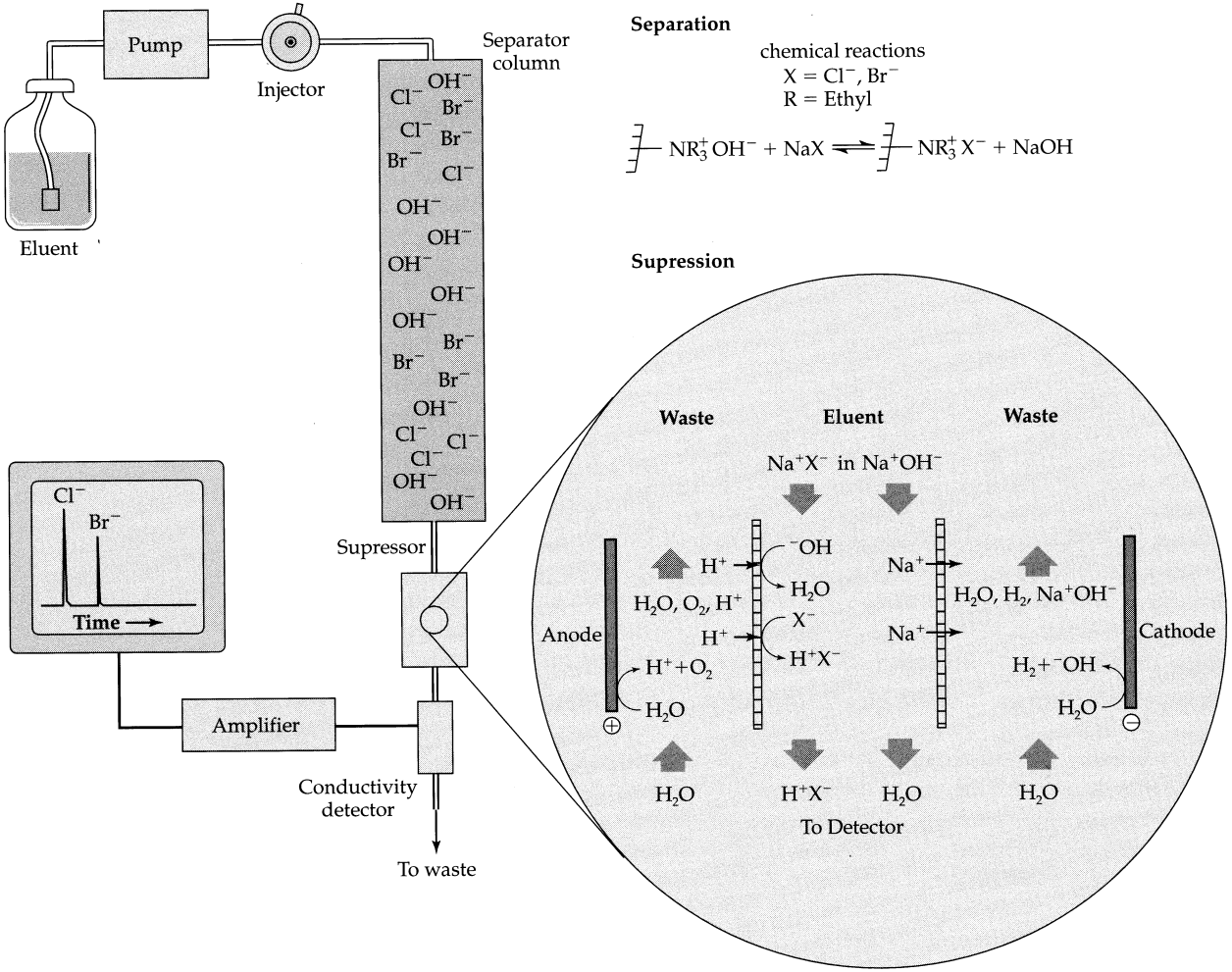


FIGURE 14.6(b) ▲
The mechanisms of ion chromatography.

Ion chromatography employs a standard HPLC apparatus and an ion-exchange column. For the anions used in this illustration, the separation is done using a quaternary ammonium resin (with $—NR_3^+$ groups). The eluent is aqueous sodium hydroxide solution. The reversible reaction shown in the figure determines the k_i for each ion. (If there were no OH^- in the eluent solution, the anions would not elute but merely bind with and remain on the resin sites with a simultaneous release of the ionically bound hydroxide that they displace.)

After many runs, the hydroxides of the chromatographic column will have been exchanged, leaving the resin predominantly in the multianion form. The resin must be **regenerated** periodically by passing a solution high in OH^- through the column, reversing the ion-exchange reaction and regenerating the hydroxy form.

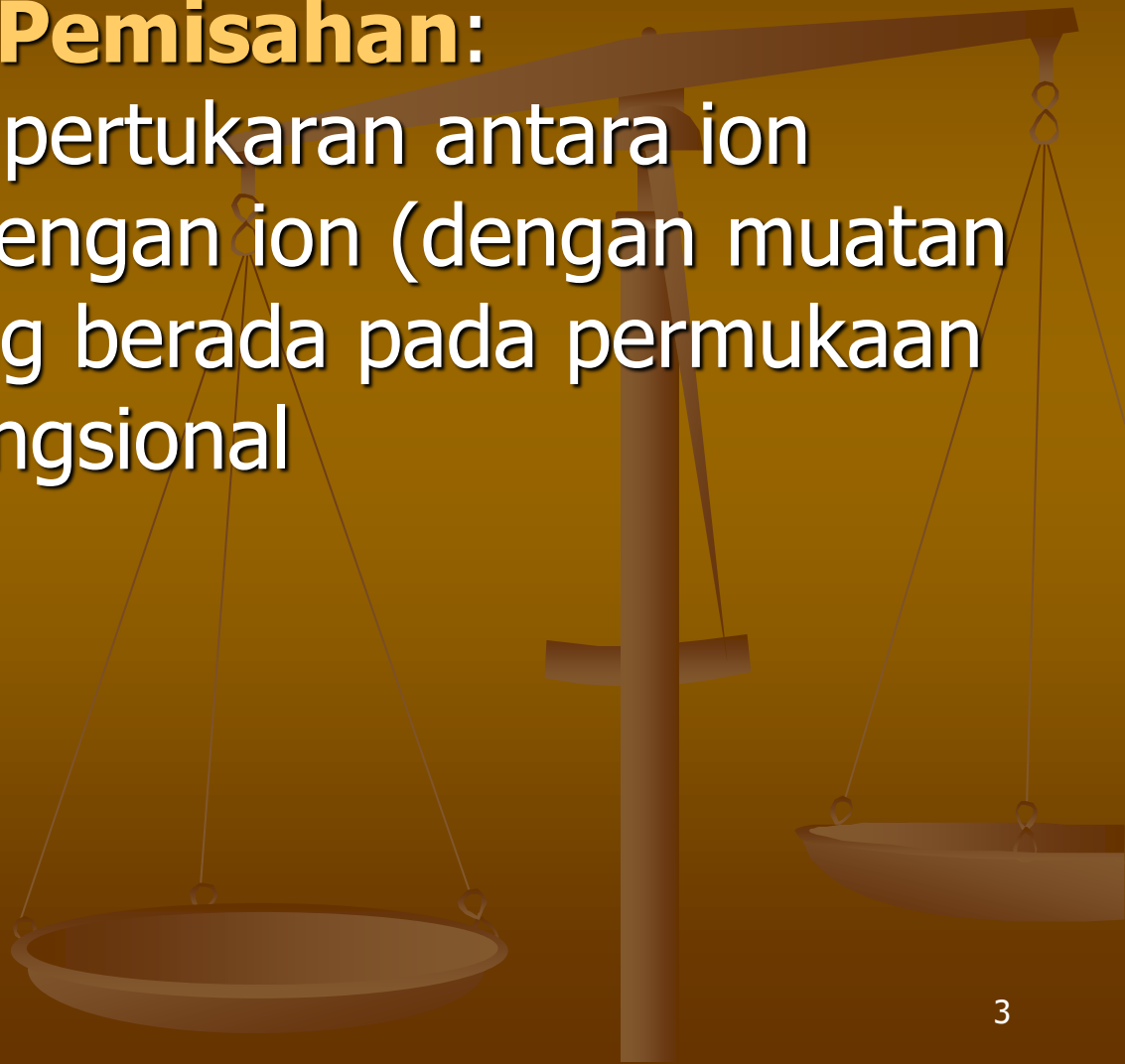
The suppressor reduces the background by neutralizing the eluent OH^- as shown, and increases the signal by substituting higher mobility H^+ ions for Na^+. The suppression is followed by conductivity detection.

Komponen

- Sama dengan instrumen HPLC
  - Reservoirs
  - Pump
  - Injector
  - Column
  - Detector
  - Chromatography Software
- Komponen Spesifik
  - Membrane Suppressor

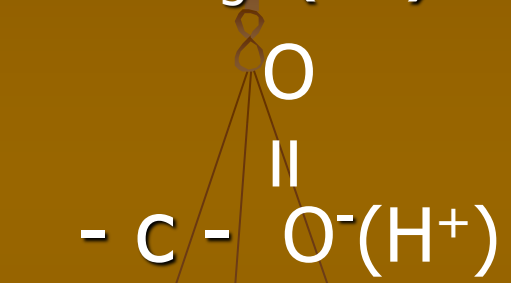
Kromatografi Penukar Ion

- **Prinsip Dasar Pemisahan:** Kesetimbangan pertukaran antara ion dalam larutan dengan ion (dengan muatan yang sama) yang berada pada permukaan ikatan gugus fungsional

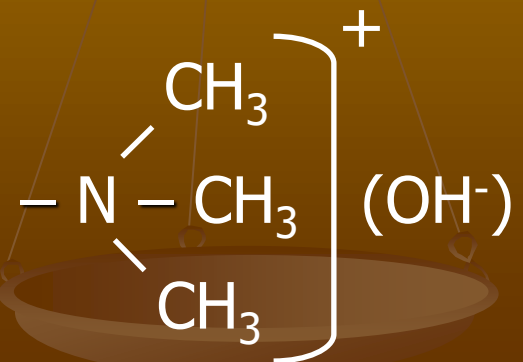


Pertukaran Ion Gugus Fungsi

- Penukar Kation
  - Sulfonic acid – SO_3^- (H^+)
  - Carboxylic Acid

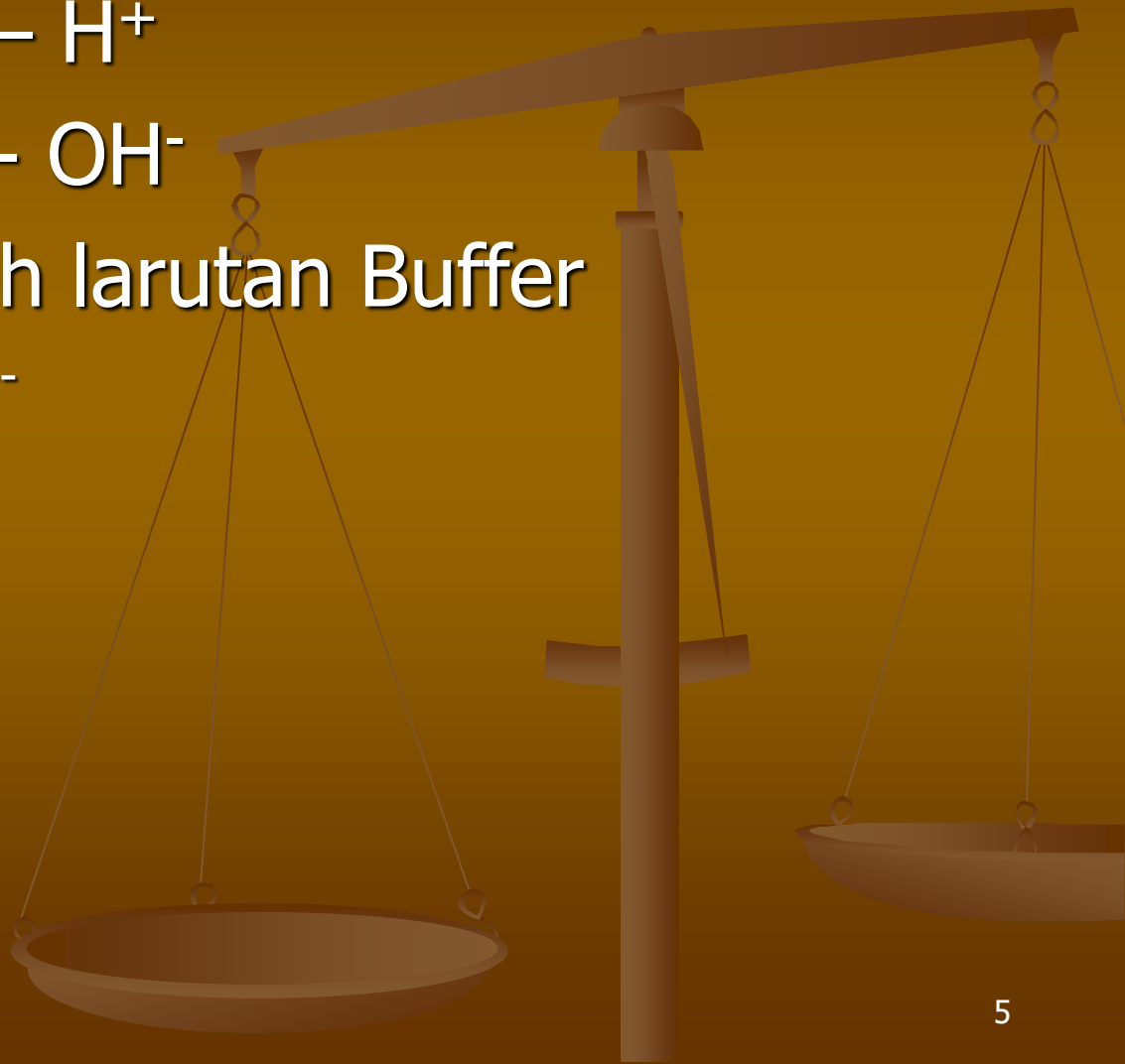


- Penukar Anion
  - Primary Amine – $NH_3^+(OH^-)$
  - Tertiary Amine

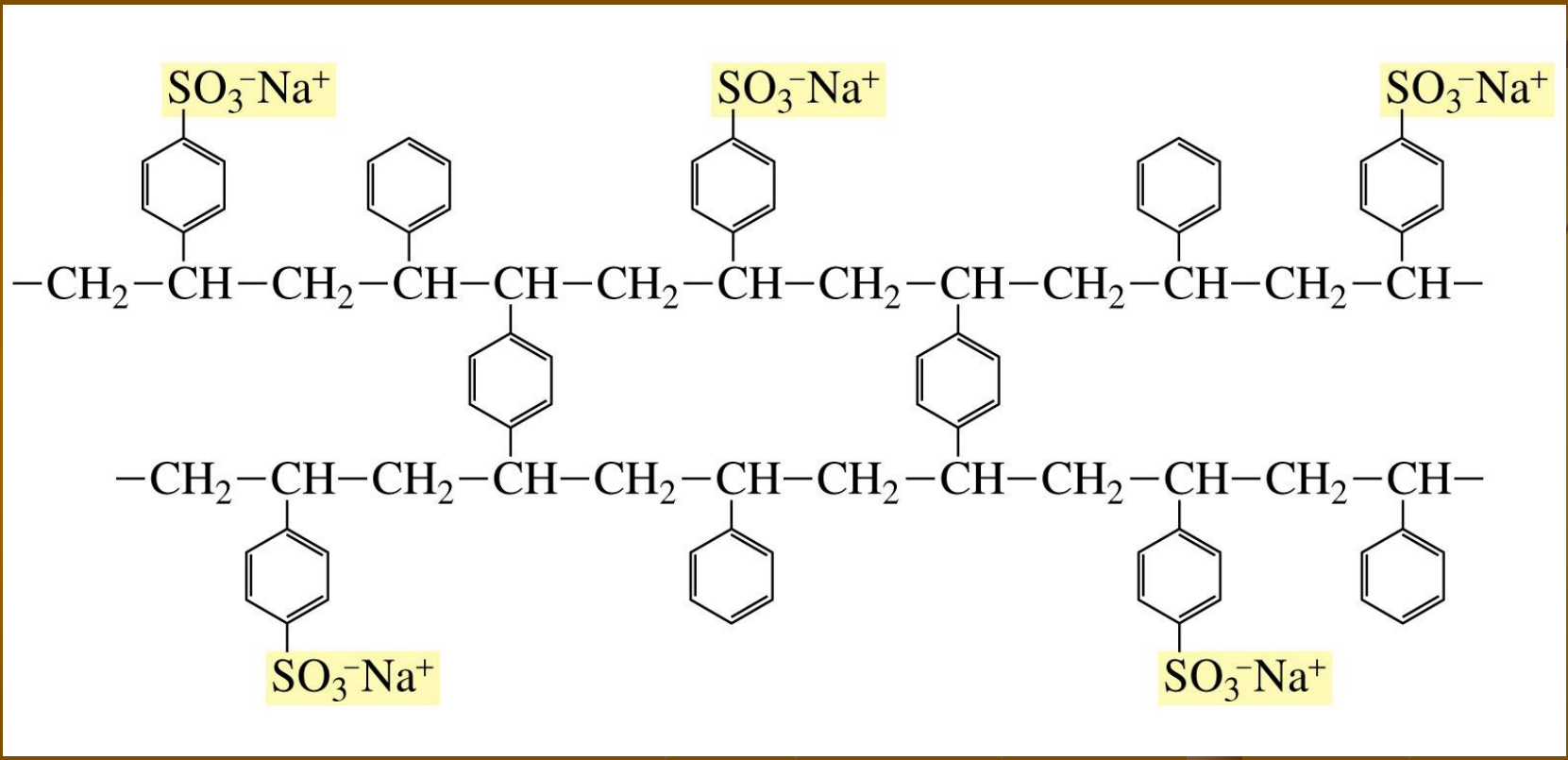


Fasa Gerak

- Penukar kation – H^+
- Penukar anion - OH^-
- pH dikontrol oleh larutan Buffer
  - e.g. HCO_3^-/CO_3^{--}



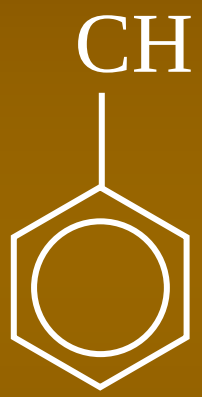
Fasa Diam – Resin Penukar Ion



Fasa Diam sintetik: Resin

- Resin adalah suatu polimer polistirena dengan berat molekul tinggi yang terangkai silang dengan gugus divinil benzena (DVB). Derajat/banyaknya %DVB yang terkandung dalam resin akan menentukan sifat ketahanan dan permeabilitas dari resin. Semakin banyak %DVB resin akan semakin solid, kaku dan sulit ditembus ion lawan (*counter ion*), sehingga efek transfer massa semakin besar dan nilai N akan semakin rendah.
- Ideal 5% - 8 % DVB

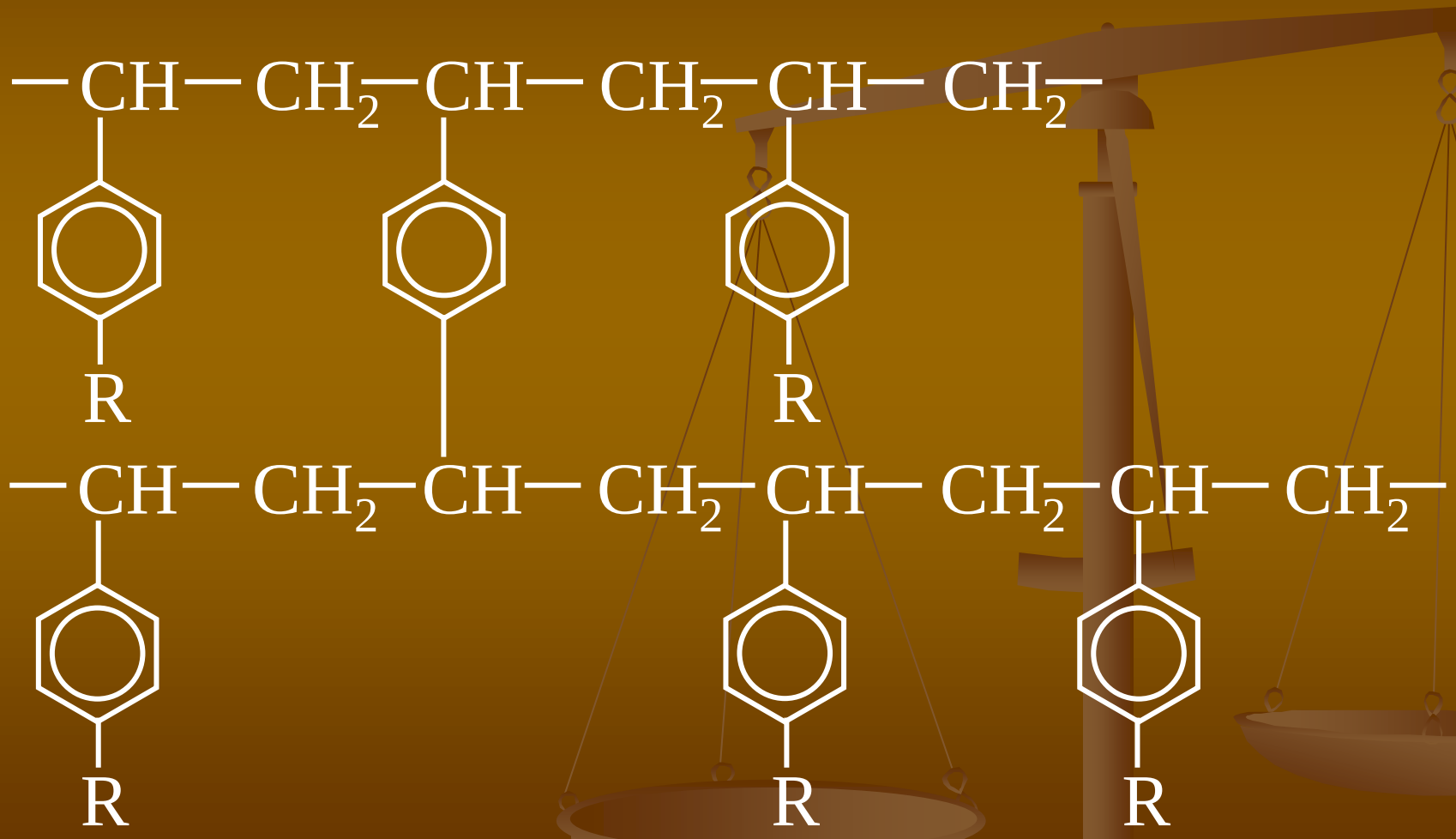
Stationary Phase – Solid Support
"Backbone"



styrene

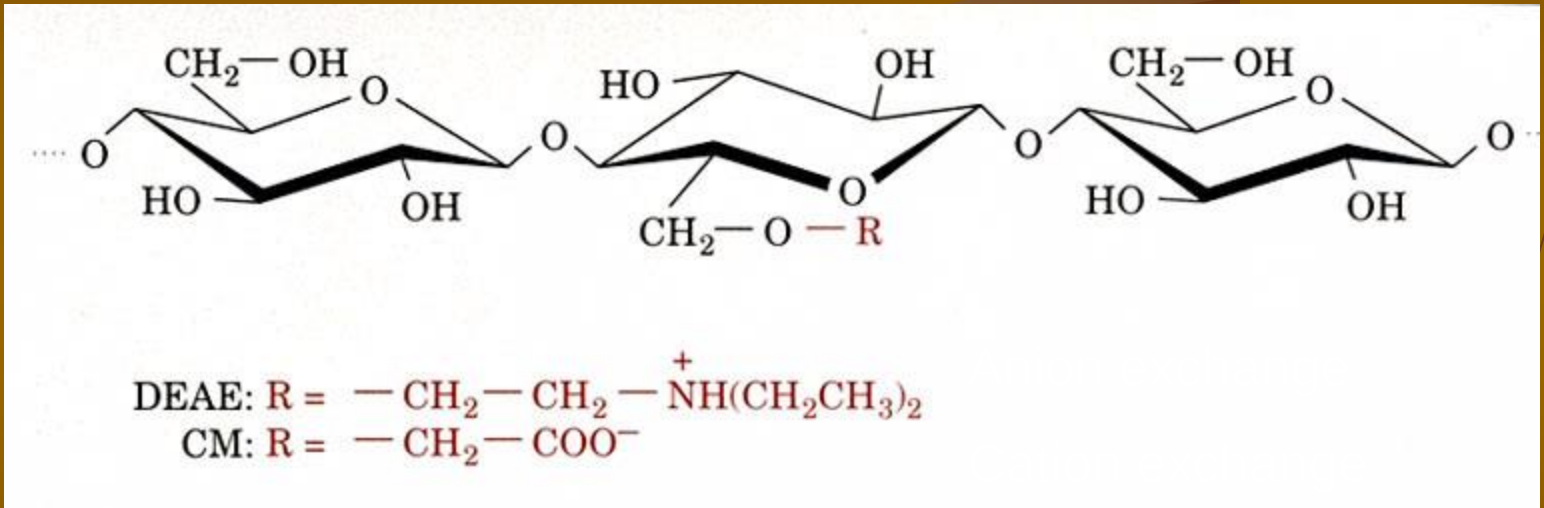
Divinylbenzene (DVB)

Polystyrene Divinylbenzene



Fasa Diam – Resin Penukar Ion

1. **Cellulose** (the cellulose, derived from wood or cotton, is lightly derivatized with ionic groups to form the ion exchanger).



2. **Gel-type ion exchangers**: combine the separation properties of gel filtration with those of ion exchange. Because of their high degree of substitution of charged groups, which results from their porous structures, these gels have a higher loading capacity than do cellulosic ion exchangers.

Pemisahan ion: Ca^{2+} Mg^{2+} Sr^{2+} dan Ba^{2+}

- Exchange equilibrium at the head of the column:

$$2(R\text{-}SO_3\text{-}H) + M^{2+} = (R\text{-}SO_3)_2\text{-}M + 2H^+$$

solid solution solid solution

- Separtion/Elution begins when acid solution is added
  - Equilibrium shifts to the left
  - Cation goes into the mobil phase (momentarily)
  - Cation desorbs/re-adsorbs many times

Pemisahan ion: Ca^{2+} Mg^{2+} Sr^{2+} dan Ba^{2+}

- The time the cation spends in each phase is governed by its unique value of $K_{exchange}$

$$K_{exchange\,reaction} = \frac{[(RSO_3^-)_2M^{2+}]_{solid}\,[H^+]^2_{aq}}{[RSO_3^-H^+]^2_{solid}\,[M^{+2}]_{aq}}$$

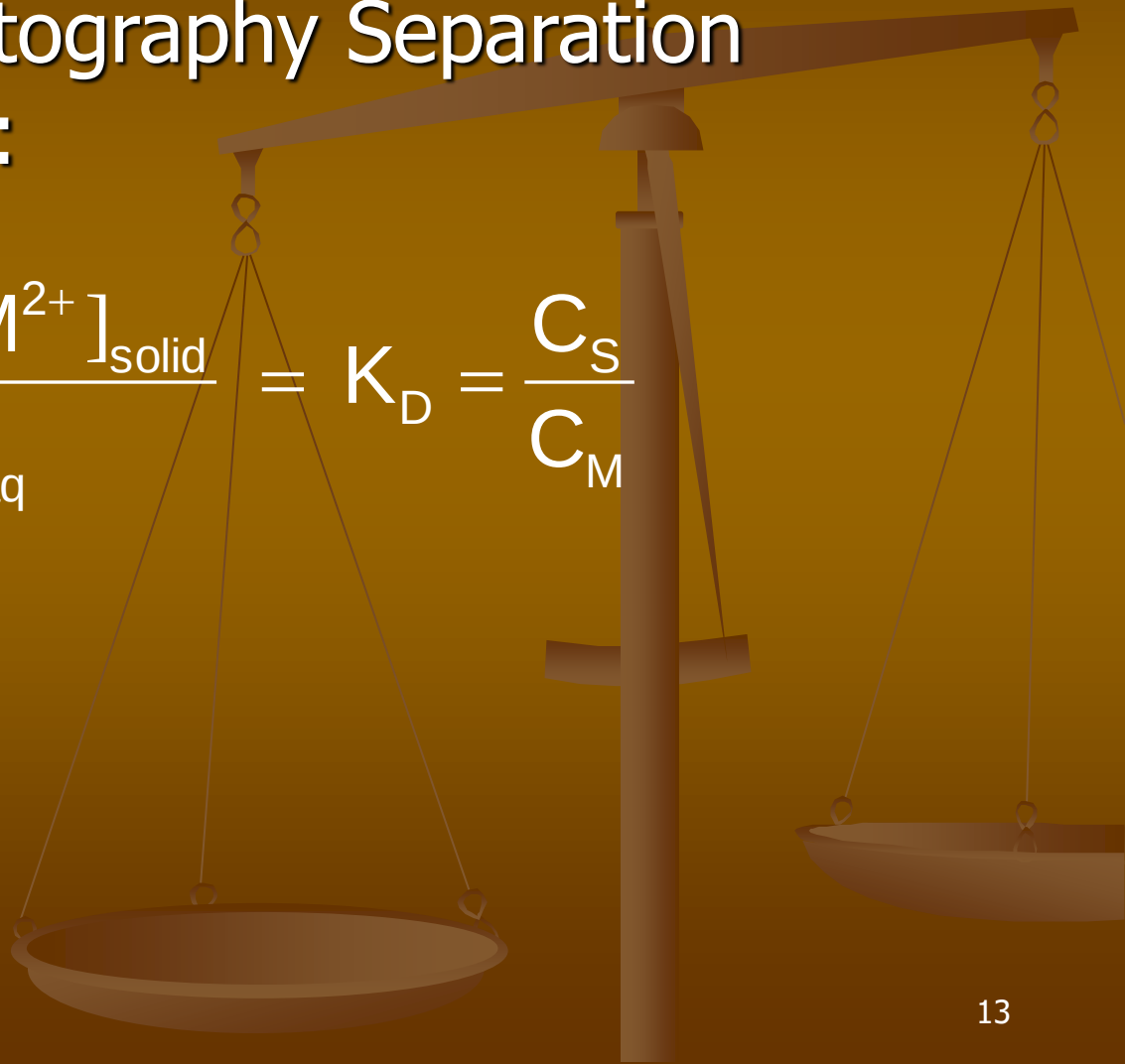
- Rearranging gives:

$$\frac{[(RSO_3^-)_2M^{2+}]_{solid}}{[M^{+2}]_{aq}} = K_{ex}\,\frac{[RSO_3^-H^+]^2_{solid}}{[H^+]^2_{aq}}$$

Pemisahan ion: Ca^{2+} Mg^{2+} Sr^{2+} dan Ba^{2+}

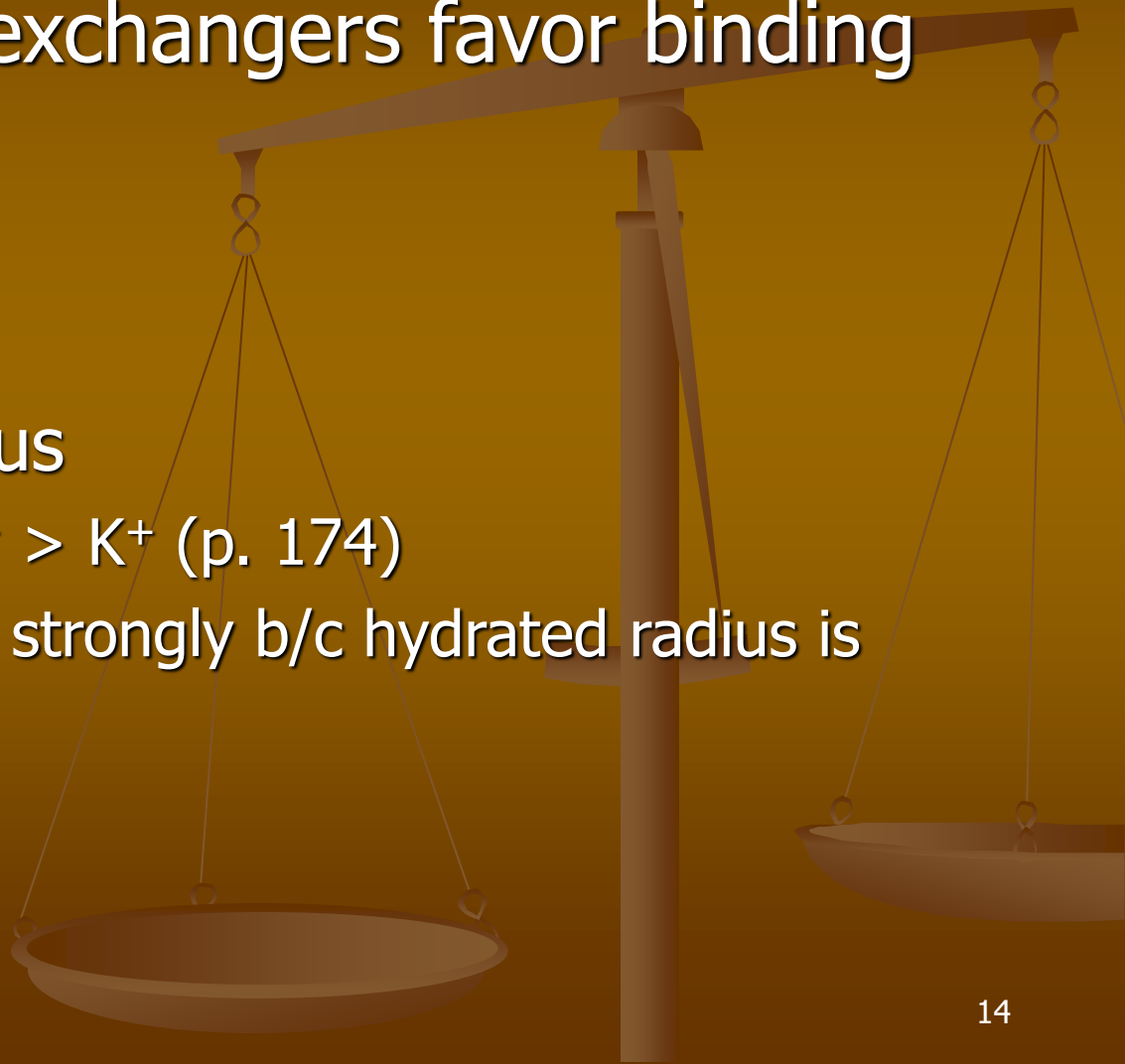
- Normal Chromatography Separation Principles Apply:

$$\frac{[(RSO_3^-)_2M^{2+}]_{solid}}{[M^{+2}]_{aq}} = K_D = \frac{C_S}{C_M}$$



Kromatografi Penukar Ion – Karakteristik Umum

- In general, ion exchangers favor binding of ions with:
  - ↑ charge
    - $3^+ > 2^+ > 1^+$
  - ↓ hydrated radius
    - $H^+ > Li^+ > Na^+ > K^+$ (p. 174)
    - H^+ bound least strongly b/c hydrated radius is highest
  - ↑ polarizability



Example Chromatograms

- Cation Exchange
- Anion Enchange

Concentrations, ppm	
F^-	3
Formate	8
BrO_3^-	10
Cl^-	4
NO_2^-	10
HPO_4^{2-}	30
Br^-	30
NO_3^-	30
SO_4^{2-}	25

Concentrations, ppm	
Ca^{2+}	3
Mg^{2+}	3
Sr^{2+}	10
Ba^{2+}	25

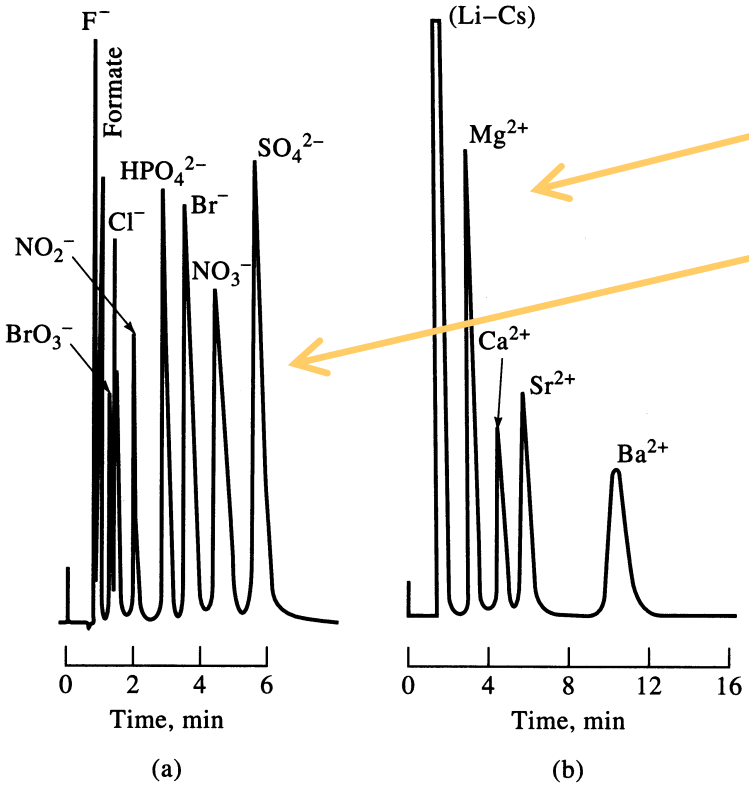


Figure 28-23 Typical applications of ion chromatography. (a) Separation of anions on an anion-exchange column. Eluent: 0.0028 M $NaHCO_3$/0.0023 M Na_2CO_3. Sample size: 50 μL. (b) Separation of alkaline earth ions on a cation-exchange column. Eluent: 0.025 M phenylenediamine dihydrochloride/0.0025 M HCl. Sample size: 100 μL. *(Courtesy of Dionex Corporation, Sunnyvale, CA.)*

Example Chromatograms

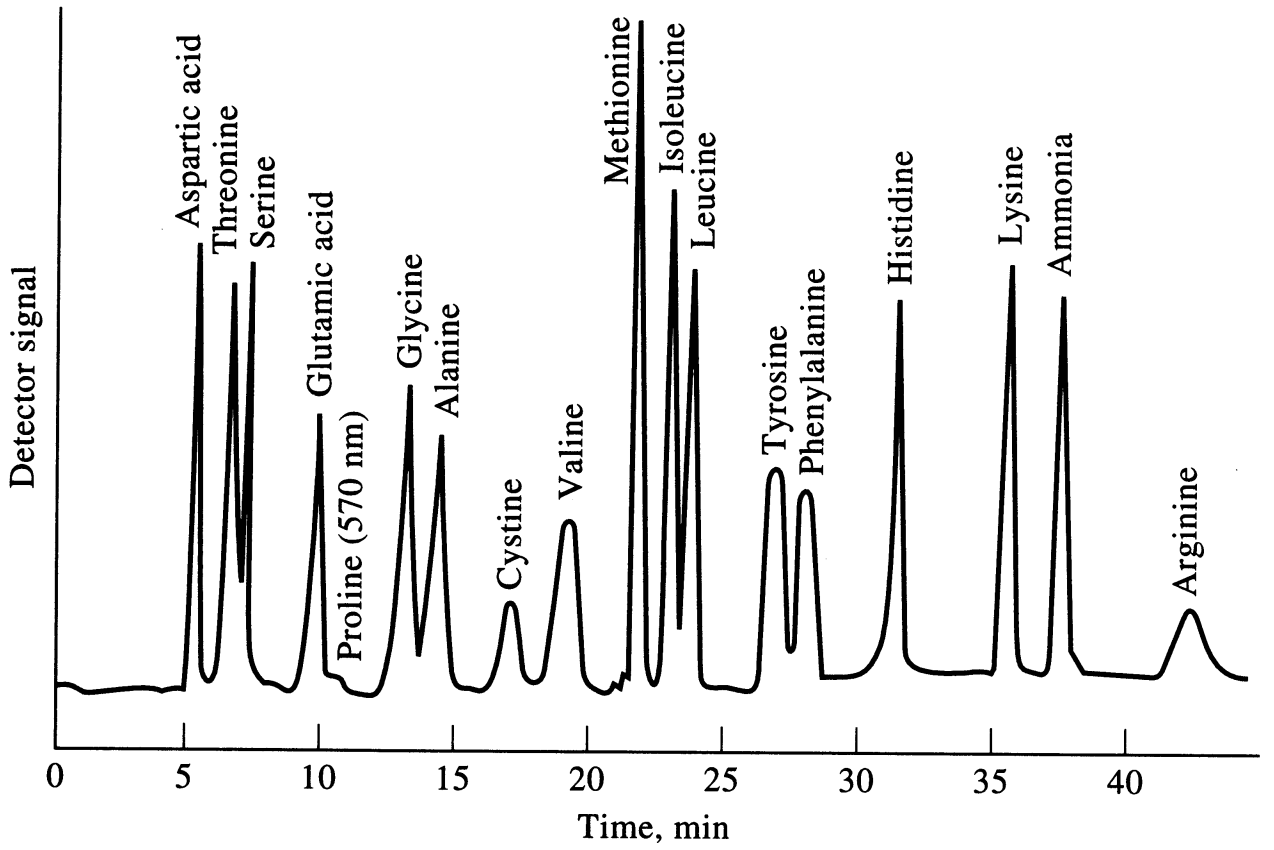
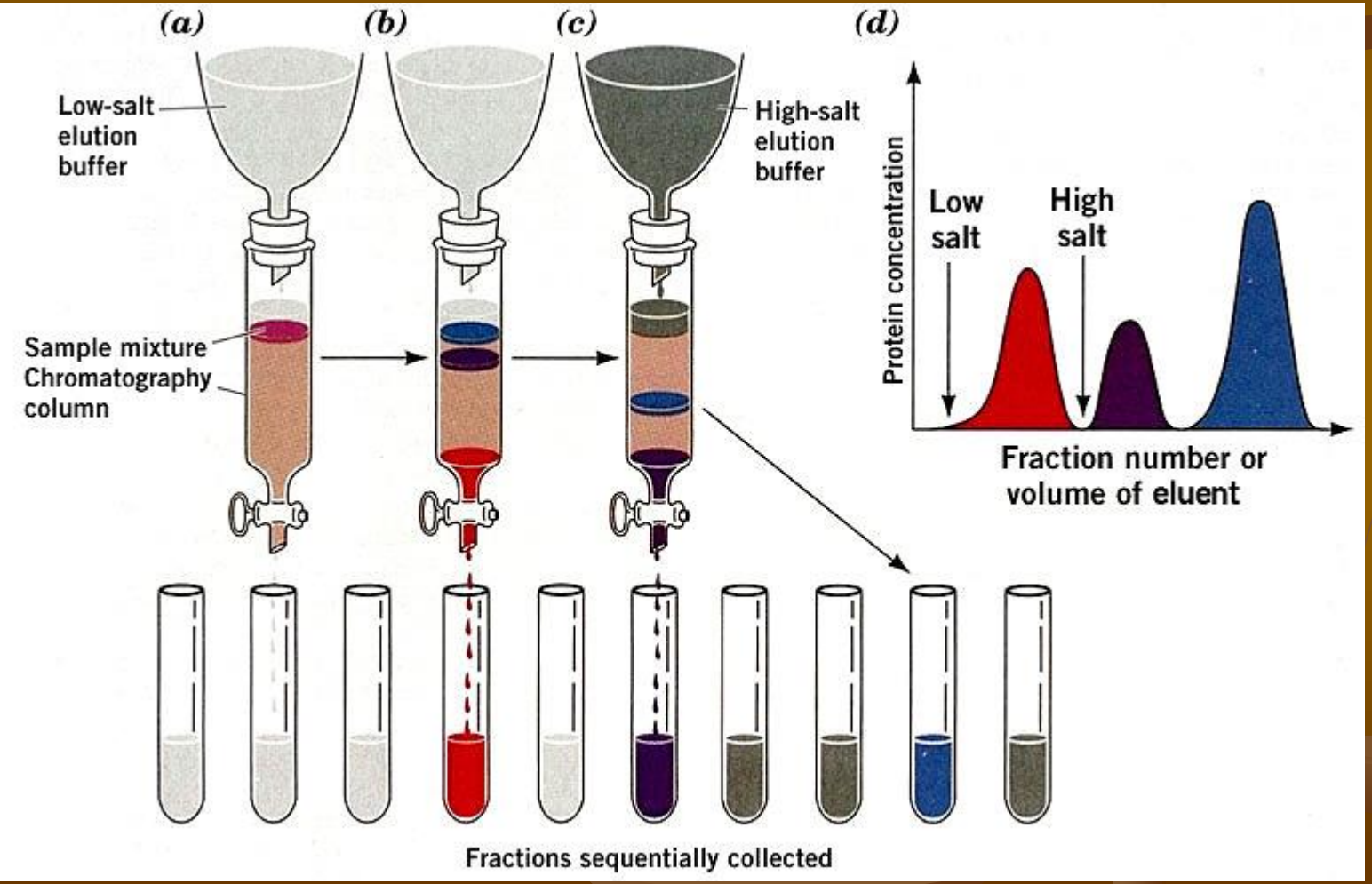


Figure 28-25 Separation of amino acids on an ion-exchange column. Packing: cation exchange with particle size of 8 μm. Pressure: 2700 psi. *(Reprinted with permission from J. R. Benson,* Amer. Lab., ***1972,*** *4(10), 60. Copyright 1972 by International Scientific Communications, Inc.)*

Illustration of Ion Exchange Chromatography



LATIHAN

1. Apa yang dimaksud dengan mode isokratik dan gradien?
2. Jelaskan fungsi kolom supressor?
3. Apa yang harus dilakukan untuk mencegah difusi eddy?
4. Mengapa dapat terjadi efek transfer massa?
5. Tuliskan persaamaan reaksi kesetimbangan pertukaran anion monovalen?
6. Dst.