10.537 Nanomaterial Characterization I

Chromatographic Methods

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UMass Lowell

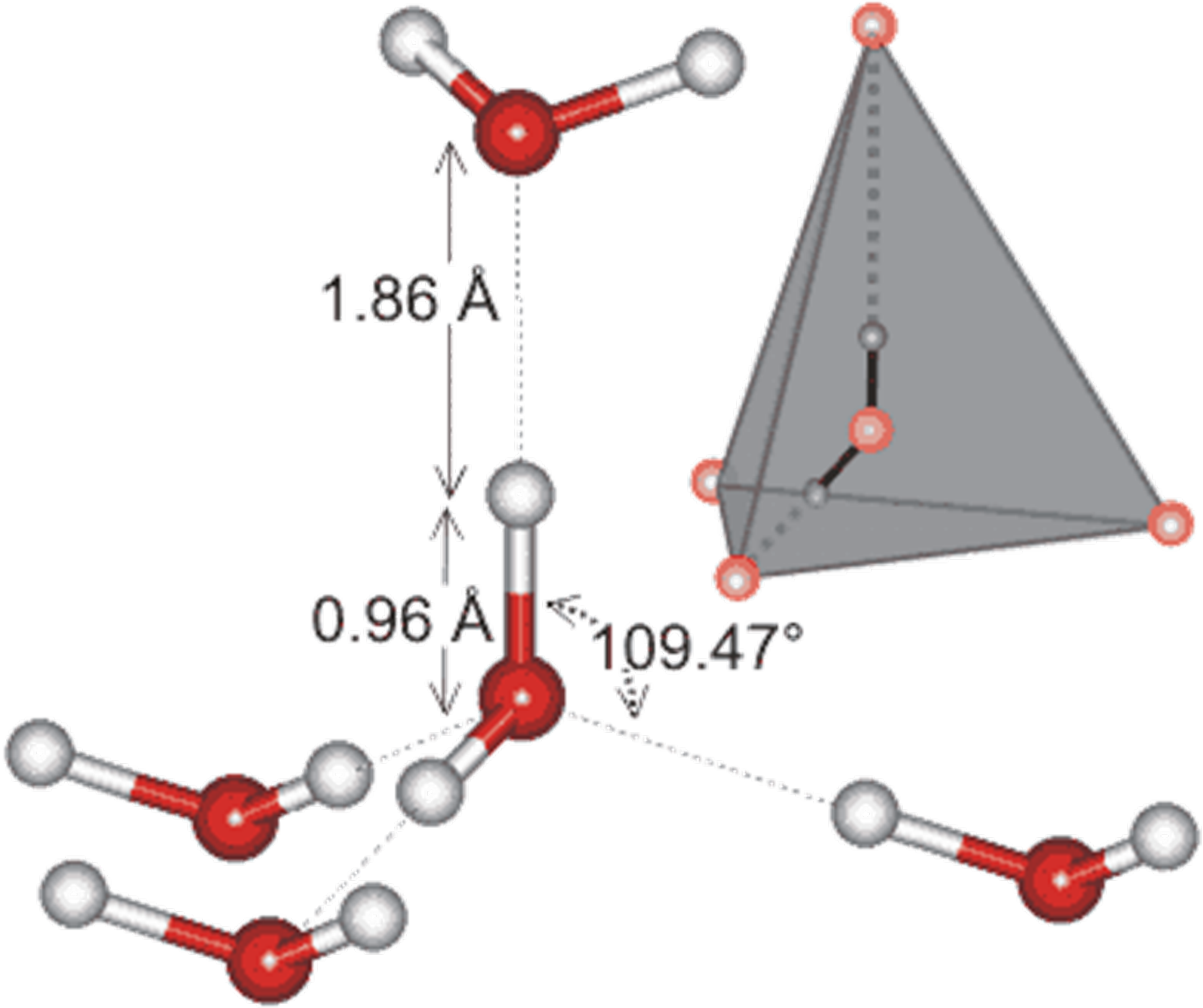
Definitions

- **Analytical Chemistry** – qualitative and quantitative measurement of chemical species
- **Chromatography** – methods for separation and analysis of complex mixtures
- **HPLC** – High Performance Liquid Chromatography
- **GC** – Gas Chromatography

Chromatographic Methods only work for dissolved molecular species

They are not directly applicable to:

- Nanoparticles
- Carbon Nanotubes
- Particulate or colloidal species including:
  - Graphene
  - Elemental nanoparticles
  - Etc.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Introduction to Chromatography

- Chromatography is a separation technique
- HPLC & GC are our primary focus
- Also discuss low pressure column chromatography, not TLC (thin layer) or SFC
- All chromatographic techniques have
  - Stationary phase – solid or viscous liquid phase typically in a column
  - Mobile phase – moves sample in contact with stationary phase

Partitioning = type of equilibrium where the analyte divides itself between two phases

For liquid-liquid extraction – two liquids

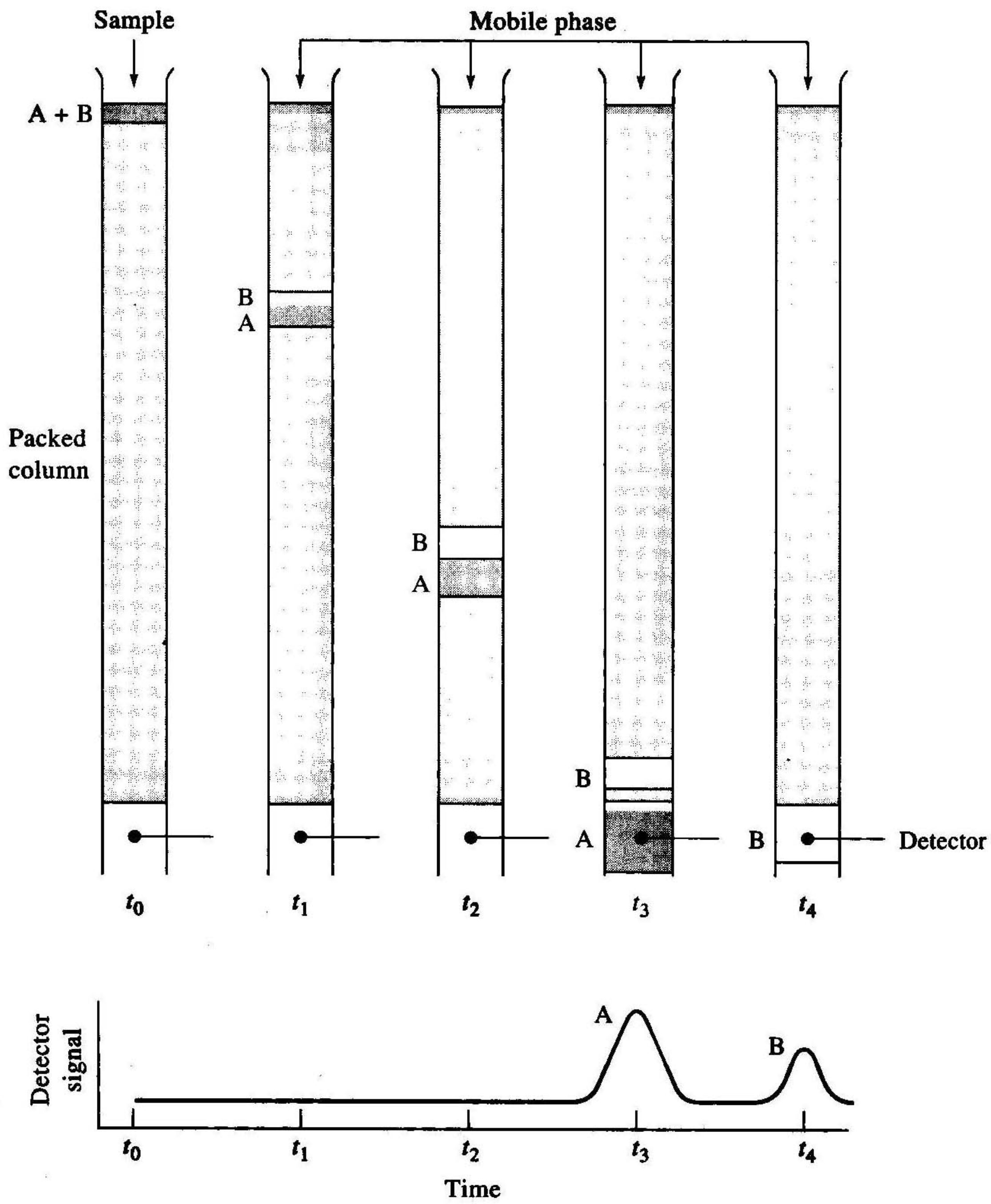
For chromatography – mobile vs. stationary phases

Define a partition ratio K (or distribution constant)

$$K = \frac{C_s}{C_M}$$

where C_s & C_M are concentrations of analyte in stationary & mobile phases

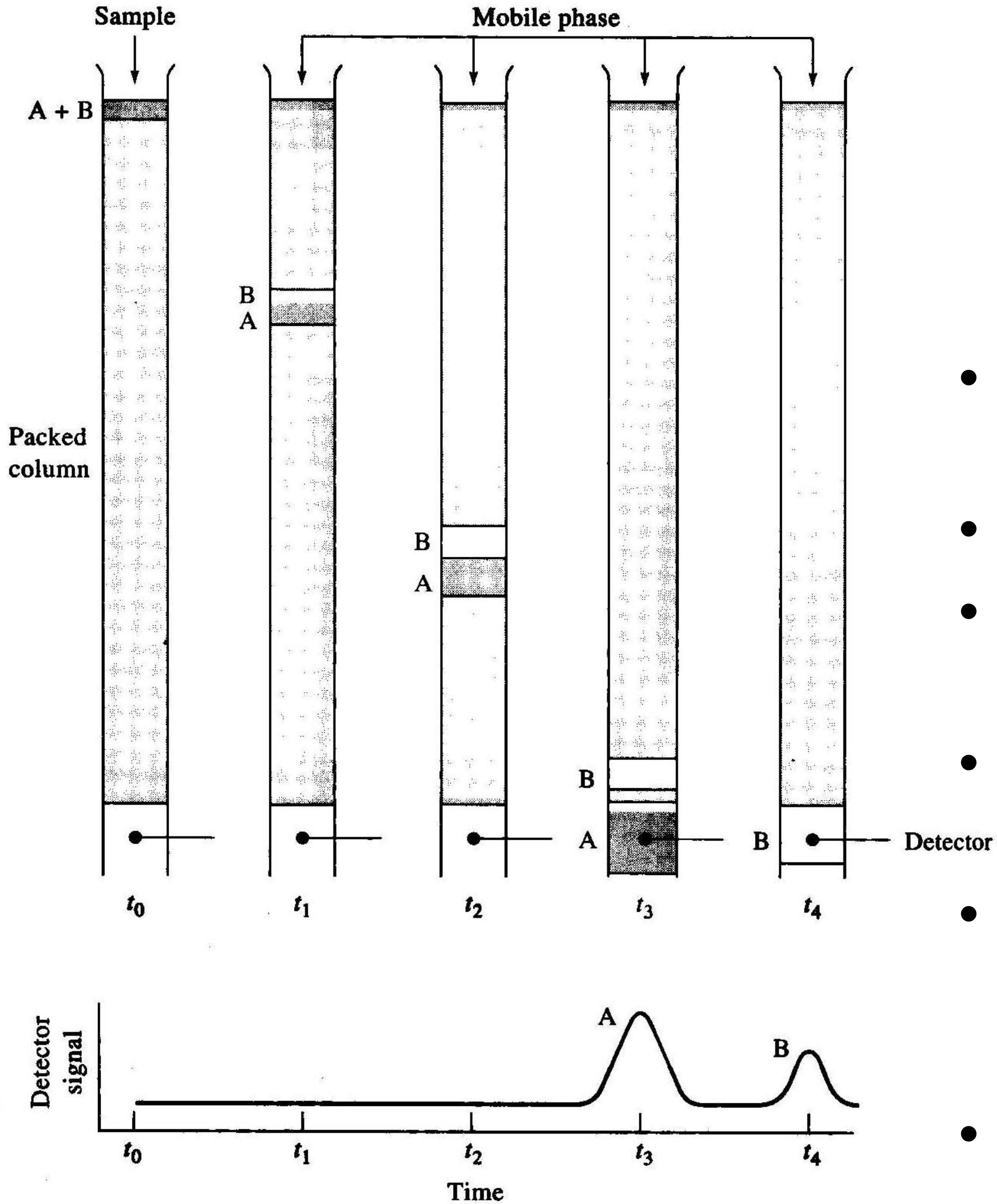
- Prefer if K is constant over conc. range
- If not constant we can work in a narrow range where it is constant
- This is linear chromatography
- In linear chromatography a constant flow rate of mobile phase moves through column
- Elution = process by which analyte is flushed through the column by mobile phase (which could be a liquid or a gas)



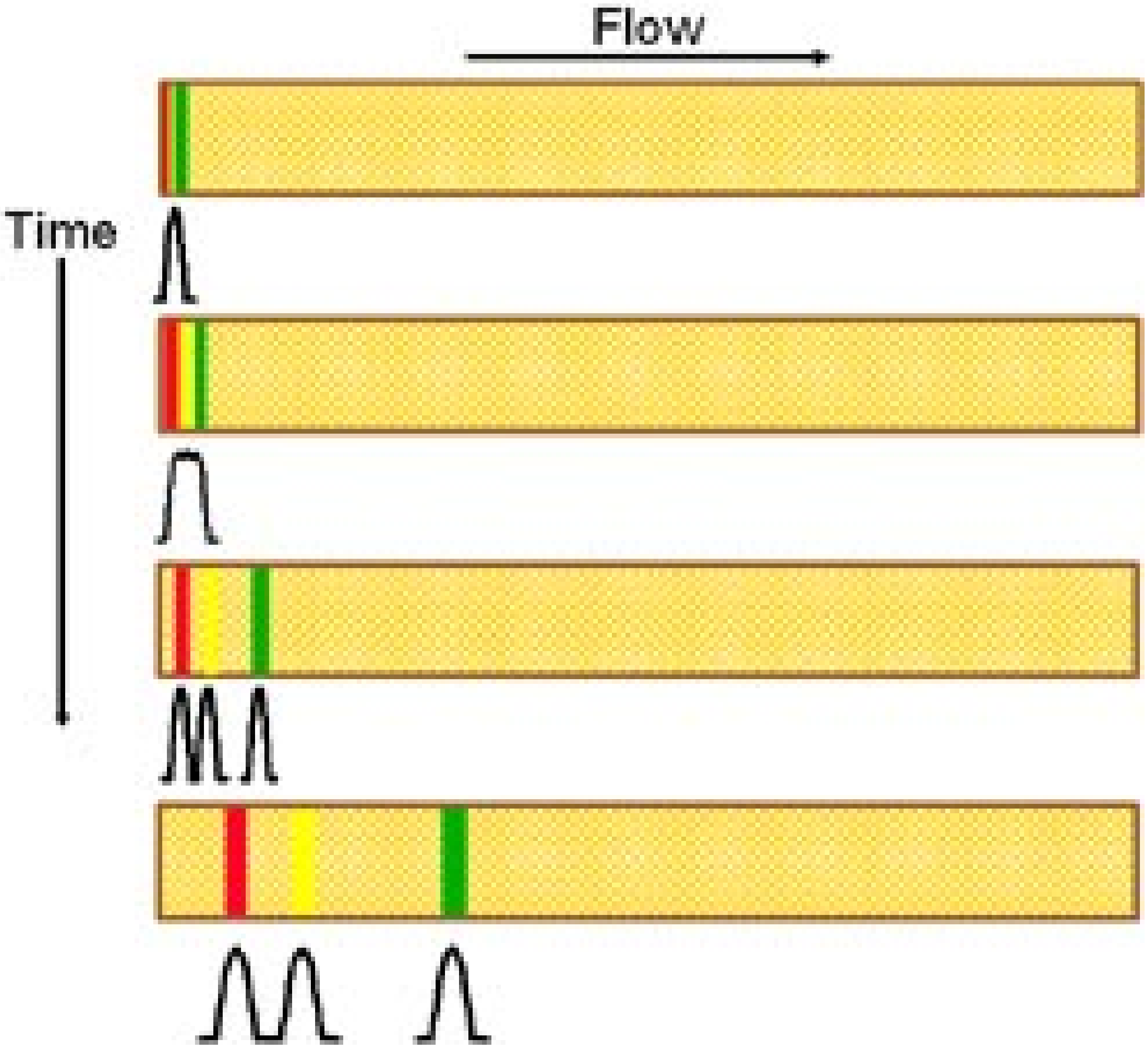
Overview of chromatographic process – packed column

- Inject at t_o
- Separate t_1 to t_3
- Detect at t_4

← Resulting chromatogram



- A & B retained by column differently
- B has higher K
- B takes longer to elute from column
- Detector sees A first then B
- Peak heights & peak areas are proportional to conc.
- Band broadening



Flow
Time

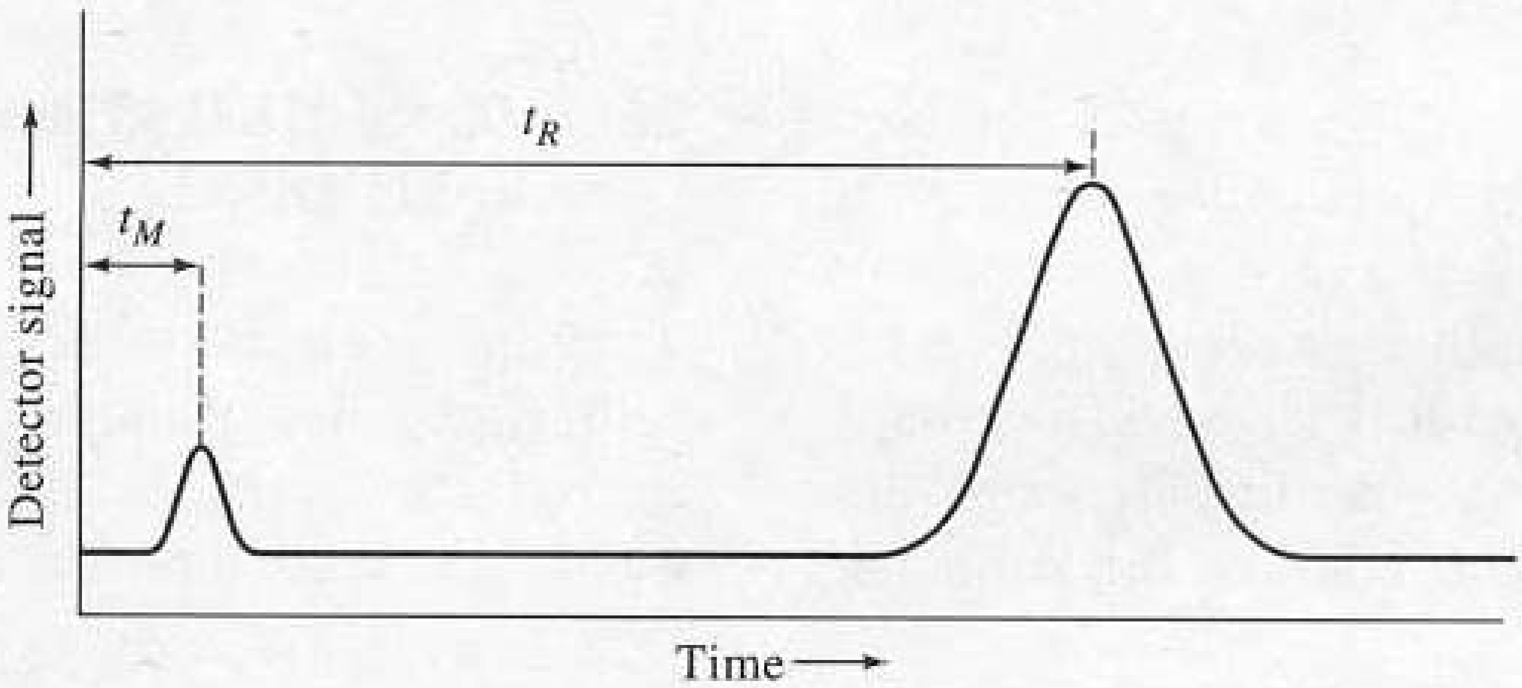
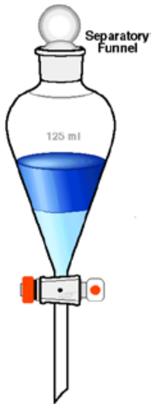


Figure 26-4 A typical chromatogram for a two-component mixture. The small peak on the left represents a species that is not retained on the column and so reaches the detector almost immediately after elution is started. Thus its retention time t_M is approximately equal to the time required for a molecule of the mobile phase to pass through the column.

t_M = time for unretained molecule to reach detector or dead time
t_R = retention time, time for retained species to reach detector

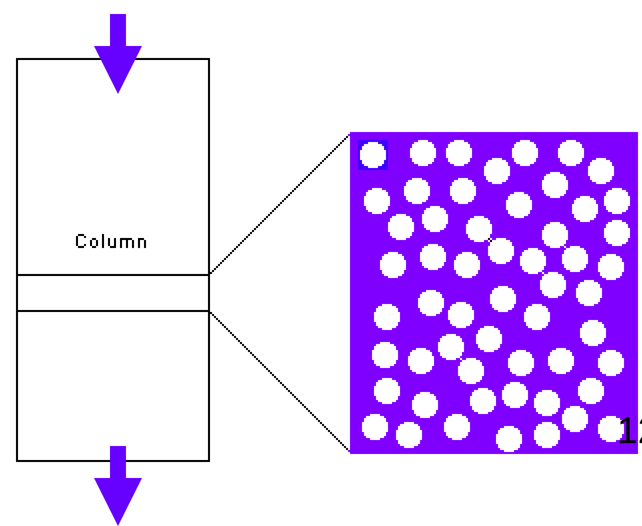
Chromatographic Plate Theory vs. Rate Theory

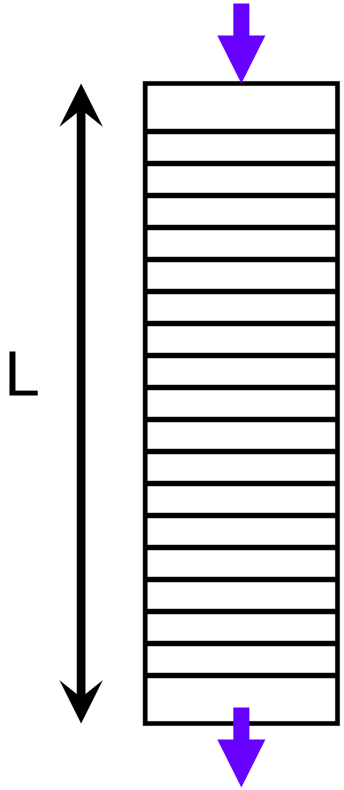


- Plate theory based in liquid-liquid extraction (successive extractions)
- $K = C_{org}/C_{water}$
- Chromatographic column can be thought of in the same way (only continuous process)
- $K = C_s/C_M$

○ Stationary phase bead

■ Mobile phase (liquid)





$L = NH$

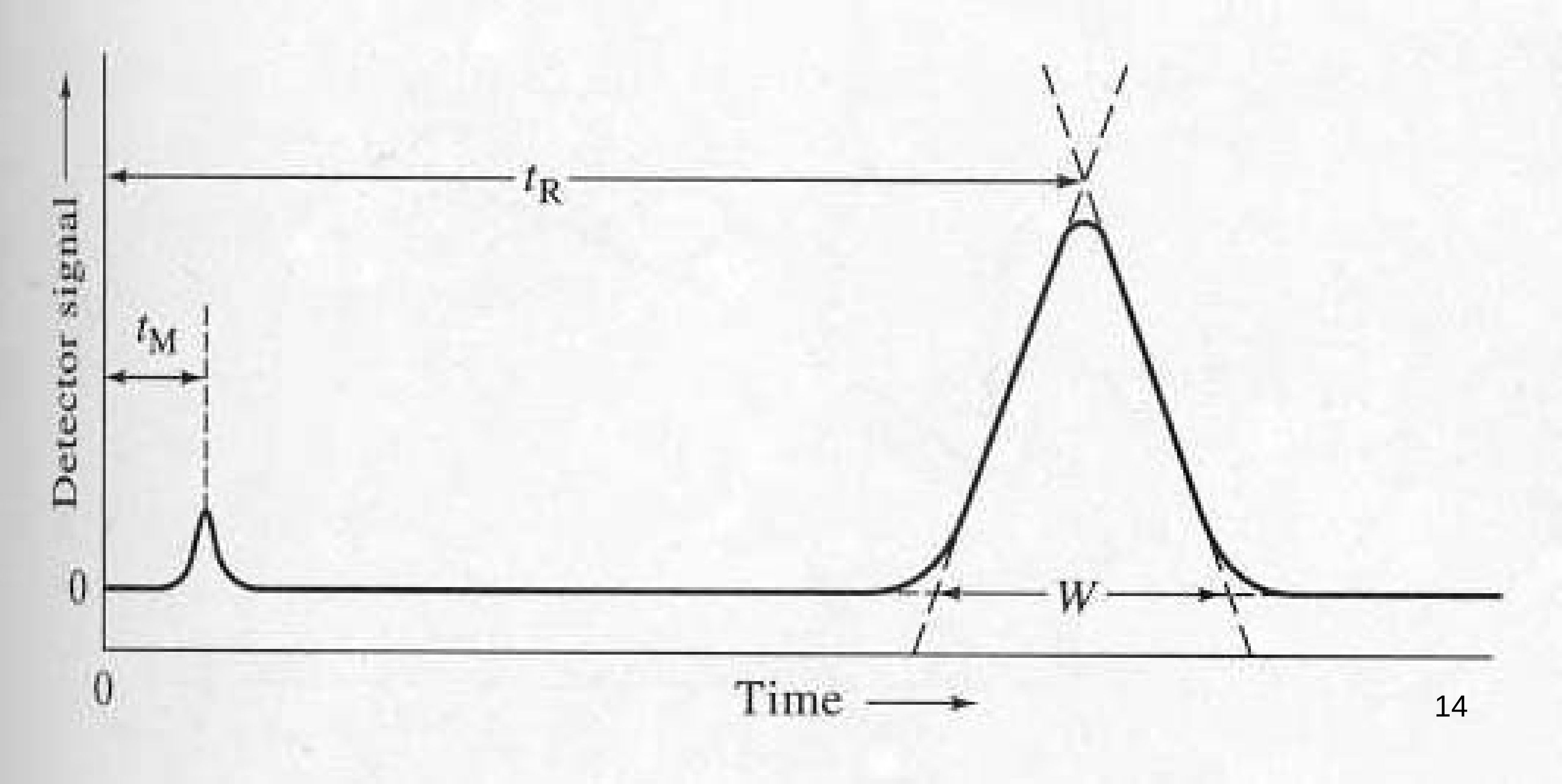
or

$N = L/H$

- Divide chromatographic column up into steps or segments called theoretical plates
- The theoretical concept is that these theoretical plates are equilibrium units for $K = C_s/C_M$
- The more theoretical plates a column has, the more efficient it is
- If column length = L & N = number of plates, then H = height equivalent to theoretical plate

Gausian distribution (bell curve)

$W = 4\sigma$



Can derive N = number of plates

$N = 16\,(t_R/W_b)^2$ W_b = base width

$N = 16\,(t_R/4\boldsymbol{\sigma})^2 = (t_R/\boldsymbol{\sigma})^2$

$N = 5.54\,(t_R/W_{½})^2$ $W_{½}$ = width at half height

Column manufacturers use N
to characterize column – N varies widely

Shortcomings of Plate Theory

- Assumes K is independent of concentration
- Assumes equilibration is rapid relative to velocity of mobile phase – not true, in reality solute may pass a plate without entering
- Assumes no longitudinal diffusion (= non ideal effect that causes band broadening)
- Does not address several factors caused by mobile phase velocity (fast or slow) Rate Theory
- Assumes discrete units or plates for equilibrium rather than a semi continuous process through the column

Rate Theory of Chromatography

$$H = H_L + H_S + H_M + H_{SM}$$

H = height equivalent to theoretical plate (as in Plate Theory)

H_L = contribution due to longitudinal diffusion

H_S = stationary phase mass transfer contribution

H_M = diffusion associated with mobile phase effects

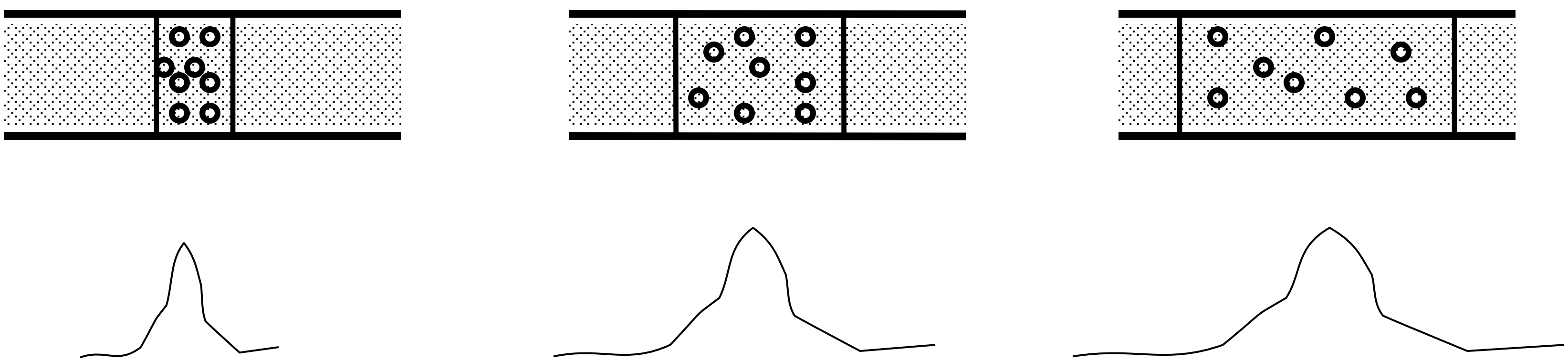
H_{SM} = diffusion into or mass transfer across a stagnant layer of mobile phase (neglect)

$$H = B/\mu + C\mu + A$$

van Deemter Equation A, B & C are coefficients, μ = velocity

1) Longitudinal Diffusion $H_L = (B/\mu)$

$t = 0$ $0 < t < t_R$ t_R

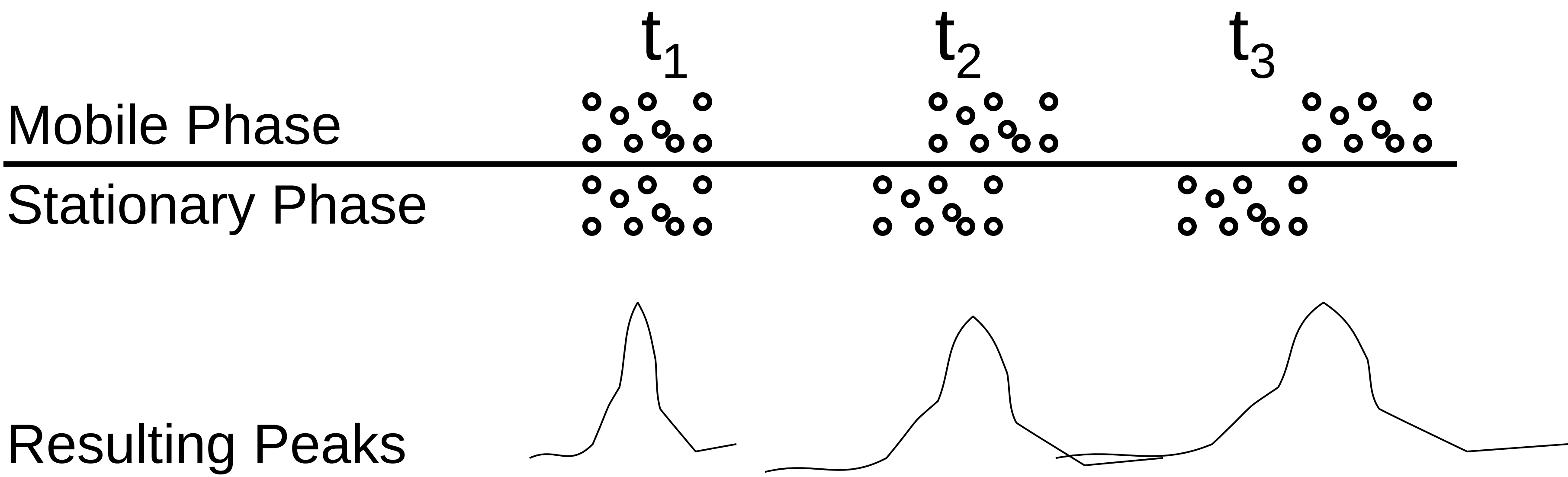


$\sigma_L^2 = 0$ $\sigma_L^2 = 2\,D_M\,t_M$

Variance due to longitudinal diffusion = 0 at start

Variance increases with time & diffusion coefficient D

2) Mass transfer in & out of stationary phase

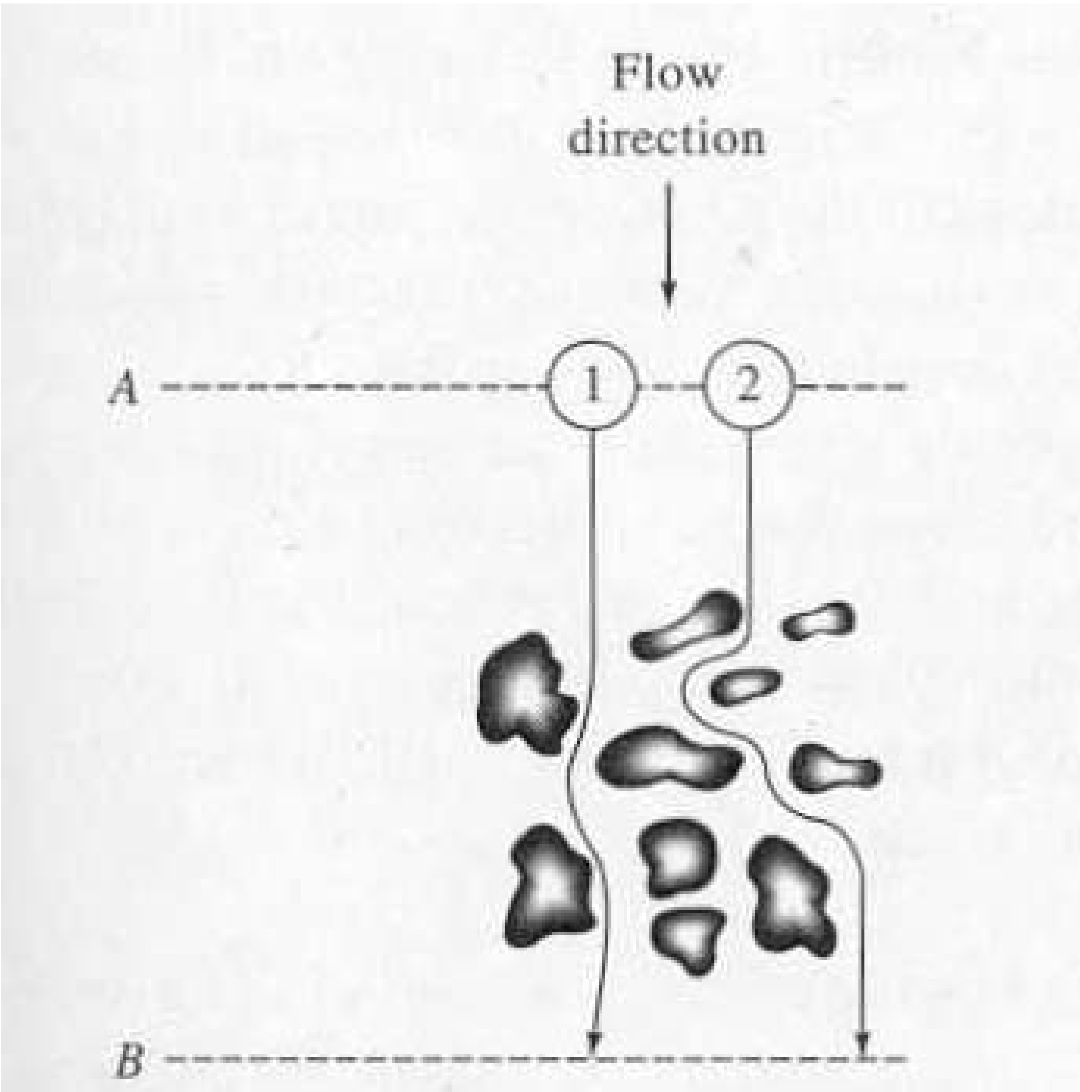


Broadening of peaks is a function of mobile phase velocity (moving molecules faster than those in stationary phase)

Not the same as longitudinal diffusion $$H_S = C\mu$$

In Plate Theory condition at t_1 assumed to hold throughout

3) Uneven Flow or Eddy Diffusion

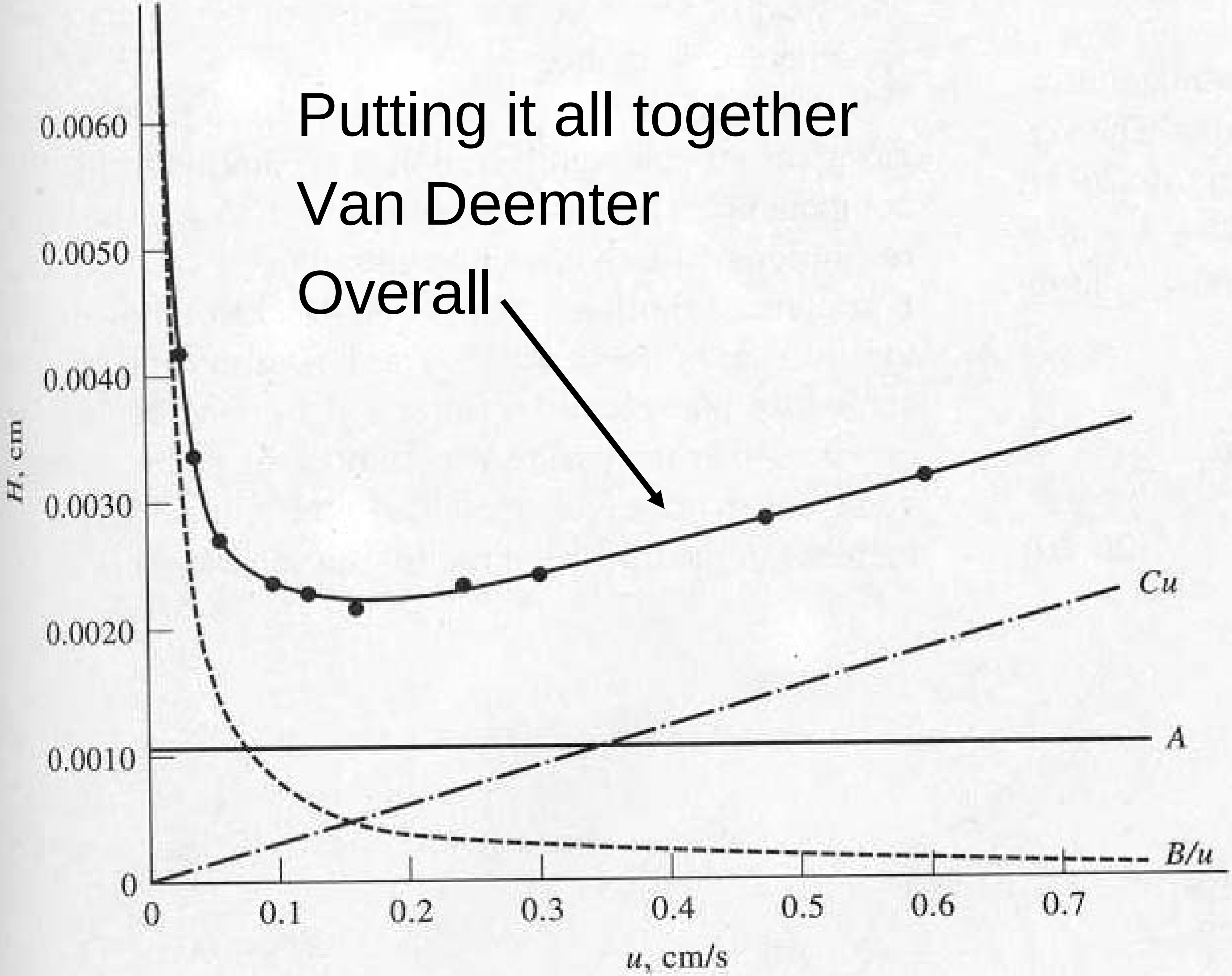


Path 1 is shorter than path 2

$H_M = A$

Putting it all together

Van Deemter



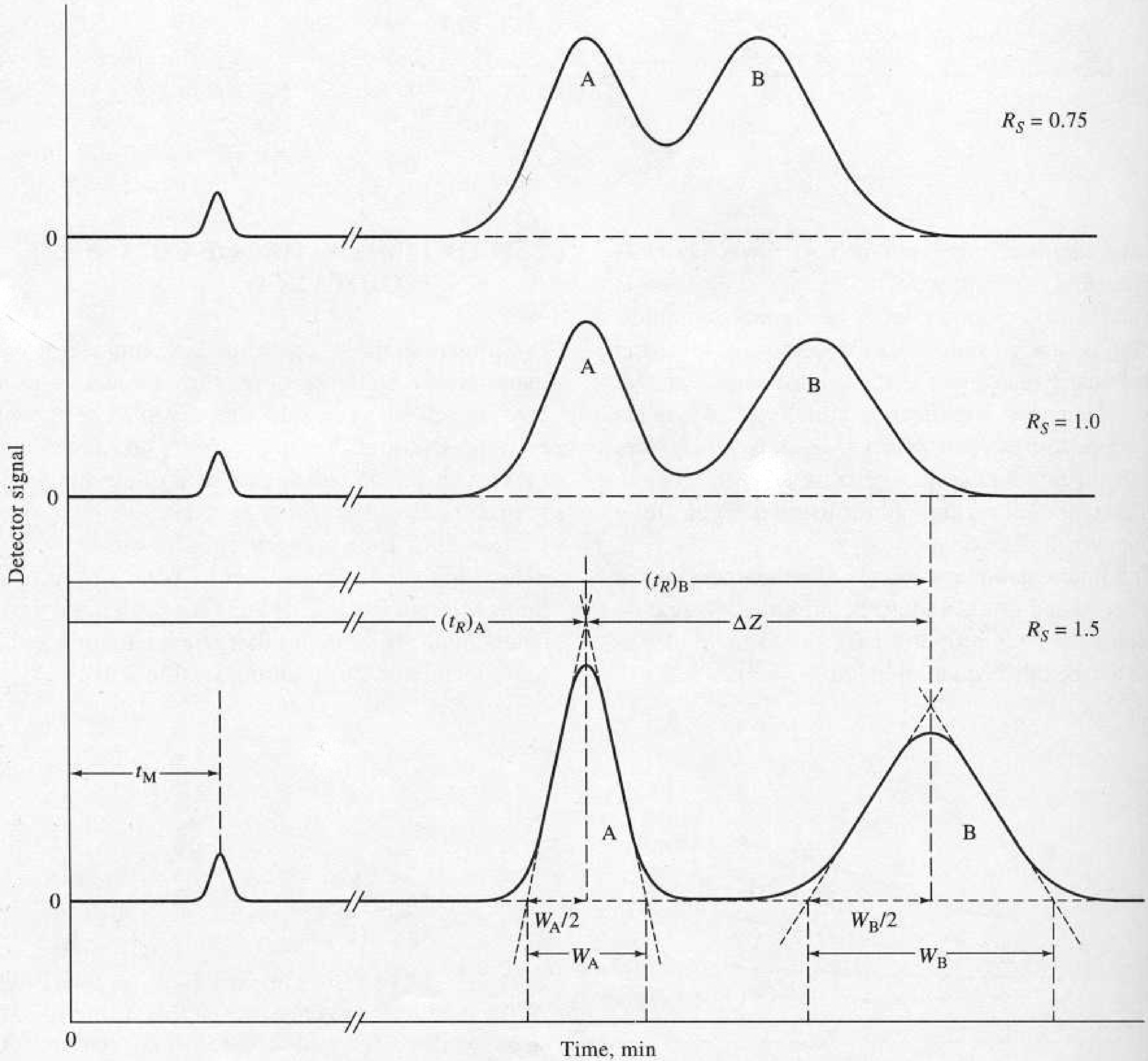
Optimizing Column Performance – seldom operate at optimum → too slow

Normally want to get required separation in shortest time, this may be at 2X μ_{opt}

Can optimize a separation by varying experimental conditions, usually goals are

1) reduce band broadening (zone)

2) alter relative migration rates of components (allowing better separation of two components)



This brings us to Resolution (R_S) = Measure of columns ability to separate 2 analytes

Note ΔZ = spread of peaks & W or W/2 = peak width

$$R_S = \frac{\Delta Z}{W_A/2 + W_B/2} = \frac{2\,\Delta Z}{W_A + W_B} = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$$

If $R_S = 1.0$ then $\Delta Z = W_A/2 + W_B/2$

and peaks touch with about 4% overlap

This is too big an error to tolerate

If $R_S = 1.5$ then about 0.3% overlap

Can lengthen column to improve resolution by increasing N → this also increases time for analysis

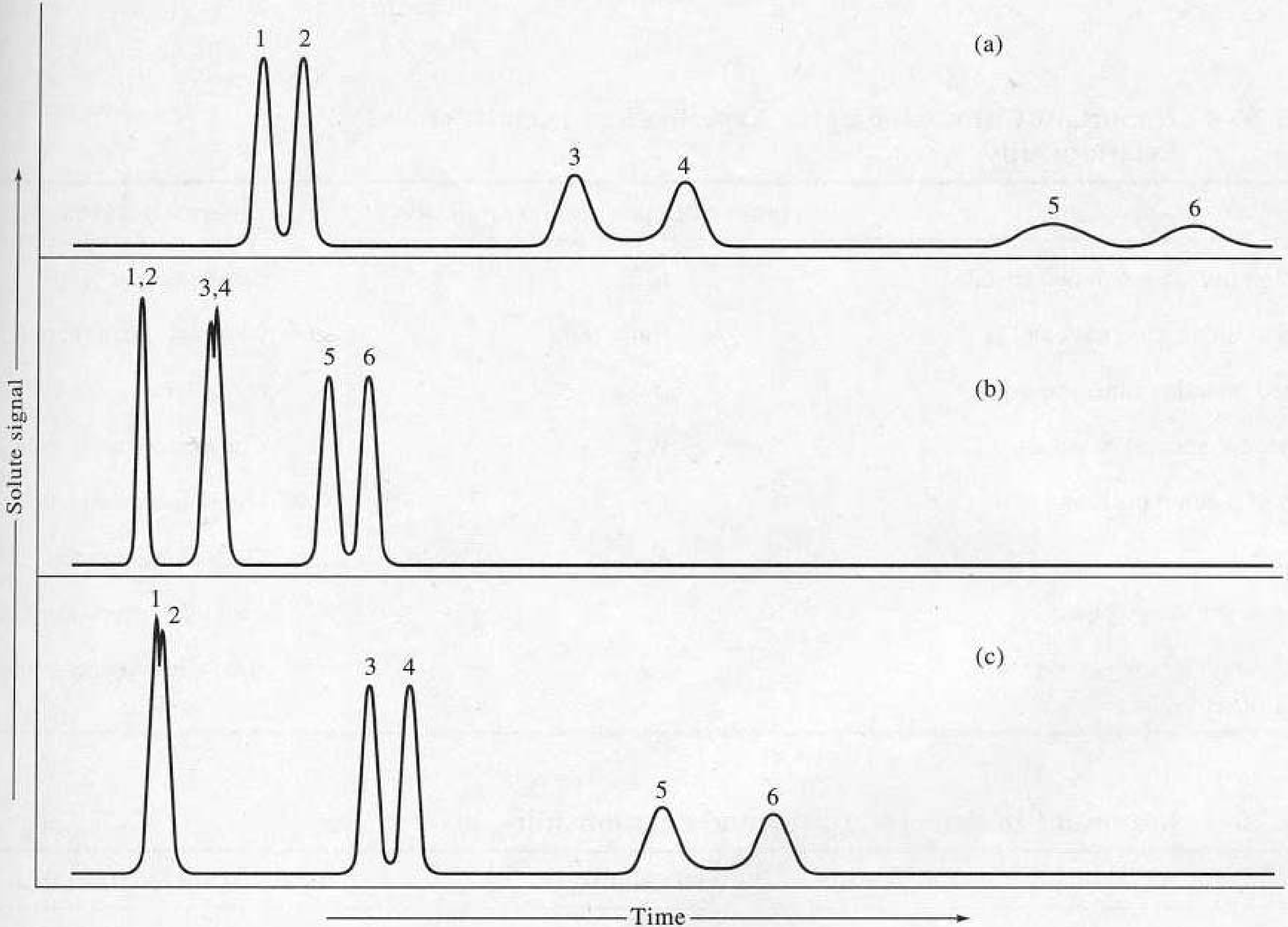


Figure 26-14 Illustration of the general elution problem in chromatography.

Commonly found problem in chromatography

General Elution Problem

Solution – change conditions during chromatographic run so that k’ changes

Start with conditions for chromatogram (a), after 1 & 2 elute

Change to conditions for chromatogram (c), after 3 & 4 elute

Change to conditions for chromatogram (b) to get 5 & 6

To Solve the General Elution Problem:

In GC do temperature programming

In HPLC do solvent programming (a.k.a. gradient elution)

Gas Chromatography

- Principles
- Instrumentation
- Detectors
- Columns and Stationary Phases
- Applications

Basic Principle of GC – sample vaporized by injection into a heated system, eluted through a column by inert gaseous mobile phase and detected

Three types (or modes)

gas – solid chromatography ⟵ early

gas – liquid " ⟵ important

gas – bonded phase " ⟵ relatively new

An estimated 200,000 GC in use worldwide

Discuss components starting here

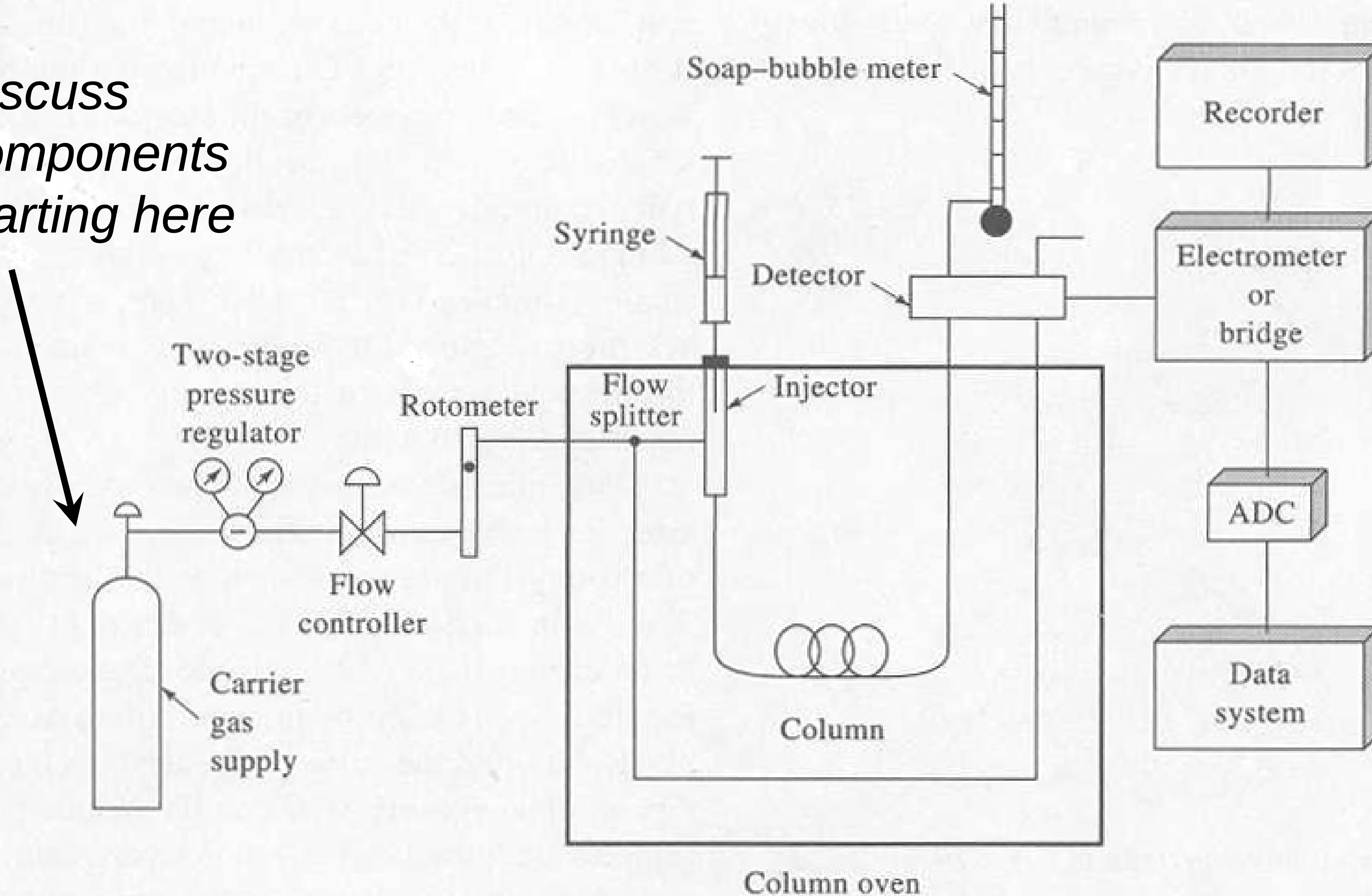


Figure 27-1 Schematic of a gas chromatograph.

Carrier gases (mobile phase) – must be chemically inert He, Ar, N_2, CO_2 even H_2 and mixtures 95/5 N_2/CH_4

Often detector dictates choice of carrier gas

In GC sample doesn’t really interact with carrier gas (unlike HPLC), temp controls partitioning

Often necessary to purify cylinder gas with a trap, scrubber or cartridge of molecular sieves (or buy high purity gas) O_2 ppm Hc

The move today is away from gas cylinders toward gas generators (extract pure carrier gas from air)

Next is gas flow control In this region

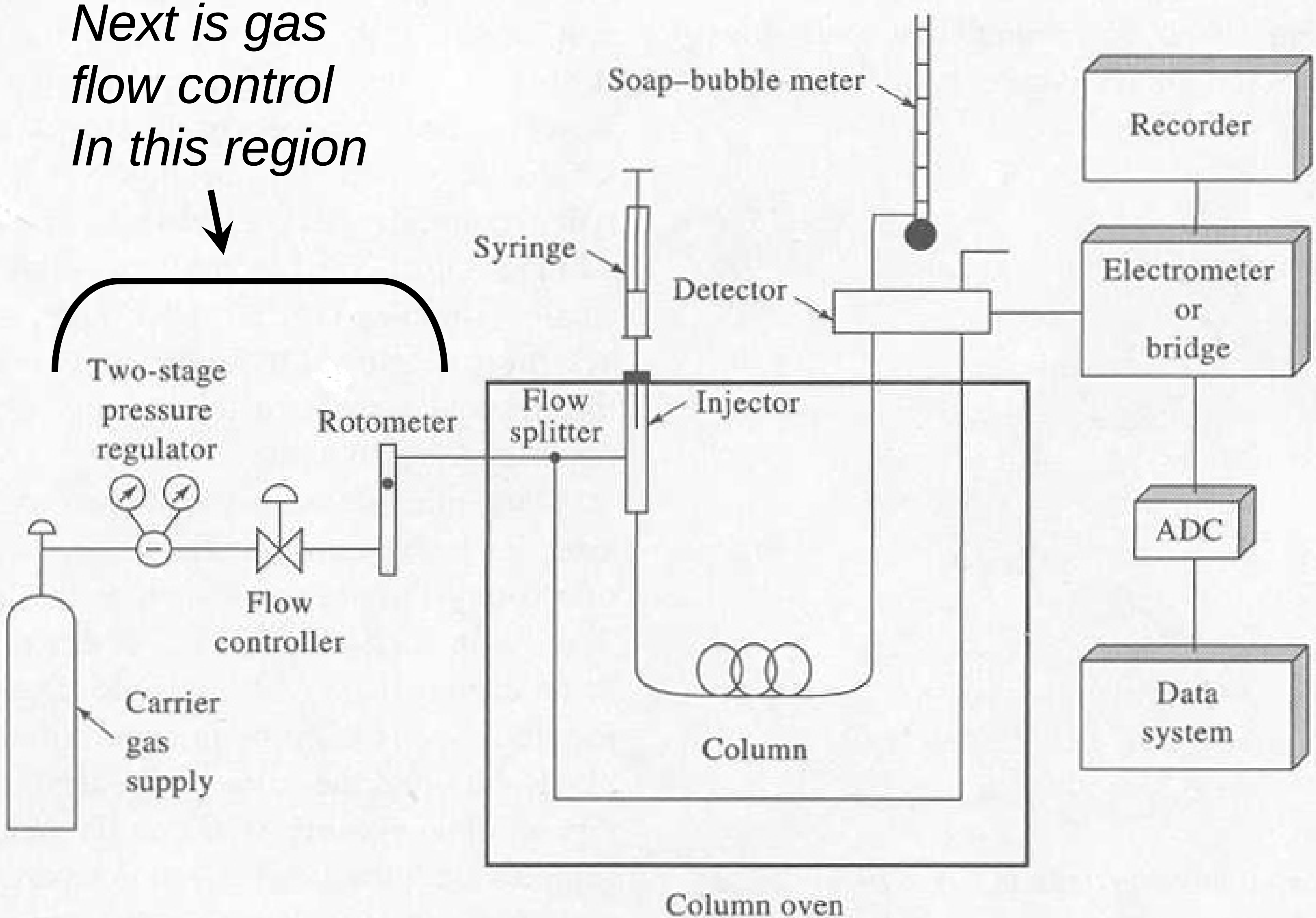


Figure 27-1 Schematic of a gas chromatograph.

Flow control – 10 to 50 psi with regulator

Regulators vary in quality, material & control, typically use a 2 stage regulator with the best material being stainless steel

Ultimately flow rate is checked by a soap bubble meter for accurate flow

Injector

Next is gas flow control In this region

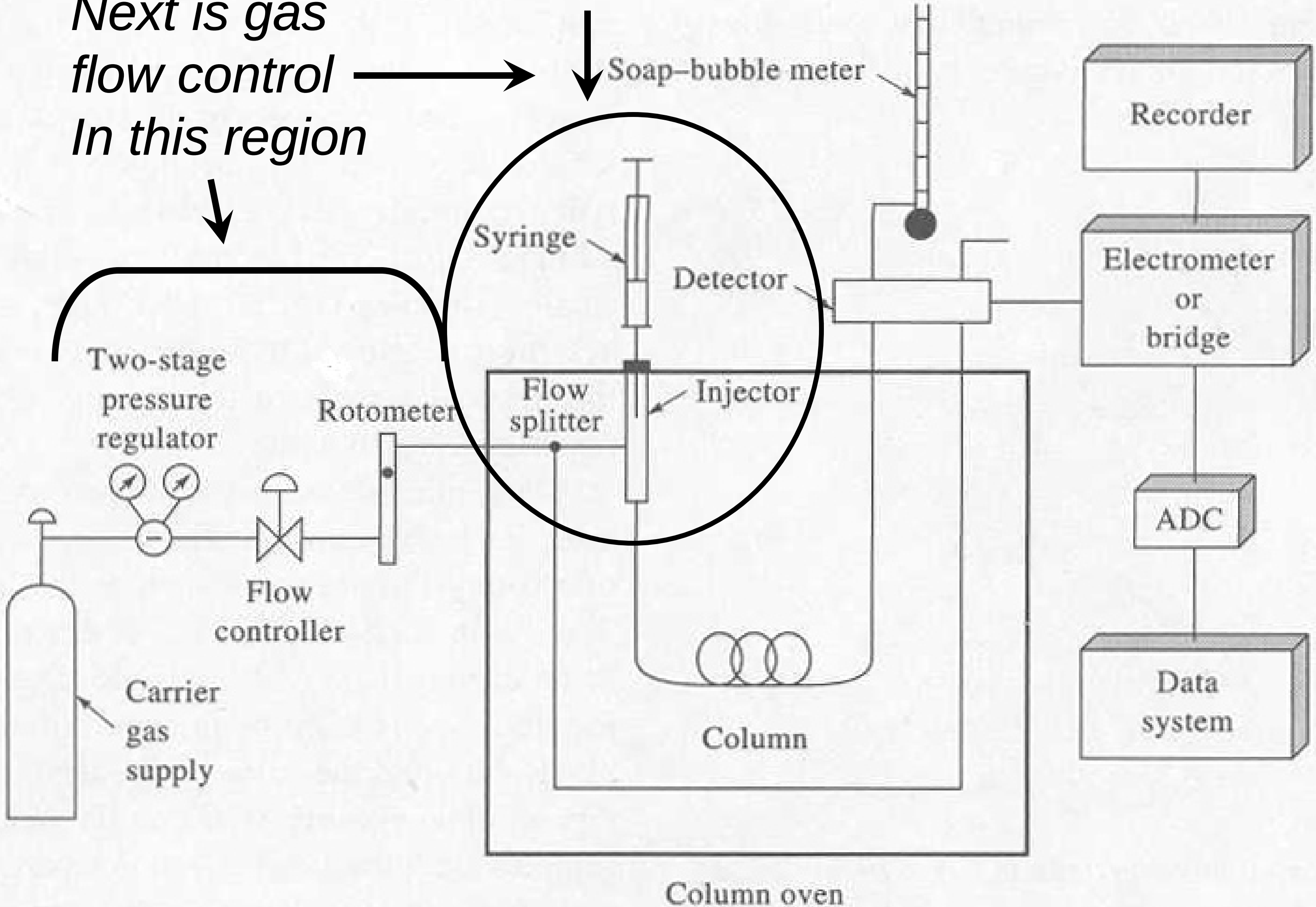


Figure 27-1 Schematic of a gas chromatograph.

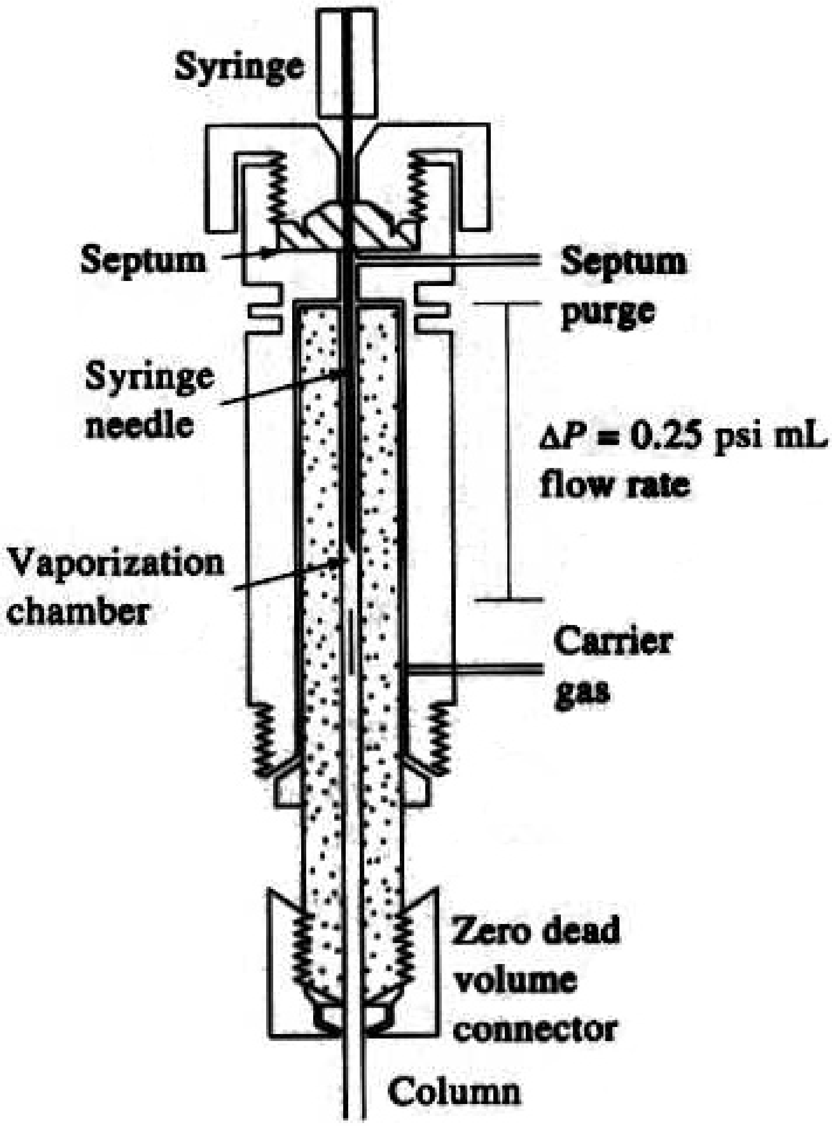


Figure 27-3 Cross-sectional view of a microflash vaporizer direct injector.

Injector – use micro syringe 99.9 % of the time injecting 1 to 20 µL, rapidly shoot in plug of sample

Old GCs had separate injection area

Today use on-column & microflash vaporizers – all have septum of synthetic rubber which is punctured by syringe

Injector usually 50 ^{o}C hotter than boiling point of sample – also hotter than column

Can use rotary injector valve (as for HPLC)

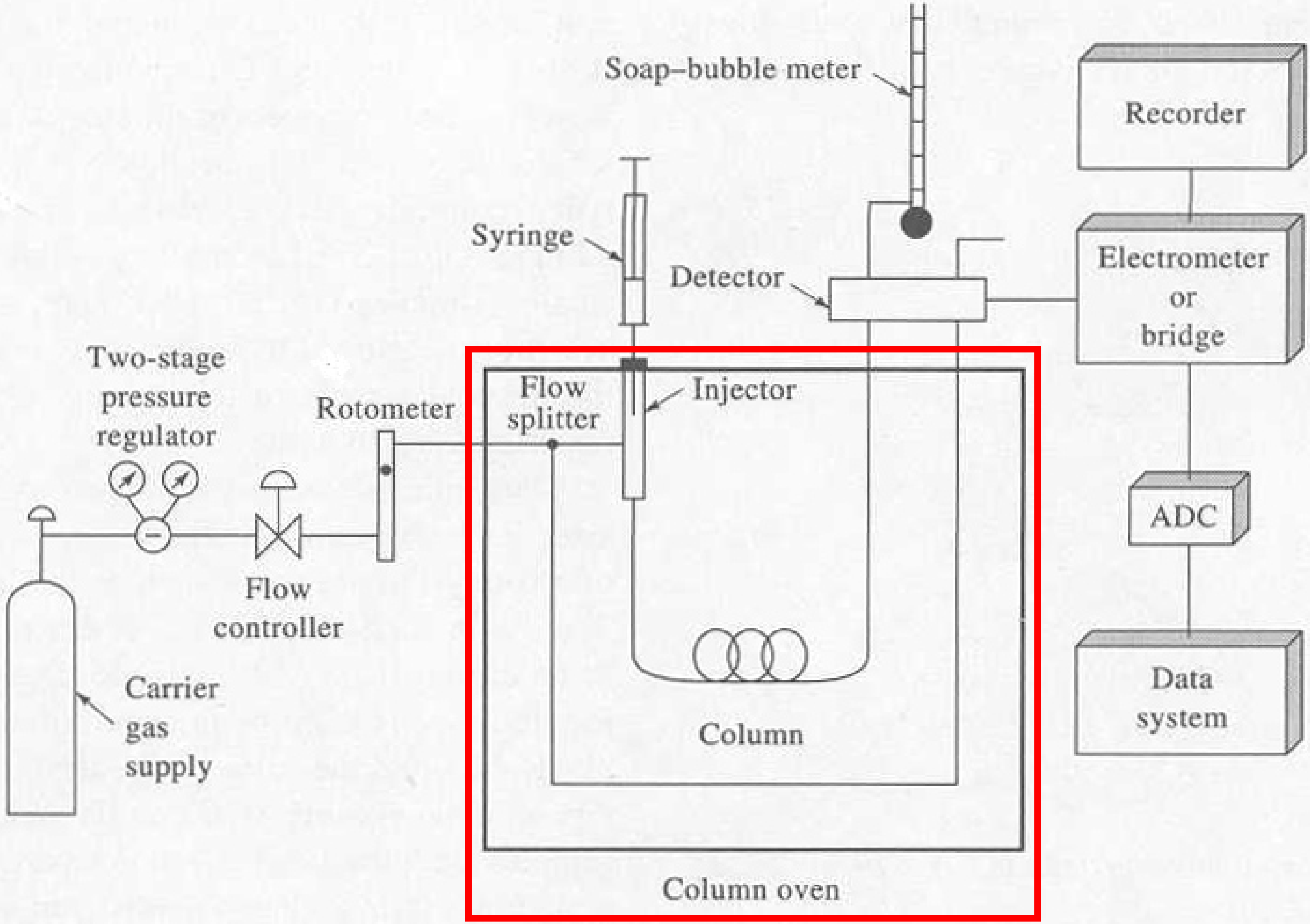


Figure 27-1 Schematic of a gas chromatograph.

Column housed in Column Oven to maintain temperature

Types – packed, open tubular, capillary

oldest ------------------- newest

Capillary columns will take over completely

Packed – tube (steel, glass, **fused silica**, Teflon) packed with material

Open Tubular – coated on walls

Capillary – coated on walls, long & narrow

Length range – 2 to 50 m (typically 30 m)

Detectors – dozens of detectors available

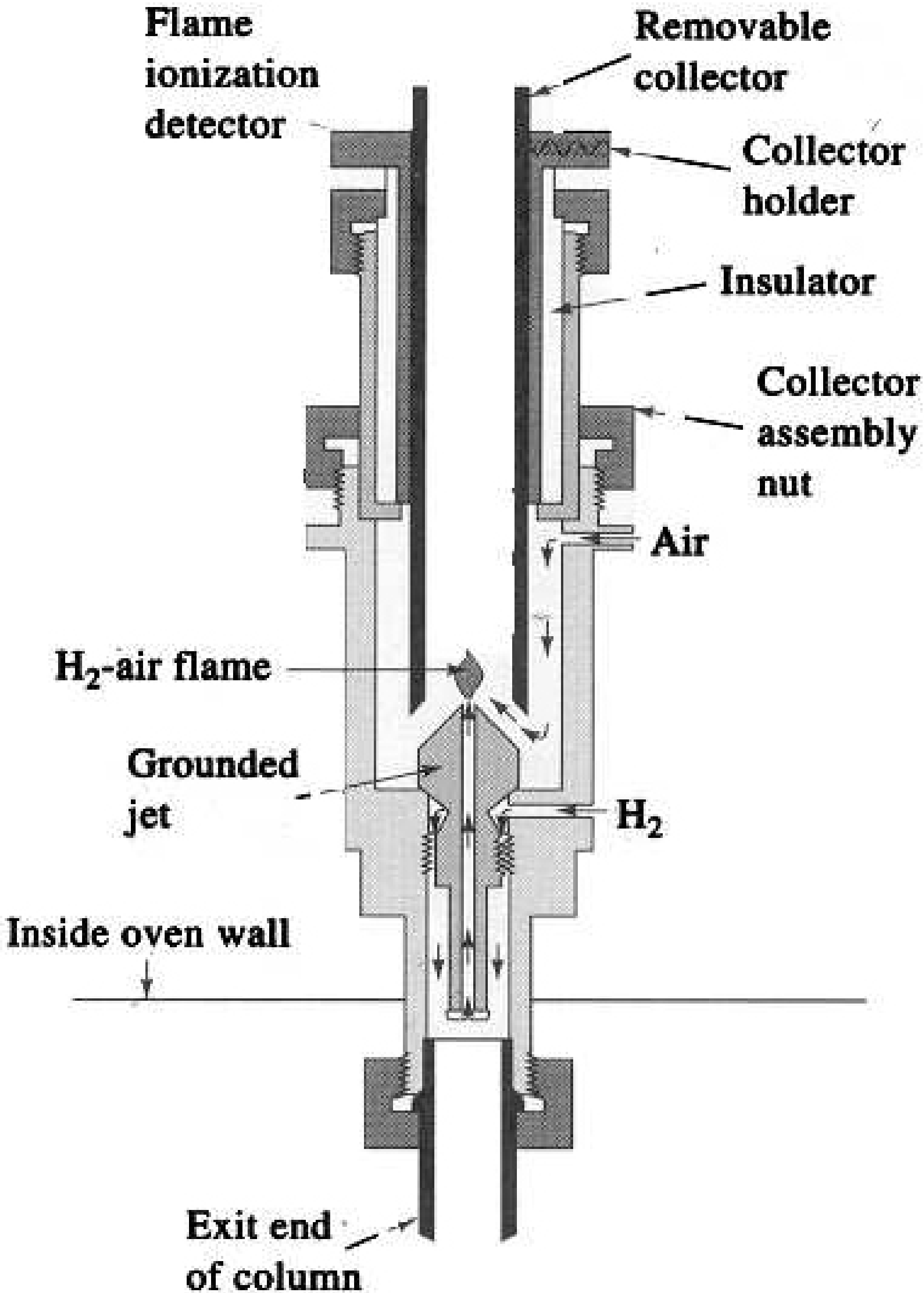
Characteristics of an ideal detector:

1) Adequate sensitivity for desired analysis (typical 10^{-8} to 10^{-15} g analyte/sec)
2) Stable – background constant with time
3) Reproducible – good precision
4) Linear response over several orders of magnitude
5) Temperature range – room temp - 400 ^{o}C

Characteristics of ideal detector: (continued)

6) Rapid response time
7) Independent of flow rate
8) Reliable
9) Easy to Use – inexperienced operators
10) Either selective or universal response
11) Nondestructive

No detector exhibits all these characteristics



Flame Ionization Detector (FID)

- one of most widely used GC detectors
- good sensitivity to almost all organic compounds

FID Basics

- column effluent mixed with air and burned in H_2 flame producing ions & electrons that conduct electricity
- a few hundred volts applied between burner tip & a collector electrode above the flame producing currents on the order of 10^{-12} amps
- amplify & measure
- signal approximately proportional to number of reduced carbon atoms in flame

FID Basics (continued)

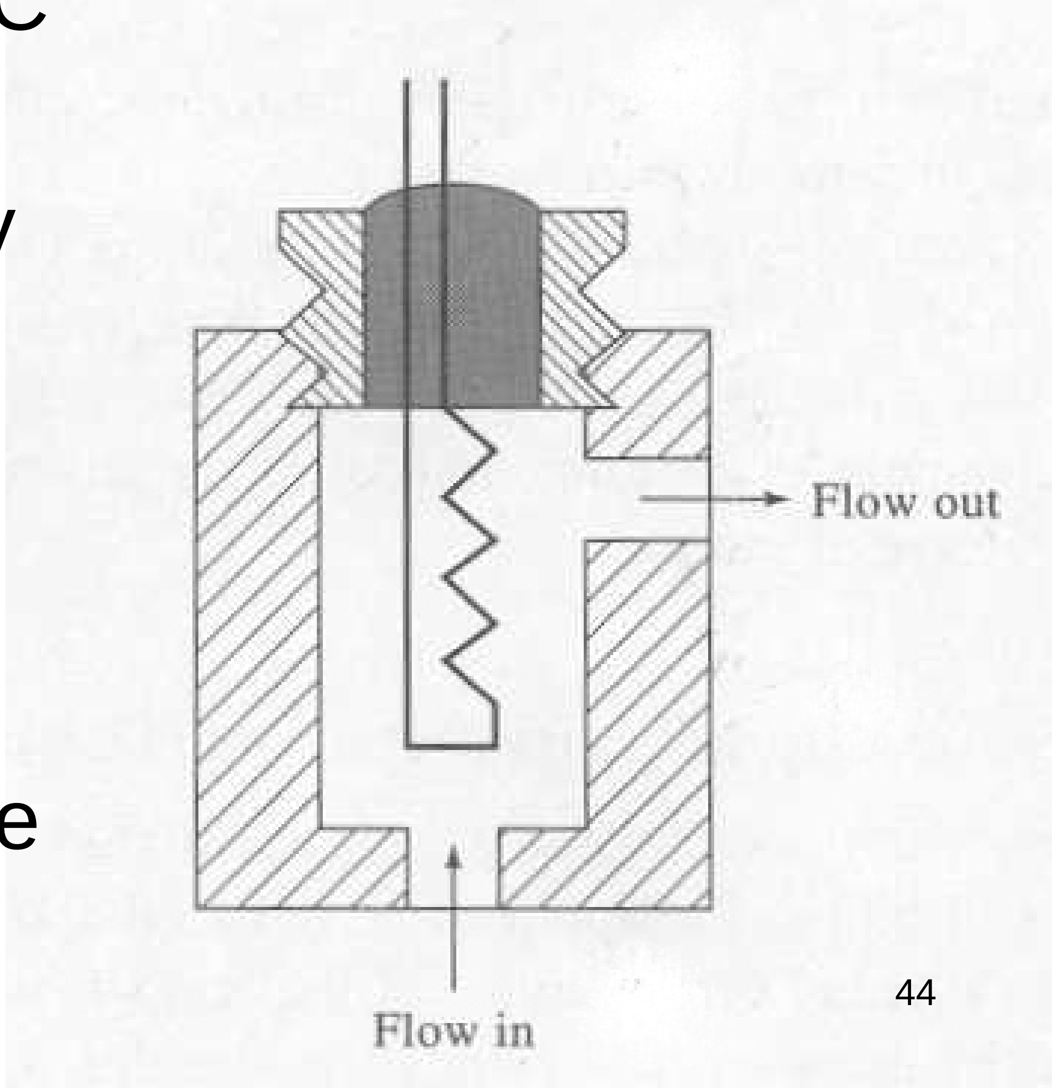
- mass sensitive rather than concentration
- insensitive to non combustible gases – H_2O, CO_2, SO_2, NO_x

FID exhibits

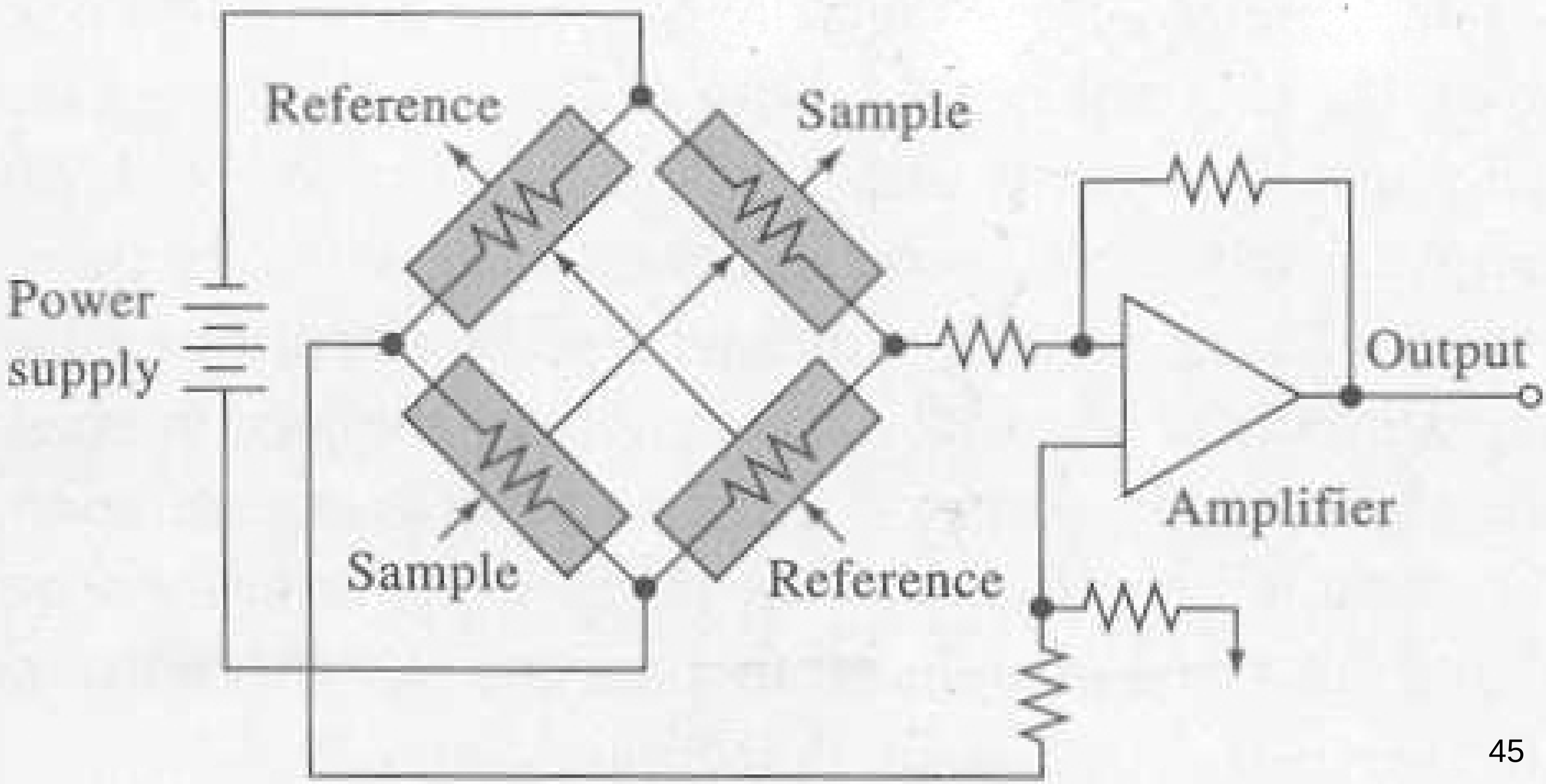
- High sensitivity (as low as 10^{-13} g/s)
- Large linear response range (10^7)
- Easy to use
- Rugged
- DESTRUCTIVE

Thermal Conductivity Detector (TCD)

- One of earliest GC detectors
- Not popular today
- Low sensitivity
- Several designs
- Use heated wire or semiconductor
- Resistance of wire changes with analyte vs carrier



TCD uses bridge circuit with Sample & Reference Cells



TCD

- New TCDs use pulsed current to increase sensitivity & reduce drift
- Thermal conductivity of He & H_2 are about 6 to 10 times greater than most organic compounds (must use these carrier gases)
- Other carrier gases (N_2, Ar, etc) have thermal conductivities too close to organics

Advantages of TCD

- Simple → Reliable & Easy to use
- Universal response (organic & inorganic)
- Large linear dynamic range 10^5
- Nondestructive, can use in tandem
- Older instruments have built-in TCD

Disadvantages

- Low sensitivity
- Often can't use with capillary columns because amount of analyte is small

ECD

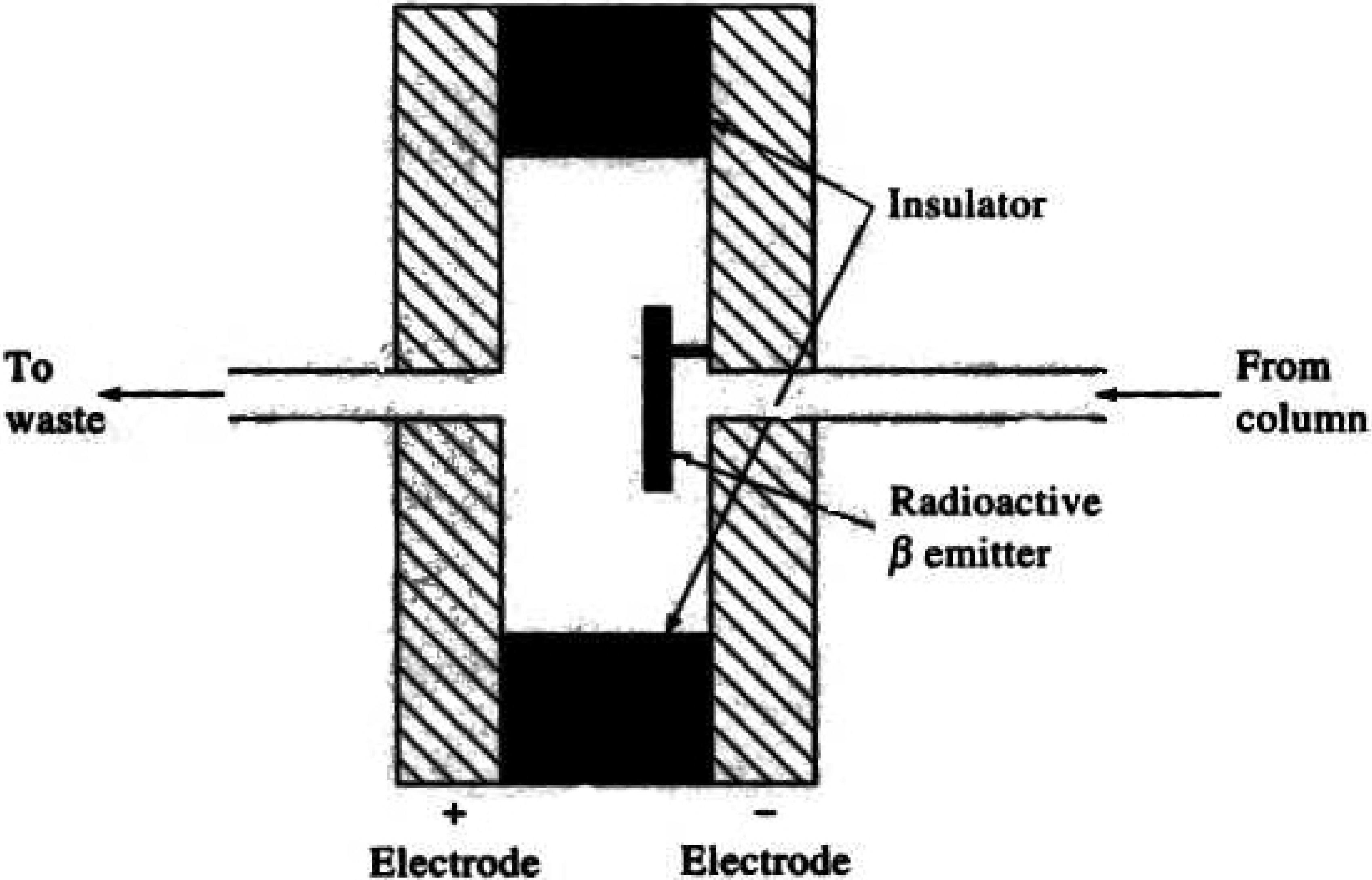


Figure 27-8 A schematic of an electron-capture detector.

Electron Capture Detector

- Sample passes over β emitter (radioactive) like ^{63}Ni foil or $^{3}H_2$ adsorbed on Pt or Ti foil
- β particles (i.e. electrons) hit carrier gas (usually N_2) causing a burst of e^- to be released & measured by electrode = standing current or constant signal
- When analyte molecule that absorbs e^- passes through, current is reduced = signal
- Response is non-linear unless pulsed

ECD Advantages

- Responds well to molecules with electronegative atoms like halogens (F, Cl, Br, I), peroxides, quinones, & nitro groups
- Insensitive to amines, alcohols, hydrocarbons
- Chlorinated pesticides are big application
- Highly sensitive
- Easy to use
- Pretty reliable, although foil can get coated
- Selective

ECD Disadvantages

- Narrow linear range
- Radioactive
- Regular wipe test
- Bake out contaminants
- Some limits to applicability because highly selective

Other Conventional Detectors

Thermionic Detector (TID)

- Selective for N & P compounds
- 500 x more sensitive than FID for P
- 50 x more sensitive than FID for N
- Bad for C
- Design similar to FID with rubidium silicate bead at 180 V vs collector → get hot plasma 600 - 800 ^{o}C
- Produces large number of ions with N & P

Flame Photometric Detector (FPD)

- Selective for P & S compounds
- Again sample goes through H_2/air flame
- Observe optical emission of HPO at 510 nm & 526 nm & S_2 at 394 nm
- Use optical filters to isolate signal
- Can also measure halogens, N, some metals (e.g. Cr, Ge, Se)

Photoionization Detector (PID)

- Column effluent irradiated with intense UV light source
- Ionizes molecules
- Measure ions with electrodes in detector cell

Unconventional Detectors

(Hyphenated Techniques)

Atomic Emission Detector (AED)

- Very powerful
- Sample eluent introduced to He microwave plasma atomizing all atoms in sample
- Uses diode array detector measuring optical emission over wide spectral range (170 - 780 nm)
- Measure many elements simultaneously

GC-AED

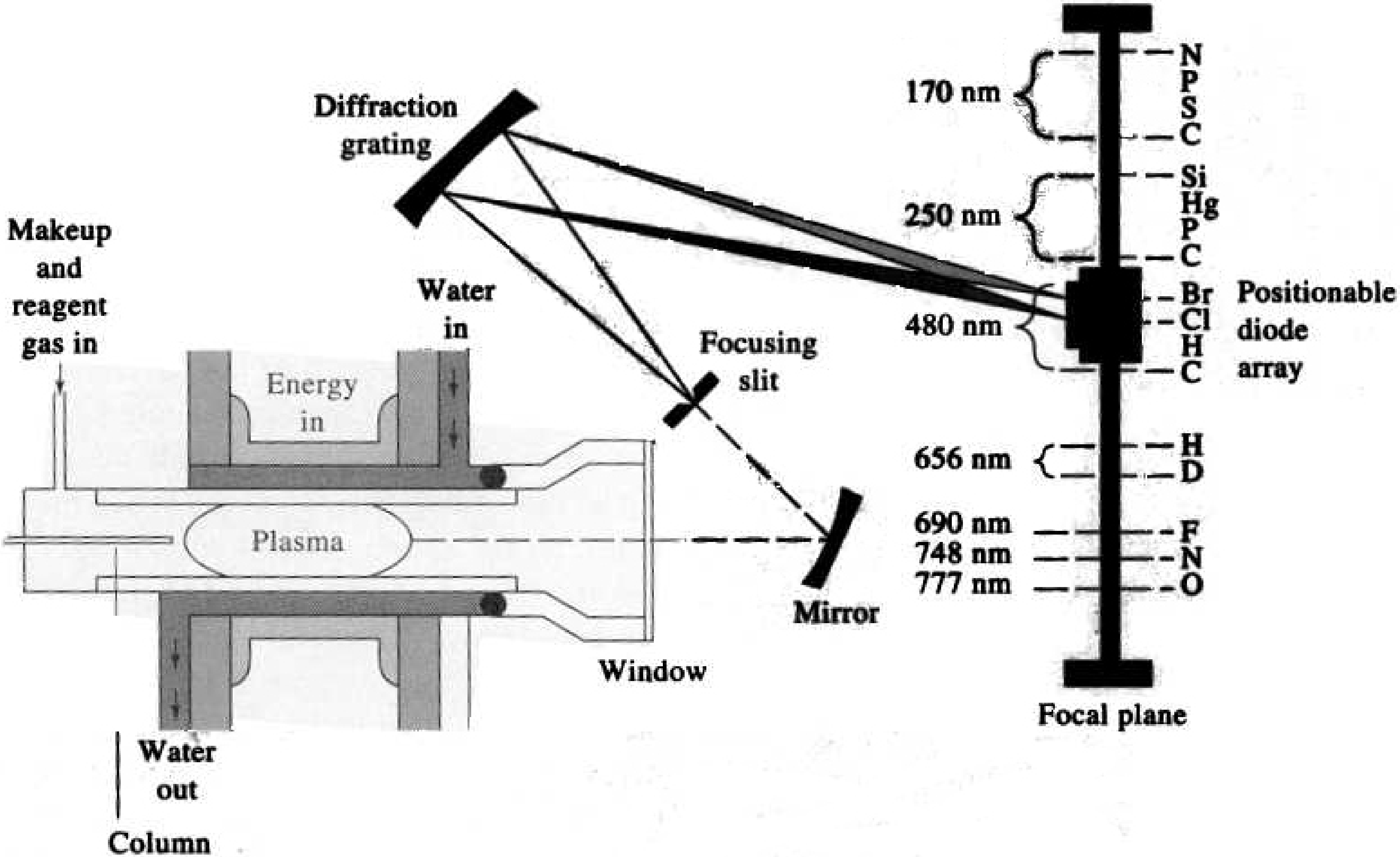


Figure 27-9 An atomic emission detector. *(Courtesy of Hewlett-Packard Company.)*

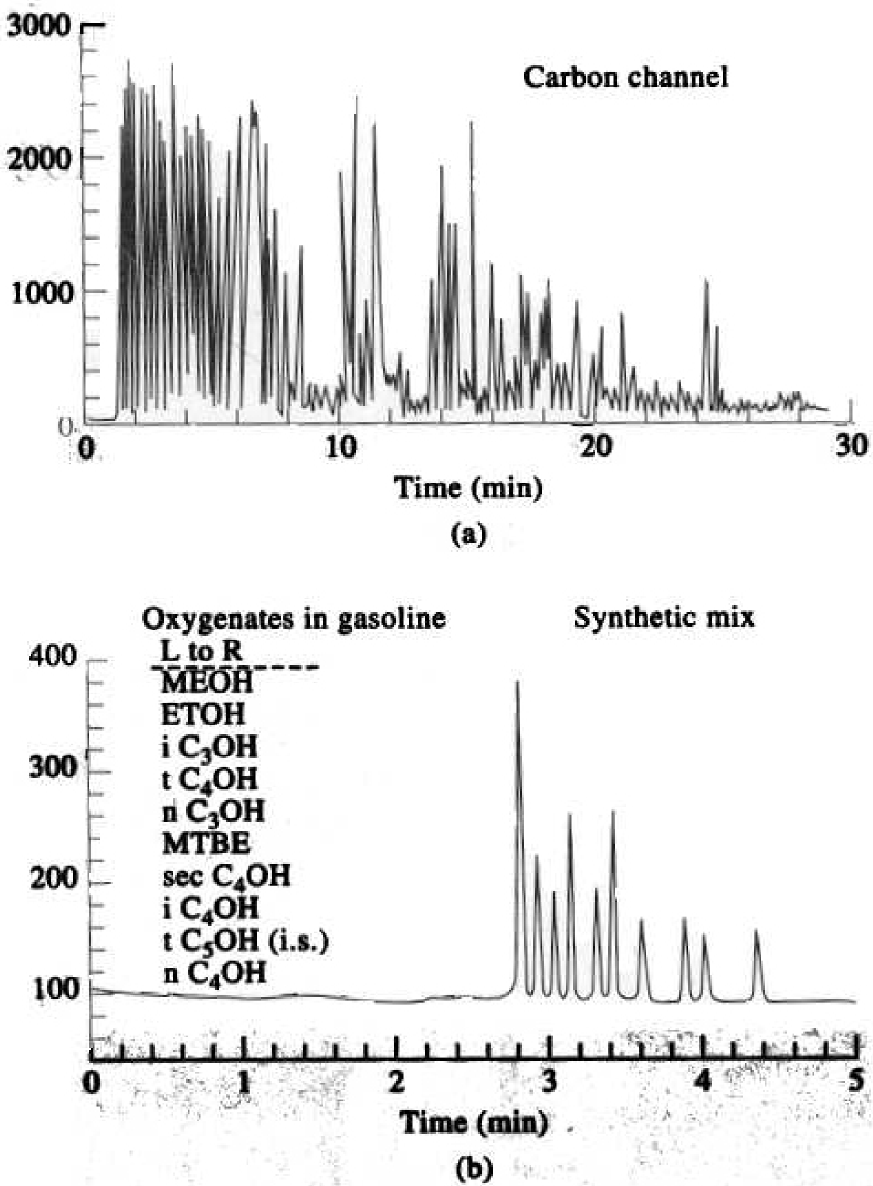


Figure 27-10 Chromatograms for a gasoline sample containing a small amount of MTBE and several aliphatic alcohols: (a) monitoring the line for carbon; (b) monitoring the line for oxygen. *(Courtesy of Hewlett-Packard Company.)*

GC-AED

- Potentially can measure 70 or more elements
- If look at C signal from AED get chromatogram with hundreds of peaks
- If look at O signal get very simple chromatogram with only a few peaks

GC – Mass Spectrometry (GC-MS)

- Interfacing GC & MS normally difficult
- GC at pressure above atmospheric while MS under high vacuum
- Need special interfaces for packed columns
  - Jet separator – discussed below
  - Membrane separator – a membrane sandwich between spiral channels, column efluent on one side under pressure, MS on other side under vacuum – relies on differential permeability of carrier gas vs analyte molecules

GC-MS Schematic

Interface less critical for capillary columns

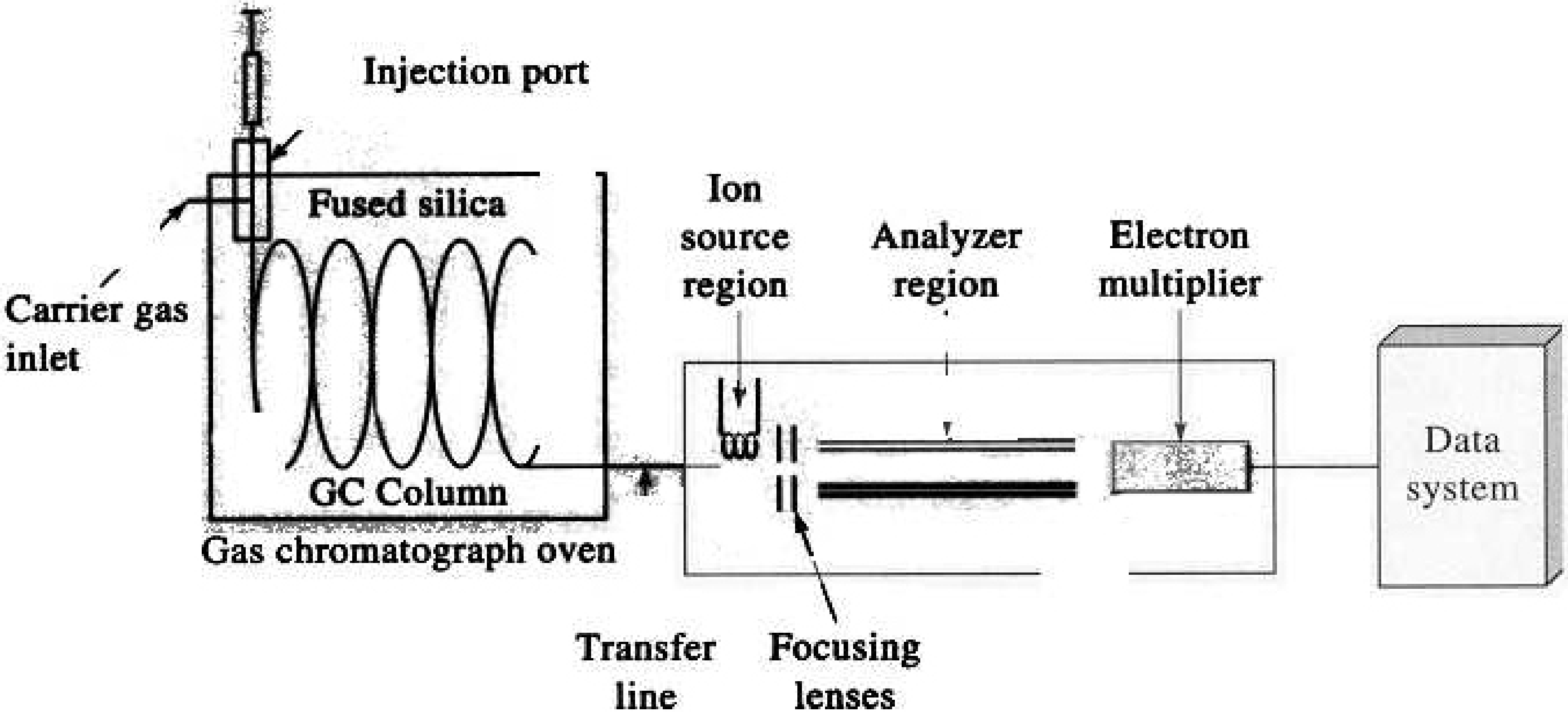


Figure 27-13 Schematic of a typical capillary gas chromatography/mass spectrometer.

Several types of Mass Specs available

- Rarely magnetic sector, time of flight (TOF) or ion cyclotron
- Usually quadrupole or ion trap for GC-MS
- Less expensive
- Less maintenance
- Easy to use
- Normally use electron multiplier as detector
- All MS systems need ion source, either electron impact or chemical ionization

Three modes of operation for GC-MS

1) Spectral mode – look at mass spectrum every second or so during chromatogram - gives most information for research or method development
2) Total ion current – sum signal for all ions as one large signal – highest sensitivity
3) Selective ion monitoring (SIM) – look at certain mass/charge ratios for compounds of interest – routine analysis

GC-MS

- sensitive
- can be very selective in SIM mode
- powerful for qualitatively & quantitatively
- used for complete unknowns
- used for court cases/expert witness

GC-FTIR

- Powerful technique for identifying compounds
- Use heated light pipe 1 to 3 mm dia

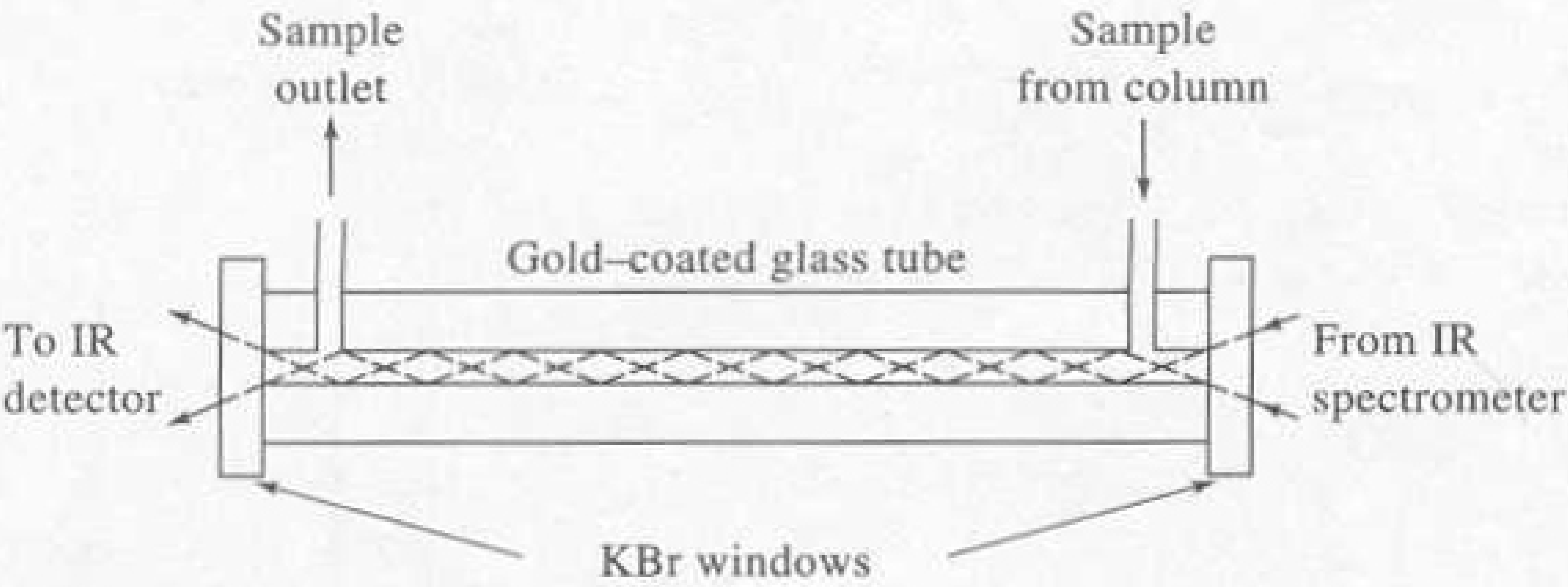


Figure 27-17 A typical light pipe for GC/IR instruments.

GC-FTIR

- Powerful technique for identifying compounds
- Use heated light pipe 1 to 3 mm dia and 10 to 40 cm long
- Heat to prevent condensation of sample
- Cool detector for sensitivity
- Gives structural information from spectrum
- Not very common

GC Columns & Stationary Phases

- Historically used packed columns
- Stationary phase coated as a thin film on a high surface area solid support
- Theoretical studies showed that unpacked columns with narrow diameters were better
- Open tubular columns first developed
- Capillary columns came later because
  - Very fragile, difficult to construct, hard to connect to GCs, small samples hard to detect, difficult to coat column walls, etc.

Packed Columns

- Tubing of metal, glass, Teflon, etc.
- 2 to 3 m long and 2 to 4 mm in dia
- Packed with diatomaceous earth (SiO_2), clay, carbon particles, glass microbeads, polymer
- Diameter 150-250 μm (60-100 mesh) 1 m^2/g
- Thin coating of liquid stationary phase

TABLE 27-2 Some Common Stationary Phases for Gas-Liquid Chromatography

Stationary Phase	Common Trade Name	Maximum Temperature, °C	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCBs
Poly(phenylmethyldimethyl) siloxane (10% phenyl)	OV-3, SE-52	350	Fatty acid methyl esters; alkaloids; drugs; halogenated compounds
Poly(phenylmethyl) siloxane (50% phenyl)	OV-17	250	Drugs; steroids; pesticides; glycols
Poly(trifluoropropyldimethyl) siloxane	OV-210	200	Chlorinated aromatics; nitroaromatics; alkyl-substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids; alcohols; ethers; essential oils; glycols
Poly(dicyanoallyldimethyl) siloxane	OV-275	240	Polyunsaturated fatty acids; rosin acids; free acids; alcohols

High-Performance Liquid Chromatography (HPLC)

- Scope
- Instrumentation – eluants, injectors, columns
- Modes of HPLC
  - Partition chromatography
  - Adsorption chromatography
  - Ion chromatography
  - Size exclusion chromatography

HPLC

- Most widely used separation technique
- Broad applicability – organic & inorganic
- Can be very sensitive, accurate & precise
- Suitable for separation of nonvolatile species
- Has found numerous uses in industry, clinical settings, environmental areas, pharmaceuticals, etc.

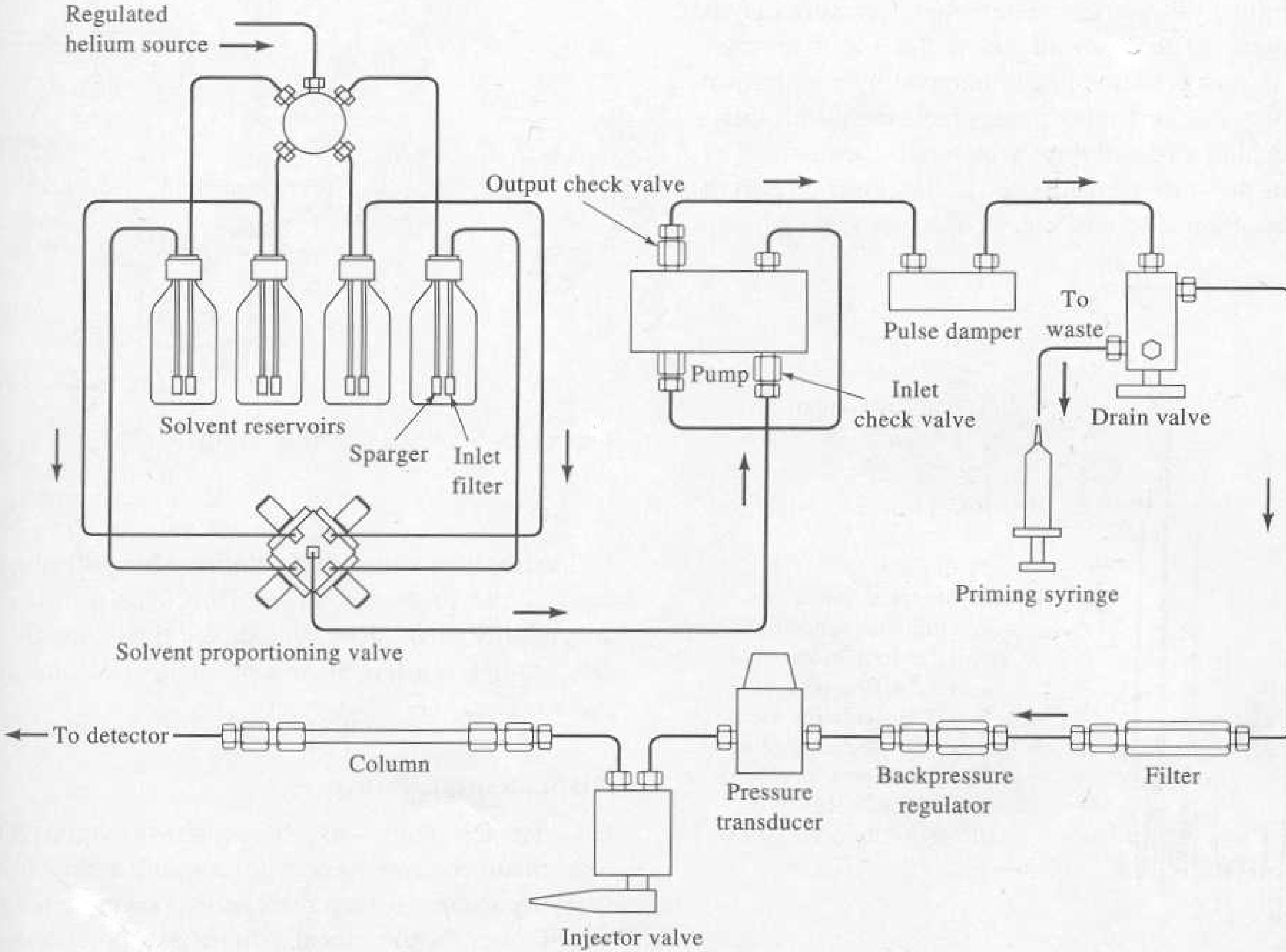


Figure 28-4 Schematic of an apparatus for HPLC. *(Courtesy of Perkin-Elmer Corporation, Norwalk, CT.)*

Solvents (mobile phase) – are stored in special reservoirs connected to the pumping system – must be free of particles that can clog components & free of bubble forming gases that get trapped in column or detector

Three basic ways to degas solvents

1) vacuum or suction filter (0.4 or 0.2 µm)
2) ultrasonicate (with vacuum)
3) He purge (sparge units often built in)

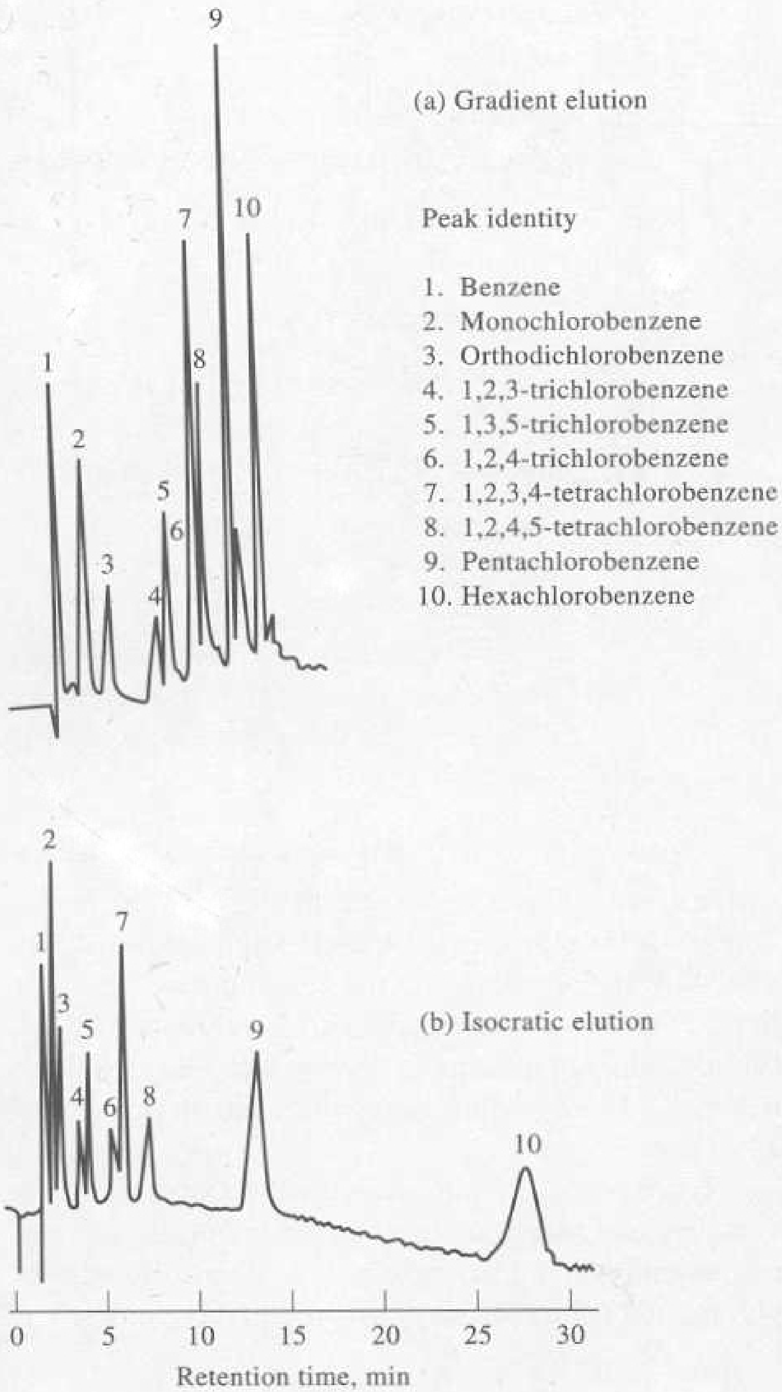
Can purchase HPLC solvents & water - still

In GC the analyte affinity for the column is influenced by temp

In HPLC the solvent strength affects an analytes retention on column

Therefore, analogous to temp programming in GC, do solvent programming in HPLC

This is also referred to as gradient elution



Gradient elution dramatically improves the efficiency of separation

HPLC sample injectors are 6 port rotary valves that are overfilled by syringe giving extreme accuracy & precision – typical volumes are 10 to 50 µL but can be larger

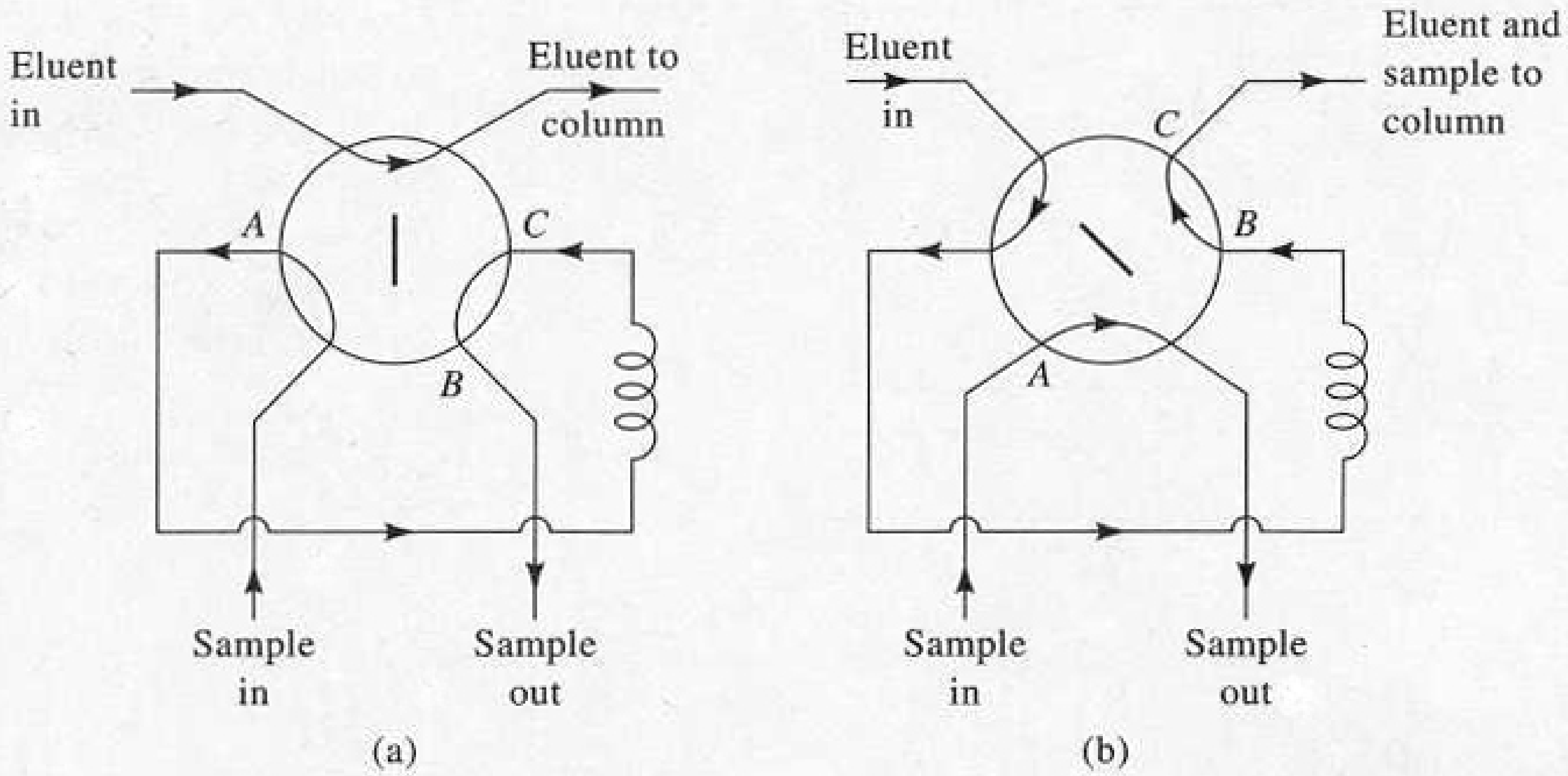
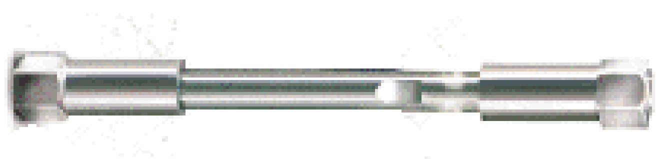


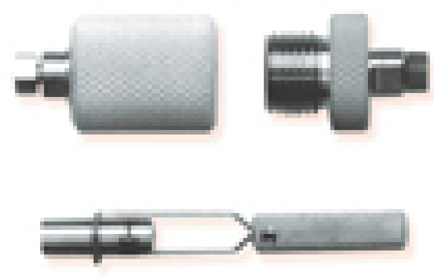
Figure 27-4 A rotary sample valve: valve position (a) for filling sample loop ACB and (b) for introduction of sample into column.

Columns

- usually stainless steel
- can be PEEK (poly ether ether ketone)
- may cost $300-$1000 packed
- Length 10-30 cm, ID 4-10 mm
- Packings are 3, 5, or 10 µm particle size
- Most common 25 cm, 5 µ, 4.6 mm ID
- N = 40,000 to 60,000
- Normally packed under 6000 psi pressure at factory as a slurry

Guard columns are normally used before the analytical column to protect & increase lifetime of column – operator usually slurry or dry packs short guard column regularly with same or similar packing used in analytical column (old column material) – can purchase guard systems, cartridges, etc.





Detectors for HPLC

- Ideal characteristics same as GC
- Exception is temp range
- Low dead volume 1 to 10 µL

Most common detector is **<u>UV-vis absorbance</u>**

Three types

1) Filter instrument – optical filters, Hg lamp
2) Variable wavelength – monochromator
3) Diode array detector- provide spectra

Many HPLC detectors available

For universal & selective detection

TABLE 28-1 Performances of LC Detectors

LC Detector	Commercially Available	Mass LOD (commercial detectors)[a]	Mass LOD (state of the art)[b]
Absorbance	Yes[c]	100 pg–1 ng	1 pg
Fluorescence	Yes[c]	1–10 pg	10 fg
Electrochemical	Yes[c]	10 pg–1 ng	100 fg
Refractive index	Yes	100 ng–1 μg	10 ng
Conductivity	Yes	500 pg–1 ng	500 pg
Mass spectrometry	Yes[d]	100 pg–1 ng	1 pg
FT–IR	Yes[d]	1 μg	100 ng
Light scattering[e]	Yes	10 μg	500 ng
Optical activity	No	—	1 ng
Element selective	No	—	10 ng
Photoionization	No	—	1 pg–1 ng

1) Filter based UV-vis detector – Typically set at 254 nm using the most prominent band in Hg spectrum – can also use 313, 365, 334 nm and other lines as well
2) Variable wavelength detectors – use continuum source like (D_2 or H_2) & a monochromator, select any λ, less sensitive
3) PDA - D_2 or H_2 source, disperse & focus on diode array, get complete spectrum every 1 sec, powerful, expensive, less sensitive, lots of data generated

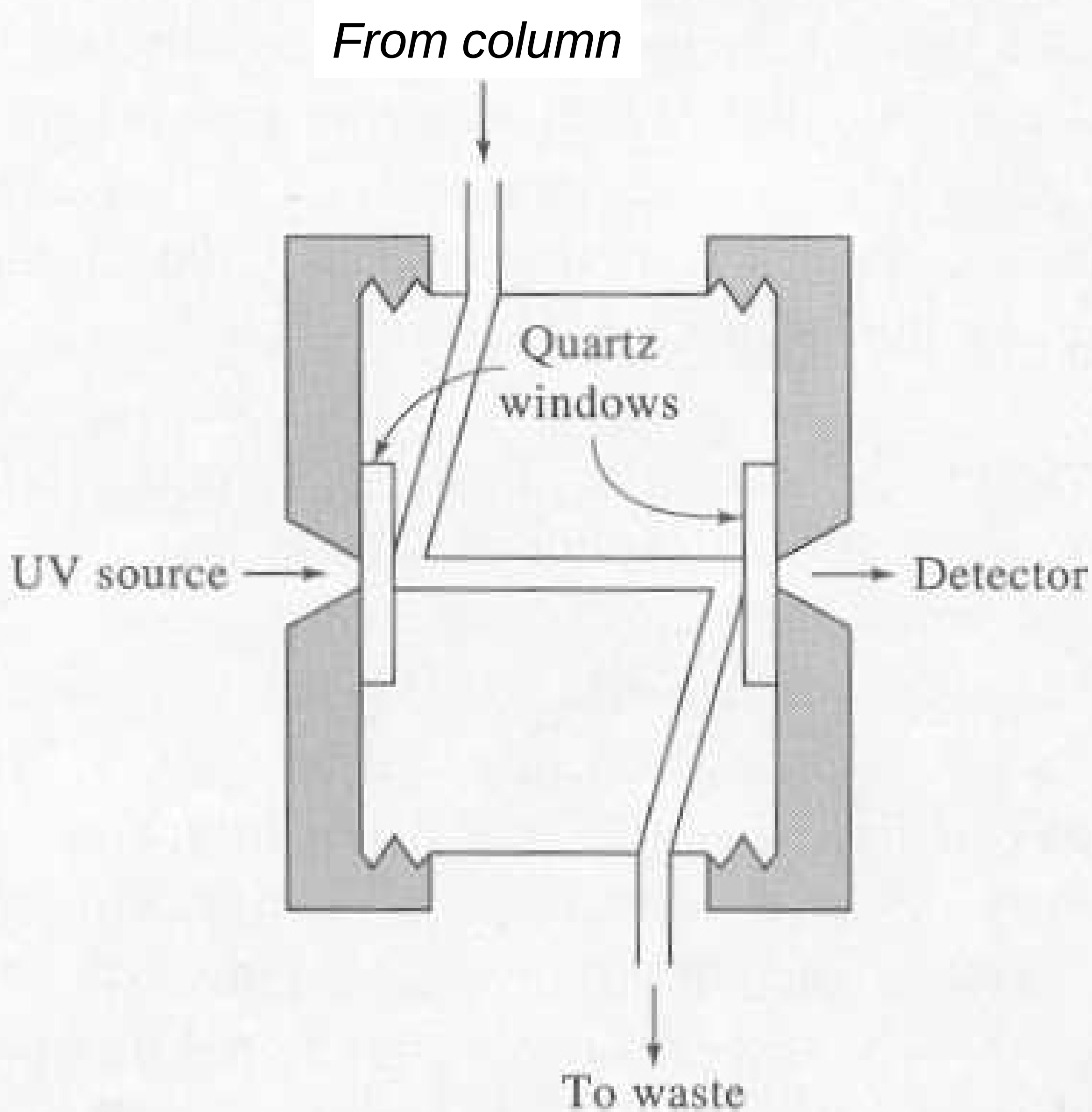


Figure 28-9 Ultraviolet detector cell for HPLC.

Cell for UV-vis detector for HPLC

- Low vol

Diode Array Detector

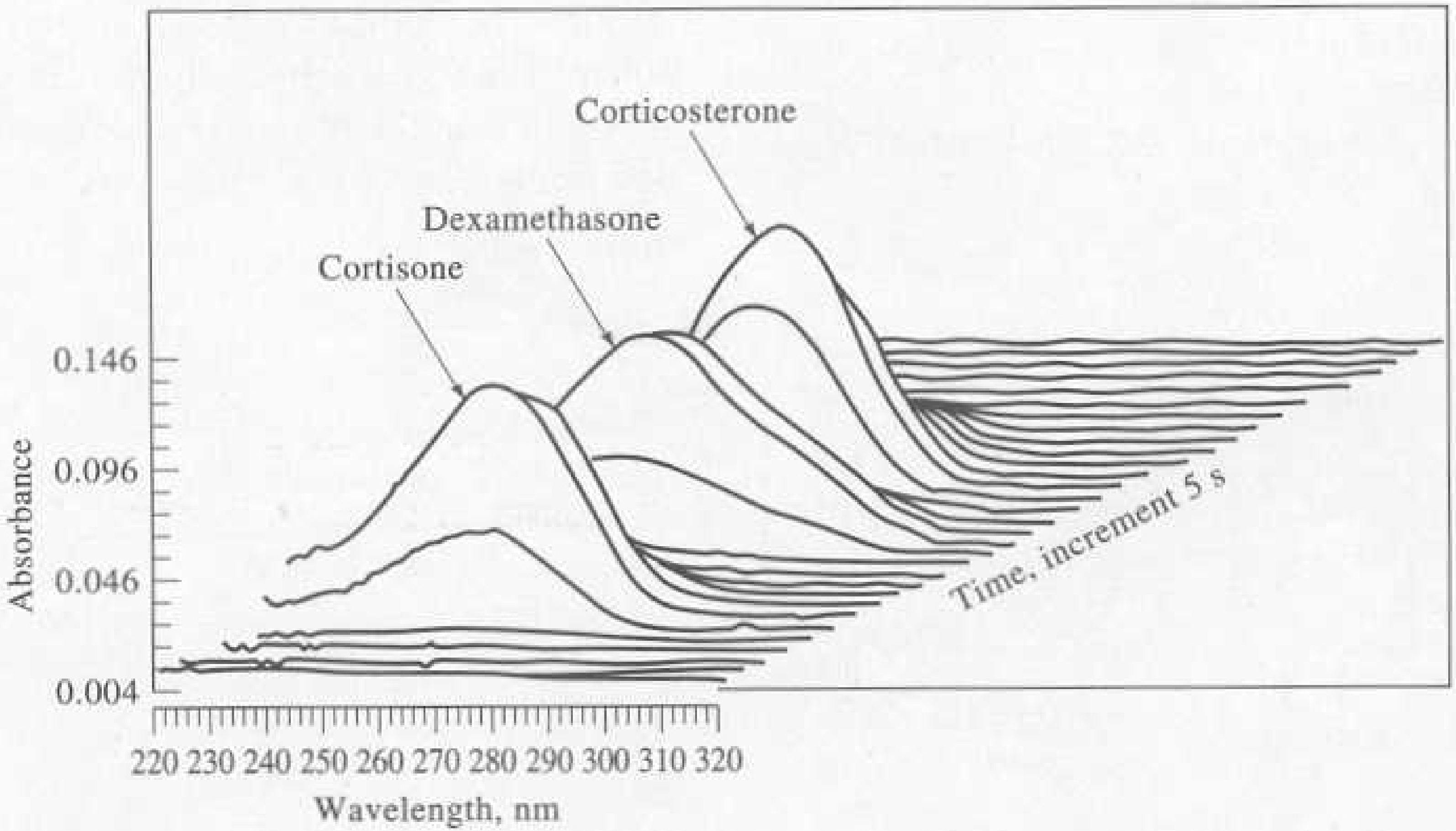


Figure 28-10 Absorption spectra of the eluent from a mixture of three steroids taken at 5-second intervals. *(Courtesy of Hewlett-Packard Company, Palo Alto, CA.)*

Fluorescence detector – normally fixed wavelength filter fluorometer
excitation filter & emission filter
can be changed for particular λ of interest
gives selectivity based on:

- ability to exhibit fluorescence
- excitation wavelength
- emission wavelength

Variable λ monochromator based fluorescence detectors also available

Filter based detectors usually more sensitive

Refractive index detector (RI) -

responds to nearly all solutes but has poor sensitivity – detects changes in refractive index as sample passes through as long as solute has different RI than solvent – analogous to TCD in GC

Electrochemical Detection

- Amperometric – fix potential & measure current (i)
- Conductometric – measure conductivity
- Coulometric – fix potential & integrate i
- Voltammetric – vary potential & measure i
- Potentiometric – measure potential

Can use 2 or 3 electrode design with Pt or carbon electrodes (glassy C or C paste)

Electrochem. detector nearly universal

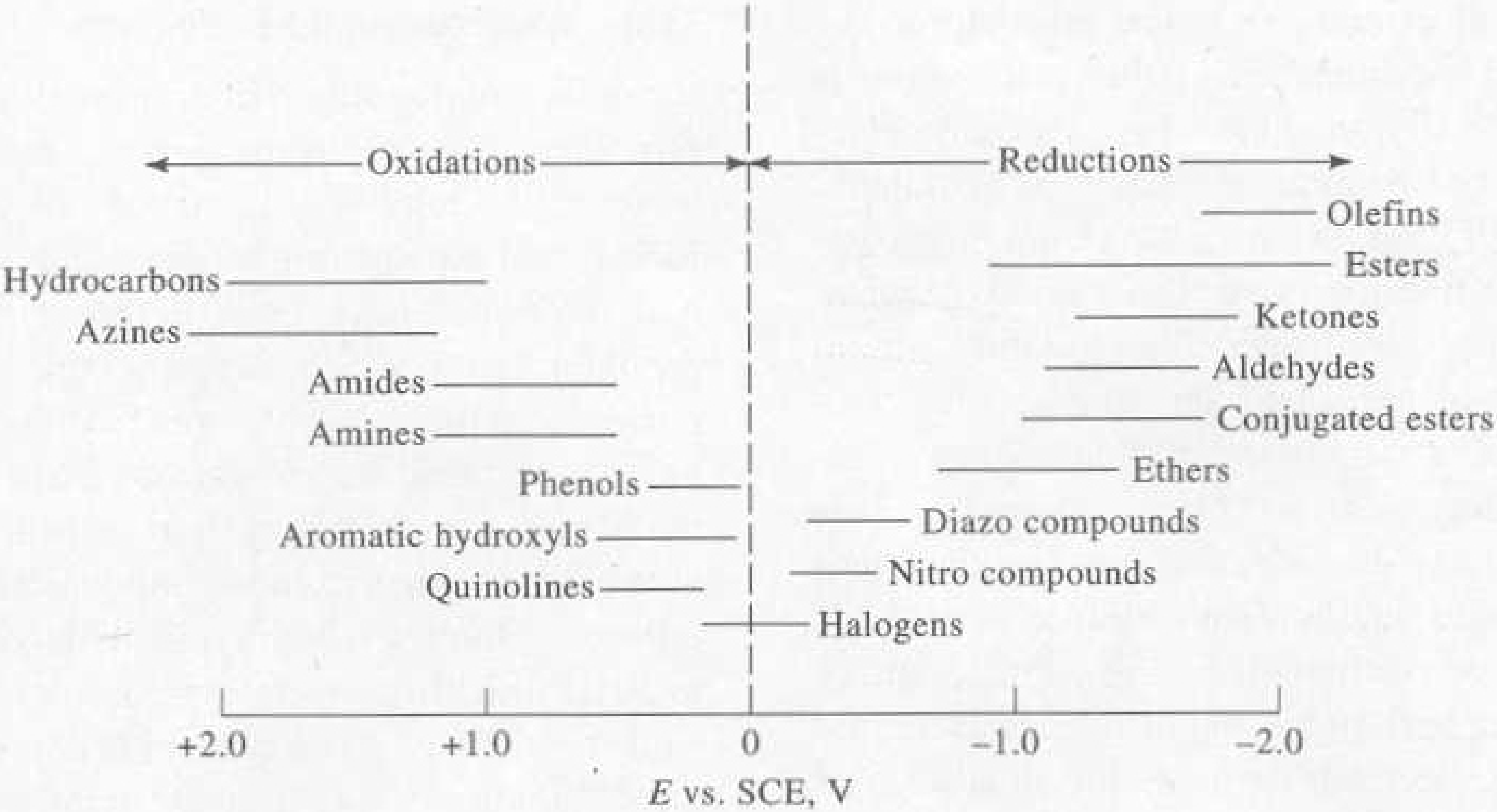


Figure 28-12 Potentially detectable organic functional groups by amperometric measurements. The horizontal lines show the range of oxidation or reduction potentials wherein compounds containing the indicated functional groups are electroactive.

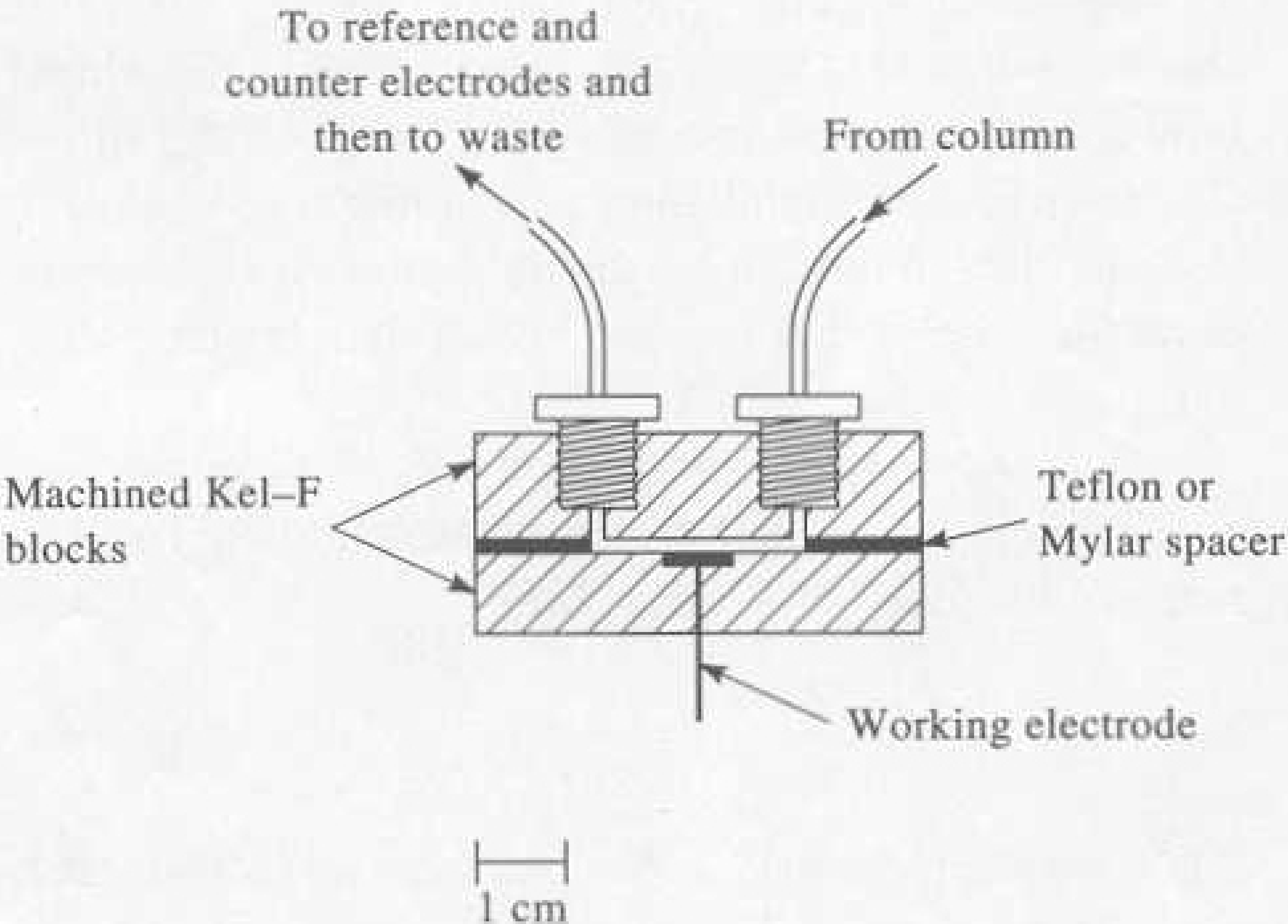


Figure 28-13 Amperometric thin-layer detector cell for HPLC.

Other HPLC detectors

- LC-MS using thermospray – new popularity (pharmaceuticals)
- Evaporative light scattering - polymers
- LC-FTIR
- LC-plasma emission or ICP-MS

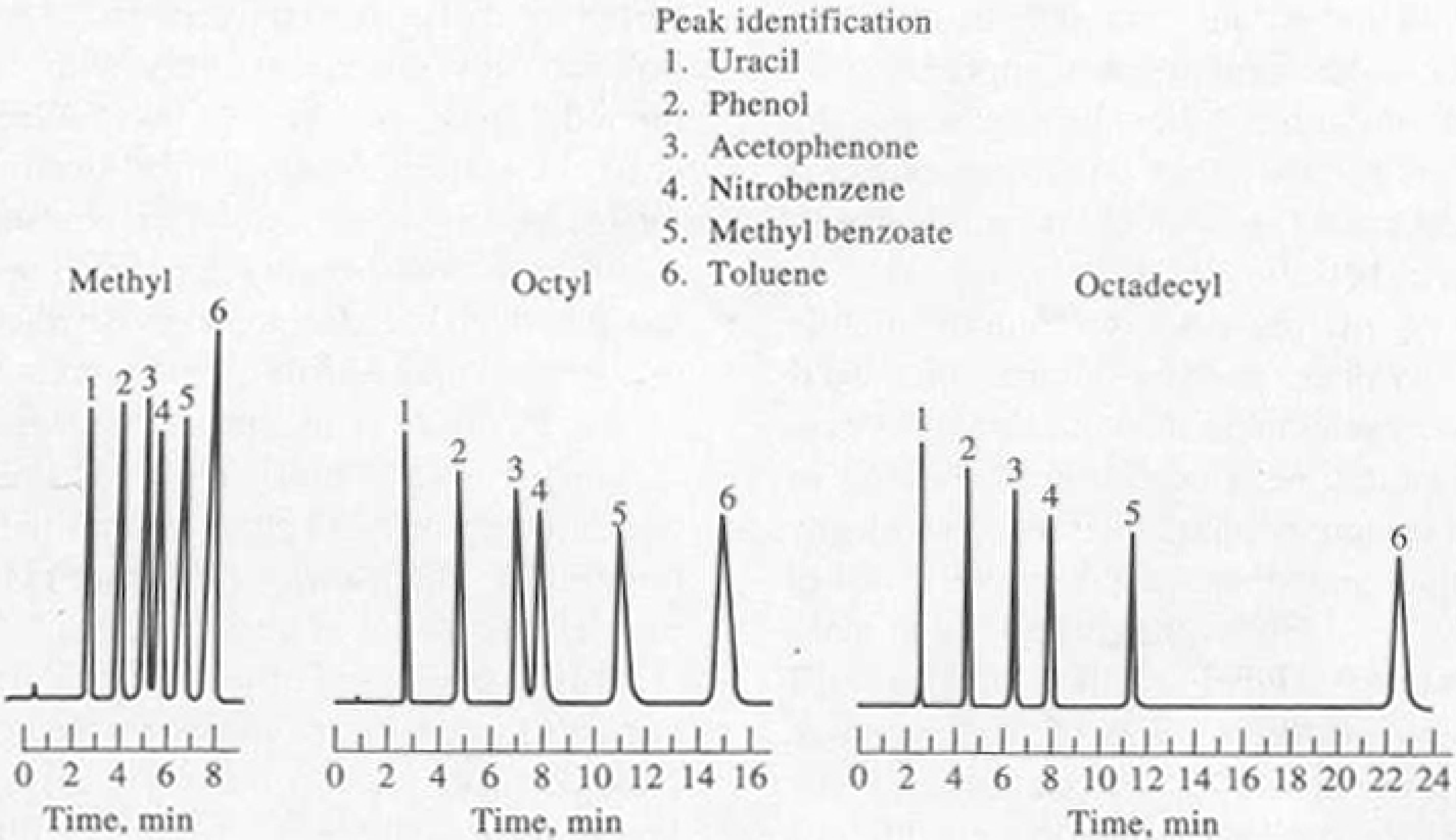


Figure 28-15 Effect of chain length on performance of reversed-phase siloxane columns packed with 5-μm particles. Mobile phase: 50/50 methanol/water. Flow rate: 1.0 mL/min.

Besides C_{18} can have C_8, C_4, C_3, C_2, C_1 plus functionalities like cyano ($-C_2H_4CN$), amino ($-C_2H_4NH_2$), diol ($-C_3H_6O-CH_2-CHOHCH_2OH$)

Each has different polarity

Can also do Ion Pair Chromatography or Paired-Ion Chromatography – type of RP-HPLC used to separate ionic species

Still partition chrom. but use a reagent like a quaternary ammonium salt $(C_4H_9)_4N^+$ to pair with analyte ions to separate by RP

Adsorption Chromatography –
bare silica or alumina to separate non-polar compounds because they adsorb to the stationary phase & are eluted by adjusting solvent strength of mobile phase – important non-linear applications

Adsorption chrom. = normal phase chromatog.

Least popular mode of separation due to:
strong adsorption, surface changes over time, with pH or water content

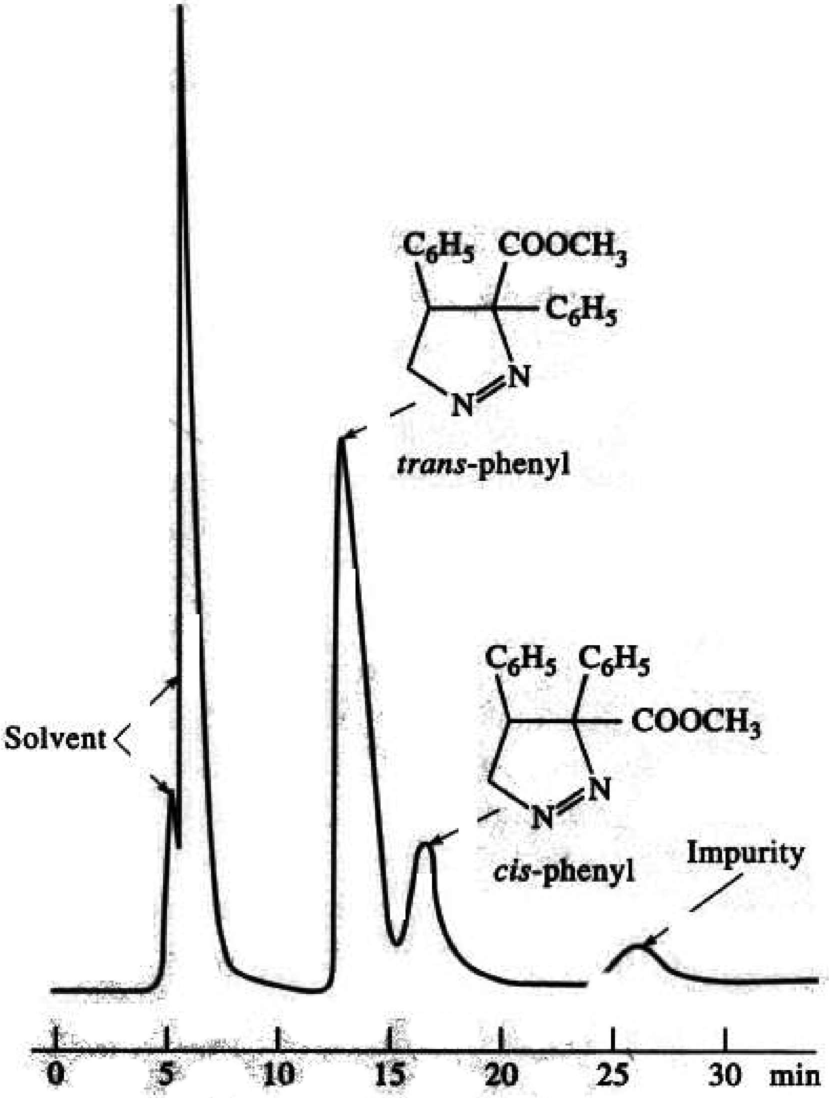


Figure 28-20 A typical application of adsorption chromatography: separations of *cis*- and *trans*-pyrazoline. Column: 100 × 0.3 cm pellicular silica. Mobile phase: 50% methylene chloride/isooctane. Temperature: ambient. Flow rate: 0.225 mL/min. Detector: UV, 254 nm.

- Sample of an application of adsorption chromatography

Ion Chromatography (Ion Exchange)

Historically was developed for the

Manhattan Project (atomic bomb)

Generally not automated because of the lack of good detectors until it was reinvented in 1970’s at Dow Chemical using conductivity detection & chemical suppression

Stationary phases are resin beads of styrene-divinylbenzene functionalized with cationic & anionic groups developed for water purification in 1930’s

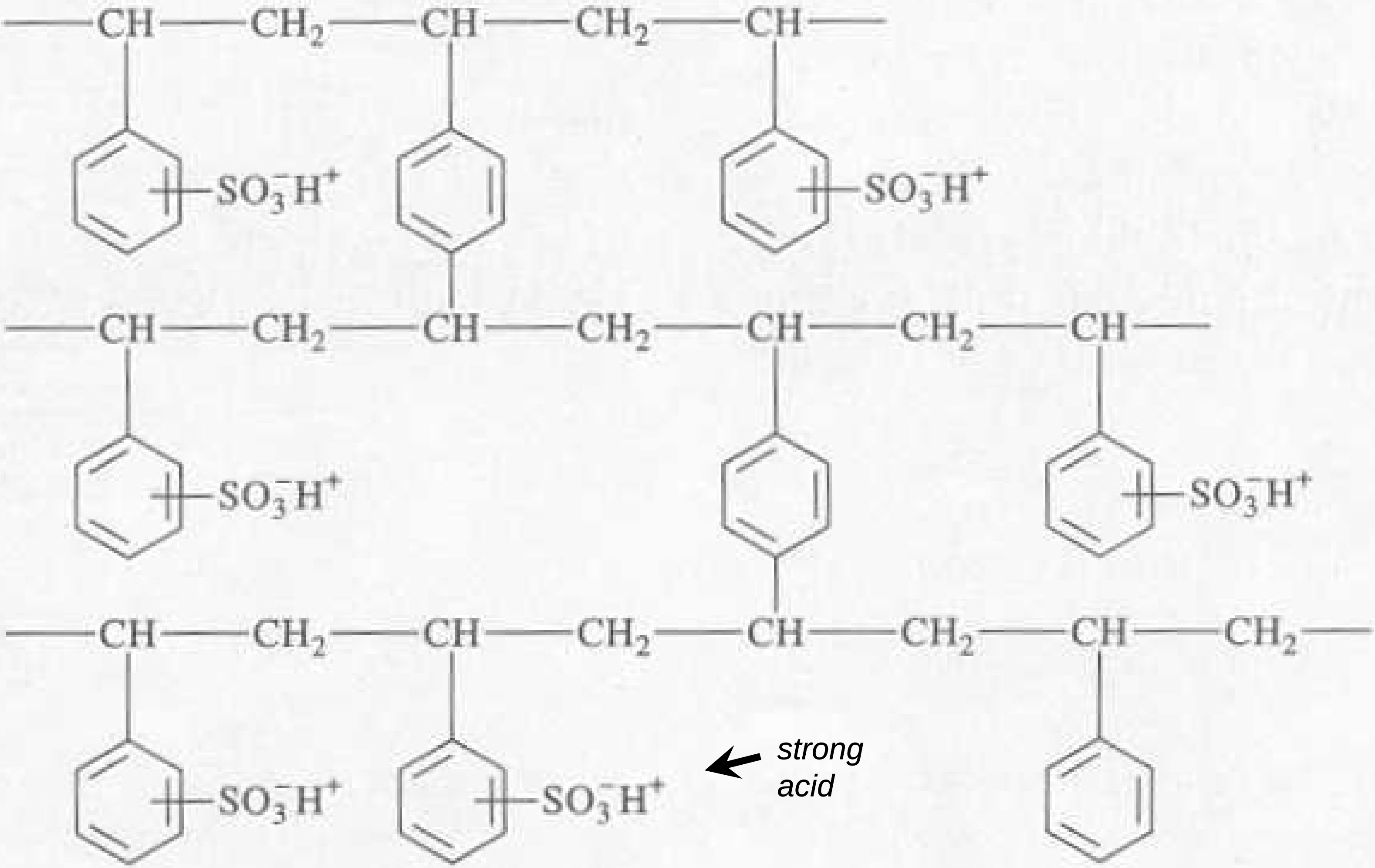


Figure 28-21 Structure of a cross-linked polystyrene ion-exchange resin. Similar resins are used in which the $—SO_3^-H^+$ group is replaced by $—COO^-H^+$, $—NH_3^+OH^-$, and $—N(CH_3)_3^+OH^-$ groups.

weak base strong base weak acid

Can write reactions in general format

$$xRSO_3^- H^+ + M^{x+} \rightleftarrows (RSO_3^-)_x M^{x+} + xH^+$$

solid   solution   solid   solution

Where R = polymer support (styrene divinylbenzene)

Can write equilibrium expression for exchange

$$K_{ex} = \frac{[(RSO_3^-)_x M^{x+}]_s [H^+]^x_{aq}}{[RSO_3^- H^+]^x_s [M^{x+}]^x_{aq}}$$

tells affinity of resin for M^+ compare to H^+

here or any ion

Ion Exchange Process

Analyte ions (M^{x+}) are passed thru column & retained on an ion-exchange site. The mobile phase contains some H^+ & this is increased sufficiently to cause <u>exchange</u> with M^{x+}.

Back to equilibrium expression

$$K_{ex} = \frac{[(RSO_3^-)_x\ M^{x+}]_s\ [H^+]^x_{aq}}{[RSO_3^-\ H^+]^x_s\ [M^{x+}]^x_{aq}}$$

Rearrange to

$$\frac{[RSO_3^-\ H^+]^x_s}{[H^+]^x_{aq}}\ K_{ex} = \frac{[(RSO_3^-)_x\ M^{x+}]_s}{[M^{x+}]^x_{aq}}$$

During elution $[H^+]$ is high & $[RSO_3^-\ H^+]_s$ is high

Left hand side of equation essentially constant

$$K = \frac{[(RSO_3^-)_x M^{x+}]_s}{[M^{x+}]^x_{aq}} = \frac{C_s}{C_M}$$

K turns out to be a distribution ratio (partition)

Order of affinity for sulfonated cation exchange

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

$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Hg^{2+}$

Ion Chromatography Detection

Basic detector is conductivity, but others are used such as UV-vis & atomic spectrometry (AA, AE) for metals

Measure conductivity change in effluent when analyte passes through

Problem – use high [H^+] to elute small [M^{x+}] which makes it difficult to detect [M^{x+}] conductivity on high background of [H^+]

This problem hindered development of IC until the innovations made at Dow in 70’s

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

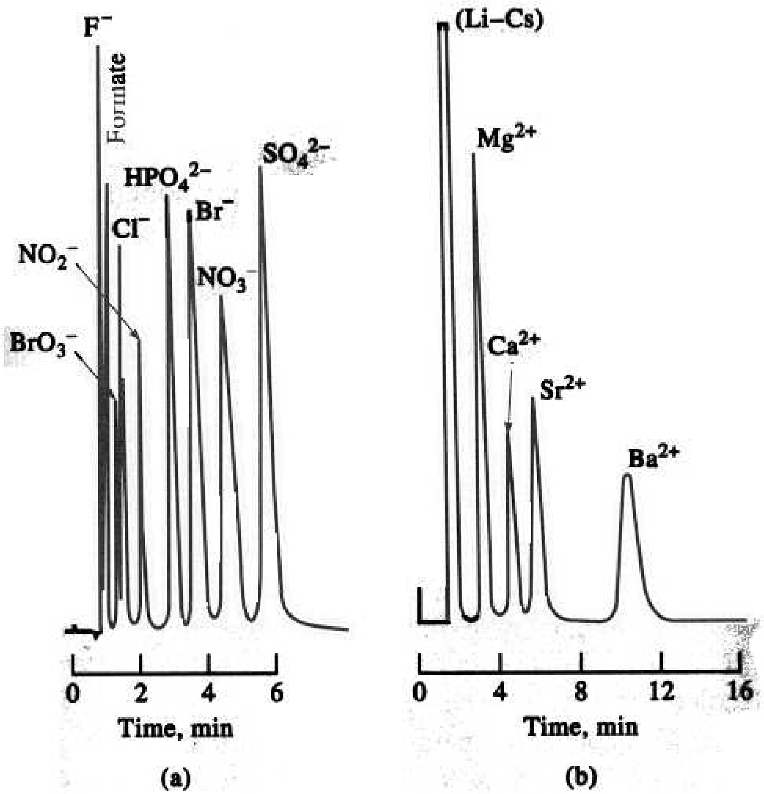


Figure 28-23 Typical applications of ion chromatography. (a) Separation of anions on an anion-exchange column. Eluent: 0.0028 M $NaHCO_3$/0.0023 M Na_2CO_3. Sample size: 50 μL. (b) Separation of alkaline earth ions on a cation-exchange column. Eluent: 0.025 M phenylenediamine dihydrochloride/0.0025 M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

- Typical IC separations

Size Exclusion Chrom. (SEC)

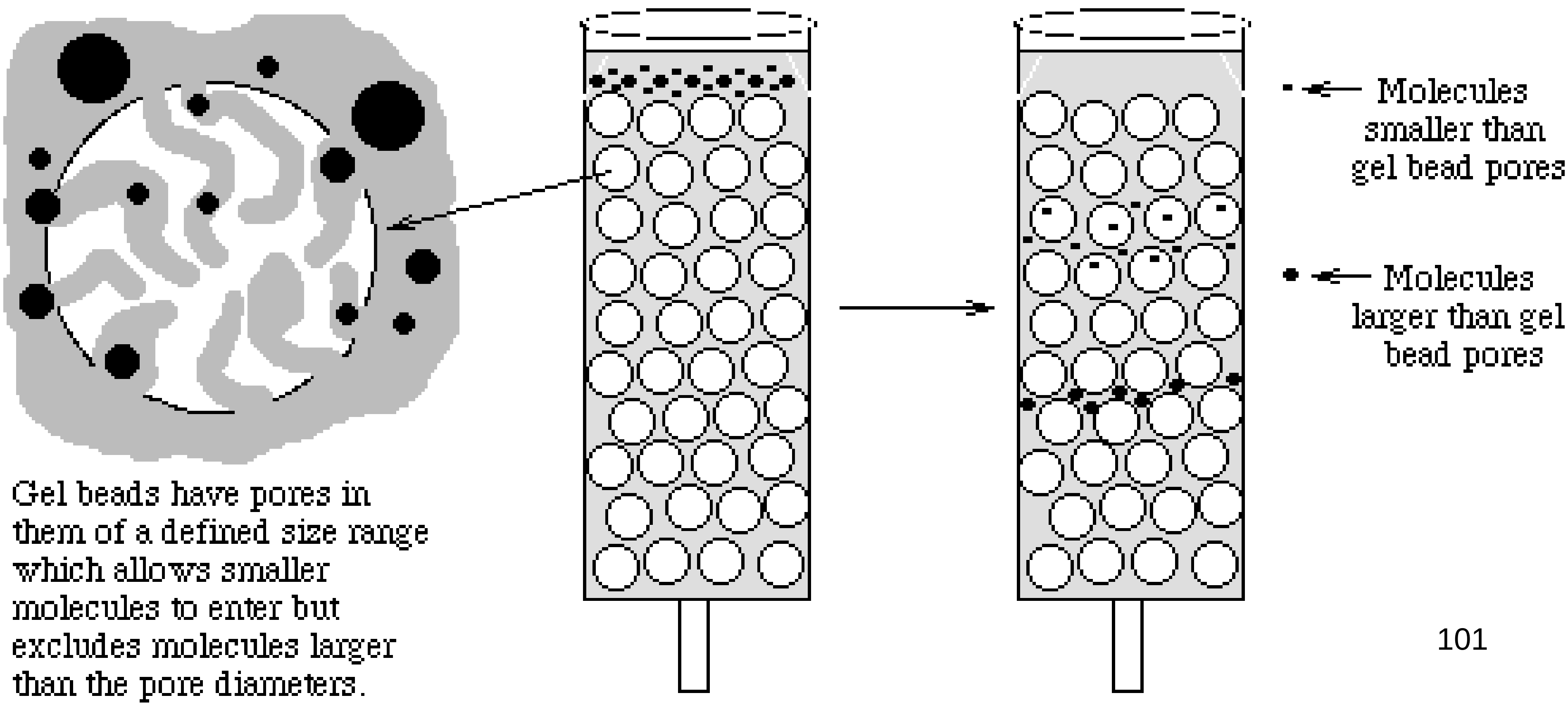
Packings are porous polymeric (resins) or silica based materials

Two names used for the same process:

1) Gel filtration chrom. = aqueous solvent
2) Gel permeation chromatography = non-aqueous mobile phase

Column packing works like a molecular filter allowing small molecules access to every pore, retarding their progress – large molecules pass thru more quickly

SEC


Molecules smaller than gel bead pores
Molecules larger than gel bead pores
Gel beads have pores in them of a defined size range which allows smaller molecules to enter but excludes molecules larger than the pore diameters.

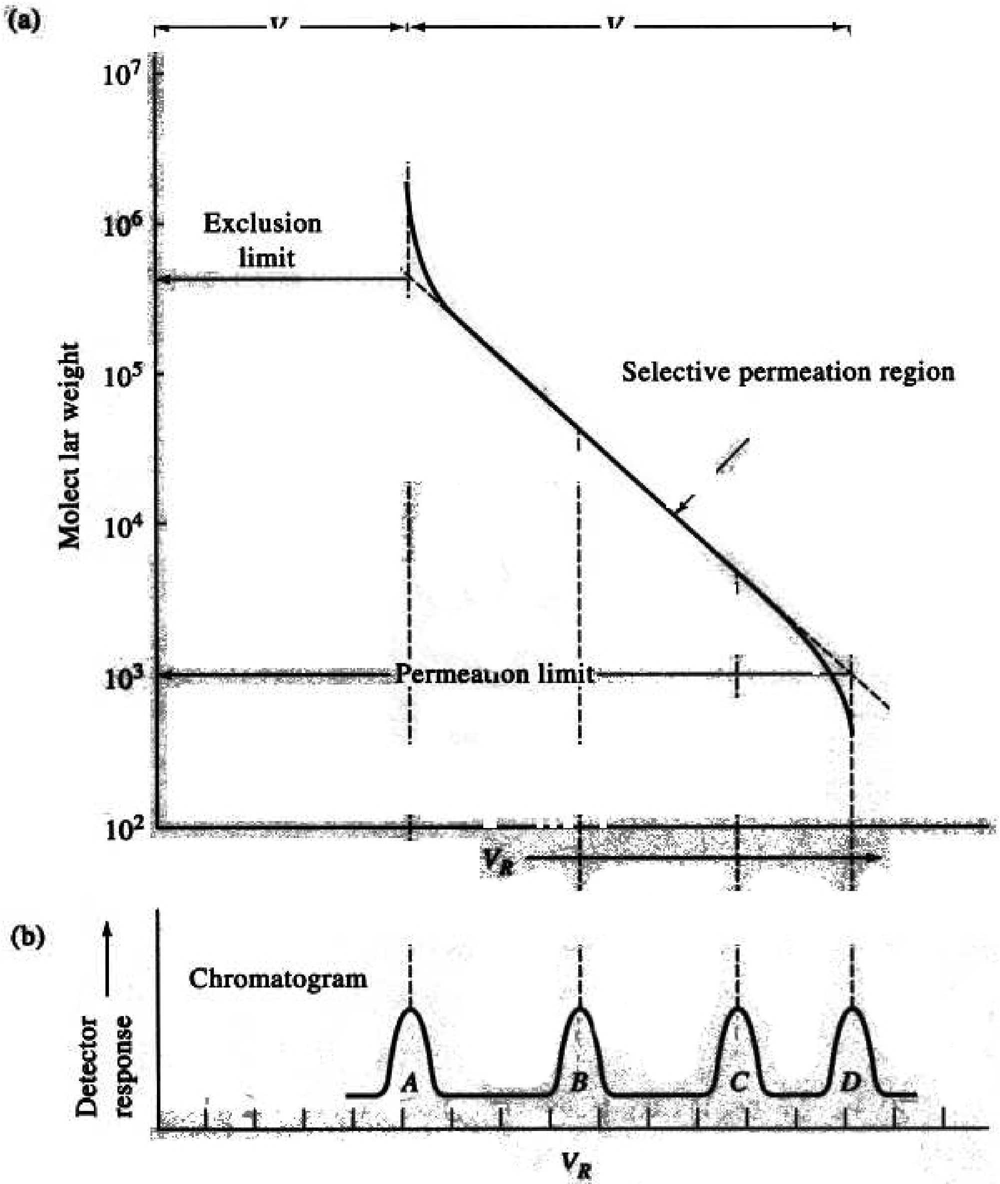


Figure 28-27 (a) Calibration curve for a size-exclusion column. (b) Chromatogram showing peak *A* containing all compounds with molecular weights greater than the exclusion limit, peaks *B* and *C* consisting of compounds within the selective permeation region, and peak *D* containing all compounds smaller than the permeation limit.