Chapter 27: Gas Chromatography

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

GC-MS Schematic

Interface less critical for capillary columns

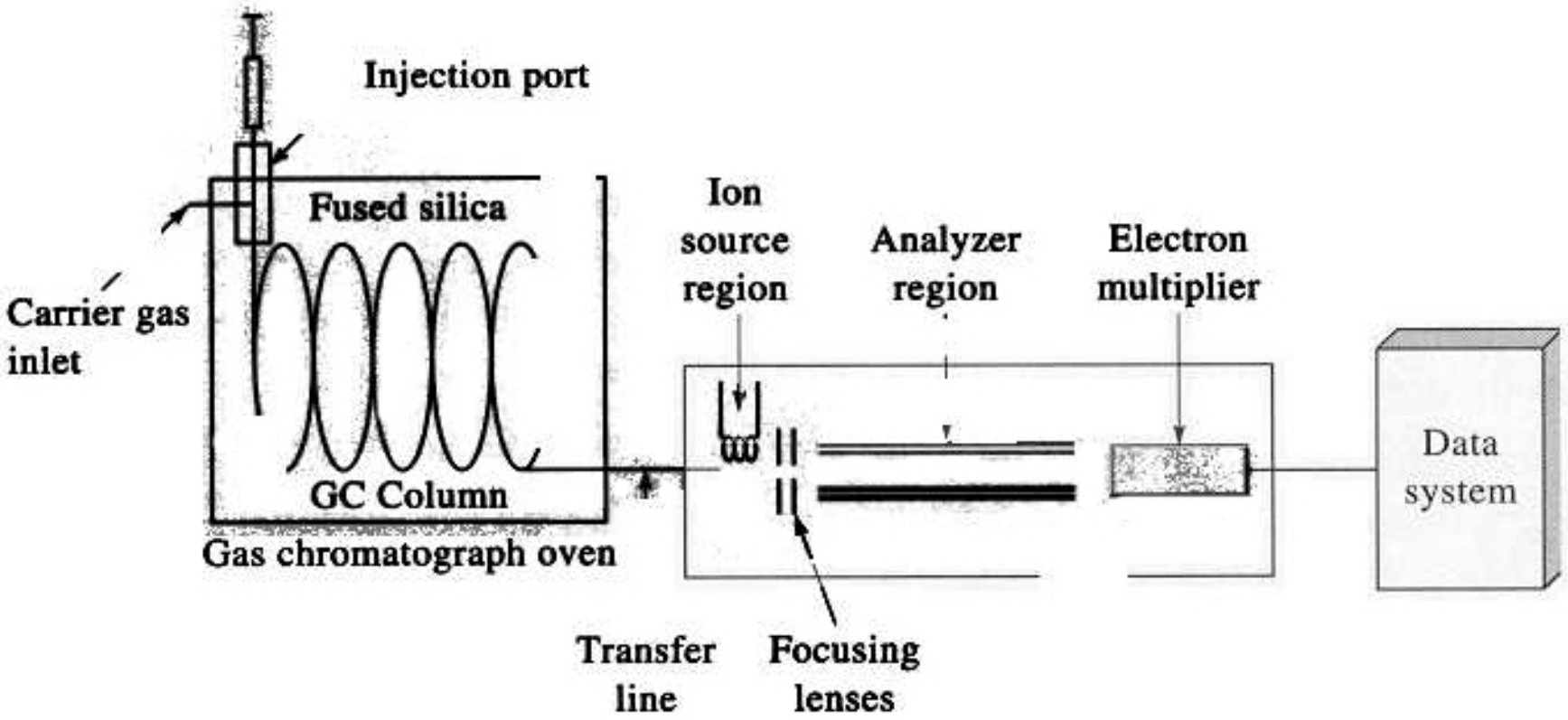


Figure 27-13 Schematic of a typical capillary gas chromatography/mass spectrometer.

Several types of Mass Specs available

- Rarely magnetic sector or time of flight
- Usually quadrapole 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

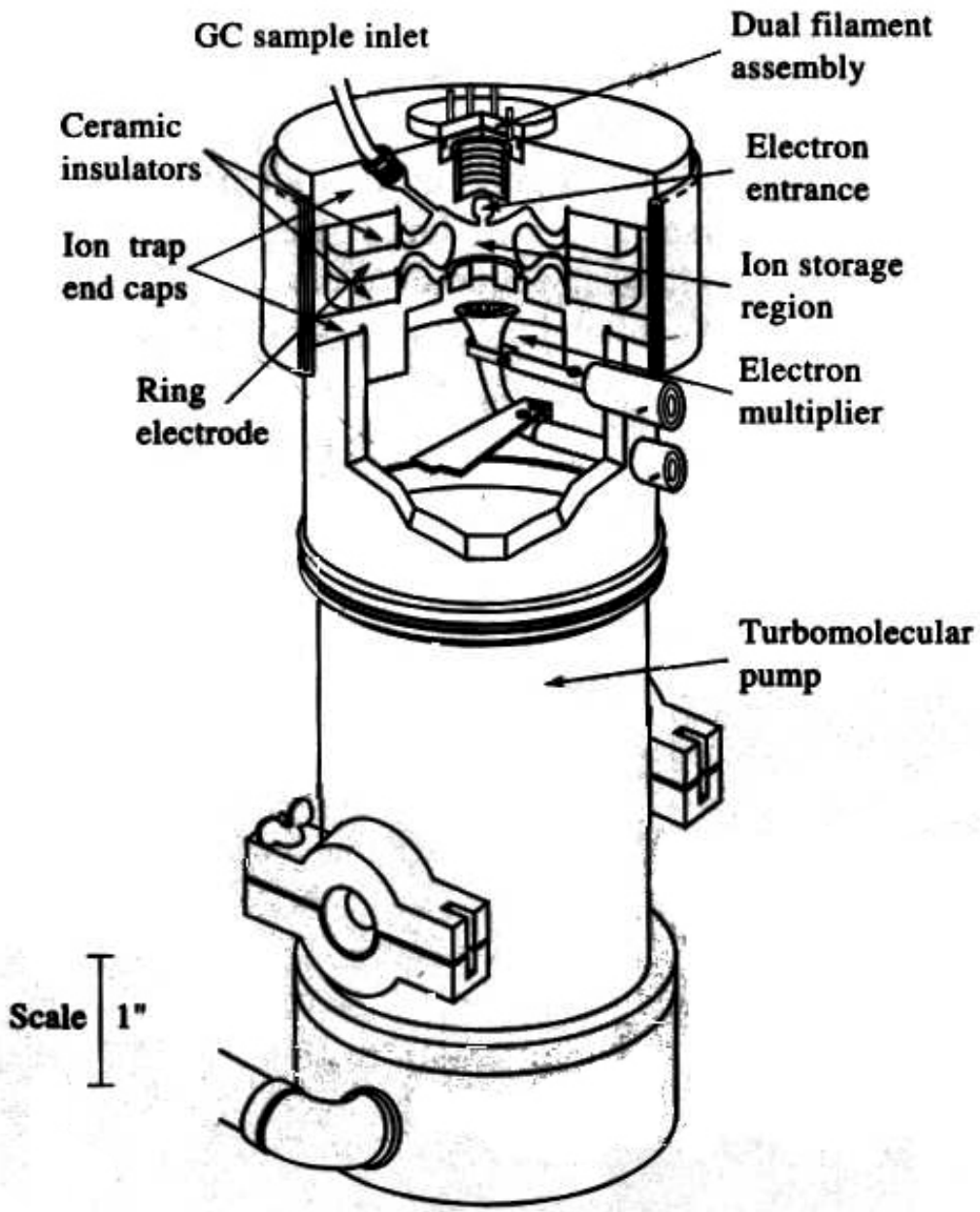


Figure 27-15 Schematic of the ion trap detector.

Ion trap uses radio frequency to trap ions, hold or store them, then ejects them to detector

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 – look at certain mass/charge ratios for compounds of interest – routine analysis

GC-FTIR

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

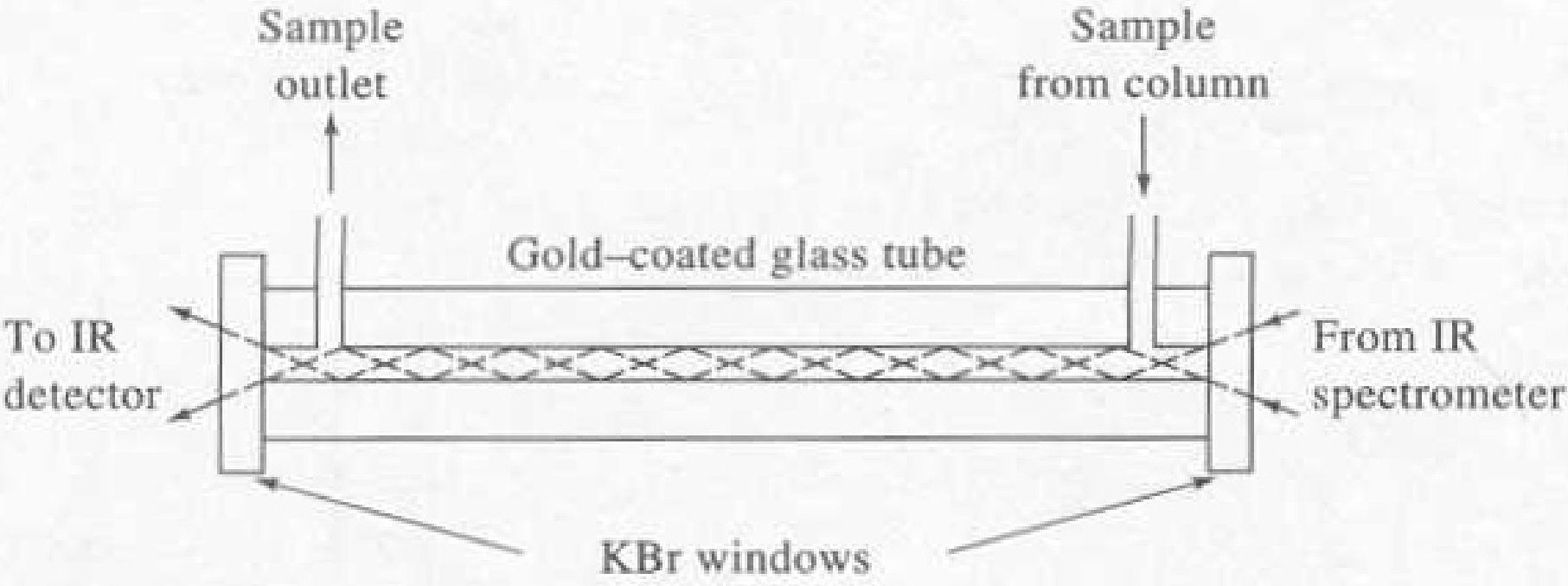


Figure 27-17 A typical light pipe for GC/IR instruments.

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

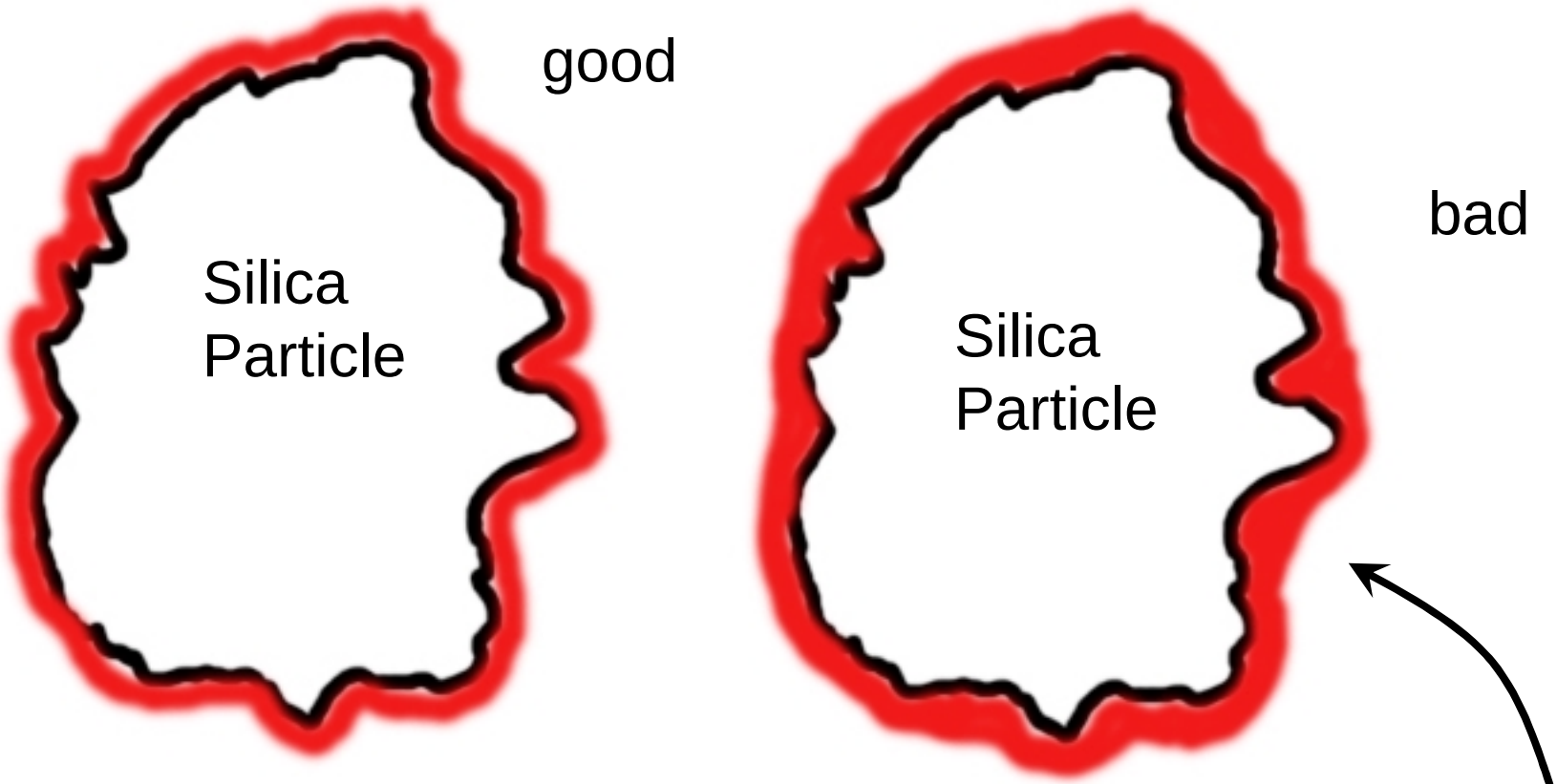
GC Columns & Stationary Phases

- 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
  - Can dissolve liquid in solvent, mix with support & evaporate solvent
  - Very tricky to do correctly
  - Condition column at 5 ^oC above operating temp

Stationary Phase Coating



Don’t want stationary phase liquid coating to bleed or puddle in column – gives zone broadening & poor resolution

Open Tubular Columns → Capillary Columns

Column evolution

Three types

Wall Coated Open Tubular (WCOT) – open tube with coating on wall – duh

Support Coated Open Tubular (SCOT) – open tube with particles of support material stuck to the walls

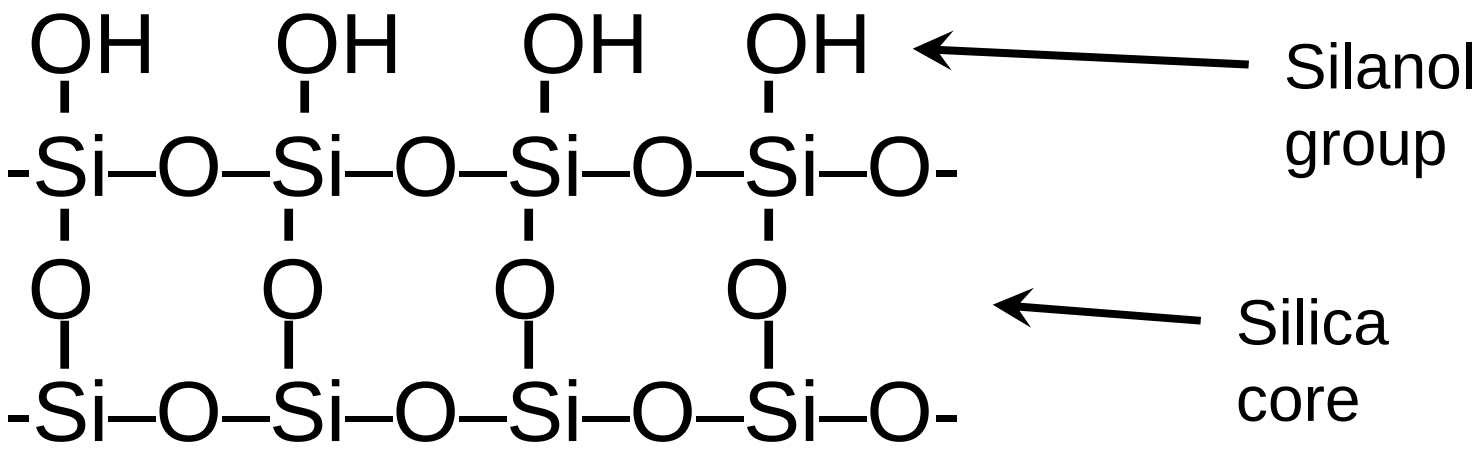
Fused Silica Open Tubular (FSOT) – WCOT made of fused silica

TABLE 27-1 Properties and Characteristics of Typical Gas-Chromatographic Columns

	Type of Column*			
	FSOT	WCOT	SCOT	Packed
Length, m	10–100	10–100	10–100	1–6
Inside diameter, mm	0.1–0.53	0.25–0.75	0.5	2–4
Efficiency, plates/m	2000–4000	1000–4000	600–1200	500–1000
Total plates	$(20–400) \times 10^3$	$(10–400) \times 10^3$	$(6–120) \times 10^3$	$(1–10) \times 10^3$
Sample size, ng	10–75	10–1000	10–1000	$10–10^6$
Relative back pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow
Chemical inertness	Best →			Poorest
Flexible?	Yes	No	No	No

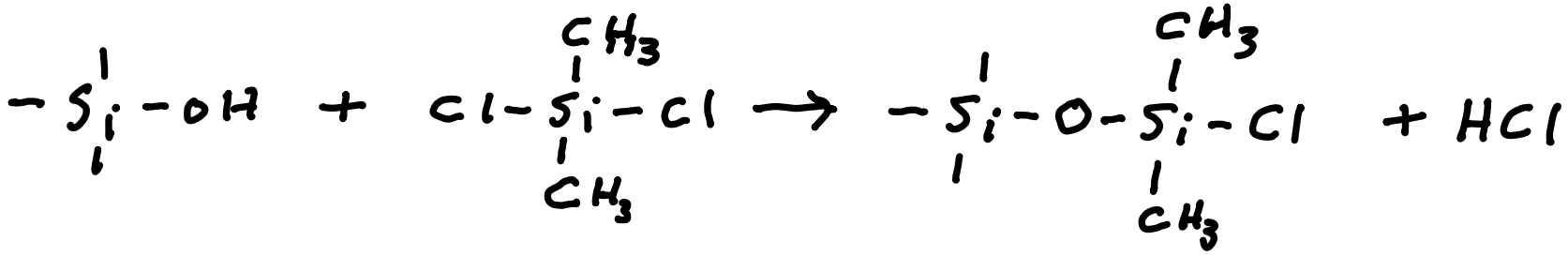
*FSOT: Fused-silica, open tubular column.
WCOT: Wall-coated, open tubular column.
SCOT: Support-coated open tubular column.

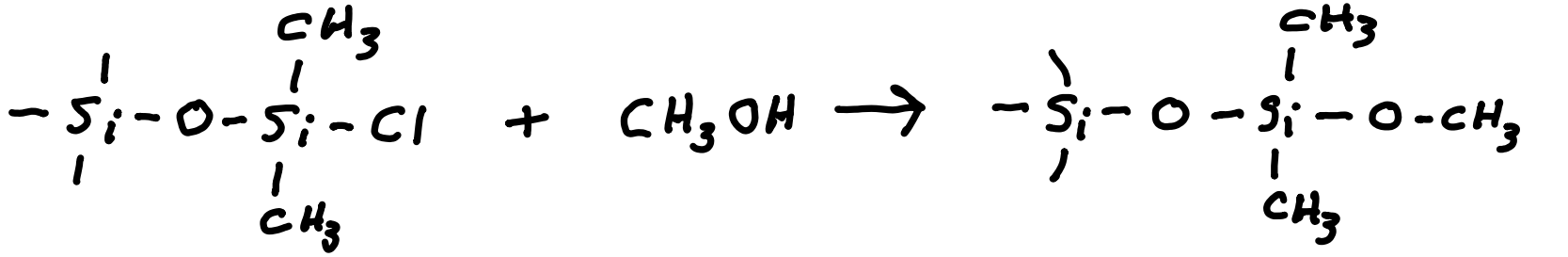
Surface chemistry – glass & silica are SiO_2 with -OH at surface



OH is a problem because it can adsorb polar substances with strong affinity causing peak tailing – must deactivate by reacting

React Si-OH groups with silane





Sometimes still have –OH groups

If silica not pure may have metal impurities M-OH
typically use high purity silica – acid wash

Same chemistry to making specialty bonded phase

Liquid coatings on stationary

phase should exhibit:

1) Chemical inertness
2) Low volatility (b.p. 100 ^{o}C > max temp)
3) Thermal stability
4) Good solvent characteristics (i.e. k' & α suitable)

Many different liquid coatings have been used or attempted for GC, only about 10 have withstood the test of time

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

Retention time of a solute depends on K (partition coefficient) which is dependent on stationary phase – must have different K's for different analytes

However, if K's too large → long retention time

if K's too small → short retention time

resulting in incomplete separation

In choosing a stationary phase use general principles such as "like dissolves like", polar groups interact with polar groups, non polar with non polar, etc.

Polar groups include –CN, –CO, –OH

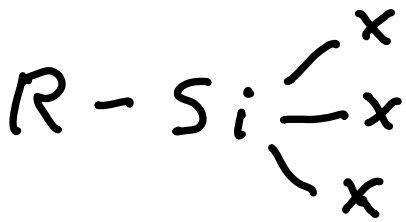
Polar analytes include alcohols, acids, amines

Non polar → hydrocarbons

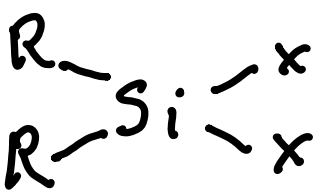
Where analyte & stationary phase match is good → elution order is determined by boiling points

Bonded Stationary Phases

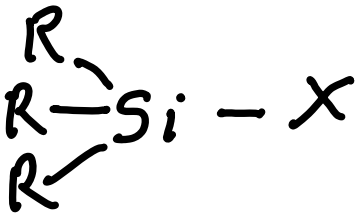
Use silylation chemistry to covalently attach stationary phase to solid support or column wall



X = Cl or -O-CH_3 or -O-CH_2-CH_3



R = stationary phase functionality



Bonded Stationary Phases

Advantages

- monolayer coverage can be obtained
- reduced bleeding of stationary phase
- longer lasting
- better stability
- can be solvent washed

Chiral Stationary Phases – separating stereo-isomers is the ultimate in chromatography, separate molecules that are mirror images

Predicting retention

I) Selectivity Factors

$$\alpha = \frac{K_B}{K_A} = \frac{(t_R)_B - t_M}{(t_R)_A - t_M} = \frac{(t'_R)_B}{(t'_R)_A}$$

If B is a standard compound & we know α, can then be able to identify compound A even if we change the the chromatographic conditions or go to another chromatograph, etc.

This is limited to specific applications where a database is available, not universally applicable

II) Retention Index (I)

Proposed by Kovats in 1968

Index based on normal alkanes

If have a mixture of 2 known alkanes & 1 unknown compound & the 2 knowns bracket unknown in t_R can then determine I for unknown & identify it

$$I = 100 \times \#\text{ of carbon atoms}$$

Regardless of column packing, temp. or other conditions

Kovats Retention Index

Doesn't work as well for other types of compounds (Hc), but useful in some cases e.g. homologous series

Plot log adjusted retention time ($t_R' = t_R - t_M$) vs number of carbon atoms is linear

Useful in particular fields – petroleum industry, cosmetics, pharmaceuticals, etc. since have their own unique "standards"

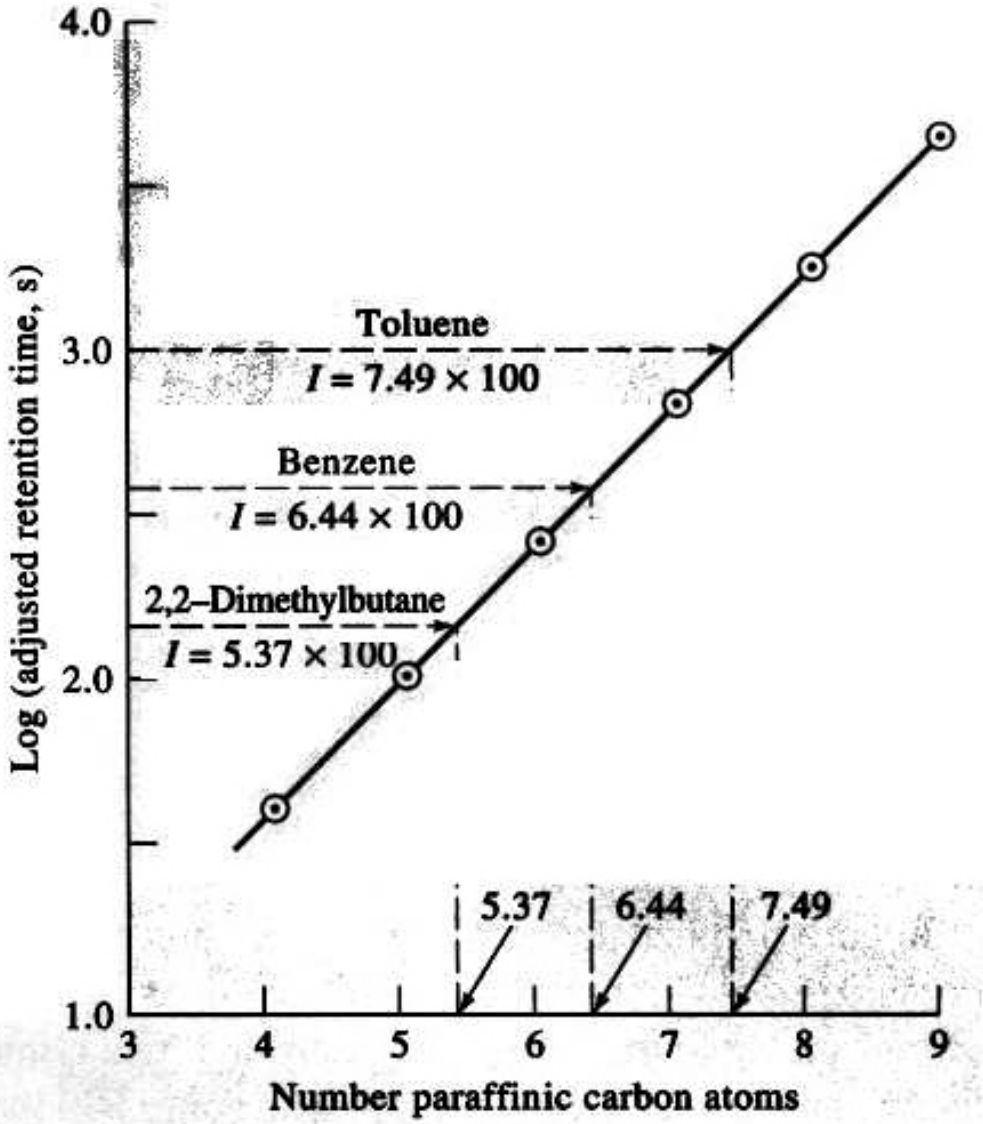


Figure 27-12 Graphical illustration of the method for determining retention indexes for three compounds. Stationary phase: squalane. Temperature: 60°C.

Note number of carbons that would be calculated for these 3 compounds based on I

Chapter 28: High-Performance Liquid Chromatography (HPLC)

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