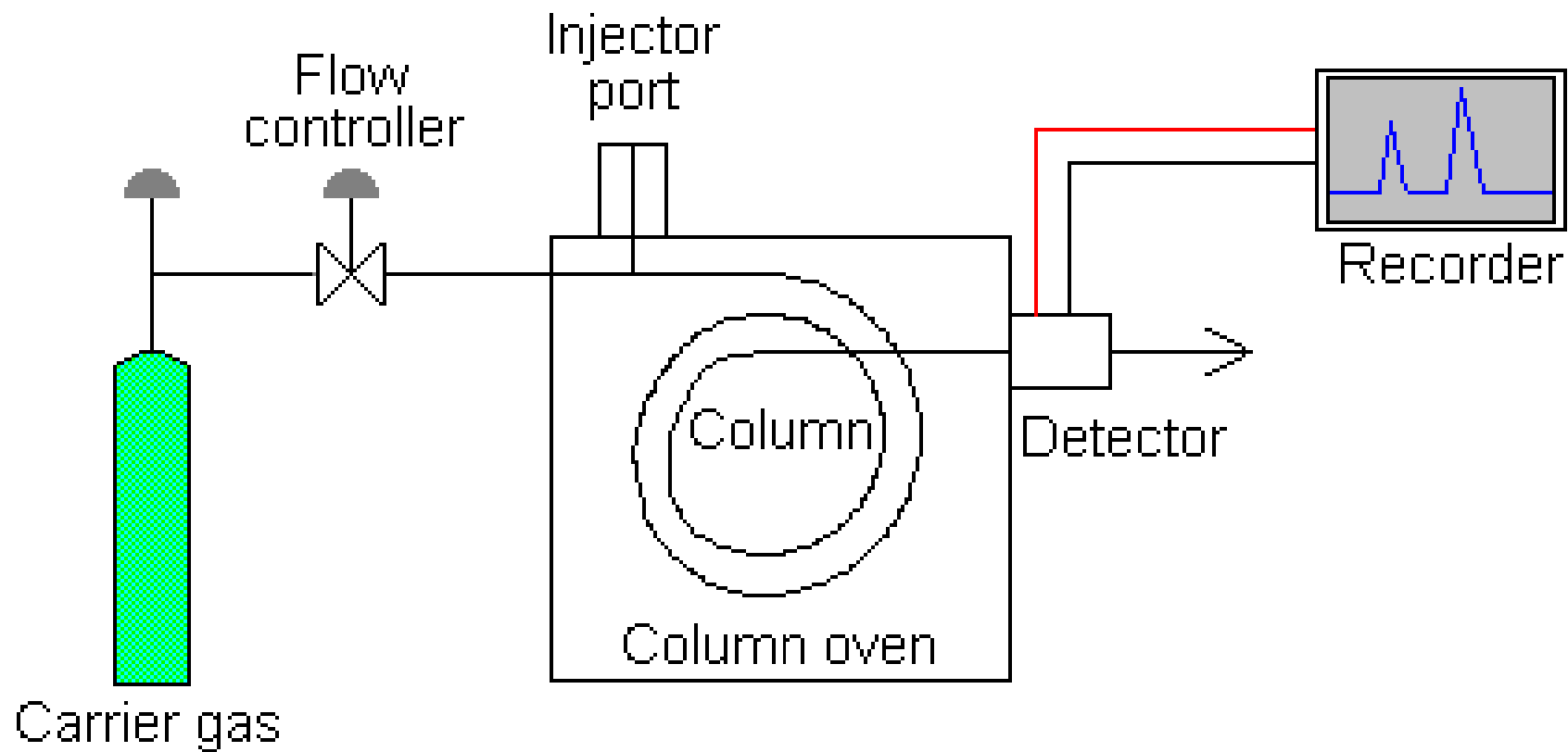# Chemistry 4631

Instrumental Analysis
Lecture 25

Gas Chromatography

Instrumentation

Gas Chromatography

Instrumentation

Columns
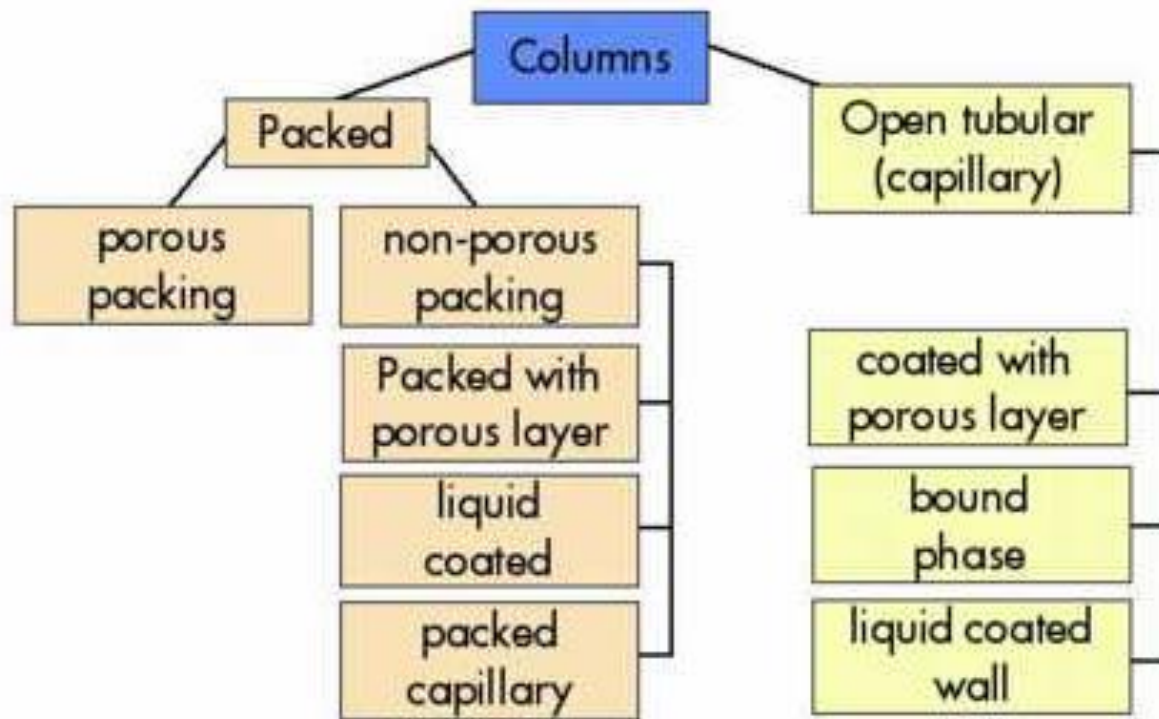
Two types in general use:
- **packed (stationary phase)**
- **open tubular or capillary**

Columns determine selectivity and efficiency of the sample.
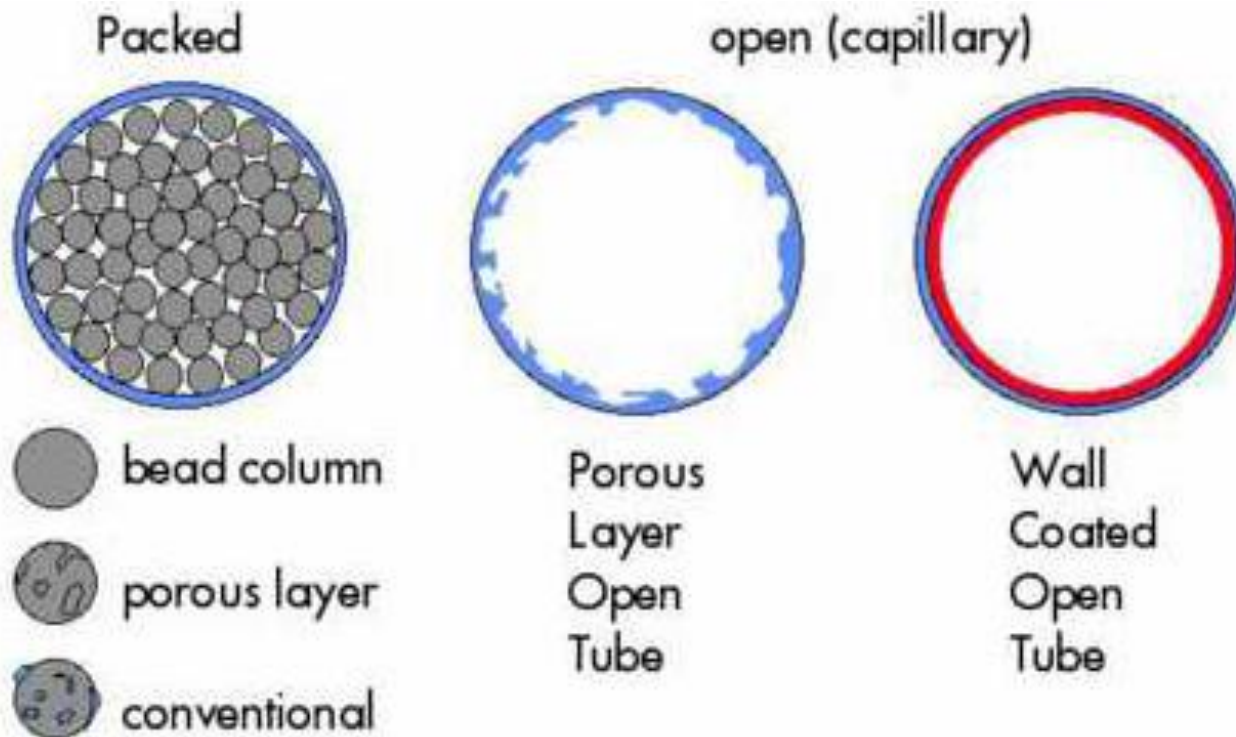
Gas Chromatography

Instrumentation

Columns

Gas Chromatography

Instrumentation

Columns

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Column Materials

- Column tubing supports the stationary phase.

- Needs to be:
  - chemically inert (to prevent sample decomposition)
  - thermally stable
  - robust
  - flexible – form a coil to fit into oven

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Column Materials

Early columns were metal (stainless steel, Cu, Al, Ni) but these were too reactive.

Glass is popular – but fragile

Fused silica columns – weak and subject to atmospheric corrosion. Used a protective outer Al sheath. These columns are used for most applications.

Gas Chromatography

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Columns

Column Activity leads to:
-**tailing or skewed peaks**
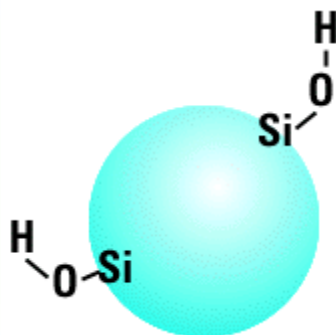-**partial or total disappearance of a solute**

The surface properties of the column – catalytic or sorptive are important to consider to eliminate column activity.
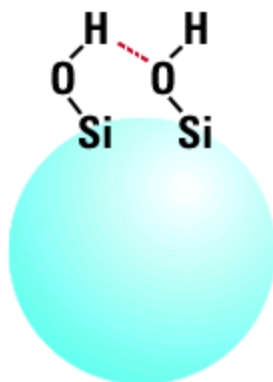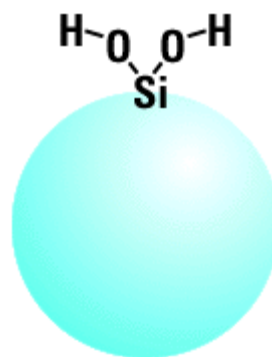
Gas Chromatography

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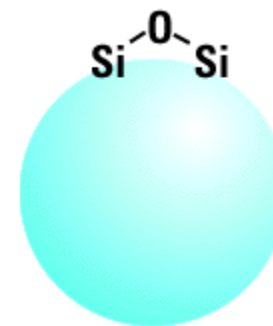**Various surface groups attributed to the silica surface have been identified:**

| Isolated Silanol | Vicinal Silanol | Geminal Silanol | Siloxane |

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Columns

- **Surface hydroxyl groups can act as proton donors in hydrogen bonding interactions**
  - -**very strong sorptive sites for molecules with localized high electron density.**

- **Surface siloxane bridge can act as**
  - -**proton acceptors functioning as sorptive sites for molecules such as alcohols**

- **Metal ions present on the surface of soda lime or borosilicate glasses can function as**
  - -**Lewis acid sites absorbing molecules that have regions of localized high electron density such olefins, aromatic compounds, alcohols, ketones and amines. (Lewis acids – a species that accepts an electron pair)**

Gas Chromatography

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Columns

**Columns are deactivated before use. One method deactivates reactive hydroxyl groups by silanizing or silylating the inner surface of the column.
Typical derivatization reactions are:**

- **Silylation**
- **Acylation**
- **Alkylation**
- **Esterification**

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Silylation - It involves the replacement of an acidic hydrogen on the compound with an alkylsilyl group, for example, $-SiMe_3$. The derivatives are generally less polar, more volatile and more thermally stable.

OH + MSTFA $\longrightarrow$ OTMS
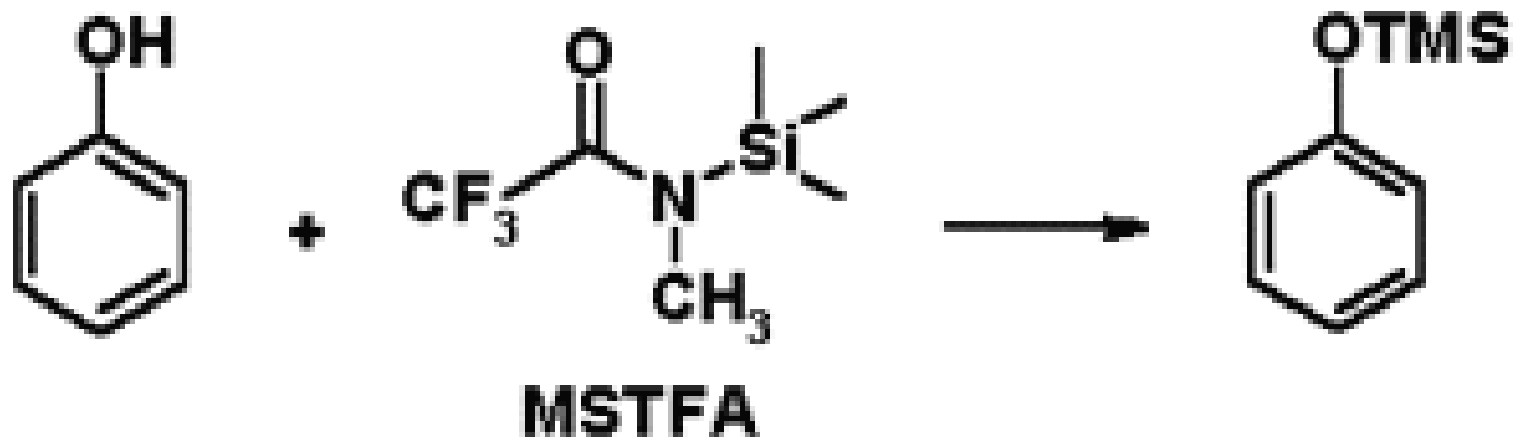
Gas Chromatography

Instrumentation

Columns

Stationary Phases (GSC)

GSC of inorganic gases is the one area where packed columns are still used almost exclusively. Main adsorbents for packed columns are based on:
-silica
-charcoal
-alumina
-molecular sieves

Gas Chromatography

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Stationary Phases (GSC)

Adsorbents for GSC

Chemical Type	Specific Surface Area (m^2g^{-1})	Pore Diameter (nm)
Silica	~ 100 – 185	15 – 30
Alumina	-	-
Carbon Black	10 – 1000	1 – 2
Molecular Sieves	700 – 1000	0.5 – 2.0
Porous Polymers	~ 100 – 800	5 – 500

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Stationary Phases (GLC)

> **Stationary Phase is a liquid either on solid support (packed columns) or the column wall.**

> **Solid Support – retains the liquid stationary phase and provides a large surface area. It must be thermally stable, mechanically strong to avoid breakage during the column packing process. Must have uniform pore and particle size.**

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Stationary Phases (GLC)

Most common supports are based on diatomaceous earths which consist mainly of silica and minor metallic impurities. Other supports are PTFE beads, glass beads, charcoal, porous silica. Without a liquid phase these supports are essentially absorbants and would be the same as GSC.

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Stationary Phases (GLC)

The support is treated to reduce activity before coating by:

- acid wash, which eliminates metal impurities
- silanization with dimethyldichlorosilane (DMCS) or hexamethyldisilazane (HMDS) to eliminate surface activity of silanol groups.

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Stationary Phases (GLC)

Liquid Phase – required properties

- low vapor pressure
- thermal and chemical stability
- low viscosity
- nonreactive toward sample components
- wide operating temperatures (-80 to 450°C)
- reasonable solvent properties

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Stationary Phases (GLC)

Categories of stationary phases

- o **non-polar**
- o **polar**
- o **specialty phases**

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Stationary Phases (GLC)

Hydrocarbons – non-polar – have been used as non-polar stationary phase.

Most have a high molecular weight for low volatility.

Examples: Squalane ($C_{30}H_{62}$), Apolane C87, long-chain n-alkanes, Apiezon L-not used much.

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Stationary Phases (GLC)

Alkylsilicone Phases – can be non-polar or polar. Polymers based on silicon-oxygen-silicone backbone – most widely used group of stationary phases. Differences in these stationary phases differ mainly in the degree of substitution on the silicon backbone.
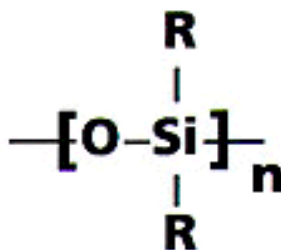
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Stationary Phases (GLC)

Standard polysiloxanes are characterized by the repeating siloxane backbone. Each silicon atom contains two functional groups. The type and amount of the groups distinguish each stationary phase and its properties.

$$-[O-Si]_n-$$

with R above and below Si

R = CH_3 methyl
$CH_2CH_2CH_2CN$ cyanopropyl
$CH_2CH_2CF_3$ trifluoropropyl

⬡ phenyl

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Stationary Phases (GLC)

Polyether Phases – polar phases – based on polyethylene glycol,

$HO\text{-}CH_2\text{-}CH_2\text{-}[O\text{-}CH_2\text{-}CH_2]_n\text{-}OH$.

Marketed under the trade name, carbowax or superox.

Advantage - Average molecular weight of 20,000, so can be used at high temperatures.

Disadvantage is that it reacts with even trace amounts of oxygen at high temperatures, as well as decomposing to acetaldehyde and acetic acid.

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Stationary Phases (GLC)

- **High-temperature phases – substituted silicone-carborane copolymers.**

- **Stable up to 450°C - 500°C.**

- **Their advantage is in their low stationary bleed – for use with highly sensitive detectors.**

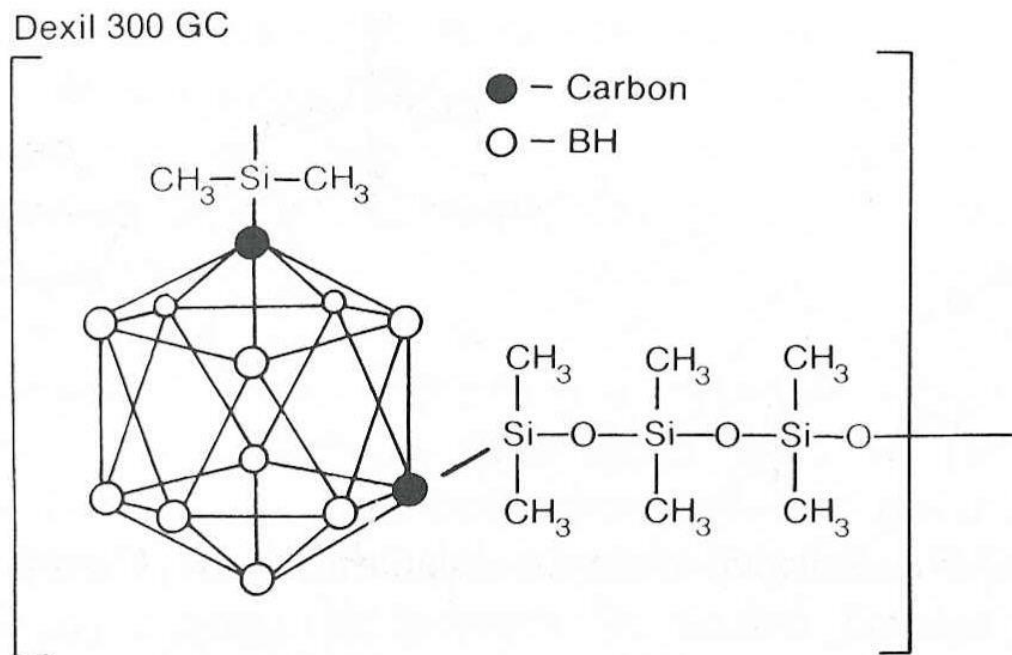# Gas Chromatography

Instrumentation

High Temperature Phases

Dexil 300 GC

● – Carbon
○ – BH

Fig. 3.18. A silicone–carborane copolymer used as a high temperature stationary phase.

Gas Chromatography

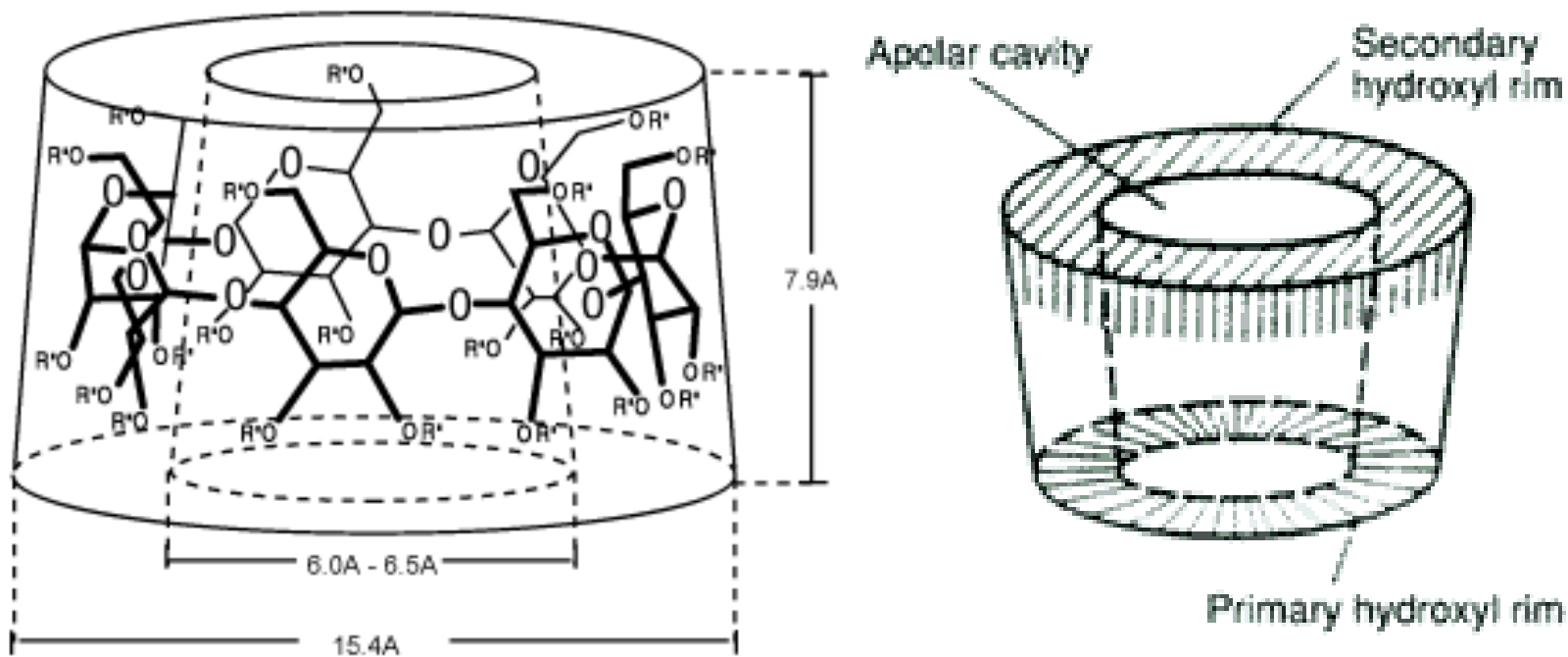## Instrumentation

Columns

Stationary Phases (GLC)

**Chiral Phases - used to distinguish between enantiomers of optically active compounds.
α,β,γ – cyclodextrins – composed of six or more D(+)-glucose units bonded through a α-(1,4) – glycosidic linkage.**

Gas Chromatography

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Chiral Phases

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Instrumentation

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Stationary Phase Film Thickness

Stationary phase loadings were 20-30% w/w prior to 1970's.

Now loadings are in the order of 1-3%.

Film thickness, d_f, has a direct effect on the retention, sample capacity and elution temperature.

For best column efficiency, the film thickness is kept as thin as possible in order to reduce resistance to mass transfer in the stationary phase, C_s.

Gas Chromatography

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Columns

Column Selection

- **Non-polar phases usually exhibit superior lifetimes – so best to select least polar phase needed for a particular separation.**

- **Most difficult factor to access is the ability of a phase to produce a good separation. In theory selection is based on knowing the types of interactions.**

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Column Selection

  Types of interactions:

- **London or dispersive forces (weak, non-specific). Temporarily induced dipole. As molecular weight increases dispersive forces increase (electrons further from nucleus)**

- **Dipole-dipole interactions (polar molecules)**

- **Acid – Base interactions (proton sharing or electron transfer)**

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Column Selection

Selection process takes experience (many years of use).

Easiest to remember "like dissolves like."

i.e.

Solvent	Phase-Choice
Alcohol (polar)	Polar
Alkane (non-polar)	Non-polar
Xylenes (non-polar)	Polar (highlights the slight difference in polarity among the isomers)

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Methods to characterize stationary phases:

Rohrschneider Constants or McReynolds Constants

Use the relative retention of a solute – plot of the logarithm of the adjusted retention time versus Kovats retention index, I (linear).
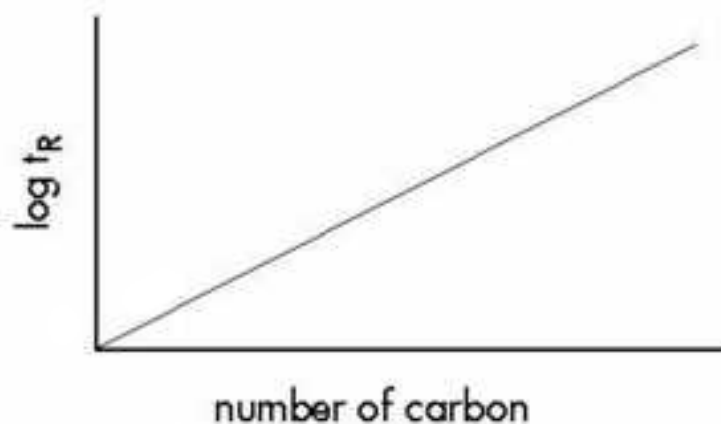
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Column Selection

Plot of the logarithm of the adjusted retention time versus Kovats retention index, I (linear).

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Kovat assigned the retention index (I) of an n-alkane to equal a value 100 times its carbon number.

n-octane = 800
n-decane = 1000
n-dodecane = 12000, etc.

An I value of something different than n-alkane can be determined by "spiking" the mixture with n-alkanes. Plot log t'$_r$ vs. I (or use equation) and I of solute is determined.

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Equation:

$$I_x = 100Z + \frac{100(\log t'_{r,x} - \log t'_{r,z})}{\log t'_{r,z+1} - \log t'_{r,z}}$$

where,

Z - carbon # of n-alkane.

t'$_{r,x}$ - adjusted retention time of component under consideration.

t'$_{r,z}$ - adjusted retention time of alkane eluting before x

t'$_{r,z+1}$ - adjusted retention time of alkane eluting after x.

Gas Chromatography

TABLE 3.4   Probes Used in the McReynolds and Rohrschneider Classifications of Liquid Phases

Symbol	McReynolds Probe	Rohrschneider Probe	Measured Interaction
X'	Benzene	Benzene	Electron density for aromatic and olefinic hydrocarbons
Y'	n-Butanol	Ethanol	Proton donor and proton acceptor capabilities (alcohols, nitriles)
Z'	2-Pentanone	2-Butanone	Proton acceptor interaction (ketones, ethers, aldehydes, esters)
U'	Nitropropane	Nitromethane	Dipole interactions
S'	Pyridine	Pyridine	Strong proton acceptor interaction
H'	2-Methyl-2-pentanol	—	Substituted alcohol interaction similar to n-butanol
J'	Iodobutane	—	Polar alkane interactions
K'	2-Octyne	—	Unsaturated hydrocarbon interaction similar to benzene
L'	1,4-Dioxane	—	Proton acceptor interaction
M'	cis-Hydrindane	—	Dispersion–interaction

Assignment

- Read Chapter 26
- HW14 Chapter 26: 1- 17
- HW14 Chapter 26 Due 04/03/24

- Read Chapter 27
- HW15 Chapter 27: 1-5, 11-19 & 21-23
- HW15 Chapter 27 Due 4/08/24

- Test 3 – PPT Lectures 15-21 - Friday April 5th