Lecture Chromo-3:

# Gas Chromatography

CHEM 5181 Fall 2004

Mass Spectrometry & Chromatography

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## Outline

- Introduction
- Instrument overview
  - Carrier gas
  - Sample injection
  - Columns & stationary phase
    - Packed columns
    - Capillary (open) columns
  - Operating conditions
- Practical ways to select and compare columns

# Review and References on GC

- Historical Basis (Review)
  - 1952; Martin and James: Packed columns
  - 1954; Commercialization
  - 1957; Golay: Open tubular (capillary) columns
  - 1980; Wide spread use of capillary GC
- GC replaced distillation as the preferred method for separating volatile materials.
  - GC separations depend upon many variables making it a powerful separation technique.

| Author | Publisher | Title | $ on Amazon | Comments |
|---|---|---|---|---|
| McNair & Miller | Wiley | Basic Gas Chromatography, 1998 *(QD79.C45M425)* | $37 | Good short reference book, read it if you use GC a lot |
| Grant | Wiley | Capillary Gas Chromatography, 1995 *(QD79.C45G73)* | $185 | Detailed reference |

# Example of Separating Power of GC

From McNair

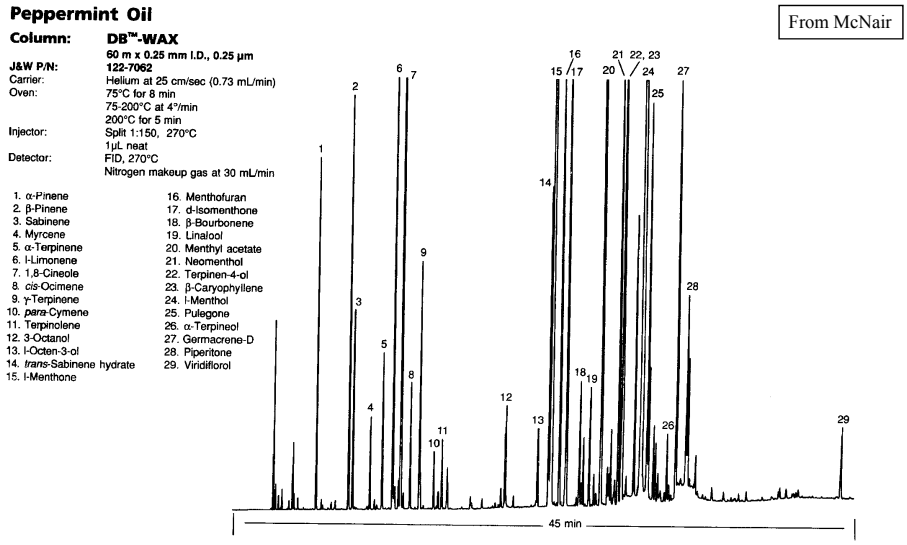



**Fig. 1.1.** Typical gas chromatographic separation showing the high efficiency of this method. Courtesy of J & W Scientific, Inc.

## Introduction

- GC is most widely used analytical technique in the world
  - Over 50 years in development
  - 2,000 instruments / yr
  - 25,000 in use
  - Worldwide market > $1billion
- GC is premier technique for separation and analysis of volatile compounds
  - Gases, liquids, dissolved solids
  - Organic and inorganic materials
  - MW from 2 to > 1,000 Daltons

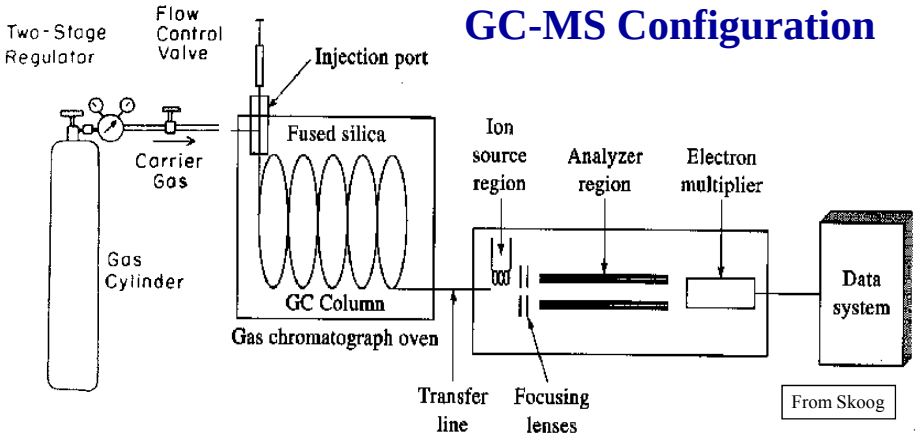
## Advantages of GC

- Fast analysis
  - Typically minutes (even sec.)
  - Can be automated
- Small samples (µl or µg needed)
- High resolution
  - Record: $N \sim 1.3 \times 10^6$
- Reliable, relatively simple and cheap (~ $20,000)
- Non-destructive
  - Allows on-line coupling, e.g. to MS
- Sensitive detectors (easy ppm, often ppb)
- Highly accurate quantification (1-5% RSD)

## Disadvantages of GC

- Limited to volatile samples
  - T of column limited to ~ 380 °C
  - Need $P_{vap}$ of analyte ~ 60 torr at that T
  - Analytes should have b.p. below 500 °C
- Not suitable for thermally labile samples
- Some samples may require intensive preparation
  - Samples must be soluble and not react with the column
- Requires spectroscopy (usually MS) to confirm the peak identity

## Instrument Overview




**Other Analyzers**: Flame ionization, Thermal conductivity, Electron-capture, Atomic Emission, Flame photometric, and more

## Carrier Gas Properties

- Carrier gas ⟷ Mobile phase
  - Flows continuously throughout instrument
  - Carries the sample vapor through the column to detector
- Necessary properties:
  - INERT
    - Does not chemically interact with sample
  - COMPATIBLE with detector
    - No noise or explosions
  - HIGHLY PURIFIED
    - Impurities will degrade column and cause noise in detector
    - "Research grade" is very expensive, so purify a cheaper grade

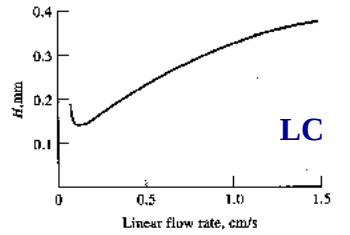
## Flow Rate of Carrier Gas

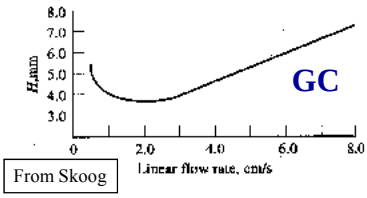
- Flow rates must be precisely controlled
  - Reproducible retention times, minimize detector drift
- Flow rates of carrier gas:
  - Linear flow rate (cm/s): $\bar{u} = L/t_r$
  - Volumetric flow rate (mL/min): $\bar{u}\ (\pi\ r^2)$

  L is length of column, $t_r$ is retention time, r is the internal radius of column
- Flow rate depends on type of column
  - Packed column: 25-100 mL/min
  - Capillary column: µL/min to 1 mL/min
- Flow rate will *decrease* as column T increases
  - Viscosity of carrier gas increases with T

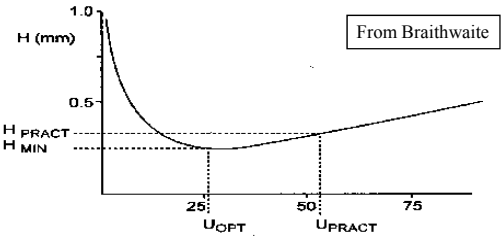
# Mobile Phase Velocity and Composition

**Plate height vs. Flow Rates**

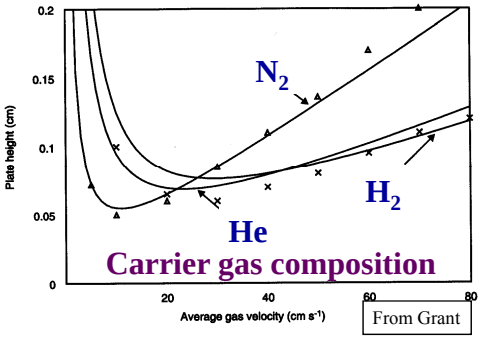



From Skoog




From Braithwaite




From Grant

Small *H*, large *N*

# Injection Process and Properties

- Properties:
  - Versatile, rapid, quantitative
  - Introduce sample to column as a sharp, symmetric band
- Heated injection port
  - Vaporize sample (50 °C > analyte b.p.)
  - Low enough to avoid degradation
- Packed columns:
  - Flash vaporizer or on-column
- Capillary columns:
  - Split: 1-2%, Higher resolution
  - Splitless: ~100%, Trace analysis

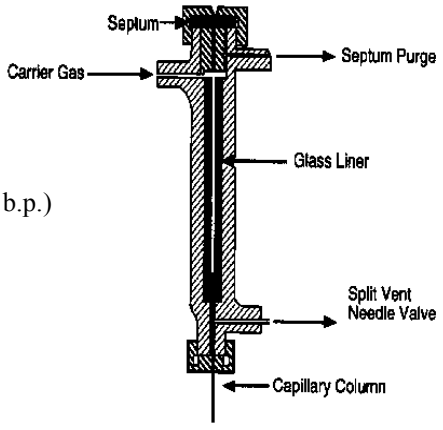



**Fig. 6.8.** Cross section of typical split injector.

*From McNair*

# Sampling Details

- For best peak shape and max resolution, the smallest possible sample size should be used
- When there are many components in a sample, generally the sample size will need to be larger
- Sample volumes:

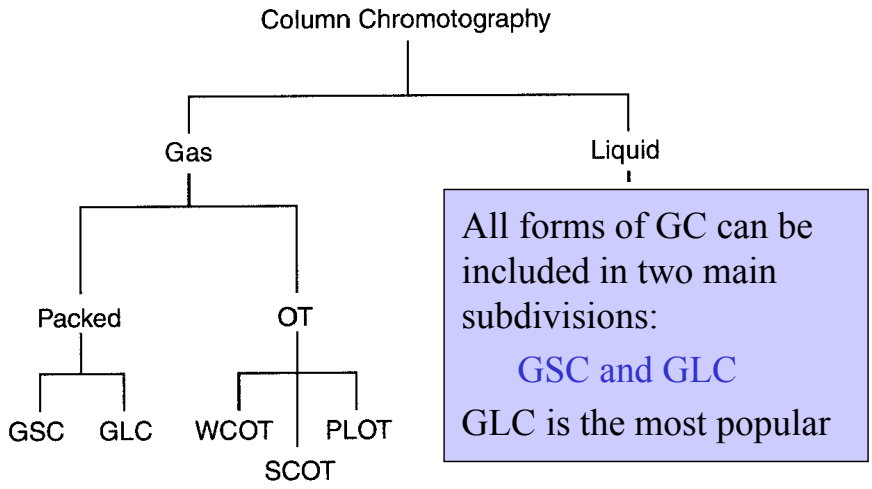
**TABLE 2.1 Sample Volumes for Different Column Types**

| Column Types | Sample Sizes (liquid) |
|---|---|
| Regular analytical packed: ¼″ o.d., 10% liquid | 0.2–20 μl |
| High efficiency packed: ⅛″ o.d., 3% liquid | 0.01–2 μl* |
| Capillary (open tubular): 250 μm i.d., 0.2 μm film | 0.01–3 μl* |

* These sample sizes are often obtained by sample splitting techniques.

From McNair

# Classification of Column Chrom.




All forms of GC can be included in two main subdivisions:

GSC and GLC

GLC is the most popular

**Fig. 1.2.** Classification of chromatographic methods.

From McNair

# Types of GC Columns

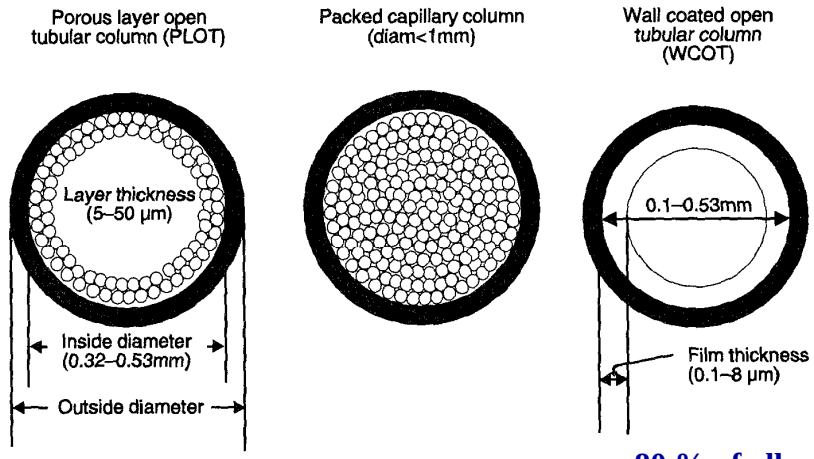
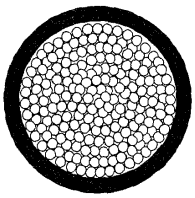



**Figure 1.4** Types of capillary column

From Grant

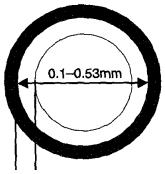
**80 % of all columns used!**

# Packed GC Columns



- Easy to make and use
- Limited resolution ($N < 8{,}000$)
- Outside: Solid tubing usually made of stainless steel
  - Because of strength
  - Glass when more inert substrate is needed
- Inside: Tightly packed with inert support
  - Solid supports should be inert and have high surface area
  - Typically diatomaceous earth or fluorocarbon polymer
- Stationary liquid phase is coated on the solid support
  - 3-10% by weight of the solid support

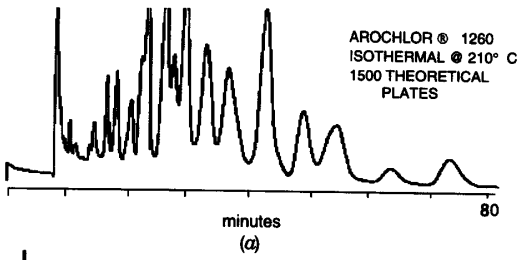
## Open (Capillary) Columns



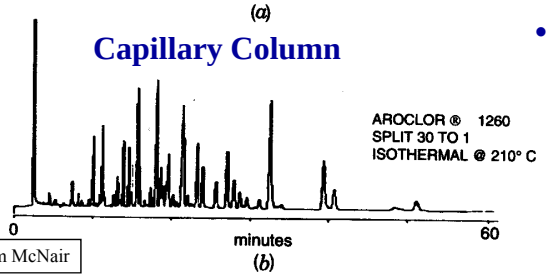

- Most common and efficient
- High resolution ($N$ > 100,000)
- Outside: Solid tubing made from fused silica
  - Inert, flexible, strong, and easy to use
- Inside: Column is an open tube
  - Very low resistance to flow
  - Long lengths possible ( L > 100 m)
- Stationary phase is a thin, uniform liquid film coated on the wall of the tubing

## Column Type vs. Separation

**Packed Column**




**Capillary Column**




From McNair

- Packed Column
  - Lower resolution
  - Fewer peaks (16)
  - Fewer plates
- Capillary Column
  - Small sample needed
  - Better resolution
  - More peaks
  - Faster Analysis

# Comparison of Columns

**TABLE 2.2 Comparison of Packed and WCOT Columns**

| | ⅛″ Packed | | WCOT |
|---|---|---|---|
| Outside diameter | 3.2 mm | **Dimensions** | 0.40 mm |
| Inside diameter | 2.2 mm | | 0.25 mm |
| $d_f$ | 5$\mu$m | | 0.25 $\mu$m |
| $\beta$ | 15–30 | | 250 |
| Column length | 1–2 m | | 15–60 m |
| Flow | 20 mL/min | | 1 mL/min |
| $N_{tot}$ | 4,000 | **Efficiency** | 180,000 |
| $H_{min}$ | 0.5 mm | | 0.3 mm |
| Advantages | Lower cost | | Higher efficiency |
| | Easier to make | | Faster |
| | Easier to use | | More inert |
| | Larger samples | | Fewer columns needed |
| | Better for fixed gases | | Better for complex mixtures |

From McNair

# Operating Conditions and T Controls

- Oven Temperatures:
  - Set by user depending on analytes and type of column
  - Should NOT be higher than b.p.of analyte
    - Column operates at a T where the sample is in the vapor state—it need not be in gas state
    - Column temp should be just above “dew point” of analyte
- Isothermal
  - Simplest mixtures and cheapest GCs
  - Temperature of oven remains constant
- Temperature programming
  - Analytes with wide range of volatilities
  - Best separation in quickest amount of time

# Effect of Temperature on Retention Time

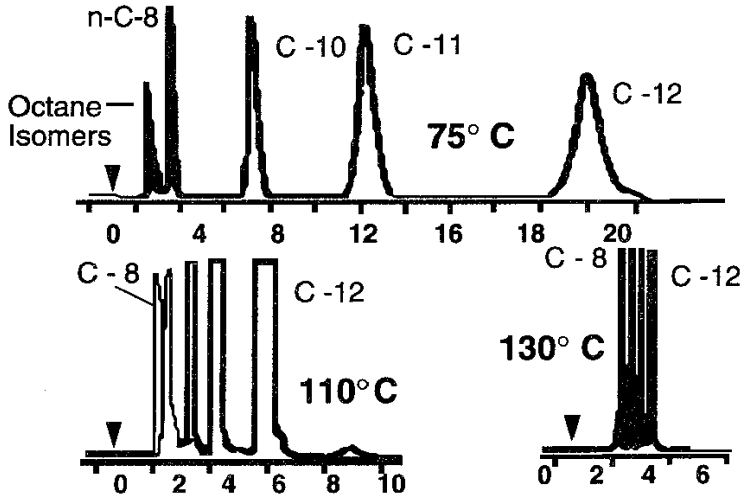
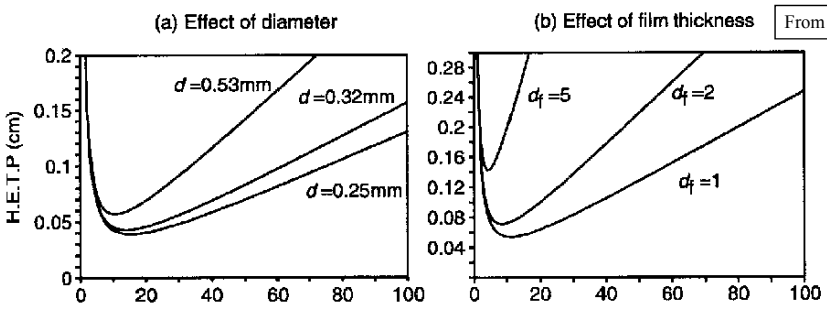



**Fig. 2.5.** Effect of temperature on retention time. From McNair

# Other Dimensional Considerations




From McNair

**TABLE 6.2 Effects of Column Diameter**

| Inside Diameter | Resolution | Speed | Capacity | Ease |
|---|---|---|---|---|
| 100 µm | Very good | Very good | Fair | Fair |
| 250 µm<br>320 µm | Good | Good | Good | Good |
| 530 µm | Fair | Good | Very good | Very good |

**TABLE 6.3 Column Length Recommendations**

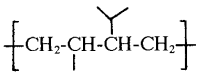
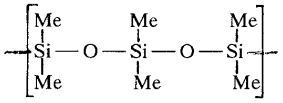
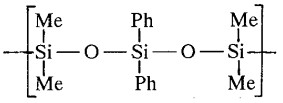
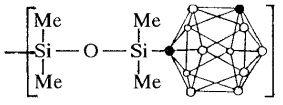
| Column Length | Resolution | Speed |
|---|---|---|
| Long (60–100 m) | High | Slow |
| Short (5–10 m) | Moderate | Fast |
| Medium (25–30 m) | Good compromise, good starting point | |

# Column Selection Parameters

- The critical parameters for GC columns:
  - **Dimensions**: Internal diameter, Column length, Film thickness
  - **Conditions**: Temperature, Flow rate
  - **Composition**: Stationary phase composition*, Carrier gas
- Given a sample, you will need to first choose the what stationary phase will work best
  - First pick the type of column, then think about dimensions
  - Conditions can be optimized for given column dimensions
- Choice of stationary phase is very important
  - It determines what kind of sample you can run
  - Critical for packed columns, but less so for OT columns because of high efficiency

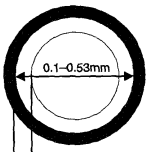
# Typical Stationary Phases

**Table 5.1** Basic stationary phases

| Stationary phase | Material | Structure |
|---|---|---|
| Apiezon L | Branched-chain alkane grease, mp 43°C |  |
| OV101 | Dimethyl silicone |  |
| OV3 | 5% Phenyldimethylsilicone |  |
| OV17 | 50% Phenyldimethylsilicone | |
| Dexil 300 | Carborane dimethyl silicone |  |
| | | ● = C, carbon, ○ = borane, B–H |
| Carbowax 20M | Polyethylene glycol | $HO-[-CH_2-CH_2-O-]_n-H$ |

From Braithwaite

# Stationary Phases for GLC




- Hundreds of SP have been used
  - Only requirements are:
    - Low vapor pressure
    - Thermal stability
    - Low viscosity (for fast mass transfer)
    - High selectivity for compounds of interest
- How do you decide?
  - Literature searches
  - Ask around, talk to manufacturers
  - Trial and error

# Most Important: SP Polarity

- Selectivity: "Like dissolves like"
  - Polar liquid better for polar analytes
  - Nonpolar liquid for NP analytes

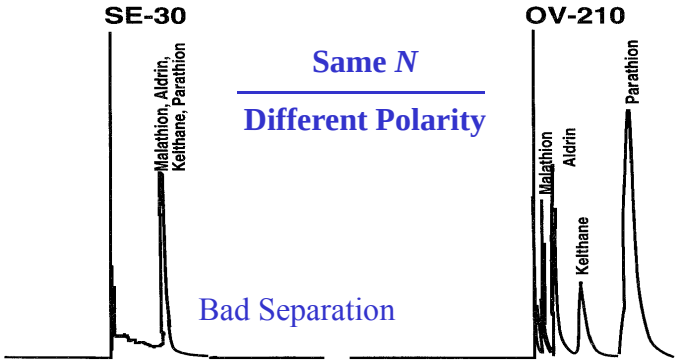



**Fig. 4.1.** Comparison of two liquid phases for an insecticide separation: (*a*) SE-30, a poor choice; *b*) OV-210®, a good choice. Both columns have the same efficiency, *N*.

From McNair

## Polarity and $t_r$

- Changing SP polarity can change the elution order
- Verify:
  - Retention times
  - Peak identity

From McNair

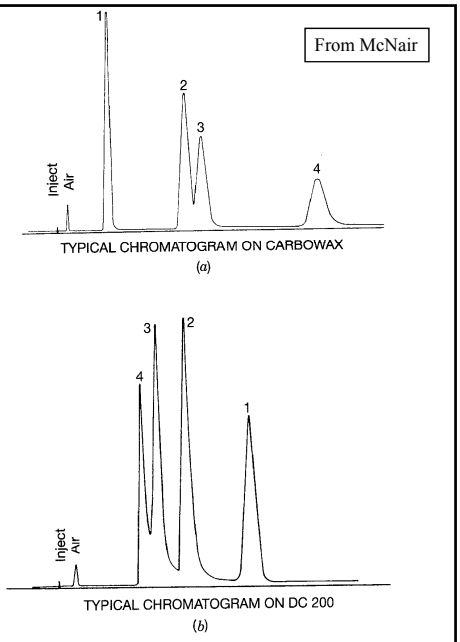



**Fig. 4.2.** Effect of stationary phase polarity on a 4-component separation: (*a*) Carbowax-20M® (polar); (*b*) DC-200 (nonpolar). Samples and their boiling points: (1) *n*-heptane (98); (2) tetrahydrofuran (64); (3) 2-butanone (80); (4) *n*-propanol (97). Reprinted with permission of the GOW-MAC Instrument Co., Bethlehem, PA, U.S.A.

## Comparing Columns/Results

- How do you know if two columns are the same?
- How do you compare $t_r$ on different columns?
  - Need a reliable method for specifying and measuring retention behavior of different solutes
  - Establish a catalogue of GC retention parameters that will allow identification of most components
- How do you express relative polarity?
  - You know lots of equations/relations…
  - However, they depend on too many variables!

$$k = K\frac{V_s}{V_M}$$

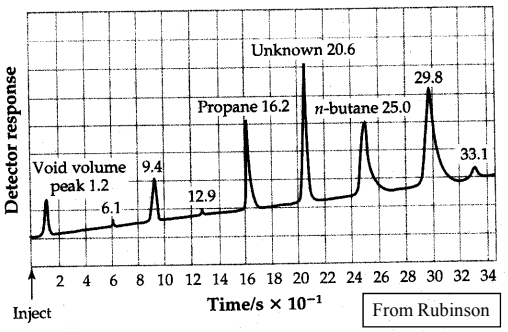
***Establish a relative scale of polarity***

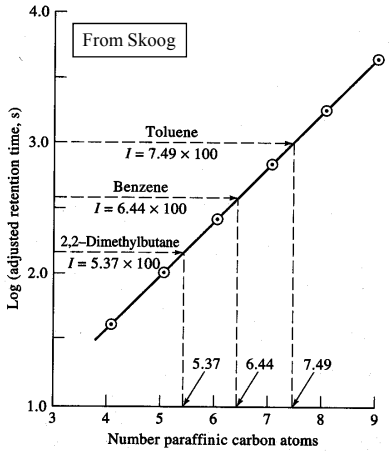
# Kovats Retention Index System

- Purpose: To quantify the retention of a test compound by comparing it with a pair of n-alkane adjacent peaks
- Retention Index (*def.*): I = 100 x Paraffin CN
  - Independent of column packing, temperature, or any other chromatographic conditions!
- Homologous series of *n*-alkanes as standards
  - Chosen because of low polarity and freedom from H-bonding
  - In all stationary phases, they follow order of vapor pressure
    - Log(*t'*) is directly proportional to the number of carbons
  - Other homologous series used for specific applications

# Kovats Retention Index System

- Compare retention time of unknowns to knowns in an effort to identify them




I = 100 x Paraffinic Carbons

## McReynolds Constants

- Purpose: To quantify the polarities and selectivities of stationary phases for specific chemical groups
- McReynolds Constant (*def.*): $\Delta I = I - I_{standard}$
  - Compare the change in the Kovats retention index, I, as a function of the type of column
  - Provides a measure of the relative polarity of one column to a standard (Squalane)
- "Probe" molecules
  - Traditionally: Benzene, n-butanol, 2-pentanone, nitropropanone, and pyridine
  - Each serves to measure the extent of intermolecular interaction between the probe molecules and SP

## McReynolds Constants: Example

- Example:
  - Kovats index of toluene:
    - 773 on SP squalene (non-polar)
    - 860 on SP dioctylphatalate
  - Define McReynolds constant as:
    - $\Delta I = 860 - 773 = 87$
  - Results:
    - Dioctylphatalate is a more polar stationary phase
    - The larger the McReynolds constant, the greater the retention time than compared to the non-polar column.

# McReynolds Constants

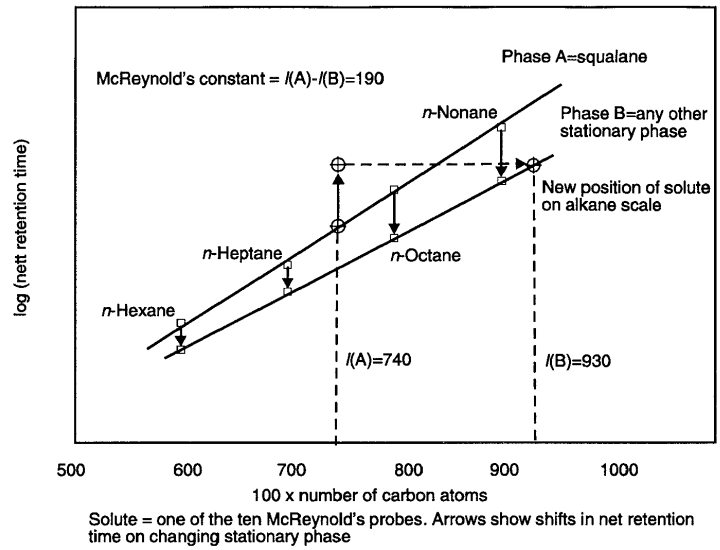



**Figure 4.21** McReynolds' constants for stationary phase classification

From Grant

# McReynolds Constants

**TABLE 4.4 McReynolds Constants and Temperature Limits for Some Common Stationary Phases**

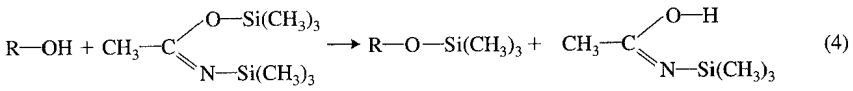
From McNair

| Stationary Phase | Probes* | | | | | Temp. Limits | | Sum of ΔI |
|---|---|---|---|---|---|---|---|---|
| | Benz | Alc | Ket | N-Pr | Pyrid | Lower | Upper | |
| Squalane | 0 | 0 | 0 | 0 | 0 | 20 | 125 | 0 |
| Apolane 87® | 21 | 10 | 3 | 12 | 25 | 20 | 260 | |
| OV-1® | 16 | 55 | 44 | 65 | 42 | 100 | 375 | |
| OV-101® | 17 | 57 | 45 | 67 | 43 | 20 | 375 | |
| Dexsil 300® | 41 | 83 | 117 | 154 | 126 | 50 | 450 | |
| OV-17® | 119 | 158 | 162 | 243 | 202 | 20 | 375 | 884 |
| Tricresylphosphate | 176 | 321 | 250 | 374 | 299 | 20 | 125 | |
| QF-1 | 144 | 233 | 355 | 463 | 305 | 0 | 250 | |
| OV-202® and OV-210® | 146 | 238 | 358 | 468 | 310 | 0 | 275 | |
| OV-225® | 228 | 369 | 338 | 492 | 386 | 20 | 300 | |
| Carbowax 20M® | 322 | 536 | 368 | 572 | 510 | 60 | 225 | |
| DEGS | 492 | 733 | 581 | 833 | 791 | 20 | 200 | |
| OV-275® | 629 | 872 | 763 | 1106 | 849 | 20 | 275 | 4219 |

Each sum is a measure of the "polarity" of the liquid phase. The higher the sum, the higher the polarity, the higher the retention time.

# Derivatization

- If changing the column won't help, you may change the separation by changing the analyte
  - Cause a non-volatile sample to become volatile
  - Improves delectability of derivative
- E.g. silylation
  - Introduce trimethylsilyl group to make sample volatile




(4)

## Effects of Oxidation on Compound Vapor Pressures

| Compound | $P^{o}_{25C}$ (torr) | Mass % in Particles* |
|---|---|---|
|  (C14) | $2 \times 10^{-2}$ | 0.004 |
|  | $3 \times 10^{-3}$ | 0.03 |
|  | $8 \times 10^{-4}$ | 0.1 |
|  | $2 \times 10^{-4}$ | 0.4 |
|  | $7 \times 10^{-6}$ | 10 |
|  (C15) | $4 \times 10^{-3}$ | 0.02 |

From Ziemann, P. Tutorial on Secondary Organic Aerosol Formation. American Association for Aerosol Research Annual Conference, Anaheim, CA 2003

*Assuming 10 μg $m^{-3}$ organic matter in particles

# References:

- Braithwaite and Smith
  - Chromatographic Methods
- Grant
  - Capillary Gas Chromatography
- McNair and Miller
  - Basic Gas Chromatography
- Rubinson
  - Contemporary Instrumental Analysis
- Skoog, Holler, and Nieman.
  - Principles of Instrumental Analysis

APPENDIX II. GUIDELINES FOR SELECTING CAPILLARY COLUMNS

I. Length
  A. Rule: Use shortest useful column
    1. Save time
    2. Cheaper
    3. Reduced side effects (reduced residence time)
    4. If more $R_S$ required, consider reducing $d_f$ and/or i.d.

II. Internal Diameter
  A. Megabore (0.53mm i.d.) preferred when high carrier flow rate desired
    1. Simple direct injection techniques
    2. Primitive equipment including dead volumes, cold spots, active materials, parts that cannot be cleaned
    3. Sample transfer from absorbent filters (head space, SFC, SPE techniques)
  B. Medium size columns (0.25–0.35mm i.d.)
    1. Commonly used as good compromise
  C. Narrow columns (0.10mm i.d.) for increased separation efficiency and speed
    1. Shorter lengths are possible and faster analysis
    2. Limitations
      a. High split ratios necessary (500/1)
      b. Limited trace analyses
      c. High carrier gas pressures required
      d. Equipment and manipulation more critical

III. Film Thickness
  A. Advantages of thick films
    1. Increased retention; frequently essential for volatiles; film thickness may replace column length
    2. Increased capacity; important for GC/MS or FTIR
    3. Elution shifted to higher temperature (all sample components see warmer column), resulting in reduced adsorption effects
  B. Advantages of thin films
    1. Maximum separation efficiency
    2. Elution shifted to lower temperature (sample sees cooler column)
    3. Faster analyses

IV. Stationary Phase
  A. Start with nonpolar phases like DB-1 or DB-5. More efficient, more inert and generally useful for most sample types. The non-polar character shows low solubility for polar compounds, thus allowing lower column temperatures to be used. This means better stability for thermolabile compounds.
  B. If greater selectivity is needed, try a more polar phase, OV-1701 or some version of Carbowax®.

V. Carrier Gases—Use $H_2$ or He (much faster than $N_2$)
  A. Advantages of $H_2$ over He
    1. Separation efficiency slightly higher
    2. Analysis time roughly 50% faster (isothermal only)
    3. Better sensitivity (sharper peaks)
    4. Columns regularly run at lower temperature, resulting in increased resolution and longer column life
  B. Limitations
    1. Potential hazard; may cause explosion if more than 5% in air and spark. Not recommended, especially not for GC/MS.

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APPENDIX III. GC: HOW TO AVOID PROBLEMS

I. Carrier Gas
- A. Use high purity gases, 99.9% minimum; 99.999 for GC–MS.
- B. Use a molecular sieve scrubber on *all gas cylinders* to remove $H_2O$ and methane.
- C. Use of an $O_2$ scrubber on carrier gas line is essential for electron capture detector; recommended for high temperature capillary columns.
- D. Use He (or $H_2$) for TCD. $N_2$ is not sensitive (also it gives both + and − peaks).
  Use He or $N_2$ for FID.
  Use bone dry, $O_2$-free $N_2$ for ECD.
- E. Know the van Deemter (or Golay) plot for your column. $\bar{u}$ opt. is 12, 20, and 40 cm/sec for $N_2$, He and $H_2$ respectively. H vs. $\bar{u}$. Measure $\bar{u}$ daily (inject methane). $\bar{u} = L$ (cm)/$t_M$ (secs).

II. Injectors
- A. Packed Column—use on-column injectors; more inert, lower temperature than off-column heated inlet. Use only a small piece of silanized glass wool. Don't pack the first few inches (see your manual) of the column to allow space for needle. Use the lowest possible inlet temperature which produces the least band broadening.
- B. Capillary Column
  1. Split—split in the range of 20/1 to 200/1. A good starting point is 50/1. Low split ratios give better sensitivity, but eventually lead to low resolution. For gas sample valves, purge and trap, and SFE interfaces increase split ratio until $R_s$ is maximized. Use a fast injection technique, preferably with an autosampler.
  2. Splitless—
     a. Dilute sample in volatile solvent like hexane, iso-octane, or methylene chloride.
     b. Set column temperature at b.p. of solvent.
     c. Inject slowly, 1–5 $\mu$l, "hot needle" technique.
     d. Start temperature program; open split valve after 1 minute.

III. Columns
- A. Buy good columns from reliable manufacturers. Don't try to save a few dollars. Check out all columns regularly. Run your test mix; measure $N$, $\alpha$, $k$, and $R_s$.
- B. Clean columns regularly. Best ways to clean a column:
  1. Bake out overnight;
  2. Cut off first 10 cm at least once a month.
  3. If necessary, take out column, rinse with solvents (only bonded phases), dry well, reinstall and condition slowly.

  Remember: Bad performance of a sample doesn't necessarily mean the column is bad; run a standard check on the column.
- C. Capillary Columns
  1. Length—start with 25m; shorter columns are faster, longer columns have more plates (but are slow). It is better to use *thinfilm, small i.d.,* and *small sample sizes* to increase column efficiency.
  2. i.d.—start with 250 or 320 $\mu$m. Megabore (530 $\mu$m) are not as efficient; 100 $\mu$m require *very* small, *very* fast injections.
  3. Carrier gas—use He or $H_2$; $N_2$ is too slow.
  4. $d_f$—start with 0.2 or 0.5 $\mu$m. Thicker films for volatiles, but usually less efficient.

IV. Detectors
- A. Always use proper carrier gas; one of high purity.
- B. Use scrubbers to remove $H_2O$ and light hydrocarbons.
- C. If necessary, use make-up gas. Essential for ECD and TCD; often increases sensitivity with FID.
- D. Keep the detector hot; avoid condensation of sample.

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# 11. Troubleshooting GC Systems

The following pages have been inserted to help the chromatographer interpret the different peak shapes encountered in gas chromatography. The various chromatograms obtained are the result of our own experiences combined with a thorough literature search.

The injection point on each chromatogram is shown by a tick mark on the baseline as shown in example 1. The time axis runs from left to right (see arrow).

| SYMPTOM | POSSIBLE CAUSE | CHECKS AND/OR REMEDY |
|---|---|---|
| 1. No peaks.<br>Injection<br>↓<br>Time → | 1a. Main power off, fuse burned out. | 1a. Plug in system, check fuses. |
| | b. Detector (or electrometer) power off. | b. Turn detector (or electrometer) switch on and adjust to desired sensitivity level. |

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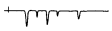
| SYMPTOM | POSSIBLE CAUSE | CHECKS AND/OR REMEDY |
|---|---|---|
| | c. No carrier gas flow. | c. Turn carrier gas flow ON and adjust to proper setting. If carrier lines are obstructed, remove obstruction. Replace carrier-gas tank if empty. |
| | d. Integrater/data system improperly connected; not turned on; not grounded. | d. Connect systems as described in manual. Remove any jumper lines connecting either input connection to ground or shield. |
| | e. Injector temperature too cold. Sample not being vaporized. | e. Increase injector temperature. Check with volatile sample such as air or acetone. |
| | f. Hypodermic syringe leaking or plugged up. | f. Squirt acetone from syringe onto paper; if no liquid comes out, then replace the syringe. |
| | g. Injector septum leaking. | g. Replace injector septum. |
| | h. Column connections loose. | h. Use leak detector, check leaks, tighten column connections. |
| | i. Flame out (FID only). | i. Inspect flame; check to see if water vapor condenses on mirror, light if necessary. |
| | j. No cell voltage being applied to detector (all ionization detectors). | j. Place CELL VOLTAGE in ON position. Also check for bad detector cables. Measure voltage with a voltmeter per instruction manual. |
| | k. Column temperature too cold. Sample condensing on column. | k. Inject volatile compound like air or acetone, increase column temperature. |
| 2. Poor sensitivity with normal retention time.  | 2a. Attenuation too high. | 2a. Reduce attenuation. |
| | b. Insufficient sample size. | b. Increase sample size; check syringe. |
| | c. Poor sample injection technique. | c. Review sample injection techniques. |
| | d. Syringe or septum leaking when injecting. | d. Replace syringe or septum. |
| | e. Carrier gas leaking. | e. Find and correct leak; usually retention time will also change. |
| | f. Thermal conductivity response low. | f. Use higher filament current; He or $H_2$ carrier gas. |
| | g. FID response low. | g. Optimize both air and $H_2$ flow rate; use $N_2$ to make up gas. |
| 3. Poor sensitivity with increased retention time.  | 3a. Carrier gas flow rate too low. | 3a. Increase carrier gas flow. If carrier gas lines are obstructed, locate and remove obstruction. |
| | b. Flow leaks downstream of injector; usually at column inlet. | b. Locate flow leak and correct. |
| | c. Injector septum leaking continuously. | c. Replace injector system. |
| 4. Negative peaks.  | 4a. Integrator/data system improperly connected. Input leads reversed. | 4a. Connect system as described in manual. |
|  | b. Sample injected in wrong column. | b. Inject sample in proper column; only on dual column systems! |
| | c. MODE switch in wrong position (ionization detectors). | c. Insure MODE switch is in correct position for column being used as analytical column. |
| | d. POLARITY switch in wrong position (thermal conductivity detector). | d. Change POLARITY switch. |
| 5. Irregular baseline drift when operating isothermally.  | 5a. Poor instrument location. | 5a. Move instrument to a different location. Instrument should not be placed directly under heater or air conditioner blower, or any other place where it is subject to excessive drafts and ambient temperature changes. |
| | b. Instrument not properly grounded. | b. Insure instrument and data system connected to good earth ground. |

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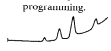
| SYMPTOM | POSSIBLE CAUSE | CHECKS AND/OR REMEDY |
|---|---|---|
| | c. Column packing bleeding. | c. Stabilize column as outlined in instrument manual. Some columns are impossible to stabilize well at the desired operating conditions. These columns will always produce some baseline drift, particularly when operating at high sensitivity conditions. |
| | d. Carrier gas leaking. | d. Locate leak and correct. |
| | e. Detector block contaminated. | e. Clean detector block. Raise temperature and bake out detector over night. |
| | f. Detector base contaminated (ionization detectors). | f. Clean detector base. See instrument manual. |
| | g. Poor carrier gas regulation. | g. Check carrier gas regulator and flow controllers to insure proper operation. Make sure carrier gas tank has sufficient pressure. |
| | h. Poor $H_2$ or air regulation (FID only). | h. Check $H_2$ and air flow to insure proper flow rate and regulation. |
| | i. Detector filaments defective (TC detector only). | i. Replace TC detector assembly or filament. |
| | j. Electrometer defective (ionization detectors). | j. See instrument manual on electrometer troubleshooting. |
| 6. Sinusoidal baseline drift.  | 6a. Detector oven temperature controller defective. | 6a. Replace detector oven temperature controller, and/or temperature sensing probe. |
| | b. Column oven temperature defective. | b. Replace oven temperature control module, and/or temperature sensing probe. |
| | c. OVEN TEMP °C control on main control panel set too low. | c. Set OVEN TEMP °C control to higher setting. Must be set higher than highest desired operating. |
| | | temperature of the column oven. |
| | d. Carrier gas flow regulator defective. | d. Replace carrier gas flow regulator; sometimes higher pressure provides better control. |
| | e. Carrier gas tank pressure too low to allow regulator to control properly. | e. Replace carrier gas tank. |
| 7. Constant baseline drift in one direction when operating isothermally.  | 7a. Detector temperature increasing (decreasing). | 7a. Allow sufficient time for detector to stabilize after changing its temperature. Particularly important with TC detector. Detector block will lag the indicated temperature somewhat because of its large mass. |
| | b. Flow leak down stream of column effluent end (TC detector only). | b. A very small diffusion leak will allow a small amount of air to enter the detector at a constant rate. This in turn will oxidize the effected elements at a constant rate while slowly changing their resistance. Locate the leak and correct. These are very often very slight leaks, and difficult to find. Use high carrier gas pressure (60–70 psig) is necessary. |
| | c. Defective detector filaments (TC detector). | c. Replace detector or filaments. |
| 8. Rising baseline when temperature programming.  | 8a. Increase in column "bleed" when temperature rises. | 8a. Use less liquid phase and lower temperature. If possible, use more temperature stable liquid phase. |
| | b. Column(s) contaminated. | b. 1) Bake out column overnight.<br>2) Break off first 10 cm of column inlet. |

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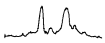
| SYMPTOM | POSSIBLE CAUSE | CHECKS AND/OR REMEDY |
|---|---|---|
| 9. Irregular baseline shifting when temperature programming.  | 9a. Excessive column "bleeding" from well conditioned columns. | 9a. Use less liquid phase and low temperatures. Use different columns. |
| | b. Columns not properly conditioned. | b. Condition columns as outlined in instruction manual. |
| | c. Column(s) contaminated. | c. See 8b. |
| 0. Baseline cannot be zeroed. | 10a. Zero on data system improperly set. | 10a. Reset zero. Short system input with piece of wire and adjust to zero. See system instruction manual. |
| | b. Detector filaments out of balance (TC detector). | b. Replace detector. |
| | c. Excessive signal from column "bleed" (especially FID). | c. Use different column with less "bleed." Use lower column temperature. |
| | d. Dirty detector (FID and EC). | d. Clean detector base and head assemblies. |
| | e. Data system improperly connected. | e. Connect system as described in instrument manual. Remove any jumper lines connecting either system input connection to ground or shield. |
| 11. Sharp "spiking" at irregular intervals.  | 11a. Quick atmospheric pressure changes from opening and closing doors, blowers, etc. | 11a. Locate instrument to minimize problem. Also do not locate under heater or air conditioner blowers. |
| | b. Dust particles or other foreign material burned in flame (FID only). | b. Take care to keep detector chamber free of glass wool, maranite, molecular sieve (from air filter), dust particles, etc. Blow out or vacuum detector to remove dust. |
| | c. Dirty insulators and/or connectors (Ionization detectors). | c. Clean insulators and connectors with residue free solvent. Do not touch with bare fingers after cleaning. |
| | d. High line voltage fluctuations. | d. Use separate electrical outlet; use stabilized transformer. |

| SYMPTOM | POSSIBLE CAUSE | CHECKS AND/OR REMEDY |
|---|---|---|
| 12. High background signal (noise).  | 12a. Contaminated column or excessive "bleed" from column. | 12a. Recondition column (see 8b.) |
| | b. Contaminated carrier gas. | b. Replace or regenerate carrier gas filter. Regenerate filter by heating to about 175–200°C and purging overnight with dry nitrogen. |
| | c. Carrier gas flow rate too high. | c. Reduce carrier gas flow rate. |
| | d. Carrier gas flow leak. | d. Locate leak and correct. |
| | e. Loose connections. | e. Make sure all interconnecting plug and screw connections are tight. Make sure modules are properly seated in their plug-in connectors. |
| | f. Bad ground connection. | f. Insure all ground connections are tight and connected to a good earth ground. |
| | g. Dirty switches. | g. Locate dirty switch, spray with a contact cleaner and rotate switch through its positions several times. |
| | h. Dirty injector. | h. Clean injector tube and replace septum. |
| | i. Dirty crossover block from column oven to detector oven. | i. Clean crossover block. |
| | j. Dirty detector (TC detector). | j. Clean detector block. |
| | k. Defective detector filaments (TC detector). | k. Replace detector assembly. |
| | l. Hydrogen flow rate too high or too low (FID detector). | l. Adjust hydrogen flow rate to proper level. |
| | m. Air flow too high or too low (FID detector). | m. Adjust air flow rate to proper level. |

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