Gas Chromatography

Excellent resource: Quantitative Chemical Analysis
By Daniel C. Harris
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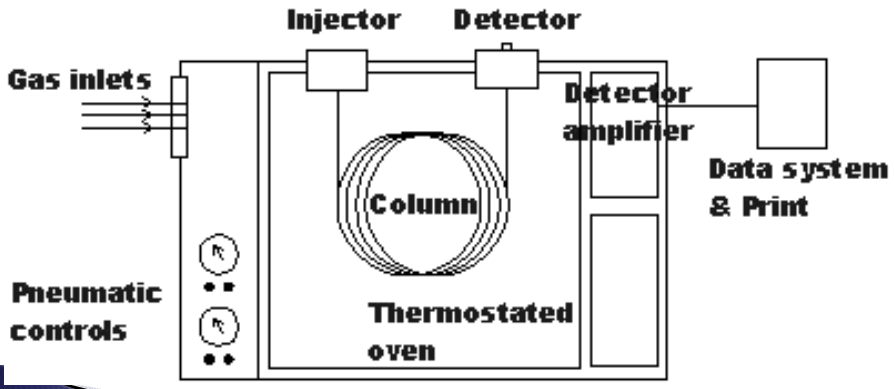
Main Components of Chromatograph

- Carrier gas (mobile phase)
  - N_2, He, H_2
- Injector
- Column
- Detector
- Integrator or Computer

oven

Gas Chromatograph

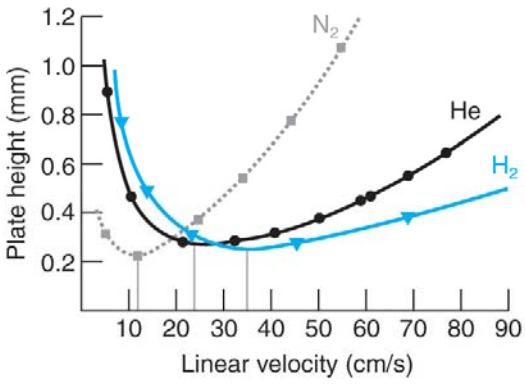


Gas Chromatography

employs gas as a mobile phase (carrier) – He, H_2, N_2

Which gas is the best ?

Based on the van Deemter curve



The best for most operation conditions is hydrogen, but it is explosive.

Helium is employed especially with MS.

The conditions for the use of nitrogen has to be carefully selected (e.g. flow rate)

GC Components

- Injector – transfers the analyte onto the column
- Column – separates the analytes
- Detector – recognizes separated analytes and translates them into graphical form (chromatogram)

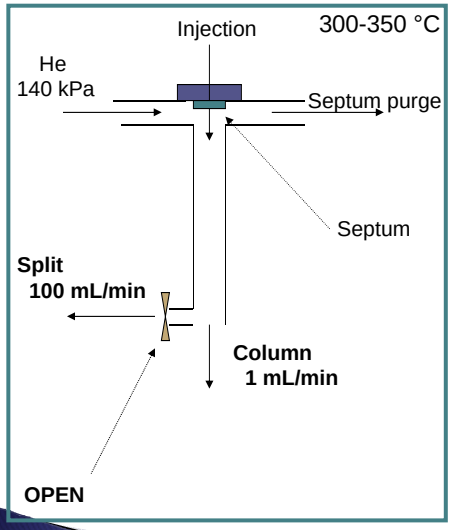
Injectors

Injectors are usually heated to **ensure analyte's transfer to a gas phase**. Volatile liquid or gaseous sample is injected through a septum. Vapor is swept through column

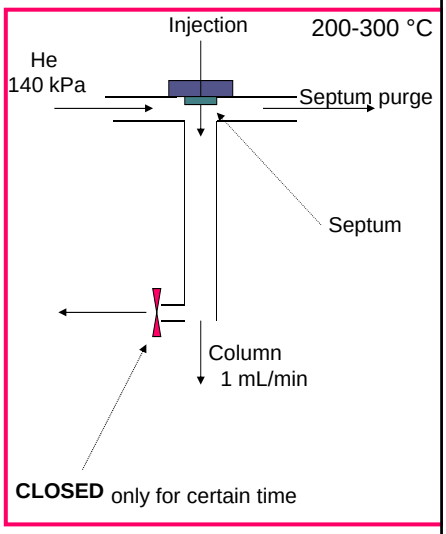
- **Split/splitless injector** usually consists of heated liner (a glass sleeve, prior to the column. (200 – 300 °C)
  - Split (dilution) only part of sample is introduced on the column
    1:25 – 1:600
  - Splitless – all the sample is introduced (but only for limited time period)
- **On-column injector** for the analytes which are thermally unstable
  - Analytes are injected directly on the column,

  This techniques is suitable for thermally unstable compounds

Split versus Splitless



1% of sample introduced on the column.
Higher precision
Eliminates interferences from matrix.



Most of the sample introduced on column.
To obtain narrow peaks a cold trapping is used.

Injection

- **Volume** Injected is Typically 0.1-3µL (liquid)
- The injected volume is limited by the volume of solvent as a vapor phase.

At 200°C and pressure on column 100 kPa

- 1 µL of hexane (l) forms 222 µL (g)
- 1 µL of methylene chloride (l) forms 310 µL
- 1 µL of water (l) form 1111 µL

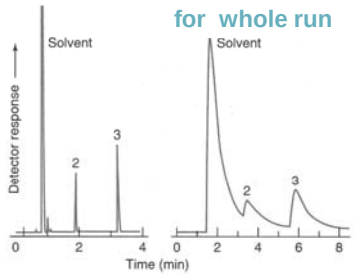
volume of vapor > then volume of injector = backflash (system contamination)

- **Concentration**
- Is defined by column retaining capacity
  - Columns with a thicker film thickness (a stationary phase) retain more of the analyte

Injection and Temperature program

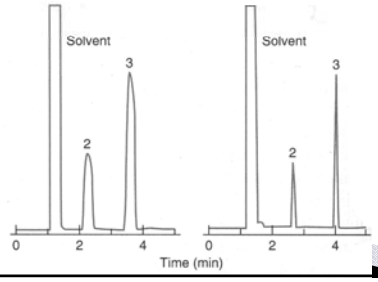
SPLIT

SPLITLESS for whole run



SPLITLESS 30 s

SPLITLESS 30 s solvent trapping



Split injection - a fraction of a solute (solvent) is injected, therefore peaks are sharp.

Splitless injection – for trace analysis
The split valve is closed and most of the sample is introduced on the column.
The volume of the gas going through the injector is only ca. 1 ml/min. Thus, sample components are transferred to the column for long time. Thus peak tailing.

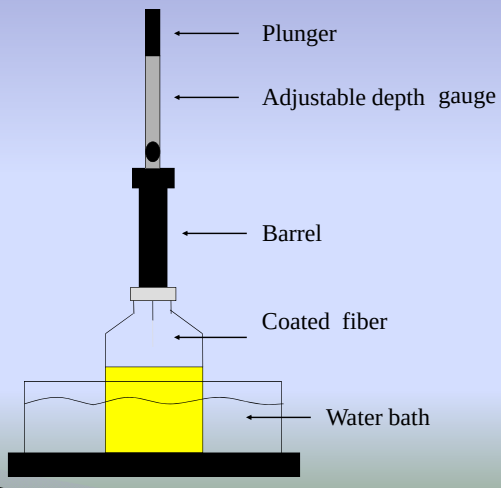
Splitless time - If the split valve is opened after certain time 20 - 120 s, the transfer of sample is stopped. Still the transfer can be long, causing an increased peak width.

Solvent trapping - Injecting the sample to the column at temperature bellow boiling point of a solvent <20°C, after 30s (splitless time) a fast increase in the temperature to 20°C above solvent's boiling point.
Fast transfer from gas to liquid and again to the gas phase sharpens the elution band.

On column injection

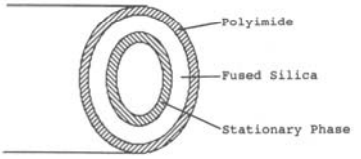
- On column injection for samples which would decompose at higher temperatures
  - Injects the sample directly on the column or the guard column.
  - All the sample is introduced on the column.
  - Also all interfering components are injected.
  - In past, the column has to be ca. 0.53 mm I.D. so the syringe needle can fit in.

Volatile Compounds Isolation by SPME



Columns

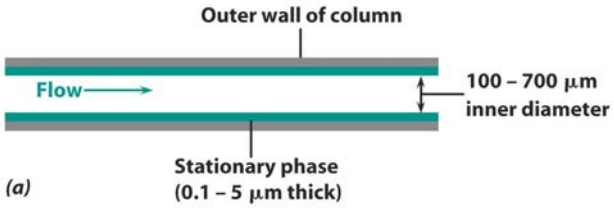
- **Packed**
  - solid particles either porous or non-porous coated with thin (1 μm) film of liquid
  - 3 – 6 mm ID; 1 – 5 m length
- **Capillary** (open tubular) silica columns
  - 0.1 – 0.5 mm I.D. (internal diameter); 15 – 100 m length
  - Inner wall modified with thin (0.1–5 μm) film of liquid (stationary phase)
  - easy to install
  - well defined stationary phase

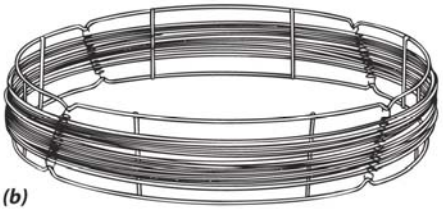


I.D. Internal diameter

Optimal flow rate depends on carrier gas, I.D., film thickness
As the linear velocity, I.D. and increases also van Deemter curve is steeper.

Open tubular columns



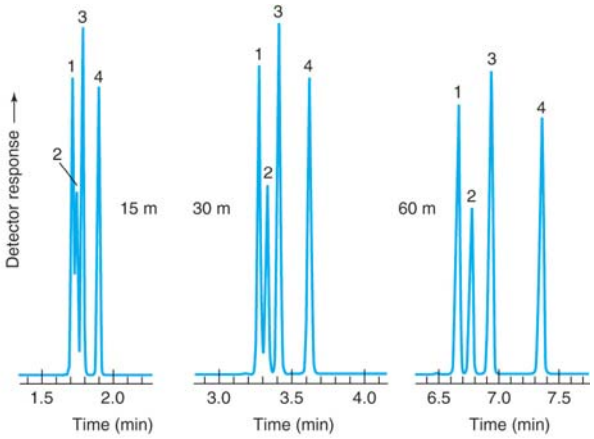


van Deemter equation for plate height:

$$H \approx \cancel{A} + \frac{B}{u} + Cu$$

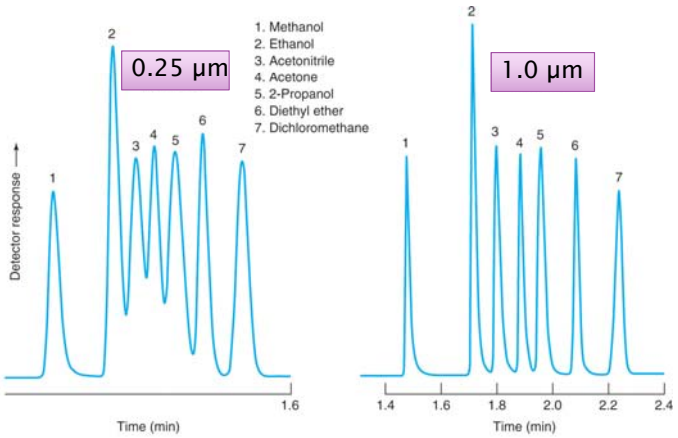
Multiple paths | Longitudinal diffusion | Equilibration time

Resolution increases in proportion to the square root of column length



$$R = \frac{\sqrt{N}}{4}(\gamma - 1) = \frac{\sqrt{N}}{4}\left(\frac{t_{r2}}{t_{r1}} - 1\right)$$

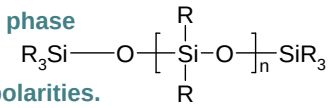
The thicker stationary phase enhances separation of volatile species



Stationary Phases

Must have:
(1) low volatility
(2) thermal stability
(3) chemical inertness
(4) solvation properties giving suitable values for k', α.

Most common are polysiloxanes stationary phase



Nature of R varied to give different polarities.

For non-polar columns R = CH_3 or phenyl
MOST FREQUENTLY USED
Best for non-polar analytes (hydrocarbons, PAHs etc.)

R = 50% CH_3 and 50% cyanopropyl have increased polarity.
Best for alcohols, acids etc.

Greater polarity using polyethylene glycols:

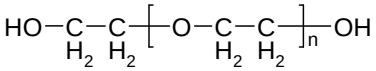
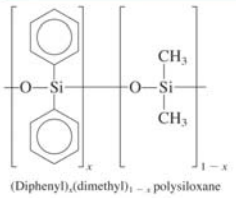
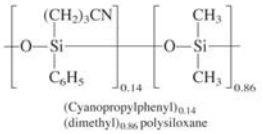
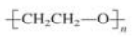
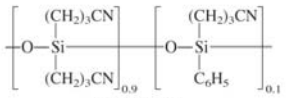


TABLE 22-1 Common stationary phases in capillary gas chromatography

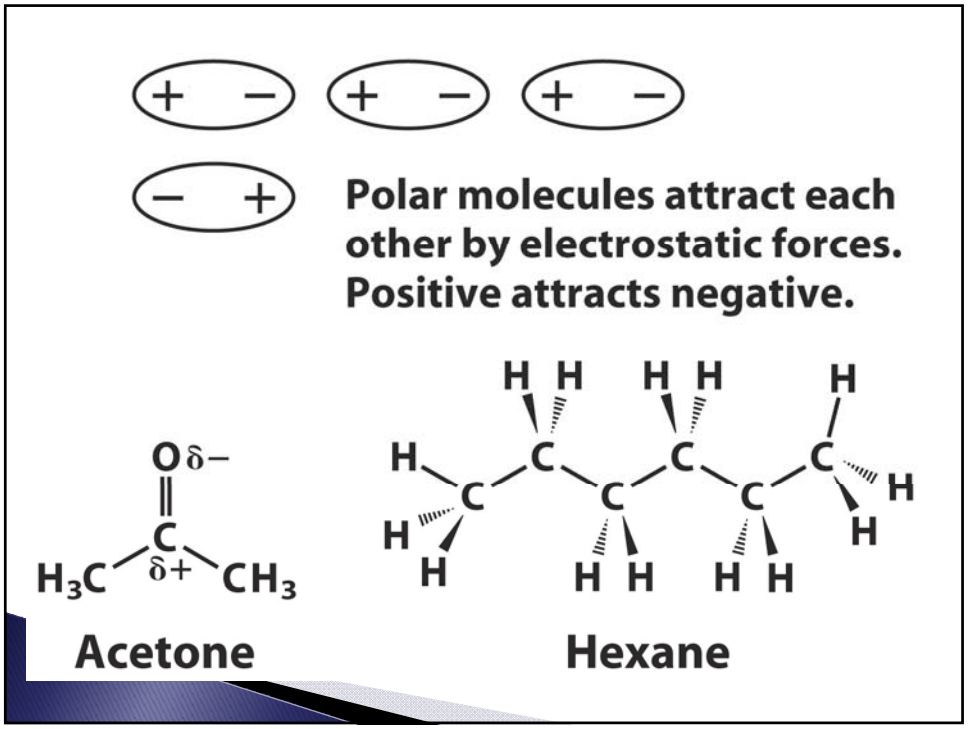
Structure	Polarity	Temperature range
 (Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$ Nonpolar	−60° to 360°C
	$x = 0.05$ Nonpolar	−60° to 360°C
	$x = 0.35$ Intermediate polarity	0° to 300°C
	$x = 0.65$ Intermediate polarity	50° to 370°C
 (Cyanopropylphenyl)$_{0.14}$ (dimethyl)$_{0.86}$ polysiloxane	Intermediate polarity	−20° to 280°C
 Carbowax (polyethylene glycol)	Strongly polar	40° to 250°C
 (Biscyanopropyl)$_{0.9}$ (cyanopropylphenyl)$_{0.1}$ polysiloxane	Strongly polar	0° to 275°C

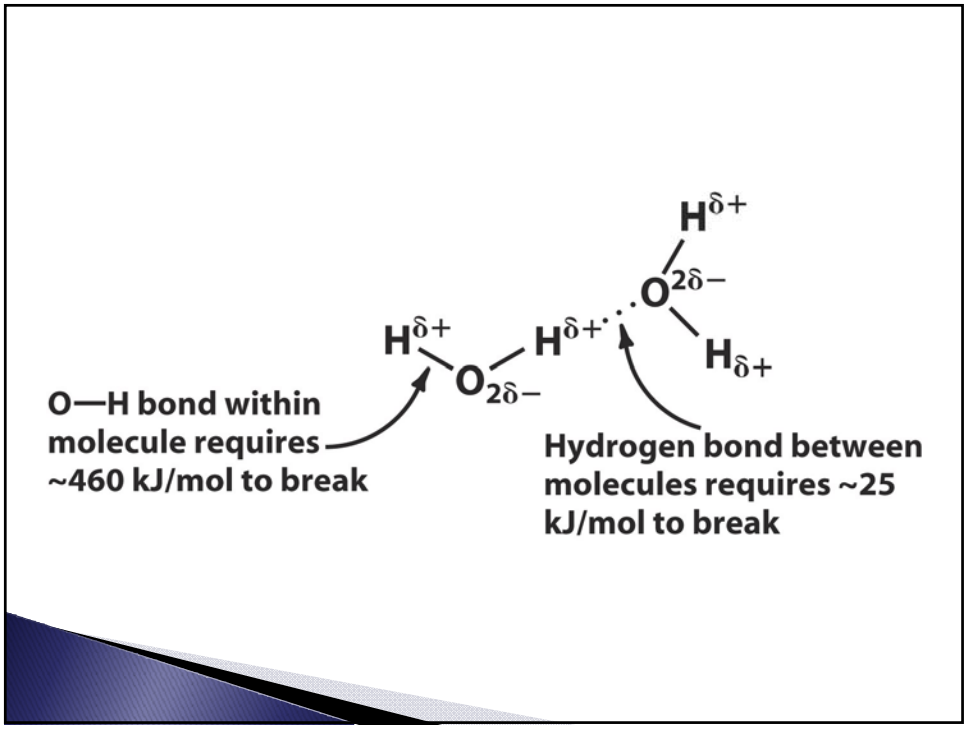
What will kill the column?

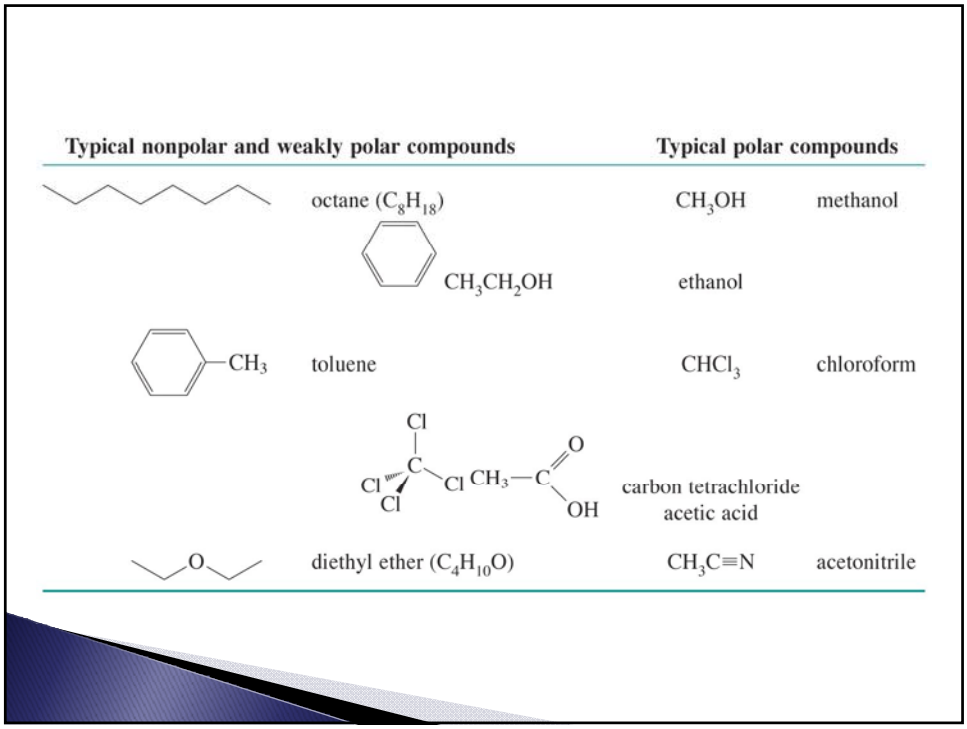
- Air leak (oxidation)
- No flow (overheat)
- Too high temperature
- Highly corrosive species

Is there solution to the problem?

- No
- Bonded stationary phases
- Cross linked siloxanes
- Guard column


Polar molecules attract each other by electrostatic forces. Positive attracts negative.
Acetone
Hexane


O—H bond within molecule requires ~460 kJ/mol to break
Hydrogen bond between molecules requires ~25 kJ/mol to break



Polarity of analytes

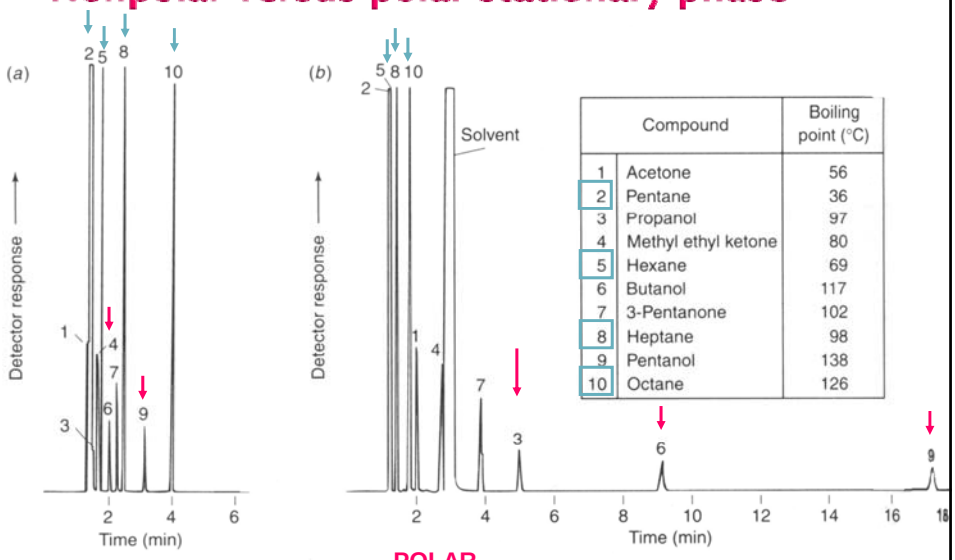
Nonpolar	Weak and intermediate polarity
Saturated hydrocarbons	Ethers
Olefinic hydrocarbons	Ketones
Aromatic hydrocarbons	Aldehydes
Halocarbons	Esters
Mercaptans	Tertiary amines
Sulfides	Nitro compounds without α-H atoms
CS2	Nitriles compounds without α-H atoms
Strong and intermediate polarity	**Strong polar**
Alcohols	Polyhydroxyalcohols
Carboxylic acids	Amino alcohols
Phenols	Hydroxy acids
Primary and secondary amines	Polyprotic acids
Oximes	Polyphenols
Nitro compounds with α-H atoms	
Nitriles compounds with α-H atoms	

Derivatization

- Nonpolar stationary phase gives more reproducible data and is stable at higher T
- To be able to analyze polar analytes on nonpolar columns a derivatization can be used. Derivatization involves a chemical modification of the analytes.
- **Methylating agents**: use of diazomethane Carboxylic acids R–COOH can be analyzed as methyl esters

  $R–COOCH_3$
- **Silylating agents** $Si(CH_3)_3$ can be also used

Nonpolar versus polar stationary phase



	Compound	Boiling point (°C)
1	Acetone	56
2	Pentane	36
3	Propanol	97
4	Methyl ethyl ketone	80
5	Hexane	69
6	Butanol	117
7	3-Pentanone	102
8	Heptane	98
9	Pentanol	138
10	Octane	126

NONPOLAR — **POLAR**

alkanes (nonpolar) are better separated on the nonpolar column depending on boiling point

alcohols (polar) are more retained on the polar st. phase

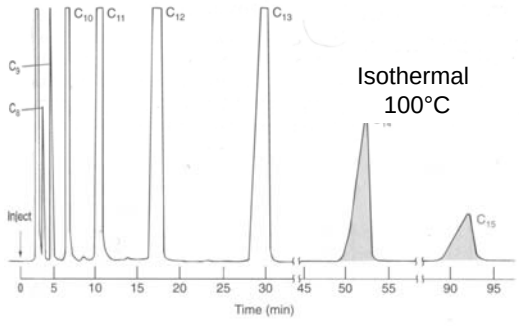
GC – Modes of Separation

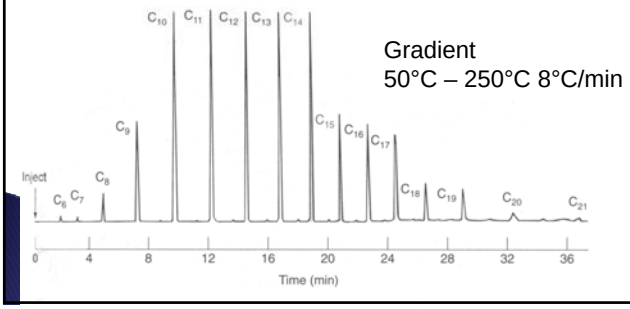
- Isothermal GC
- Programmed temperature GC
  - Raising column temperature (GC oven)
    - Decreases retention time
    - Sharpens peaks
    - only thermally stable compounds
- Programmed pressure GC

Always check for the **column temperature limit.**

Nonpolar columns are more heat resistant.

Temperature Effect





Increase in temperature
- **Decreases retention time**
- **Sharpens peak**

Selecting temperature conditions

- Temperature of injector

  ensures evaporation of sample,
  but do not decompose it (200 – 300 °C)

- Temperature of the column (GC oven)

  Effect of injection

  For the split injection– no specific requirements

  For the splitless and on column injection – solvent trapping technique

  Oven temperature – optimized to improve the separation

- Temperature of the detector

  has to be high enough to prevent condensation of analytes on the detector

Detectors for GC

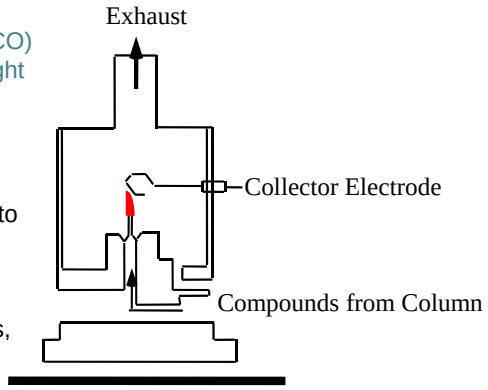
- Flame ionization detector (FID)
  - destruction of combustible sample in flame produces measurable current
- Electron capture detector (ECD)
  - radioactive
  - good for X^-, NO_2^-
- Thermal conductivity detector (TCD)
  - change in resistance of heated wire
- Mass spectrometr (MS)

Flame Ionization Detector (FID)

Eluate is burned/ionized in the mixture of hydrogen and air
Carbon atoms (except -COOH and -CO) produce CH radicals, which are thought to produce CHO^+ ions

Cations are collected on the cathode producing current (signal)
The response is directly proportional to the solute mass over 7 orders of magnitude.

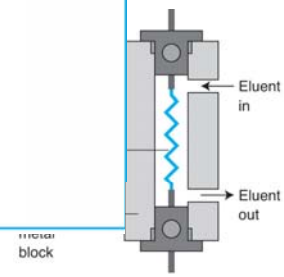
FID is insensitive to nonhydrocarbons, CO, CO_2, NH_3 H_2S etc.



Thermal conductivity detector (TCD)

TABLE 23-5 Thermal conductivity at 273 K and 1 atm

Gas	Thermal conductivity J/(K · m · s)
H_2	0.170
He	0.141
NH_3	0.021 5
N_2	0.024 3
C_2H_4	0.017 0
O_2	0.024 6
Ar	0.016 2
C_3H_8	0.015 1
CO_2	0.014 4
Cl_2	0.007 6



Low-volume thermal conductivity detector for open tubular column

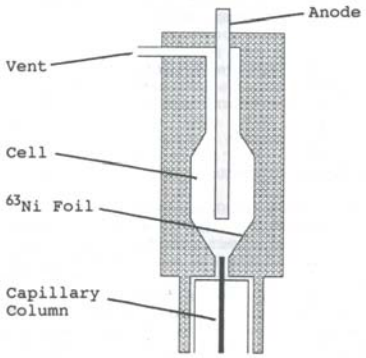
Universal detector
Measures the ability of substance to **transport heat** from a hot region to a cold region.

The carrier (he) has high conductivity thus any analyte will decreases it .
In system with reference cell carrier without the sample goes through a reference cell. The difference between amount of heat loss from carrier alone and from carrier with a sample is the measured signal.

The sensitivity is inversely proportional to a flow rate, TCD is more sensitive at lower flow rate.

Electron Capture Detector (ECD)

- **Selective detector for electron capturing compounds** – halogens, carbonyls, nitriles, nitro, organometallic compounds
- Radioactive ^{63}Ni emits high energ electrons β–rays which ionize a "makeup gas" nitrogen or 5% CH_4 Ar – forming plasma containing th "thermal electrons". Thermal electrons are captured on the electrode – signal. If electron capturing compound is present th number of thermal electrons on th electrode is decreased.
- The amount of the loss of detecto background current is translated into a detector signal

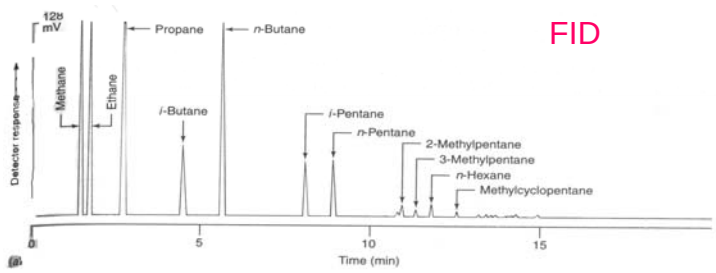


Other detectors – SELECTIVE

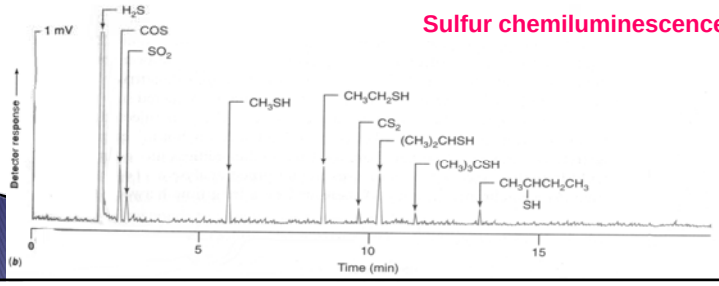
- **Photoionization detector (PID)** – Uses vacuum UV source to ionize aromatic and unsaturated compounds. Electrons produced by ionization are collected and measured.
- **Nitrogen phosphorus detector** (alkali flame) Sensitive to compounds containing N and P. Ions produced by those compounds in contact with Rb_2SO_4 (or cesium) glass beads form great current.
- **Sulfur chemiluminescence detector** – Exhaust from FID where S is oxidized to SO which reacts with O_3, and forms excited SO_2, which emits blue light and UV radiation.
- **Atomic emission detector** – eluate goes through a Helium plasma in microwave cavity, the atoms are excited and emission is monitored. This technique can detect most of the elements.

Detector Selectivity

FID

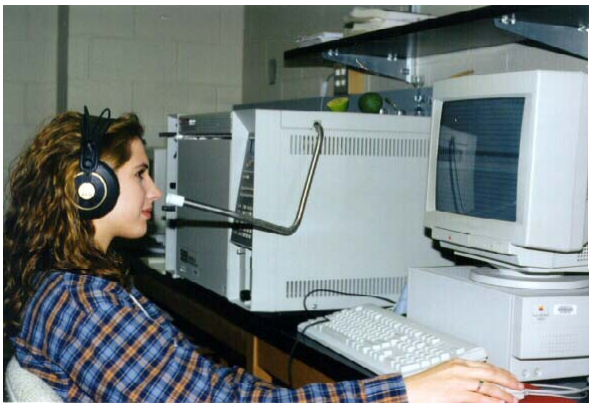


Sulfur chemiluminescence detector



GC/Olfactometry

For the determination of fragrances



Gas chromatography/Mass Spectrometry

- The Mass spectrometer is the only detector which does not require higher temperature than is the temperature of GC column.
- The outlet of capillary column of GC is placed directly to ionization source

  The MS employed consists of EI or CI ionization and RF analyzer such as quadrupole or ion trap.

MS

Mass spectrometer is the detector which fragments the molecules of eluting compounds. The individual fragments are than detected.

using GC/MS

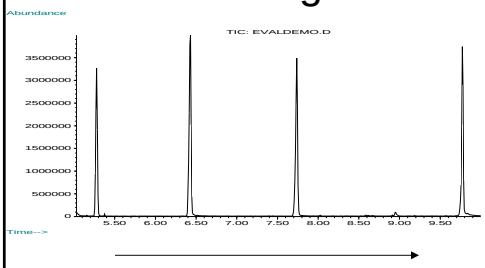
qualitative information : retention times
masses of fragments of the compound

Chromatogram versus Mass spectrum

The analytes can be monitored as **total ion current** (TIC) each data point in the chromatogram is represented by spectra of ions from MS

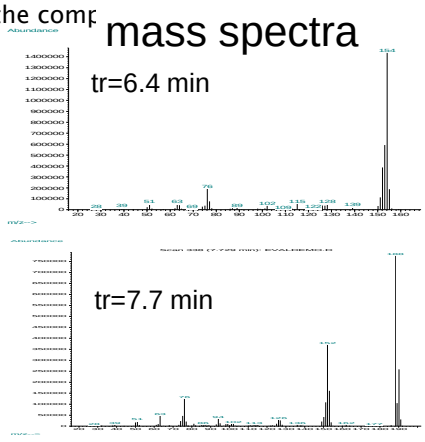
Therefore for each peak on the chromatogram we can get the spectrum and attempt to identify the comp

chromatogram

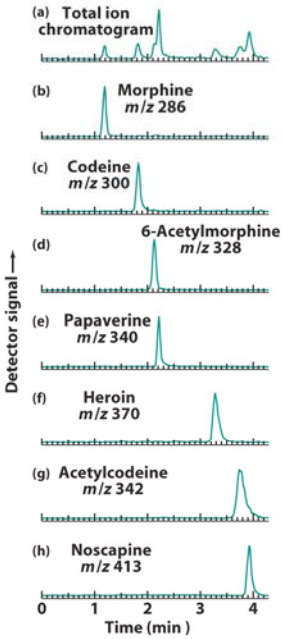


tr (min)

mass spectra



m/z



Detectors

- Universal (TCD, MS)
- Selective (FID, ECD, PID, N and P detector, Sulfur chemiluminiscence)

- Destructive
- Non destructive (TCD)

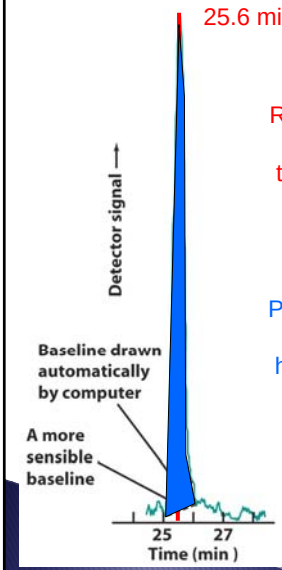
Quantification in chromatography

- Area or height of the peak is proportional to the concentration of the analyte.

- The area is a more precise measure. Nevertheless when peaks coelute (are not separated on the baseline), the height may be used.

- Both the external and internal method of calibrations are often employed.

Qualitative and quantitative analysis



Retention time

tell as about compound identity = qualitative

Peak Area or height

how much of compound is there = quantitative