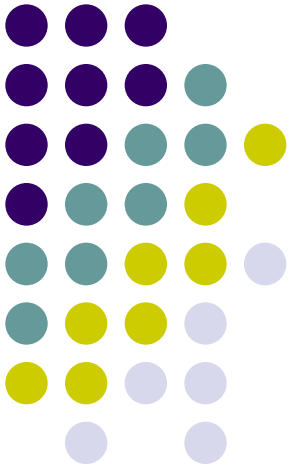
Chap 4. Water Analysis– Trace Pollutants

Analysis of the constituents of water found at ug/L

(Organic chemicals and Metal)



- Organic trace pollutants

  - Naturally occurring compounds from decaying organic material

  - Pollutants discharged into the environment

  - Degradation and inter-reaction products of the pollutants

  -substances introduced during sewage treatment

- types of organic compounds

  - pesticides, PCBs, dioxin etc

General Guidelines of Environmental Sampling Techniques

Sample Preservation and Storage

- Purpose – minimize physical, chemical and biological changes
- 3 approaches:
  - Refrigeration, Use of proper sample container, Addition of preserving chemicals

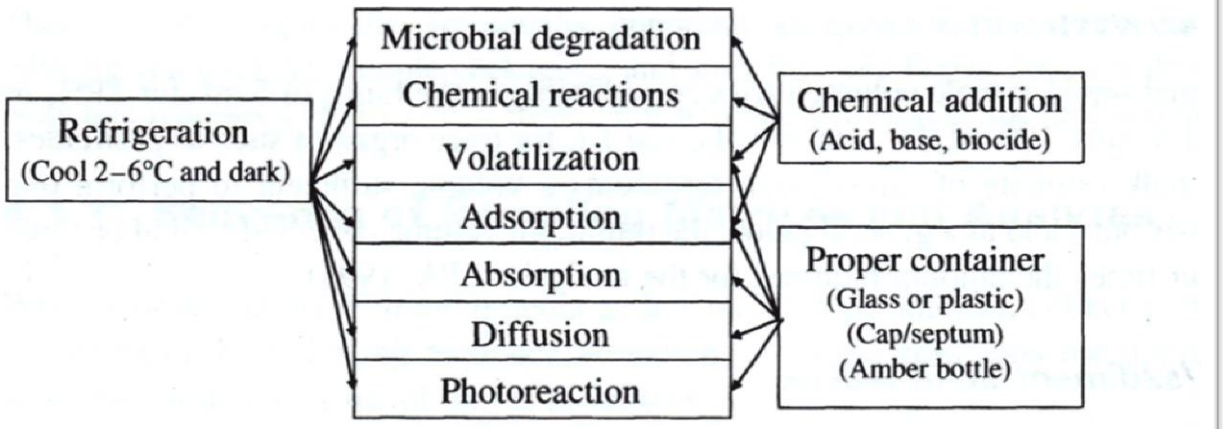


Figure 4.1 Methods of sample preservation to minimize potential changes of analytes during sample transportation and storage

Storage of samples

- The volatility of organic compounds ; filled and kept at sub-ambient T
- Microbial degradation : storage below 0°C
- Photolytic decomposition : store in dark
- Contamination from the container : glass bottle
- Maximum Holding Time (MHT) is the length of time a sample can be stored after collection and prior to analysis (refer to Korean standard method)

Table 4.1 Preservation methods of selected analytes and their physicochemical and biological changes during sample storage

Analytes	Change during storage	Preservation
Metals (M)	Adsorption to glass wall	Use plastic bottle
	Precipitation (MO, $M(OH)_2$)	Add HNO_3 to pH < 2
Phthalate ester	Diffusion from plastics	Use Teflon or glass bottle
Oil	Adsorption to plastics	Use glass bottle
VOCs	Volatilization	Avoid headspace
NH_3	Volatilization	Add H_2SO_4 to pH < 2
S^{2-}	Volatilization	Add zinc acetate and NaOH to pH > 9
CN^-	Volatilization	Add NaOH to pH > 12
	Chemical reaction with Cl_2	Add ascorbic acid to remove free Cl_2
Organic (drinking water)	Chemical reaction with Cl_2	Add $Na_2S_2O_3$ to remove free Cl_2
PAH	Photochemical degradation	Use amber glass container
Organic	Biodegradation	Low pH and temperature; add $HgCl_2$ to kill bacteria
Total phenolics	Bacterial degradation	Add H_2SO_4 to stop bacterial degradation

Adapted from Keith (1988) and Popek (2003).

QA/QC

- Experiment in a clean laboratory (free from the analytes)
- Prevent contamination of stock solvent,
- prevent contamination of samples and working standards
- Use pesticides free grade solvent
- Clean the glassware

→ Need Method blank

Field blank ; this undergoes the full handling and shipping process of an actual samples. to detect sample contamination that can occur during field operation or during shipment.
prepare with certified clean water or clean sand or soil in the field

What is GC?

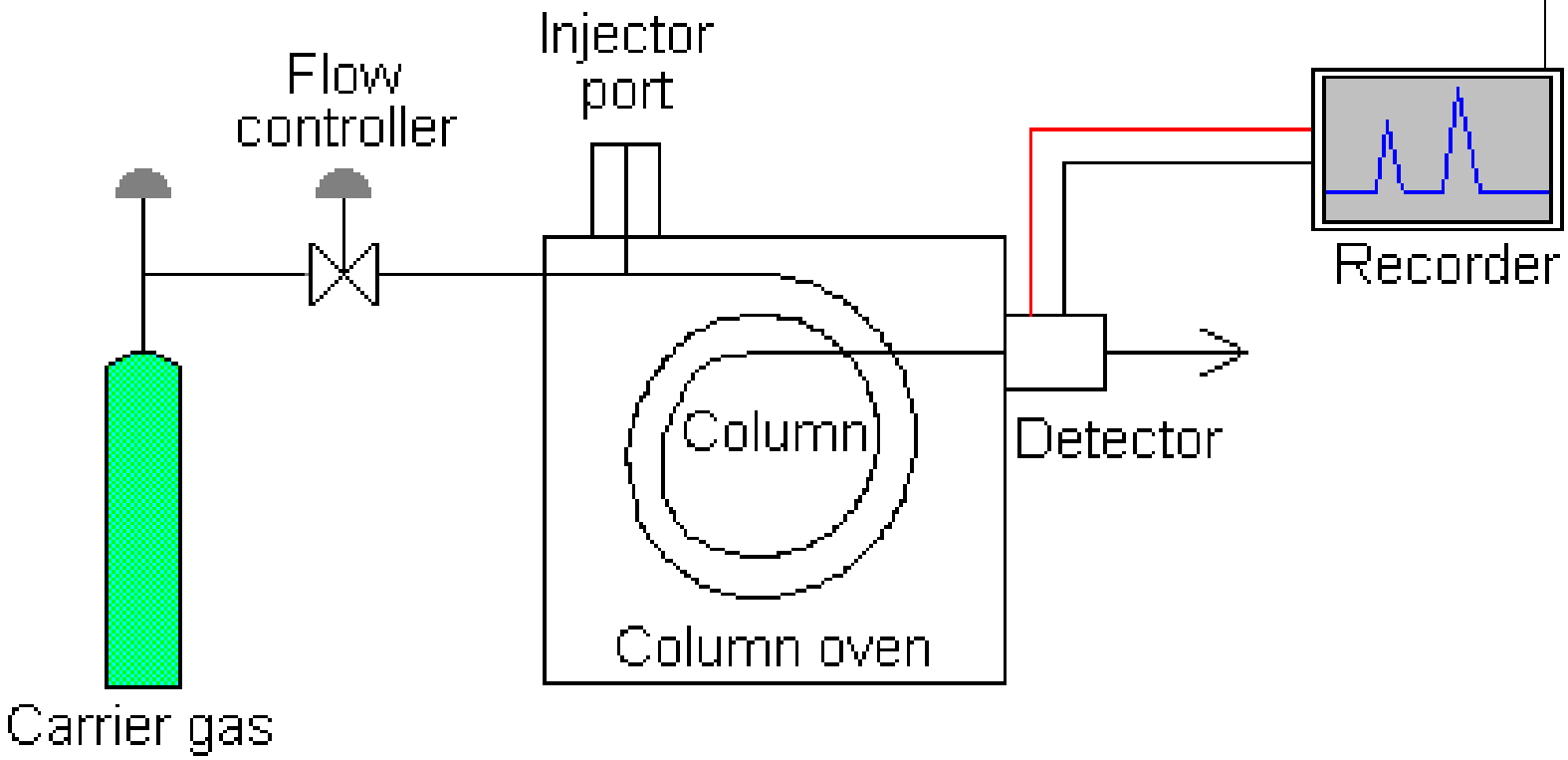
- GC ; gas chromatography (GLC ; gas-liquid chromatography)

  –Mobile phase ; gas
  –Stationary phase ; microscopic layer of liquid or polymer on an inert solid support

Chromatography ; The collective term for a family of laboratory techniques for the separation of mixtures

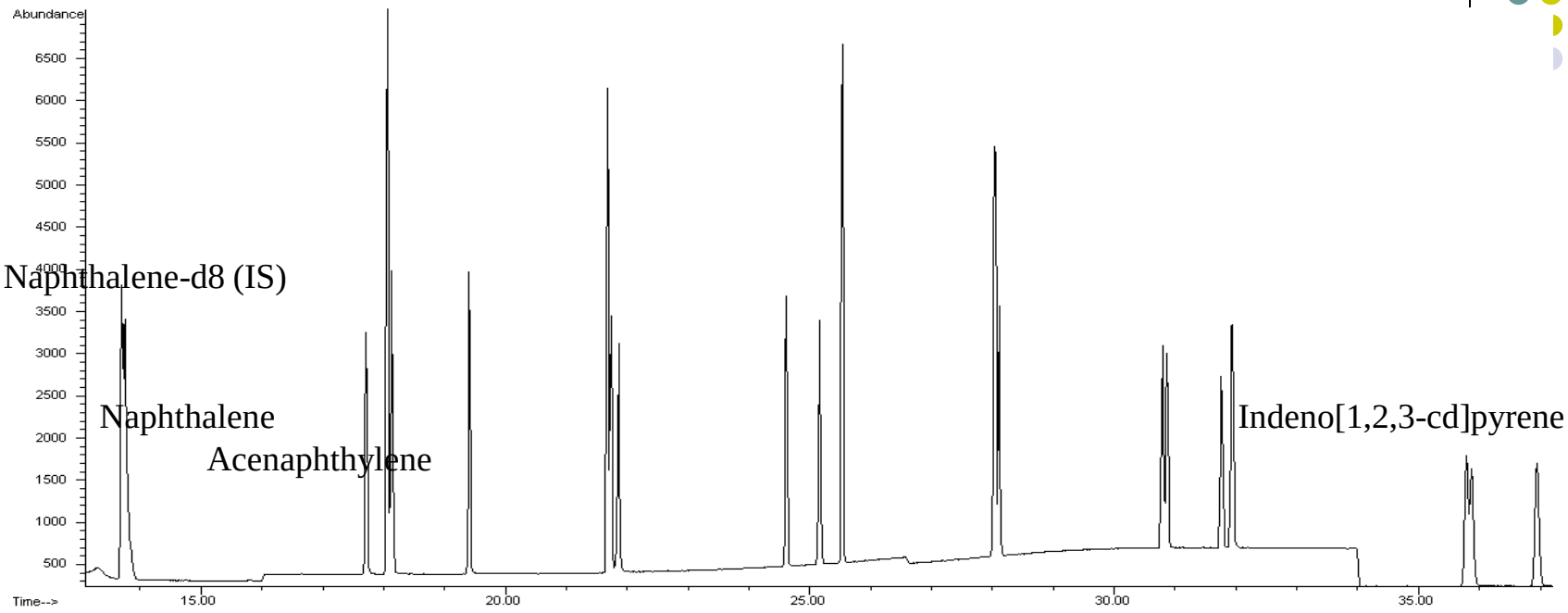
- Gas Chromatograph ; Equipment

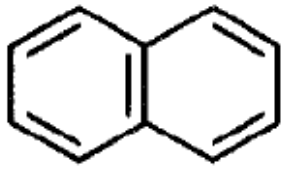
Schematic diagram of GC



Carrier gas

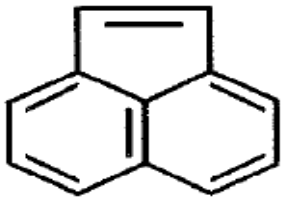
- inert gas like nitrogen, helium, hydrogen etc





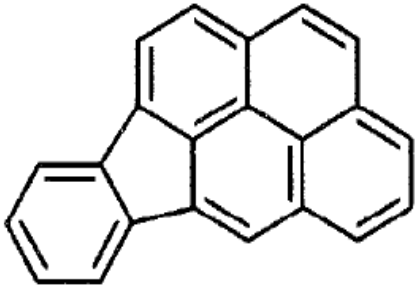
Naphthalene

(M.W., 128)



Acenaphthylene

(M.W., 152)

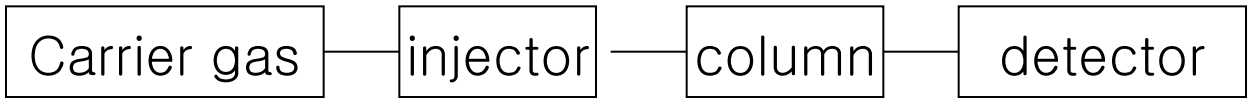


Indeno(1,2,3−c,d)pyrene

(M.W., 276)

• Gas Chromatography

He, N, H2



- Separation ; differential retention of the components between stationary phase and a mobile phase

–**Volatility of compound**: Low boiling (volatile) components will travel faster through the column than will high boiling components

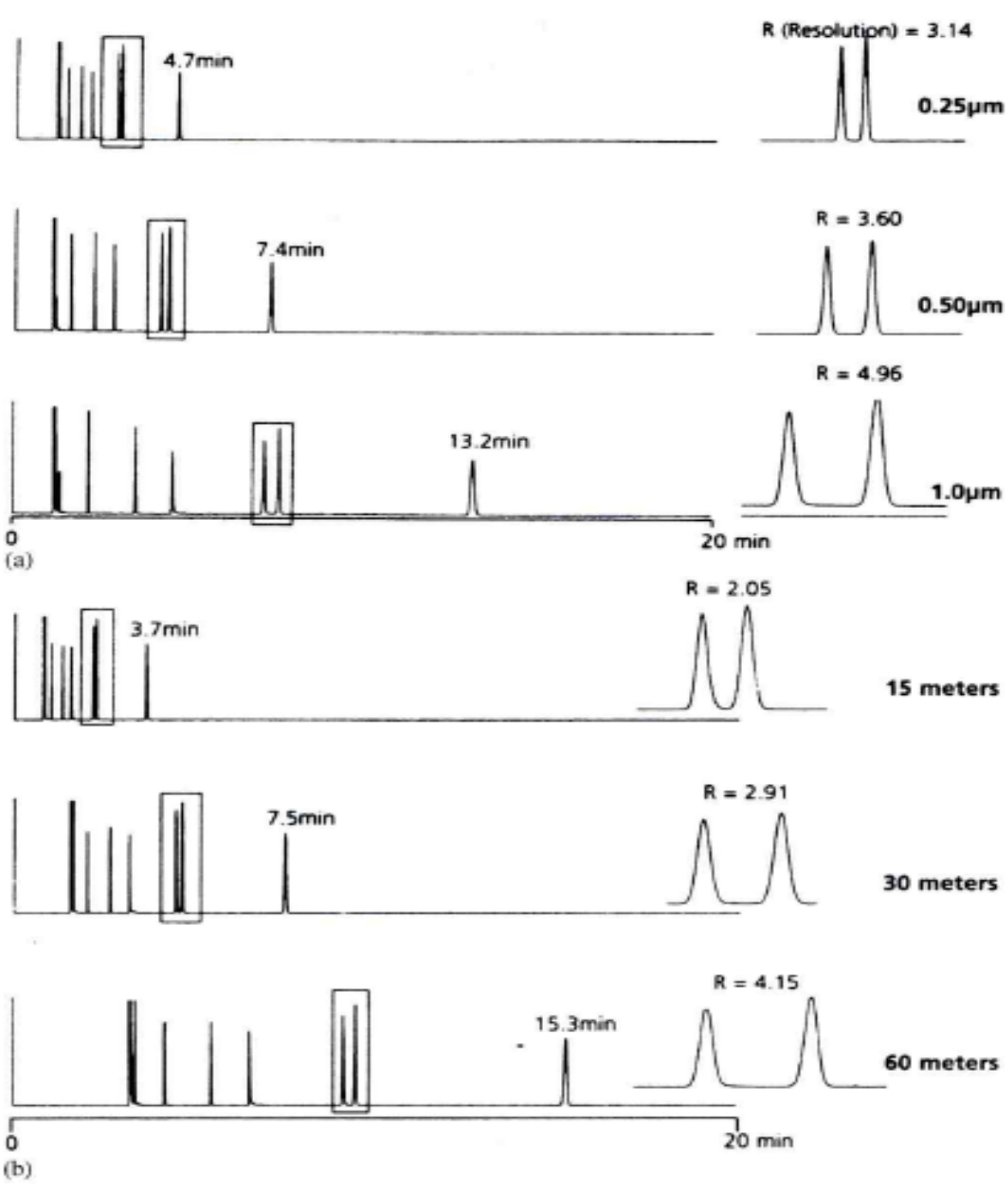
–**Polarity of compounds**: Polar compounds will move more slowly, especially if the column is polar.

-**Column temperature**: Raising the column temperature speeds up all the compounds in a mixture

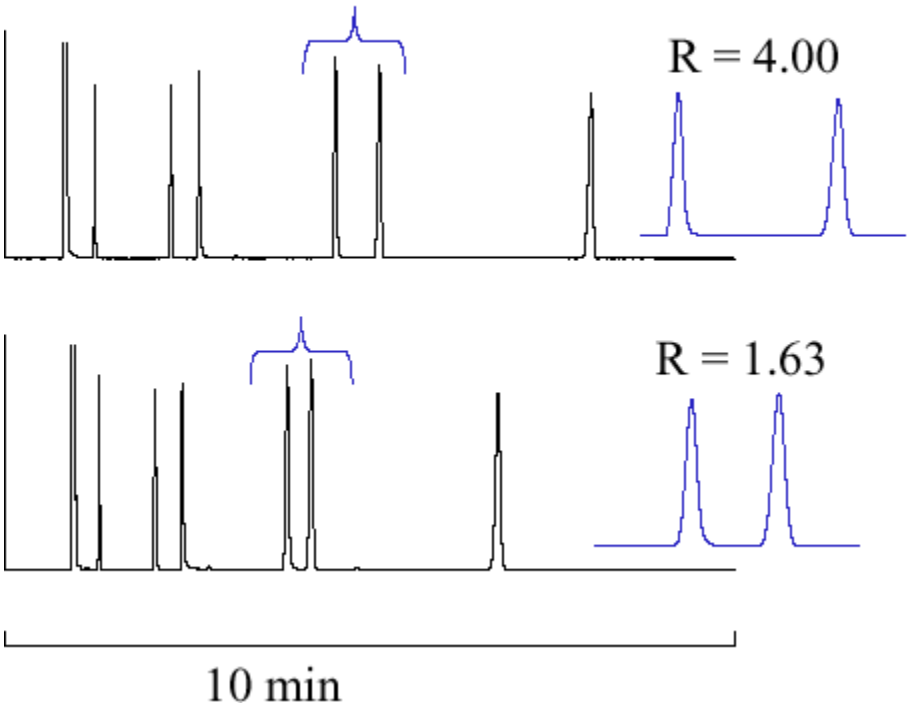
–**Column packing polarity**: Usually, all compounds will move slower on polar columns, but polar compounds will show a larger effect

-**Flow rate of the gas through the column**: Speeding up the carrier gas flow increases the speed with which all compounds move through the column

-**Length of the column**: The longer the column, the longer it will take all compounds to elute. Longer columns are employed to obtain better separation

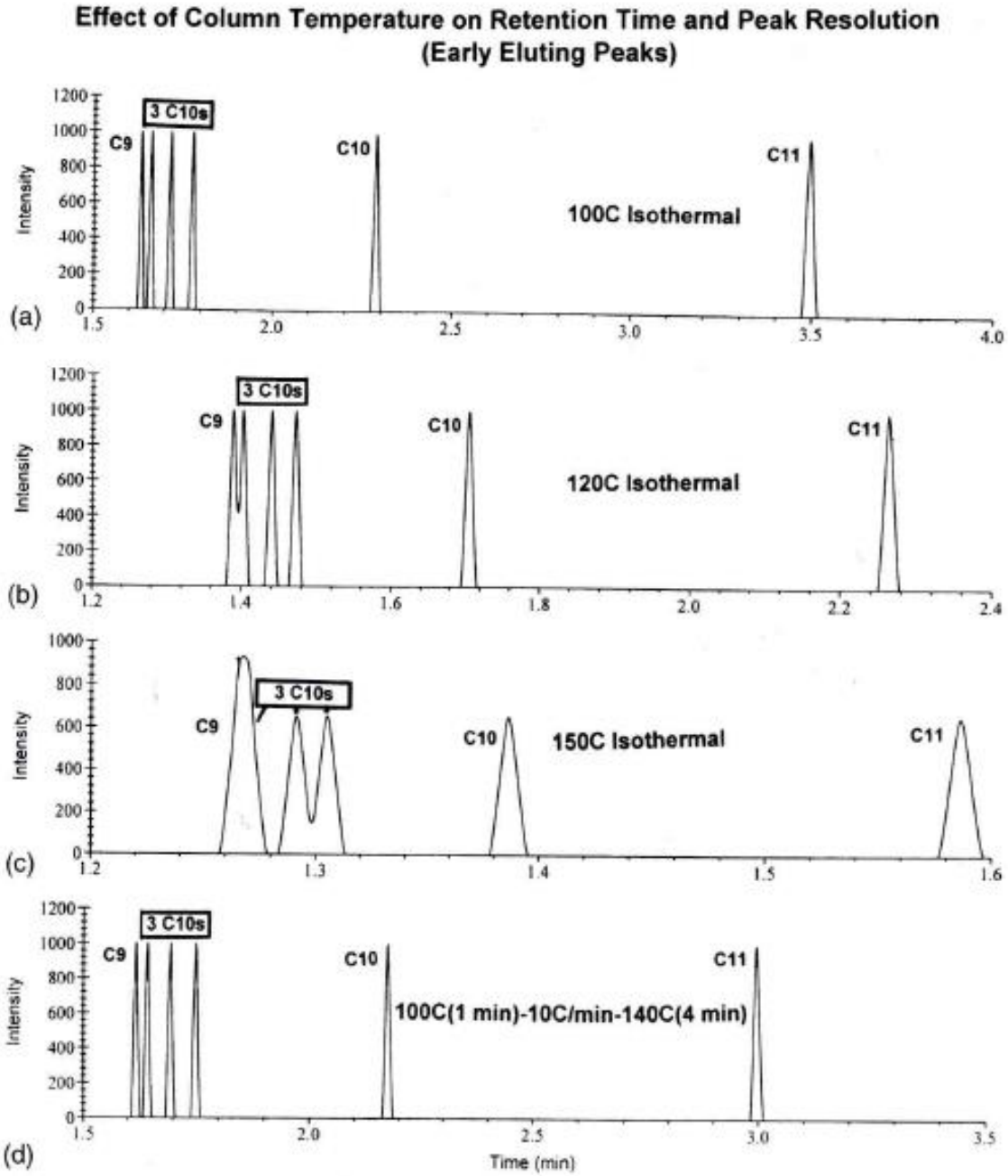

4.7min
R (Resolution) = 3.14
0.25μm
7.4min
R = 3.60
0.50μm
13.2min
R = 4.96
1.0μm
0
20 min
(a)
3.7min
R = 2.05
15 meters
7.5min
R = 2.91
30 meters
15.3min
R = 4.15
60 meters
0
20 min
(b)

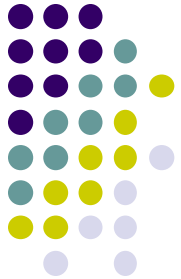
Effect of Column Diameter



0.1 mm ID

0.25 mm ID


Effect of Column Temperature on Retention Time and Peak Resolution
(Early Eluting Peaks)
Intensity
3 C10s
C9
C10
C11
100C Isothermal
(a)
120C Isothermal
(b)
150C Isothermal
(c)
100C(1 min)-10C/min-140C(4 min)
(d)
Time (min)



- Columns and Stationary phases

- Consider stationary phase and column dimension
  ; affect separation efficiency

- Column types

1. narrow-bore capillary columns ; 30~60m, 0.2mm id, 0.4ml/min
   The greatest detection sensitivity, suitable for mass detector
   Direct injection is not possible (overload), need splitting device

2. Wide-bore capillary column ; 15~30m, 0.53mm id, 25ml/min
   Large sample capacity, direct syringe injection

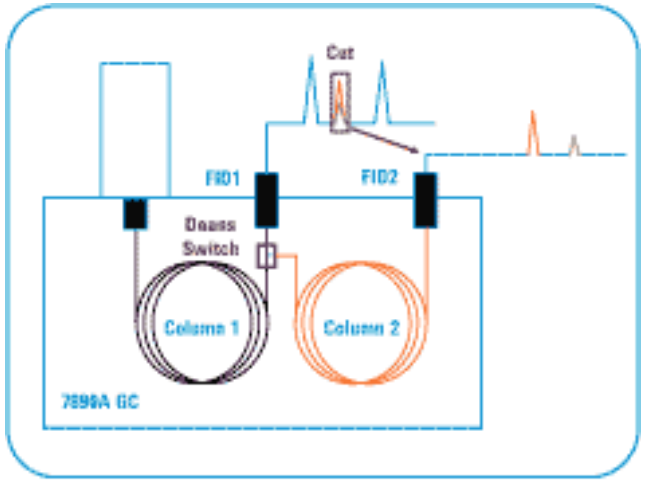
   Less affected by contamination from non-volatile components in the sample so suitable for highly contaminated samples

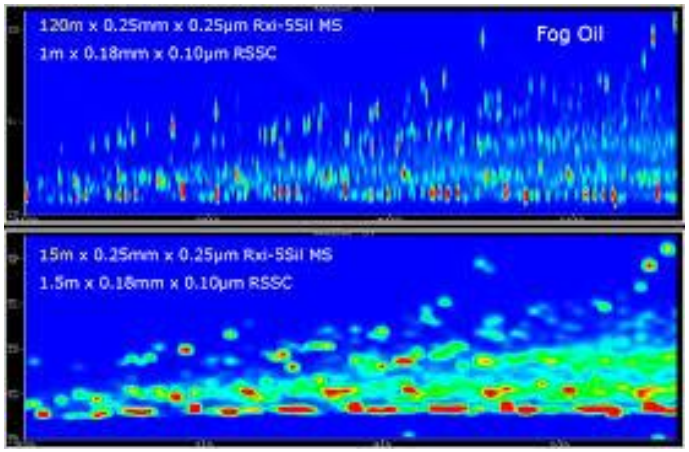
3. Packed column ; 2m, 2mm id, 20ml/min

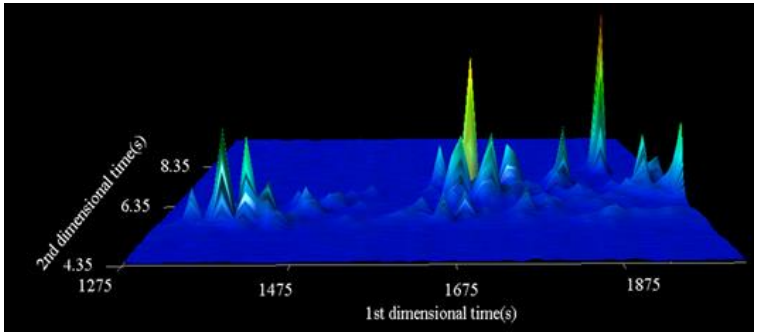
- Column bleeding ; background signal generated by the column stationary phase

* Use two columns of different polarities for resolving compounds

Two dimensional GC (GC X GC)

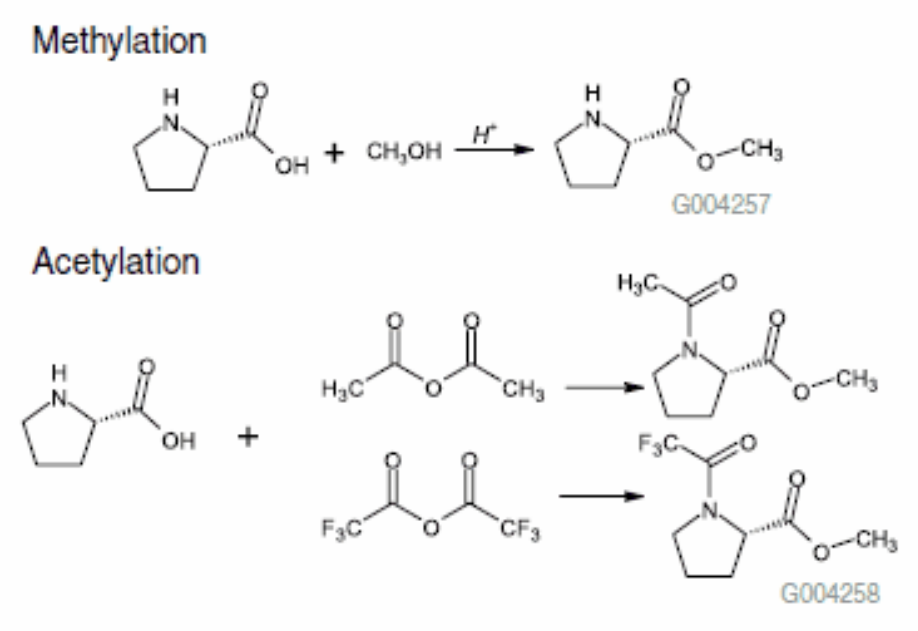






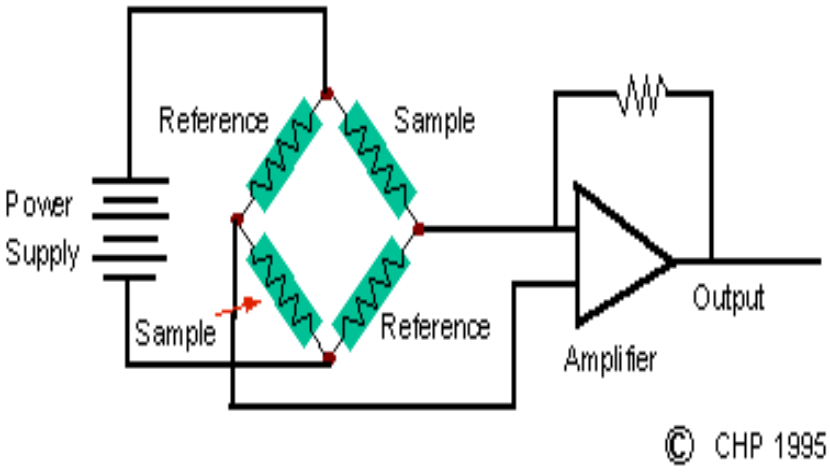
- some compounds are needed a derivatization for analysis

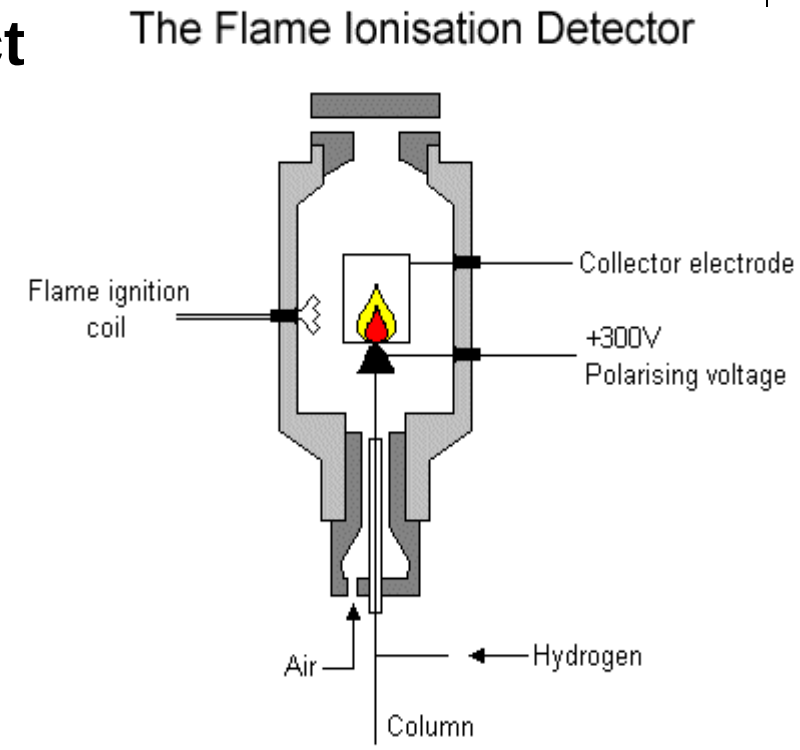
Polar N-H and O-H groups on which give hydrogen bonding may be converted to relatively nonpolar groups on a relatively nonvolatile compound.
The resultant product may be less polar, thus more volatile, allowing analysis by GC. (ex ; alkylation)



- Detectors

-Thermal Conductivity Detect

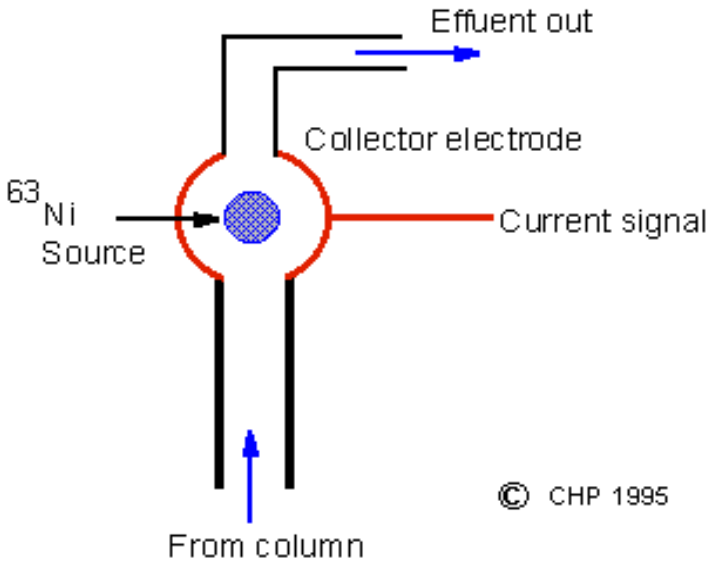




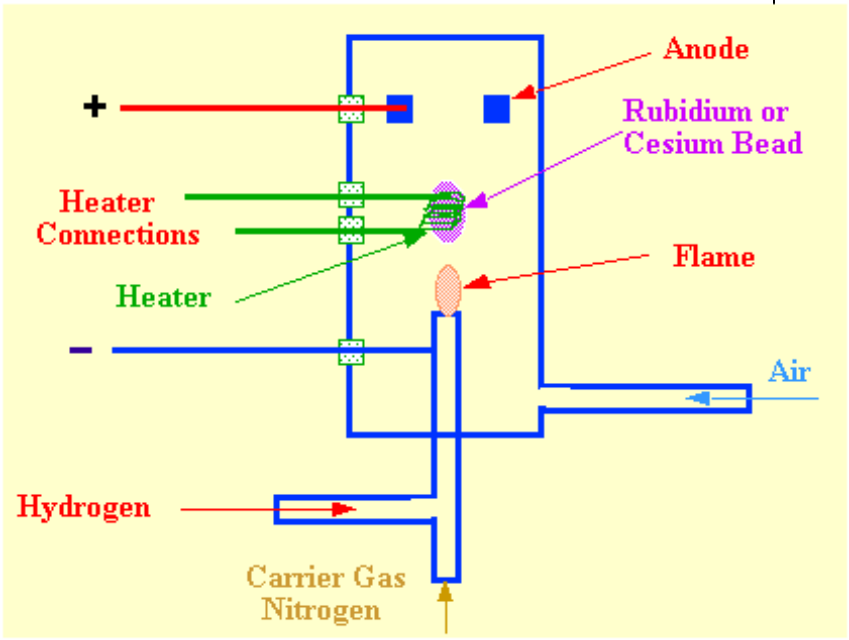
-TCD ; universal, non-destructive, insensitive, limited dynamic range
Measurement of major constituents of air (H_2O, CO, CO_2, H_2)

-FID ; micro hydrogen/oxygen burner that continuously maintain a hydrogen flame sensitive universal detector for organic compounds(suitable for hydrocarbon) nearly universal, destructive, sensitive with dynamic range

Electron capture detector



Nitrogen phosphorus detector



- ECD ; highly sensitive specific detector responding to atoms with a high electron affinity like halogen, nitro and some other oxygen containing functional groups very selective and sensitive, limited dynamic range

-NPD ; selective for organic compounds with N or P atoms, destructive, less dynamic range than the FID

- Detectors

-TCD ; universal detector

-FID ; micro hydrogen/oxygen burner that continuously maintain a hydrogen flame sensitive universal detector for organic compounds

-ECD ; highly sensitive specific detector responding to atoms with a high electron affinity like chlorine

-Hall electrolytic conductivity detector (EICD)
; highly sensitive specific detector for halogens, nitrogen and sulpher

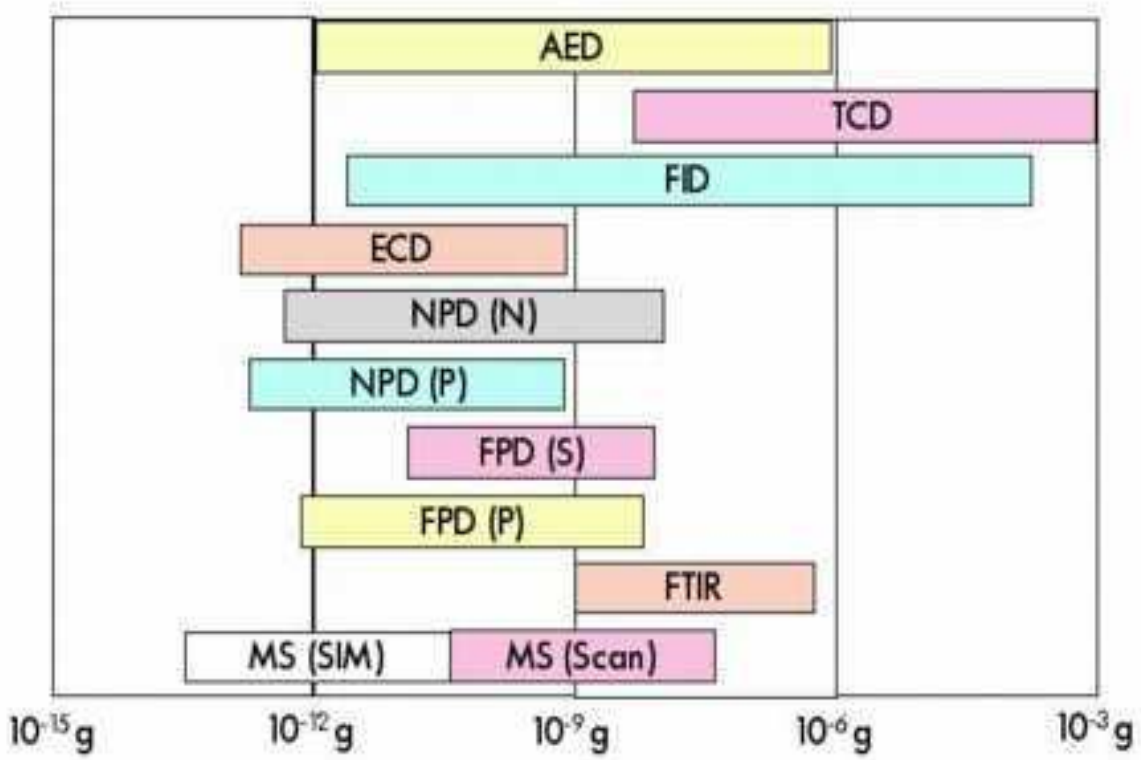
- Thermionic detector ; element specific detector for nitrogen and phosphorus

- Flame photometric detector ; sulphur and phosphorus

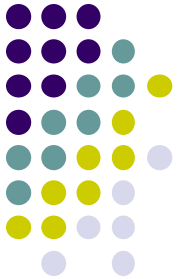
- photo-ionisation detector ; aromatic rings or double bonds

-mass spectrometric detector ; highly specific and sensitive detection for all organic compounds

GC detectors sensitivities and ranges



Comparison of GC and LC



- All gases and volatile compounds can be analyzed via GC not by HPLC
- Nonvolatiles and thermally unstable compounds cannot be analyzed via GC unless their structures are changed through derivatization
- For some semivolatile compounds (e.g. PAHs, nitroaromatics and explosives) both GC and HPLC can be used
- HPLC is preferred when direct analysis of aqueous sample is needed to avoid time consuming extractions
- In other cases, GC is instrument of choice due to variety of detection methods