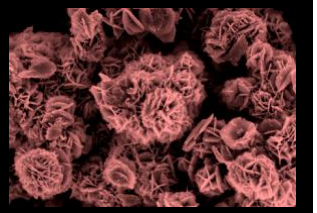
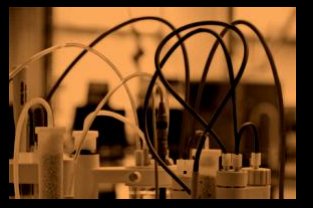




Chemical Engineering

Inspiring Potential · Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

Gas Chromatography-Principles and Instrumentation

CEB 4032/CFB3032: ANALYTICAL CHEMISTRY/ANALYTICAL INSTRUMENTATION

TS CHM DR. MOHD DZUL HAKIM WIRZAL

Chemical Engineering
Inspiring Potential · Generating Futures

Introduction

UNIVERSITI TEKNOLOGI PETRONAS

- GC is is widely used for the determination of organic/volatile compounds.

- For example: the separation of benzene (bp. 80.1ºC) and cyclohexane (bp. 80.8 ºC) is extremely simple by gas chromatography, but it is virtually impossible by conventional distillation.

- Very complex mixture can be separated by this technique.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- Two types of gas chromatography (GC):
  i. Gas-solid (adsorption) chromatography (GSC)
  ii. Gas-liquid (partitioning) chromatography (GLC)

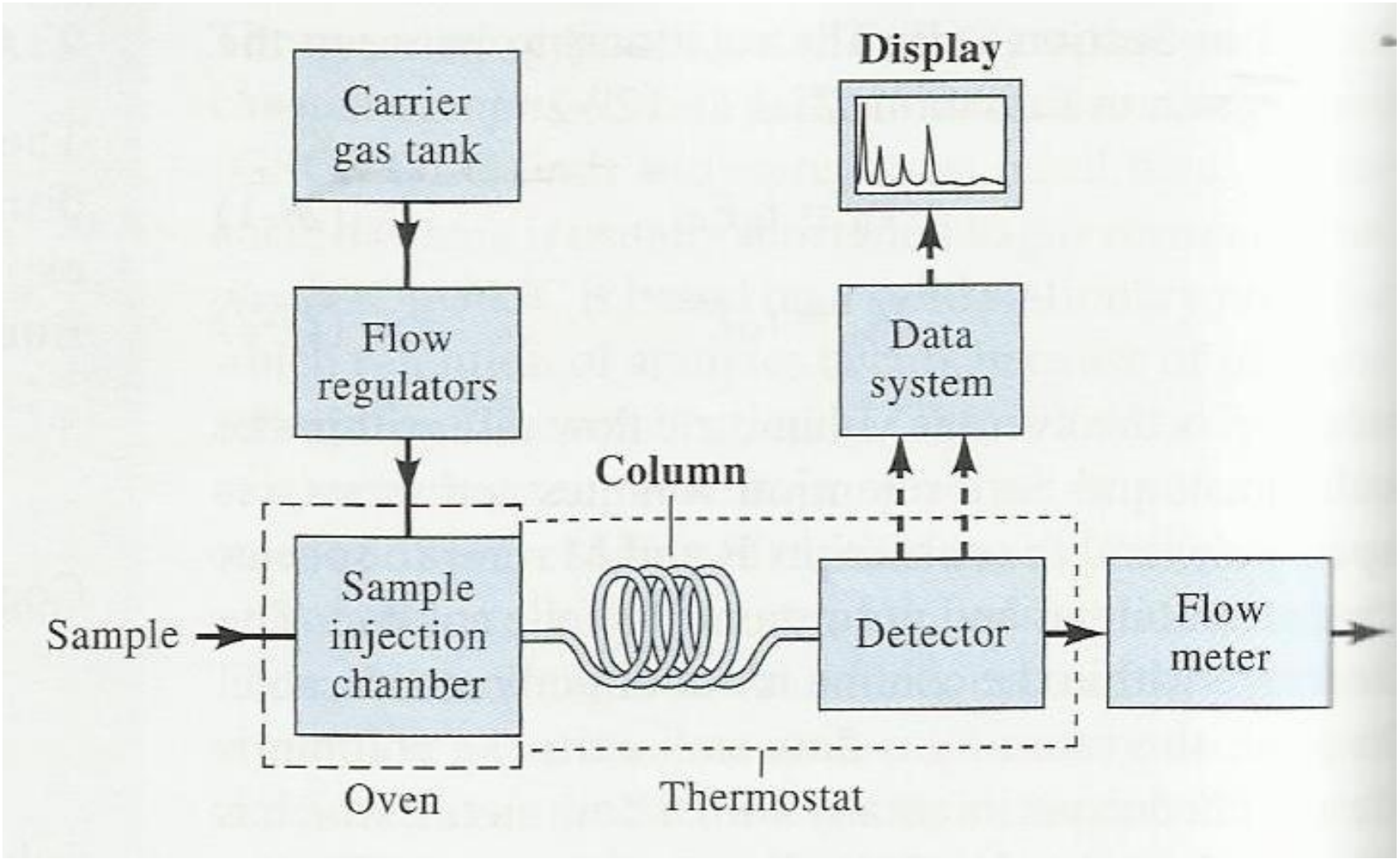
- In GSC, analyte is adsorbed directly on solid particles of stationary phase.

- In GLC, the stationary phase is a nonvolatile liquid coated on the inside of the column or on a fine solid support.

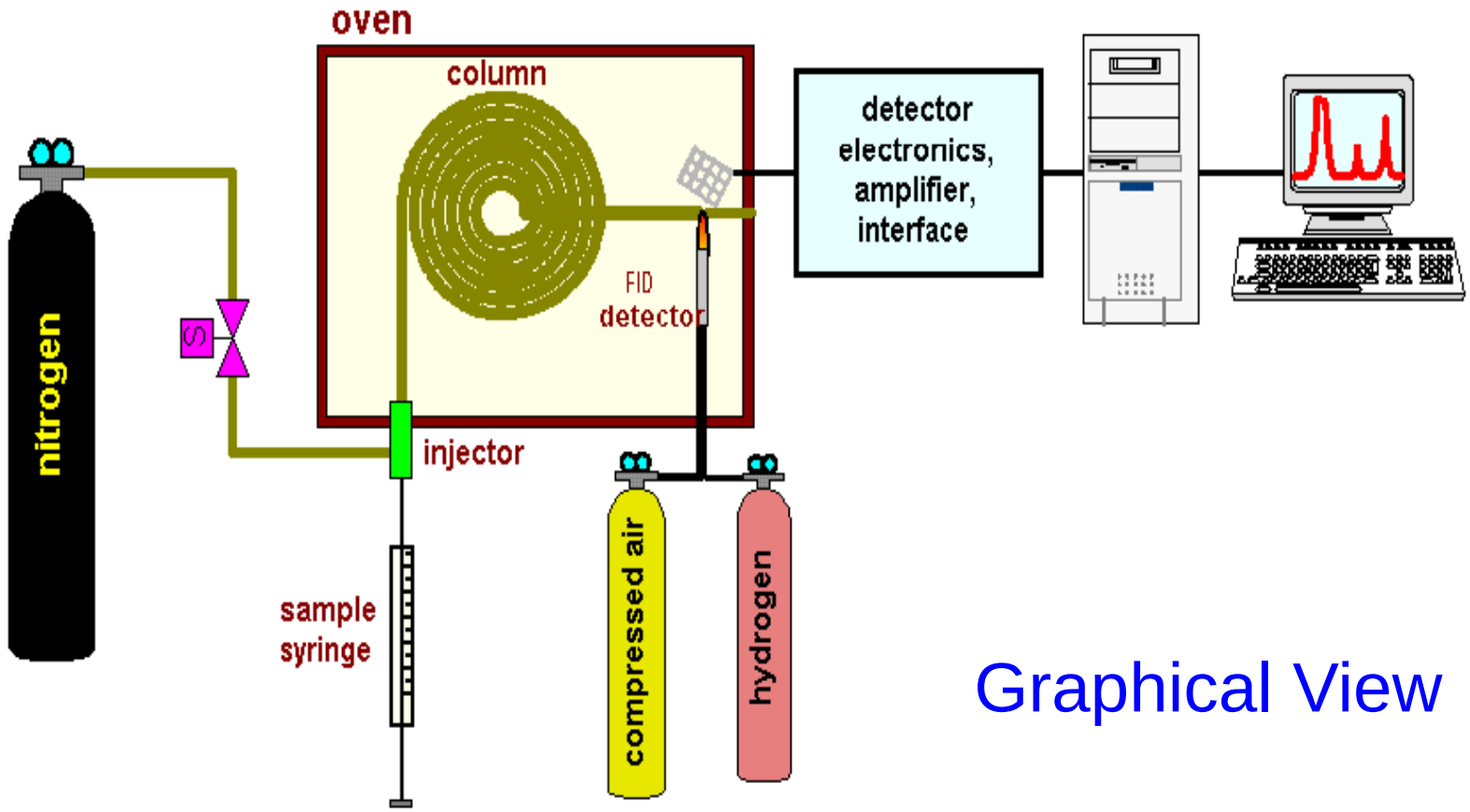
The basic components of a typical instrument for performing GC are:

i. Carrier gas system
ii. Sample injection system
iii. Column
iv. Column oven
v. Detection system

Instrumentation of GC



Block diagram of a typical Gas Chromatography



Graphical View

Chemical Engineering
Inspiring Potential · Generating Futures

Principles Operation of GC

UNIVERSITI TEKNOLOGI PETRONAS

- Volatile liquid or gaseous sample is injected through a septum into a heated port, in which it rapidly evaporated.
- Vapor is swept through the column (stationary phase) by carrier gas (mobile phase→ usually He, N_2 or H_2)
- The column must be hot enough to provide sufficient temperature for analytes to be eluted in a reasonable time.
- Separation occurs as the vapor constituents equilibrate between carrier gas and the stationary phase.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- The sample is automatically detected as it emerges from the column → using a variety of detectors whose response is dependent upon the composition of the vapor.

- The detector is maintained at a higher temperature than the column, so that all analytes will be gaseous.

- The signal is fed to a recording device where the chromatographic peaks are recorded as a function of time → chromatogram.

Chemical Engineering
Inspiring Potential · Generating Futures

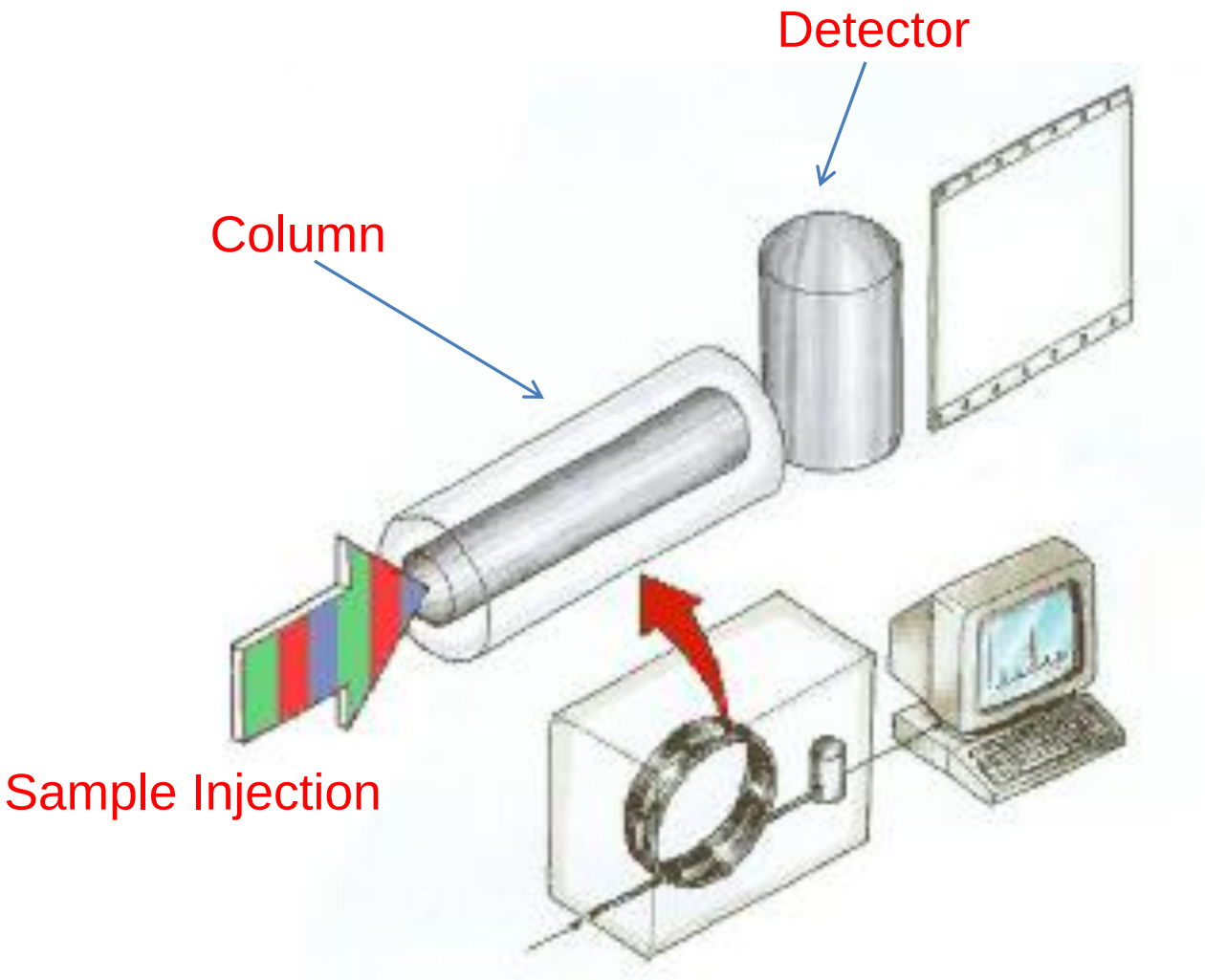
UNIVERSITI TEKNOLOGI PETRONAS

- By measuring the retention time and comparing this time with that of a standard of the pure substance, it can identify the peak.

- The area under the peak is proportional to the concentration, and so the amount of the substance can be quantitatively determined.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS



GC Operation

Modern Gas Chromatography System

These include software for recording retention time, taking peak areas and calculating concentrations.

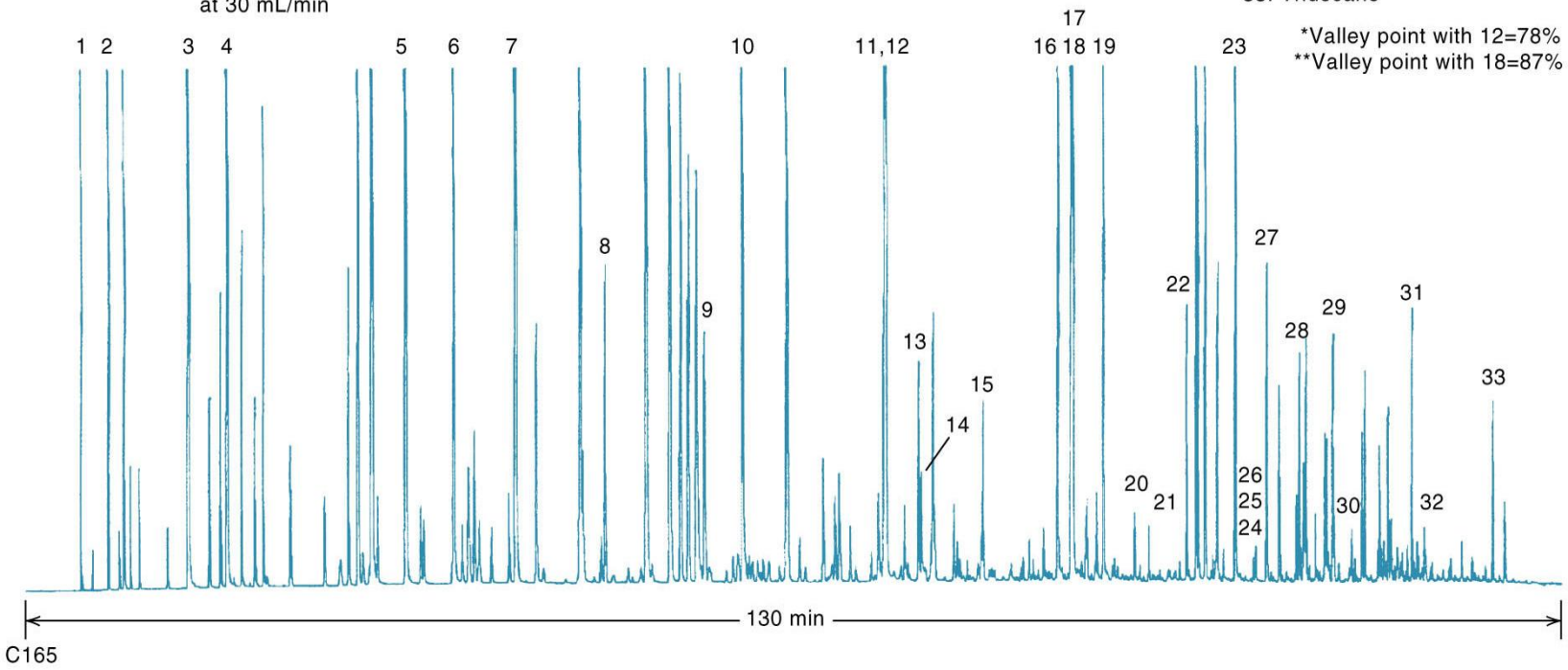
Chemical Engineering
Inspiring Potential • Generating Futures

Unleaded Gasoline

Column: **DB-Petro 100**
100 m × 0.25 min I.D., 0.5 µm
J&W P/N: **122-10A6**
Carrier: Helium at 25.6 cm/sec
Oven: 0°C for 15 min
0-50°C at 1°/min
50-130°C at 2°/min
130-180°C at 4°/min
180°C for 20 min
Injector: Split 1:300, 200°C
1 µL of neat sample
Detector: FID, 250°C
Nitrogen makeup gas
at 30 mL/min

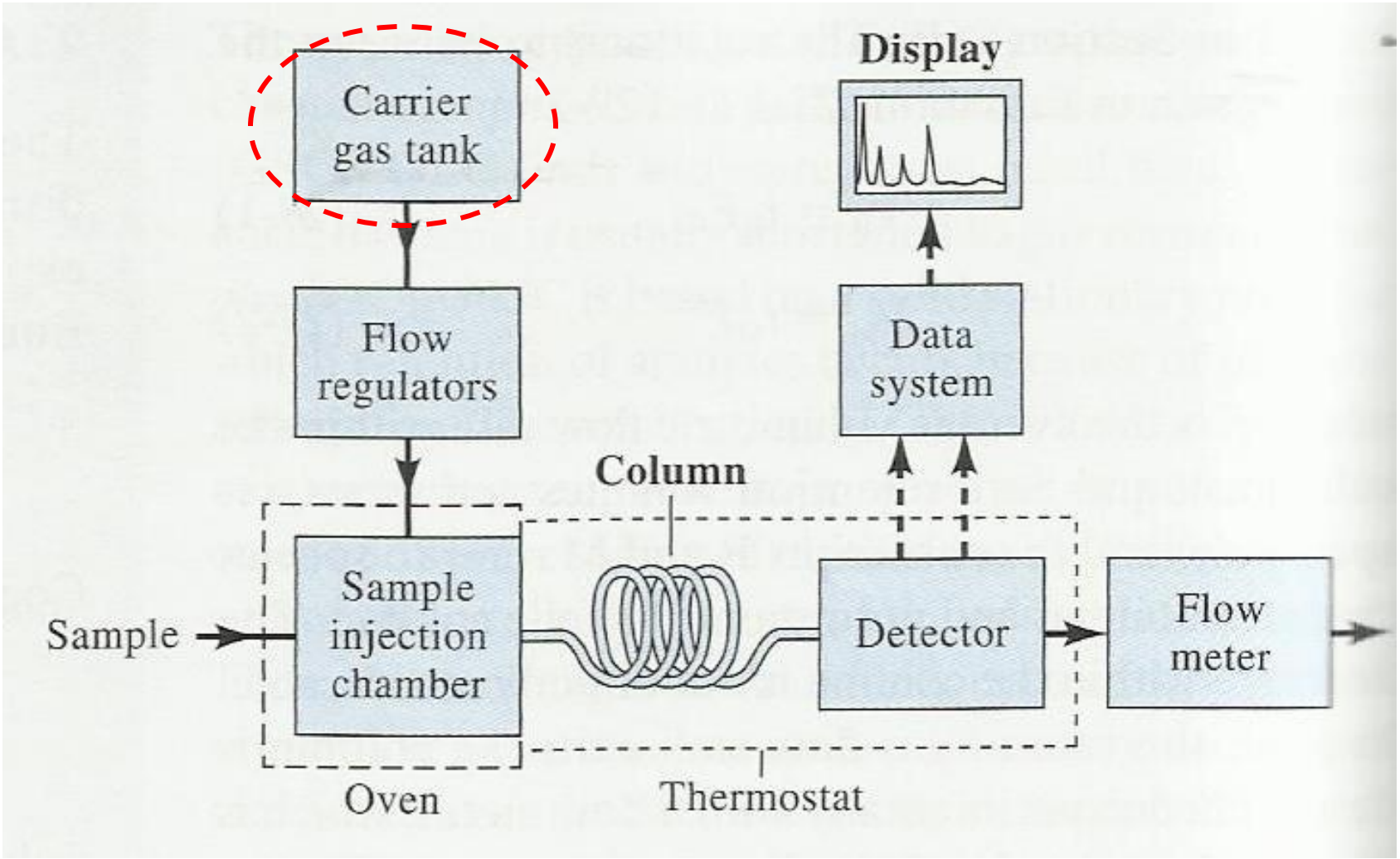
1. Methane
2. *n*-Butane
3. Isopentane
4. *n*-Pentane
5. *n*-Hexane
6. Methylcyclopentane
7. Benzene
8. Cyclohexane
9. Isooctane
10. *n*-Heptane
*11. Toluene
12. 2,3,3-Trimethylpentane
13. 2-Methylheptane
14. 4-Methylheptane
15. n-Octane
16. Ethylbenzene
**17. *m*-Xylene
18. *p*-Xylene
19. *o*-Xylene
20. *n*-Nonane
21 Isopropylbenzene
22. Propylbenzene
23. 1,2,4-Trimethylbenzene
24. Isobutylbenzene
25. *sec*-Butylbenzene
26. *n*-Decane
27. 1,2,3-Trimethylbenzene
28. Butylbenzene
29. *n*-Undecane
30. 1,2,4,5-Tetramethylbenzene
31. Naphthalene
32. Dodecane
33. Tridecane

*Valley point with 12=78%
**Valley point with 18=87%



Typical gas chromatogram of complex mixture using a capillary column

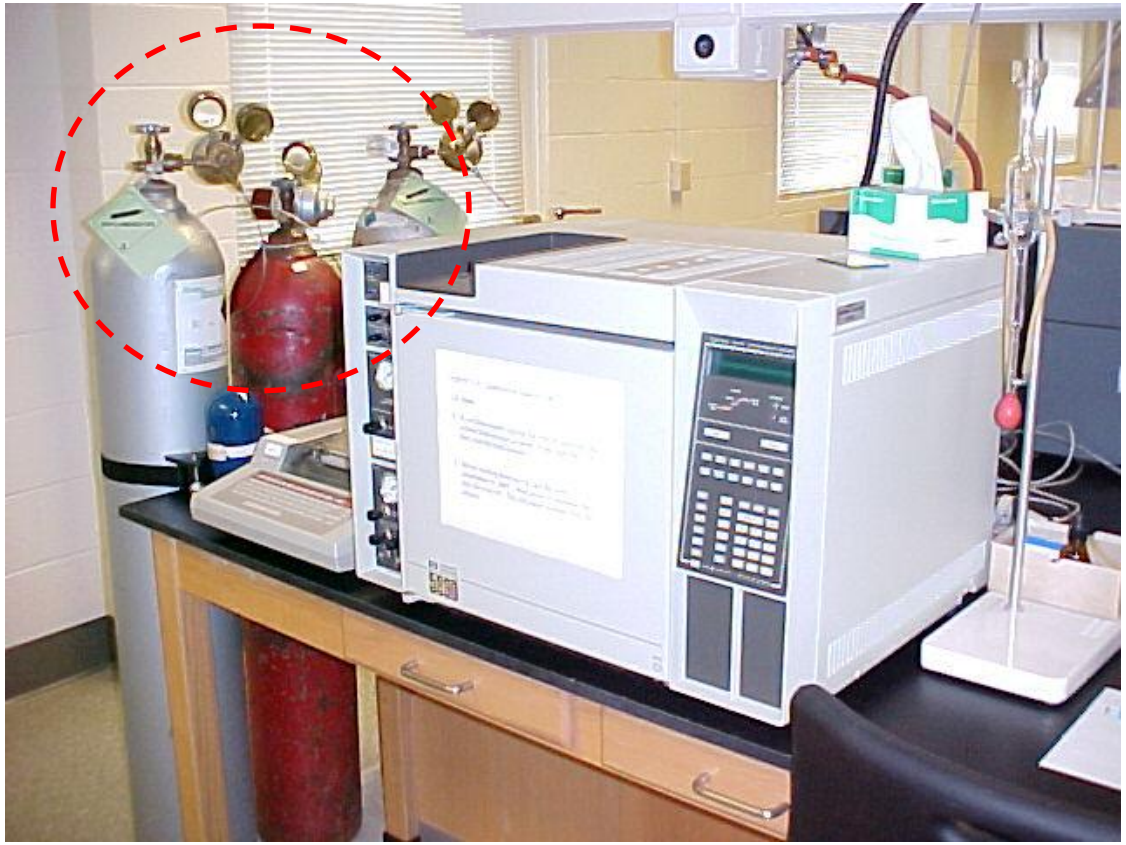
Carrier Gas System



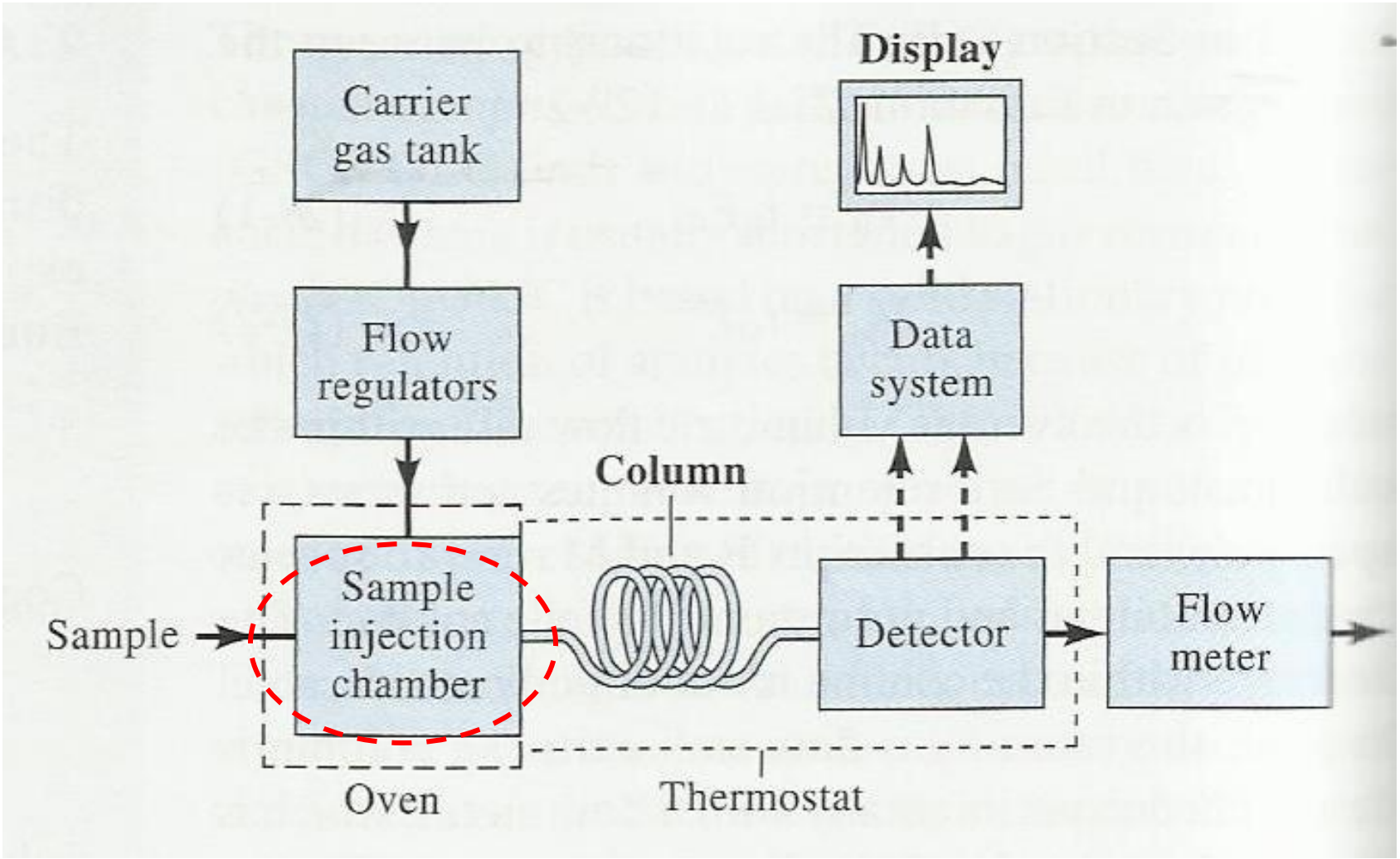
Carrier Gas System

- The mobile-phase gas in GC is called carrier gas and must be chemically inert.
- Example gases: helium, argon, nitrogen and hydrogen.
- The choice of the gas → dictated by the type of detector.
- These gases are available in pressurized tanks.
- Pressure regulators, gauges, and flow meters, are required to control the flow rate of the gas.

Carrier Gas System / Gas Supply



Sample Injection System



Sample Injection System

- Calibrated microsyringes → used to inject samples into a heated sample port located at the head of the column.
- For liquid samples, the injection system are heated to temperatures about 50 ºC above the boiling point of the highest boiling solute.
- The injection port are usually kept warmer than the column to promote rapid vaporization of the injected sample and prevent sample condensation in the detector.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- To achieve high column efficiency, the sample must be of a suitable size.

- Slow injection or oversize samples cause band spreading and poor resolution.

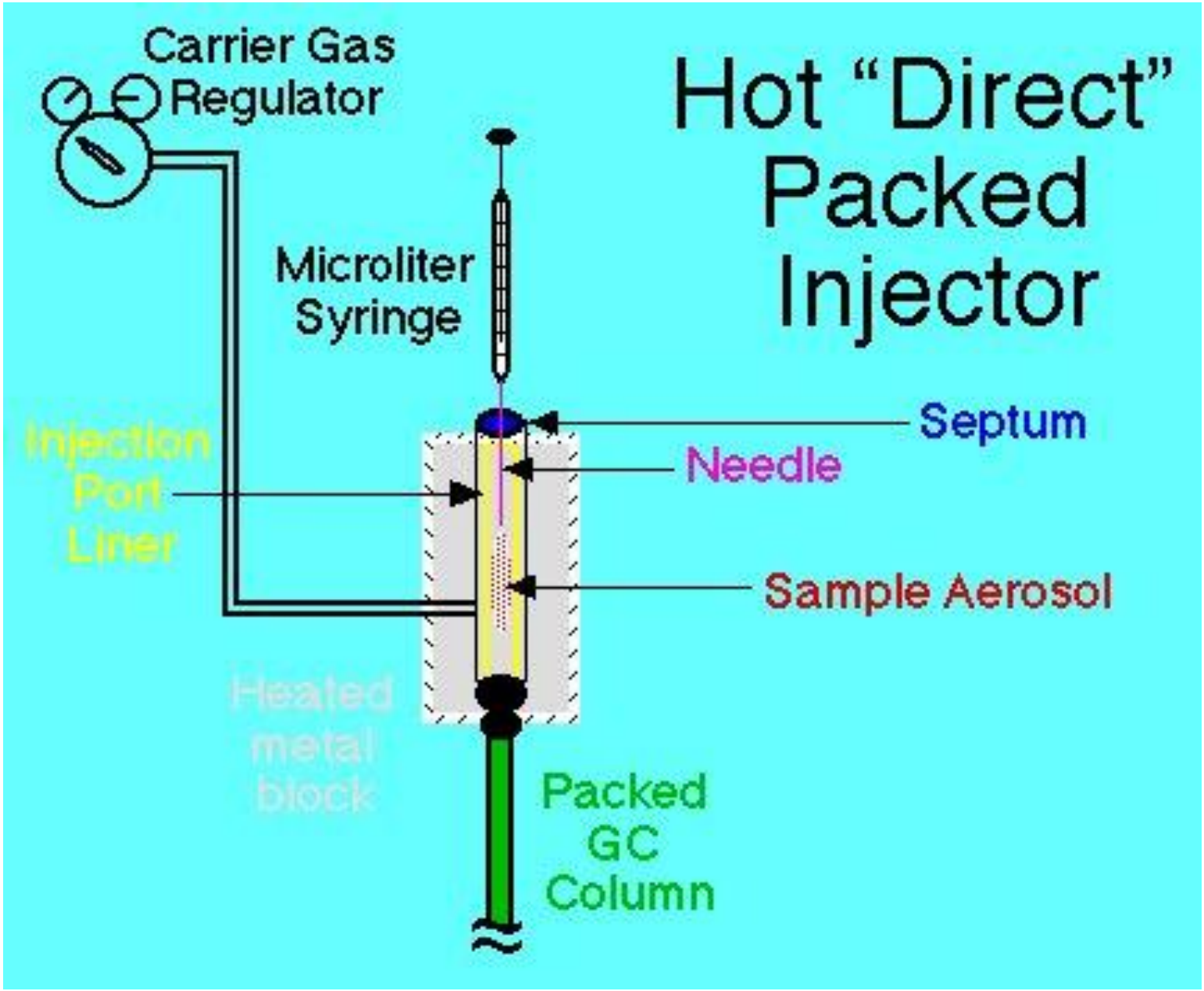
- Sample size→ depends on the column and sample.

- For i) packed column:
  - liquid samples of 0.1 to 10 µl are injected
  - for gas samples, 1-10 mL are injected

- Gases may be injected by means of gas-tight syringe or through a special gas inlet chamber of constant volume (gas sampling valve).

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS



Chemical Engineering
Inspiring Potential • Generating Futures

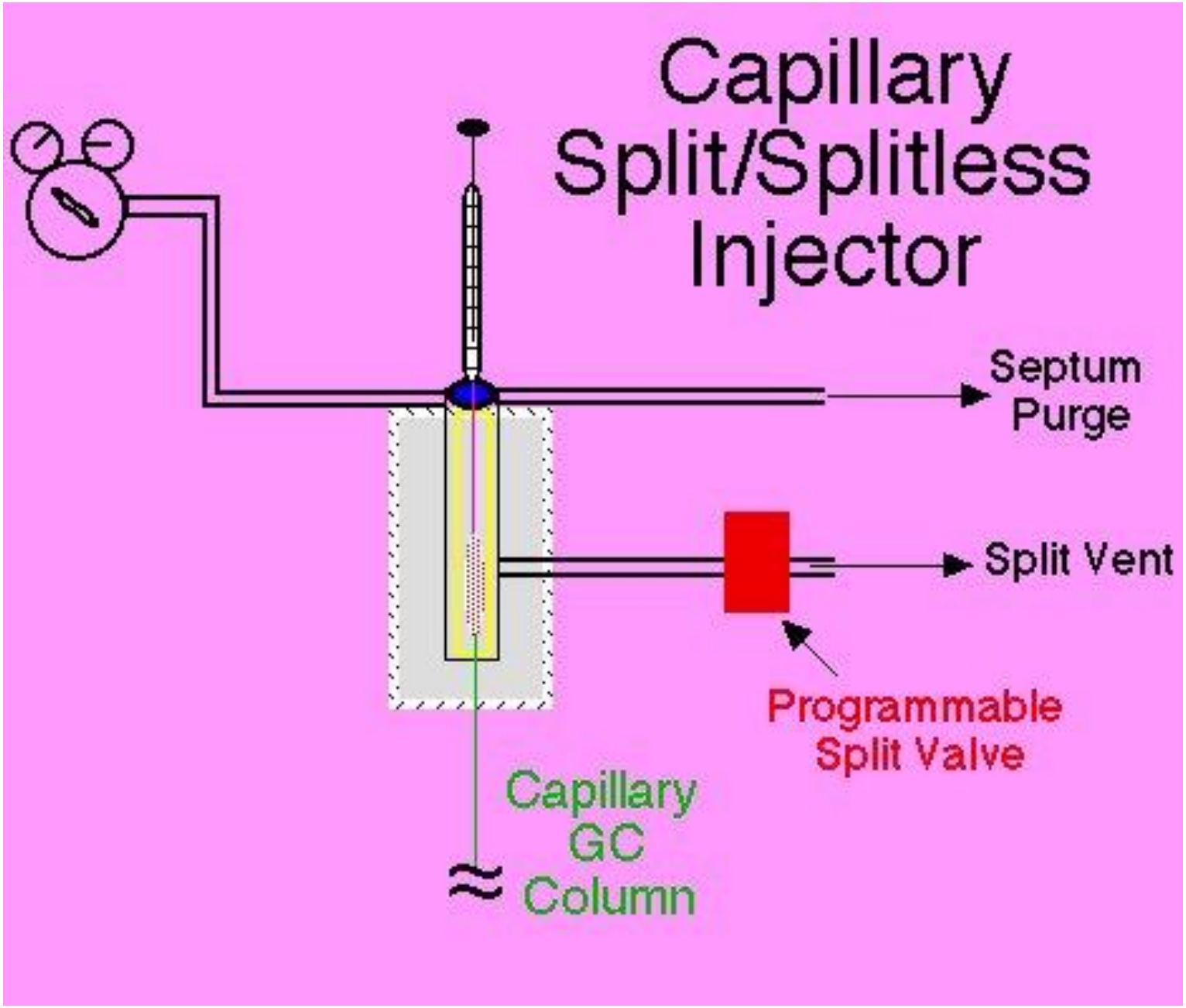
UNIVERSITI TEKNOLOGI PETRONAS

- For ii) capillary column → volumes of only about 1/100 size of packed column must be injected because of the lower capacity of the columns.

- Sample splitters are included in the gas chromatography system designed for use with capillary columns that deliver a small fixed fraction of the sample to the column, with the remainder going to the waste.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS



Chemical Engineering
Inspiring Potential · Generating Futures

Syringes

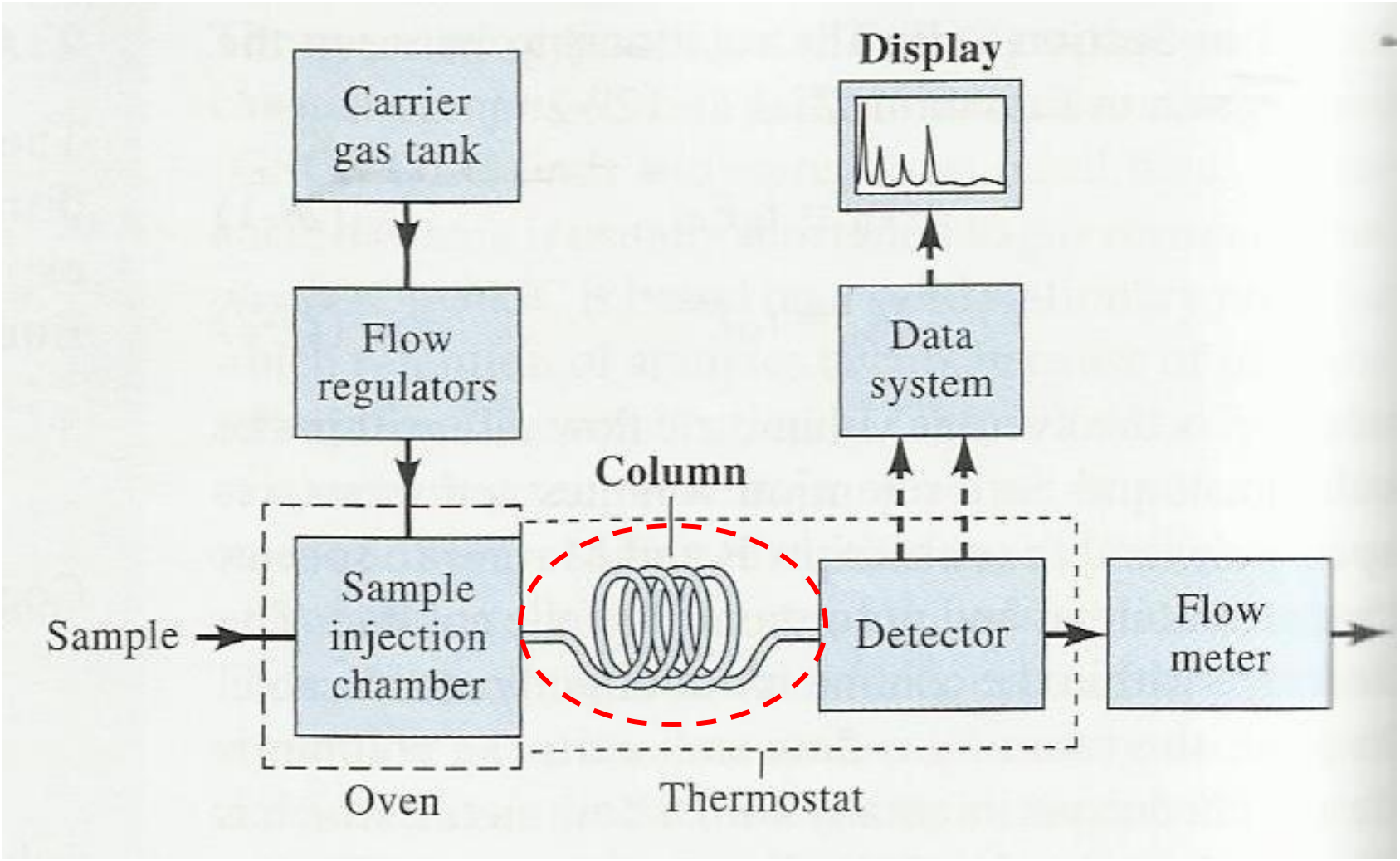
Autosampler

UNIVERSITI TEKNOLOGI PETRONAS

Injector Port

Injection

GC Columns


Carrier gas tank
Flow regulators
Sample injection chamber
Sample
Oven
Column
Thermostat
Detector
Display
Data system
Flow meter

Chemical Engineering
Inspiring Potential • Generating Futures

GC Columns

UNIVERSITI TEKNOLOGI PETRONAS

- Two types of columns used in GC are:
  i. Packed column
  ii. Capillary column (open tubular)

- Capillary columns are more commonly used today, but packed columns are still used for applications that do not require high resolution or when increased capacity is needed.

Chemical Engineering
Inspiring Potential · Generating Futures

i) Packed Column

UNIVERSITI TEKNOLOGI PETRONAS

- The column contain a fine solid support coated with a nonvalatile liquid stationary phase (partitioning chromatography); or the solid itself may be the stationary phase (adsorption chromatography).

- useful for the separation of small gaseous species such as H_2, N_2, CO_2, CO, O_2, NH_2 and CH_4 and volatile hydrocarbons.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- Small particle size of fine solid decreases the time required for solute equilibration → improve column efficiency, but higher pressure required to force mobile phase through the column.

- Packed column are usually made of stainless steel, nickel, glass and are typically 3-6 mm in diameter and 1-5 m in length.

Chemical Engineering
Inspiring Potential · Generating Futures

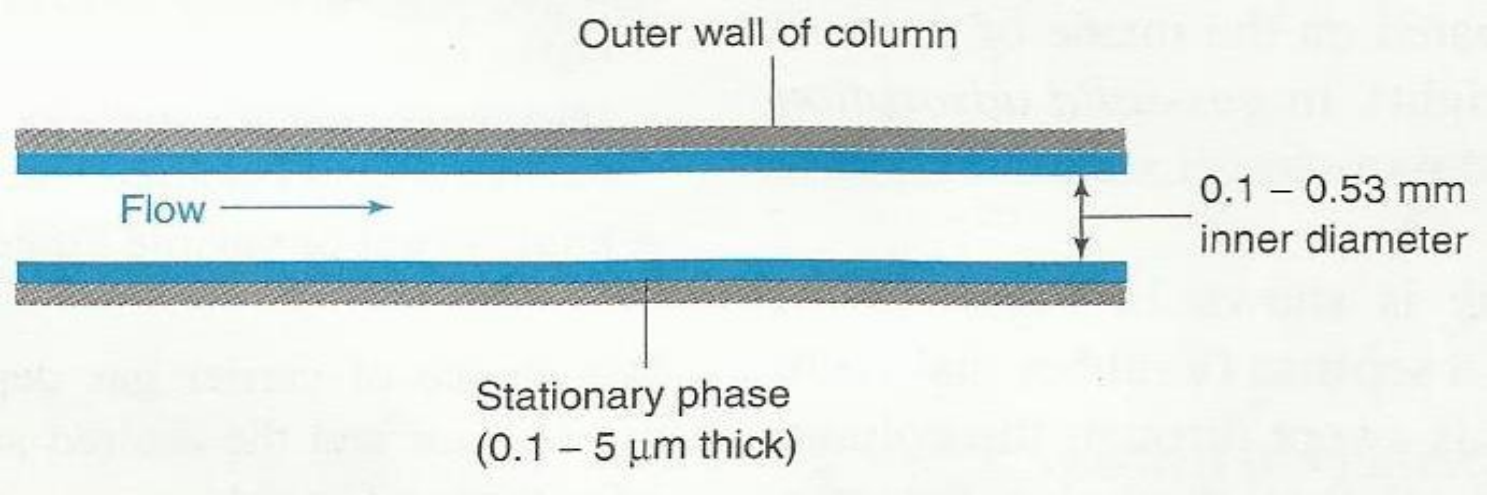
UNIVERSITI
NOLOGI
RONAS

Glass Packed GC Column

Stainless Steel GC

ii) Capillary Column (Open Tubular)

- Most widely use.
- Long, narrow open tubular columns made of fused silica (SiO_2).
- Column inner diameter = 0.10-0.53 mm and typical length = 15-100 m.



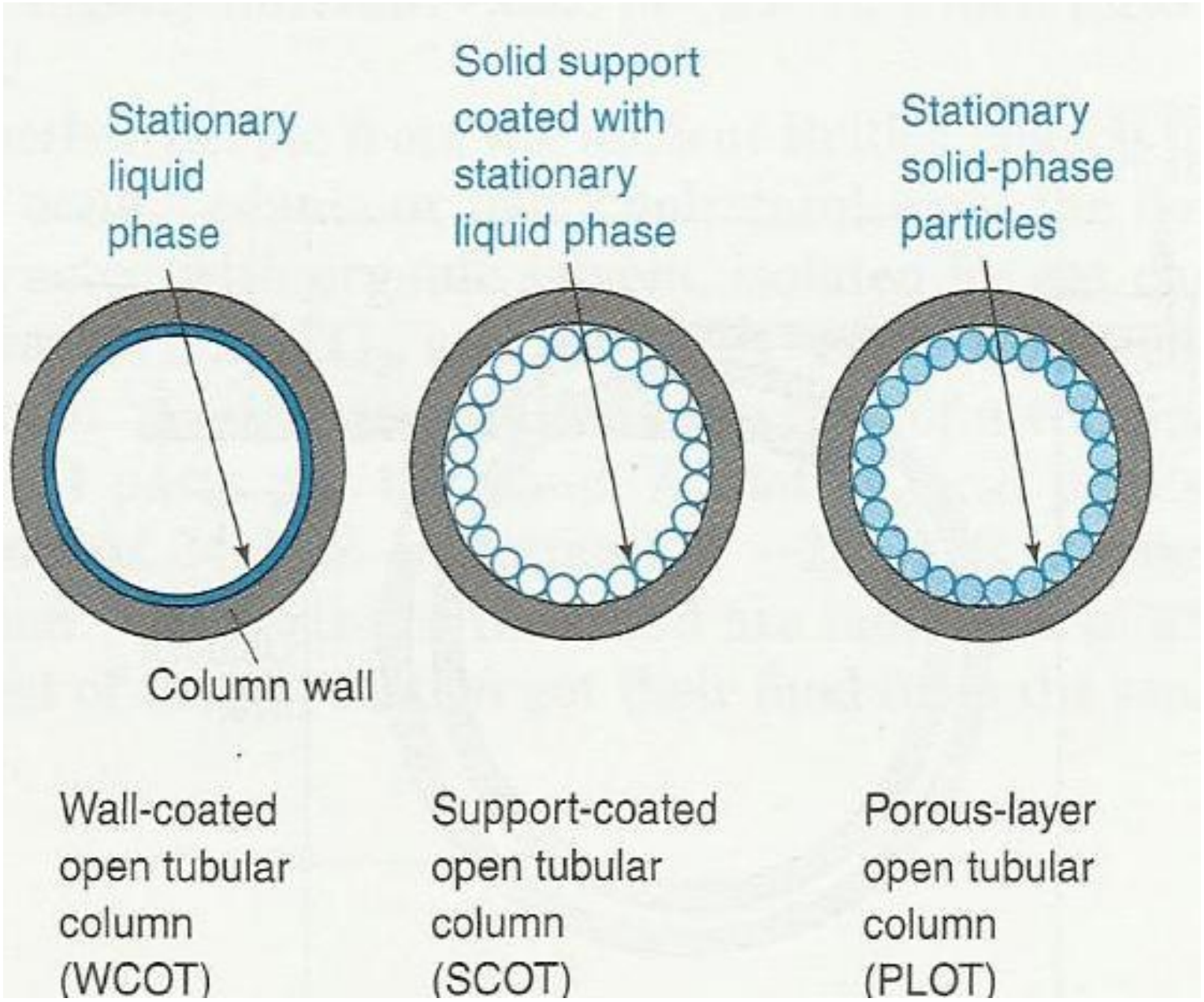
Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- Compared with packed columns, open tubular columns offer:
  i. Higher resolution
  ii. Shorter analysis time
  iii. Greater sensitivity
  iv. Lower sample capacity

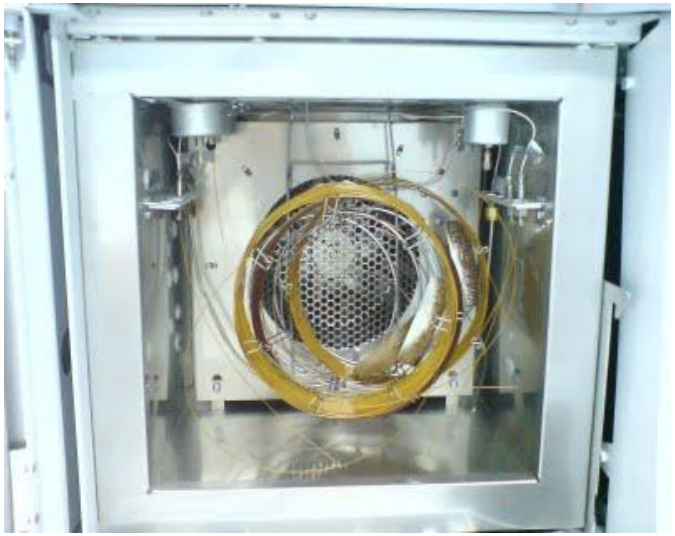
- Drawback: require higher pressure to operate.

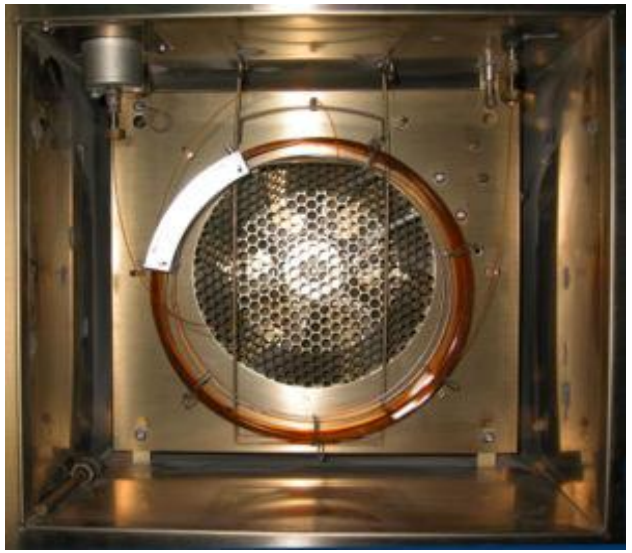
- Three types of open-tubular columns:
  i. Wall coated open tubular column (WCOT)
  ii. Support-coated open tubular column (SCOT)
  iii. Porous layer tubular column (PLOT)


Stationary liquid phase
Solid support coated with stationary liquid phase
Stationary solid-phase particles
Column wall
Wall-coated open tubular column (WCOT)
Support-coated open tubular column (SCOT)
Porous-layer open tubular column (PLOT)

Capillary Columns

Columns placed in the Oven



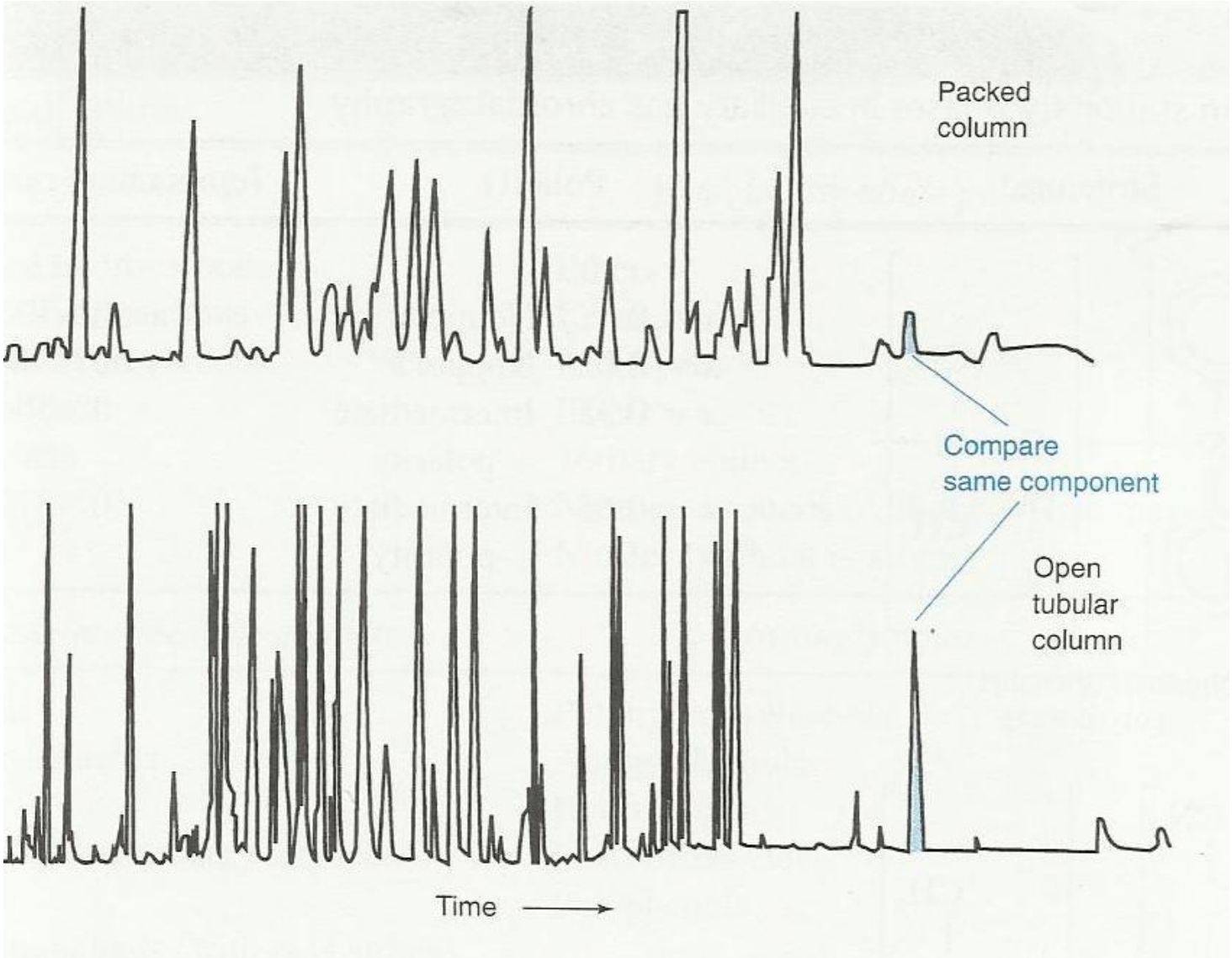


Dual-column Configuration

Single-column Configuration

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

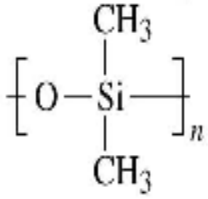
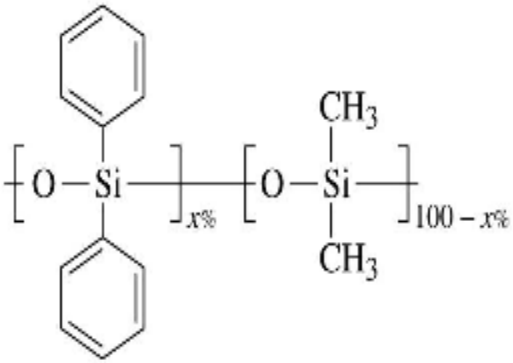
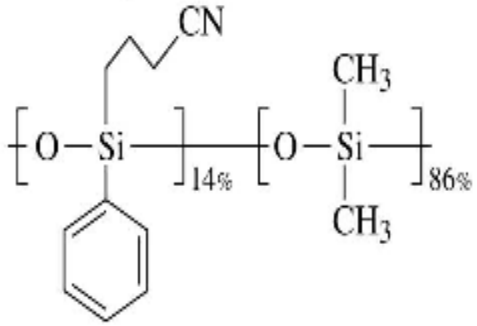


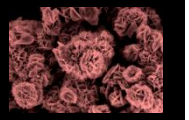
Gas Chromatographic separation of a perfume oil on a packed column and tubular column

Stationary Phases in GC columns

- The stationary phases are high molecular weight, thermally stable polymers that are liquids or gums.
- The stationary phase are selected based on their polarity on the rule "like dissolve like".
- Nonpolar columns are best for nonpolar solutes, and vice versa.
- The most common phases are polysiloxanes and polyethylene glycols (Carbowax).

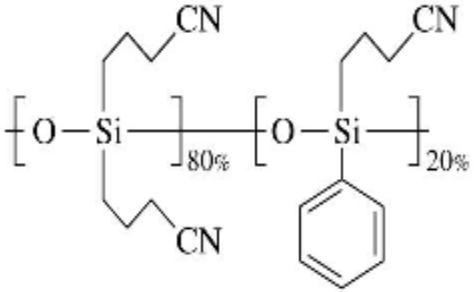
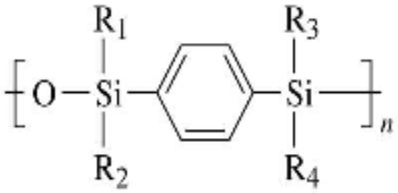
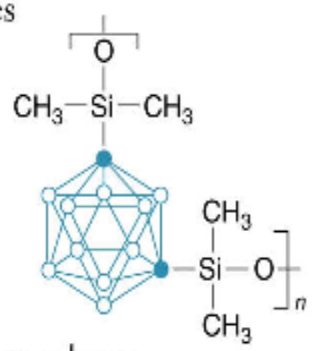
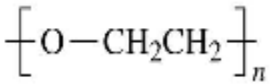
Capillary Fused Silica Stationary Phases

Phase	Polarity	Use	Max. Temp. (°C)
100% Dimethyl polysiloxane 	Nonpolar	Basic general-purpose phase for routine use. Hydrocarbons, polynuclear aromatics, PCBs.	320
Diphenyl, dimethyl polysiloxane 	5% Low 35%, 65% Intermediate 65%, 35% Intermediate	General-purpose, good high-temperature characteristics. Pesticides.	320 300 370
14% Cyanopropylphenyl–86% dimethylsiloxane 	Intermediate	Separation of organochlorine pesticides listed in EPA 608 and 8081 methods. Susceptible to damage by moisture and oxygen.	280

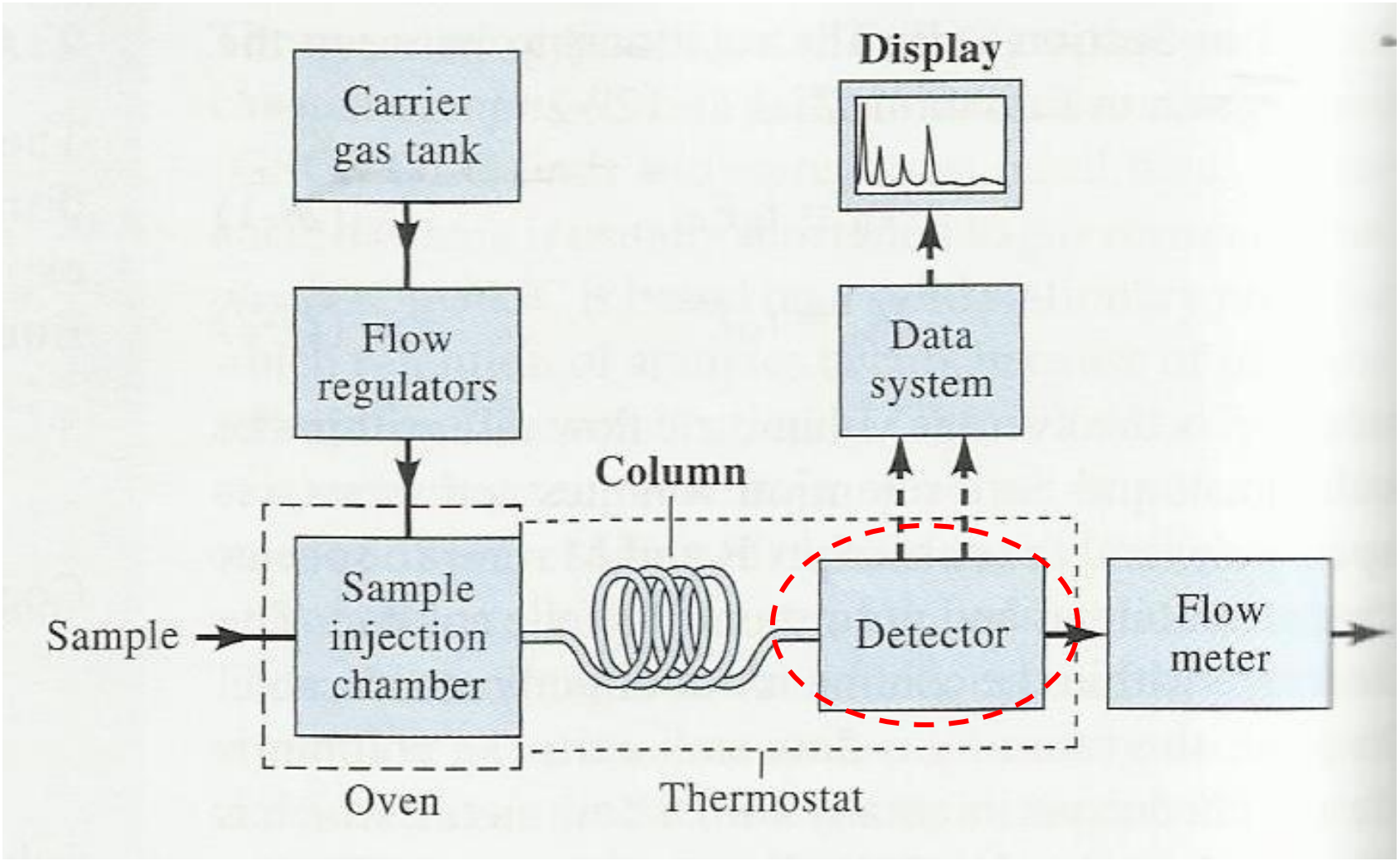




Chemical Engineering
Inspiring Potential • Generating Futures

80% Biscyanopropyl–20% cyanopropylphenyl polysiloxane 	Very polar	Free acids, polysaturated fatty acids, alcohols. Avoid polar solvents such as water and methanol.	275
Arylenes 	Vary R as above to vary polarity	High temperature, low bleed	300–350
Carboranes  open circles = boron filled circles = carbon	Vary R as above to vary polarity	High temperature, low bleed	430
Poly(ethyleneglycol) (Carbowax) 	Very polar	Alcohols, aldehydes, ketones, and separation of aromatic isomers, e.g., xylenes	250

GC Detectors



Chemical Engineering
Inspiring Potential • Generating Futures

GC Detectors

UNIVERSITI TEKNOLOGI PETRONAS

- After the components of a mixture are separated in the chromatography column, they must be detected at the outlet so that they can be identified and measured.

- A detector does not identify what is eluted form column → only tells us that something is emerging.

- Most common types of detectors:
  i. Thermal Conductivity Detector (TCD)
  ii. Flame Ionization Detector (FID)

Chemical Engineering
Inspiring Potential · Generating Futures

Thermal Conductivity Detector (TCD)

UNIVERSITI TEKNOLOGI PETRONAS

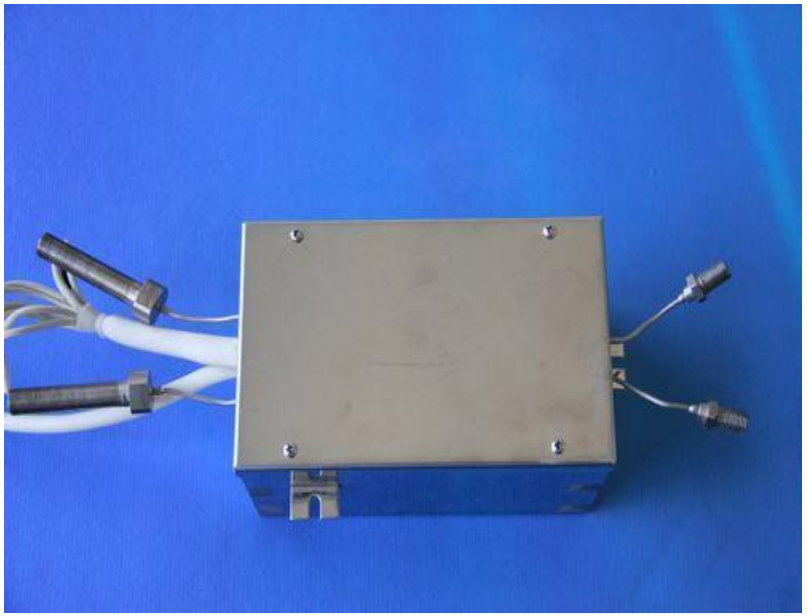
- The operating principle relies on the thermal conductivity of gas mixture as a function of their composition.
- Measures the ability of a substance to transport heat from a hot region to cold region.
- Helium → carrier gas commonly used in TCD → 2nd highest thermal conductivity of the gas stream.

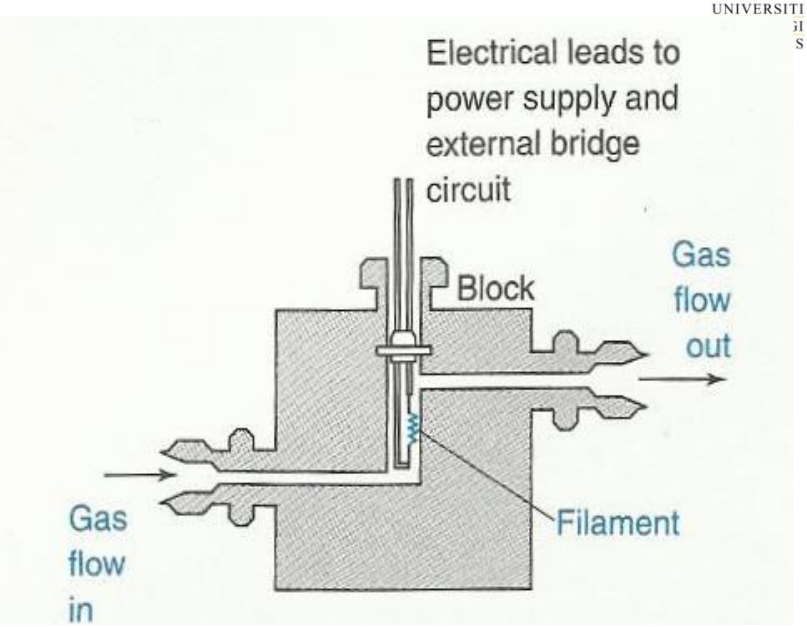
Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

Thermal Conductivity at 273 K , 1 atm

Gas	Thermal conductivity J/(K · m · s)	**Molecular Weight**
H_2	0.170	2
He	0.141	4
NH_3	0.021 5	17
N_2	0.024 3	28
C_2H_4	0.017 0	28
O_2	0.024 6	32
Ar	0.016 2	40
C_3H_8	0.015 1	44
CO_2	0.014 4	44
Cl_2	0.007 6	71





- Eluate from the column flows over a hot filament.
- The filament gets hotter → its electrical resistance increases, and the voltage across the filament changes.
- The detector measures the change in voltage.

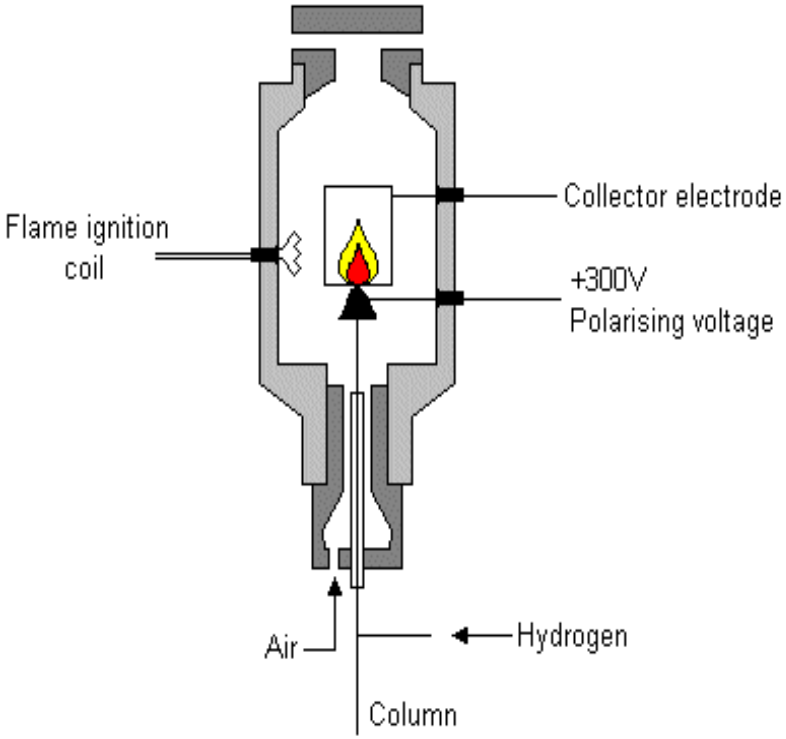
Chemical Engineering
Inspiring Potential • Generating Futures

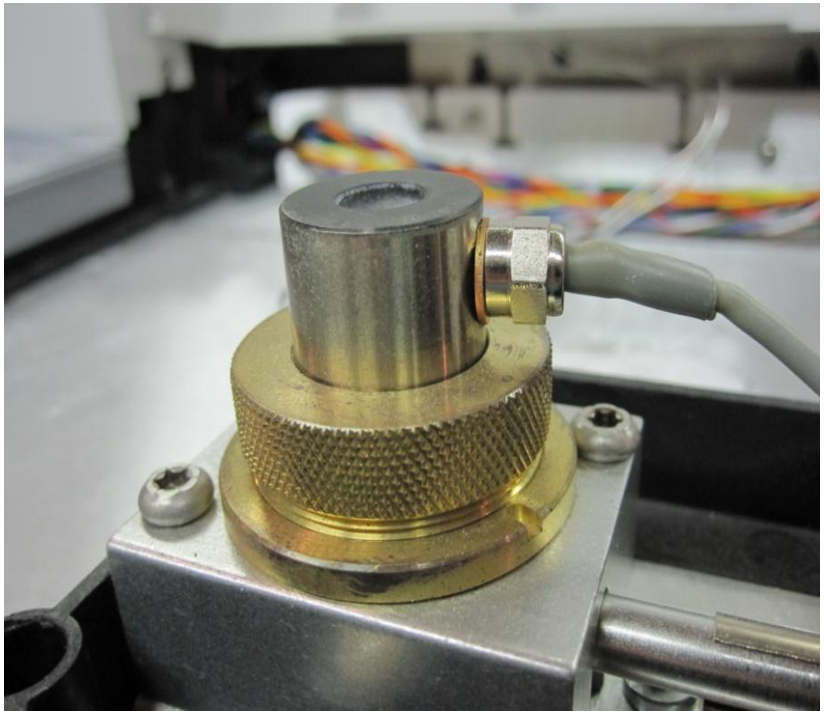
Flame Ionization Detector (FID)

UNIVERSITI TEKNOLOGI PETRONAS

- Relies on the creation of ion/charged particles produced from the sample/compound when they are burnt by temperature in a flame.
- Eluate is burned in a mixture of H_2 and air.
- Carbon atoms produce CH radicals, which are thought to produce CHO^+ ions in the flame.
- Cations produced in the flame carry electric current from the anode flame tip to the cathode collector → detector signal.

FID Detector





Chemical Engineering
Inspiring Potential·Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- In the absence of organic solutes, the current is almost 0.
- The detection limit is 100 times smaller than that of the TCD.
- FID responds to most hydrocarbons, which constitute the vast majority of GC analytes.
- Insensitive to nonhydrocarbon such as H_2, He, N_2, O_2, CO, CO_2, H_2O, NH_3, NO, H_2S and SiF_4.

Chemical Engineering
Inspiring Potential · Generating Futures

Other Detectors

UNIVERSITI TEKNOLOGI PETRONAS

- Nitrogen-Phosphorus Detector (NPD)
- Flame Photometric Detector (FPD)
- Photoionization Detector (PD)
- Sulfur Chemiluminescence Detector (SCD)
- Nitrogen Chemiluminescence Detector (NCD)
- Electron Capture Detector (ECD)

Comparison of Gas-Chromatographic Detectors

Detector	Application	Sensitivity Range	Linearity	Remarks
Thermal conductivity	General, responds to all substances	Fair, 5–100 ng, 10 ppm–100%	Good, except thermistors at higher temperatures	Sensitive to temperature and flow changes; concentration sensitive
Flame ionization	All organic substances; some oxygenated products respond poorly. Good for hydrocarbons	Very good, 10–100 pg, 10 ppb–99%	Excellent, up to 10^6	Requires very stable gas flow; response for water is 10^4–10^6 times weaker than for hydrocarbons; mass-sensitive
Flame photometric	Sulfur compounds (393 nm), phosphorus compounds (526 nm)	Very good, 10 pg S, 1 pg P	Excellent	
Flame thermionic	All nitrogen- and phosphorus-containing substances	Excellent, 0.1–10 pg, 100 ppt–0.1%	Excellent	Needs recoating of sodium salts on screen; mass sensitive
Electron capture	All substances that have affinity to capture electrons; no resonse for aliphatic and naphthenic hydrocarbons	Excellent for halogen-containing substancs, 0.05–1 pg, 50 ppt–1 ppm	Poor	Very sensitive to impurities and temperature changes; quantitative analysis complicated; concentration sensitive

Chemical Engineering
Inspiring Potential • Generating Futures

Characteristics of the Ideal Detector

UNIVERSITI TEKNOLOGI PETRONAS

- Adequate sensitivity.
- Good stability and reproducibility.
- A linear response to solutes that extends over several order of magnitude.
- A temperature range from room temperature to at least 400 ºC.
- A short response time and independent flow rate.
- High reliability and ease of use.
- Non destructive.

Chemical Engineering
Inspiring Potential • Generating Futures

Quantitative Analyses based on GC Chromatogram

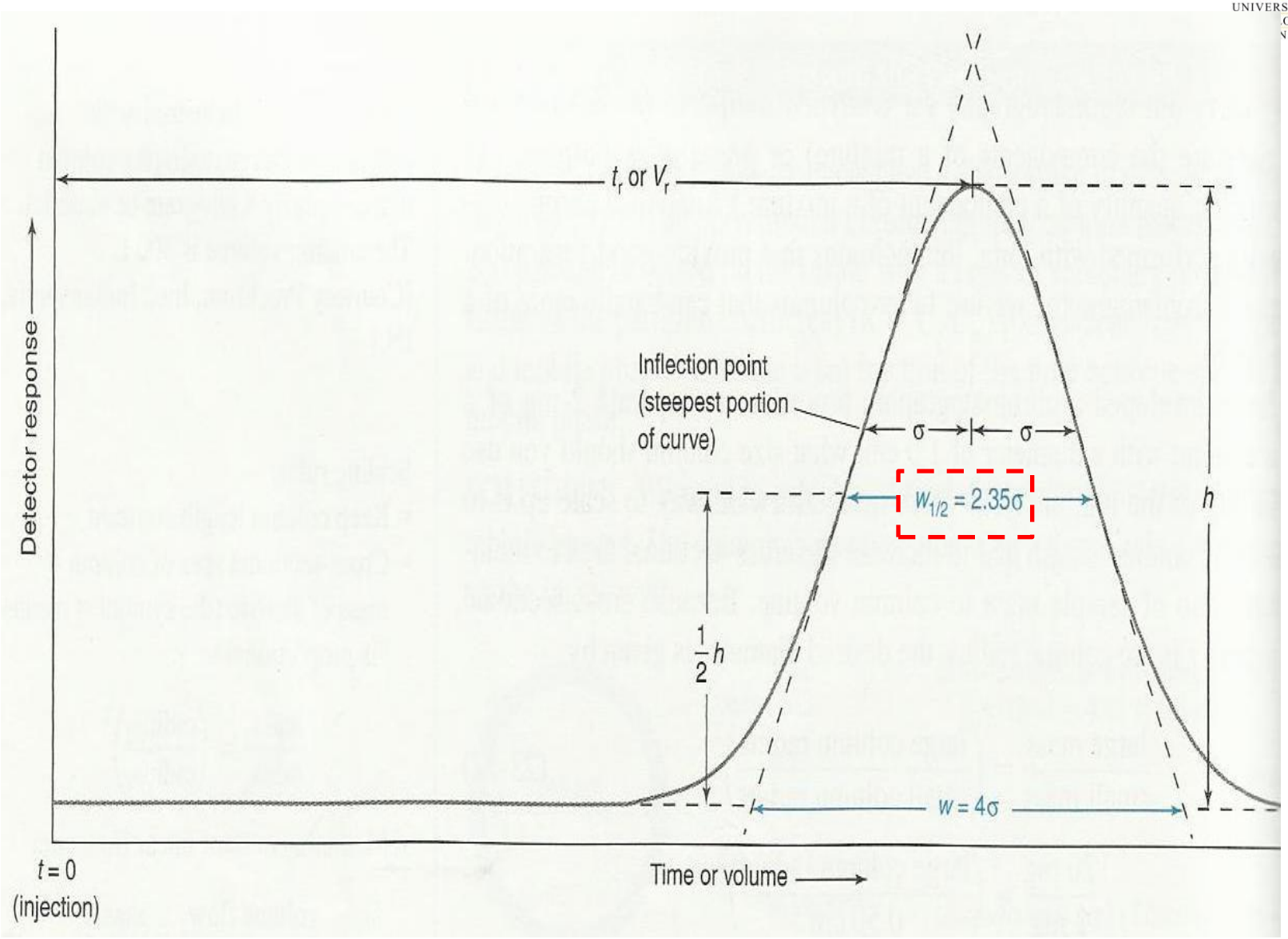
UNIVERSITI TEKNOLOGI PETRONAS

1) Analyses based on Peak Areas (or Peak Height)

- The area of a peak is proportional to the concentration of that component.
- In most of the computer-controlled system, the peak area is measured automatically by the computer.
- If the peak area must be measured by hand, and if the peak has a Gaussian shape, then the area is:

Area of Gaussian peak = 1.064 x peak height x $w_{1/2}$

Recall:


t_r or V_r
Detector response
Inflection point
(steepest portion
of curve)
σ
σ
$w_{1/2} = 2.35\sigma$
h
$\frac{1}{2}h$
$w = 4\sigma$
$t = 0$
(injection)
Time or volume

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

2a) Analyses based on Internal Standard Method (single point)

- After measuring the response factor with standard mixture, the quantity of unknown is:

$$\frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right)$$

A_x = area of analyte signal

A_s = area of internal standard

[X] = concentration of analyte

[S] = concentration of standard

F = response factor

Example

When 1.06 mM of pentanol and 1.53 mM of hexanol were separated by gas chromatography, they gave relative peak areas of 922 and 1570 units, respectively.

When 0.570 mM of pentanol was added to an unknown containing hexanol, the relative chromatographic peak areas were 843:816 (pentanol:hexanol).

How much hexanol did the unknown contain?

Chemical Engineering
Inspiring Potential • Generating Futures

Solution

UNIVERSITI TEKNOLOGI PETRONAS

Equation: $\frac{A_X}{[X]}=F\left(\frac{A_S}{[S]}\right)$

S = [pentanol]

X = [hexanol]

For the standard mixture,

$$\frac{A_X}{[X]}=F\left(\frac{A_S}{[S]}\right)$$

$$\frac{1570}{1.53}=F\left(\frac{922}{1.06}\right)$$

F = 1.18

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

For an unknown mixture,

$$\frac{A_x}{[X]} = F\left(\frac{A_s}{[S]}\right)$$

$$\frac{816}{[X]} = 1.18\left(\frac{843}{0.571}\right)$$

[x] = 0.468 mM

Chemical Engineering
Inspiring Potential • Generating Futures

Exercise

UNIVERSITI TEKNOLOGI PETRONAS

- A standard solution containing 6.30×10^{-8} M iodoacetone and 2.00×10^{-7} M p-dichlorobenzene (an internal standard) gave peak areas of 395 and 787, respectively, in a gas chromatogram. A 3.00-mL unknown solution of iodoacetone was treated with 0.100 mL of 1.60×10^{-5} M p-dichlorobenzene and the mixture was diluted to 10.00 mL. Gas chromatography gave peaks areas of 633 and 522 for iodoacetone and p-dichlorobenzene, respectively. Find the concentration of iodoacetone in the 3.00 mL of original solution.

Chemical Engineering
Inspiring Potential · Generating Futures

2b) Analyses based on Internal Standard Method (calibration curve)

UNIVERSITI TEKNOLOGI PETRONAS

A 5.00 mL blood sample from a suspect is spiked with 0.500 mL of aqueous 1% propanol internal standard. A 10.0-microliter portion of the mixture is injected into the GC, and the peak areas are recorded. Standards are treated in the same way. The following results were obtained:

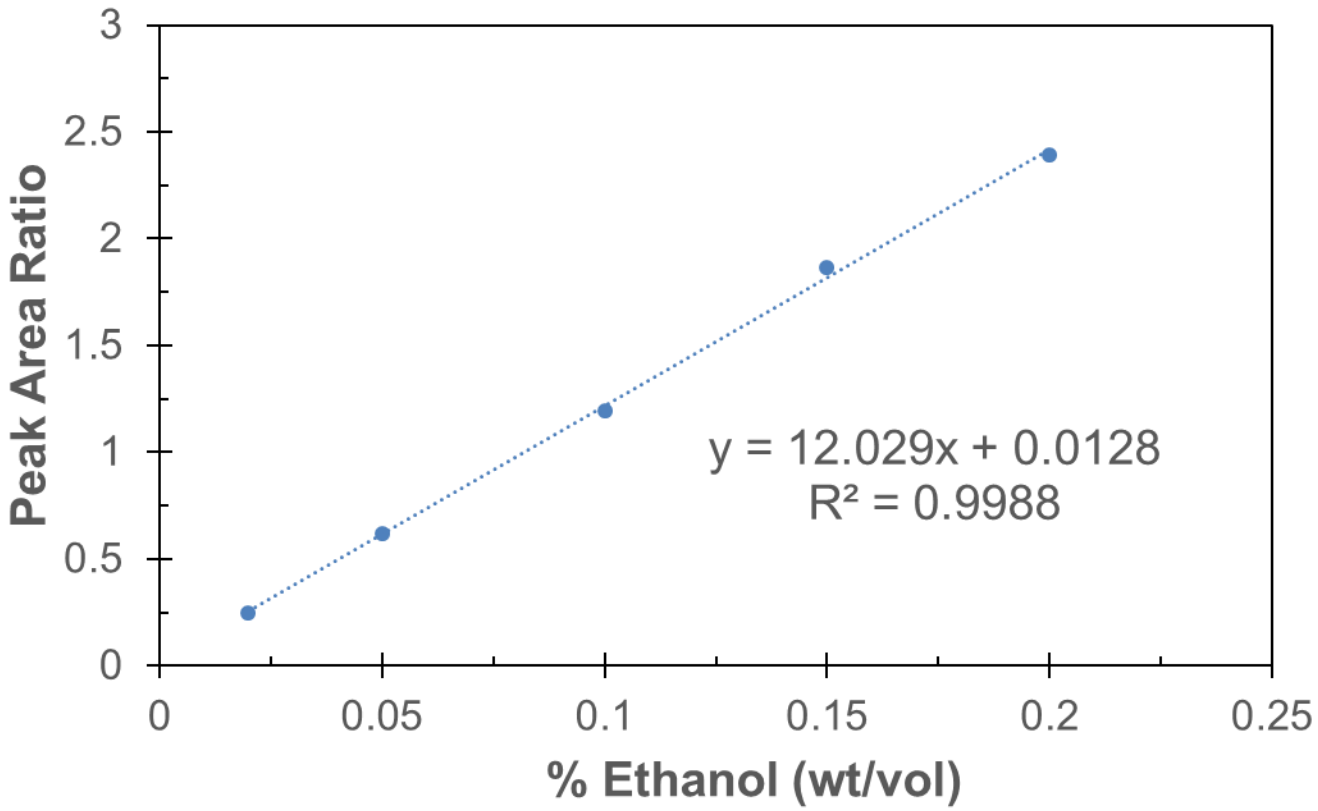
% Ethanol (wt/vol)	Peak Area Ethanol	Peak Area Propanol
0.0200	114	457
0.0500	278	449
0.100	561	471
0.150	845	453
0.200	1070	447
Unknown	782	455

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

Construct a calibration curve of the ratio of the Ethanol/Propanol area vs ethanol concentration and calculate the unknown concentration.

% Ethanol (wt/vol)	Peak Area Ethanol	Peak Area Propanol	Peak Ratio
0.0200	114	457	0.249
0.0500	278	449	0.620
0.100	561	471	1.19
0.150	845	453	1.87
0.200	1070	447	2.39
Unknown	782	455	1.72



Correlation, y = 12.029 x + 0.0128, by substitution of y = 1.72 into the equation, concentration of unknown, x = 0.142 % wt/vol

Chemical Engineering
Inspiring Potential • Generating Futures

3) Area Normalization method

UNIVERSITI TEKNOLOGI PETRONAS

- Complete elution of all the sample constituents is necessary.

- The area of each peak is then measured and corrected for differences in detector response to the different eluates.

- The correction involves dividing the area by the response factor.

- The concentration of the analyze is found from the ratio of its corrected area to the total corrected area of all peaks.

Chemical Engineering
Inspiring Potential • Generating Futures

Example

UNIVERSITI TEKNOLOGI PETRONAS

For a chromatogram containing three peaks, the relative areas were found to be 16.4, 45.2 and 30.2 in order of increasing retention time. Calculate the percentage of each compound if the relative detector responses were 0.600, 0.780 and 0.880, respectively.

Chemical Engineering
Inspiring Potential · Generating Futures

Solution

UNIVERSITI TEKNOLOGI PETRONAS

Compound	Relative Peak Area	Relative detector Response	Corrected Area(peak area/detector response)	% Compound
1	16.4	0.600	27.33	22.9
2	45.2	0.780	57.95	48.4
3	30.2	0.880	34.32	28.7
Corrected area summation			119.6	

Chemical Engineering
Inspiring Potential · Generating Futures

Temperature Selection

UNIVERSITI TEKNOLOGI PETRONAS

- The proper temperature selection in gas chromatography→ depends on several factors.

- The injection temperature should be
  1. relatively high
  2. consistent with thermal stability of the sample
  3. give faster rate of vaporization to get the sample into the column in small volume.
  4. decrease spreading and increase resolution results.

- Too high an injection temperature → tend to degrade the rubber septum and cause dirtying of the injection port.

Chemical Engineering
Inspiring Potential • Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

- The column temperature is compromise between
  1. speed
  2. sensitivity
  3. resolution

- At high column temperature → sample components spend most of their time in the gas phase →eluted quickly →poor resolution.

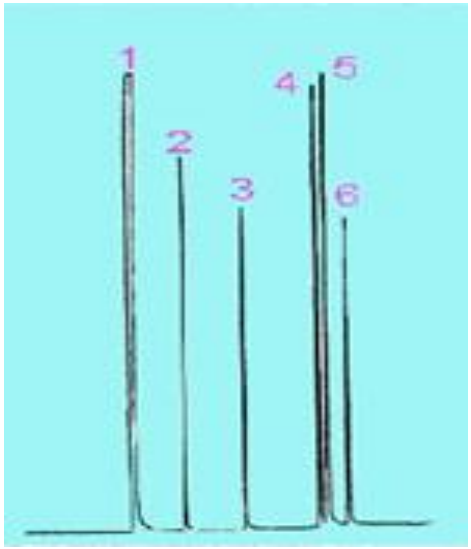
- At low temperature → sample spend more time in the stationary phase and elute slowly → resolution increased but sensitivity is decreased due to increased spreading of the peaks.

- The detector temperature must be high enough → prevent condensation of the sample components.

- Separations can be facilitated by temperature programming → the compounds eluted with more difficulty can be eluted in a reasonable time without forcing the others from the column too quickly.

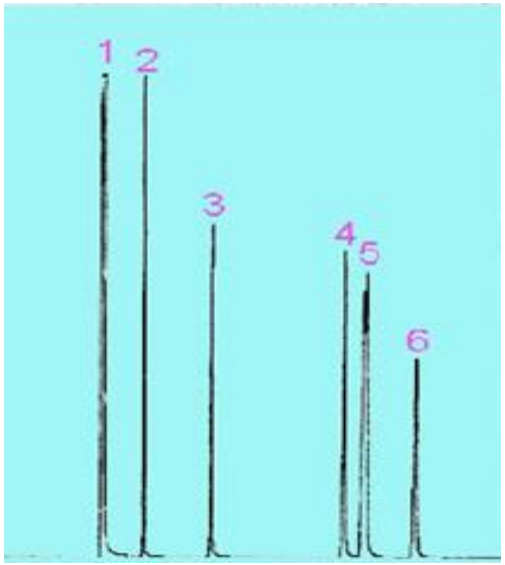
Example: GC analysis results for the same mixture using different temperature-programmed

Temperature Program:
50 °C -100 °C,
10 ° C/min

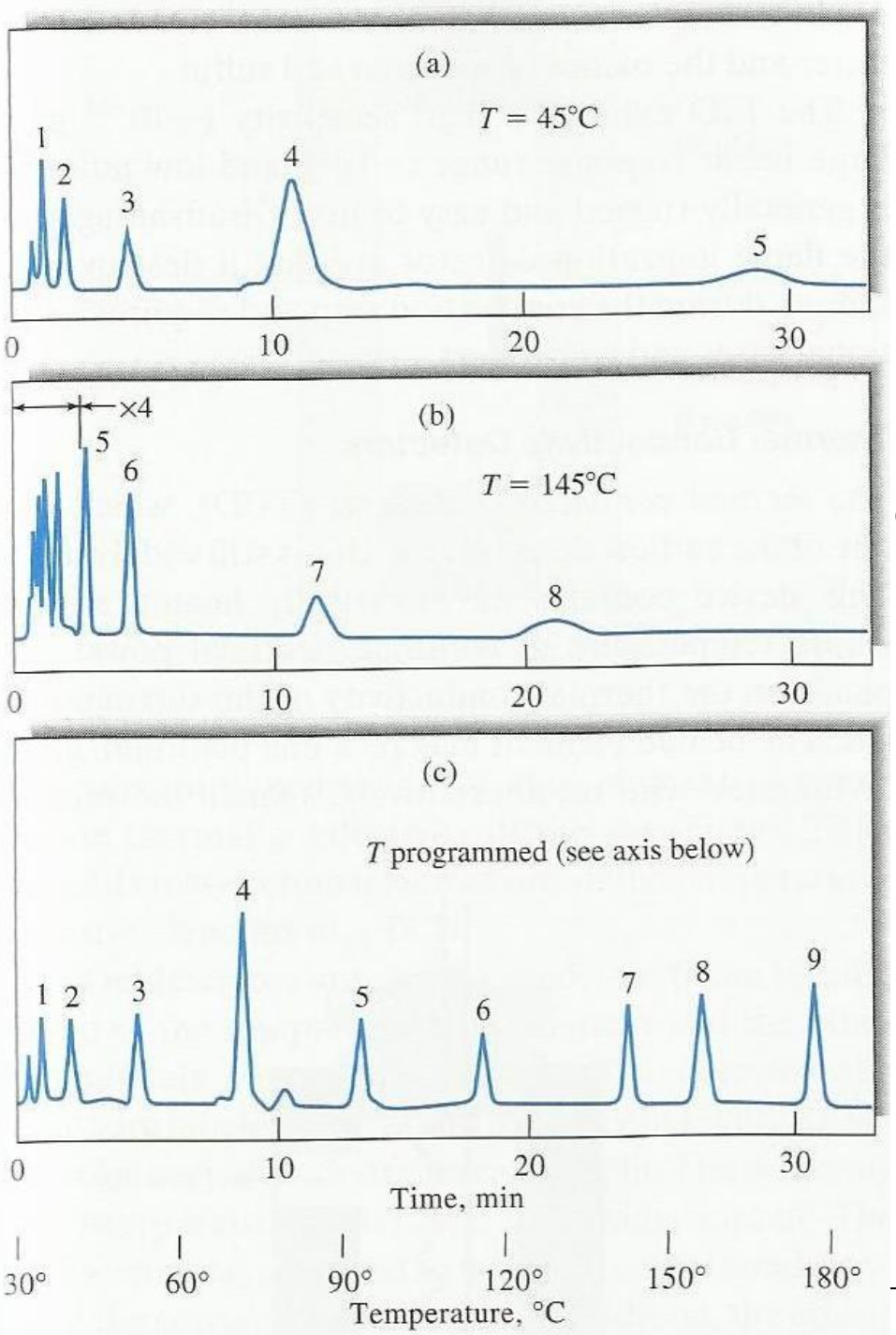


Peak#	Compound	Retention Time
1	Methanol	2.244 min
2	Benzene	3.260 min
3	Toluene	4.455 min
4	Ethyl Benzene	5.941 min
5	Para-xylene Meta-xylene	6.115 min
6	Ortho-xylene	6.524 min

Temperature Program:
60°C - isothermal



Peak#	Compound	Retention Time
1	Methanol	2.245 min
2	Benzene	3.176 min
3	Toluene	4.616 min
4	Ethyl Benzene	7.486 min
5	Para-xylene Meta-xylene	7.895 min 7.957 min
6	Ortho-xylene	9.050 min



Effect of temperature on gas chromatography:

(a)Isothermal at 45 °C
(b)Isothermal at 145 °C
(c)Programmed at
30 °C to 180 °C

Chemical Engineering
Inspiring Potential • Generating Futures

Method Development in Gas Chromatography

UNIVERSITI TEKNOLOGI PETRONAS

- Order of decisions:
  1. Goal of analysis
     - what is require?
     - qualitative or quantitative?
     - need high resolution?
  2. Sample preparation
  3. Choosing the detector
  4. Choosing the column
  5. Choosing the injection method
     - split/splitless/on-column injection

Chemical Engineering
Inspiring Potential · Generating Futures

UNIVERSITI TEKNOLOGI PETRONAS

End of GC topic