Gas Chomatography

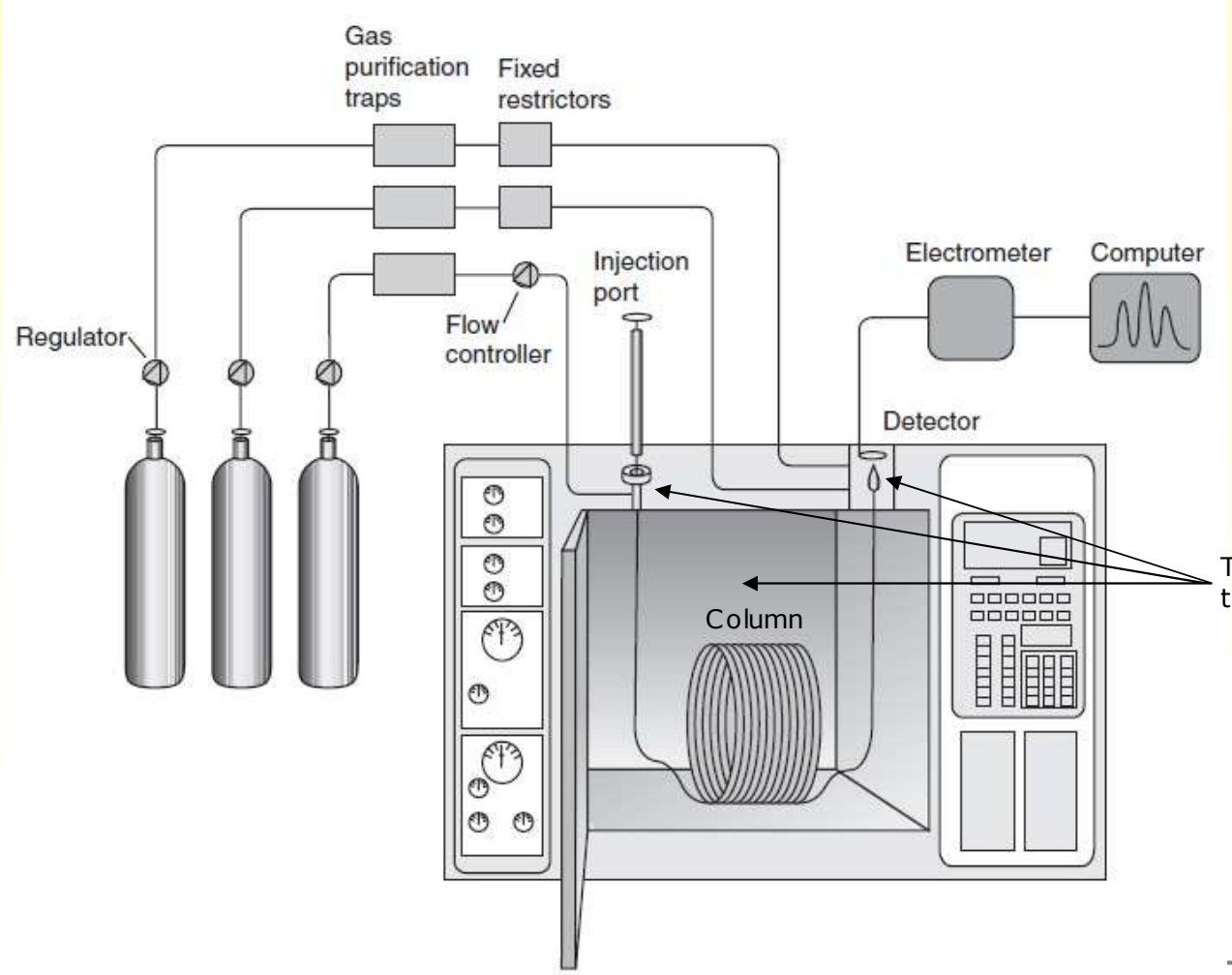
Introduction

The method of gas chromatography (GC) was developed in 1947 and found a very broad application in chemical analysis due to its high separation power.

The area of compounds capable of analyzing by GC is limited to volatile compounds vapor pressure of which is at least 60 torr at achievable temperature usually 350-400 C

The range of compounds can be broadened by the use of preliminary derivatization that can increase volatility and thermal stability of analytes

Gaschromatograph



Carrier gas in GC

The purpose – to move analyte molecules through the column

Must be inert and pure to avoid any interactions in the column

The most common mobile phases in GC are He, N_2 and H_2

Carrier rate depends on the column and is usually 1-25 mL/min for capillary and 25-150 mL/min for packed columns.

Sample introduction in GC

Cool on-column – for thermally labile compounds

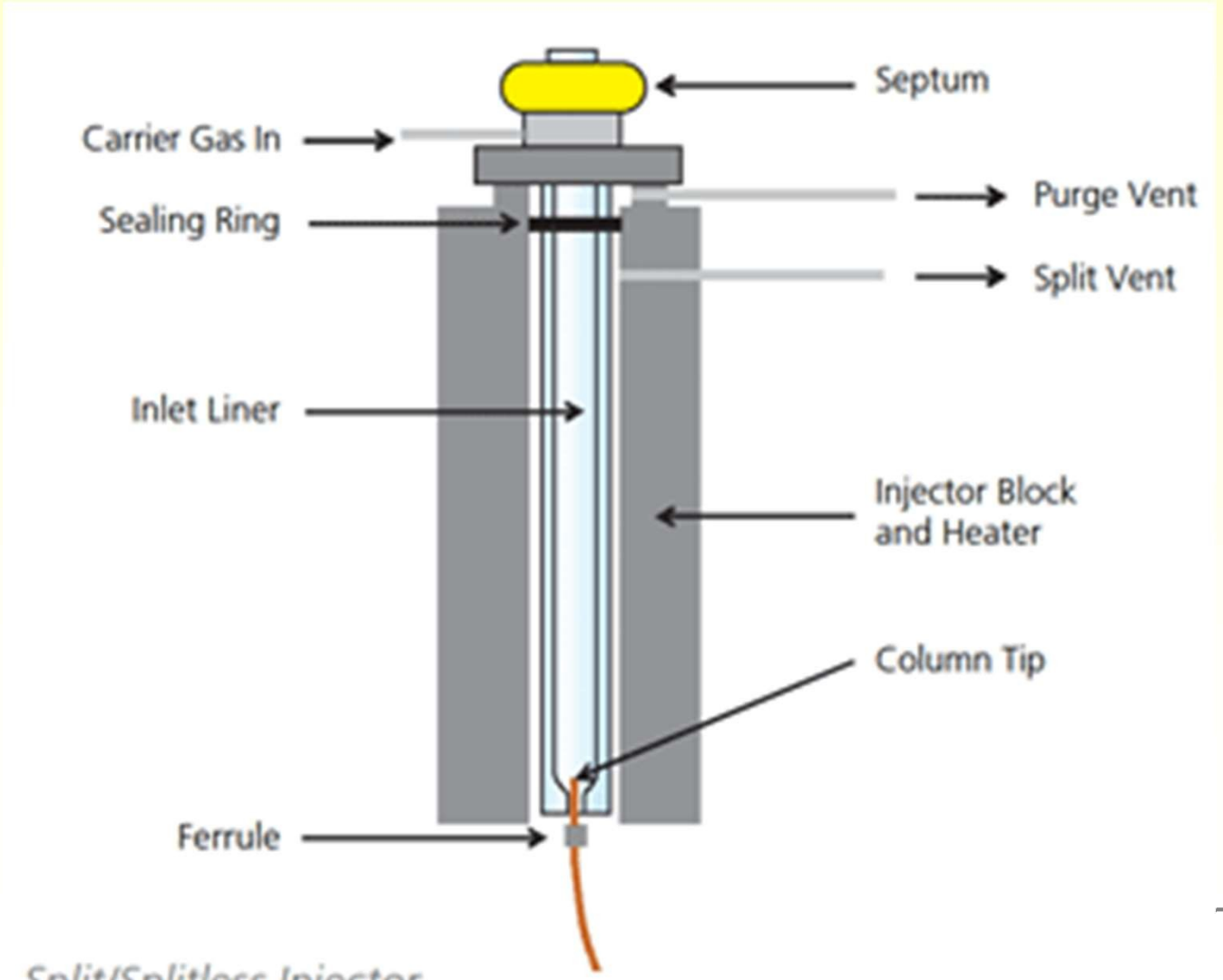
Split/splitless – classic for capillary columns

Programmable temperature vaporization – provides maximum flexibility

Only gaseous and liquid samples can be directly injected into GC

All solid and dirty liquid samples require sample preparation

Split/splitless GC inlet



Split/Splitless Injector

Split injection

Only small part of injected sample (1:1000-1:10) reaches the column

Other part of sample is sent to split vent

Very fast injection > narrow peaks

Required for analysis of high concentrations (to avoid detector overload)

Split injection animation

Open "Split Injection" video

https://www.restek.com/Injector-Animations

Task 1

One microliter of vodka sample having concentration of methanol 125 mg/L was injected to gas chromatograph in 1:50 split mode. How many nanograms of methanol reached the column?

$$m = \frac{V \times C}{S}$$

Where:

m – mass of analyte reached the column, ng

V – sample volume injected, µL;

C - analyte concentration, ng/µL;

S – split factor (50 in our case)

Task 2

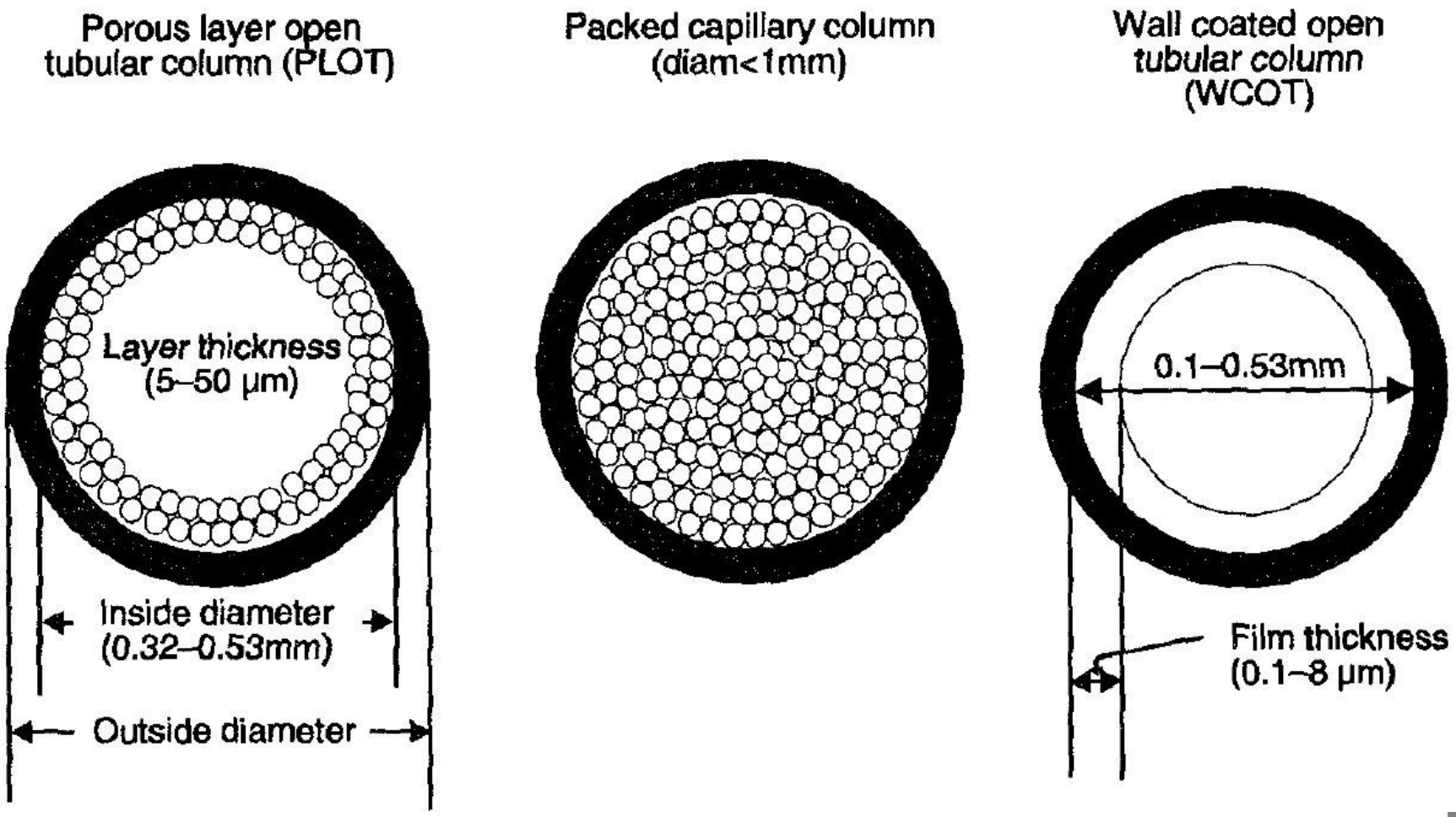
One microliter of naphthalene solution (10 mg/L) in methanol was injected into inlet of gas chromatograph. What volume of gas will be formed in the inlet at temperature 240 °C and pressure 0.49 bar (relative to ambient). Can this sample be injected into a liner having length 68.5 mm and internal diameter 4 mm (vapor volume must be lower than liner volume)?

Absolute Pressure = Ambient Pressure (bar) + 0.49 bar

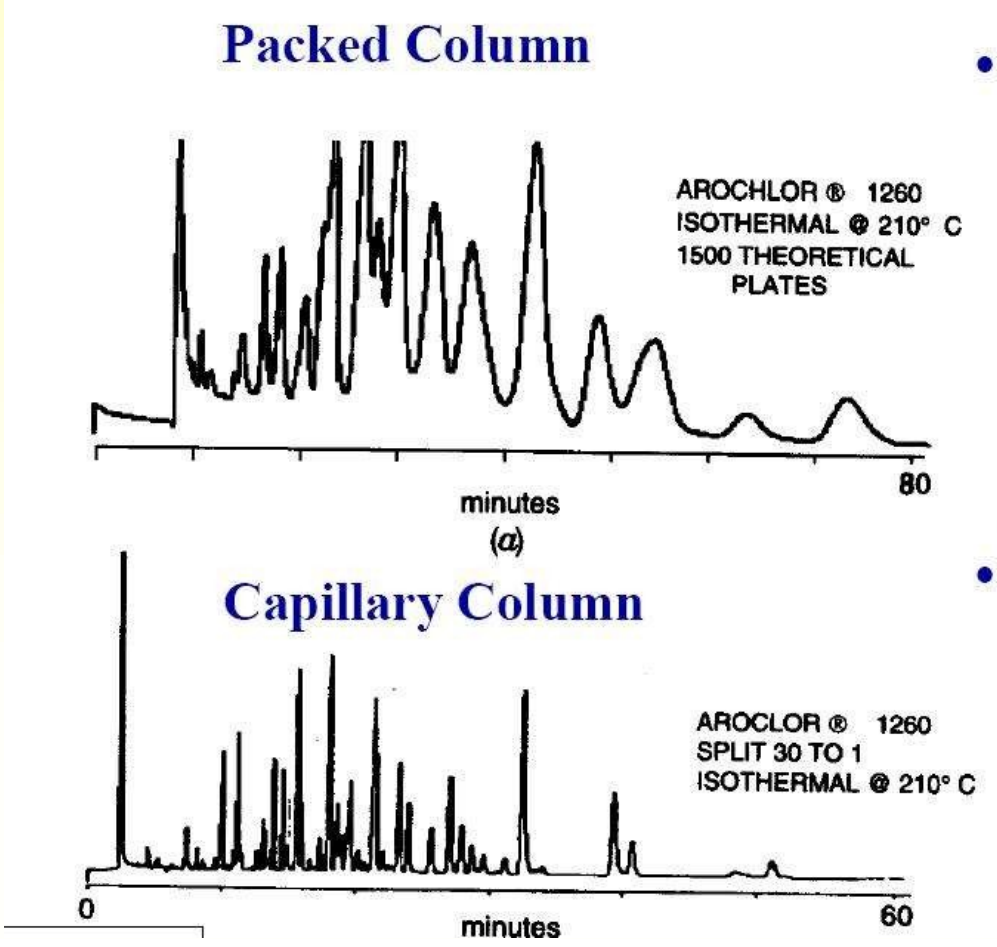
Main formula:

$$p\,V = \frac{m}{M}\,R\,T$$

Columns in GC

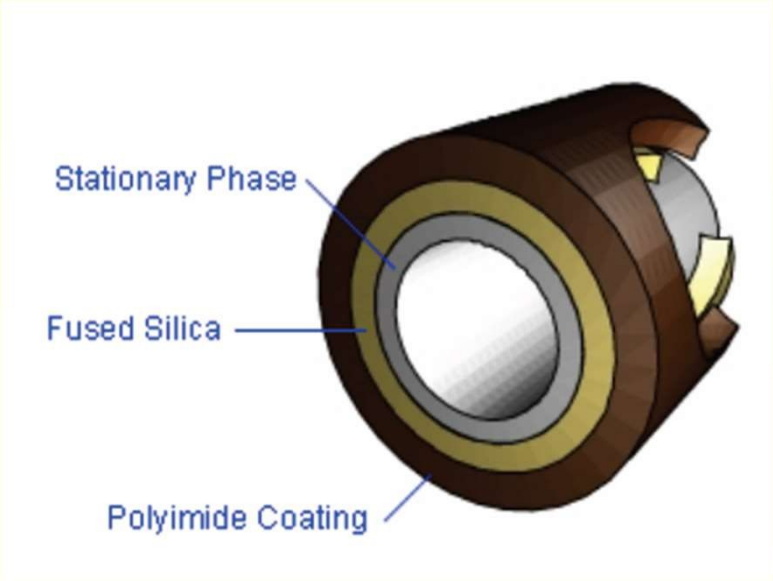


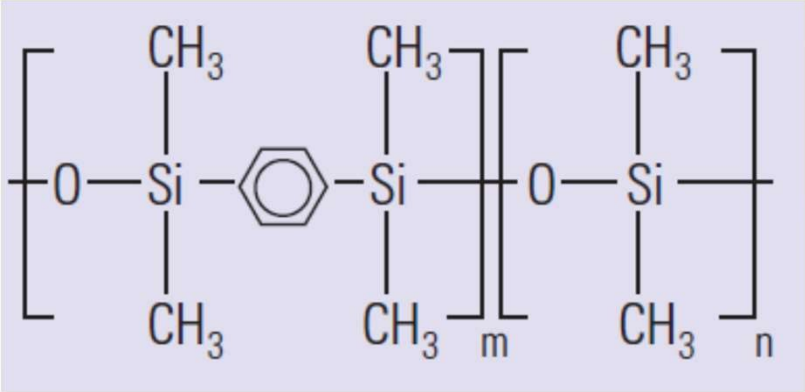
Packed vs capillary columns



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

Capillary columns in GC





Stationary phases:

Non-polar to polar polymers

Polydimethylsiloxane and polyethyleneglycol are mostly used non-polar and polar stationary phases, respectively

Aromatic and other functional groups are implemented into polymeric composition to change polarity of the phase

GC columns

Internal Diameter (mm)	Efficiency: Plates/Meter (N/m)	Efficiency: Total Plates (N)	Capacity Each Analyte (ng)
0.53	1,300	39,000	1000-2000
0.32	2,300	69,000	400-500
0.25	2,925	87,750	50-100
0.20	3,650	109,500	<50
0.18	4,050	121,500	<50
0.10	7,300	219,000	<10
Note: Theoretical values for 30 meter columns, calculated @ a k = 6.00 and 85% coating efficiency			

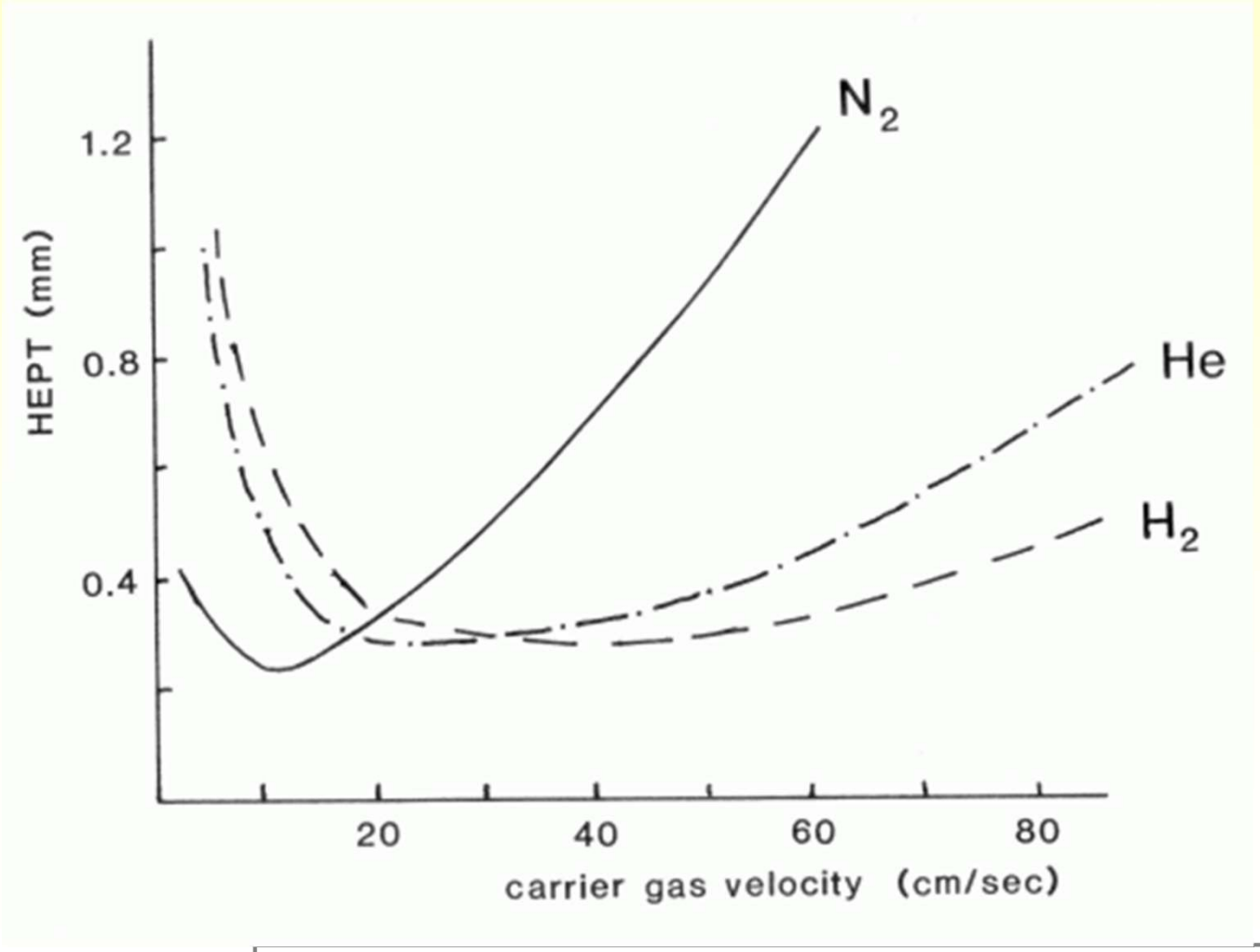
Fast gas chromatography

Effect of the column length

Column Length (m)	Inlet Pressure (psi)	Peak 1 Retention (min)	Peak 1/2 Resolution (R)	Efficiency: Total Plates (N)
15	5.9	8.33	0.8	43,875
30	12.0	16.68	1.2	87,750
60	24.9	33.37	1.7	175,500

Note: Theoretical values for 0.25 mm I.D. columns with 85% coating efficiency, 145 Â°C isothermal analyses, helium at 21 cm/sec, k (peak 1) = 6.00

Effect of carrier gas velocity (van Deemter plots)



Main GC parameters

Injection

Mode (split or splitless)

Split ratio (for split mode)

Temperature

Column

Mode (constant flow or constant pressure)

Flow or pressure

Compound retention in GC

Physical properties of analyte (boiling point, molecular weight, diffusion coefficient, polarity)

Column temperature (higher temperature =lower retention)

Carrier flow rate (higher flow rate = lower retention)

Polarity of stationary phase (polar stationary phase stronger retains polar compounds)

If peaks are not separated

Lower temperature

Decrease flow rate

Change stationary phase

Increase column length

If compounds are not retained

Use thicker stationary phase

Use PLOT or packed column

Separate at cryogenic temperatures (use liquid N_2 or CO_2)

Main detectors in GC

Thermal conductivity (TCD)

Flame ionization (FID)

Nitrogen phosphorus (NPD)

Electron capture (ECD)

Photo ionization (PID)

Infrared (IR)

Mass spectrometric (MSD)

Flame ionization detector

The Flame Ionization Detector

Electron capture detector

GC detector comparison

Name	Type	Selectivity	Sensitivity	Linear range
FID	Universal	-	10 pg C	10^7
ECD	Selective	Halogen containing compounds	0,2 pg Cl	10^4
NPD	Selective	Compounds of nitrogen and phosphorus	1 pg N, 5 pg P	10^4
PID	Selective	Aromatic hydrocarbons		10^7
IR	Universal	Any IR absorbing compounds	1 ng	10^3
MSD	Universal	Characteristic ions	1 pg	10^5

GC detectors

Universal:

quantification by normalization

analysis of unknown samples

lower sensitivity;

longer and worse separation

VS

Selective:

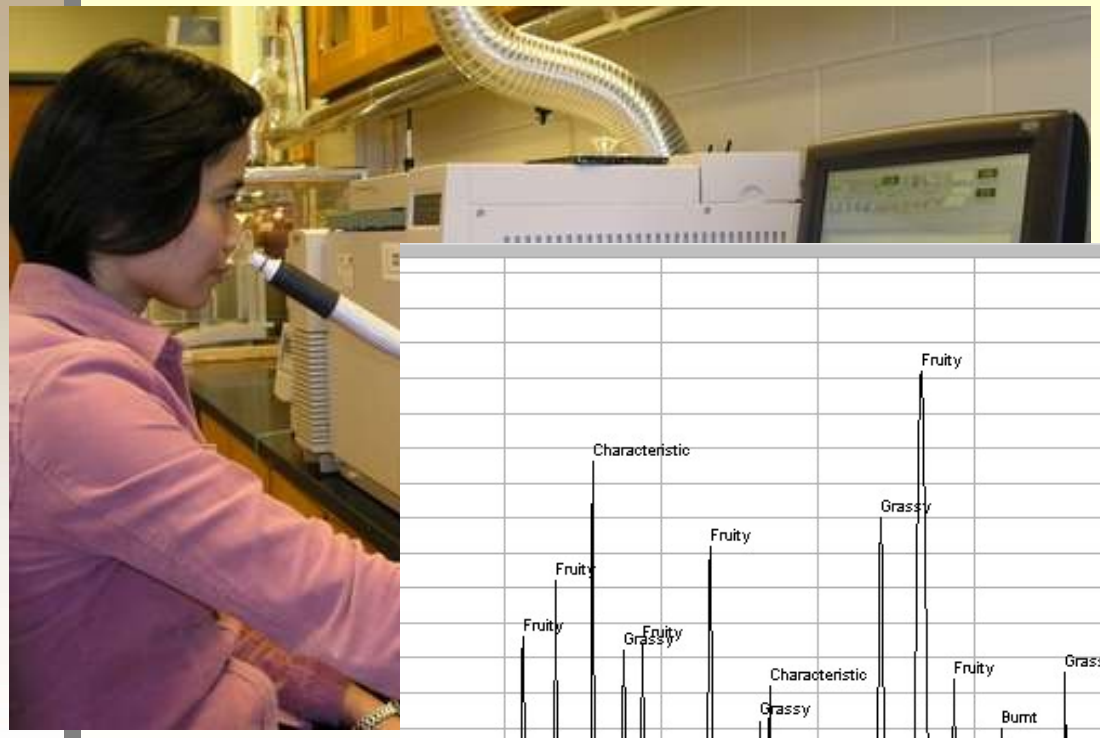
better and faster selectivity

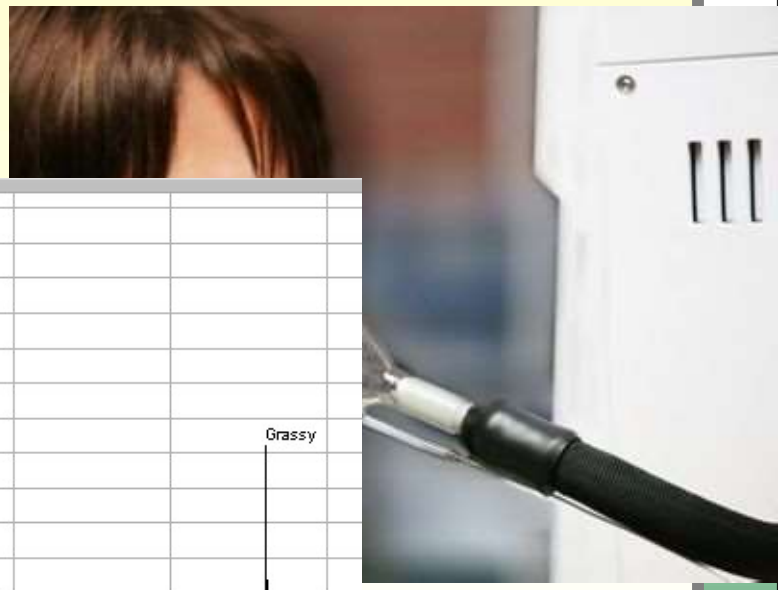
higher sensitivity

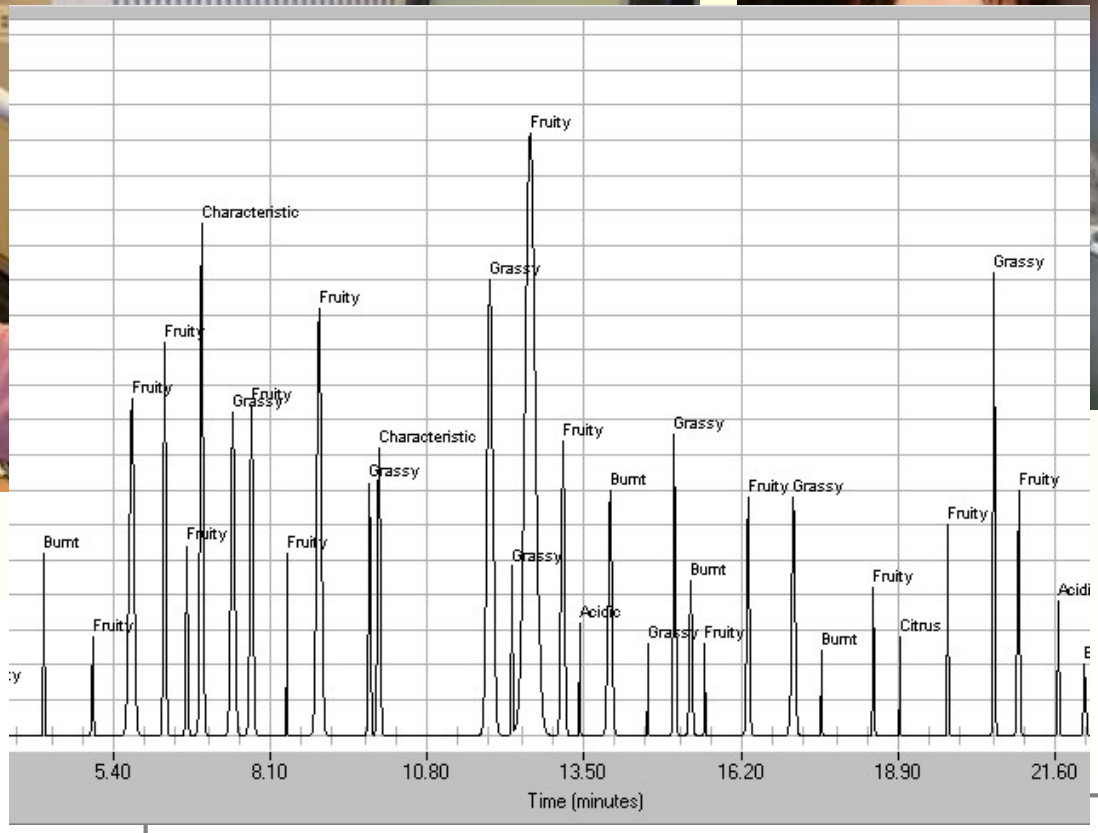
lower noise

normalization impossible

Olfactory detector







Characterizing odor caused by separated chemicals from one sample

Odor Character

Hedonic tone

Odor Intensity

Task 3

Twenty microliters of air were injected into GC inlet in splitless mode. Expected benzene concentration is 5 ppb (v/v). Will benzene be detected on chromatogram if detector (MS) sensitivity to benzene in 5 pg at signal to noise ratio 5:1?

Task 4

Sample of solvent (V =0.2 µL) was injected into GC-MS instrument at 700:1 split. On the obtained chromatogram, four peaks were detected: ethyl acetate, toluene, iso-propanol and o-xylene with corresponding areas 4260, 3120, 11600 и 700 a.u. Calculate mass fraction of each compound if their response factors relative to toluene are 0.77; 1.00; 0.45 и 1.11.