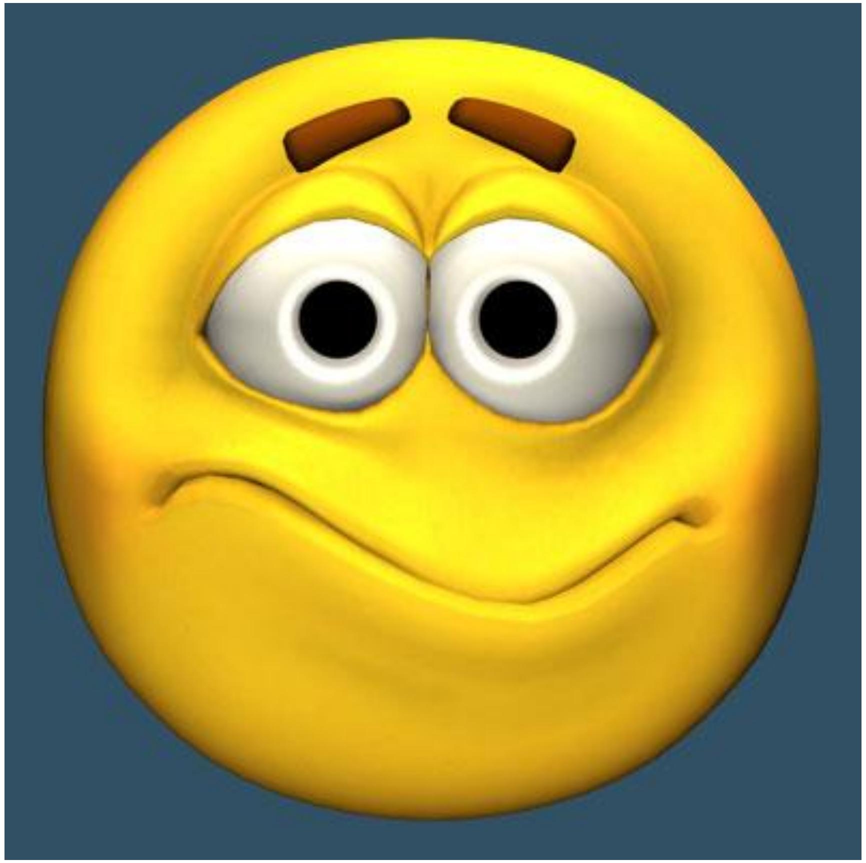
Basics in Gas Chromatography

GC-Training

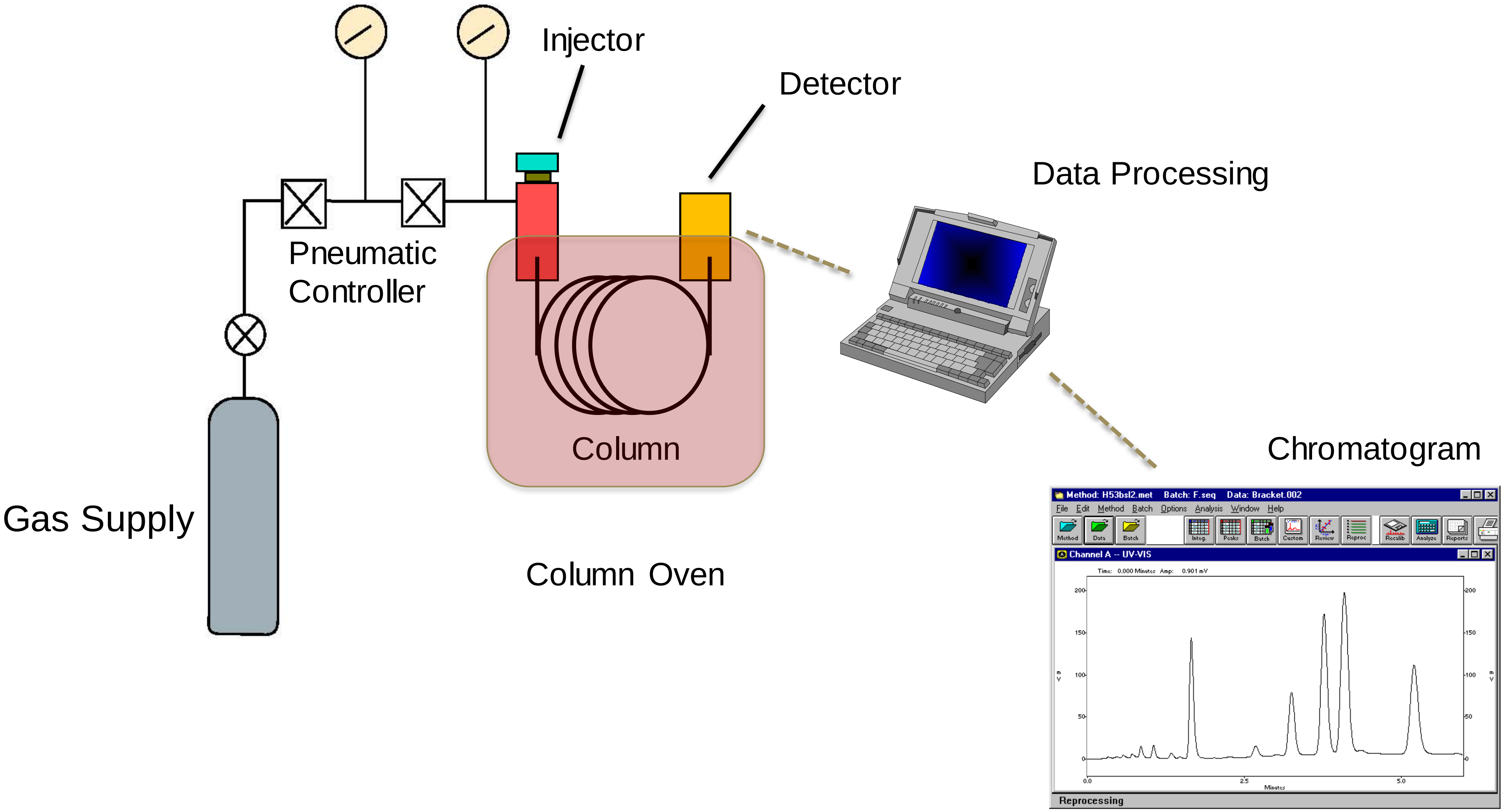
Basics in Gas Chromatography

Chromatography is a technique for separating a mixture of substances, using different moving speeds of the substances

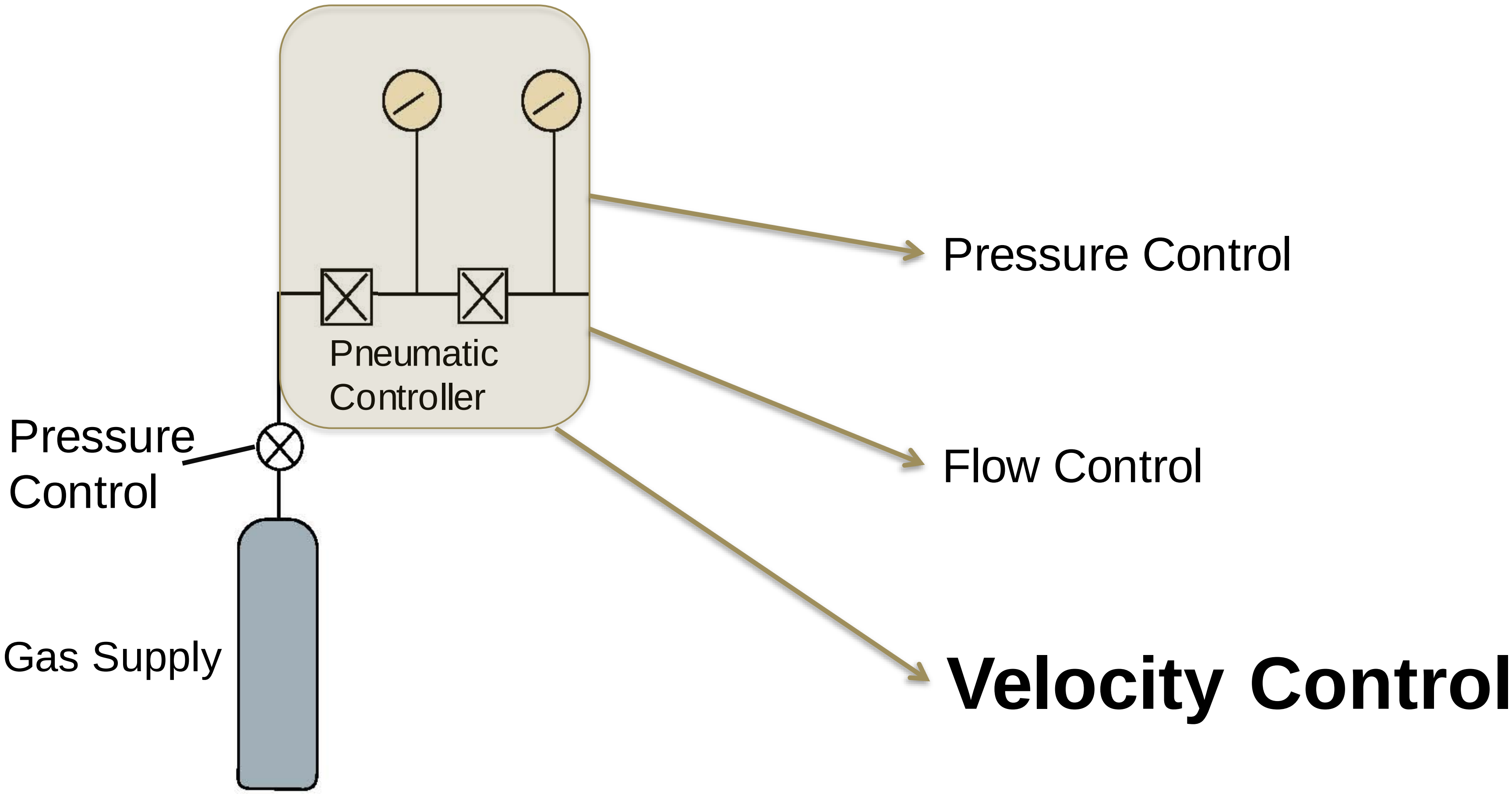
(Translation from Brockhaus 2005)



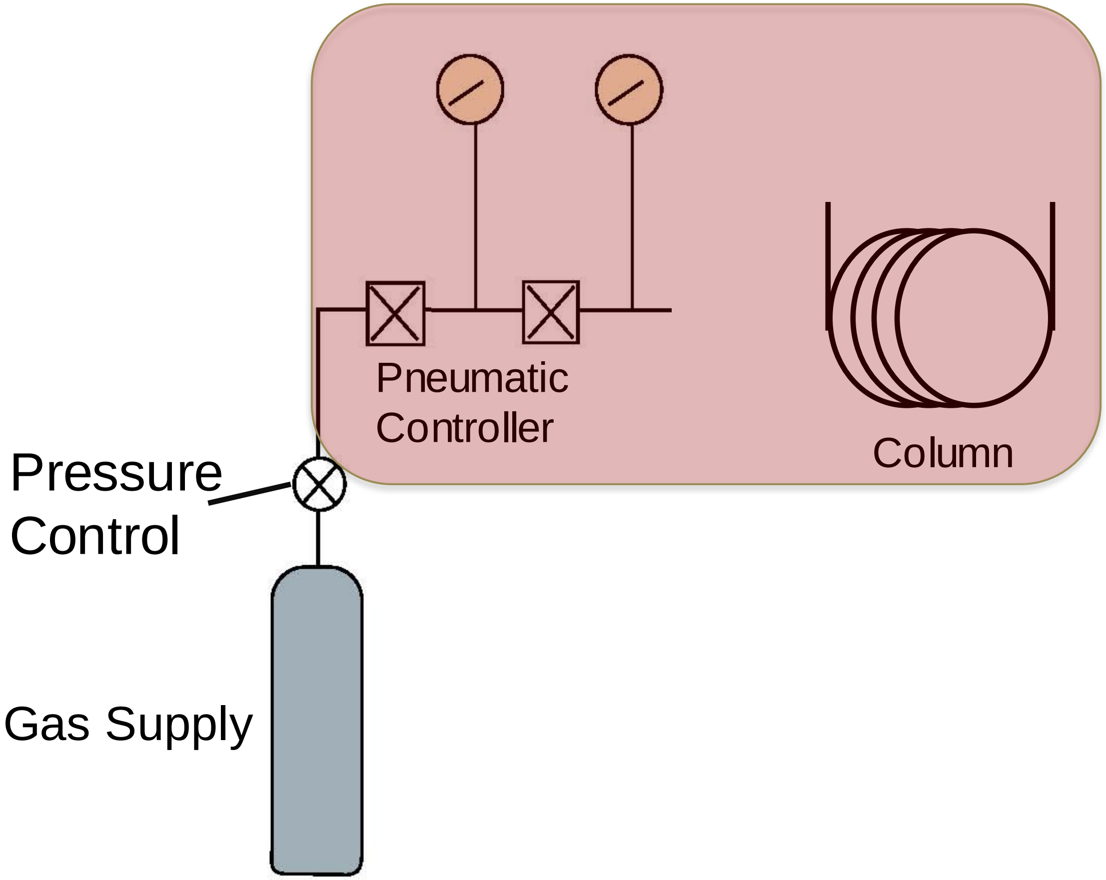
GC-System


Injector
Detector
Data Processing
Pneumatic
Controller
Column
Chromatogram
Gas Supply
Column Oven
Method: H53bsl2.met Batch: F.seq Data: Bracket.002
Channel A -- UV-VIS
Reprocessing

Pneumatic Control



Pneumatic Control



Pneumatic Control

Column = Tube = Restrictor

Flow rate and Linear Velocity:

1. Flow rate [cm³/min],

Typically related to Column Outlet under SATP (Standard Ambient Temperature and Pressure)

2. Average Linear Velocity [cm/sec]

$$\bar{u} = L / t_u$$

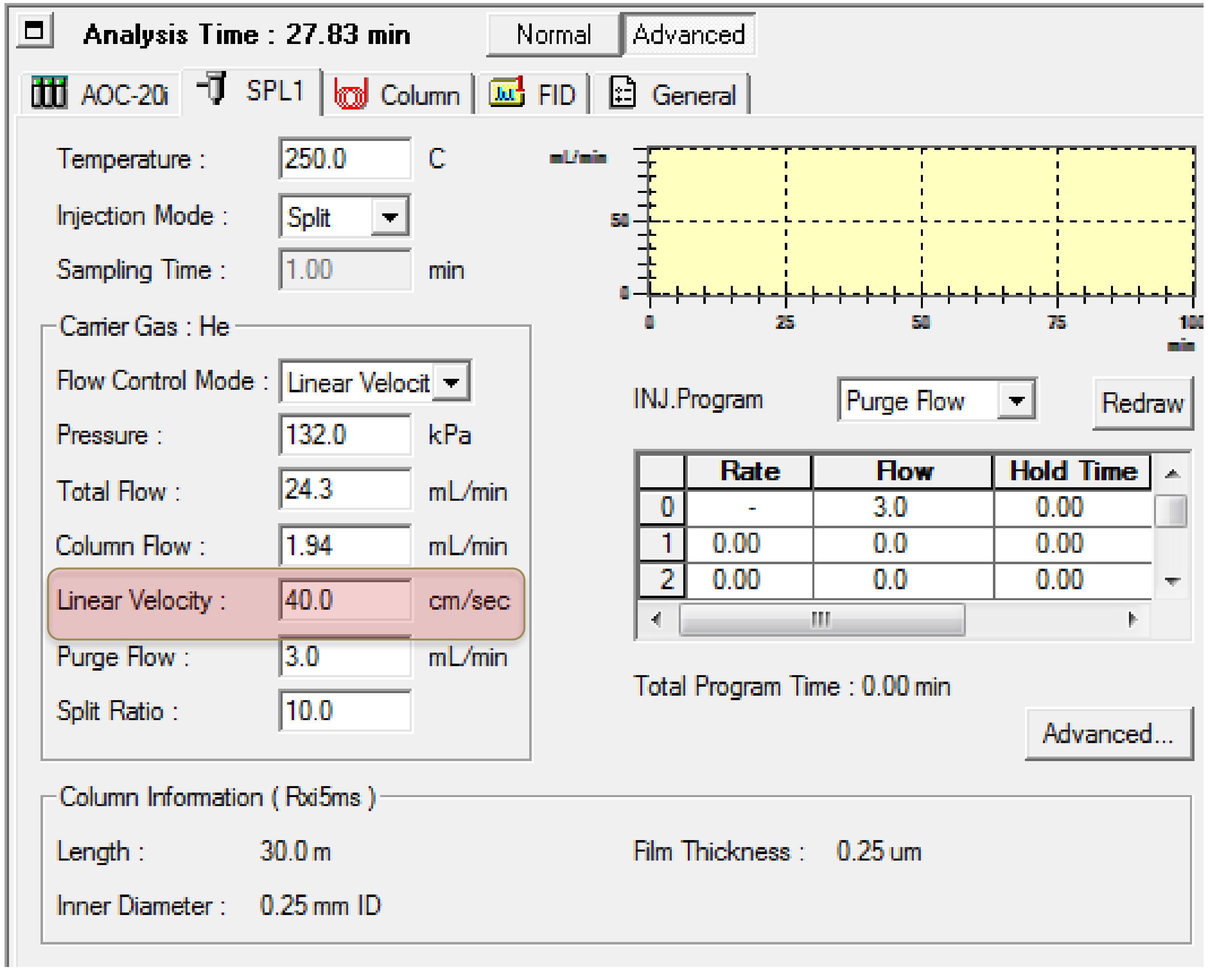
L = length of column [cm]

t_u = retention time for an unretained peak [sec]

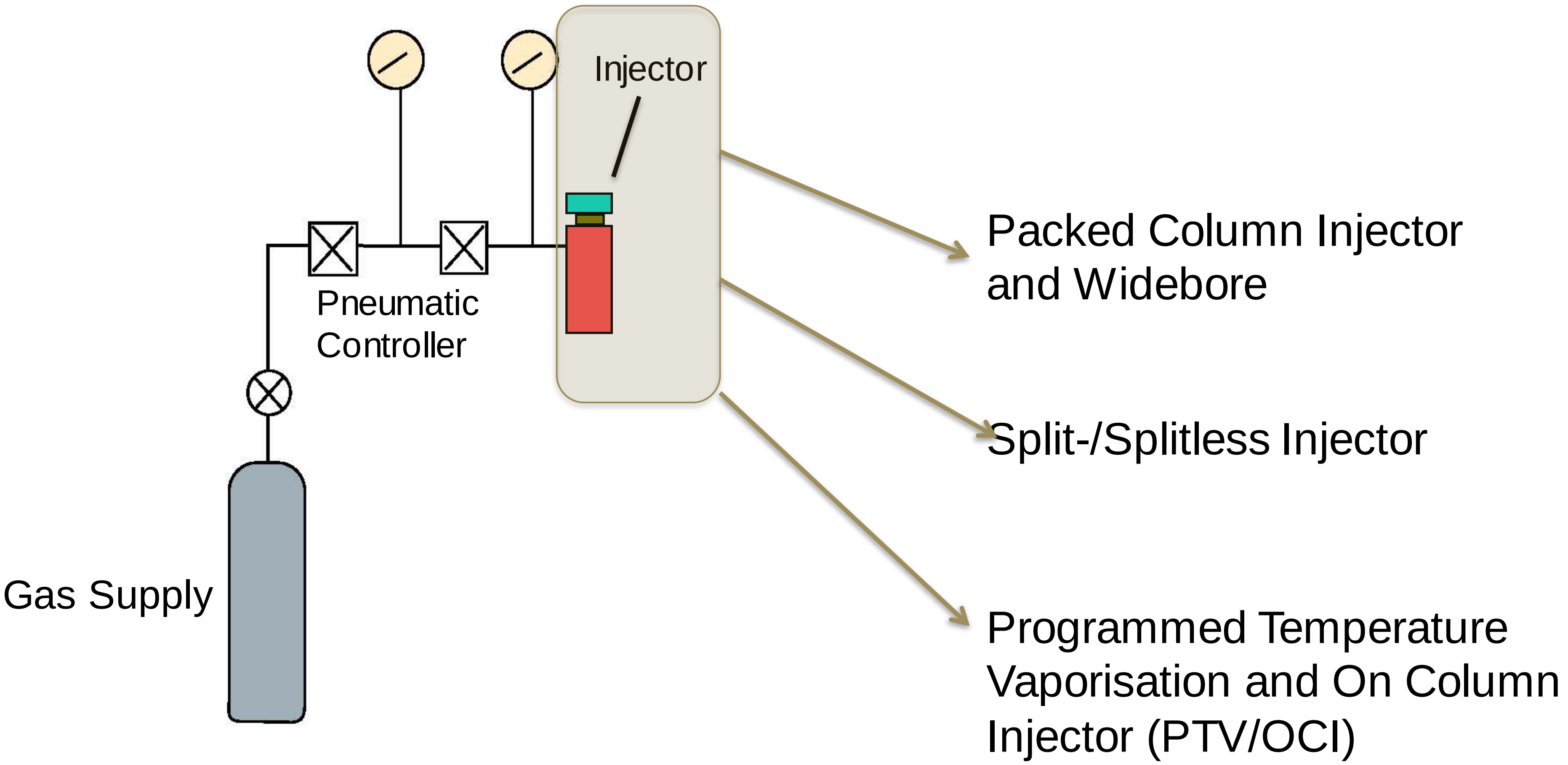
Flow rate and Linear Velocity:

Linear Velocity

can be set as a control parameter for GC-2010 Series, GC-2014 and GC2025



Headline for slide (Text only)



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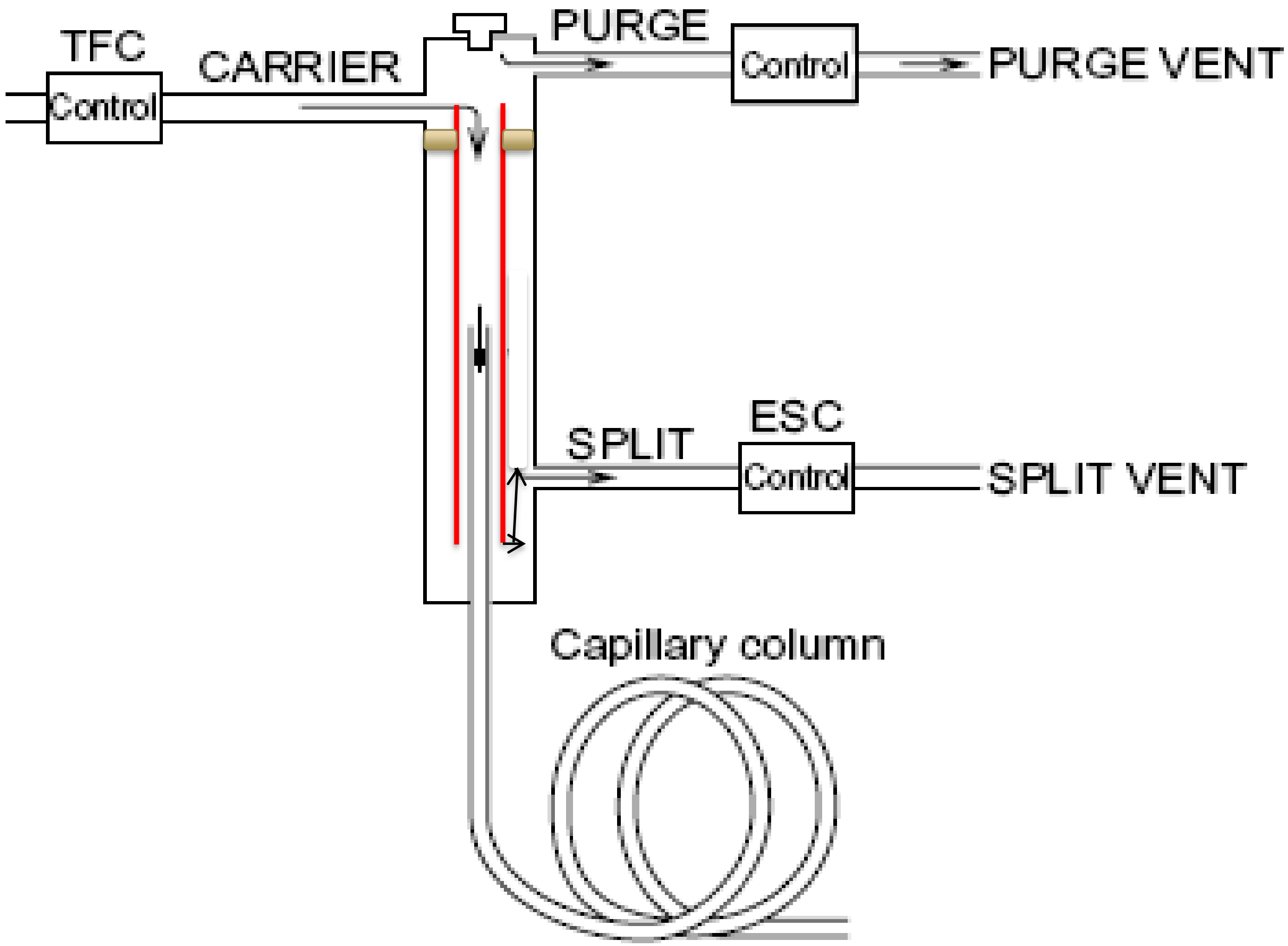
Split-/Splitless Injector

The total flow is the summery of purge, split and column flow

Split Injection System is to inject a sample with high concentration

Only a defined part of the sample go through the column. the rest go through the Split out

The purge flow is to purge the septum



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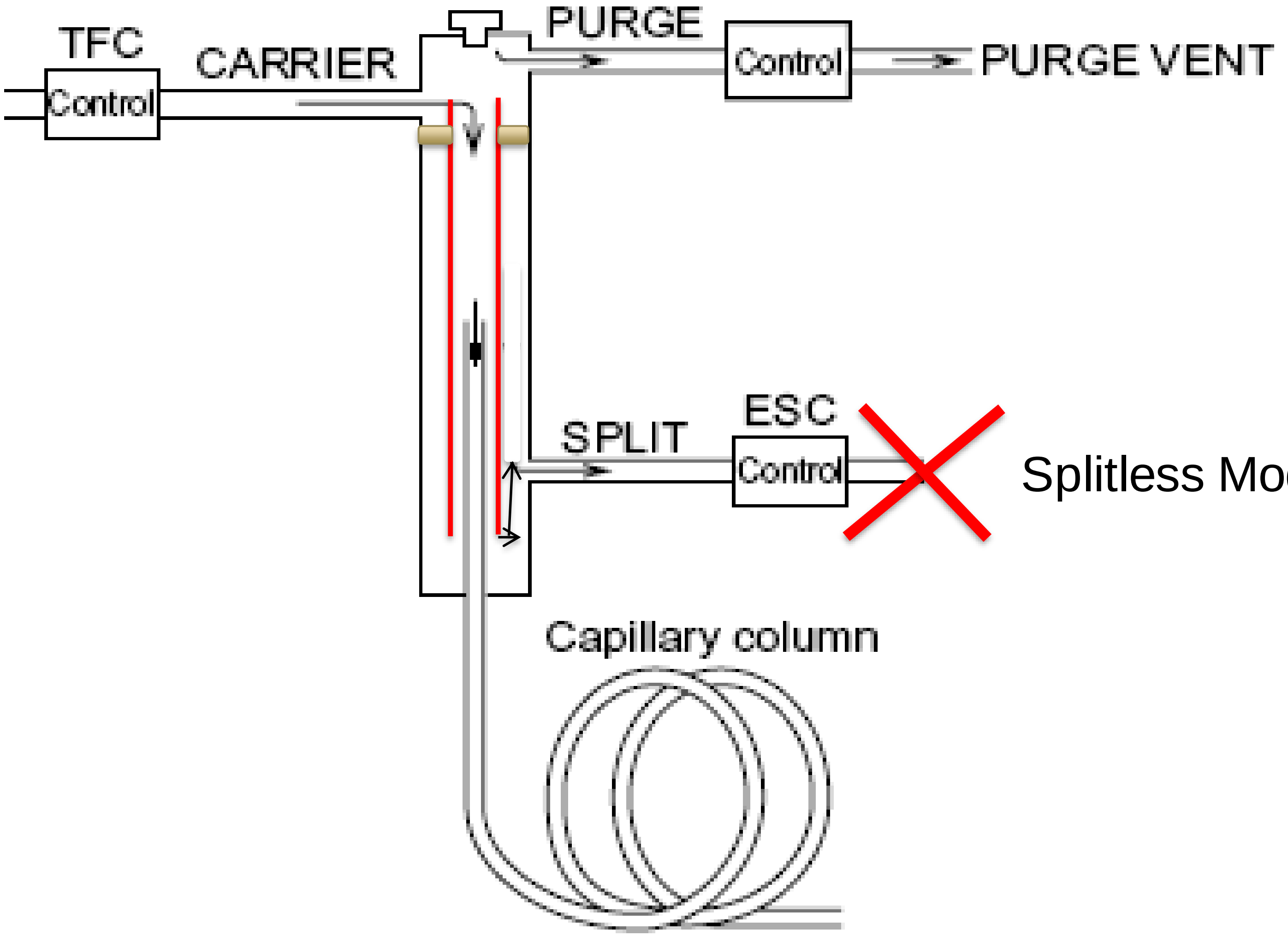
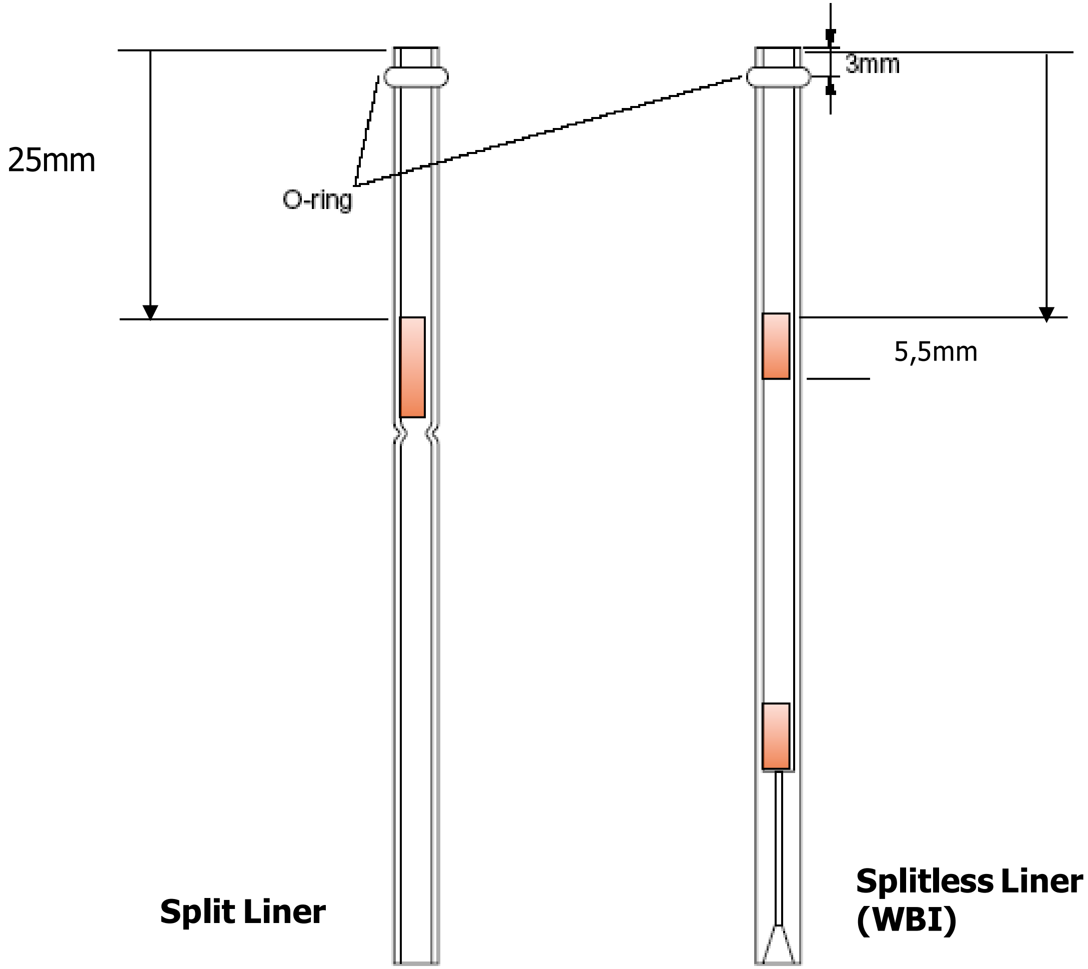
Split-/Splitless Injector



Splitless Mode

Split-/Splitless Injector

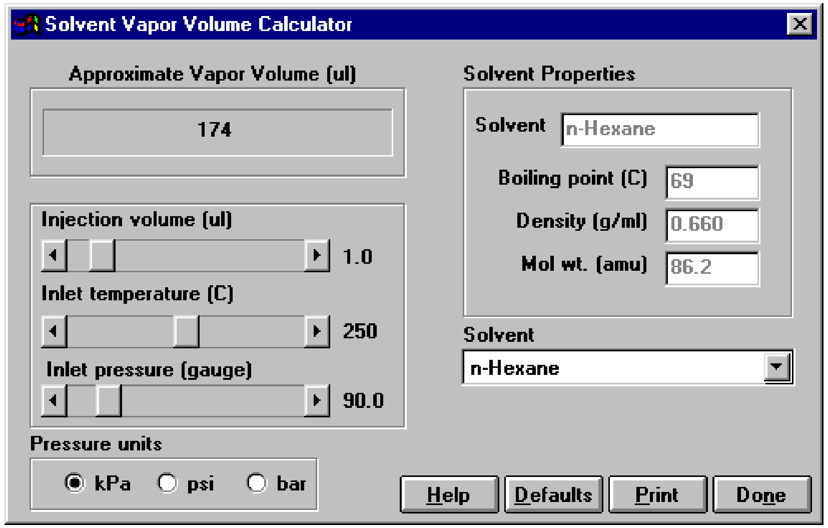
Two Types of Liner

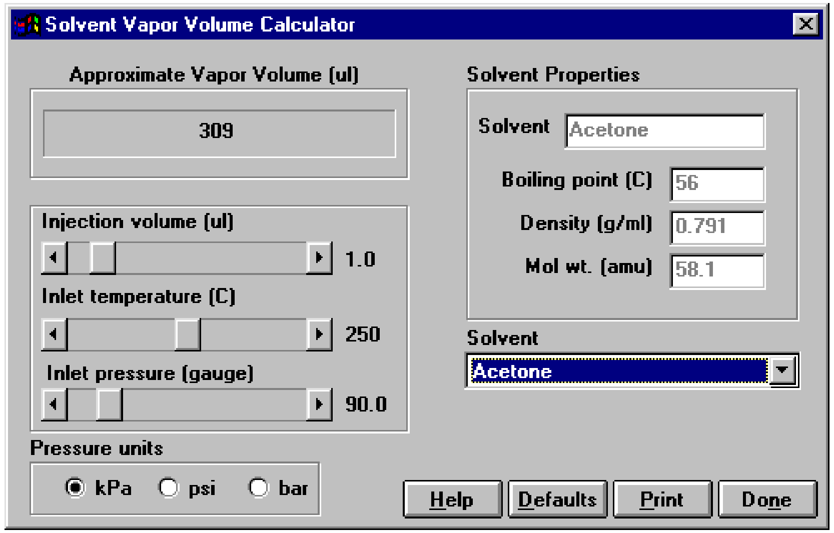


Very Important !

The glaswool must be
In the correct possition

Injection Efficiency





Bad sample transfer on the column can be due to an overloaded liner. Important is the volume of the evaporated sample not liquid.

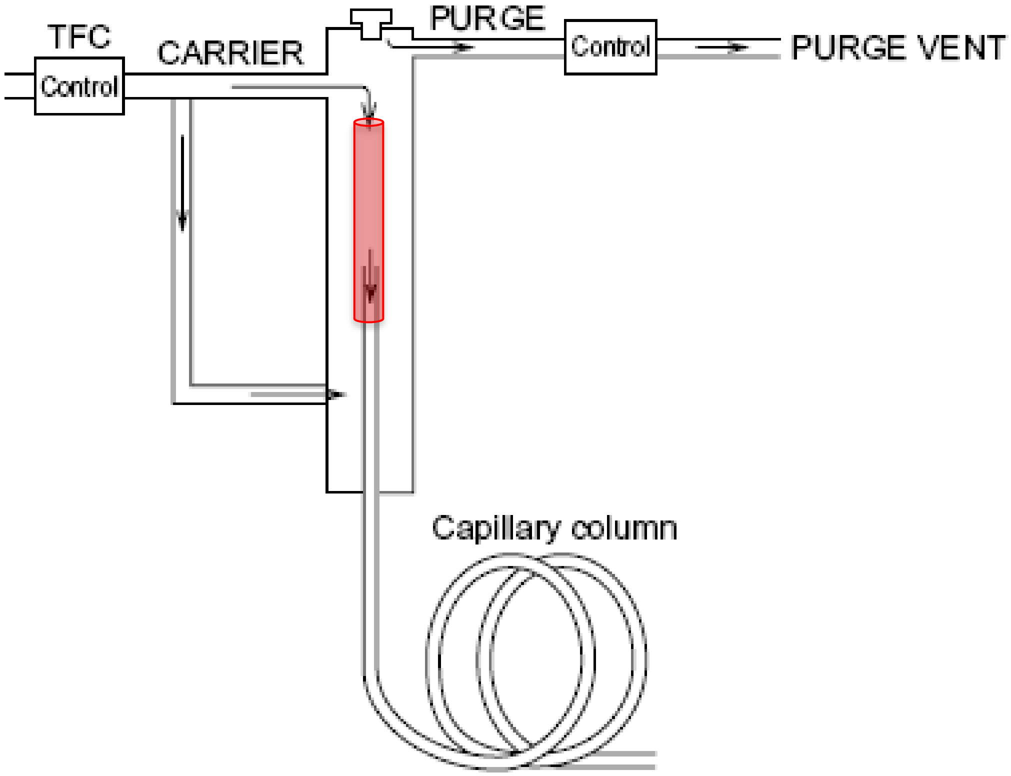
Typical liner volume might vary from 1.0 to 0.1ml

SPL-2010 Plus liner 0.86ml

Wide Bore Injector

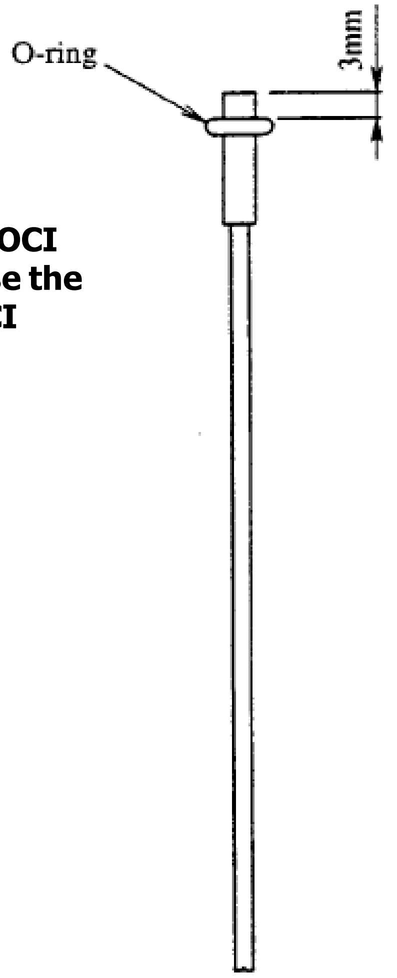
In a direct injection system, a wide-bore column is used. Nearly the entire amount of sample injected is inrtoduced on the column. This usually results in better sensitivity than narrow-bore columns with split injections. However, peak shapes are broad, which decreases resolution and can lead to a higher S/N ratio. The direct injection system uses a WBI (wide-bore injection) injection port. When WBI is specified, DIRECT injection mode is automatically used and split mode is not available on the [INJ] key main screen.

Direct Injection System

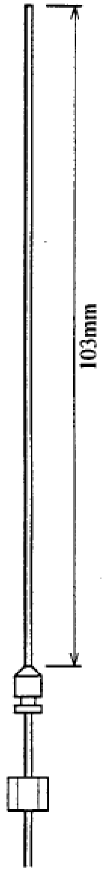


OCI/PTV

(On Column/Programmable Temperature Injector)



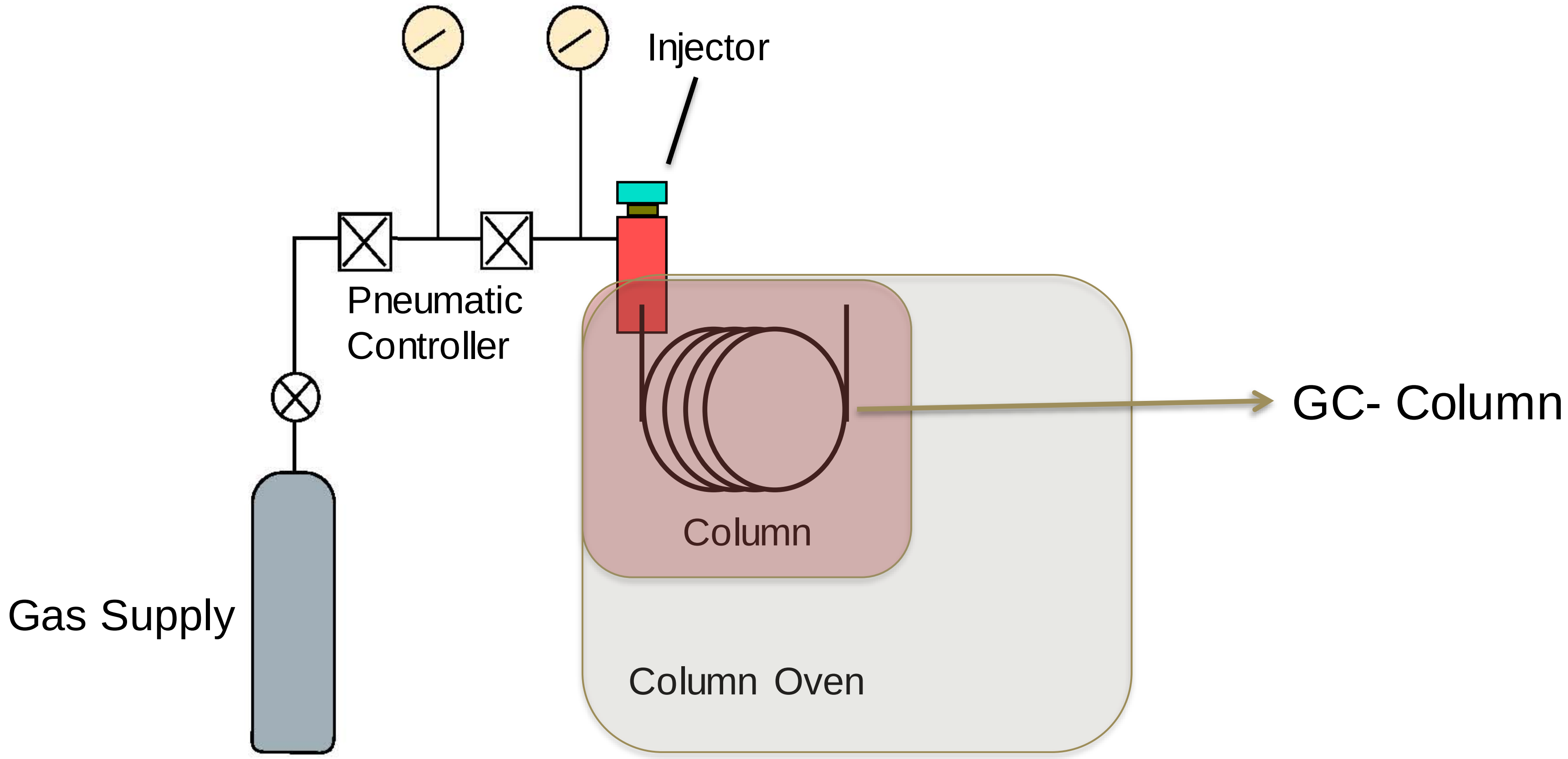
In the case of OCI you have to use the adapter for OCI



To install the column you have to fix the graphite ferrule with the corect lenght. Then insert the column until it reaches the top end of the adapter for OCI

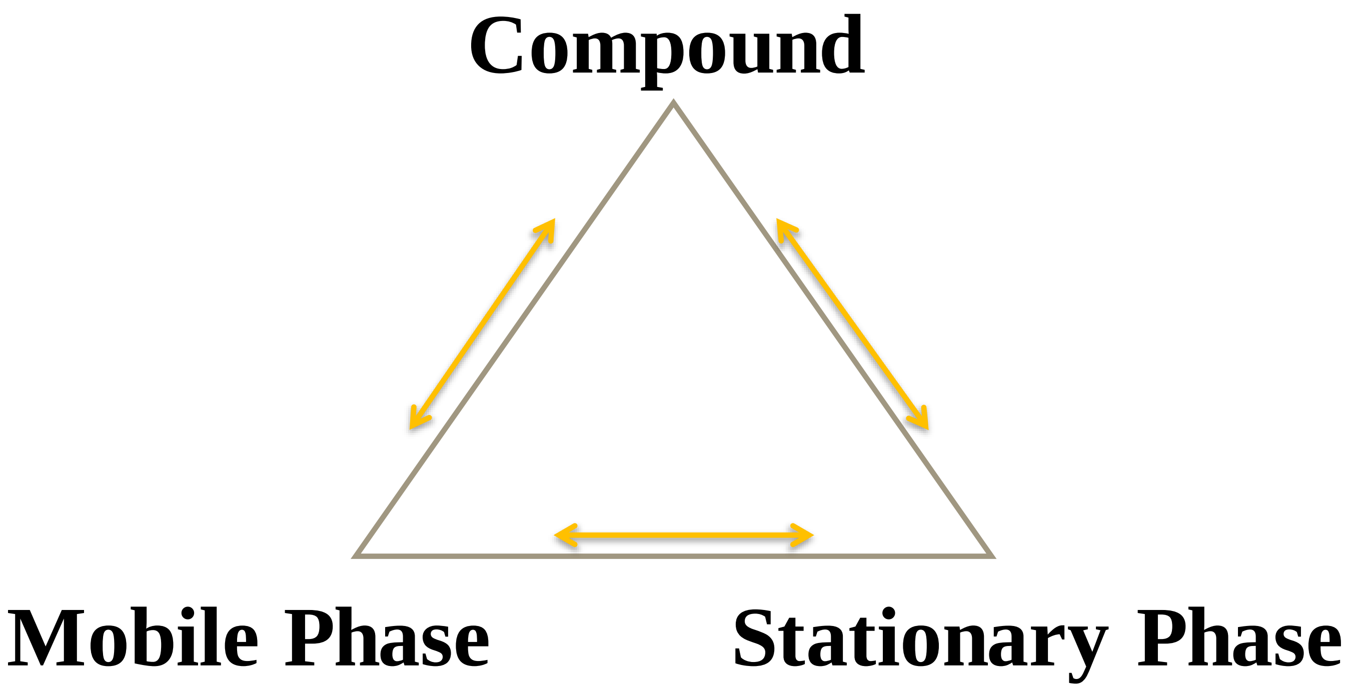
A short coffee break

GC-System


Injector
Pneumatic
Controller
GC- Column
Column
Gas Supply
Column Oven

Gas Chromatography Separation

Interaction of Forces



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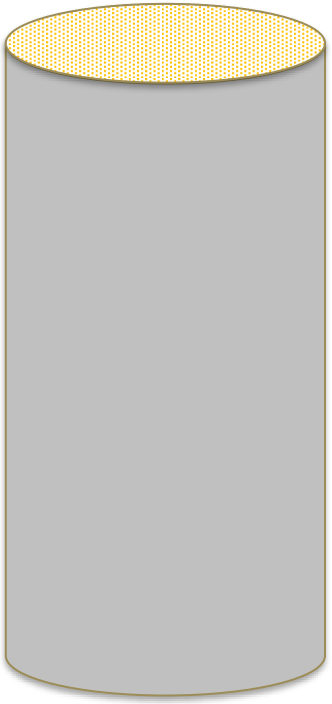
GC Columns:

Packed Column



Stainless Steel
Glass
Teflon

Typical size:
1/8 or 1/4 inch o.d.
1 to 3 m lengh

10 to 60 ml/min flowrate

Capillary Column

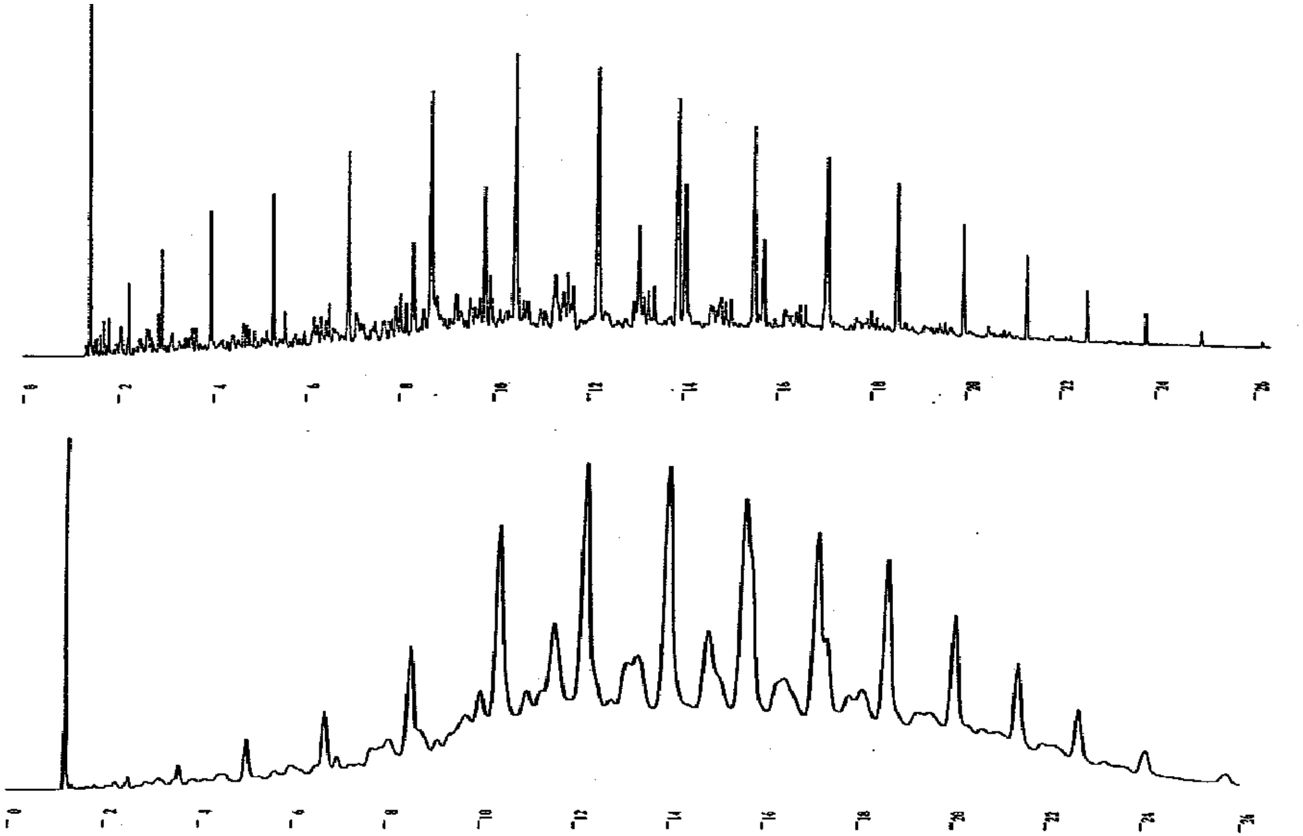
Fused Silica
Stainless Steel
Glass

Typical size:
0.25 or or 0.32 mm i.d.
10 to 100 m lengh (30m typ.)
0.5 to 3 ml/min flowrate

0.1 mm i.d. for Fast GC
0.53 mm i.D. for Wide Bore

Packed vs Capillary

Analysis of light oil



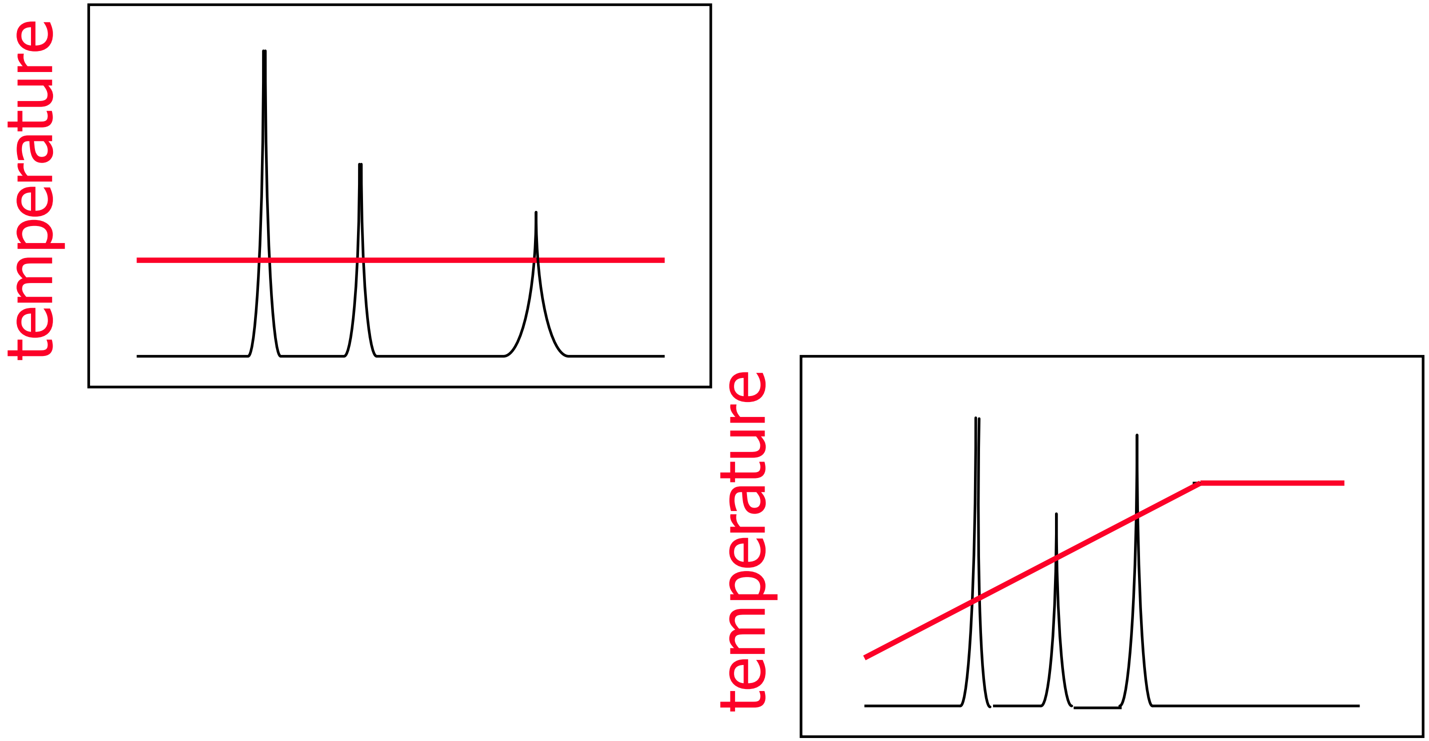
Capillary

Packed

Influence of temperature on separation efficiency

Isothermal Analysis

Temperature Programming Analysis



Classification of Capillary Colunms

Mobile Phase	Stationary Phase	
- **Gas**	**- Liquid**	**(GLC)**
- **Gas**	**- Solid**	**(GSC)**

- **Application Fields:**

  (Examples)

  – Environment
  – Chemistry
  – Petrochem
  – Food
  – Pharmacy
  – Drugs
  – ……………………..

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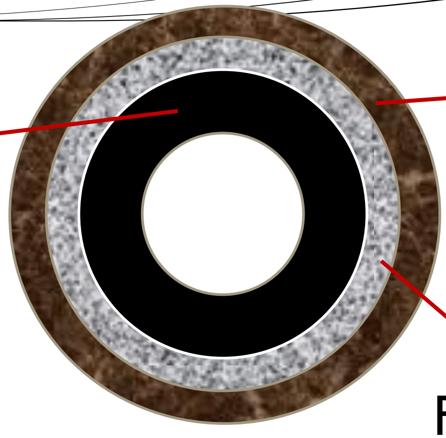
Capillary columns



Capillary column types

- **WCOT** = (GLC) Wall coated open tubular columns
- **PLOT** = (GSC) Porous layer open tubular columns
- **SCOT** = (GLC) support coated open tubular columns (Special PLOT columns, stationaly phase is additionally coated with a special liquid)

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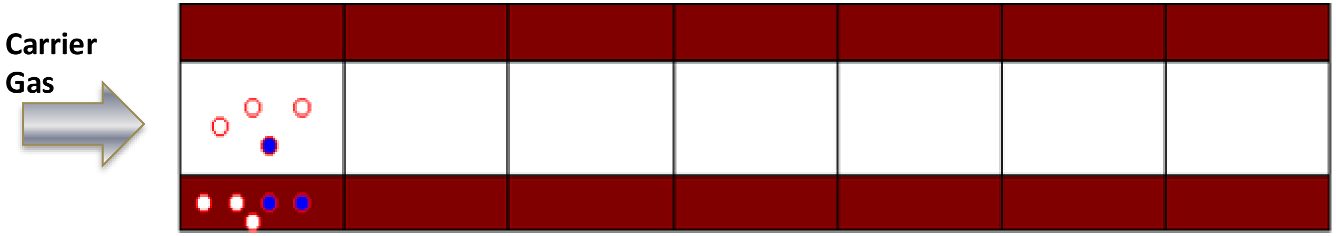
Classification of WCOT Capillary Colunms

Bore,I.Dmm	Length (m)	Film Thickness um	Application
0.1	10-20	0.1-0.4	High Separation, Fast analysis, very small column load
0.25	25-100	0.25-1.0	High separation, generally used in split type analysis
0.32	25-60	0.25-3.0	Used in splitless, on-column injection method
0.53	10-60	0.25-6.0	Separation ability equal to that of packed column. Large column load, on-column injection method

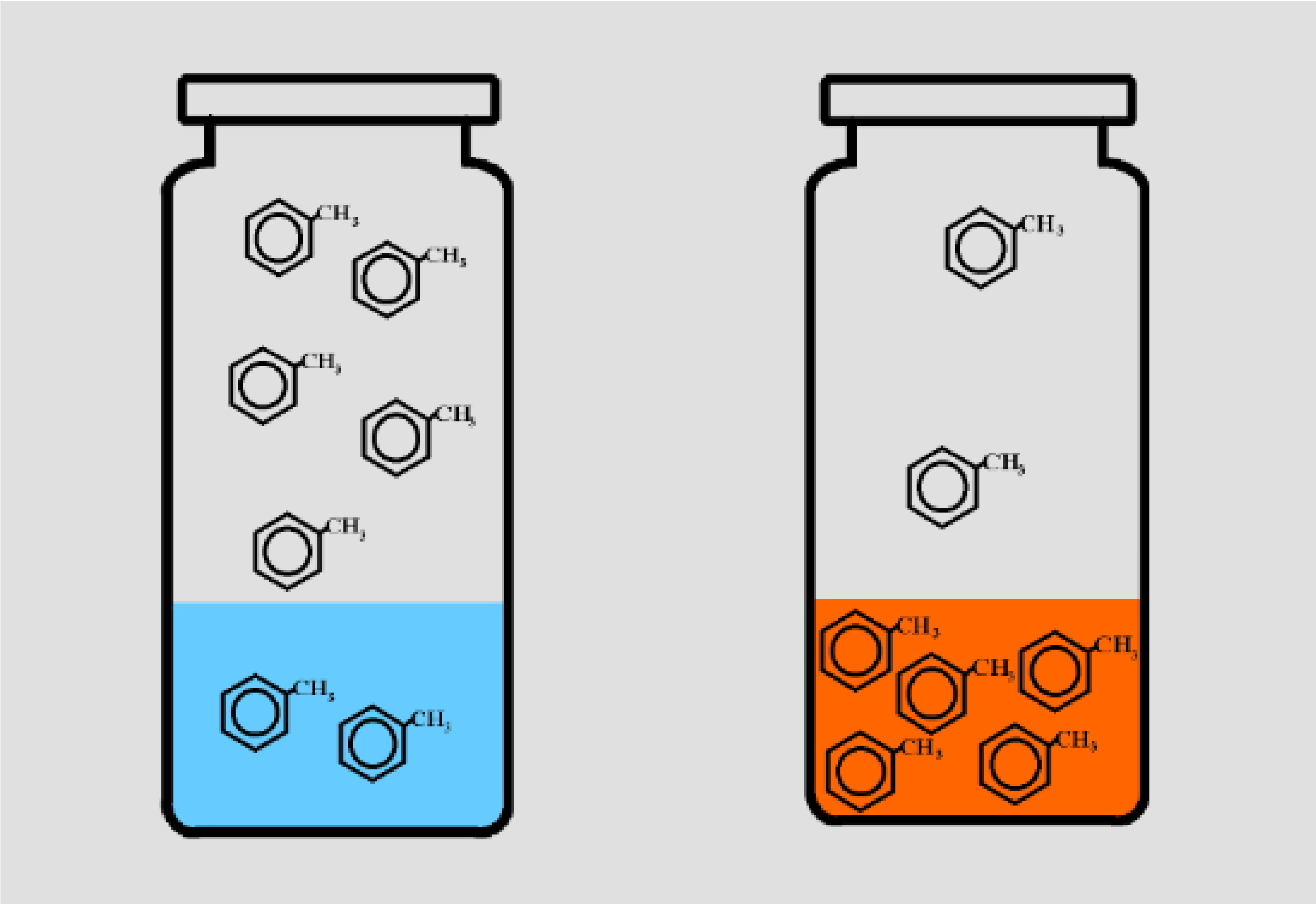
Capillary Column

Gas - Liquid - Chromatography (GLC)



Different compounds should be separated on the GLC Capillary Column

Phase Distribution



$$K_i = \frac{C_{iL}}{C_{iG}}$$

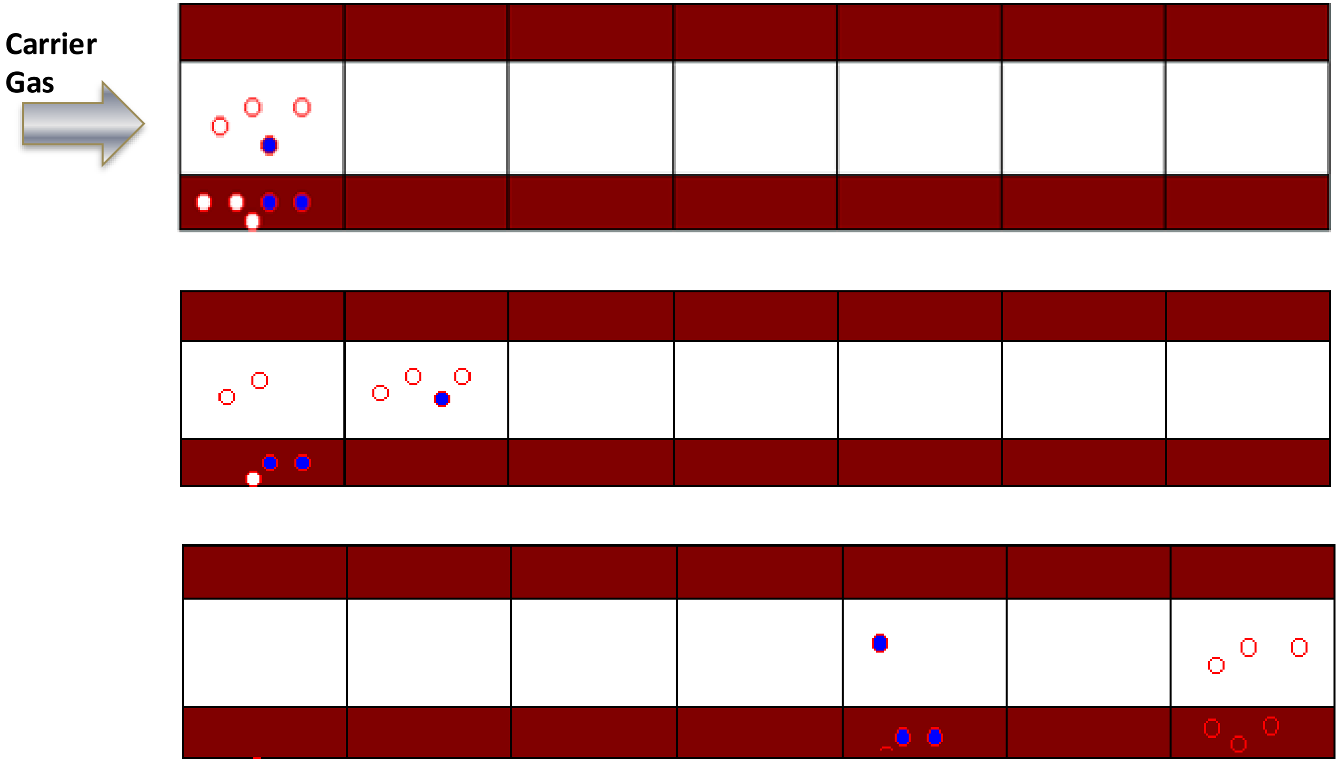
K_i : Distribution Coefficient compound **i**

C_{iL} : Concentration of compound **i** in liquid phase

C_{iG} : Concentration of compound **i** in gas phase

Capillary Column

Gas - **L**iquid - **C**hromatography (GLC)



Separation Mechanism:

1. **Vapor Pressure**
2. **Polarity**

Theory for GLC

Henry´s Law:

$$\boxed{p_i = p_{0i} \cdot x_{si} \cdot \gamma_i}$$

$\gamma = 1$: No interaction of compounds due to Polarity

$\gamma =$ konstant: Non saturated Solution

$\gamma = f(x_i)$: High Concentration of Compounds In the mixture (saturation)

$p_{0i} \longrightarrow$ Vapor Pressure

$\gamma_i \longrightarrow$ Polarity

Optimizing Capillary Column Parameters

-Stat. Phase

-Length

-Inner Diameter (I.D.)

-Film I.D.

Selectivity

Resolution

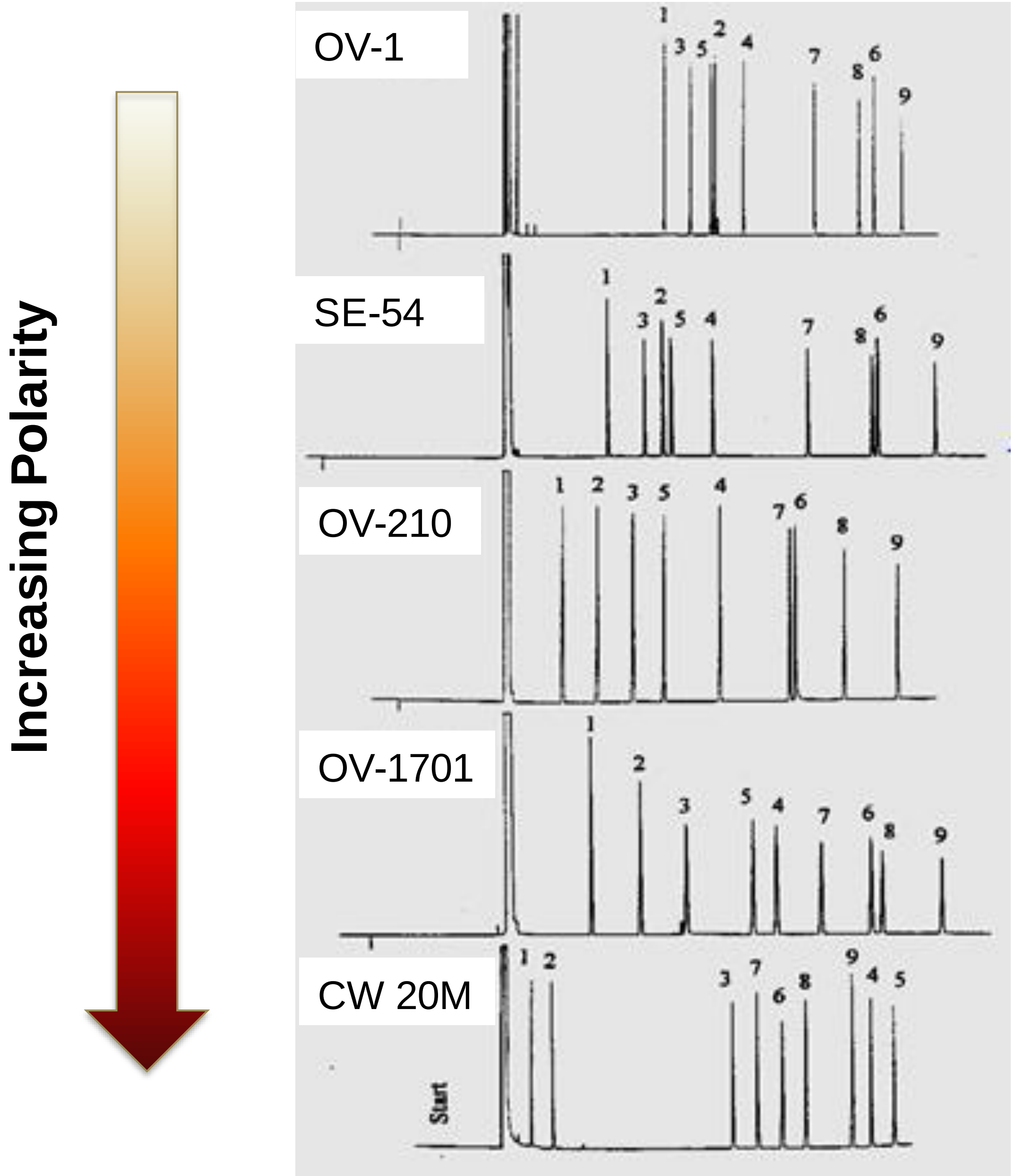
Analysis Time

Sampleamount for Injection

Stationary Phase

	Phase	Chemical name	Synonyms (Supplier)	Typical Application
Non Polar	OV-101	100% Methyl	SP-2100	Hydrocarbons
				Fraktioning Gasoline and Diesel
	OV-1		DB-1, SPB-1, RTX-1	Triglyceride
		100% Methyl	CP-SIL 5	
	SE 30			
	SE-52	95% Methyl	CP-SIL 8, SPB-5	Universal (e.g. PAH, PCB, LHKW)
		5% Phenyl	DB-5, RTX-5	
	SE-54	94% Methyl		
		5% Phenyl		
		1% vinyl		
	OV-1701	86% Methyl	DB-1701, SPB-7	Aromatic Compounds, Phenoles
		7% Phenyl	CP-SIL 19	PCB, Pesticides, LHKW
		7% Cyanopropyl		
Medium Polar	OV-210	50% Methyl	DB-210	
		50% Triflourpropyl	RSL-400	same as before
	OV-225	50% Methyl	DB-225,BP-15	same as before
		25% Phenyl	CP-SIL 43	
		25% Cyanopropyl		
High Polar	CW 20M	Polyethylenglycol	DB-WAX, Supelcowax 20	Alcoholes, Flavors, FAME, Free Fatty Acids
		PEG 20000	BP-20	
	FFAP	PEG 20000	AT-1000,SP-1000	same as before

Stationary Phase defines Selectivity

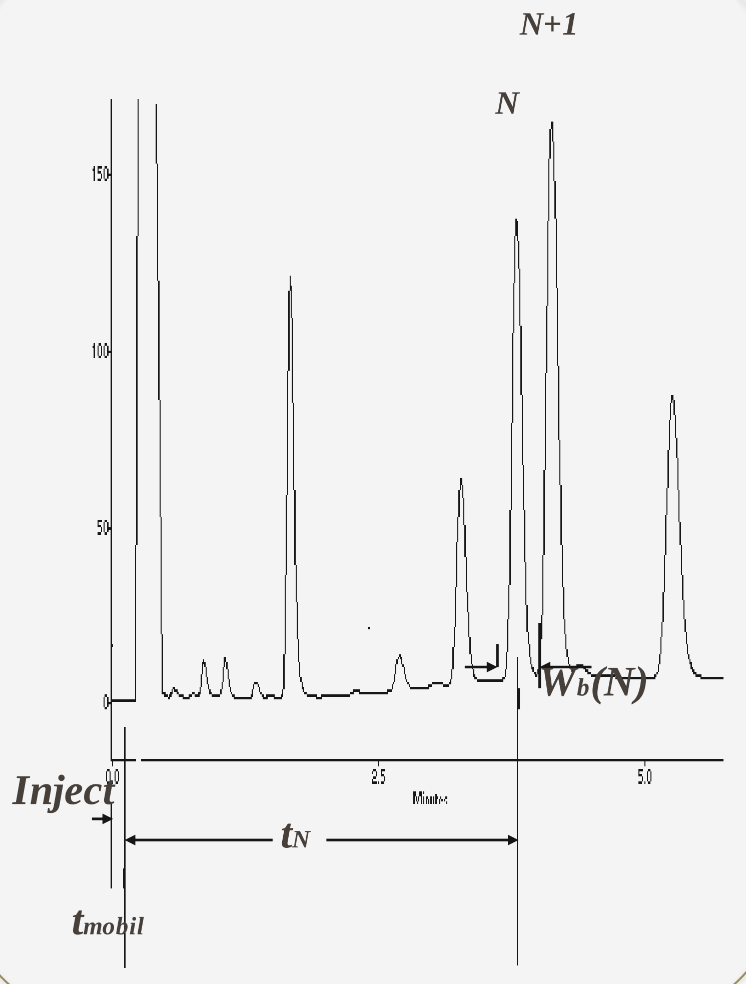


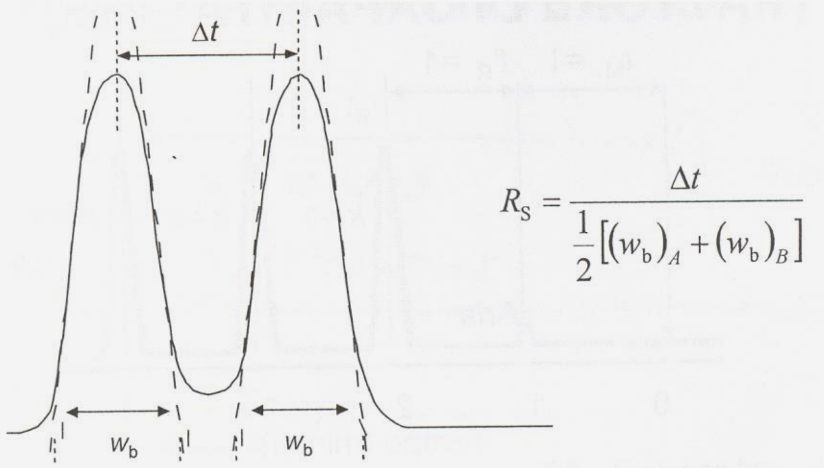
Grob-Mix Compounds

1 n-C10
2 n-C11
3 N-Octanol
4 2,6-Dimethyleaniline
5 2,6-Dimethylephenol
6 Dicyclohexyleamine

7,8,9 Methyle-Esters from C10,C11,C12

Resolution R_S and Column

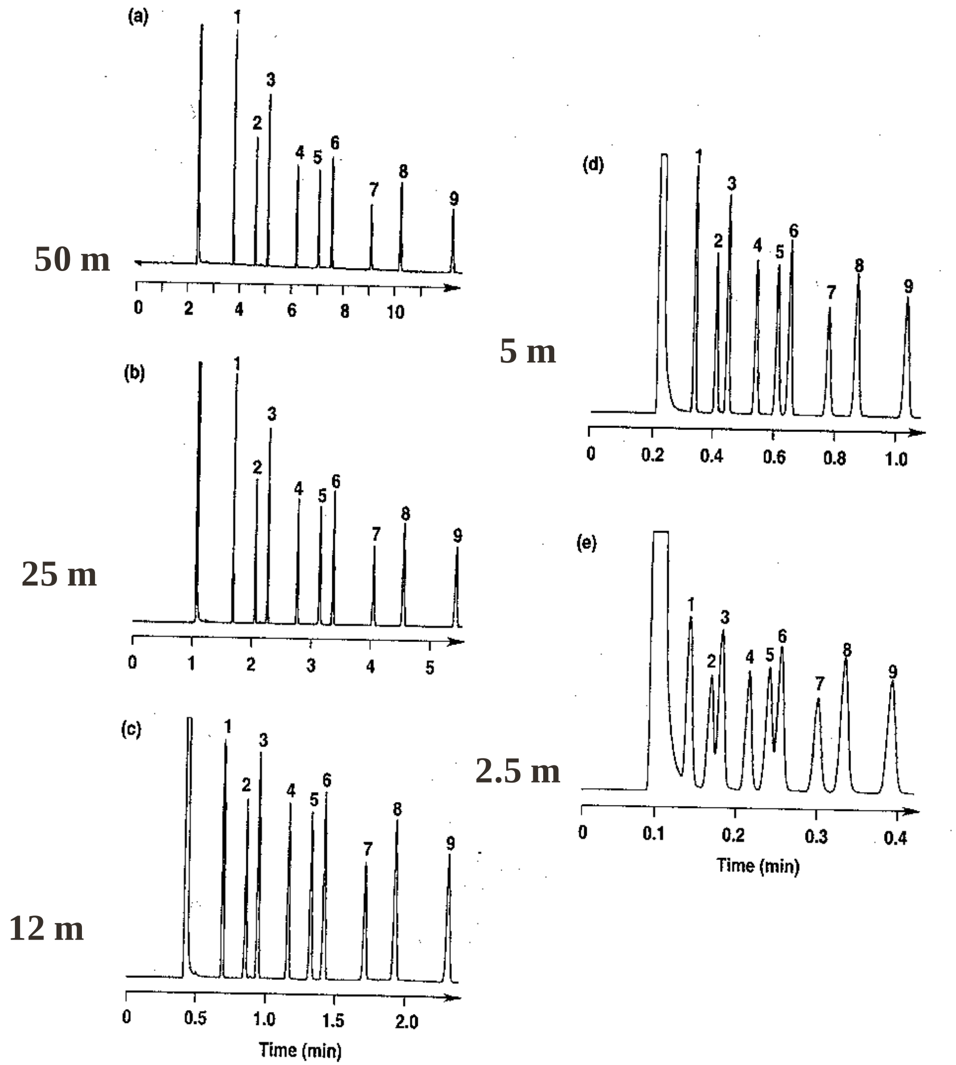




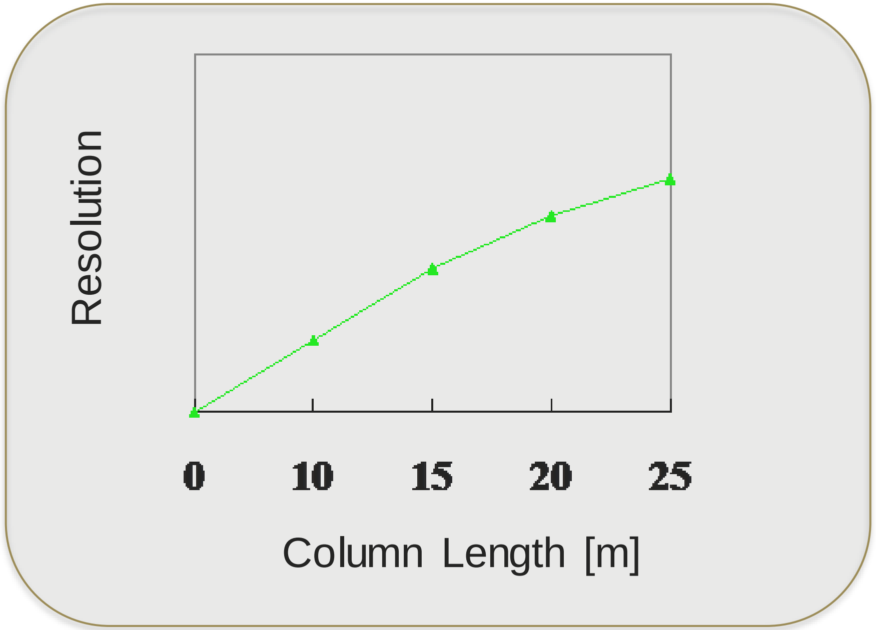
Optimizing Resolution by Colunm Parameters:

- Column Length
- I.D. of the Column
- Thickness of inner Film

Resolution vs. Column Length



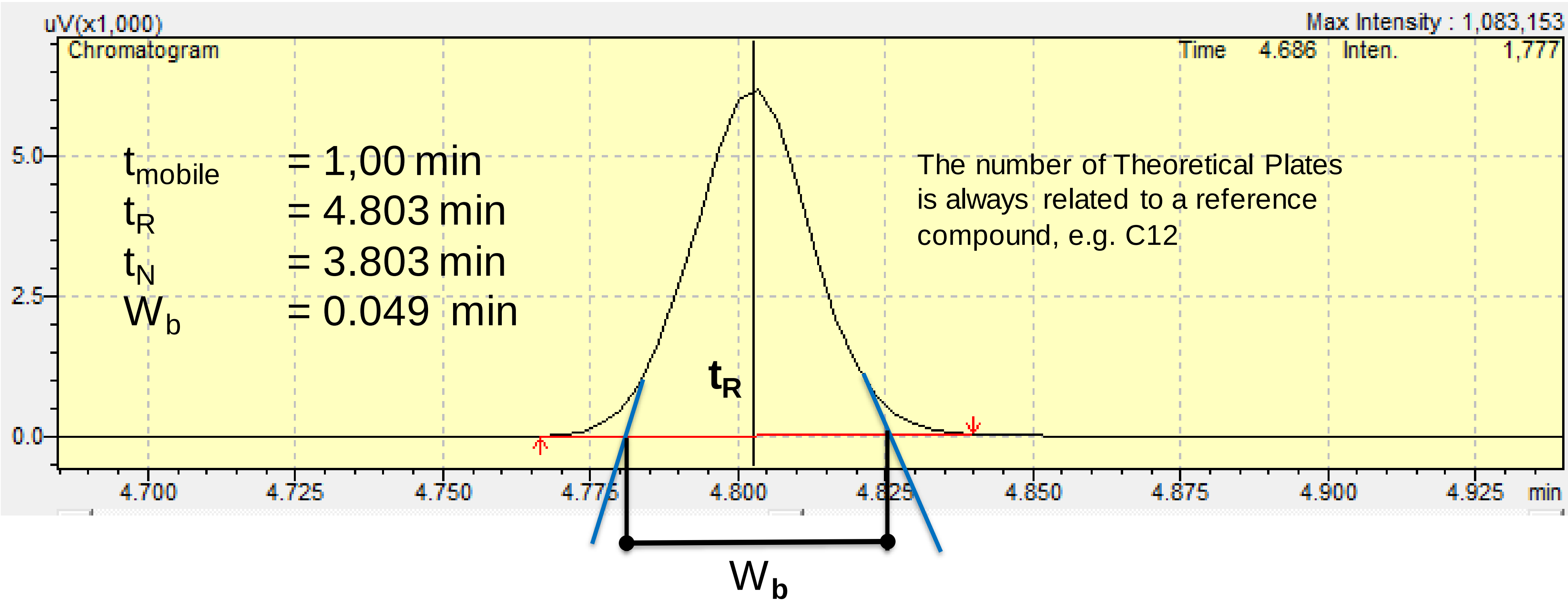
$$Resolution \sim \sqrt{Length}$$



Increasing the Column Length is **<u>less efficient</u>** due to Peak Resolution

Theoretical Plates of a Column

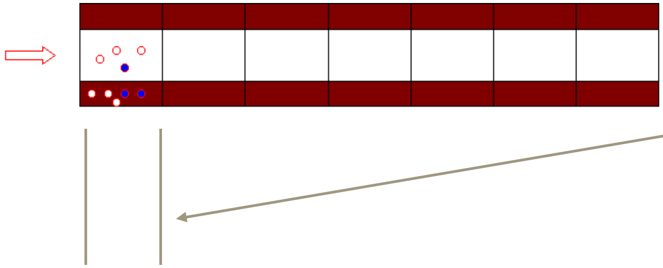
Theor. Plates: $N = 16 \times (t_N / w_b)^2$ **Describing Separation Efficiency**



Example: **N = 96.000**

HETP

HETP = Height Equivalent of a Theoretical Plate



$$HETP = L/N$$

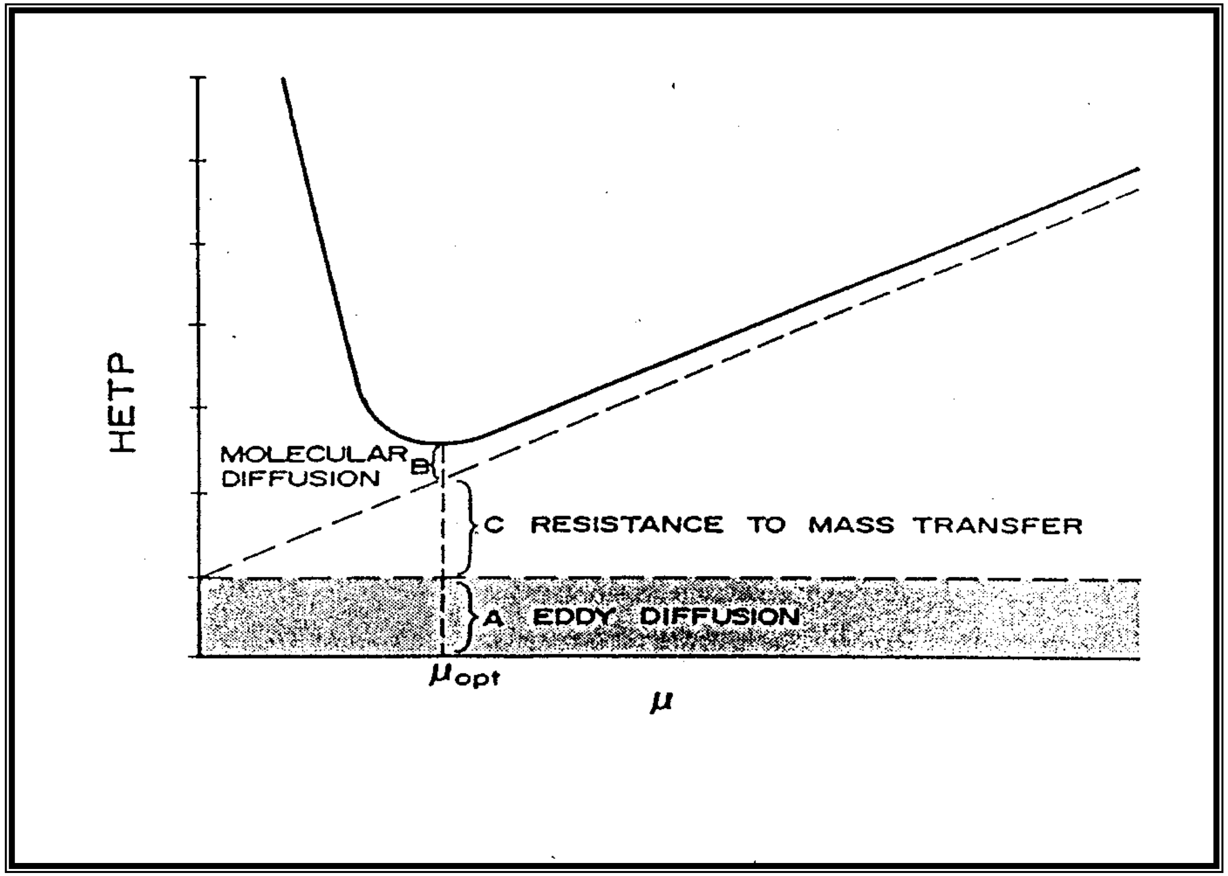
L = Length of a Column

HETP is a suitable Parameter describing the efficiency of separation

Decreasing value for HETP = Increasing separation efficiency

Linear Velocity vs. HETP

Van Deemter Curve



HETP = A + B/u + Cu

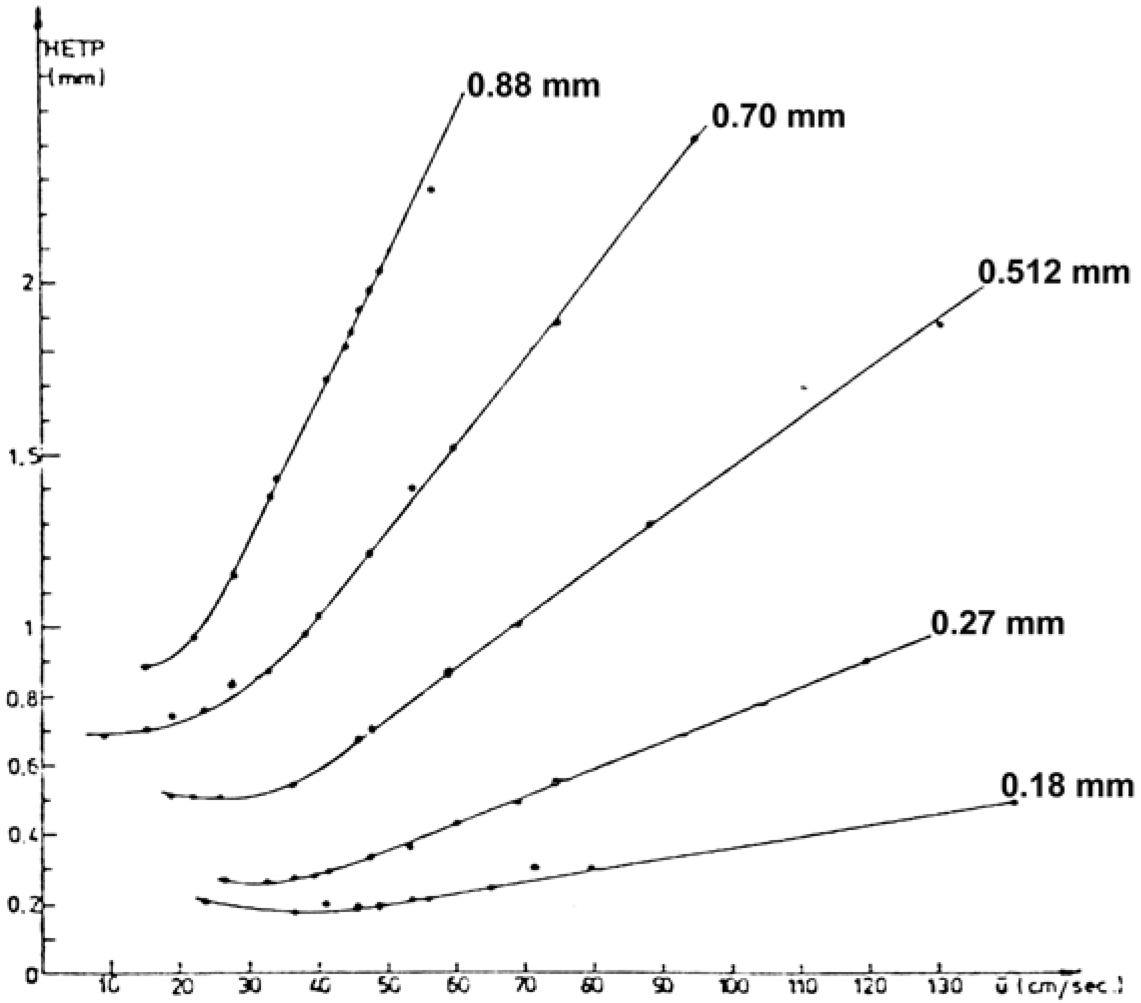
A: Eddy Diffusion

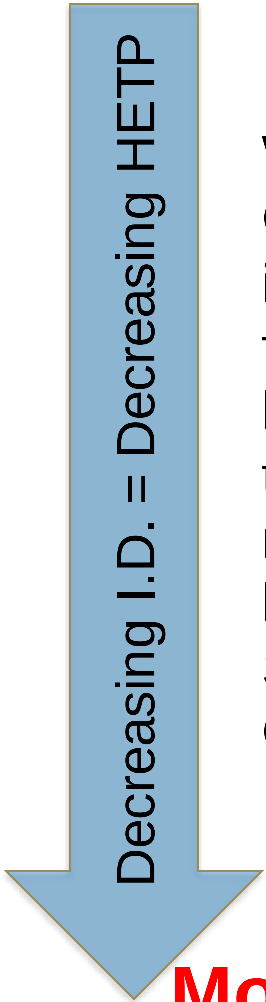
(konstant, only Packed Column)

B: Axial Diffusion of Molecules

C: Molecules transferring Phases

HETP and Column I.D.





With smaller Column I.D. the influence of higher flow rates is much less, due to faster transfer of sample molecules between the Stationary- and Gasphase

Most Effective

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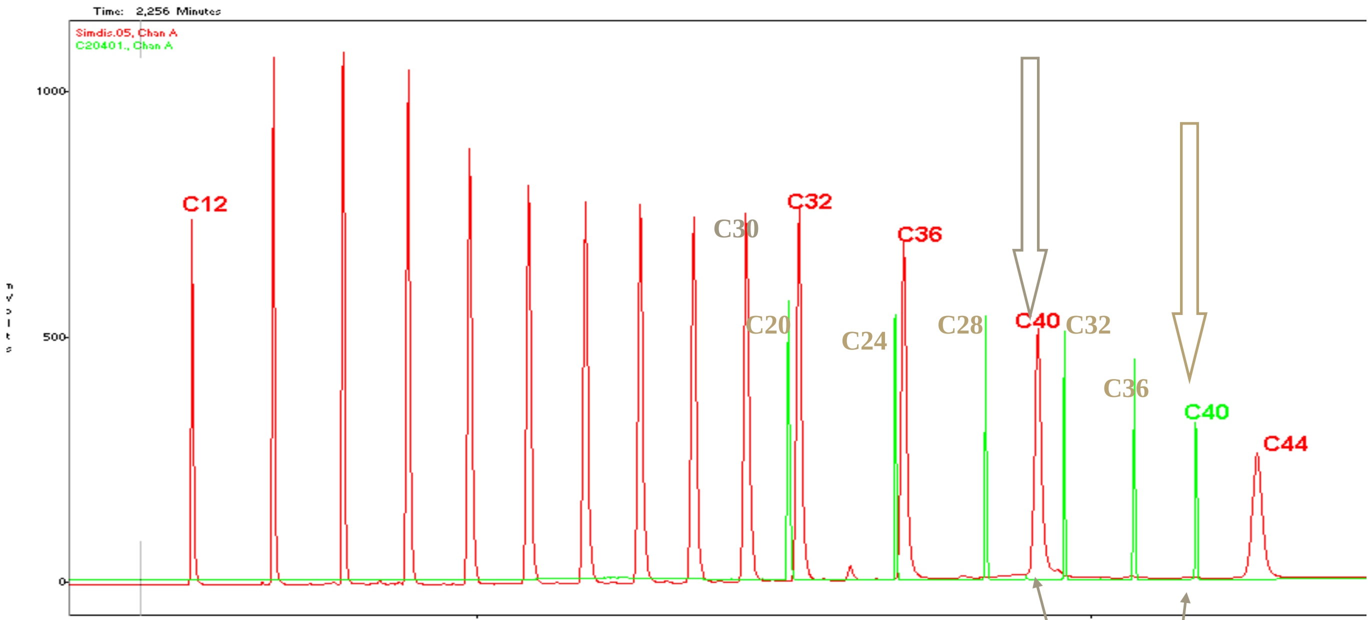
Example – Using different Columns



Red: 0.53mm I.D. , 0.25µm Film , 15 m

Green: 0.22mm I.D. , 0.25µm Film , 25m

Base With C40

Conclusuion:

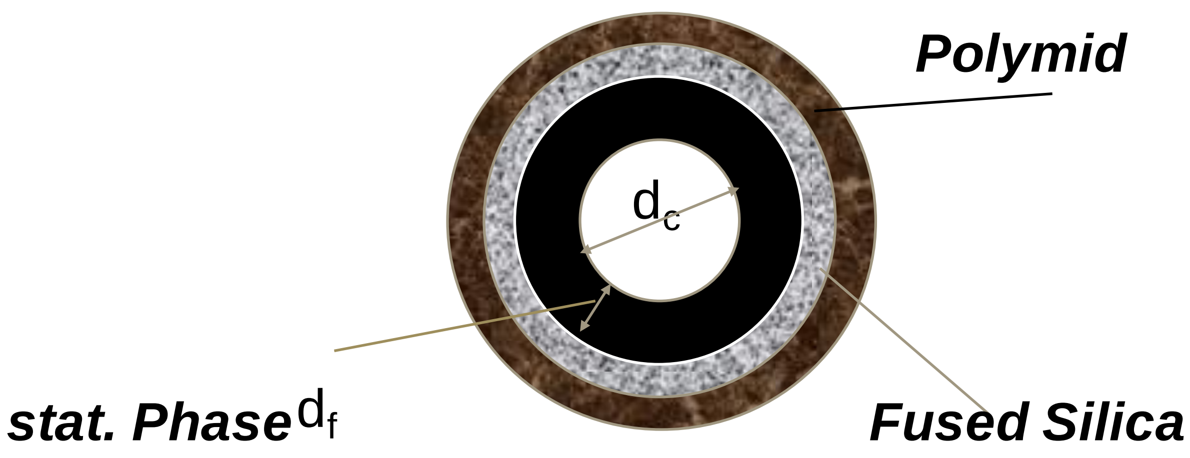
Much more Separation Efficiency with 0,22 mm I.D.

Film Thickness of Stationary Phase

The relevance of the Film Thickness is depending on the Column I.D.

Phase Ratio

Phase Ratio **ß ≈ $d_c/4d_f$**
Volume ratio gas volume to liquid volume



Tendency:

ß is high

- ➢ Good separation for high boiling Componds

ß is low

- ➢ Good separation for low boiling Componds

Film Thickness of Stationary Phase

Phase Ratios for different d_f , d_c

d_f (µm)	d_c (mm) 0,2	0,25	0,32	0,53
0,1	500	625	800	1325
0,2	250	313	400	663
0,33	152	190	250	400
0,5	100	125	160	265
1		63	80	133
2			40	66

Film Thickness of Stationary Phase

For rough Orientation

ß	Application
< 100	Compounds with high Vapor Pressure (Low boiling)
100 - 400	Intermediate Range
> 400	Compounds with low Vapor Pressure (High boiling)

HETP and Carrier Gas

Fig. 1 shows the HETP–u curve for C_{17} at 175 °C analysed by a glass WCOT capillary column (OV–101, 0.4 um, 0.25 mm ID x 25 m) with k = 4.95.

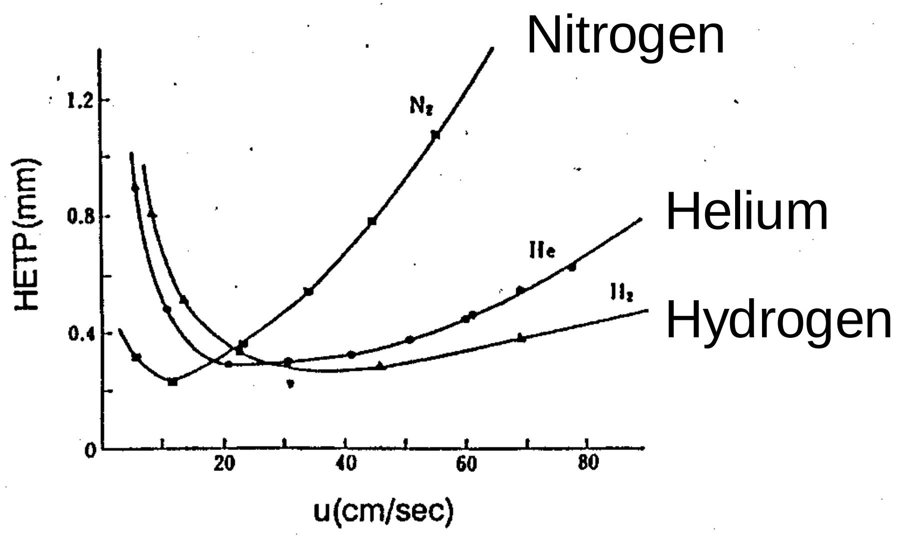


Fig. 1

Conclusion:

Approximately no difference for minimum HETP comparing the Gases

Major differences due to higher flowrates

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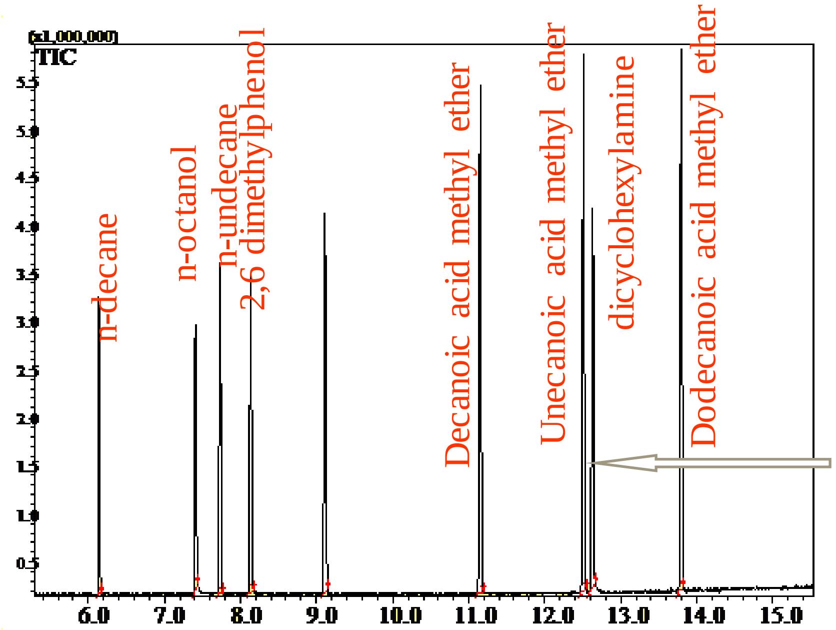
Example – Normal GC vs. Fast GC



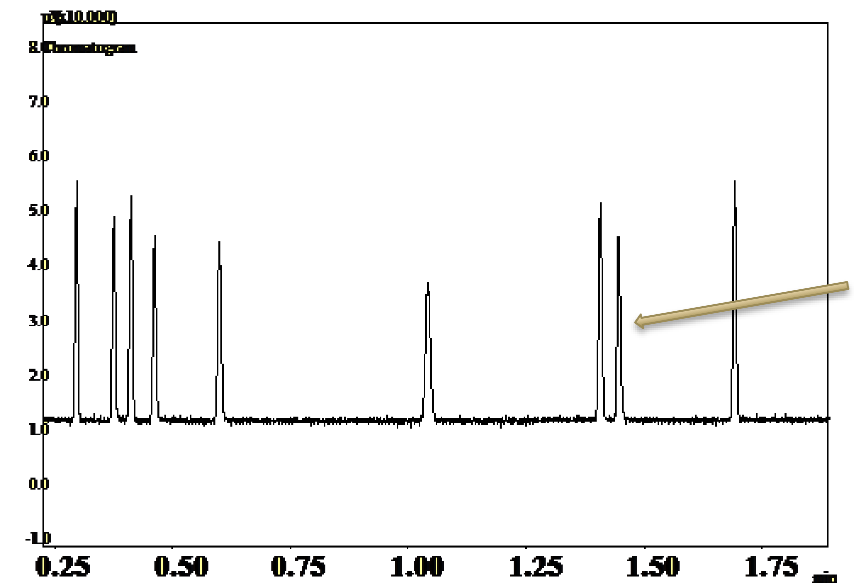
FWHM = 3 s

15 min

DB-5 MS: 30m, 0.25 mm, 0.25 μm

140°C 1 min, 10°C/min to 280 °C,2 min

He 40 cm/s, split 20:1



FWHM = 0.48s

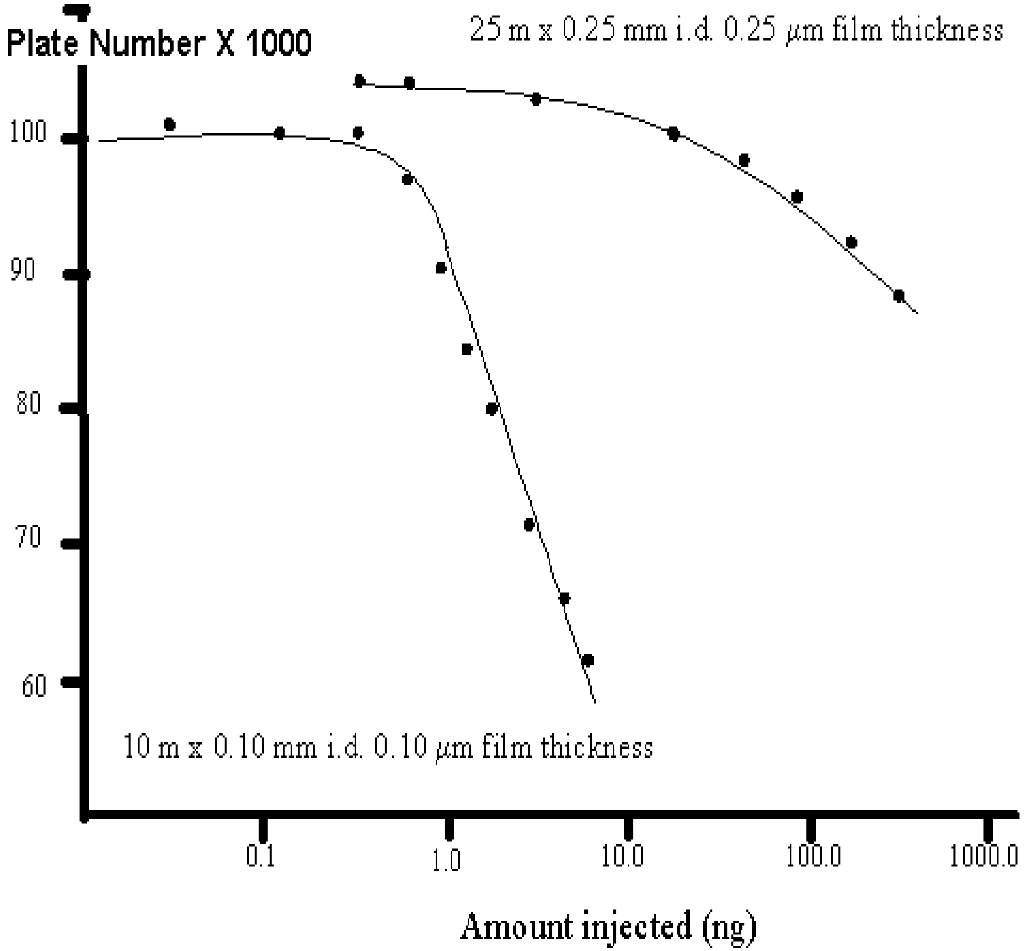
1,75 min

RTX-5 : 10m, 0.1 mm, 0.4 μm

140°C, 1 min
60°C/min to 280 °C, 2min

H2 120 cm/s, diluted 10:1, split 200:1

Sample Amount and Column I.D.



Sample Amount and Column I.D.

ID [mm]	Film thickness DF [µm]	Phase Ratio ß=ID/4DF	Capacity [ng/component]
0.20	0.25	200	70 - 80
0.25	0.25	250	100 - 150
0.25	0.50	125	200 - 250
0.32	0.10	800	60 - 70
0.32	0.32	320	150 - 200
0.32	0.50	160	250 - 300
0.32	1.00	80	400 - 450
0.32	3.00	27	1200 - 1500
0.32	5.00	16	2000 - 2500
0.53	1.00	133	1000 - 1200
0.53	5.00	27	5000 - 6000

Finish