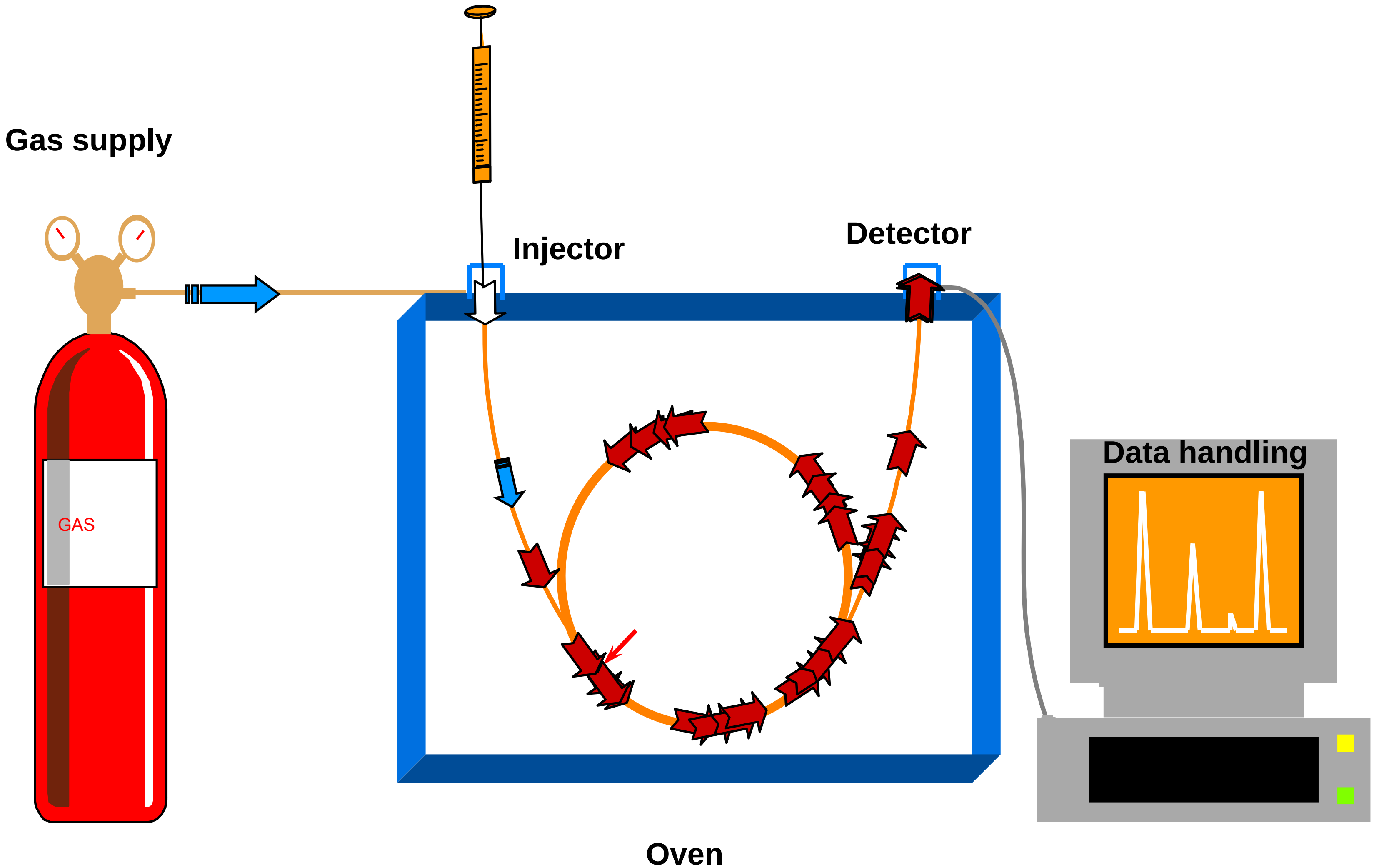
Introduction to Capillary GC

Typical GC System

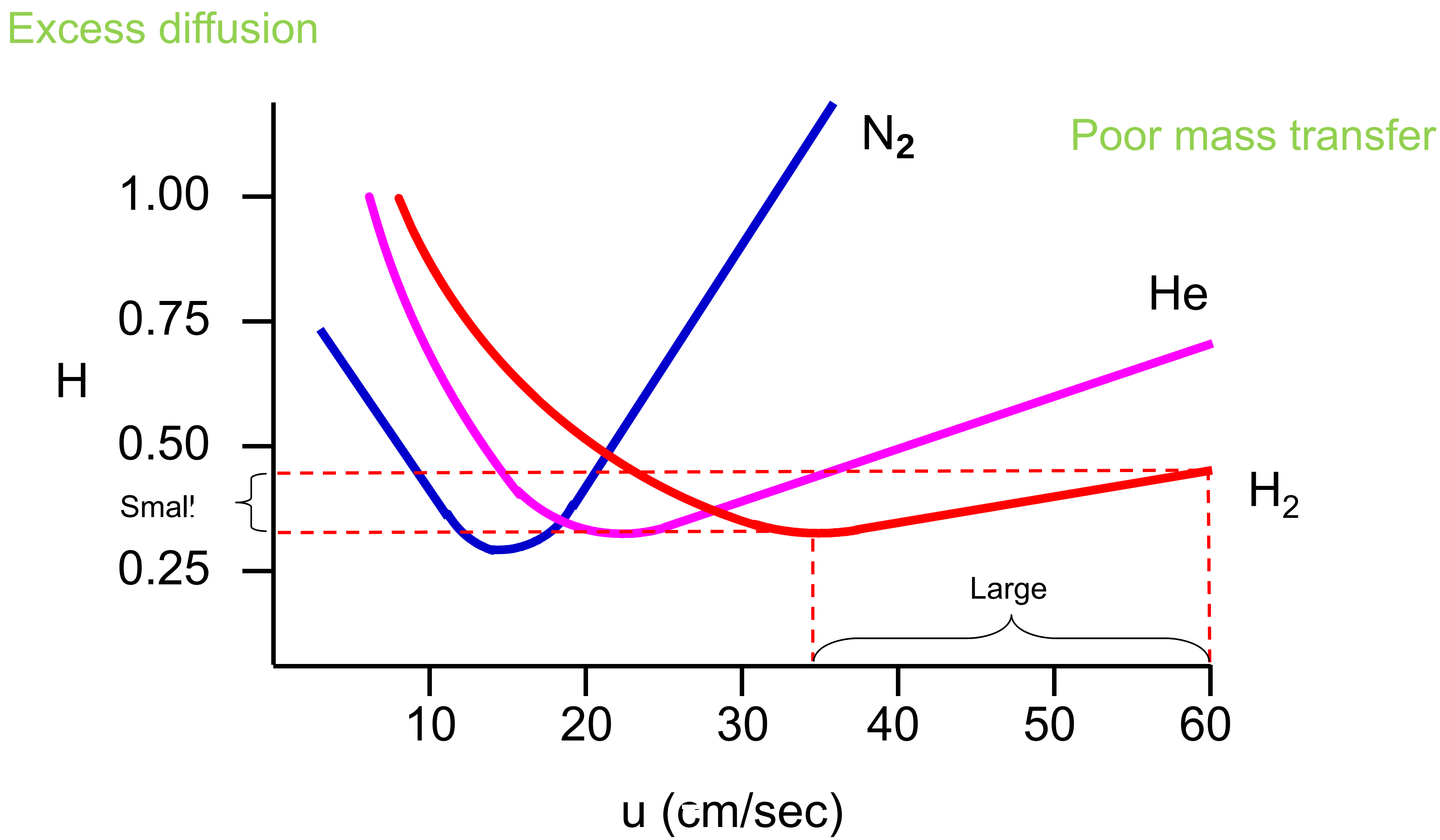


CARRIER GAS

Carries the solutes down the column

Selection and velocity influences efficiency and retention time

VAN DEEMTER CURVES



CARRIER GAS

Type	Velocity Range (u_{opt} – OPGV)
Nitrogen	8-16
Helium	20-40
Hydrogen	30-55

μ_{opt} Opimal Carrier Gas Velocity

OPGV Optimal Practical Gas Velocity
1.5-2 times the μ_{opt}

SAMPLE INJECTION

Goals:

Introduce sample into the column

Reproducible

No efficiency losses

Representative of sample

Sample Introduction

Purpose: To introduce a representative portion of sample onto the column in a reproducible manner, while minimizing sample bandwidth

Syringe Injection

Autosampler injection

Valve Injection

- **Gas sampling valve**
- **Liquid sampling valves**

Objective: The sample must not be chemically altered , unless desired (e.g., derivatization). Success is no contamination, degradation, or discrimination.

Types of Inlets

Purged Packed

Split / Splitless

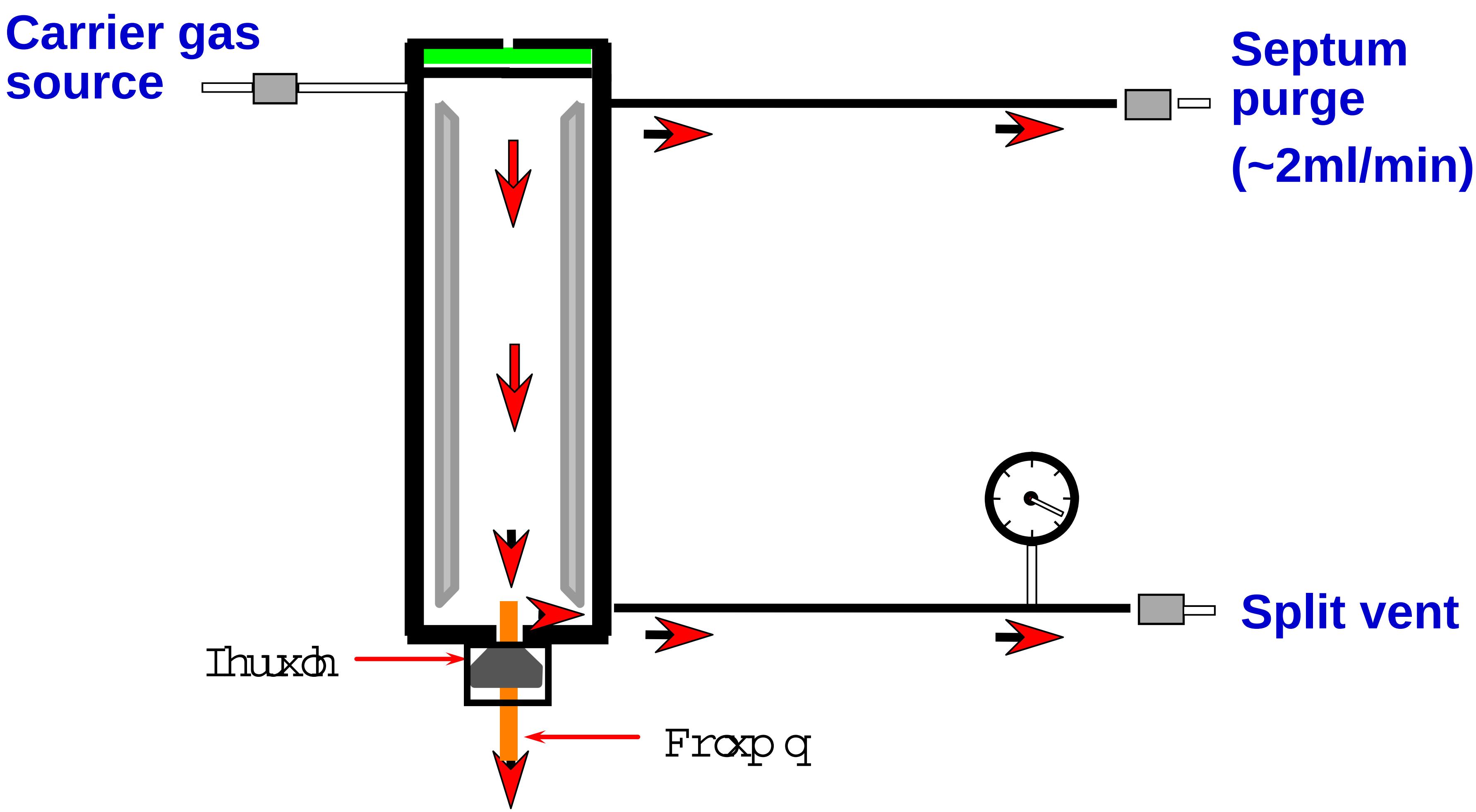
Cool On Column

Programmable Temperature Vaporization

Volatiles Interface

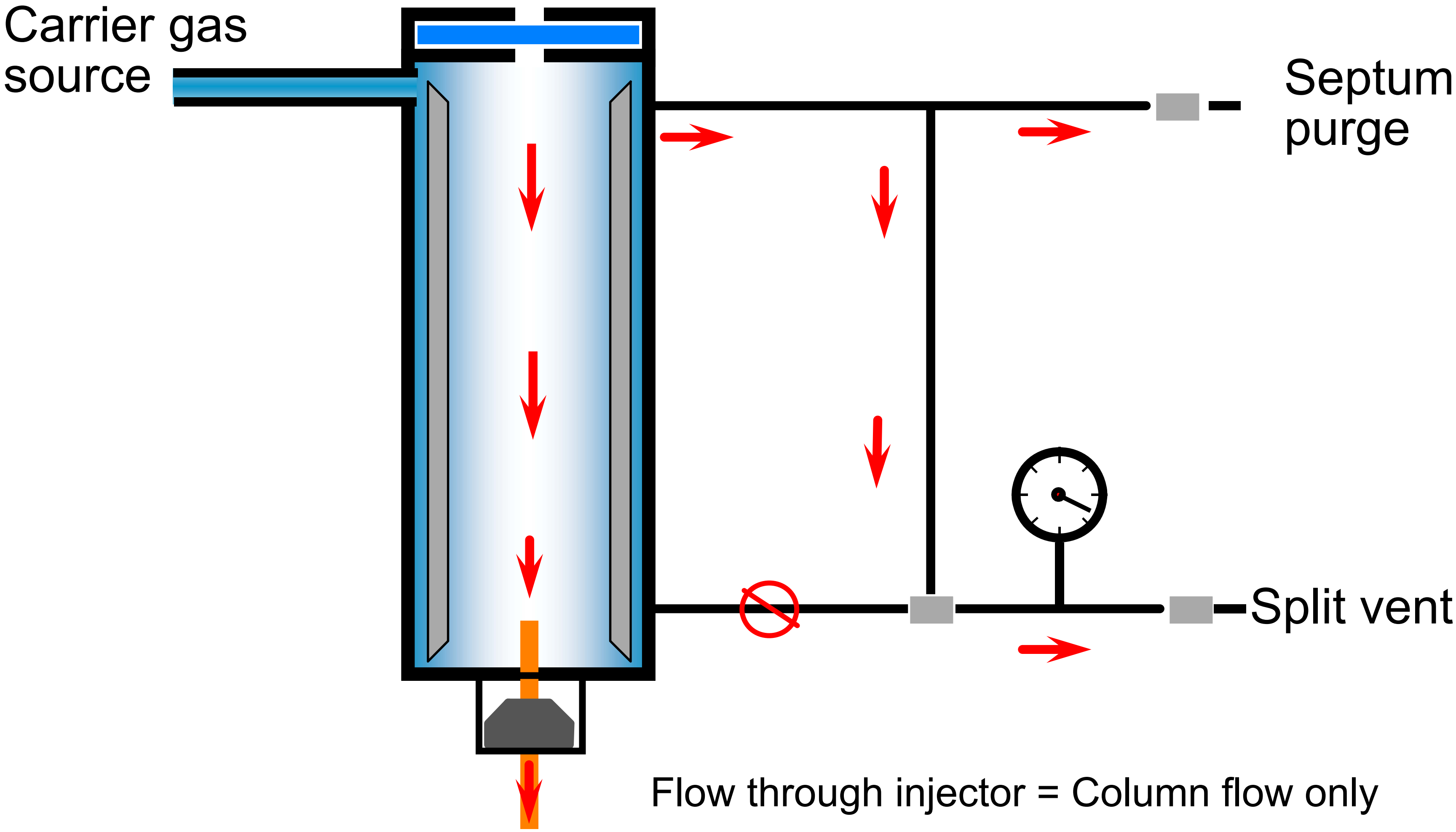
Multi Mode Inlet

SPLIT/SPLITLESS INJECTOR



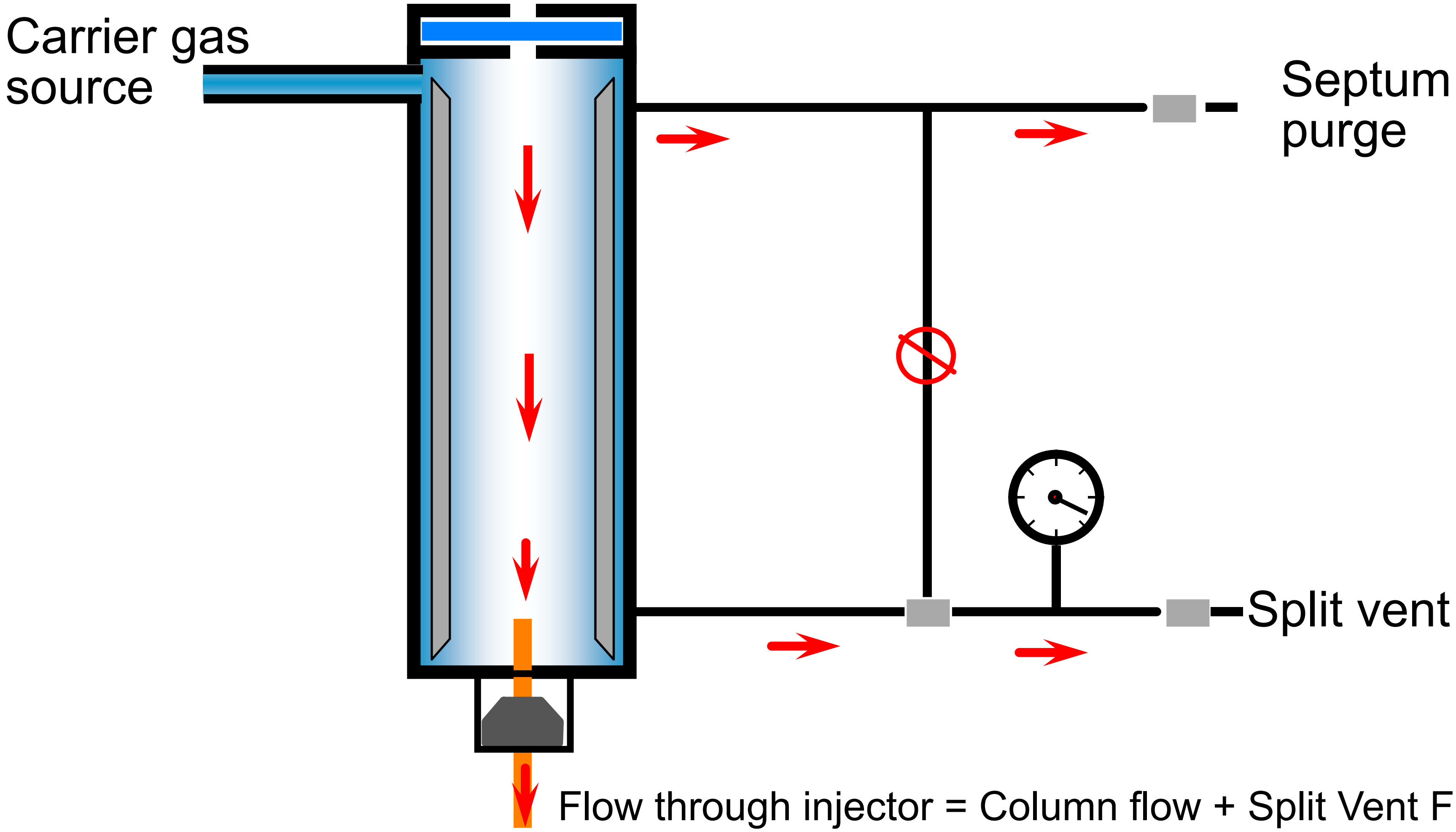
Flow through injector = Column flow + Split Vent Flow

Splitless Injector
Purge Off At Injection



Flow through injector = Column flow only

Splitless Injector
Purge On After Injection



Flow through injector = Column flow + Split Vent Flow

DETECTORS

Purpose:

Responds to some property of the solutes

Converts the interaction into a signal

Immediate

Predictable

Detectors

Detector	Dynamic Range		MDL
TCD	10^5	Universal	400 pg Tridecane
FID	10^7	Responds to C-H bonds	1.8 pg Tridecane
ECD	$5x10^5$	Responds to free electrons	6 fg/mL Lindane
NPD	10^5	Specific to N or P	0.4 pgN/s 0.06 pg P /s
FPD	10^3S, 10^4P	Specific to S or P	60 fg P/s 3.6 pg S/s
SCD	10^4	Specific & Selective to S	0.5 pg S/s
NCD	10^4	Specific & Selective to N	3 pg N/s
MSD		Universal	S/N 400:1 1 pg/uL OFN

DATA HANDLING

Converts the detector signal into a chromatogram

- **Integrator**
- **Software Program**

COMPOUND REQUIREMENTS FOR GC

Only 10-20% of all compounds are suitable for GC analysis

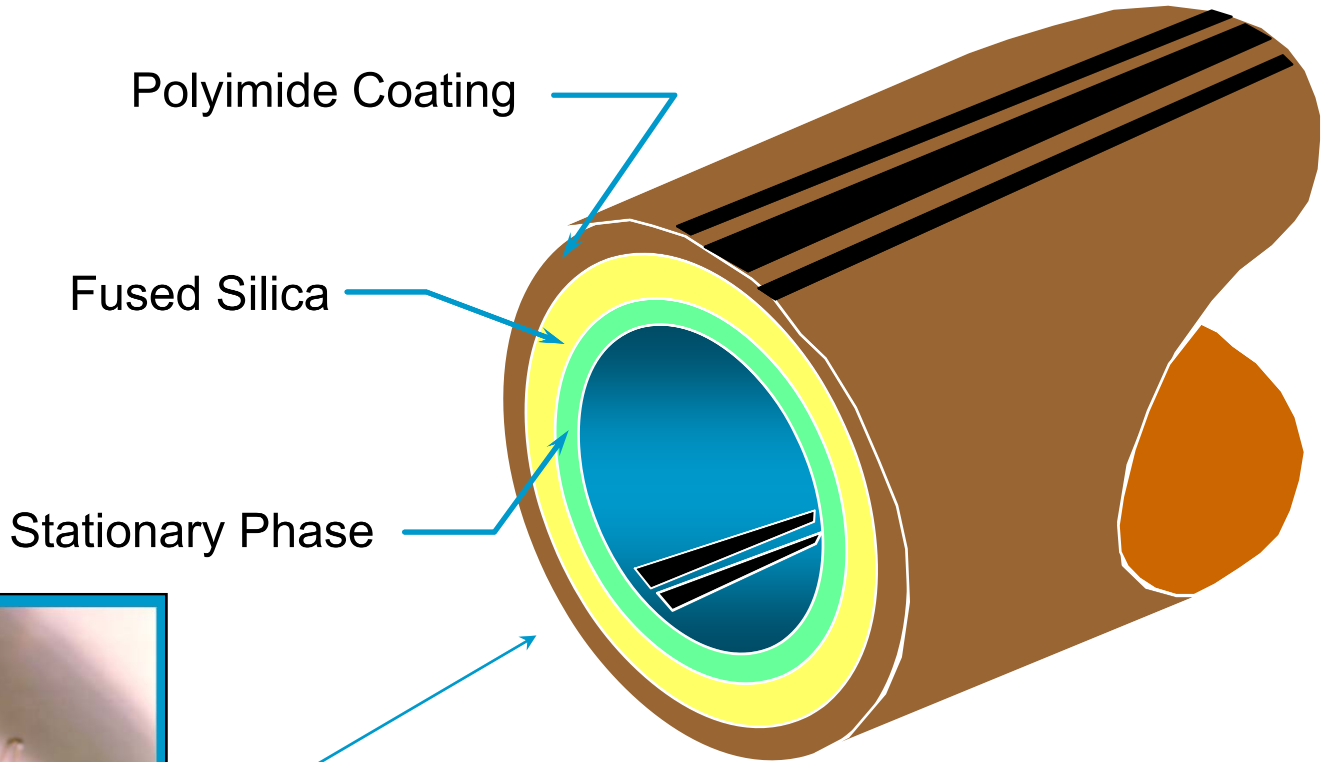
The compounds must have:

- ✓ Sufficient volatility
- ✓ Thermal stability

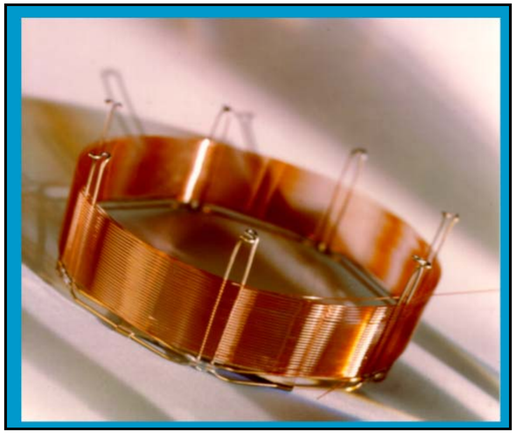
NO Inorganic Acids and Bases

Be mindful of salts!

Typical Capillary Column

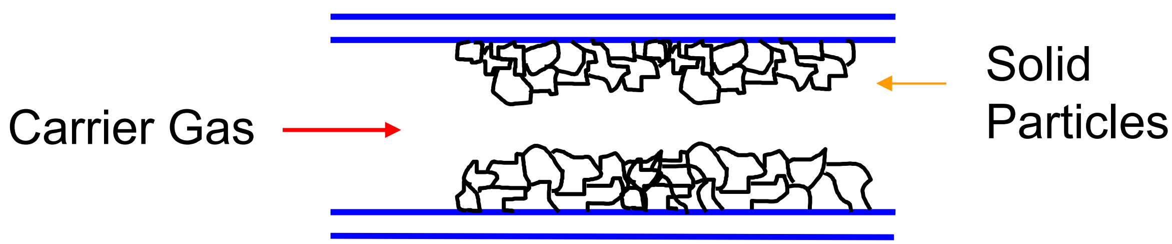


Expanded view of capillary tubing

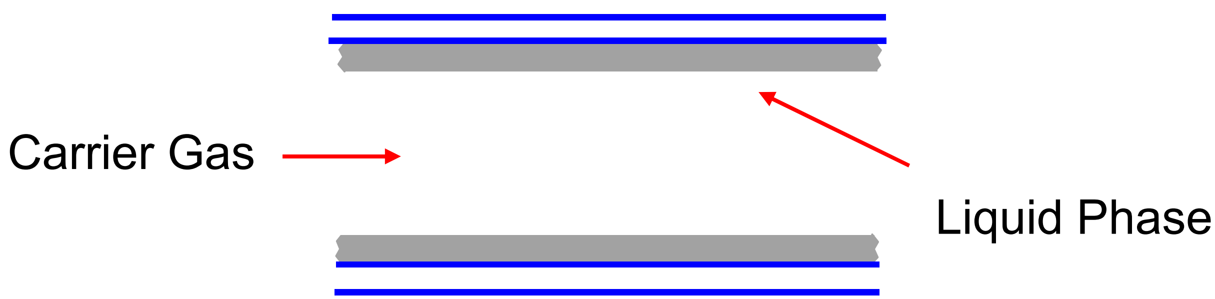


CAPILLARY COLUMN TYPES

Porous Layer Open Tube (PLOT)



Wall Coated Open Tube (WCOT)

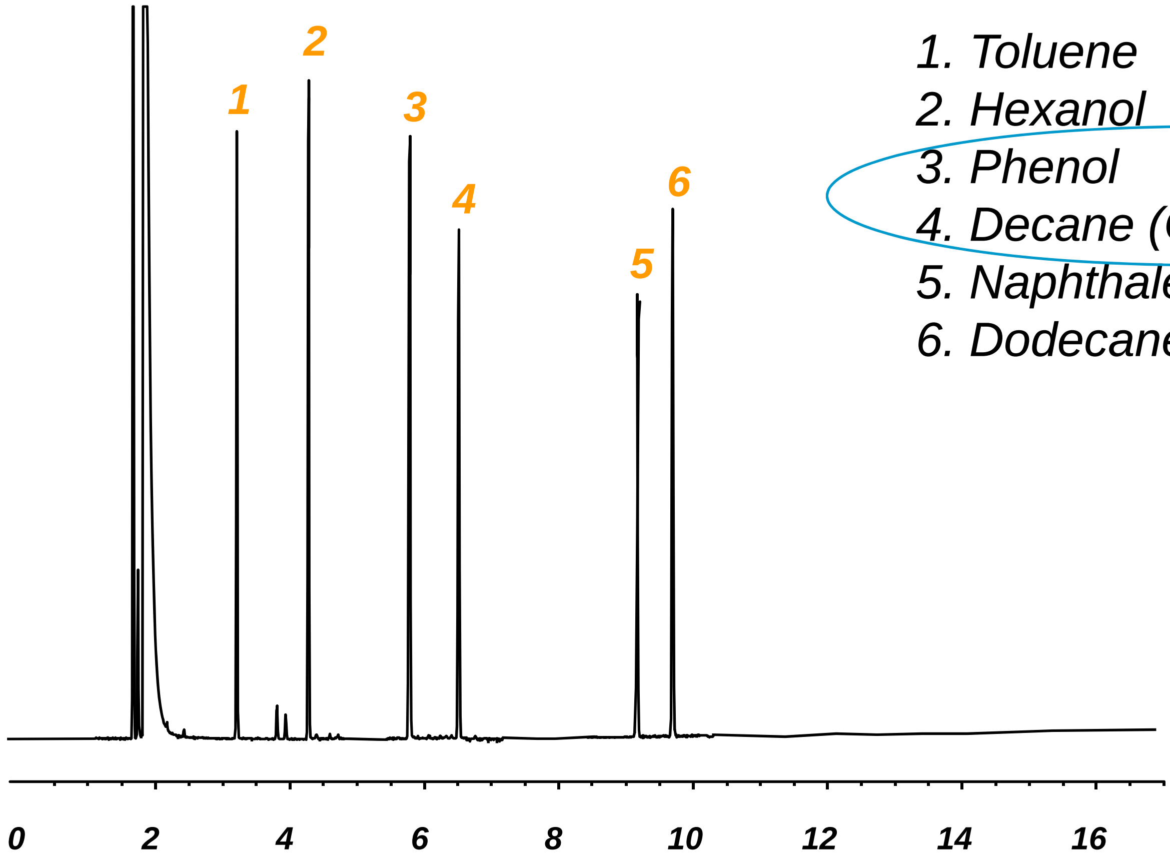


WCOT Column Types

Agilent J&W has <u>over 50 different stationary phase offerings</u>

Low Polarity			Mid Polarity			High Polarity		
CP-Sil 2	DB & HP-1ms UI	DB & HP-5ms UI	DB-XLB	DB-225ms	DB-ALC1	HP-88	DB-WAX	CP-TCEP
DB-MTBE	DB & HP-1ms	DB & HP-5ms	VF-Xms	DB-225	DB-Dioxin	CP-Sil 88	DB-WAXetr	
CP-Select CB MTBE	VF-1 ms	VF-5ms	DB-35ms UI	CP-Sil 43 CB	DB-200	DB-23	HP-INNOWax	
	DB & HP-1	DB & HP-5	DB & VF-35ms	VF-1701 ms	VF-200ms	VF-23 ms	VF-WAXms	
	CP-Sil 5 CB	CP-Sil 8 CB	DB & HP-35	DB-1701	DB-210		CP-Wax 57 CB	
	Ultra 1	Ultra 2	DB & VF-17ms	CP-Sil 19 CB	DX-4		DB & HP-FFAP	
	DB-1ht	VF-DA	DB-17	HP-Blood Alcohol			DB-WAX FF	
	DB-2887	DB-5.625	HP-50+	DB-ALC2			CP-FFAP CB	
	DB-Petro/ PONA	DB & VF-5ht	DB-17ht	DX-1			CP-WAX 58 FFAP CB	
	CP-Sil PONA CB	CP-Sil PAH CB	DB-608				CP-WAX 52 CB	
	DB-HT SimDis	Select Biodiesel	DB-TPH				CP-WAX 51	
	CP-SimDis	SE-54	DB-502.2				CP-Carbowax 400	
	CP-Volamine		HP-VOC				Carbowax 20M	
	Select Mineral Oil		DB-VRX				HP-20M	
	HP-101		DB-624				CAM	
	SE-30		VF-624ms					
			CP-Select 624 CB					
			DB-1301					
			VF-1301ms					
			CP-Sil 13 CB					

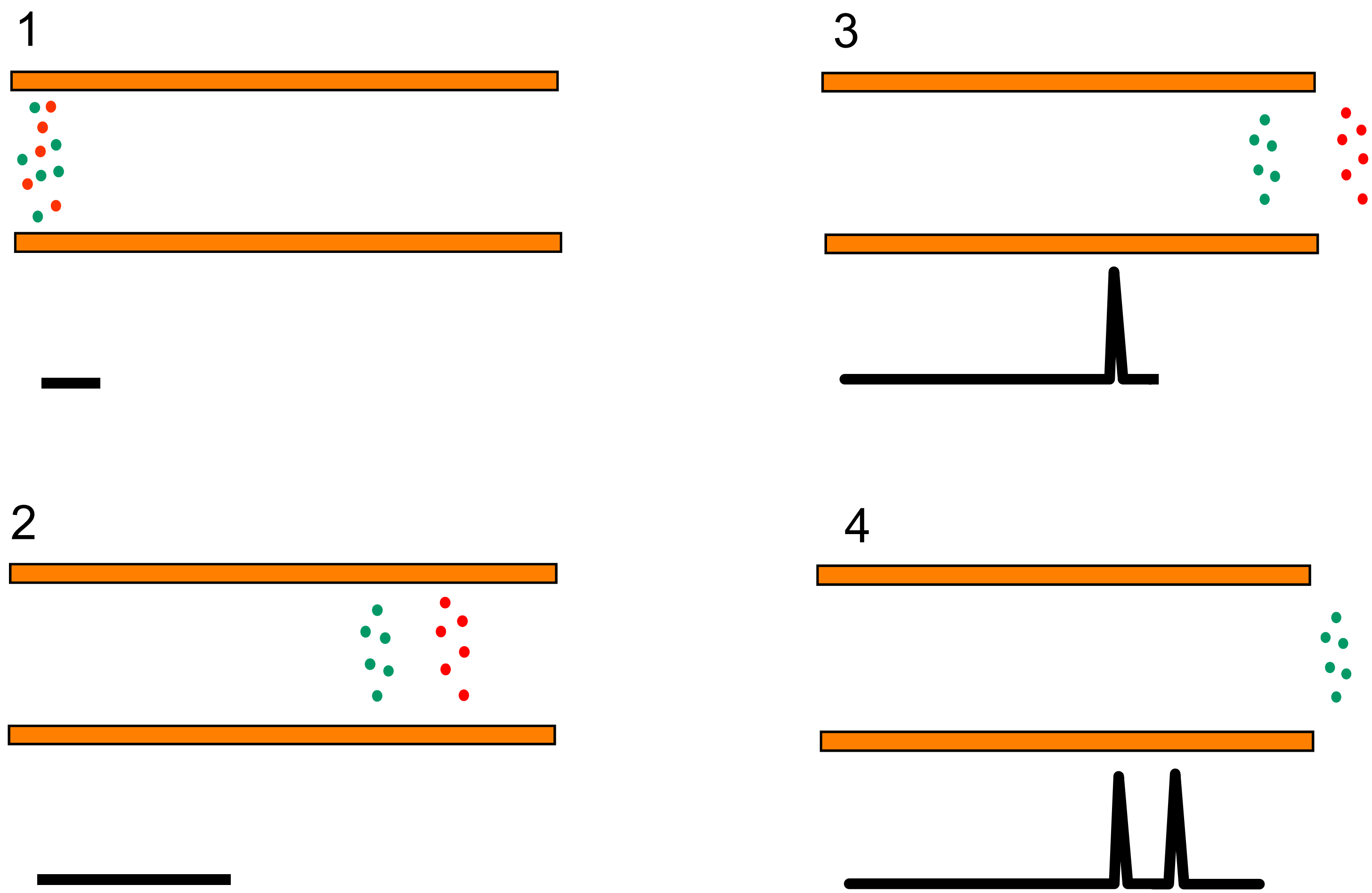
100% Methyl Polysiloxane “boiling point column”



1. Toluene 110°C
2. Hexanol 158°C
3. Phenol 181°C
4. Decane (C10) 174°C
5. Naphthalene 218°C
6. Dodecane (C12) 216°C

Strong Dispersion
No Dipole
No H Bonding

SEPARATION PROCESS



TWO PHASES

Solute molecules distribute into the two phases

DISTRIBUTION CONSTANT (K_C)

$$N_C \; @ \; \frac{\text{conc. of solute in stationary phase}}{\text{conc. of solute in mobile phase}}$$

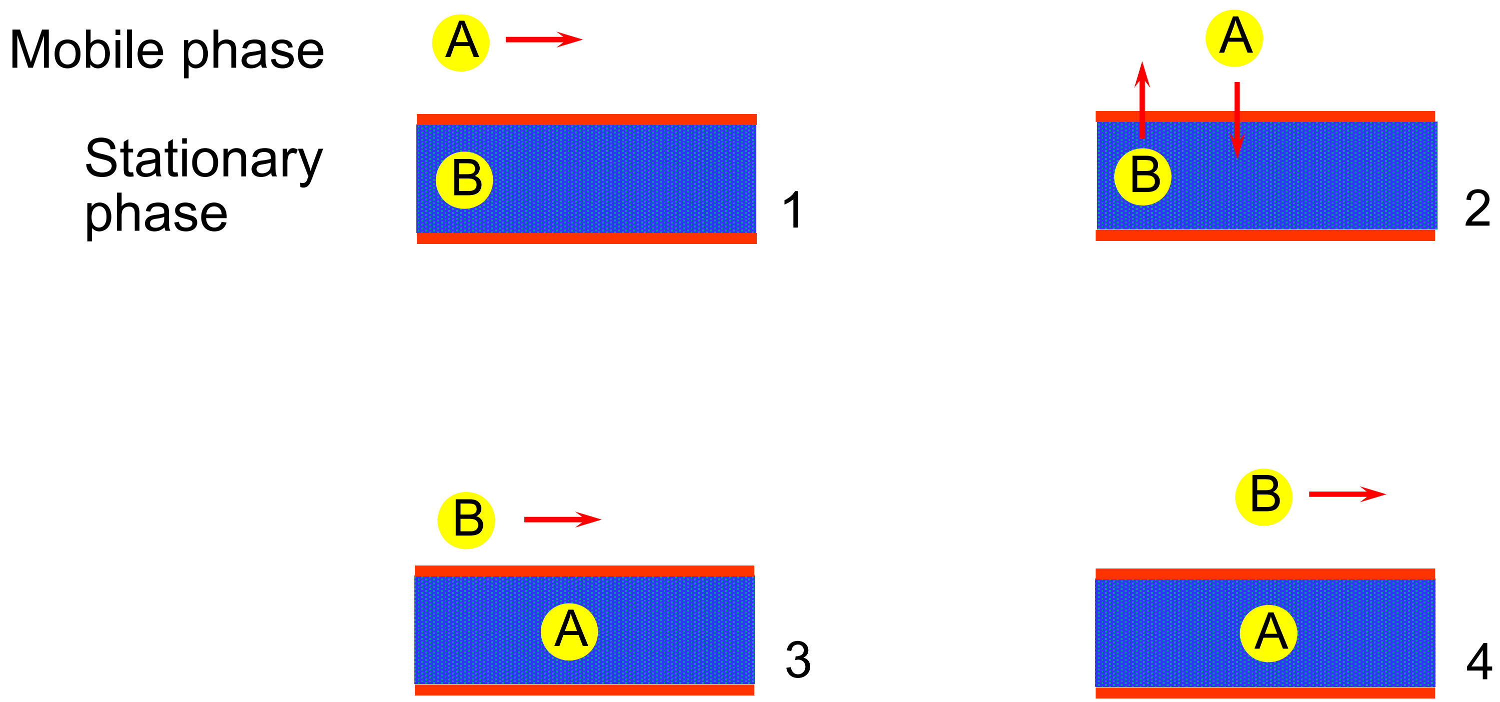
K_C formerly written as K_D

SOLUTE LOCATION

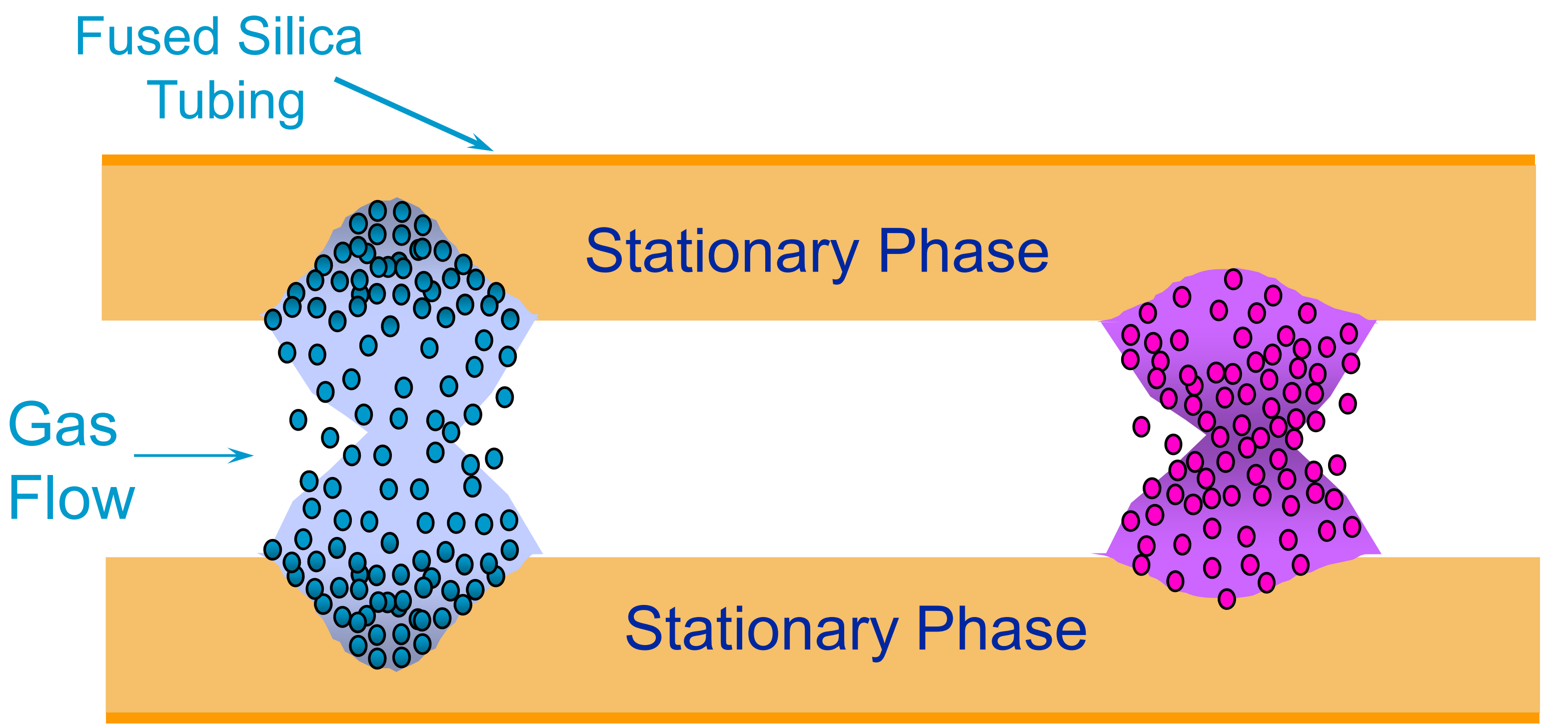
In stationary phase = Not moving down the column

In mobile phase = Moving down the column

SEPARATION PROCESS
Movement Down the Column



K_C AND RETENTION



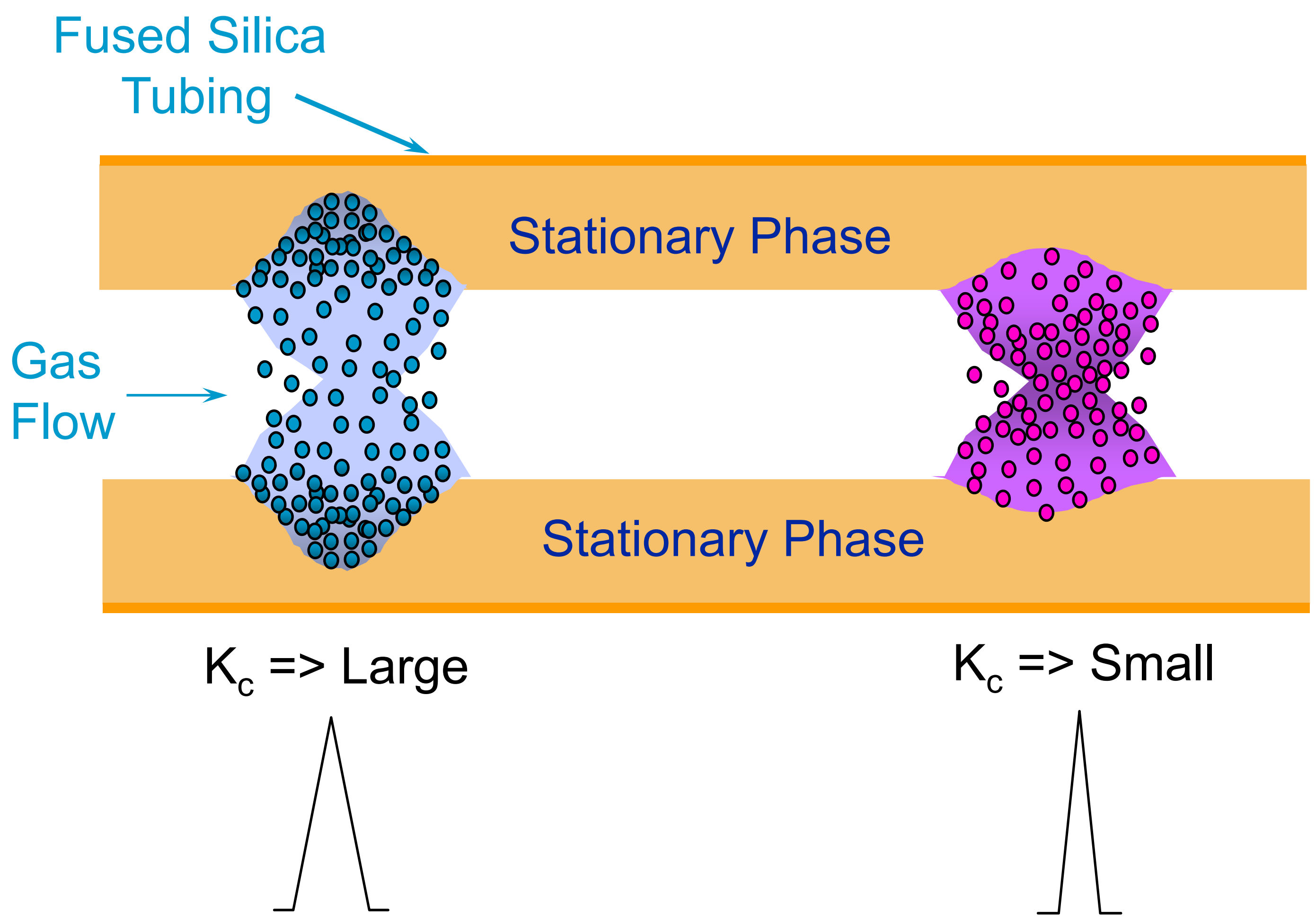
K_c => Large

retention

K_c => Small

retention

K_C AND PEAK WIDTH
Time of Elution



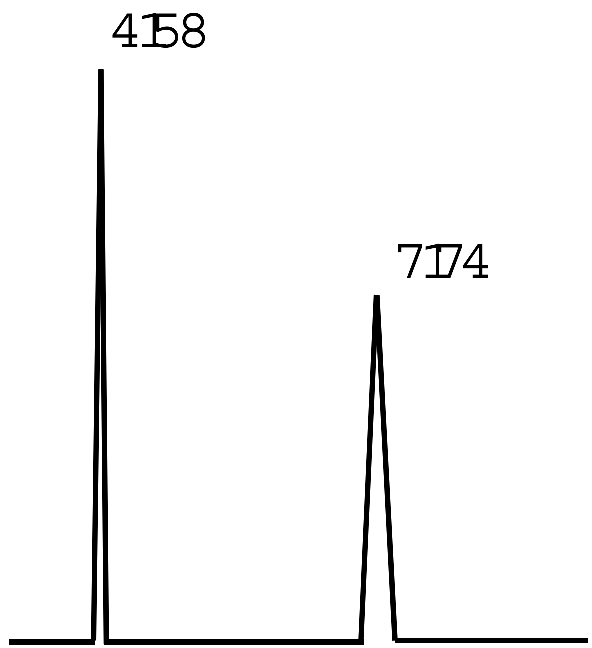
THREE PARAMETERS THAT AFFECT K_C

Solute:
different solubilities in a stationary phase

Stationary phase:
different solubilities of a solute

Temperature:
K_C decreases as temperature increases

RETENTION TIME t_r



Time for a solute to travel through the column

ADJUSTED RETENTION TIME t_r'

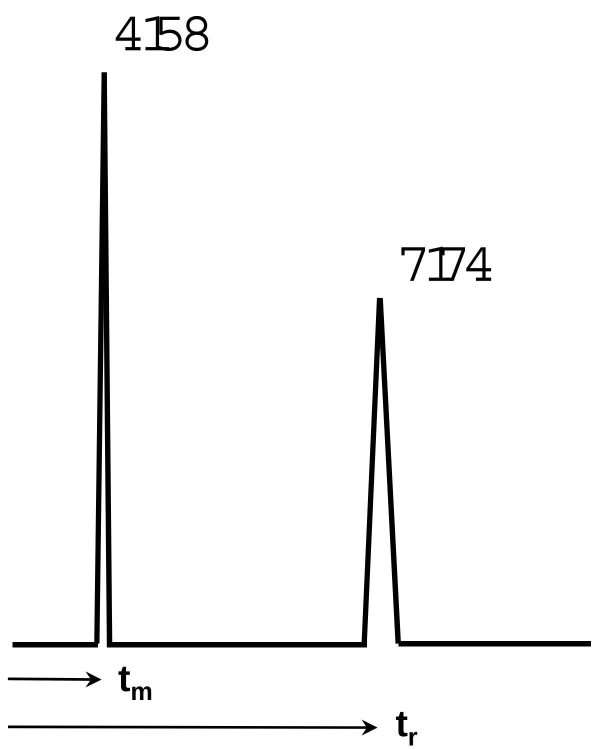
Actual time the solute spends in the stationary phase

$$t_r' = t_r - t_m$$

t_r = retention time
t_m = retention time of a non-retained solute

ADJUSTED RETENTION TIME

t_r'



t'_r = tr - tm

t'_r = 4.41 - 1.25

t'_r = 3.16 min = time spent in stationary phase

TIME IN THE MOBILE PHASE

All solutes spend the same amount of time in the mobile phase.

RETENTION FACTOR (k)

Ratio of the time the solute spends in the stationary and mobile phases

$$k = \frac{t_r - t_m}{t_m}$$

t_r = retention time
t_m = retention time of non-retained compound
Formerly called partition ratio; k'

RETENTION FACTOR (k)

Relative retention

Linear

Factors out carrier gas influence

PHASE RATIO
(β)

$$\beta = \frac{u}{5g_i}$$

r = radius (μm)

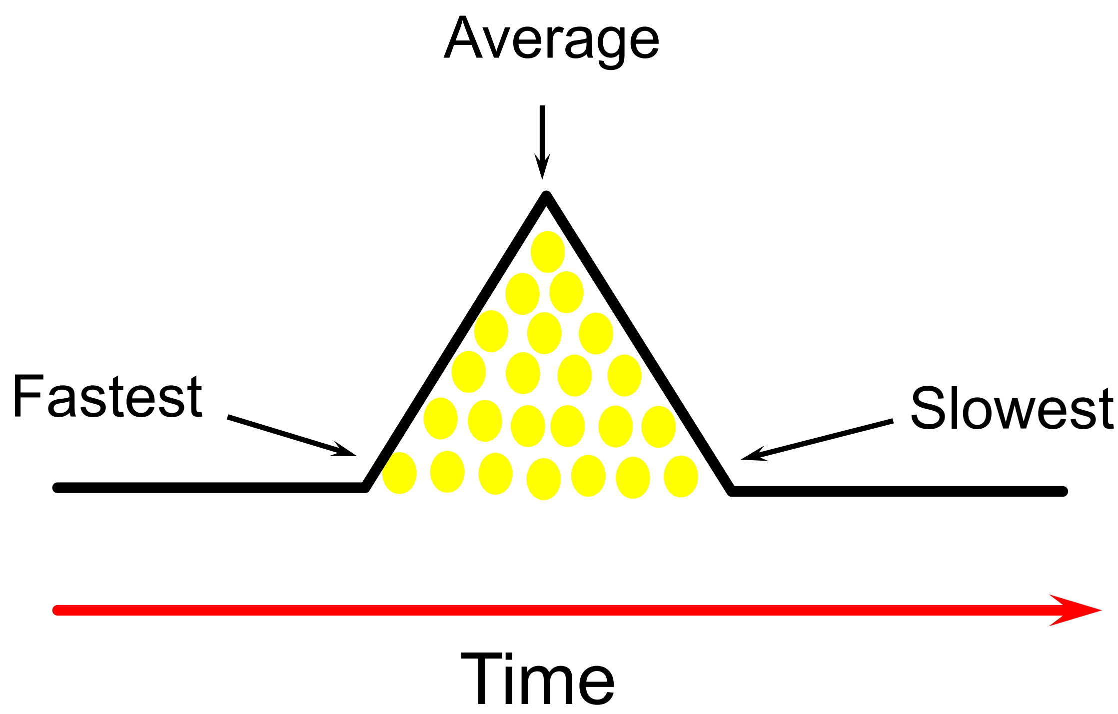
d_f = film thickness (μm)

DISTRIBUTION CONSTANT (K_c)

$$K_c = k\beta$$

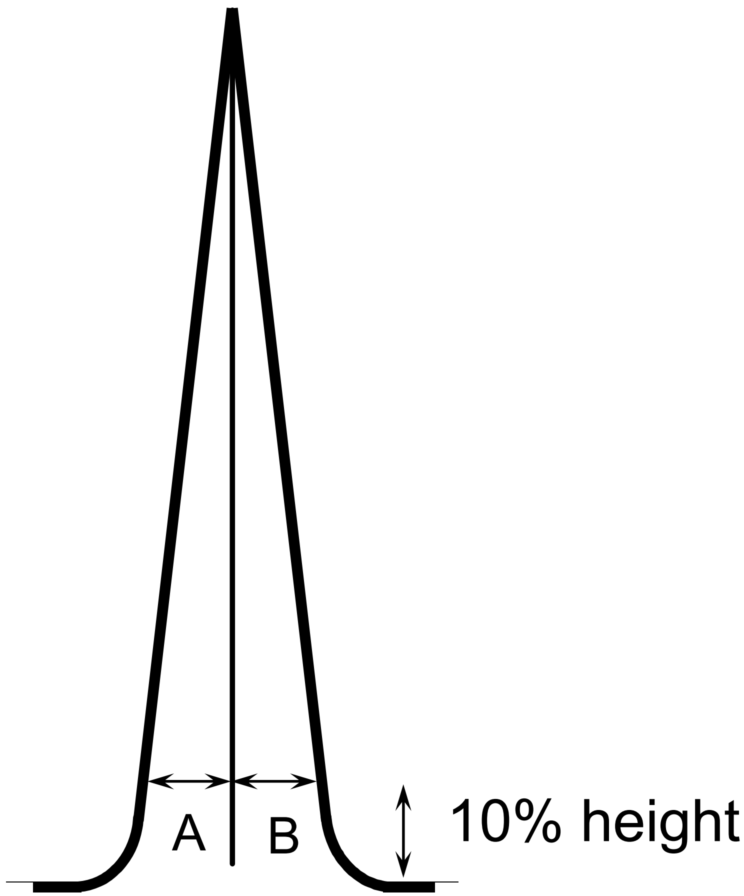
$$n \;@\; \frac{t_r'}{t_m} \qquad \beta \;@\; \frac{r}{2d_f}$$

RANGE OF RETENTION



PEAK SYMMETRY

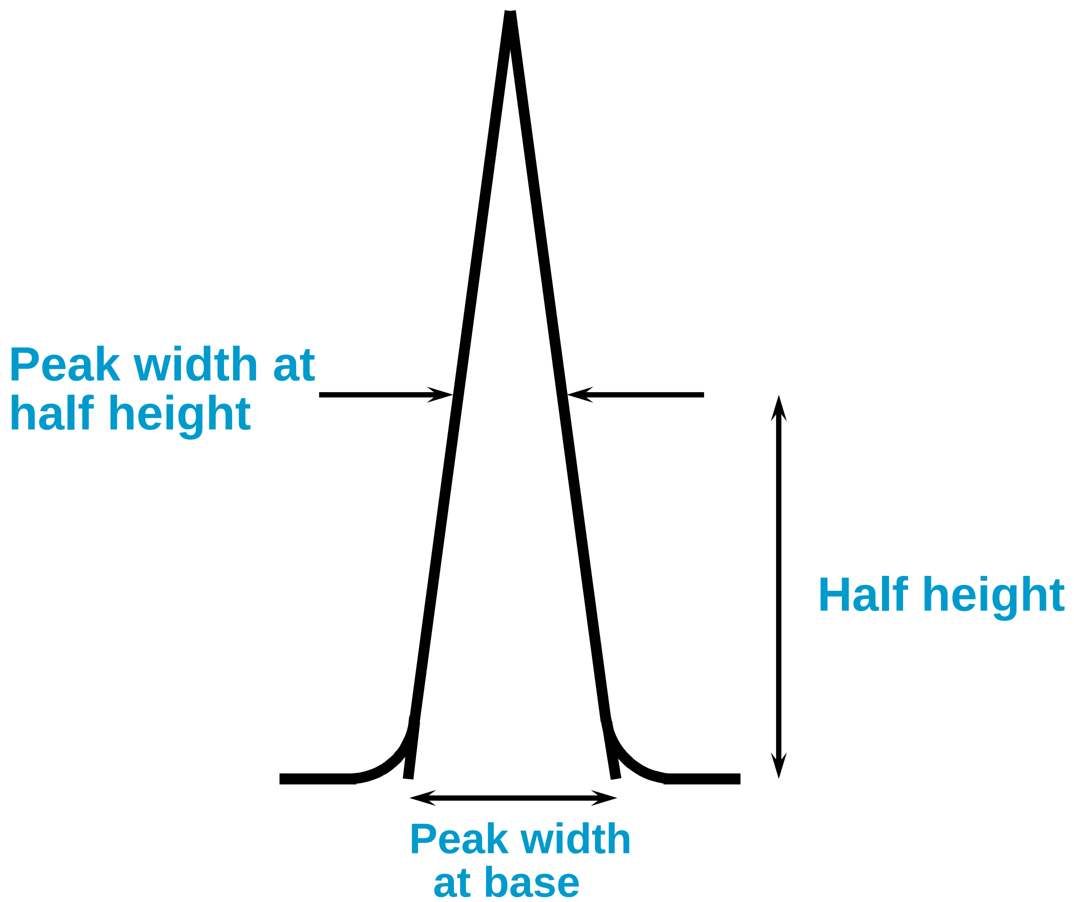
$$\text{Symmetry} = \frac{A}{B}$$



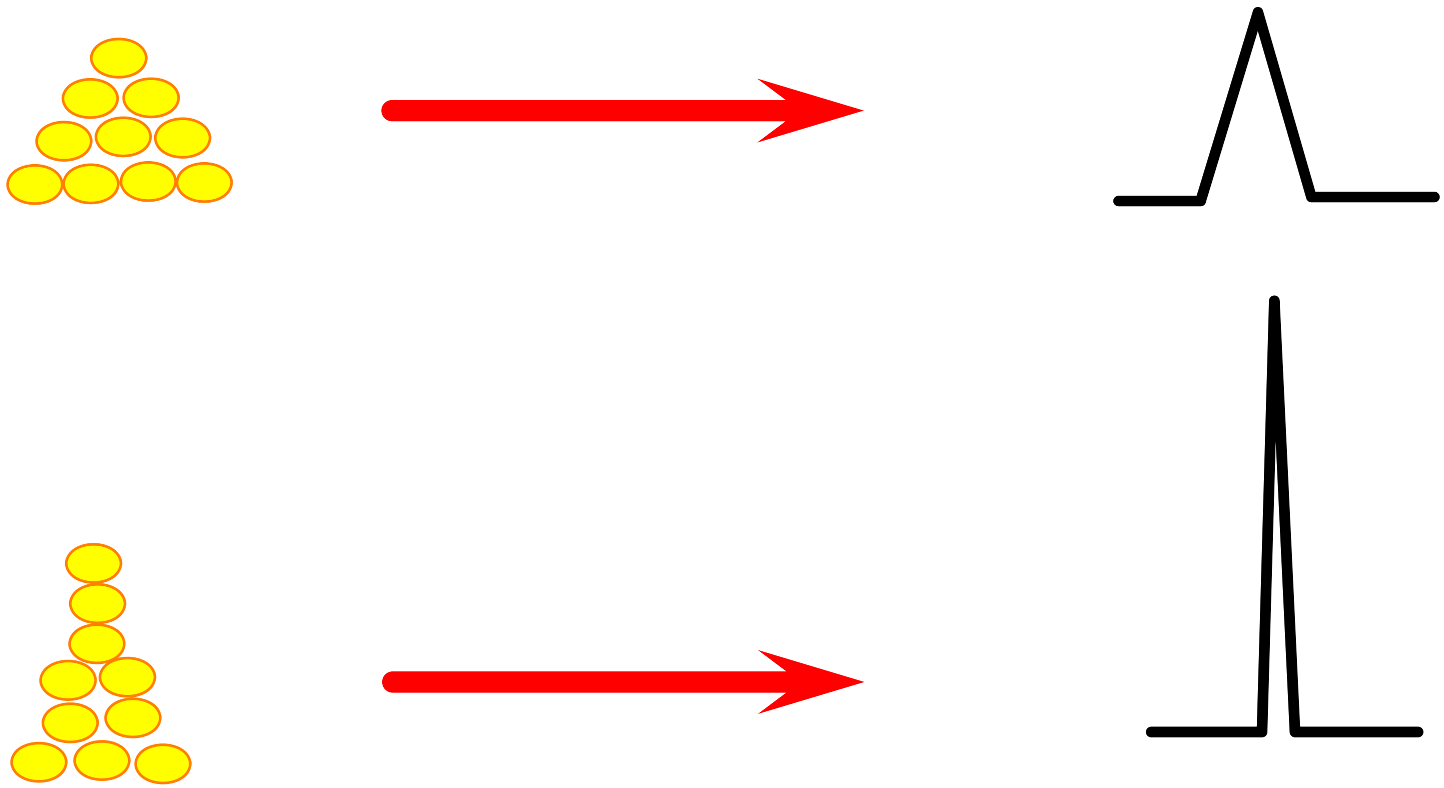
Tailing : Symmetry <1

Fronting : Symmetry >1

PEAK WIDTH



PEAK WIDTH



EFFICIENCY
Theoretical Plates (N)

Large number implies a better column

Often a measure of column quality

Relationship between retention time and width

THEORETICAL PLATES (N)

$$N = 5.545 \left(\frac{t_r}{W_h} \right)^2$$

t_r = retention time
W_h = peak width at half height (time)

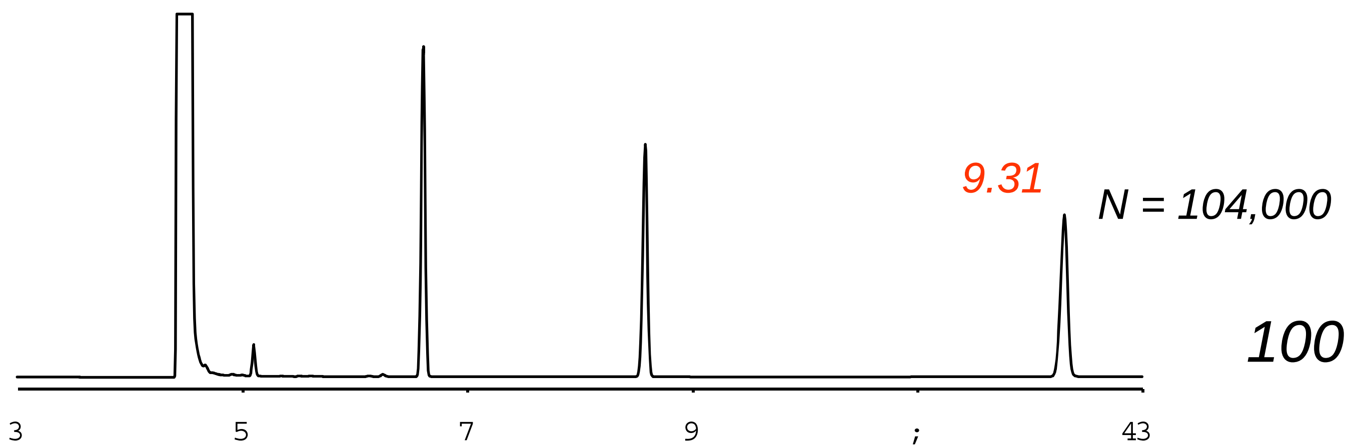
EFFICIENCY MEASUREMENT
Cautions

Actually, measurement of the GC system

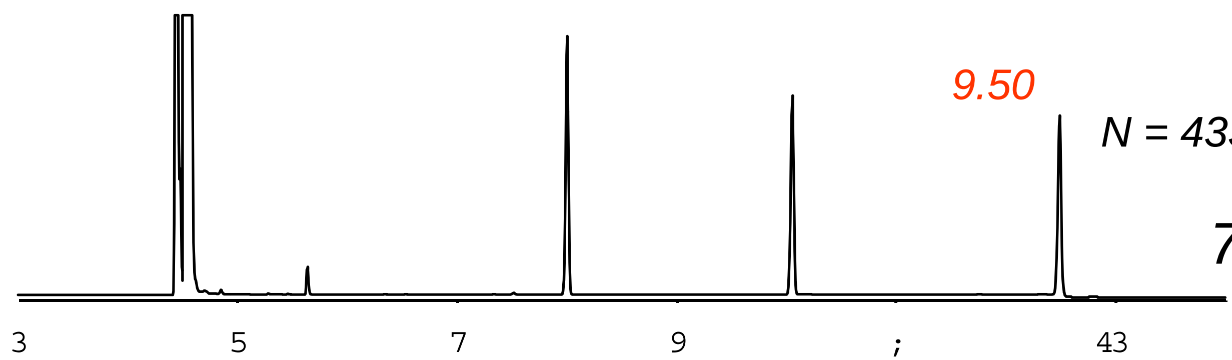
Condition dependent

Use a peak with k>5

ISOTHERMAL VS. TEMPERATURE PROGRAMMING
Efficiency



100°C isothermal



75-135°C at 5°/min

DB-1, 30 m x 0.25 mm ID, 0.25 um
He at 37 cm/sec
C10, C11, C12

SEPARATION VS. RESOLUTION

Separation: time between peaks

Resolution: time between the peaks while considering peak widths

SEPARATION FACTOR (α)

$$\alpha = \frac{k_2}{k_1}$$

co-elution: $\alpha = 1$

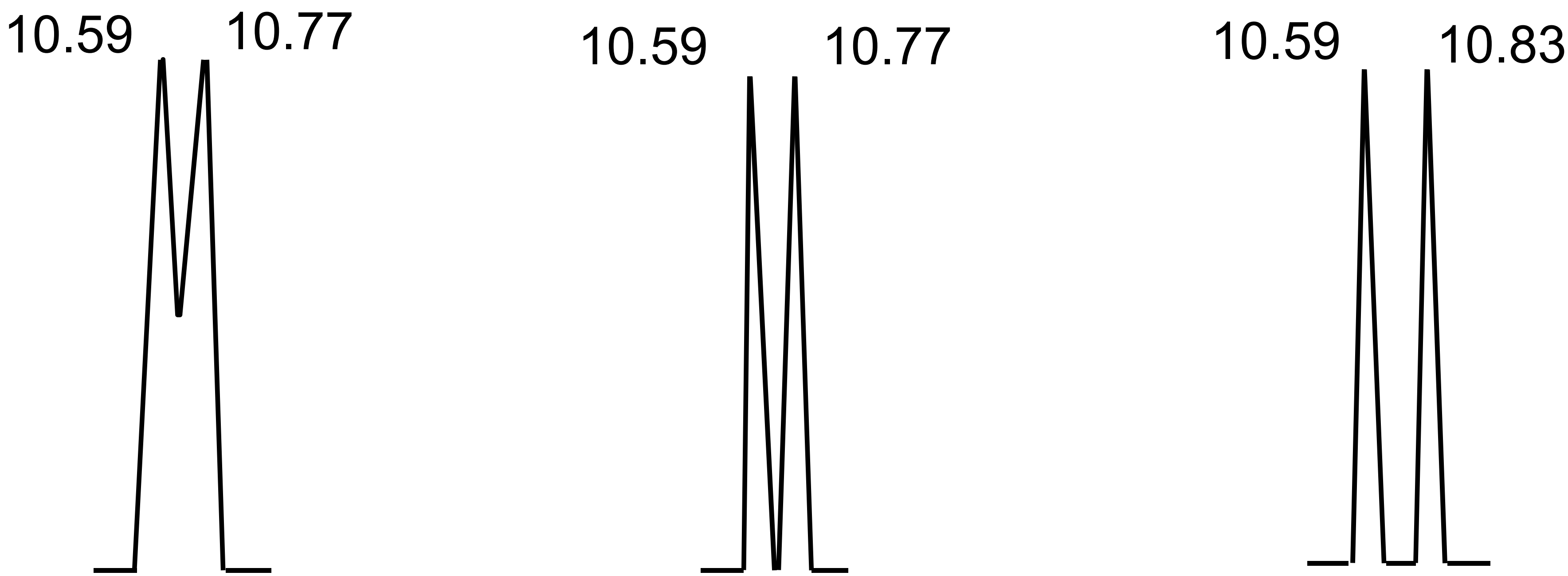
k_2 = retention factor of 2nd peak
k_1 = retention factor of 1st peak

RESOLUTION (Rs)

$$R_s = 1.18 \left(\frac{t_{r2} - t_{r1}}{W_{h1} + W_{h2}} \right)$$

t_r = retention time
W_h = peak width at half height (time

RESOLUTION
Baseline Resolution: Rs = 1.5



$W_h = 0.105$

R = 0.84

% = 50

$W_h = 0.059$

R = 1.50

% = 100

$W_h = 0.059$

R = 2.40

% = 100

Resolution

$$R_s = \frac{\sqrt{N}}{4}\left(\frac{k}{k+1}\right)\left(\frac{\alpha-1}{\alpha}\right)$$

N	= Theoretical plates
k	= Retention factor
α	= Separation factor

INFLUENCING RESOLUTION

Variables:

N: column dimensions, carrier gas

a: stationary phase, temperature

k: stationary phase, temperature,
column dimensions

Conclusions

The GC is comprised of an inlet, column and detector that all work together to produce good chromatography

Separation (via K_c) is based on 3 things:

- Solute: different solubilities/interaction in a given stationary phase
- Stationary phase: different solubilities/interaction of a solute (correct column selection is critical!)
- Temperature: K_C decreases as temperature increases

When in doubt, contact Agilent Technical Support!

Additional Recorded –Seminars

http://www.chem.agilent.com/en-US/Training-Events/eSeminars/14736A/Pages/default.aspx

Advanced Topic: Trace Level Analysis for Active Compounds Made Routine with Agilent J&W Ultra Inert Capillary GC Columns

Advanced Topic – Tips and Tricks of Injector Maintenance

Advanced Topic – Practical, Faster GC Applications

Carrier Gases in Capillary GC

Selection of a Capillary GC Column

Secrets of GC Column Dimensions

Techniques for Making Your GC Analysis More Repeatable and Robust

Techniques, Tips and Tricks of Troubleshooting GC Capillary Systems

Practical Steps in GC Method Development

Understanding the Inlets - How to Choose the Right One

Agilent J&W Scientific Technical Support

800-227-9770 (phone: US & Canada)*

**** Select option 3..3..1***

866-422-5571 (fax)

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