Understanding Gas Chromatography

What is Really Going on Inside the Box?

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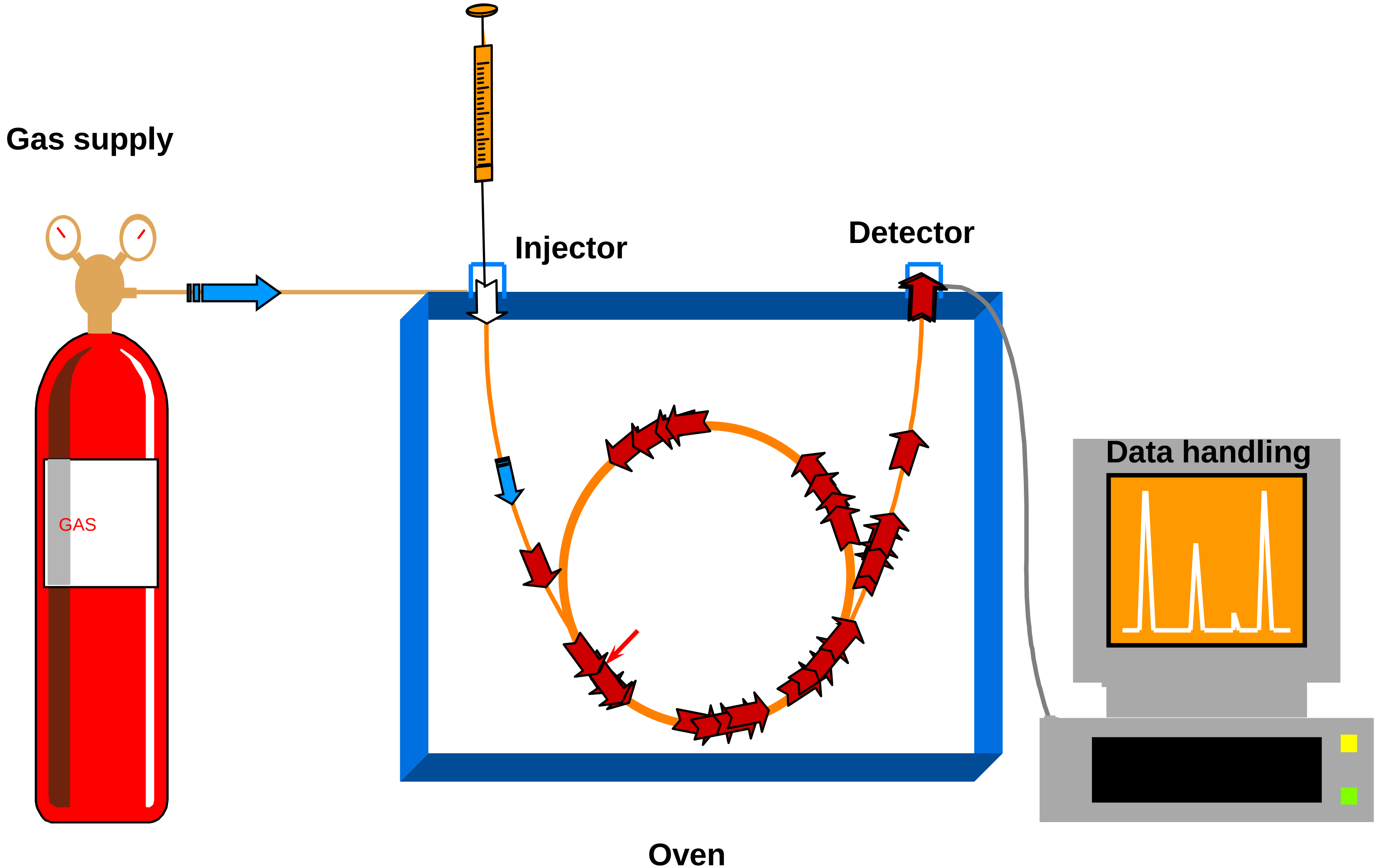
t_r
?
$k = \frac{t_r - t_m}{t_m}$
K_c
?
Kβ
?
R_s

Typical GC System

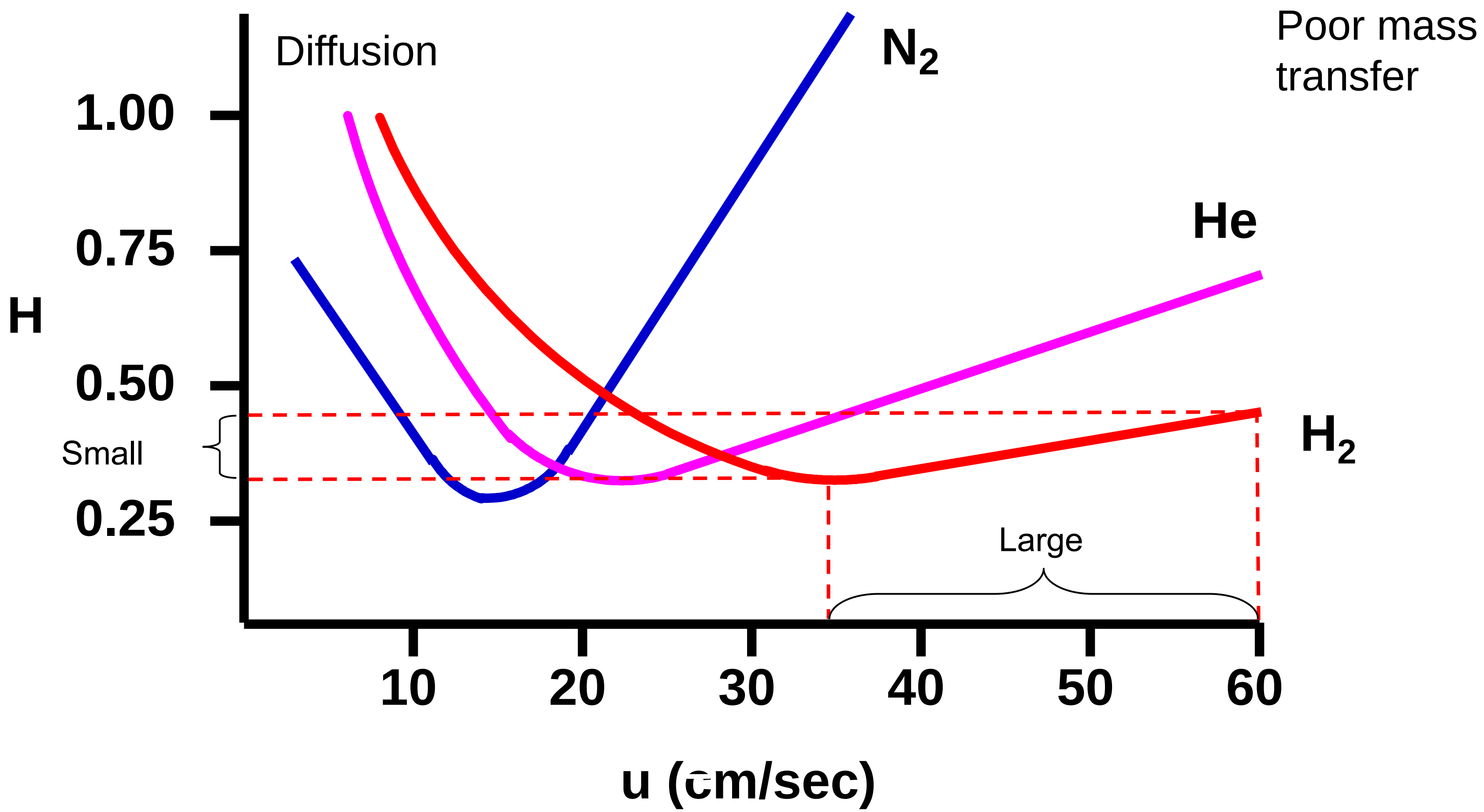


CARRIER GAS

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

Sample Introduction

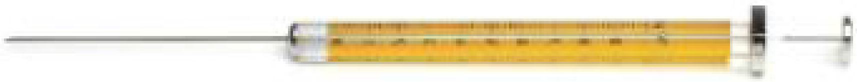
Purpose: To introduce a representative portion of sample onto the column in a reproducible manner, while minimizing sample bandwidth

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 not contamination, degradation, or discrimination.

Injection Port Types

Purged Packed

Split/Splitless

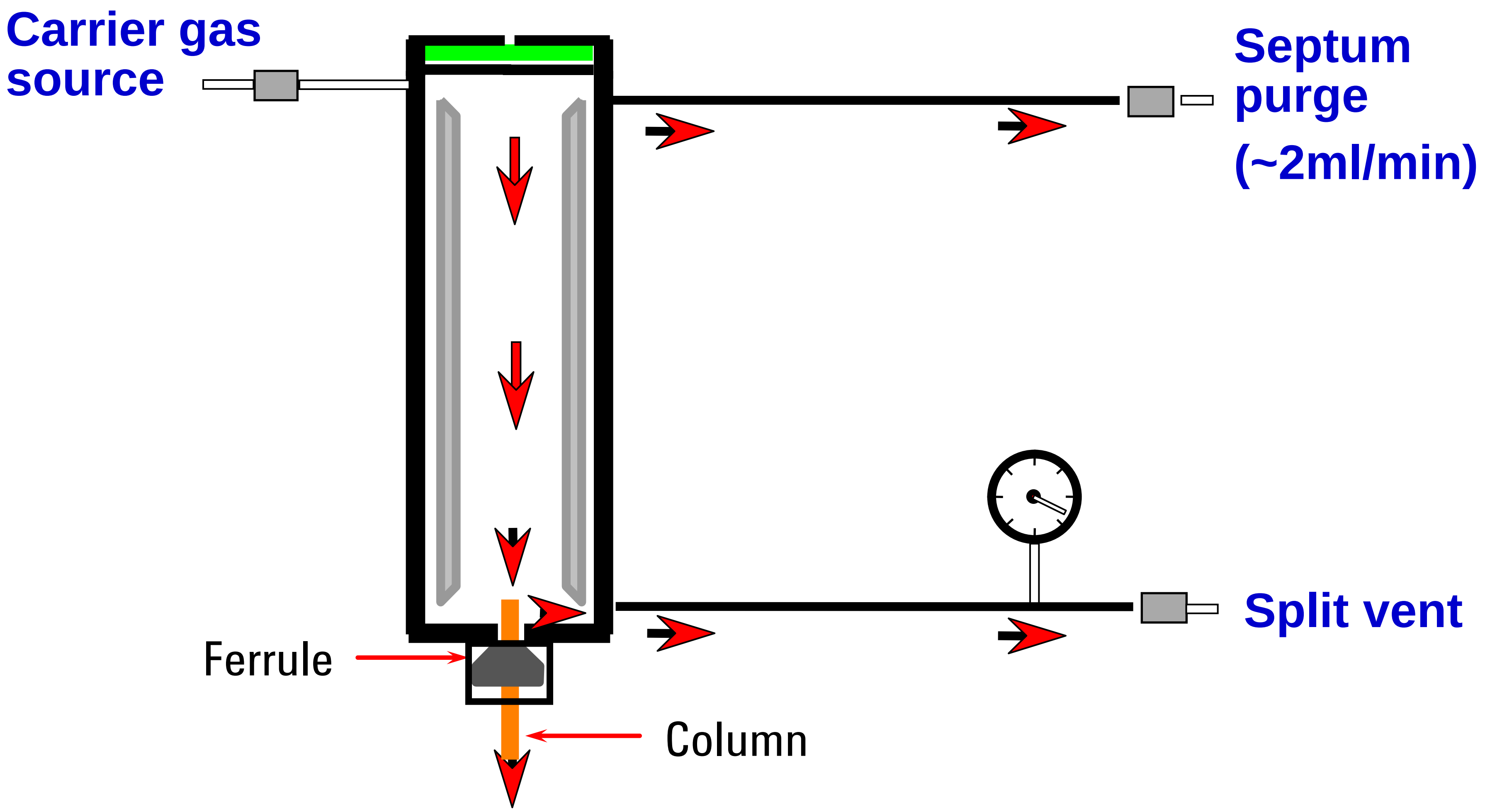
Cool-On-Column

PTV

MMI

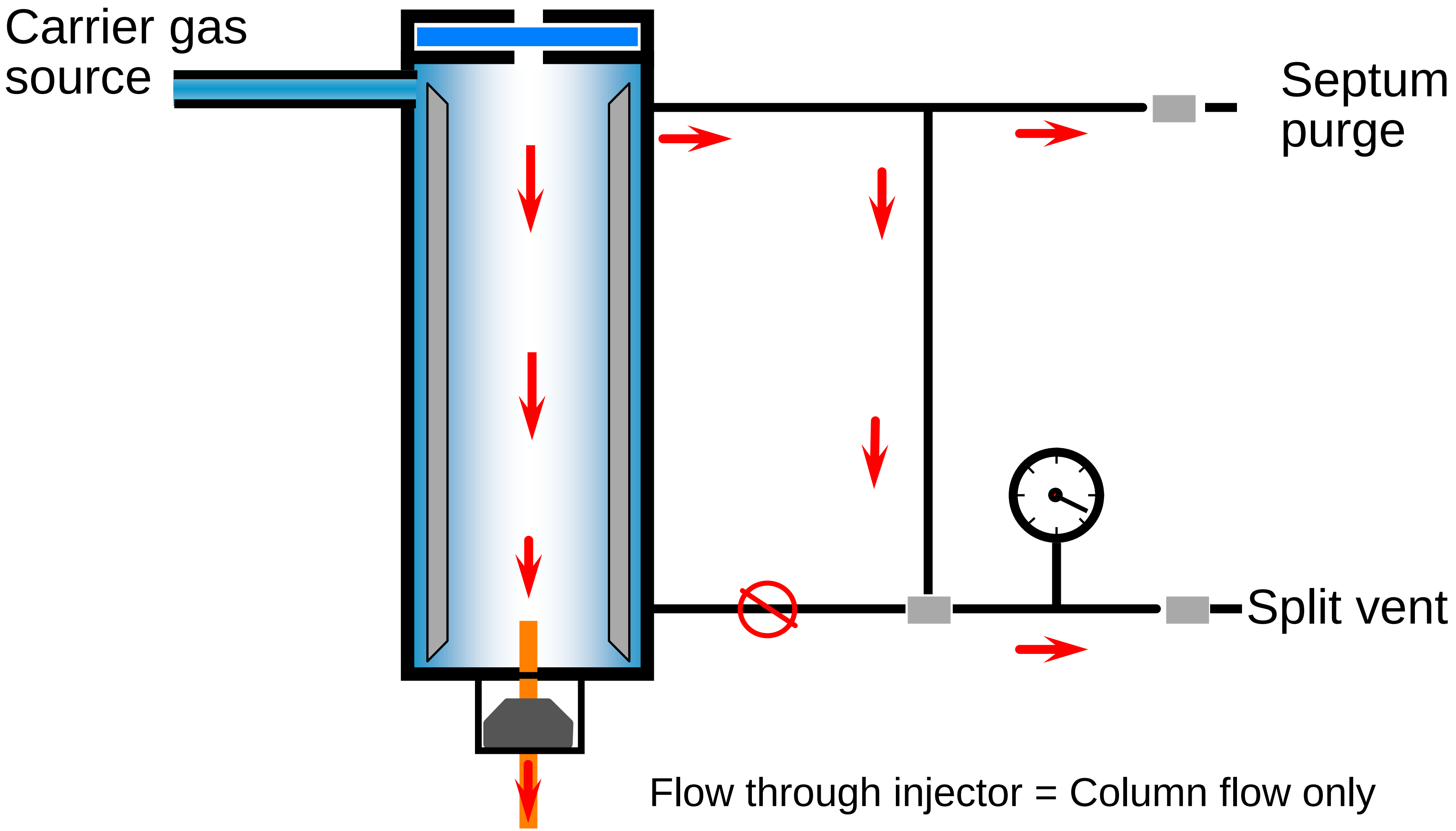
Volatiles Inlet

SPLIT/SPLITLESS INJECTOR



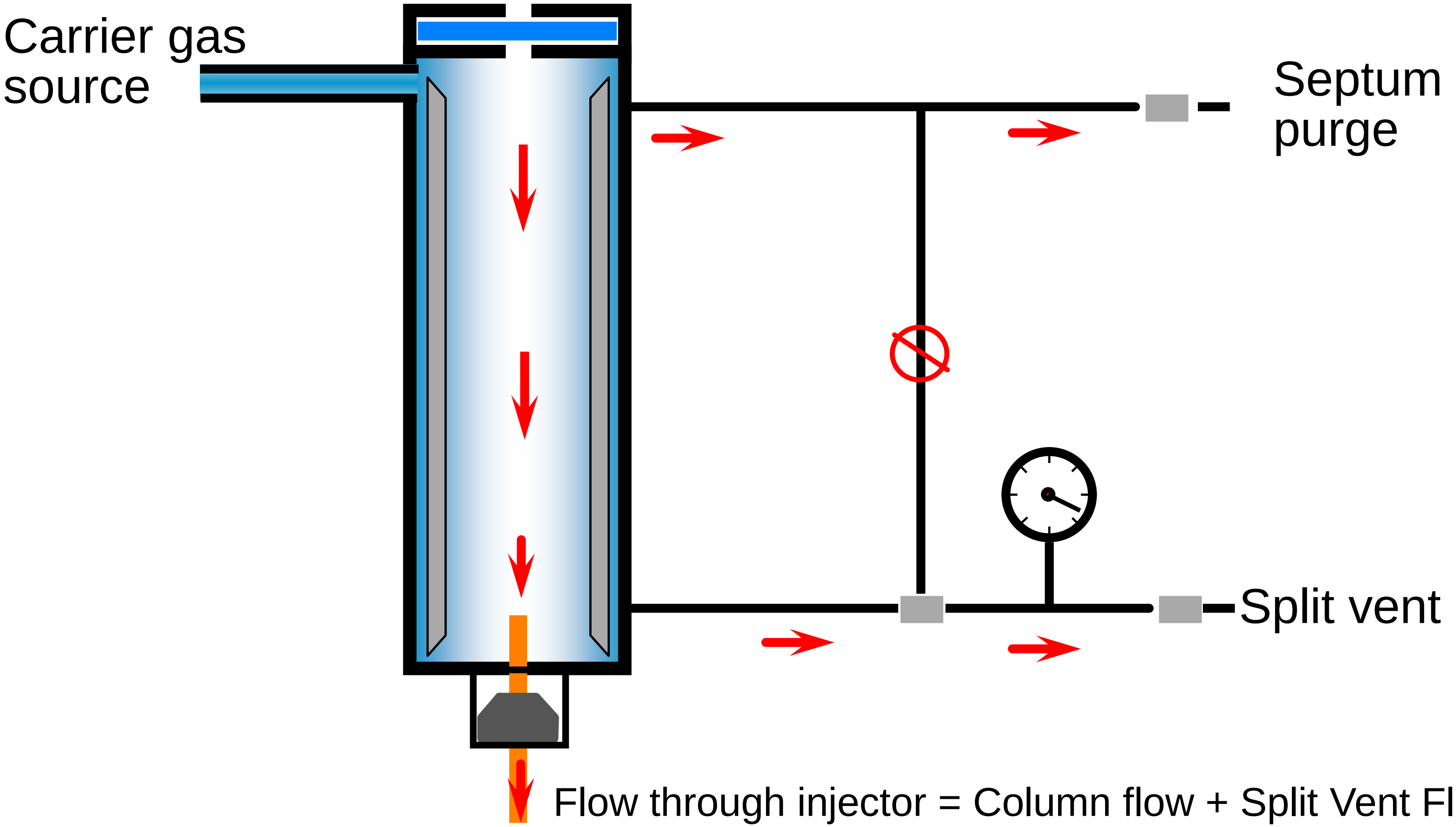
Flow through injector = Column flow + Split Vent Flow

Splitless Injector
Purge Off At Injection



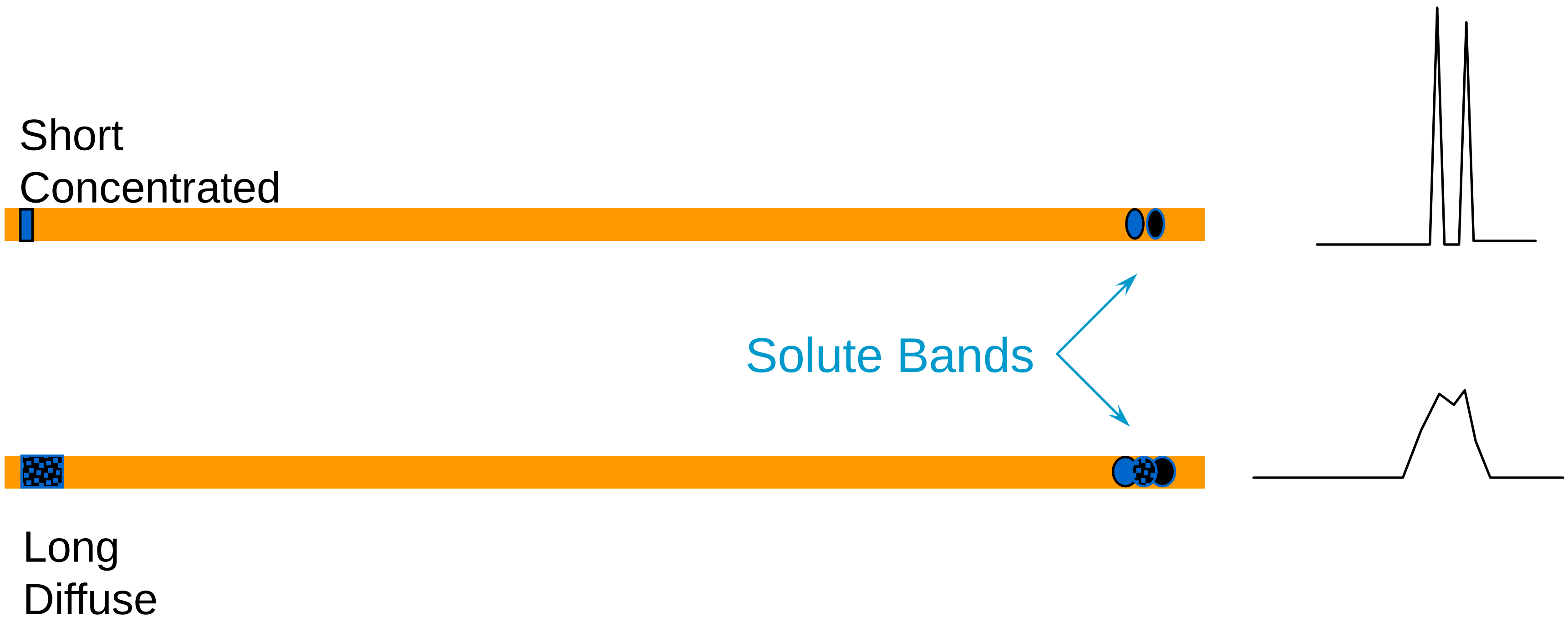
Splitless Injector

Purge On After Injection



Flow through injector = Column flow + Split Vent Flow

Influence of Injection Efficiency



Same column, same chromatographic conditions

Split Injector
Major Variables

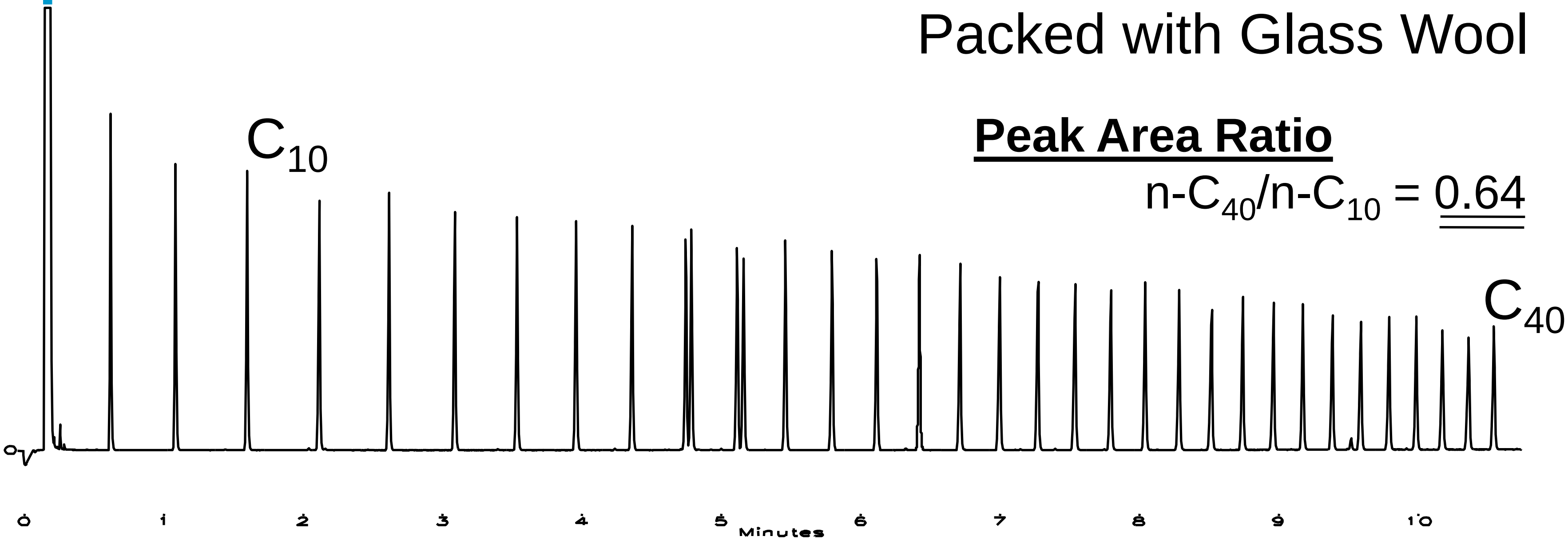
Split ratio - determines amount of sample onto column and efficiency of injection (sensitivity vs peak shape)

Liner - influences efficiency of vaporization/discrimination

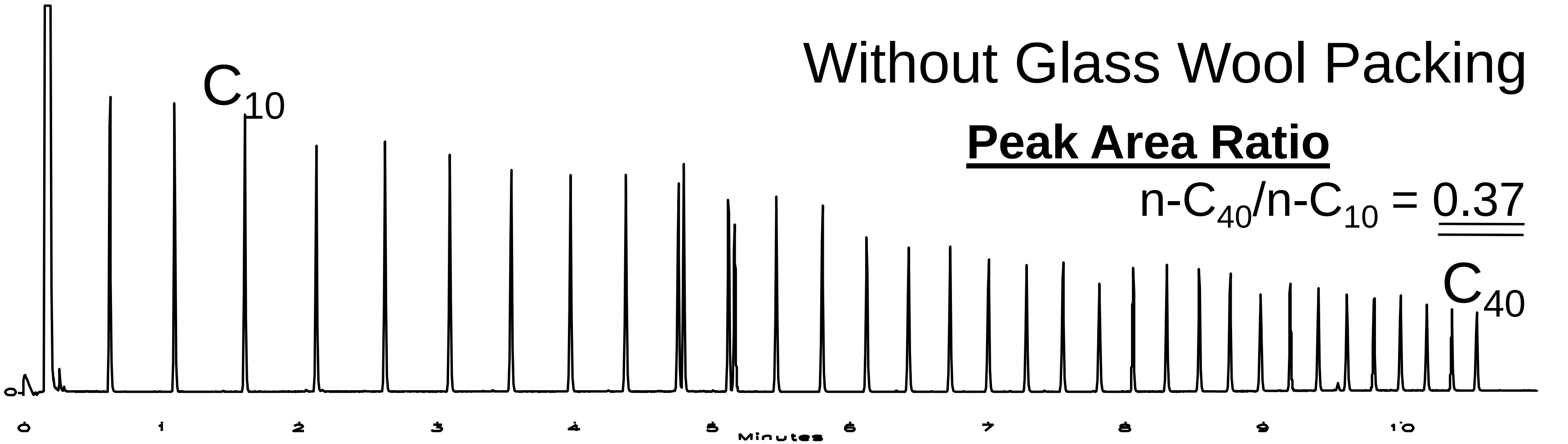
Temperature - hot enough to vaporize sample without degradation or causing backflash

Injection volume - typically 1-3uL, increasing it does not have as much of an effect as one might think

Split Liner

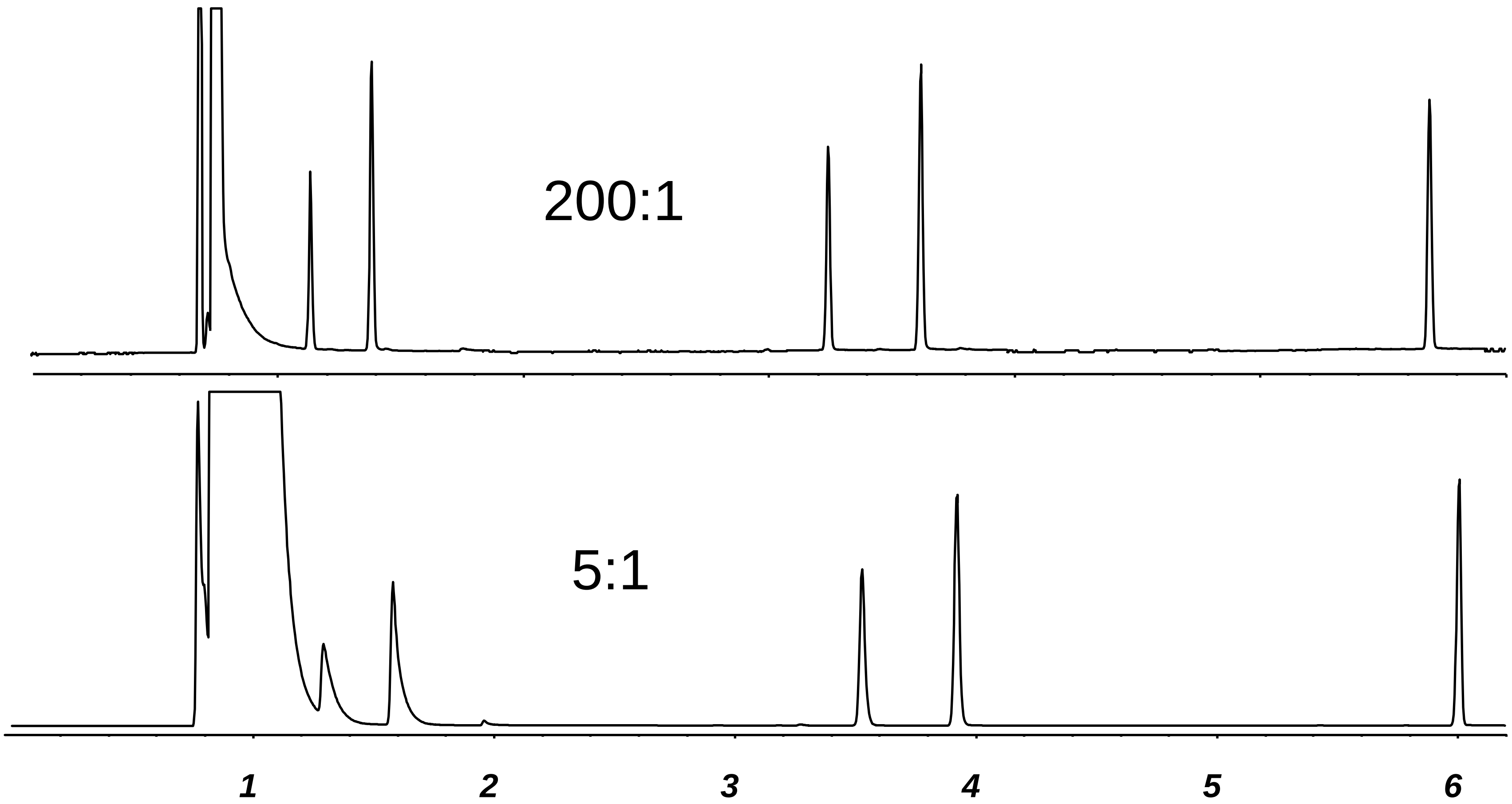


Packed with Glass Wool
C10
Peak Area Ratio
n-C40/n-C10 = 0.64
C40
0
1
2
3
4
5
Minutes
6
7
8
9
10



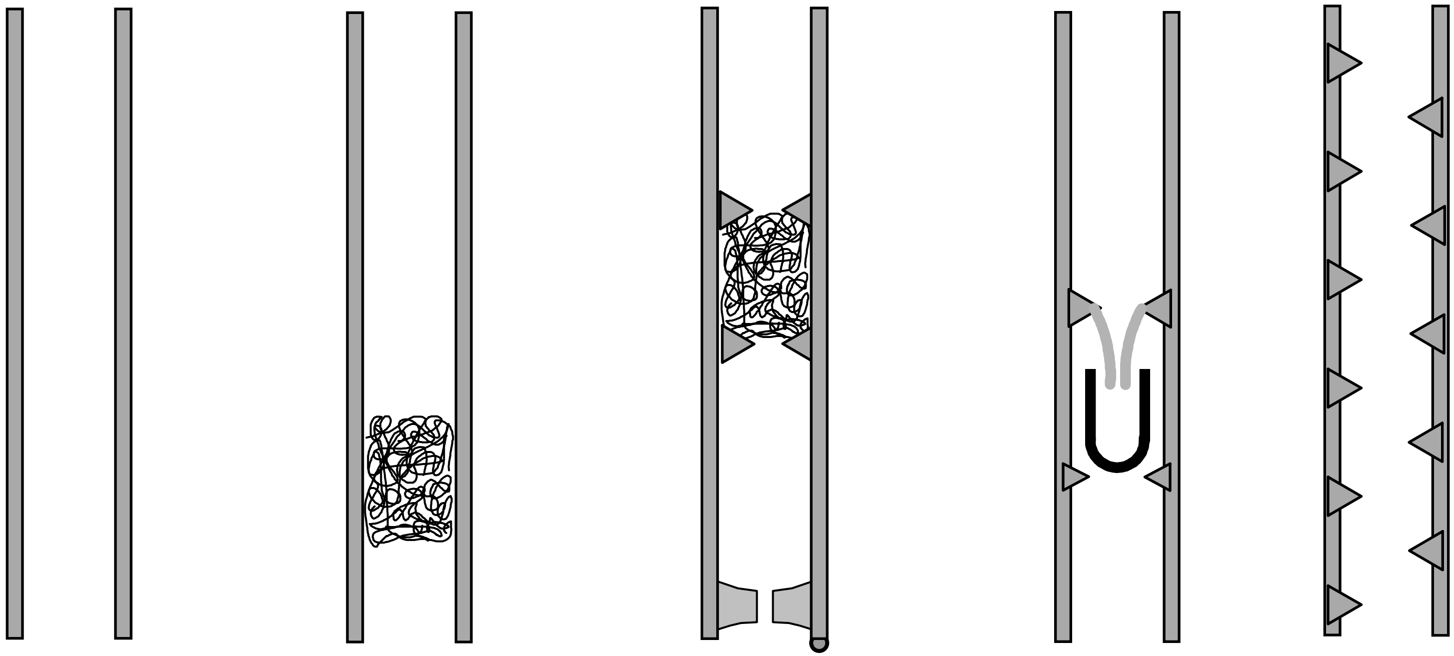
Without Glass Wool Packing
C10
Peak Area Ratio
n-C40/n-C10 = 0.37
C40
0
1
2
3
4
5
Minutes
6
7
8
9
10

Split Injector - 200:1 vs 5:1



DB-1, 15 m x 0.25 mm I.D., 0.25 µm
60°C for 1 min, 60-180°C at 20°/min; Helium at 30 cm/sec
1. n-heptane   2. toluene   3. n-decane   4. n-butylbenzene   5. n-tridecane

Split Liners – What's What?



Straight tube

Straight tube with glass wool

Fixed glass wool

Inverted cup

Baffle

GLASS WOOL

Placement in Liner

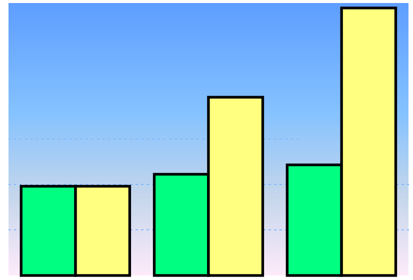
Near top of liner:

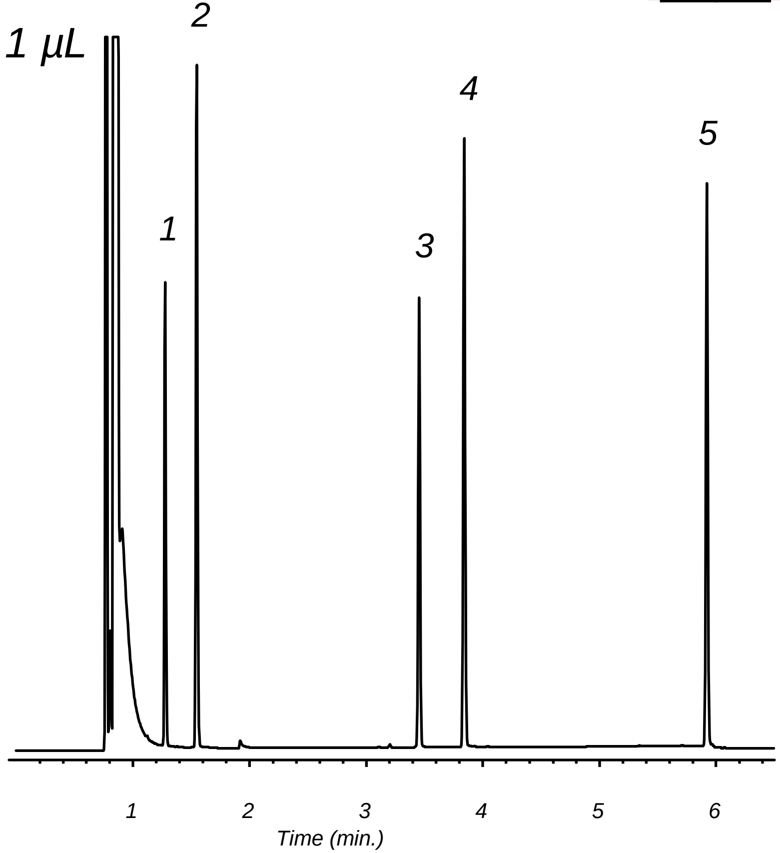
- Wipes syringe needle of sample
- More thermal mass
- Aids in sample volatilization
- Can improve injector precision
- Helps to prevent backflash

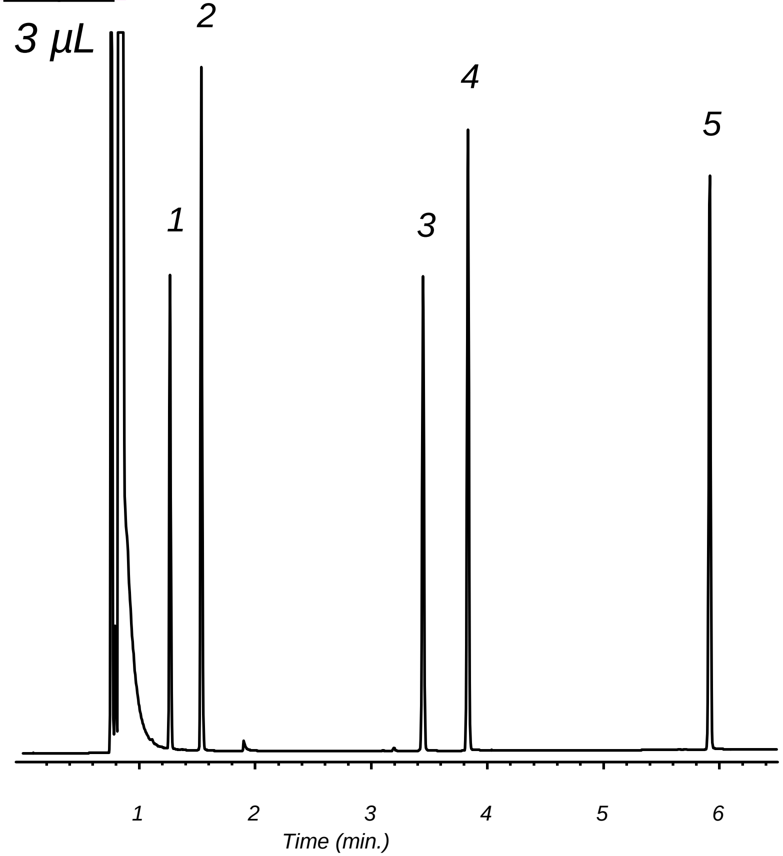
Near bottom of liner:

- Helps in volatilization of high MW components
- Increases mixing

Split Injector
Injection Volume







DB-1, 15 m x 0.25 mm I.D., 0.25 µm
60°C for 1 min, 60-180°C at 20°/min; Helium at 30 cm/sec
1. n-heptane   2. toluene   3. n-decane   4. n-butylbenzene   5. n-tridecane

Splitless Injector
Overview

Most of the sample is introduced into the column

Used for low concentration samples

Wider peaks are obtained than for split injections

Splitless Injector
Major Variables

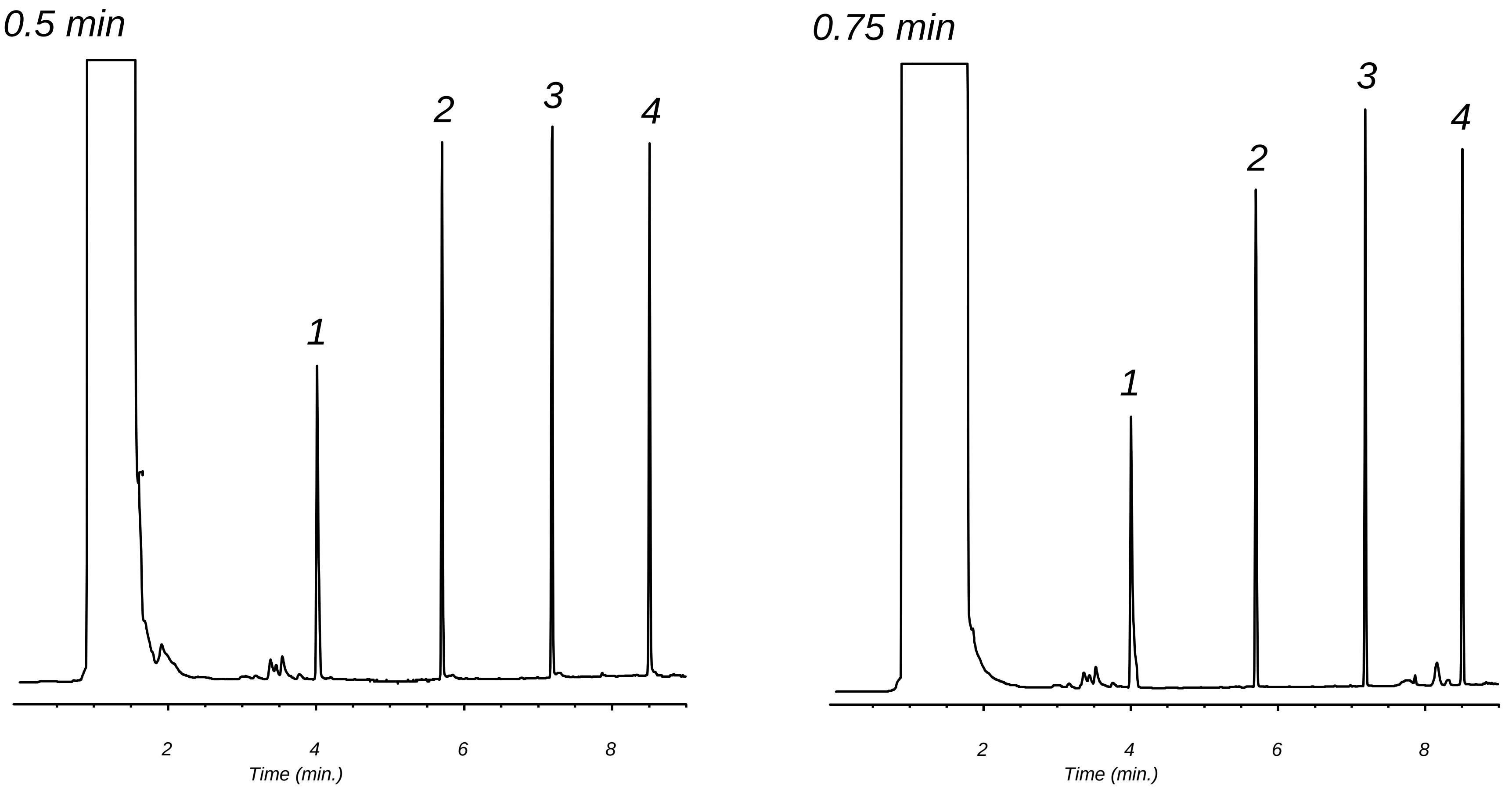
Purge activation time - determines amount of sample onto column and efficiency of injection (sensitivity vs peak shape)

Liner - preventing backflash more critical than vaporization properties (double tapered type recommended)

Injection volume - typically 1uL or less (backflash)

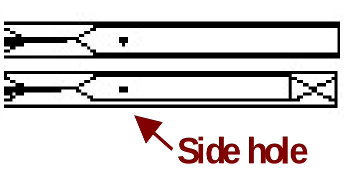
Temperature – long residence times allow for lower temps

Splitless Injector
Purge Activation Time

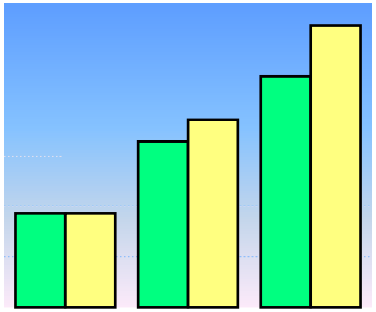


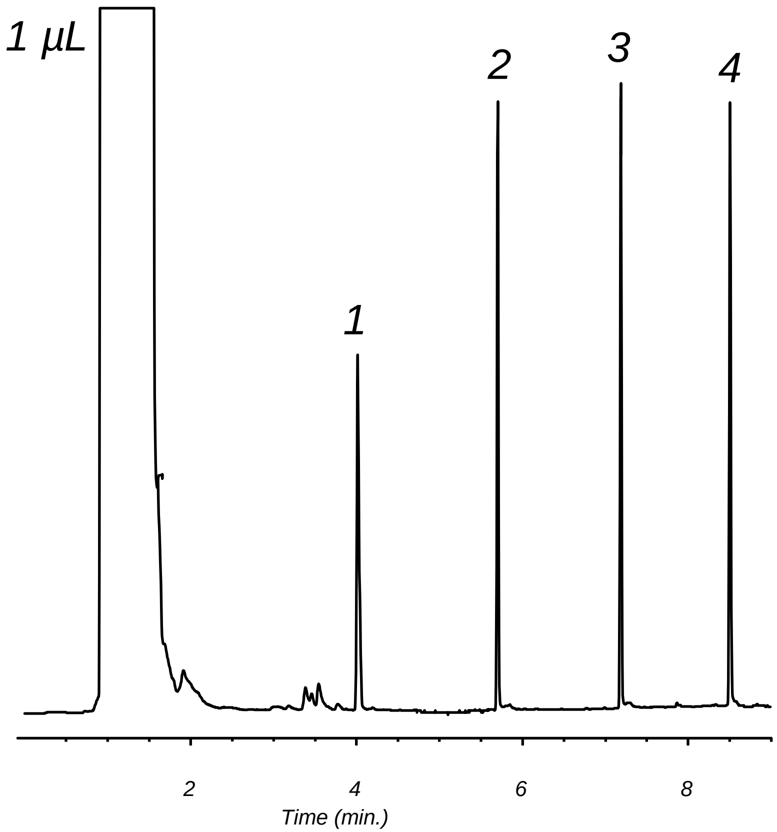
DB-1, 15 m x 0.25 mm I.D., 0.25 µm
60°C for 1 min, 60-180°C at 20°/min; Helium at 30 cm/sec
1. n-decane 2. n-dodecane 3. n-tetradecane 4. n-hexadecane

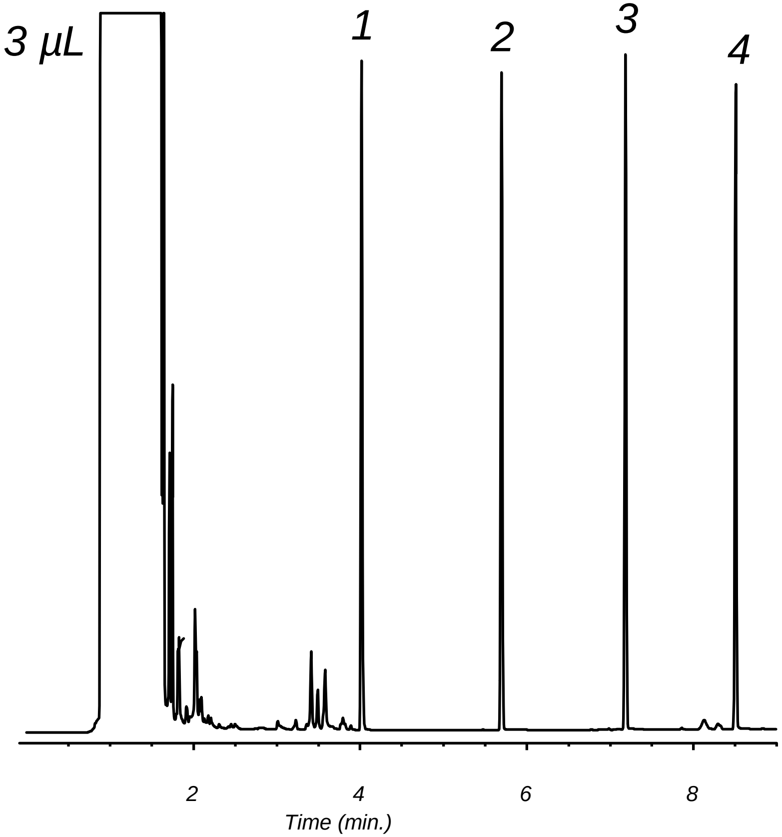
Splitless Injection Liners

Liner	Part No.	Comments
	5181-3316	Single taper, deactivated, 900μL volume. Taper isolates sample from metal seal, reducing breakdown of compounds that are active with metals. For trace samples, general application.
	5062-3587	Single taper, deactivated, with glass wool, 900μL volume. Glass wool aides volatilization and protects column. For trace (dirty) samples.
	5181-3315	Double taper, deactivated, 800μL volume. Taper on inlet reduces chance for backflash into carrier gas lines. High efficiency liner for trace, active samples.
	G1544-80730 G1544-80700	Direct connect liners, single and dual taper, deactivated. Capillary column press fits into liner end, eliminating sample exposure to inlet. Ultimate protection for trace, active samples. Side hole permits use with EPC.

Splitless Injector
Injection Volume

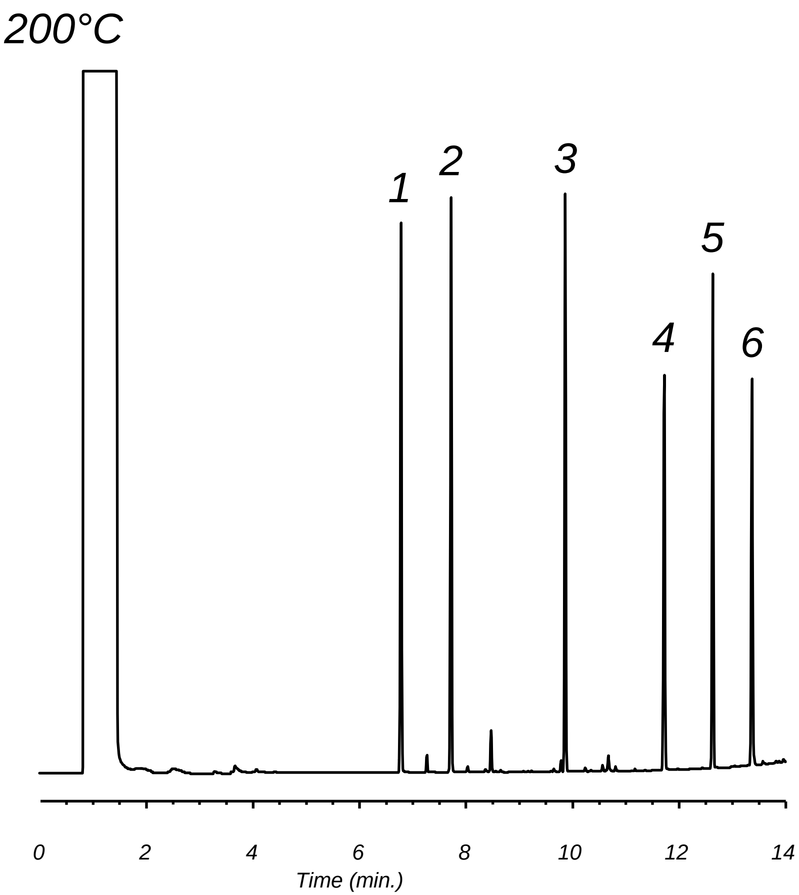


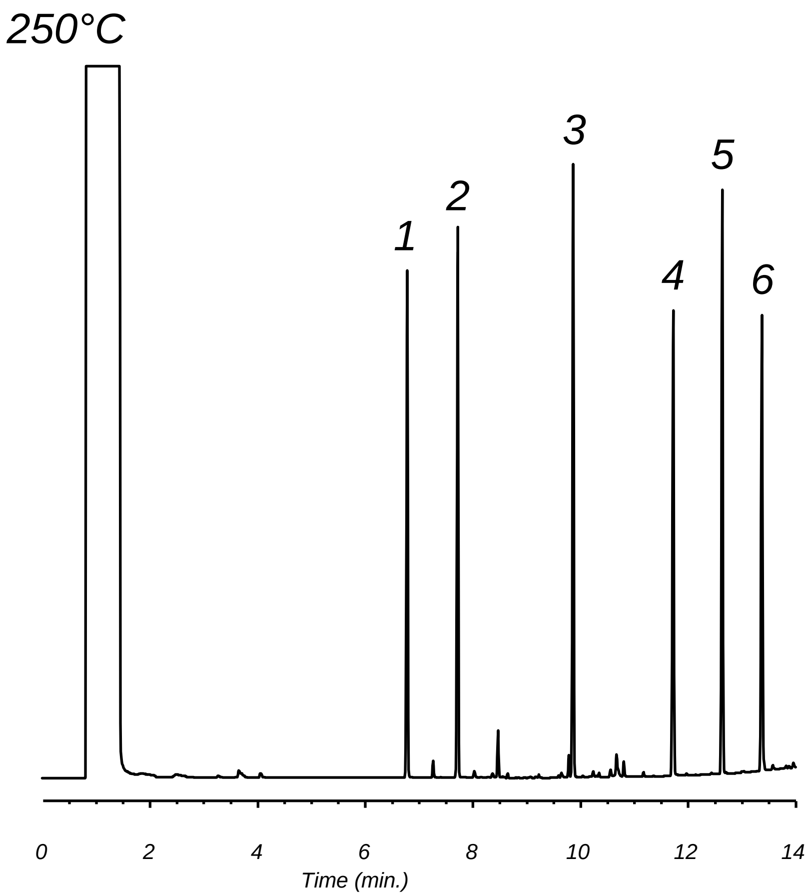




DB-1, 15 m x 0.25 mm I.D., 0.25 µm
60°C for 1 min, 60-180°C at 20°/min; Helium at 30 cm/sec
1. n-decane   2. n-dodecane   3. n-tetradecane   4. n-hexadecane

Splitless Injector
Injector Temperature





DB-1, 15 m x 0.25 mm I.D., 0.25 µm
50°C for 0.5 min, 50-325°C at 20°/min; Helium at 30 cm/sec
Phthalates: 1. dimethyl 2. diethyl 3. dibutyl 4. benzylbutyl 5.bis(2-ethylhexyl) 6. dioctyl

Splitless Injector
Sample Re-focusing

Sample re-focusing improves efficiency

Use low column temperature to refocus solvent
 - called the *solvent effect*

Use cold trapping

Splitless Injector

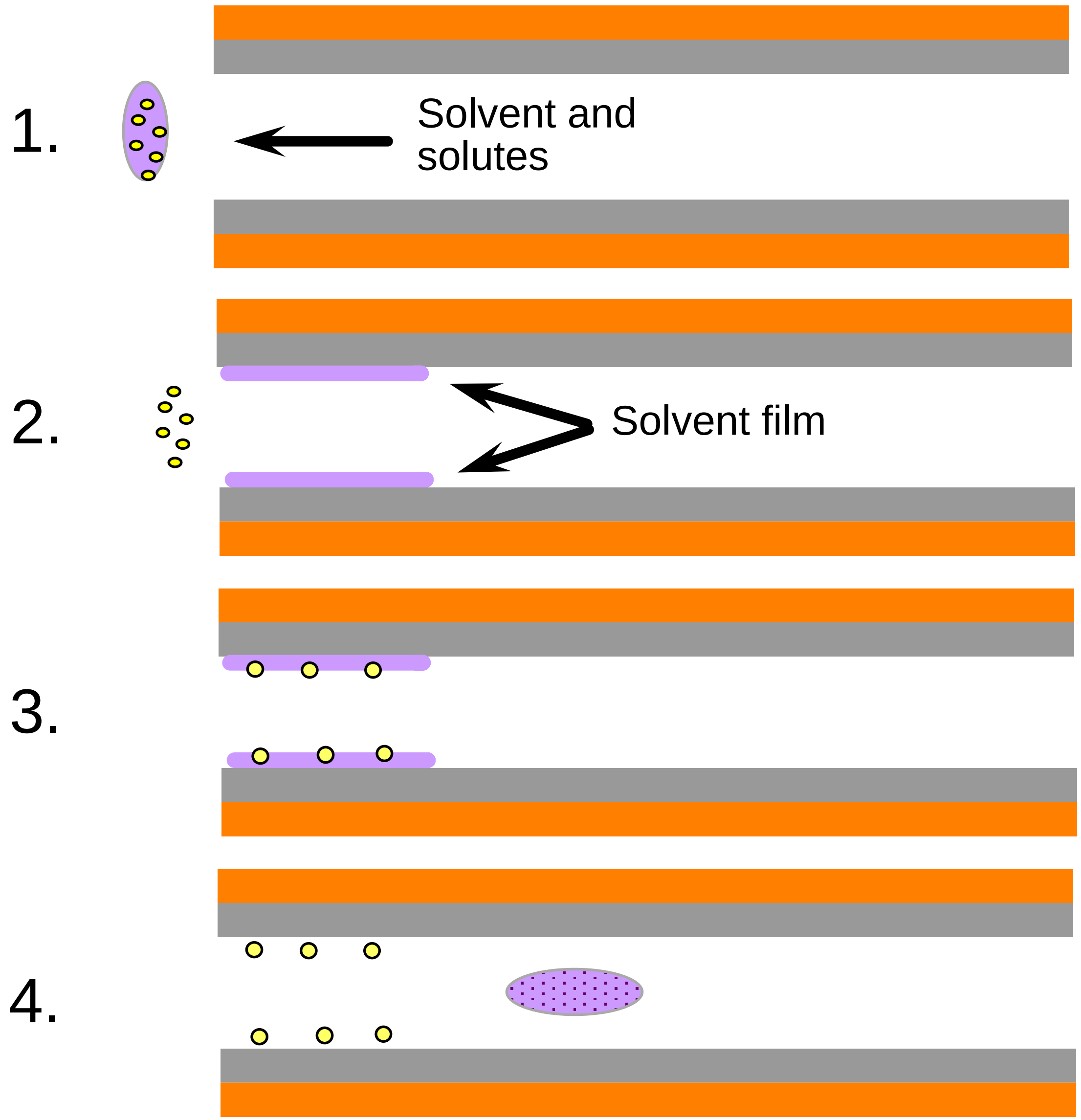
Solvent Effect

Initial column temperature at least ***10°C below*** sample solvent boiling point

Required to obtain good peak shapes unless cold trapping occurs

Rule of thumb, if solute BP >150°C above initial column temperature, the solute will cold trap

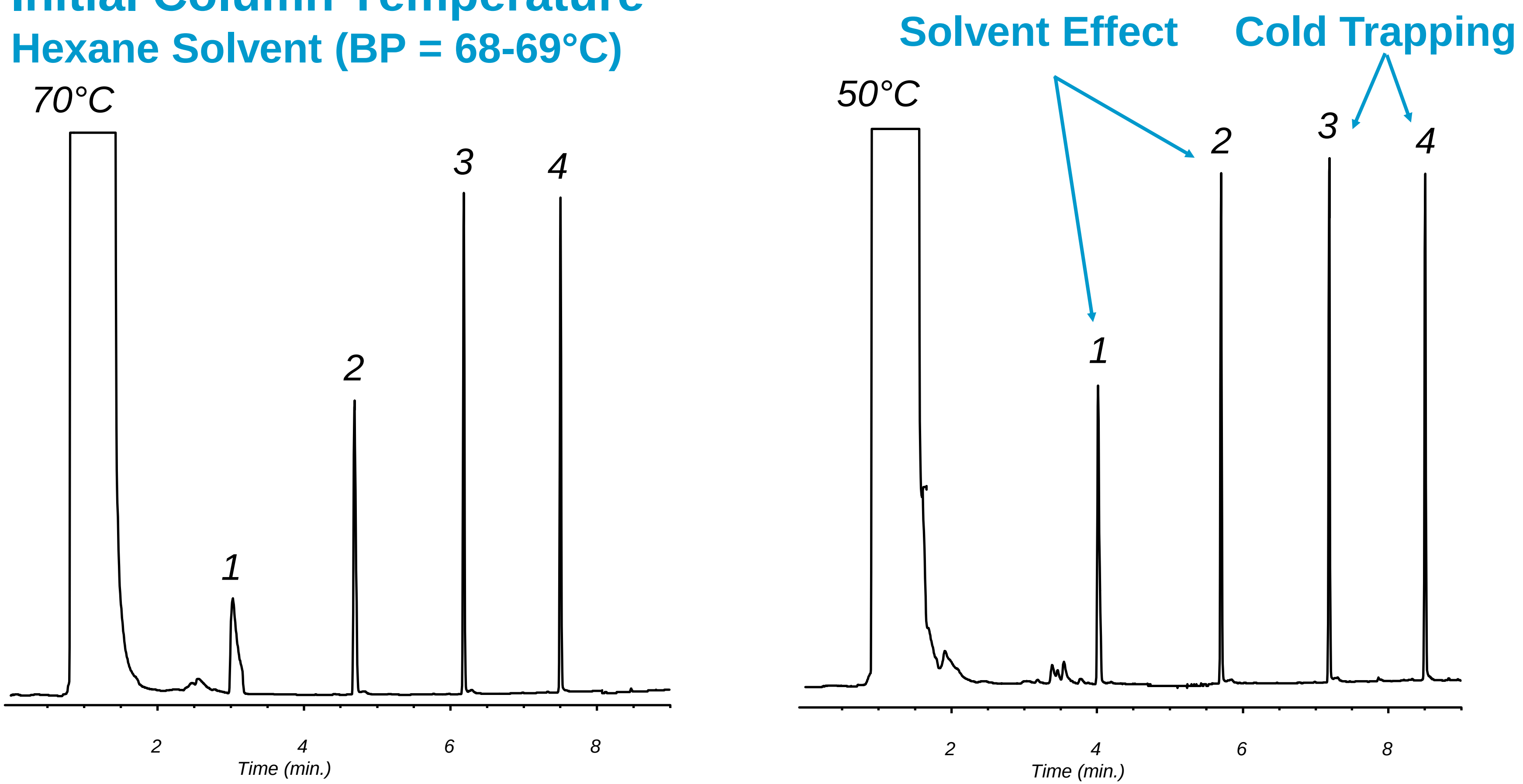
Cold trapping has greater efficiency than solvent effect



Splitless Injector

Initial Column Temperature

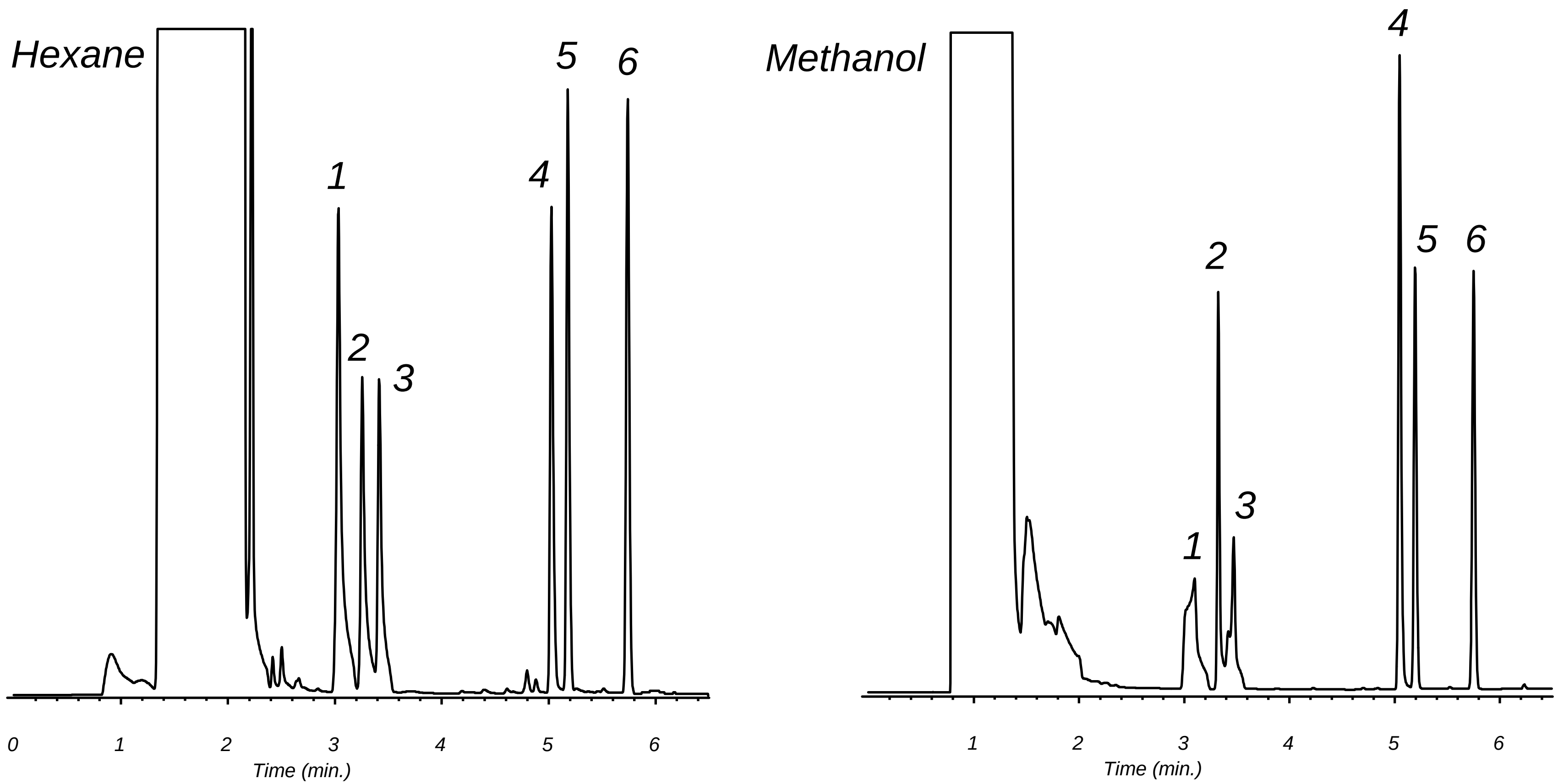
Hexane Solvent (BP = 68-69°C)



DB-1, 15 m x 0.25 mm I.D., 0.25 µm
50°C or 70°C for 0.5 min, to 210°C at 20°/min; Helium at 30 cm/sec
1. n-decane 2. n-dodecane 3. n-tetradecane 4. n-hexadecane

Splitless Injector

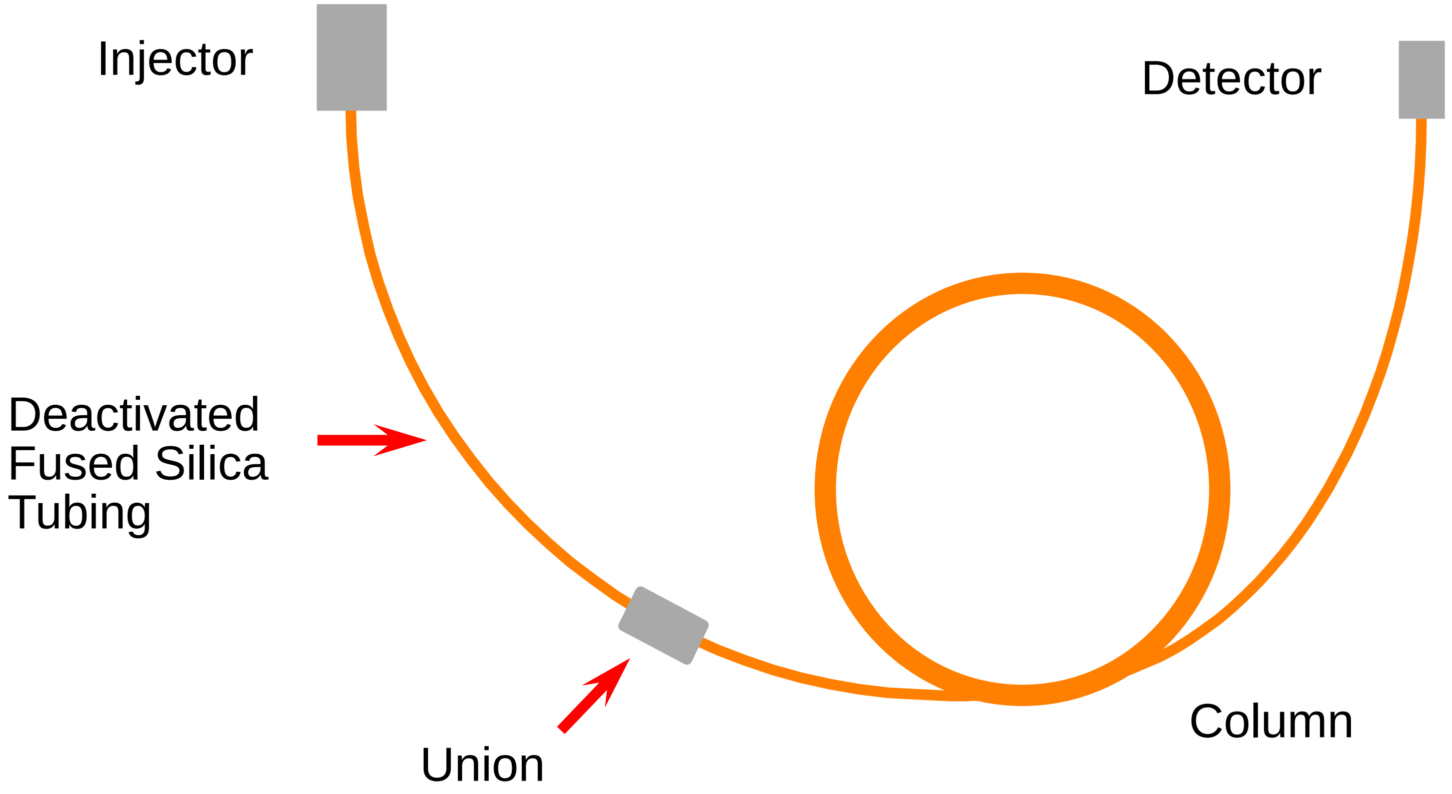
Reverse Solvent Effect



DB-1, 15 m x 0.25 mm I.D., 0.25 µm
50°C for 1 min, 50-210°C at 20°/min; Helium at 30 cm/sec
1. 1,3-DCP 2. 3-hexanol 3. butyl acetate 4. 1-heptanol 5. 3-octanone 6. 1,2-dichlorobenzene

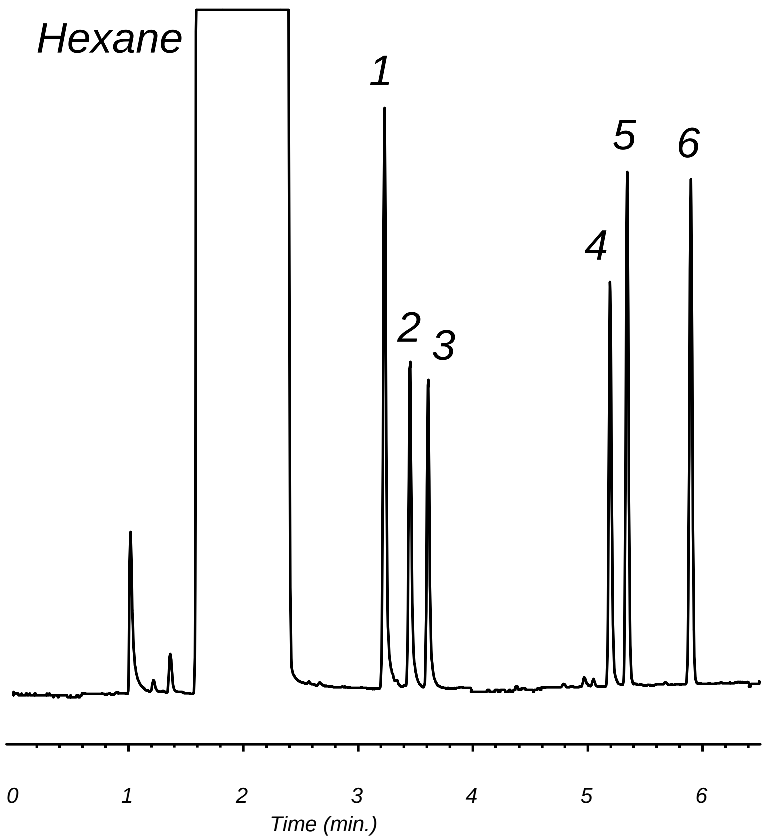
Retention Gap

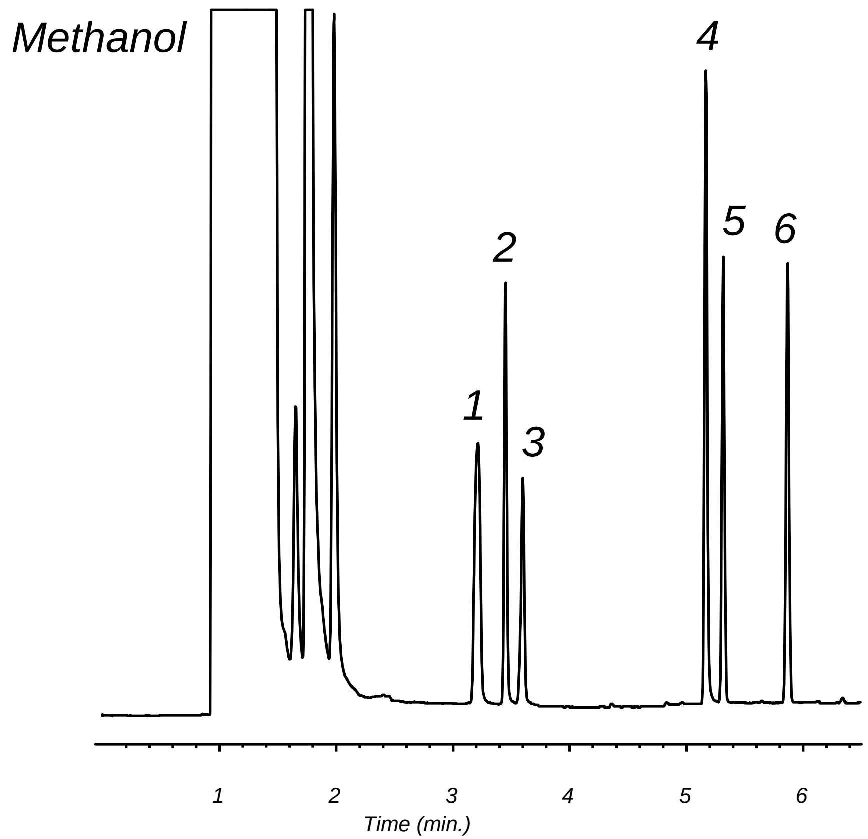
Also Called A Guard Column



Usually 2-10 meters long and same diameter as the column (or larger if needed)

Splitless Injector
3 m x 0.25 mm I.D. Retention Gap





DB-1, 15 m x 0.25 mm I.D., 0.25 µm
50°C for 1 min, 50-210°C at 20°/min; Helium at 30 cm/sec
1. 1,3-DCP 2. 3-hexanol 3. butyl acetate 4. 1-heptanol 5. 3-octanone 6. 1,2-dichlorobenzene

COMPOUND REQUIREMENTS FOR GC

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

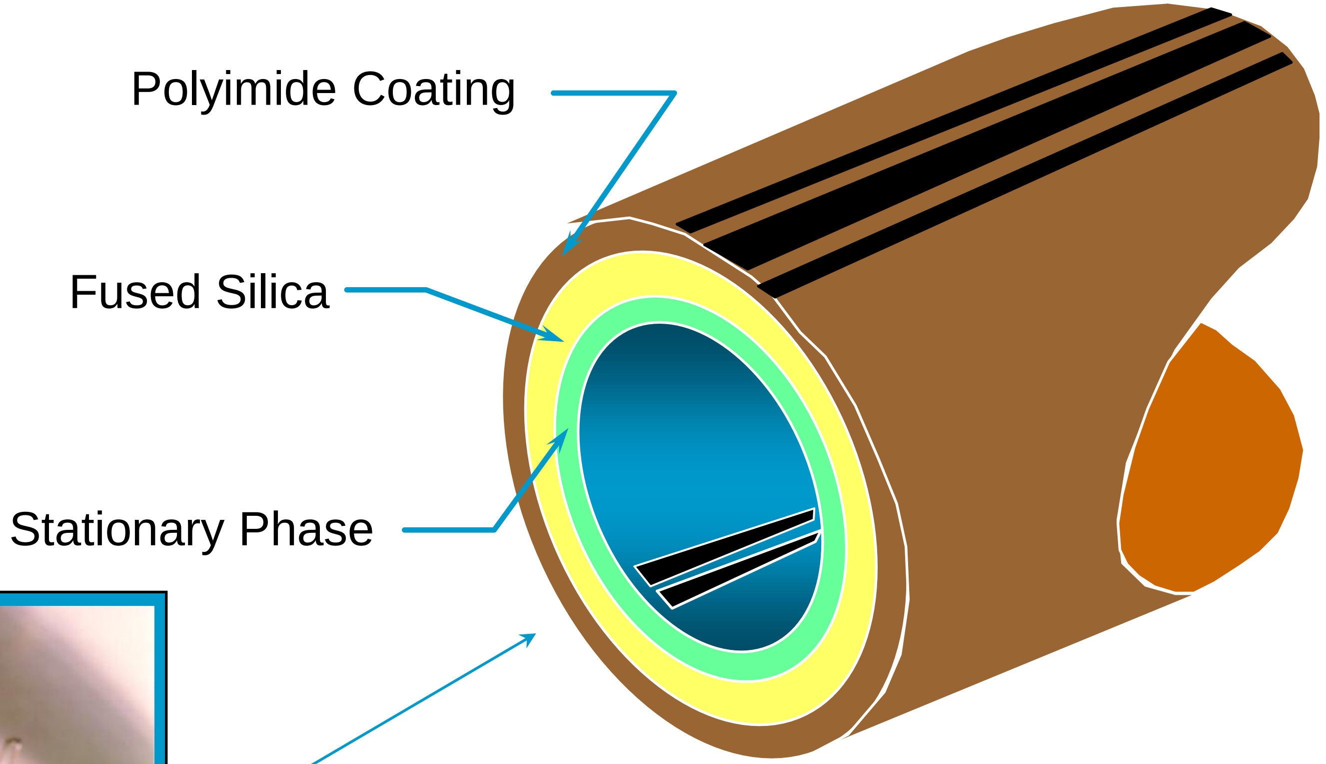
The compounds must have:

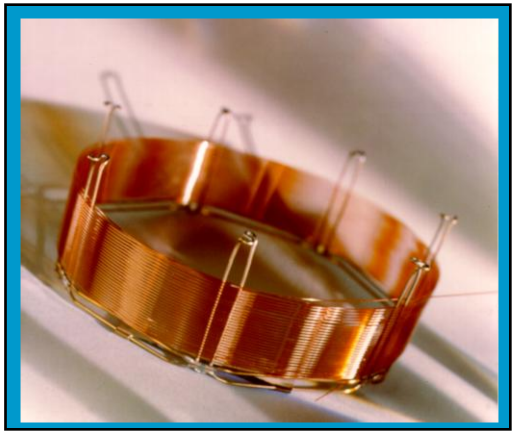
- ✓ Sufficient volatility
- ✓ Thermal stability

NO Inorganic Acids and Bases

Be mindful of salts!

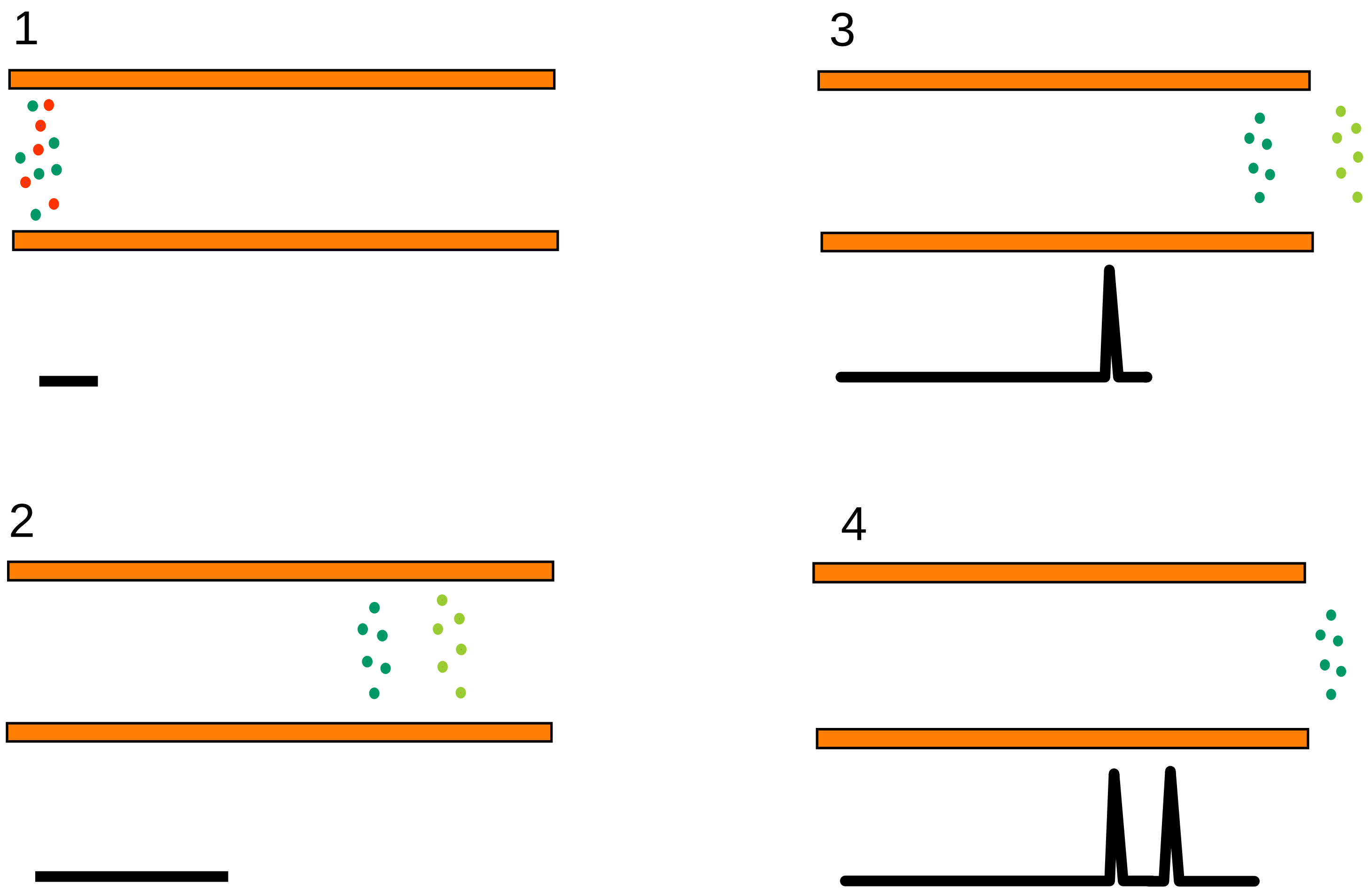
Typical Capillary Column





Expanded view of capillary tubing

SEPARATION PROCESS



TWO PHASES

Solute molecules distribute into the two phases

DISTRIBUTION CONSTANT (K_C)

$$K_C = \frac{\text{conc. of solute in stationary phase}}{\text{conc. of solute in mobile phase}}$$

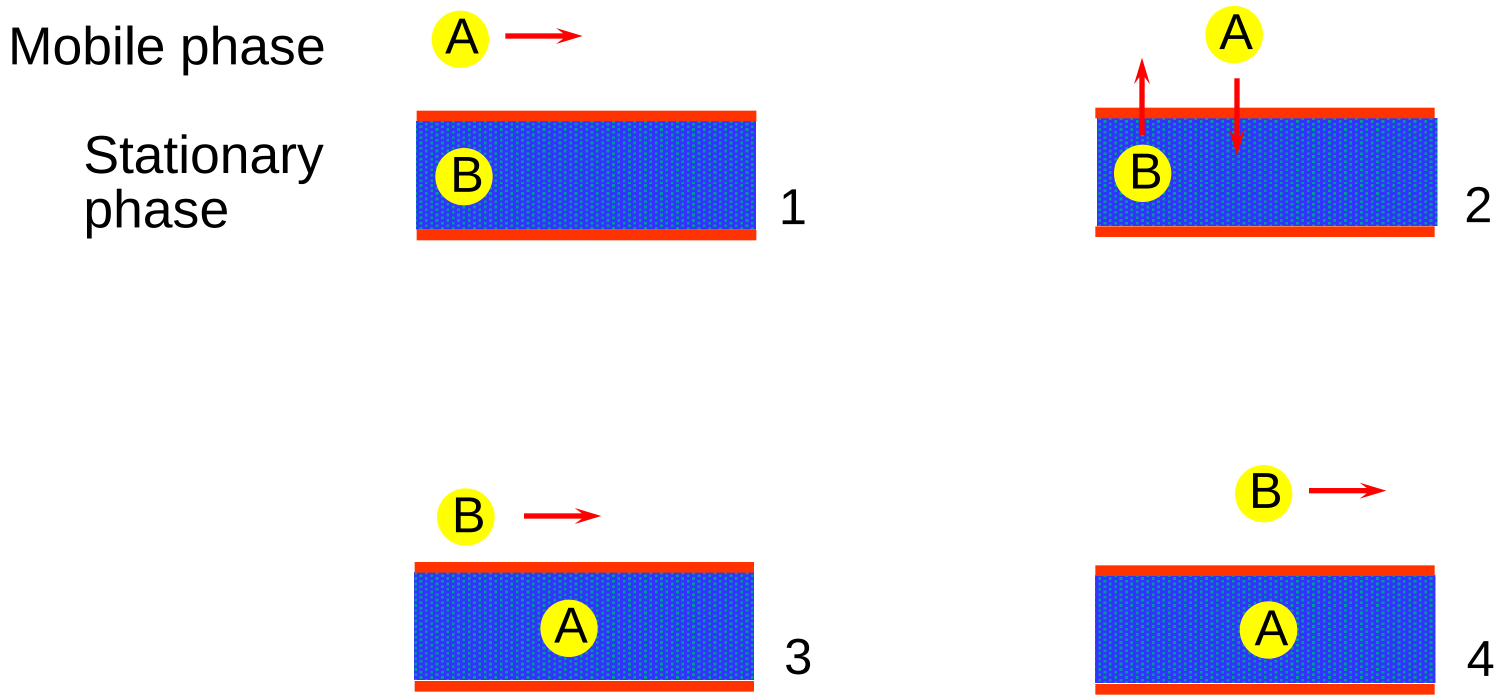
K_C formerly written as K_D

SOLUTE LOCATION

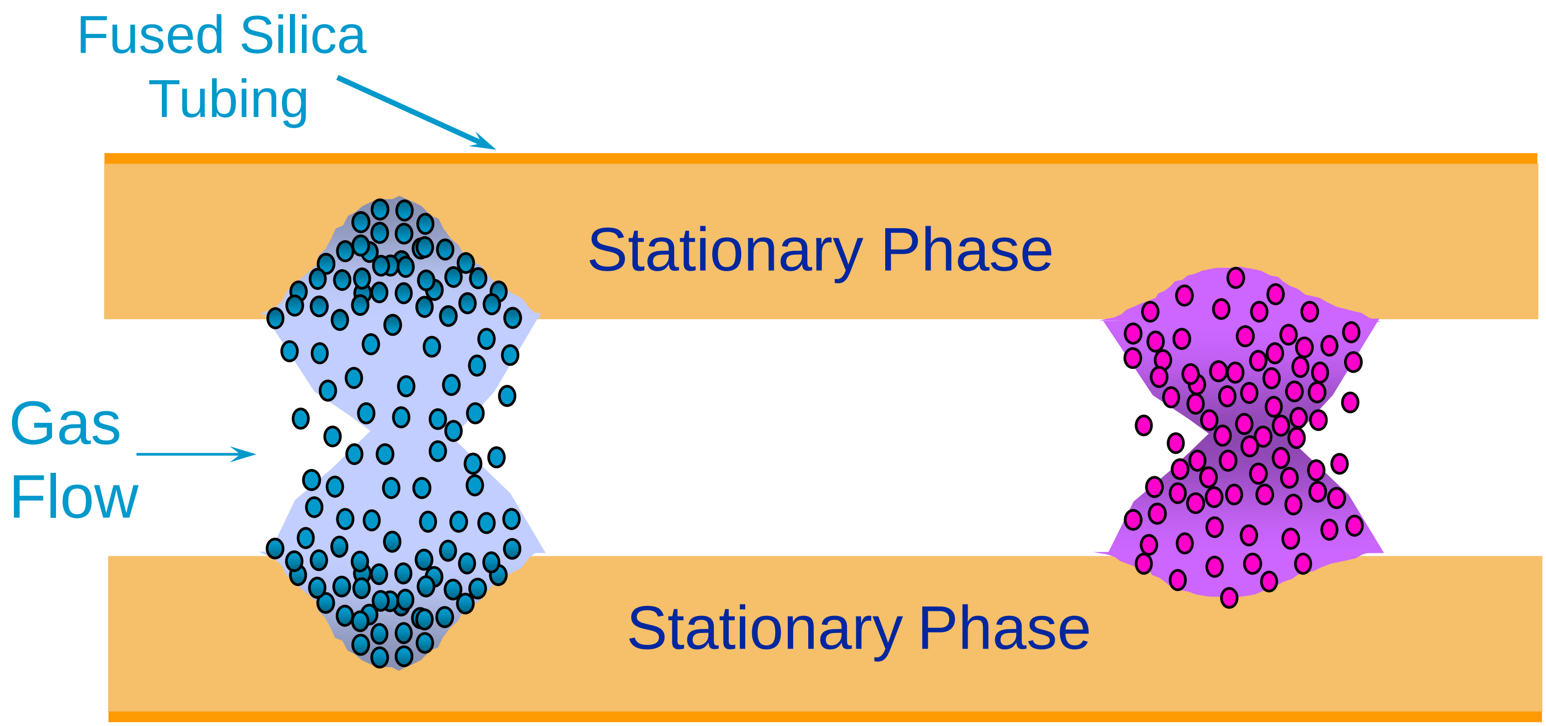
In stationary phase = Not moving down the column

In mobile phase = Moving down the column

SEPARATION PROCESS
Movement Down the Column



KC AND RETENTION



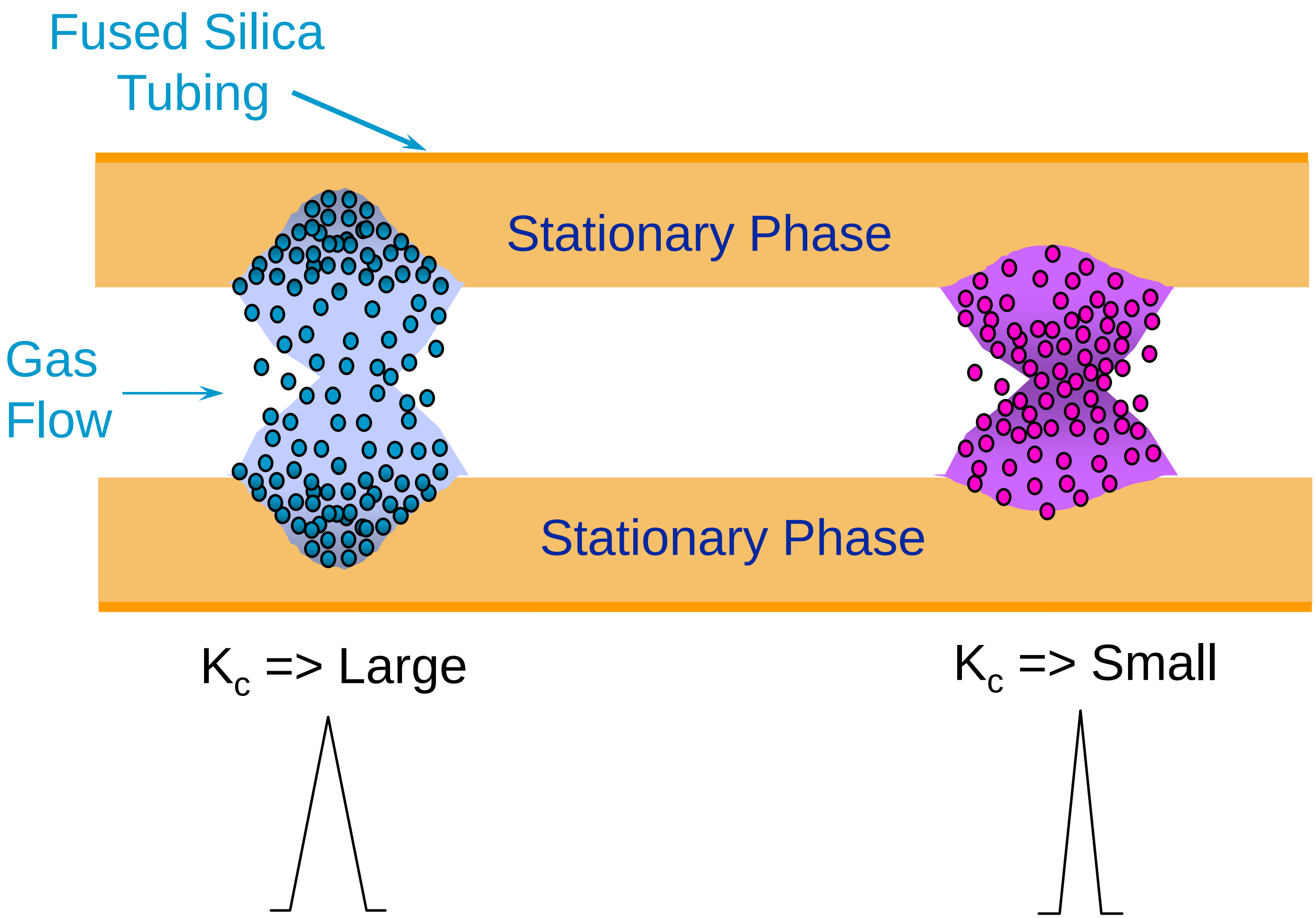
K_c => Large

retention

K_c => Small

retention

KC AND PEAK WIDTH
Time of Elution



THREE PARAMETERS THAT AFFECT K_C

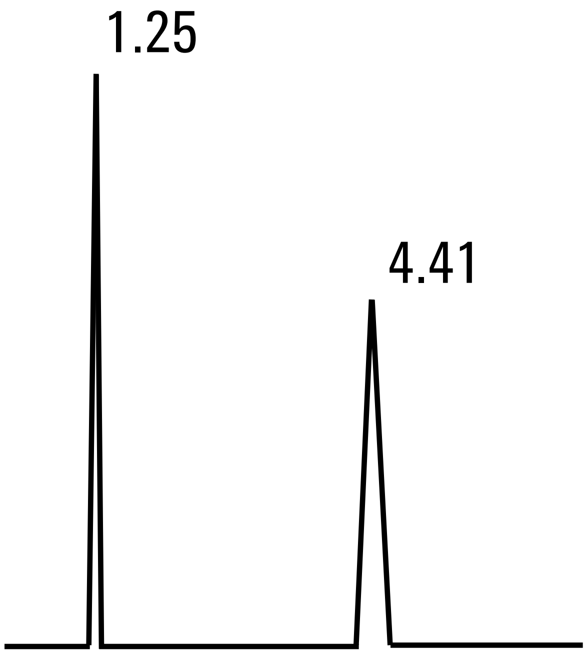
Solute:
different solubilities in a stationary phase

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

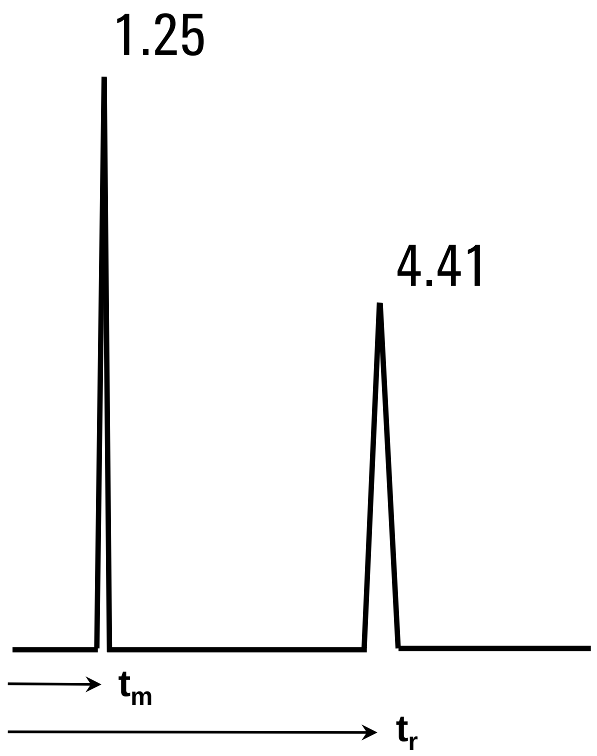
ADJUSTED RETENTION TIME
t_r'

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
tr



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)

$$\beta = \frac{r}{2d_f}$$

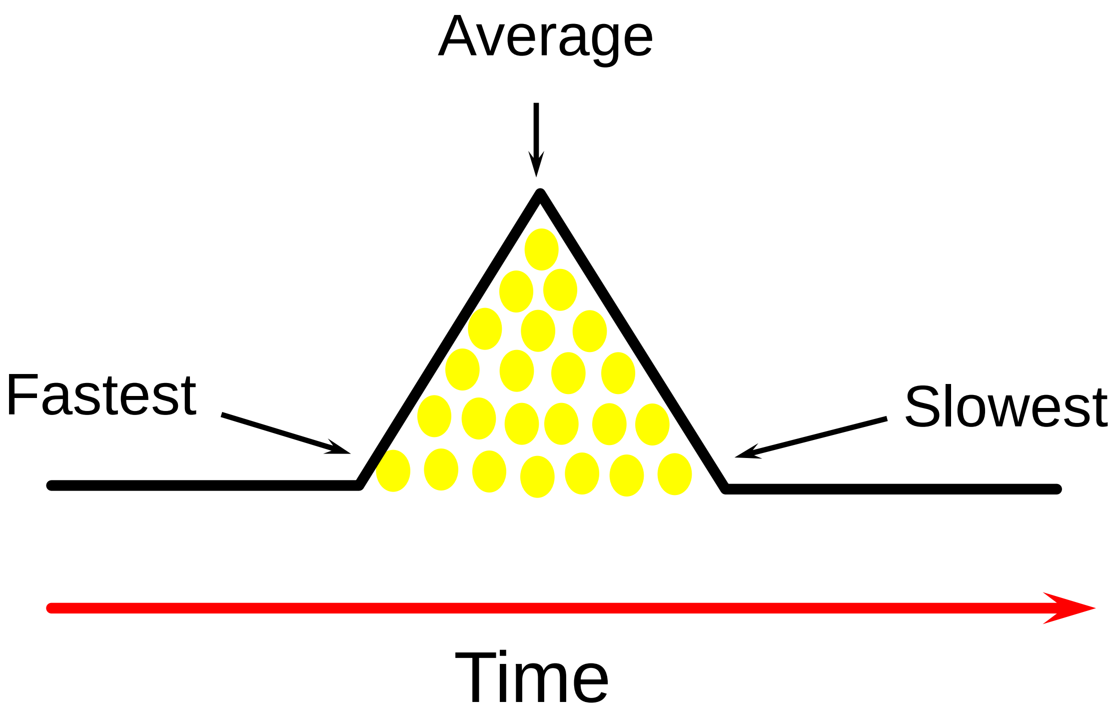
r = radius (µm)
d_f = film thickness (µm)

DISTRIBUTION CONSTANT (Kc)

$$K_c = k\beta$$

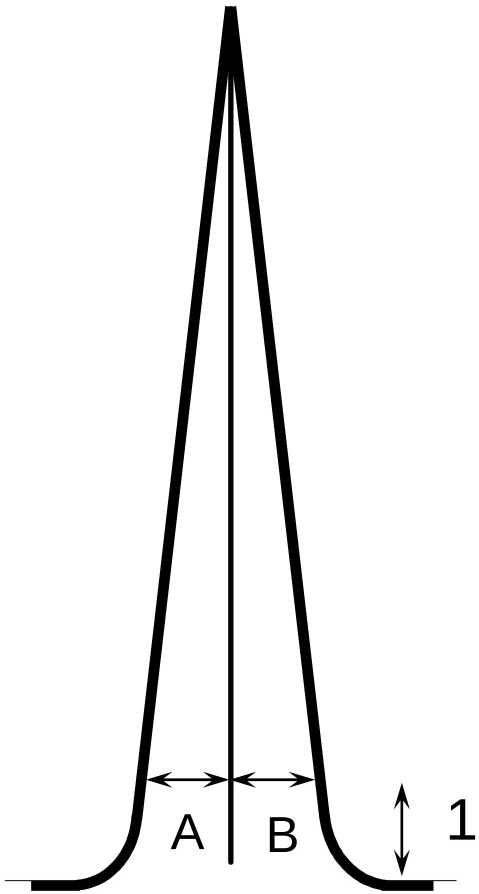
$$k = \frac{t_r'}{t_m} \qquad \beta = \frac{r}{2d_f}$$

RANGE OF RETENTION



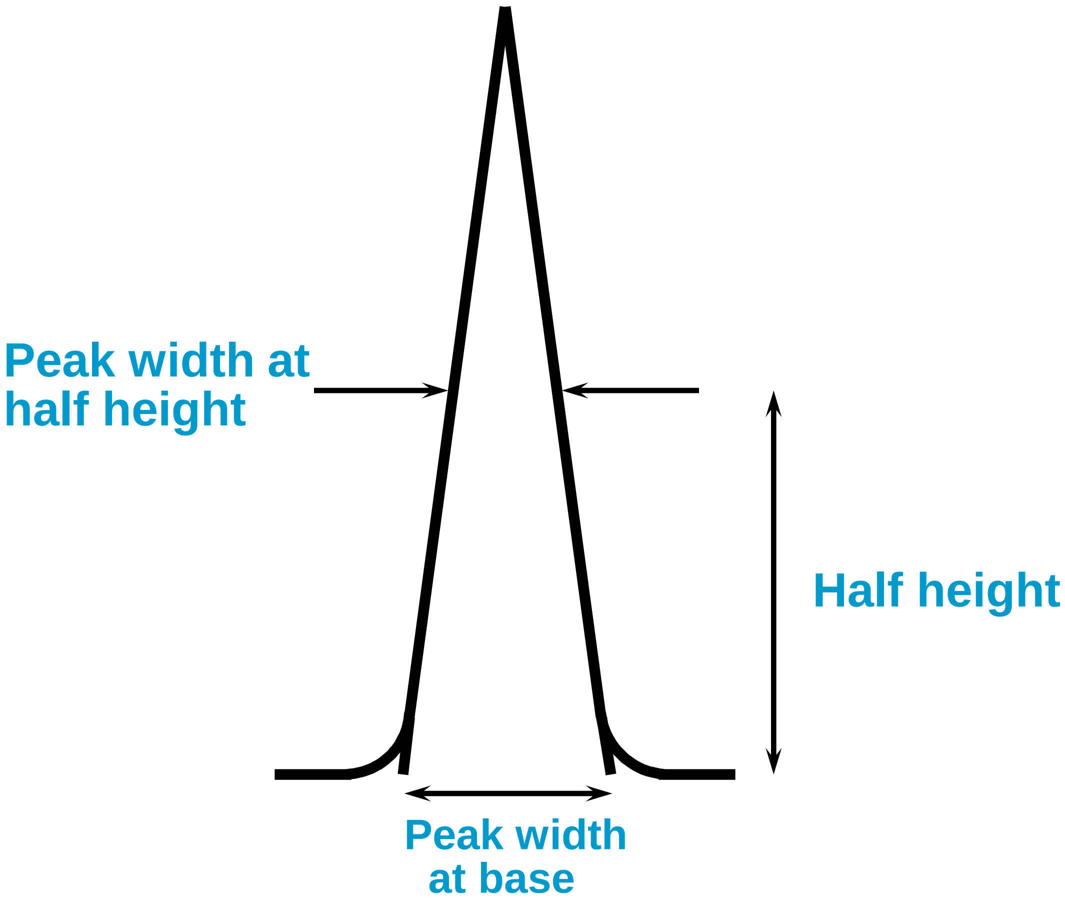
PEAK SYMMETRY

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

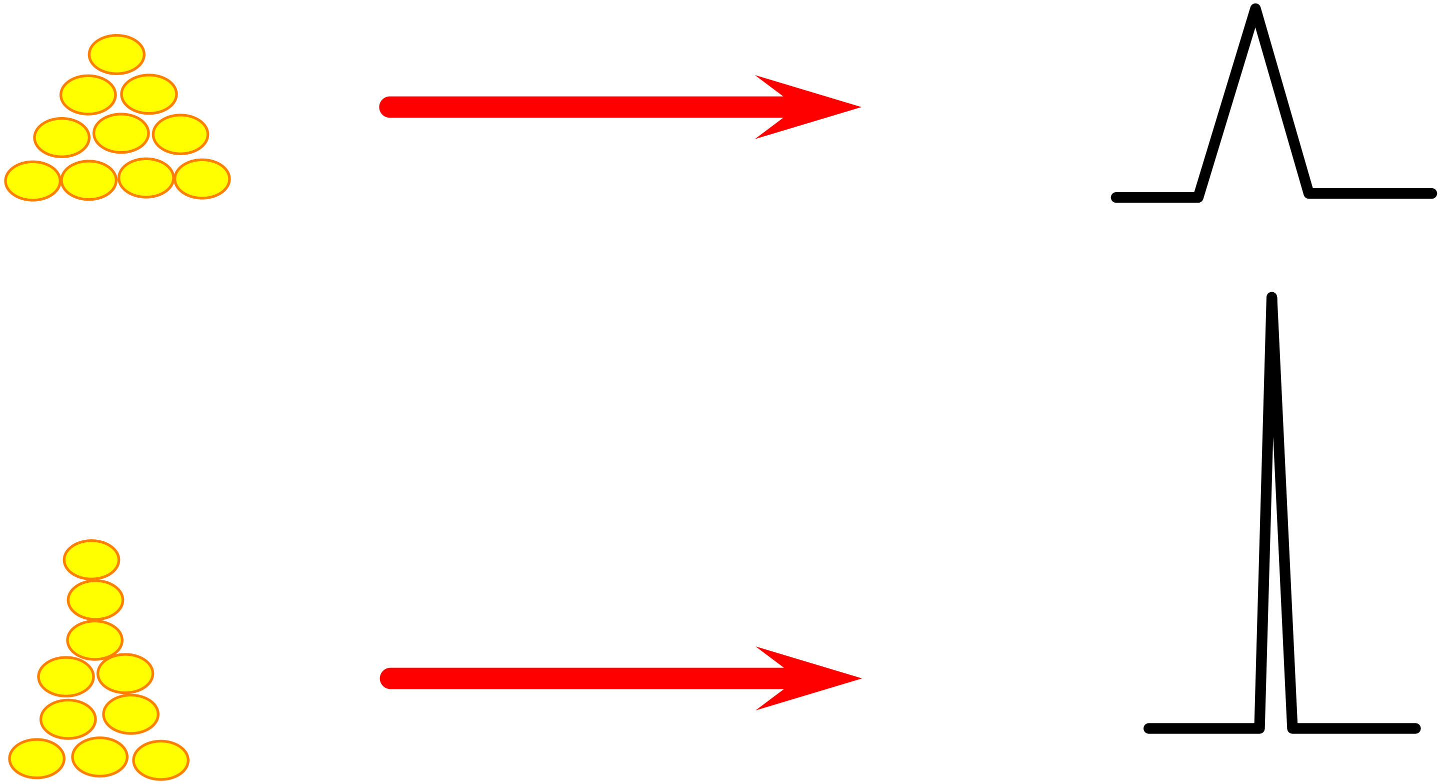


Tailing : Symmetry <1
Fronting : Symmetry >1

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)

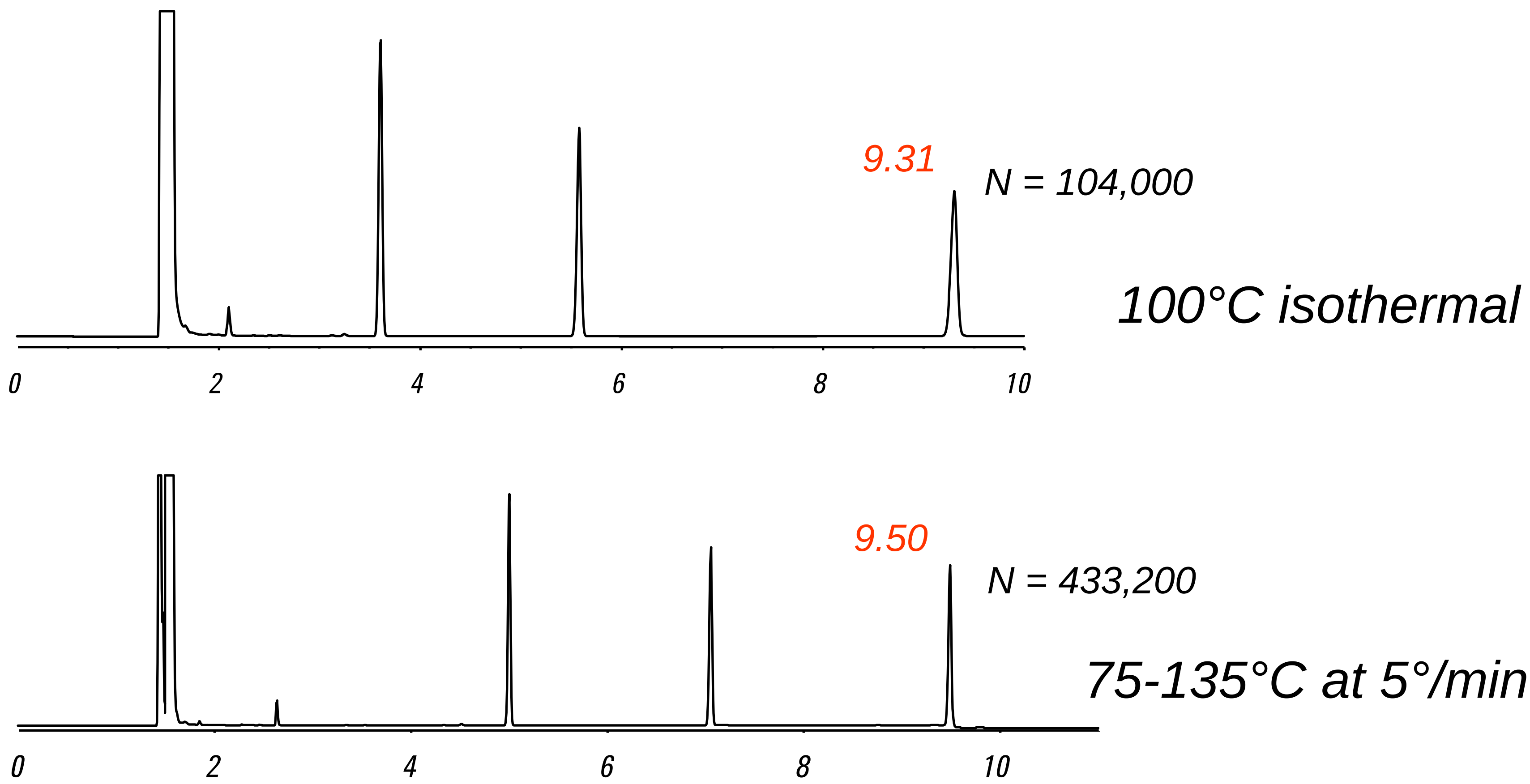
EFFICIENCY MEASUREMENT
Cautions

Actually, measurement of the GC system

Condition dependent

Use a peak with k>5

ISOTHERMAL VS. TEMPERATURE PROGRAMMING
Efficiency



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: $\alpha = 1$

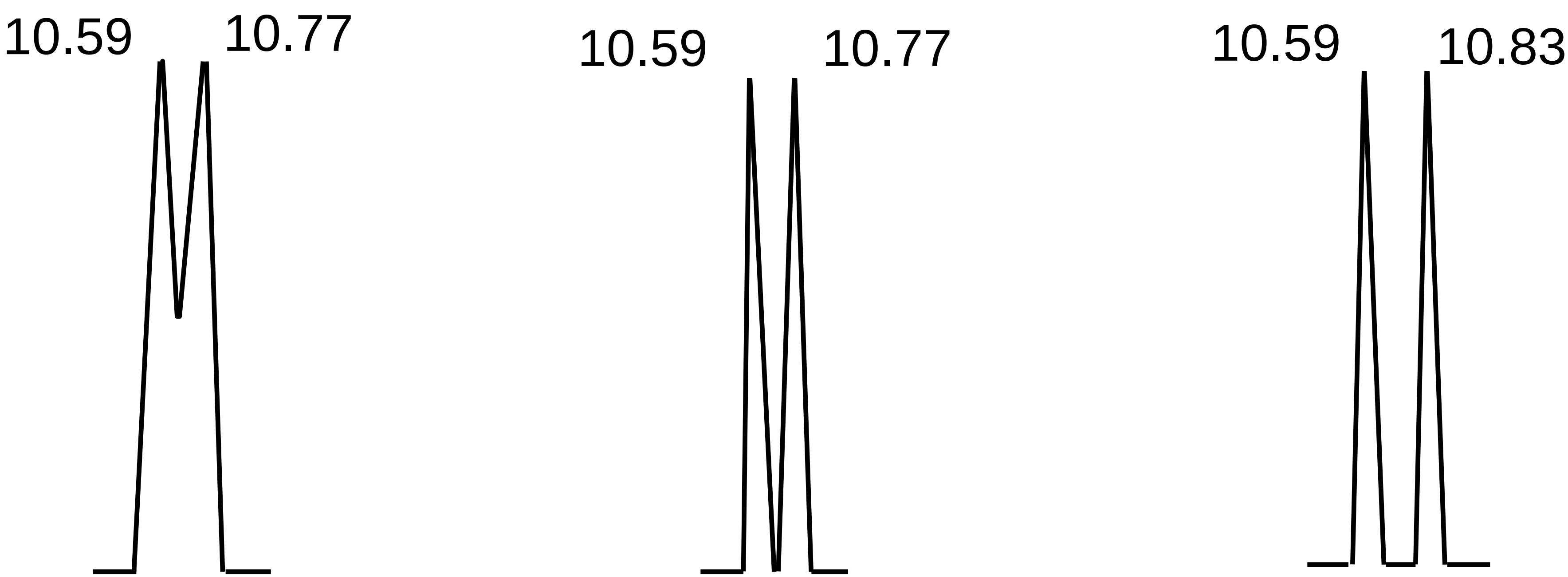
k_2 = retention factor of 2nd peak
k_1 = retention factor of 1st peak

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



$W_h = 0.105$	$W_h = 0.059$	$W_h = 0.059$
R = 0.84	R = 1.50	R = 2.40
% = 50	% = 100	% = 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

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**

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!

Agilent J&W Scientific Technical Support

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

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

866-422-5571 (fax)

GC-Column-Support@agilent.com

www.chem.agilent.com