Understanding the Capillary GC Column:

How to Choose the Correct Type and Dimension

Simon Jones
Application Engineer

Agilent Technologies

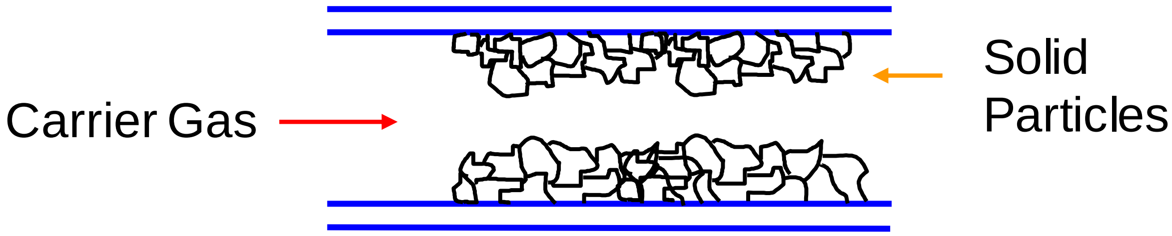
Things to Consider…

- Is it Volatile enough to chromatograph by GC?
- Is it a Gas or a Liquid?
- How are we getting the Sample Injected?
- What is the sample Matrix?
  – Can we do sample clean up?
- Is it an established method?
  -- EPA, ASTM, USP
- What do we Know about the analytes?

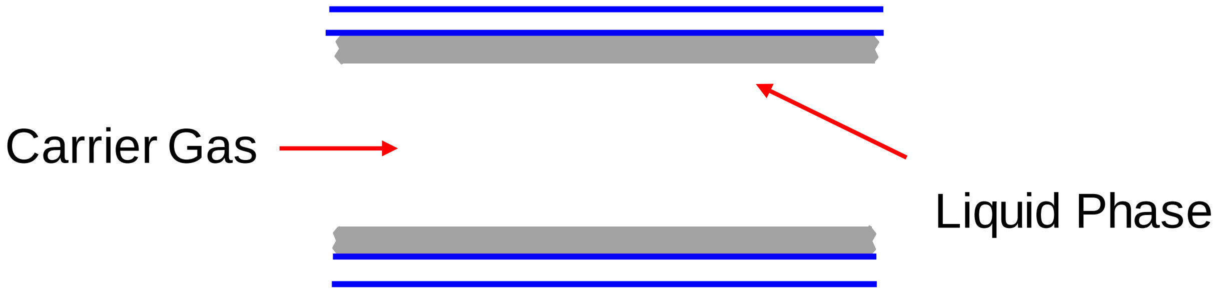
- What else ‘MAY’ be present in the sample?

CAPILLARY COLUMN TYPES

Porous Layer Open Tube (PLOT)

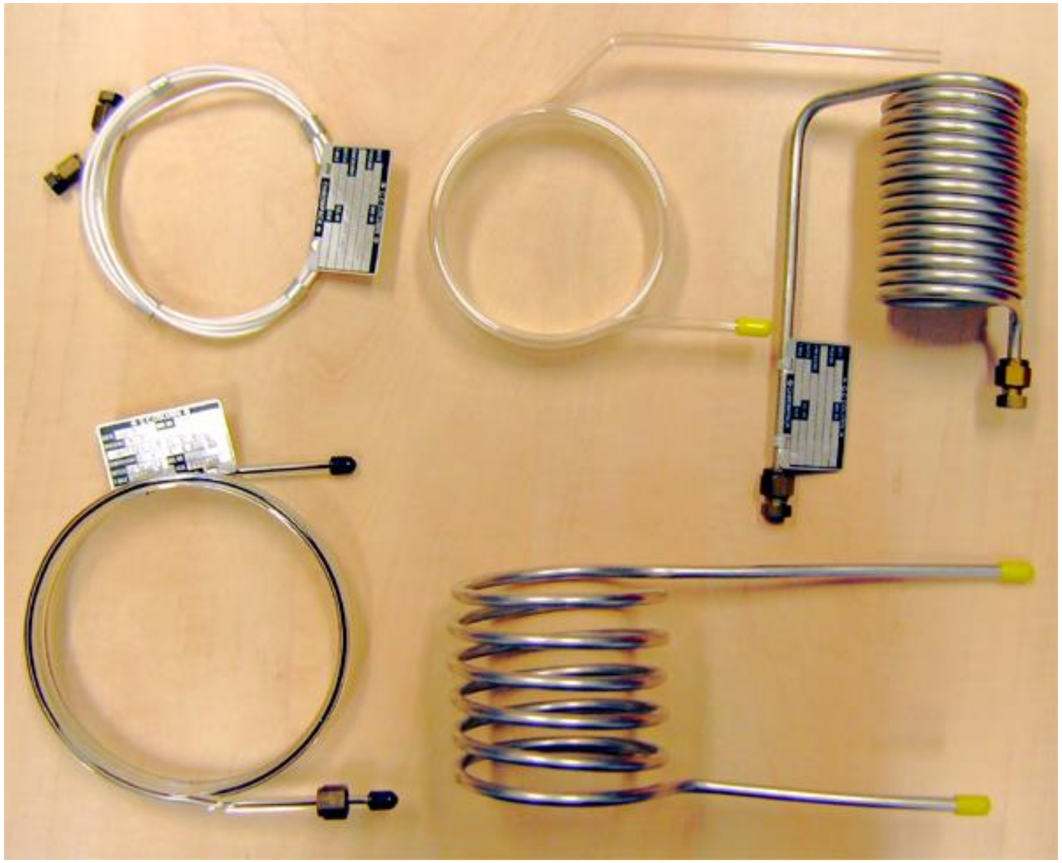


Wall Coated Open Tube (WCOT)



Packed Columns

1950 Introduction with the first gas chromatographs



Packed Column Designs and Materials

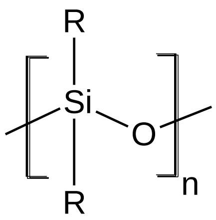
Packed Column Anatomy

- Packed Columns

- 1 – 12 m length
- Internal Diameter 0.5 – 4mm
- Tubing
  – Stainless Steel, Ultimetal™ SS, Glass, Nickel, PTFE
- Packing
  – Coated packing WCOT Capillary
    - Inert, solid support (diatomaceous earth) coated with liquid stationary phase (e.g. OV-1, SE-30, Carbowax 20M, FFAP)

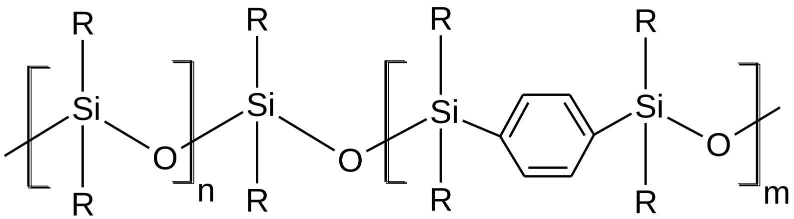
  – Porous packing PLOT Capillary
    - Porous polymers (PoraPak Q, N, HayeSep Q, R, S, etc.)
    - Porous carbons (Carboxens, Carbosieves, Carbotraps)

STATIONARY PHASE POLYMERS

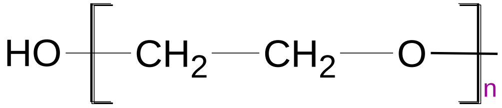


Siloxane

R=methyl, phenyl, cyanopropyl, trifluoropropyl



Siarylene backbone

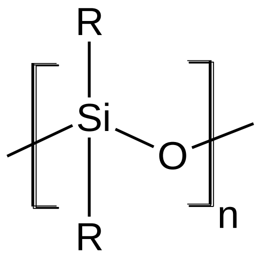


Polyethylene Glycol

Stationary Phase
% Substitution -- polysiloxanes

% = # of sites on silicon atoms occupied

Balance is methyl



Siloxane

R=methyl, phenyl, cyanopropyl, trifluoropropyl

Stationary Phase

Poly(ethylene) Glycol

$$HO-(CH_2-CH_2-O)-H$$

100% PEG (DB-WAX)

Less stable than polysiloxanes

Unique separation characteristics

Poly(Ethylene) Glycol
Modified

- Base deactivated (CAM)
- Acid Modified (DB-FFAP)
- Extended Temperature Range

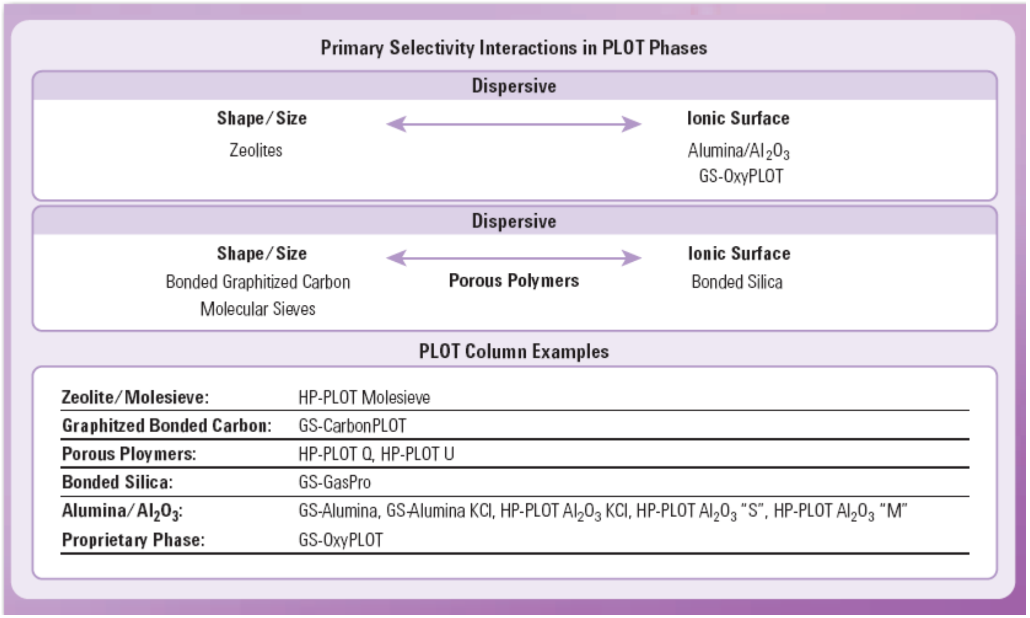
WCOT Column Types

Agilent J&W has over 50 different stationary phase offerings

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					

PLOT Column Types

PLOT columns are primarily, but not exclusively, used for the analysis of gases and low boiling point solutes (i.e., boiling point of solute is at or below room temperature).



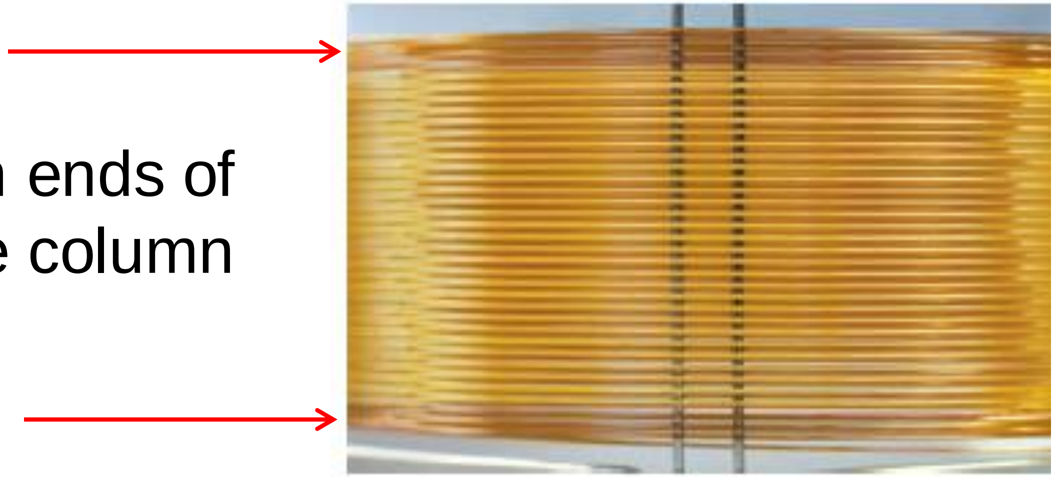
Zeolite/Molesieve:	HP-PLOT Molesieve
Graphitzed Bonded Carbon:	GS-CarbonPLOT
Porous Ploymers:	HP-PLOT Q, HP-PLOT U
Bonded Silica:	GS-GasPro
Alumina/Al_2O_3:	GS-Alumina, GS-Alumina KCl, HP-PLOT Al_2O_3 KCl, HP-PLOT Al_2O_3 "S", HP-PLOT Al_2O_3 "M"
Proprietary Phase:	GS-OxyPLOT

- GS-OxyPLOT: oxygenates
- HP-PLOT Molesieve: O2, N2, CO, Methane
- HP-PLOT Alumina and GS-Alumina: complex hydrocarbon gas matrices, ethylene and propylene purity, 1,4-butadiene
- HP-PLOT Q: freons, sulfides
- HP-PLOT U: C1 to C7 hydrocarbons, CO2, Polar Hydrocarbons
- GS-GasPro: freons, sulfurs, inorganic gases
- GS-CarbonPLOT: inorganic and organic gases

- Agilent J&W PLOT columns begin with the designation of
  - GS (Gas Solid) or
  - HP-PLOT followed by a specific name
  - CP (ChromPack) followed by name
  - **10 stationary phases**
    - GS-OxyPLOT / CP-Lowox
    - GS-Alumina
    - HP-PLOT Al_2O_3 "M"
    - HP-PLOT Al_2O_3 "S"
    - HP-PLOT Al_2O_3 "KCl" / CP-AL_2O_3/KCl
    - HP-PLOT MoleSieve / CP-Molsieve 5A
    - GS-CarbonPLOT / CP-CarboBOND
    - HP-PLOT Q / CP PoraBOND Q
    - HP-PLOT U / CP-PoraBOND U
    - GS-GasPro / CP-SilicaPLOT

Integrated Particle Trap PLOT Columns

Particle trap is on both ends of the column



On the front end to help facilitate backflushing without blowing particles back into the inlet / valve

Specialty Phases

Columns developed for particular applications

Examples: DB-UI 8270D, DB-624UI <467>,DB-VRX, DB-MTBE, DB-TPH, DB-ALC1, DB-ALC2, DB-HTSimDis, DB-Dioxin, Select Low Sulfur, CP-Volamine, Select PAH, DB-EUPAH, DB-CLP1 & 2, DB-Select 624 UI 467, CP-LowOx, Select Permanent Gases……….

Ultra Inert Phases

DB-1msUI

HP-1msUI

DB-5msUI

HP-5msUI

DB-17msUI

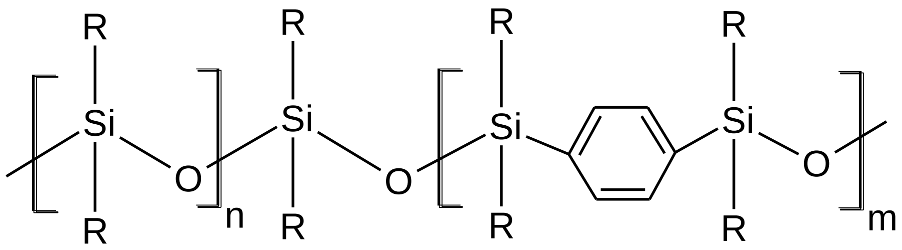
DB-624UI

DB-Select 624UI 467

Same Selectivity, more Inertness!

Three Types Of Low Bleed Phases

- Phases tailored to "mimic" currently existing polymers
  Examples: DB-5ms, DB-35ms, DB-17ms, VF-1701ms



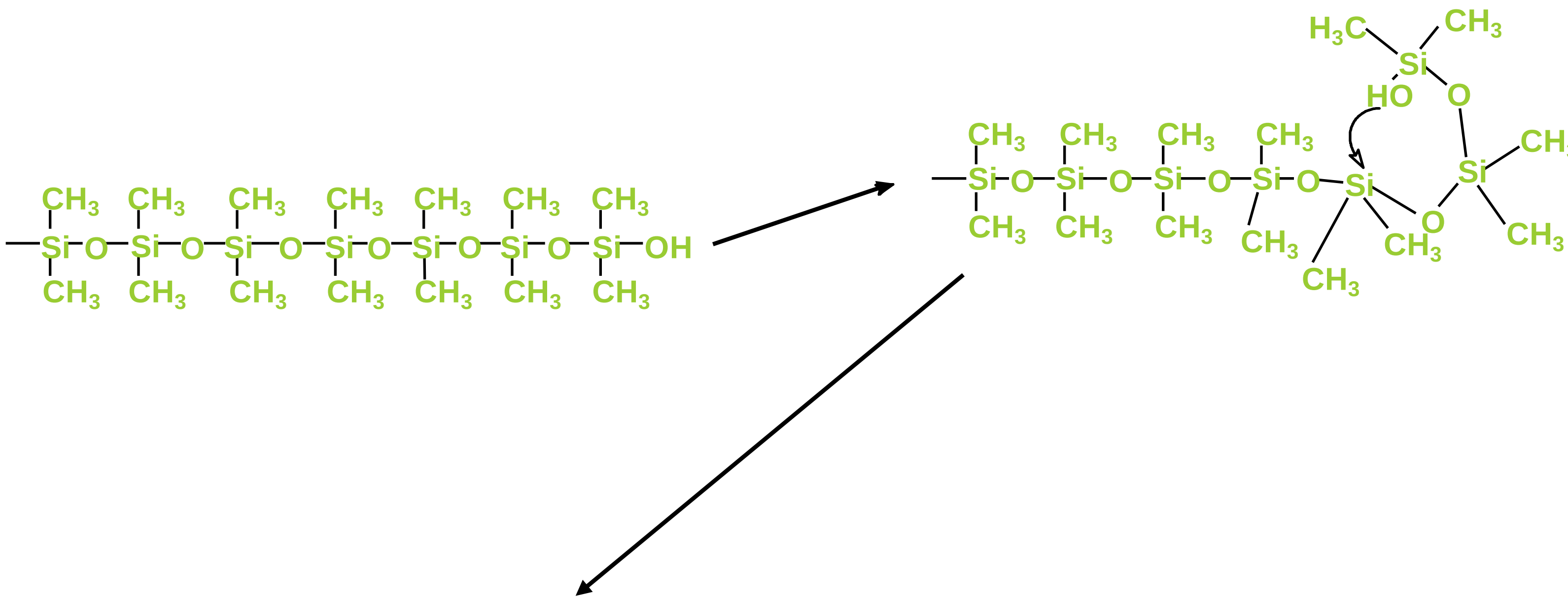
Siarylene backbone

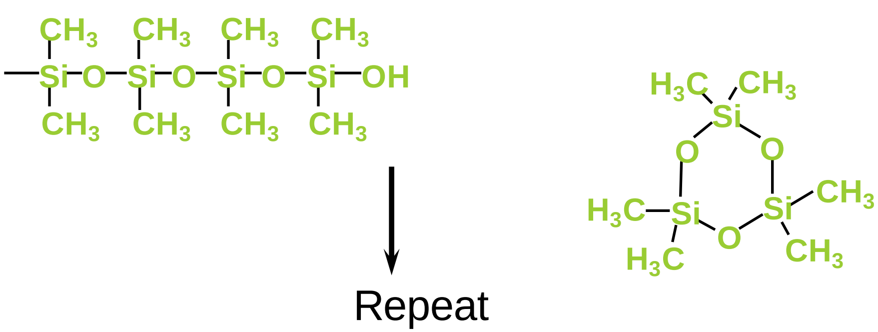
- New phases unrelated to any previously existing polymers
  Examples: DB-XLB

- Optimized manufacturing processes
  DB-1ms, HP-1ms, HP-5ms, VF-5ms

What is Column Bleed???

"Back Biting" Mechanism of Product Formation

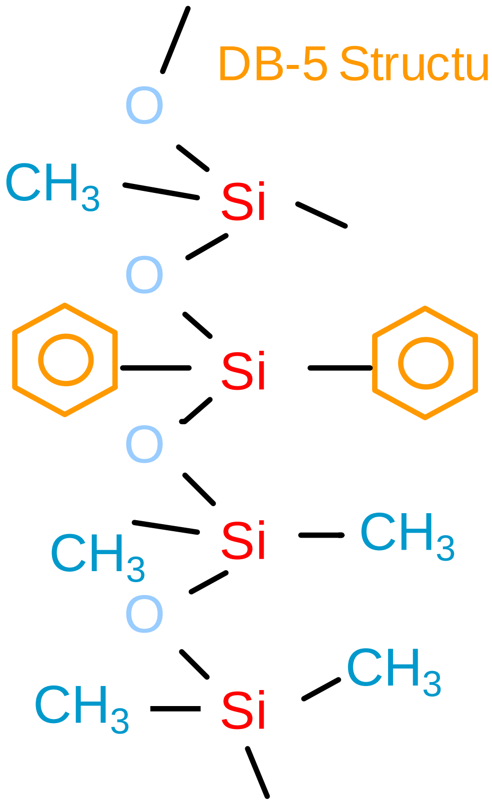




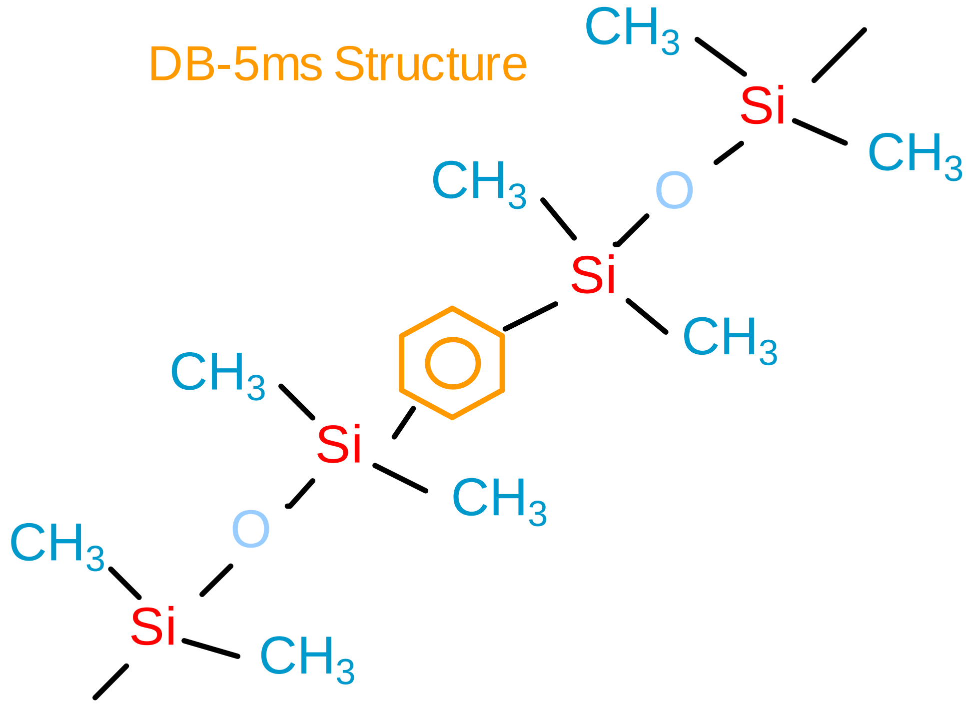
Cyclic products are thermodynamically more stable!

DB-5ms Structure

DB-5 Structure



DB-5ms Structure

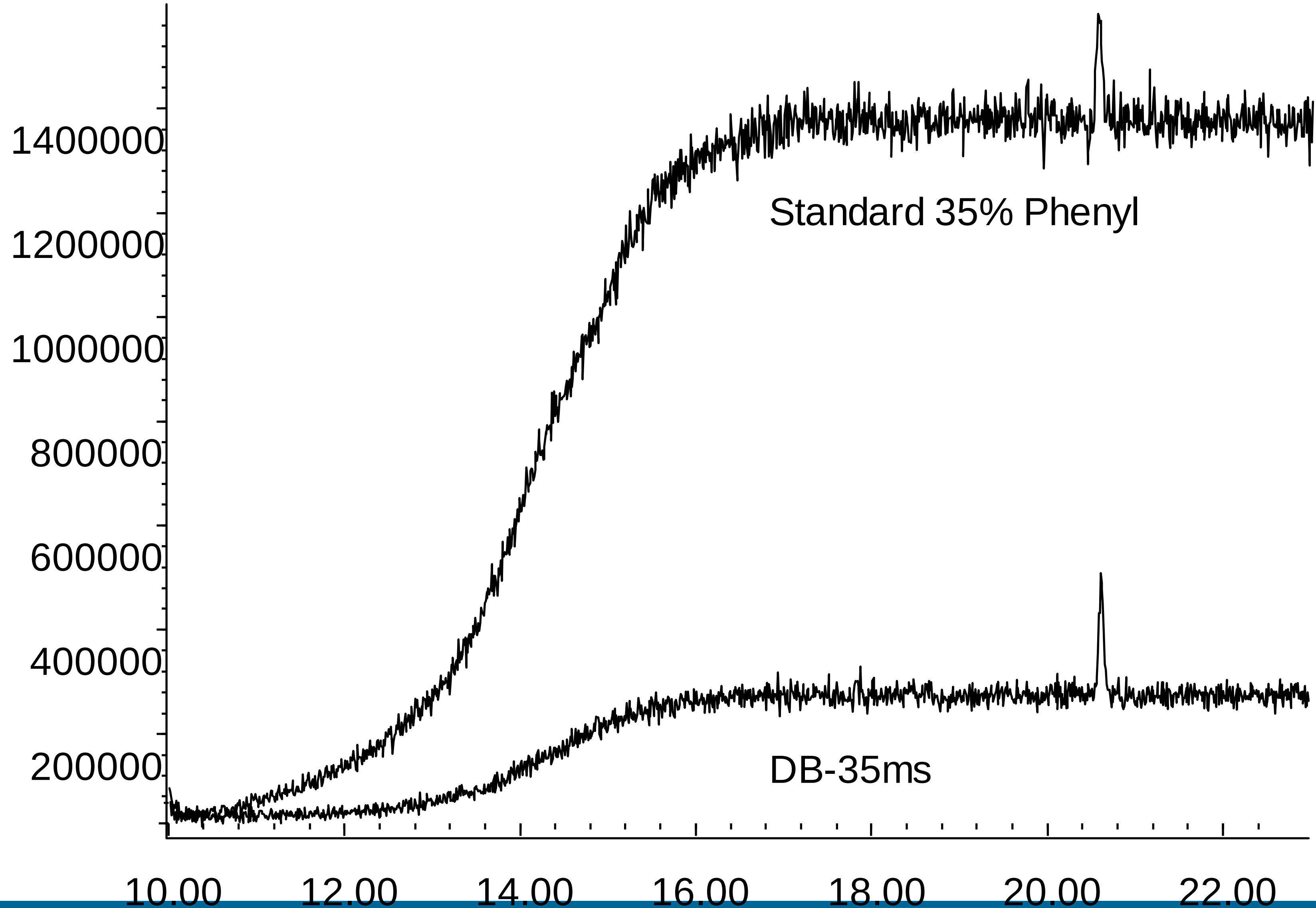


DB-5
5% Phenyl

DB-5ms
1. Increased stability
2. Different selectivity
3. Optimized to match DB-5

DB-35MS VS STANDARD 35% PHENYL

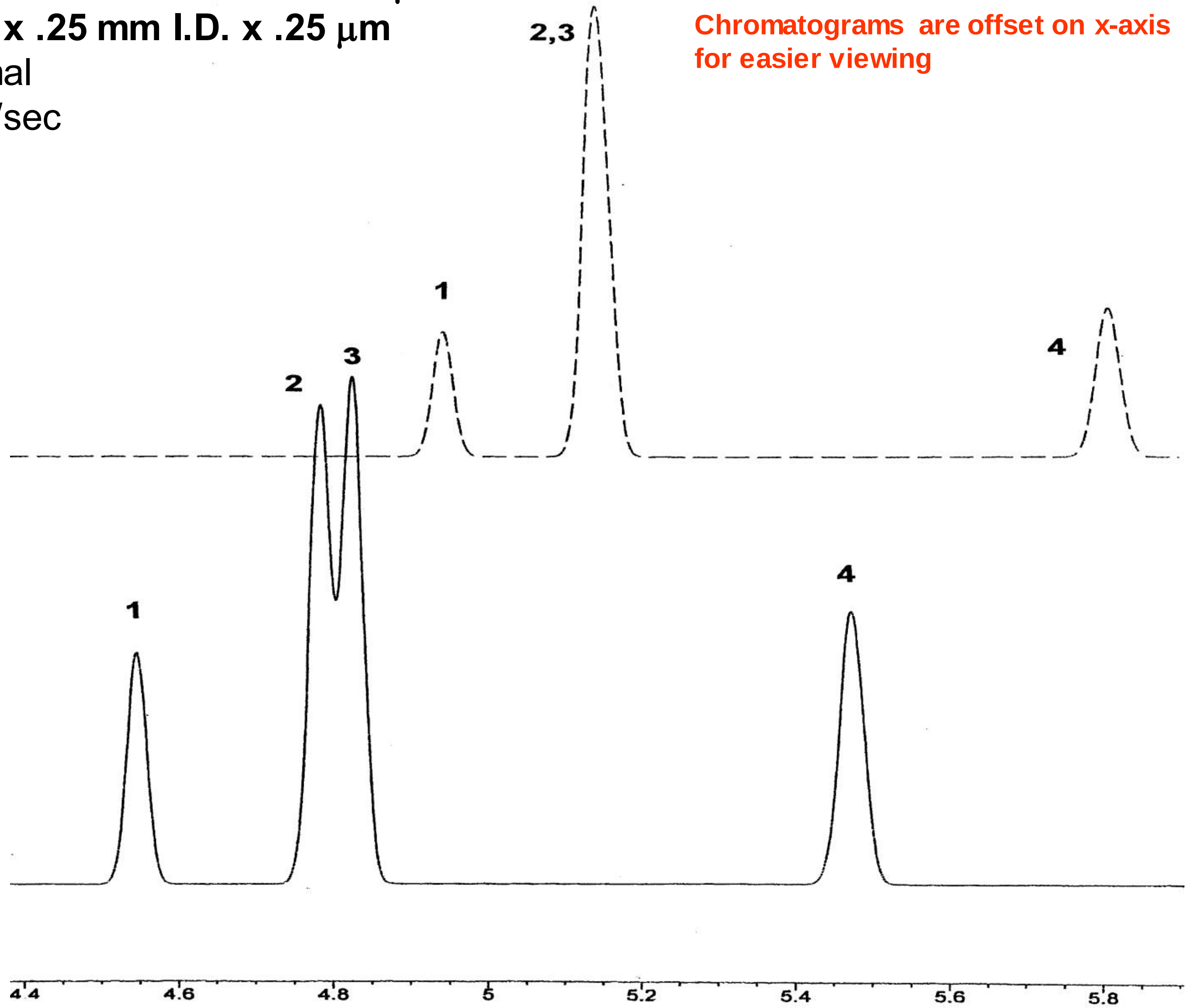
Benzo[g,h,i]perylene, 1ng



Solid line: **DB-5ms 30 m x .25 mm I.D. x .25 μm**
Dashed line: **DB-5 30 m x .25 mm I.D. x .25 μm**
Oven: 60° C isothermal
Carrier gas: H_2 at 40 cm/sec

1: Ethylbenzene
2: m-Xylene
3: p-Xylene
4: o-Xylene

Chromatograms are offset on x-axis for easier viewing



Why is stationary phase type important?

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

Influence on α

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

k_2 = partition ratio of 2nd peak
k_1 = partition ratio of 1st peak

Selectivity

- Relative spacing of the chromatographic peaks

- The result of all non-polar, polarizable and polar interactions that cause a stationary phase to be more or less retentive to one analyte than another

Optimizing Selectivity (α)

Match analyte polarity to stationary phase polarity

-'like dissolves like'

Take advantage of unique interactions between analyte and stationary phase functional groups

Analyte Polarity

Nonpolar Molecules - generally composed of only carbon and hydrogen and exhibit no dipole moment (Straight-chained hydrocarbons (n-alkanes))

Polar Molecules - primarily composed of carbon and hydrogen but also contain atoms of nitrogen, oxygen, phosphorus, sulfur, or a halogen (Alcohols, amines, thiols, ketones, nitriles, organo-halides, etc. Includes dipole-dipole interactions and H-bonding)

Polarizable Molecules - primarily composed of carbon and hydrogen, but also contain unsaturated bonds (Alkenes, alkynes and aromatic compounds)

Selectivity Interactions

- Dispersion
- Dipole
- Hydrogen bonding

Dispersion Interaction

ΔH_{vap}

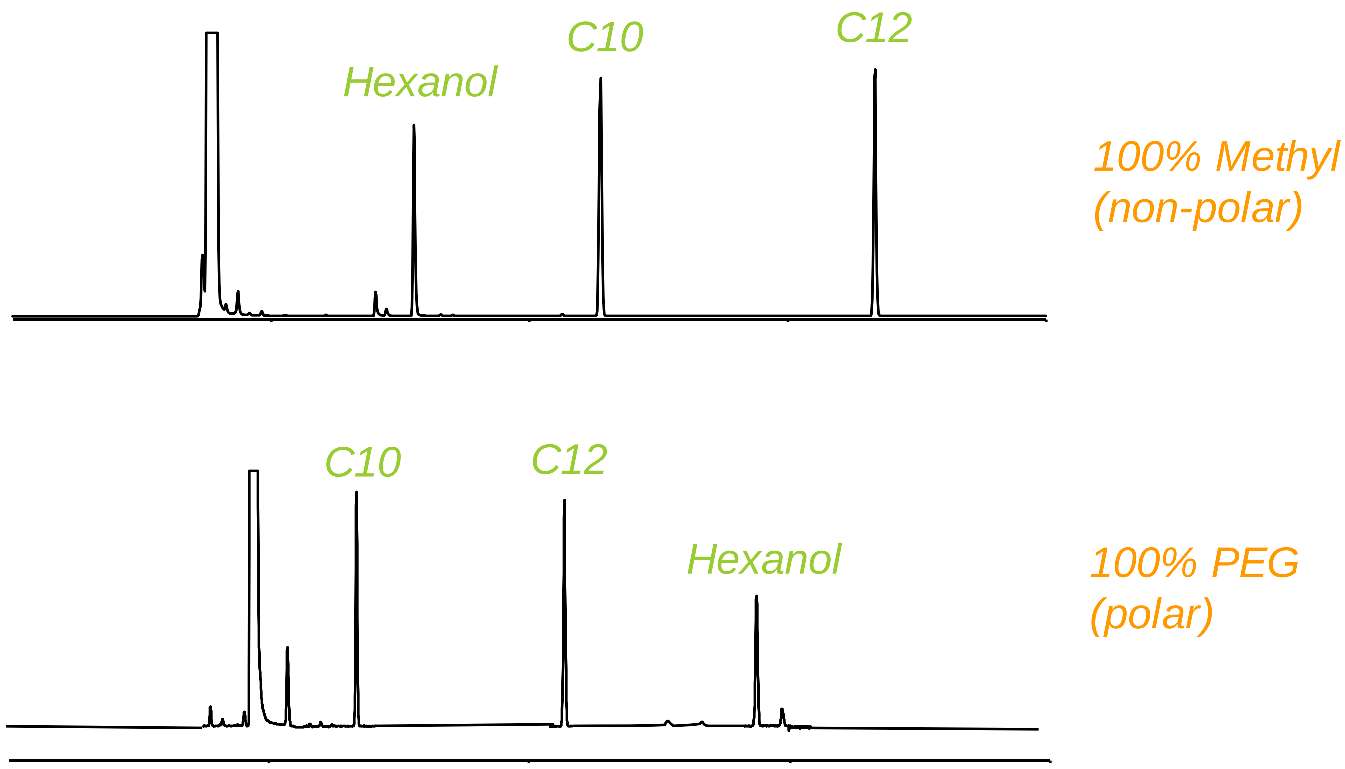
- Separation by differences in analyte heat of vaporizations (ΔH_{vap})

- Heat necessary to convert a liquid into a gas (at the same temperature)

Dispersion Interaction

Solubility And Retention

Hexanol	158°C
Decane	174°C
Dodecane	216°C



30 m x 0.32 mm ID, 0.25 µm
He at 35 cm/sec
50-170°C at 15°/min

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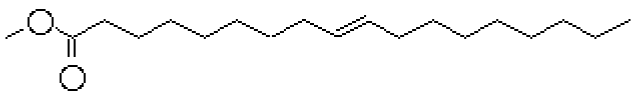
Dispersion Interaction

ΔH_{vap}

Vapor pressure: good approximation

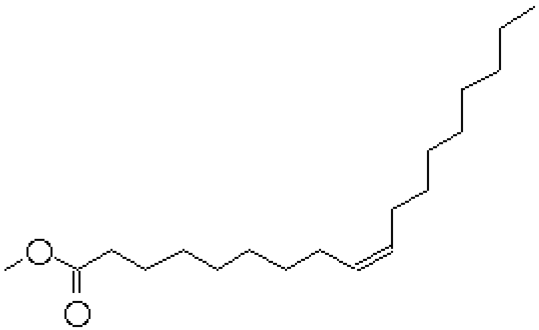
Boiling point: poor approximation

Dipole Interaction



C18:1 (Methyl *trans*-9-octadecenoate)

B.Pt. 186°C



C18:1 (Methyl *cis*-9-octadecenoate)

B.Pt. 186°C

Smaller differences require a stronger dipole phase

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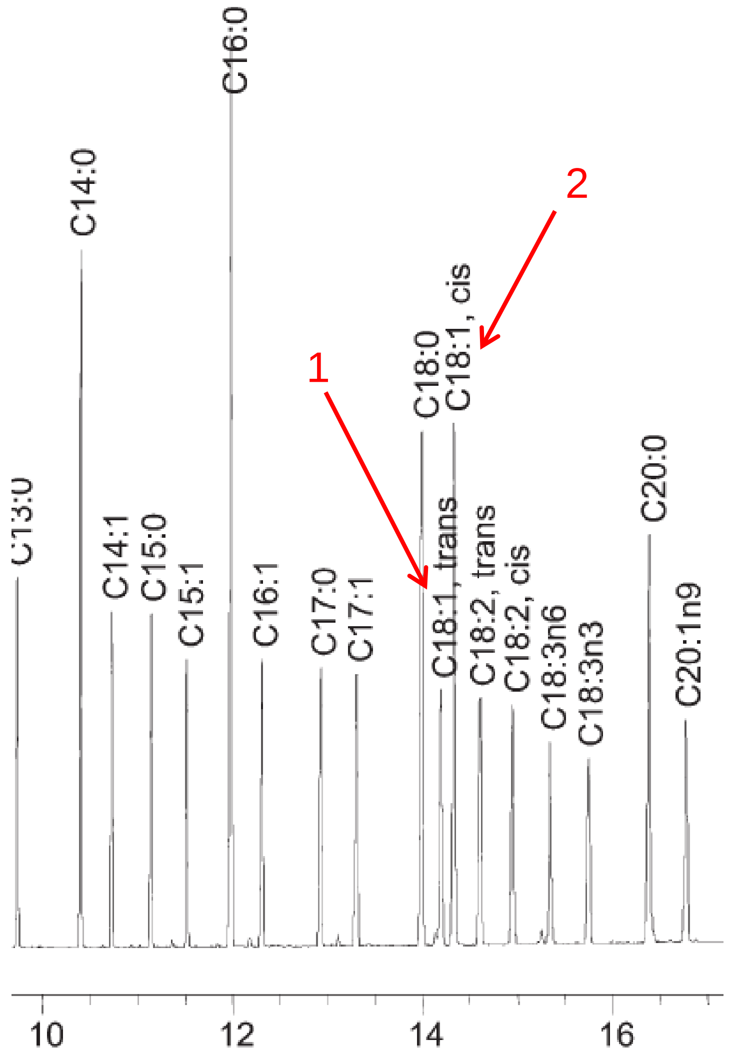
Fames – 37 Component Standard

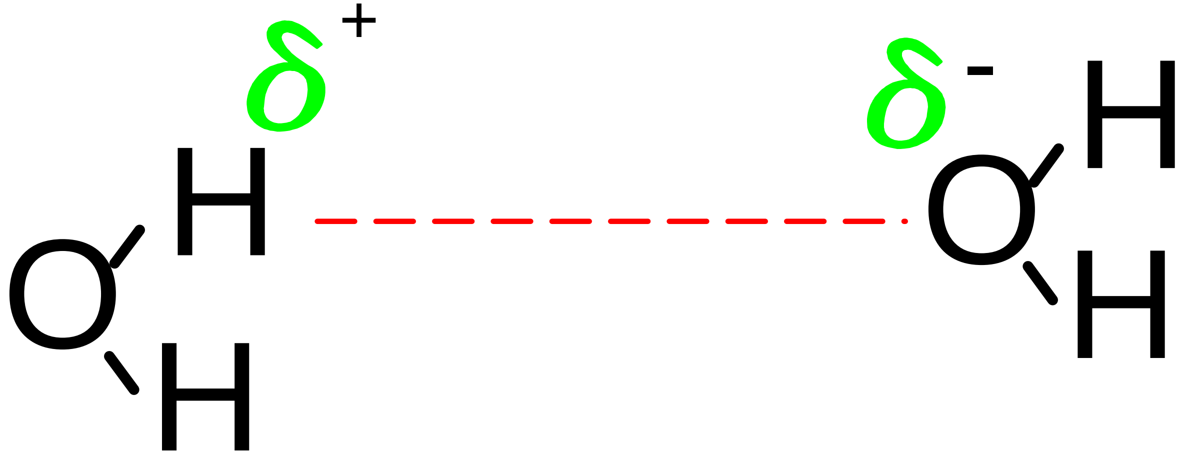
Column: DB-23
60 m X 0.25 mm X 0.15 µm
Agilent P/N 122-2361
Carrier: He , 33 cm/sec @ 50°C
Oven: 50°C for 1 min
25°C/min to 175 (no hold)
4°C/min to 230°C hold 5 min
Injector: 250°C, Split 50:1, 1uL
Detector: FID, 250°C

1 C18:1 (Methyl *trans*-9-octadecenoate)
2 C18:1 (Methyl *cis*-9-octadecenoate)



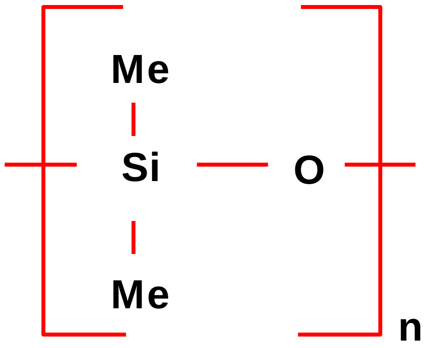
Hydrogen Bonding Interaction

Dipole-Dipole interaction with H bound to O or N interacting with an O or N



NONPOLAR PHASES

Typified by 100% polydimethylsiloxanes such as HP-1, DB-1, DB-1ms, HP-1ms, VF-1ms, CP-Sil 5 CB

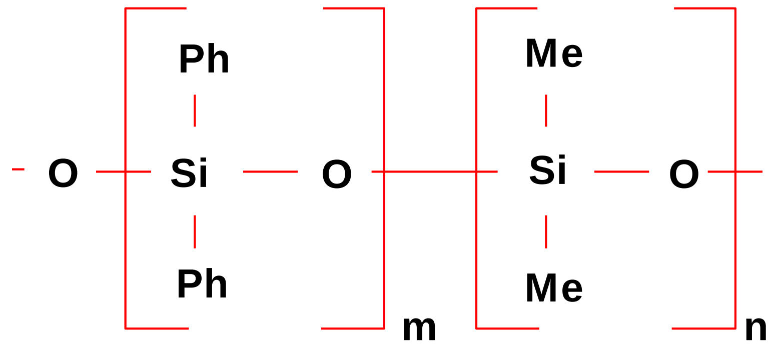


Separation Mechanisms:

- Dispersion only

POLARIZABLE PHASES

Typified by phenyl substituted siloxanes, substituted at 5-50% (HP-5, HP-5ms, DB-35, DB-35ms, DB-17, DB-17ms)



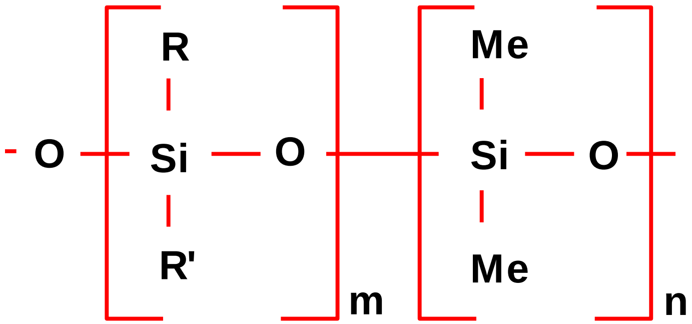
5%--weakly polar, rest--mid polar

Separation Mechanisms:

- Dispersion
- Inducible dipole at phenyl groups

STRONG DIPOLE PHASES

Typified by cyanopropyl or trifluoropropyl substituted siloxanes, substituted 6-50% (DB-1701, DB-1301, DB-200, DB-23, DB-225)



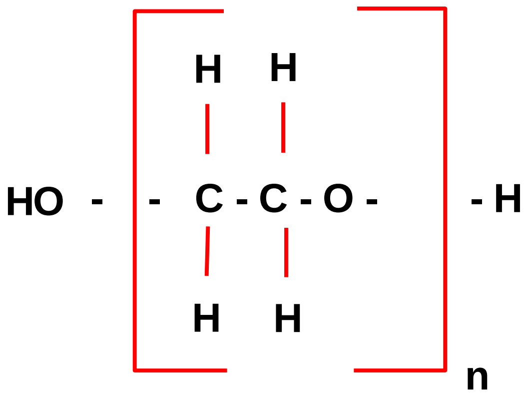
R = cyanopropyl or trifluoropropyl
R′ = phenyl or methyl

Separation Mechanisms:

- Dispersion
- Inducible dipole at phenyl groups
- Strong permanent dipole
- Hydrogen bonding

HYDROGEN BONDING PHASES

Typified by polyethylene glycol polymers (Carbowax, HP-INNOWax, DB-WAX, DB-FFAP, VF-WAXms, CP-WAX52CB….)



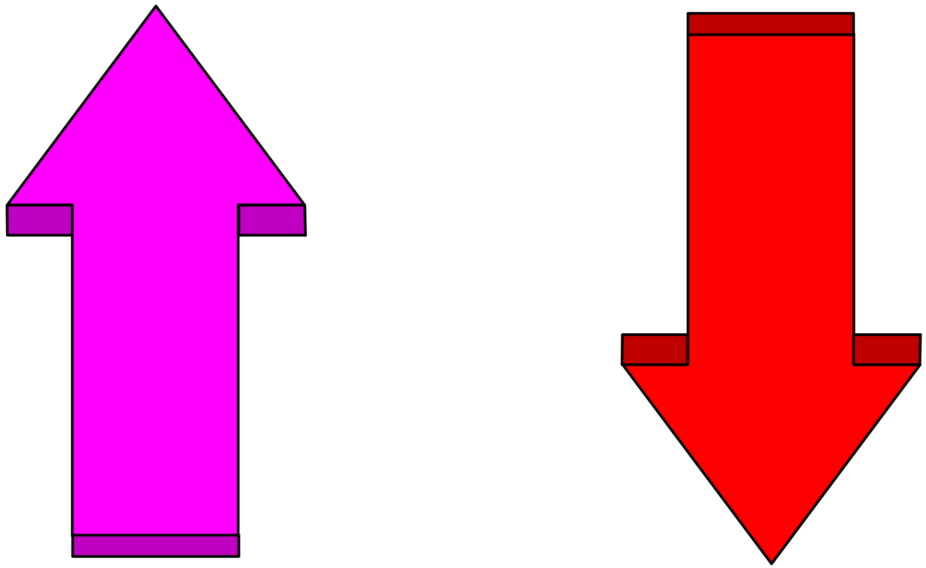
Separation Mechanisms:

- Dispersion
- Strong permanent dipole
- Hydrogen bonding

Selectivity
Interaction Strengths

Phase	Dispersion	Dipole	H Bonding
Methyl	Strong	None	None
Phenyl	Strong	None	Weak
Cyanopropyl	Strong	Very Strong	Moderate
Trifluoropropyl	Strong	Moderate	Weak
PEG	Strong	Strong	Moderate

Polarity



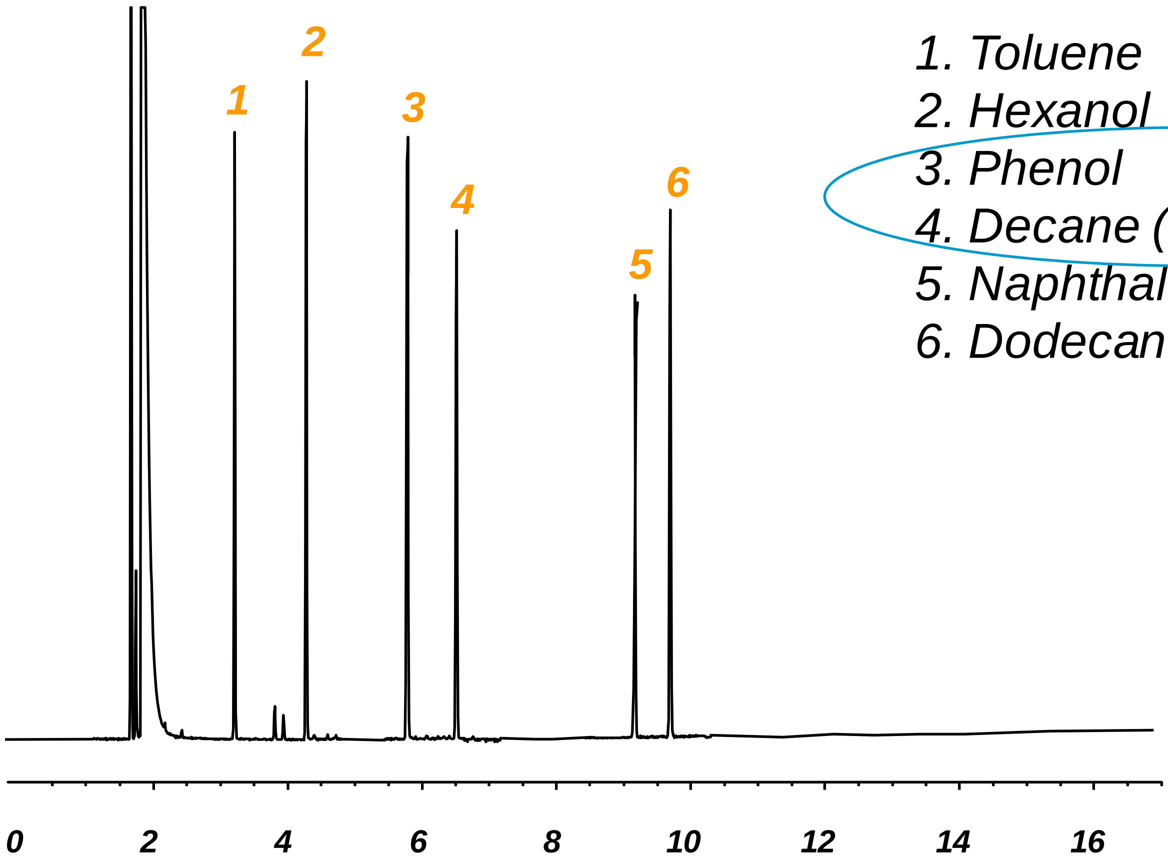
Polarity

Stability
Temperature Range

Compounds Properties

Compounds	Polar	Aromatic	Hydrogen Bonding	Dipole
Toluene	no	yes	no	induced
Hexanol	yes	no	yes	yes
Phenol	yes	yes	yes	yes
Decane	no	no	no	no
Naphthalene	no	yes	no	induced
Dodecane	no	no	no	no

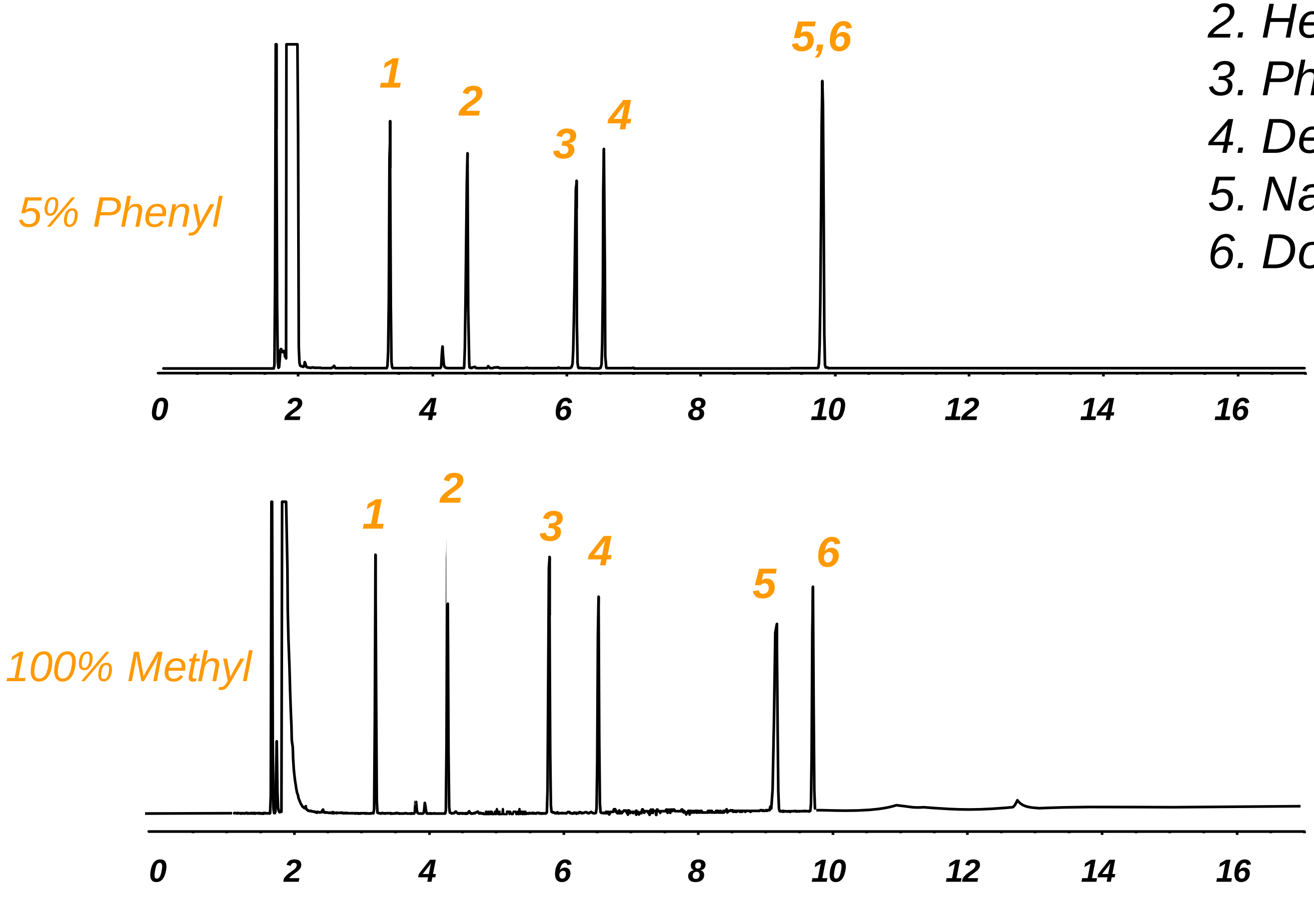
100% Methyl Polysiloxane



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

5% Phenyl

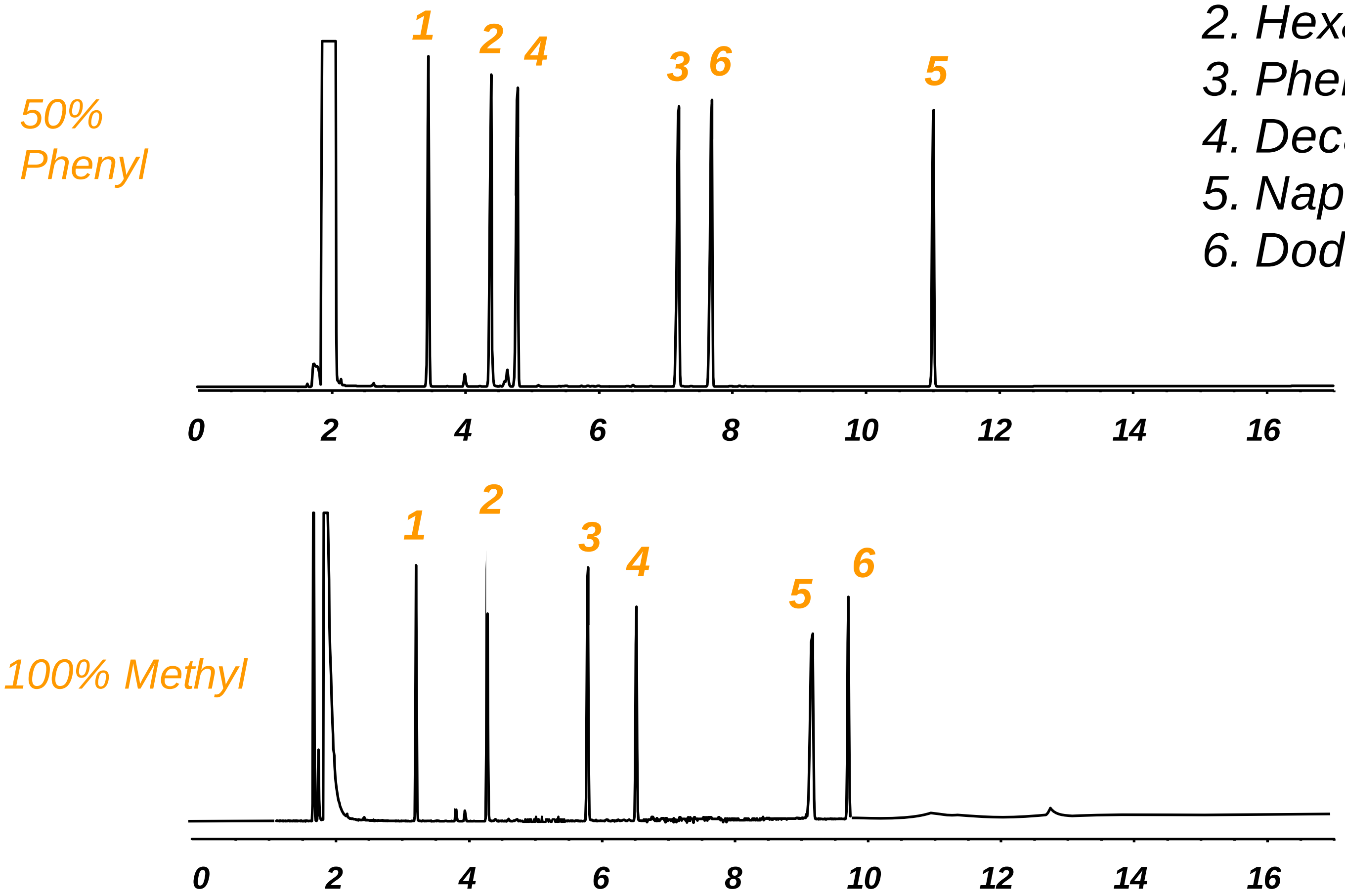


1. *Toluene* 110°C
2. *Hexanol* 158°C
3. *Phenol* 181°C
4. *Decane (C10)* 174°C
5. *Naphthalene* 218°C
6. *Dodecane (C12)* 216°C

Strong Dispersion
No Dipole
Weak H Bonding

50% Phenyl

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

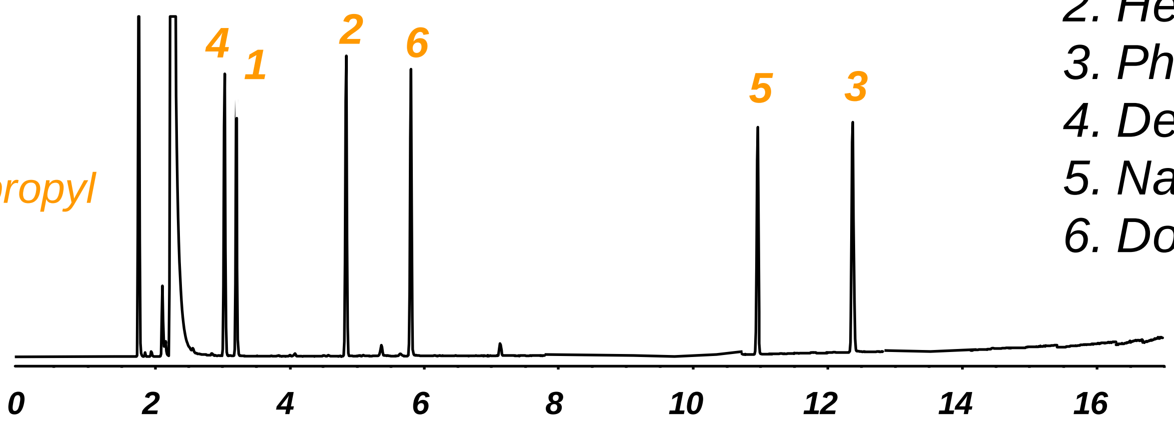


Strong Dispersion
No Dipole
Weak H Bonding

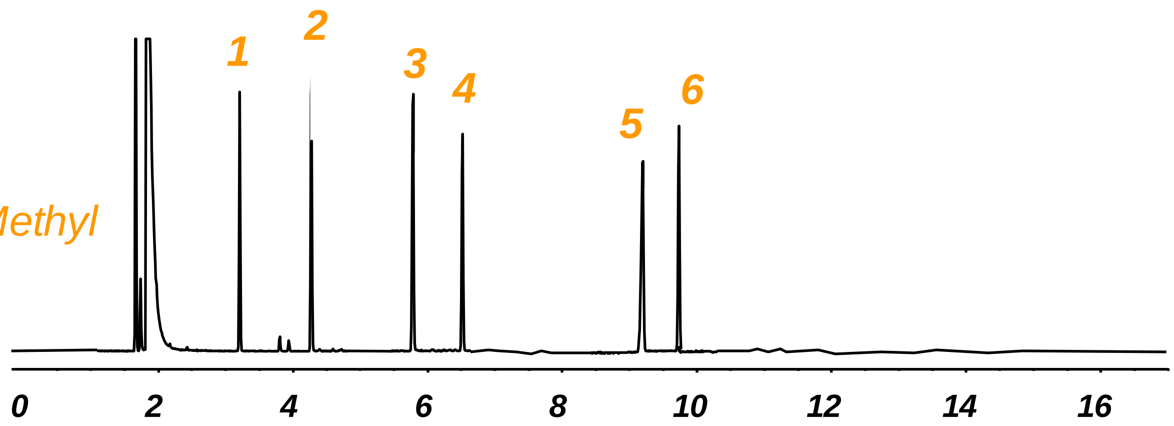
50% Cyanopropyl

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

50% Cyanopropyl

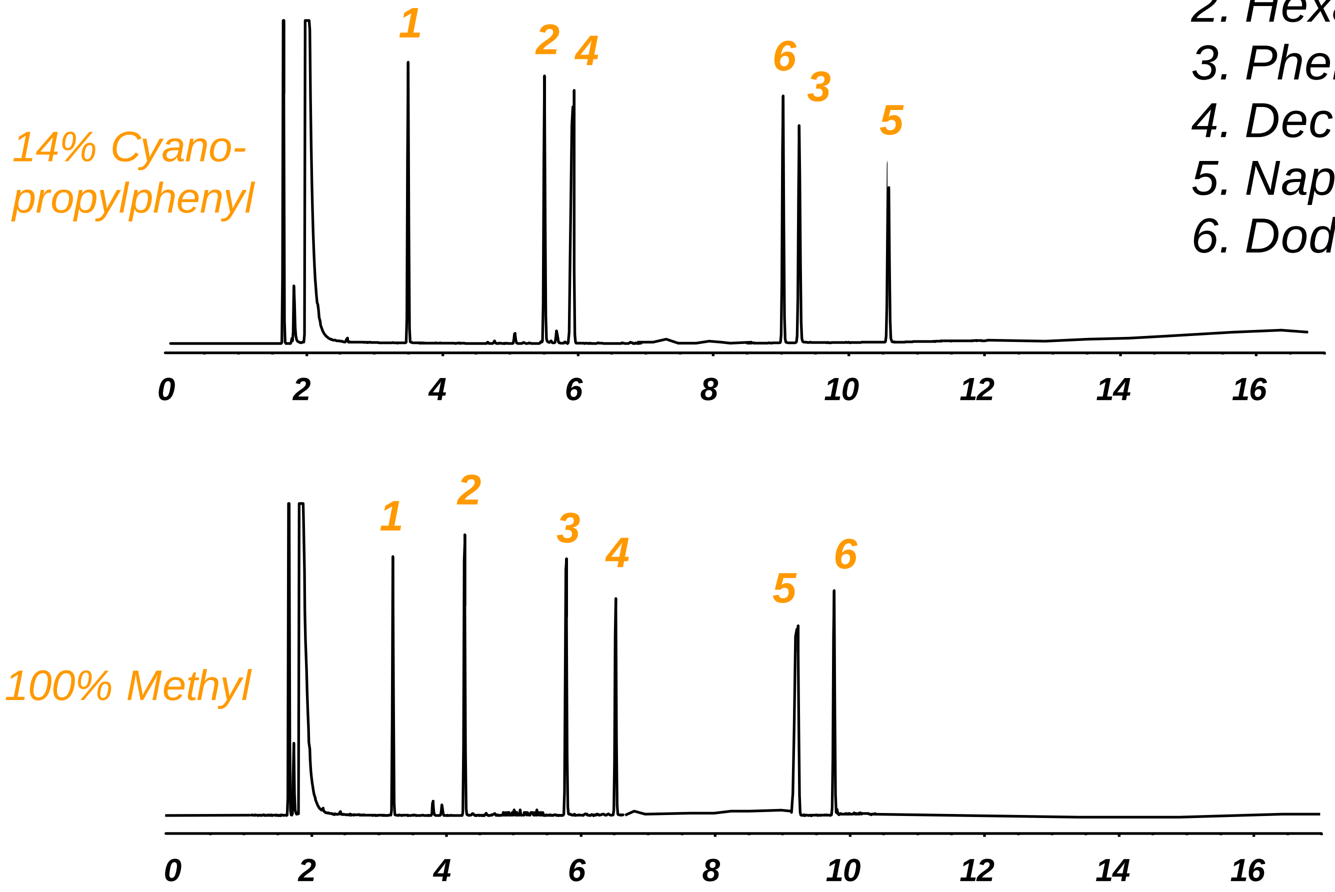


100% Methyl



Strong Dispersion
Strong Dipole
Moderate H Bonding

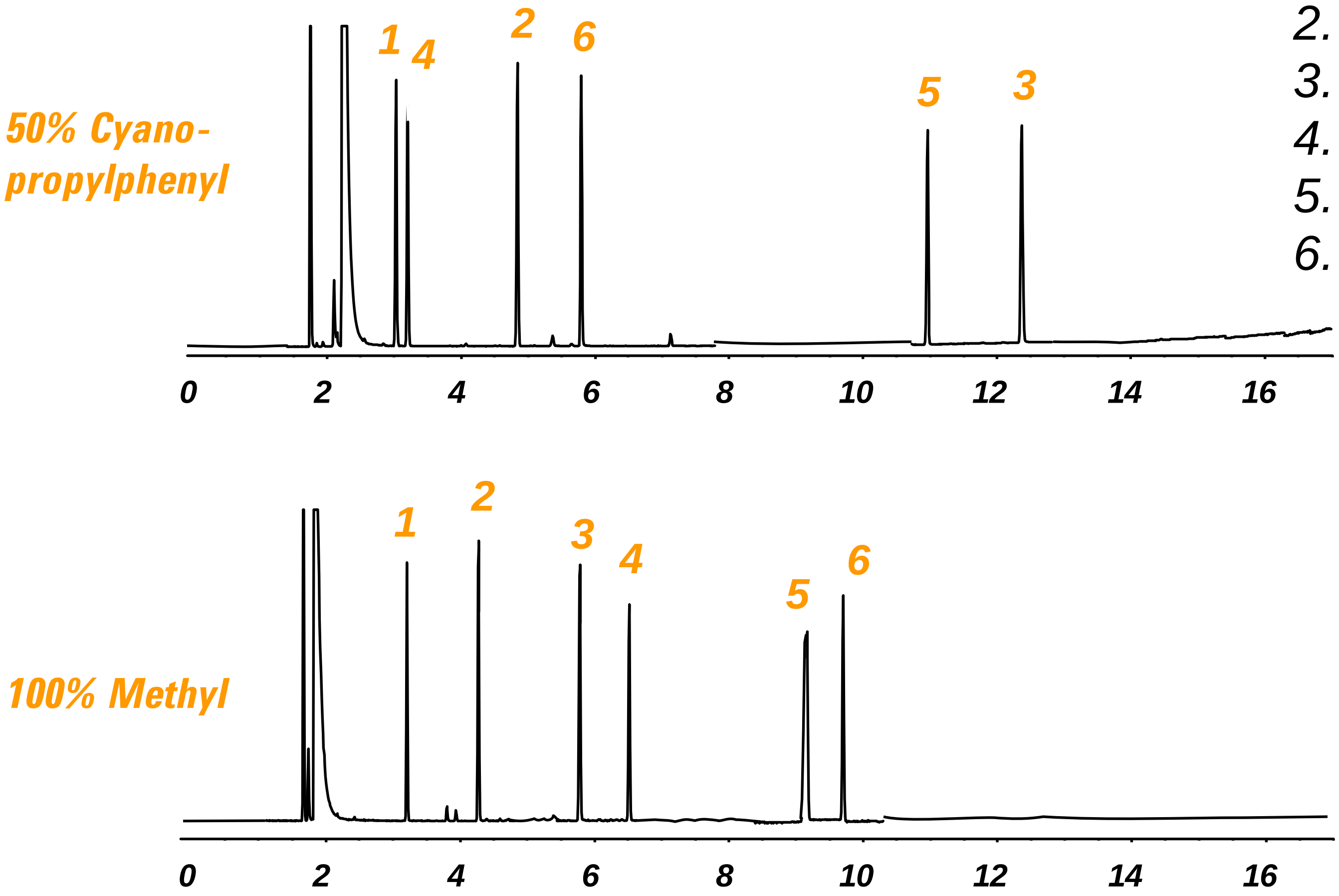
14% Cyanopropylphenyl



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
None/Strong Dipole (Ph/CNPr)
Weak/Moderate H Bonding (Ph/CNPr)

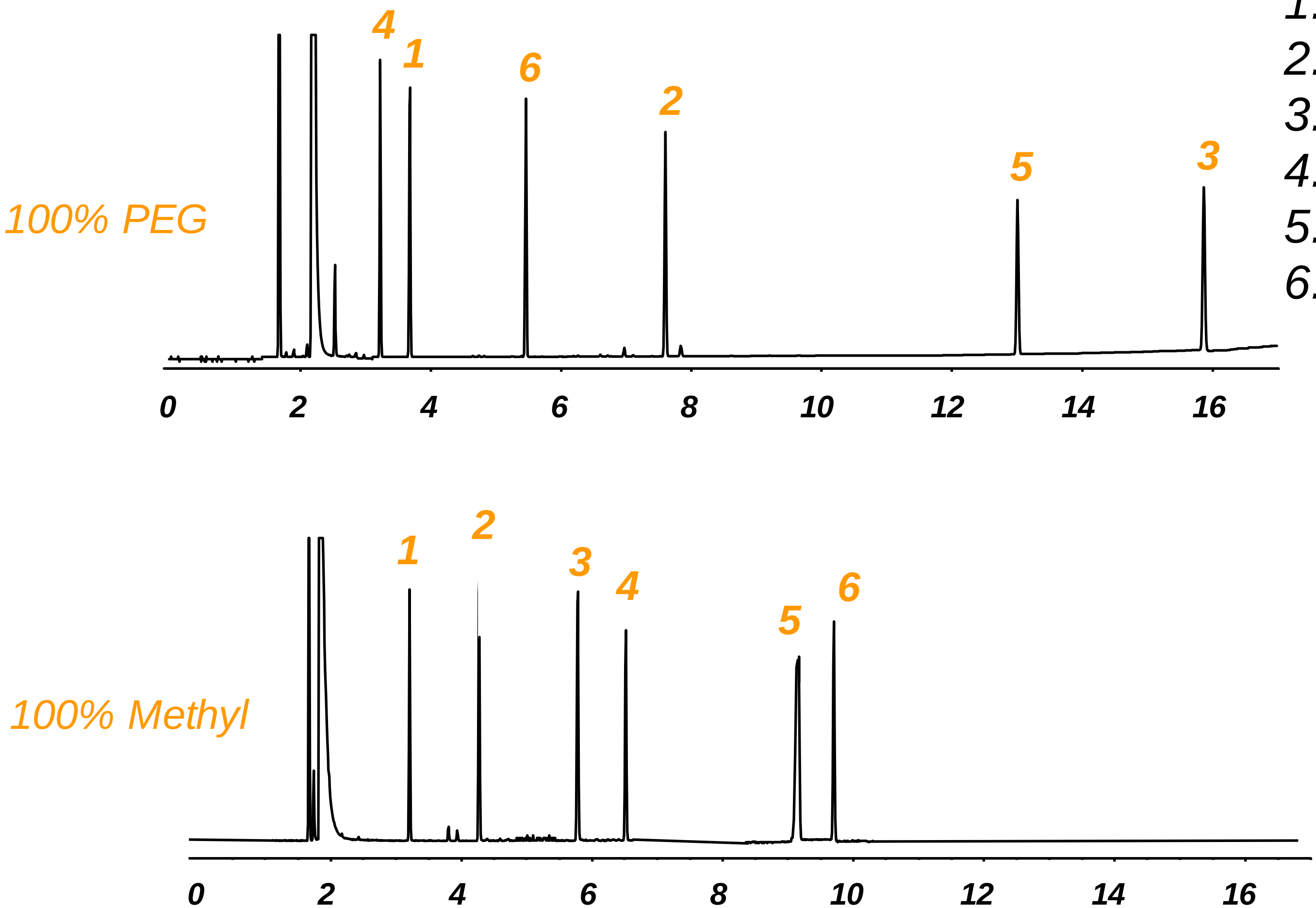
50% Cyanopropylphenyl



1. Toluene
2. Hexanol
3. Phenol
4. Decane (C10)
5. Naphthalene
6. Dodecane (C12)

Strong Dispersion
None/Strong Dipole (Ph/CNPr)
Weak/Moderate H Bonding (Ph/CNPr)

100% Polyethylene Glycol



1. Toluene
2. Hexanol
3. Phenol
4. Decane (C10)
5. Naphthalene
6. Dodecane (C12)

Strong Dispersion
Strong Dipole
Moderate H Bonding

Stationary Phase Selection
Part 1

- Existing information
- Selectivity
- Polarity
- Critical separations
- Temperature limits

Stationary Phase Selection
Part 2

- Capacity
- Analysis time
- Bleed
- Versatility
- Selective detectors

Column Dimensions

- Inner diameter
- Length
- Film Thickness

Column Diameter

Capillary Columns

I.D. (mm)	Common Name
0.53	Megabore
0.45	High speed Megabore
0.32	Wide
0.20-0.25	Narrow
0.18	Minibore

Column Diameter

Theoretical Efficiency

I.D. (mm)	N/m
0.10	11905
0.18	6666
0.20	5941
0.25	4762
0.32	3717
0.53	2242

k = 5

Efficiency and Resolution
Relationship

$$\sqrt{N} \propto R_s$$

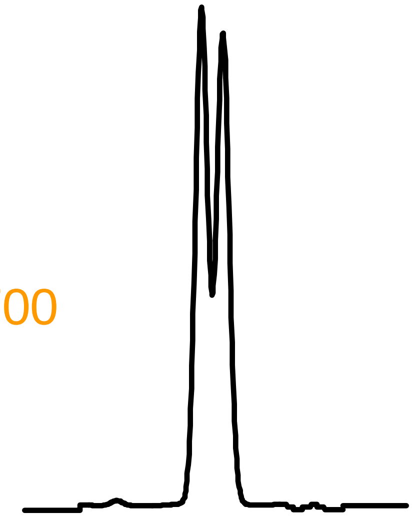
Efficiency X 4 = Resolution X 2

Column Diameter

Resolution
180°C isothermal

R=0.87

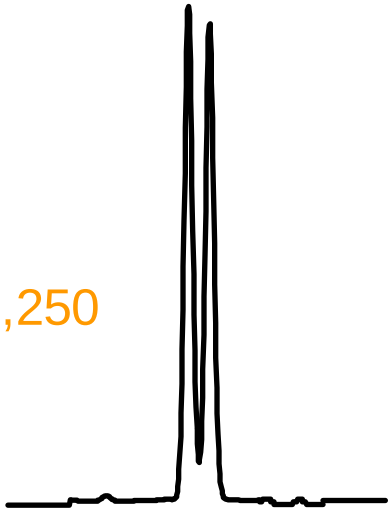
n =58,700



0.53 mm

R=1.01

n =107,250



0.32 mm

Square root of resolution is inversely proportional to column diameter

Column Diameter

Inlet Head Pressures
Helium

I.D (mm)	Pressure (psig)
0.10	225-250
0.20	25-35
0.25	15-25
0.32	10-20
0.53	2-4

30 meters
Hydrogen pressures x 1/2

Column Diameter

Capacity

Like Polarity Phase/Solute

I.D. (mm)	Capacity (ng)
0.20	50-100
0.25	75-150
0.32	125-250
0.53	200-400

0.25 µm film thickness

Column Diameter
Carrier Gas Flow Rate

Smaller diameters for low flow situations
(e.g., GC/MS)

Larger diameters for high flow situations
(e.g., purge & trap, headspace, gas sample valve)

Column Length

Most common: 15-60 meters

Available: 5-200 meters

Column Length

Resolution and Retention
210°C isothermal

R=0.84
2.29 min

R=1.16
4.82 min

R=1.68
8.73 min

15 m

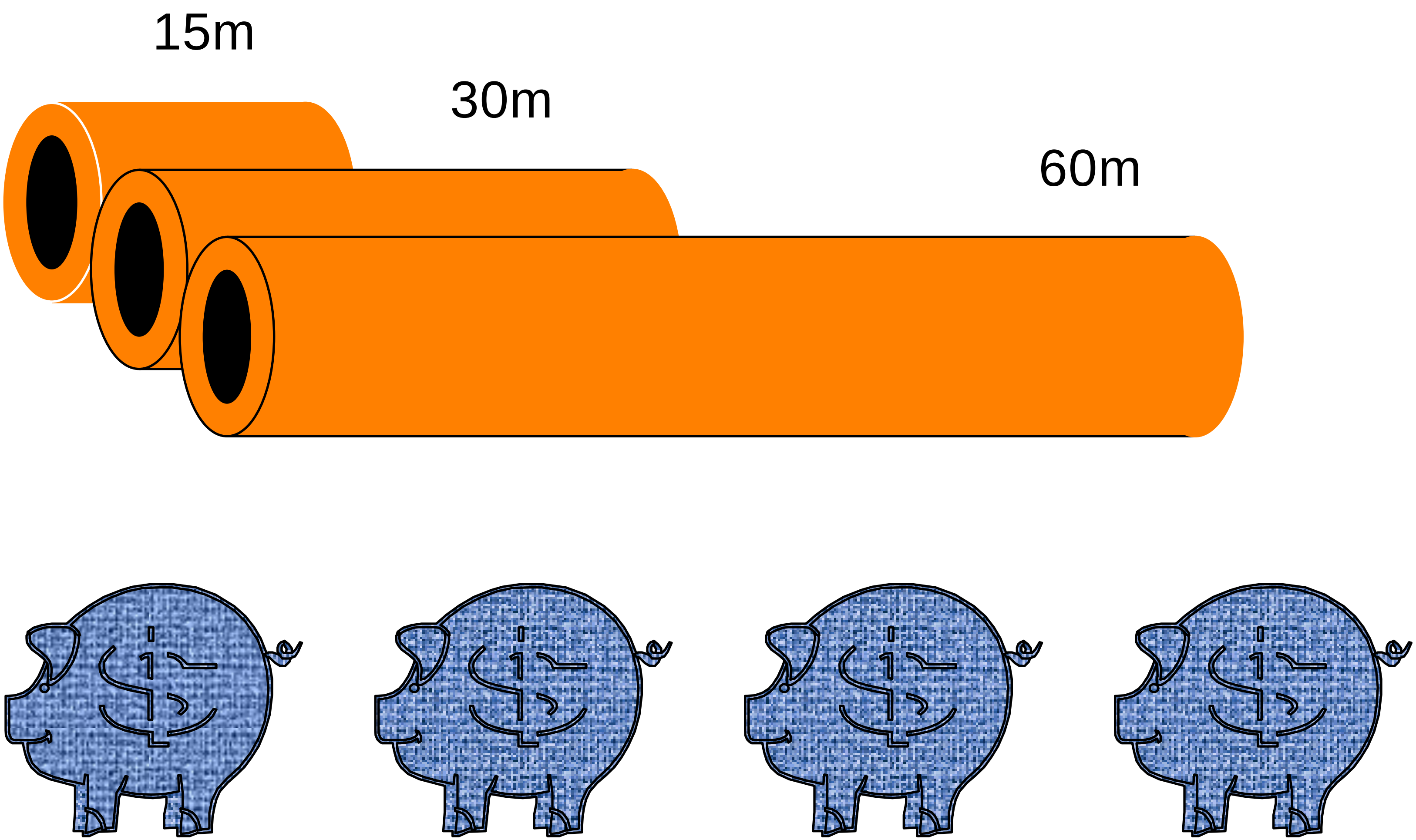
30 m

60 m

Resolution is proportional to the square root of column length
Isothermal: Retention is proportional to length
Temperature program: 1/3-1/2 of isothermal values

Column Length

Cost



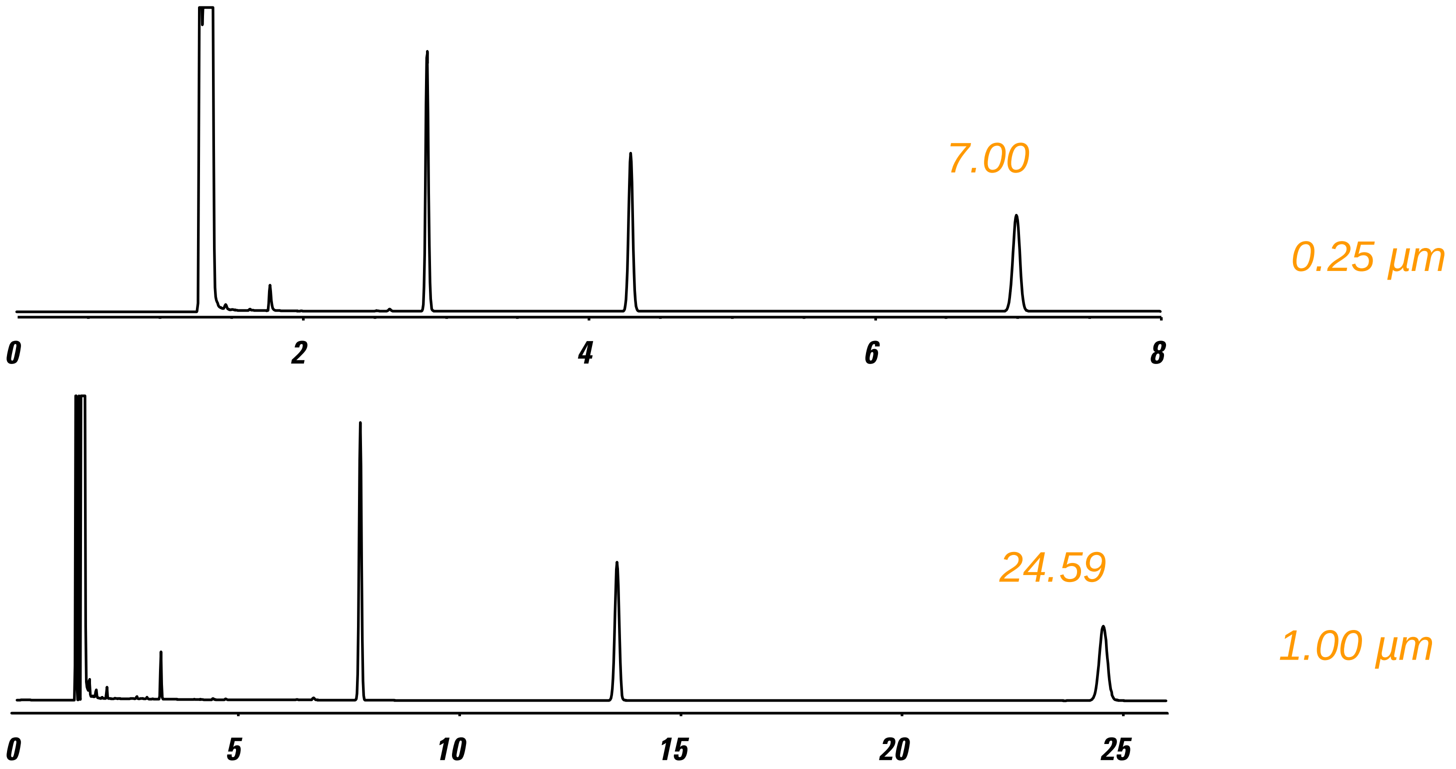
Film Thickness

Most common: 0.1-3.0 µm

Available: 0.1-10.0 µm

Film Thickness

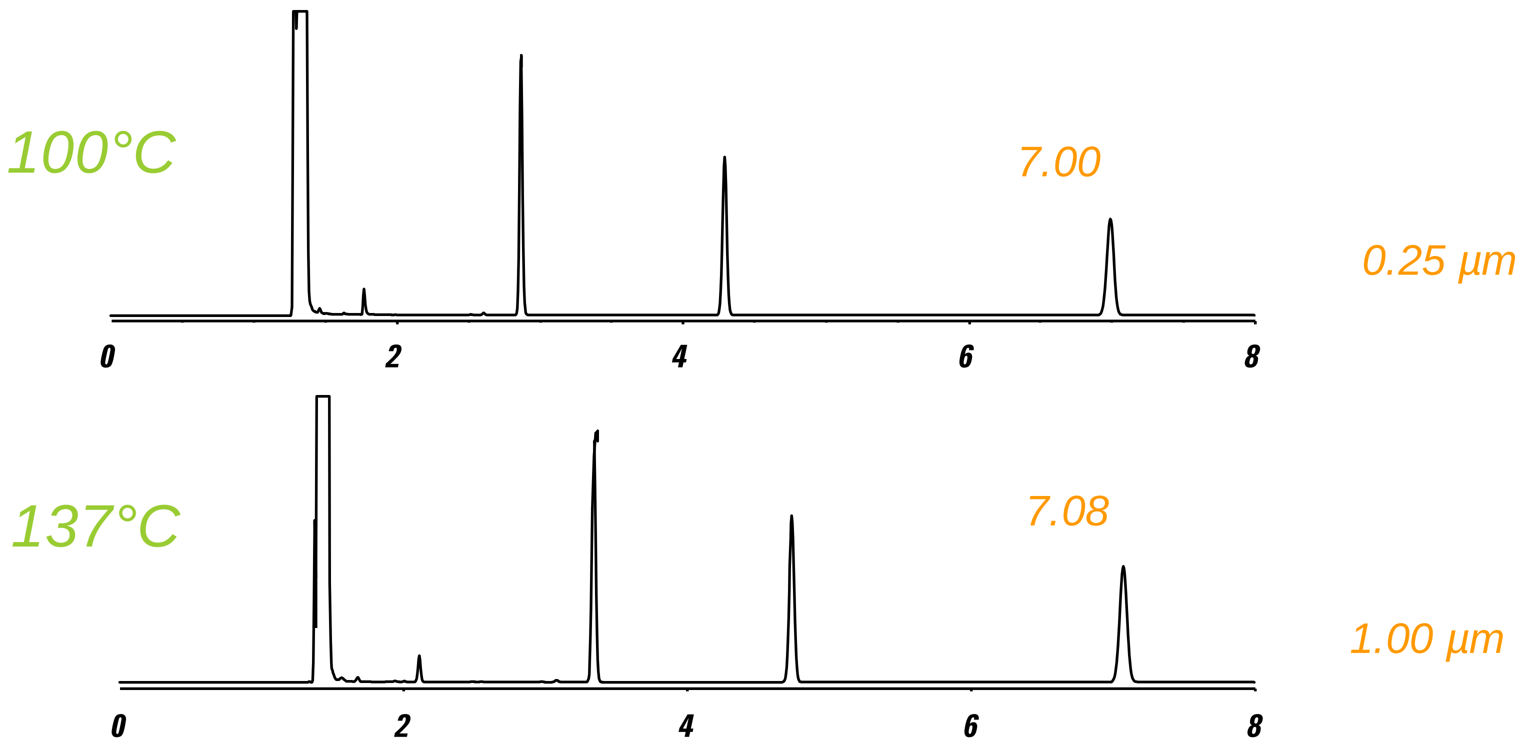
Retention
100°C Isothermal



Isothermal: Retention is proportional to film thickness
Temperature program: 1/3-1/2 of isothermal values

Film Thickness

Equal Retention: Isothermal

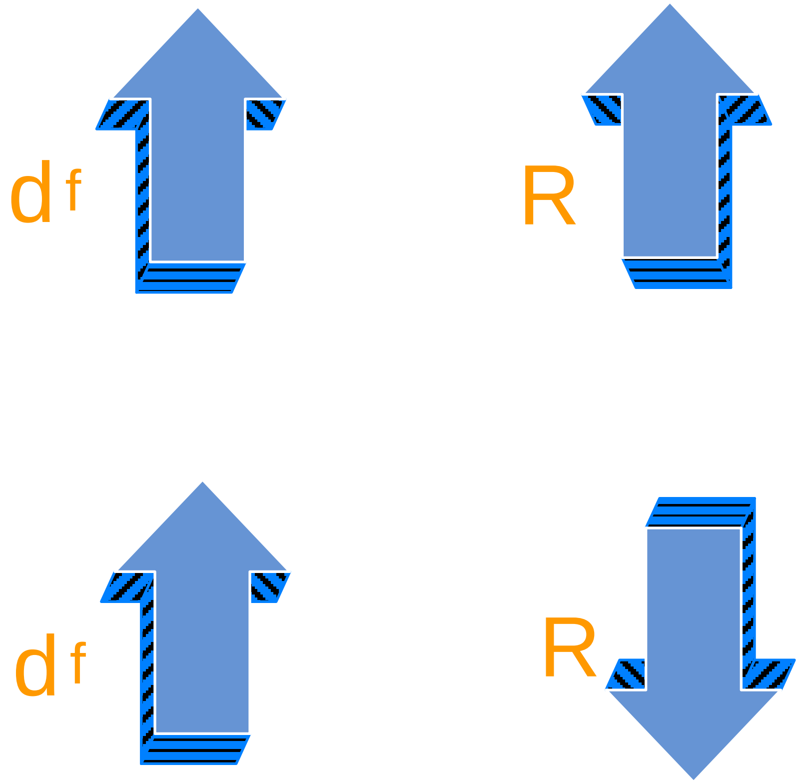


DB-1, 30 m x 0.32 mm ID
He at 37 cm/sec
C10, C11, C12

Film Thickness
Resolution

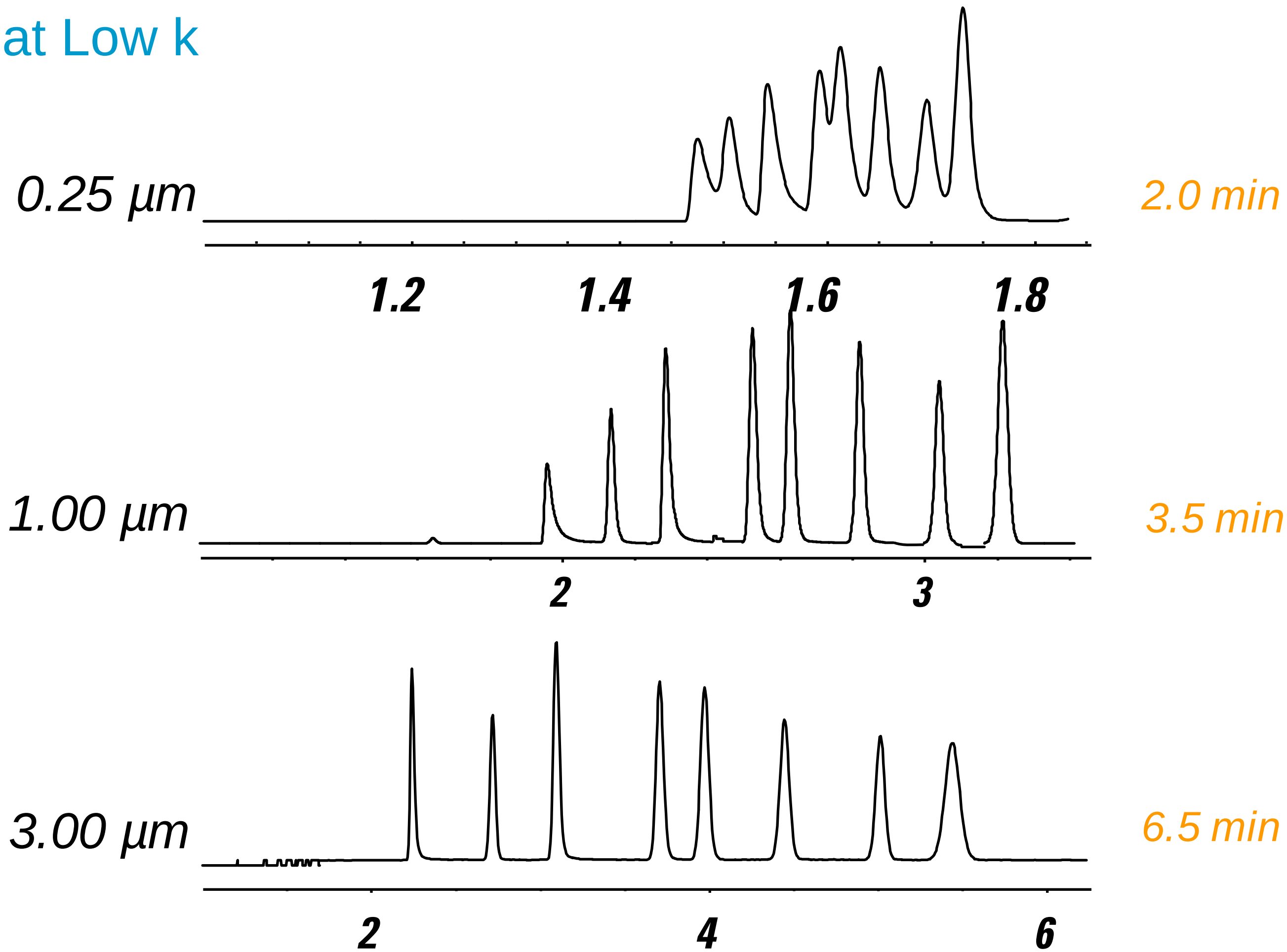
When solute k < 5

When solute k > 5



Film Thickness

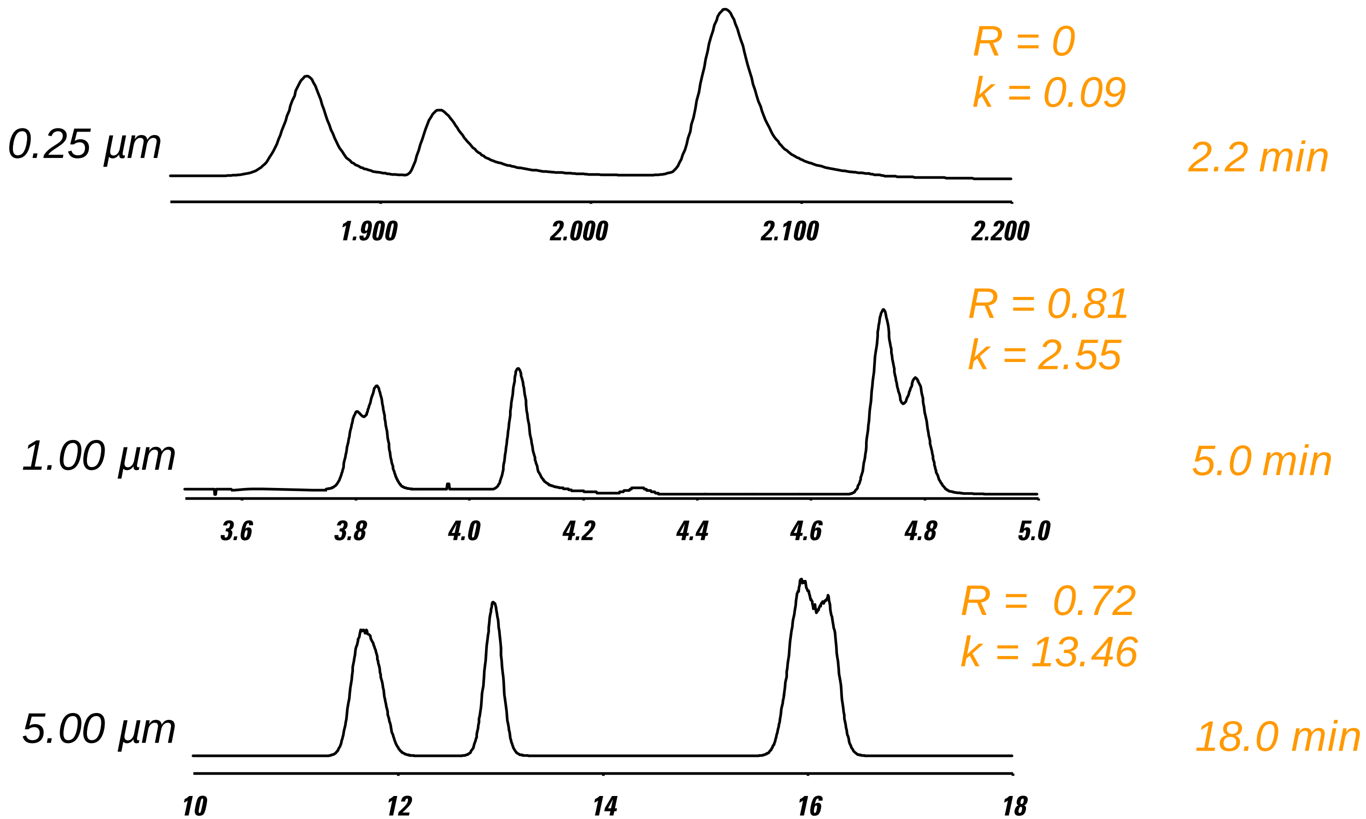
Resolution at Low k



DB-1, 30 m x 0.32 mm ID
40°C isothermal, He at 35 cm/sec
Solvent mixture

Film Thickness

Resolution at High k



DB-1, 30 m x 0.32 mm ID
40°C isothermal, He at 35 cm/sec
Solvent mixture

Film Thickness

Capacity

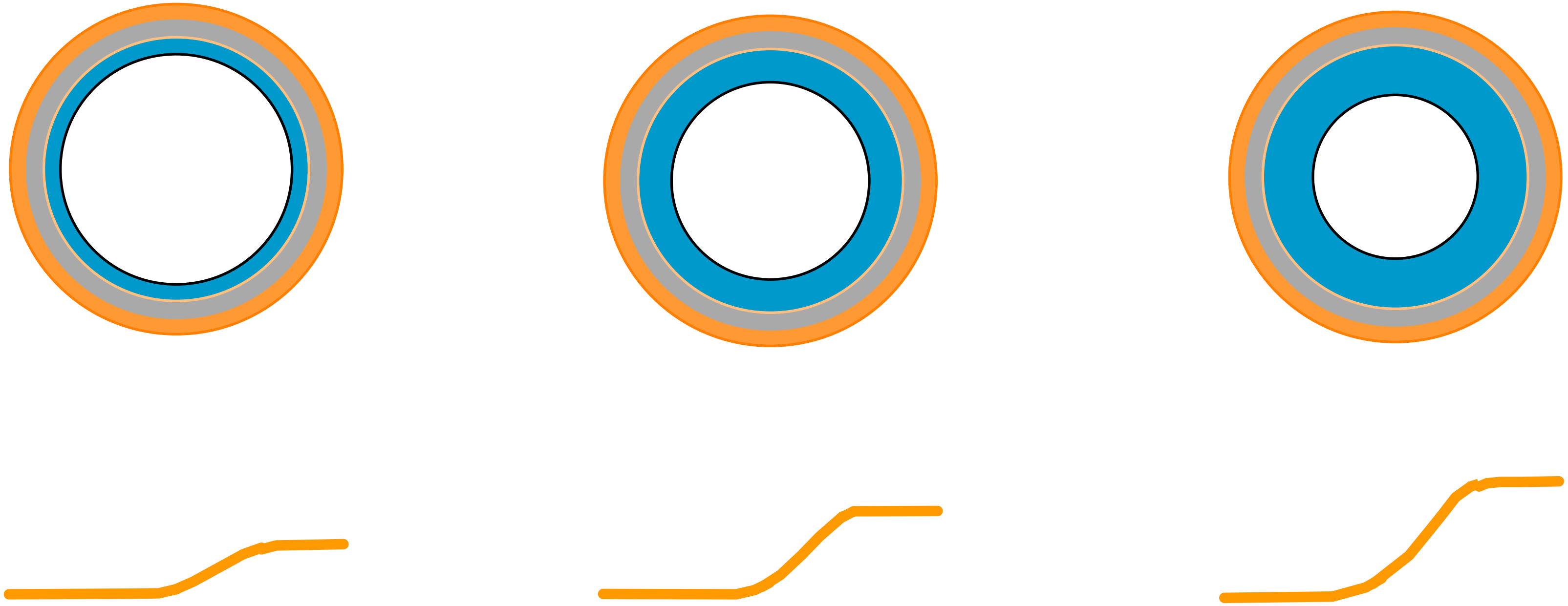
Like Polarity Phase/Solute

Thickness (um)	Capacity (ng)
0.10	50-100
0.25	125-250
1.0	500-1000
3.0	1500-3000
5.0	2500-5000

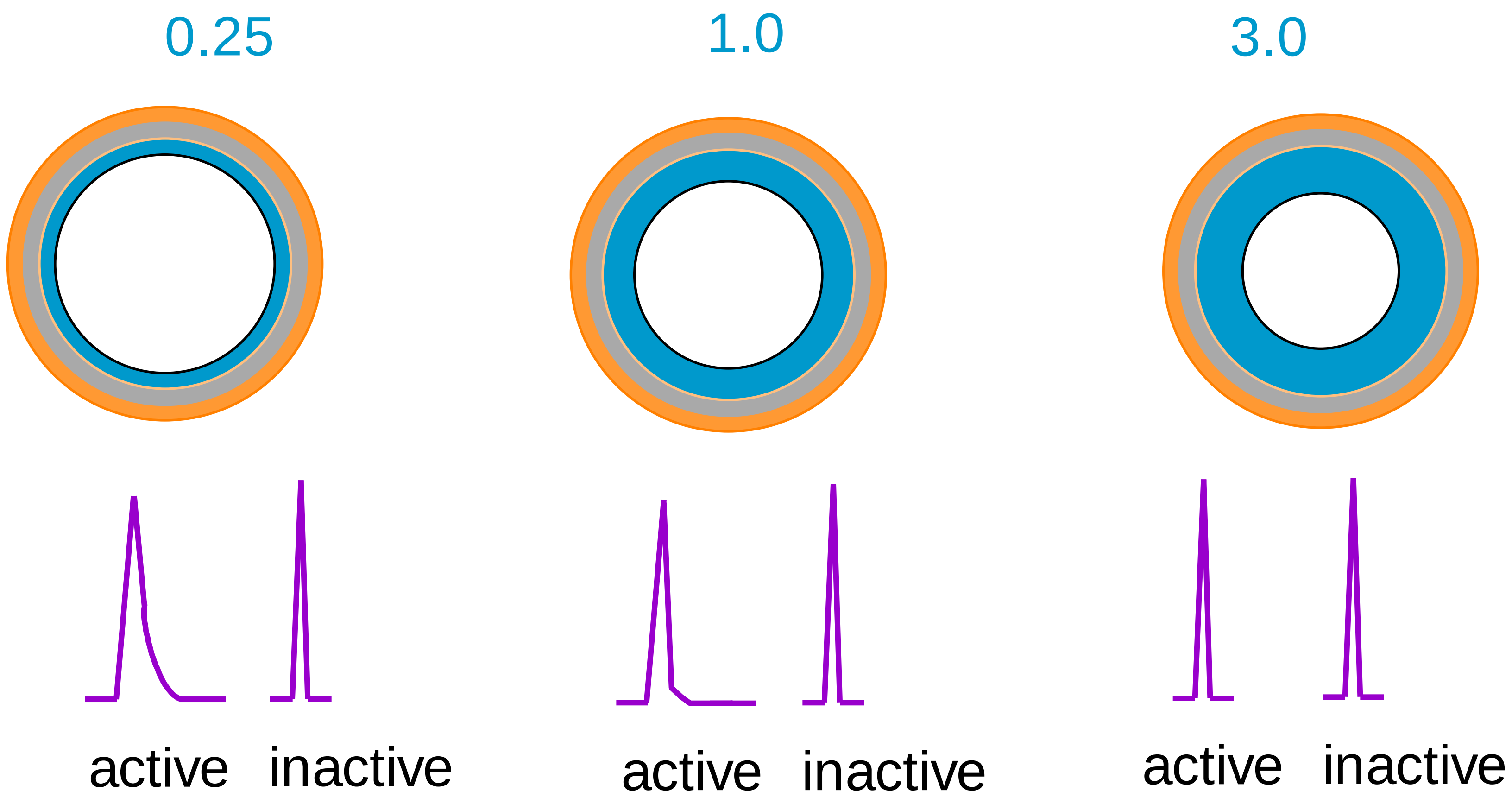
0.32 mm I.D.

Film Thickness
Bleed

More stationary phase = More degradation products



Film Thickness
Inertness Summary



Column Dimensions
Diameter Summary

To Increase	Make Diameter
Resolution	Smaller
Retention	Smaller
Pressure	Smaller
Flow rate	Larger
Capacity	Larger

Column Dimensions
Length Summary

To Increase	Make Length
Resolution	Longer
Retention	Longer
Pressure	Longer
Cost	Longer

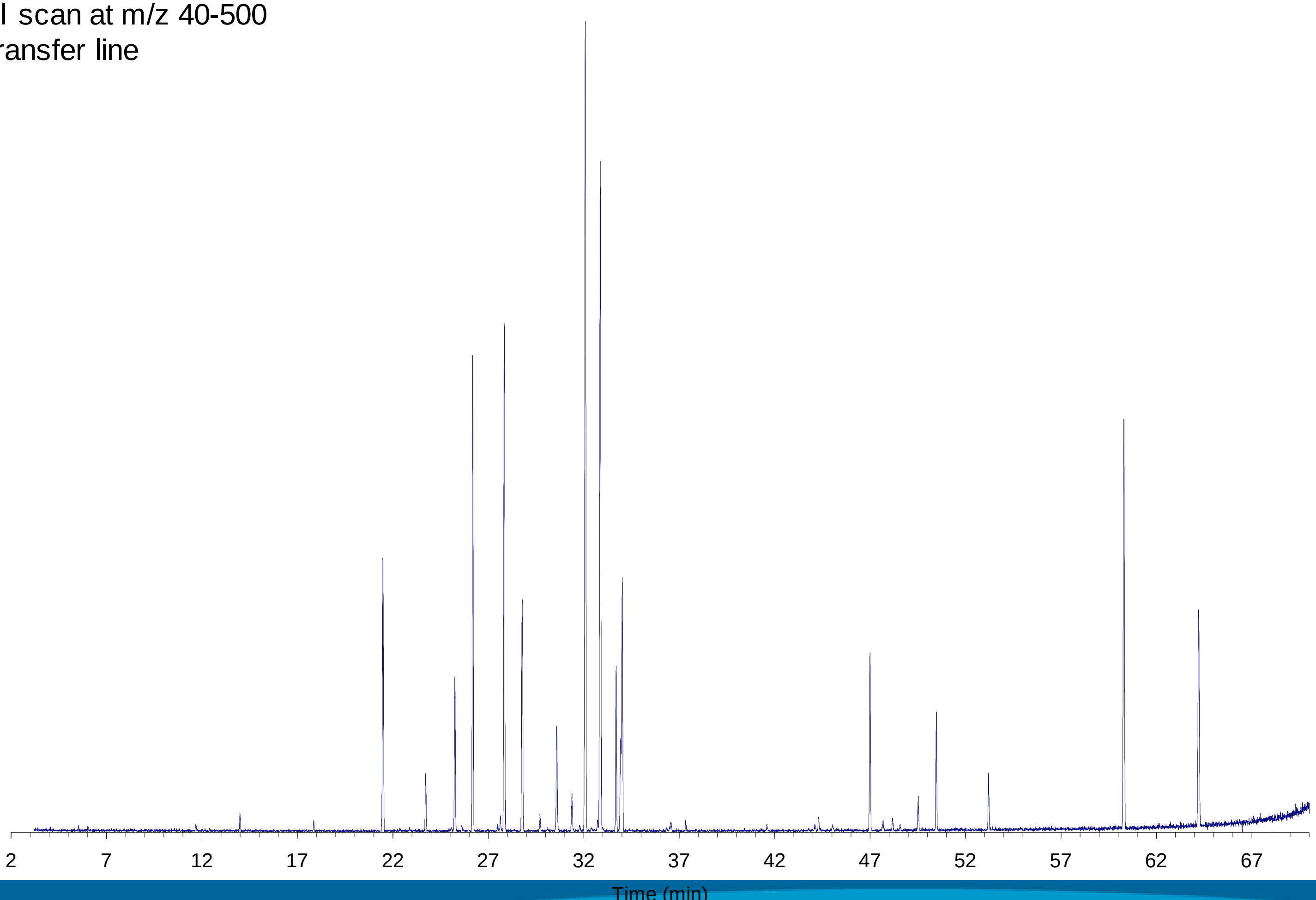
Column Dimensions

Film Thickness Summary

To Increase	Make Film
Retention	Thicker
Resolution (k<5)	Thicker
Resolution (k>5)	Thinner
Capacity	Thicker
Inertness	Thicker
Bleed	Thicker

Column: DB-WAX 30 m X 0.25 mm X 0.25 µm

Carrier: Helium at 25.4 cm/sec measured at 45°C
Oven: 45°C for 2 min
45 to 250°C at 3°C/min
250°C for 34 min
Injector: Split 1:30, 250°C
1µL of 1:35 Oil in Acetone
Detector: MSD full scan at m/z 40-500
250°C transfer line



Column: DB-WAX 20m X 0.18mm X 0.18um

Carrier: Helium at 26.3 cm/sec measured at 45°C

Oven: 45°C for 1.28 min

45 to 250°C at 4.67°C/min

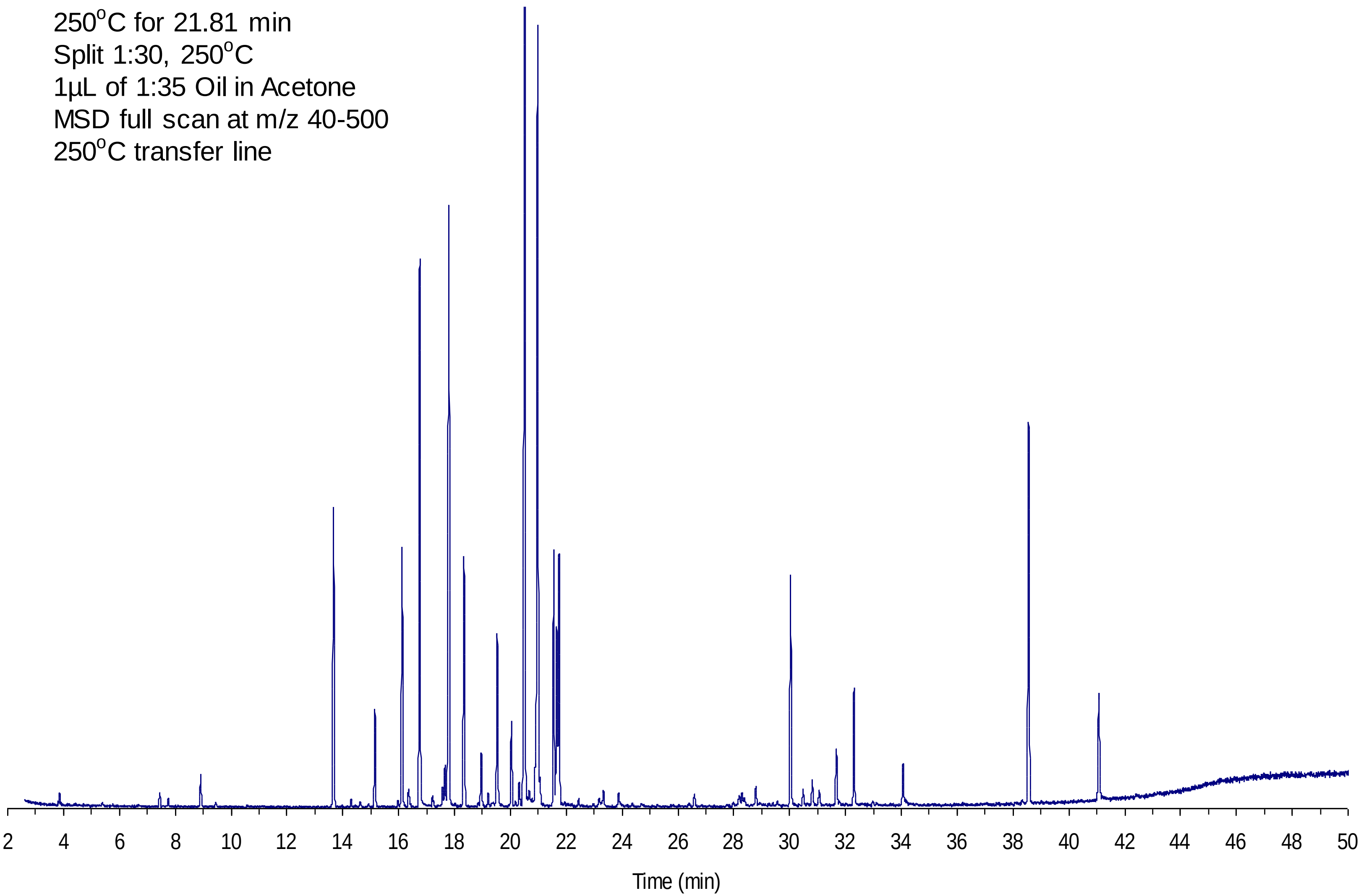
250°C for 21.81 min

Injector: Split 1:30, 250°C

1µL of 1:35 Oil in Acetone

Detector: MSD full scan at m/z 40-500

250°C transfer line



Conclusions:

Understand the Sample

Is it volatile and thermally stable enough to chromatograph by GC?

Try to match polarity – oil and water don't mix!

Look for unique characteristics of compounds and match them to a phase

If you have the correct selectivity, change the dimensions to improve resolution – consider a smaller ID

If you need better peak shape for difficult compounds, try the 'UI' version

Look for available information for a particular application

Call Tech Support!

References:

GC Column Selection Guide: 5990-9867EN

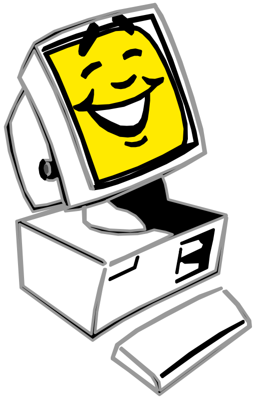
Integrated Particle Trap PLOT columns: 5991-1174EN

Agilent/J&W Technical Support

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

- *Select option 3, then option 3, then option 1.*

GC-Column-Support@Agilent.com



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