Understanding the Capillary GC Column

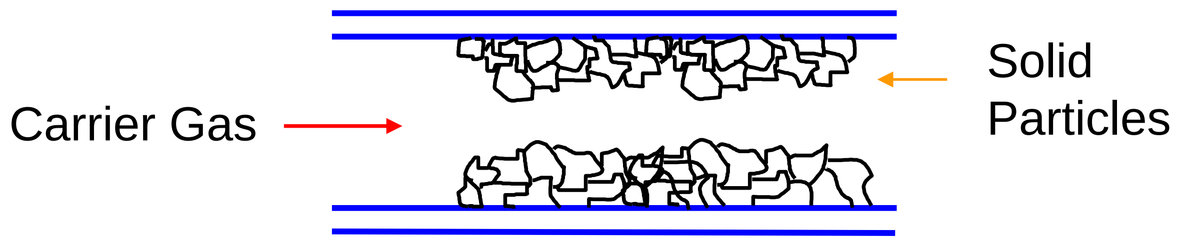
Mark SInnott
Application Engineer

Things to Consider…

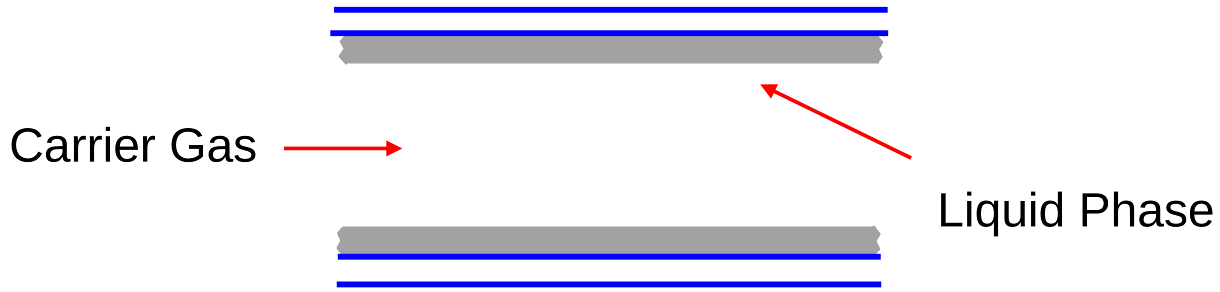
- Is it Volatile enough to chromatograph by GC?
- Is it stable enough to "survive" vaporization?
- Is it a Gas or a Liquid?
- How are we getting the Sample Injected?
- What is the sample Matrix?
  – Can we do sample clean up?
- Is it an established method?
  -- EPA, ASTM, USP
- What do we Know about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

CAPILLARY COLUMN TYPES

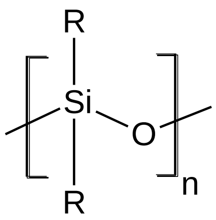
Porous Layer Open Tube (PLOT)



Wall Coated Open Tube (WCOT)

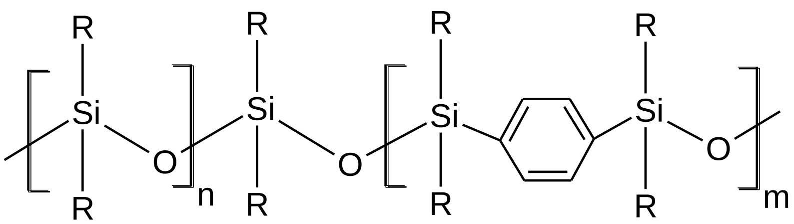


STATIONARY PHASE POLYMERS

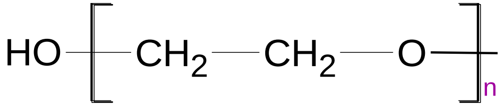


Siloxane

R=methyl, phenyl, cyanopropyl, trifluoropropyl



Siarylene backbone



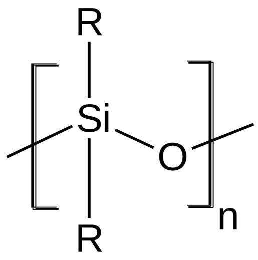
Polyethylene Glycol

Stationary Phase

% Substitution -- polysiloxanes

% = # of sites on silicon atoms occupied

Balance is methyl



Siloxane

R=methyl, phenyl, cyanopropyl, trifluoropropyl

Stationary Phase

Poly(ethylene) Glycol

$$HO\text{—}\left(CH_2\text{—}CH_2\text{—}O \right)\text{—}H$$

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

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).

Primary Selectivity Interactions in PLOT Phases

Dispersive

Shape/Size ⟷ **Ionic Surface**

Zeolites — Alumina/Al_2O_3, GS-OxyPLOT

Dispersive

Shape/Size ⟷ **Ionic Surface**

Bonded Graphitized Carbon, Molecular Sieves — **Porous Polymers** — Bonded Silica

PLOT Column Examples

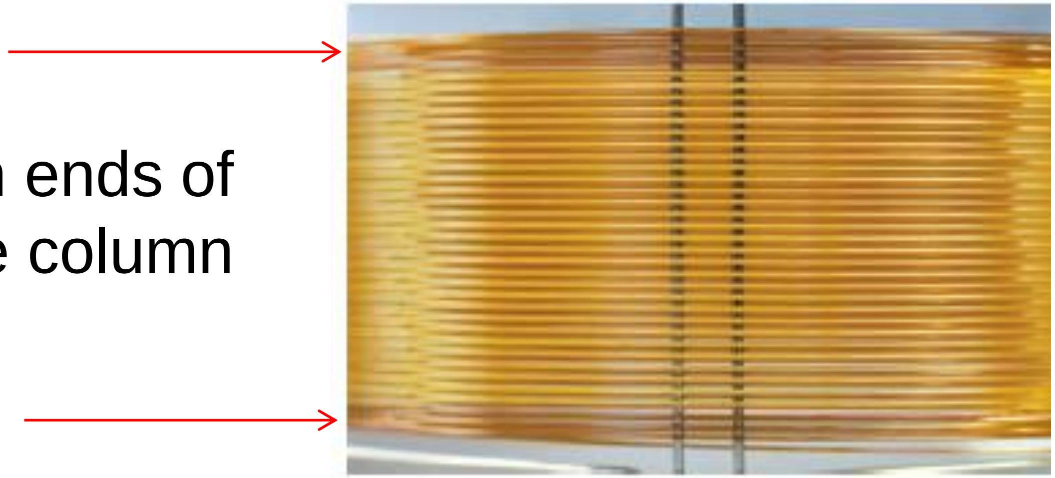
Zeolite/Molesieve:	HP-PLOT Molesieve
Graphitzed Bonded Carbon:	GS-CarbonPLOT
Porous Ploymers:	HP-PLOT Q, HP-PLOT U
Bonded Silica:	GS-GasPro
Alumina/Al_2O_3:	GS-Alumina, GS-Alumina KCl, HP-PLOT Al_2O_3 KCl, HP-PLOT Al_2O_3 "S", HP-PLOT Al_2O_3 "M"
Proprietary Phase:	GS-OxyPLOT

- 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

Ultra Inert Phases

DB-1msUI

HP-1msUI

DB-5msUI

HP-5msUI

DB-17msUI

DB-624UI

DB-Select 624UI 467

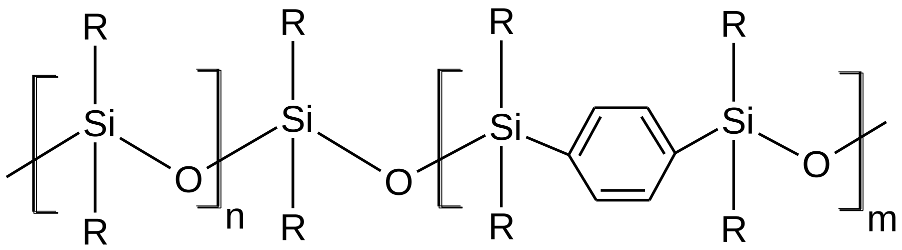
DB-WaxUI

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

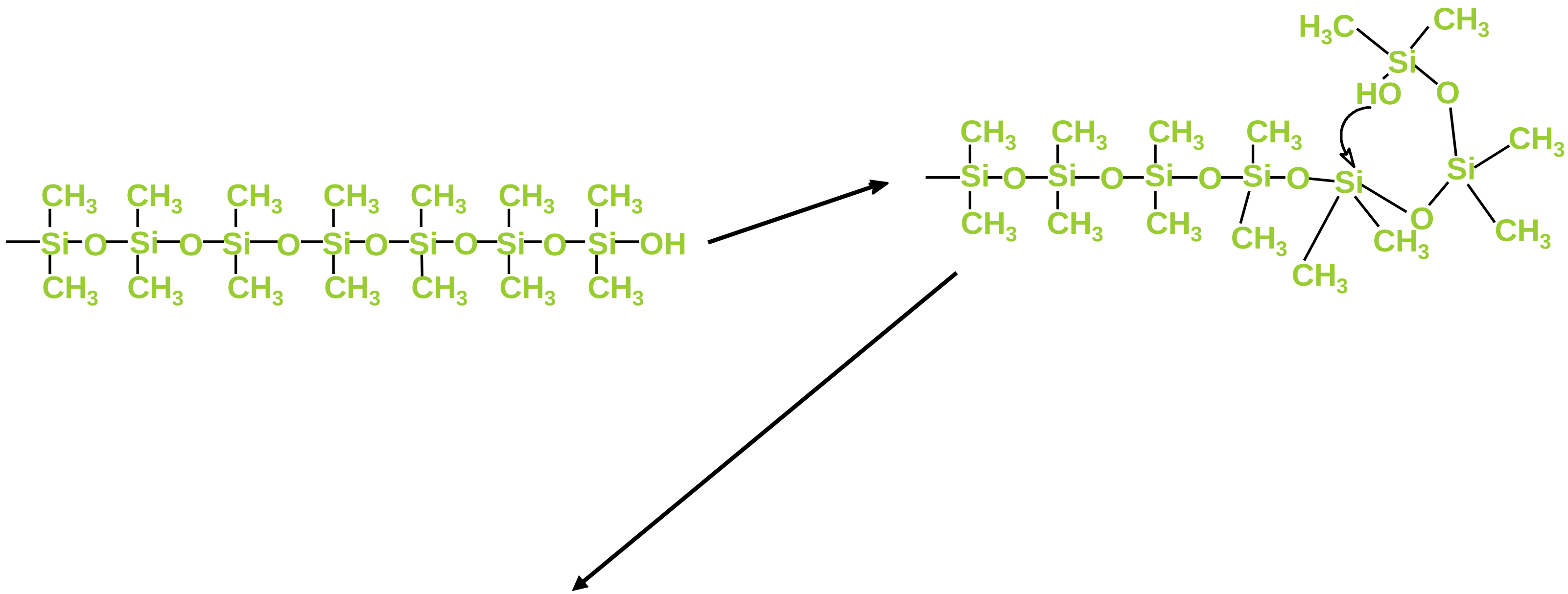
Examples: DB-XLB

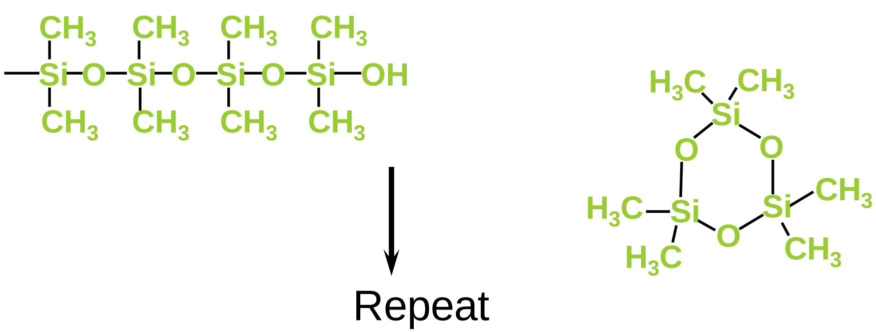
•Optimized manufacturing processes

DB-1ms, HP-1ms, HP-5ms, VF-5ms

What is Column Bleed???

“Back Biting” Mechanism of Product Formation

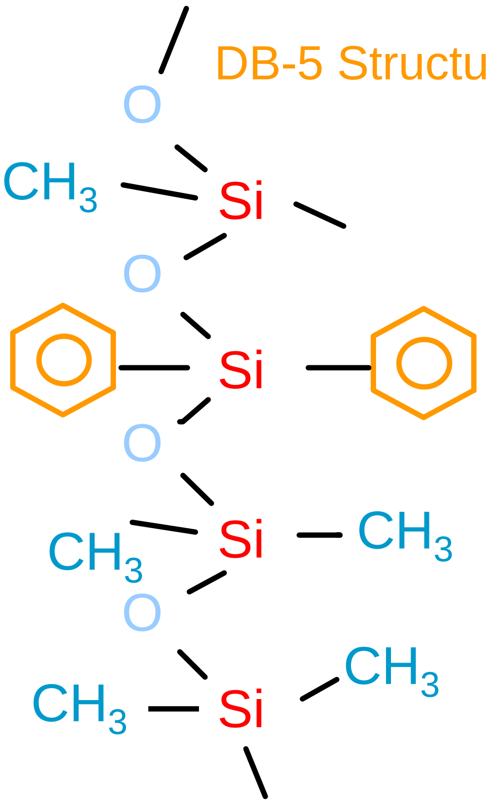




Cyclic products are thermodynamically more stable!

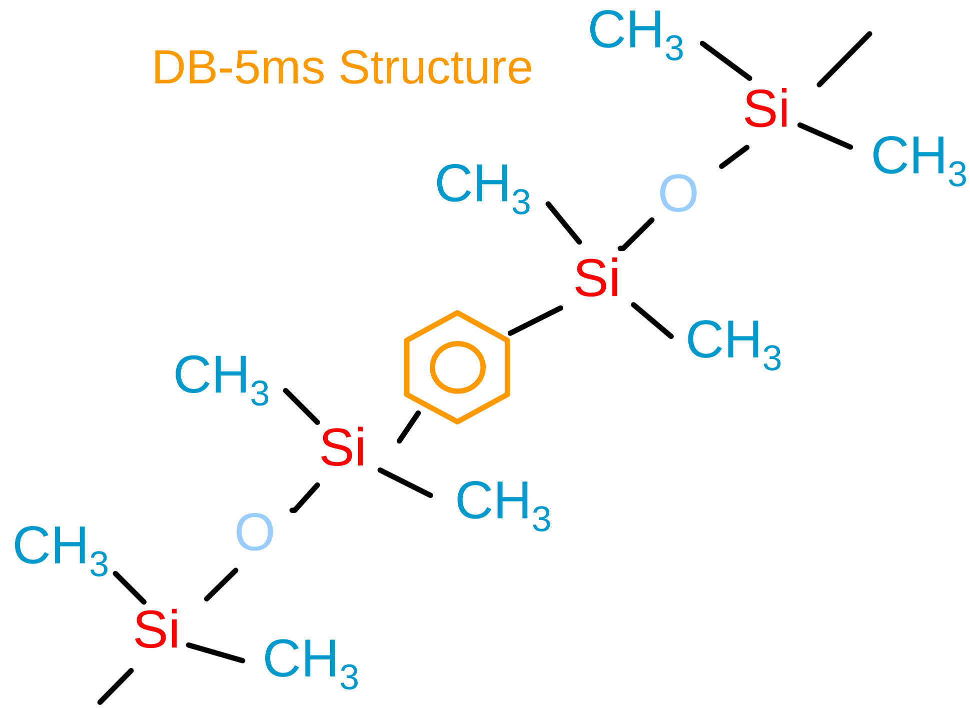
DB-5ms Structure

DB-5 Structure



DB-5
5% Phenyl

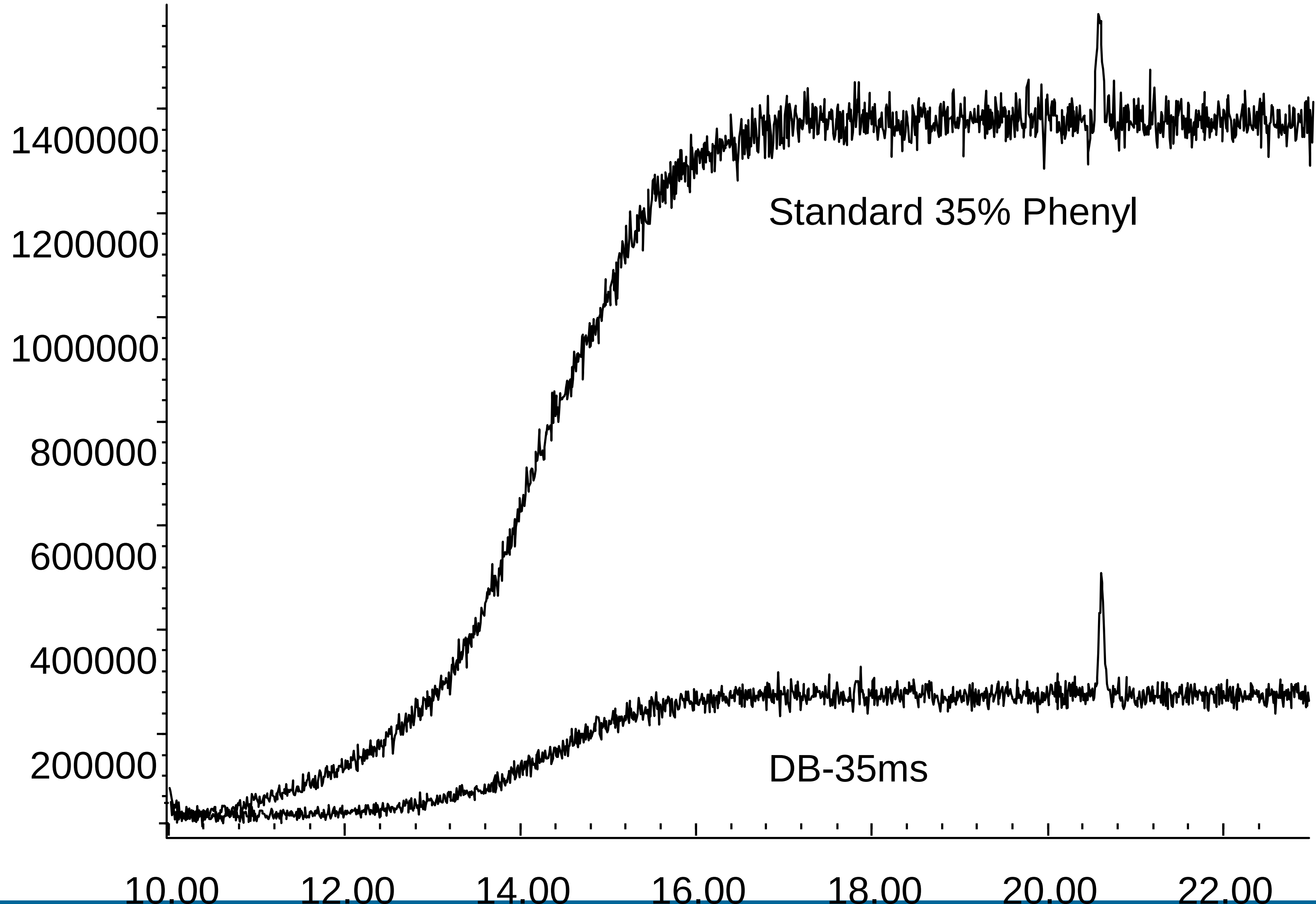
DB-5ms Structure



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

DB-35MS VS STANDARD 35% PHENYL

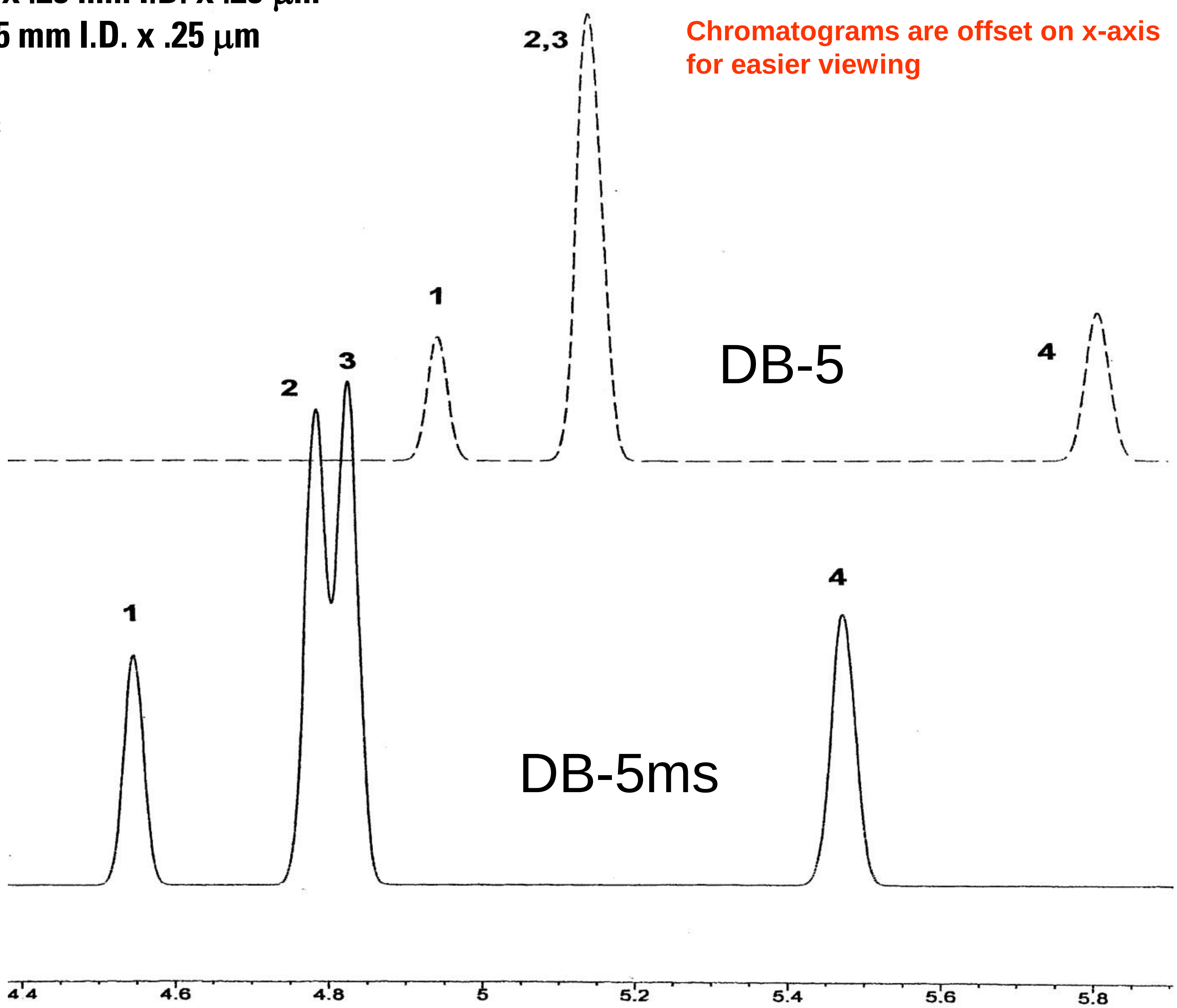
Benzo[g,h,i]perylene, 1ng



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: 60º 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)

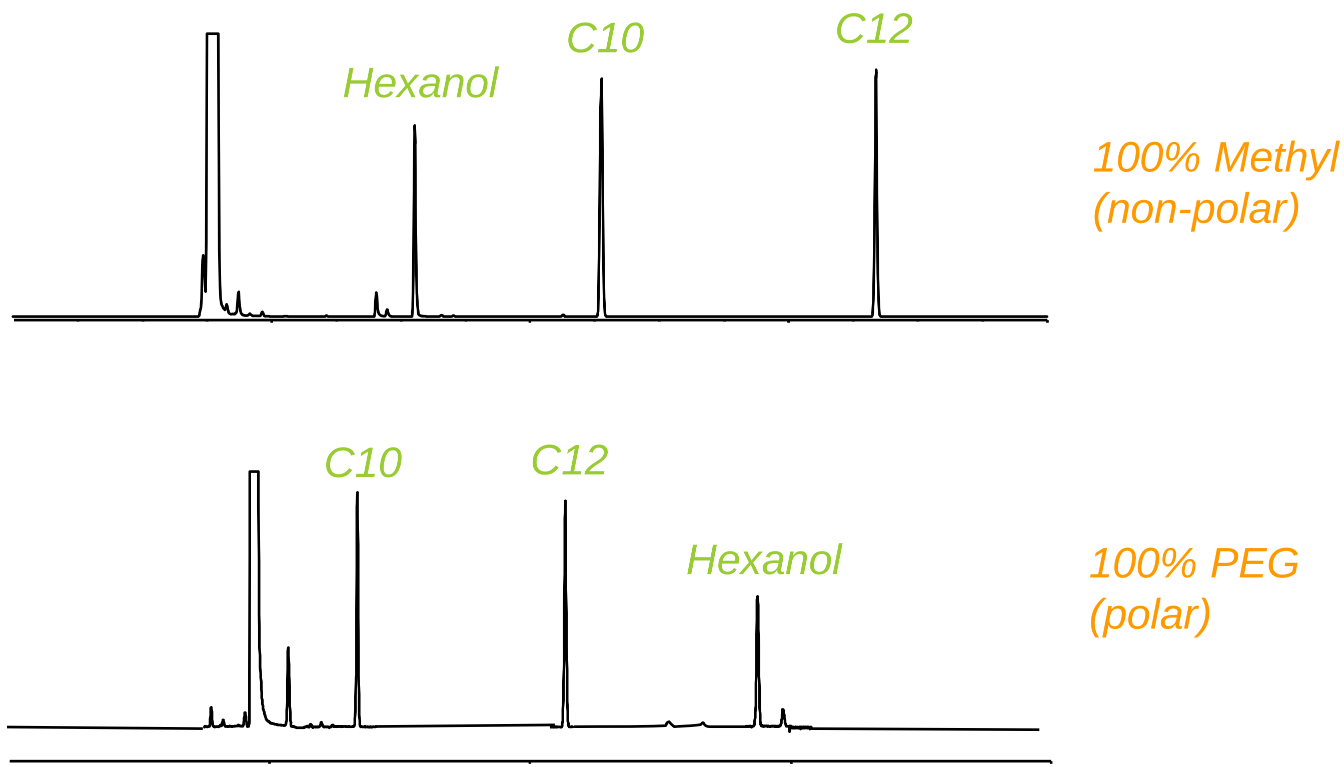
Selectivity Interactions

- Dispersion
- Dipole
- Hydrogen bonding

Dispersion Interaction

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

Dispersion Interaction

ΔH_{vap}

Vapor pressure: good approximation

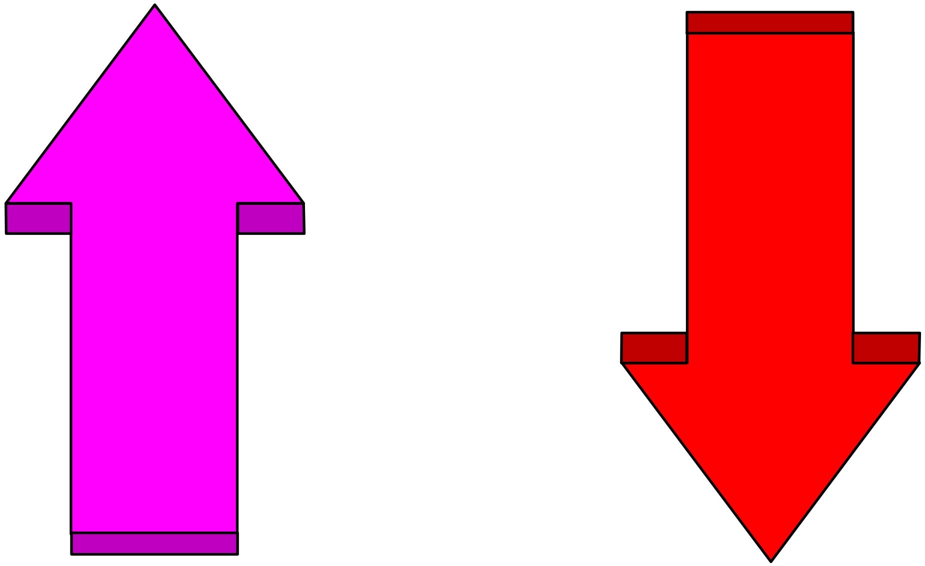
Boiling point: poor approximation

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

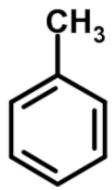
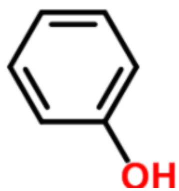
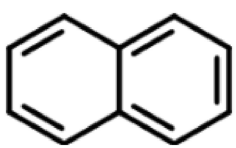
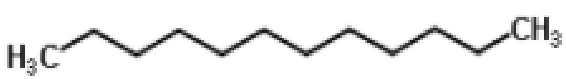
Polarity



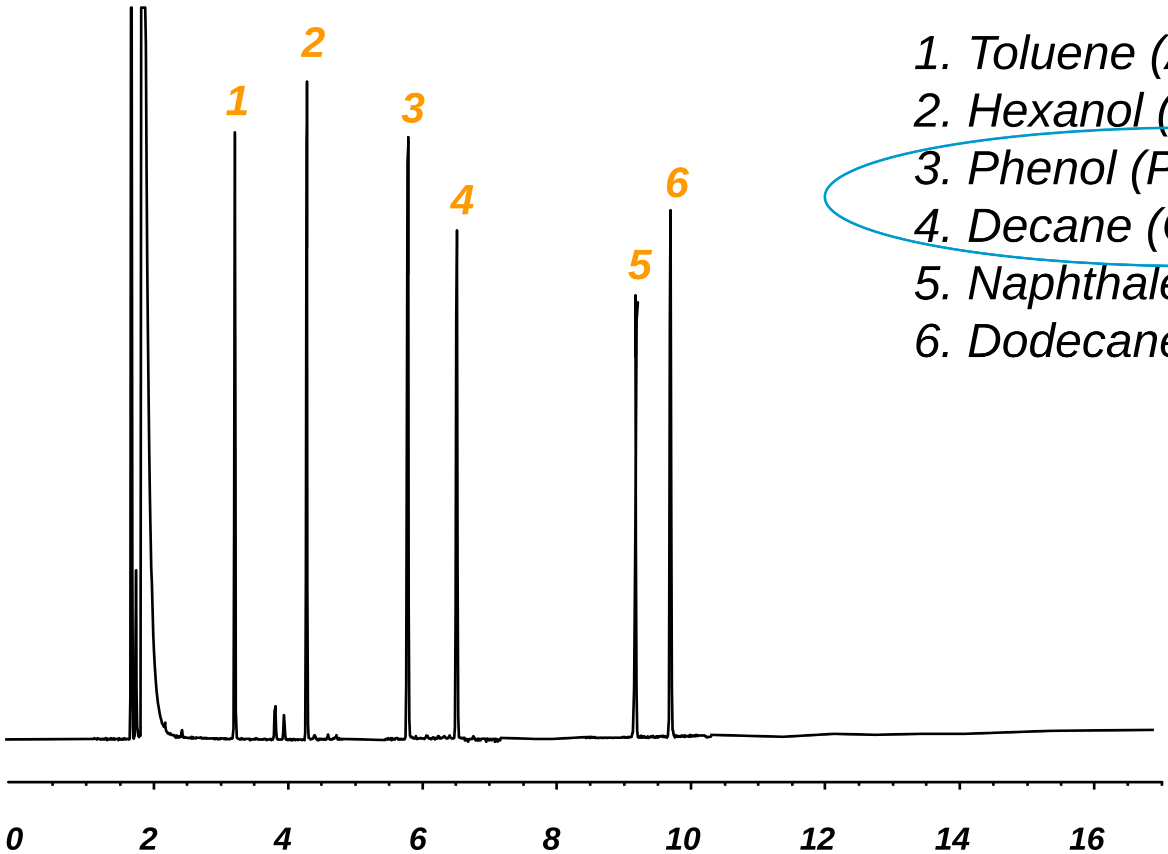
Polarity

Stability
Temperature Range

Compounds Properties

Compound	Structure	Polar	Aromatic	H-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

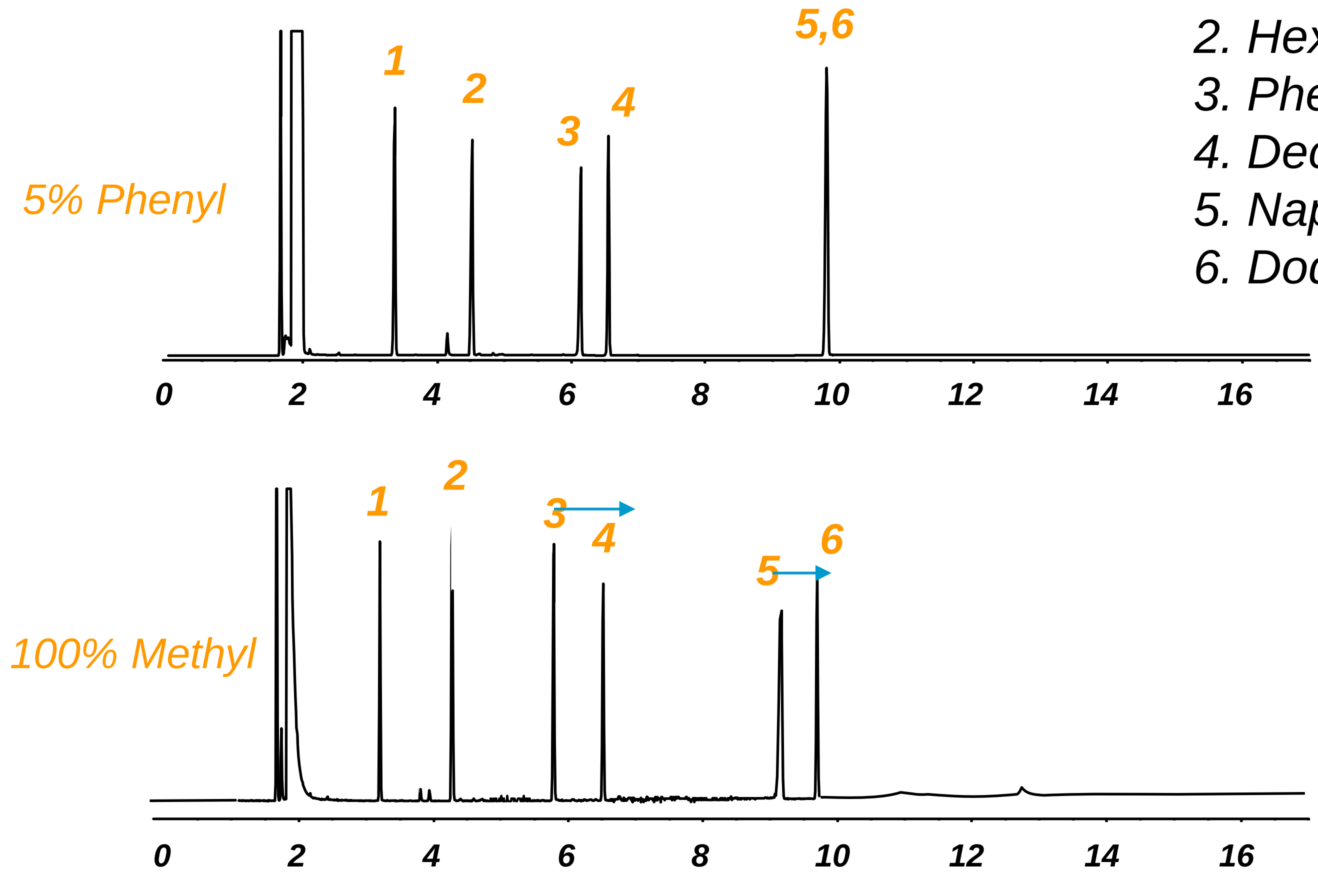
100% Methyl Polysiloxane



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

Strong Dispersion
No Dipole
No H Bonding

5% Phenyl (aromatic phase)

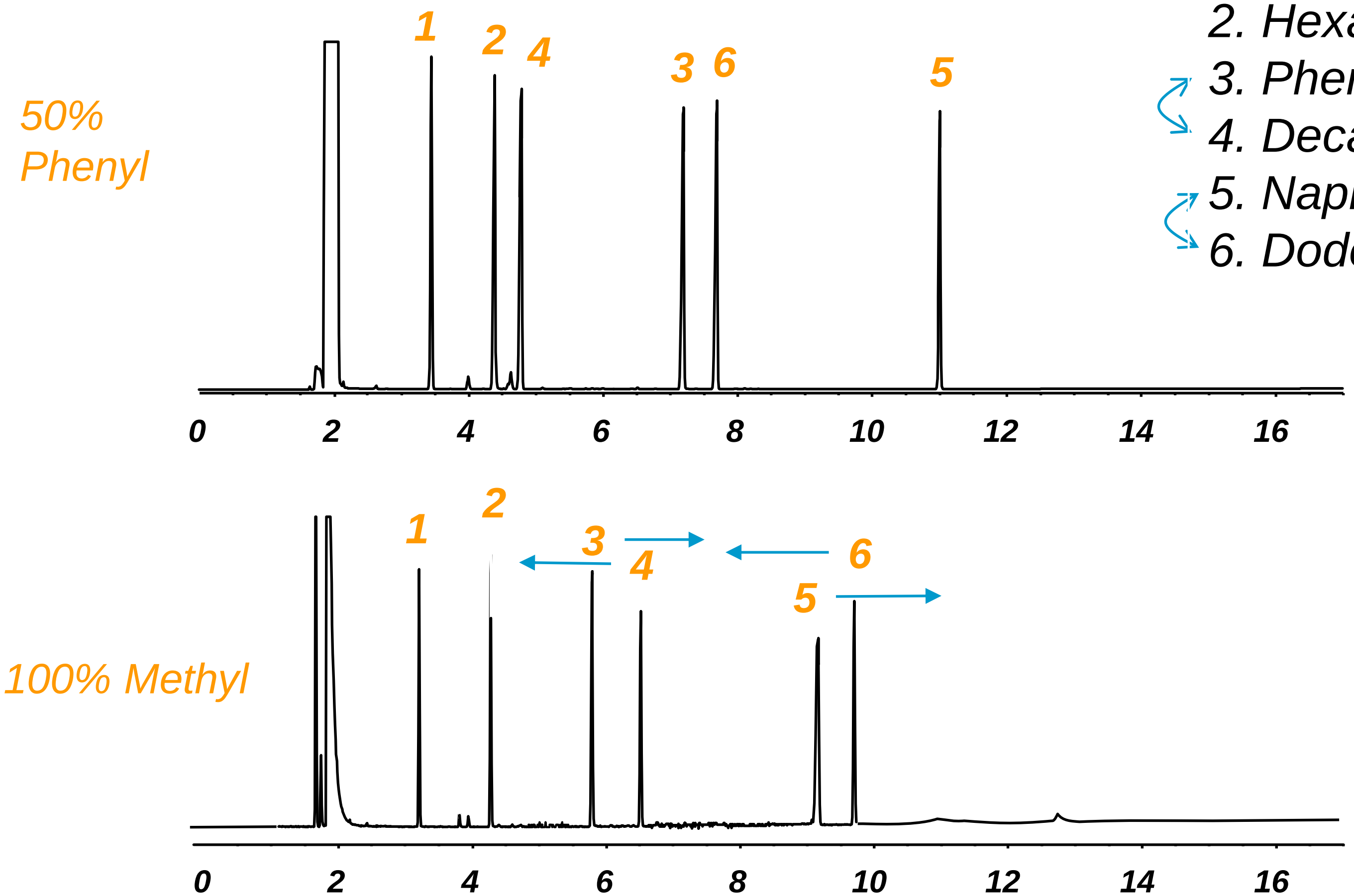


1. Toluene (A-ID) 110°C
2. Hexanol (P-H-D) 158°C
3. Phenol (P-A-H-D) 181°C
4. Decane (C10) 174°C
5. Naphthalene (A-D) 218°C
6. Dodecane (C12) 216°C

Strong Dispersion
No Dipole
Weak H Bonding

50% Phenyl (more aromatic)

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



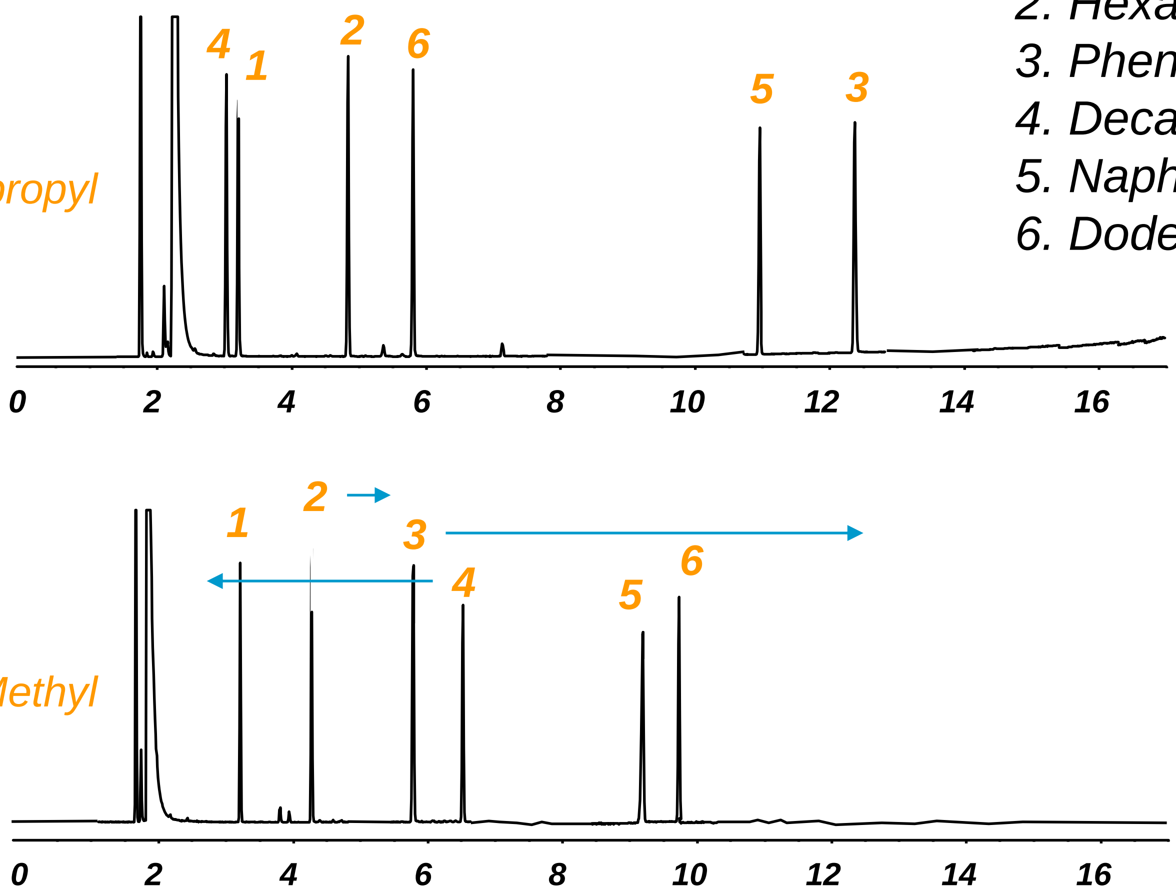
Strong Dispersion
No Dipole
Weak H Bonding

50% Cyanopropyl

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

50% Cyanopropyl

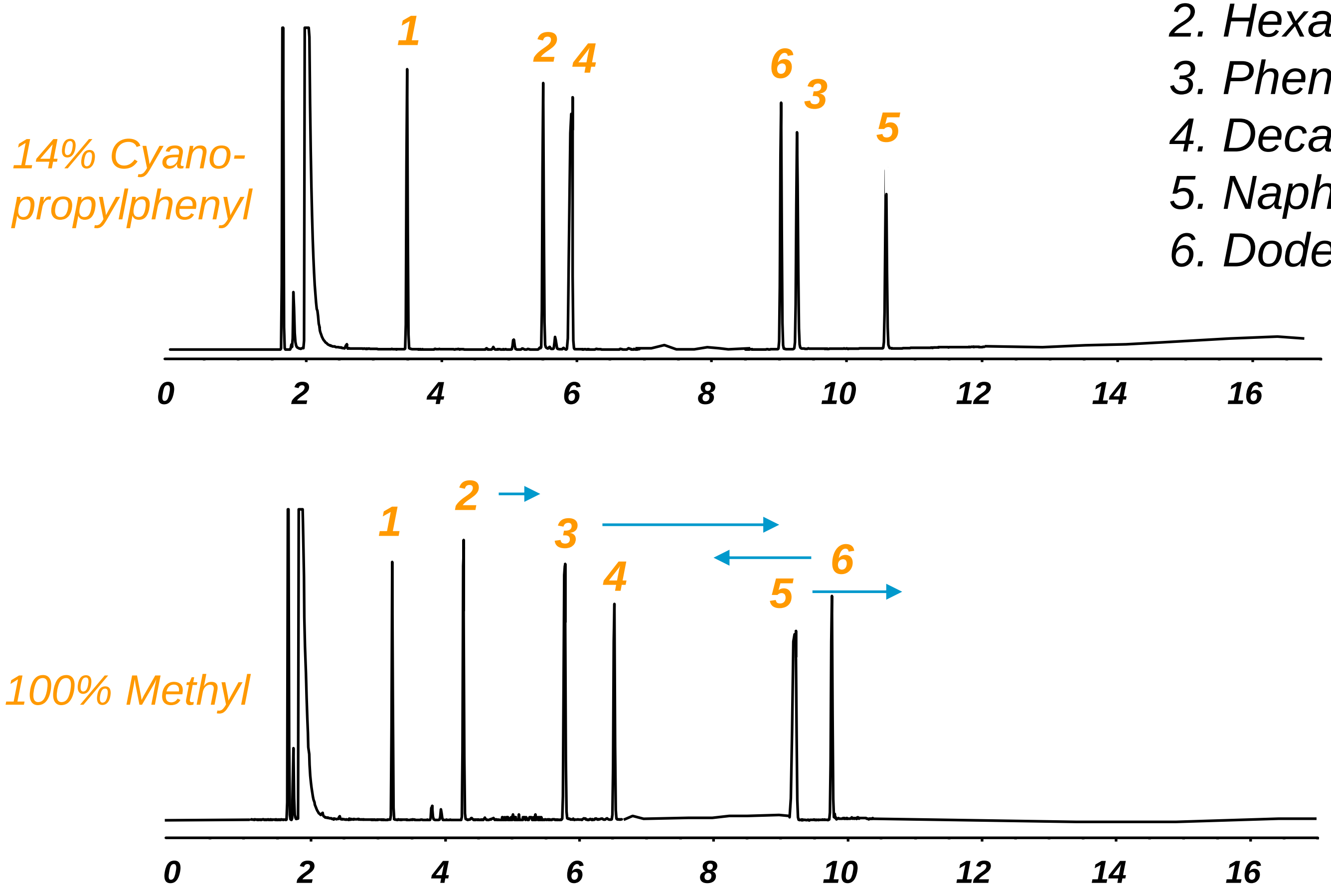
100% Methyl



Strong Dispersion
Strong Dipole
Moderate H Bonding

14% Cyanopropylphenyl

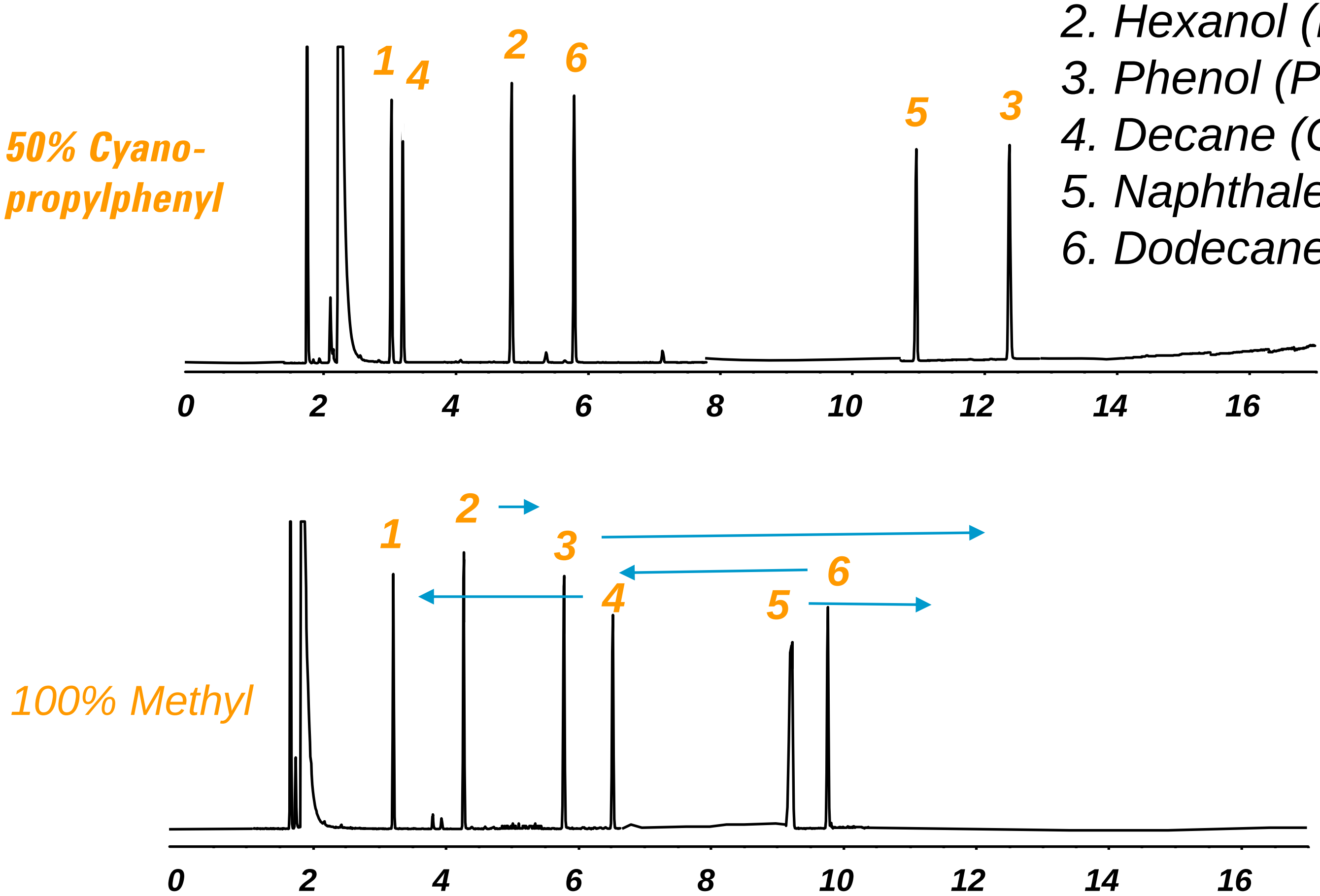
1. Toluene (A-ID) 110°C
2. Hexanol (P-H-D) 158°C
3. Phenol (P-A-H-D) 181°C
4. Decane (C10) 174°C
5. Naphthalene (A-D) 218°C
6. Dodecane (C12) 216°C



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

50% Cyanopropylphenyl

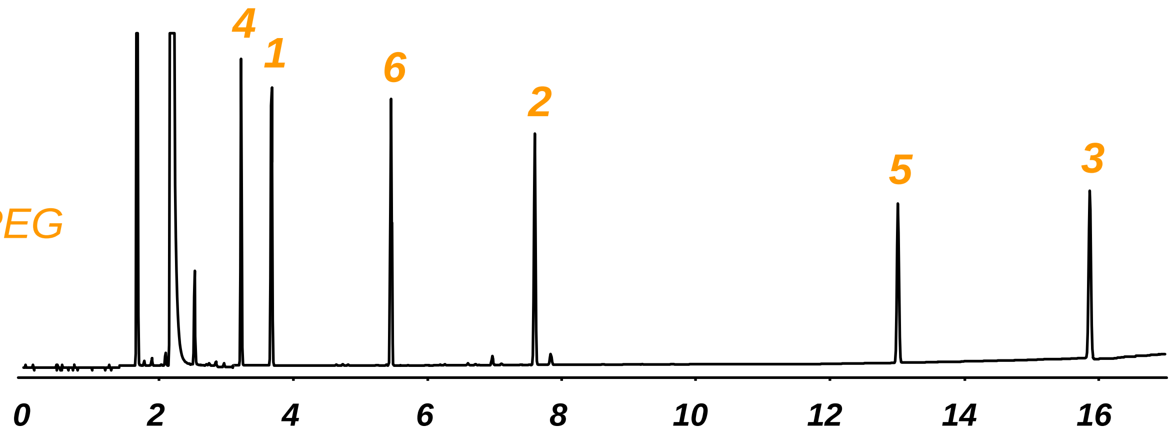
1. *Toluene (A-ID)* 110°C
2. *Hexanol (P-H-D)* 158°C
3. *Phenol (P-A-H-D)* 181°C
4. *Decane (C10)* 174°C
5. *Naphthalene (A-D)* 218°C
6. *Dodecane (C12)* 216°C



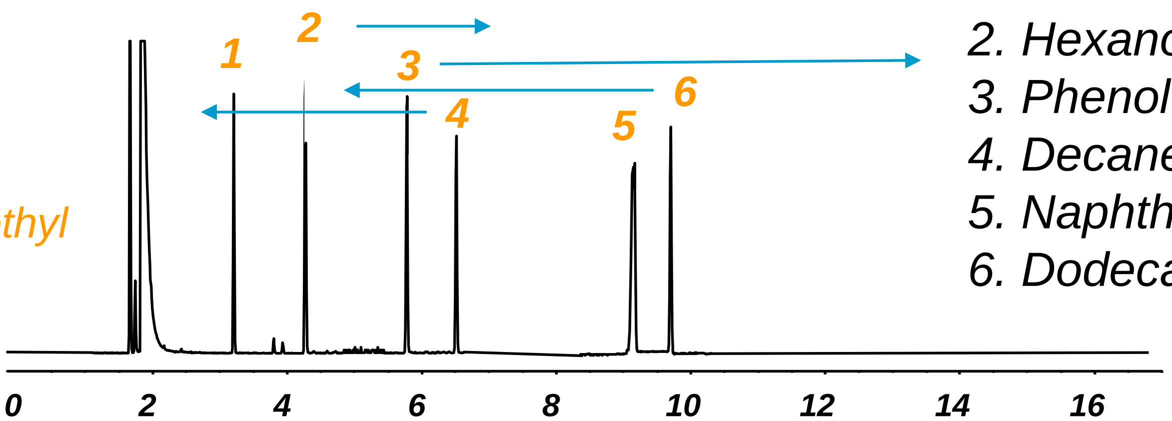
Strong Dispersion
None/Strong Dipole (Ph/CNPr)
Weak/Moderate H Bonding (Ph/CNPr)

100% Polyethylene Glycol

100% PEG



100% Methyl



1. *Toluene (A-ID)* *110^{o}C*
2. *Hexanol (P-H-D)* *158^{o}C*
3. *Phenol (P-A-H-D)* *181^{o}C*
4. *Decane (C10)* *174^{o}C*
5. *Naphthalene (A-D)* *218^{o}C*
6. *Dodecane (C12)* *216^{o}C*

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

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

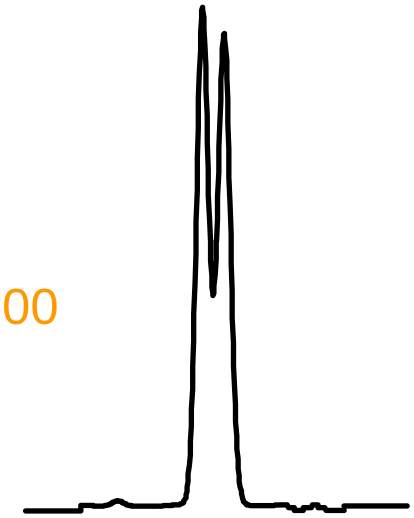
Efficiency X 4 = Resolution X 2

Column Diameter

Resolution
180°C isothermal

R=0.87

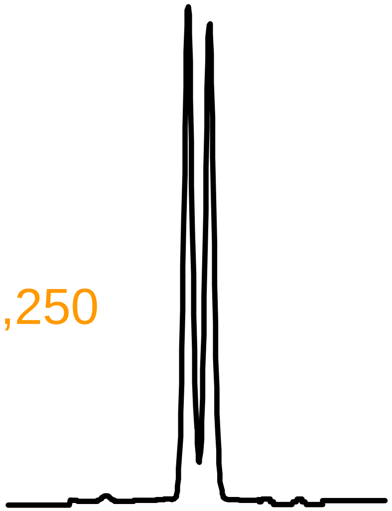
n =58,700



0.53 mm

R=1.01

n =107,250



0.32 mm

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

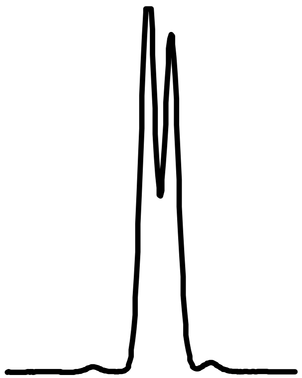
Most common: 15-60 meters

Available: 5-200 meters

Column Length

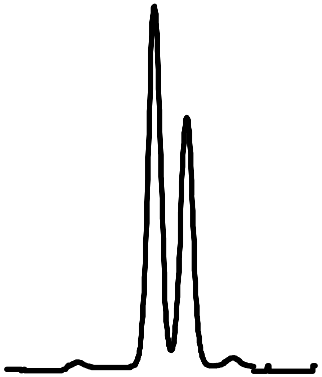
Resolution and Retention
210°C isothermal

R=0.84
2.29 min



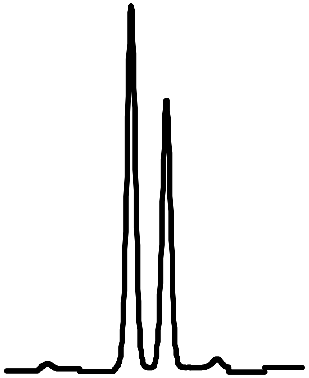
15 m

R=1.16
4.82 min



30 m

R=1.68
8.73 min



60 m

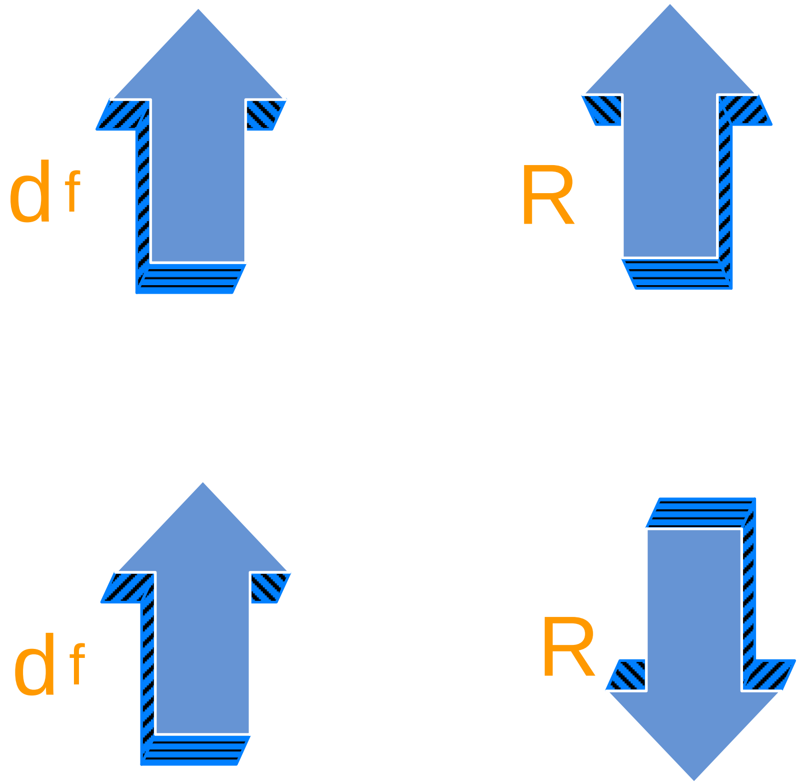
Resolution is proportional to the square root of column length
Isothermal: Retention is proportional to length

Film Thickness

Resolution

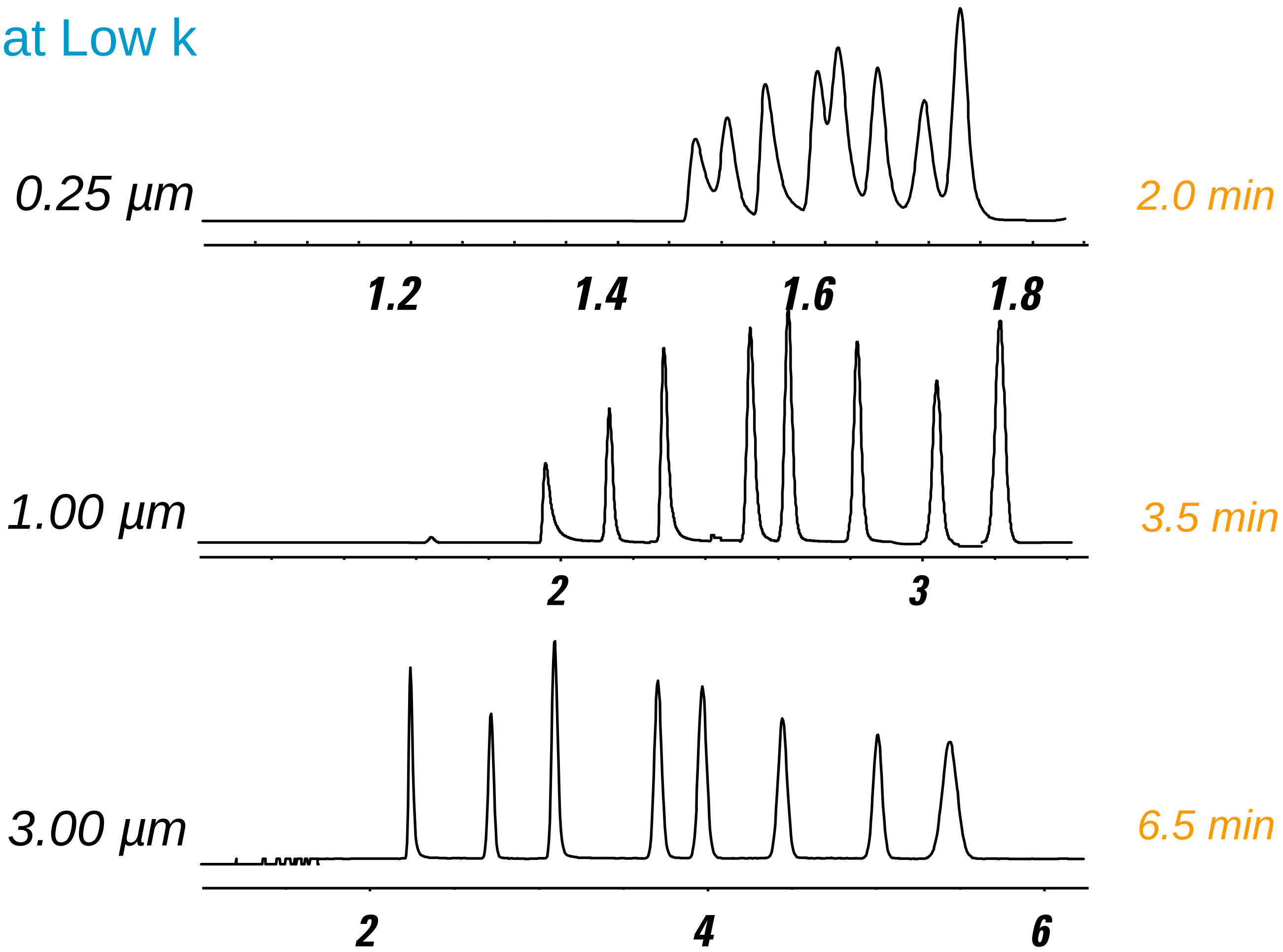
When solute k < 5

When solute k > 5



Film Thickness

Resolution at Low k

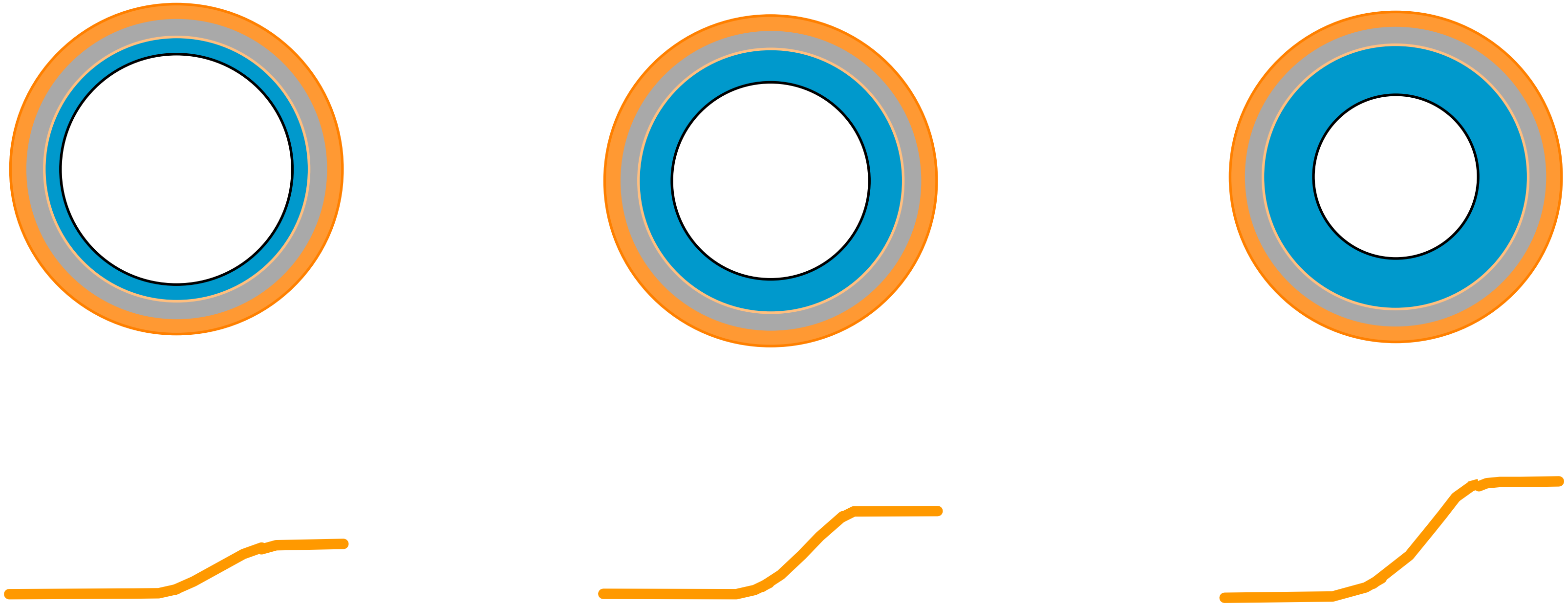


DB-1, 30 m x 0.32 mm ID
40°C isothermal, He at 35 cm/sec
Solvent mixture

Film Thickness

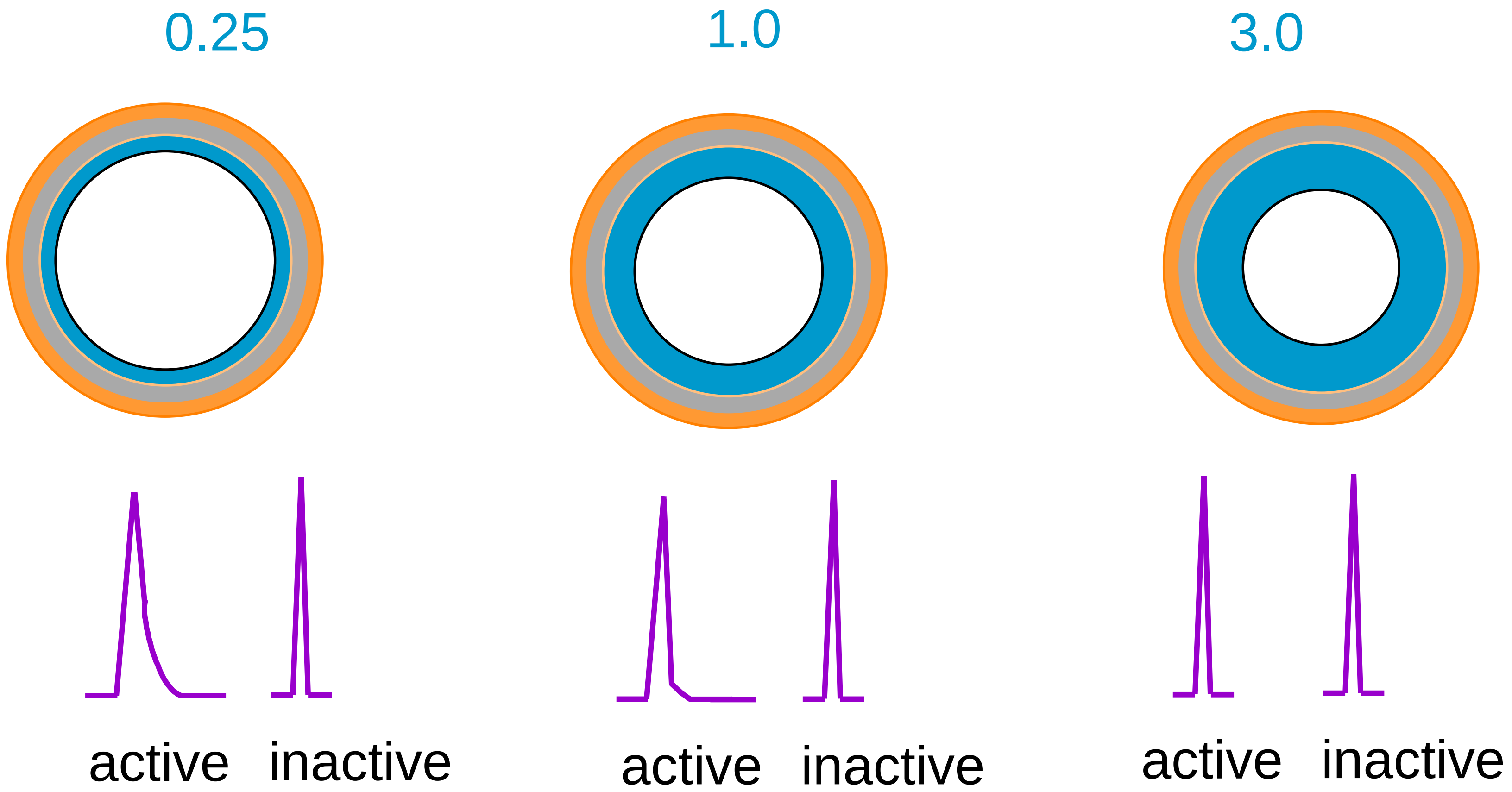
Bleed

More stationary phase = More degradation products



Film Thickness

Inertness Summary



Column Dimensions
Diameter Summary

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

Column Dimensions

Length Summary

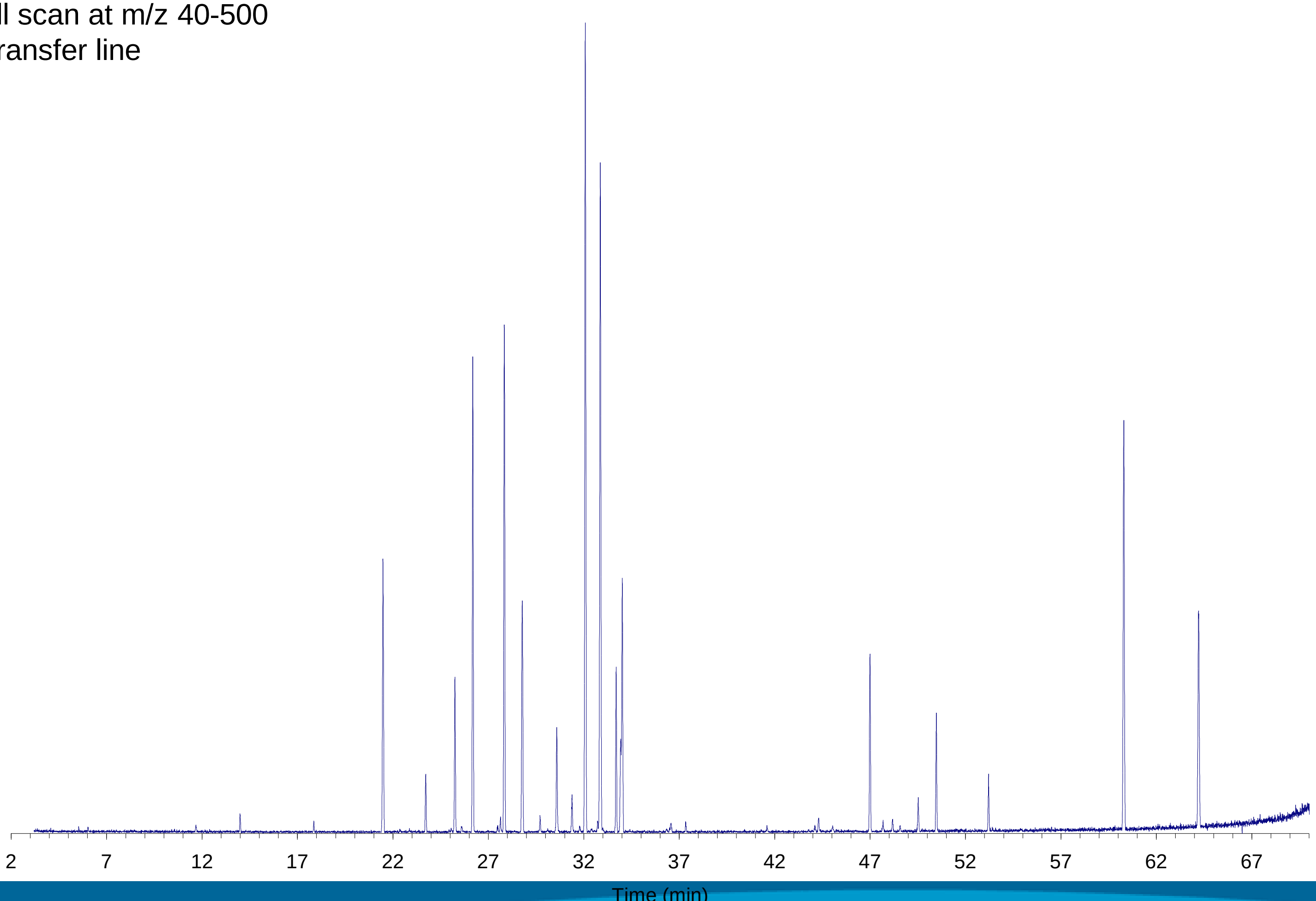
To Increase	Make Length
Resolution	Longer
Retention	Longer
Pressure	Longer
Cost	Longer

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

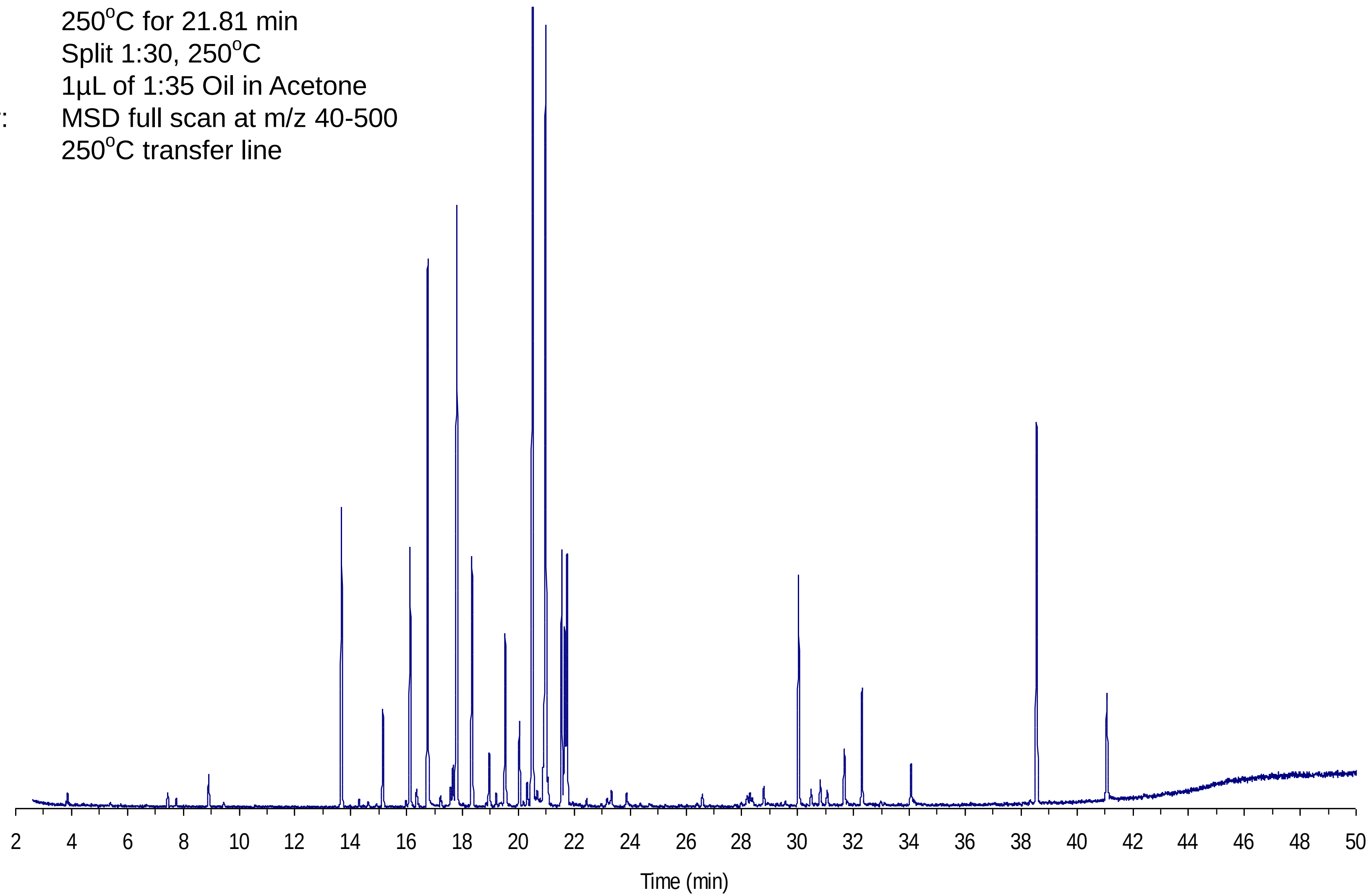
Column: DB-WAX 30 m X 0.25 mm X 0.25 µm

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!

Contact Agilent Chemistries and Supplies Technical Support

- 1-800-227-9770 Option 3, Option 3:
- Option 1 for GC/GCMS Columns and Supplies
- Option 2 for LC/LCMS   Columns and Supplies
- Option 3 for Sample Preparation, Filtration and QuEChERS
- Option 4 for Spectroscopy Supplies
- Available in the USA 8-5 all time zones

- gc-column-support@Agilent.com
- lc-column-support@agilent.com
- spp-support@agilent.com
- spectro-supplies-support@agilent.com