Choosing the “Correct” GC Column Dimensions and Stationary Phase

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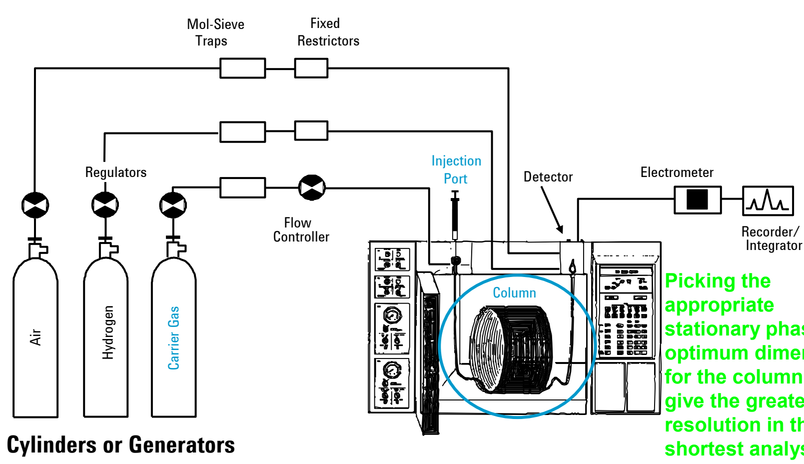
Agilent Technologies

Typical Gas Chromatographic System



Picking the appropriate stationary phase and optimum dimensions for the column will give the greatest resolution in the shortest analysis time.

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Column Selection

Four Primary Selection Areas

Stationary Phase Type

Column Internal Diameter

Stationary Phase Film Thickness

Column Length

Resolution

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

Efficiency	$N = f$ (gas, L, r_c)	L = Length
Retention	$k = f$ (T, d_f, r_c)	r_c = column radius
Selectivity	$\alpha = f$ (T, phase)	d_f = film thickness
		T = temperature

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Column Selection

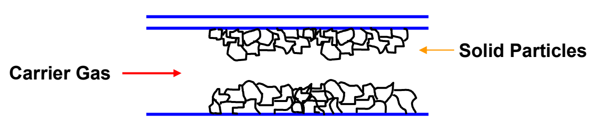
Stationary Phase - Common Types

Siloxane polymers

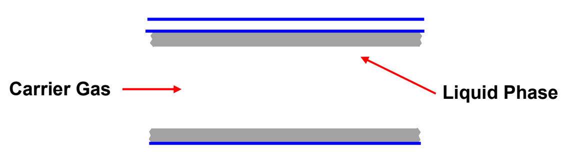
Poly(ethylene) glycols

Porous polymers

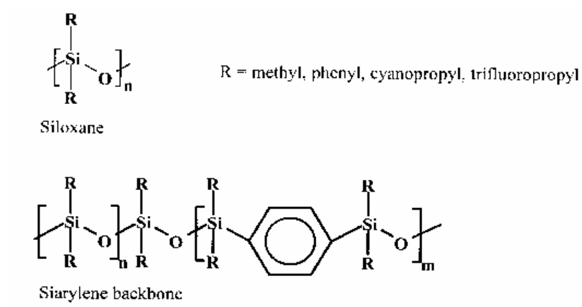
Capillary Column Types

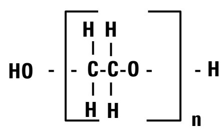


Wall Coated Open Tube (WCOT)



Stationary Phase Polymers





Polyethylene glycol backbone

Why Is Stationary Phase Type Important?

Influence of 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

Match analyte polarity to stationary phase polarity

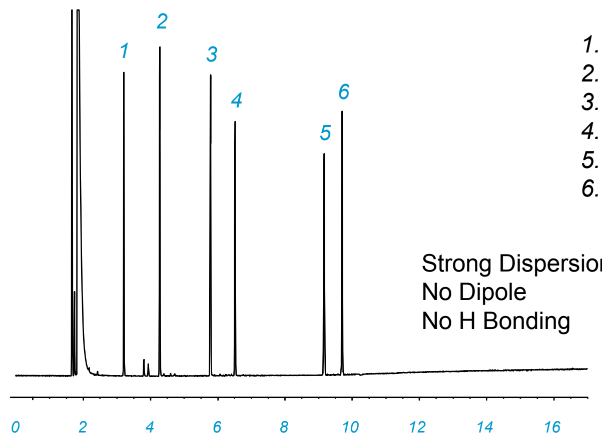
-like dissolves like(oil and water don’t mix)

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

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

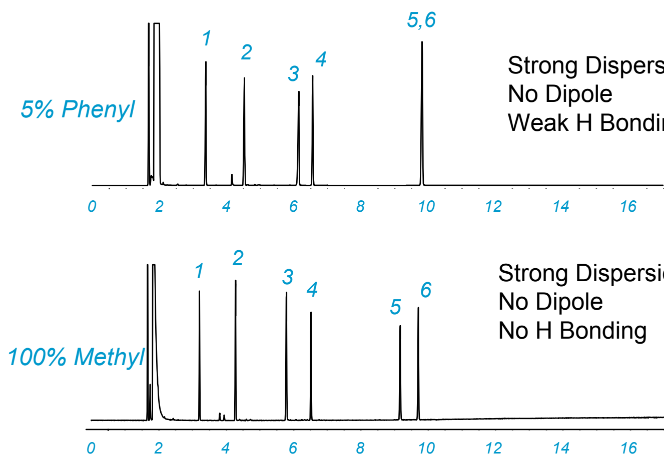
100% Methyl Polysiloxane (boiling point column?)



1. Toluene 110^o
2. Hexanol 156^o
3. Phenol 182^o
4. Decane (C10) 174^o
5. Naphthalene 218^o
6. Dodecane (C12) 216^o

Strong Dispersion
No Dipole
No H Bonding

5% Phenyl

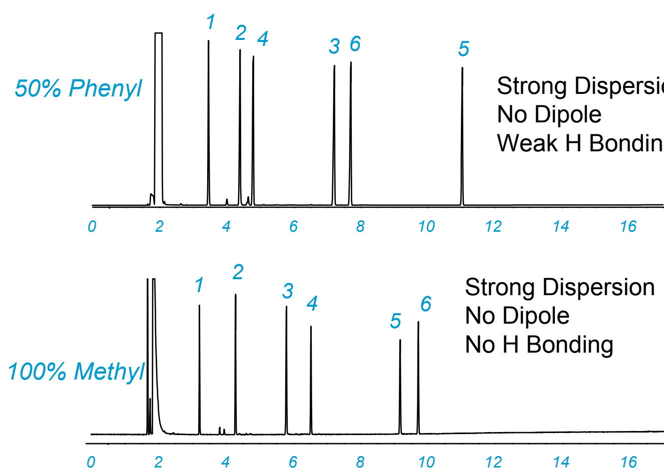


Strong Dispersion
No Dipole
Weak H Bonding

Strong Dispersion
No Dipole
No H Bonding

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

50% Phenyl

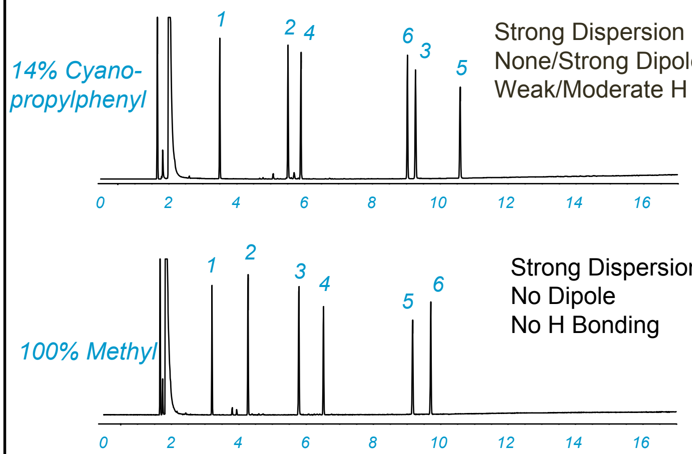


Strong Dispersion
No Dipole
Weak H Bonding

Strong Dispersion
No Dipole
No H Bonding

1. Toluene	*110°*
2. Hexanol	*156°*
3. Phenol	*182°*
4. Decane (C10)	*174°*
5. Naphthalene	*218°*
6. Dodecane (C12)	*216°*

14% Cyanopropylphenyl

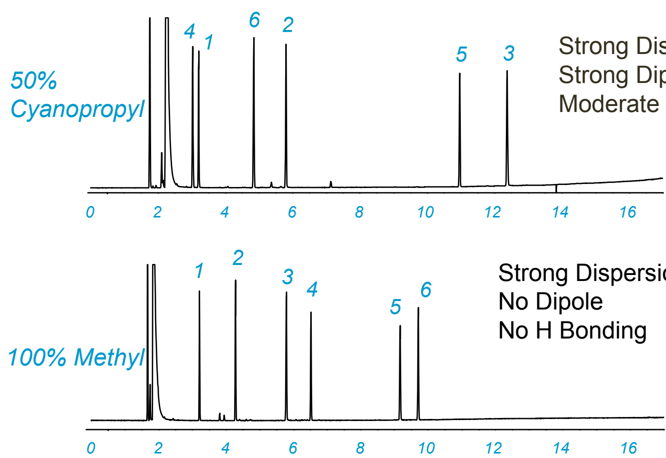


Strong Dispersion
None/Strong Dipole (Ph/CNPr)
Weak/Moderate H Bonding (Ph/CNPr)

Strong Dispersion
No Dipole
No H Bonding

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

50% Cyanopropyl

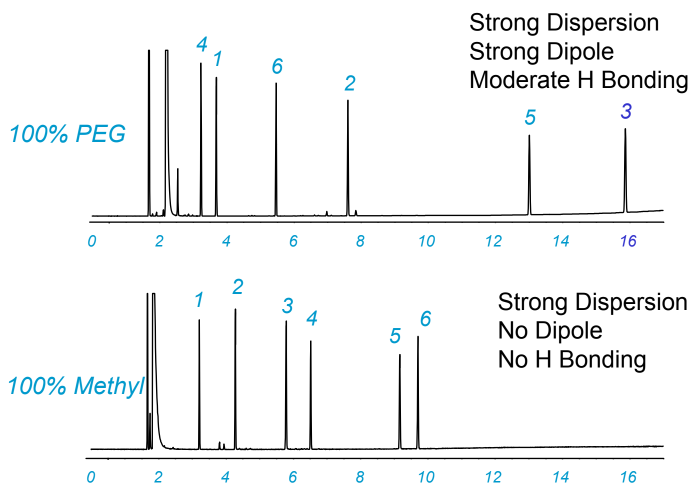


Strong Dispersion
Strong Dipole
Moderate H Bonding

Strong Dispersion
No Dipole
No H Bonding

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

100% Polyethylene Glycol



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

Selectivity is important but not everything…

Inertness and Bleed can be critical factors in column selection.

Temperature limits will play a role as well.

Stationary Phase Bleed

A thermodynamic equilibrium process that occurs to some degree in all columns, and is proportional to the mass amount of stationary phase inside the capillary tubing/carrier gas flow path

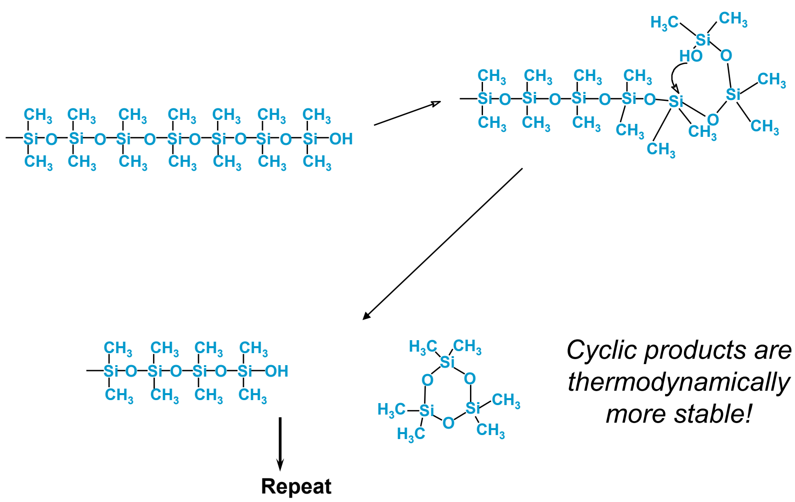
Polysiloxane backbone releases low molecular weight, cyclic fragments

Is negligible in low temperature, O2-free, clean GC systems

Increased by increased temperature, oxygen exposure, or chemical damage

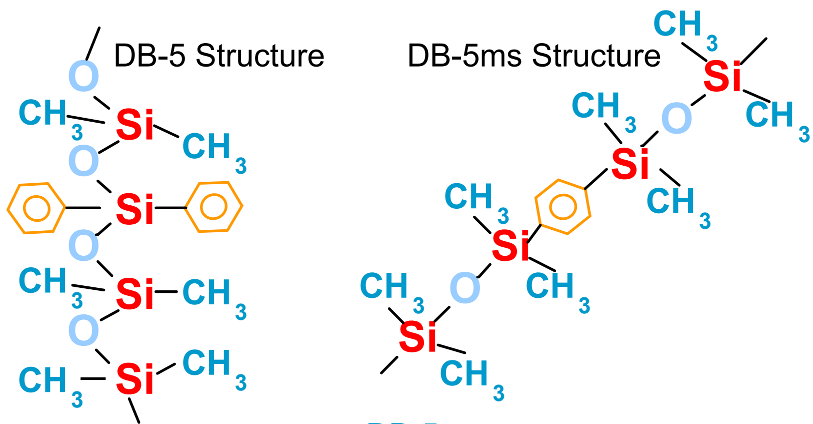
Bleed: Why Does It Happen?

"Back Biting" Mechanism of Product Formation



Cyclic products are thermodynamically more stable!

DB-5ms Structure



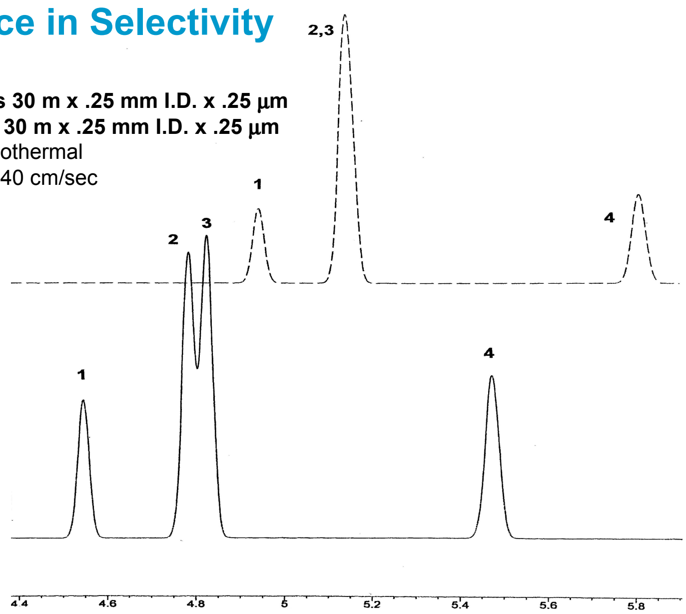
DB-5
5% Phenyl

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

Difference in Selectivity

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



Four Types Of Low Bleed Phases

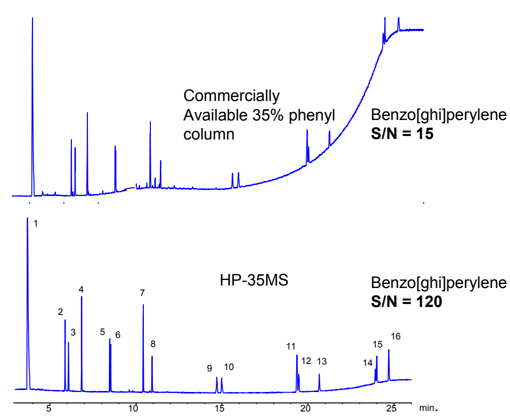
Phases tailored to “mimic” currently existing polymers
- -Examples: DB-5ms, DB-35ms, DB-17ms, DB-225ms

Phases unrelated to any previously existing polymers
- -Examples: DB-XLB

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

Hand selected columns

Benefits of Low Bleed Phases
PAH Sensitivity Using HP-35MS



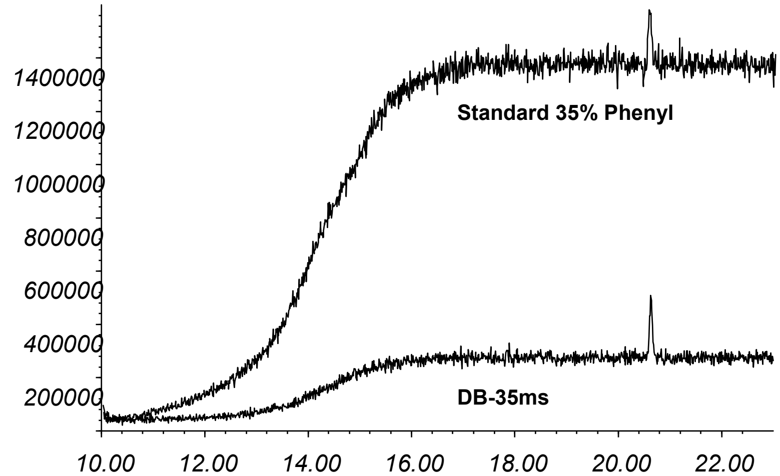
1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benz[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Indeno[1,2,3,-c,d]anthracene
15. Dibenz[a,h]anthracene
16. Benzo[g,h,i]perylene

Columns: 30 m x 0.32 mm x 0.35 um.
Carrier: H2, constant flow, 5 psi at 100 ºC.
Injector: 275 ºC, splitless, 1 ul , 0.5-5ppm.
Oven: 100 ºC to 250 ºC (5 min.) at 15 ºC/min.,; then to 320 ºC (10 min.) at 7.5 ºC/min.
Detector: FID, 320 ºC.

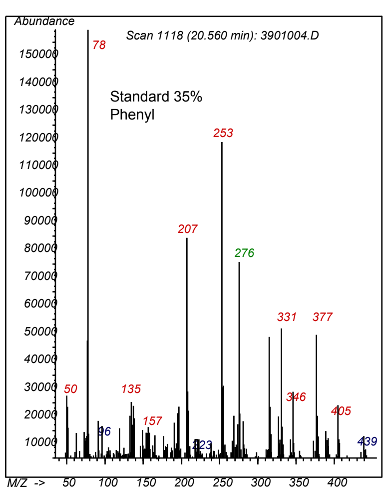
Benefits of Low Bleed Phases

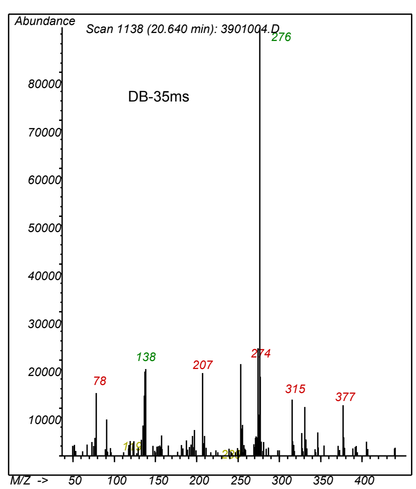
DB-35ms vs Standard 35% Phenyl

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

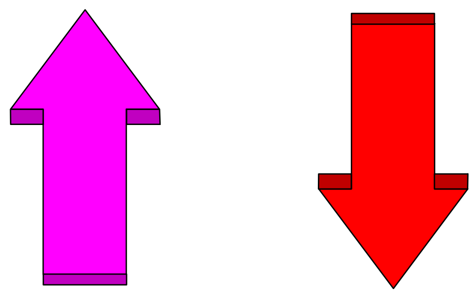


Higher Spectral Purity





Polarity vs Stability/Temperature Range



Polarity

Stability
Temperature Range

Stationary Phase Selection

Existing information

Selectivity/Polarity

Critical separations

Temperature limits

Application designed

Examples: DB-VRX, DB-MTBE, DB-TPH, DB-ALC1, DB-ALC2, DB-HTSimDis, DB-Dioxin, HP-VOC, etc.

Choose the column phase that gives the best separation but not at the cost of robustness or ruggedness.

Resolution

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

Efficiency	$N = f$ (gas, L, r_c)	L = Length
Retention	$k = f$ (T, d_f, r_c)	r_c = column radius
Selectivity	$\alpha = f$ (T, phase)	d_f = film thickness
		T = temperature

Column Diameter - Theoretical Efficiency

I.D. (mm)	n/m
0.05	23,160
0.10	11,580
0.18	6,660
0.20	5830
0.25	4630
0.32	3660
0.45	2840
0.53	2060

Column Diameter and Capacity

I.D. (mm)	Capacity (ng)
0.05	1-2
0.10	6-13
0.18	25-55
0.20	35-70
0.25	80-160
0.32	110-220
0.45	600-800
0.53	1000-2000

Like Polarity
Phase/Solute
0.25 µm film thickness

Column Diameter - Inlet Head Pressures (Helium)

I.D (mm)	Pressure (psig)
0.05	275-400
0.10	90-130
0.18	30-45
0.20	25-40
0.25	15-25
0.32	10-20
0.45	3-7
0.53	2-4

30 meters
Hydrogen pressures x 1/2

Column Diameter and Carrier Gas Flow

Lower flow rates: Smaller diameter columns

Higher flow rates: Larger diameter columns

Low flow rates : GC/MS
High flow rates: Headspace, purge & trap

Diameter Summary

To increase	Diameter
Efficiency	Smaller
Resolution	Smaller
Pressure	Smaller
Capacity	Larger
Flow rate	Larger

Resolution

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

Efficiency	$N = f$ (gas, L, r_c)	L = Length
Retention	$k = f$ (T, d_f, r_c)	r_c = column radius
Selectivity	$\alpha = f$ (T, phase)	d_f = film thickness
		T = temperature

Film Thickness and Retention: Isothermal

Thickness (µm)	Retention Change
0.10	0.40
0.25	*1.00*
1.0	4.00
3.0	12.0
5.0	20.0

Constant Diameter
Normalized to 0.25 µm

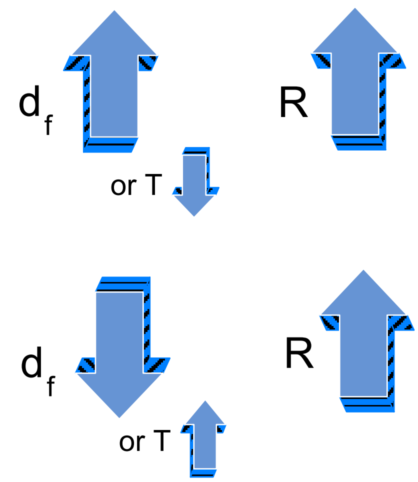
Film Thickness and Resolution

When solute k < 5

(early eluters)

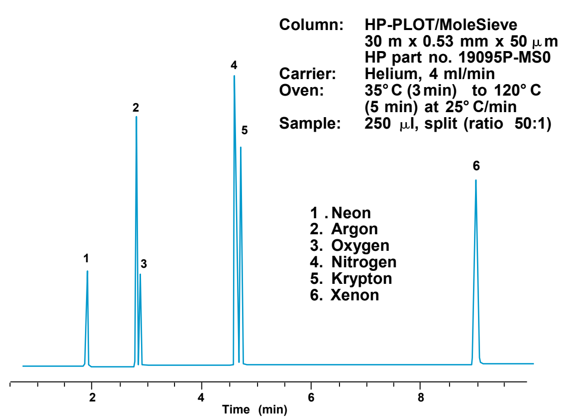
When solute k > 5

(later eluters)



Other Retention - Adsorption

Analysis of Noble & Fixed Gases
Using HP PLOT MoleSieve



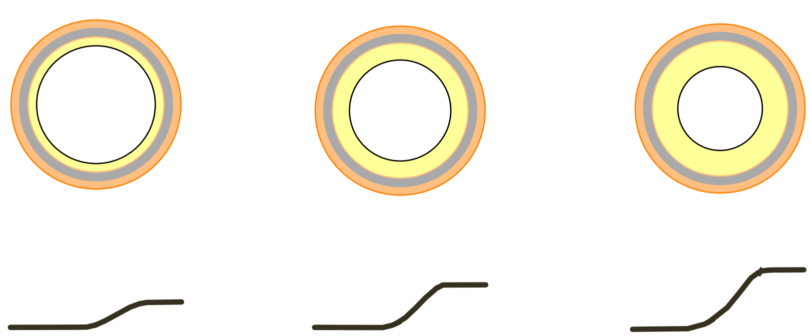
Film Thickness and Capacity

Thickness (µm)	Capacity (ng)
0.10	50-100
0.25	125-250
0.50	250-300
1	500-1000
3	1500-3000
5	2500-5000

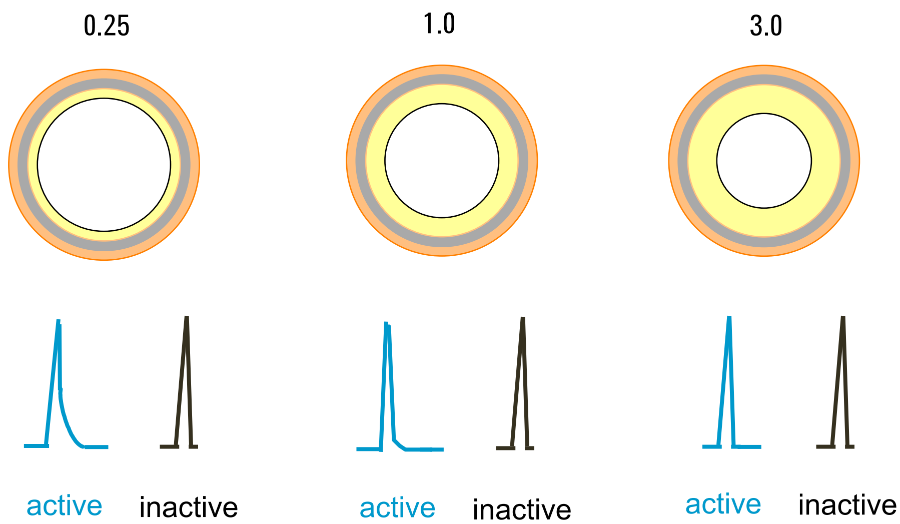
0.32 mm I.D.
Like Polarity Phase/Solute

Film Thickness and Bleed

More stationary phase = More degradation products



Film Thickness and Inertness



Film Thickness Summary

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

Resolution

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

Efficiency $N = f\ (\text{gas}, L, r_c)$

Retention $k = f\ (T, d_f, r_c)$

Selectivity $\alpha = f\ (T, \text{phase})$

L = Length

r_c = column radius

d_f = film thickness

T = temperature

Column Length and Efficiency (Theoretical Plates)

Length (m)	n
15	69,450
30	138,900
60	277,800

0.25 mm ID
n/m = 4630 (for k = 5)

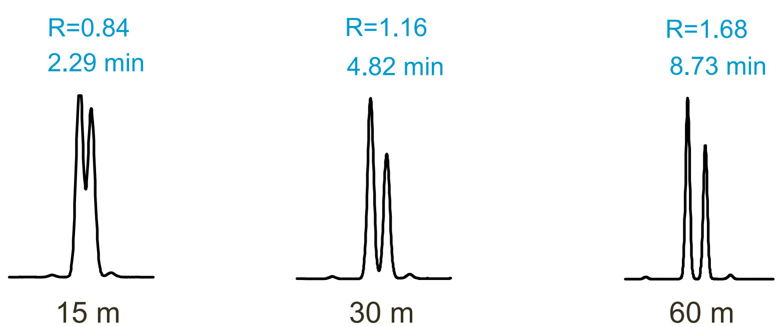
Column Length and Resolution

$$R \alpha \sqrt{n} \alpha \sqrt{L}$$

Length X 4 = Resolution X 2

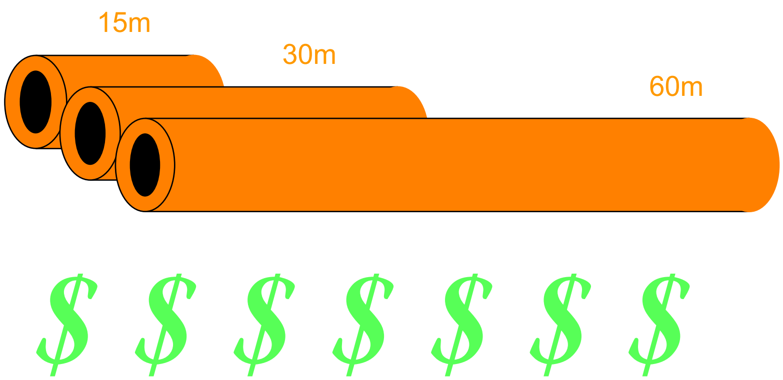
$$t \alpha L$$

Column Length VS Resolution and Retention: Isothermal



Double the plates, double the time but not double the the resolution

Column Length and Cost

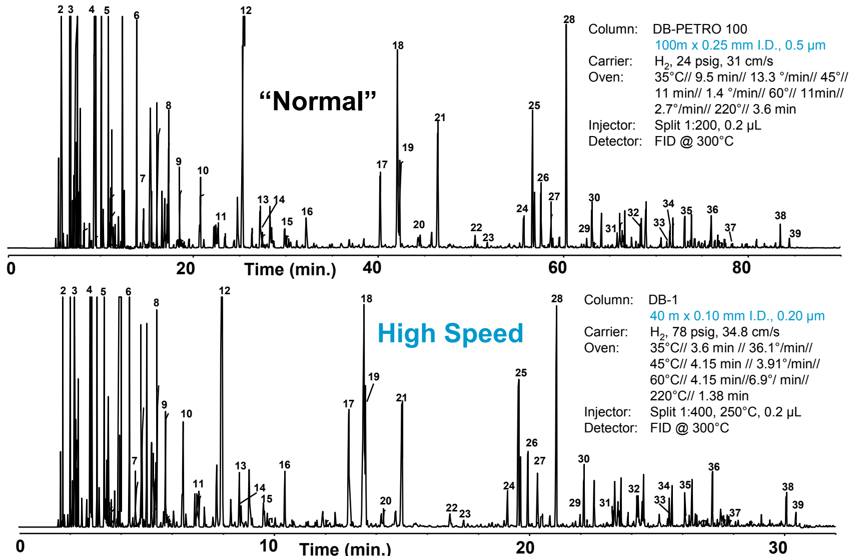


Length Summary

To Increase	Length
Efficiency	Longer
Resolution	Longer
Analysis Time	Longer
Pressure	Longer
Cost	Longer

Regular Unleaded Gasoline

California Phase I



Still Can't Decide Which Column to Use?????
…Call Us!!!

TECHNICAL SUPPORT

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E-mail: Daron_Decker@Agilent.com