Decisions, Decisions: How to Select the Correct GC Column for Your Application

Alexander Ucci Online Application Engineer July 21, 2021





# Things to Consider When Choosing a Column

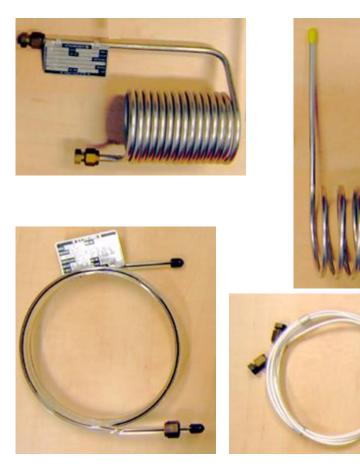
- Is it volatile enough to chromatograph by GC?
- Is it a gas or a liquid?
- How are we getting the sample injected?
- What is the sample matrix?
  - Can we do sample cleanup?
- Is it an established method?
- What do we know about the analytes?
- What else *may* be present in the sample?





# **Column History**

1969:





#### **1977:** First glass capillary columns

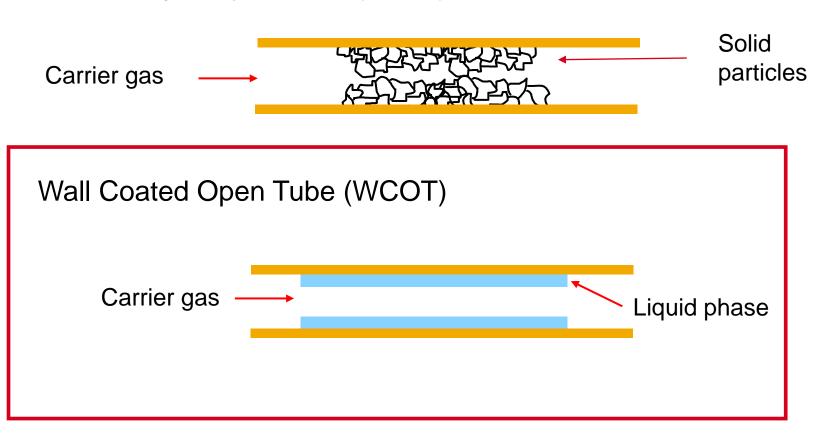


#### **1979:** First WCOT fused silica capillary columns



# Capillary Column Types

#### Porous Layer Open Tube (PLOT)



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# **Column Construction**

#### Polyimide coating

Flexible polymeric coating; adds mechanical strength and temperature stability to fused silica

#### Fused silica

Amorphous glass-like tubing comprised of silicon dioxide; high temperature resistance, low reactivity. May contain rough edges creating active sites.

#### Deactivation

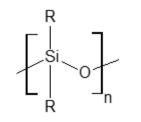
Chemical treatment layer; smooths fused silica surface to enhance inertness

#### Stationary phase

Polymeric coating atop deactivation layer; commonly comprised of polysiloxane- or polyethyleneglycol-based compounds

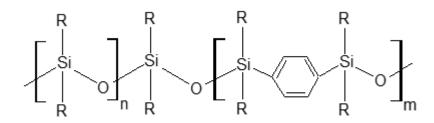


# **Stationary Phase Polymers**

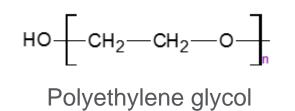


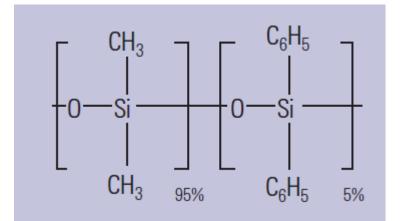
Siloxane

- R= methyl, phenyl, cyanopropyl, trifluoropropyl
- % = number of sites on silicon atoms occupied



Siarylene backbone





Structure of Agilent J&W HP-5ms

5% phenyl / 95% methyl





### Polyethylene Glycol Phases

$$HO \left( CH_2 - CH_2 - O \right) H$$



Less Stable than Polysiloxanes

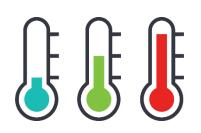


Unique Separation Characteristics  $\bigcirc$ 

Agilent J&W DB-WAX UI Agilent J&W DB-HeavyWAX Agilent J&W DB-FATWAX UI



### Another New Column: J&W DB-HeavyWAX The WAX column you've been waiting for!







Increased temperature limit (280 °C / 290 °C)

Increased thermal stability

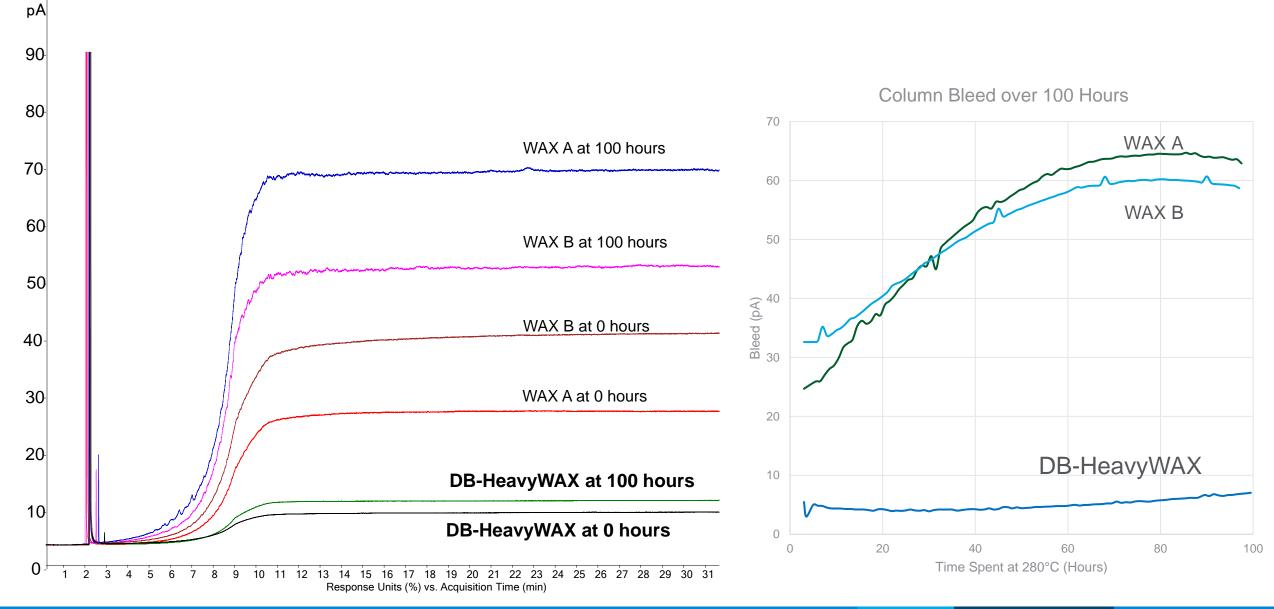
Lower bleed



www.agilent.com/chem/db-heavywax



# Bleed Summary at 280 °C Over 100 Hours





# JW Column Portfolio- DB, HP, CP, VF

Low Polarity			Mid Polarity			High Polarity		
CP-Sil 2	DB-1ms UI HP-1ms UI	DB & HP-5ms UI	DB-XLB	DB-225ms	DB-ALC1	HP-88	DB-WAX	DB-WAX UI
DB-MTBE	DB-1ms HP-1ms	DB & HP-5ms	VF-Xms	DB-225	DB-Dioxin	CP-Sil 88	DB-WAXetr	DB-HeavyWAX
CP-Select CB MTBE	VF-1ms	VF-5ms	DB-35ms UI	CP-Sil 43 CB	DB-200	DB-23	HP-INNOWax	DB-FATWAX UI
	DB & HP-1	DB & HP-5	DB & VF-35ms	VF-1701ms	VF-200ms	VF-23ms	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-FFAP 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-TCEP	
			CP-Select 624 CB	Agilent J&W has <u>over 50 different</u> stationary phase offerings				
			DB-1301					
			VF-1301ms	Stationary phase offerings				
	Finding the Pe	rfect Match: Practical Advic	CP-Sil 13 CB	Agilent Restricted				

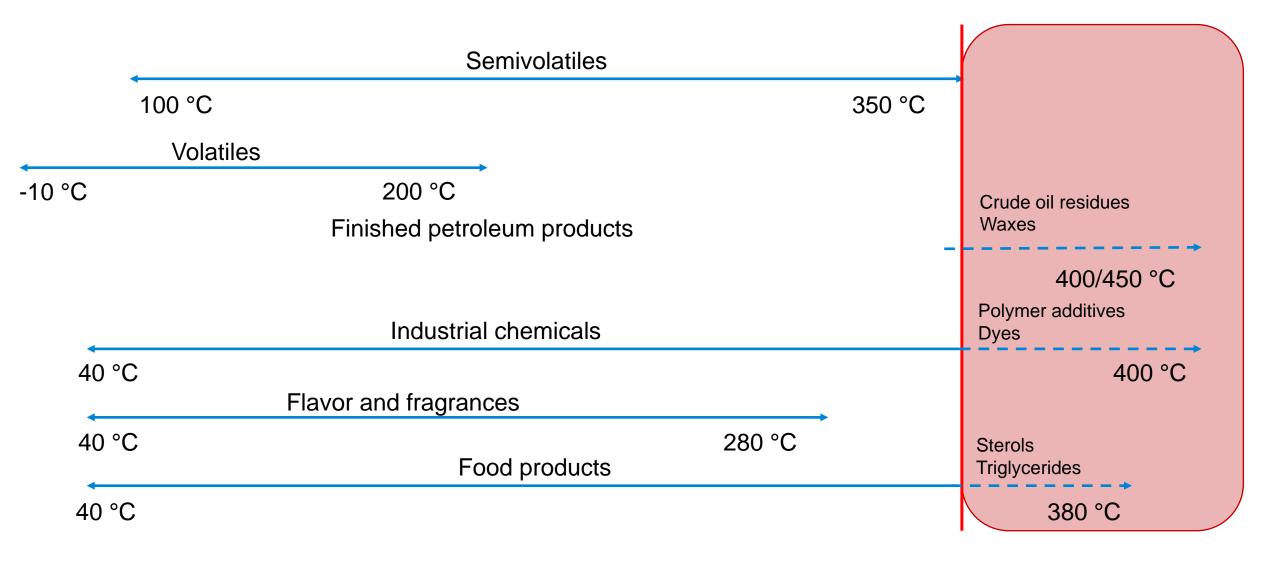
### Specialty Phases Columns developed for specific applications

- Examples:
  - DB-8270D UI
  - DB-624 UI <467>
  - DB-MTBE
  - DB-TPH
  - DB-BAC1 UI & DB-BAC2 UI
  - DB-HT SimDis
  - Select Low Sulfur
  - CP-Volamine
  - Select PAH
  - DB-EUPAH
  - DB-CLP1 & DB-CLP2
  - DB-Select 624 UI <467>
  - CP-LowOx
  - Select Permanent Gases
  - ...and more!



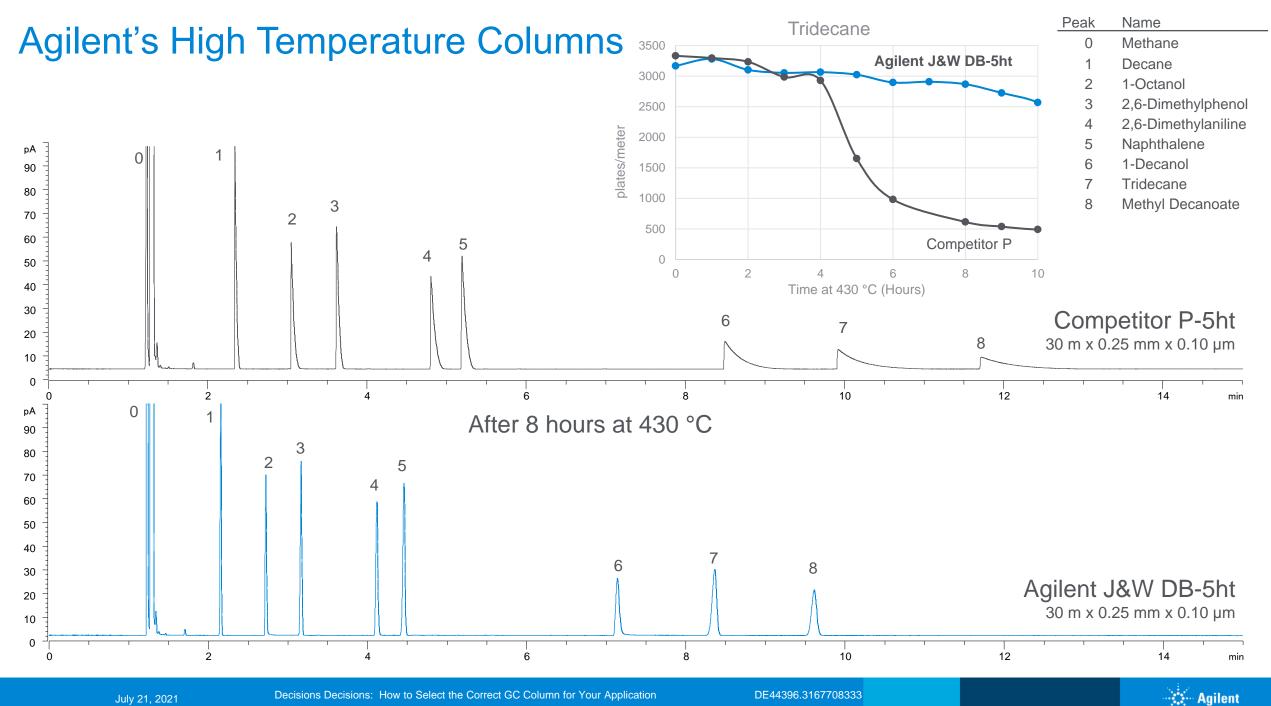


# **High Temperature Applications**



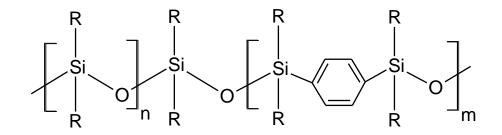
#### You only need a high-temperature column for temperatures above 350 °C





### Low Bleed Phases

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



Siarylene backbone

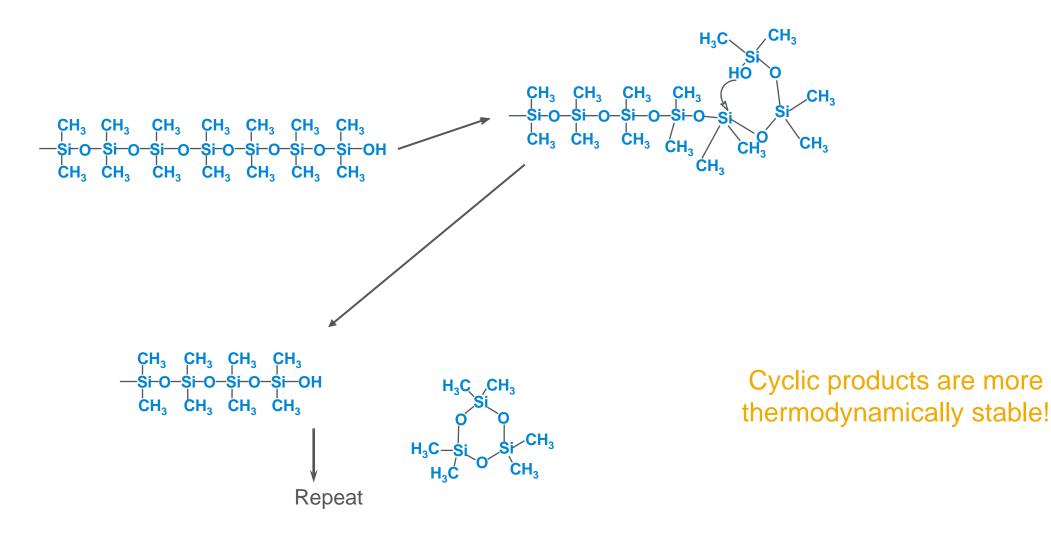
•New phases unrelated to any previously existing polymers Examples: DB-XLB

•Optimized manufacturing processes Examples: DB-1ms, HP-1ms, HP-5ms, VF-5ms



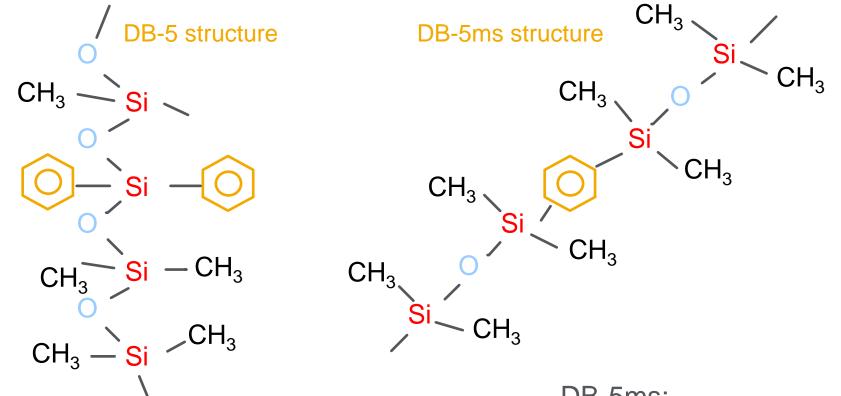
# What is Column Bleed?

"Back biting" mechanism of product formation





# Agilent J&W DB-5ms Structure



DB-5ms:

- Increased stability
- Different selectivity
- Optimized to match DB-5 as much as possible

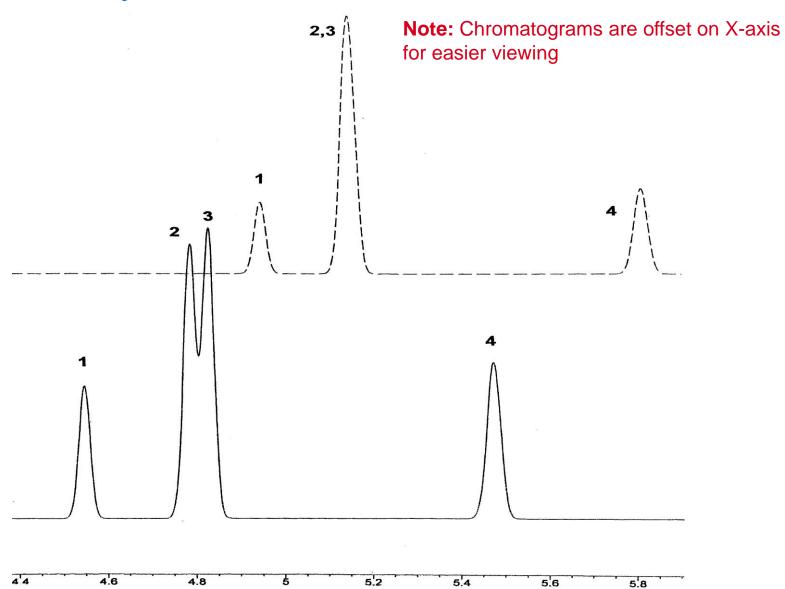


## **DB-5ms versus DB-5 Selectivity**

Solid line: Agilent J&W **DB-5ms 30 m x 0.25 mm id x 0.25 µm** Dashed line: Agilent J&W **DB-5 30 m x 0.25 mm id x 0.25 µm** Oven: 60 °C isothermal Carrier gas: H<sub>2</sub> at 40 cm/sec

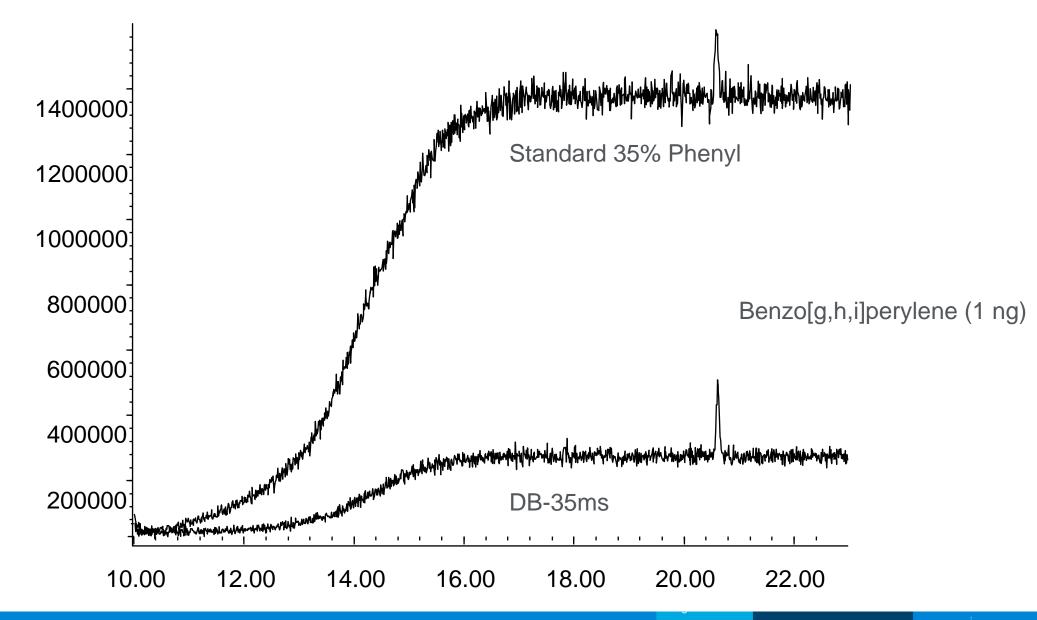
1: Ethylbenzene 2: m-Xylene

3: p-Xylene 4: o-Xylene





### Comparison of Agilent J&W DB-35ms Versus Standard DB-35



Month ##, 200X

#### Agilent Ultra Inert GC Columns Column inertness: What does it mean?

- Easier to describe "lack of inertness"
  - Peak tailing (reversible interaction)
  - Complete loss of compound (irreversible interaction)
- A high level of flow path inertness will produce peaks from active compounds that are not degraded and will look "normal"/symmetrical.
- The negative effects the column has towards challenging compounds:
  - Acids
  - Bases
  - Hydrogen bonding
  - Compounds such as 2,4-DNP, Endrin, etc.

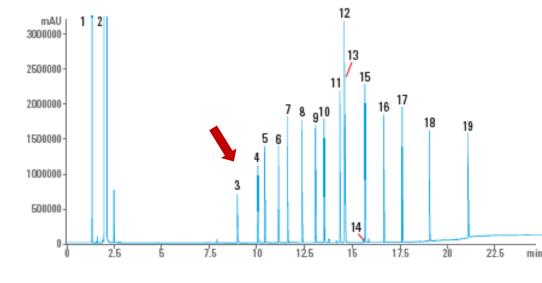


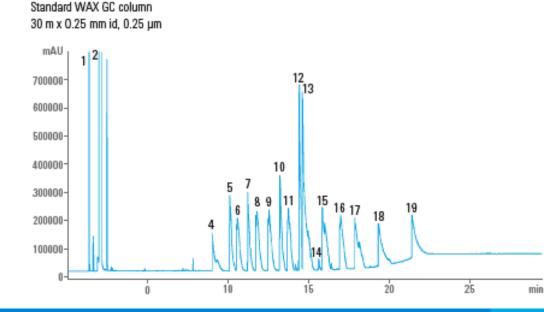
# DB-WAX Ultra Inert and Free Fatty Acid

- Peak identification:
- 1. Methane
- 2. Acetone (solvent)
- 3. Acetic acid
- 4. Propionic acid
- 5. Isobutyric acid
- 6. Butyric acid
- 7. Isovaleric acid
- 8. Valeric acid
- 9. 4-Methylvaleric acid
- 10. Hexanoic acid
- 11. 4-Methylhexanoic acid
- 12. 2-Ethylhexanoic acid
- 13. Heptanoic acid
- 14. Pyruvic acid
- 15. Octanoic acid
- 16. Nonanoic acid
- 17. Decanoic acid
- 18. Undecylenic acid
- 19. Myristic acid (Tetradecanoic)

#### Competitive comparison: free fatty acids

DB-WAX Ultra Inert GC column 30 m x 0.25 mm id, 0.25 µm (p/n 122-7032Ul)









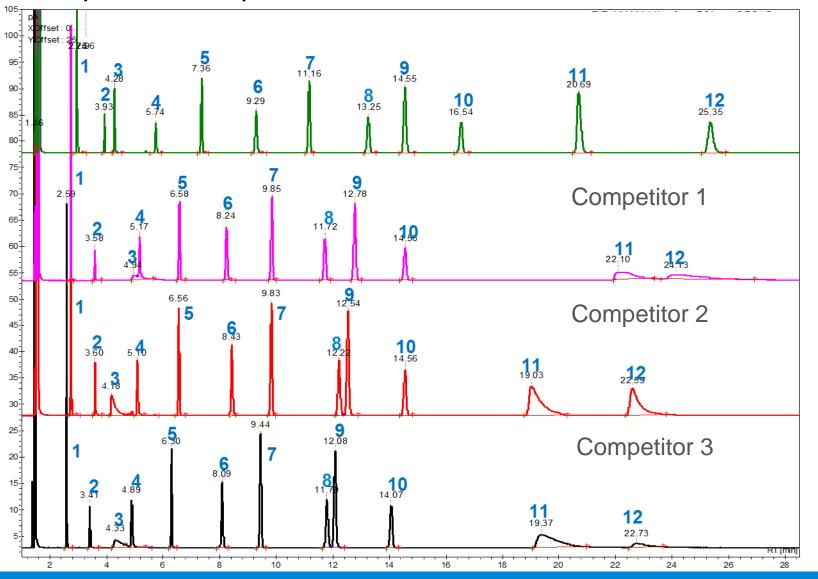
# Application note: 5991-6709EN

July 21, 2021



# Let's Make a Better WAX column: DB-WAX Ultra Inert

Competitor comparison DB-WAX UI test mix after 50 hours at 250 °C



Compound I.D.

\*. Methane

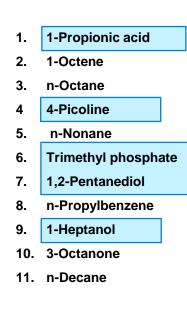
- 1. 5-Nonanone
- 2. Decanal
- 3. Propionic Acid
- 4. Ethylene Glycol
- 5. Heptadecane
- 6. Aniline
- 7. Methyl Dodecanoate
- 8. 2-Chlorophenol
- 9. 1-Undecanol
- 10. Nonadecane

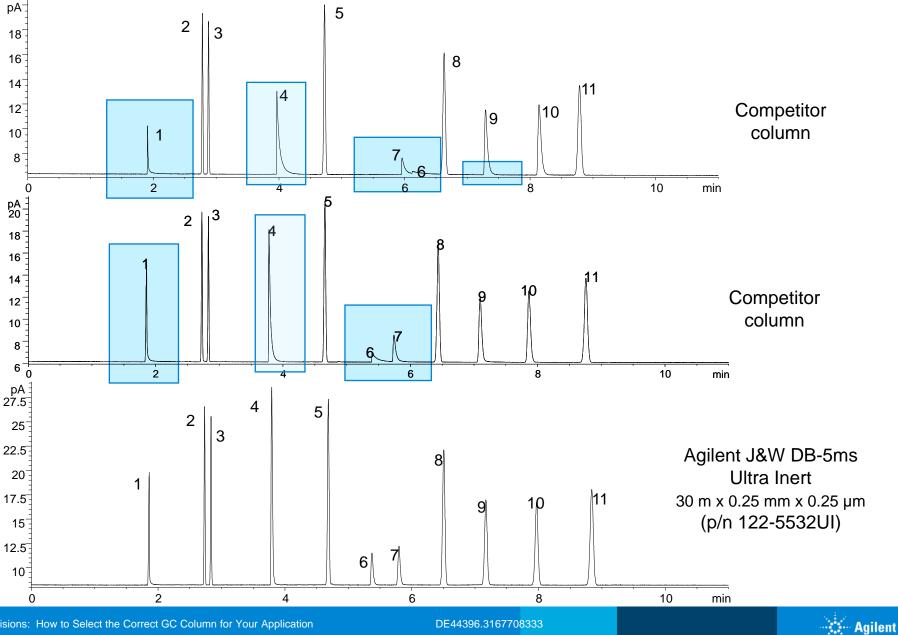
11. 2-Ethylhexanoic Acid12. Ethyl Maltol

Application note: 5991-6683EN



# Ultra Inert Test Mix – DB-5MS Ultra Inert versus Competitors





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  $\alpha$ 

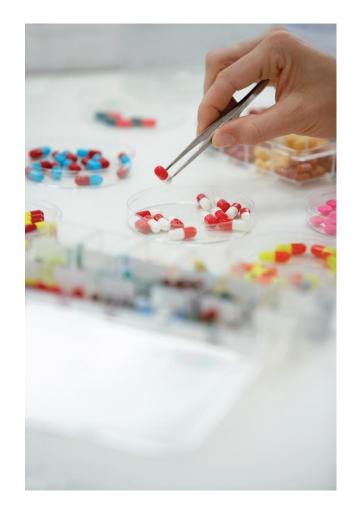
$$\alpha = \frac{k_2}{k_1}$$

 $k_2$  = partition ratio of 2<sup>nd</sup> peak  $k_1$  = partition ratio of 1<sup>st</sup> peak



# Selectivity

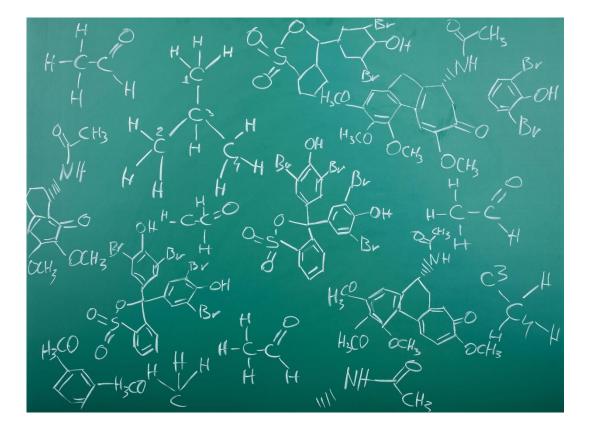
- Relative spacing of the chromatographic peaks
- The result of all nonpolar, polarizable, and polar interactions that cause a stationary phase to be more or less retentive to one analyte than another





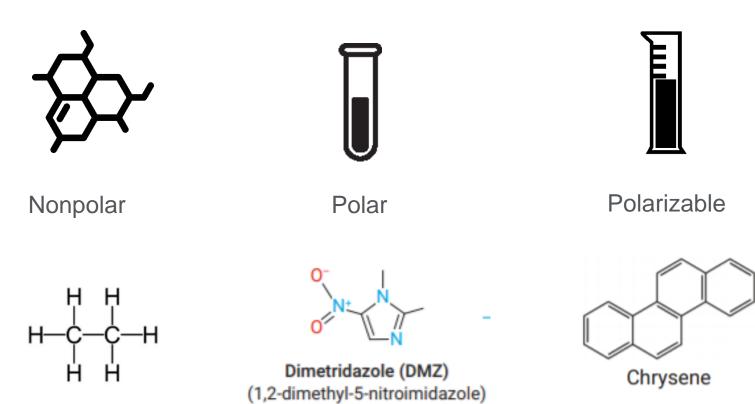
# Optimizing Selectivity ( $\alpha$ )

- Match analyte polarity to stationary phase polarity
  - "Like dissolves like"
- Take advantage of unique interactions between analyte and stationary phase functional groups





# Analyte Polarity





Decisions Decisions: How to Select the Correct GC Column for Your Application

# **Selectivity Interactions**



Dispersion



Dipole



Hydrogen bonding



# Dispersion Interaction ( $\Delta H_{vap}$ )

- Separation by differences in analyte heat of vaporizations (  $\Delta H_{vap}$  )
- Heat necessary to convert a liquid into a gas (at the same temperature)

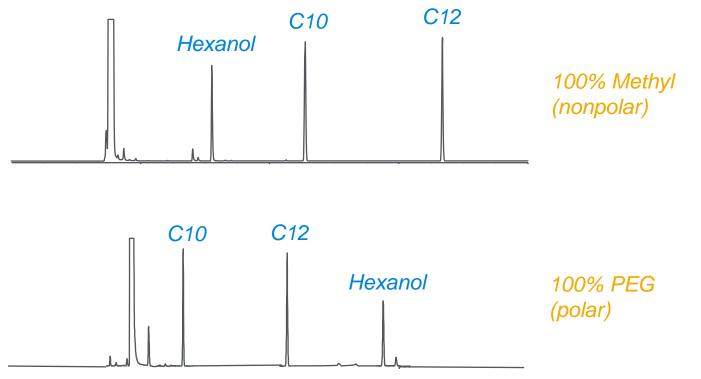






### **Dispersion Interaction** Solubility and retention

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 °C/min



# Dispersion Interaction ( $\Delta H_{vap}$ )



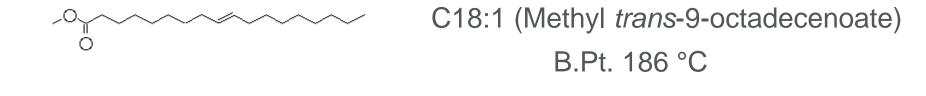


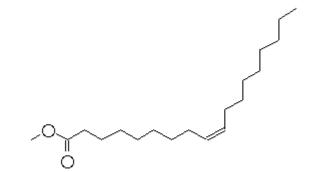
Vapor pressure: good approximation

Boiling point: poor approximation



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C18:1 (Methyl *cis*-9-octadecenoate) B.Pt. 186 °C

Smaller differences require a stronger dipole phase

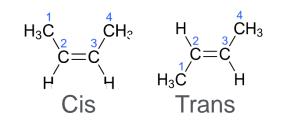


### **DB-FastFAME** 20 m x 0.18 mm x 0.20 µm

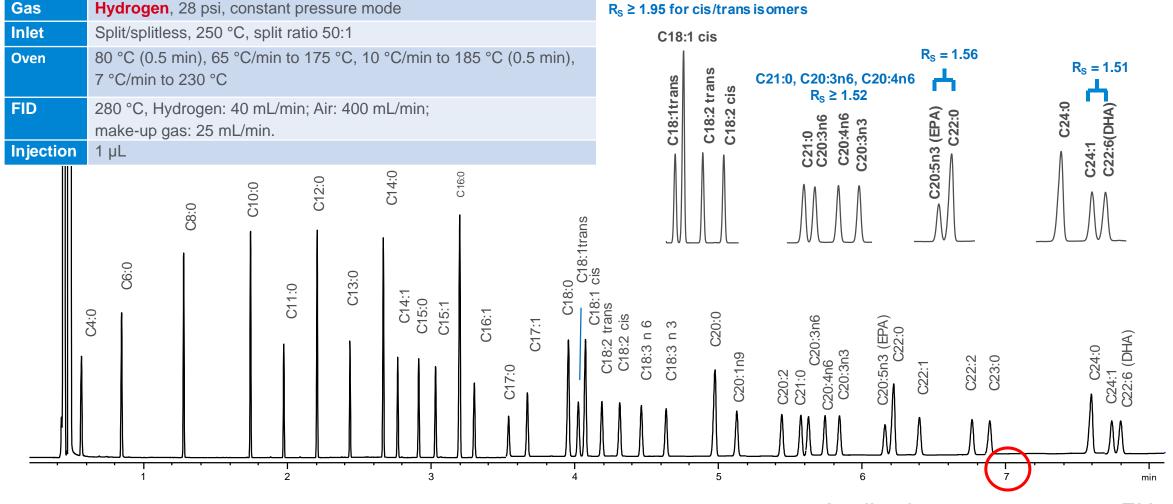
Agilent J&W DB-FastFAME, 20 m x 0.18 mm, 0.20 µm

Column

Strong interaction between cis isomers and the dipoles of the cyanopropyl ligands. That allows the trans to elute after the cis isomers.



#### $R_s \ge 1.95$ for cis/trans isomers

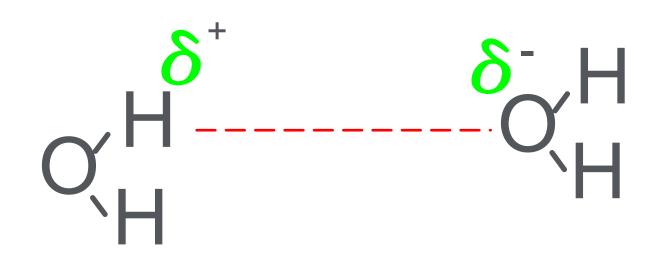


Application note: 5991-8706EN



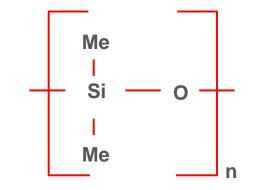
# Hydrogen Bonding Interaction

Dipole-Dipole interaction with hydrogen bound to oxygen or nitrogen interacting with an oxygen or nitrogen-atom



### **Nonpolar Phases**

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



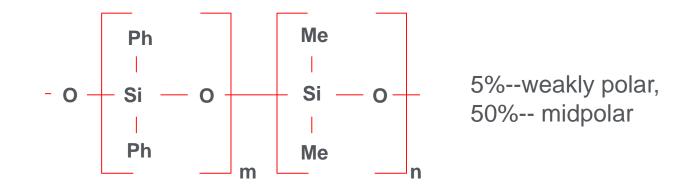
Separation mechanisms:

• 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)

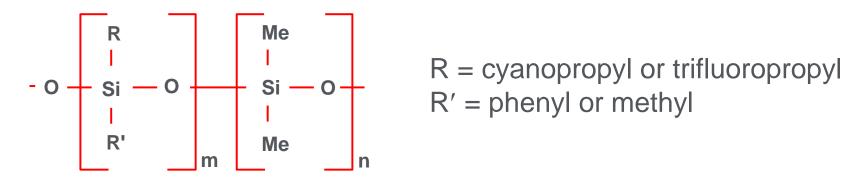


Separation mechanisms:

- 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)



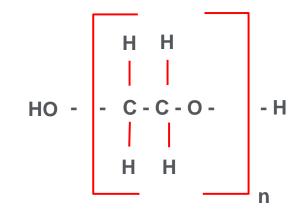
Separation mechanisms:

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



#### Hydrogen Bonding Phases

Typified by polyethylene glycol polymers (HP-INNOWax, DB-WAX UI, DB-HeavyWAX, DB-FFAP, VF-WAXms, CP-Wax 52 CB...)



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

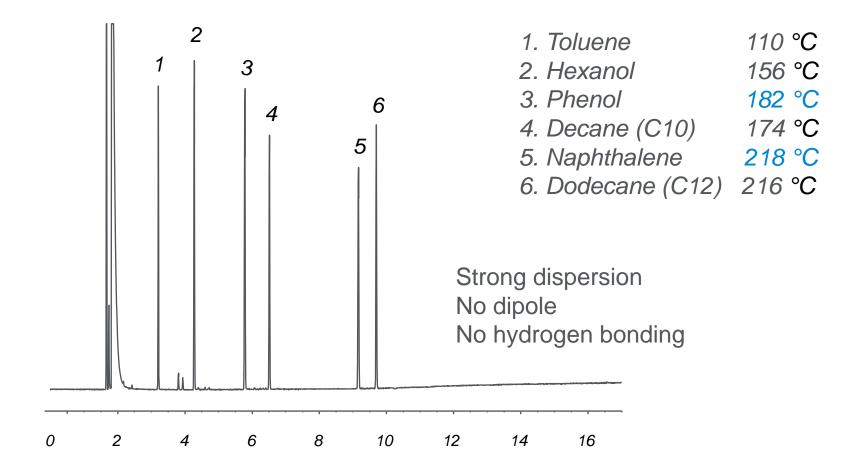


#### **Compounds and Properties**

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

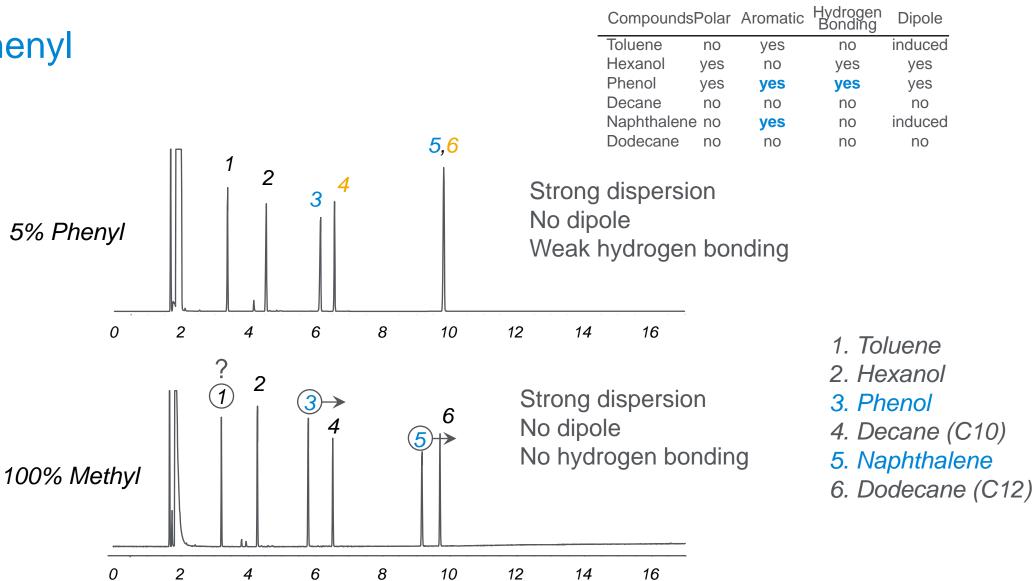


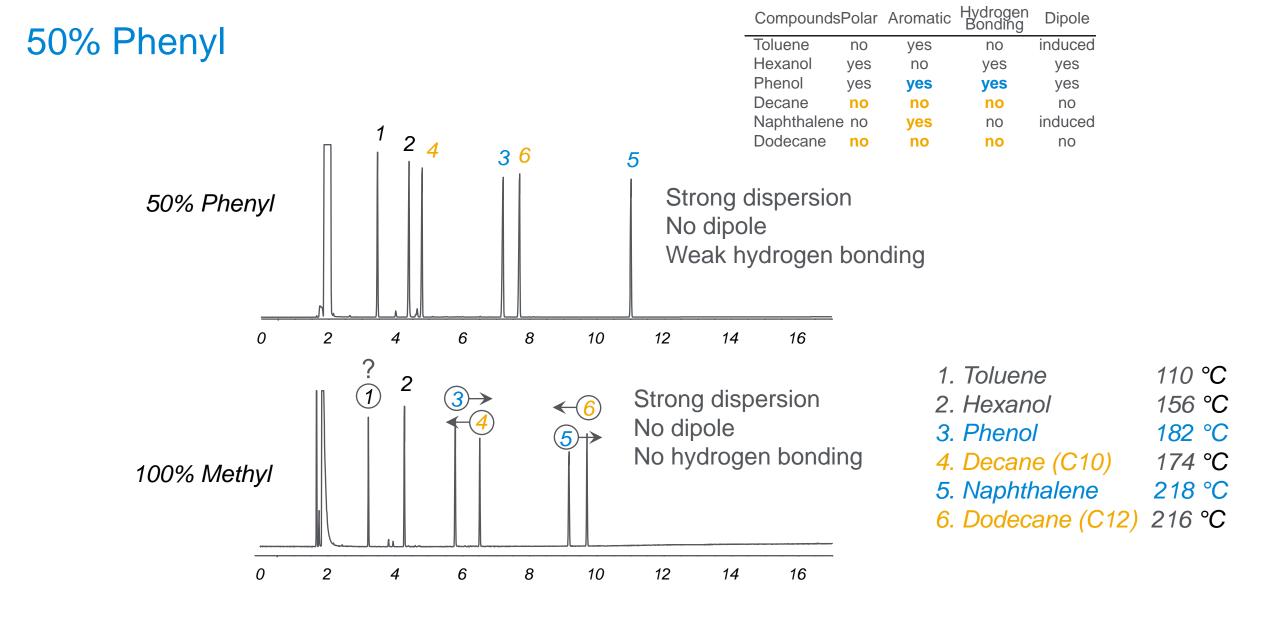
#### 100% Methyl Polysiloxane





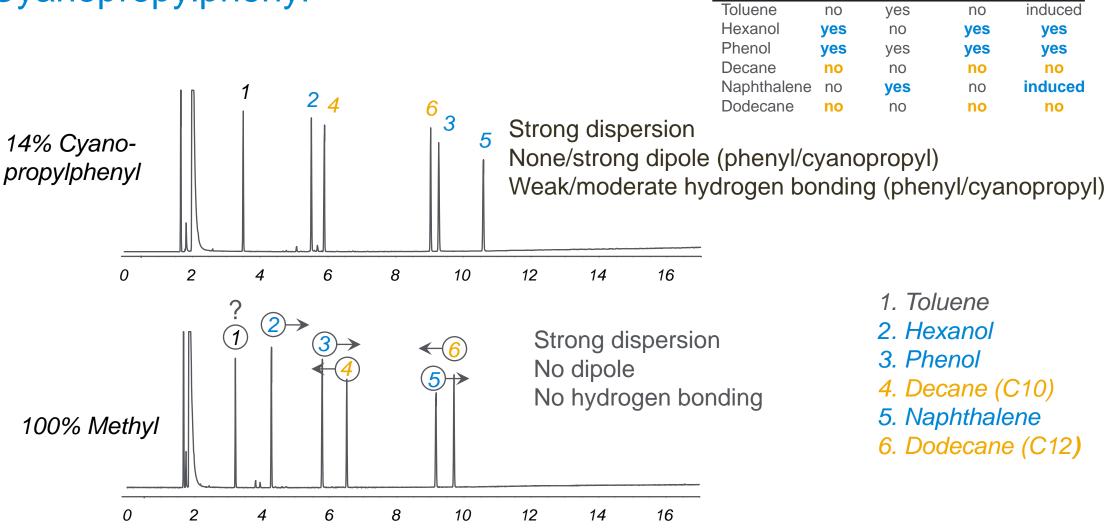
# 5% Phenyl







## 14% Cyanopropylphenyl

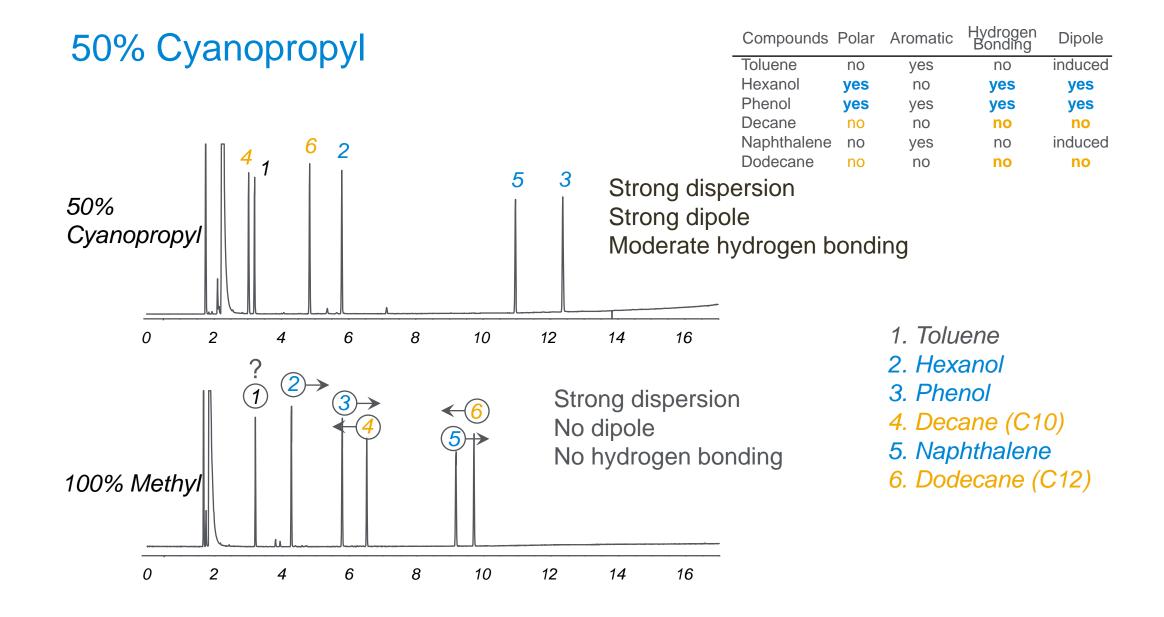




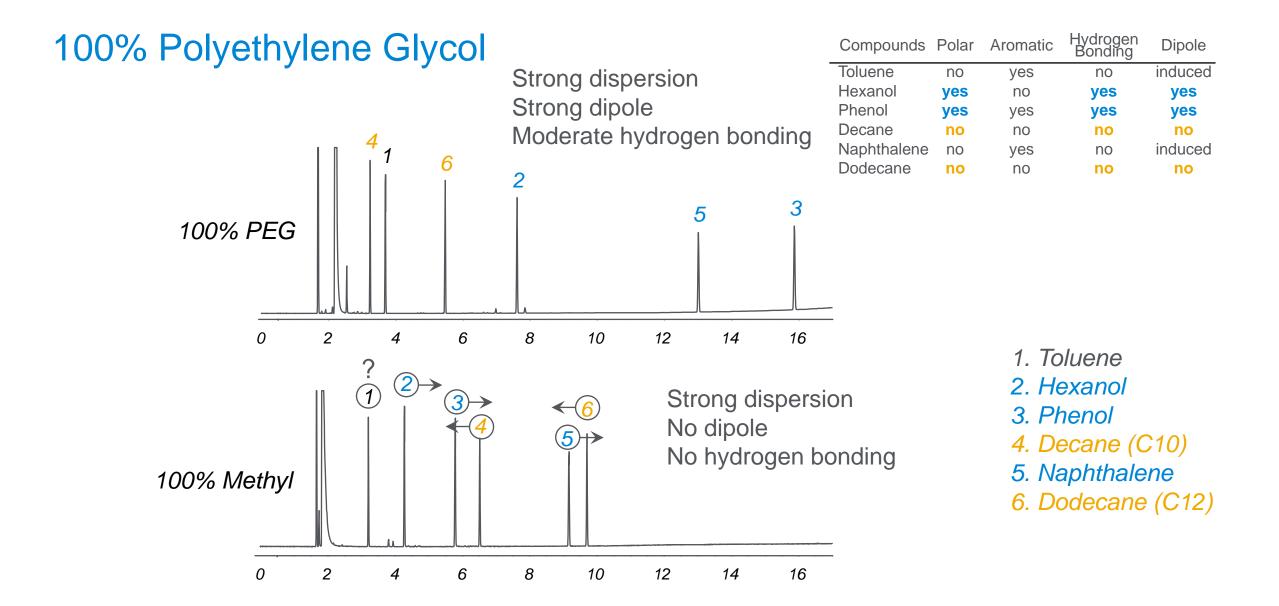
Hydrogen Bonding

Dipole

Compounds Polar Aromatic









#### Stationary Phase Selection Part 1

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



## Agilent Bond Elut Sample Cleanup Products

Solid Phase Extraction cartridges and plates





#### Synthetic Chem Elut S

# Filtration cartridges and plates





#### Captiva EMR Lipid



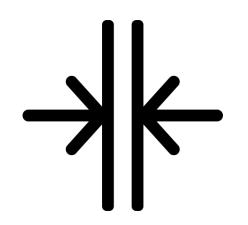
#### Stationary Phase Selection Part 2

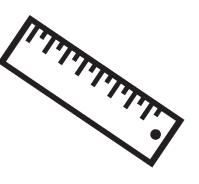
- Capacity
- Analysis time
- Bleed
- Versatility
- Selective detectors

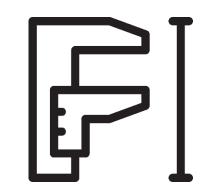




## **Column Dimensions**







Inner Diameter

Length

Film thickness



#### Column Diameter Capillary Columns

id (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

 id (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

 $\sqrt{N} \propto R_{s}$ 

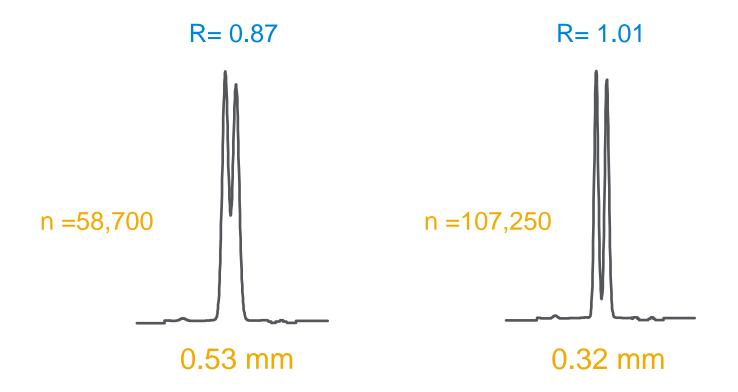
#### efficiency x 4 = resolution x 2



Decisions Decisions: How to Select the Correct GC Column for Your Application

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#### Column Diameter Resolution (180 °C isothermal)



Square root of resolution is inversely proportional to column diameter



#### **Column Diameter**

Inlet head pressures for 30 meter column (helium)

id (mm)	Pressure (psig)
0.10	225–250
0.20	25–35
0.25	15–25
0.32	10–20
0.53	2–4

Hydrogen would produce about half the amount of pressure



#### Column Diameter Capacity (0.25 µm film thickness)

id (mm)	Capacity (ng)
0.20	50–100
0.25	75–150
0.32	125–250
0.53	200–400

#### Like polarity phase/solute





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

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





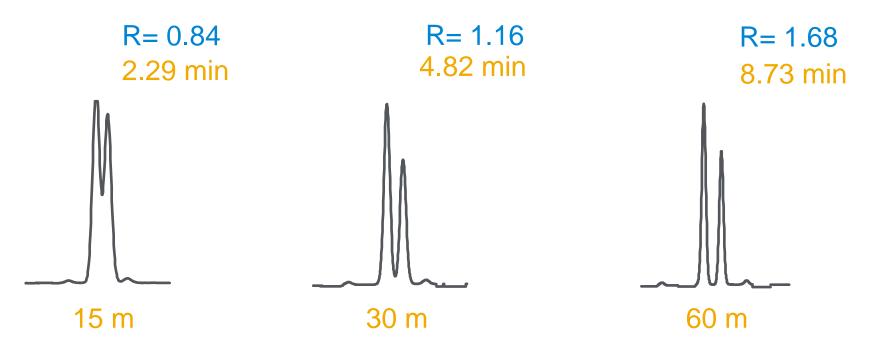
#### Column Length

#### Most common: 15–60 meters

Available: 5–200 meters



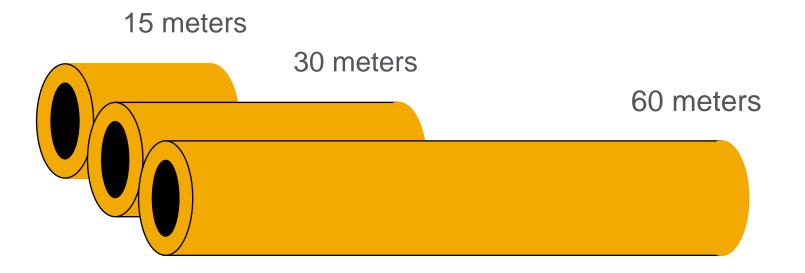
#### Column Length Resolution and retention 210 °C isothermal



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 and Cost**



#### \$ \$ \$ ¢ C C P



#### Film Thickness

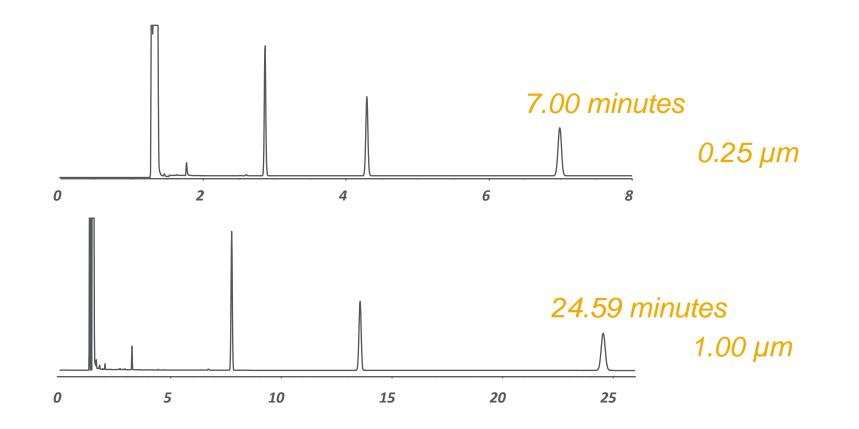
Most common: 0.1–3.0 µm

Available: 0.1–10.0 µm





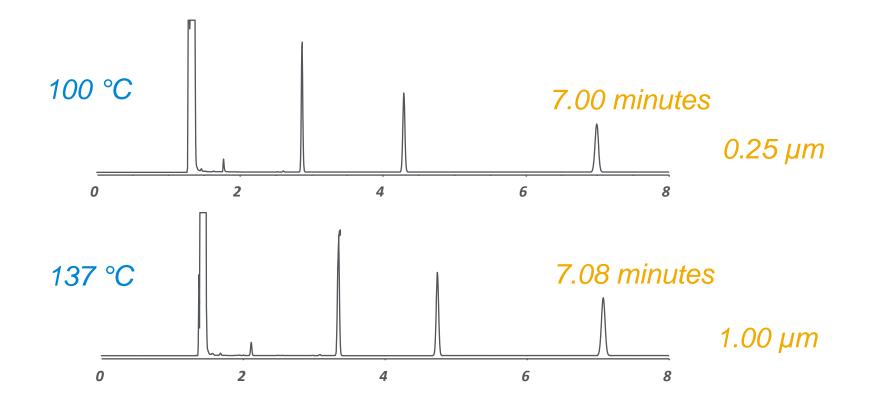
#### Film Thickness and Retention (100 °C Isothermal)



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



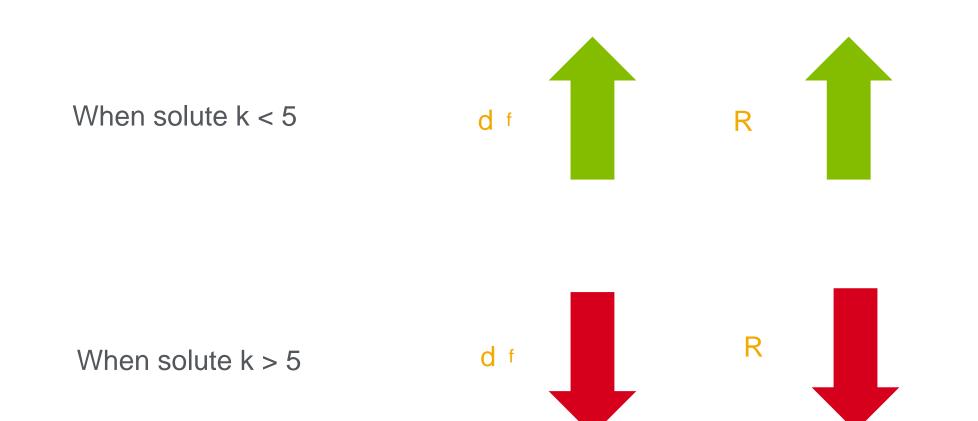
#### Film Thickness Equal retention: Isothermal



Agilent J&W DB-1, 30 m x 0.32 mm id He at 37 cm/sec C10, C11, C12



#### Film Thickness and Resolution

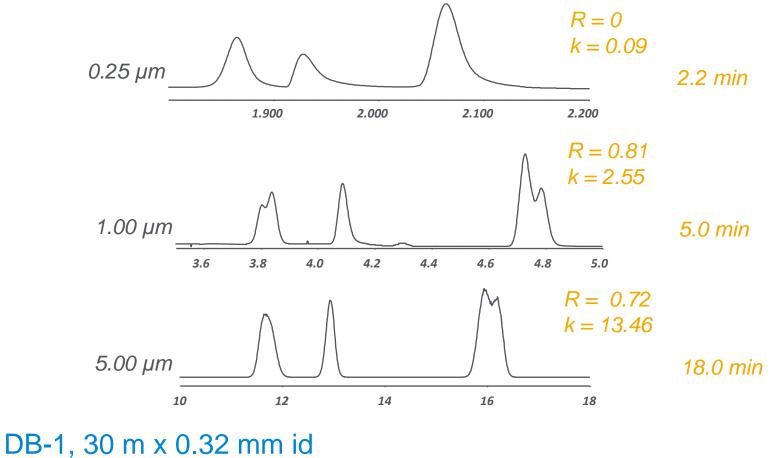




#### Film Thickness Resolution at low k 0.25 µm\_ 2.0 min **1.2** 1.4 1.6 1.8 1.00 µm 3.5 min 2 3 3.00 µm 6.5 min 2 6 4 DB-1, 30 m x 0.32 mm id 40 °C isothermal, He at 35 cm/sec Solvent mixture



#### Film Thickness Resolution at high k



40 °C isothermal, He at 35 cm/sec Solvent mixture



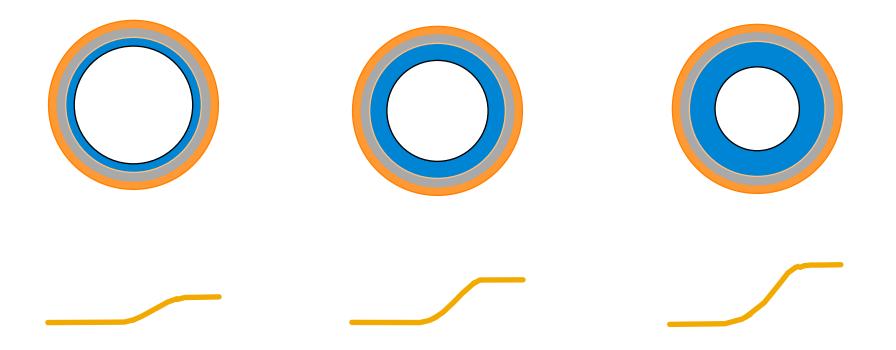
## Film Thickness (Capacity)

	Thickness (µm)	Capacity (ng)
	0.10	50-100
	0.25	125-250
	1.0	500-1000
	3.0	1500-3000
0.32 mm column id	5.0	2500-5000
Like polarity phase/s	solute	

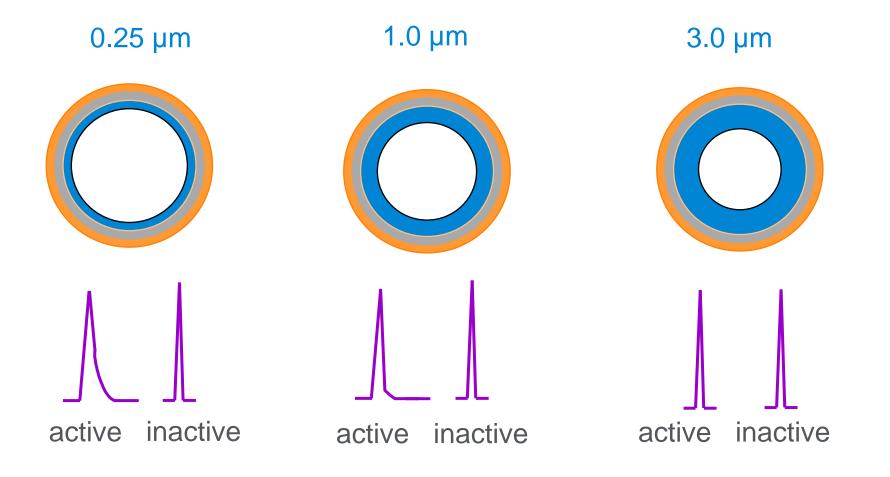


#### Film Thickness (Bleed)

More stationary phase = More degradation products



#### Film Thickness (Inertness)





#### Column Dimensions Diameter summary

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



Decisions Decisions: How to Select the Correct GC Column for Your Application

#### Column Dimensions Length summary

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



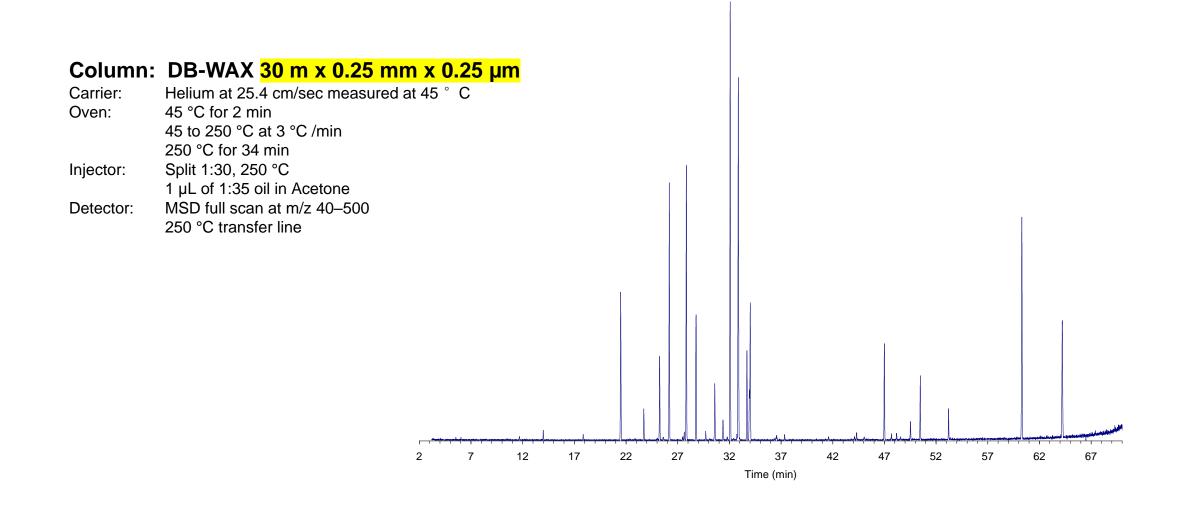
Decisions Decisions: How to Select the Correct GC Column for Your Application

#### 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



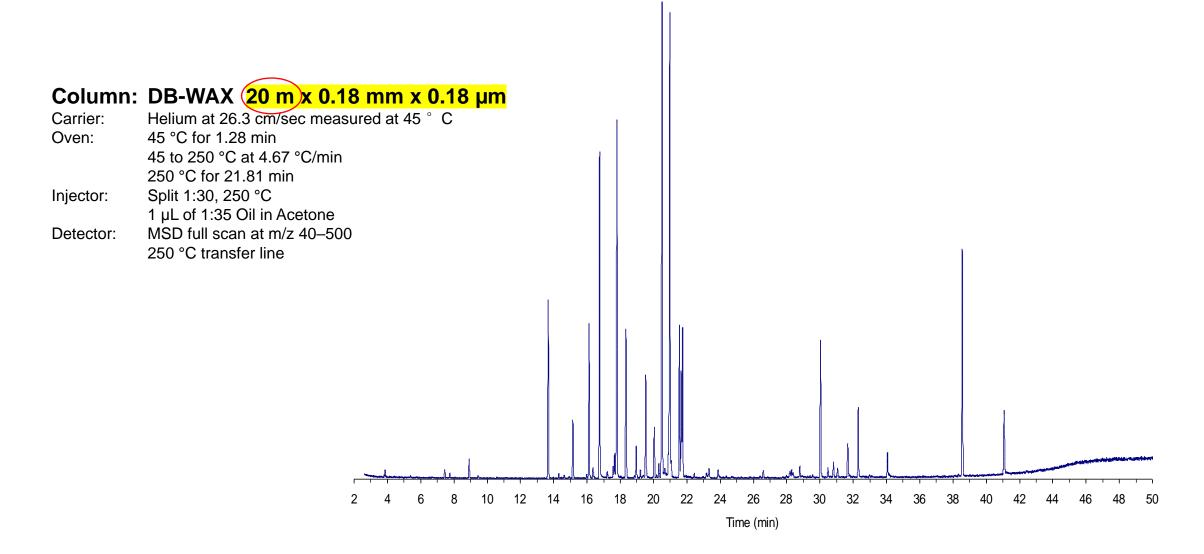
#### Example of Changing Dimensions to Achieve Faster Chromatography Before







#### Example of Changing Dimensions to Achieve Faster Chromatography After





# **Agilent University**

#### Why training? What can we help with?

Agilent University:

- Trained over 38K students FY19
- 98% customer recommended ٠
- 4.6 out of 5 customer satisfaction •
- 94% excellent & very good •

Labs who want faster and more efficient learning options to help overcome training challenges

#### Overtasked staff

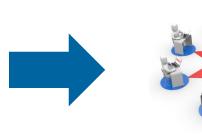
Staff turnover

Pressure to improve quality and productivity

Daily consistency with output and results

Reduce costs associated with lab operations

Flexible and convenient training options when and where you need it:





eLearning self-paced

#### **In-person Training**



Classroom



On-site or Virtual On-site

Trust Agilent for answers leveraging up-to-date knowledge and generally accepted practices for all your training needs

Virtual

Instructor Led



#### **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 and GC/MS columns and supplies Option 2 for LC and LC/MS columns and supplies Option 3 for sample preparation, filtration, and QuEChERS Option 4 for spectroscopy supplies Option 5 for chemical standards Available in the USA and Canada 8–5, all time zones



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



# Test Your Knowledge

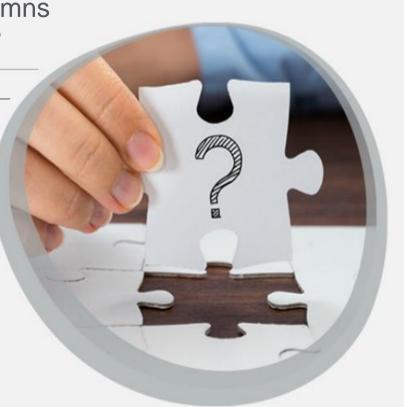
Which one of these Agilent HP-5ms columns have the highest theoretically efficiency?

A. 0.53 i.d. X 30 meters X 3.00 um

B. 0.18 i.d. X 20 meters X 0.18 um

C. 0.18 i.d. x 40 meters X 0.18 um

D. 0.25 i.d. X 15 meters X 0.25 um





# Test Your Knowledge

Which column below is the most inert?

A. Agilent DB-5ms UI 0.25 i.d. X 30 meters X 0.25 um

B. Agilent HP-5ms 0.25 X 60 meters X 0.25 um

C. Agilent DB-WAX 0.32 i.d. X 30 meters X 0.50 um

D. Agilent DB-5ms UI 0.25 X 30 meters X 0.50 um



DE44396.3167708333



# Test Your Knowledge

If I double my column length, my resolution will also double.

True

Or

False

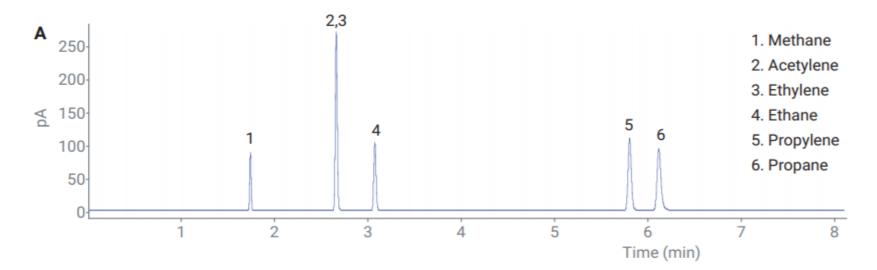




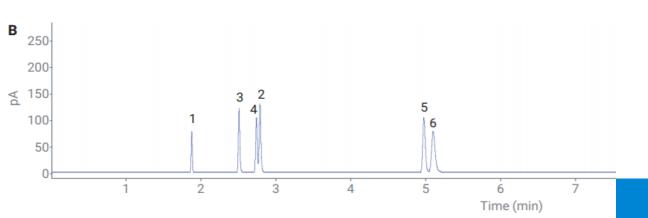


# Separation of Volatile Organic Hydrocarbons with Agilent J&W PLOT GC Columns and Selectivity Tuning (5994-3485EN)

PoraPLOT Q







PoraPLOT U

