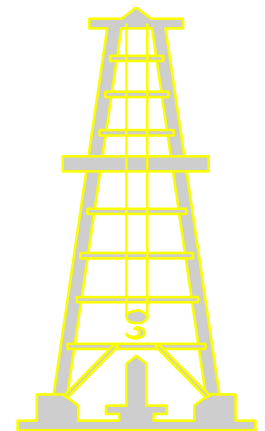
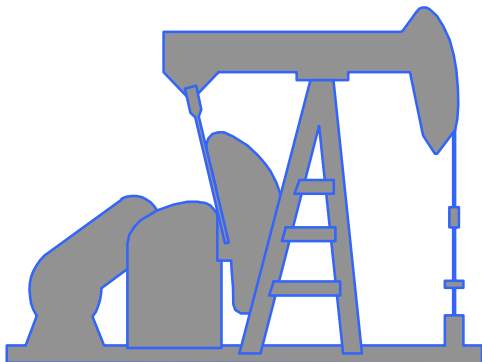


# Analysis of Refinery and Petrochemical Products by Capillary GC



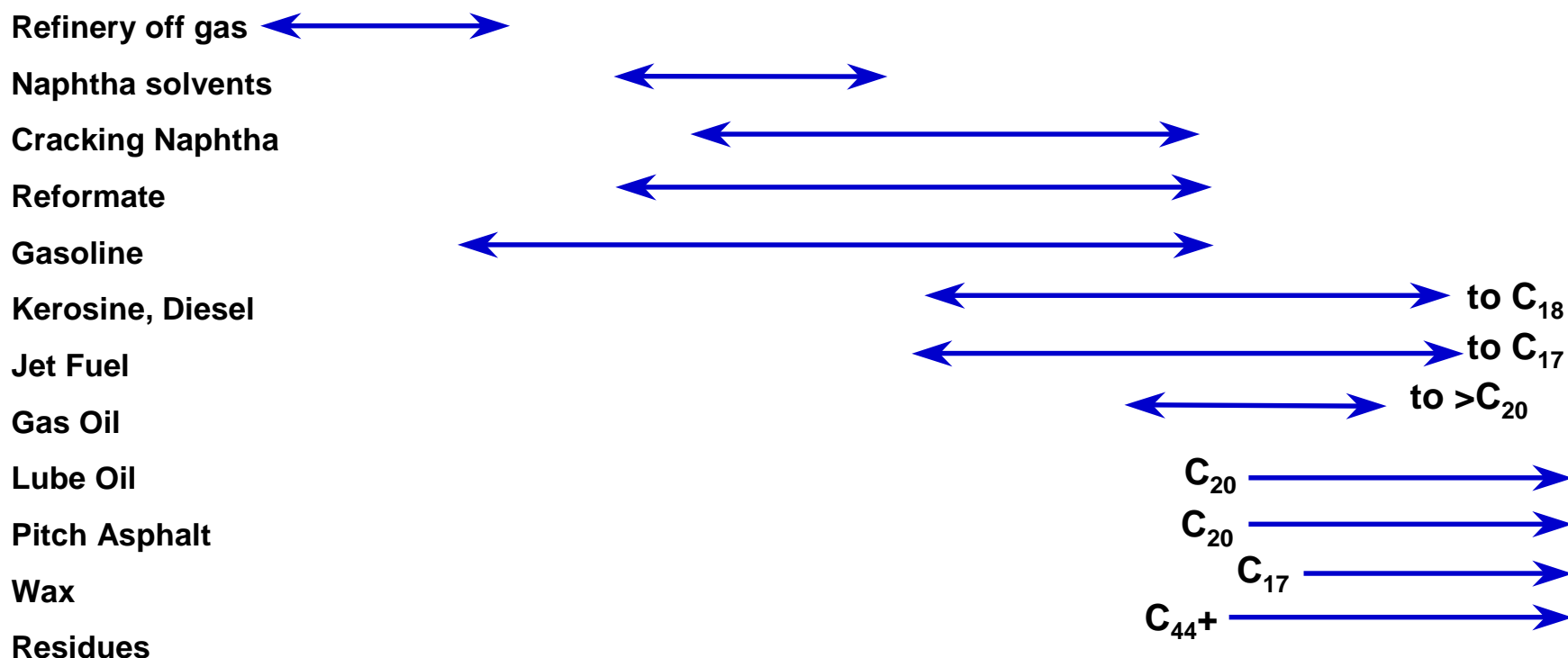
# System Optimization

- GC theory (**painful, but necessary**)
- Phase selectivity “tuning”
- High-speed GC
- Method Translation Software (**free on Agilent’s website!**)
- Retention Time Locking



## Table of Boiling Point Fractions

Carbon #	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>
Bpt of n-Paraffin @ 760 mm Hg																
Centigrade	-161	-89	-42	-0.5	+36	69	98	126	151	174	196	216	235	253	270	287
Fahrenheit	-259	-127	-44	+31	97	156	209	258	303	345	384	421	421	488	519	548



# Are These *Really* Tools for Improving Chromatography?

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

$$K_c = \frac{W_{i(s)} / V_s}{W_{i(M)} / V_M}$$

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

$$k = \frac{t'_R}{t_m}$$

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



## Chromatography is *Just Two Things*

$$K_c = \frac{\text{Conc. solute in stationary phase}}{\text{Conc. solute in mobile phase}}$$

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



# Distribution Constant ( $K_c$ )



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



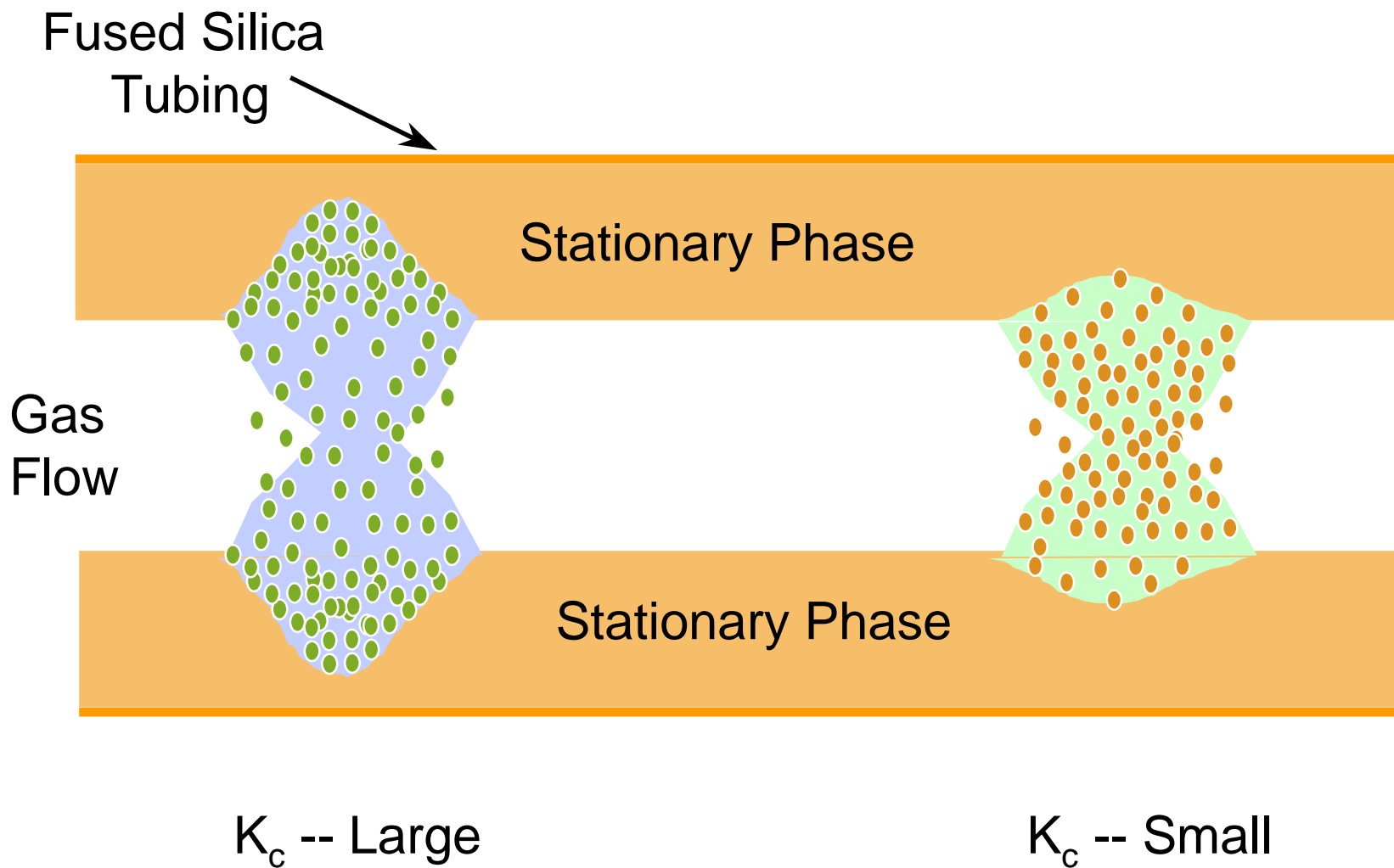
## $K_c$ Describes a Solute's Location

Solute in stationary phase -- Not moving

Solute in mobile phase -- Moving towards detector



# $K_c$ Is Dynamic



# Manipulation of Retention

$$K_c = k\beta$$

Distribution Constant

$$k = K_c / \beta$$

Retention Factor

$$\beta = K_c / k$$

Phase Ratio

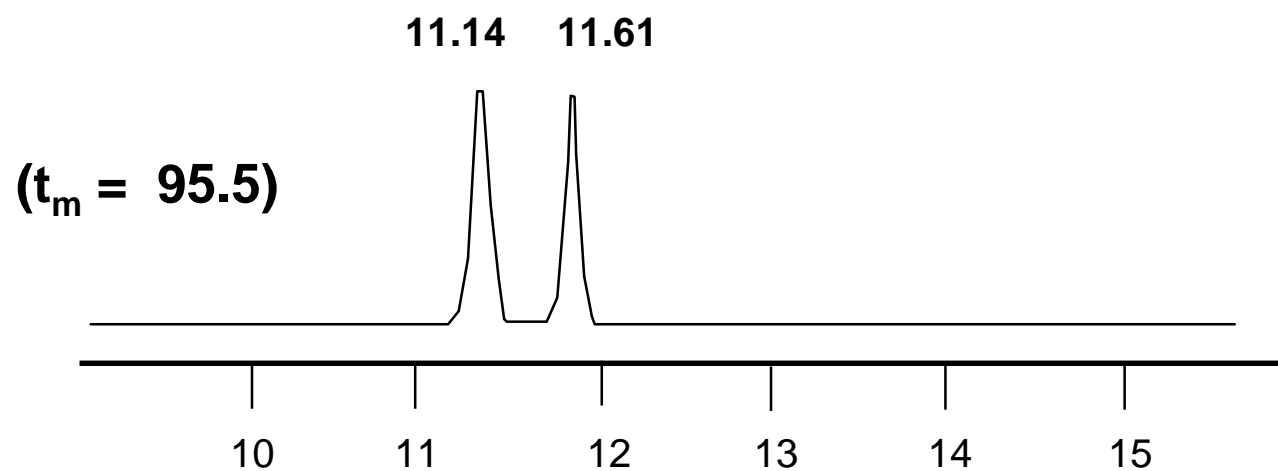
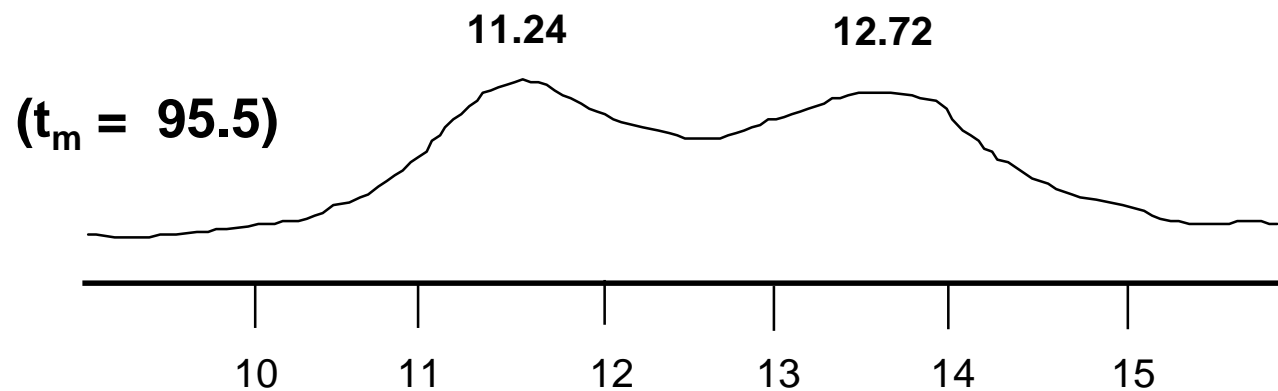


# Resolution vs Separation

- Separation: Time between the 2 peaks
- Resolution: Describes how well 2 peaks are separated with respect to their widths



# Which pair of solutes have better separation?

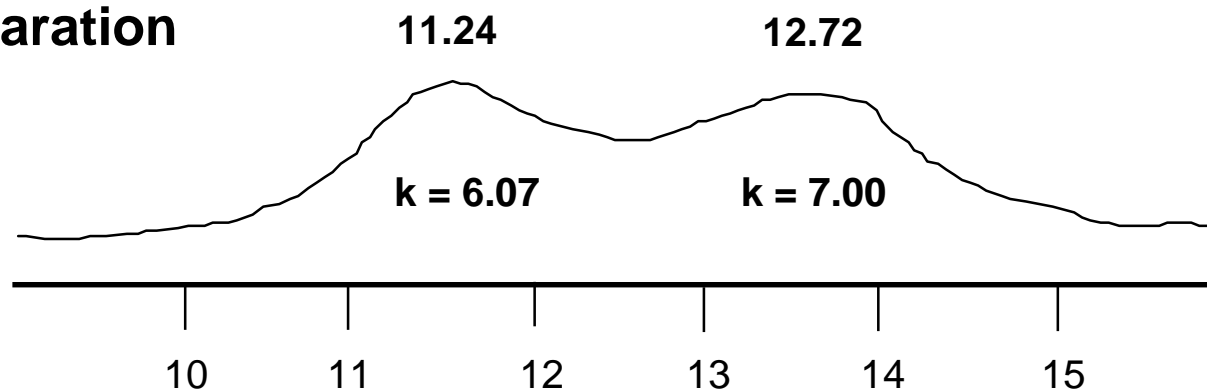


# Resolution vs Separation

**Better Separation**

$$\alpha = 1.17$$

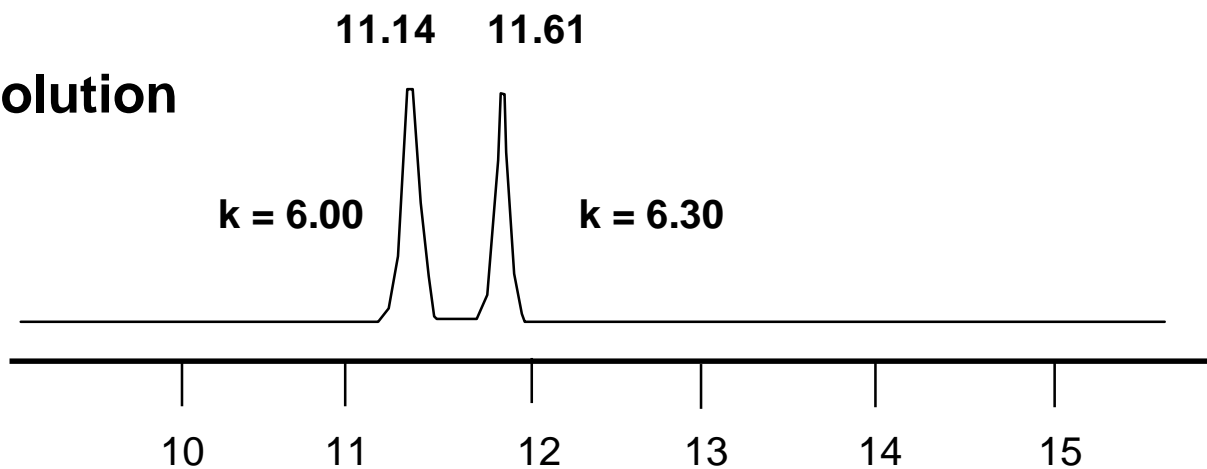
$$R_s = 0.6$$



**Better Resolution**

$$\alpha = 1.05$$

$$R_s = 2.7$$



## Resolution

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

$$N = f(L, r_c)$$

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

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



# Detailed Analysis of Gasoline

- Well over 400 components
- Solute differences are subtle
- Intended to identify the majority of HC types in a sample

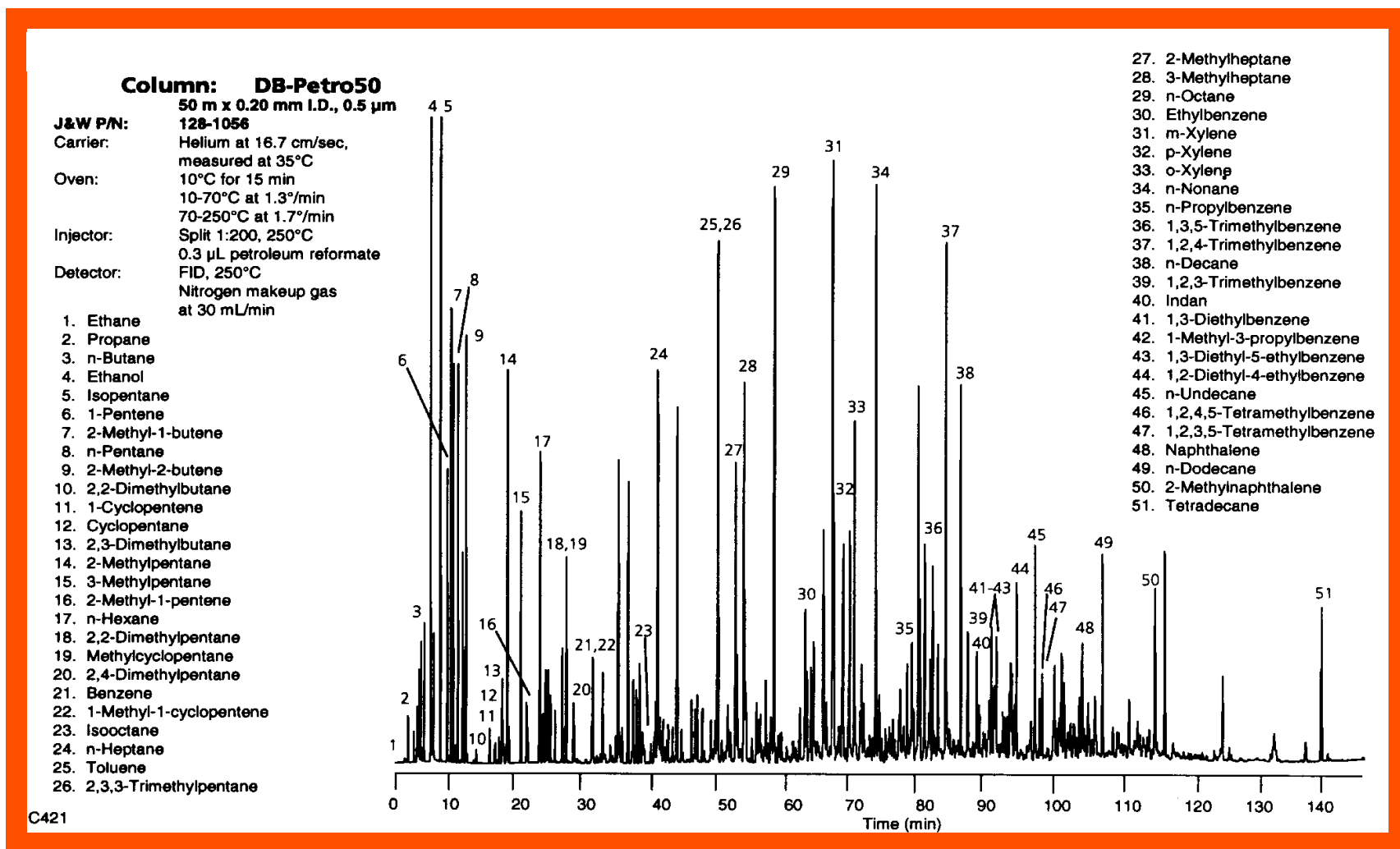


# Methods for Refinery Stream Characterization by Hydrocarbon Type Analysis

- ASTM 5134: Detailed Analysis of Petroleum Naphthas through n-Nonane by CGC
- AFNOR NF M07-086: Determination of HC Group Type in Motor Gasolines from Detailed Analysis by CGC
- CAN/ C.G.S.B.: 3.0, no. - 14.3 - 94: Detailed Analysis of Gasoline
- ASTM D6730
- PONA-BAMA: Paraffins, Olefins, Naphthenes and Aromatics - By Any Means Available



# Detailed Analysis of Gasoline by AFNOR Method #2



# "Single" Methyl Silicone Column for Hydrocarbon Type Analysis

- $N > 400,000$
- Oven programming finesse
- Can miss certain key resolutions



# Key Solute Resolutions \*

## Desired in Reformulated Fuel

- MTBE - 2,3-Dimethylbutane
- Benzene - 1-Methylcyclopentane
- Toluene - 2,3,3-Trimethylpentane
- m,p-Xylene - 2,3-Dimethylheptane

\* Not readily achieved on methyl siloxane columns



**Agilent Technologies**

# Detailed Hydrocarbon Analysis (DHA)-ASTM Method D6730-01, tuned column

- Applicable to liquid HC mixtures
- Includes analysis of reformulated gasolines
- Intent is to identify the majority of HC types in a sample



# DHA Method General Guidelines

- GC/FID with split injection
- Oven programming from 5 to 200°C (0.1°/min)
- Capillary column: 100 m x 0.25 mm I.D., 0.5 µm methyl siloxane meeting minimum performance requirements
- "Tuning" the methylsiloxane column to achieve key separations



# “Tuning” the Methylsiloxane Column To Achieve Key DHA Separations

- Step 1: Add a length of (5% phenyl)-methylsiloxane pre-column for aromatic selectivity
- Step 2: Reduce length of pre-column to achieve all key separations
- Step 3: Adjust oven temperature program if needed



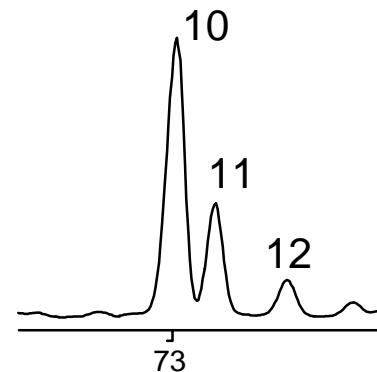
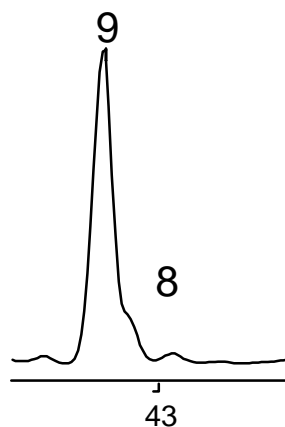
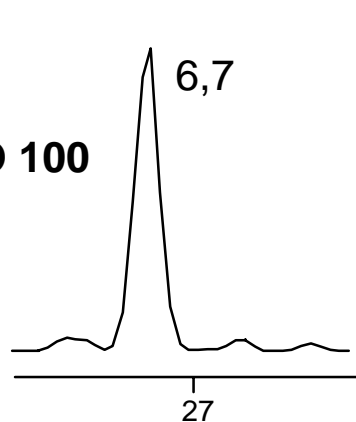
## Compound List - critical resolutions

- |                           |                              |
|---------------------------|------------------------------|
| 6. 1-Methylcyclopentane   | 12. 2,3-Dimethylheptane      |
| 7. Benzene                | 13. Unidentified isoparaffin |
| 8. 2,2,3-Trimethylpentane | 14. 1,2-Methylethylbenzene   |
| 9. Toluene                | 15. 2-Methylnaphthalene      |
| 10. m-Xylene              | 16. 1-Methylnaphthalene      |
| 11. p-Xylene              | 17. Tridecane                |

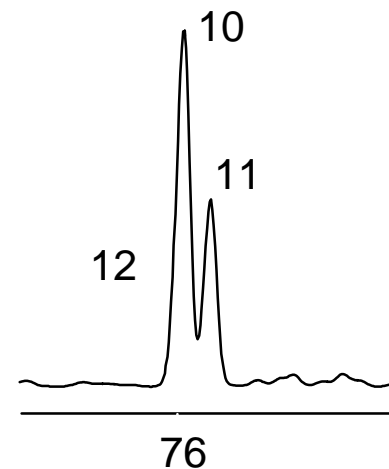
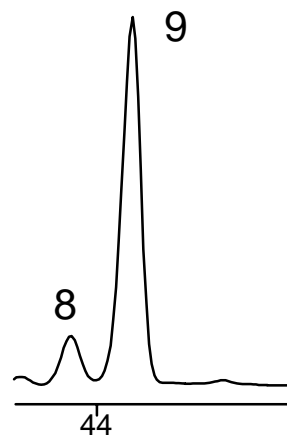
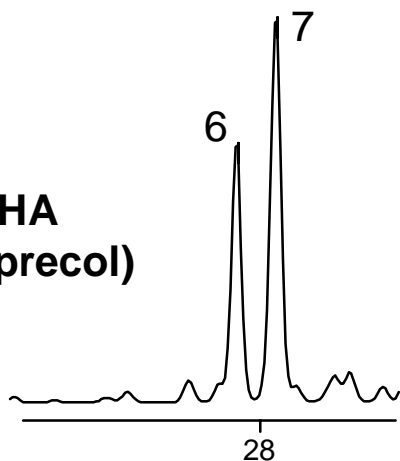


# STEP 1 - Adding 5m DB-5 Pre-column

DB-PETRO 100



HP-DHA  
(5 m precol)

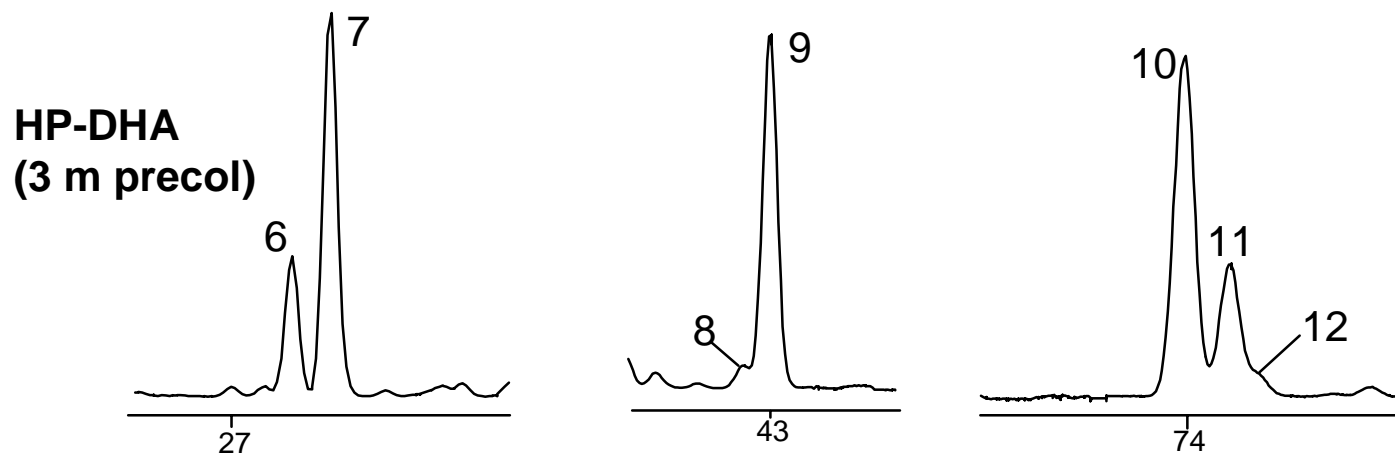
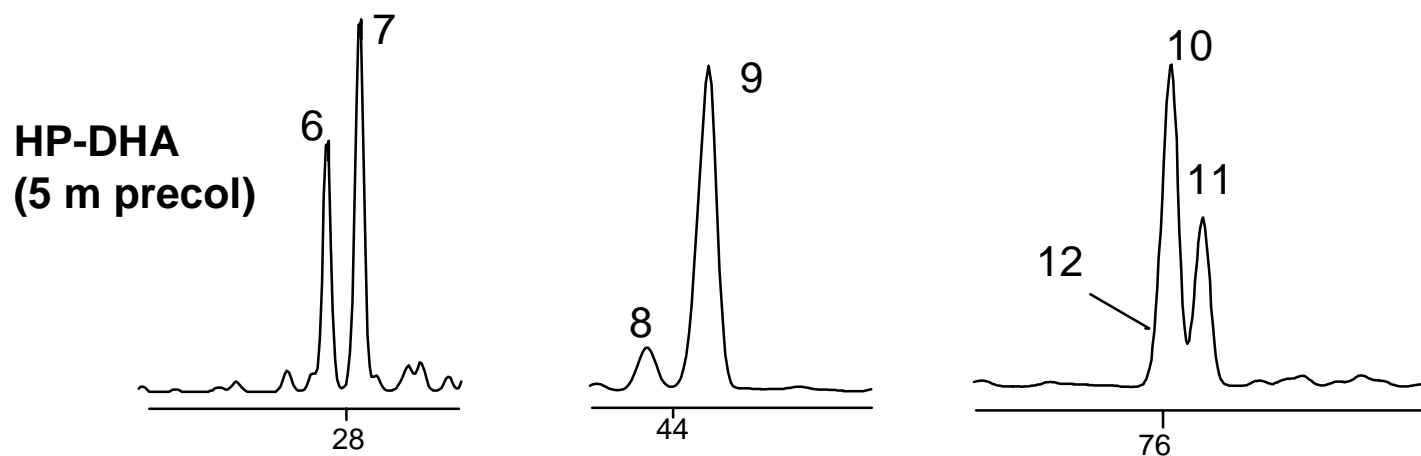


Oven Program: 5°C// 10 min// 5°/min// 50°C// 50 min// 1.5°/min // 200°C



Agilent Technologies

## STEP 2 - Tuning HP-DHA Selectivity

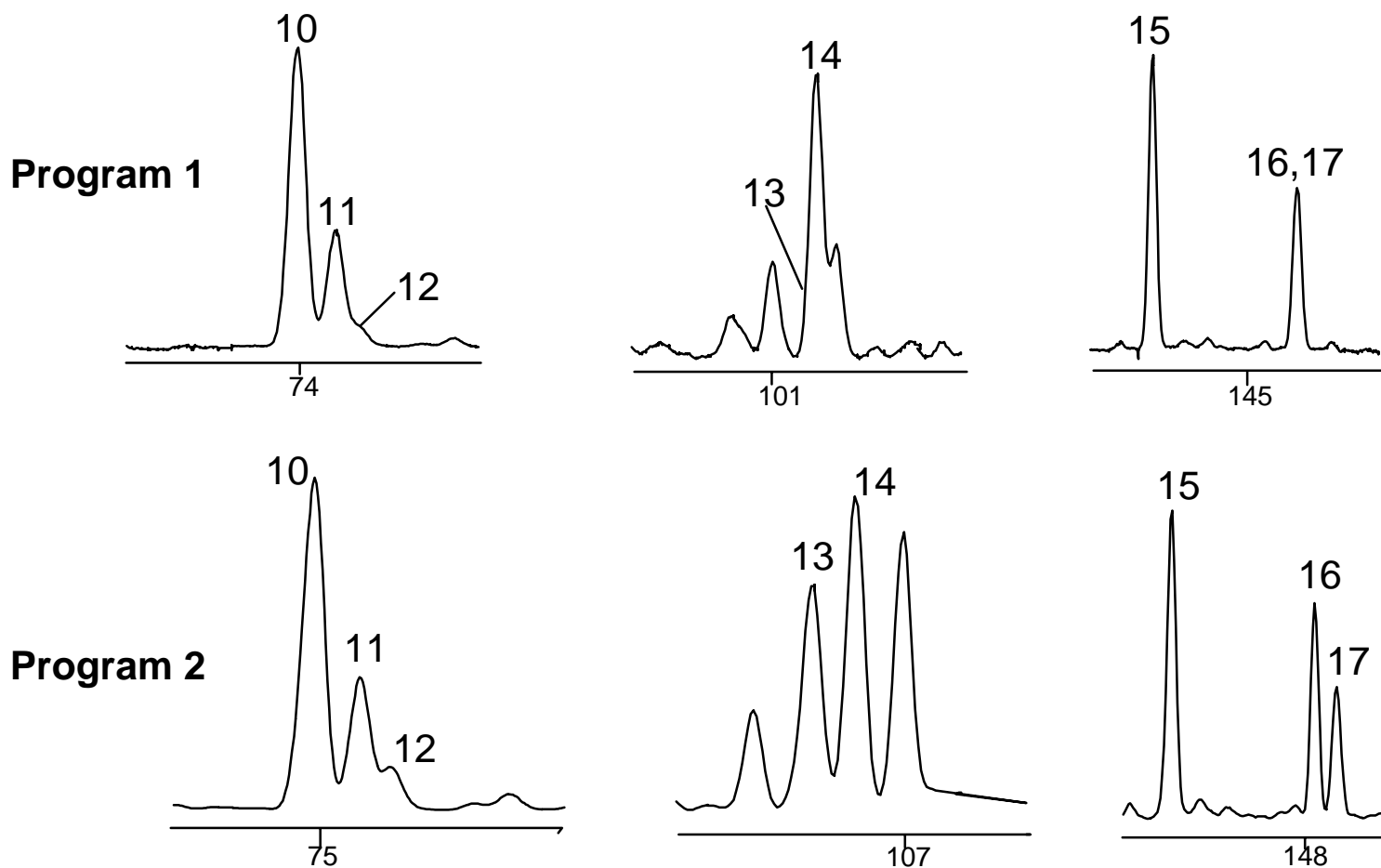


Oven Program: 5°C// 10 min// 5°/min// 50°C// 50 min// 1.5°/min // 200°C



Agilent Technologies

# STEP 3 - Tuning Oven Temperature for "3-meter - DHA"

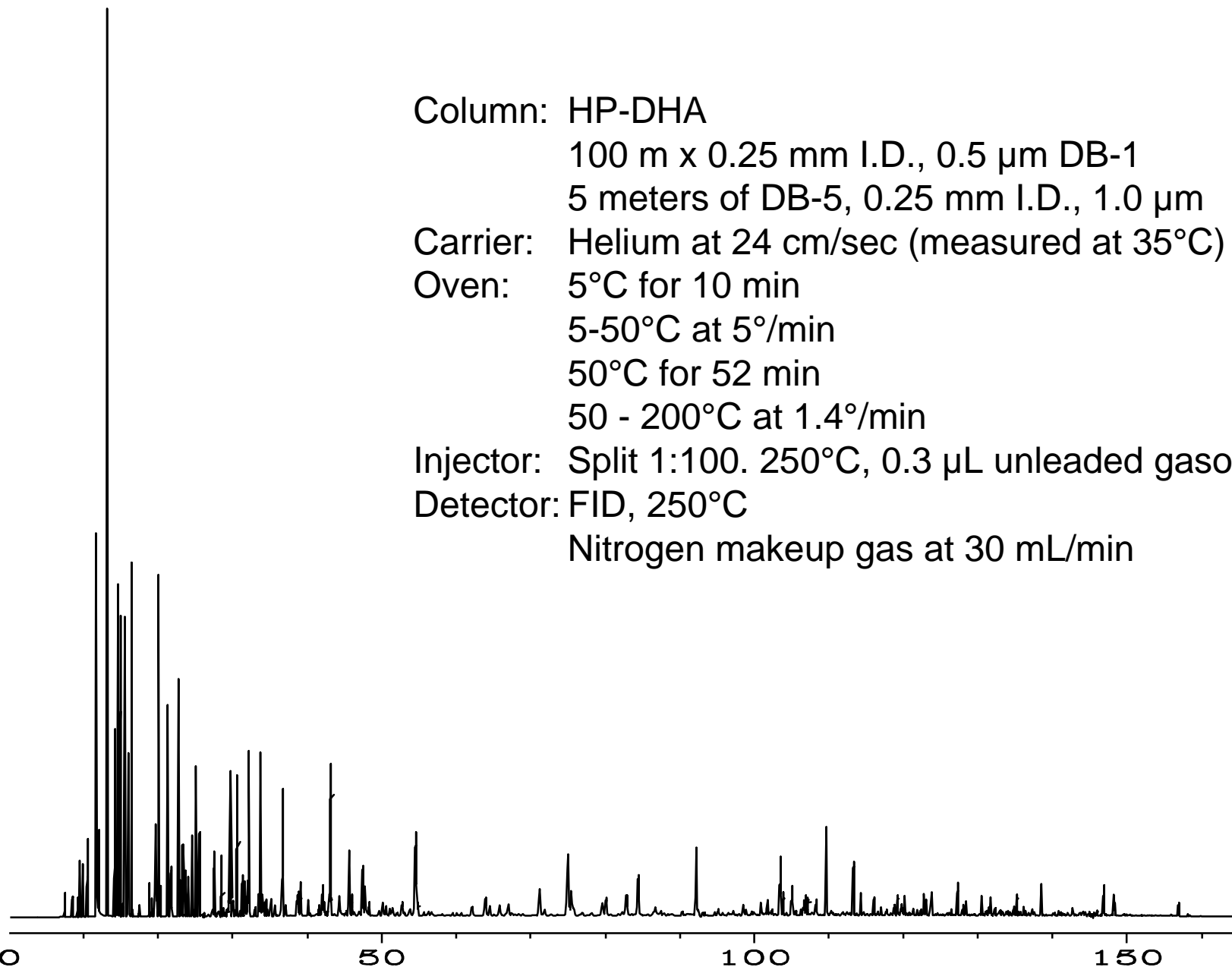


Oven Program 1: 5°C// 10 min// 5°/min// 50°C// 50 min// 1.5°/min// 200°C

Oven Program 2: 5°C// 10 min// 5°/min// 50°C// 59 min// 1.7°/min// 200°C



Agilent Technologies



Column: HP-DHA

100 m x 0.25 mm I.D., 0.5  $\mu$ m DB-1

5 meters of DB-5, 0.25 mm I.D., 1.0  $\mu$ m

Carrier: Helium at 24 cm/sec (measured at 35°C)

Oven: 5°C for 10 min

5-50°C at 5°/min

50°C for 52 min

50 - 200°C at 1.4°/min

Injector: Split 1:100. 250°C, 0.3  $\mu$ L unleaded gasoline

Detector: FID, 250°C

Nitrogen makeup gas at 30 mL/min



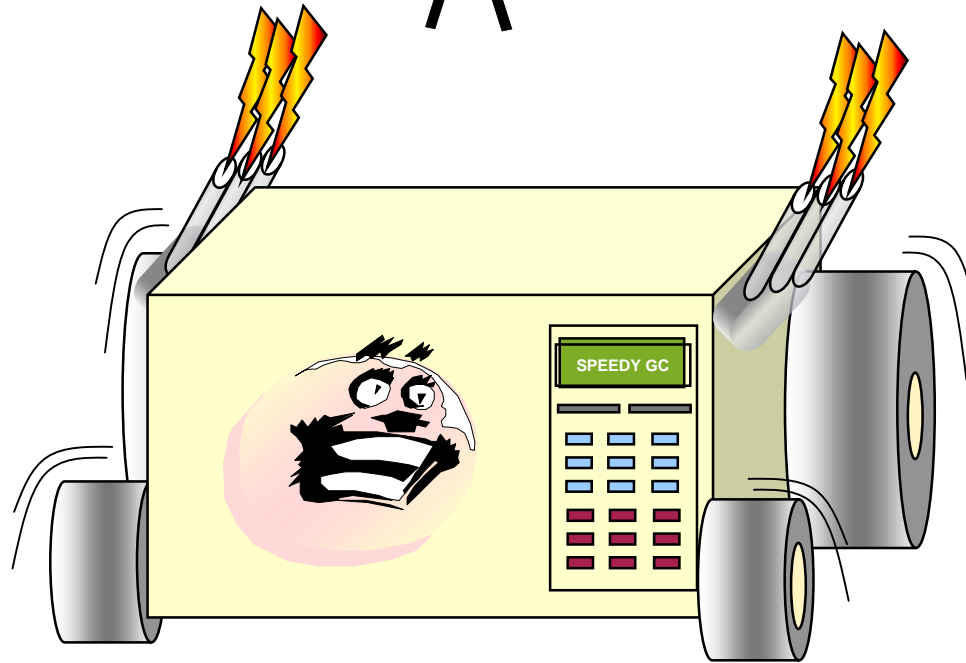
**Agilent Technologies**

# Key Considerations for HC Type Analysis

- What is your sample stream?
- What are your final product specifications?
- Capillary columns with a high N are essential but may not be enough.



# Speeding Things Up



**Agilent Technologies**

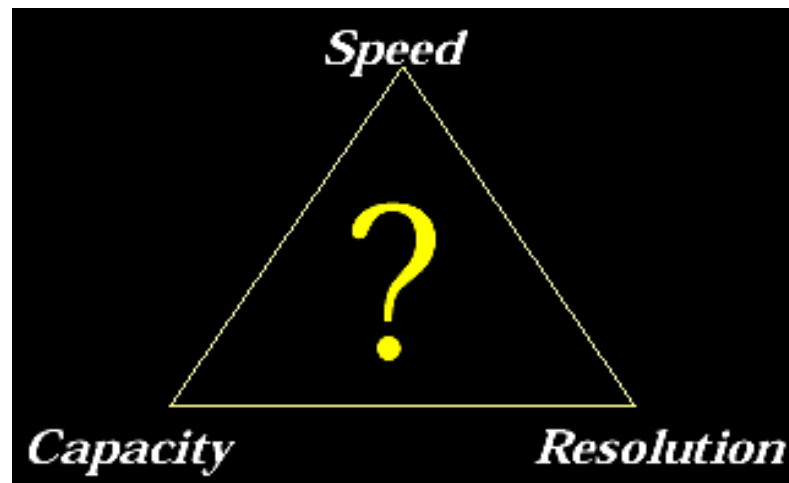
## Questions to Ask

- What information do you need from your analysis?
- Do you have more baseline than needed between your peaks?
- Do you need to resolve all of the components?

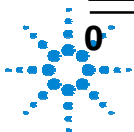
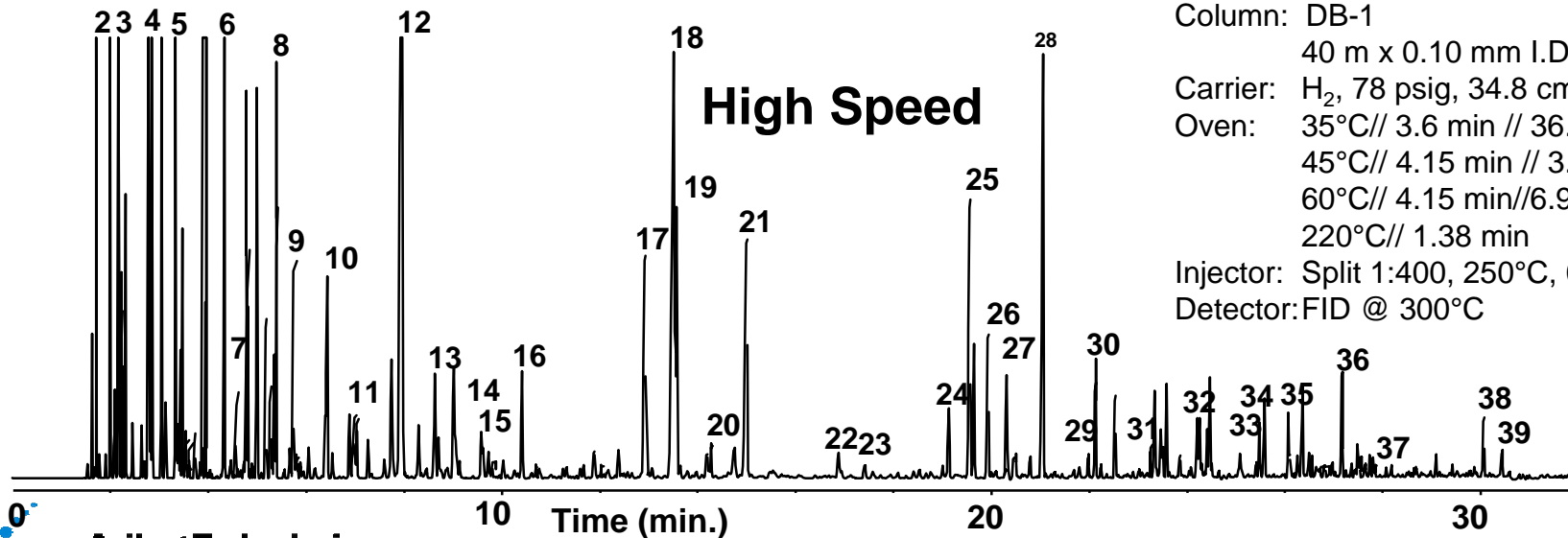
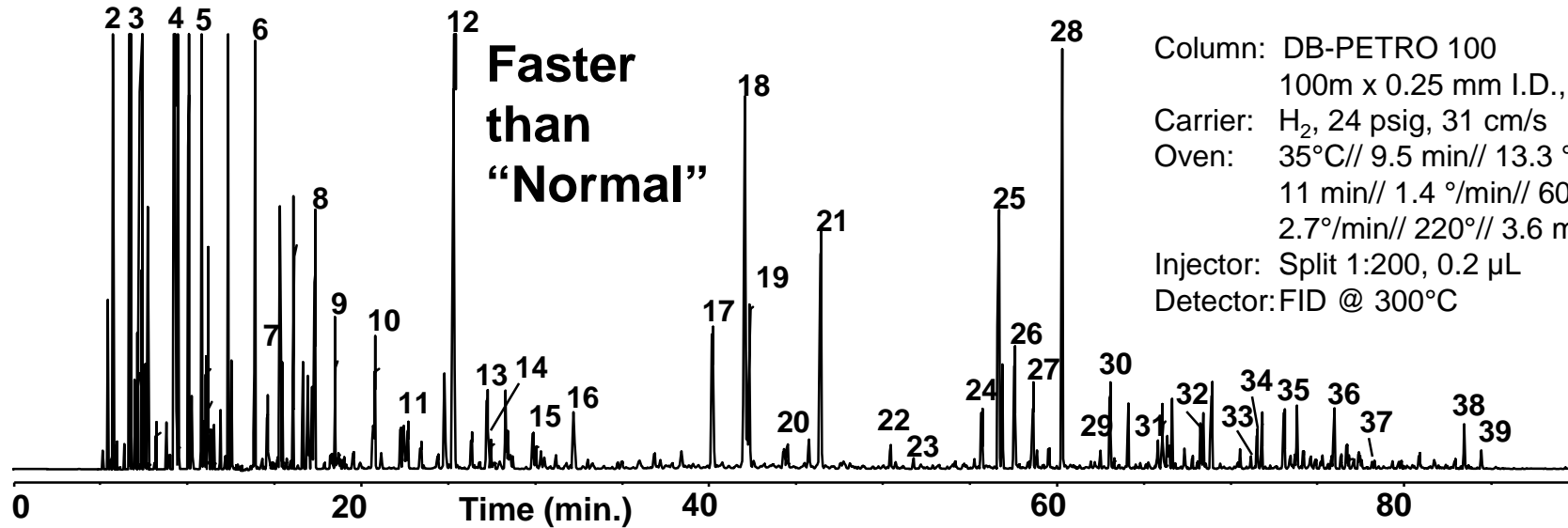


# Variables for Shortening Run Times

- Stationary Phase
- Temperature Programming
- Carrier Gas: type and linear velocity
- Shorten Column Length
- Decrease Film Thickness
- Decrease Internal Diameter

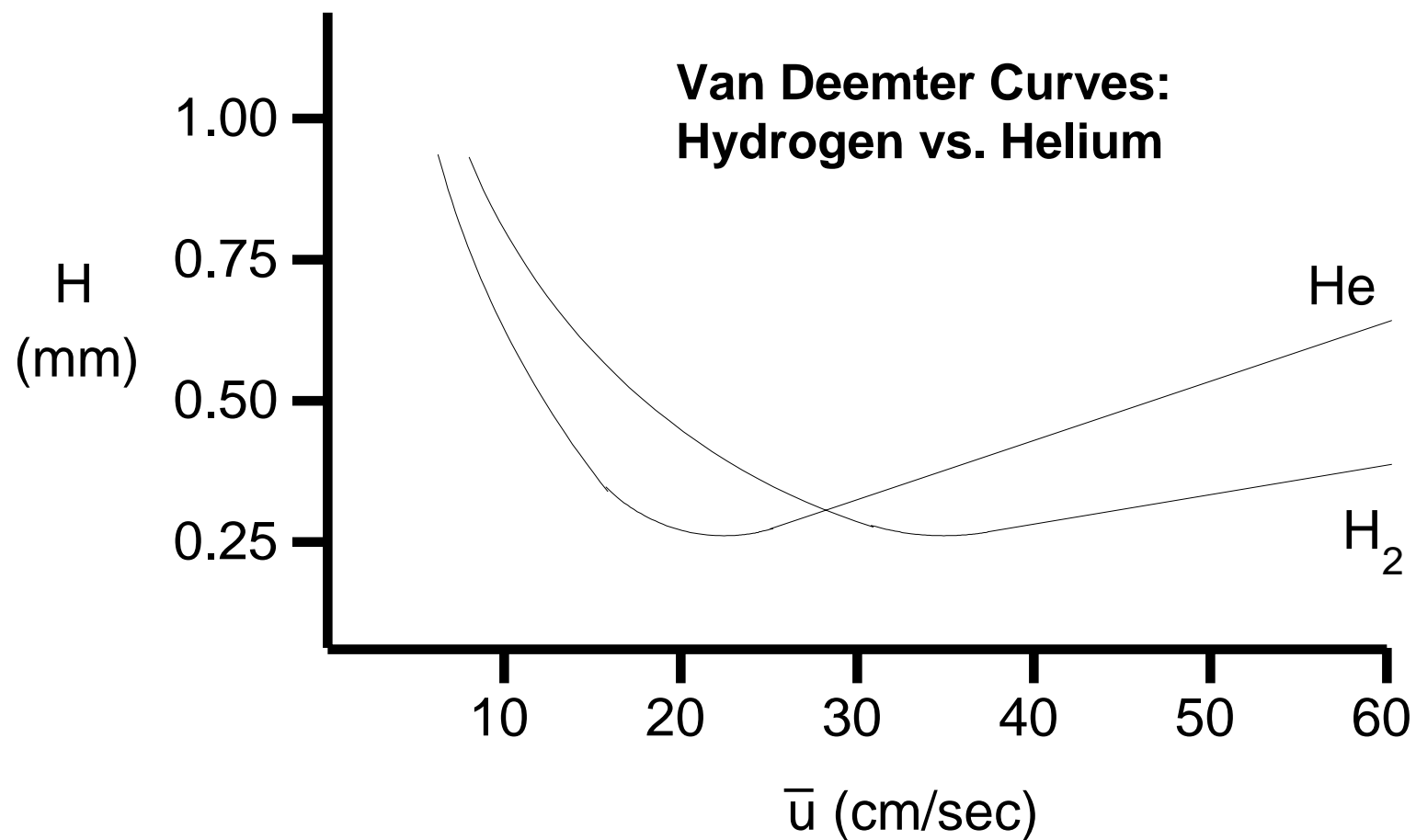


# Regular Unleaded California Phase I



Agilent Technologies

# Carrier Gas Type

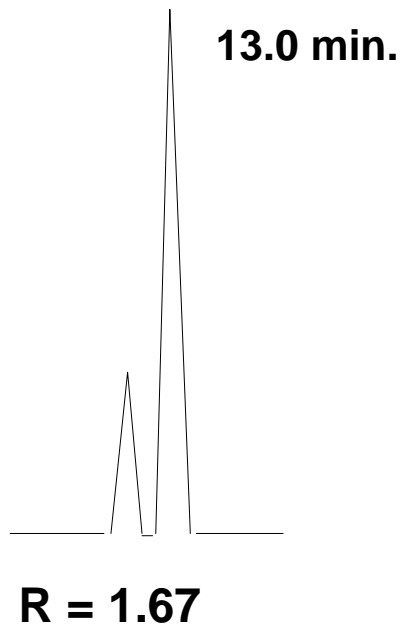


# Hydrogen vs. Helium

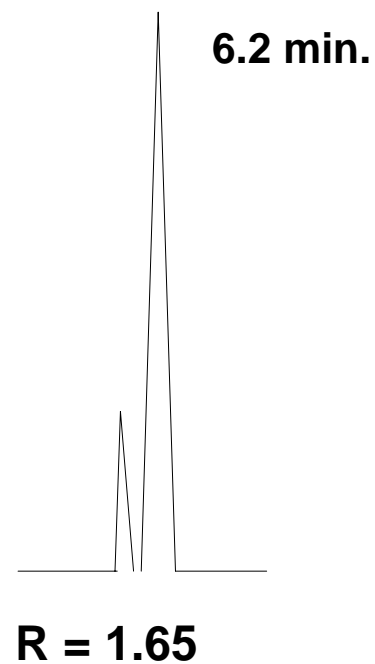
SE-52  
15m x 0.25mm  
150°C isothermal

Compounds:  
C17  
Pristane

Helium  
23.2 cm/sec



Hydrogen  
48 cm/sec



Agilent Technologies

## Factors Affecting Resolution

$$R_s = [(N)^{1/2}/4] [k/(k+1)] [(\alpha-1)/\alpha]$$

Efficiency: N = theoretical plates

Retention: k = retention factor

Selectivity:  $\alpha$  = separation factor



# Distribution Constant

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

**Change in  $K_c$  affects retention**

**Co-elution if solute  $K_c$ 's are equal**

**$K_c$  is determined by:**

**solute**

**stationary phase**

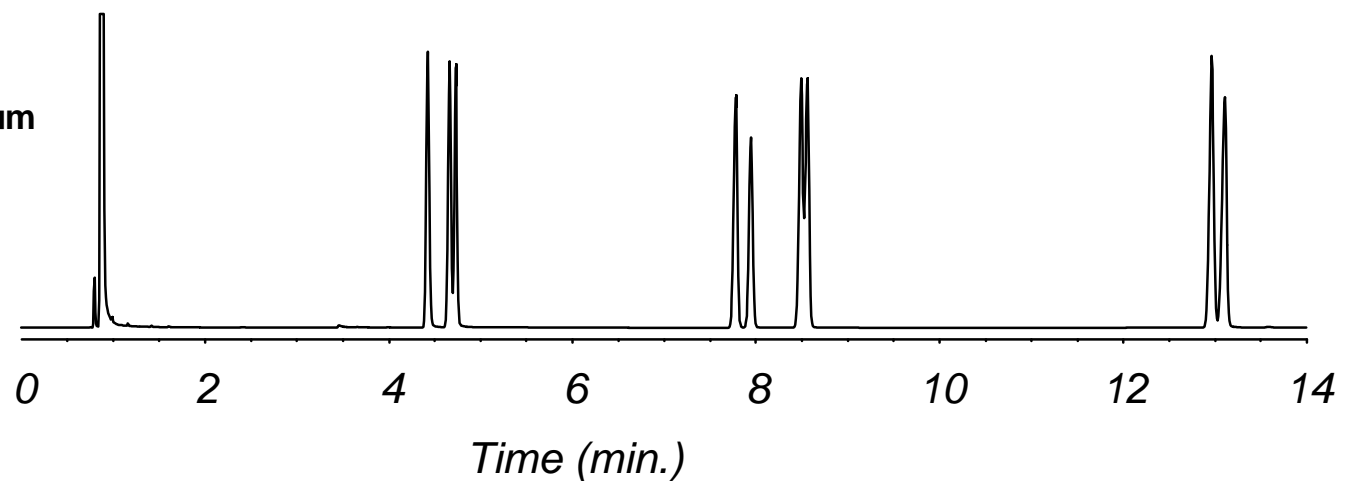
**temperature**

Stationary phase and temperature changes do not affect the  $K_c$  of all solutes equally.

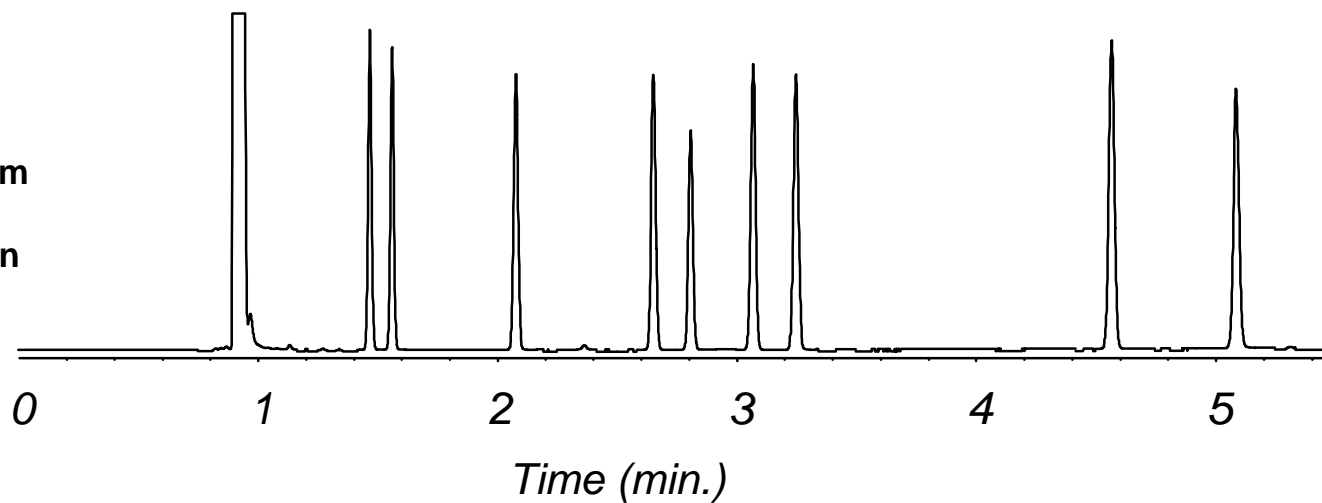


# Start with the Right Phase

DB-1  
15m x 0.32mm, 0.25 $\mu$ m  
Oven:  
40°C for 2 min  
40-120°C at 5°C/min



DB-Wax  
15m, 0.32mm, 0.25 $\mu$ m  
Oven:  
80-190°C at 20°C/min



**Agilent Technologies**

## Change retention by changing temperature: $K_C$ and Temperature

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

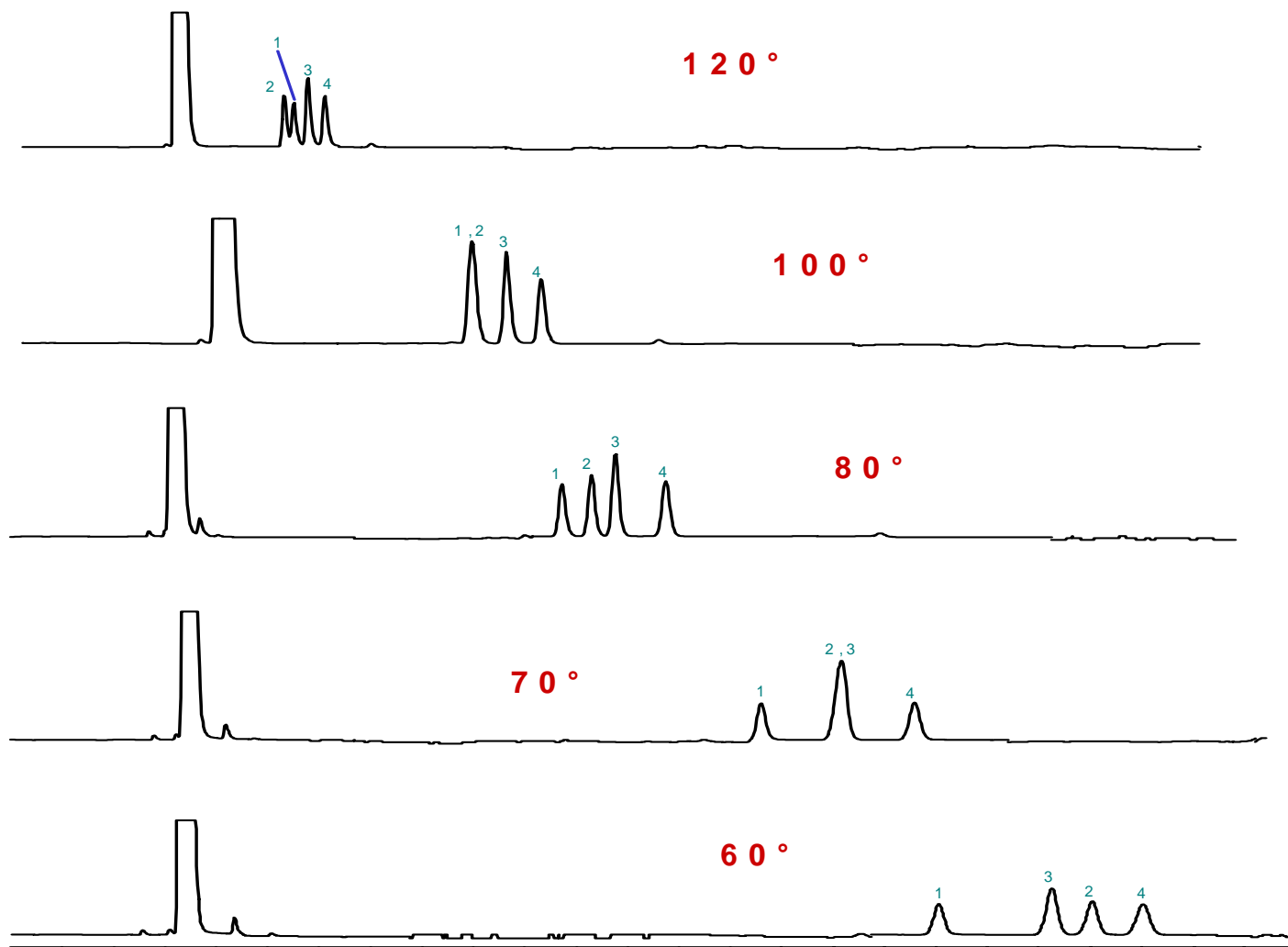
**$K_C$  decreases with an increase in temperature**  
**Each solute's  $K_C$  may change at it's own rate**



# DB-WAX

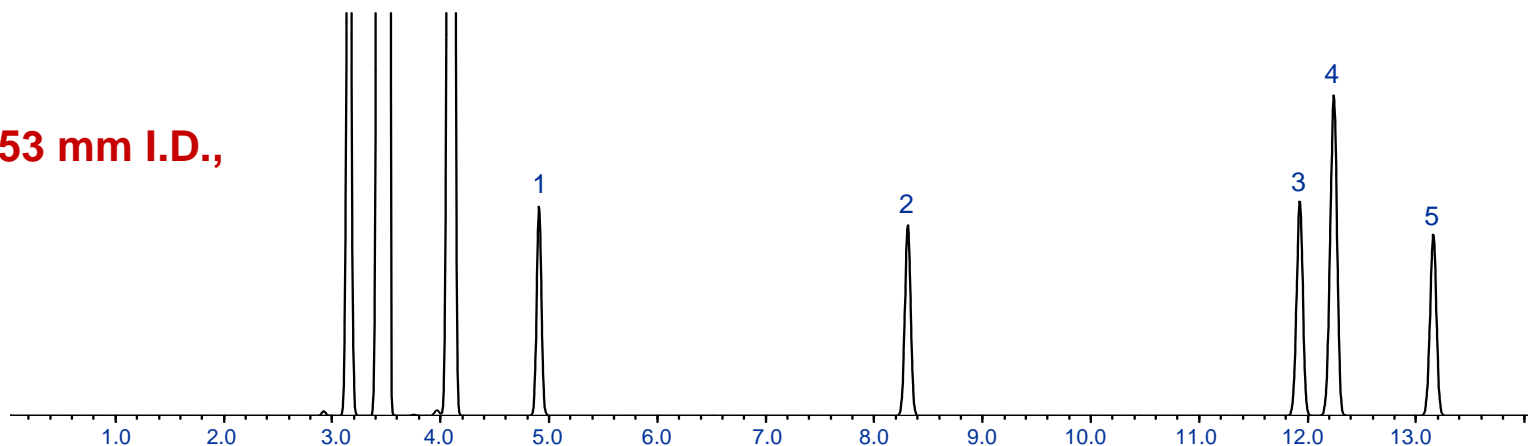
## Temperature Dependence

1.  $\alpha$ -Terpinene
2. Dodecane
3. Limonene
4. 1,8-Cineole

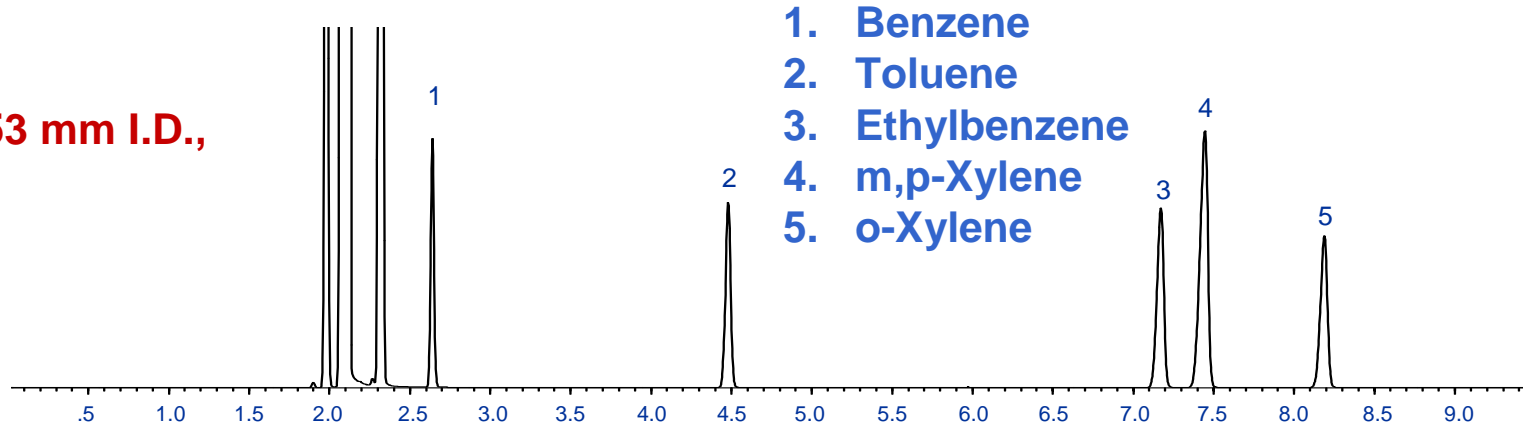


# Decreasing Film Thickness

**DB-5**  
**30 m, 0.53 mm I.D.,**



**DB-5**  
**30 m, 0.53 mm I.D.,**



1. Benzene
2. Toluene
3. Ethylbenzene
4. m,p-Xylene
5. o-Xylene

**BTEX**

**Carrier: Helium, 36 cm/sec at 40°C**

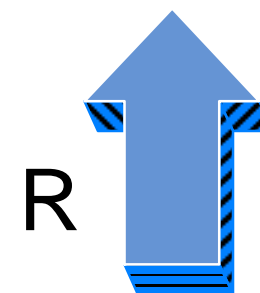
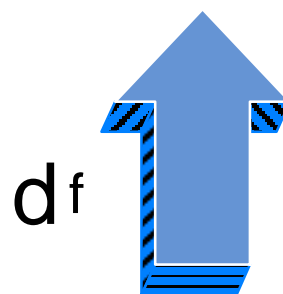
**Oven: 40°C for 3 min, 5°/min to 100°C**



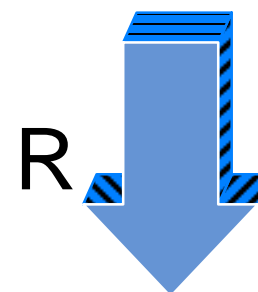
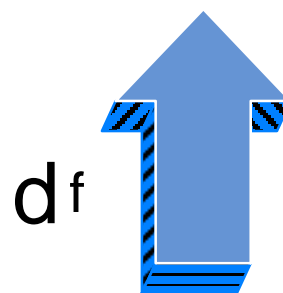
**Agilent Technologies**

# Effect of Film Thickness on Resolution

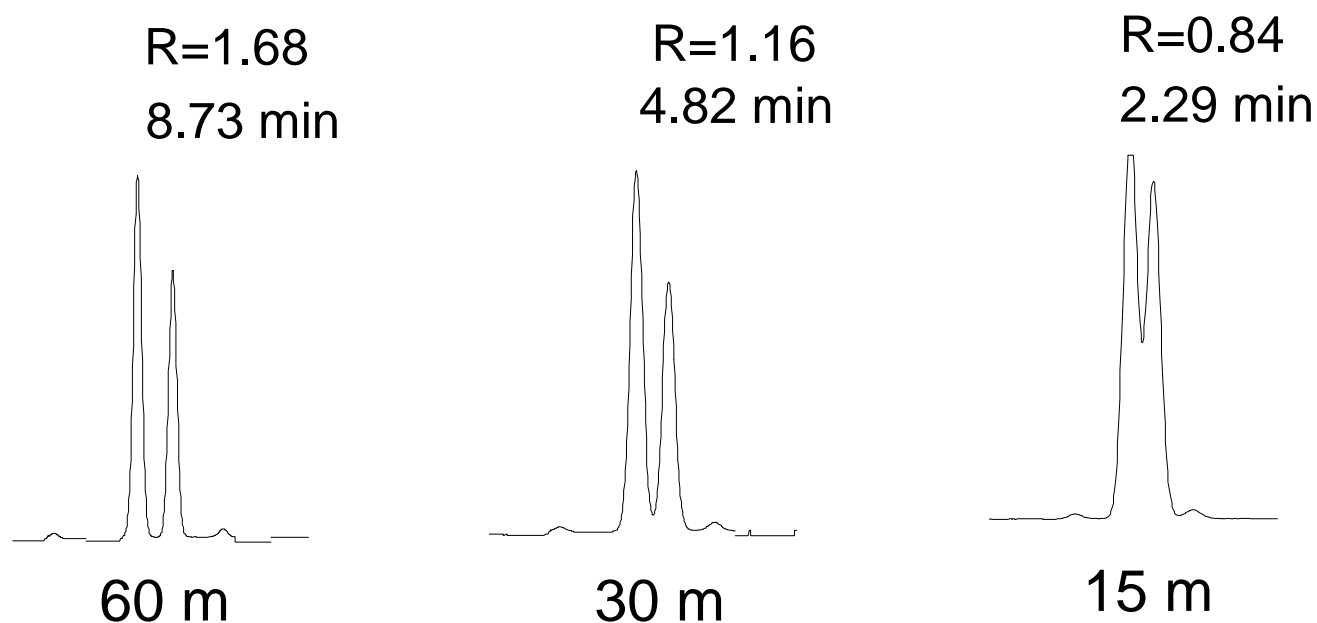
When solute  $k < 5$



When solute  $k > 5$



# Column Length Resolution and Retention 210°C isothermal



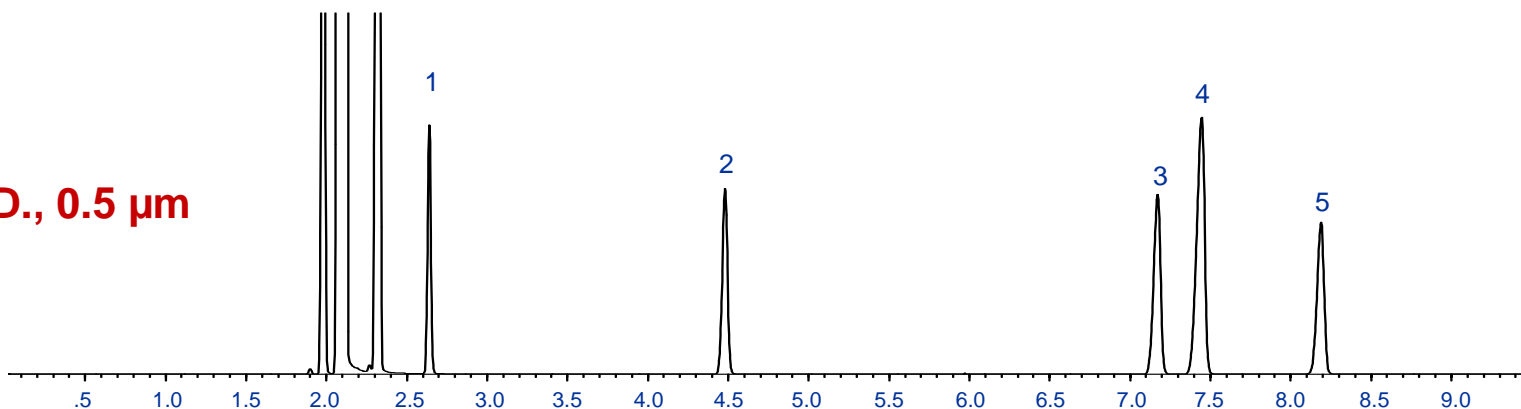
Resolution is proportional to square root of length  
Isothermal: Retention is proportional to length  
Temperature program: 1/3-1/2 of isothermal values



# Decreasing Column Length

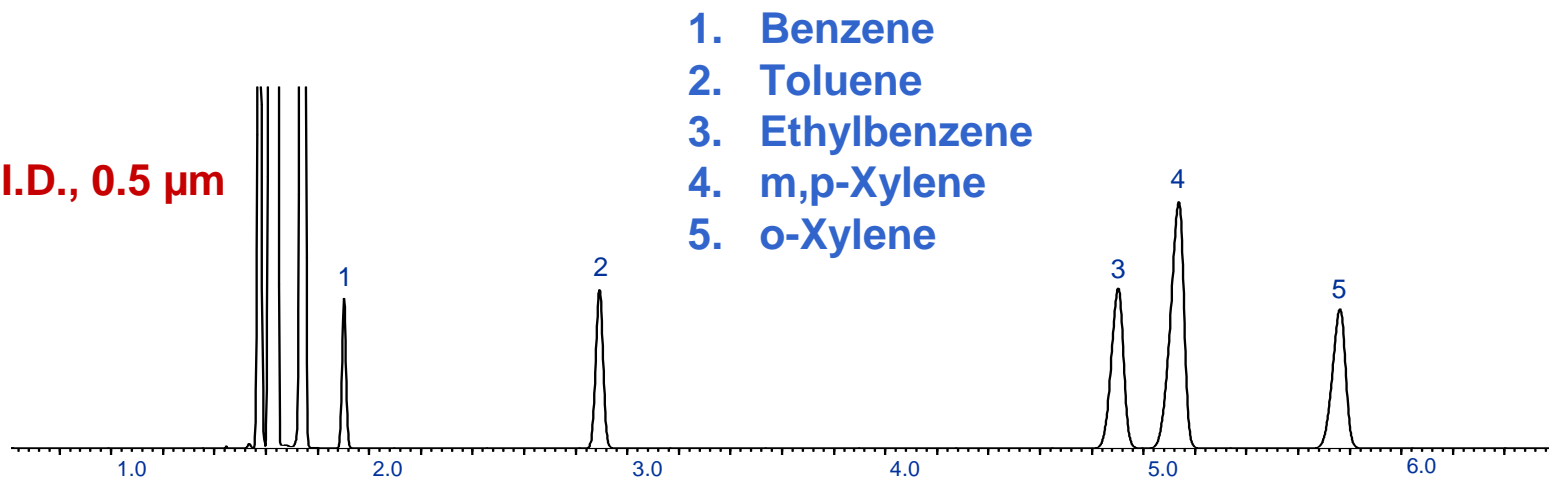
DB-5

0.53 mm I.D., 0.5  $\mu$ m



DB-5

0.53 mm I.D., 0.5  $\mu$ m



1. Benzene
2. Toluene
3. Ethylbenzene
4. m,p-Xylene
5. o-Xylene

**BTEX**

**Carrier: Helium, 36 cm/sec at 40°C**

**Oven: 40°C for 3 min, 5°/min to 100°C**



**Agilent Technologies**

# Column Diameter Theoretical Efficiency

	I.D. (mm)	N/m
	0.10	11905
	0.18	6666
	0.20	5941
	0.25	4762
	0.32	3717
k = 5	0.53	2242



# Considerations For “Extreme” Dimension Changes

**Shorten column length to decrease run time**

**Increase plates/meter by decreasing column diameter**

**For similar retention and selectivity keep the stationary phase and phase ratio ( $\beta = r/d_f$ ) the same.**



# Considerations of using 0.1mm ID Columns

**Carrier Gas**

**Temperature Program**

**Injection efficiency**

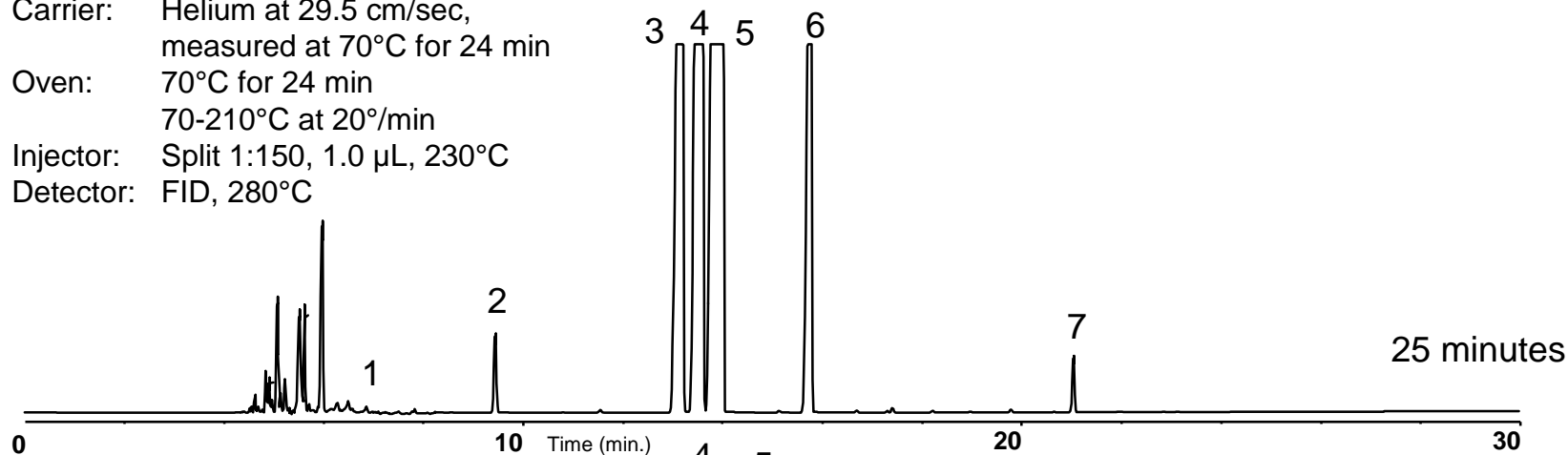
**Instrument considerations**

**Working Range**

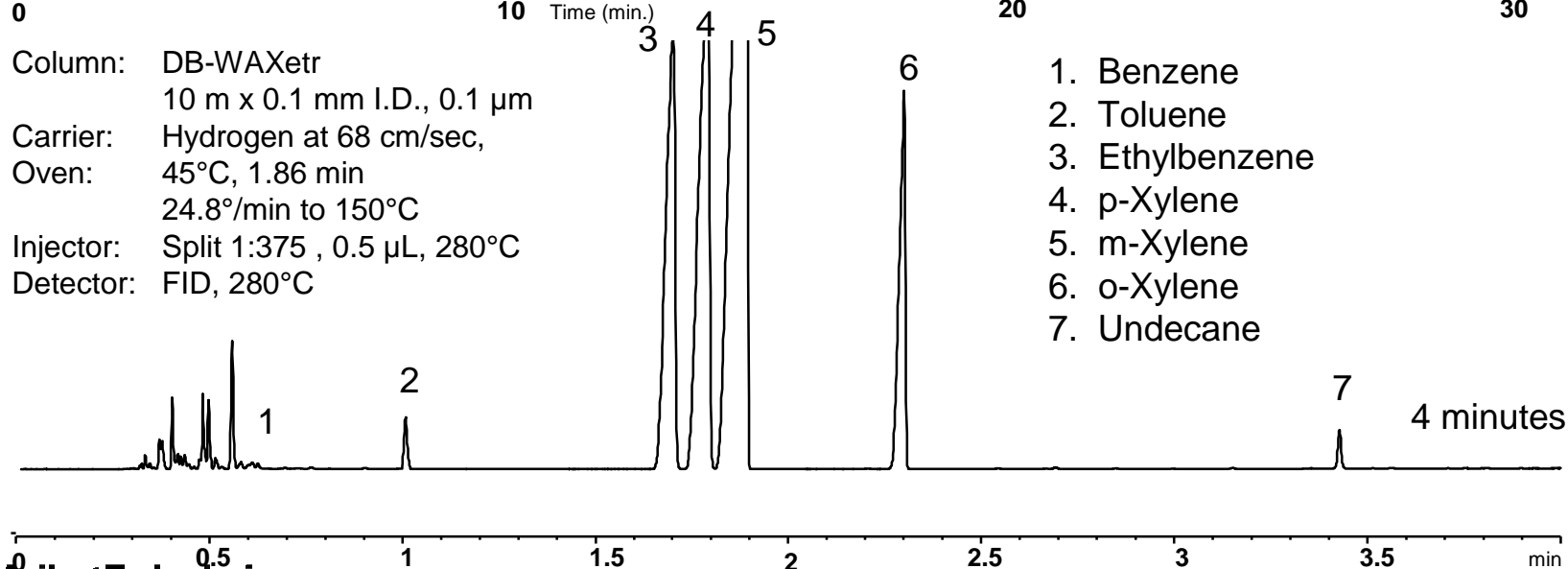


# Normal vs High Speed Analysis of Xylene (ASTM D2360)

Column: DB-WAXetr  
60 m x 0.32 mm I.D., 0.25  $\mu$ m  
Carrier: Helium at 29.5 cm/sec,  
measured at 70°C for 24 min  
Oven: 70°C for 24 min  
70-210°C at 20°/min  
Injector: Split 1:150, 1.0  $\mu$ L, 230°C  
Detector: FID, 280°C



Column: DB-WAXetr  
10 m x 0.1 mm I.D., 0.1  $\mu$ m  
Carrier: Hydrogen at 68 cm/sec,  
Oven: 45°C, 1.86 min  
24.8°/min to 150°C  
Injector: Split 1:375, 0.5  $\mu$ L, 280°C  
Detector: FID, 280°C



1. Benzene
2. Toluene
3. Ethylbenzene
4. p-Xylene
5. m-Xylene
6. o-Xylene
7. Undecane



## $K_c$ and Temperature

$K_c$  of analytes must be maintained  
Temperature programs must be accurately  
scaled to maintain relative analyte retention



# Method Translation Software

- What is Method Translation (MTL)?
  - A calculation technique used to scale a method to different column sizes, speeds, carrier gases, and detectors while maintaining the same elution order .
- How is Method Translation Done?
  - By using Agilent Technologies' free software for method translation (see note at end of this seminar section)
- Why does Method Translation Work?
  - The calculations maintain the same temperature ( $^{\circ}\text{C}$ ) per void time in the oven program, which maintains elution order

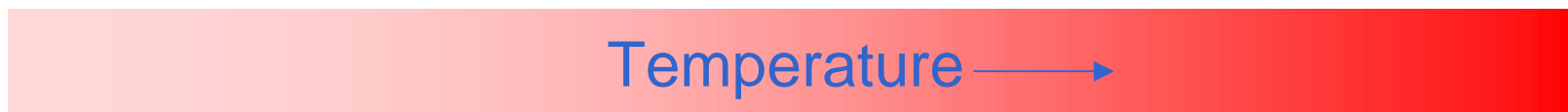


# Temperature Programming

30m, 0.25mm ID

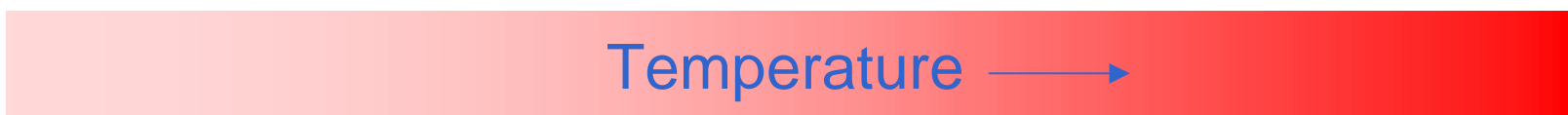


10m, 0.1mm ID

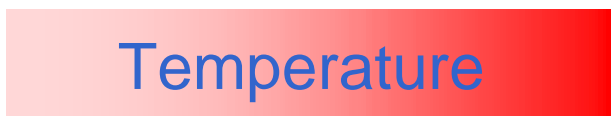


# Temperature Programming

30m, 0.25mm ID



10m, 0.1mm ID



Temperature program must be modified to give same temperature of elution (i.e. faster ramps, shorter hold times)



# Method Translation Software

**Tool allowing GC methods to be translated to different conditions & maintain selectivity/resolution**

new column configuration  
different carrier gas  
faster separation

## **Translates:**

- inlet pressure, temp program, hold times

## **Benefits**

- reduces methods development time
- help assess if GC method compatible with GC hardware



**Agilent Technologies**

# Method Translation Software

**GC Method Translation**

Criterion:  Translate Only  Best Efficiency  Fast Analysis  None **Speed gain: 4.43545**

	Original Method	Translated Method																																										
<b>Column</b>																																												
Length, m	100.0	<input type="checkbox"/> 40.00																																										
Internal Diameter, $\mu\text{m}$	250.0	<input type="checkbox"/> 100.0																																										
<b>Film</b>		<input type="radio"/> Unlock																																										
Thickness, $\mu\text{m}$	0.500	<input type="radio"/> 0.200																																										
Phase Ratio	125.0	<input checked="" type="radio"/> 125.0																																										
<b>Carrier Gas</b>	Helium	<input type="checkbox"/> Hydrogen																																										
<b>Enter one Setpoint</b>																																												
Head Pressure, psi	40.000	85.242																																										
Flow Rate, mLn/min	1.7619	0.8810																																										
Outlet Velocity, cm/sec	62.33	194.77																																										
Average Velocity, cm/sec	23.77	42.17																																										
Hold-up Time, min	7.01259	1.58103																																										
Outlet Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696																																										
Ambient Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696																																										
<b>Oven Temperature</b> 3-ramp Program																																												
	<table border="1"> <thead> <tr> <th>Ramp Rate</th> <th>Final Temp.</th> <th>Final Time</th> </tr> <tr> <th><math>^{\circ}\text{C}/\text{min}</math></th> <th><math>^{\circ}\text{C}</math></th> <th>min</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td>35.00</td> <td>13.000</td> </tr> <tr> <td>Ramp 1</td> <td>10.000</td> <td>45.00</td> <td>15.000</td> </tr> <tr> <td>Ramp 2</td> <td>1.000</td> <td>60.00</td> <td>15.000</td> </tr> <tr> <td>Ramp 3</td> <td>2.000</td> <td>220.00</td> <td>5.000</td> </tr> </tbody> </table>	Ramp Rate	Final Temp.	Final Time	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min	Initial	35.00	13.000	Ramp 1	10.000	45.00	15.000	Ramp 2	1.000	60.00	15.000	Ramp 3	2.000	220.00	5.000	<table border="1"> <thead> <tr> <th>Ramp Rate</th> <th>Final Temp.</th> <th>Final Time</th> </tr> <tr> <th><math>^{\circ}\text{C}/\text{min}</math></th> <th><math>^{\circ}\text{C}</math></th> <th>min</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td>35.00</td> <td>2.931</td> </tr> <tr> <td>Ramp 1</td> <td>44.354</td> <td>45.00</td> <td>3.382</td> </tr> <tr> <td>Ramp 2</td> <td>4.435</td> <td>60.00</td> <td>3.382</td> </tr> <tr> <td>Ramp 3</td> <td>8.871</td> <td>220.00</td> <td>1.127</td> </tr> </tbody> </table>	Ramp Rate	Final Temp.	Final Time	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min	Initial	35.00	2.931	Ramp 1	44.354	45.00	3.382	Ramp 2	4.435	60.00	3.382	Ramp 3	8.871	220.00	1.127
Ramp Rate	Final Temp.	Final Time																																										
$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min																																										
Initial	35.00	13.000																																										
Ramp 1	10.000	45.00	15.000																																									
Ramp 2	1.000	60.00	15.000																																									
Ramp 3	2.000	220.00	5.000																																									
Ramp Rate	Final Temp.	Final Time																																										
$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min																																										
Initial	35.00	2.931																																										
Ramp 1	44.354	45.00	3.382																																									
Ramp 2	4.435	60.00	3.382																																									
Ramp 3	8.871	220.00	1.127																																									
<b>Sample Information</b> None																																												



# Injector Efficiency

**Narrow columns generate narrow peaks**

**Injection band must be narrow to take advantage of the column efficiency**

**This usually means using split injection with high split ratios**



# Instrument Considerations

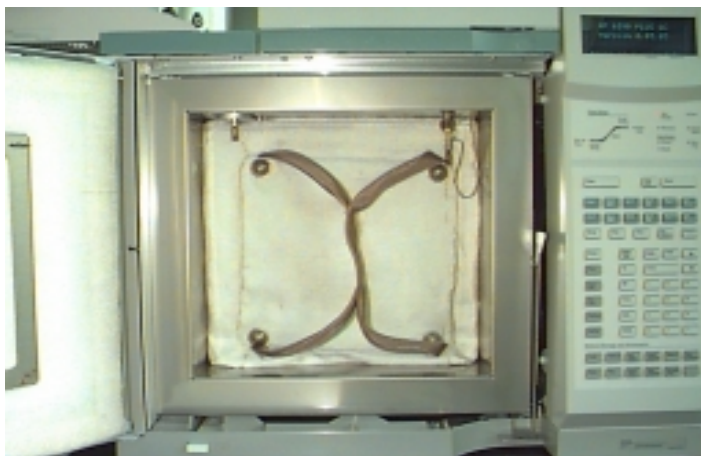
## ***6890/6850 Optimized For Fast GC***

- Sample Introduction/ Inlets
  - fast automatic injector (0.1 sec injection time)
  - high pressure, high flow capability
    - 100 psi inlet (optional 150 psi inlet for 6890)
    - up to 1000 mL/min flow rates
- Fast Oven - up to 120 °C/min ramp rates
- Fast detector electronics
  - FID, NPD, FPD to 200 Hz
  - ECD to 50 Hz



# Instrument Considerations

## *Oven insert for the 6890*



- The insert reduces the 6890 effective oven volume by 50%.
- Allows 120V 6890 to achieve ramp rate equal to a 240V 6890 or a 6850.
- Allows faster oven cool down over std 6890.
- Part No. G2646-60500



# 6890/6850 Oven Ramp Rates

	“Standard”	“Fast”			“Turbo”
Temp. Range (°C)	6890 120V	6890 240V	6890 120V Insert	6850 120V	6890 240V Insert
50 to 70	75	120	120	120	120
70 to 115	45	95	95	95	120
115 to 175	40	65	65	65	110
175 to 300	30	45	45	45	80
300 to 450	20	35	35	35*	65

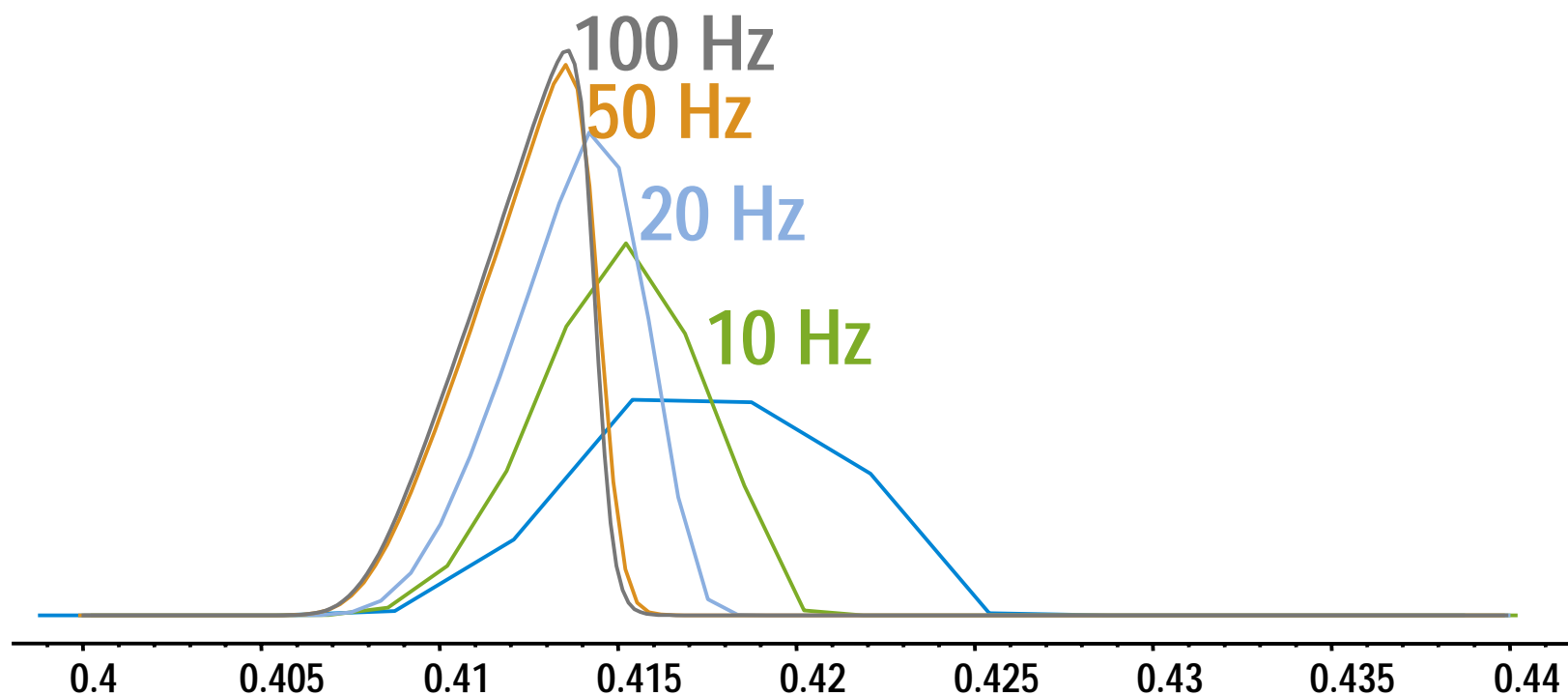
\* Maximum temperature for 6850 is 350 °C

- Allows sharing of fast GC methods across platforms



# Effect of Data Rate on Peak Height

Set data rate to give 10 points across halfwidth of peak. Peak is 0.23 sec at 1/2 width, so use 50 Hz



## Working Range

$$W = Q_s \div Q_o$$

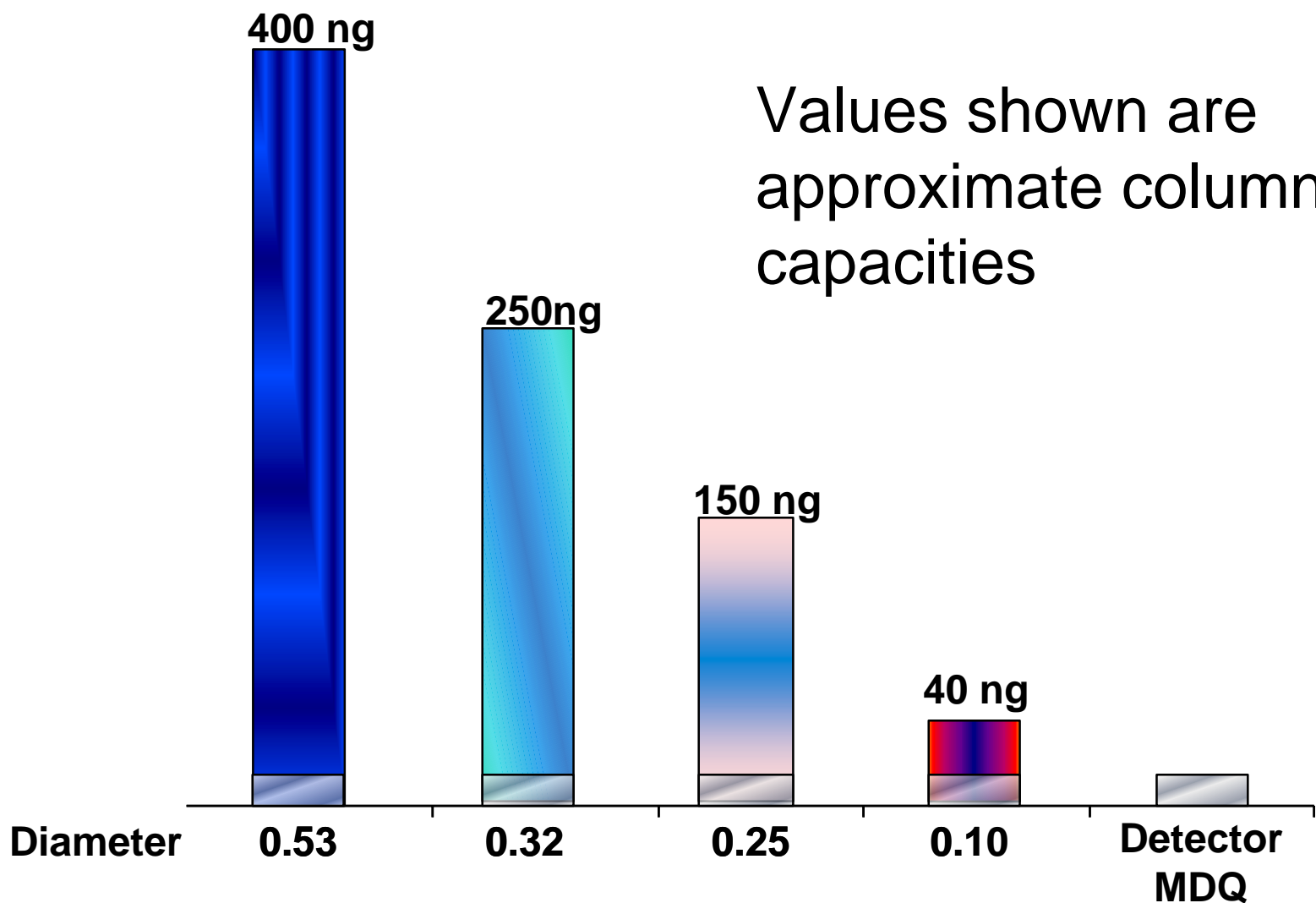
$Q_s$  = maximum column capacity

$Q_o$  = minimum amount that can be reliably detected

**Column capacity is proportional to column diameter**  
**Column diameter will have little effect on detector sensitivity**

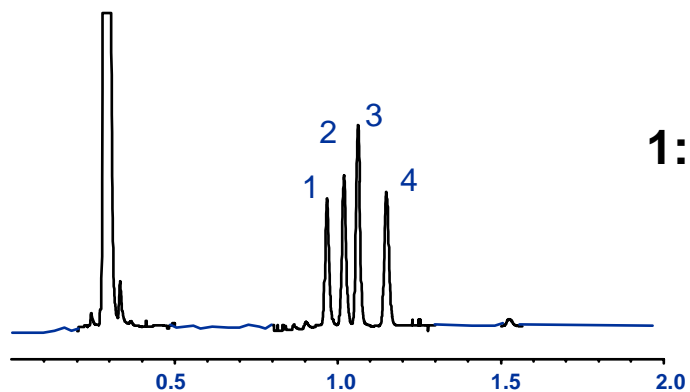


# Working Range

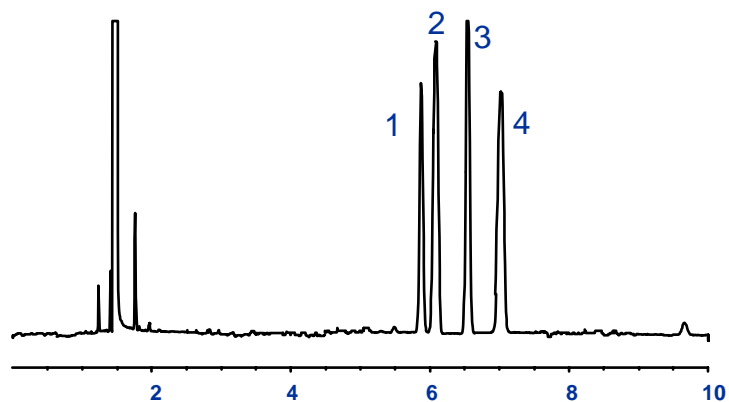


# Capacity: Effect on Resolution

10 m x 0.1 mm, 0.2  $\mu$ m

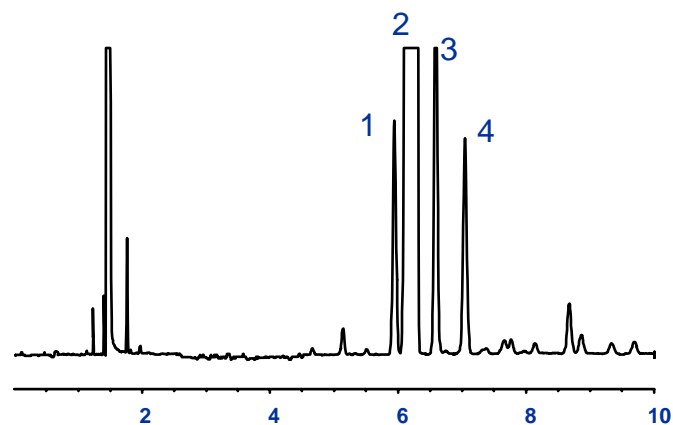
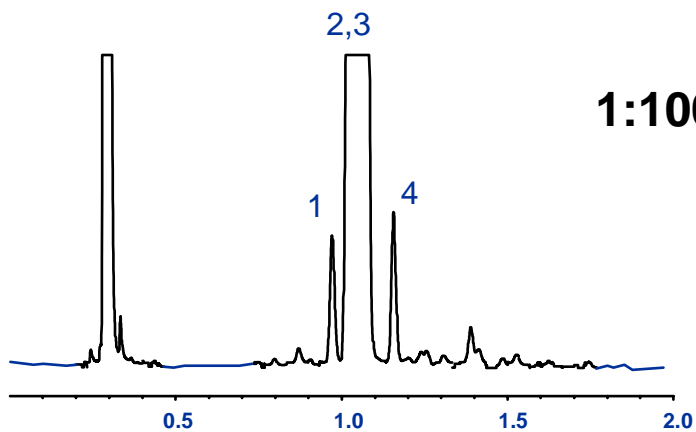


30 m x 0.25 mm, 0.5  $\mu$ m



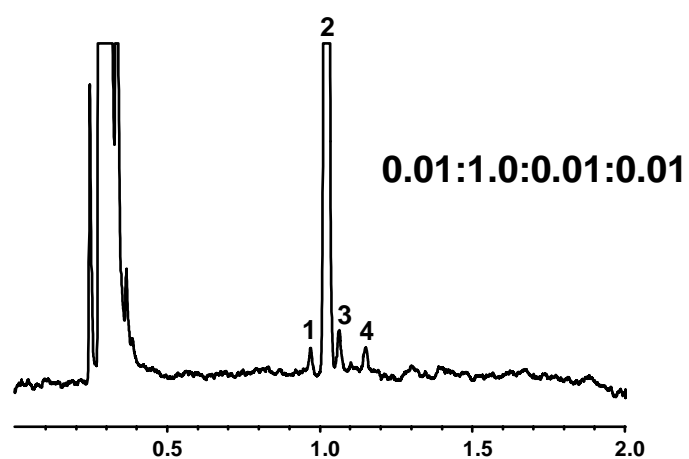
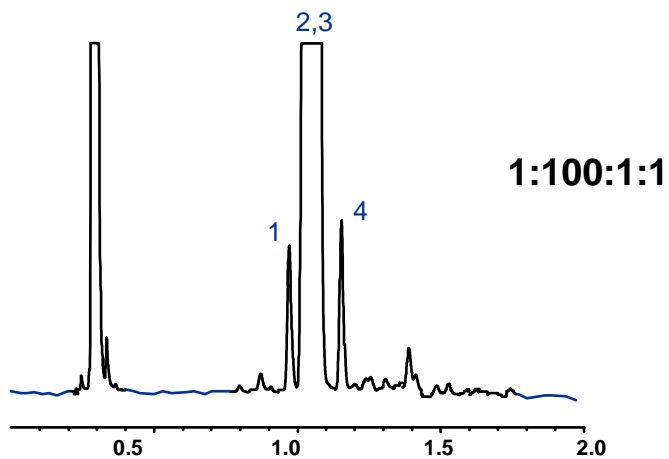
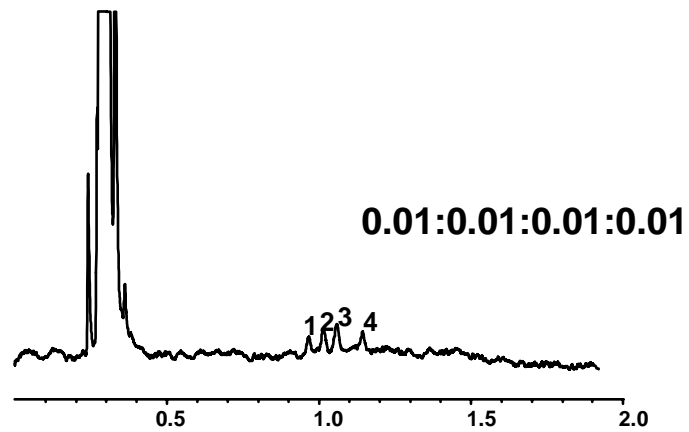
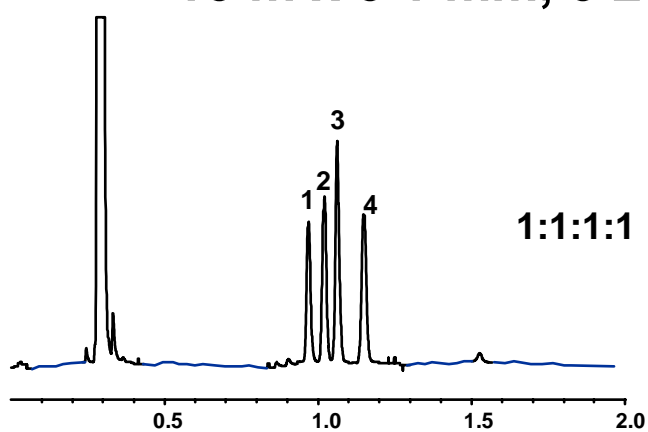
1:1:1:1

1:100:1:1



# Is Dilution the Solution?

10 m x 0.1 mm, 0.2  $\mu$ m



# Requirements for Microbore High Speed GC Analysis

- Rapid injection speed (100 ms) - split
- High pressure inlet and pressure regulators (150 psi max)
- H<sub>2</sub> carrier gas (for efficiency, speed and practicality)
- Fast oven programming rate
- Fast detector sample rate (200 Hz)



# Microbore High Speed GC Analysis Considerations

- Column capacity (25 - 40 ng)
- Carrier gas - type, pressure and plumbing
- GC System
- Method translation
- Discrimination
- Sensitivity



# Retention Time Locking



**Agilent Technologies**

# What does RTL provide?

Compound retention times become...

## Permanent and Universal

### *Unchanging RTs*

- Fast & Easy Compound Identification
- Better QA/QC
- Simpler SOPs
- Proprietary Locked Compound Databases

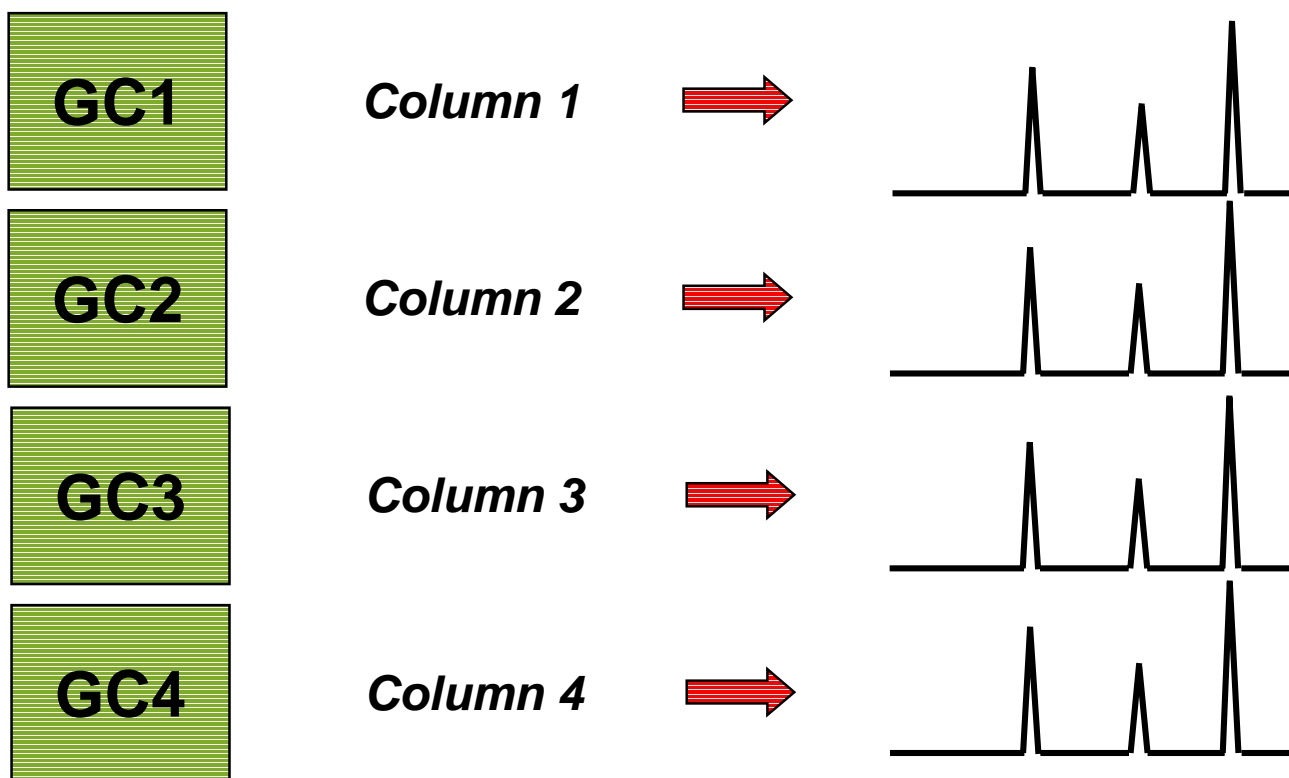
### *Shared Methods*

- Rapid and Simple Method exchange
- Intra- & Inter- laboratory SOPs
- Higher Assuredness / Confidence
- Shared Locked Compound Databases

***Lowered costs, higher quality and increased productivity***

# Retention Time Locking

Retention times match from column-to-column and instrument-to-instrument to 0.030 min or better...



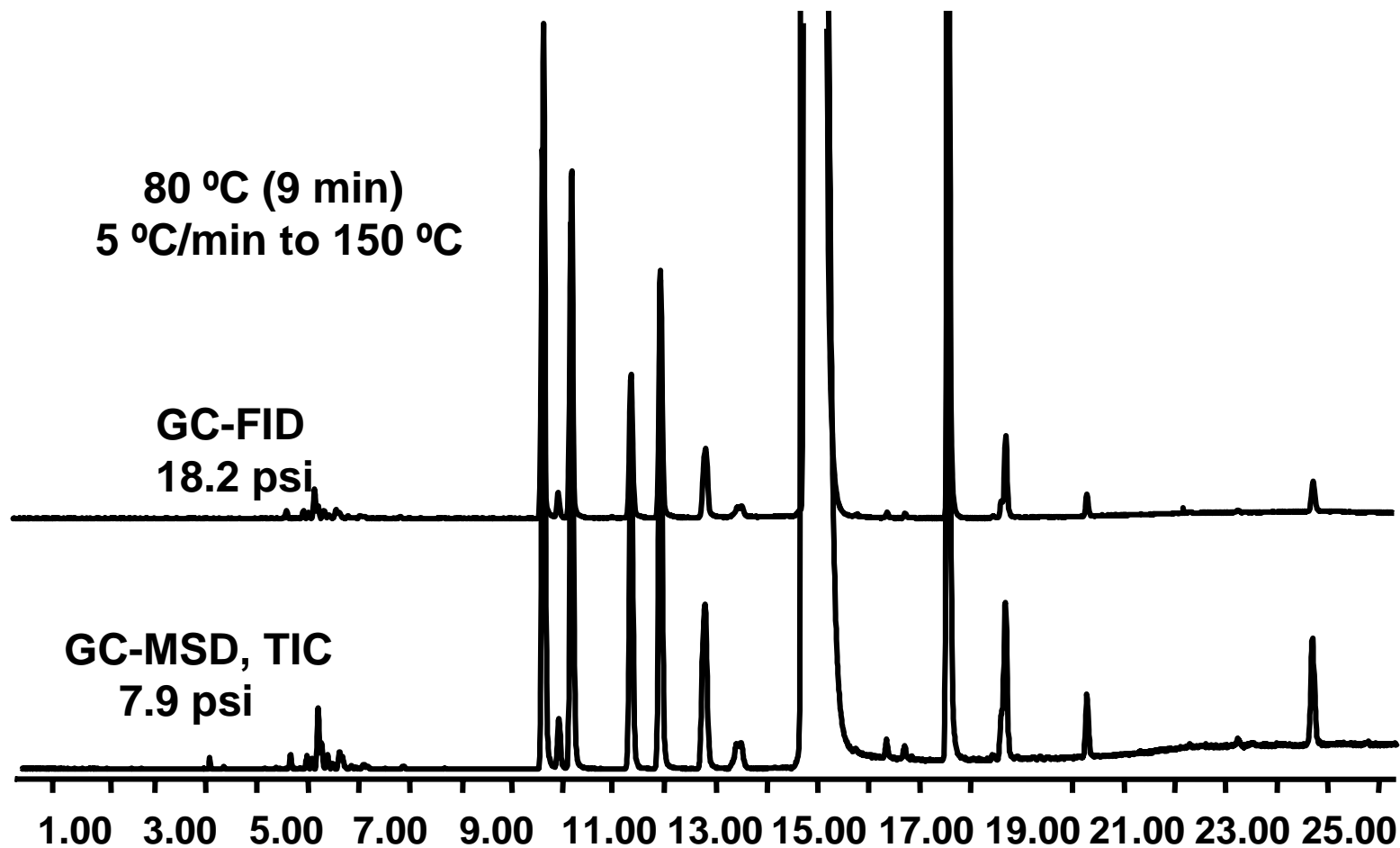
# Retention Time Locking

- Can be used with the Method Translation Software
  - different column dimensions (0.53, 0.32, 0.18, 0.10, etc.)
  - different detectors (MSD, AED, FID, etc.)
- Higher level of confidence in peak identification, especially between different instruments and different laboratories.
- Reduction in data analysis time.
- Greatly reduces problems associated with adjusting RT windows in method, peak misidentification, timed events such as valve switching, adjusting “special” integration events for problem areas in chromatogram.



# RT-Locked GC-FID and GC-MSD

## Impurities in styrene analysis



# Same Method, Different Column Sizes

- **Why?**
  - **530  $\mu\text{m}$  - Ease of use, robustness**
  - **320  $\mu\text{m}$  - Good all around compromise**
  - **250  $\mu\text{m}$  - Meets MSD flow requirements**
  - **100  $\mu\text{m}$  - Fast GC with no resolution loss**
- **How**
  - **Use MTL software to calculate changes in pressure**
  - **Generate new RTL calibration for new column**
  - **Lock system**



# Designing Global Methods...

- Designed for use in multiple:
  - instruments
  - configurations (FID, AED, micro-ECD, MSD, PTV, S/S)
  - locations
- Provides known retention times and elution order
  - Easy setup and maintenance of method
  - Easy data analysis and interpretation
- Accurately scalable
  - Adjustable for optimal speed/resolution/capacity



## With Global Methods...

- Faster method transfer & validation
- Reduce / eliminates need to update RTs in calibration tables
- Easier review of data
- Faster identification of unknowns
- More efficient troubleshooting
- Scalable methods link chromatography in QA labs with that in support labs
- Scalable methods allow optimization of speed, resolution and capacity of method for specific analysis

