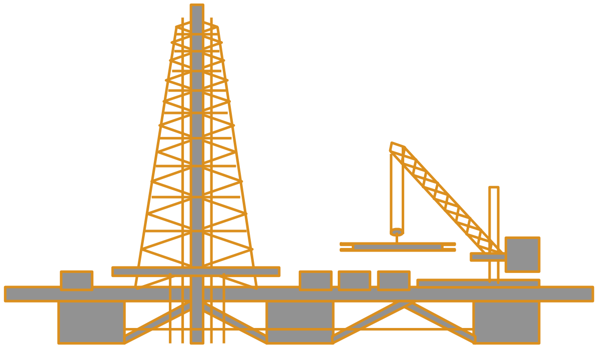
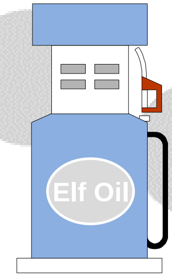
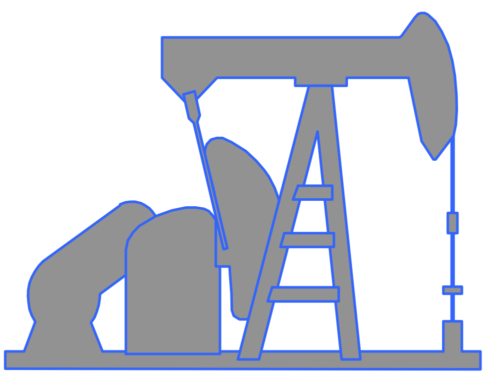




Analysis of Refinery and Petrochemical Products by Capillary GC

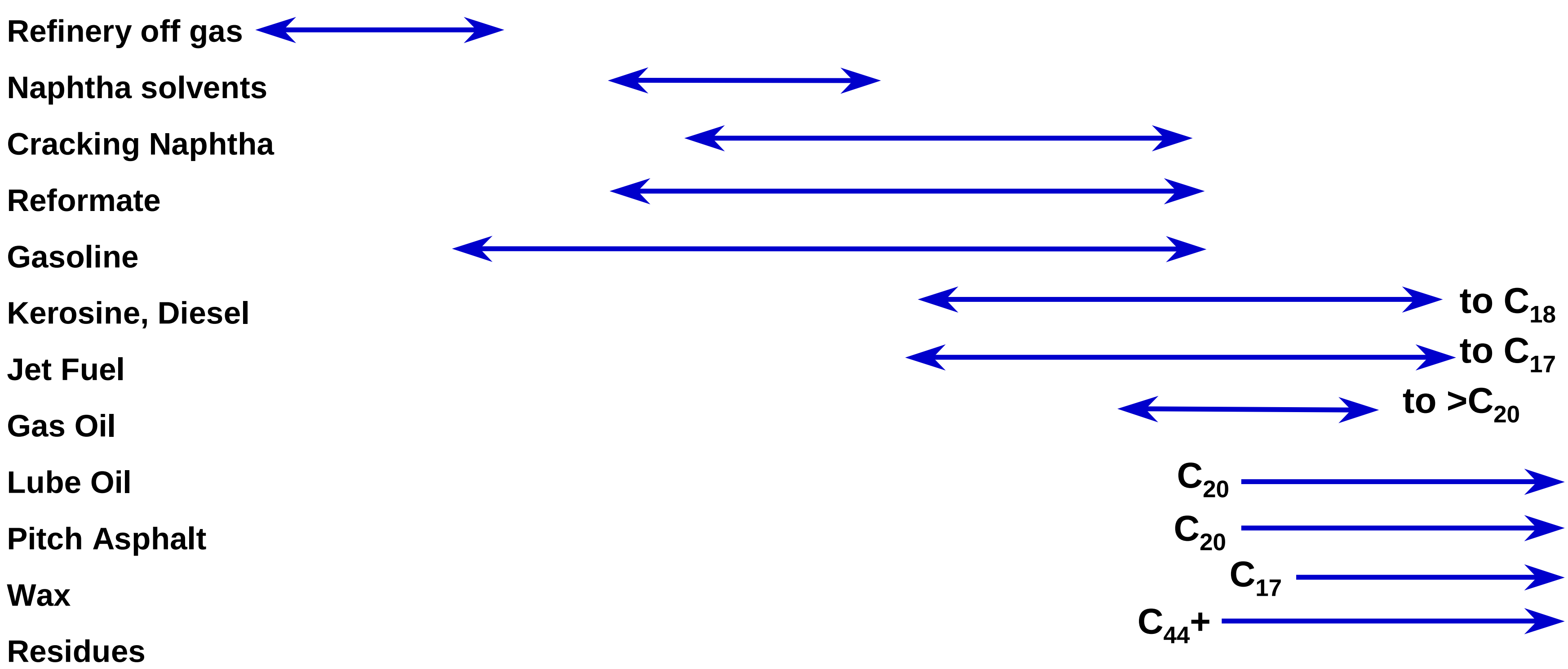


System Optimization

- 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_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
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



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Are These *Really* Tools for Improving Chromatography?

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

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

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

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

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

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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)

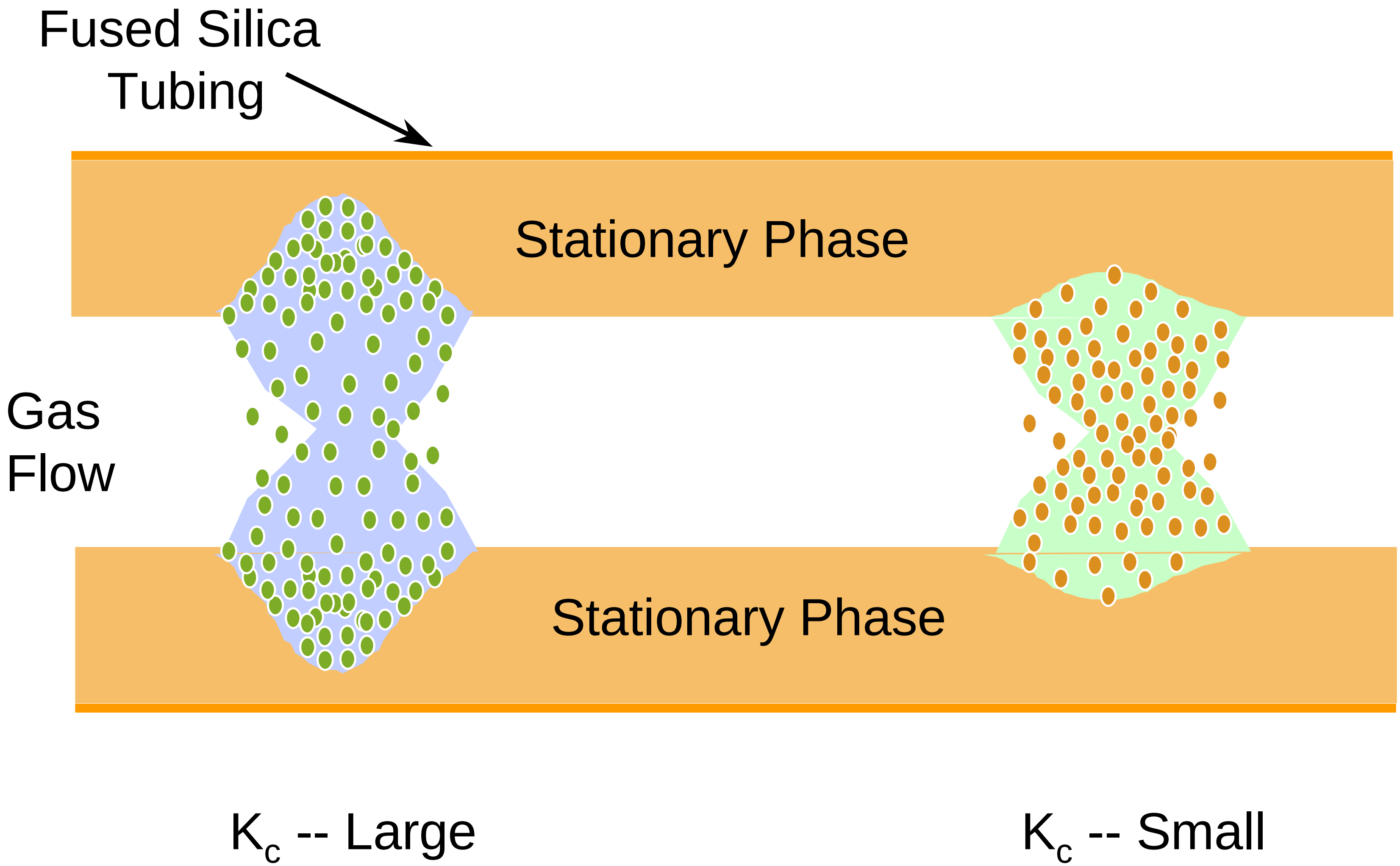
$$K_c = \frac{\text{conc. of solute in stationary phase}}{\text{conc. of solute in mobile phase}}$$

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

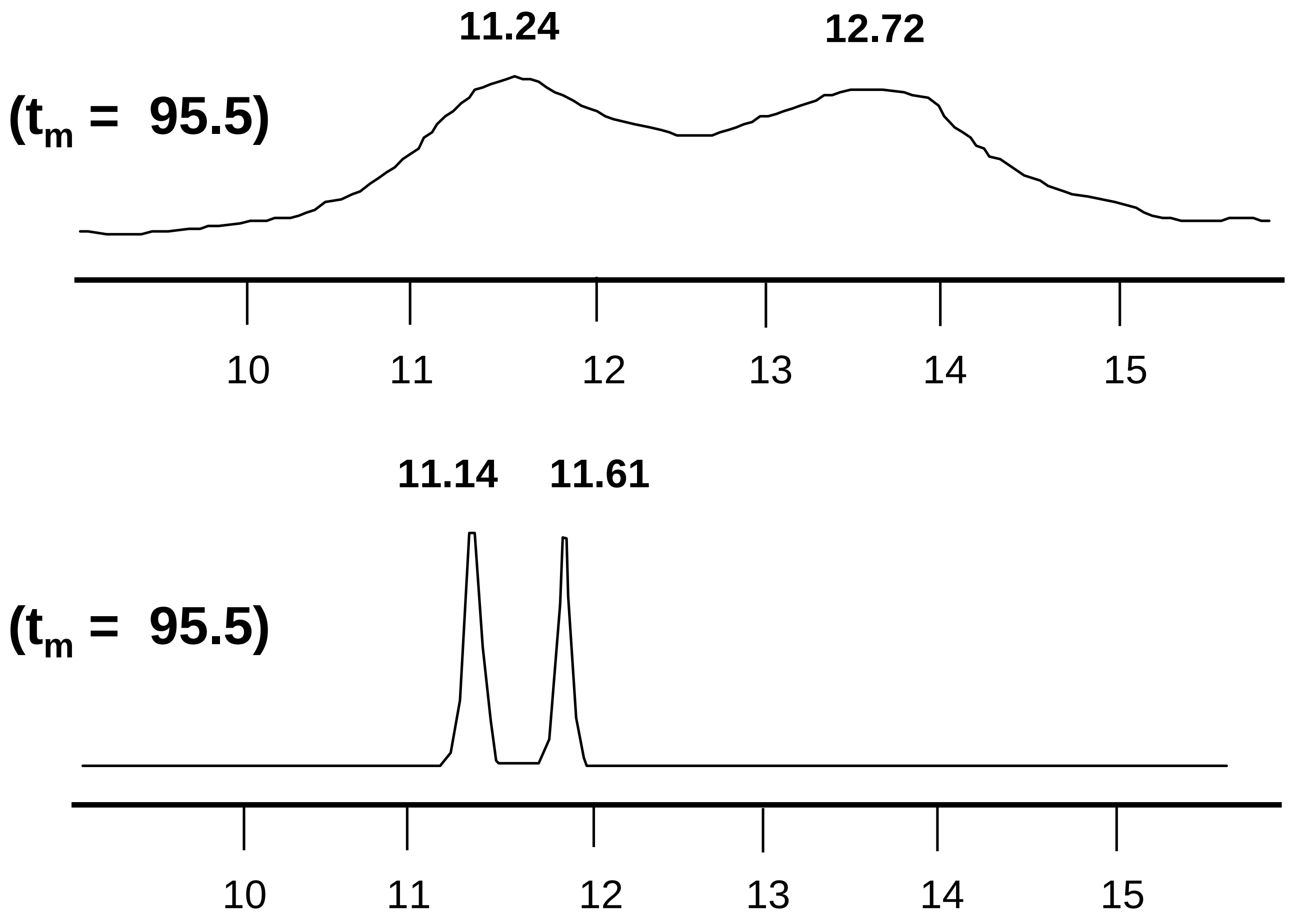
$$\beta = K_c/k$$ Phase Ratio

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?

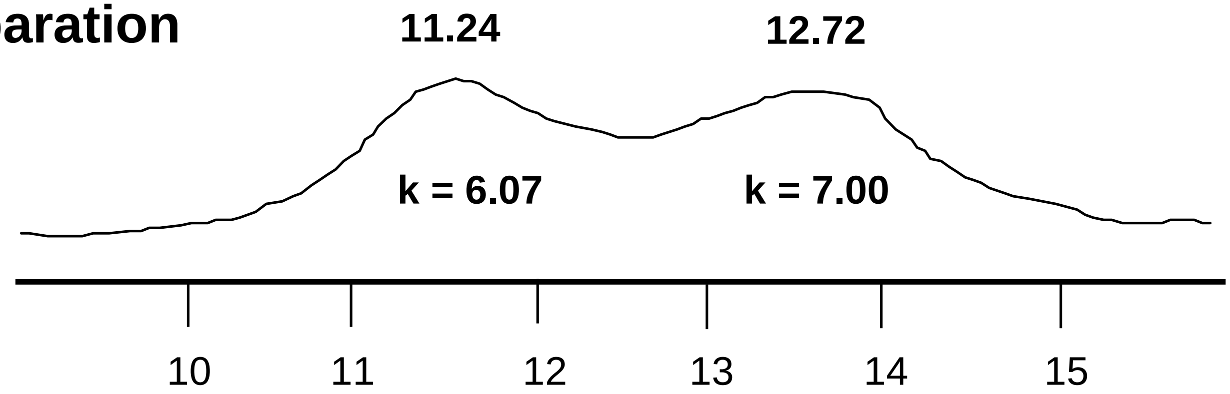


Resolution vs Separation

Better Separation

α = 1.17

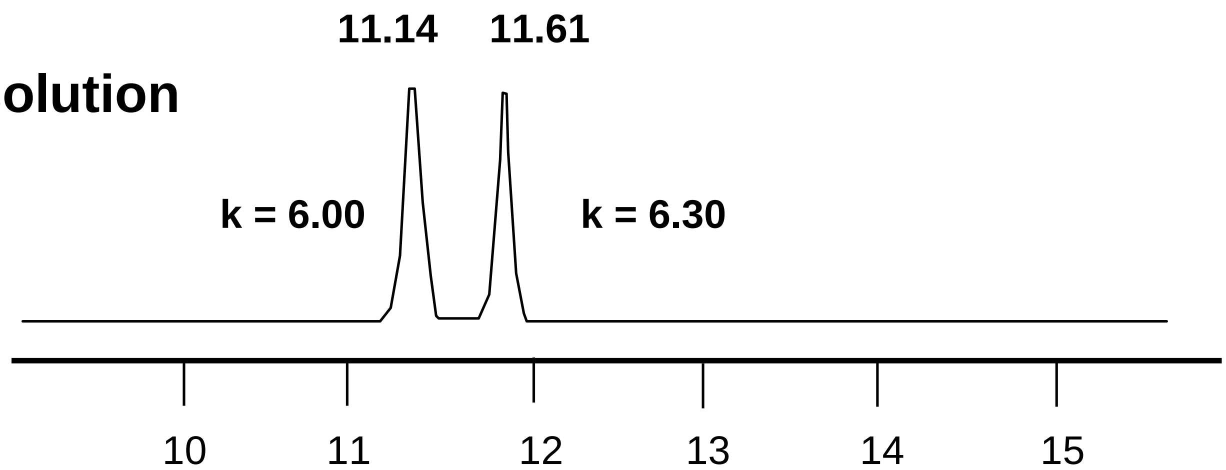
R_s = 0.6



Better Resolution

α = 1.05

R_s = 2.7



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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)

α = f (T, phase)

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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

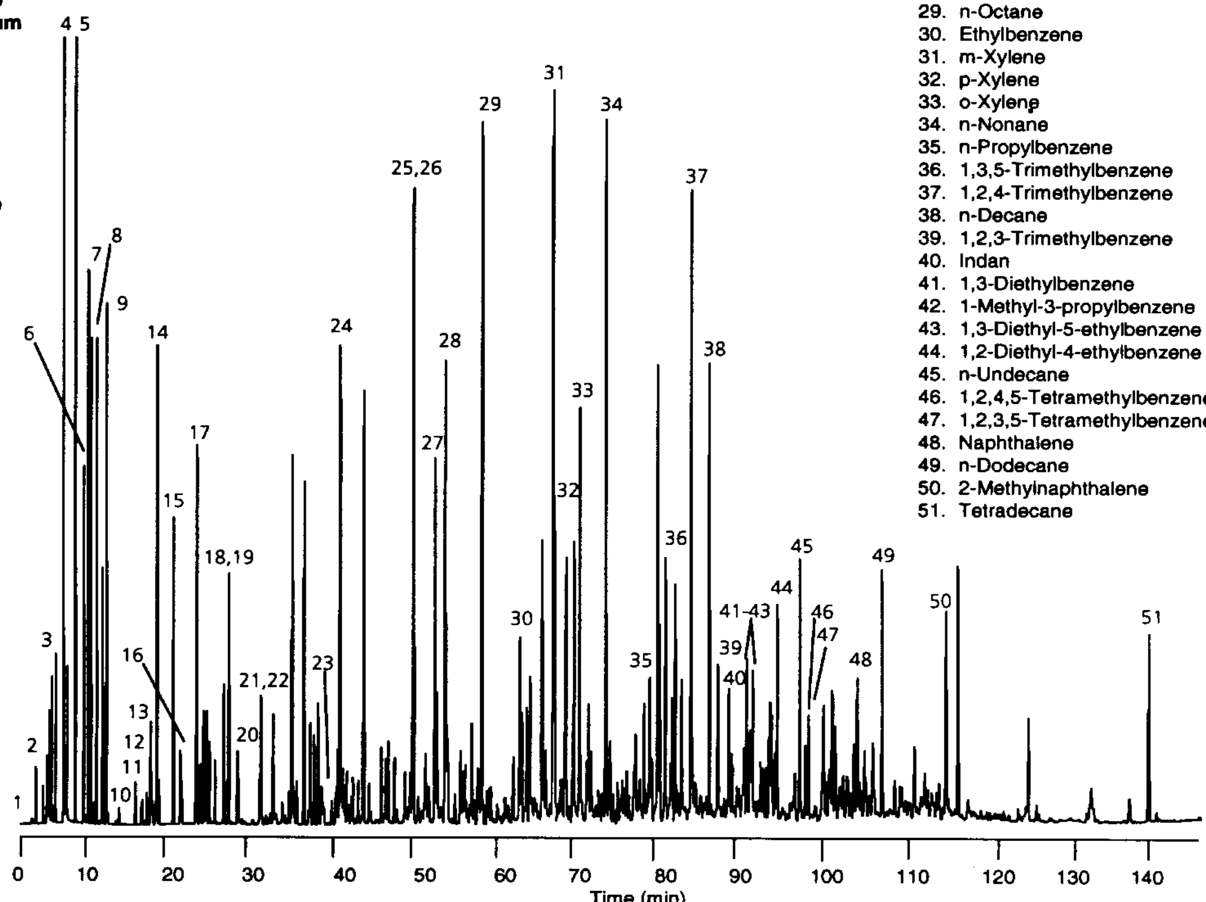
- ASTM 5134: Detailed Analysis of Petroleum Naphthas through n-Nonane by CGC
- AFNOR NF M07-086: Determination of HC Group Type in Motor Gasolines from Detailed Analysis by CGC
- CAN/ C.G.S.B.: 3.0, no. - 14.3 - 94: Detailed Analysis of Gasoline
- ASTM D6730
- PONA-BAMA: Paraffins, Olefins, Naphthenes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

Detailed Analysis of Gasoline by AFNOR Method #2

Column: DB-Petro50

	50 m x 0.20 mm I.D., 0.5 µm
J&W P/N:	**128-1056**
Carrier:	Helium at 16.7 cm/sec, measured at 35°C
Oven:	10°C for 15 min 10-70°C at 1.3°/min 70-250°C at 1.7°/min
Injector:	Split 1:200, 250°C 0.3 µL petroleum reformate
Detector:	FID, 250°C Nitrogen makeup gas at 30 mL/min

1. Ethane
2. Propane
3. n-Butane
4. Ethanol
5. Isopentane
6. 1-Pentene
7. 2-Methyl-1-butene
8. n-Pentane
9. 2-Methyl-2-butene
10. 2,2-Dimethylbutane
11. 1-Cyclopentene
12. Cyclopentane
13. 2,3-Dimethylbutane
14. 2-Methylpentane
15. 3-Methylpentane
16. 2-Methyl-1-pentene
17. n-Hexane
18. 2,2-Dimethylpentane
19. Methylcyclopentane
20. 2,4-Dimethylpentane
21. Benzene
22. 1-Methyl-1-cyclopentene
23. Isooctane
24. n-Heptane
25. Toluene
26. 2,3,3-Trimethylpentane
27. 2-Methylheptane
28. 3-Methylheptane
29. n-Octane
30. Ethylbenzene
31. m-Xylene
32. p-Xylene
33. o-Xylene
34. n-Nonane
35. n-Propylbenzene
36. 1,3,5-Trimethylbenzene
37. 1,2,4-Trimethylbenzene
38. n-Decane
39. 1,2,3-Trimethylbenzene
40. Indan
41. 1,3-Diethylbenzene
42. 1-Methyl-3-propylbenzene
43. 1,3-Diethyl-5-ethylbenzene
44. 1,2-Diethyl-4-ethylbenzene
45. n-Undecane
46. 1,2,4,5-Tetramethylbenzene
47. 1,2,3,5-Tetramethylbenzene
48. Naphthalene
49. n-Dodecane
50. 2-Methylnaphthalene
51. Tetradecane



C421

"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**

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

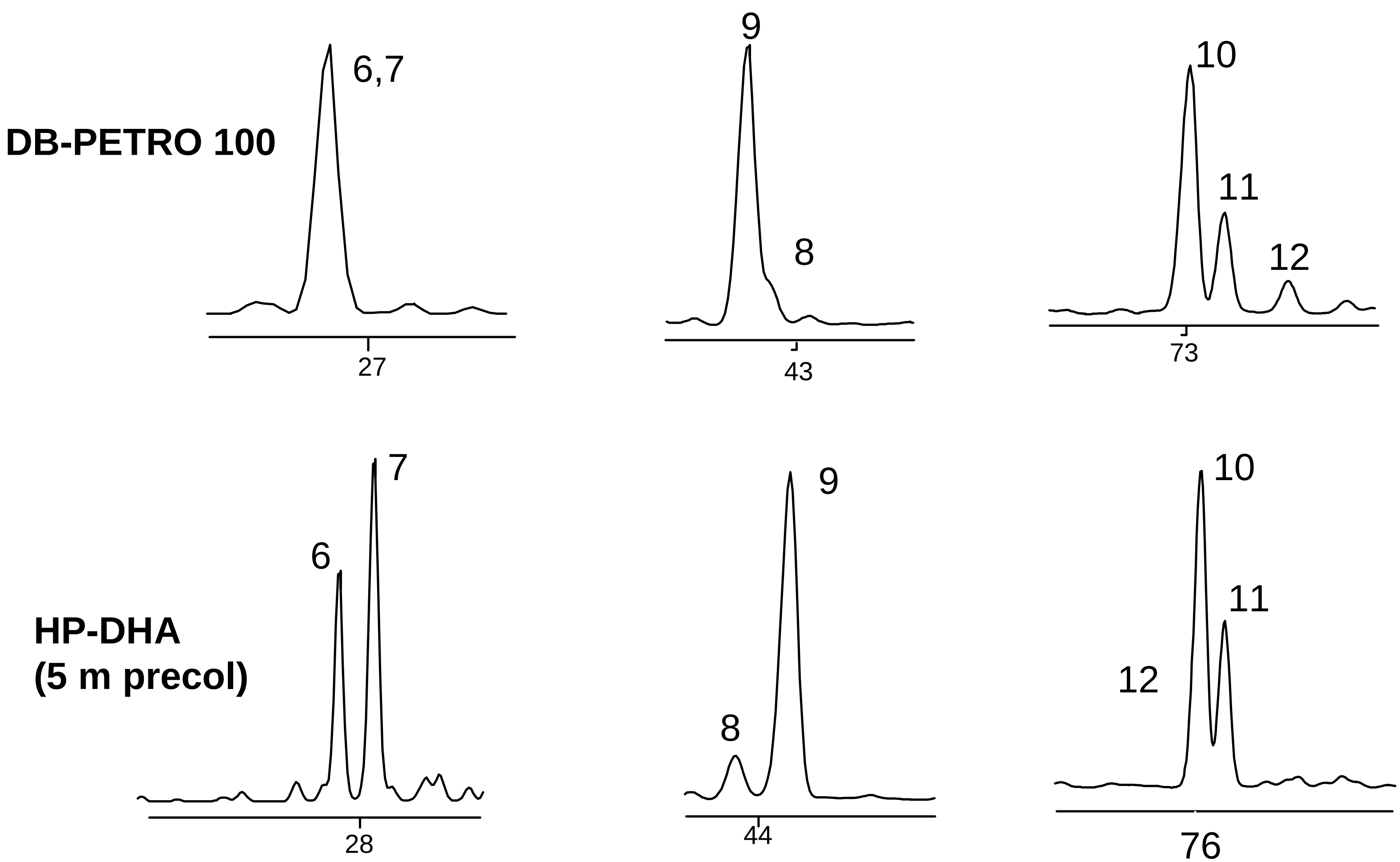
"Tuning" the Methylsiloxane Column To Achieve Key DHA Separations

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

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

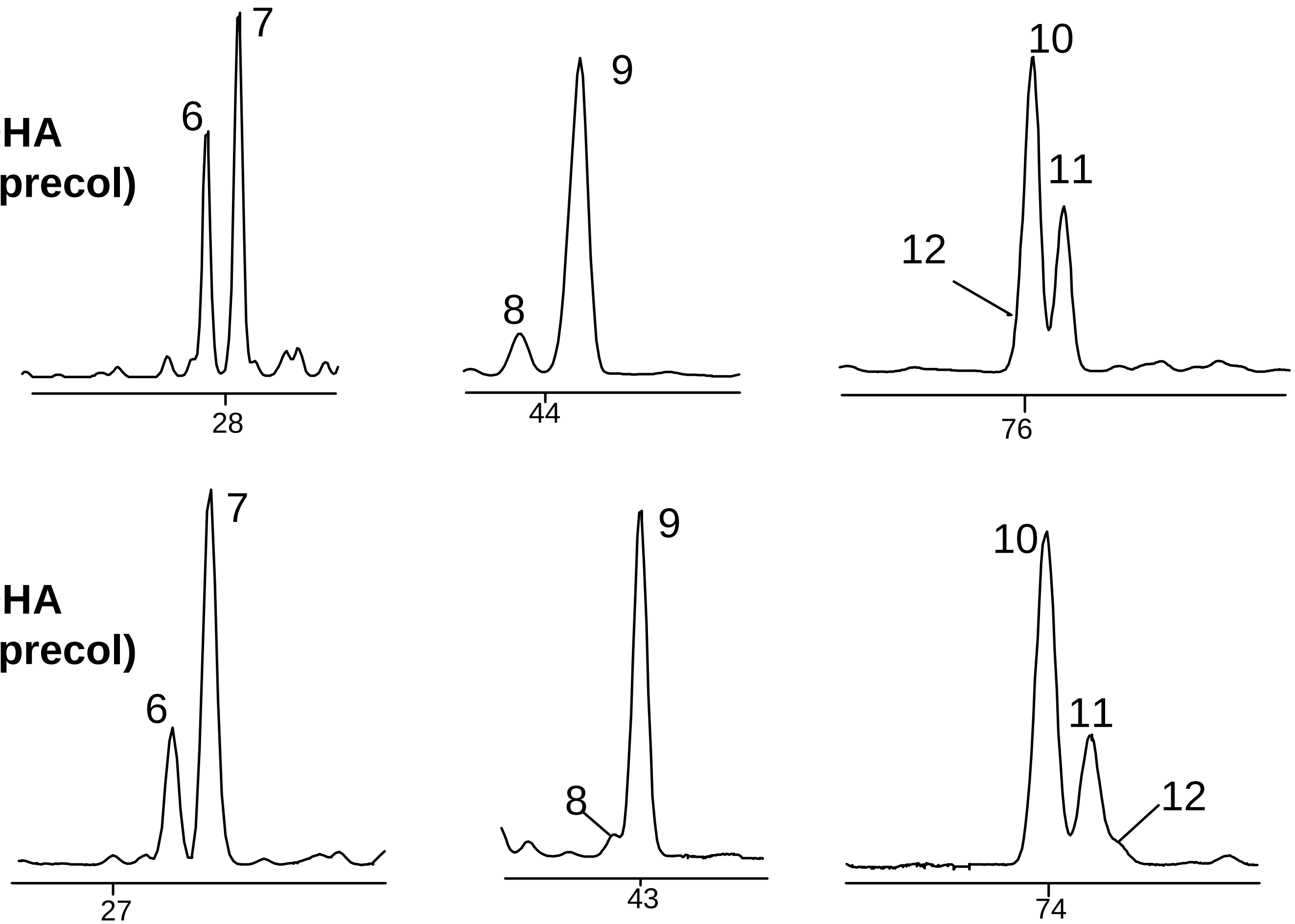


Oven Program: 5°C// 10 min// 5°/min// 50°C// 50 min// 1.5°/min // 200°C

STEP 2 - Tuning HP-DHA Selectivity

HP-DHA
(5 m precol)

HP-DHA
(3 m precol)



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

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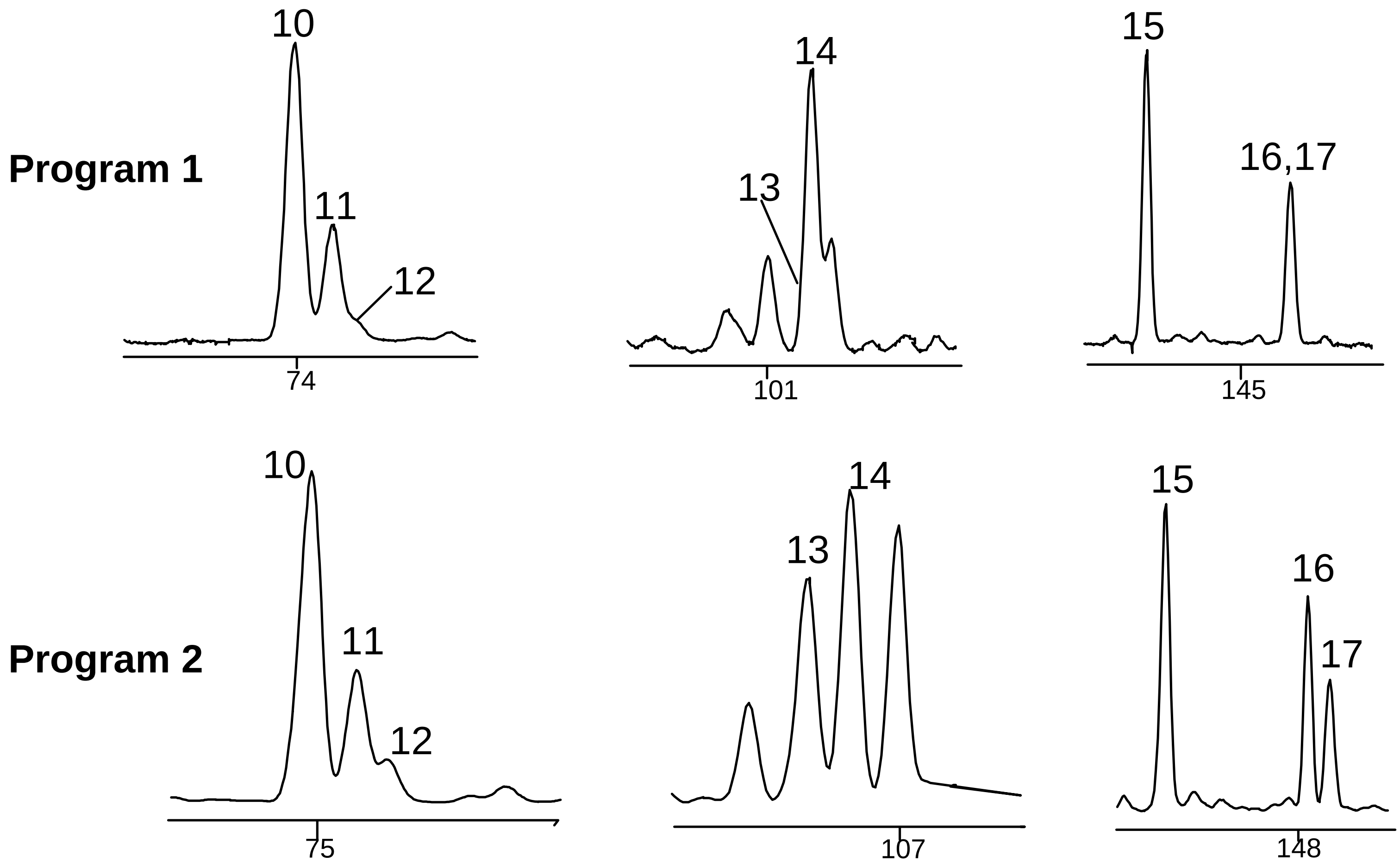
STEP 3 - Tuning Oven Temperature for "3-meter - DHA"



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

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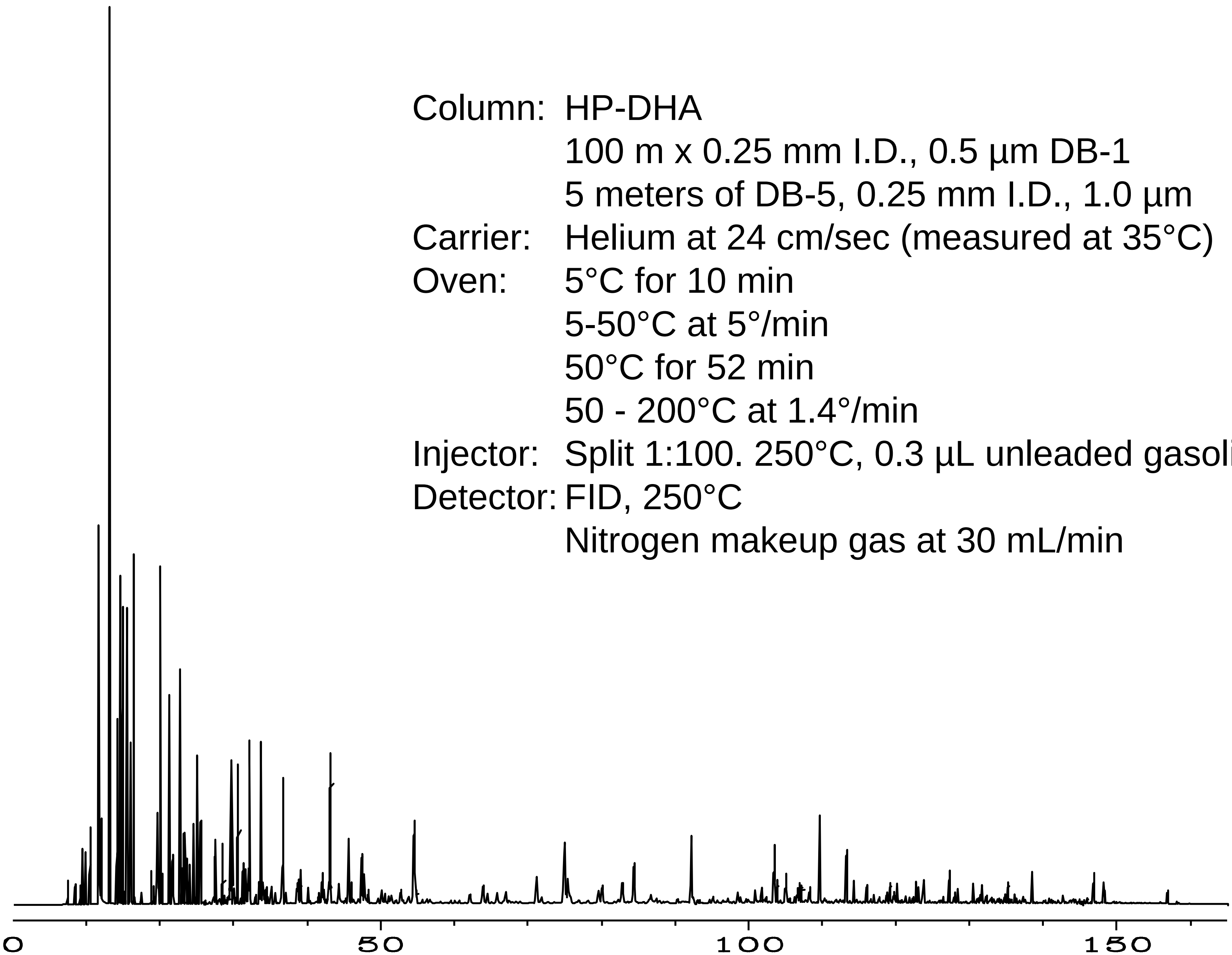

Column:	HP-DHA
	100 m x 0.25 mm I.D., 0.5 µm DB-1
	5 meters of DB-5, 0.25 mm I.D., 1.0 µm
Carrier:	Helium at 24 cm/sec (measured at 35°C)
Oven:	5°C for 10 min
	5-50°C at 5°/min
	50°C for 52 min
	50 - 200°C at 1.4°/min
Injector:	Split 1:100. 250°C, 0.3 µL unleaded gasoline
Detector:	FID, 250°C
	Nitrogen makeup gas at 30 mL/min

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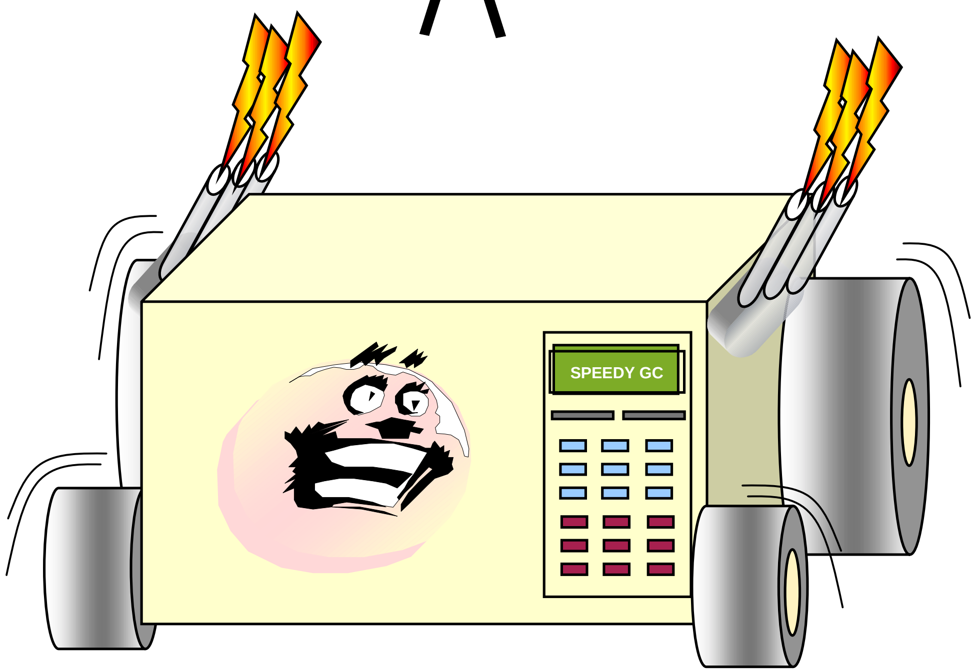
Key Considerations for HC Type Analysis

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

Break Number 1

For Questions and Answers
Press 1 on Your Phone to
Ask a Question

Speeding Things Up



Questions to Ask

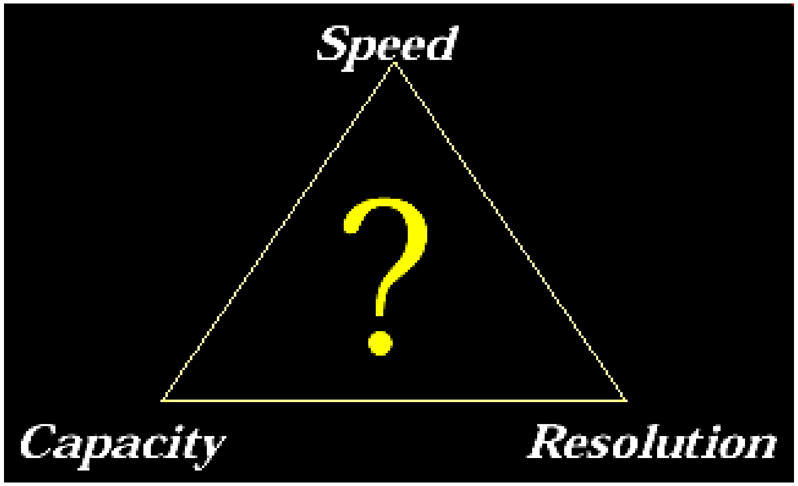
•What information do you need from your analysis?

•Do you have more baseline than needed between your peaks?

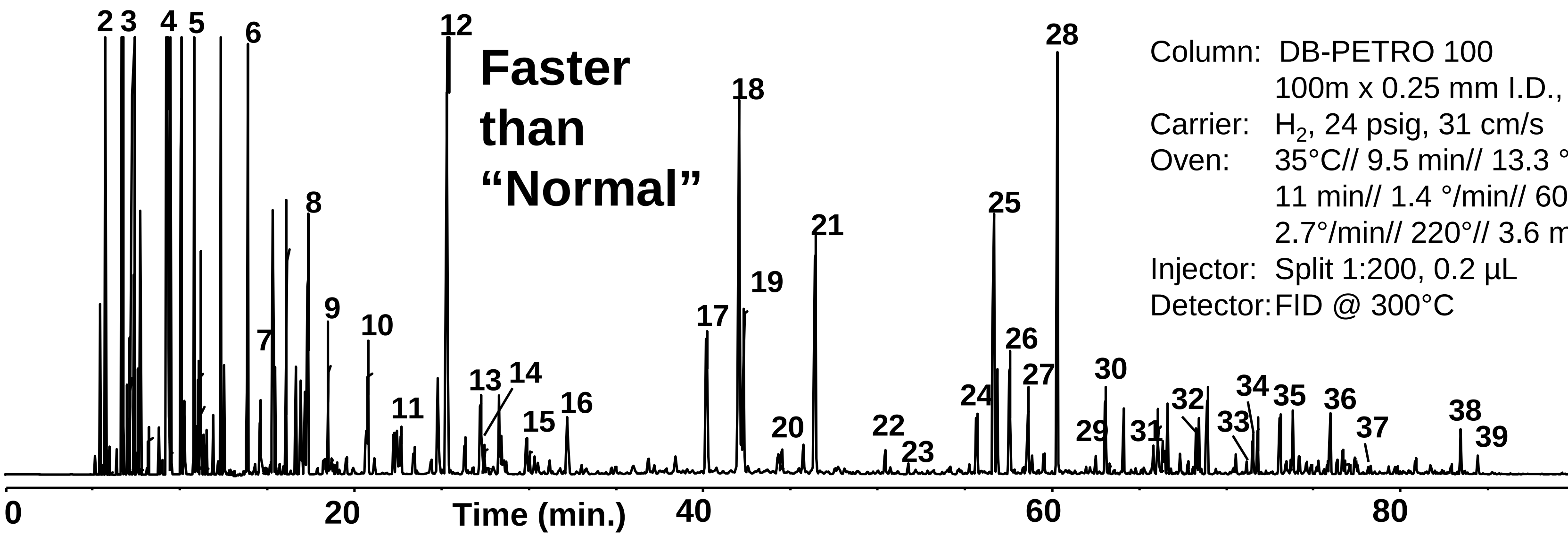
•Do you need to resolve all of the components?

Variables for Shortening Run Times

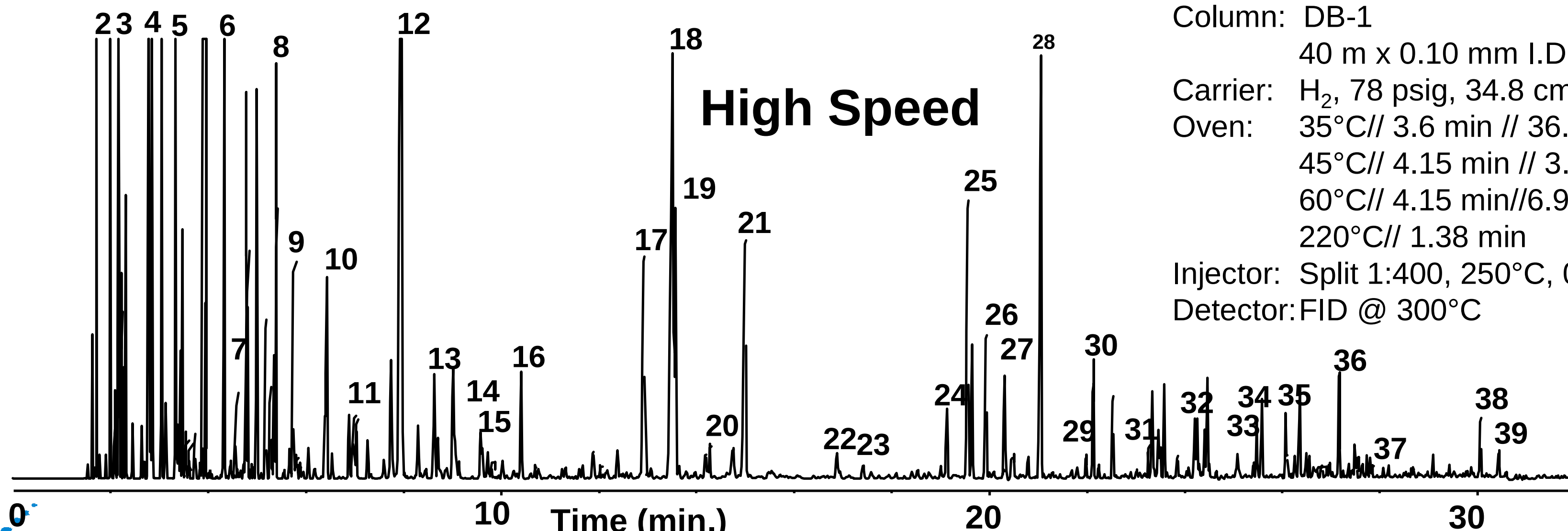
- Stationary Phase
- Temperature Programming
- Carrier Gas: type and linear velocity
- Shorten Column Length
- Decrease Film Thickness
- Decrease Internal Diameter



Regular Unleaded
California Phase I

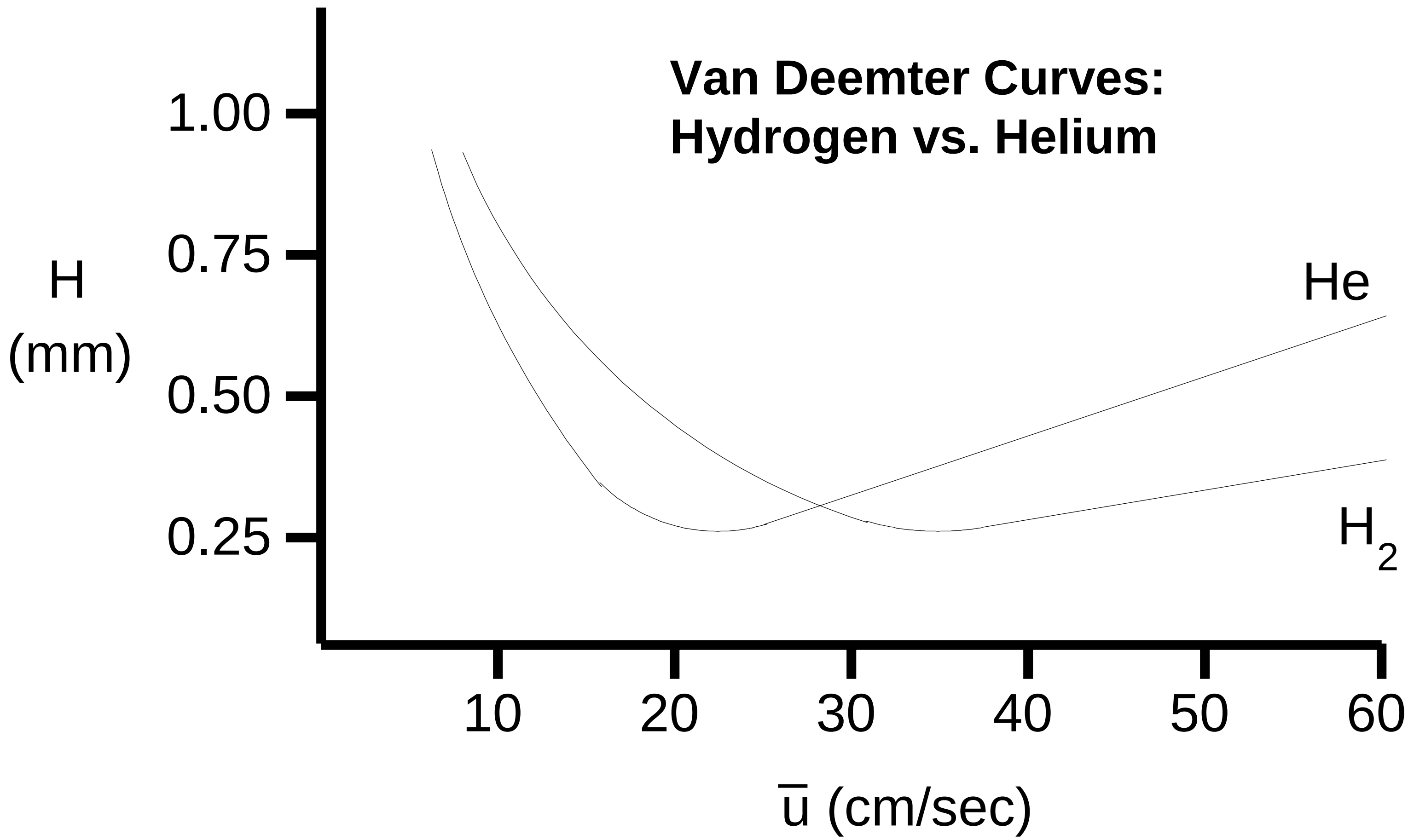


Column: DB-PETRO 100
100m x 0.25 mm I.D., 0.5 µm
Carrier: H_2, 24 psig, 31 cm/s
Oven: 35°C// 9.5 min// 13.3 °/min// 45°// 11 min// 1.4 °/min// 60°// 11min// 2.7°/min// 220°// 3.6 min
Injector: Split 1:200, 0.2 µL
Detector: FID @ 300°C



Column: DB-1
40 m x 0.10 mm I.D., 0.20 µm
Carrier: H_2, 78 psig, 34.8 cm/s
Oven: 35°C// 3.6 min // 36.1°/min// 45°C// 4.15 min // 3.91°/min// 60°C// 4.15 min//6.9°/ min// 220°C// 1.38 min
Injector: Split 1:400, 250°C, 0.2 µL
Detector: FID @ 300°C

Carrier Gas Type

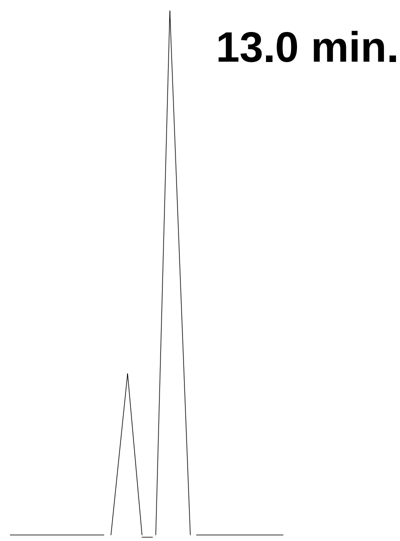


Hydrogen vs. Helium

SE-52
15m x 0.25mm
150°C isothermal

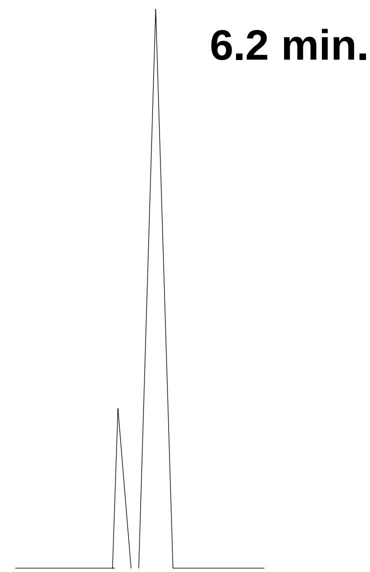
Compounds:
C17
Pristane

Helium
23.2 cm/sec



R = 1.67

Hydrogen
48 cm/sec



R = 1.65

Factors Affecting Resolution

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

Efficiency: N = theoretical plates

Retention: k = retention factor

Selectivity: α = 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

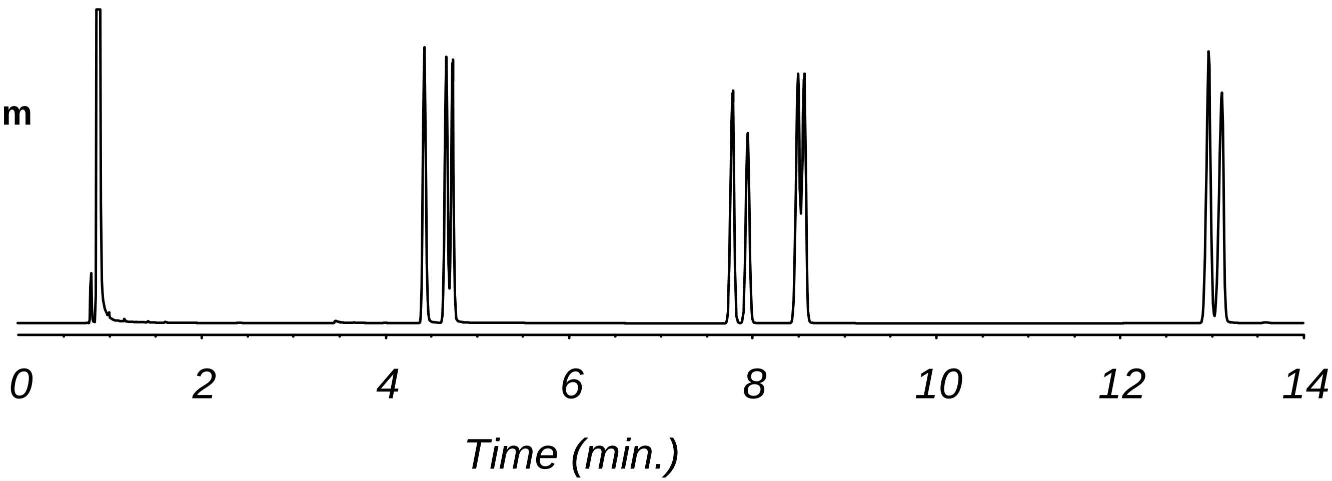
K_c is determined by:

- **solute**
- **stationary phase**
- **temperature**

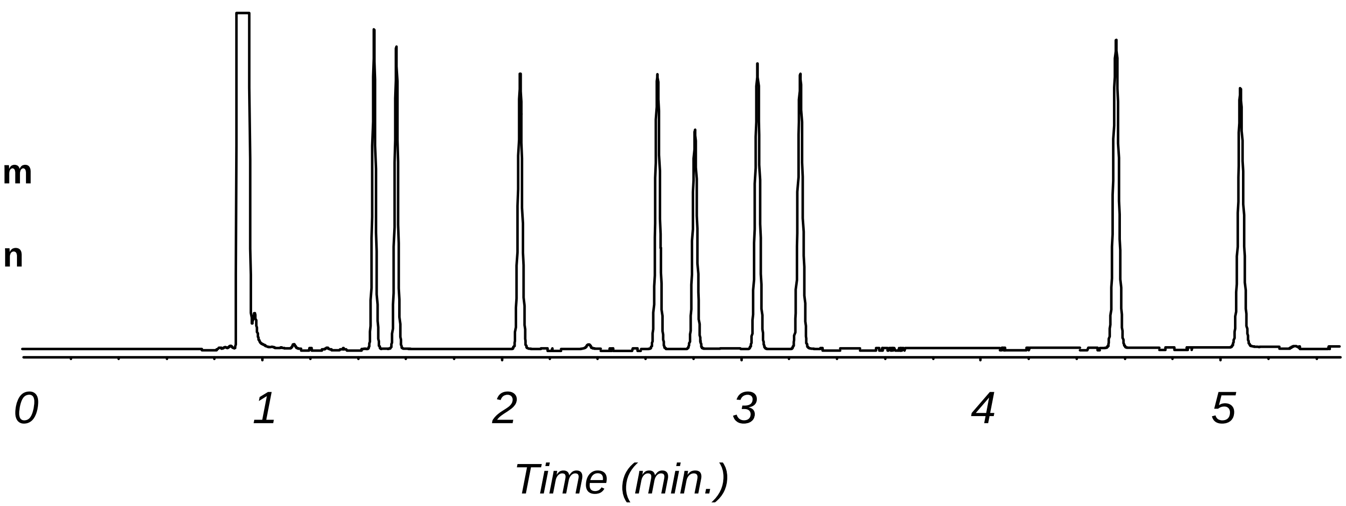
Stationary phase and temperature changes do not affect the K_c of all solutes equally.

Start with the Right Phase

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



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



Change retention by changing temperature: K_c and Temperature

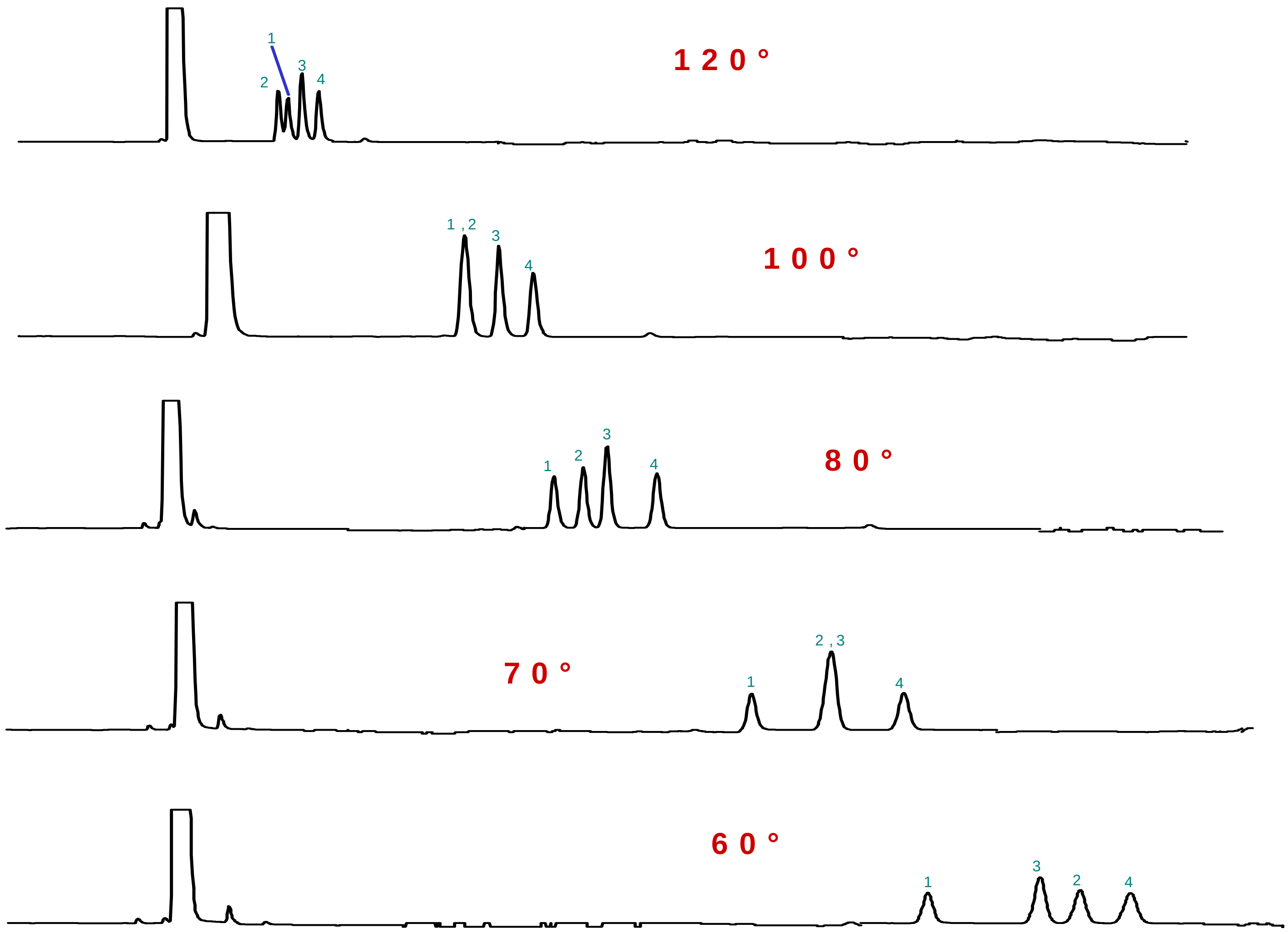
$$K_C = \frac{\text{conc. of solute in stationary phase}}{\text{conc. of solute in mobile phase}}$$

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. α-Terpinene
2. Dodecane
3. Limonene
4. 1,8-Cineole



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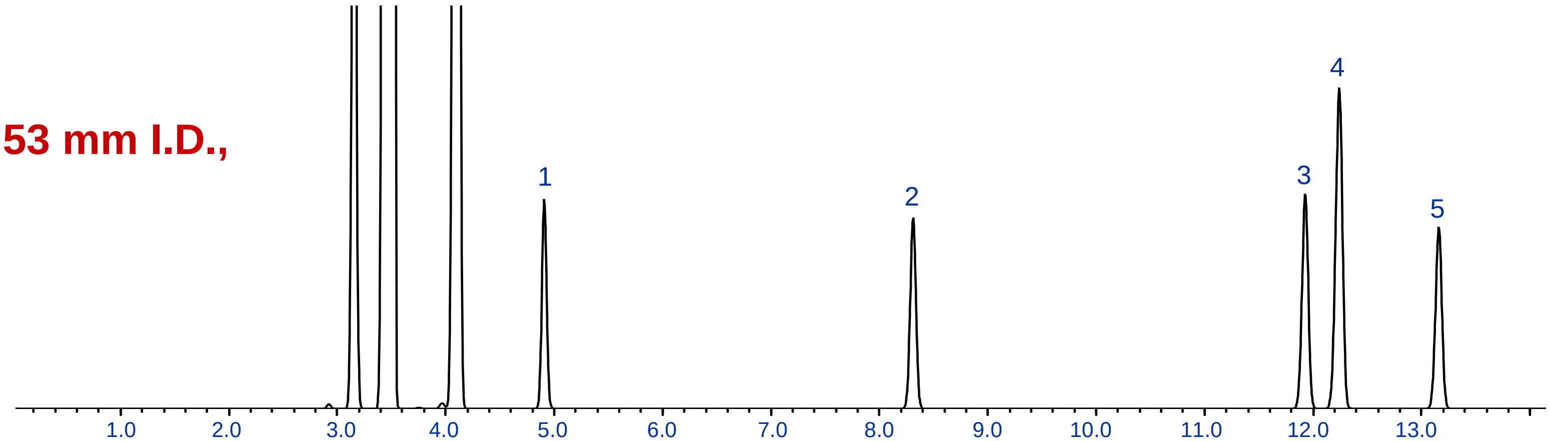
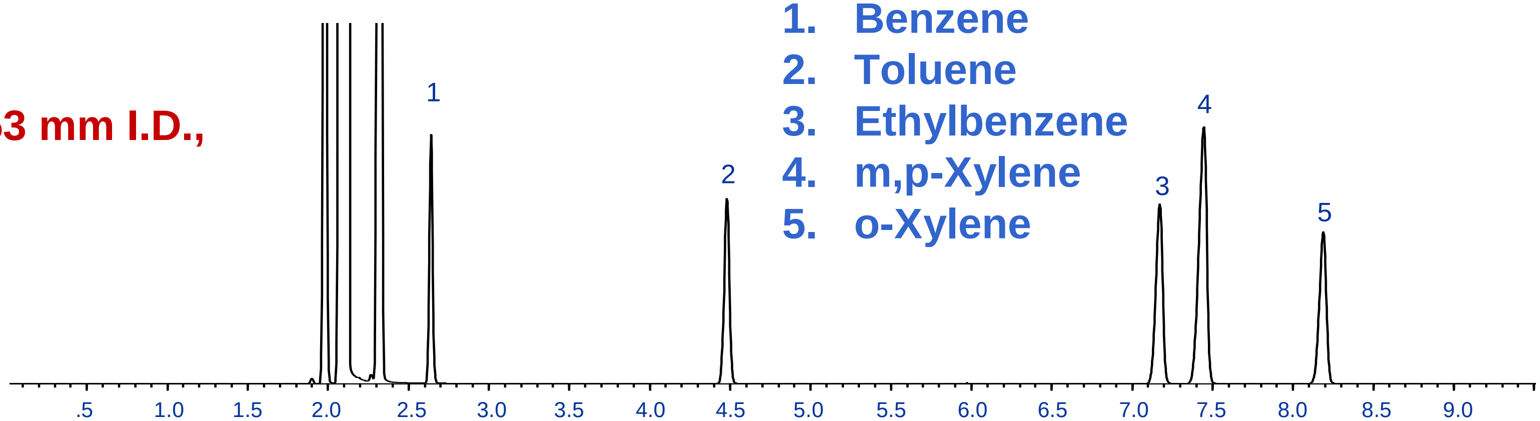
Decreasing Film Thickness

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

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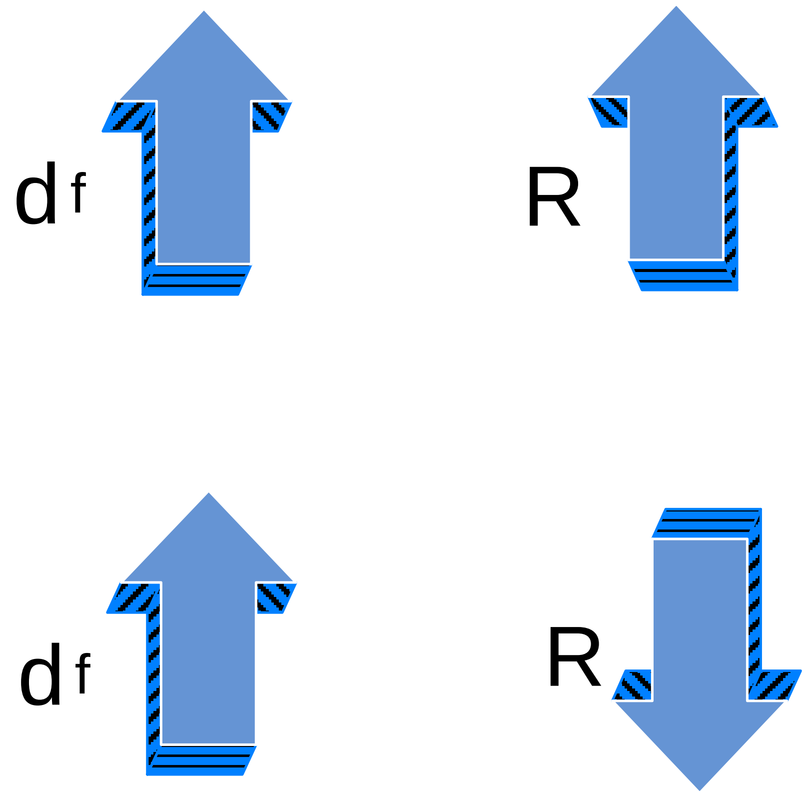
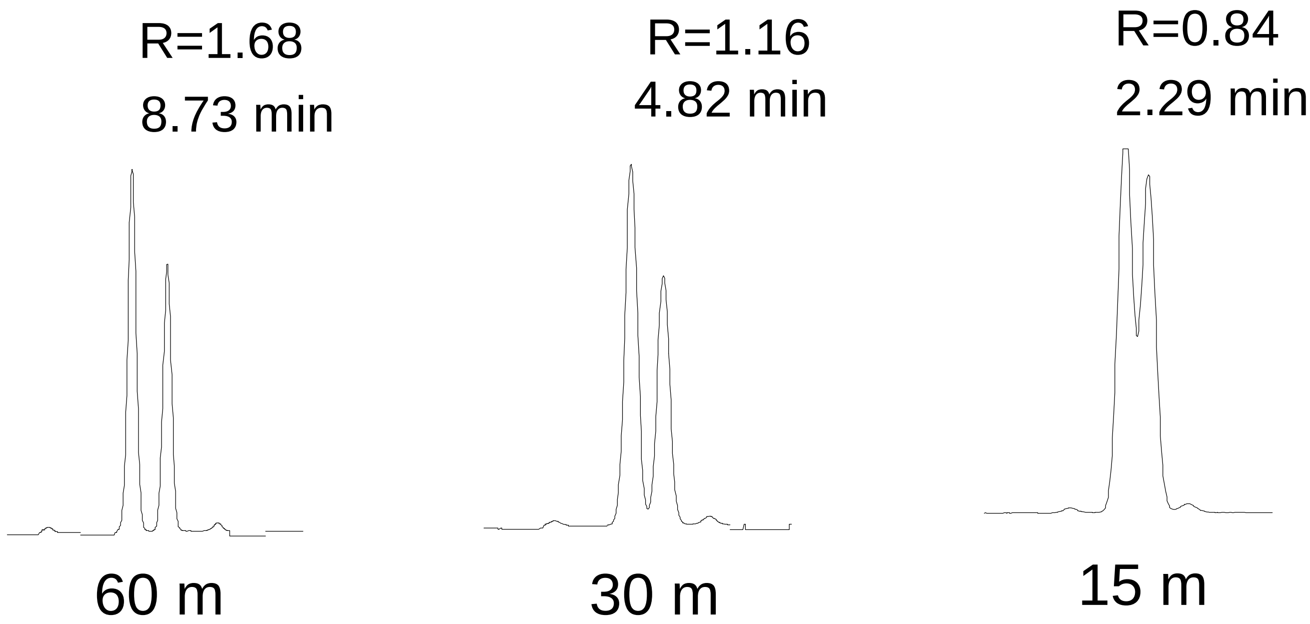
Effect of Film Thickness on Resolution

When solute k < 5

When solute k > 5



Column Length
Resolution and Retention
210°C isothermal

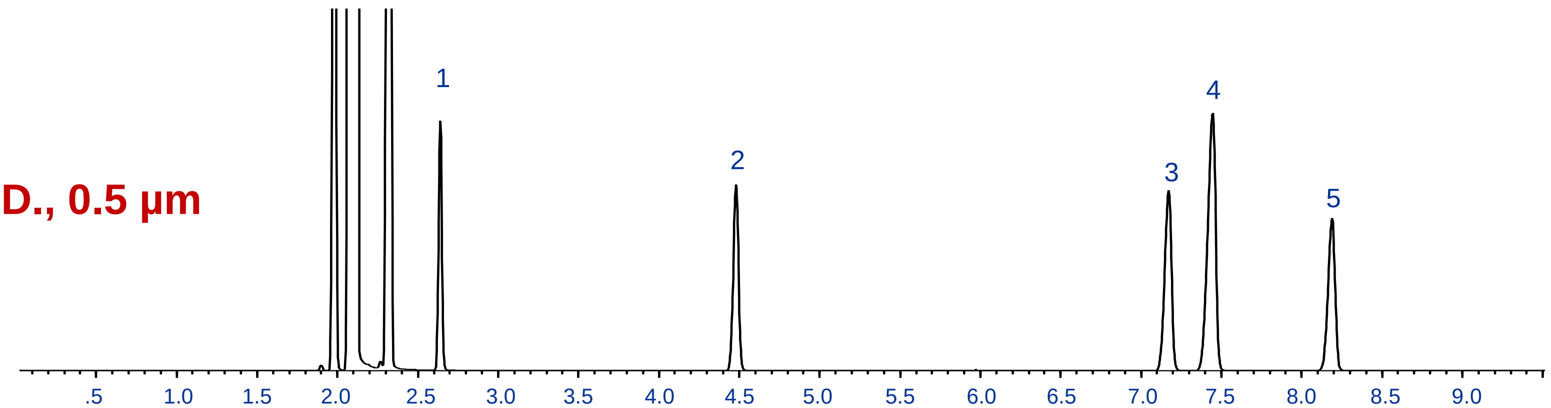


Resolution is proportional to square root of length
Isothermal: Retention is proportional to length
Temperature program: 1/3-1/2 of isothermal values

Decreasing Column Length

DB-5

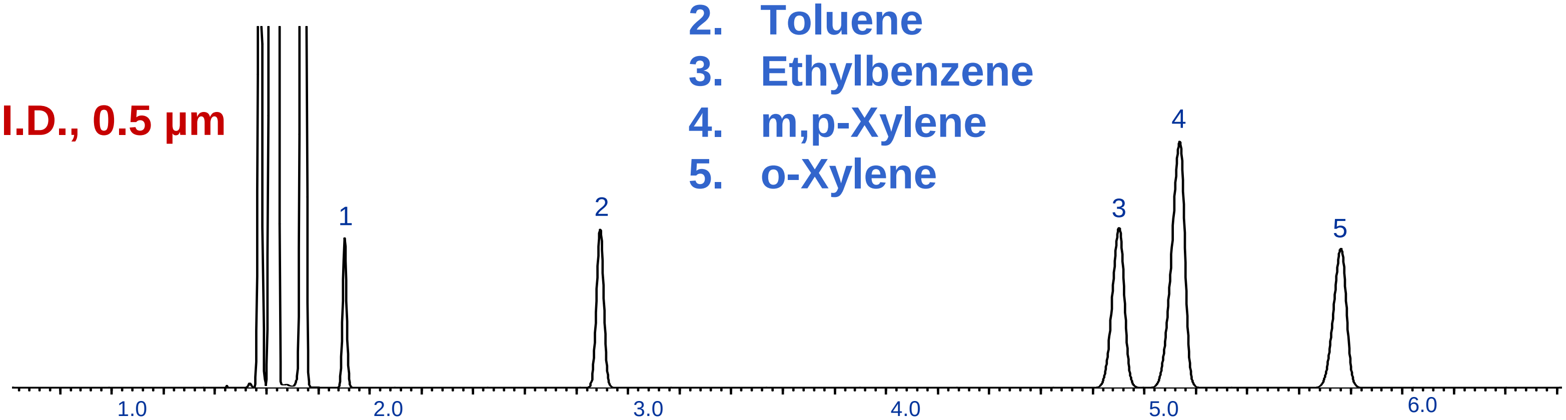
0.53 mm I.D., 0.5 µm



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

DB-5

0.53 mm I.D., 0.5 µm



BTEX
Carrier: Helium, 36 cm/sec at 40°c
Oven : 40°C for 3 min, 5°/min to 100°C

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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

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

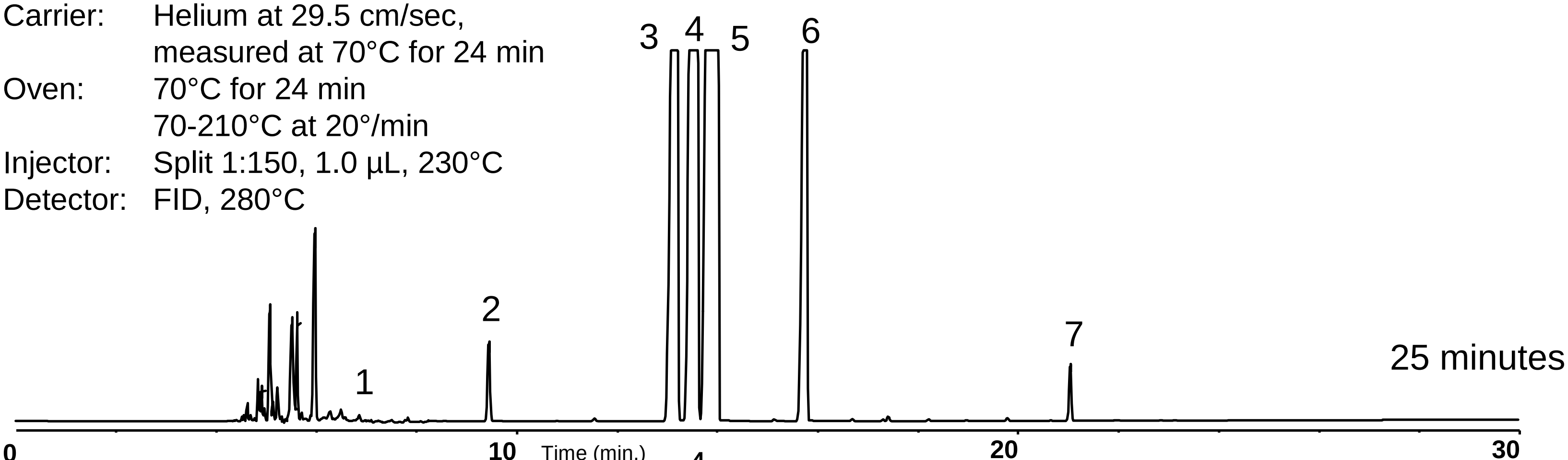
Injection efficiency

Instrument considerations

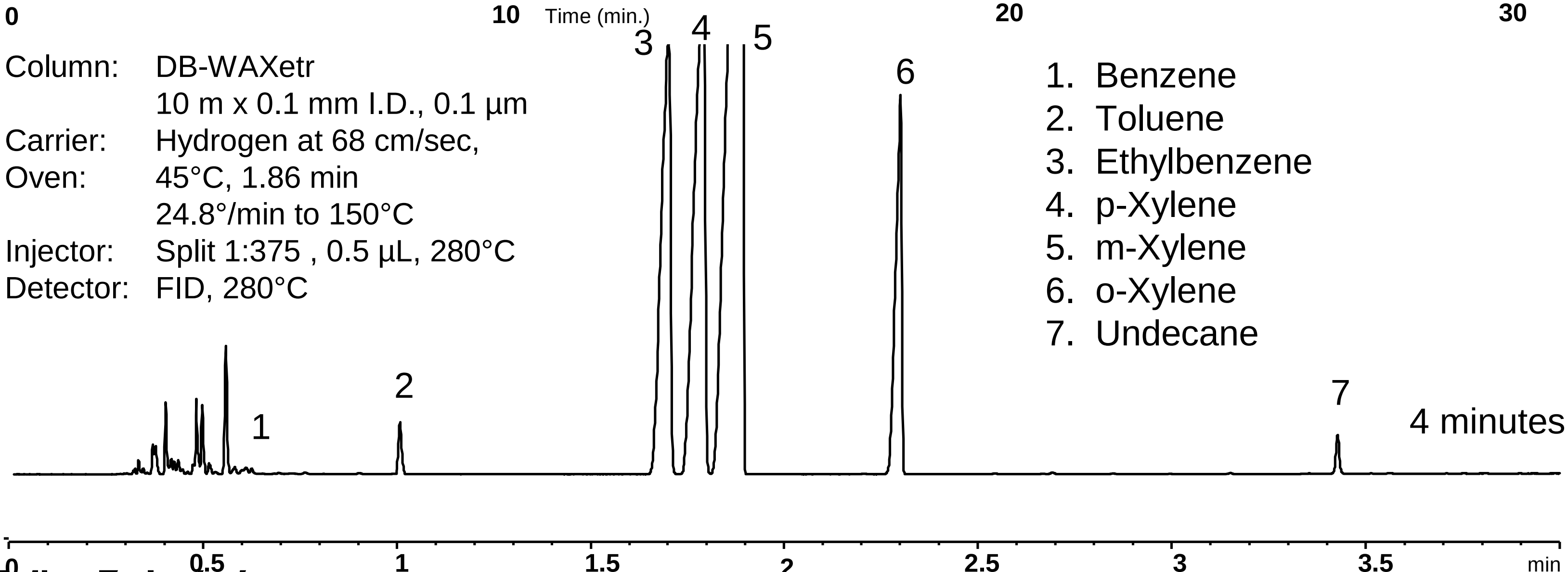
Working Range

Normal vs High Speed Analysis of Xylene (ASTM D2360)

Column: DB-WAXetr
60 m x 0.32 mm I.D., 0.25 µm
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 µL, 230°C
Detector: FID, 280°C



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



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

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K_c and Temperature

K_c of analytes must be maintained

Temperature programs must be accurately scaled to maintain relative analyte retention

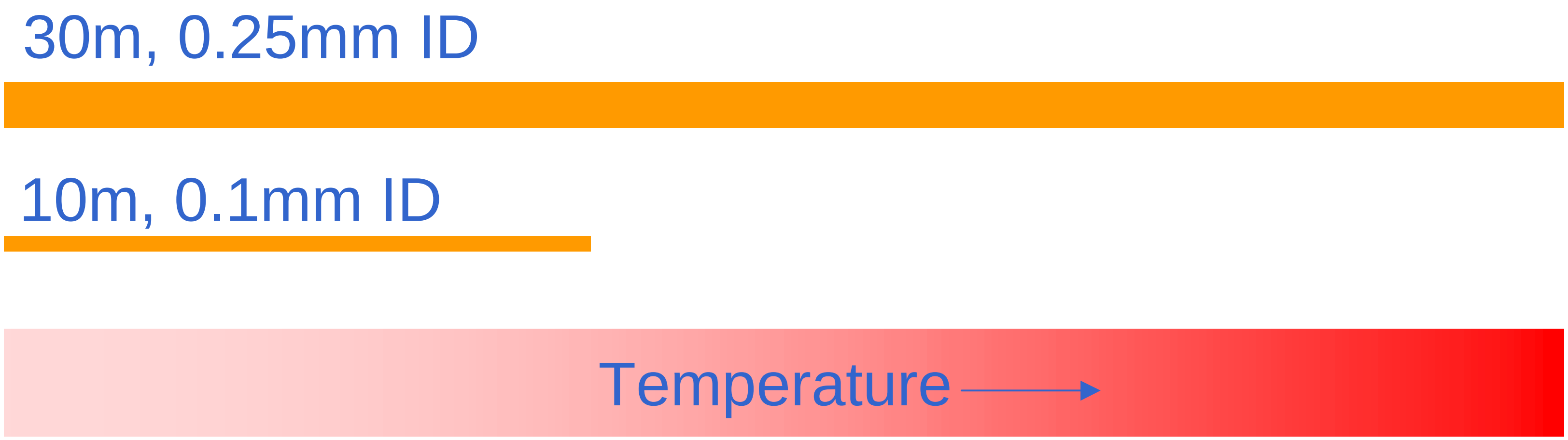
Break Number 2

For Questions and Answers
Press *1 on Your Phone to
Ask a Question

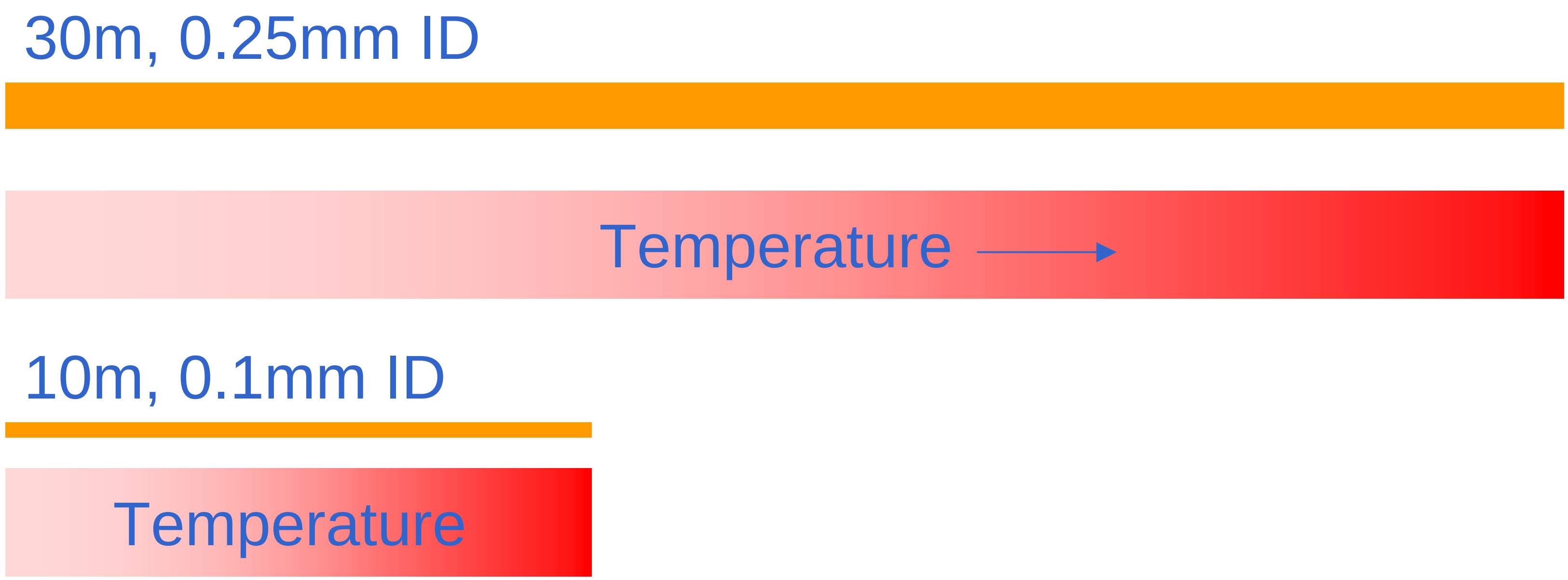
Method Translation Software

- 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 (ºC) per void time in the oven program, which maintains elution order

Temperature Programming



Temperature Programming



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

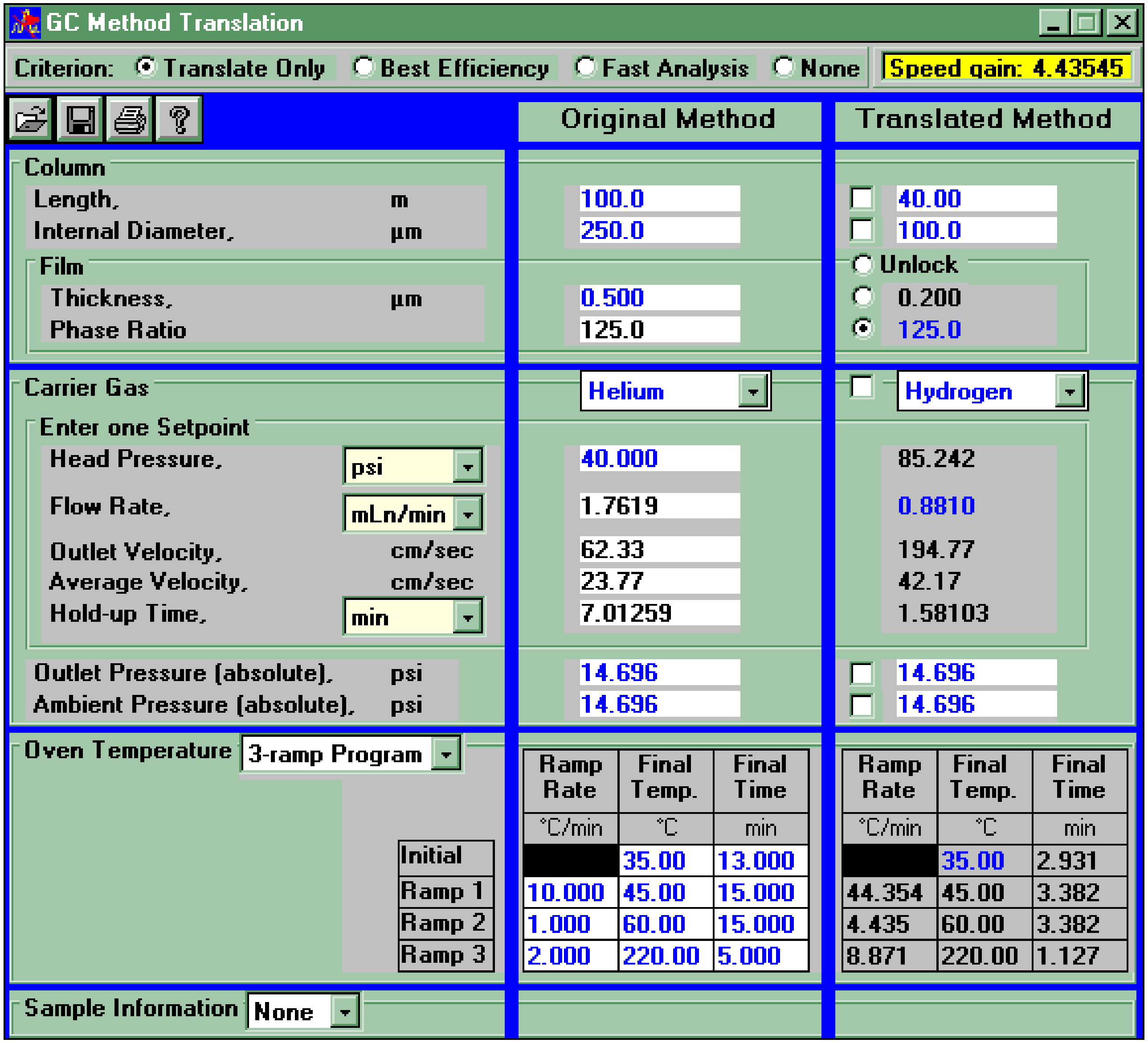
Translates:

- inlet pressure, temp program, hold times

Benefits

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

Method Translation Software



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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

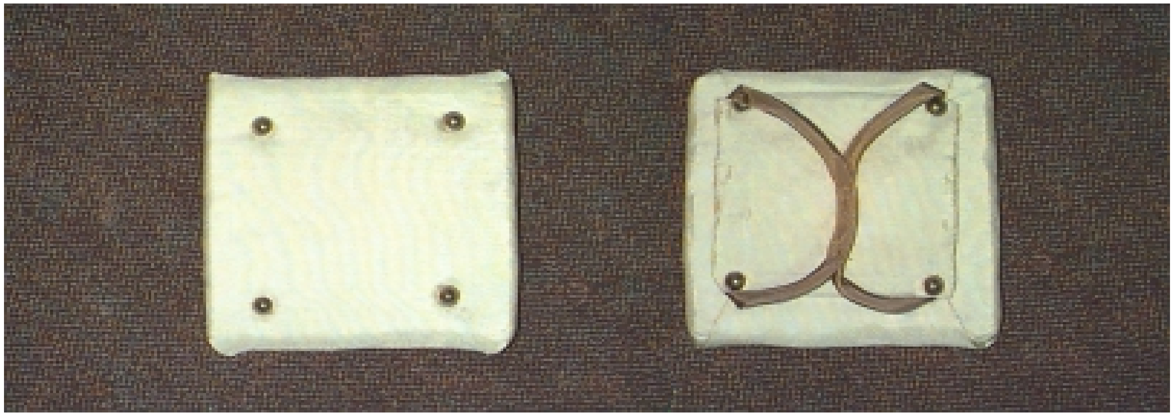
Instrument Considerations

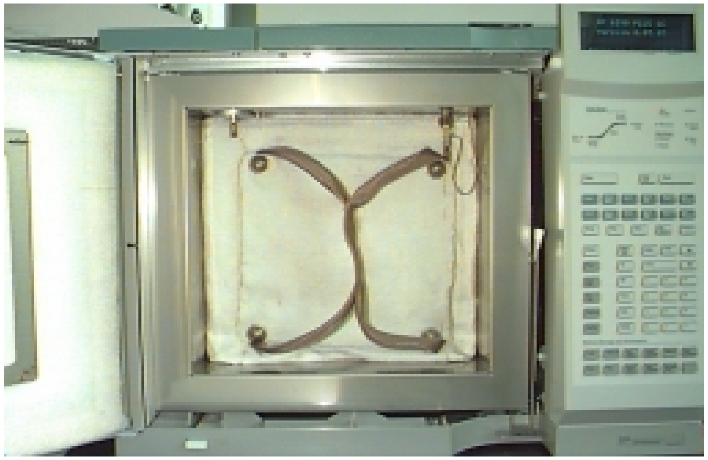
6890/6850 Optimized For Fast GC

- 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 ^{o}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

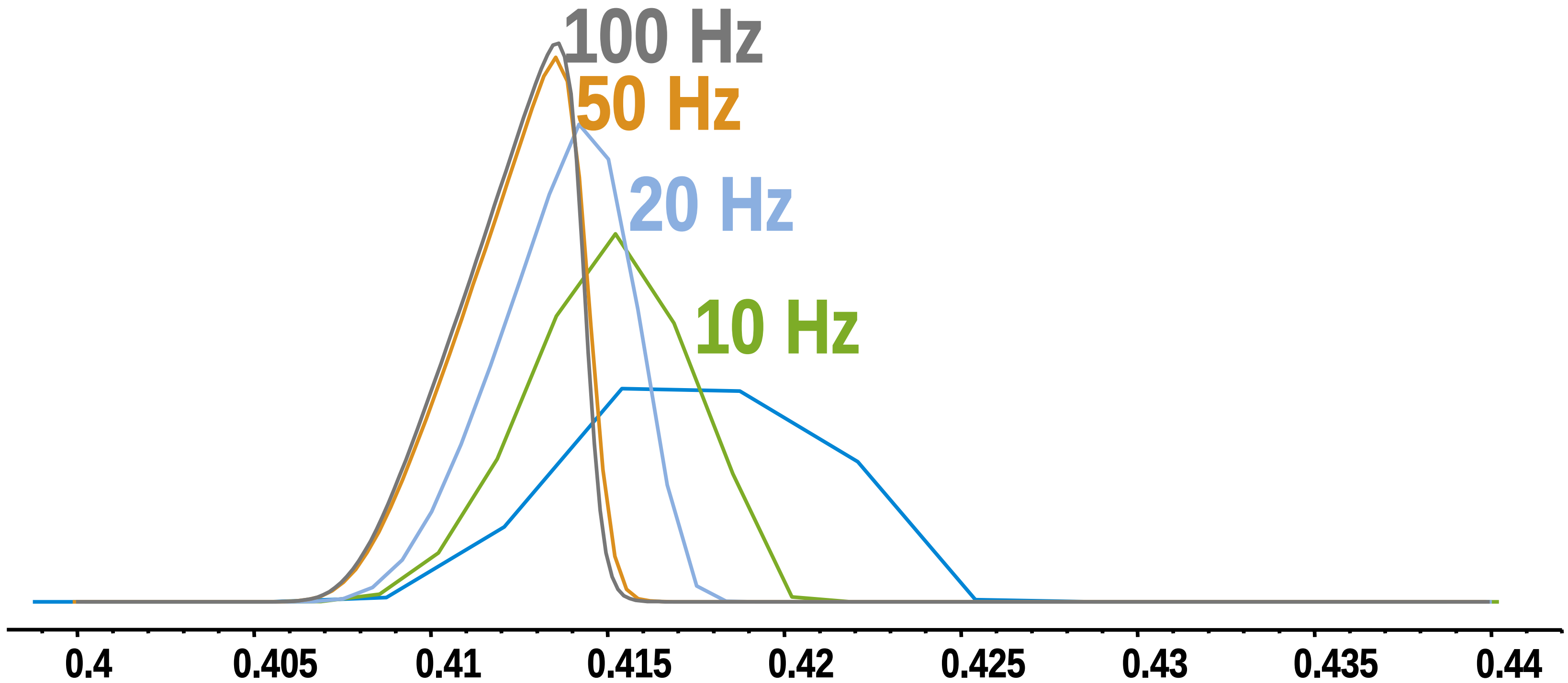
	"Standard"	"Fast"			"Turbo"
Temp. Range (°C)	6890 120V	6890 240V	6890 120V Insert	6850 120V	6890 240V Insert
50 to 70	75	120	120	120	120
70 to 115	45	95	95	95	120
115 to 175	40	65	65	65	110
175 to 300	30	45	45	45	80
300 to 450	20	35	35	35*	65

** 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



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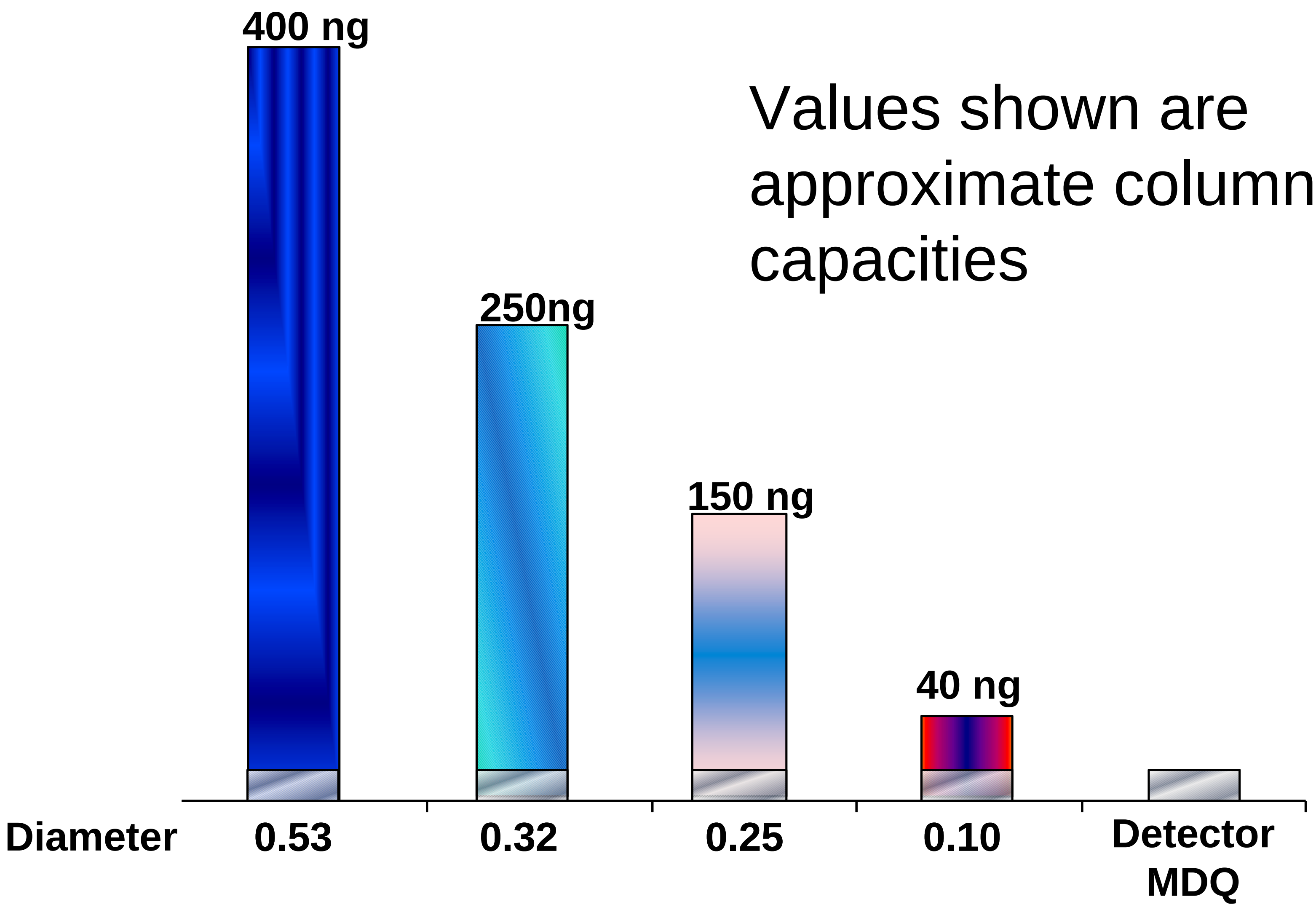
Working Range

$$W = Q_s \div Q_o$$

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

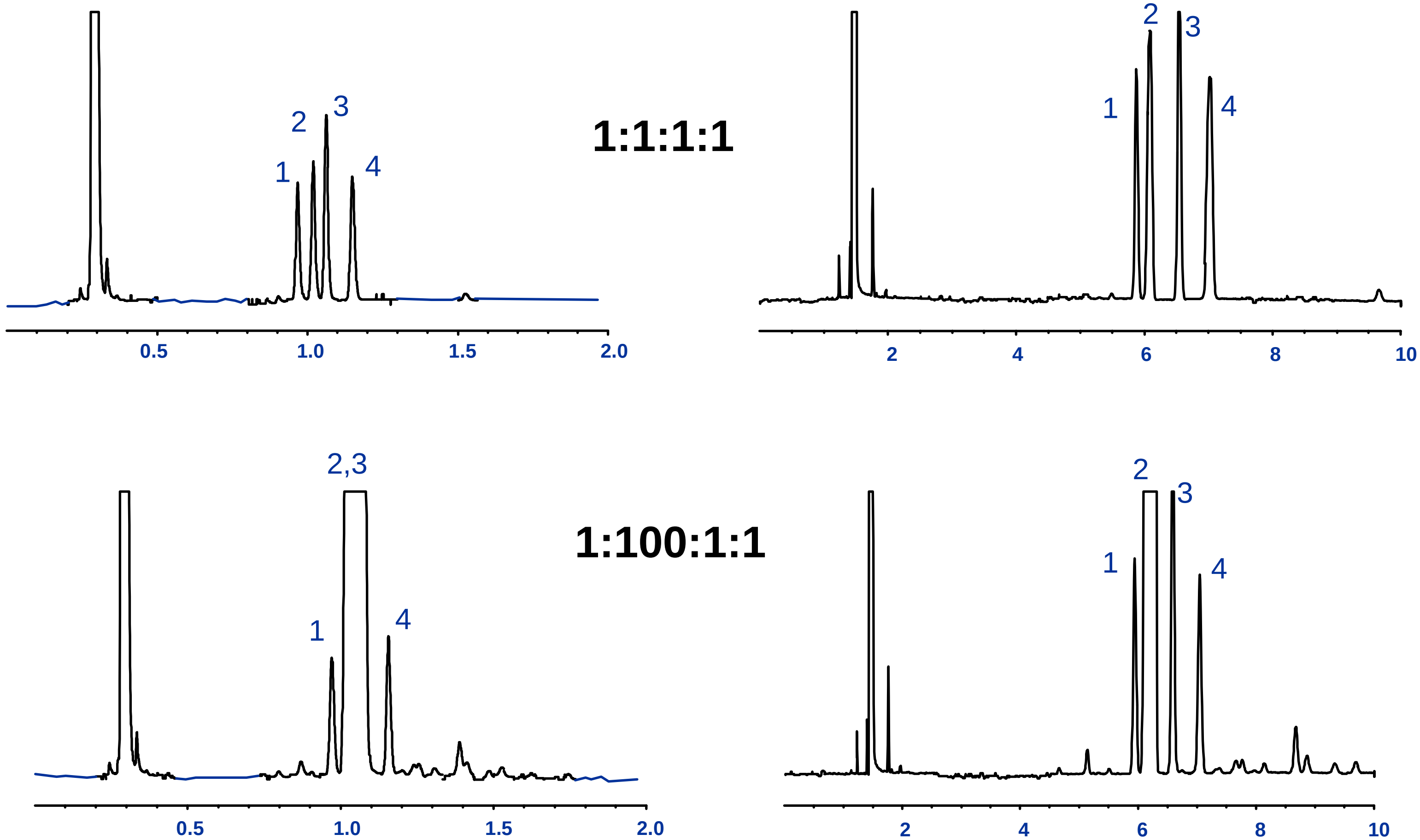
Working Range



Values shown are approximate column capacities

Capacity: Effect on Resolution

10 m x 0.1 mm, 0.2 µm | **30 m x 0.25 mm, 0.5 µm**



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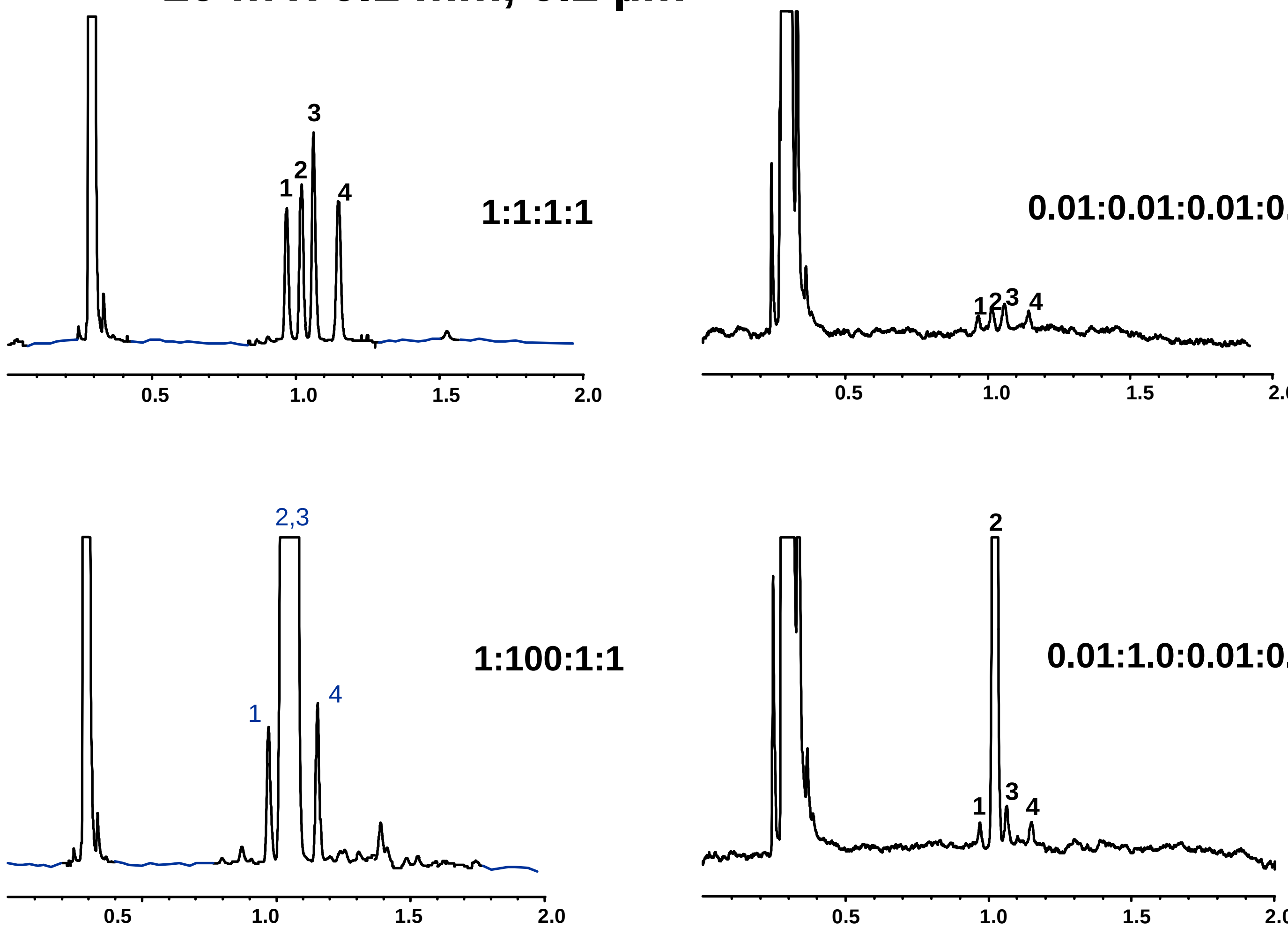
Is Dilution the Solution?

10 m x 0.1 mm, 0.2 µm



Requirements for Microbore High Speed GC Analysis

- Rapid injection speed (100 ms) - split
- High pressure inlet and pressure regulators (150 psi max)
- H_2 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

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What does RTL provide?

Compound retention times become…

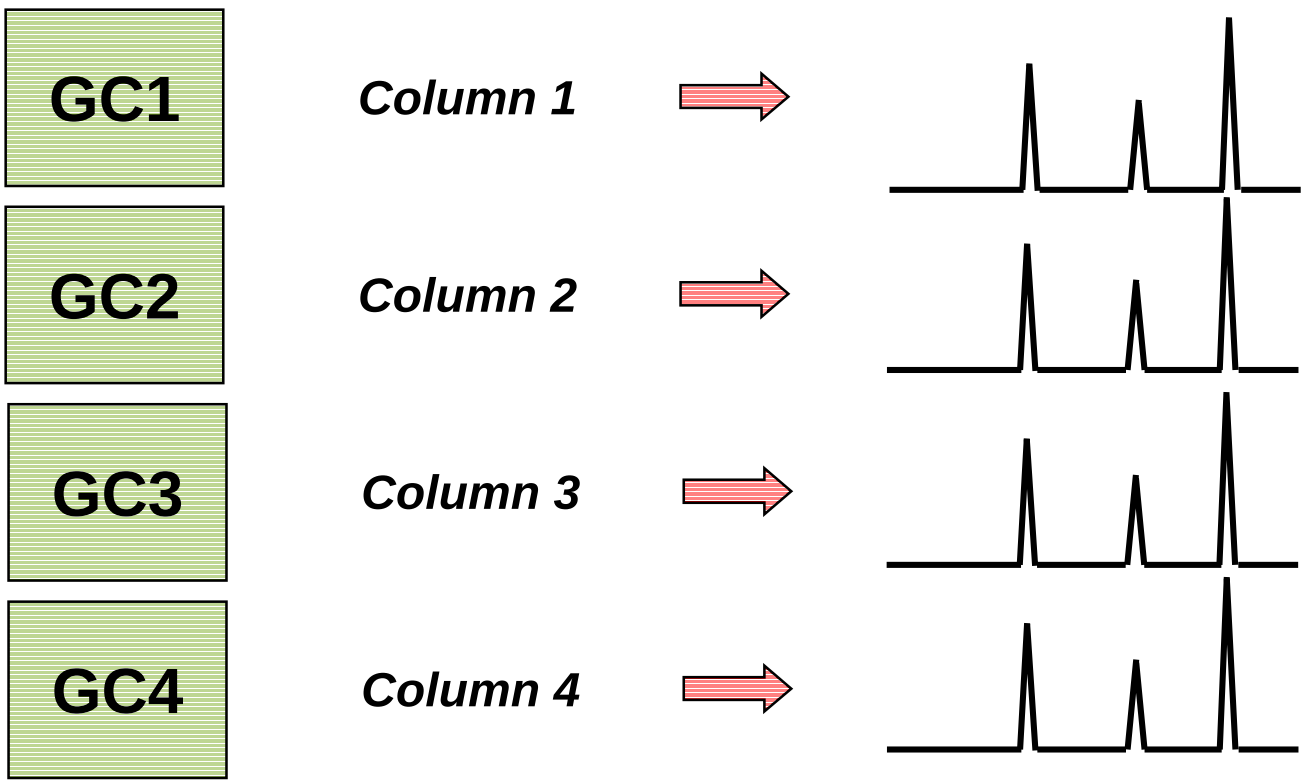
Permanent and Universal

Unchanging RTs	*Shared Methods*
➢Fast & Easy Compound Identification	➢Rapid and Simple Method exchange
➢Better QA/QC	➢Intra- & Inter- laboratory SOPs
➢Simpler SOPs	➢Higher Assuredness / Confidence
➢Proprietary Locked Compound Databases	➢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...

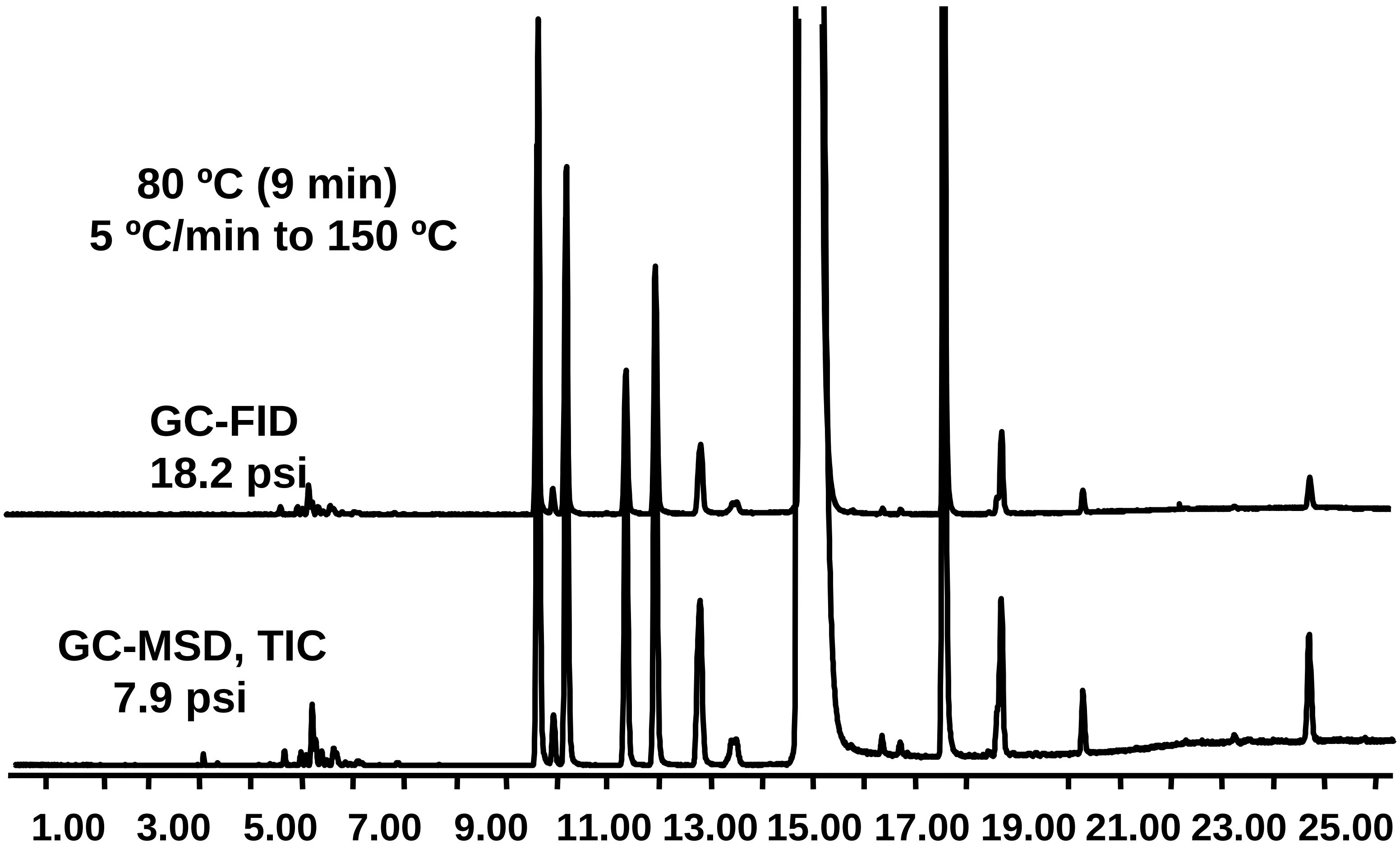


Retention Time Locking

- 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 µm - Ease of use, robustness
  - 320 µm - Good all around compromise
  - 250 µm - Meets MSD flow requirements
  - 100 µm - 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...

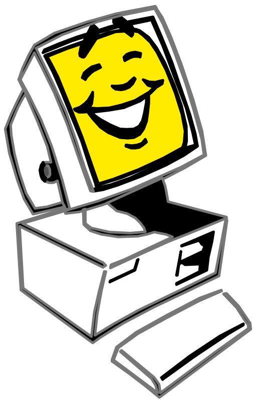
- Designed for use in multiple:
  - instruments
  - configurations (FID, AED, micro-ECD, MSD, PTV, S/S)
  - locations
- Provides known retention times and elution order
  - Easy setup and maintenance of method
  - Easy data analysis and interpretation
- Accurately scalable
  - Adjustable for optimal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

Agilent J&W Technical Support

800-227-9770 (phone: US & Canada)*
302-993-5304 (phone)*
** Select option 4, then option 1*



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