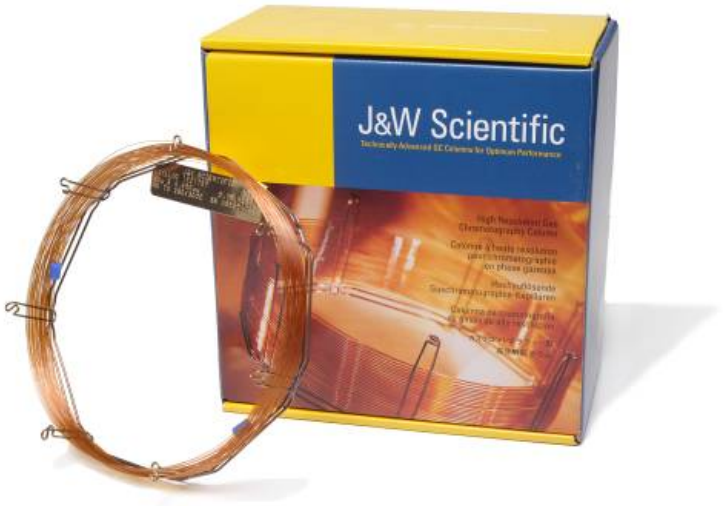
Practical Faster GC Applications with High-Efficiency GC Columns and Method Translation Software



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Presentation outline

Background and terminology

High Efficiency Capillary GC Columns

Utility of Method Translation Software

Faster GC application examples

Summary

Acknowledgments

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

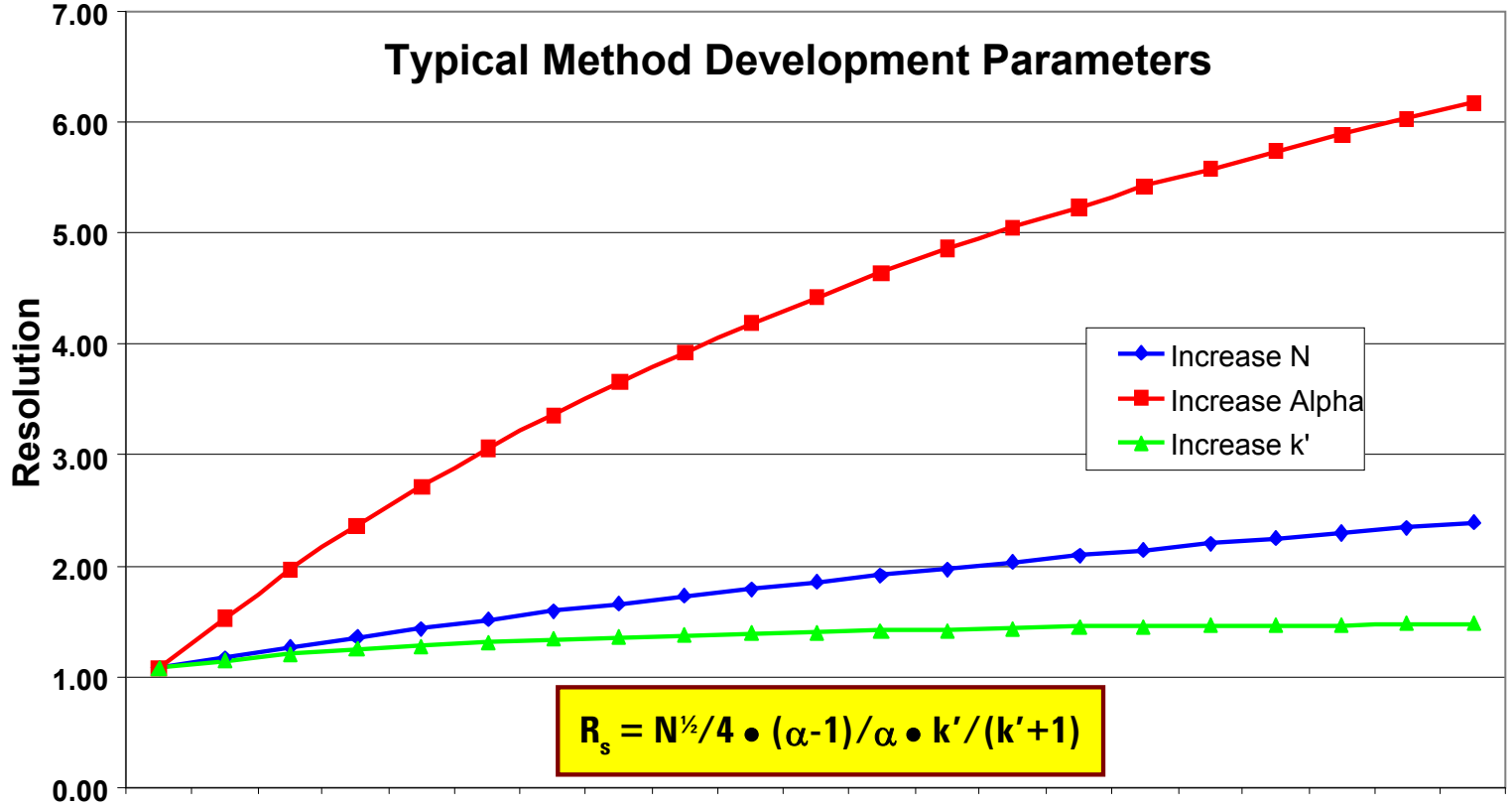
L = Length

r_c = column radius

d_f = film thickness

T = temperature

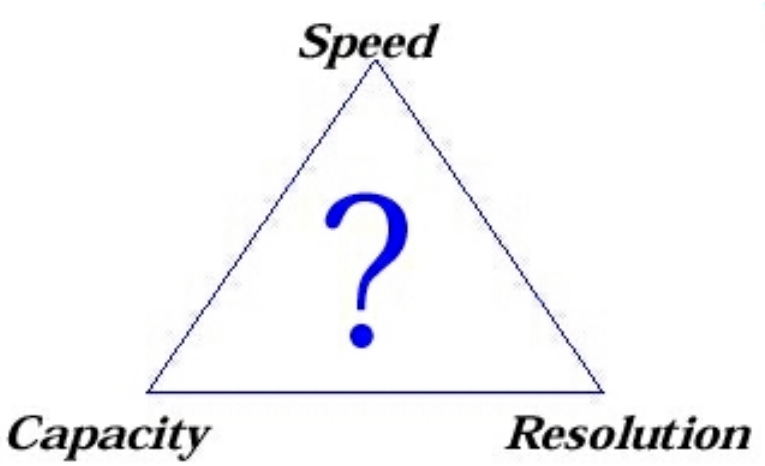
Impact of Efficiency, Selectivity and Retention on Resolution



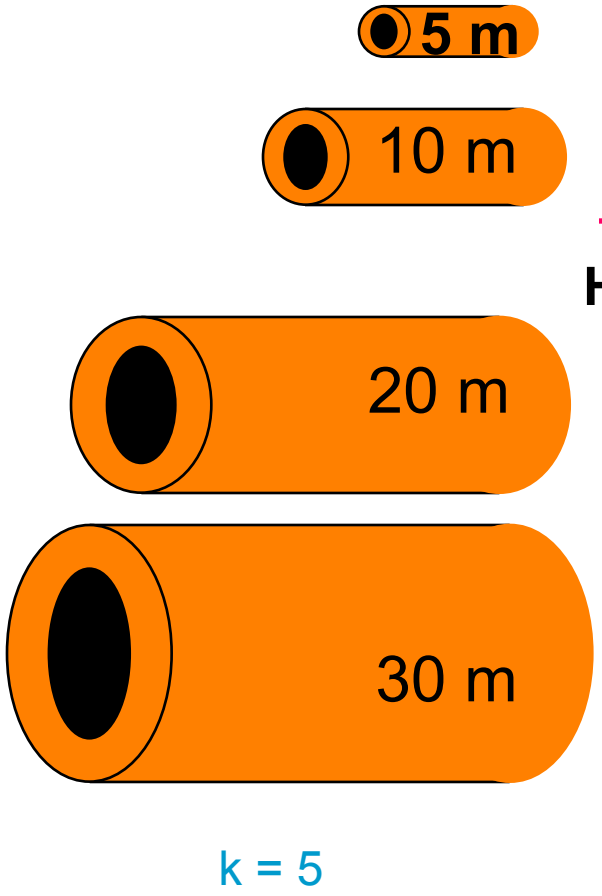
Plates:	5000	10000	15000	20000	25000
Alpha:	1.10	1.35	1.60	1.85	2.1
k':	2.0	4.5	7.0	9.5	12.0

Variables for Speeding Up an Analysis

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



Column Diameter - Theoretical Efficiency



Total Plates	I.D. (mm)	n/m
N ~ 112,000	0.05	23,160
N ~ 112,000	0.10	11,580
High-efficiency GC	0.18	6,660
N ~ 112,000	0.20	5830
	0.25	4630
N ~ 112,000	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

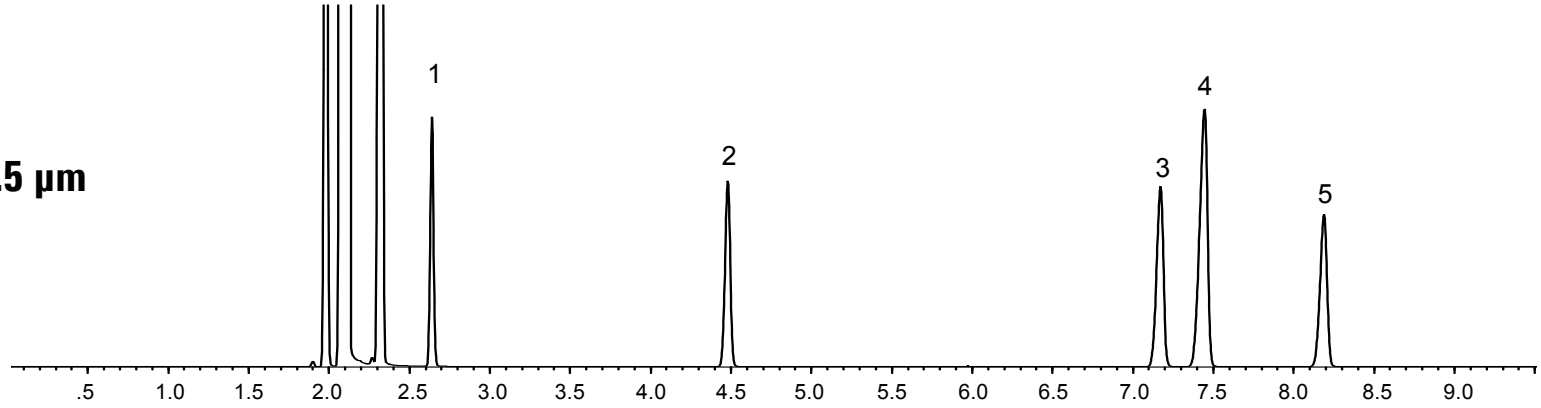
Column Diameter - Inlet Head Pressures (Helium)

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

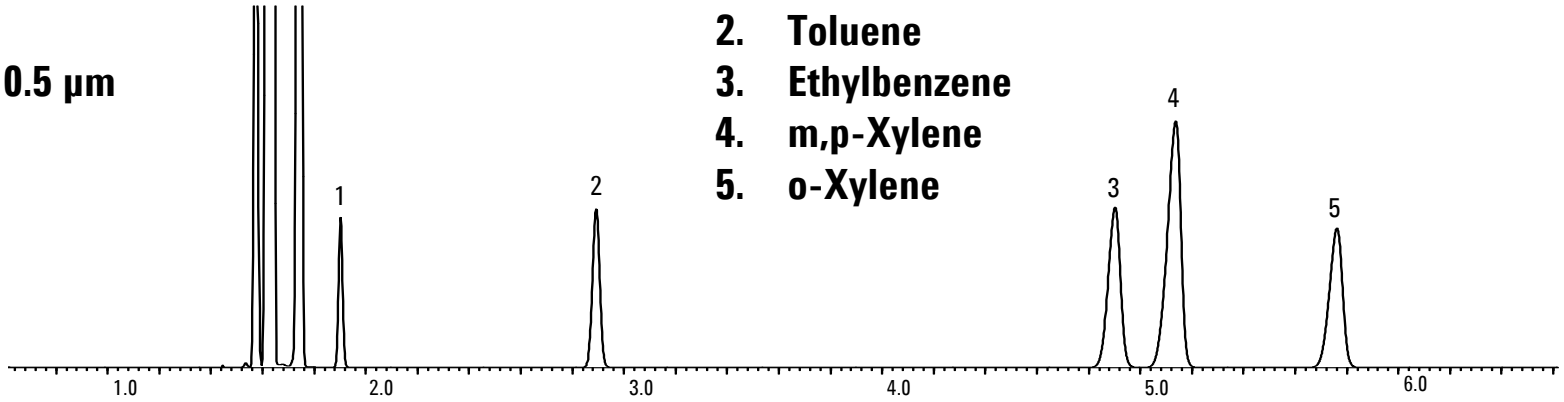
30 meters
Hydrogen pressures x 1/2

DECREASE THE LENGTH

DB-5
30 m
0.53 mm I.D., 0.5 µm



DB-5
15 m
0.53 mm I.D., 0.5 µm

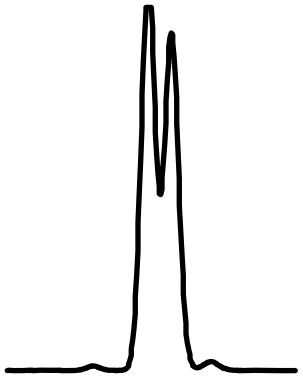


1. **Benzene**
2. **Toluene**
3. **Ethylbenzene**
4. **m,p-Xylene**
5. **o-Xylene**

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

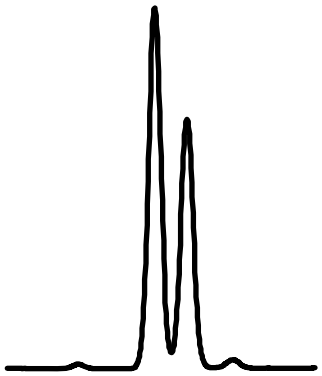
Column Length VS Resolution and Retention: Isothermal

R=0.84
2.29 min



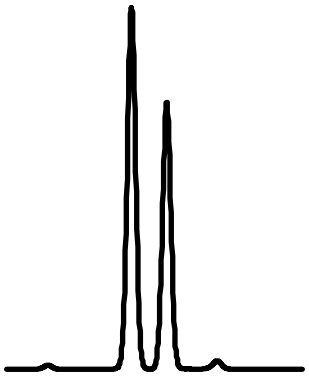
15 m

R=1.16
4.82 min



30 m

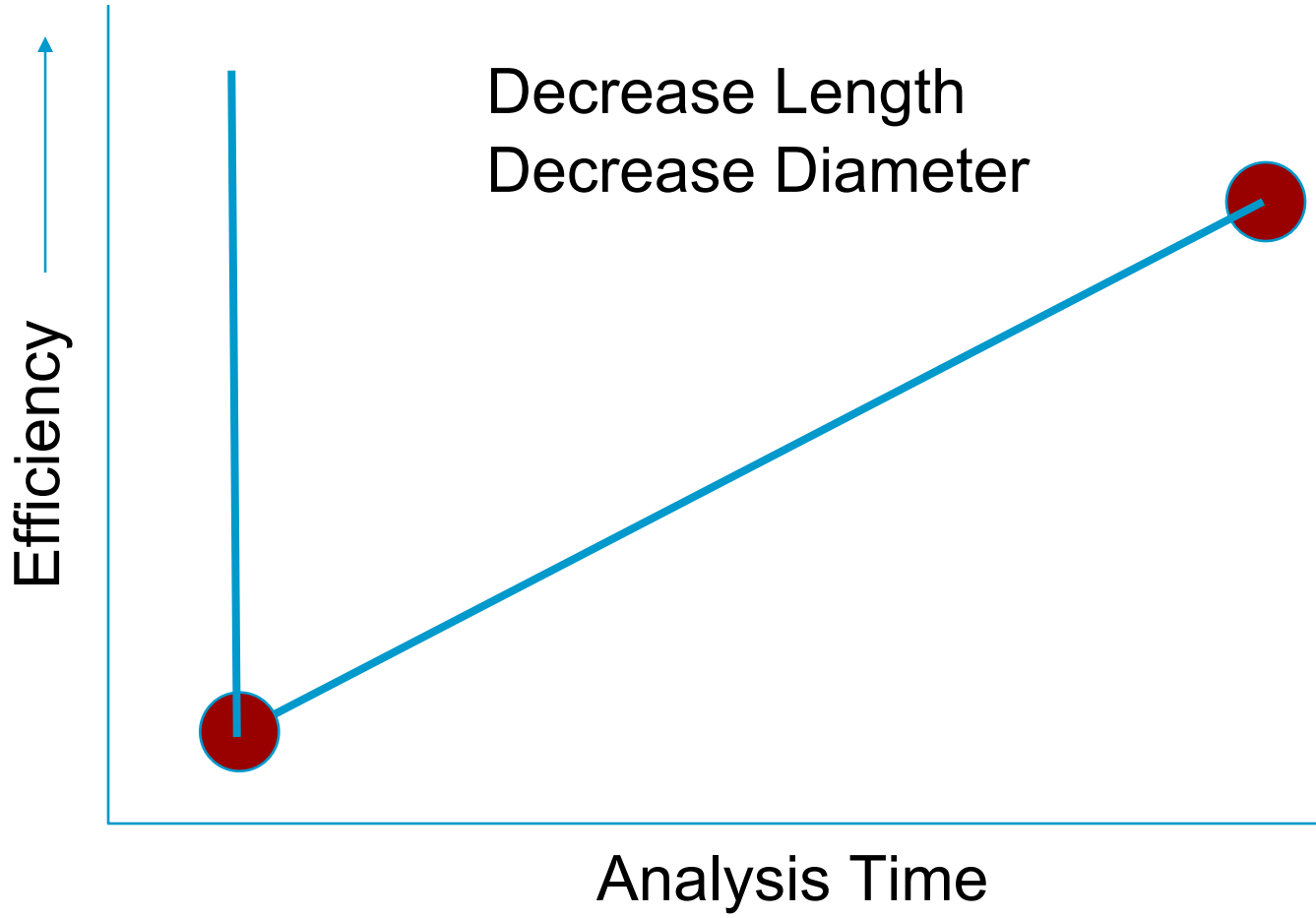
R=1.68
8.73 min



60 m

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

Combining a change in Length with a change in Diameter



PHASE RATIO (β)

$\beta = r/2\ d_f$ where

r = column radius in mm

d_f = film thickness in μm

Column Dimensions	Phase Ratio β
30 m x 0.25 mm x 0.25 μm	250
20 m x 0.18 mm x 0.18 μm	250

Example calculation for 0.32 mm ID column

$\beta = 125\ mm / (2 \times 0.25\ \mu m) = 250$

Carrier Gas Considerations
Best velocity?

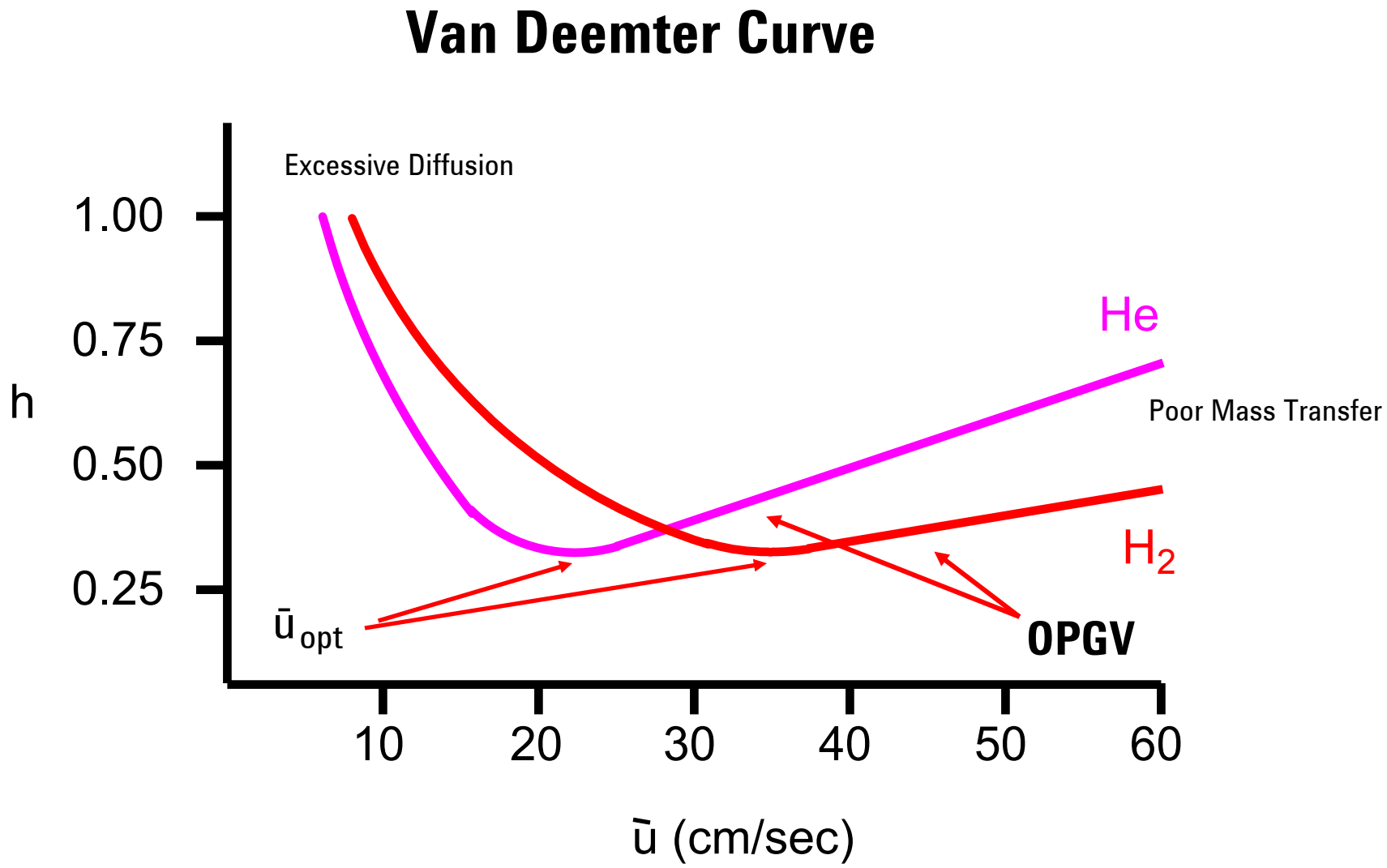
Optimal range of velocities

Too low or high results in loss of resolution

Balance resolution and analysis time

Faster still works? put the hammer down

Carrier Gas Considerations



Easy Options with Method Translation Software

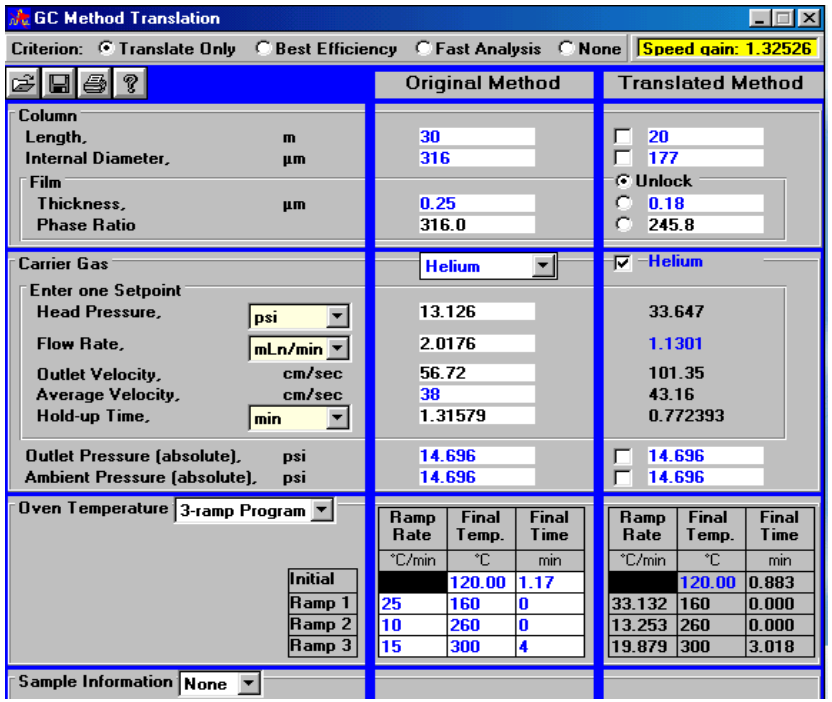
Different Column Dimensions

Same Column & Gas Type but Faster Velocities

Switch He to H_2 Carrier Gas and Try Faster Velocities

Combination of all of the above

Method Translation Software



- Four translation modes
  - Translation only
  - Best efficiency
  - Fast analysis

  } Lock all carrier gas parameters, making the flow rate an independent parameter.

  - None (unlock all carrier gas parameters)

- If translating to a different ID column, phase ratio should be maintained for the most reliable results
- If there are significant differences in phase ratio, Method Translation Software can still be used but elution order should be confirmed.
- Stationary phase of a new column must be the same as the original – the Method Translation Software cannot account for differences in selectivity.

Method Translation Made Simple

- Agilent Method Translation Software
  - A **FREE, stand-alone** software running on a PC
  - Download at: http://www.chem.agilent.com/cag/servsup/usersoft/files/GCTS.htm
  - Method Translation allows easy “tweaking” of method parameters to speed up run time.
  - It preserves relative elution order by properly scaling gas velocity and temperature program to maintain equivalent elution pattern.

- Can Change
  - column dimensions (i.e. ID, column length, film thickness, or phase ratio)
  - carrier gas type (i.e. hydrogen, helium, nitrogen)
  - pneumatic set points (i.e. flow rates, head pressure, or holdup time).
  - The software then generate a translated method (new temperature program), which will attempt to maintain the resolution and selectivity of the original method.

- Benefits
  - reduces method development time
  - helps assess if GC method is compatible with hardware

High-Efficiency GC Columns – Part Numbers

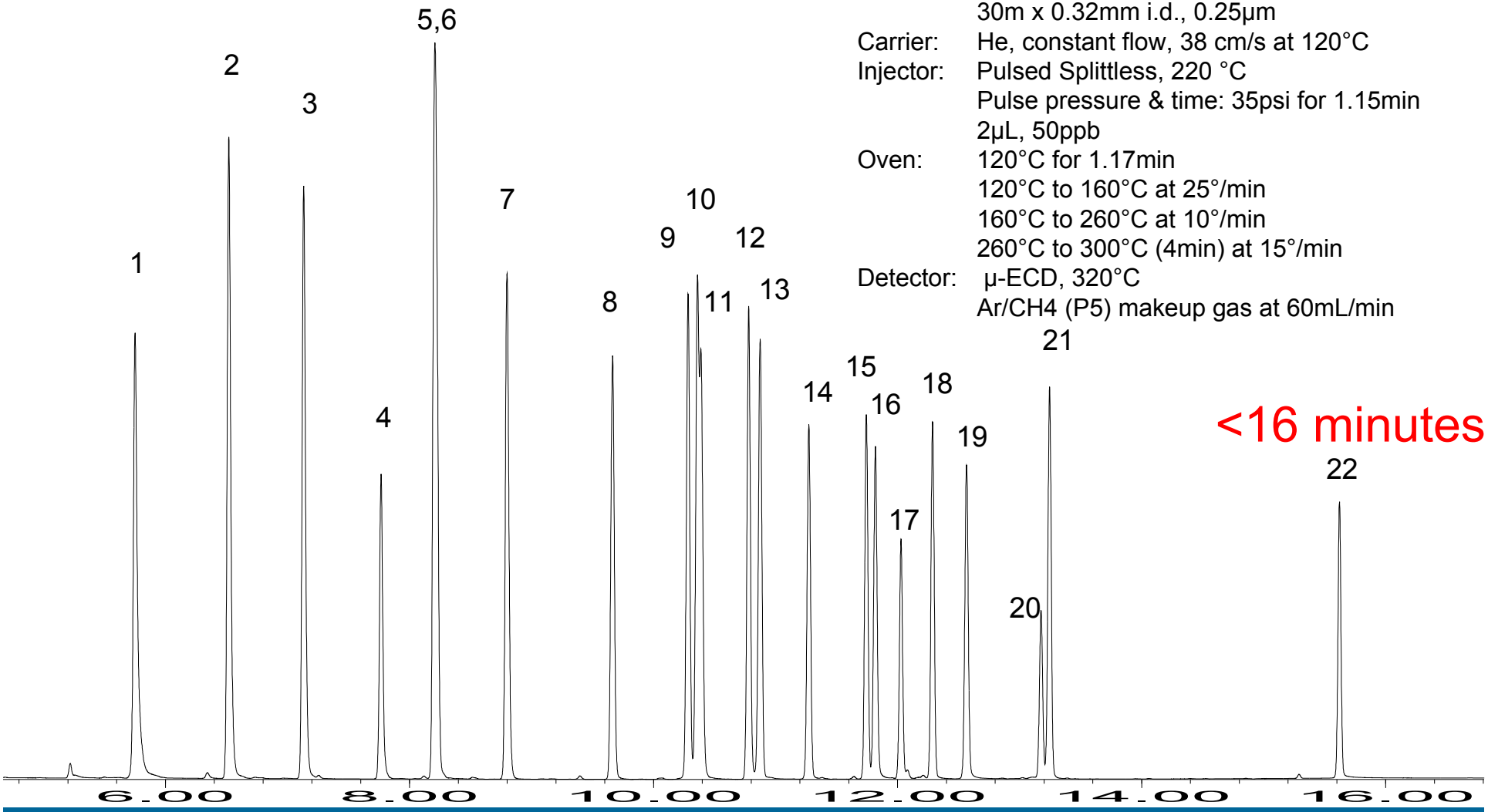
65 columns available with **43 7” cage** columns, and **22 5” cage** columns

Stationary Phase	Part Number (7" cage)	I.D. (mm)	Length (m)	Film Thickness (µm)	Part Number (5" cage)
DB-1	121-1012	0.18	10	0.18	121-1012E
	121-1013	0.18	10	0.40	121-1013E
	121-101A	0.18	10	0.20	
	121-1022	0.18	20	0.18	121-1022E
	121-1023	0.18	20	0.40	
	121-1043	0.18	40	0.40	121-1043E
HP-1	19091Z-577	0.18	20	0.18	19091Z-577E
DB-1ms	121-0122	0.18	20	0.18	121-0122E
HP-1ms	19091S-677	0.18	20	0.18	19091S-677E
DB-5	121-5012	0.18	10	0.18	121-5012E
	121-5013	0.18	10	0.40	
	121-5022	0.18	20	0.18	121-5022E
	121-5023	0.18	20	0.40	121-5023E
	121-5042	0.18	40	0.18	
HP-5	19091J-577	0.18	20	0.18	19091J-577E
DB-5ms	121-5522	0.18	20	0.18	121-5522E
	121-5542	0.18	40	0.18	
	121-5523	0.18	20	0.36	
HP-5ms	19091S-577	0.18	20	0.18	19091S-577E
DB-XLB	121-1222	0.18	20	0.18	121-1222E
	121-1232	0.18	30	0.18	

Stationary Phase	Part Number (7" cage)	I.D. (mm)	Length (m)	Film Thickness (µm)	Part Number (5" cage)
DB-35ms	121-3822	0.18	20	0.18	121-3822E
DB-17	121-1722	0.18	20	0.18	
	121-1723	0.18	20	0.30	
DB-17ms	121-4722	0.18	20	0.18	121-4722E
HP-50+	19091L-577	0.18	20	0.18	
DB-23	121-2323	0.18	20	0.20	
DB-225	121-2223	0.18	20	0.20	
DB-624	121-1324	0.18	20	1.00	121-1224E
DB-1301	121-1313	0.18	10	0.40	
DB-1701	121-0713	0.18	10	0.40	
	121-0722	0.18	20	0.18	
DB-WAX	121-7012	0.18	10	0.18	
	121-7022	0.18	20	0.18	121-7022E
	121-7023	0.18	20	0.30	121-7023E
	121-7042	0.18	40	0.18	121-7042E
	121-7043	0.18	40	0.30	
HP-INNOWax	19091N-577	0.18	20	0.18	19091N-577E
DB-5.625	121-5621	0.18	20	0.18	
	121-5622	0.18	20	0.36	
DB-VRX	121-1524	0.18	20	1.00	
	121-1544	0.18	40	1.00	121-1544E
DB-608	121-6822	0.18	20	0.18	

CLP-Pesticides - Original "Improved" Method
0.32mm I.D., Helium Carrier Gas

Column:	DB-XLB
	30m x 0.32mm i.d., 0.25µm
Carrier:	He, constant flow, 38 cm/s at 120°C
Injector:	Pulsed Splittless, 220 °C
	Pulse pressure & time: 35psi for 1.15min
	2µL, 50ppb
Oven:	120°C for 1.17min
	120°C to 160°C at 25°/min
	160°C to 260°C at 10°/min
	260°C to 300°C (4min) at 15°/min
Detector:	µ-ECD, 320°C
	Ar/CH4 (P5) makeup gas at 60mL/min



<16 minutes

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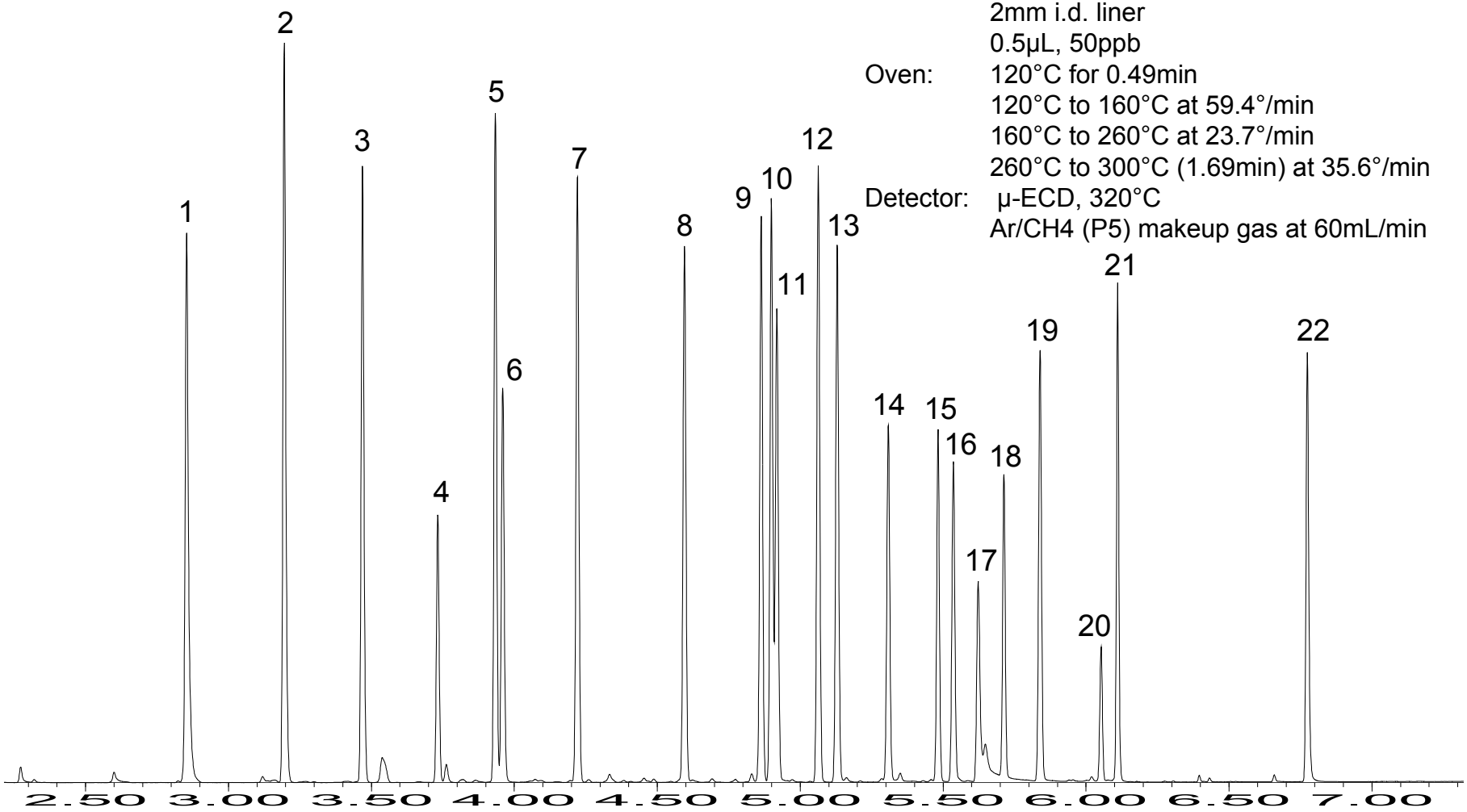
Final Method Used at EPA

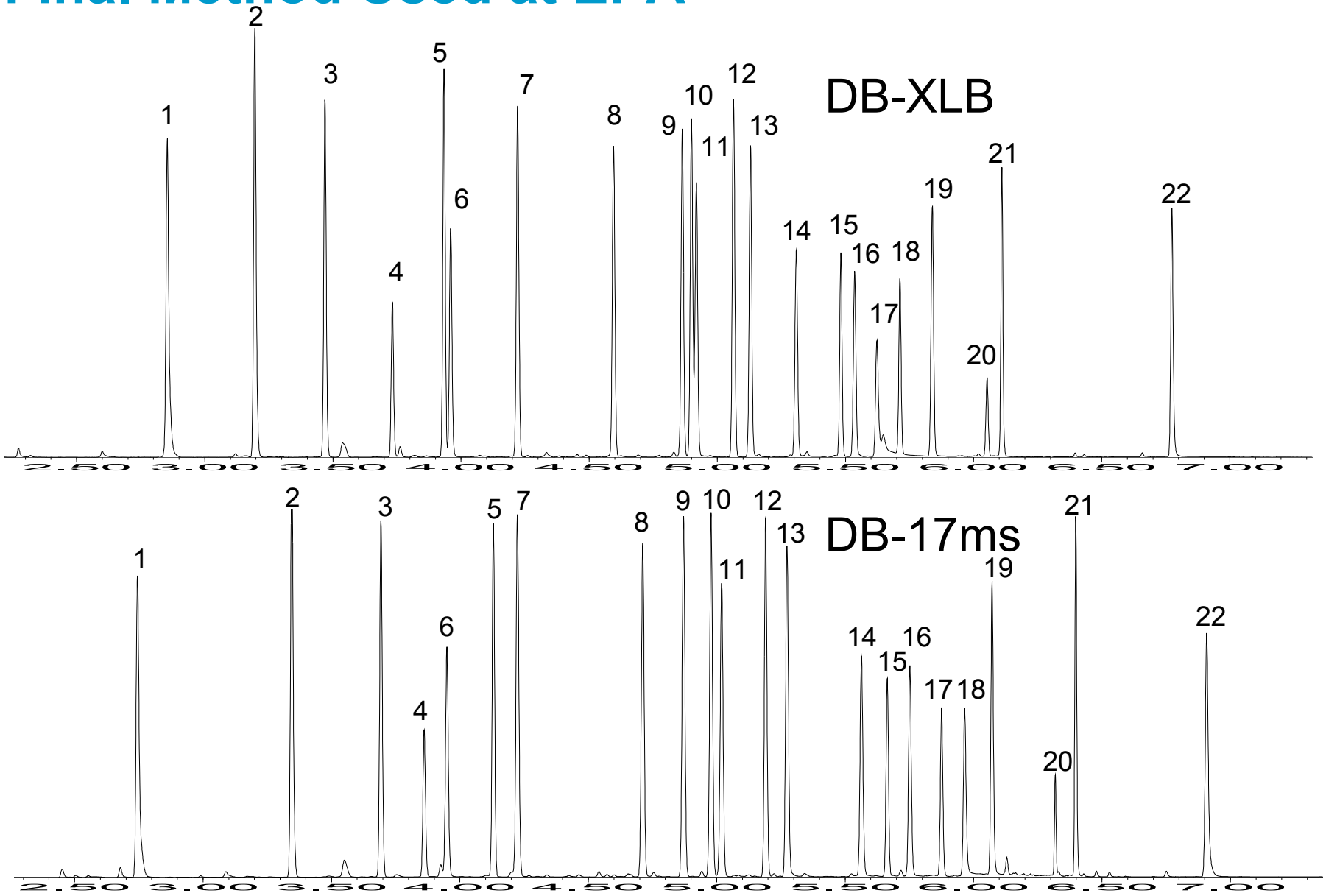
Column: DB-XLB
20m x 0.18mm i.d., 0.18µm
Carrier: H2, constant flow, 77.3cm/s at 120°C
Injector: Pulsed Splittless, 220 °C
Pulse pressure & time: 35psi for 0.5min
Flow ramp at 6.25min of 99mL/min^2 to 3mL/min
2mm i.d. liner
0.5µL, 50ppb
Oven: 120°C for 0.49min
120°C to 160°C at 59.4°/min
160°C to 260°C at 23.7°/min
260°C to 300°C (1.69min) at 35.6°/min
Detector: µ-ECD, 320°C
Ar/CH4 (P5) makeup gas at 60mL/min



CLP Pesticide Standard Key List

1. TCMX
2. Alpha BHC
3. Gamma BHC
4. Beta BHC
5. Delta BHC
6. Heptachlor
7. Aldrin
8. Heptachlor Epoxide
9. Gamma Chlordane
10. Alpha Chlordane
11. Endosulfan I
12. 4,4’ DDE
13. Dieldrin
14. Endrin
15. 4,4’ DDD
16. Endosulfan II
17. 4,4’ DDT
18. Endrin Aldehyde
19. Endosulfan Sulfate
20. Methoxychlor
21. Endrin Ketone
22. DCB

Final Method Used at EPA



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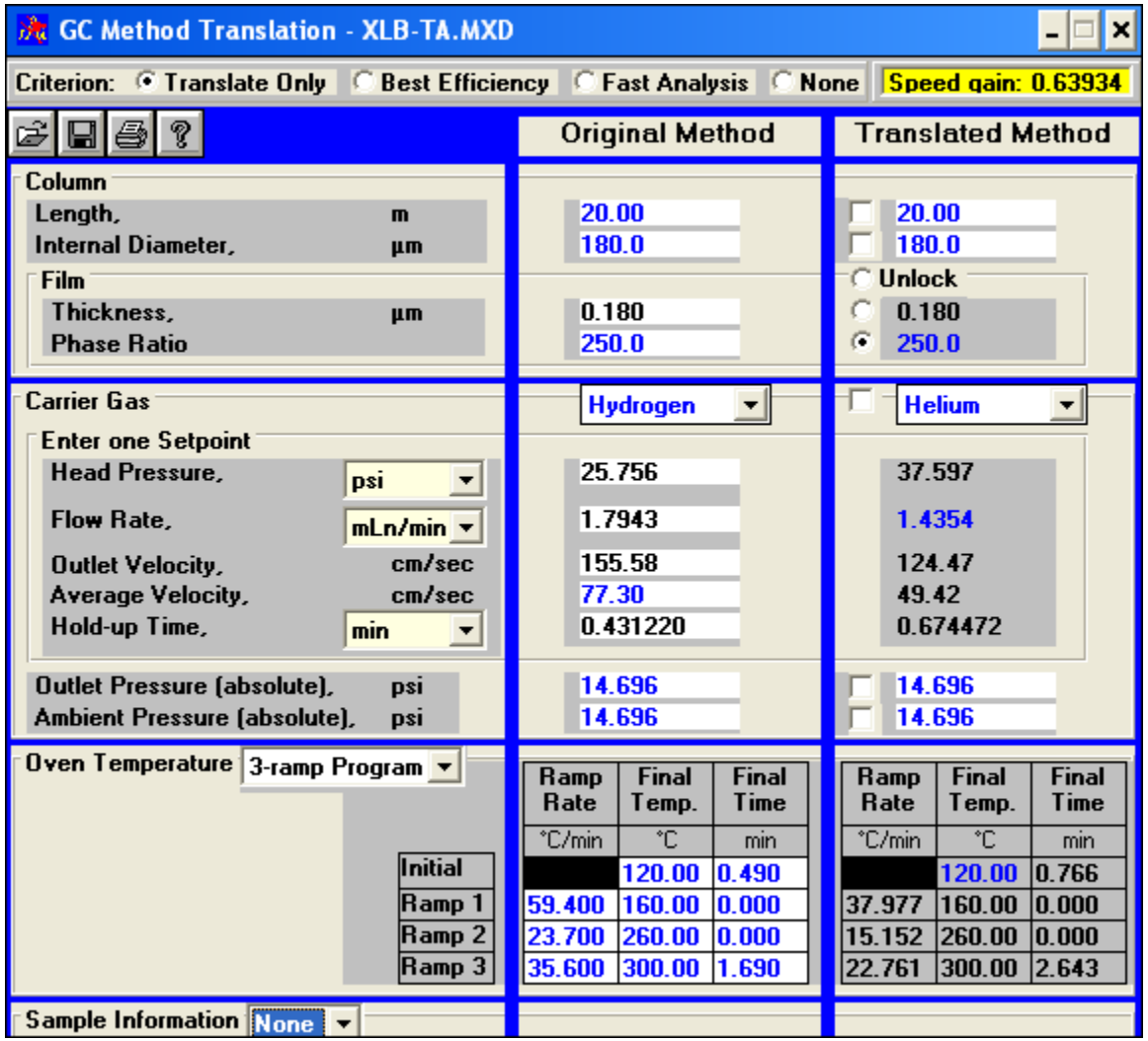
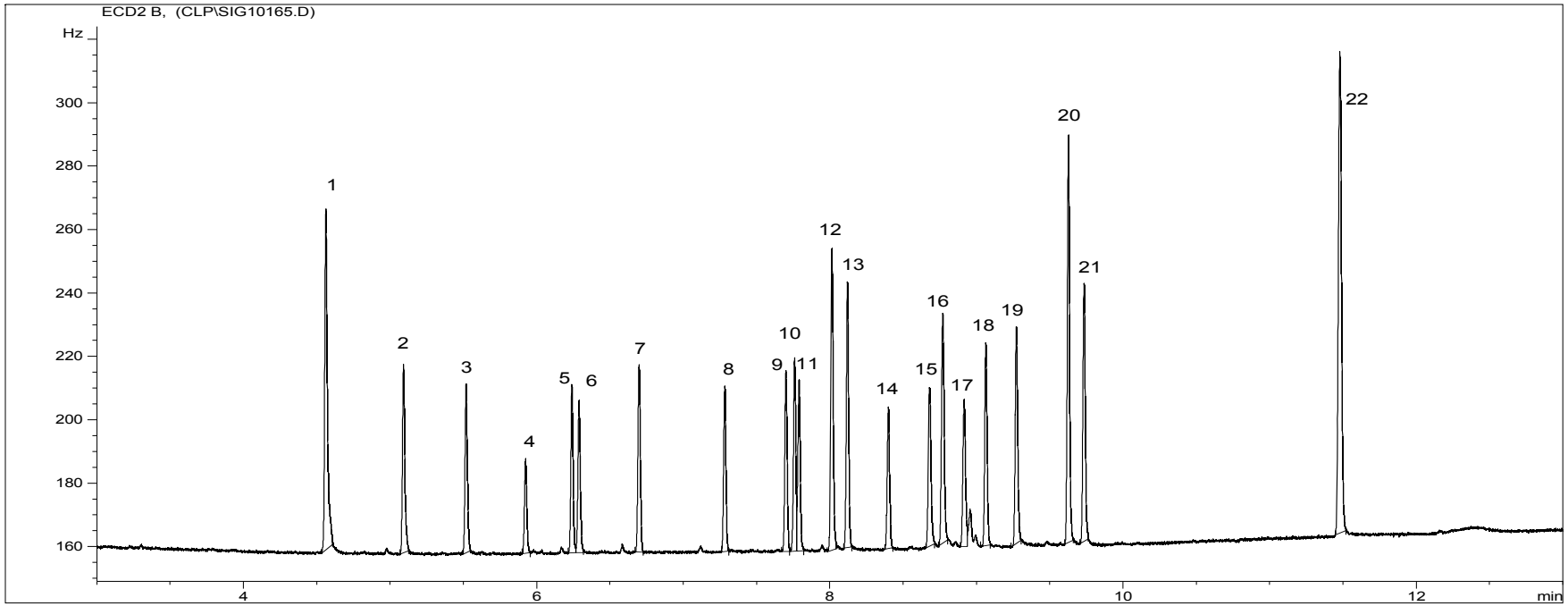
CLP Pesticide Method Translation from H_2 to He Carrier



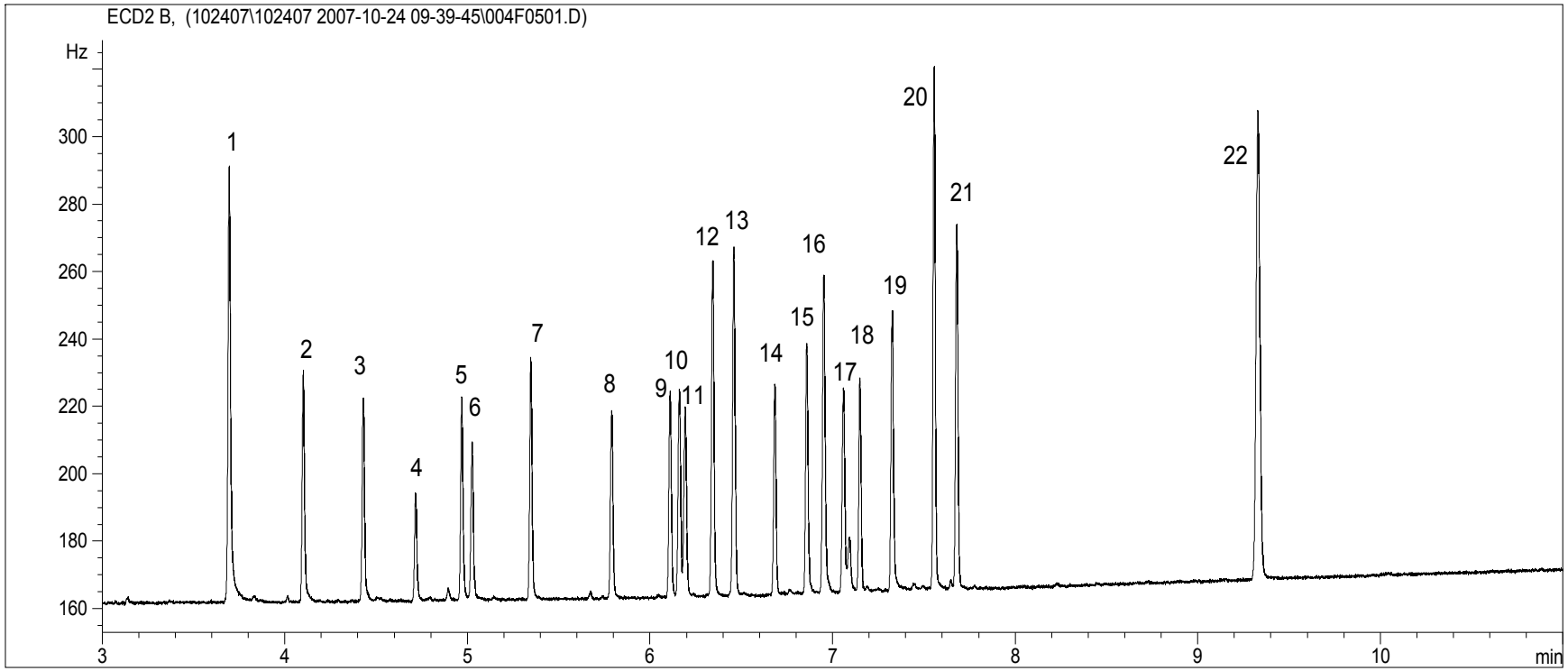
EPA Method Translated to Helium Carrier Use

Column:	DB-XLB
	20m x 0.18mm i.d., 0.18µm
Carrier:	He, constant flow, 49.5 cm/s at 120°C
Injector:	Pulsed Splittless, 220 °C
	Pulse pressure & time: 35psi for 0.5min
	single taper direct connect liner
	0.5µL, 0.4 pg on column
Oven:	120°C for 0.49min
	120°C to 160°C at 59.4°/min
	160°C to 260°C at 23.7°/min
	260°C to 300°C (1.69min) at 35.6°/min
Detector:	µ-ECD, 320°C
	N2 makeup gas at 60mL/min



Optimized Conditions Using Helium Carrier

Column:	DB-XLB 20m x 0.18mm i.d., 0.18µm
Carrier:	He, constant flow, 49.5 cm/s at 120°C
Injector:	Pulsed Splittless, 220 °C Pulse pressure & time: 35psi for 0.5min single taper direct connect liner 0.5µL, 0.4 pg on column
Oven:	120°C (0.49min); 85°/min to 160°C; 20.0°/min to 260°C (0.2 min): 40°C to 300°C (3.5min)
Detector:	µ-ECD, 320°C N2 makeup gas at 60mL/min



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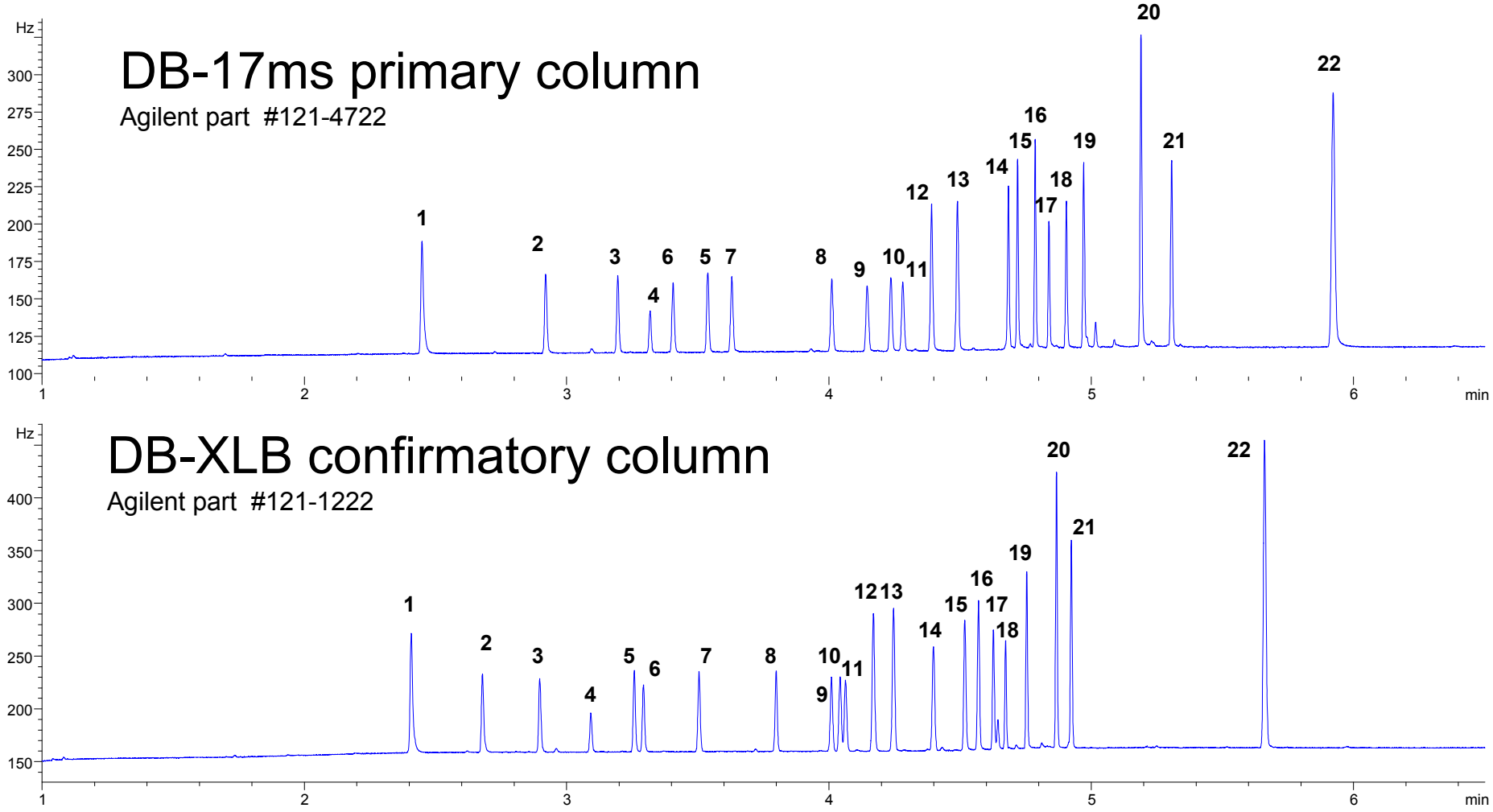
Translation Back to H_2 Carrier with Flow Ramping

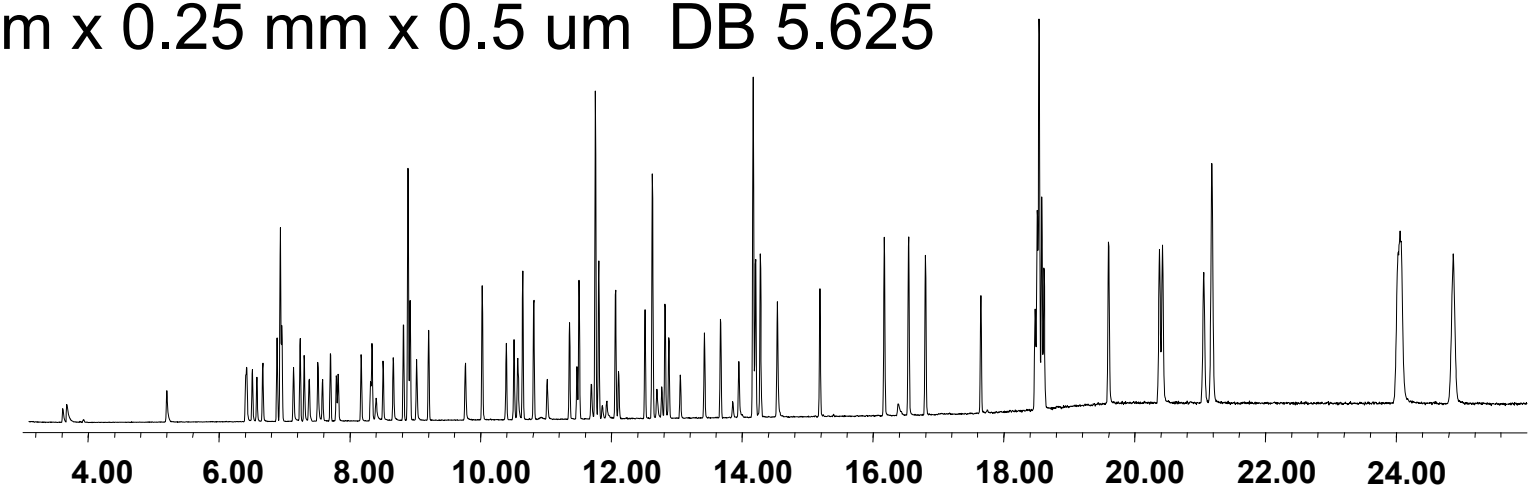


Chromatographic Conditions for Previous Slide

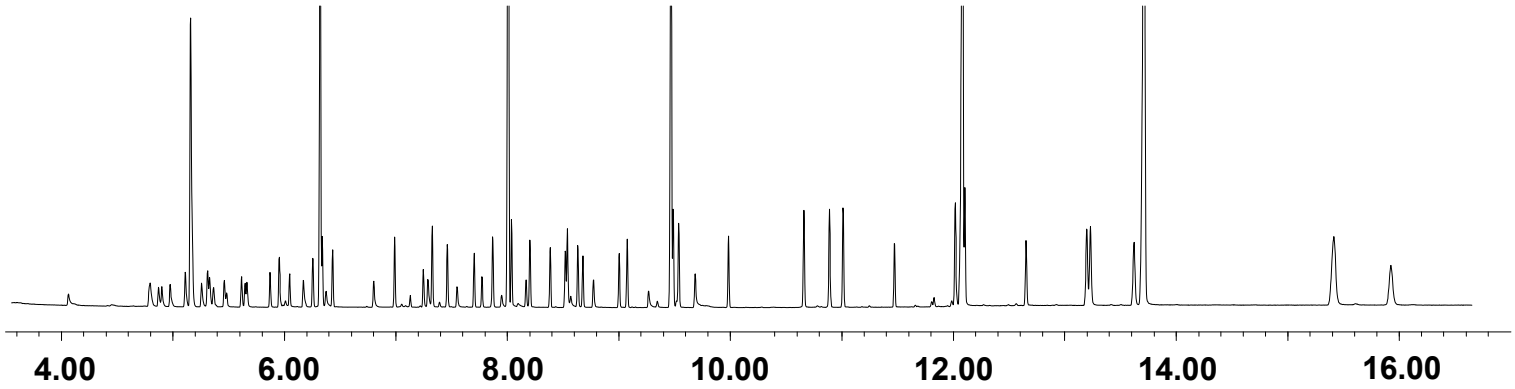
GC :	Agilent 6890N
Sampler:	Agilent 7683B, 5 µL syringe (Agilent part # 5181-1273), 0.5 µL injection
Carrier:	Hydrogen (flow programmed , 69 cm/sec at 120° C, ramped at 99ml/min to 106 cm/sec at 4.4 minutes, purified through a Big Universal Trap Agilent part # RMSH-2)
Inlet:	Split/splitless; 220° C, pulsed splitless (35 psi for 0.5 min, purge flow of 40 ml/min on at 1 minute, gas saver flow 20 ml/min on 3 minutes
Inlet Liner:	Deactivated single taper direct connect (Agilent part # 1544-80730)
Retention Gap:	5m x 0.25 mm ID deactivated (Agilent part # 160-2255-5)
Y-splitter :	Quartz deactivated (Agilent part # 5181-3398)
Columns:	
1	20m x 0.18mm x 0.18µm DB-17ms (Agilent part # 121-4722)
2	20m x 0.18mm x 0.18µm DB-XLB (Agilent part # 121-1222)
Oven:	120° C (0.32 min); 120 ° C/min to 160° C; 30 ° C/min to 258°C (0.18 min); 38.81° C/min to 300° C (1.5 min)
Detection:	µECD 320° C; nitrogen makeup; constant column + makeup flow 60 (ml/min)

Semi-Volatile Example-U.S EPA Method 8270

30 m x 0.25 mm x 0.5 um DB 5.625



20 m 0.18 mm x 0.18 um DB 5.625



PCBs in Fish Oil- Example Application

Environmental / Food Safety

- 209 possible PCB congeners
- No single-column method separates them all
- “Indicator” congeners measured in fish oil are: 28, 52, 101, 138, 153, 180 – can be difficult to resolve from other PCBs
- Recommended method uses extraction followed by GC with High Resolution MS $$$$$
- Problems when trying to GC fish oil
- High boilers stay on column causing:
  - carryover
  - dramatic shifts in PCB retention times

Fish Oil Sample Preparation is “Dilute and Shoot”

Fish oil supplement capsule

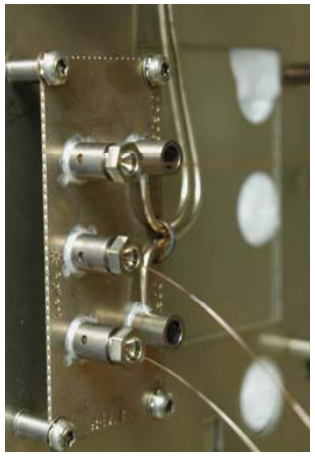
Dilute 1:10 with isooctane

Transfer to 2 mL vial

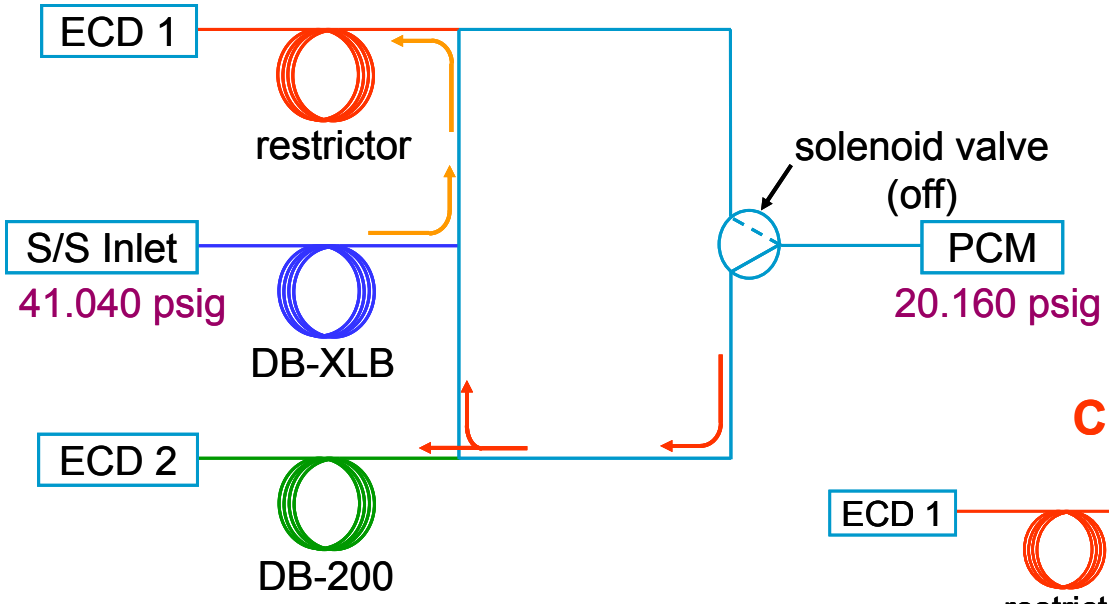
Add ISTD

7683B Auto-sampler

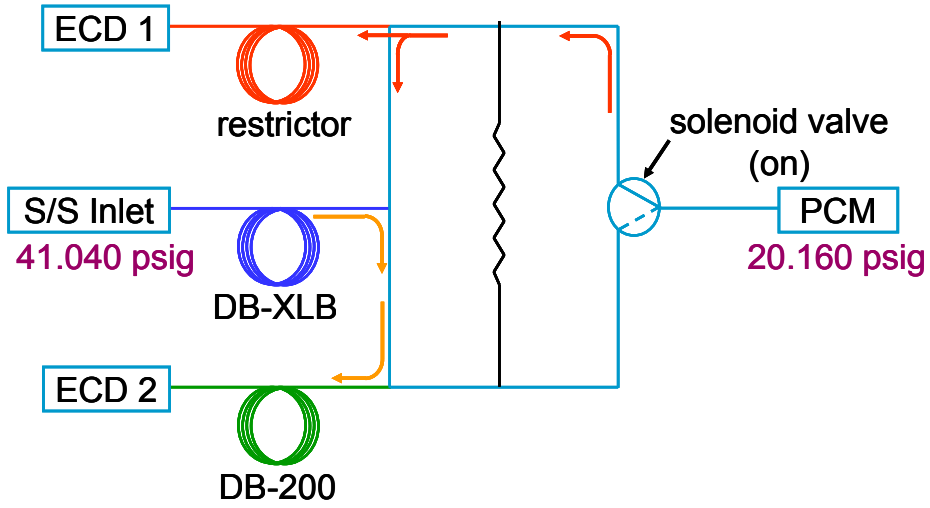
The Solution: Agilent 7890A with Deans Switch for Heart Cutting and Backflushing



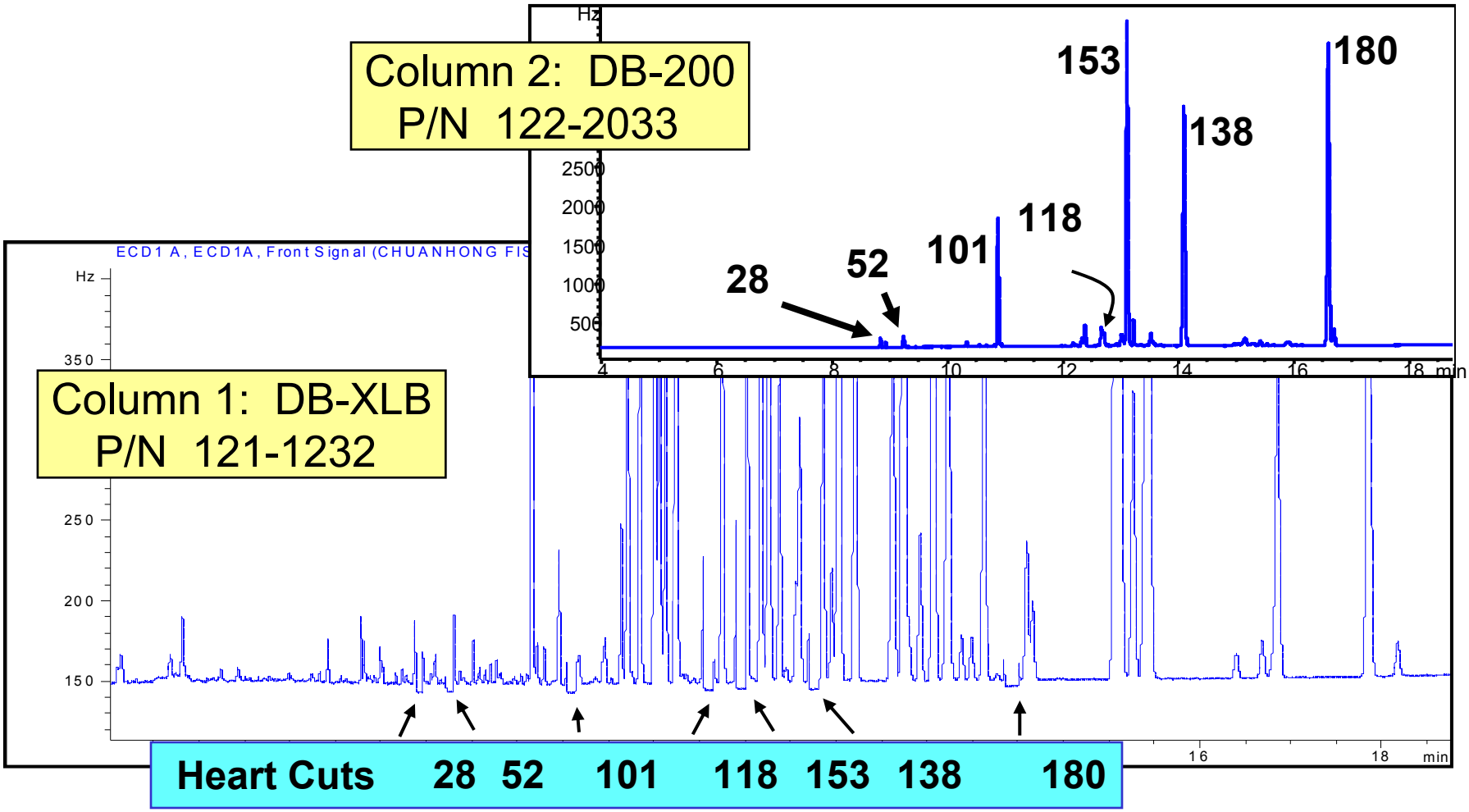
No Cut



Cut to Column 2

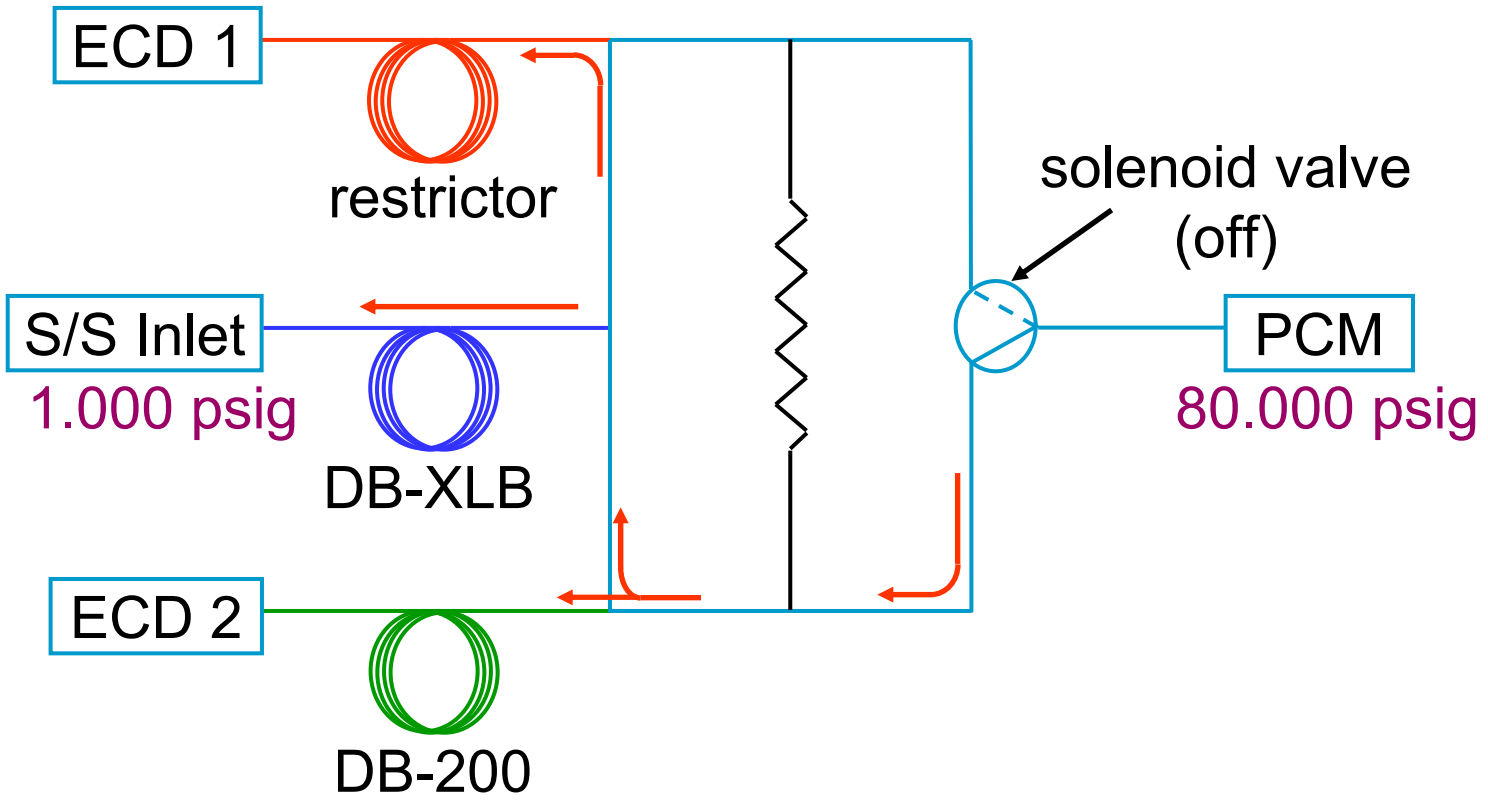


Heart Cutting with the Deans Switch to Isolate Target PCBs from Fish Oil Spiked with Aroclor 1260



Deans Switch in Backflush Mode

Backflushing Column (3 min @ 295 °C)



Application Examples – Aromatic Solvents

- ASTM Unified aromatic solvent methods D16
  - Combines 10 ASTM aromatic methods into one
  - One method can be used for up to 16 different sample types
  - One capillary GC column replaces up to 6 different columns.

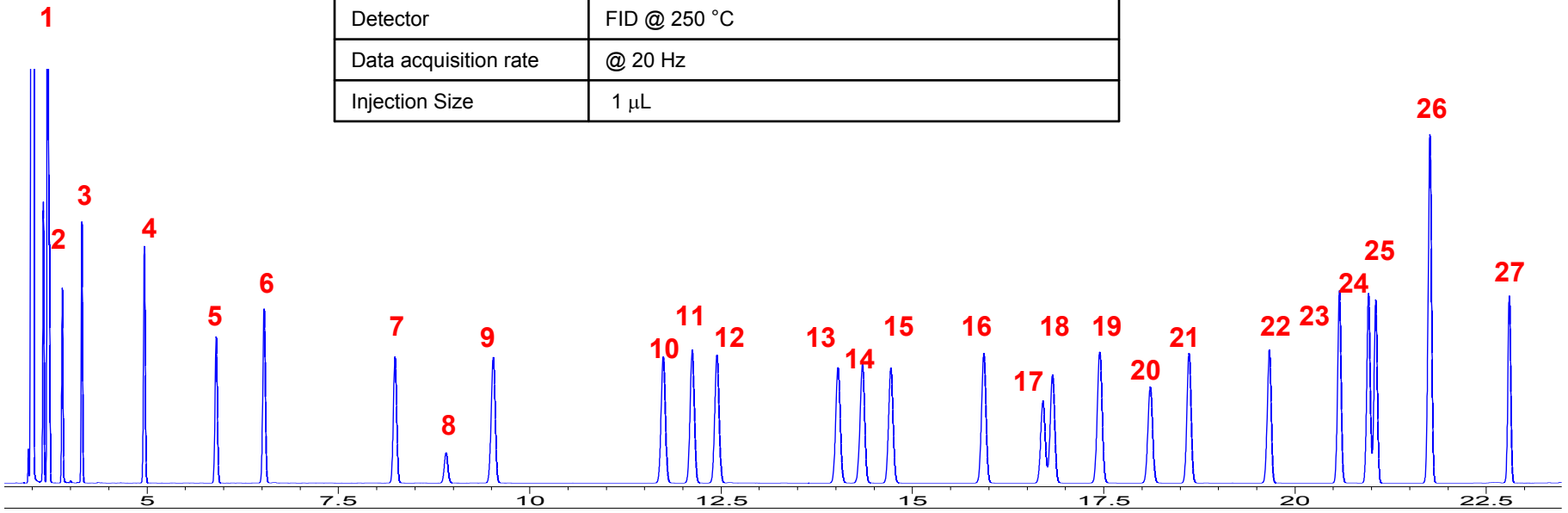
  - Due to demands for increased productivity, many QC / QA laboratories need to analyze large number of samples every day. Faster analysis is highly desirable for increased sample throughput and therefore lower cost per sample.

1 heptane
2 cyclohexane
3 octane
4 nonane
5 benzene
6 decane
7 toluene
8 1,4-dioxane
9 undecane
10 ethylbenzene
11 p-xylene
12 m-xylene
13 cumene
14 dodecane
15 o-xylene
16 propylbenzene
17 p-ethyltoluene
18 m-ethyltoluene
19 t-butylbenzene
20 s-butylbenzene
21 styrene
22 tridecane
23 diethylbenzene isomer
24 diethylbenzene isomer
25 n-butylbenzene
26 a-methylstyrene
27 phenylacetylene

Application Examples – Aromatic Solvents

Unified Aromatics Method 1

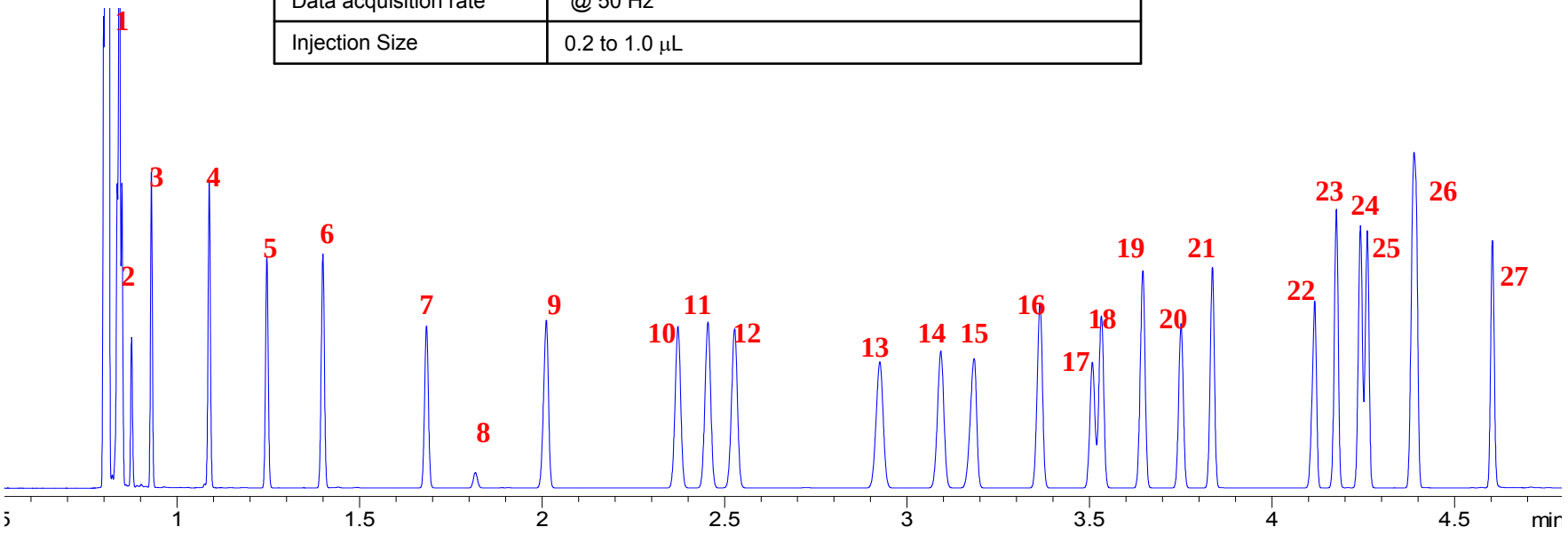
Column	HP-INNOWax, 60m × 0.32mm × 0.50 mm
Carrier Gas	Helium @ 20.00 psi constant pressure mode
Inlet	Split/Splitless @ 250°C 100:1 split ratio
Oven Temp	75°C (10 min); 3 °C/min to 100 °C (0 min) 10 °C/min to 145 °C (0 min)
Detector	FID @ 250 °C
Data acquisition rate	@ 20 Hz
Injection Size	1 µL



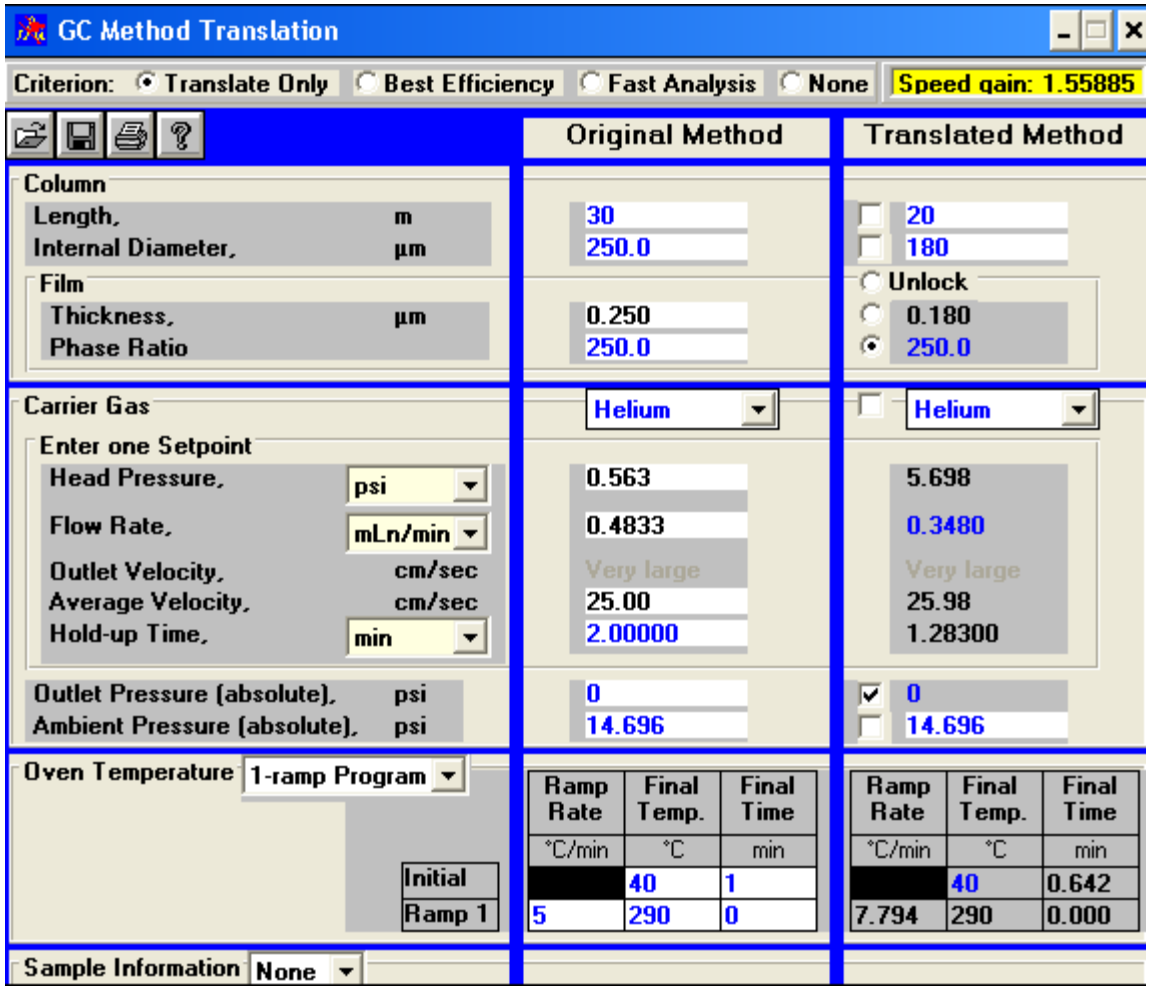
Application Examples – Aromatic Solvents

Unified Aromatics Method 2

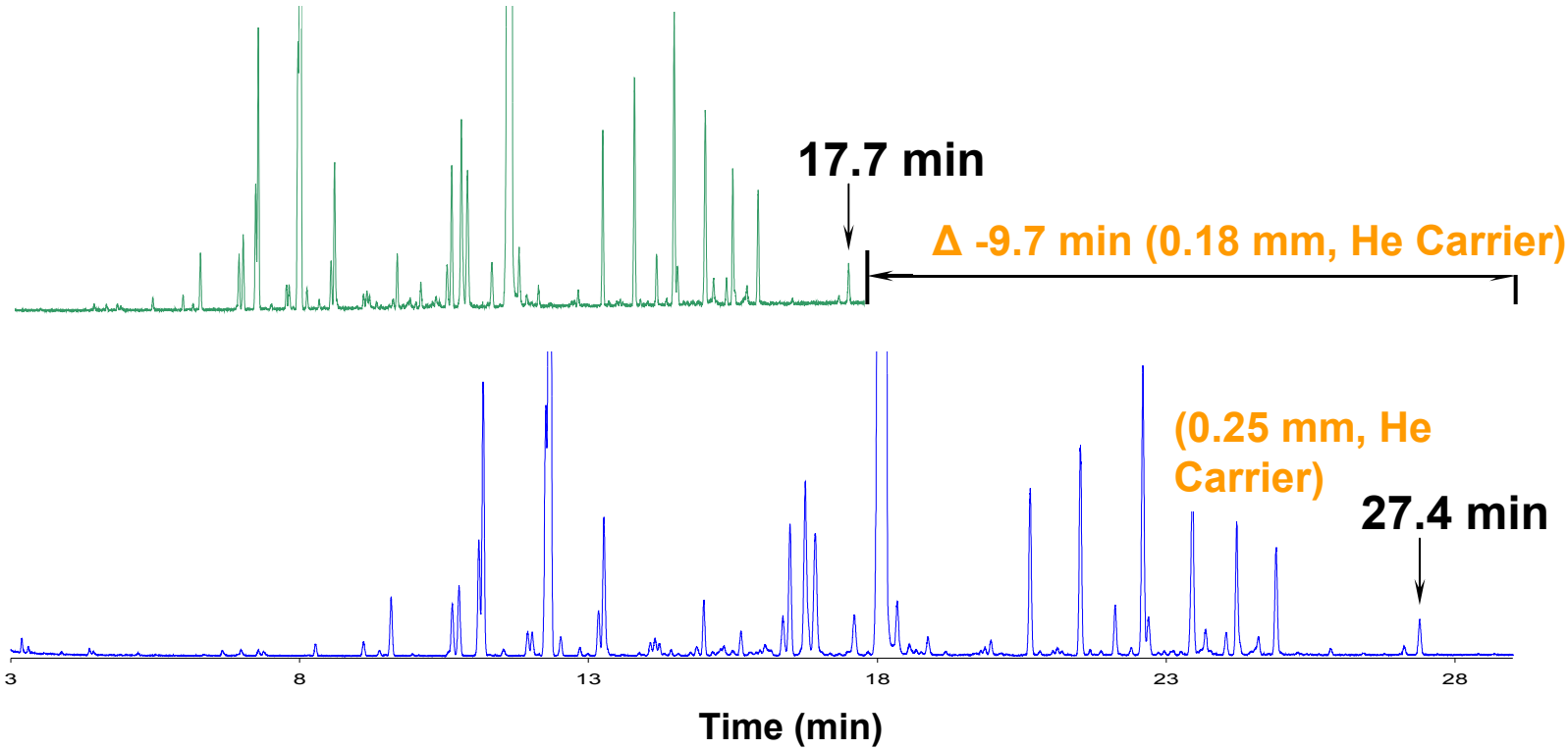
Column	HP-Innowax, 20 m x 0.18 mm x 0.18 μm
Carrier Gas	Helium @ 33.00 psi constant pressure mode
Inlet	Split/Splitless @ 250 °C
	100:1 to 600:1 split ratio
Oven Temp	70 °C (3 min); 45 °C/min to 145 °C (1 min)
Detector	FID @ 250 °C
Data acquisition rate	@ 50 Hz
Injection Size	0.2 to 1.0 μL



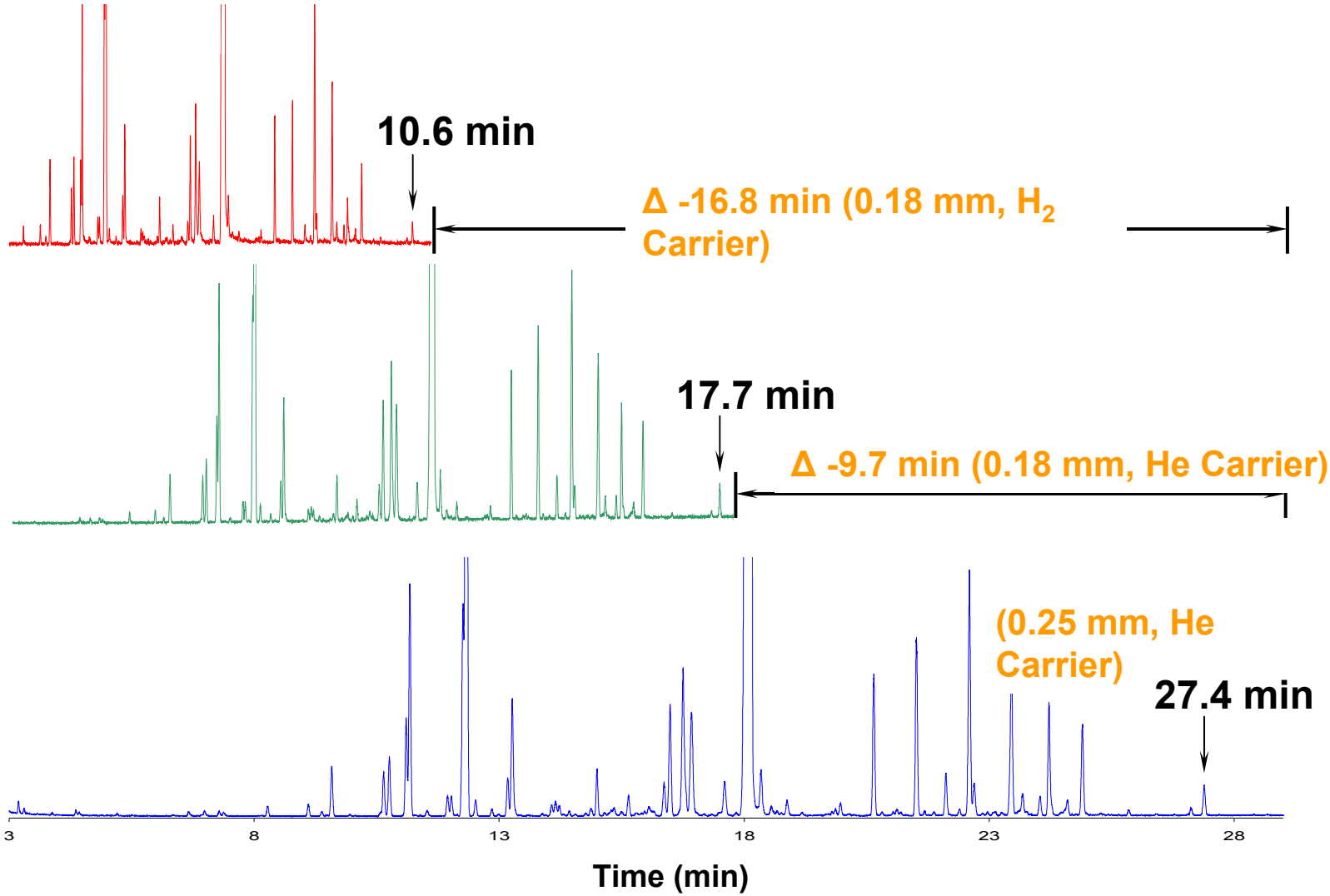
Food/Fragrance – Method translation



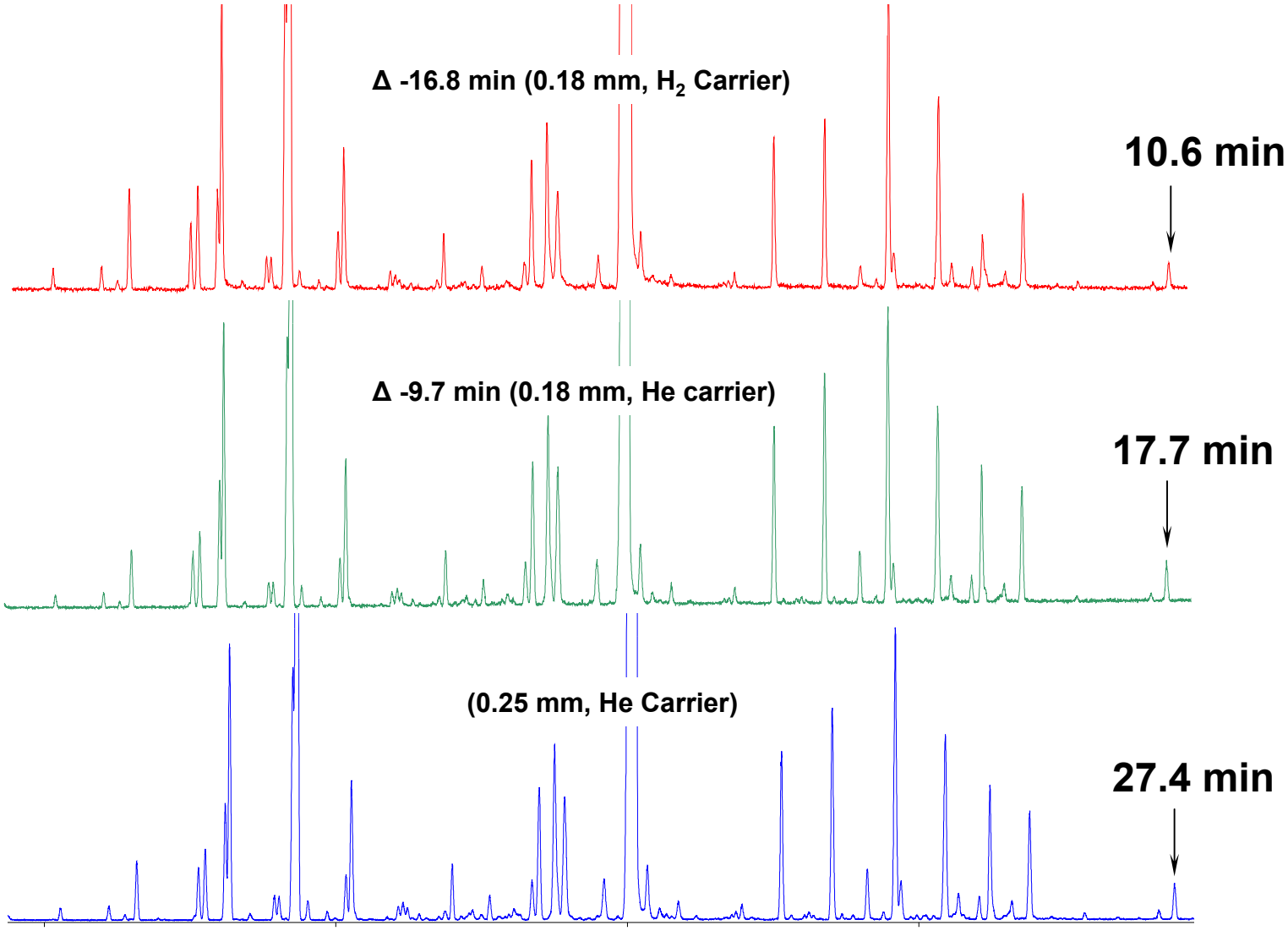
Spearmint Oil



Spearmint Oil



Spearmint Oil – Resolution Check



Resolution Maintained

Compound Resolution			
Compounds	**0.25 mm Helium**	**0.18 mm Helium**	**0.18 mm Hydrogen**
Sabinene β-Pinene	1.52	1.59	1.56
α-Terpinene p-Cymene	1.61	1.73	1.86
Speed Gain	**N/A**	35%	61%

Conclusion

You can do this!

Adapting high-efficiency GC columns into your methods is:

Practical with free method translation software and a wide range of available phases

Feasible and demonstrated for a wide range of analytes

Faster without loss of resolution

Helpful References

1. High Efficiency Column website: www.agilent.com/chem/HEColumns

2. Method translation software: free download for Method Translation Software available at http://www.chem.agilent.com/cag/servsup/usersoft/files/GCTS.htm.

3. Mike Szelewski, *Significant Cycle Time Reduction Using the Agilent 7890A/7975C GC/MSD for EPA Method 8270*, Agilent Technologies Inc., 5989-6026EN

4. Ken Lynam and Yun Zou, *A Faster Solution for Unified Volatile Organic Analysis with 0.18 mm ID GC Columns*, Agilent Technologies Inc., Separation Times 20-05

5. James D. McCurry, *A Unified Gas Chromatography Method for Aromatic Solvent Analysis"* Agilent Technologies Inc., 5988-3741EN

6. Yun Zou, "Fast Analysis of Aromatic Solvent with 0.18 mm ID GC Columns", Agilent Technologies Inc., 5898-7623EN

7. Philip L. Wylie, *Direct Injection of Fish Oil for the GC-ECD Analysis of PCBs: Results Using A Deans Switch with Backflushing*, Agilent Technologies Inc., 5989-6095EN

8. Lisa Wool & and Daron Decker, "*Practical Fast Gas Chromatography for Contract Laboratory Program Pesticide Analysis*" Journal of Chromatographic Science, Vol. 40 September 2002

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TECHNICAL SUPPORT

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