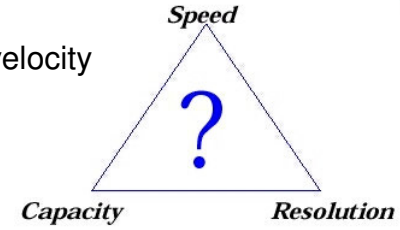
Practical Faster GC Applications with High-Efficiency GC Columns and Method Translation Software

Variables for Shortening Run Times

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



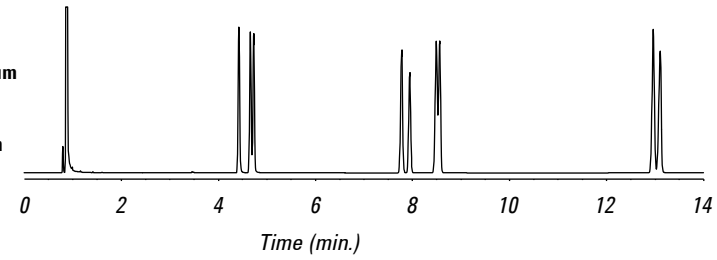
Resolution

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

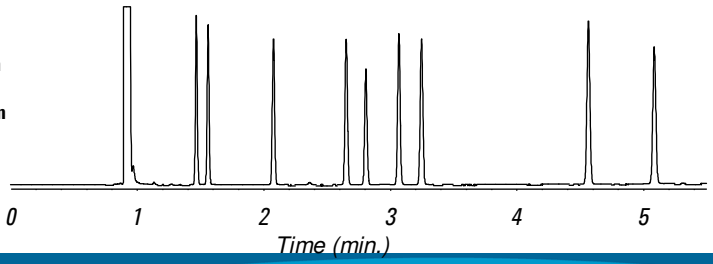
Efficiency	N = f (gas, L, r_c)	L = Length
Retention	k = f (T, d_f, r_c)	r_c = column radius
Selectivity	α = f (T, phase)	d_f = film thickness
		T = temperature

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



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

Column Length and Efficiency (Theoretical Plates)

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

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

Column Length and Resolution

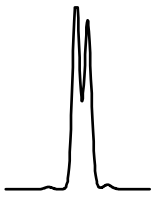
$$R \alpha \sqrt{n} \alpha \sqrt{L}$$

Length X 4 = Resolution X 2

$$t \alpha L$$

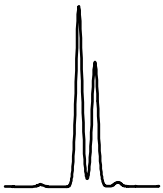
Column Length VS Resolution and Retention: Isothermal

R=0.84
2.29 min



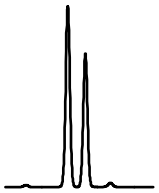
15 m

R=1.16
4.82 min



30 m

R=1.68
8.73 min

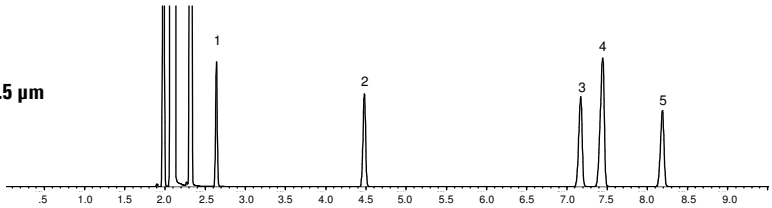


60 m

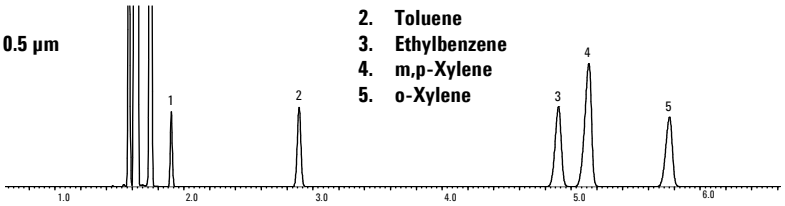
Double the plates, double the time but not double the the resolution

DECREASE THE LENGTH

DB-5
30 m
0.53 mm I.D., 0.5 µm



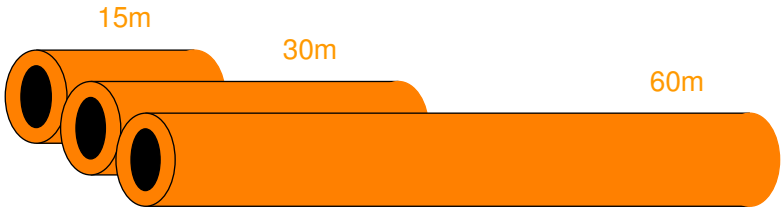
DB-5
15 m
0.53 mm I.D., 0.5 µm



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 and Cost



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Length Summary

If you Decrease Length:

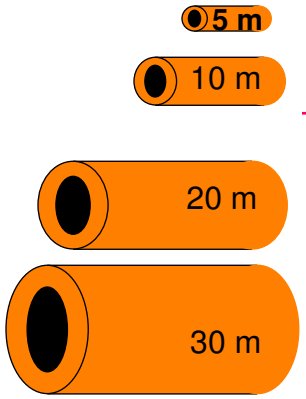
Efficiency	Decrease
Resolution	Decrease
Analysis Time	Decrease
Pressure	Decrease
Cost	Decrease

Resolution

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

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

Column Diameter - Theoretical Efficiency

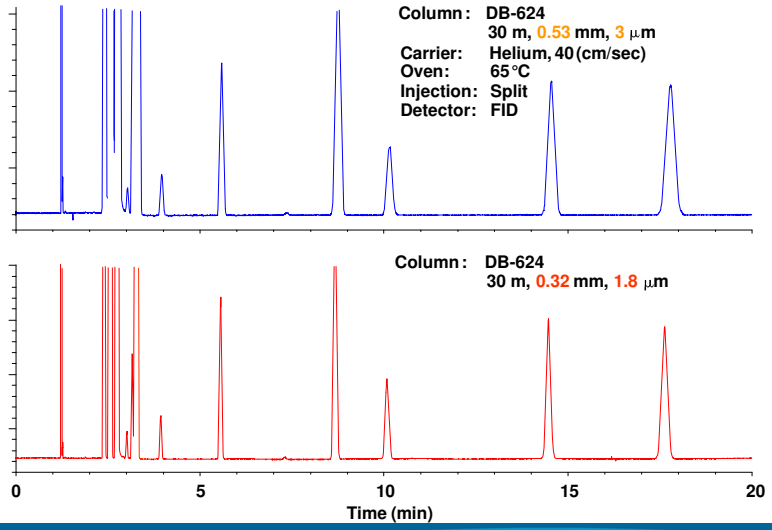


	Total Plates	I.D. (mm)	n/m
5 m	N ~ 112,000	0.05	23,160
10 m	N ~ 112,000	0.10	11,580
		0.18	6,660
20 m	N ~ 112,000	0.20	5830
		0.25	4630
30 m	N ~ 112,000	0.32	3660
		0.45	2840
		0.53	2060

k = 5

Different Column I. D.

Equal Phase Ratios



PHASE RATIO (β)

Film Thickness

Column Dimensions	Phase Ratio β
30 m x .53 mm x 3.0 µm	44
30 m x .32 mm x 1.8 µm	44

$$K_C = k\,\beta$$

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

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

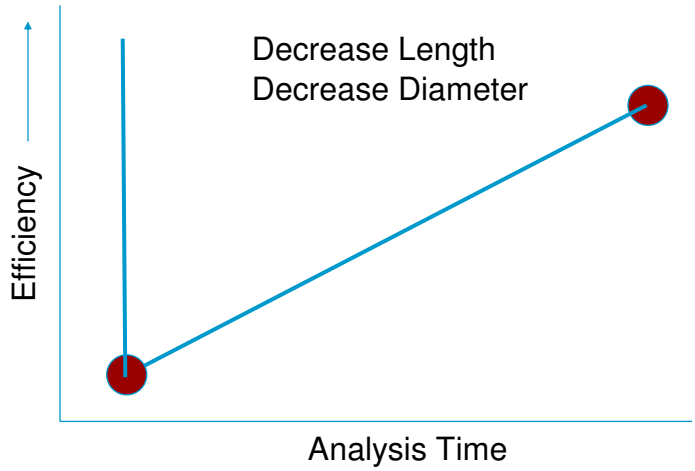
Like Polarity
Phase/Solute
0.25 µm film thickness

Diameter Summary

If you decrease the inside diameter:

Efficiency	Increase
Resolution	Increase
Pressure	Increase
Capacity	Decrease
Flow rate	Decrease

Combining a change in Length with a change in Diameter



Resolution

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

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

Carrier Gas Considerations
Best velocity?

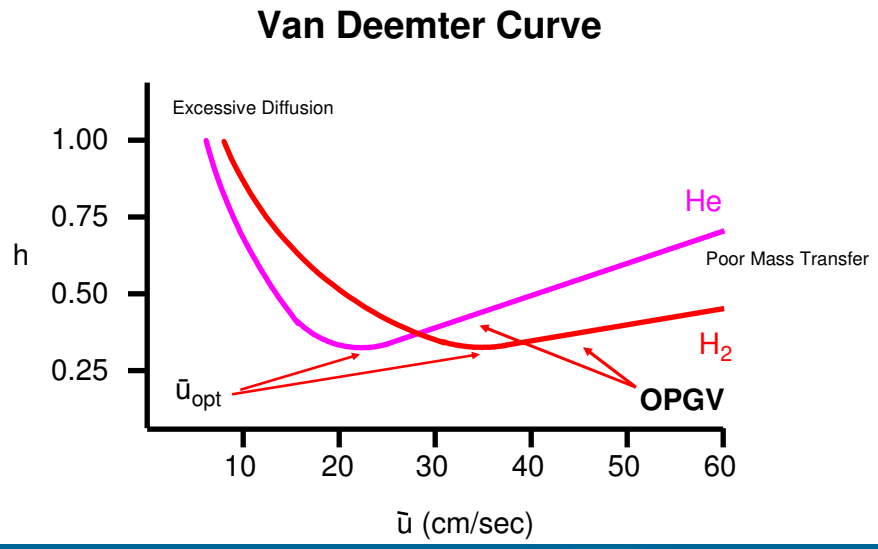
Optimal range of velocities

Too low or high results in loss of resolution

Balance resolution and analysis time

BUT... there is no LAW against going FASTER

Carrier Gas Considerations



Carrier Gas - Hydrogen Comments

Hydrogen is extremely diffusive in air

Difficult to reach explosive level of ~4 %

Most GC's flow regulated with safety shutdown

Spring loaded/Explosion proof doors

Carrier Gas Considerations
Utilizing Computer Controlled Flow Ramping (EPC)

Lonely Late Eluters? = P 

Decrease retention and overall run time by increasing pressure (speed up the gas!)

Easy Options with Method Translation Software

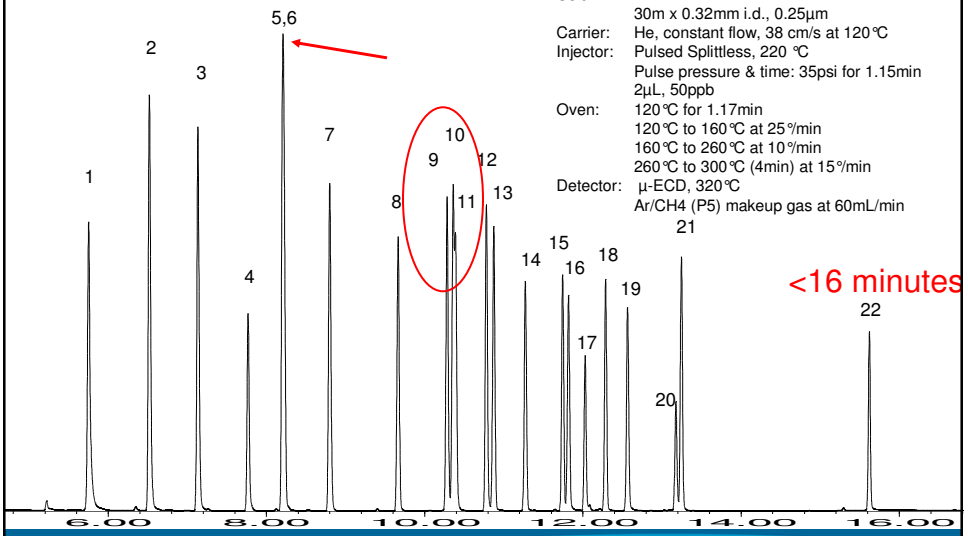
Different Column Dimensions

Switch He to H_2 Carrier Gas and Try Faster Velocities

Same Column & Gas Type but Faster Velocities

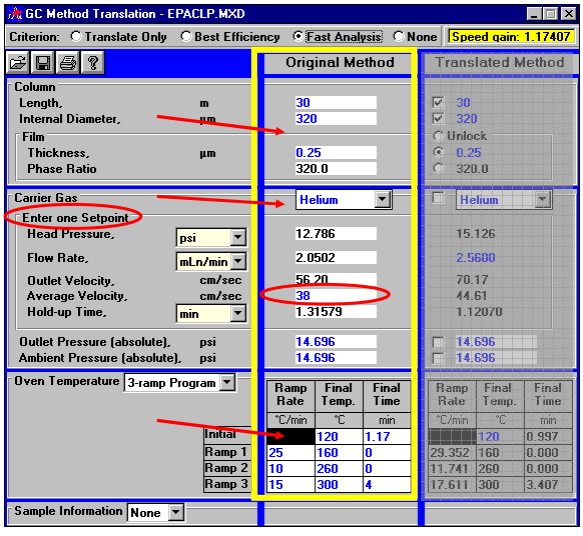
Combination of all of the above

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

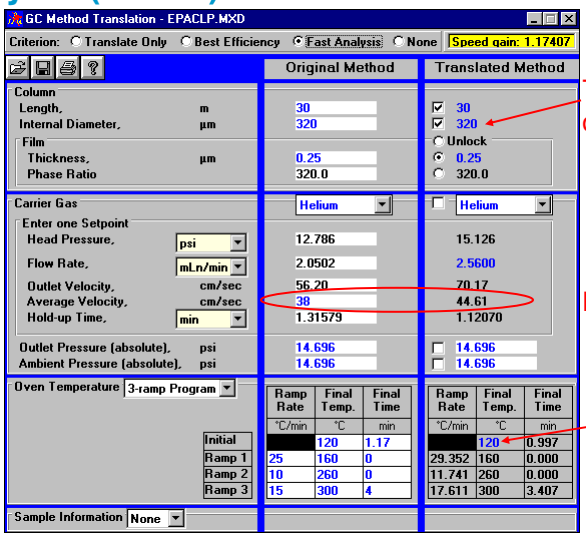


Column: DB-XLB
30m x 0.32mm i.d., 0.25µm
Carrier: He, constant flow, 38 cm/s at 120°C
Injector: Pulsed Splittless, 220 °C
Pulse pressure & time: 35psi for 1.15min
2µL, 50ppb
Oven: 120°C for 1.17min
120°C to 160°C at 25°/min
160°C to 260°C at 10°/min
260°C to 300°C (4min) at 15°/min
Detector: µ-ECD, 320°C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

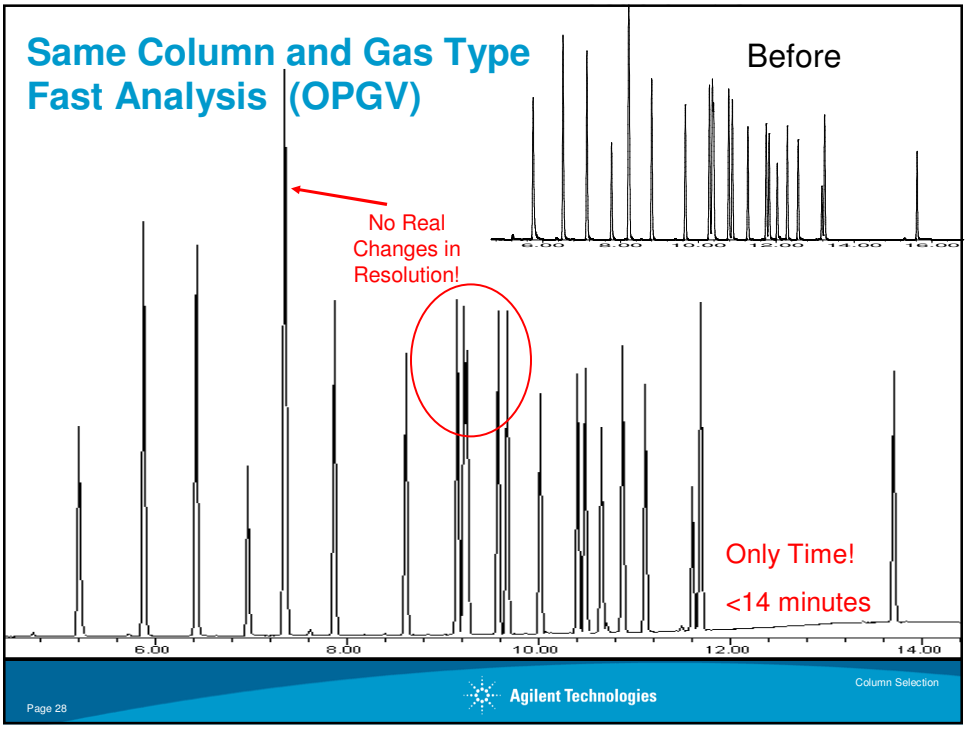
Input Original Method Parameters



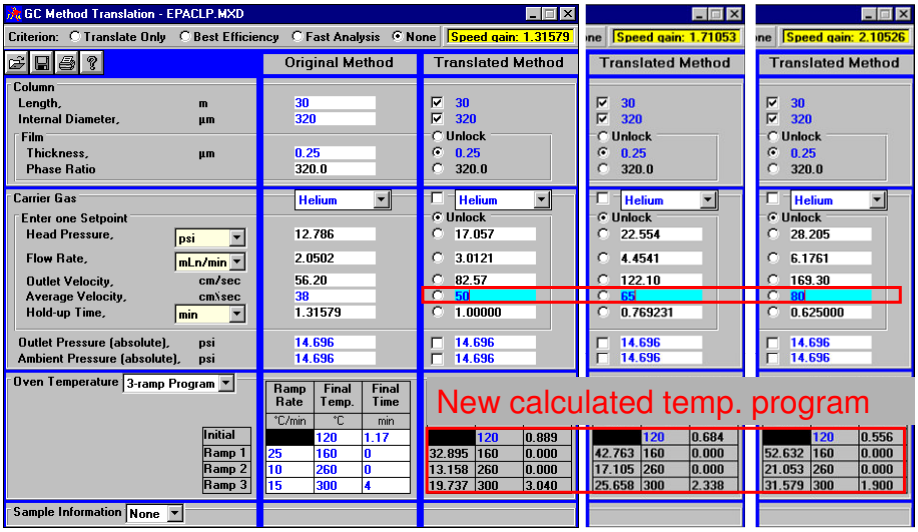
Same Column and Gas Type Fast Analysis (OPGV)



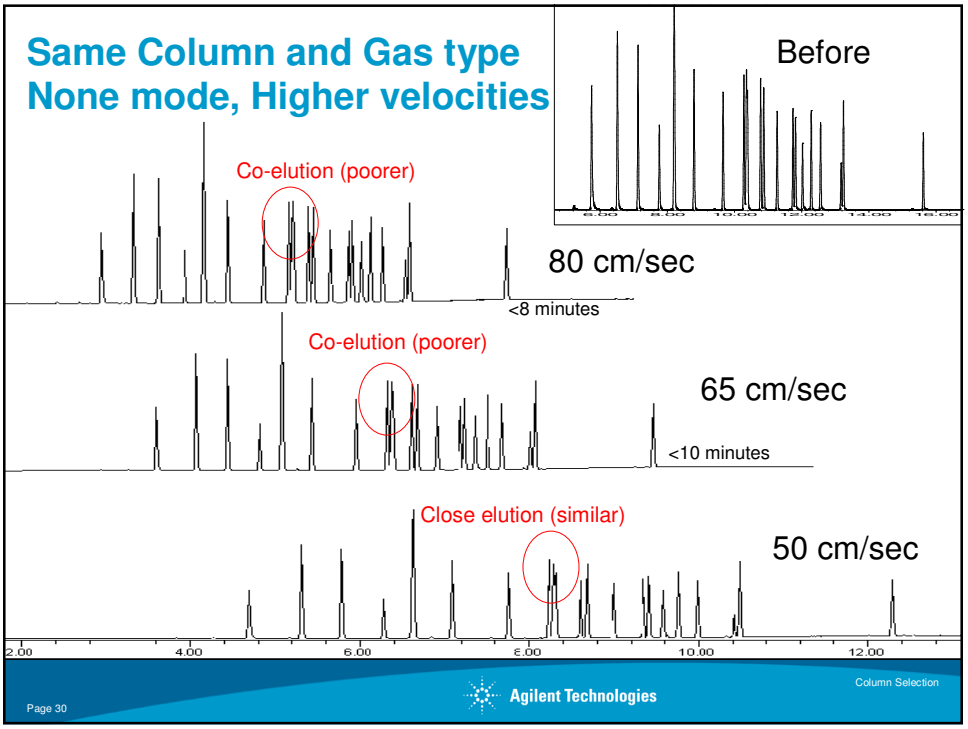
Same Column and Gas Type Fast Analysis (OPGV)



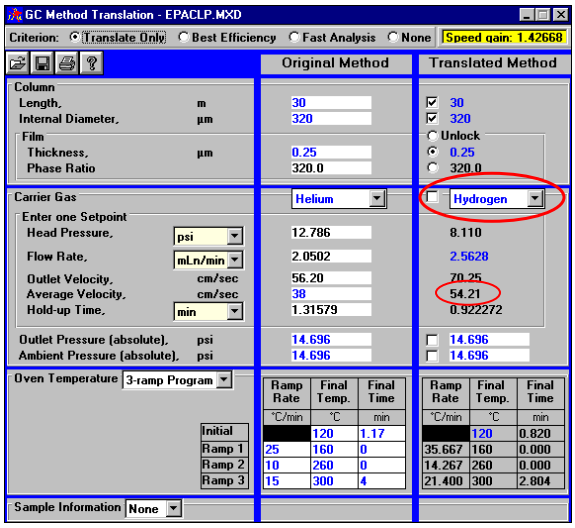
Same Column and Gas type
None mode, Try higher velocities



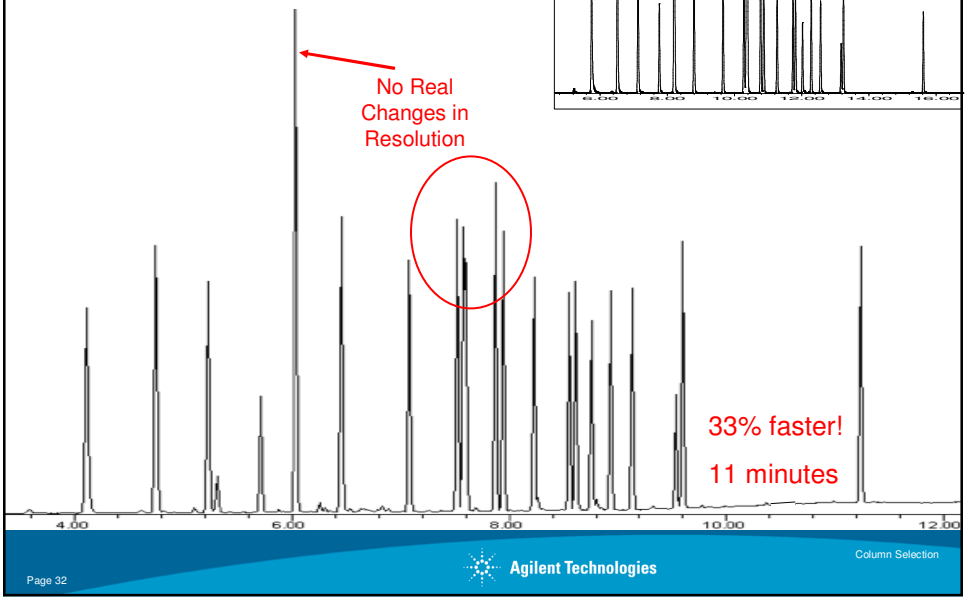
Same Column and Gas type
None mode, Higher velocities



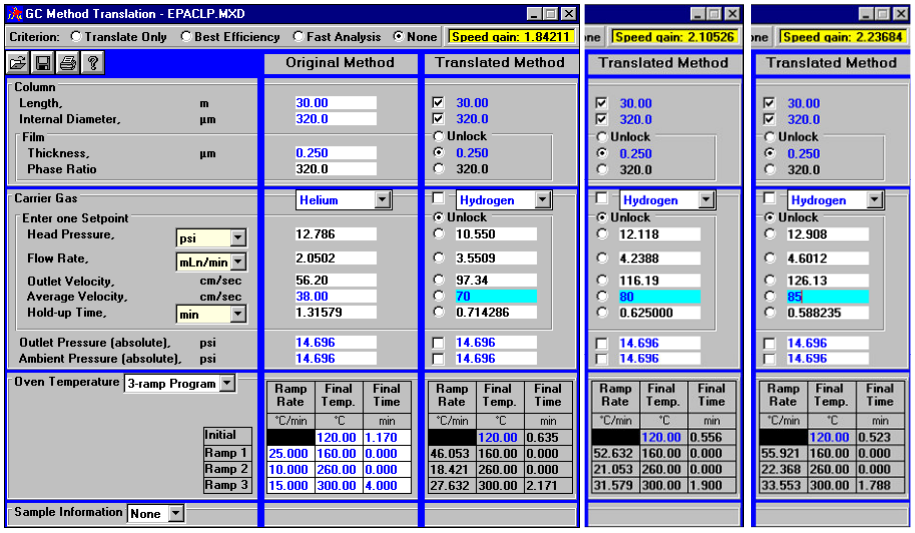
Same Column, Hydrogen Carrier Gas Translate Only



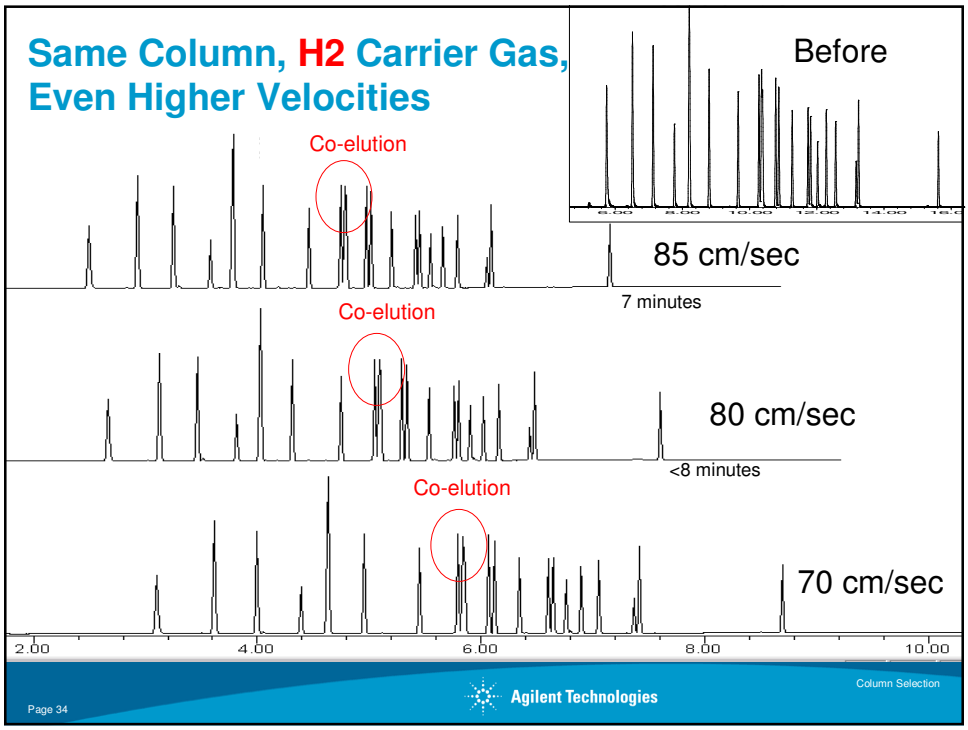
Same Column, H_2 Carrier Gas Translate Only



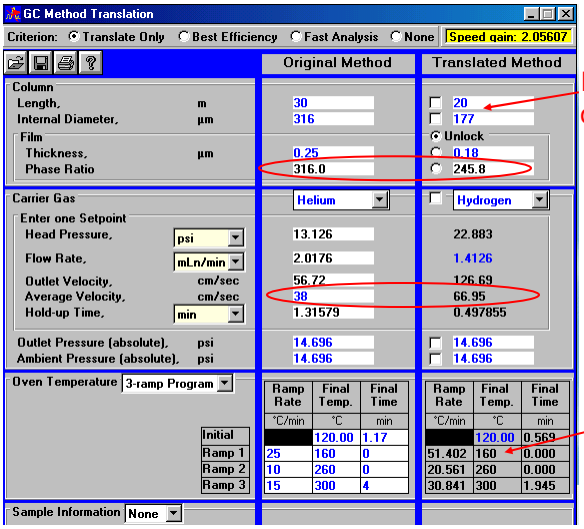
Same Column, H2 Carrier Gas, Higher Velocities



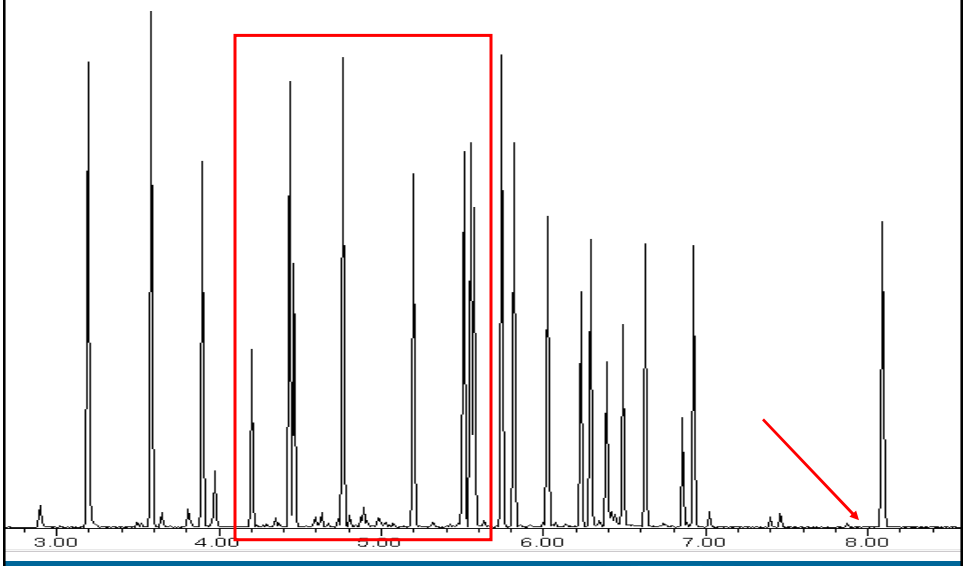
Same Column, H2 Carrier Gas, Even Higher Velocities



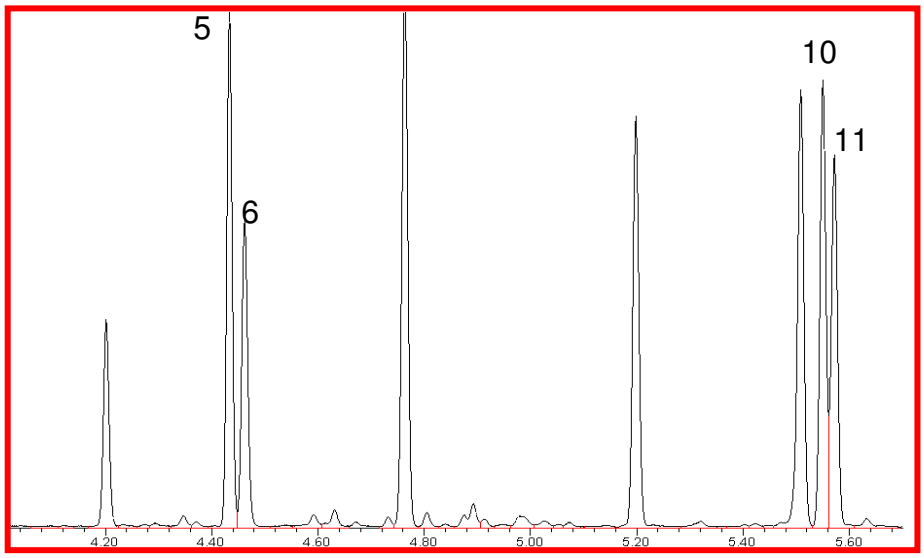
New Column Dimensions, H_2 Gas, Translate Only



New Column Dimensions, H2 Gas, Translate Only



New Column Dimensions, H2 Gas, Translate Only



New Column Dimensions, H2 Gas, Fast Analysis

GC Method Translation - EPACLP.MXD

Criterion: ○ Translate Only ○ Best Efficiency ● Fast Analysis ○ None Speed gain: 2.34453

		Original Method	Translated Method
Column			
Length,	m	30	☐ 20
Internal Diameter,	µm	320	☐ 177
Film			● Unlock
Thickness,	µm	0.25	○ 0.18
Phase Ratio		320.0	○ 245.8
Carrier Gas		Helium	☐ Hydrogen
Enter one Setpoint			
Head Pressure,	psi	12.786	26.714
Flow Rate,	mL/min	2.0502	1.7700
Outlet Velocity,	cm/sec	56.20	158.74
Average Velocity,	cm/sec	38	77.31
Hold-up Time,	min	1.31579	0.431144
Outlet Pressure (absolute),	psi	14.696	☐ 14.696
Ambient Pressure (absolute),	psi	14.696	☐ 14.696

Oven Temperature: 3-ramp Program

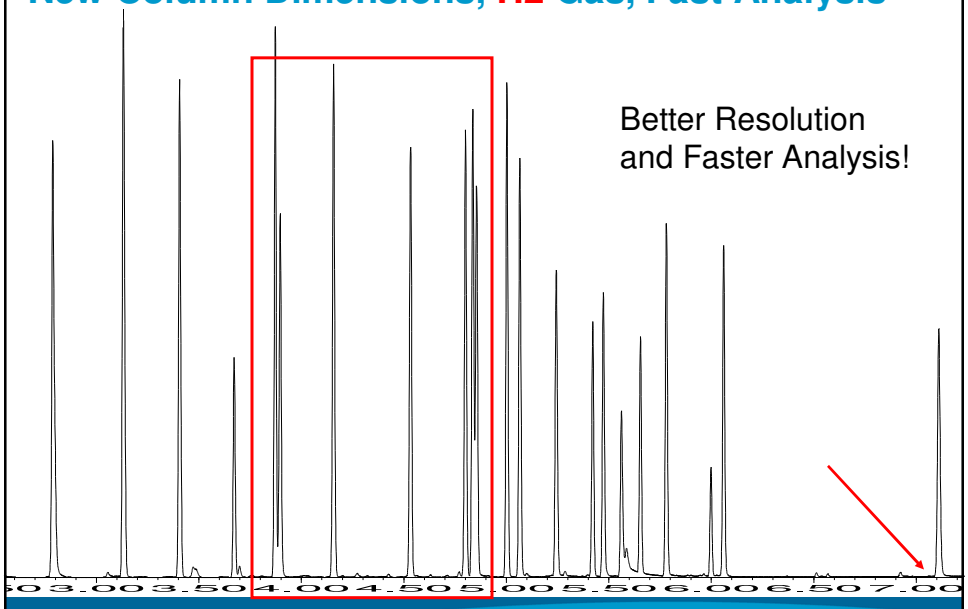
	Original Method Ramp Rate °C/min	Original Method Final Temp. °C	Original Method Final Time min	Translated Method Ramp Rate °C/min	Translated Method Final Temp. °C	Translated Method Final Time min
Initial		120	1.17		120	0.499
Ramp 1	25	160	0	58.613	160	0.000
Ramp 2	10	260	0	23.445	260	0.000
Ramp 3	15	300	4	35.168	300	1.706

Sample Information: None

New Velocity

New Temp. Program

New Column Dimensions, H2 Gas, Fast Analysis



New Column Dimensions, H2 Gas, Higher Velocities

GC Method Translation - EPACLP.MXD

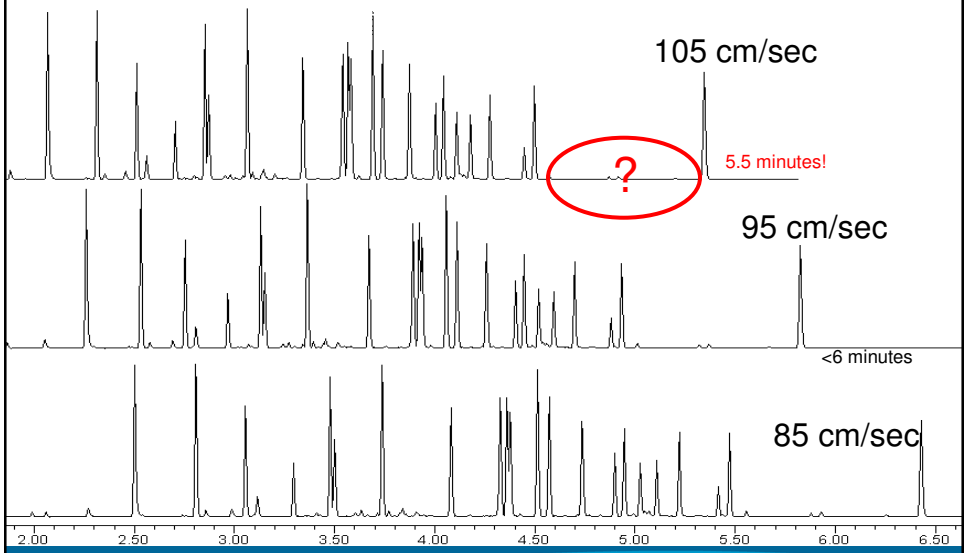
Criterion: ○ Translate Only ○ Best Efficiency ○ Fast Analysis ◉ None

	Original Method	Translated Method	Translated Method	Translated Method
		Speed gain: 2.57761	Speed gain: 2.88086	Speed gain: 3.18411
Column				
Length, m	30	20	20	20
Internal Diameter, µm	320	177	177	177
Film		Unlock	Unlock	Unlock
Thickness, µm	0.25	0.18	0.18	0.18
Phase Ratio	320.0	245.8	245.8	245.8
Carrier Gas	Helium	Hydrogen	Hydrogen	Hydrogen
Enter one Setpoint		Unlock	Unlock	Unlock
Head Pressure, psi	12.786	29.598	33.397	37.244
Flow Rate, mL/min	2.0502	2.0619	2.4764	2.9308
Outlet Velocity, cm/sec	56.20	184.91	222.08	262.84
Average Velocity, cm/sec	38	85	95	105
Hold-up Time, min	1.31579	0.392157	0.350877	0.317460
Outlet Pressure (absolute), psi	14.696	14.696	14.696	14.696
Ambient Pressure (absolute), psi	14.696	14.696	14.696	14.696
Oven Temperature 3-ramp Program				

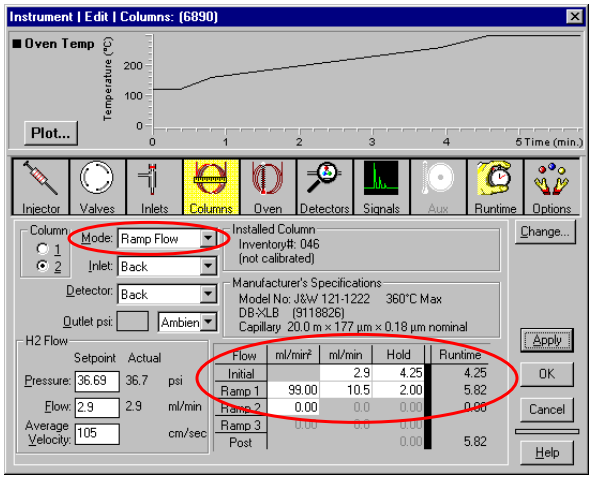
	Ramp Rate °C/min	Final Temp. °C	Final Time min	Ramp Rate °C/min	Final Temp. °C	Final Time min	Ramp Rate °C/min	Final Temp. °C	Final Time min	Ramp Rate °C/min	Final Temp. °C	Final Time min
Initial		120	1.17		120	0.454		120	0.406		120	0.367
Ramp 1	25	160	0	64.440	160	0.000	72.021	160	0.000	79.603	160	0.000
Ramp 2	10	260	0	25.776	260	0.000	28.809	260	0.000	31.841	260	0.000
Ramp 3	15	300	4	38.664	300	1.552	43.213	300	1.388	47.762	300	1.256

Sample Information None

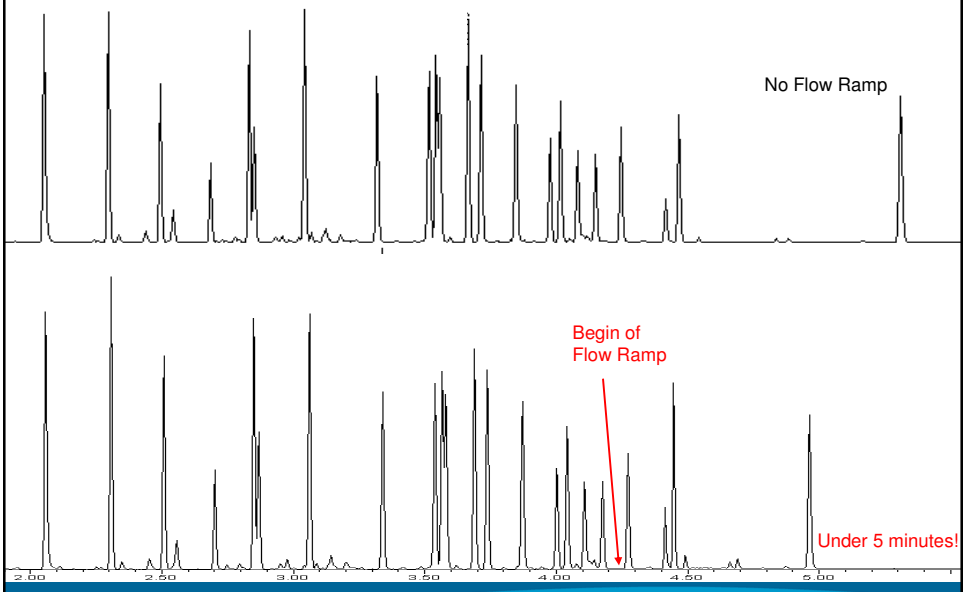
New Column Dimensions, H2 Gas, Higher Velocities



Flow Ramp (EPC) for Late Eluters and Faster Bake Outs

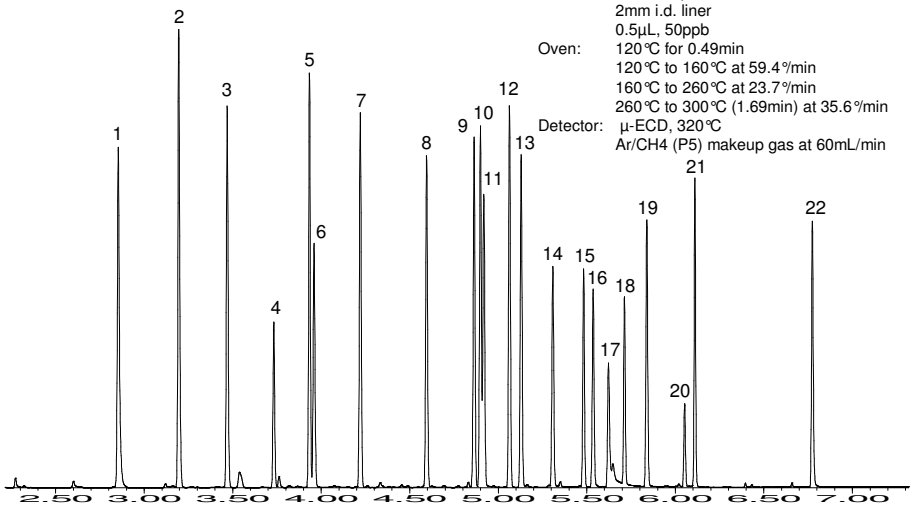


Flow Ramp

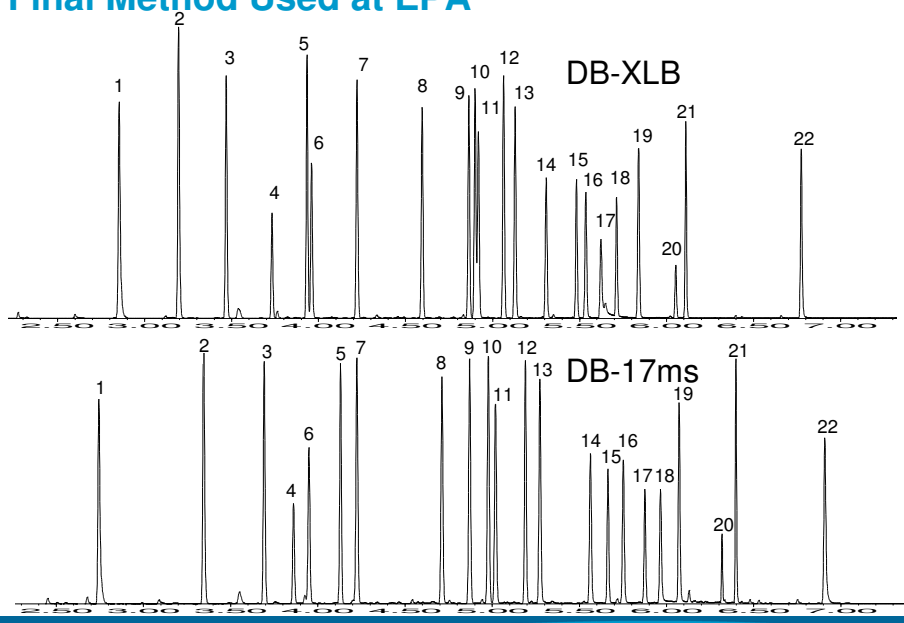


Final Method Used at EPA

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/min² 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



Final Method Used at EPA



Further Work (App. Note 5989-7818EN)

20m x 0.18mm ID, Fast Even in Helium

GC Method Translation - XLB-TA.MXD

Criterion: Translate Only | Best Efficiency | Fast Analysis | None — Speed gain: 0.63934

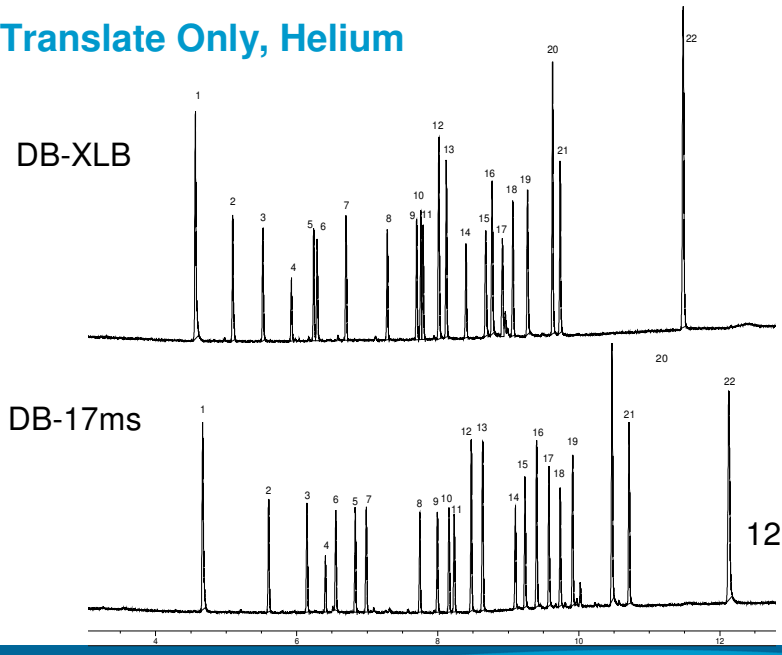
		Original Method	Translated Method
Column			
Length,	m	20.00	20.00
Internal Diameter,	µm	180.0	180.0
Film			Unlock
Thickness,	µm	0.180	0.180
Phase Ratio		250.0	250.0
Carrier Gas		Hydrogen	Helium
Enter one Setpoint			
Head Pressure,	psi	25.756	37.597
Flow Rate,	mL/min	1.7943	1.4354
Outlet Velocity,	cm/sec	155.58	124.47
Average Velocity,	cm/sec	77.30	49.42
Hold-up Time,	min	0.431220	0.674472
Outlet Pressure (absolute),	psi	14.696	14.696
Ambient Pressure (absolute),	psi	14.696	14.696

Oven Temperature: 3-ramp Program

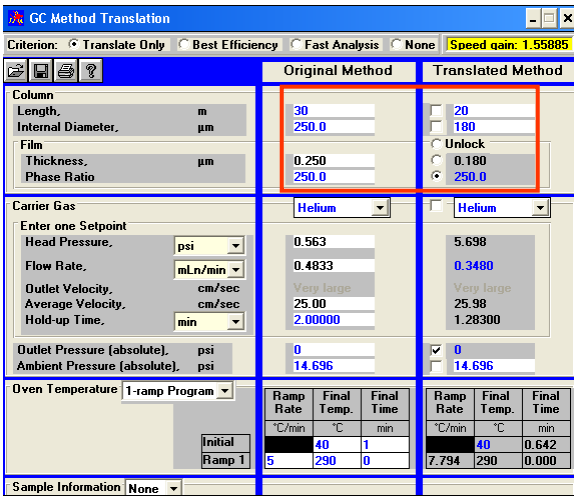
	Original Method Ramp Rate (°C/min)	Original Method Final Temp. (°C)	Original Method Final Time (min)	Translated Method Ramp Rate (°C/min)	Translated Method Final Temp. (°C)	Translated Method Final Time (min)
Initial		120.00	0.490		120.00	0.766
Ramp 1	59.400	160.00	0.000	37.977	160.00	0.000
Ramp 2	23.700	260.00	0.000	15.152	260.00	0.000
Ramp 3	35.600	300.00	1.690	22.761	300.00	2.643

Sample Information: None

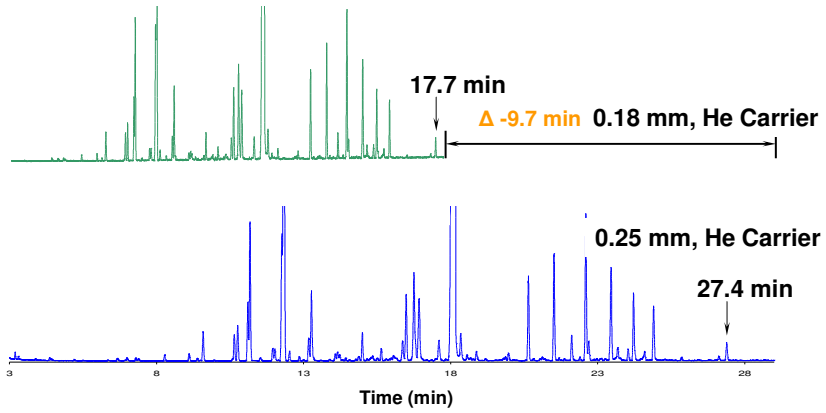
Translate Only, Helium



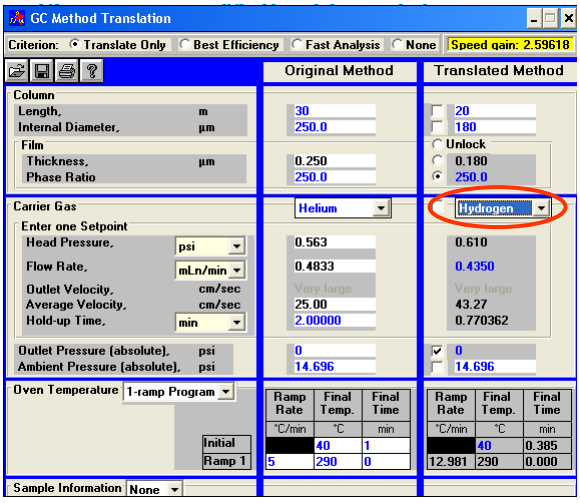
Food/Fragrance – Method translation



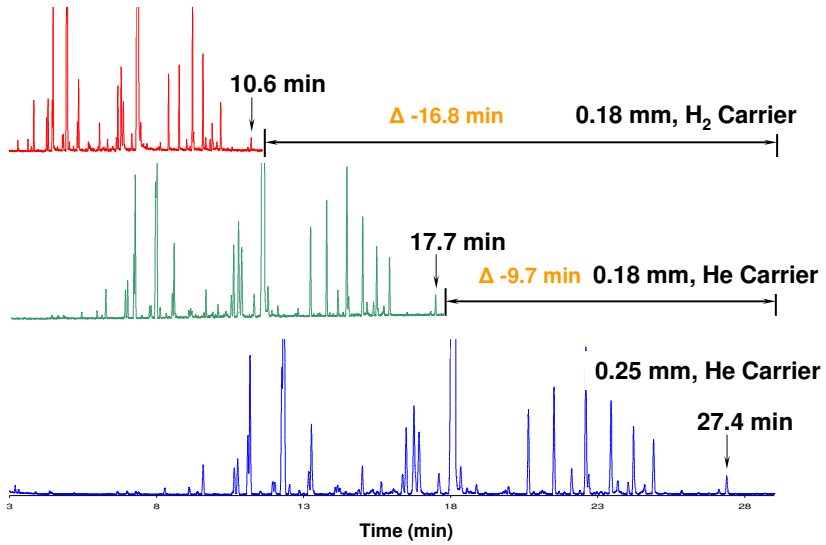
Spearmint Oil on DB-1



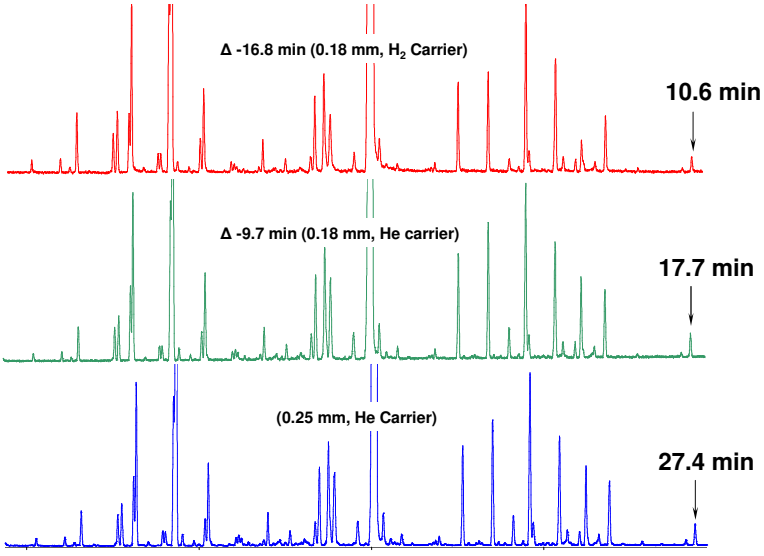
Food/Fragrance – Method translation, Hydrogen



Spearmint Oil on DB-1, (App. Note 5989-7509EN)



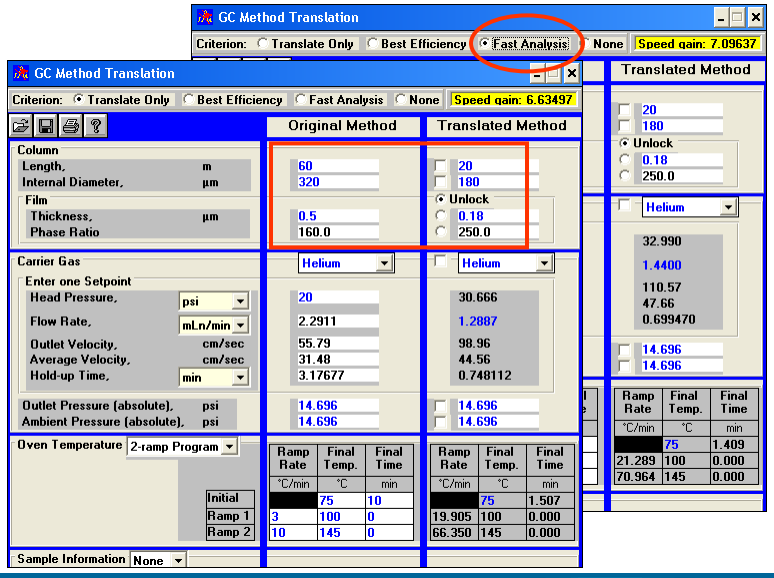
Spearmint Oil on DB-1 – Resolution Check



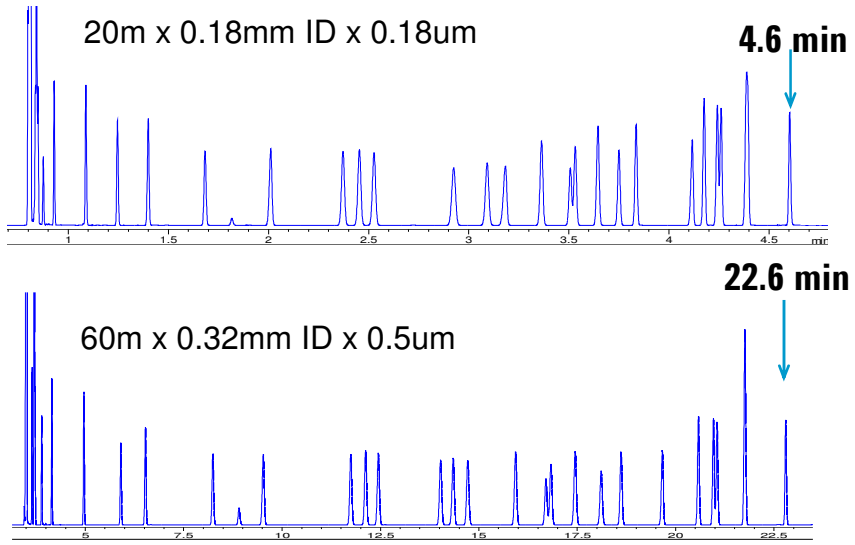
Resolution Maintained

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%

Aromatic Solvents on HP-INNOWax

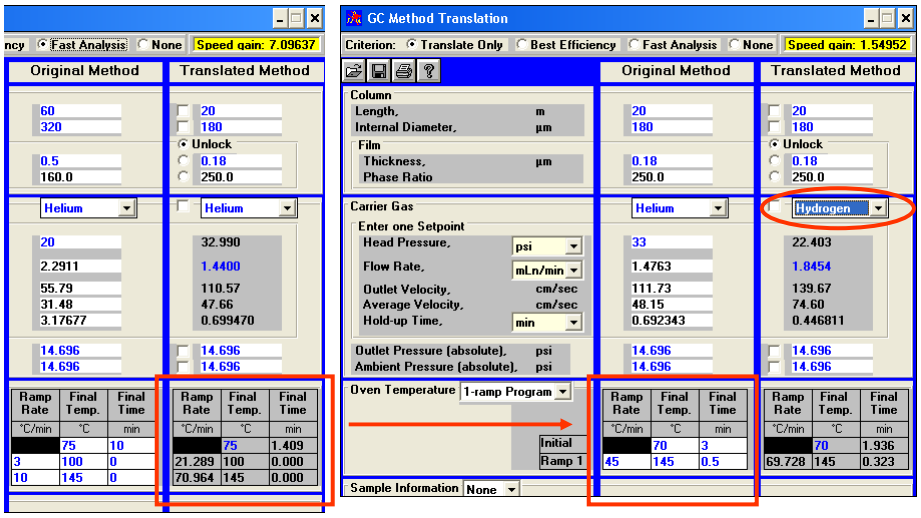


Aromatic Solvents on HP-INNOWax

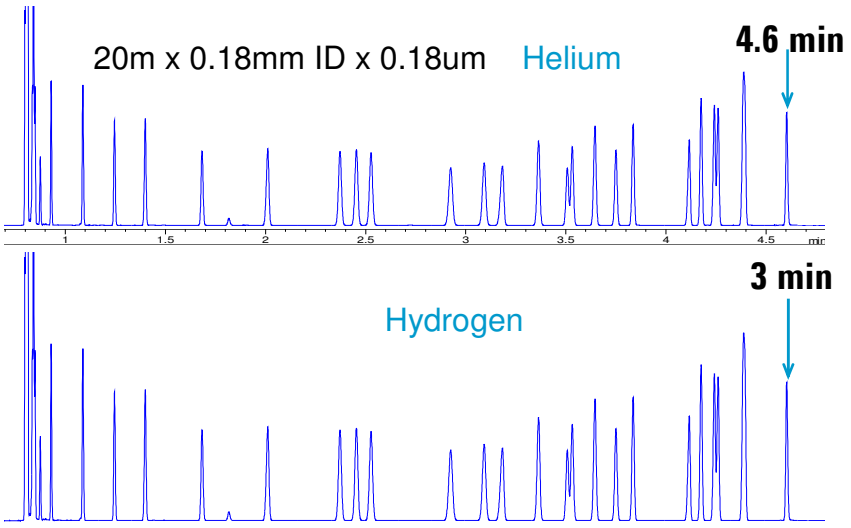


Aromatic Solvents on HP-INNOWax

Modified Temp then converted to Hydrogen



Aromatic Solvents on HP-INNOWax (App. Note 5989-7623EN)



CONCLUSIONS

Stationary Phase – Chosen for optimized selectivity

Length – Shorter might be possible without losing a lot of R

Carrier Gas – Helium can still go fast but Hydrogen has the most advantage at high velocities

Flow Ramp – Increase at end of run for lonely late eluters

Temperature Program – Use MTS to scale temps properly

Method Translation Software – FREE, reliable

Diameter – Smaller allows shorter length but has less capacity

Small Change in ID Easier to Translate – Again think capacity

TECHNICAL SUPPORT

1-800-227-9770, #4, #1

E-mail: gc_column_support@Agilent.com

1-972-699-6423 (Daron)

1-866-912-6701 (toll free)

E-mail:
Daron_Decker@Agilent.com

For More Detailed Information

"Fast Analysis if Aromatic Solvent with 0.18 mm ID GC Column" (5989-7623EN)

"Analysis of Semivolatiles Using High Efficiency Capillary GC Columns" (5989-7500EN)

Rapid Analysis of Food and Fragrances Using High-Efficiency Capillary GC Columns" (5989-7509EN)

Agilent J&W High-Efficiency Capillary columns: Productivity-Enhancing Tools for Fast GC Applications" (5989-7499EN)

www.agilent.com/chem/HEColumns