Tips and Tricks of Faster GC Analysis

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Application Engineer
E-seminar
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Questions to Ask

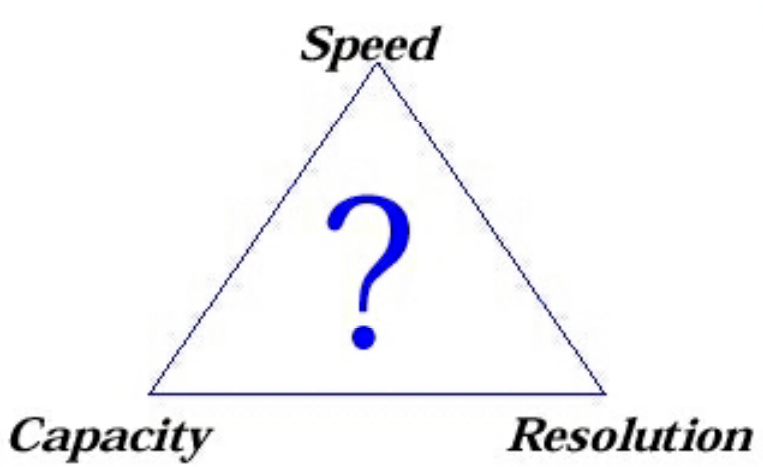
What information do you need from your analysis?

Do you have more baseline than you need 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



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

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Selectivity	$\alpha = f$ (T, phase)	d_f = film thickness
		T = temperature

Stationary Phase - Common Types

Siloxane polymers

Poly(ethylene) glycols

Porous polymers

Selectivity

Relative spacing of the chromatographic peaks

The result of all non-polar, polarizable and polar interactions that cause a stationary phase to be more or less retentive to one analyte than another

Optimizing Selectivity

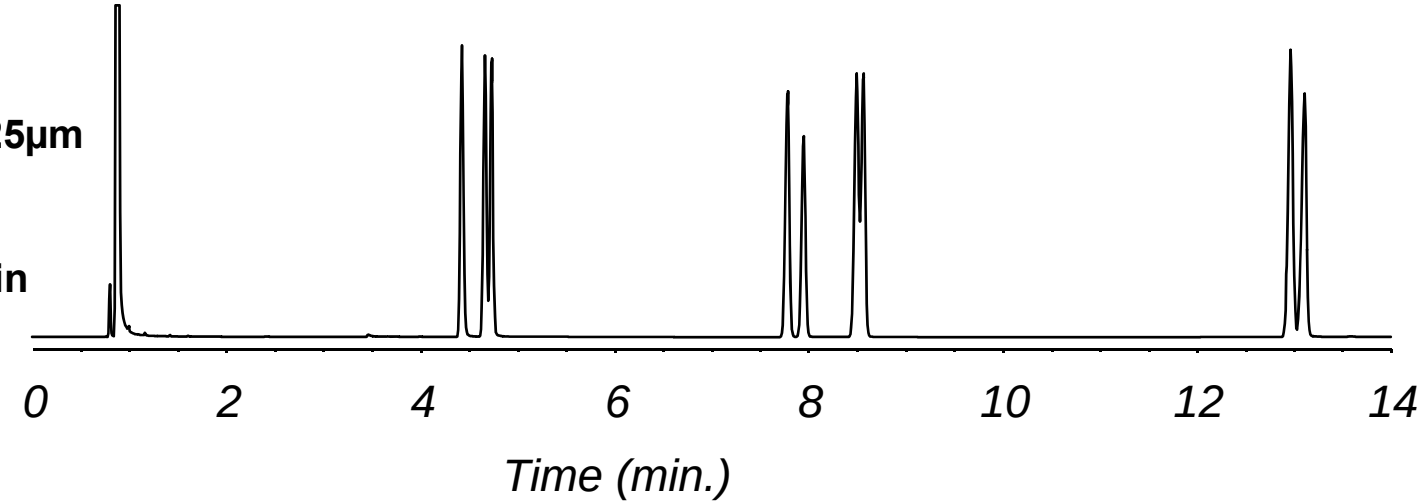
Match analyte polarity to stationary phase polarity

-like dissolves like(oil and water don’t mix)

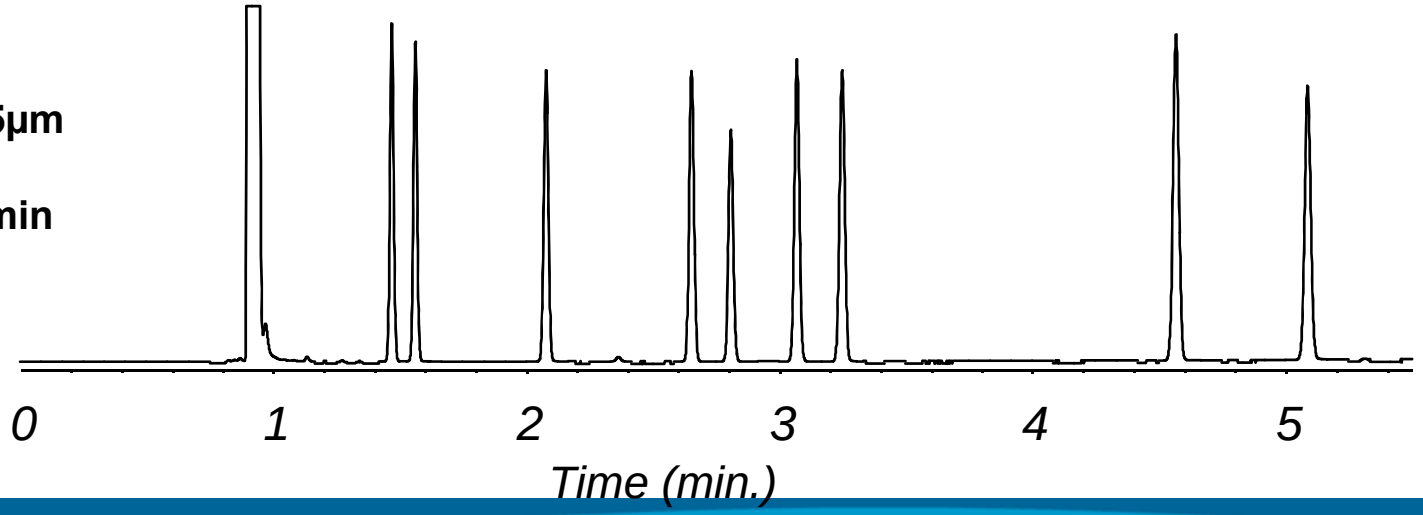
Take advantage of unique interactions between analyte and stationary phase functional groups

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



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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

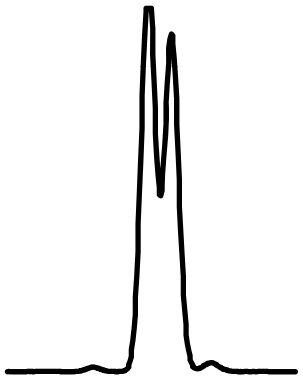
$$R \alpha \sqrt{n} \alpha \sqrt{L}$$

Length X 4 = Resolution X 2

$$t \alpha L$$

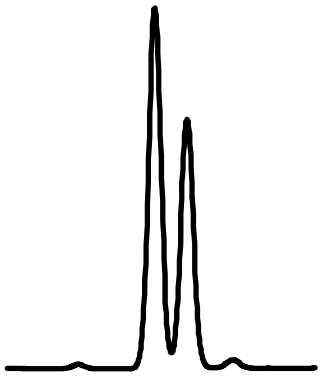
Column Length VS Resolution and Retention: Isothermal

R=0.84
2.29 min



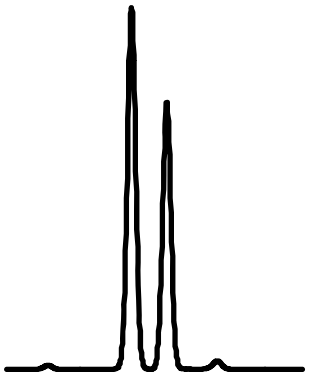
15 m

R=1.16
4.82 min



30 m

R=1.68
8.73 min

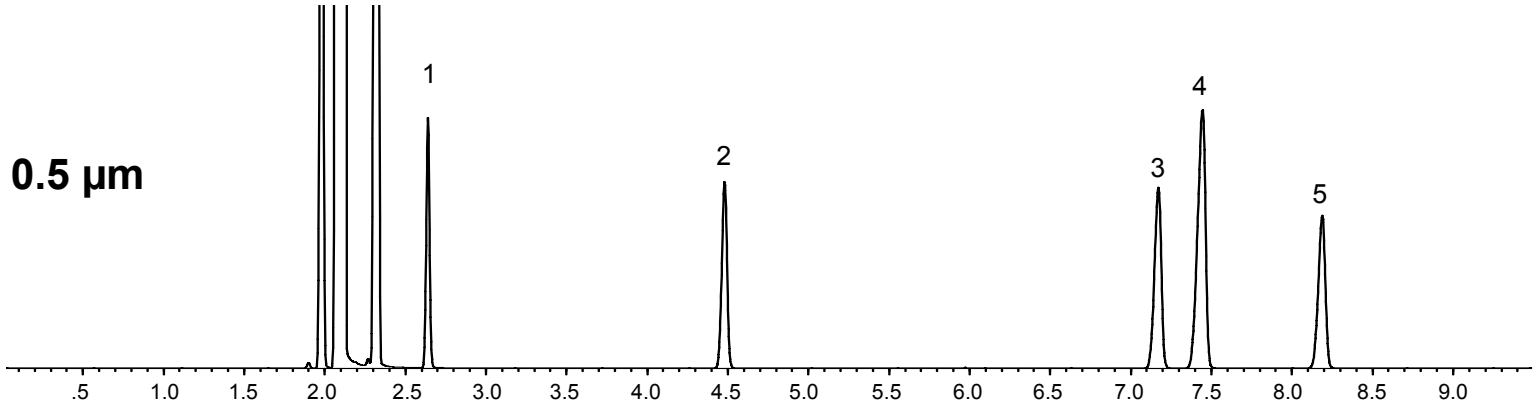


60 m

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
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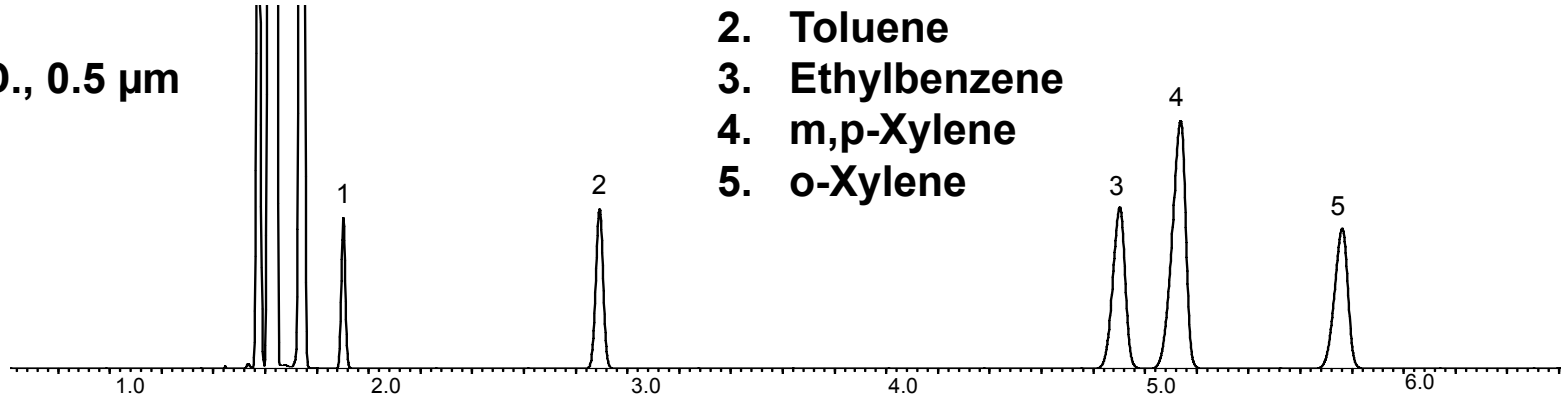
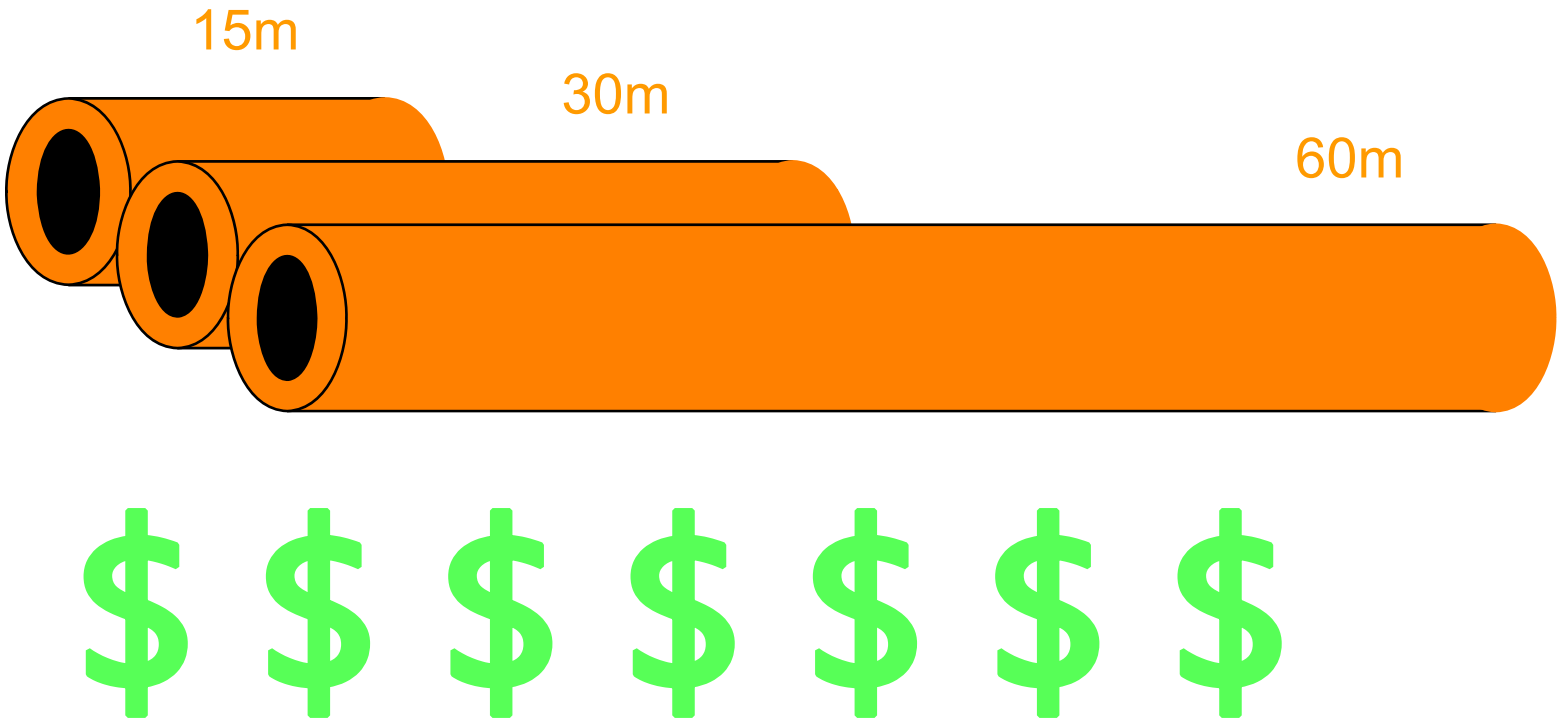


1. **Benzene**
2. **Toluene**
3. **Ethylbenzene**
4. **m,p-Xylene**
5. **o-Xylene**

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

Column Length and Cost



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

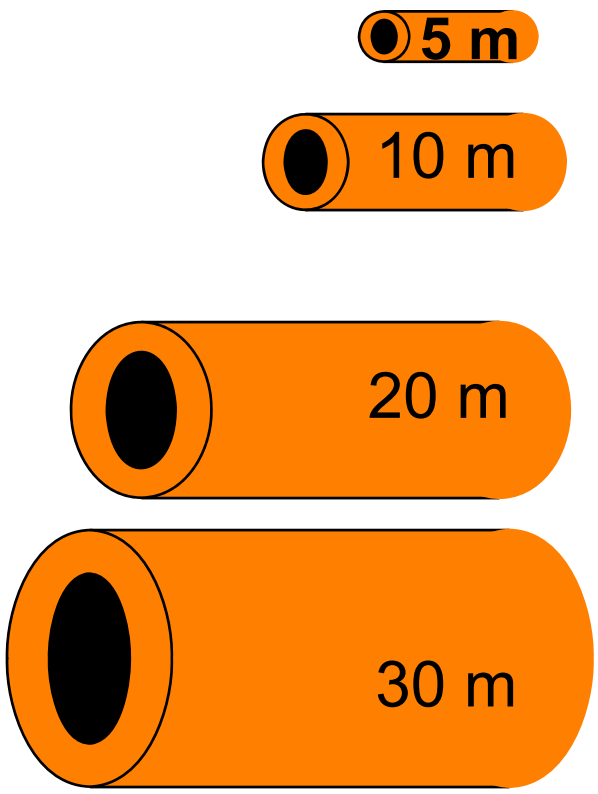
L = Length

r_c = column radius

d_f = film thickness

T = temperature

Column Diameter - Theoretical Efficiency

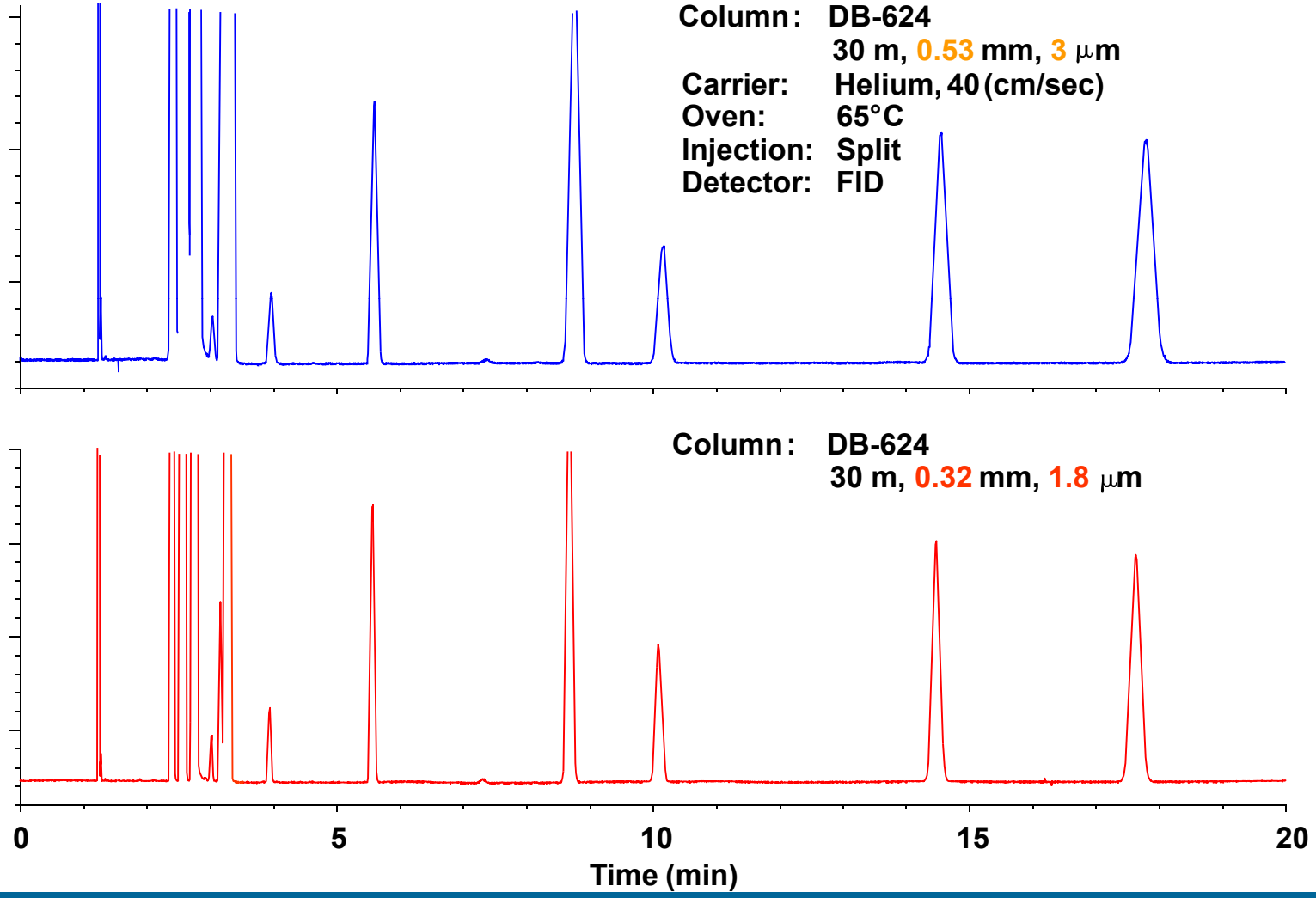


Total Plates	I.D. (mm)	n/m
N ~ 112,000	0.05	23,160
N ~ 112,000	0.10	11,580
	0.18	6,660
N ~ 112,000	0.20	5830
	0.25	4630
N ~ 112,000	0.32	3660
	0.45	2840
	0.53	2060

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

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

Column Diameter and Carrier Gas Flow

Lower flow rates: Smaller diameter columns

Higher flow rates: Larger diameter columns

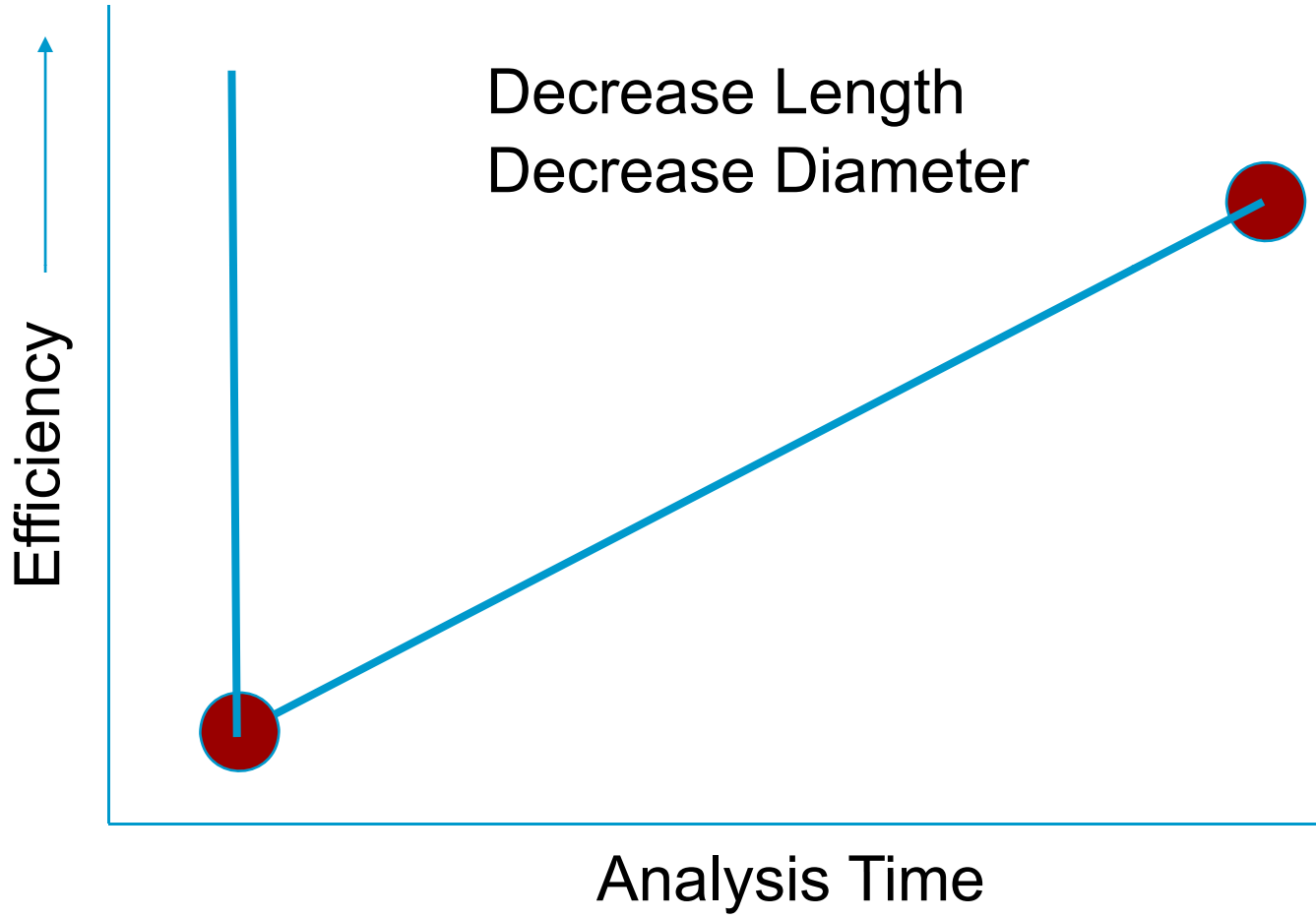
Low flow rates : GC/MS
High flow rates: Headspace, purge & trap

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



Carrier Gas Considerations
Best velocity?

Optimal range of velocities

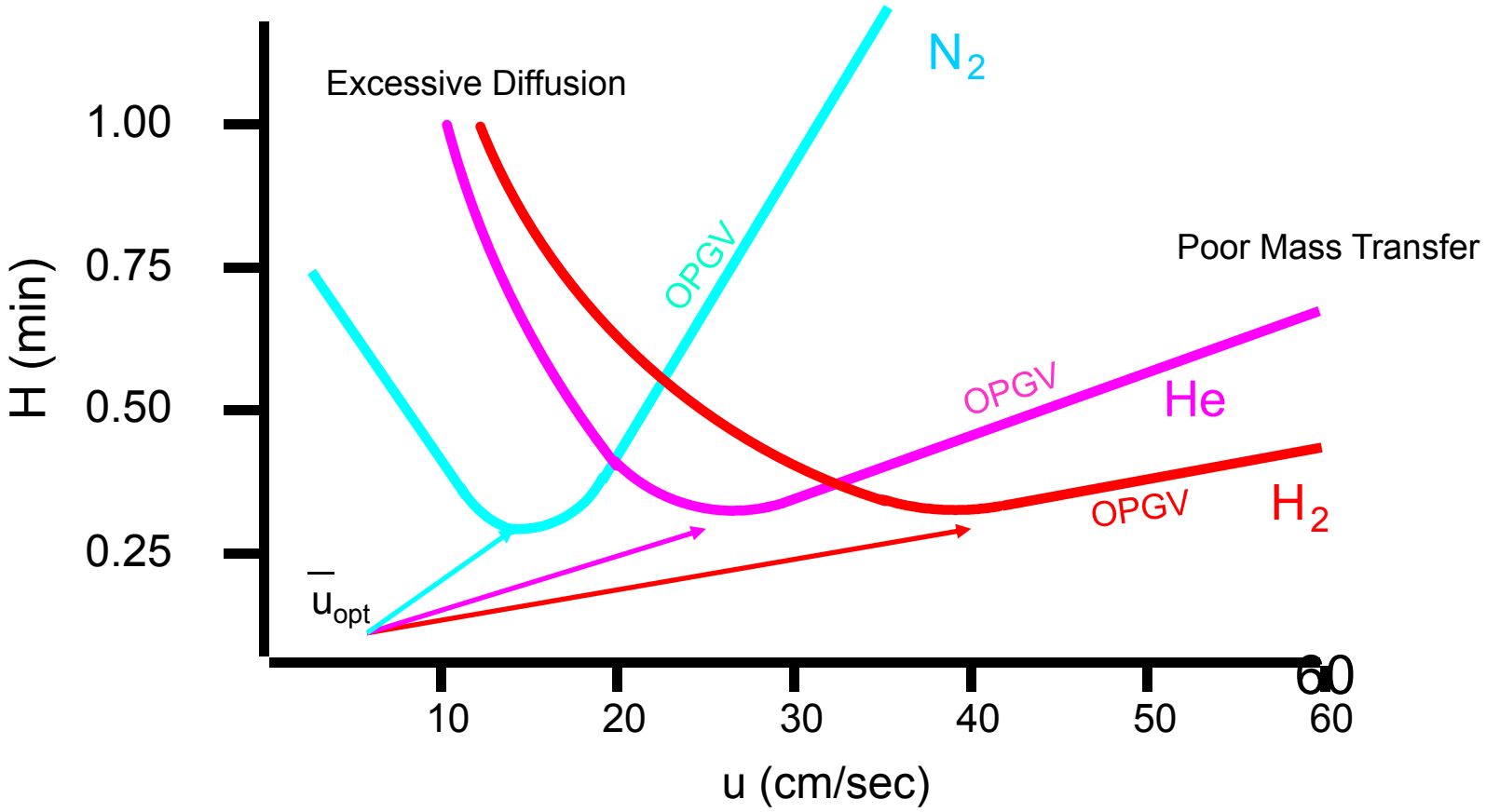
Too low or high results in loss of resolution

Balance resolution and analysis time

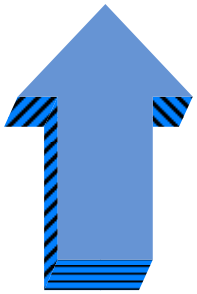
BUT... there is no LAW against going FASTER

Carrier Gas Considerations

Van Deemter Curve



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

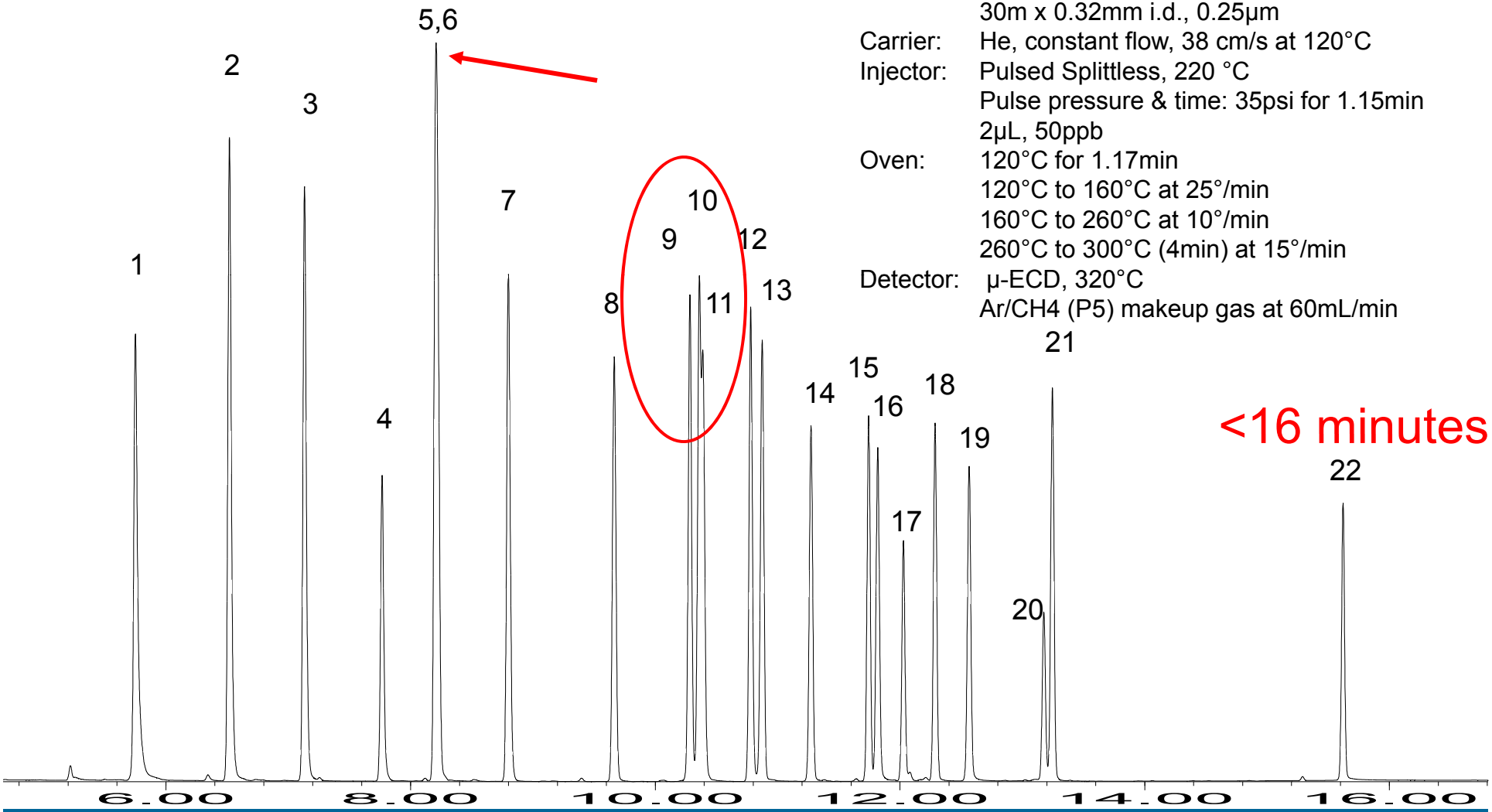
Switch He to H_2 Carrier Gas and Try Faster Velocities

Same Column & Gas Type but Faster Velocities

Combination of all of the above

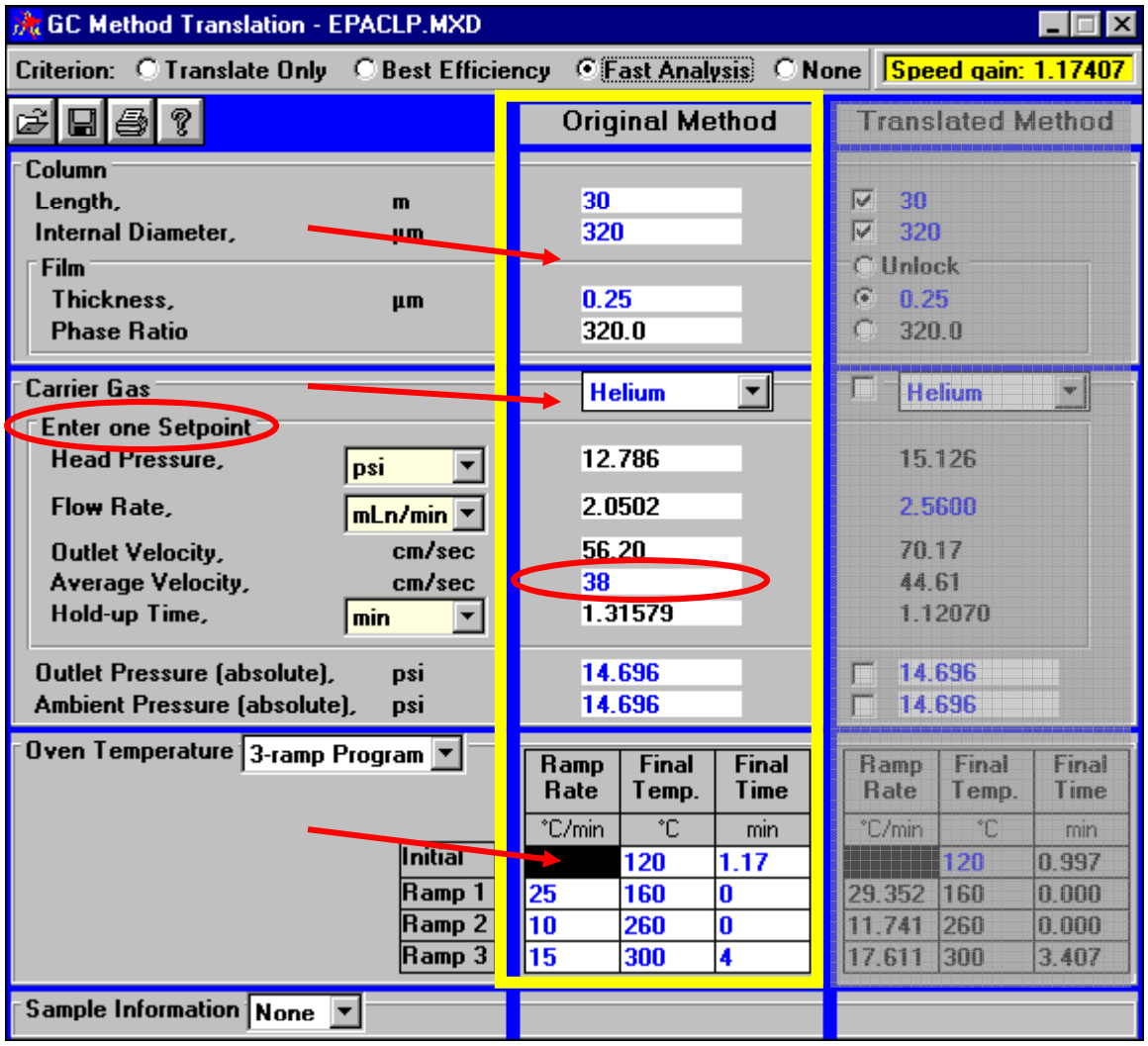
CLP-Pesticides - Original "Improved" Method
0.32mm I.D., Helium Carrier Gas

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

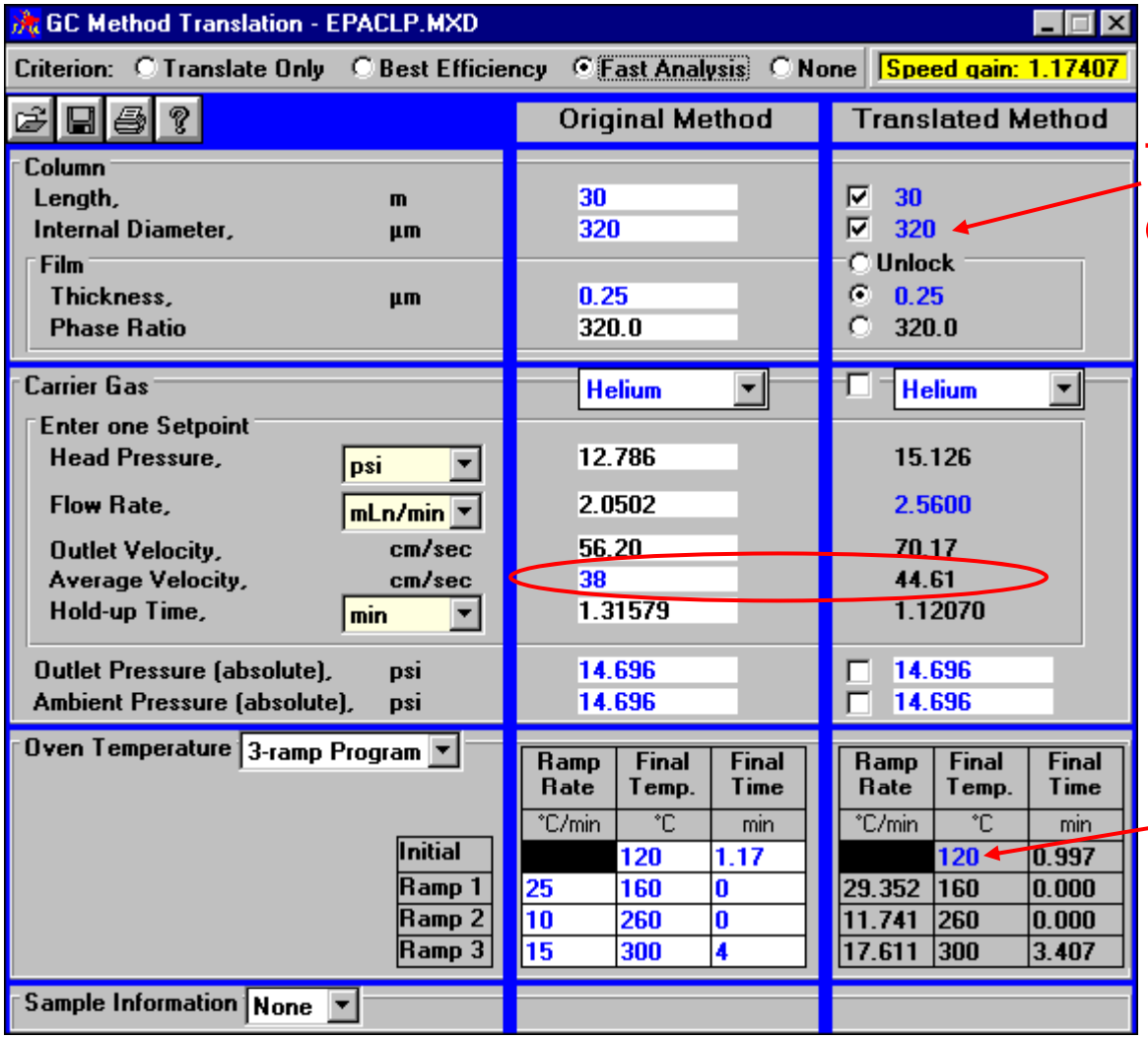


<16 minutes

Input Original Method Parameters



Same Column and Gas Type
Fast Analysis (OPGV)



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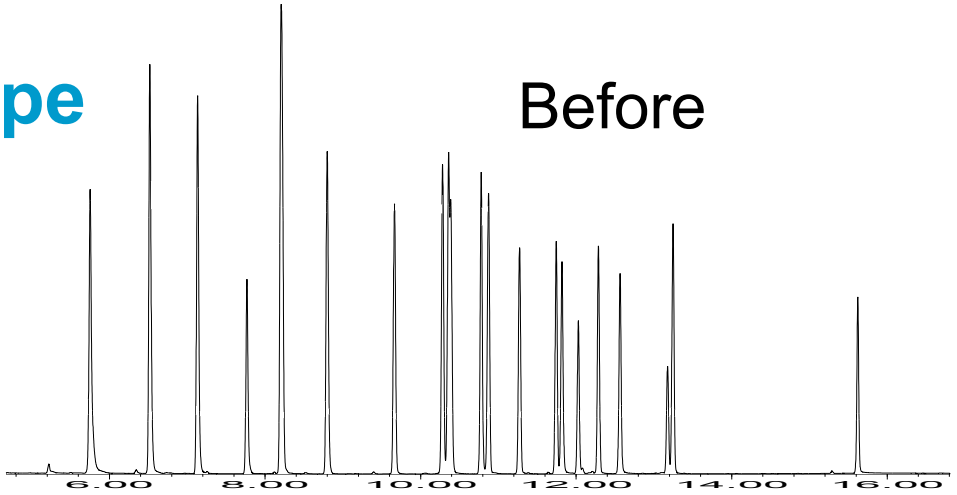


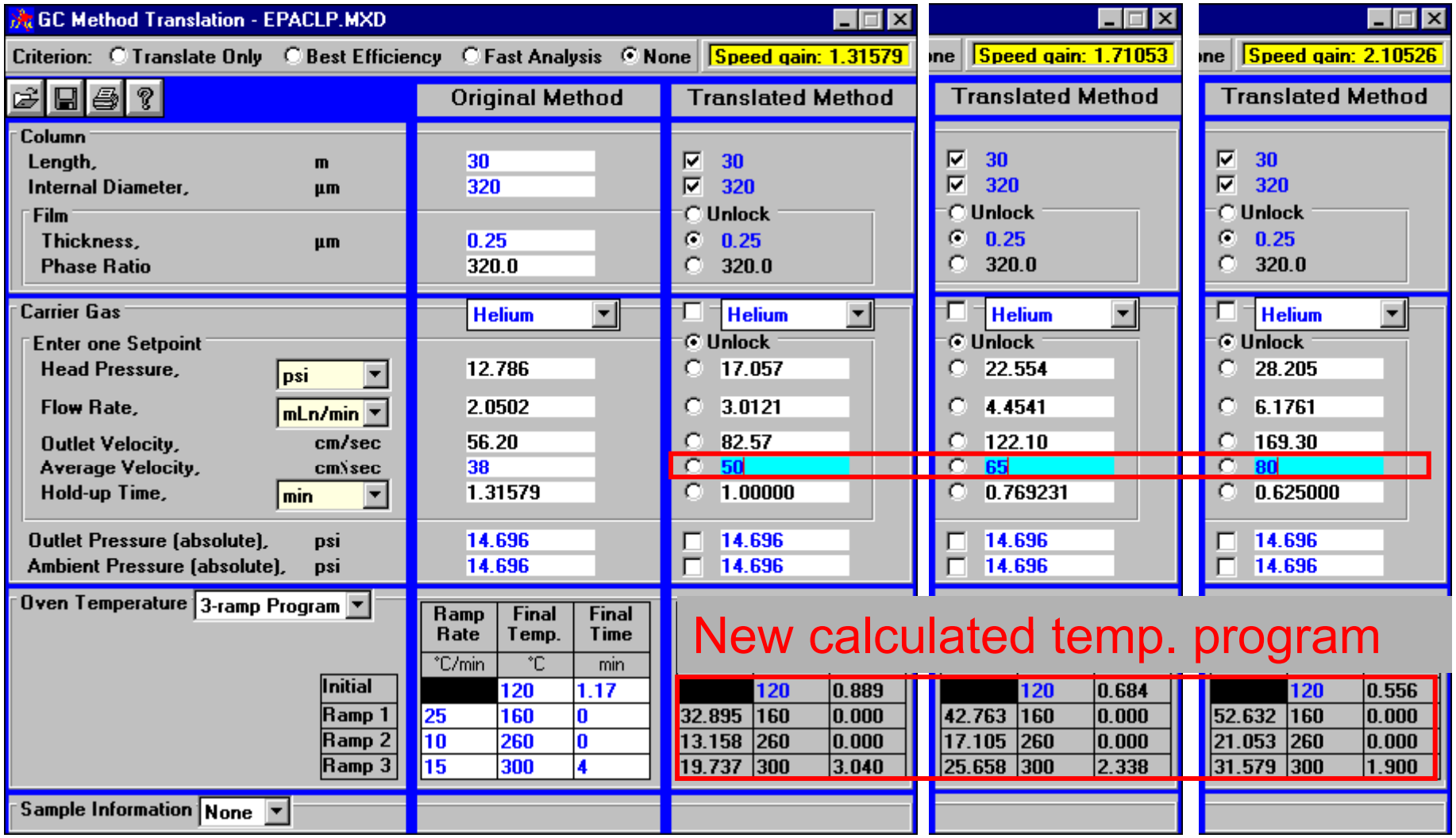
No Real Changes in Resolution!

Only Time!

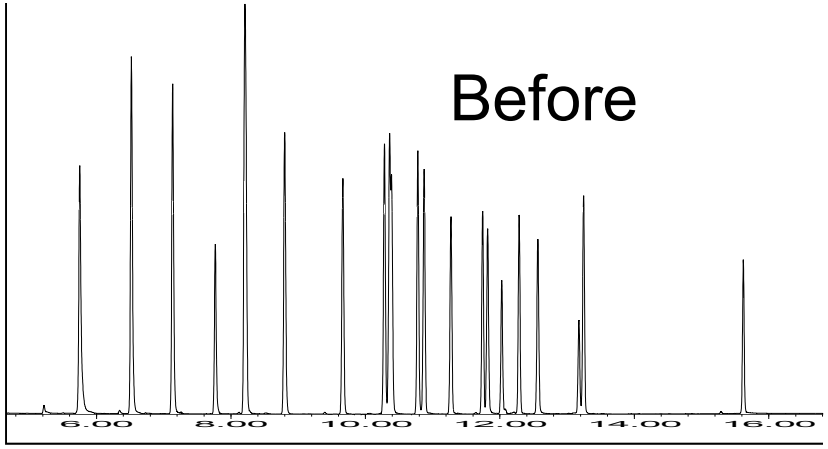
<14 minutes

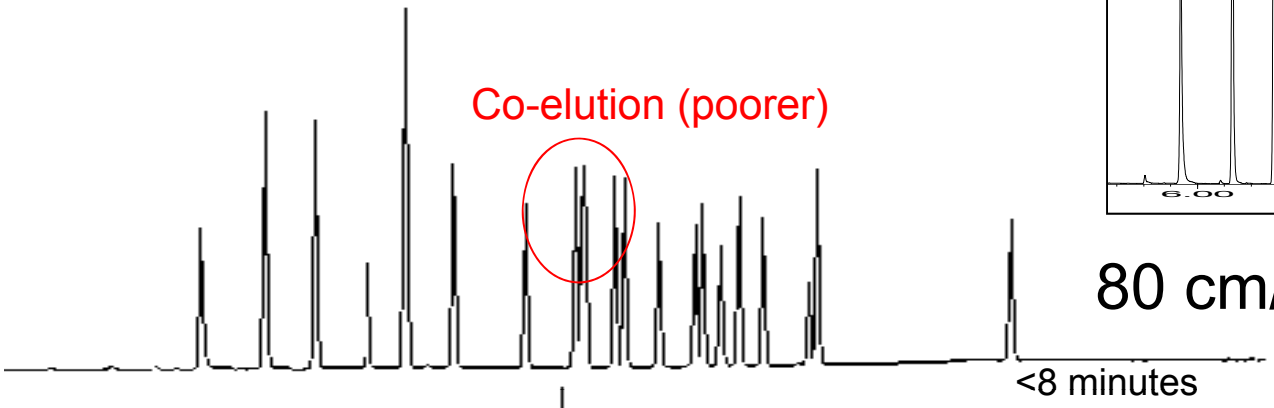
6.00
8.00
10.00
12.00
14.00

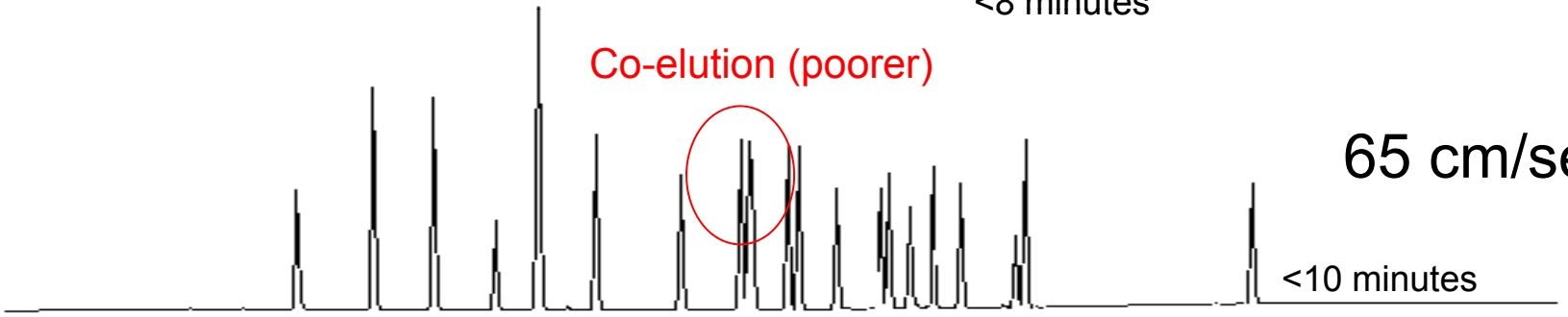
Same Column and Gas type
None mode, Try higher velocities

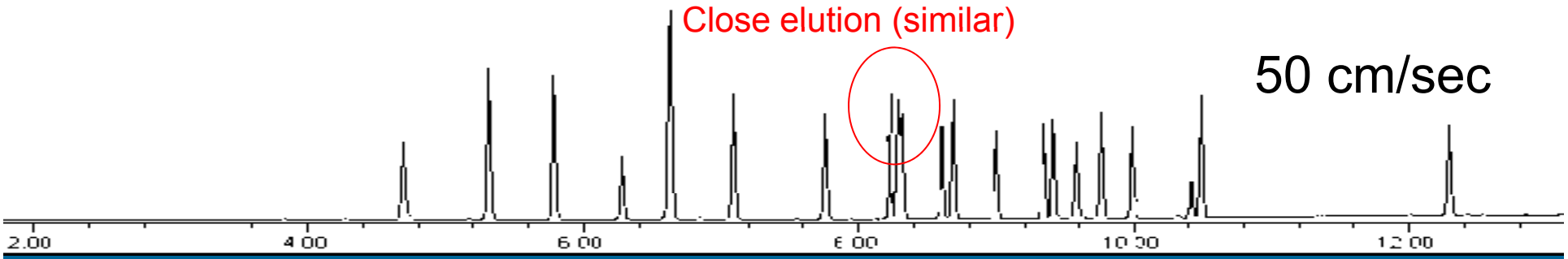


Same Column and Gas type
None mode, Higher velocities

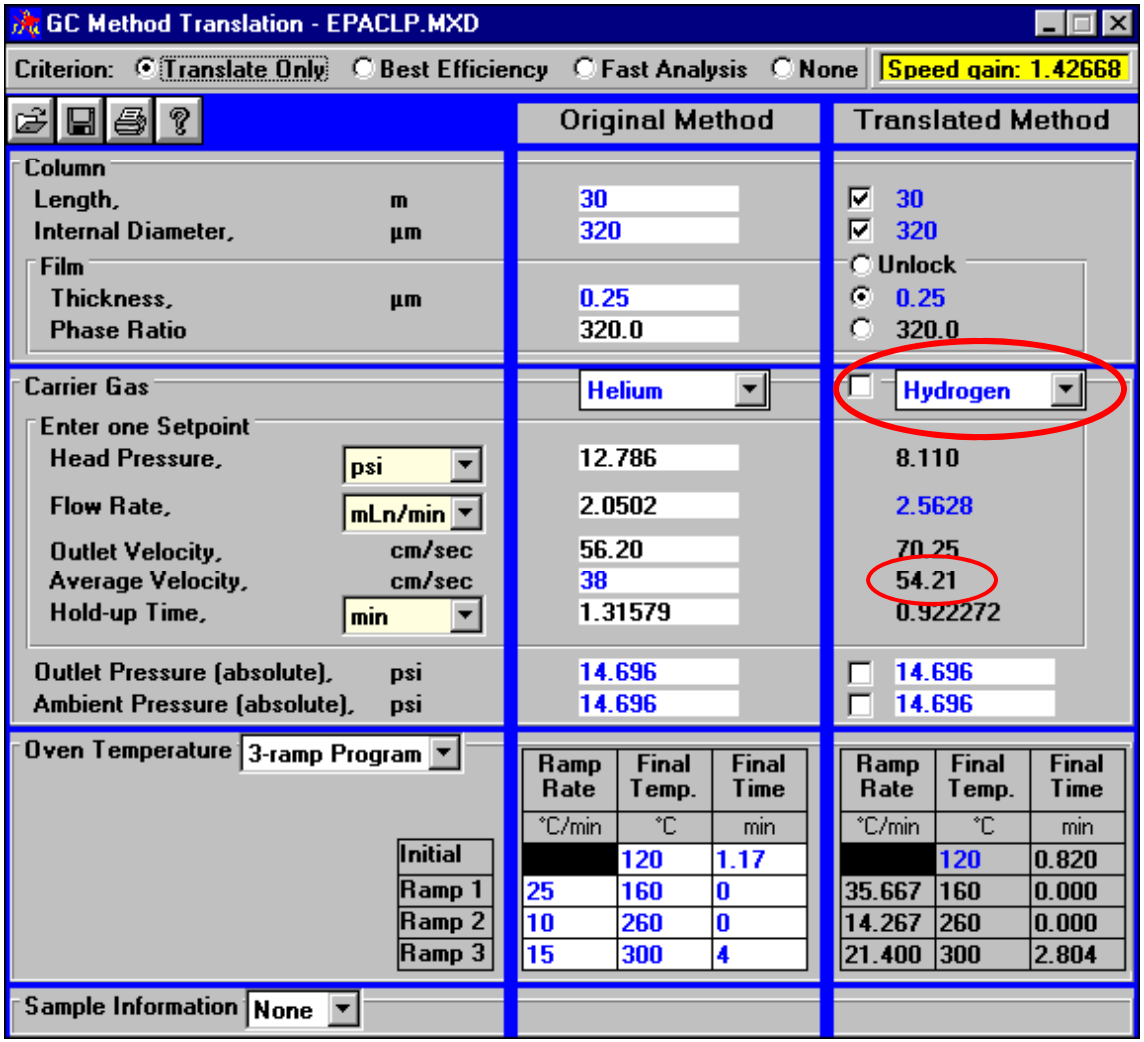




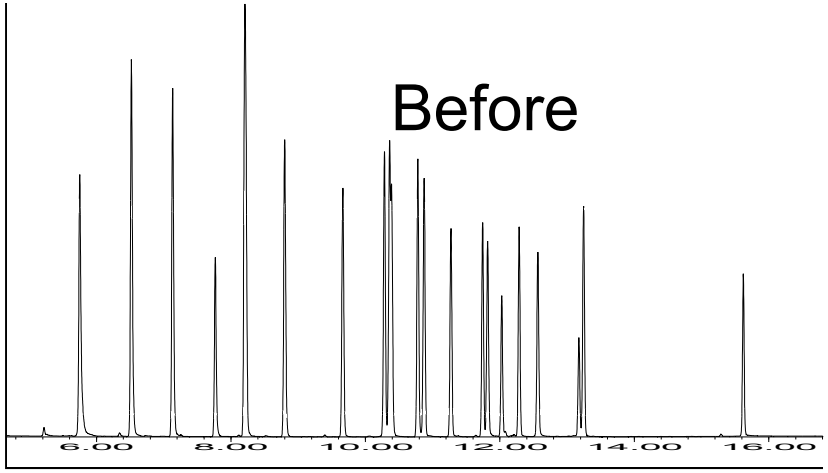




Same Column, Hydrogen Carrier Gas Translate Only



Same Column, H_2 Carrier Gas Translate Only



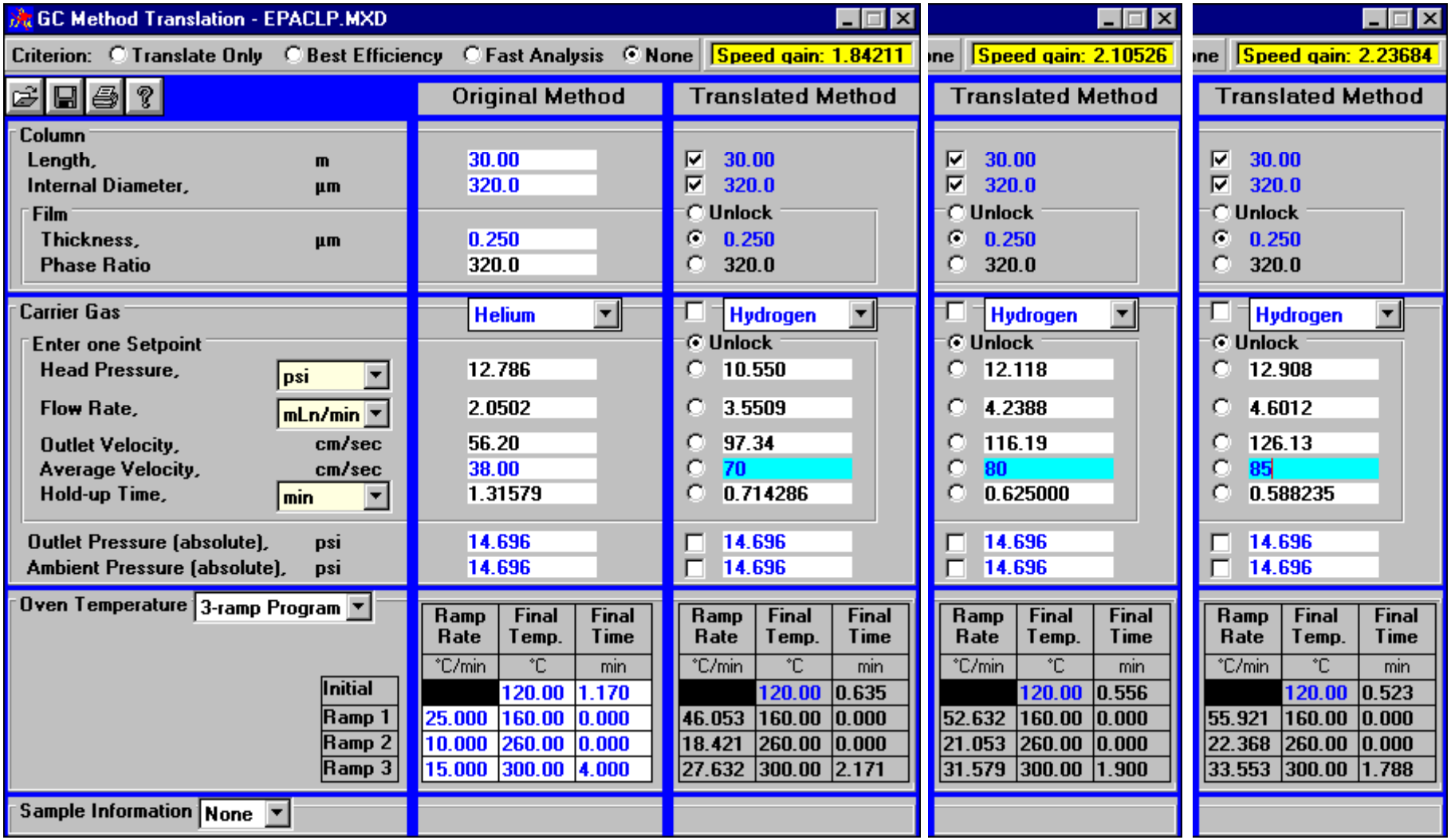
No Real Changes in Resolution

33% faster!

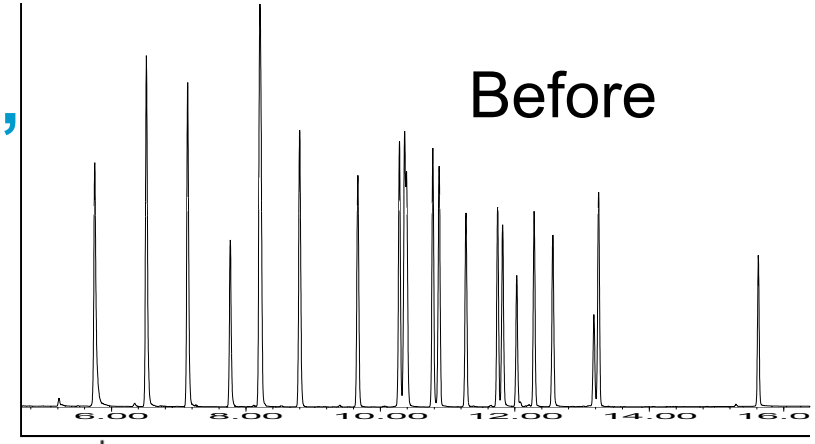
11 minutes

4.00
6.00
8.00
10.00
12.00

Same Column, H2 Carrier Gas, Higher Velocities



Same Column, H2 Carrier Gas, Even Higher Velocities



Co-elution

85 cm/sec

7 minutes

Co-elution

80 cm/sec

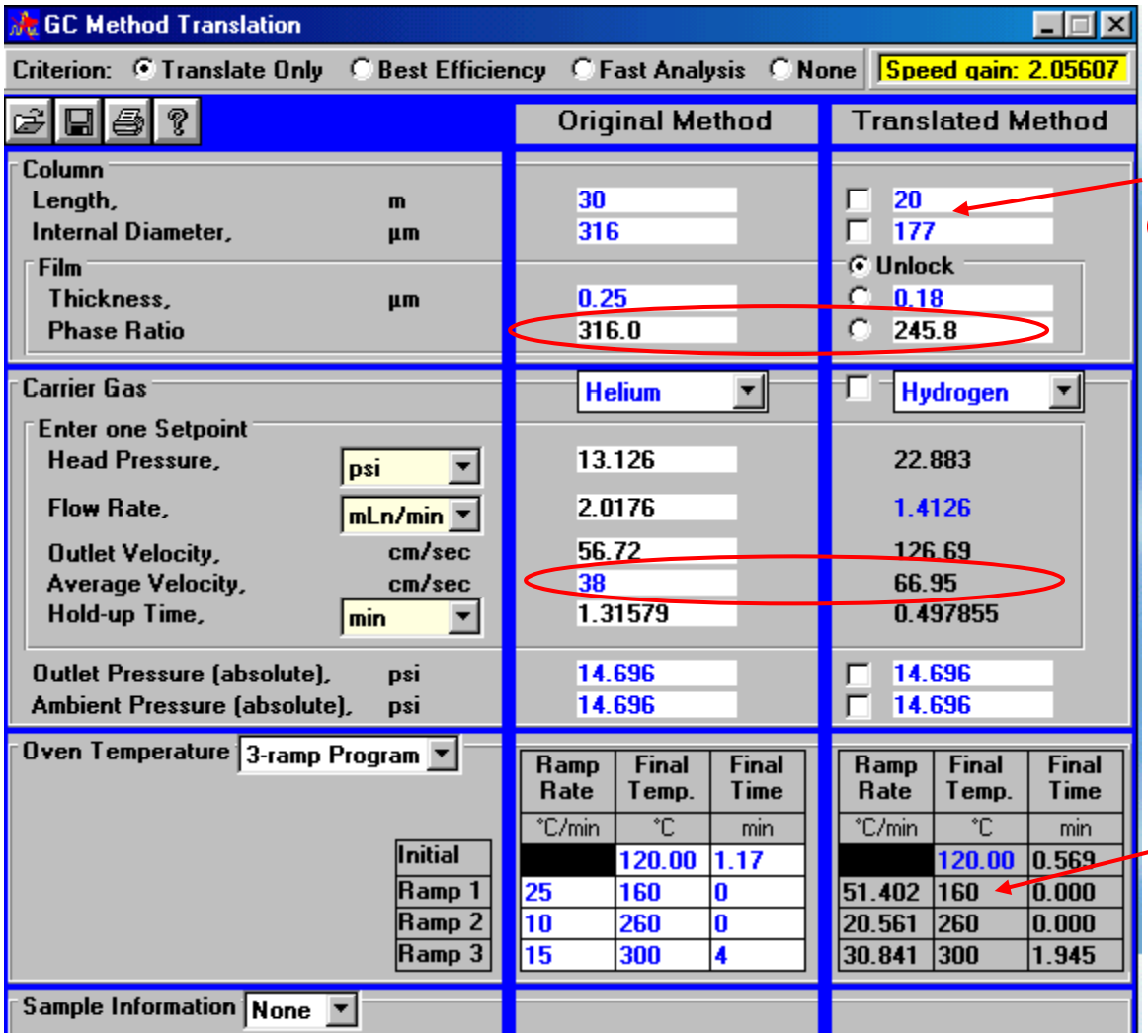
<8 minutes

Co-elution

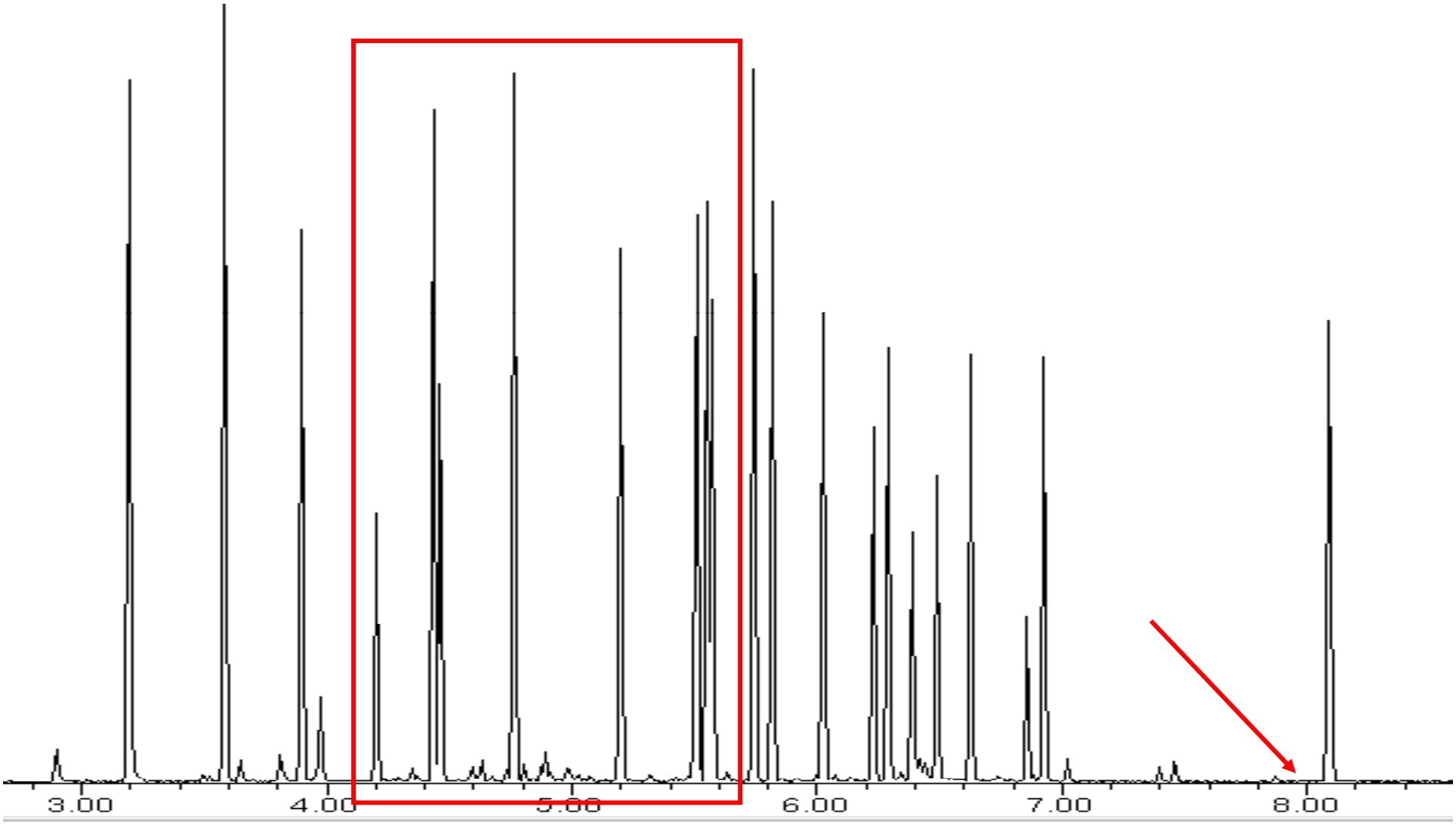
70 cm/sec

2.00 4.00 6.00 8.00 10.00

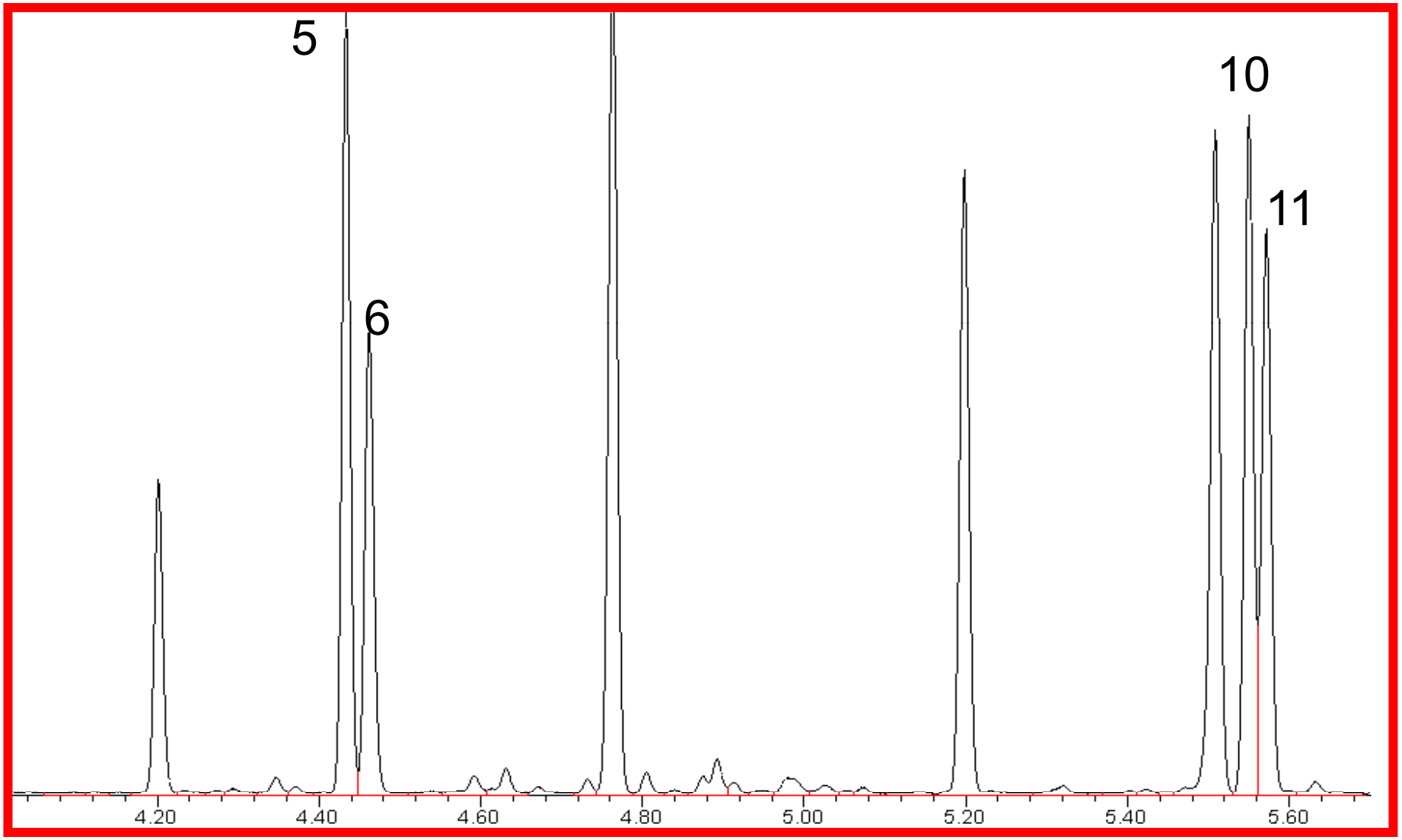
New Column Dimensions, H_2 Gas, Translate Only



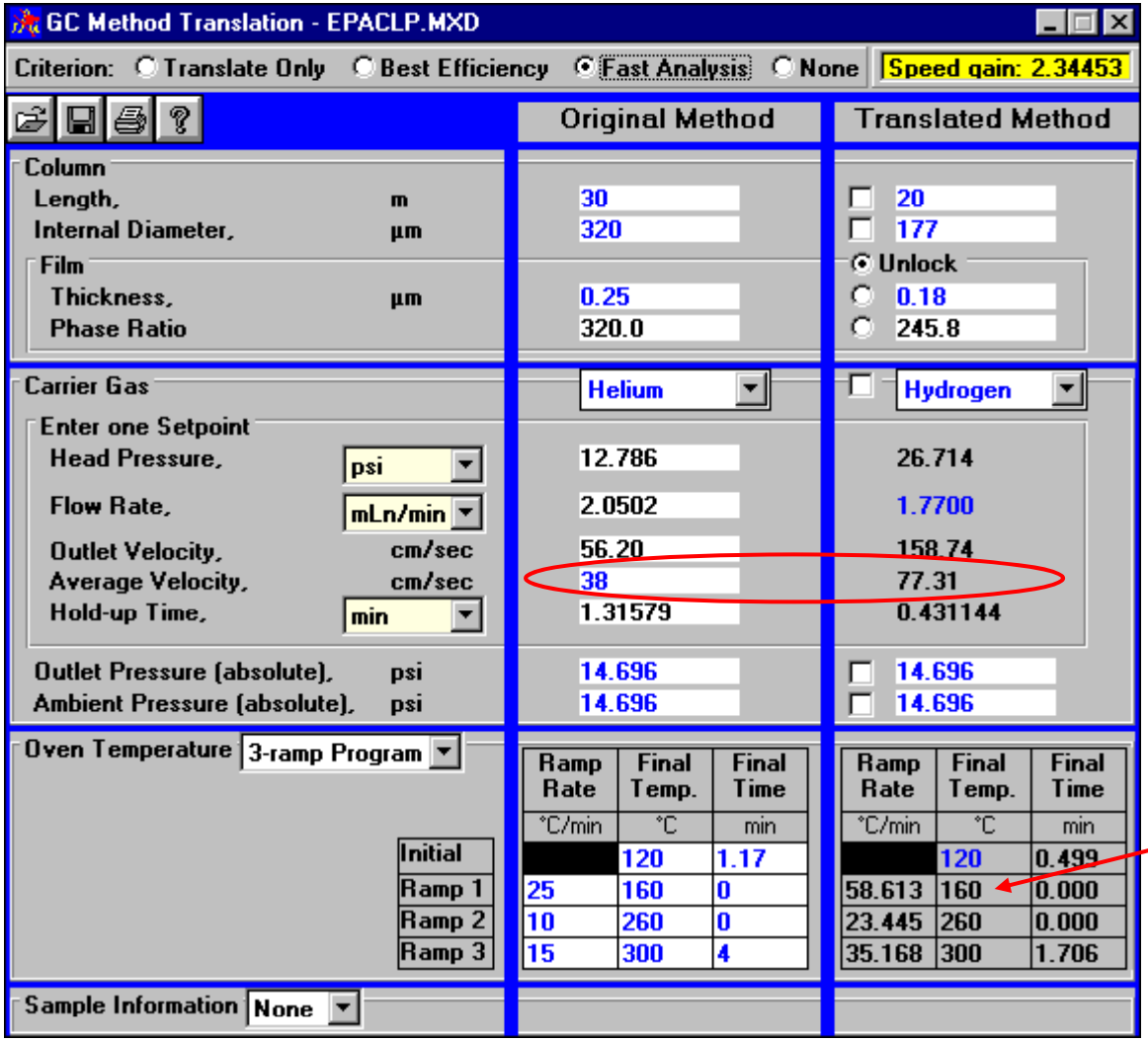
New Column Dimensions, H2 Gas, Translate Only



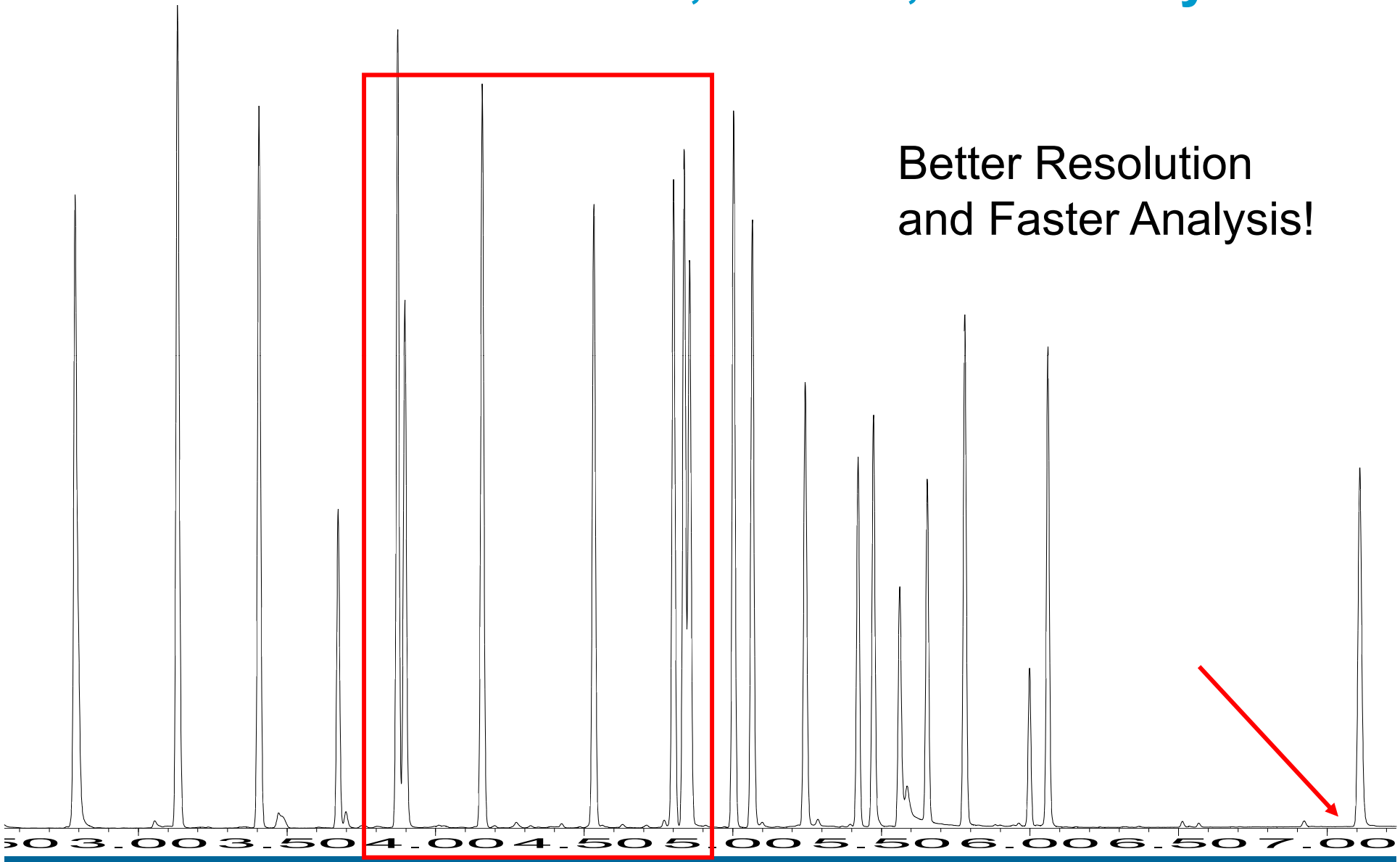
New Column Dimensions, H2 Gas, Translate Only



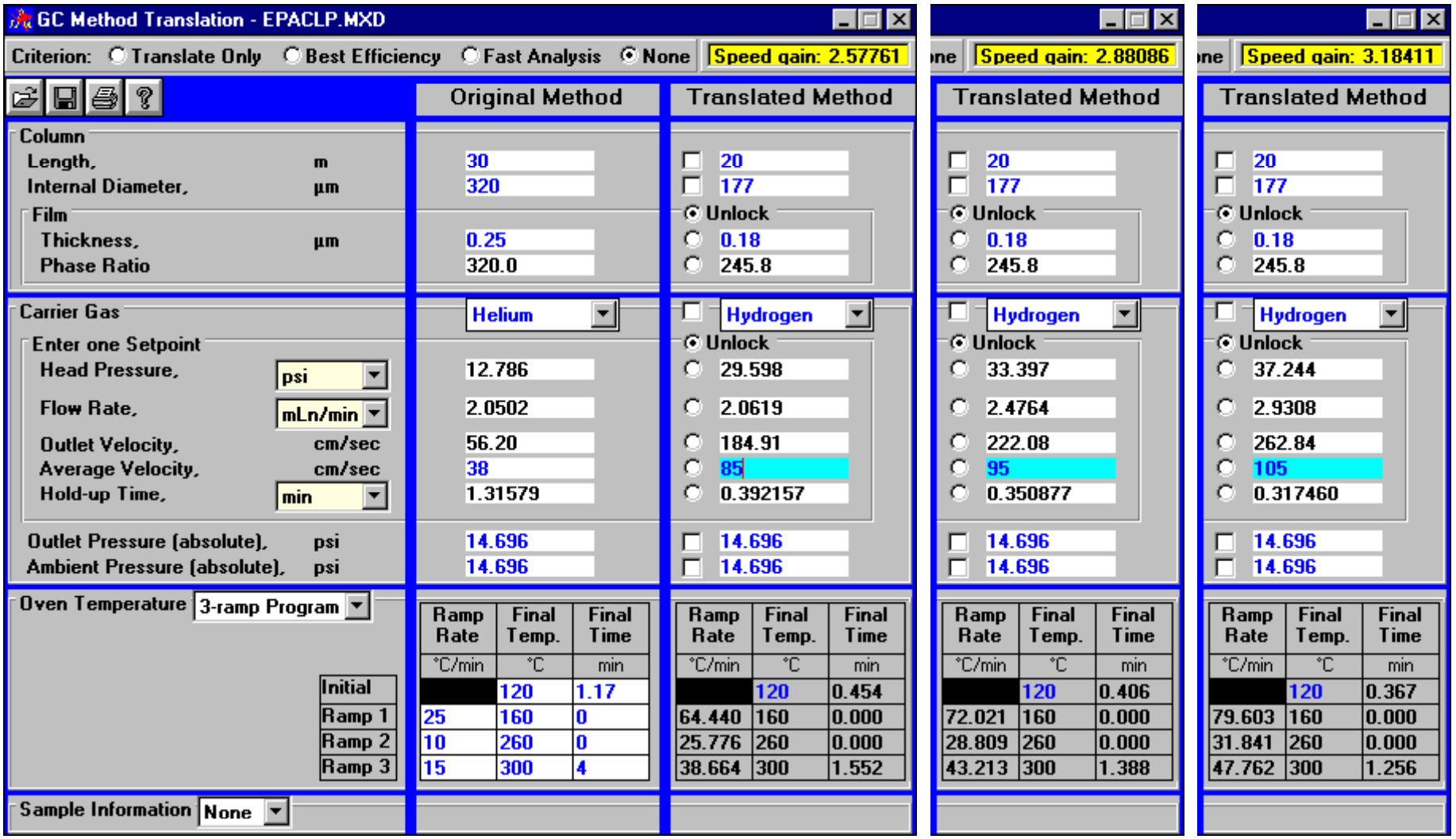
New Column Dimensions, H2 Gas, Fast Analysis



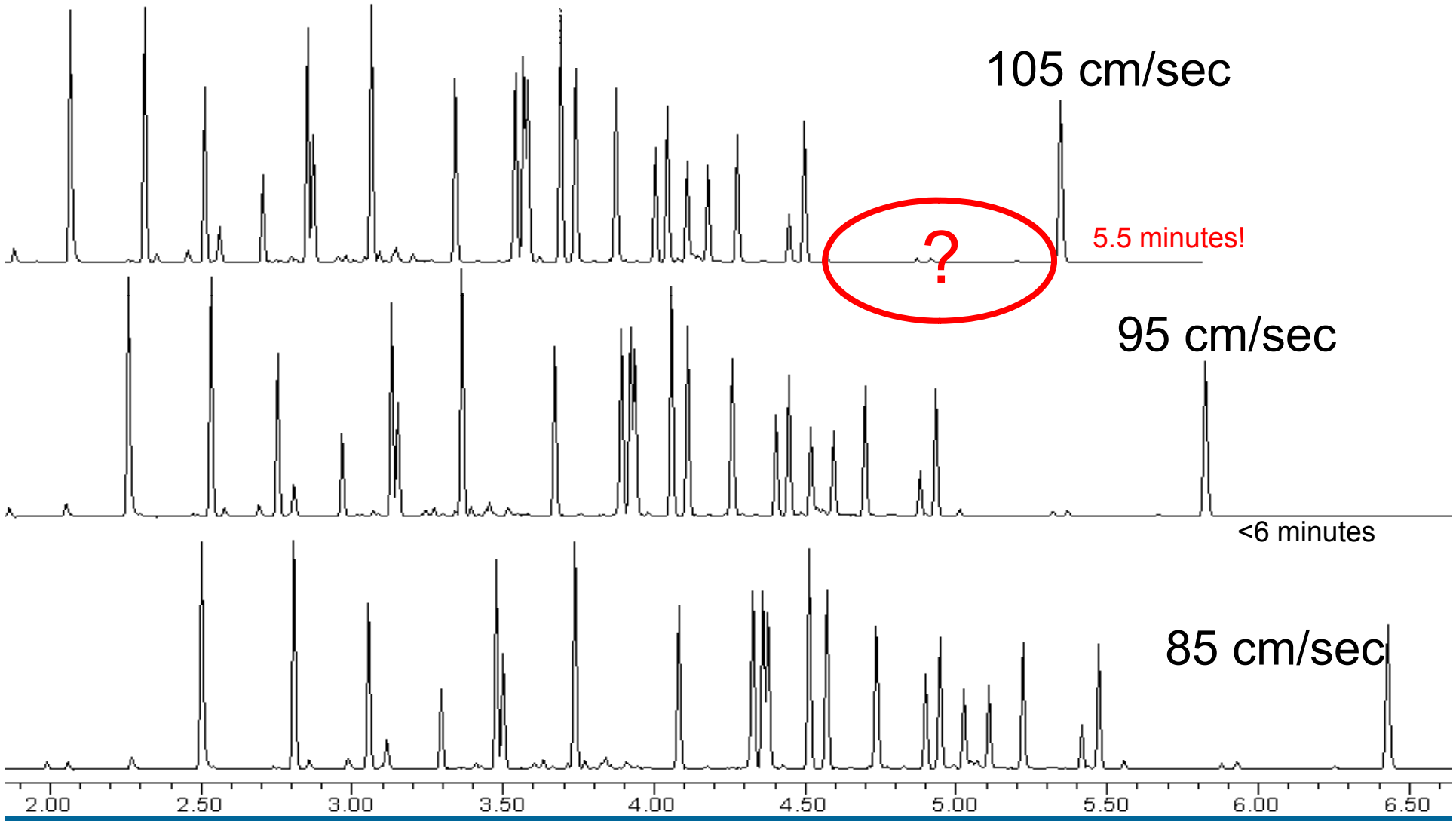
New Column Dimensions, H2 Gas, Fast Analysis



New Column Dimensions, H2 Gas, Higher Velocities

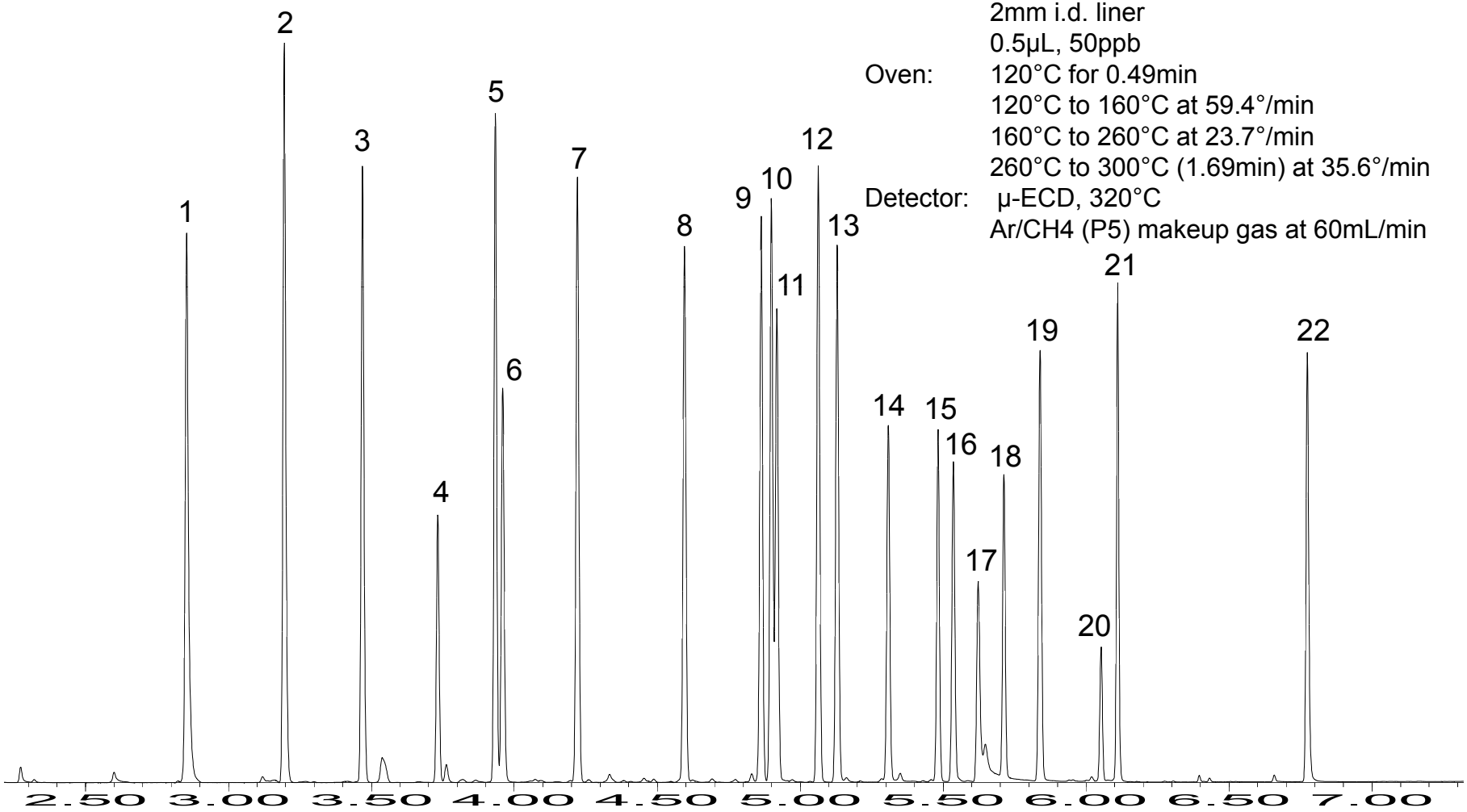


New Column Dimensions, H2 Gas, Higher Velocities



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



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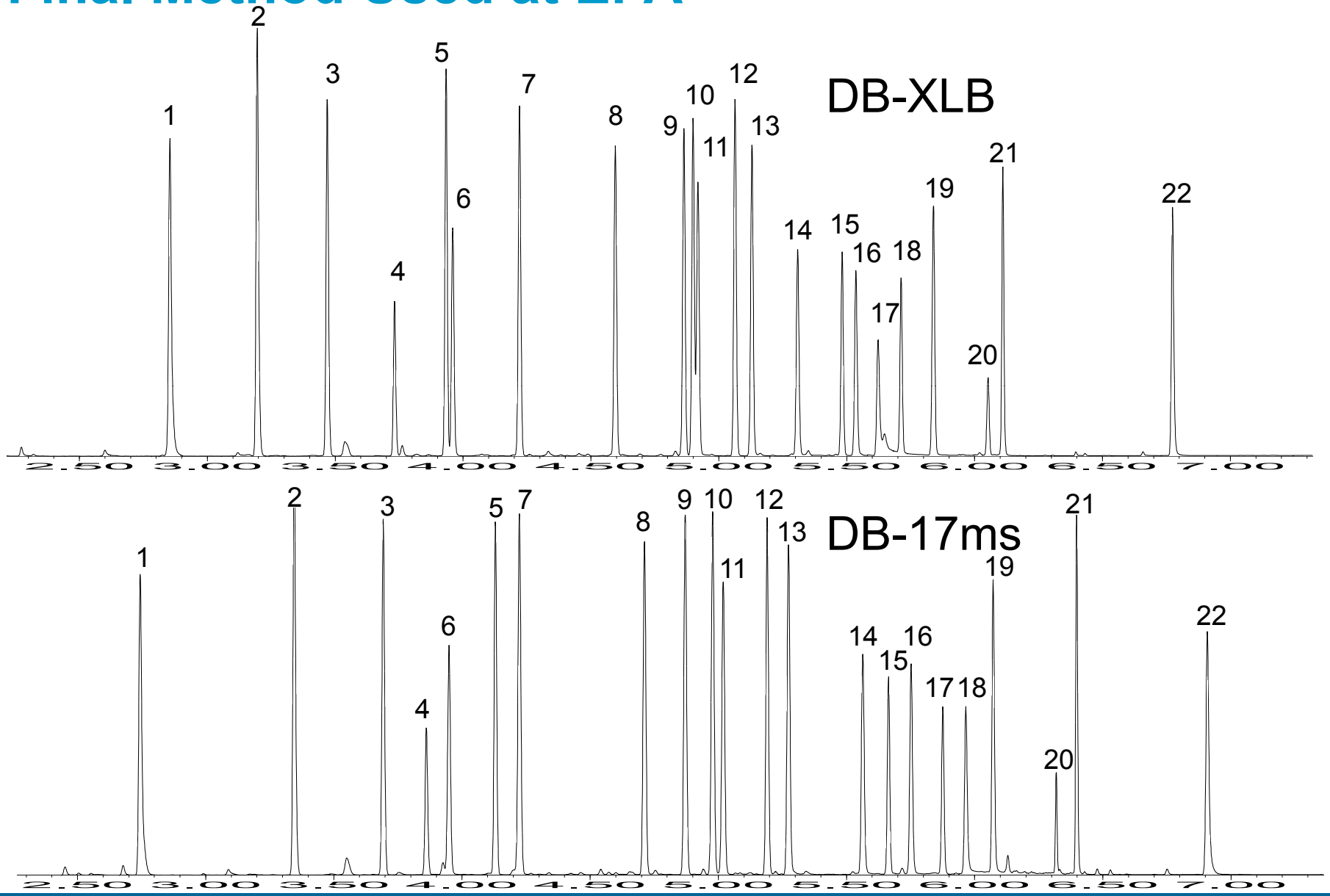
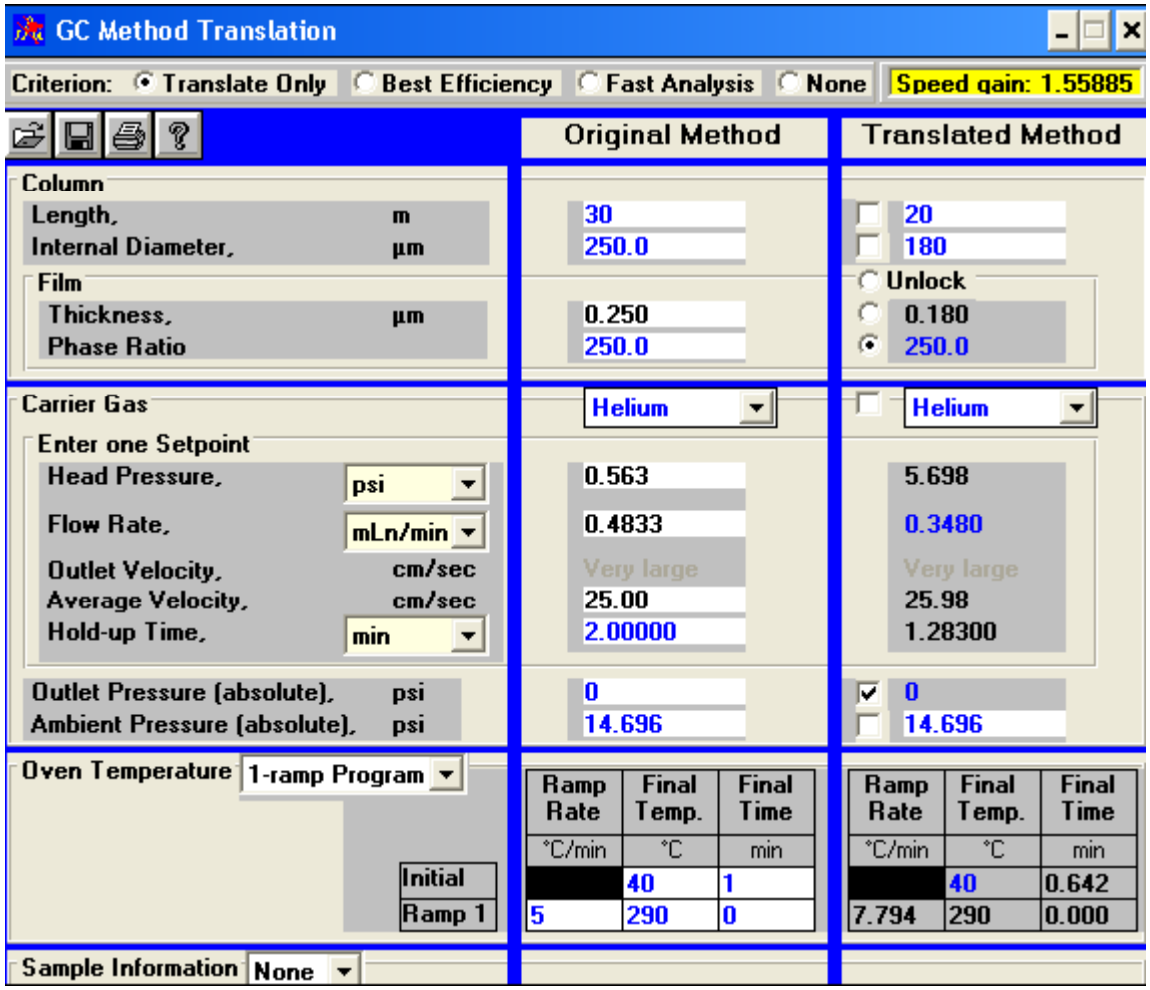
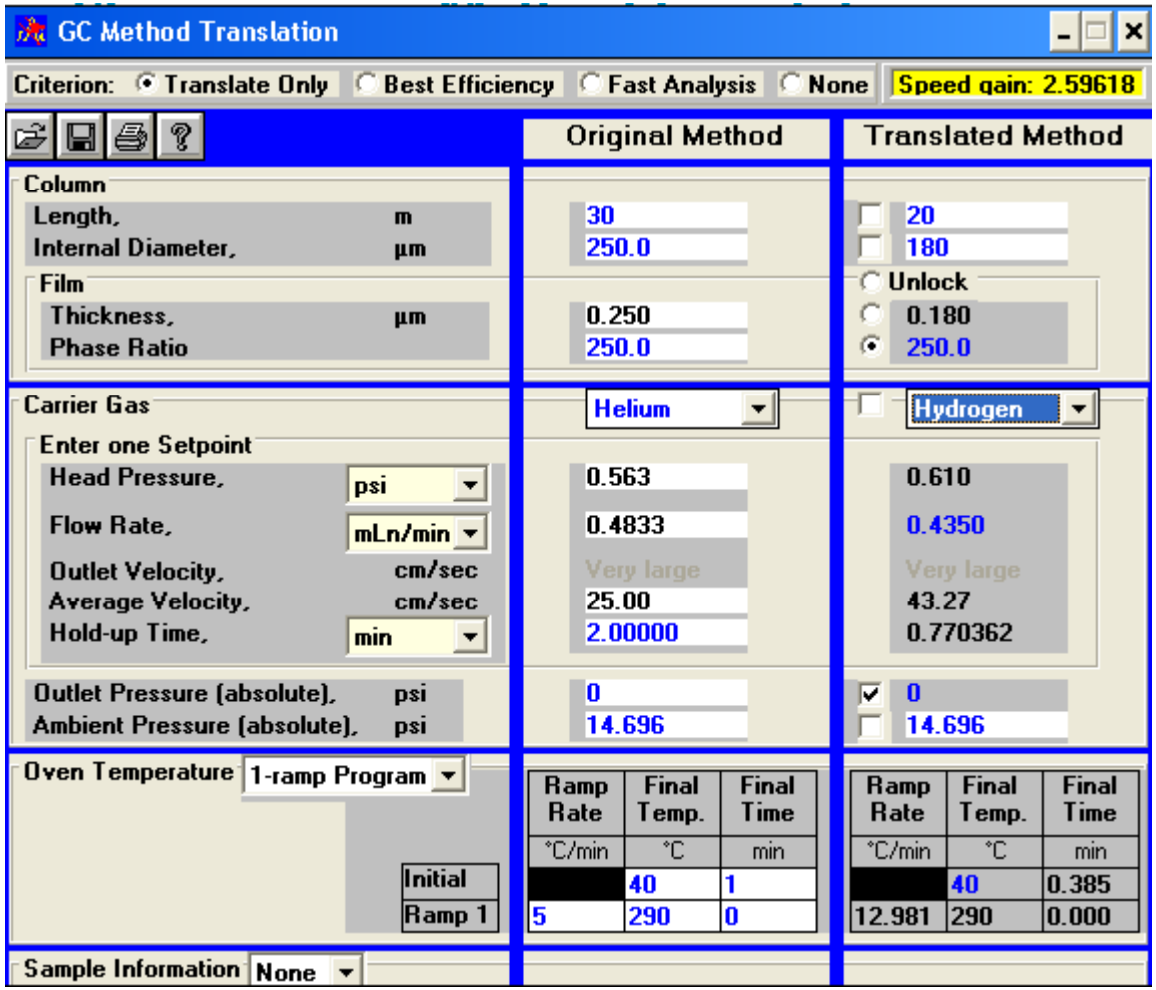


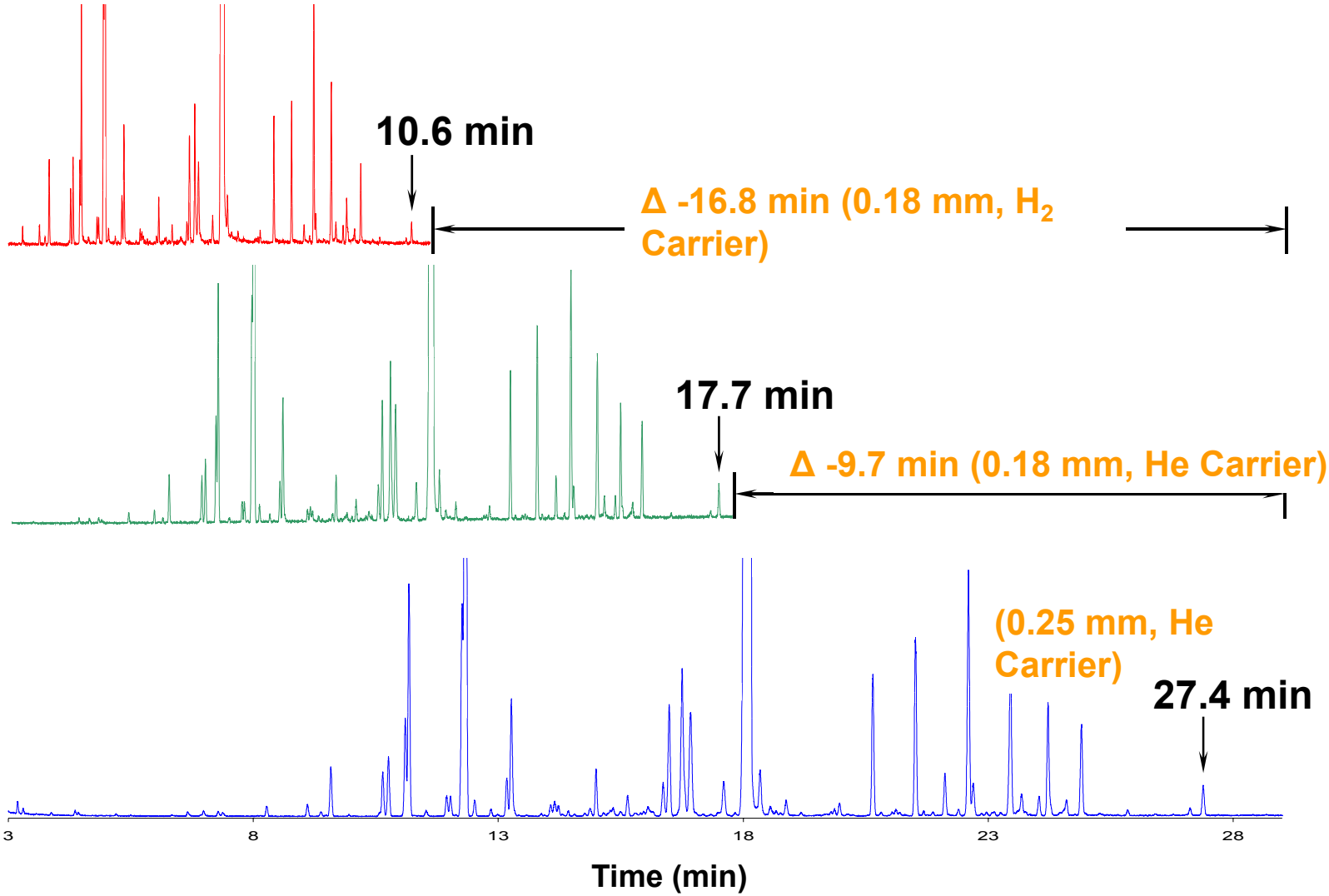
Food/Fragrance – Method translation



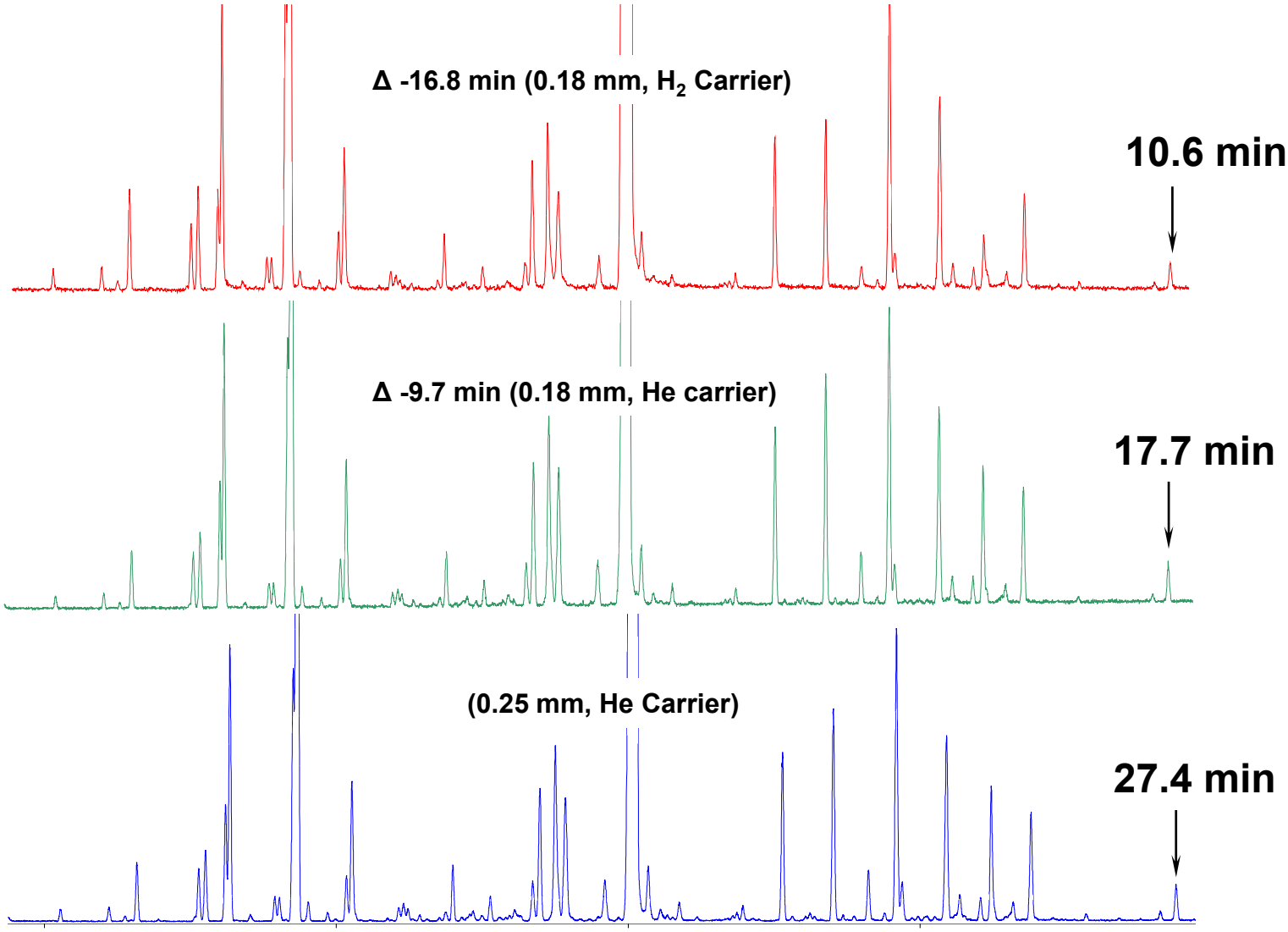
Food/Fragrance – Method translation



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%

CONCLUSIONS

Stationary Phases – Chosen for optimized selectivity

Diameter – Smaller allows shorter length but has less capacity

Make Small Changes – Again think capacity

Carrier Gas – Hydrogen, high velocity, but can still go fast with He

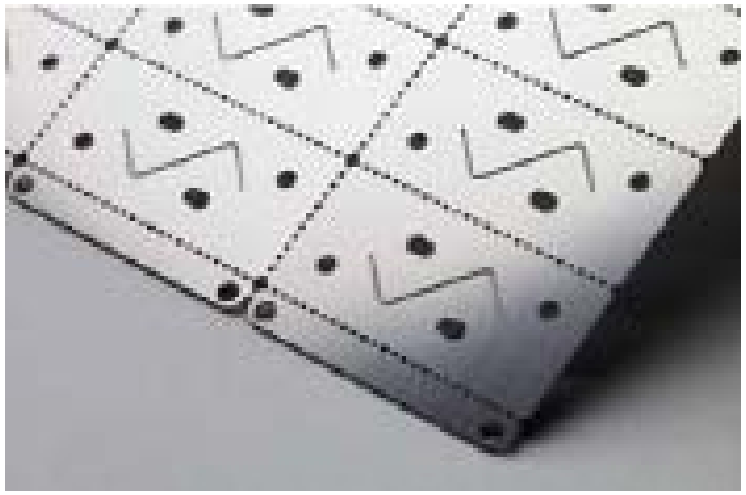
Temperature Program – Scale properly to preserve elution pattern

Method Translation Software – FREE, reliable

Flow Ramp – Increase at end of run for late eluters (if necessary)

New Devices & Instrument Improvements Provide Even Faster Analytical Cycle Times

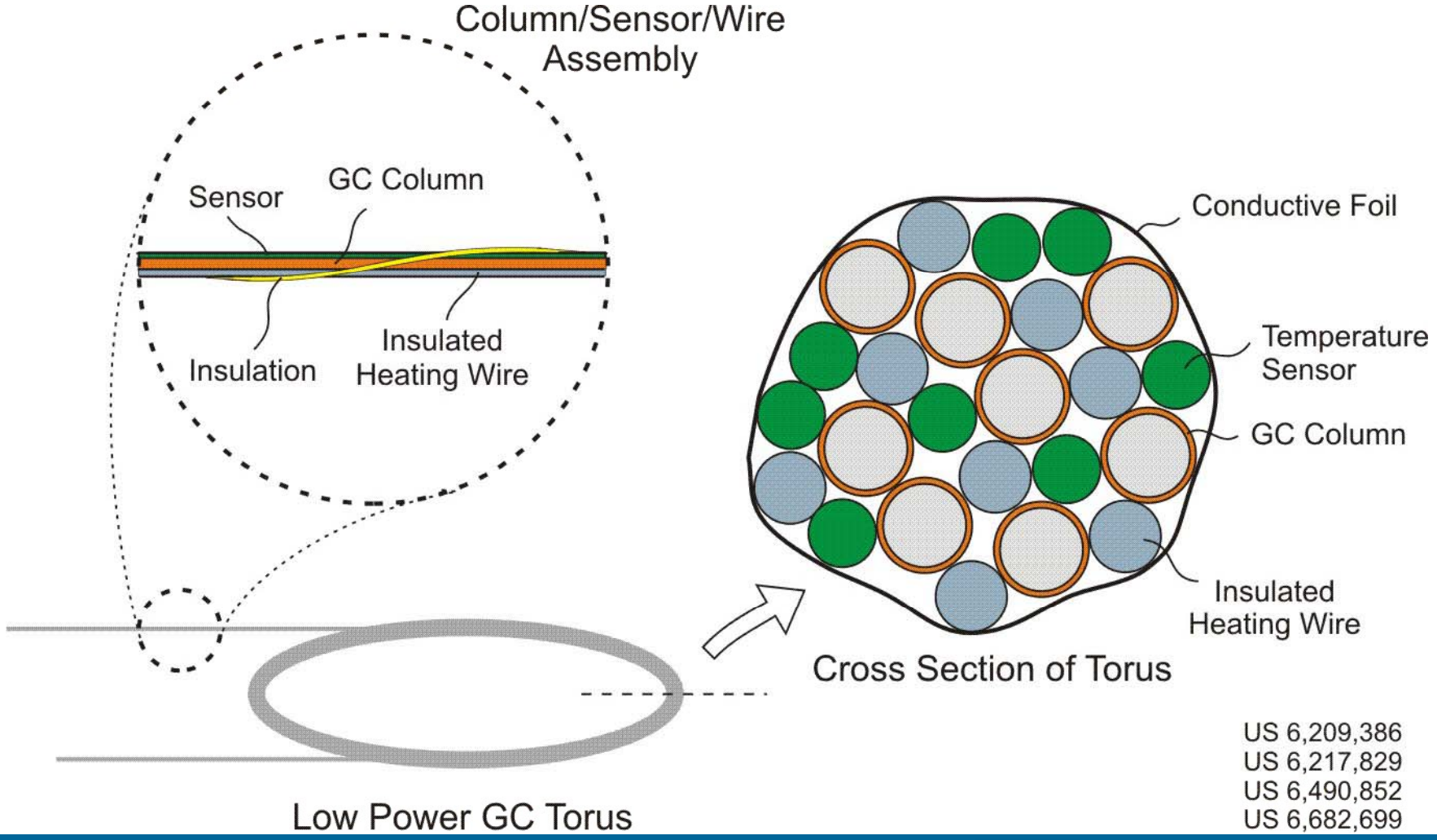
Low Thermal Mass Technology



Capillary Flow Technology

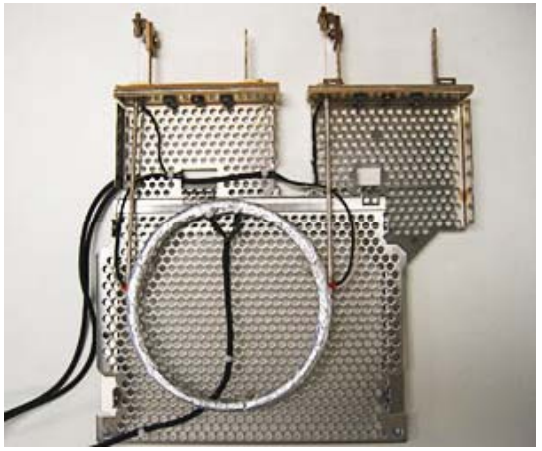
“LTM” (Low Thermal Mass) Technology (Patented)

Directly heat/cool fused silica GC columns



US 6,209,386
US 6,217,829
US 6,490,852
US 6,682,699

A Closer Look



LTM Column

LTM Retrofit Door

LTM Column Module

TECHNICAL SUPPORT

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