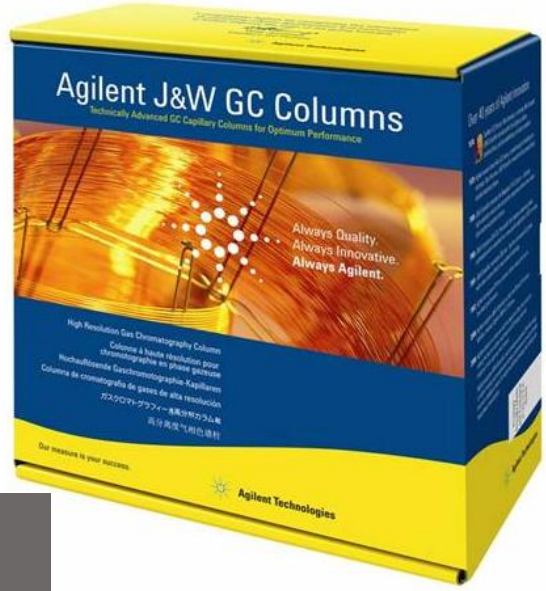
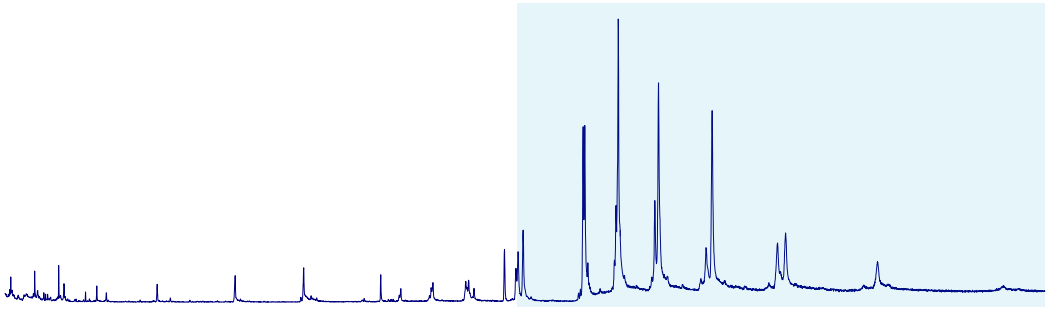
Alternate Carrier Gas Considerations and Faster GC Analysis



Faster GC Total Analytical Cycle Times – A Variety of Approaches



Included in HW/SW

"ALS Sample Overlap" in ChemStation SW

7890 GC Faster Cool-down

Column & Gas Selection, Method Translation

New Devices
***Signficantly* Faster GC Analytical Cycle Times**

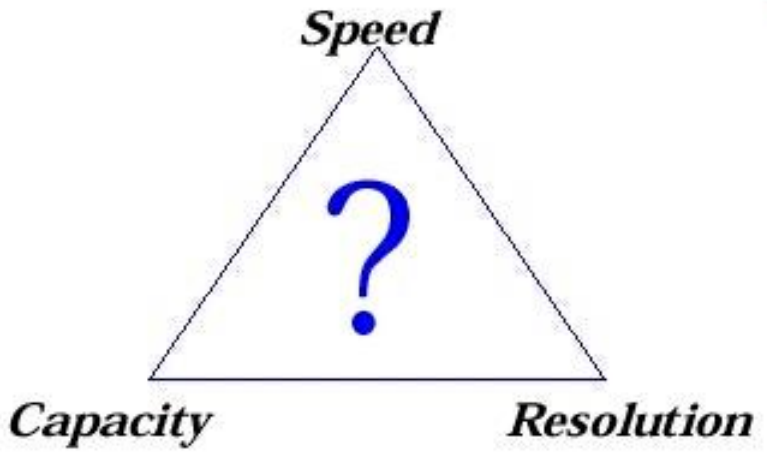
Capillary Flow Technology *(Backflush)*

LTM Technology *(Rapid Heating)*

LTM Technology *(Rapid Cooling)*

Variables for Shortening GC Run Times

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



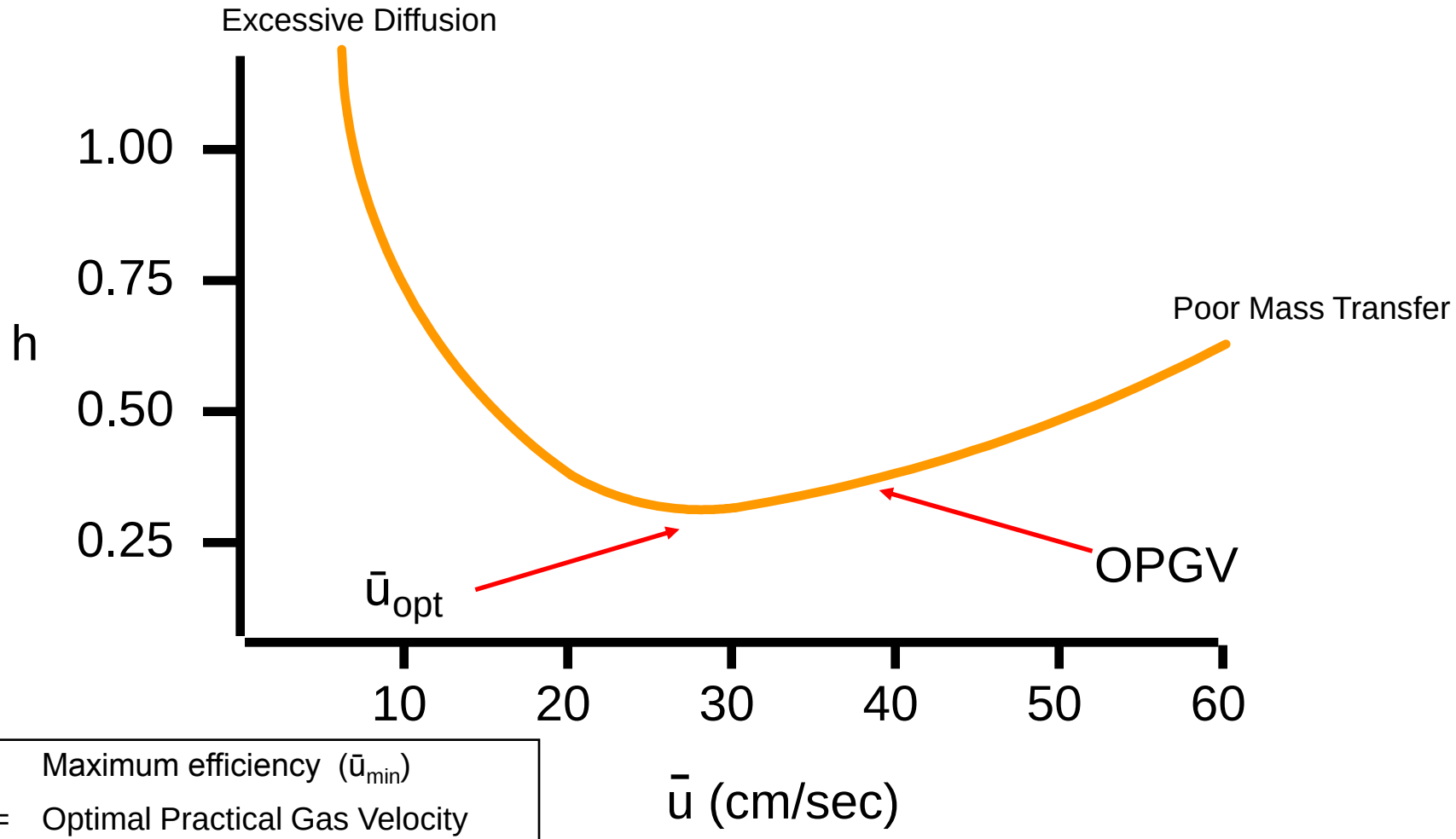
Carrier Gas

Affects resolution and retention time

Optimal range of velocities

Too low or high results in loss of resolution

van Deemter Curve



- $\bar{u}_{opt}$ = Maximum efficiency ($\bar{u}_{min}$)
- OPGV = Optimal Practical Gas Velocity
  Maximum efficiency per unit time
  ($1.5 – 2 \times \bar{u}_{opt}$)

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Diffusion Constants for Dodecane @ 150ºc

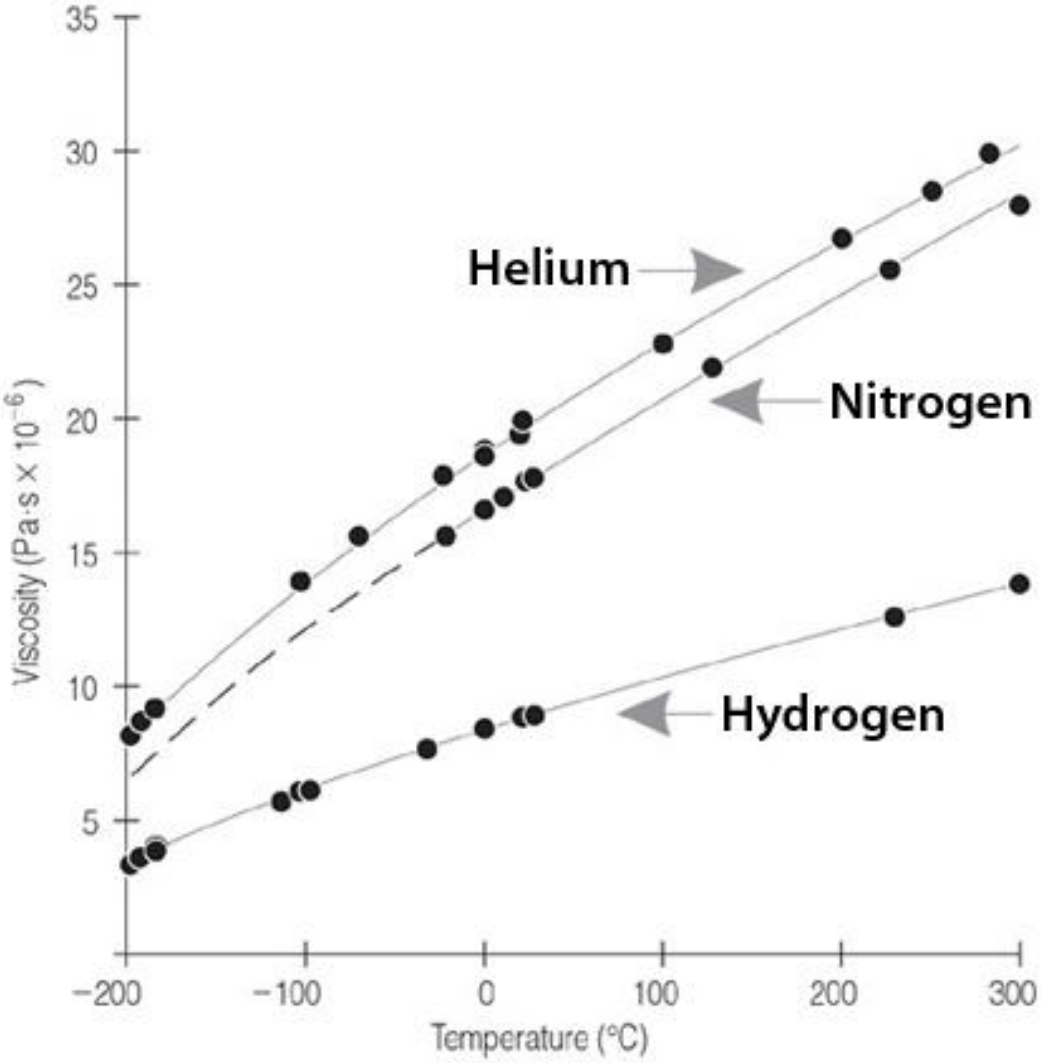
Nitrogen = 0.15 cm^2/sec

Helium = 0.4 cm^2/sec

Hydrogen = 0.6 cm^2/sec

© Walter Jennings, 1999

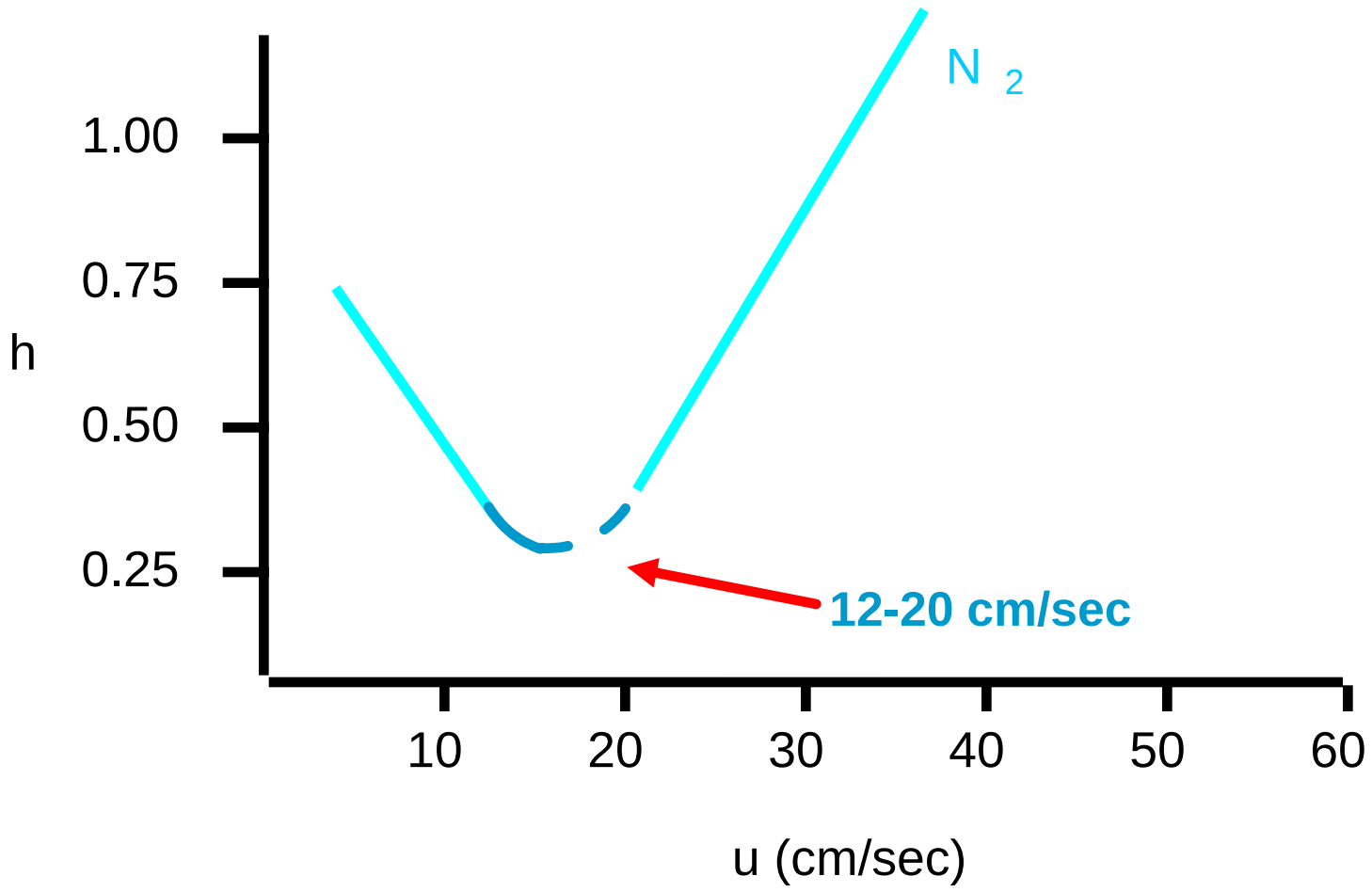
Gas Viscosity vs Temperature



J.V. Hinshaw, Column Connections, LCGC Asia Pacific, 12(2), 1100 (2009).

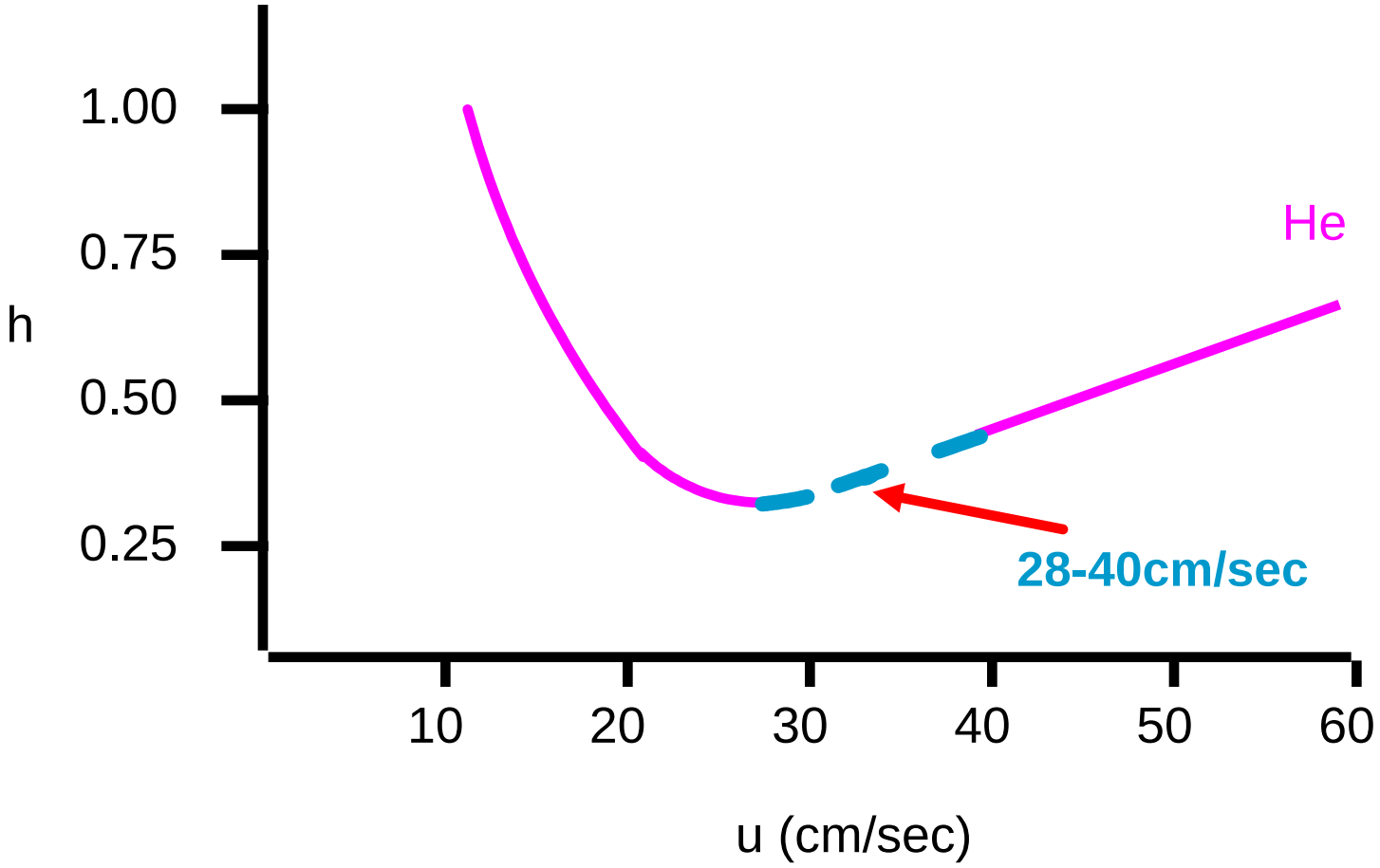
van Deemter Curve

Nitrogen



van Deemter Curve

Helium



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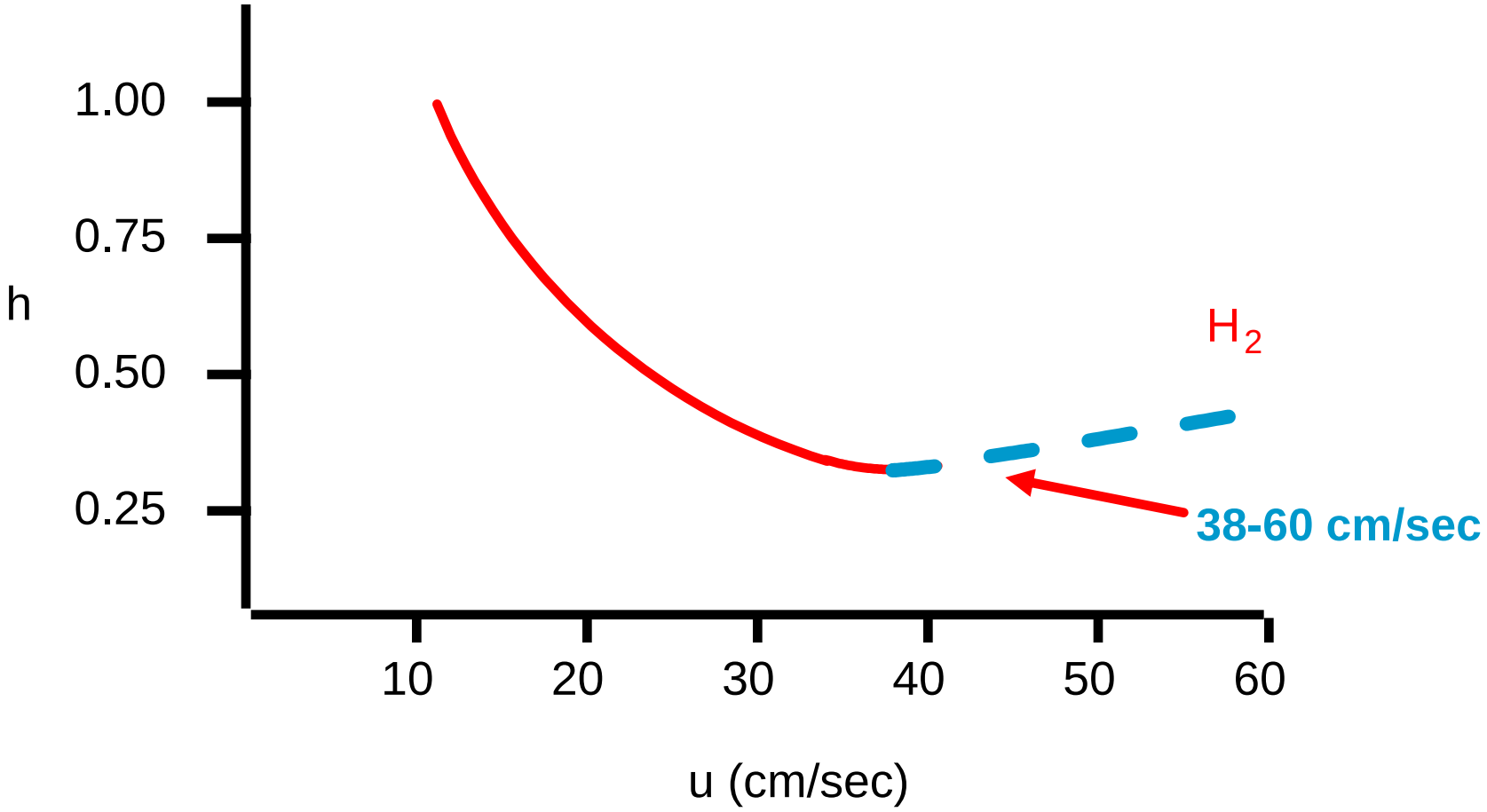
van Deemter Curve

Hydrogen



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 ready doors

Hydrogen as Carrier – Contamination?

Contamination of GC flow modules and lines.

Hydrogen acts as a scrubber.

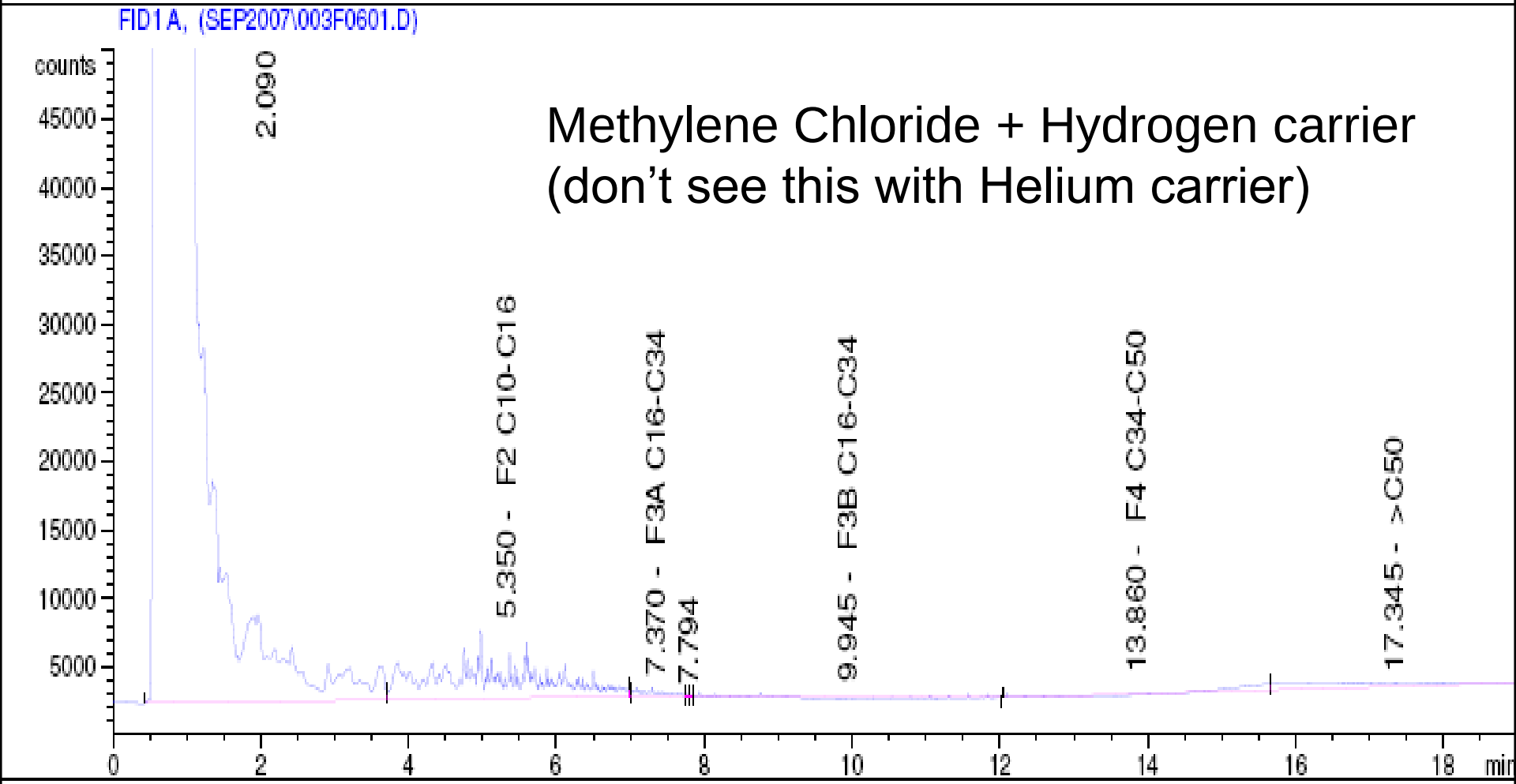
On the MS this typically looks like Hydrocarbon contamination

Most people report that it takes 2-4 weeks to clean out, depending on flows.

The FID only sees a high background for that time.

Other issues? H2 + Cl Solvent + Heat = HCl?

Contamination?! – scrubbing, vapor volume or HCl



Methylene Chloride + Hydrogen carrier
(don't see this with Helium carrier)

Hydrogen as Carrier – MS and Lower Pressures

Hydrogen is more difficult for the MS vacuum system to pump away as compared to Helium.

Be careful not to get to a “negative” head pressure situation. (pulling instead of pushing flow is not good).

Trace level work on the MS requires low flow rates.

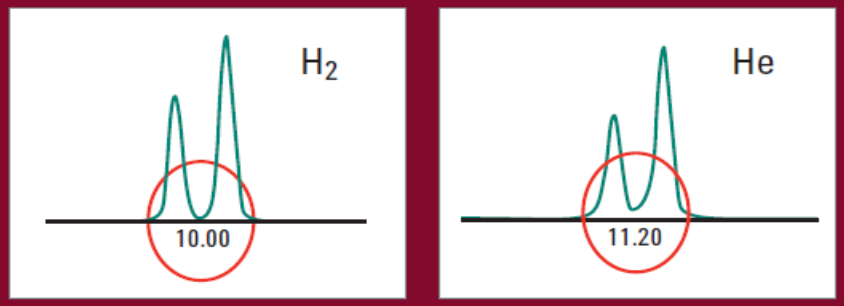
Must use smaller ID columns so you don’t have higher flow rates. (length plays a role as well)

0.18mm ID or smaller is ideal for trace level MS work when using Hydrogen.

The Only GC-MS Engineered for Hydrogen Carrier Gas to Reduce Operating Costs

Use hydrogen to lower your cost per analysis

The new hydrogen signal-to-noise specification for the 5975C Series GC/MSD makes Agilent the first and only instrument manufacturer to certify the performance and safety of hydrogen as a carrier gas. In fact, hydrogen often provides faster analysis times and resolution greater than GC/MS systems operating in helium mode.



Analysis of polyaromatic hydrocarbons using H_2 and He. In this example, H_2 actually provides better resolution.

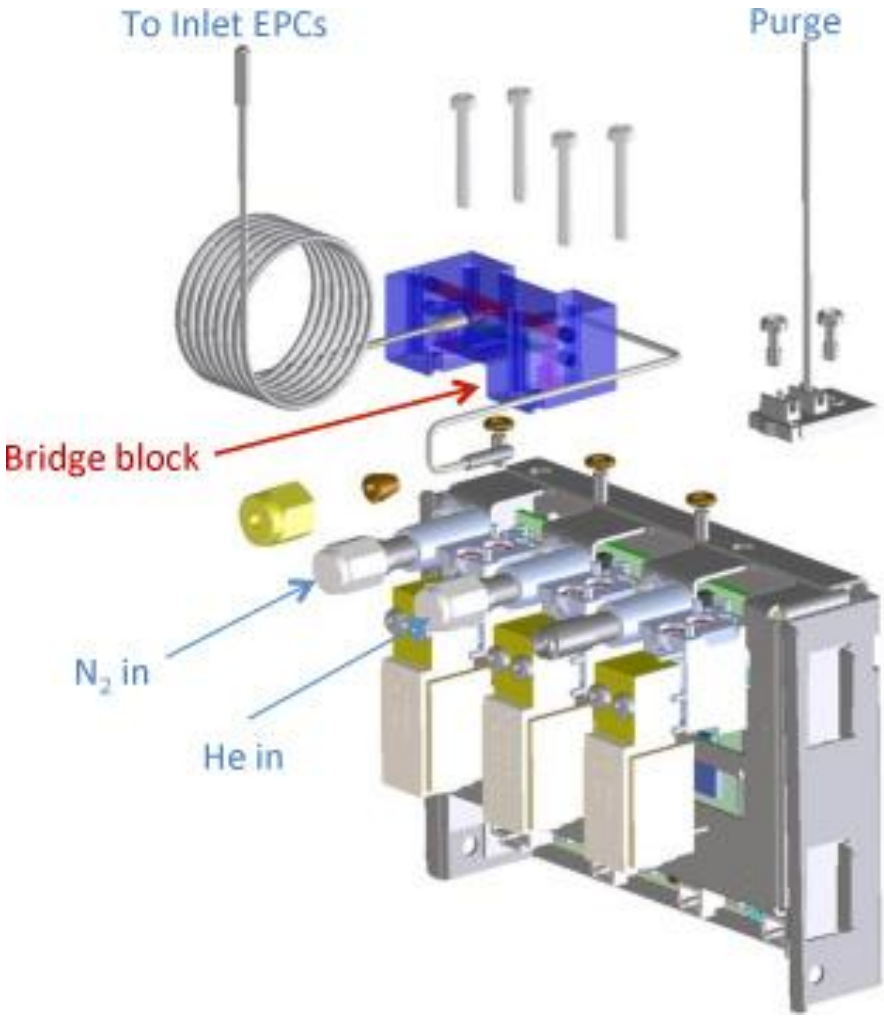
NEW Presentation!

"Conversion of Agilent EI GC/MSD Systems To Hydrogen Carrier Gas"

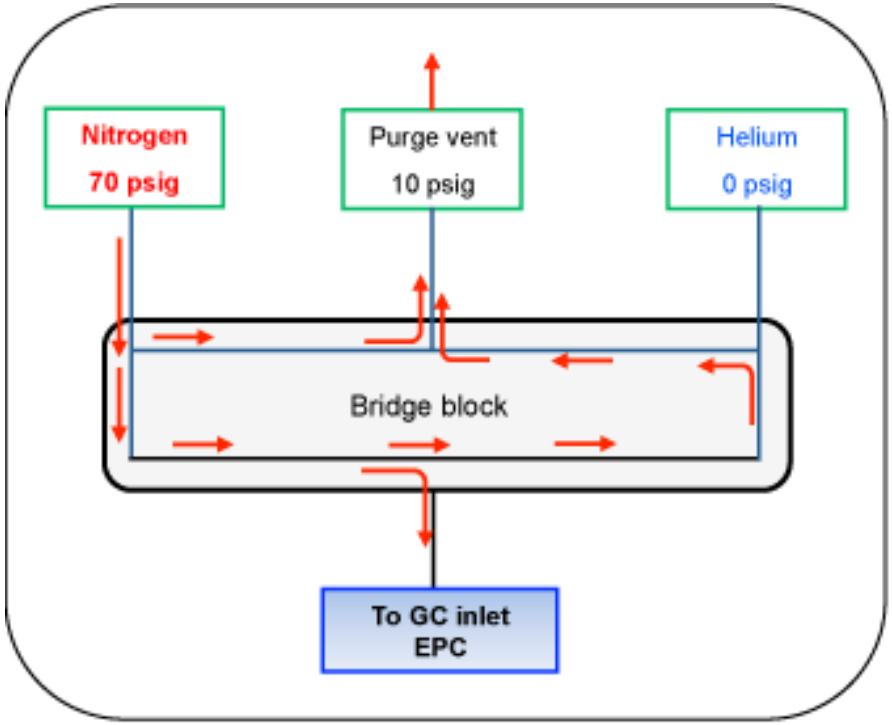
(make a note on your evaluation sheet to send)

http://www.chem.agilent.com/en-US/Promotions/pages/alternate-carrier-gas.aspx

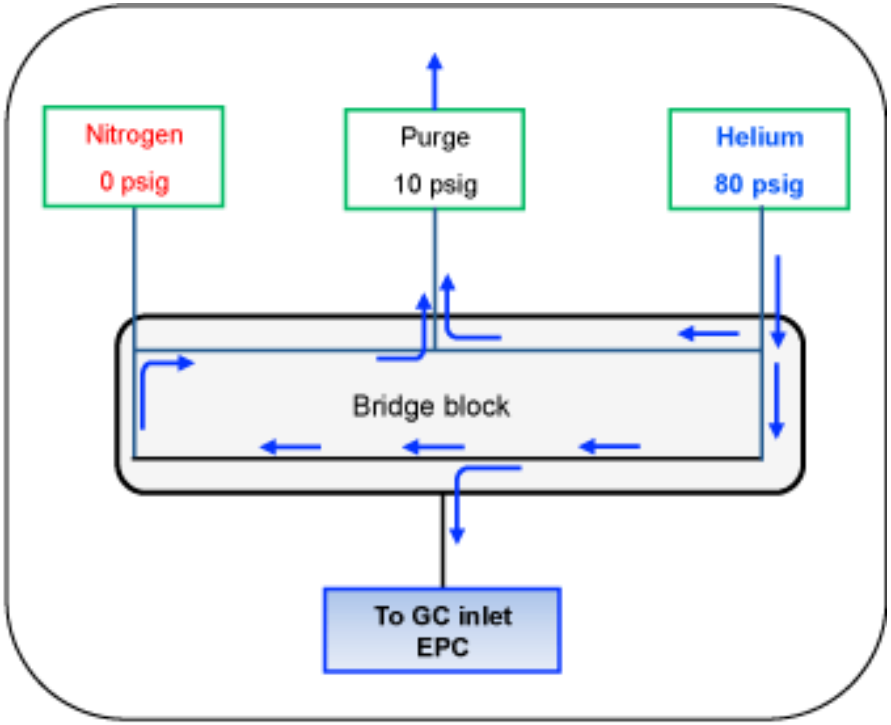
Programmable Helium Conservation Module



Programmable Helium Conservation Module

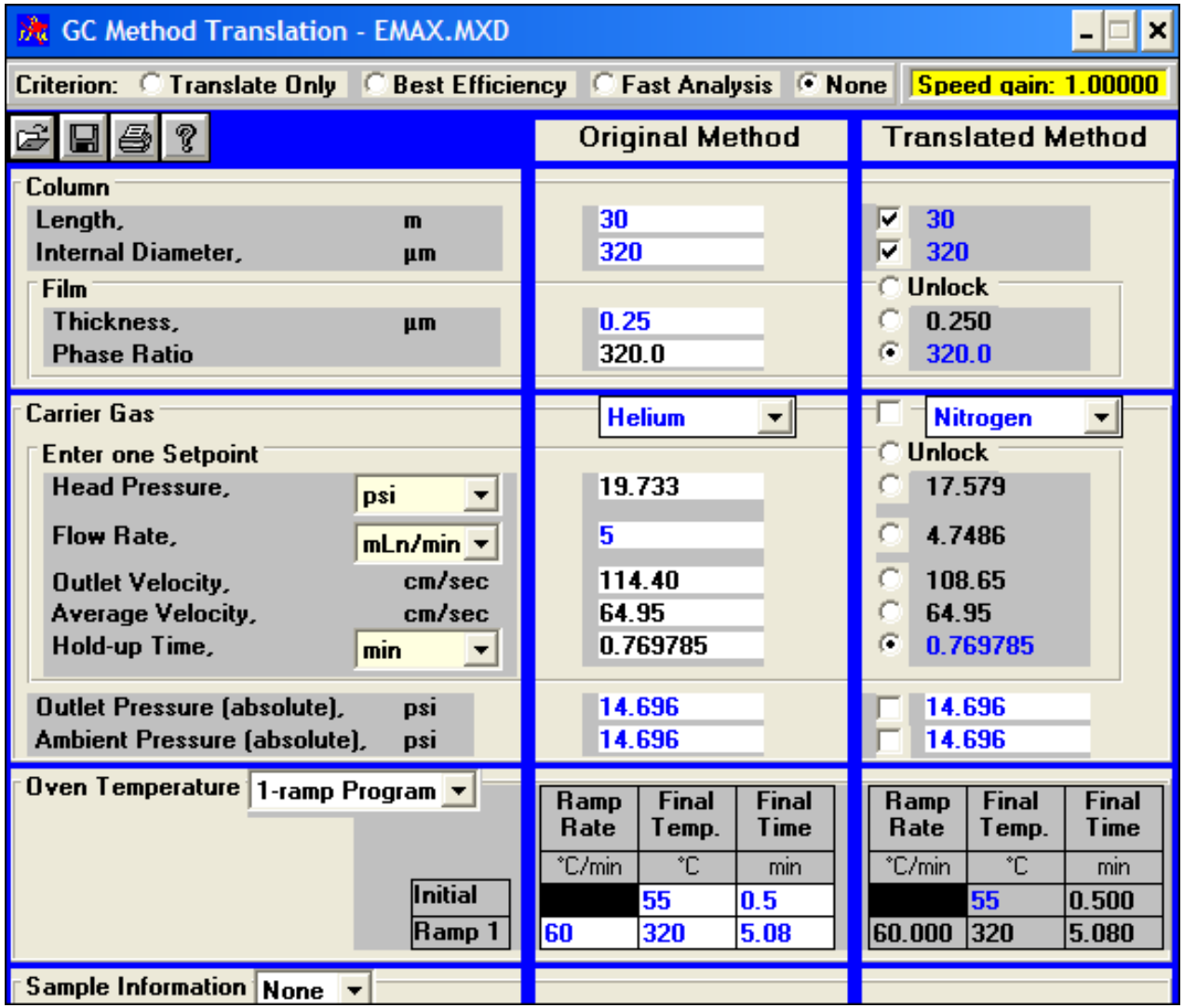


Helium savings mode
(N_2 on, He off)

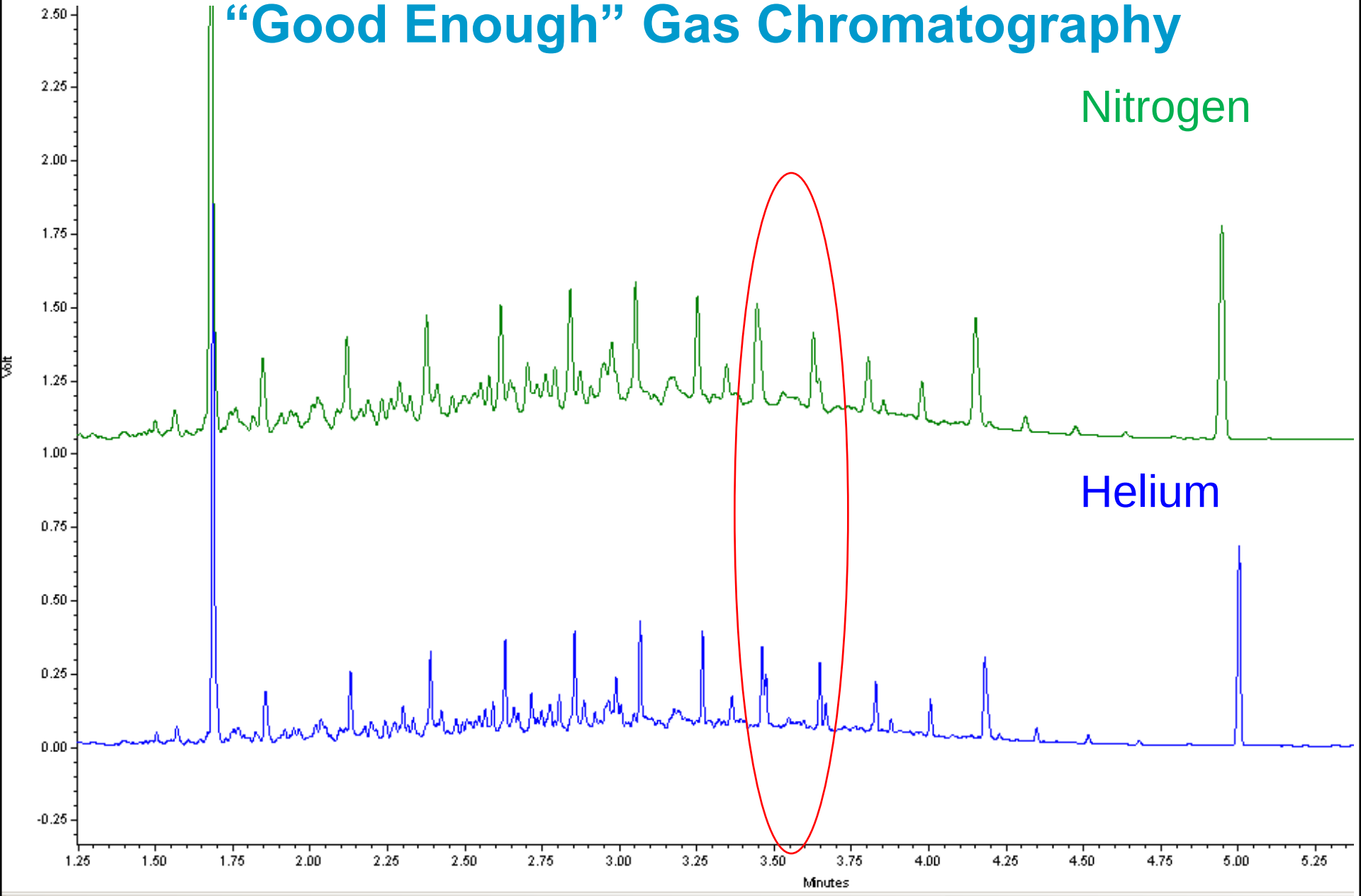


Helium operation mode
(He on, N_2 off)

He to N2 Conversion (E-Max, Diesel)



“Good Enough” Gas Chromatography



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Column Dimensions

Diameter

Length

The Secrets Are In There

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

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

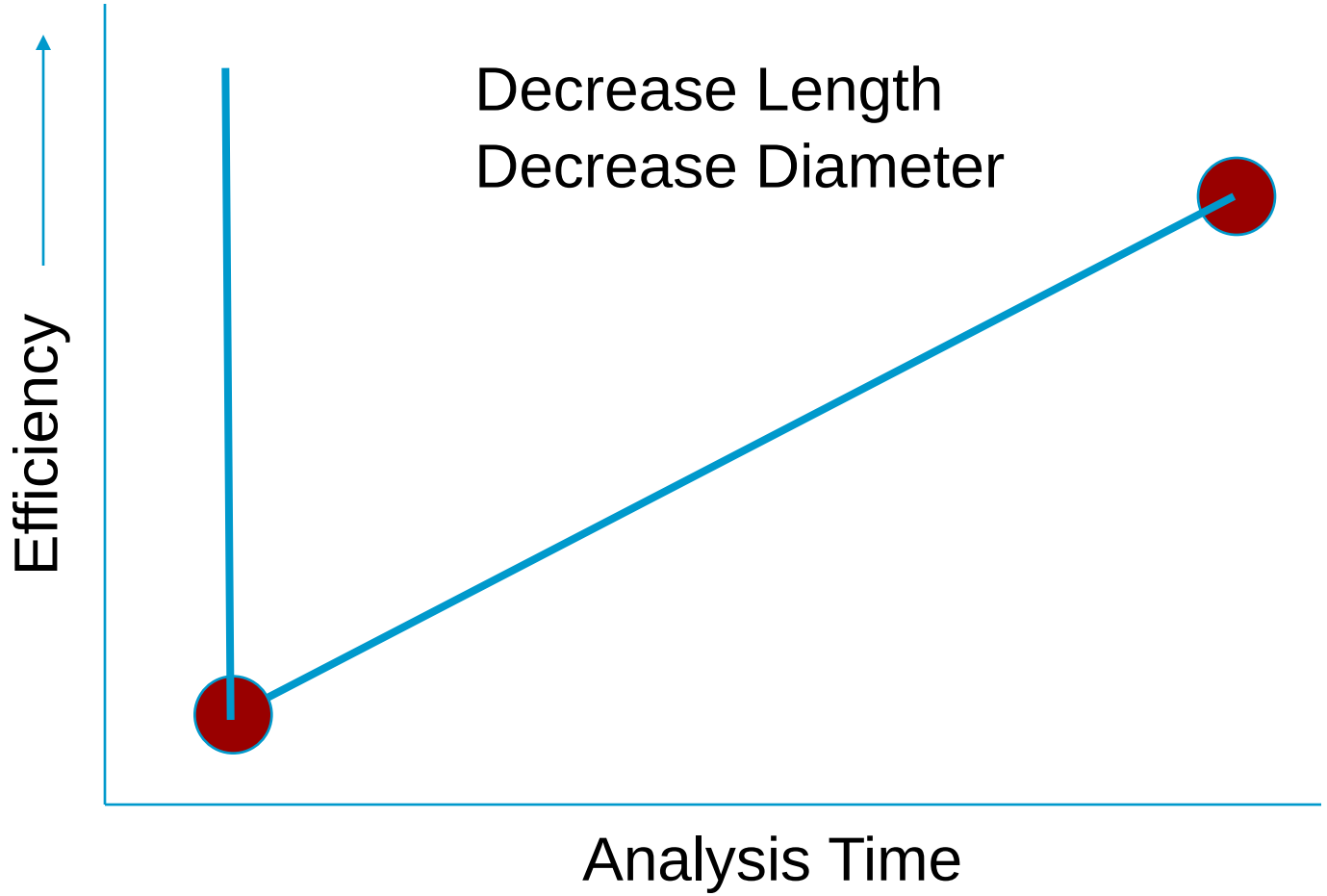
T = temperature

Column Diameter - Theoretical Efficiency

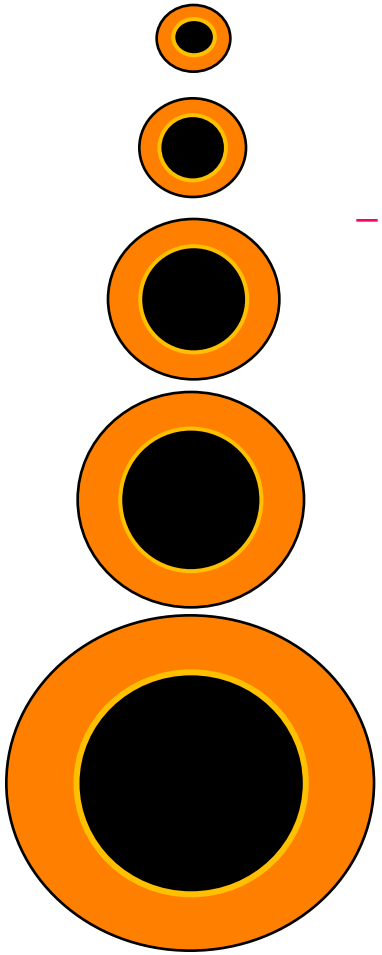
I.D. (mm)	n/m
0.05	23,160
0.10	11,980
0.18	6,660
0.20	5830
0.25	4630
0.32	3760
0.45	2840
0.53	2060

k = 5

Combining a change in Length with a change in Diameter



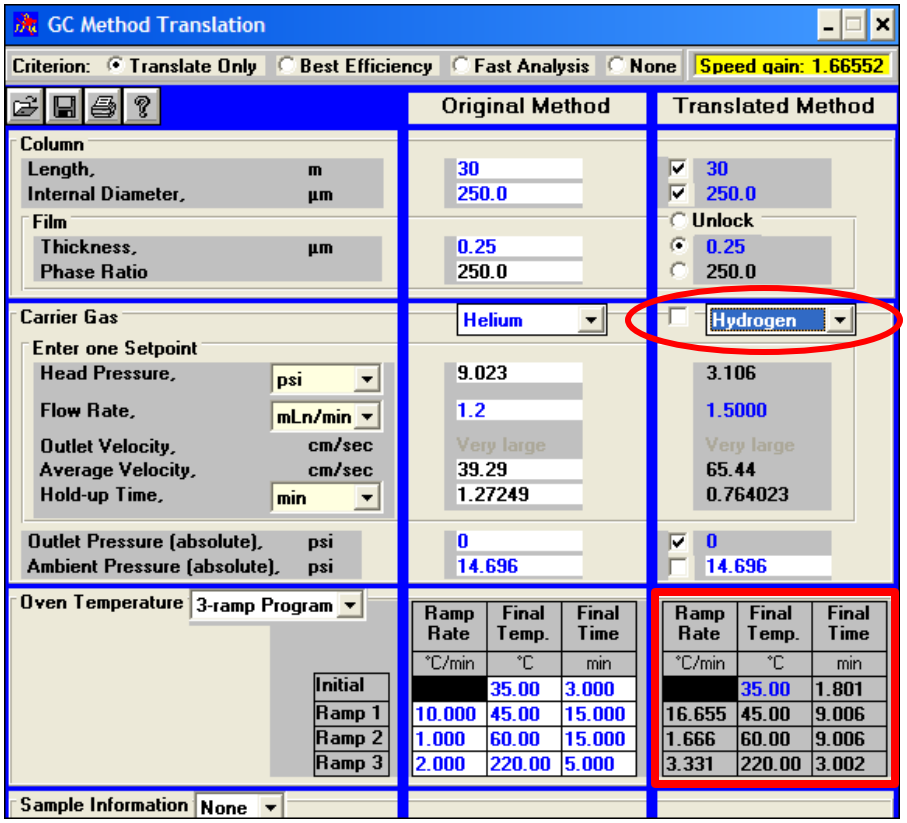
Column Diameter and Capacity

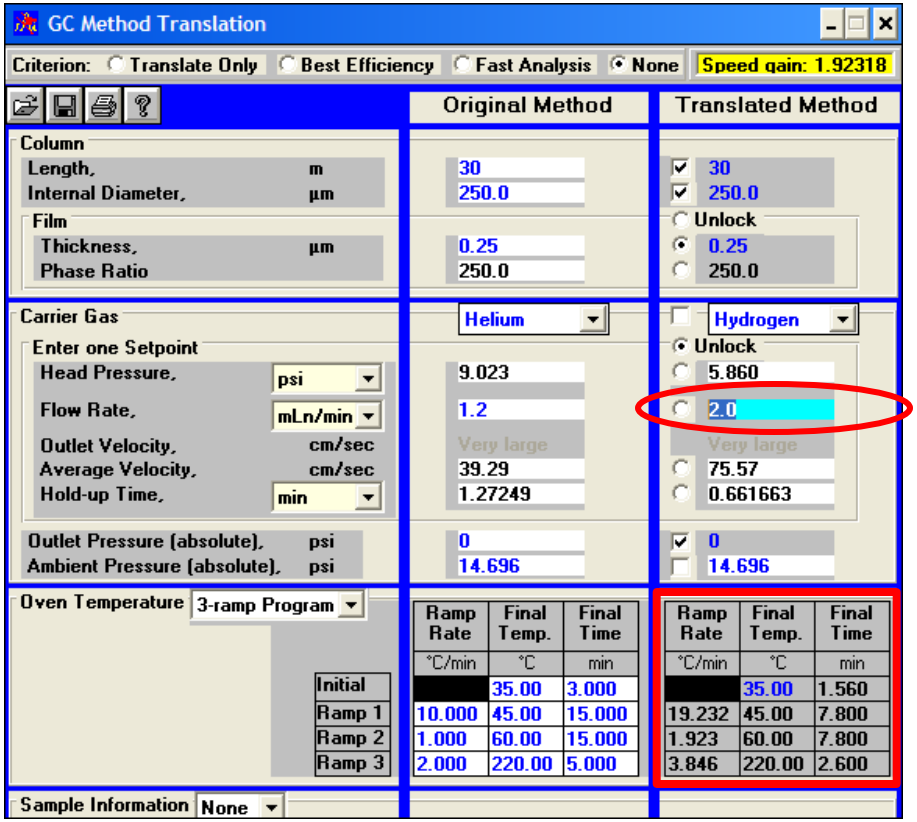


I.D. (mm)	Capacity (ng)
0.05	1-2
0.10	6-13
0.18	25-55
0.20	35-70
0.25	80-160
0.32	110-220
0.45	600-800
0.53	1000-2000

Like Polarity
Phase/Solute
0.25 µm film thickness

Changes in Column Dimensions, Gas Type or Velocity Require Changes in Temp Program Rates





Method Translation Software to the Rescue!

Agilent Technologies

To Get the Software:

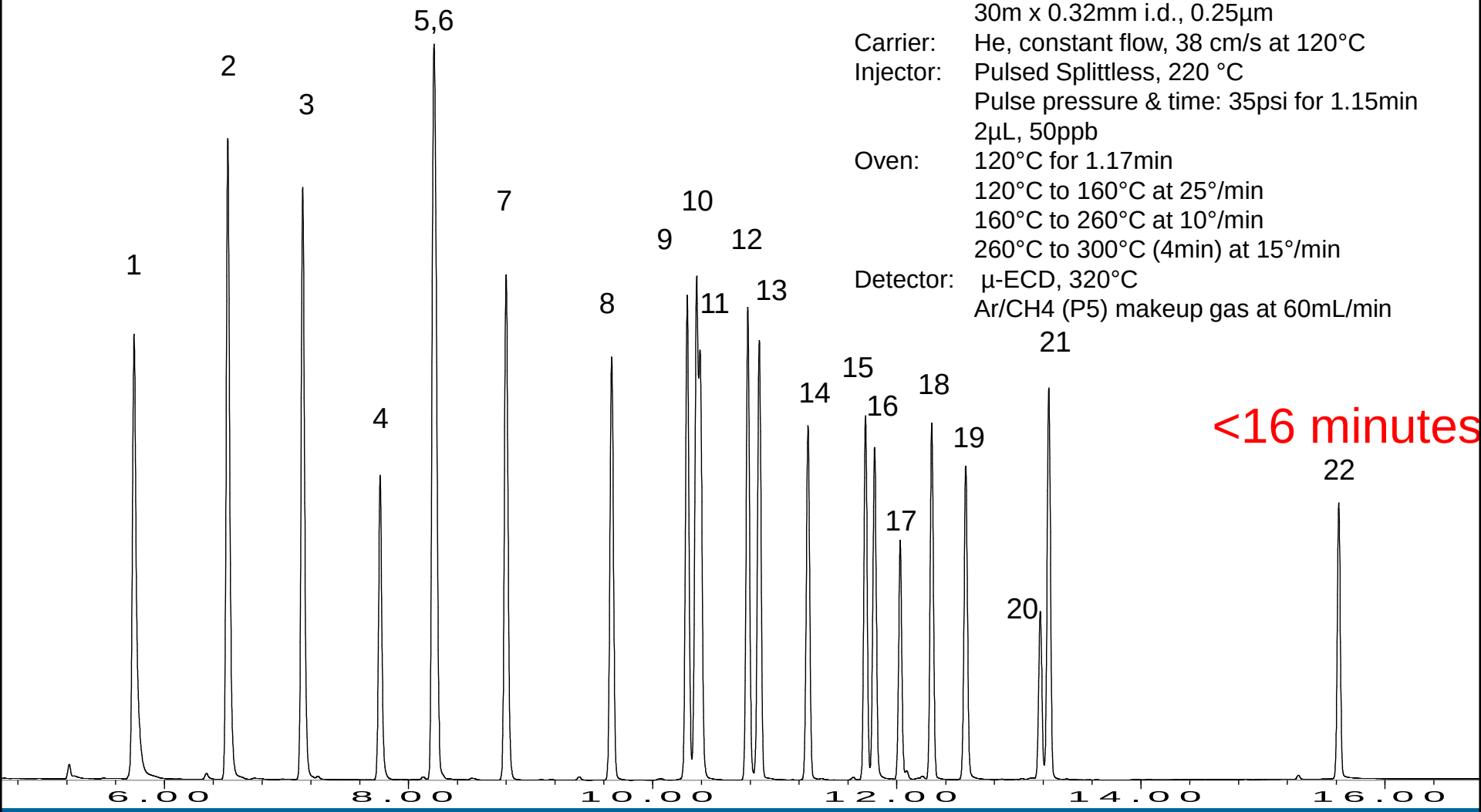
http://www.chem.agilent.com/en-US/Technical-Support/Instruments-Systems/Gas-Chromatography/Pages/gcmethodtranslation.aspx

OR

Google → Agilent GC Method Translation Software

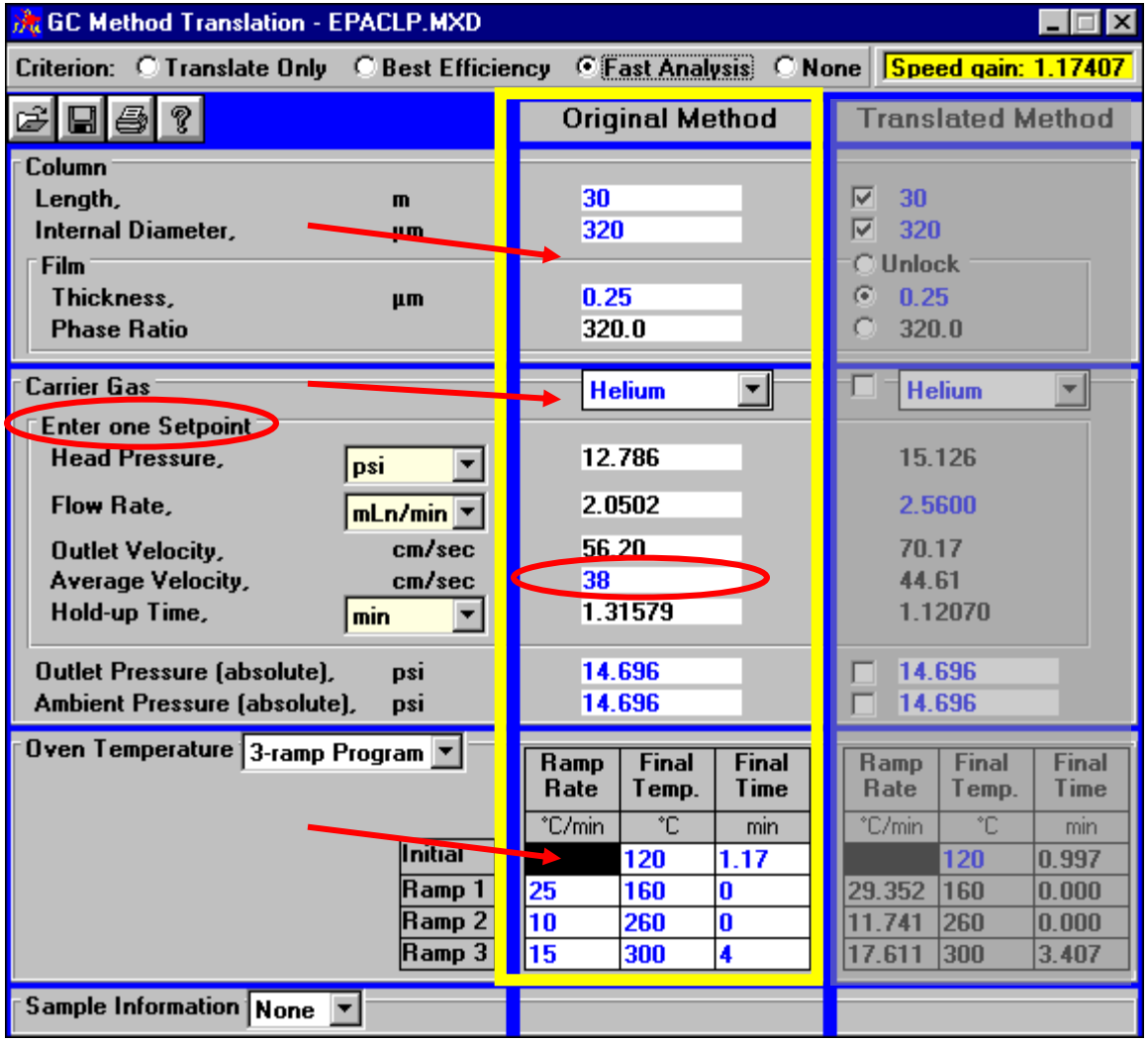
CLP-Pesticides - Original “Improved” Method 0.32mm I.D., Helium Carrier Gas

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

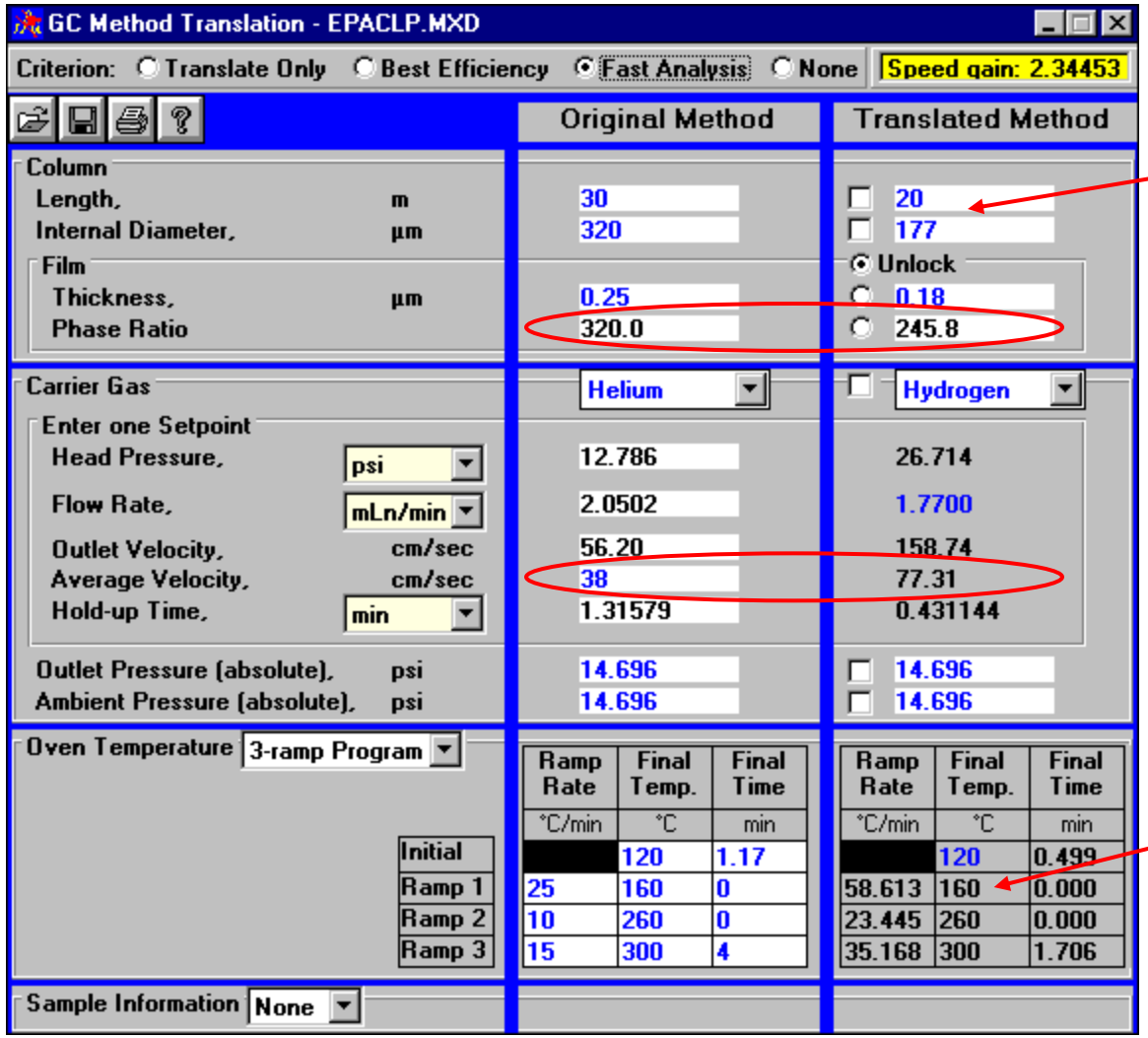


<16 minutes

Input Original Method Parameters

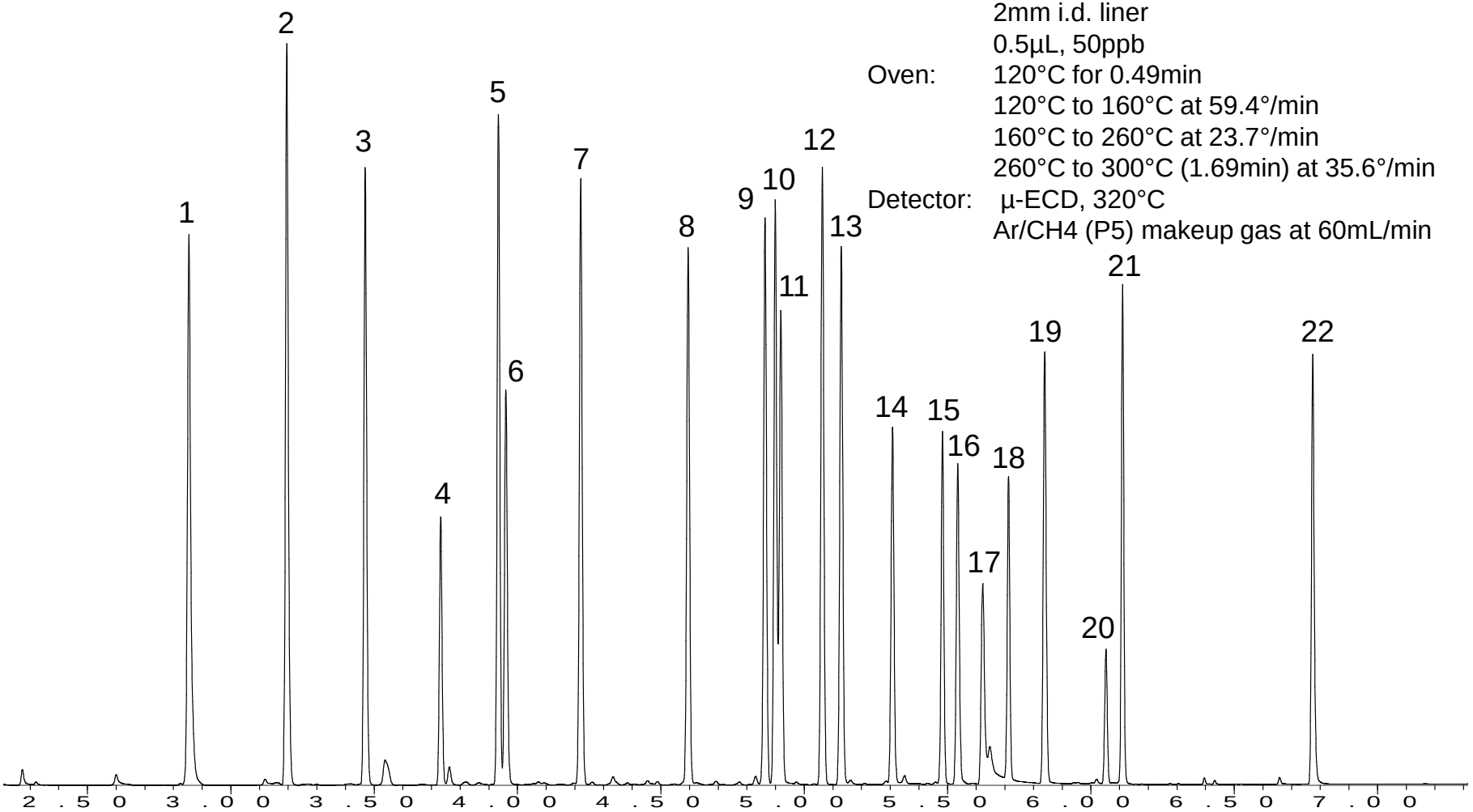


New Column Dimensions, H2 Gas, Fast Analysis



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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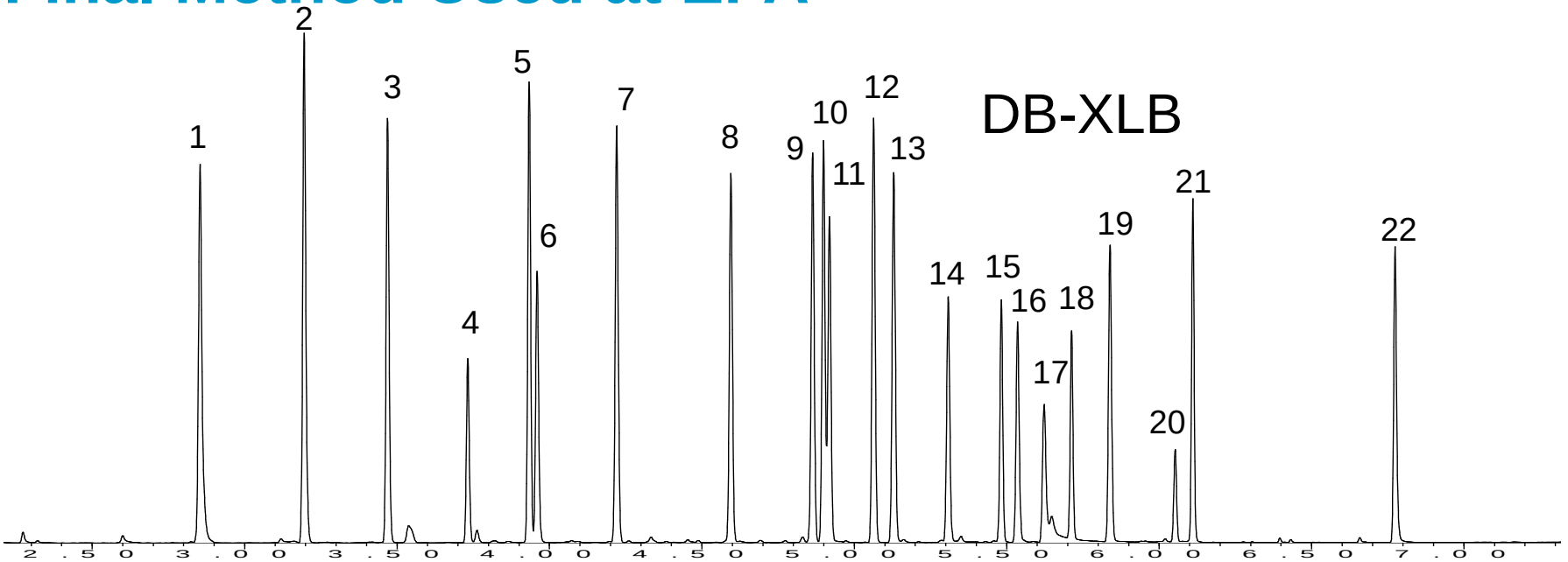
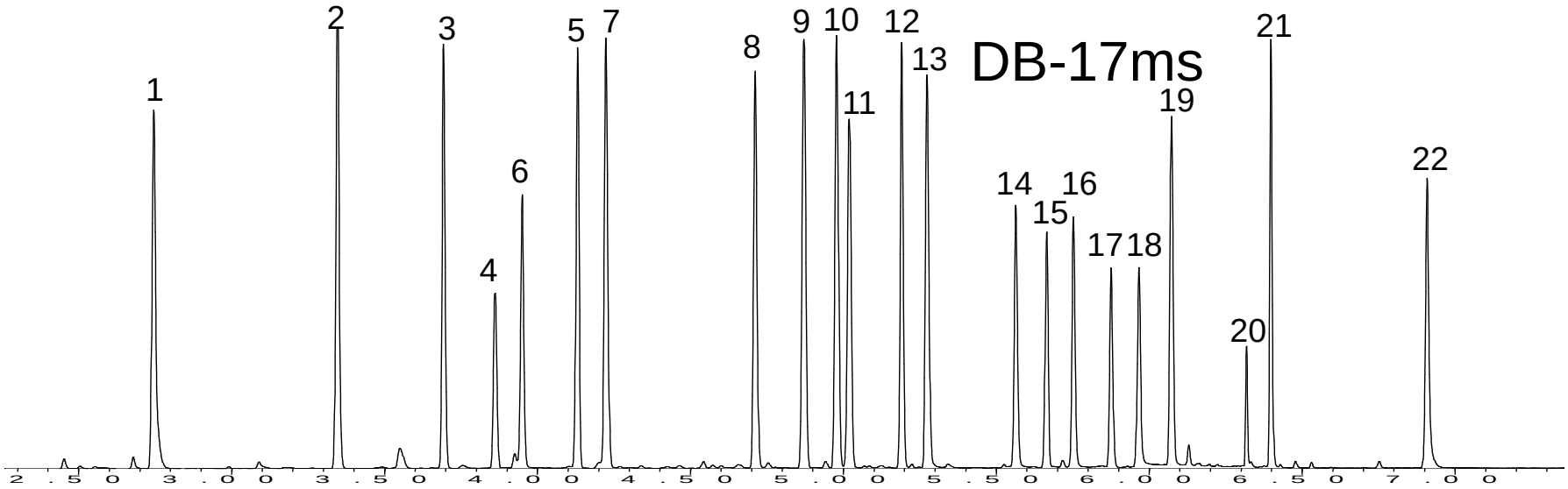
Final Method Used at EPA

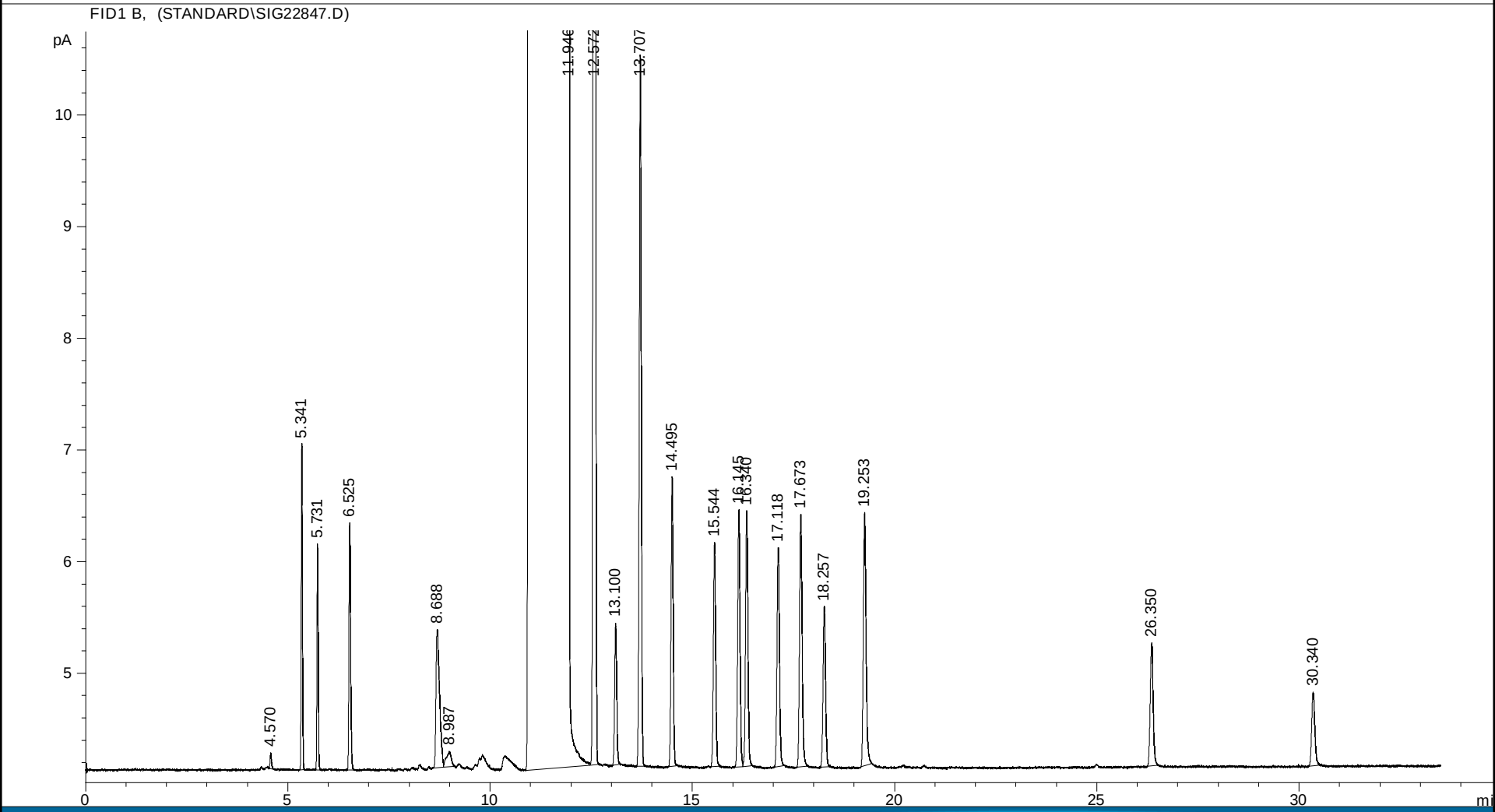




Agilent Technologies

Cumene Analysis

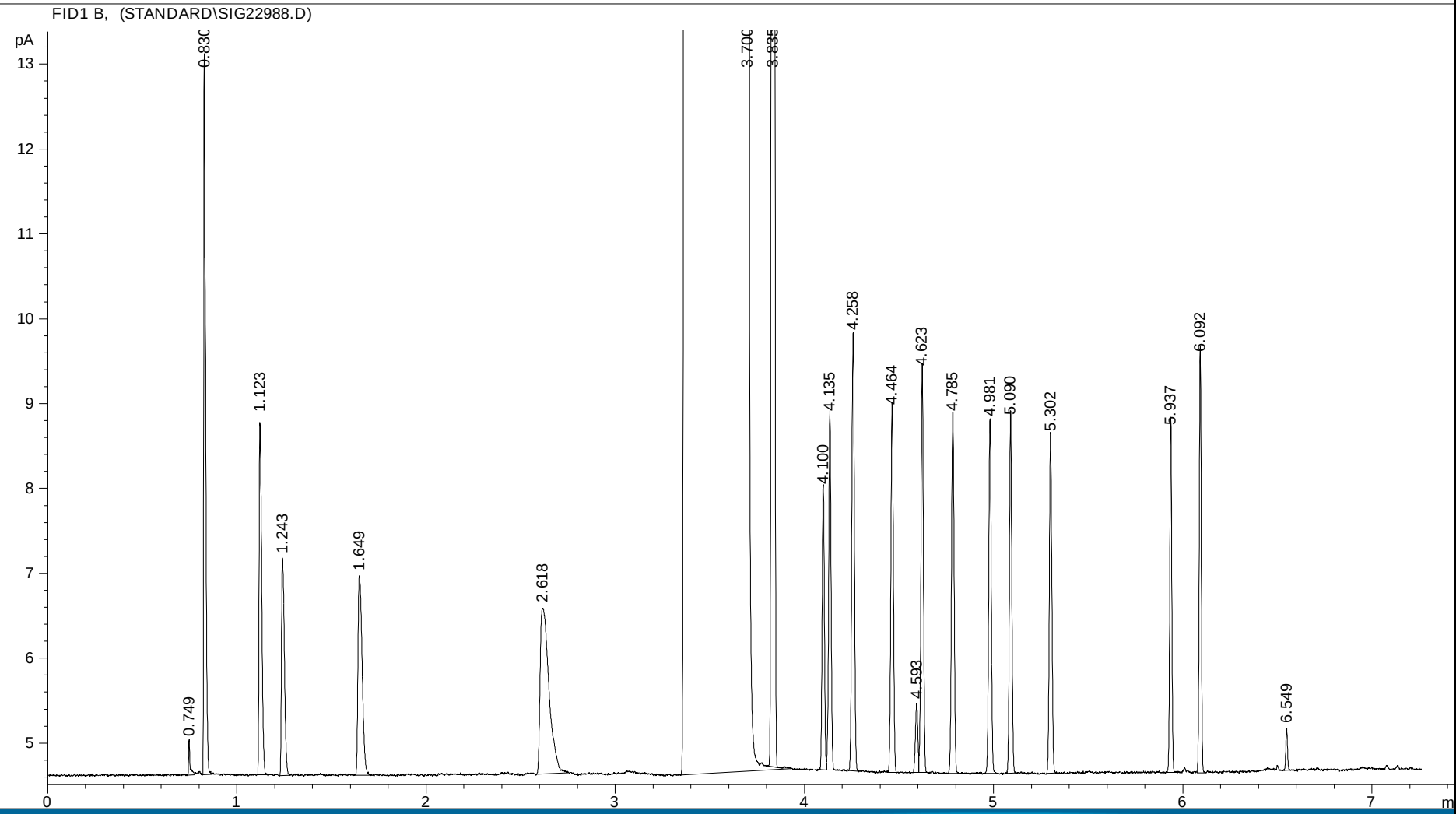
-60m x 0.32mm ID (overkill)



Agilent Technologies

Cumene Analysis

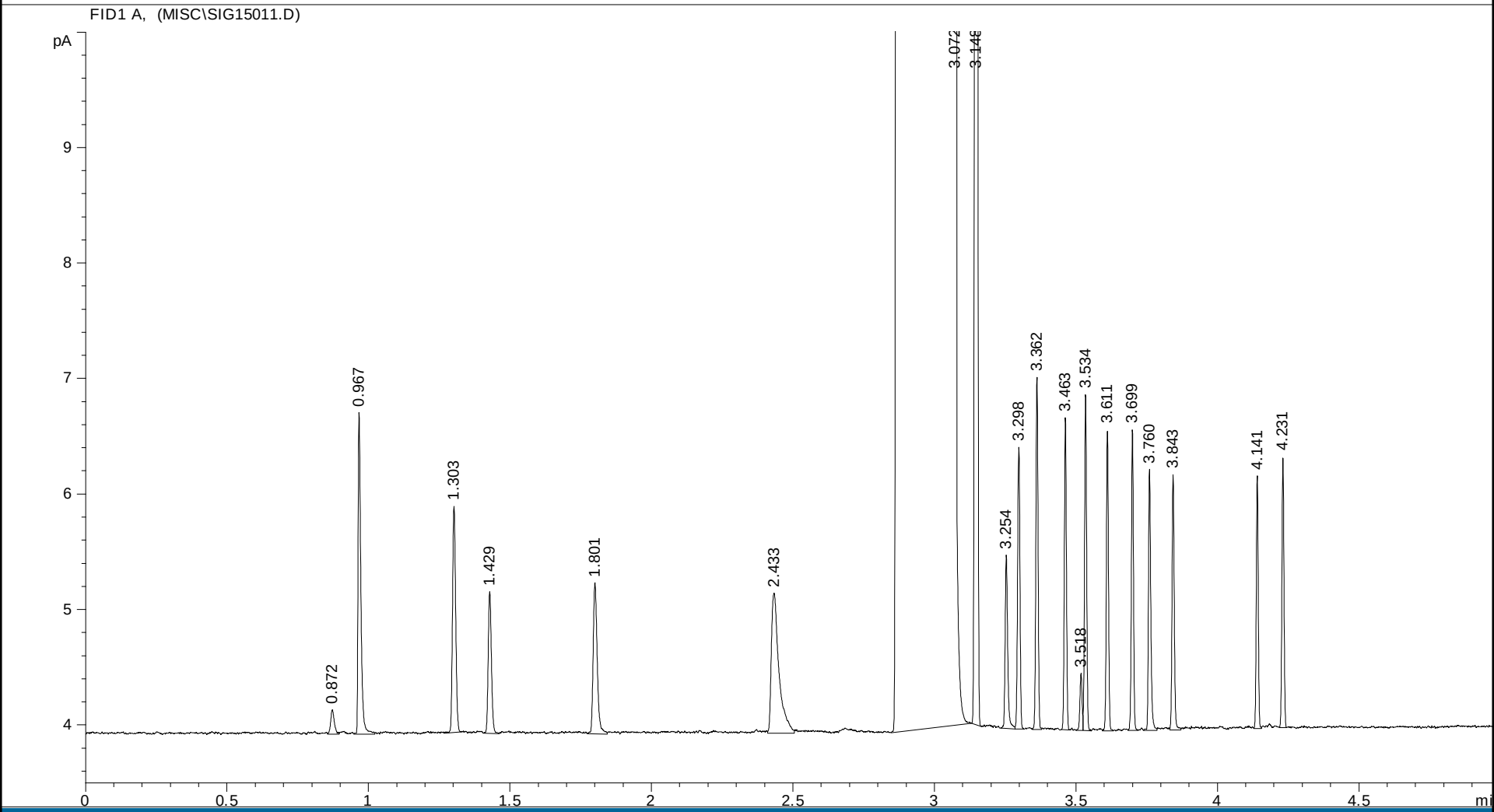
-30m x 0.25mm ID



Agilent Technologies

Cumene Analysis

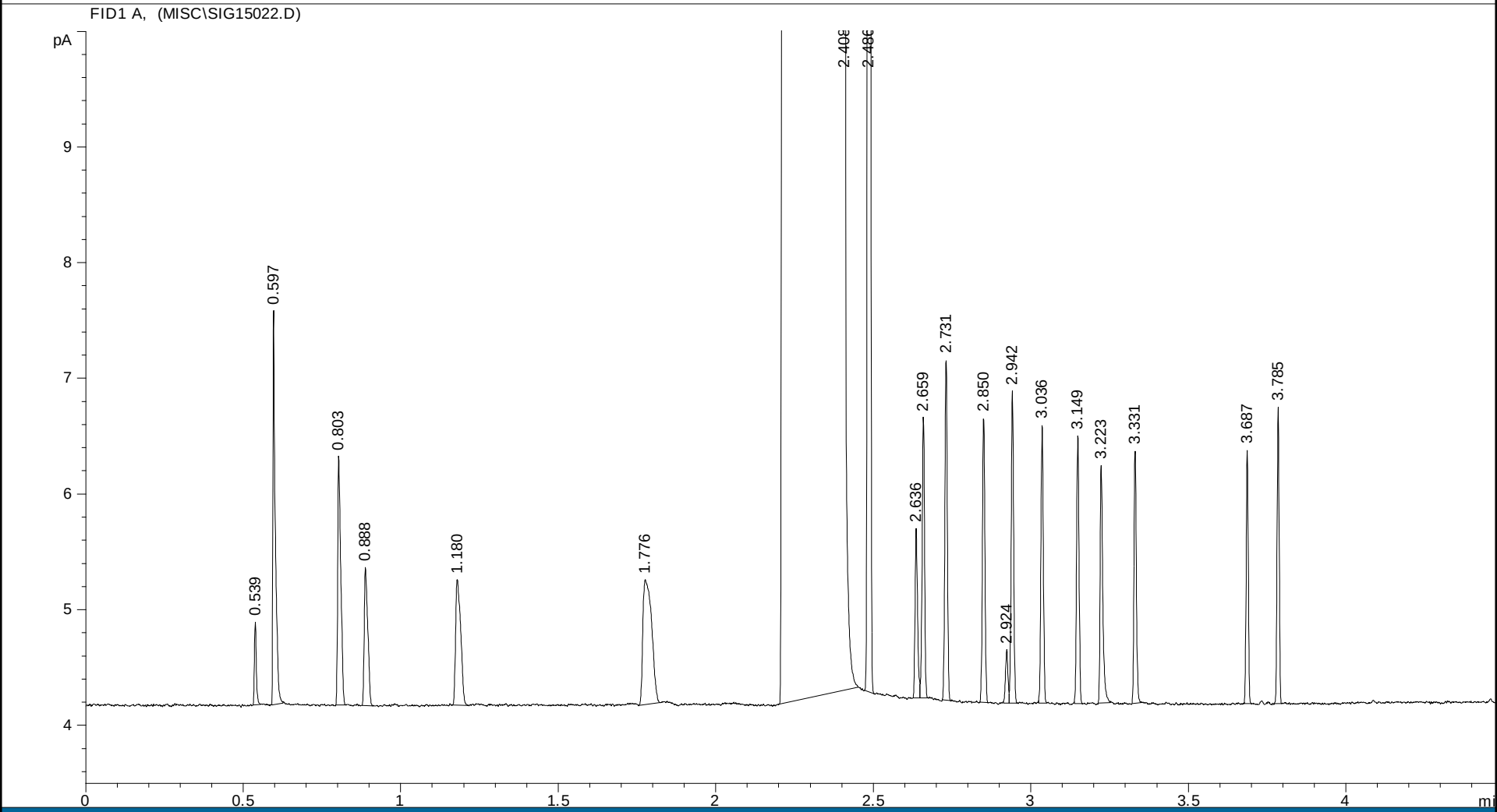
-20m x 0.18mm ID



Agilent Technologies

Cumene Analysis

-20m x 0.18mm ID, Hydrogen Carrier



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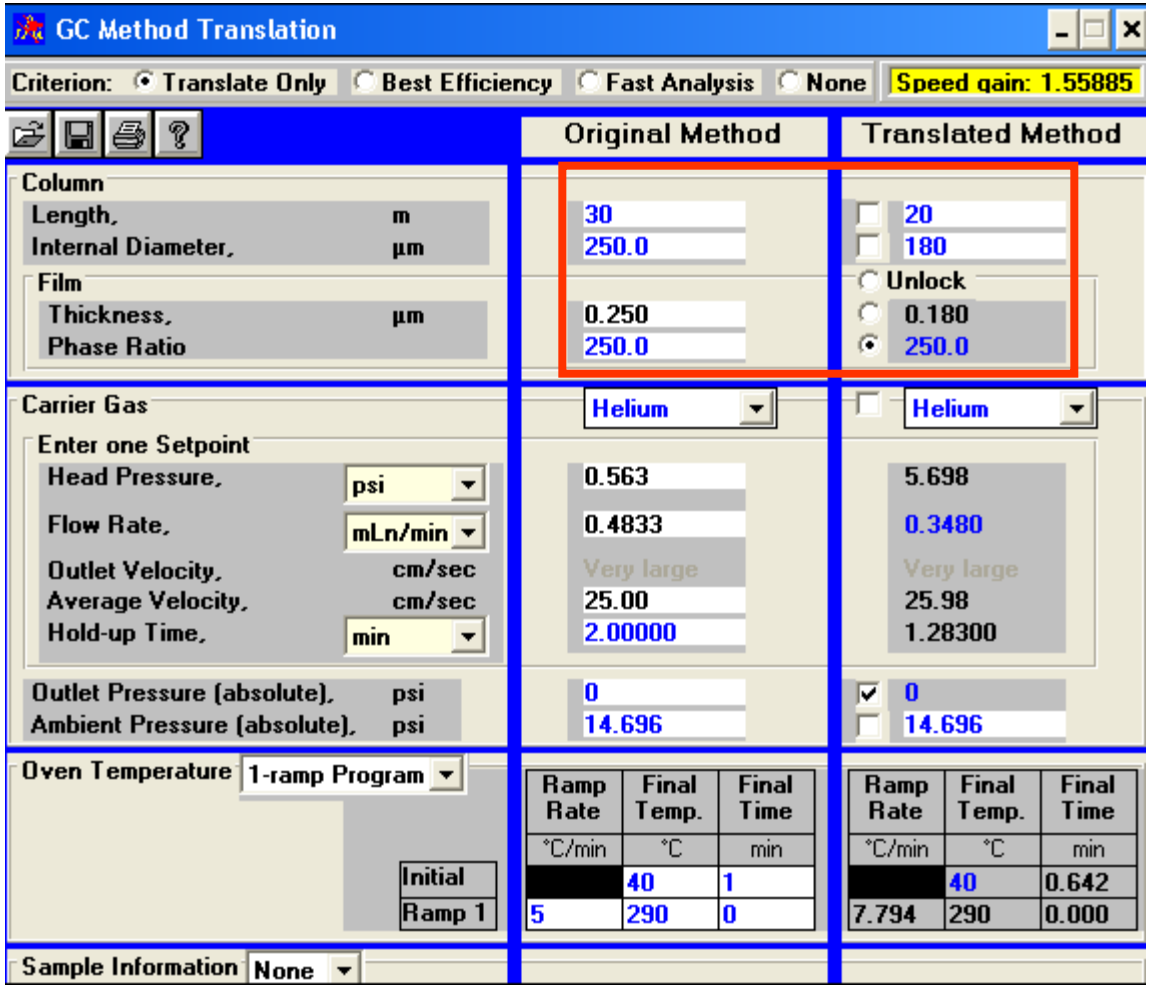
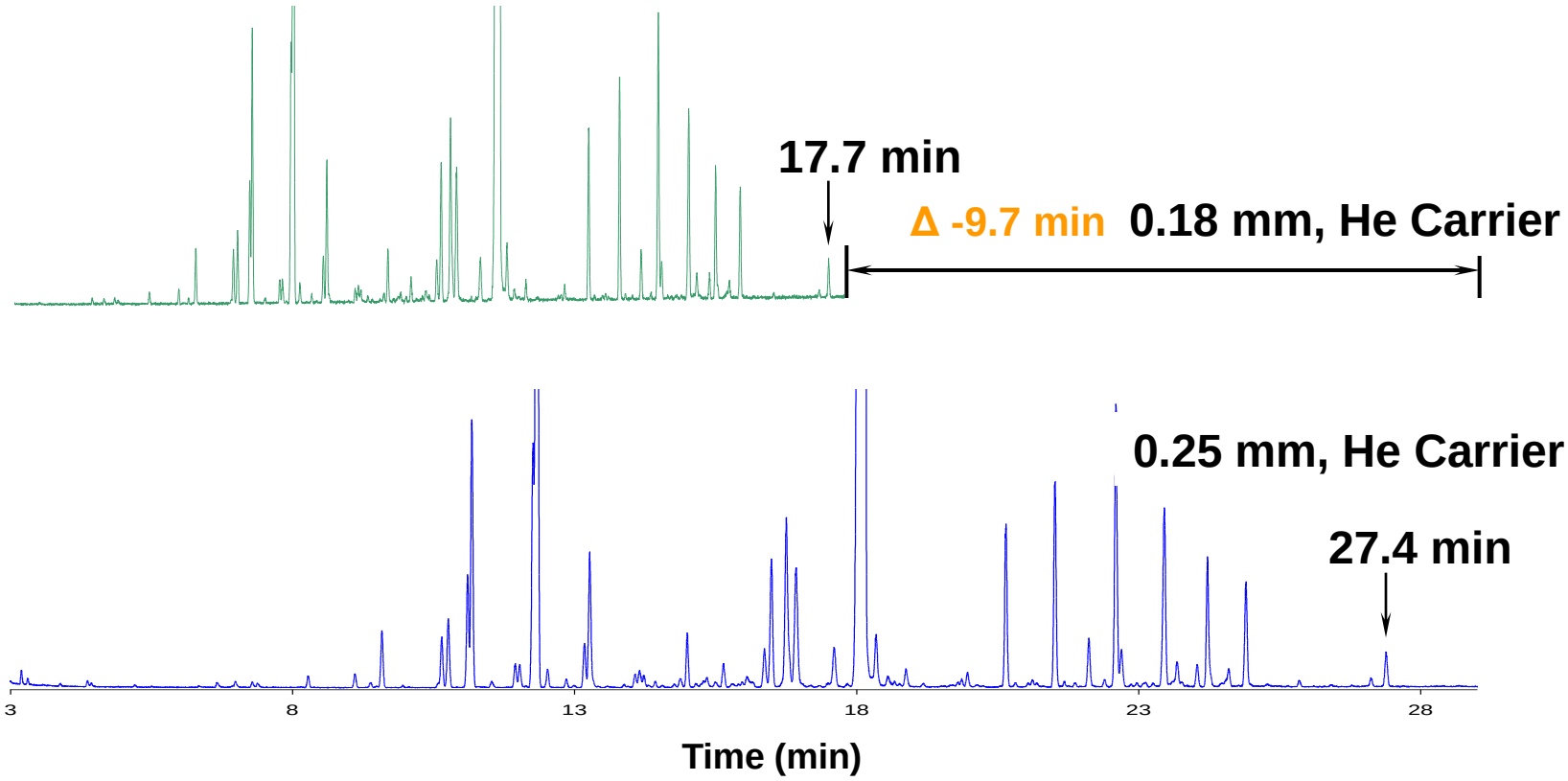
Food/Fragrance – Method translation

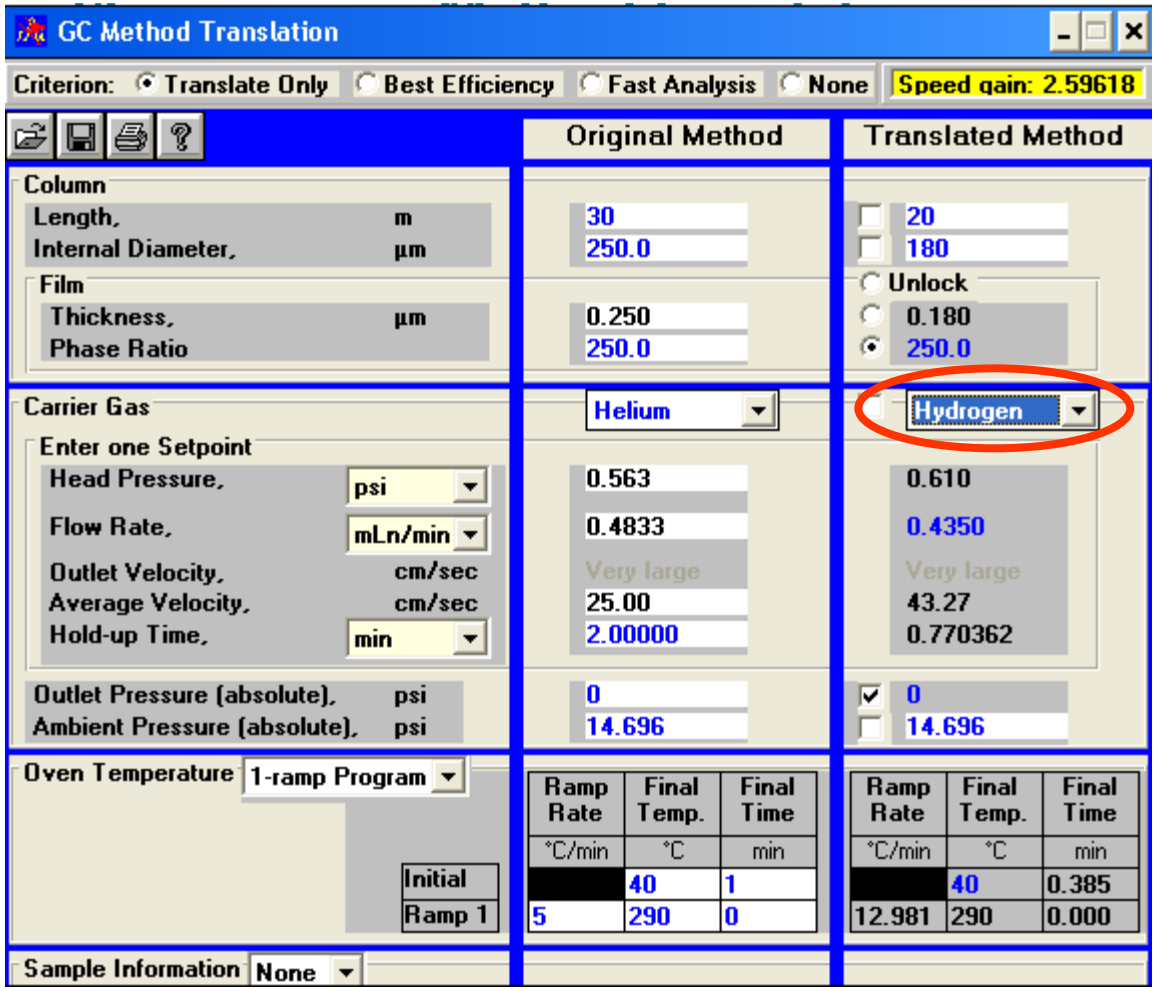


Spearmint Oil on DB-1



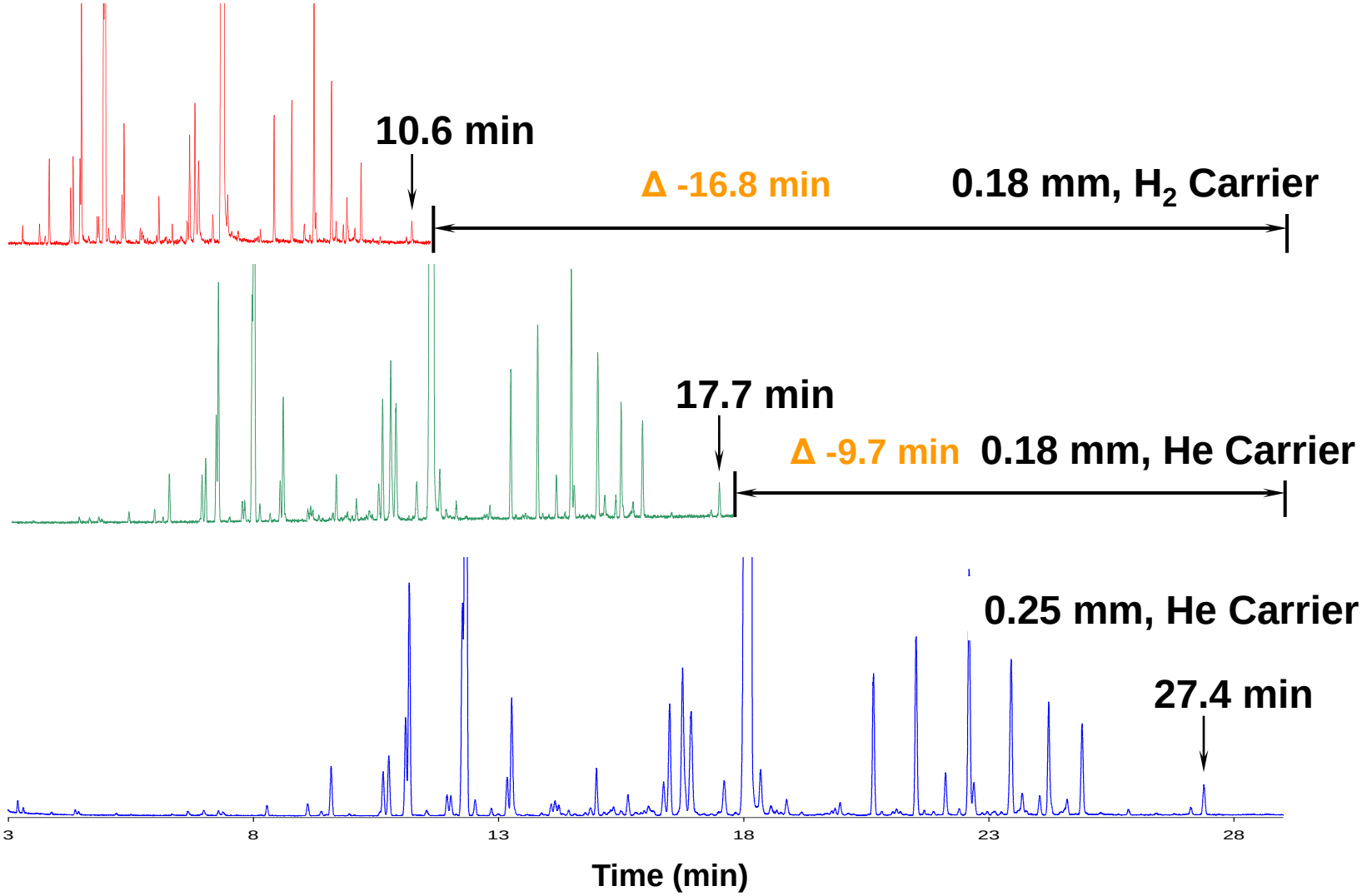
Agilent Technologies

Food/Fragrance – Method translation, Hydrogen



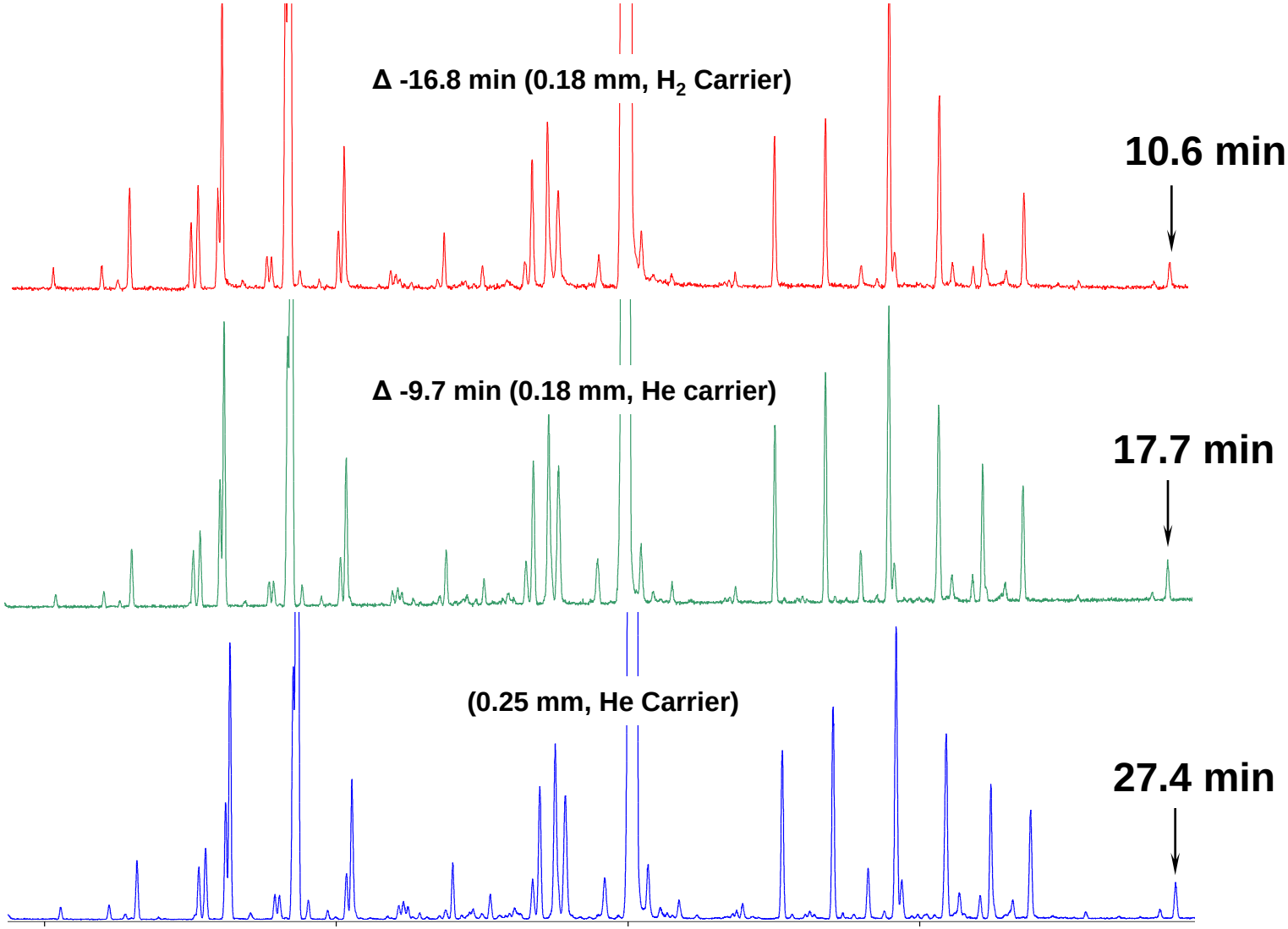
Agilent Technologies

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

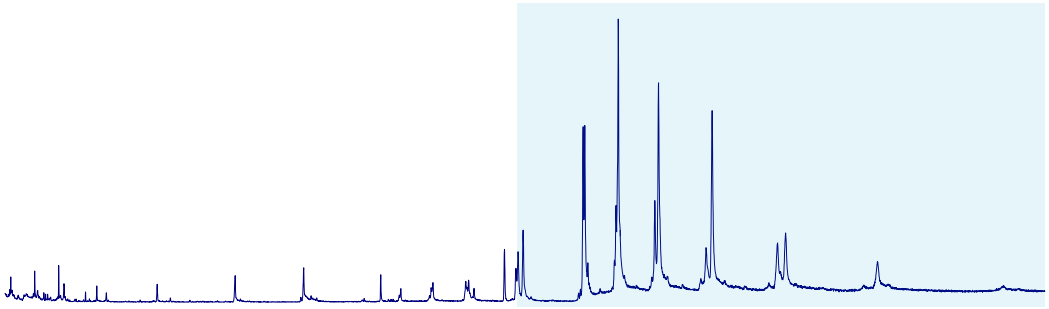


Agilent Technologies

Spearmint Oil on DB-1 – Resolution Check



Faster GC Total Analytical Cycle Times – A Variety of Approaches



Pre-Run ALS Set-Up	Chromatographic Run	Post-Run Bake-Out	Post-Run Cool-Down

Included in HW/SW

"ALS Sample Overlap" in ChemStation SW

7890 GC Faster Cool-down

Column & Gas Selection, Method Translation

New Devices
***Signficantly* Faster GC Analytical Cycle Times**

Capillary Flow Technology *(Backflush)*

LTM Technology *(Rapid Heating)*

LTM Technology *(Rapid Cooling)*

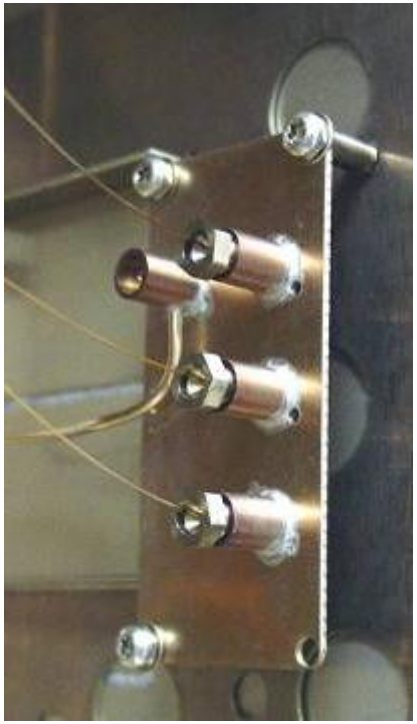
New Devices for Faster Analyses

Capillary Flow Technology

Low Thermal Mass Technology

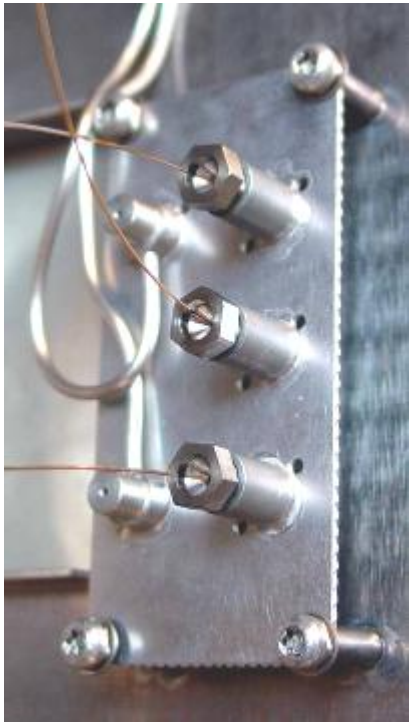
Purged Capillary Flow Devices

2-Way Splitter with Makeup



3-Way Splitter with Makeup

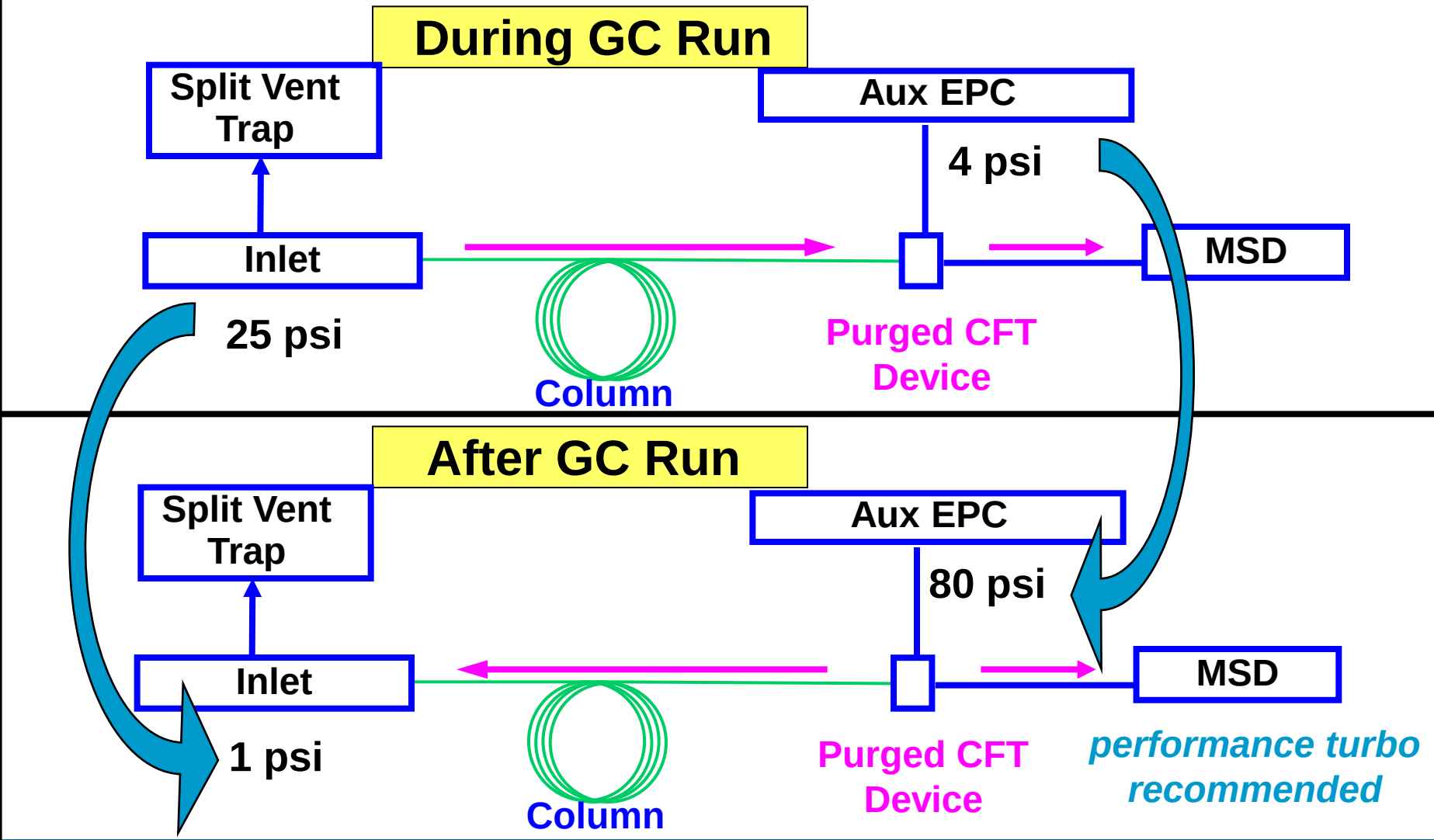
Deans Switch



Purged Union (most recent)

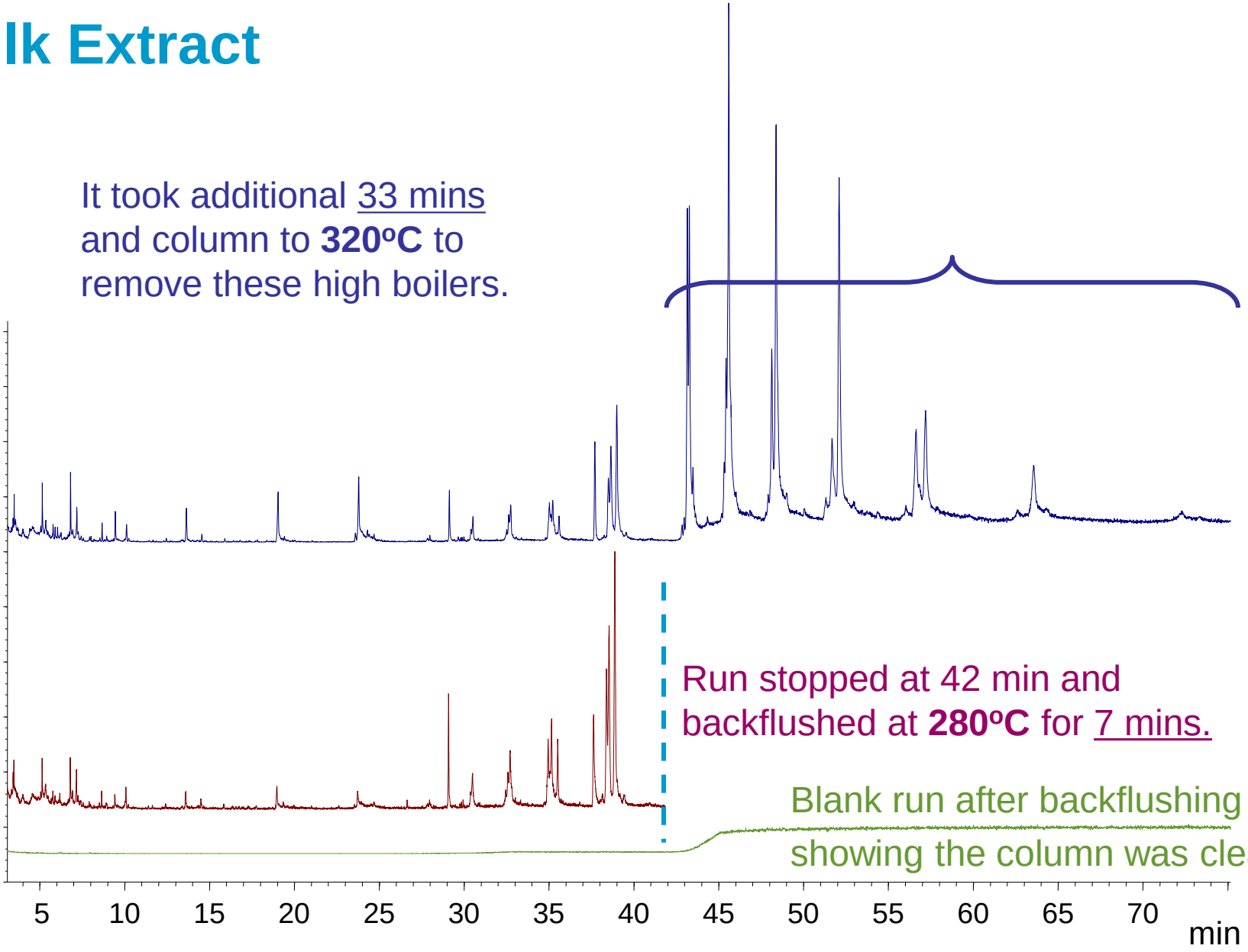
All Purged Capillary Flow Devices are Capable of Backflushing

Backflush with Purged Union or Any Purged Capillary Flow Technology Device



Milk Extract

It took additional 33 mins and column to **320ºC** to remove these high boilers.



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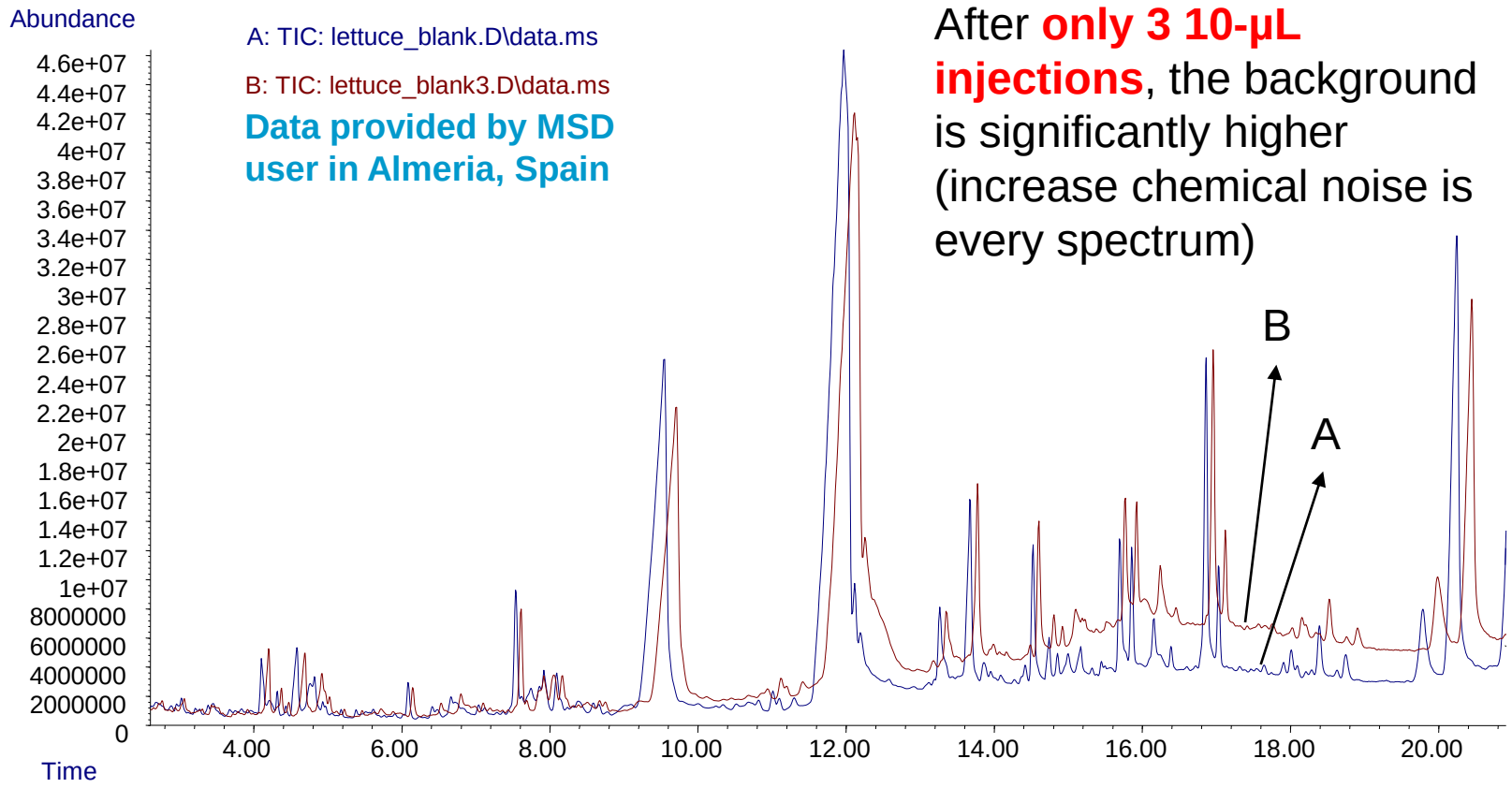
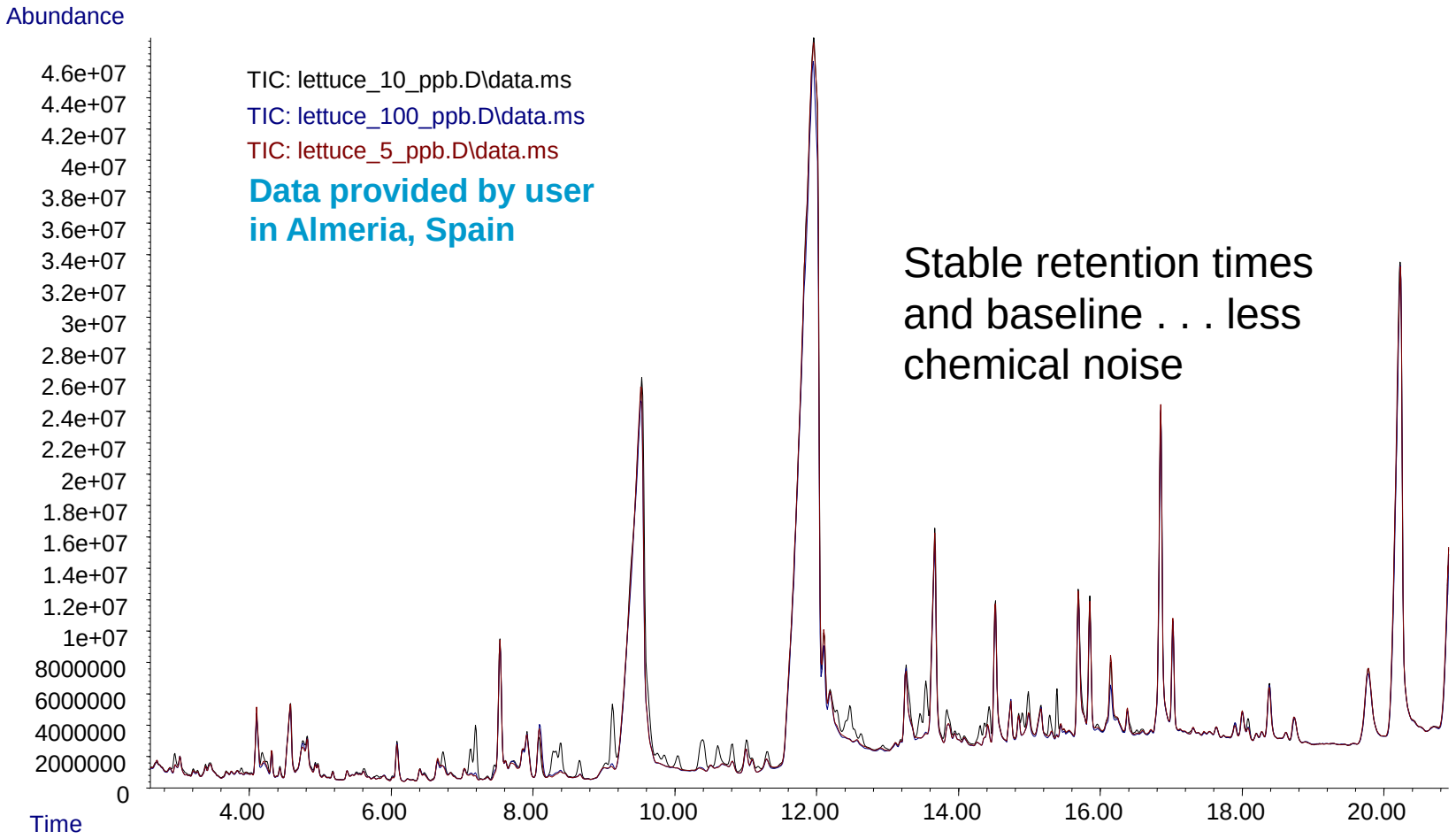
Without Backflush: A Serious Problem



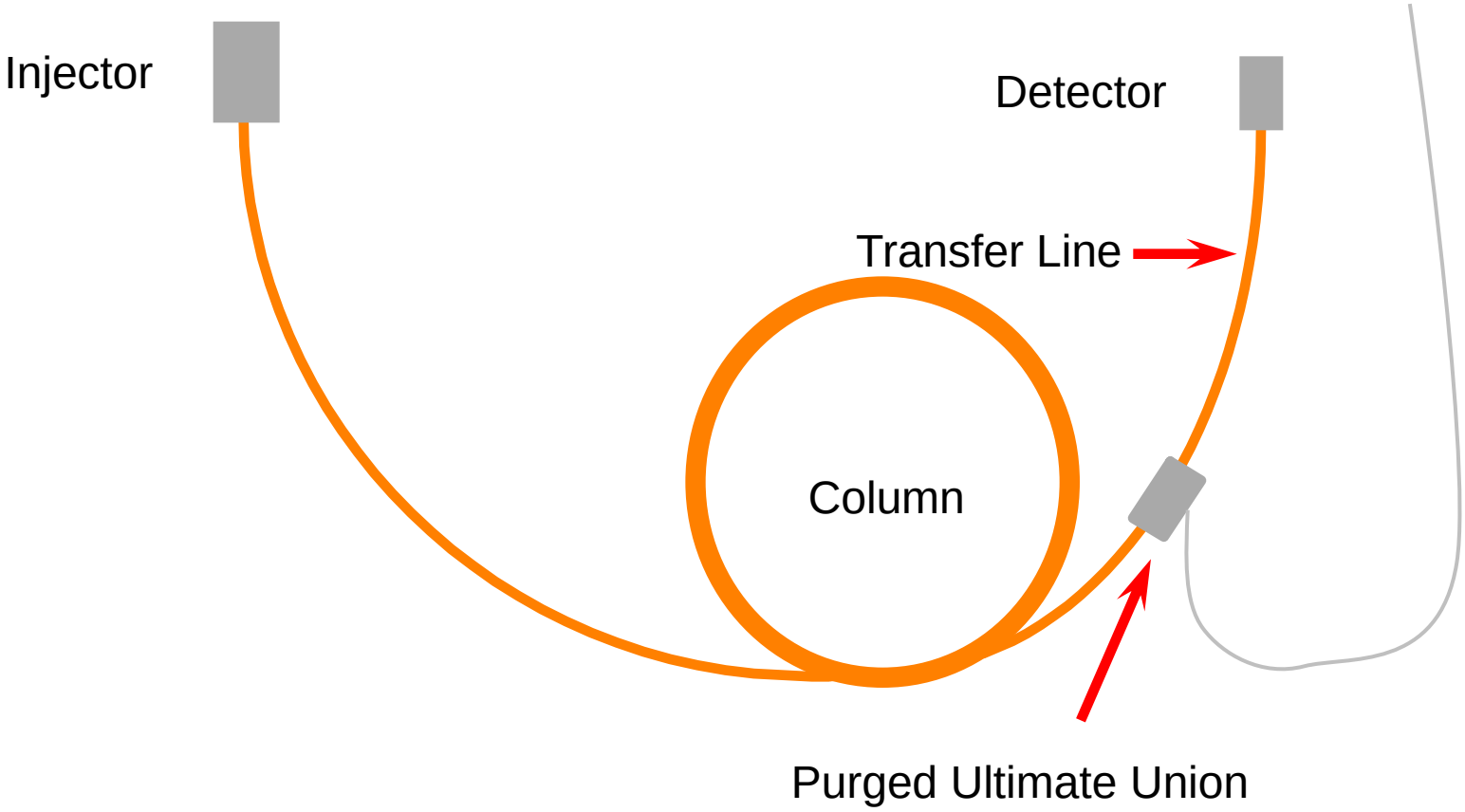
Overlay of two chromatograms of a blank extract injected BEFORE (A) and AFTER (B) three injections without backflush

With Backflush: No Increased Background (Less Spectral Noise) and Consistent Retention Times

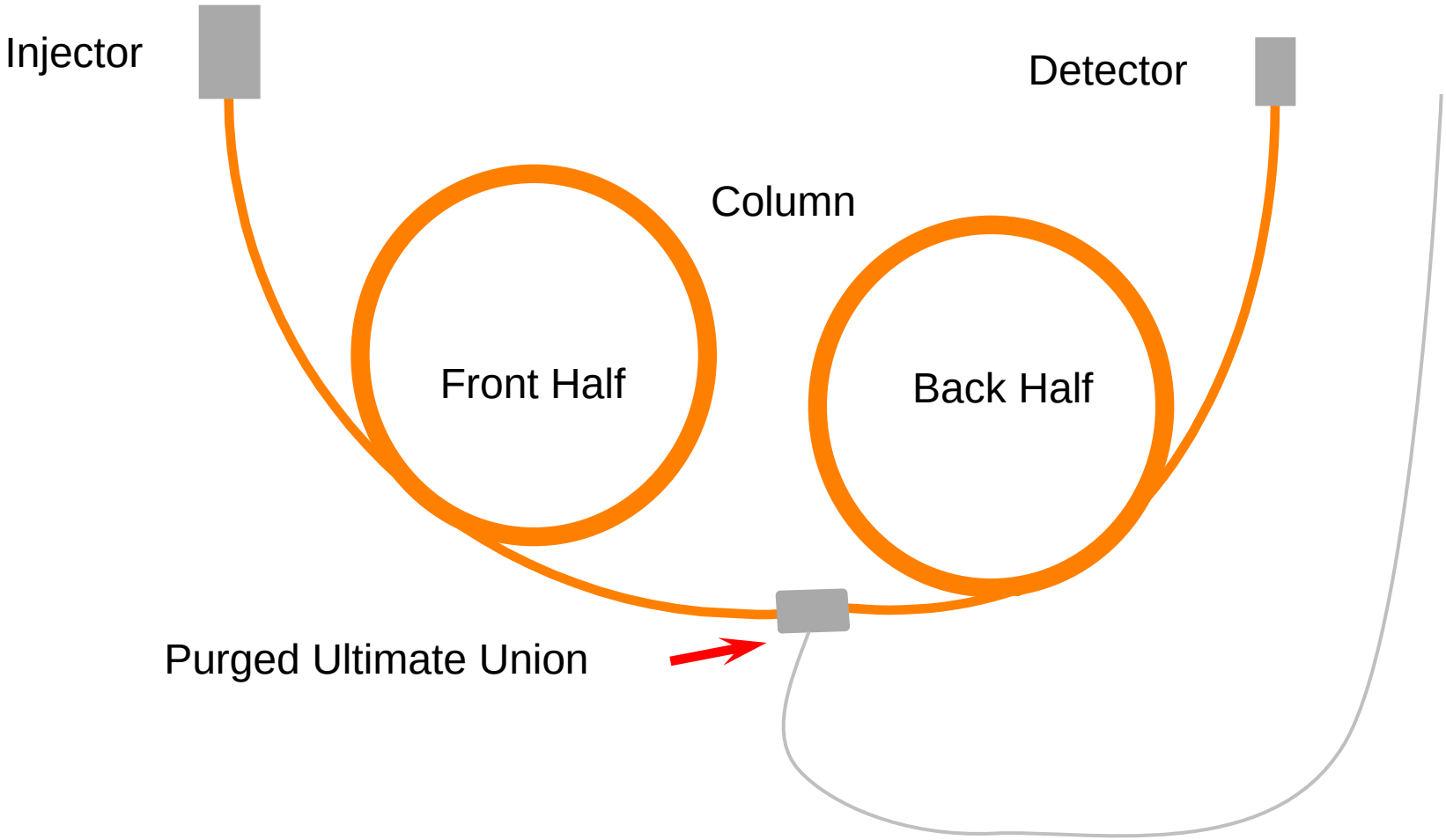


Overlay of three chromatograms of lettuce extract run with 2 min of back flush

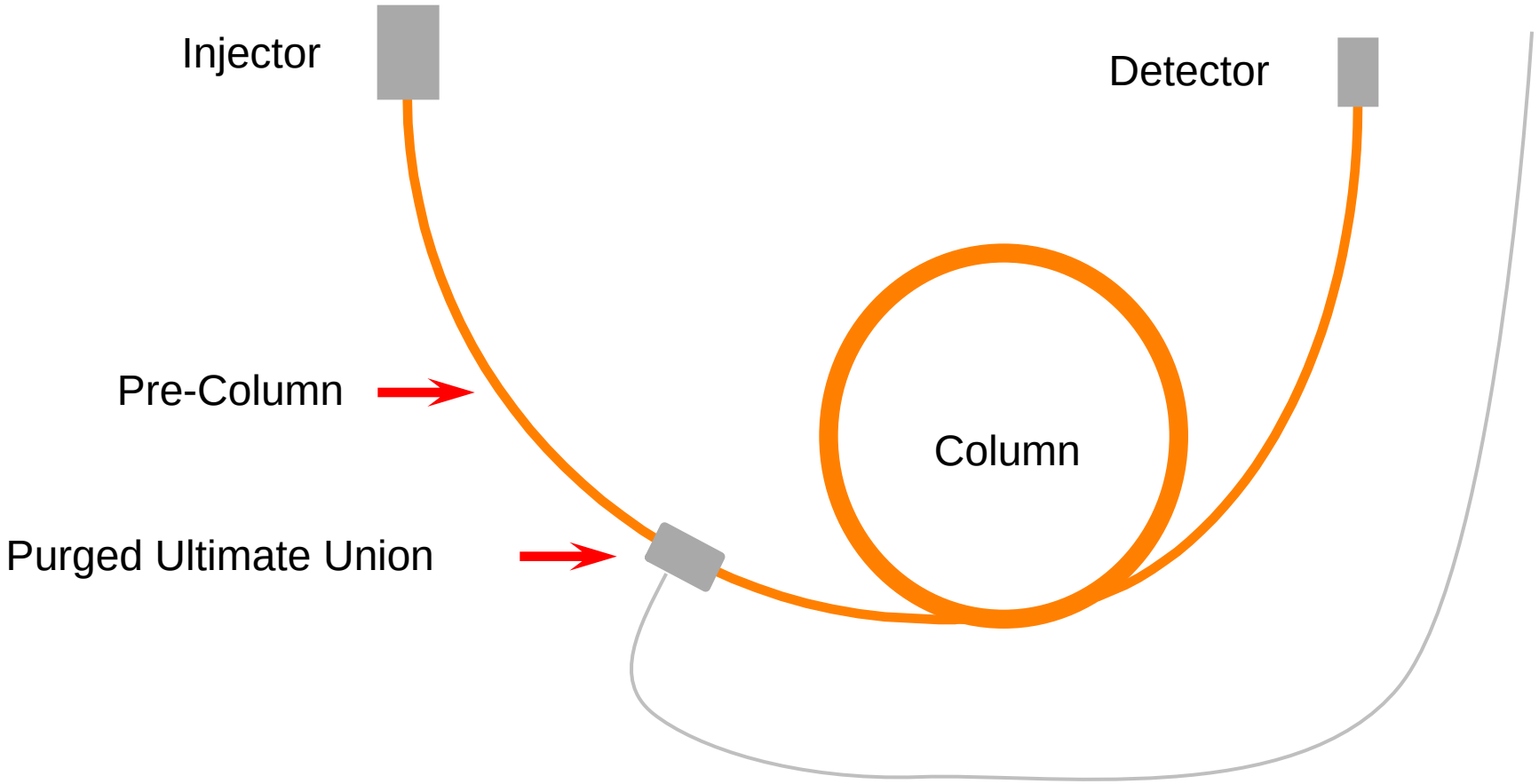
Post-Column Backflush



Mid-Column Backflush

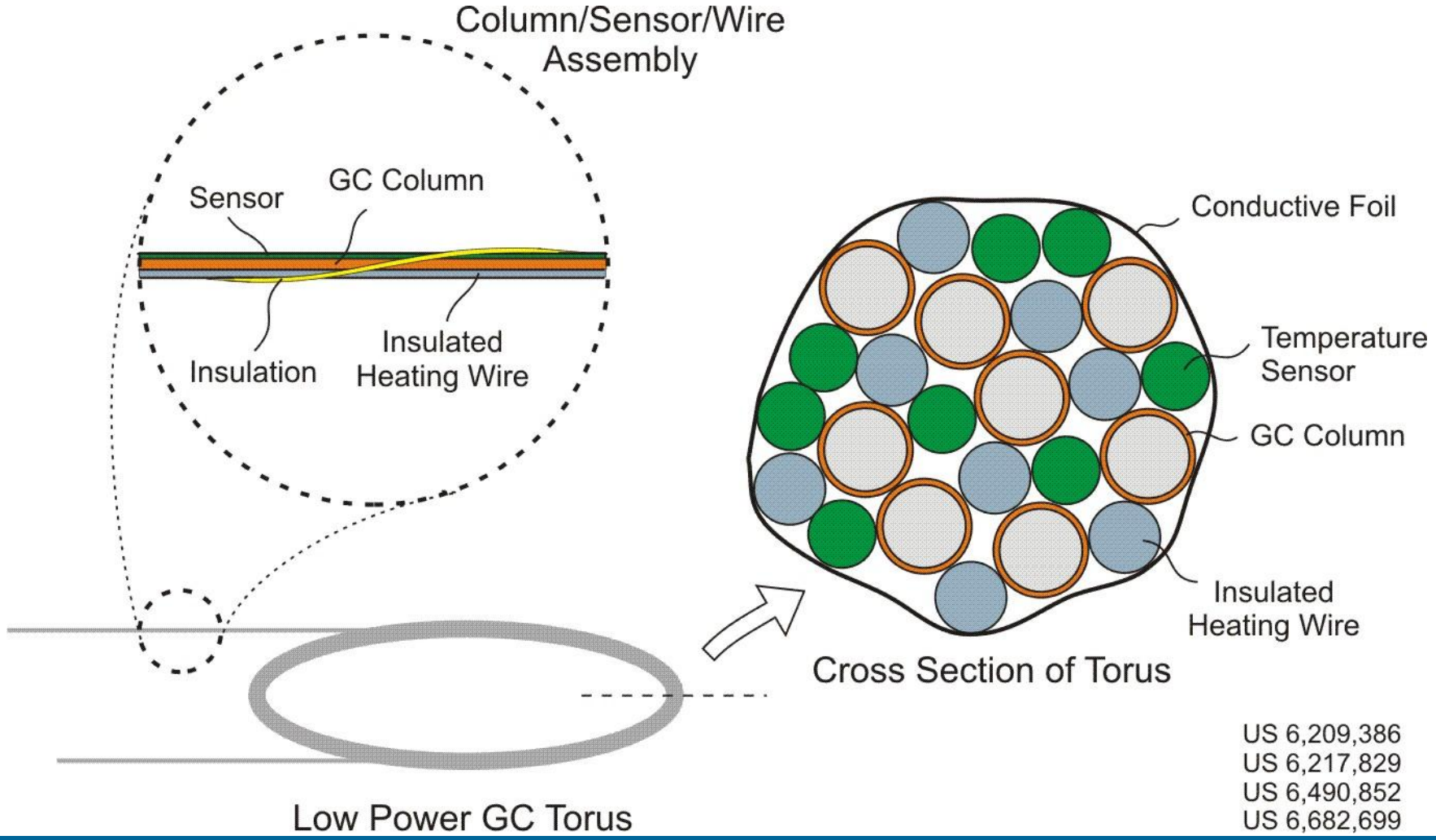


Pre-Column Backflush



“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

Interfacing LTM GC to an Agilent 7890 or 6890 GC

GC oven door replaced with LTM-ready GC oven door (easy)
Use same GC injectors, detectors, autosamplers, software, …

Column Modules mount outside isothermal GC oven for fast heating and cooling

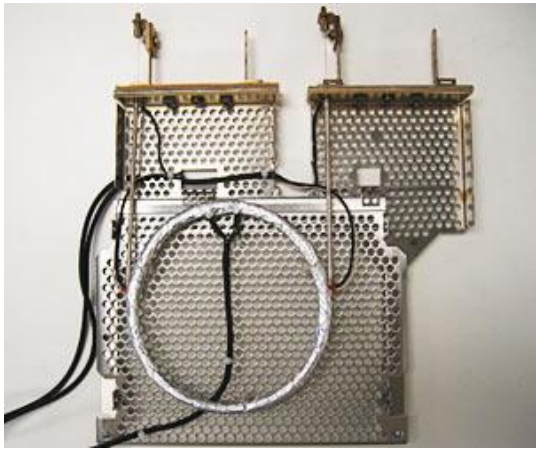
Independent and simultaneous temperature programming of 1-4 column modules

LTM Column Modules

LTM Control System
w/ Keypad User Interface
(LTM Control SW for ChemStation
Available from Agilent Nov/Dec'08)

Note: Front thermal shield removed to show LTM column modules
Entire thermal shield should always be in place during operation

A Closer Look



LTM Column Assembly

LTM Retrofit Door

LTM Column Module

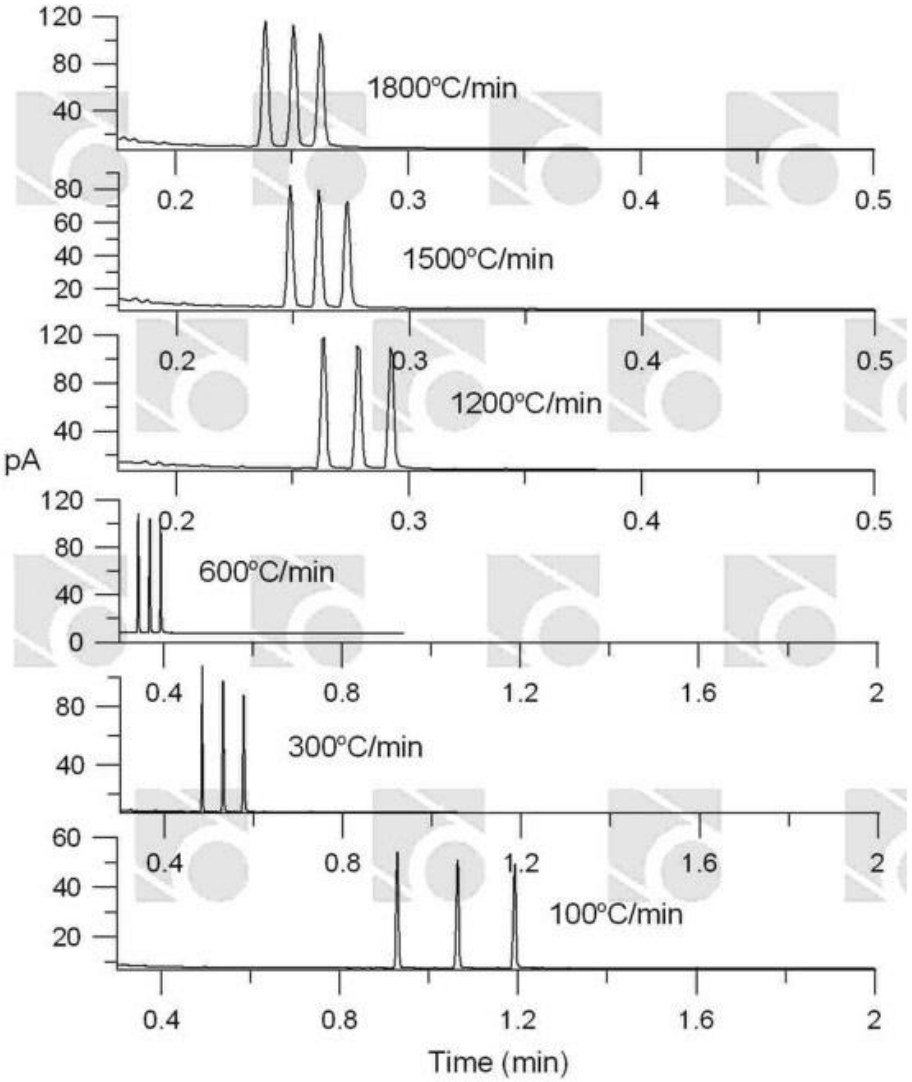
Inside View

LTM Heating Speeds

Heating speeds can be set up to 1800°C/min

- achievable rates depend on column mass, configuration and column void times

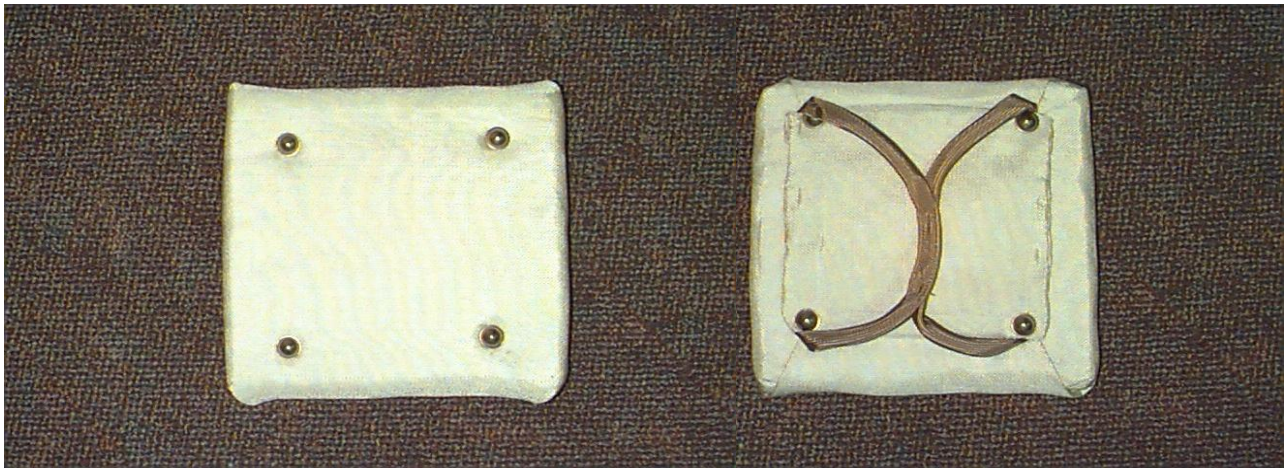
- … also including practical trade-offs of speed vs resolution

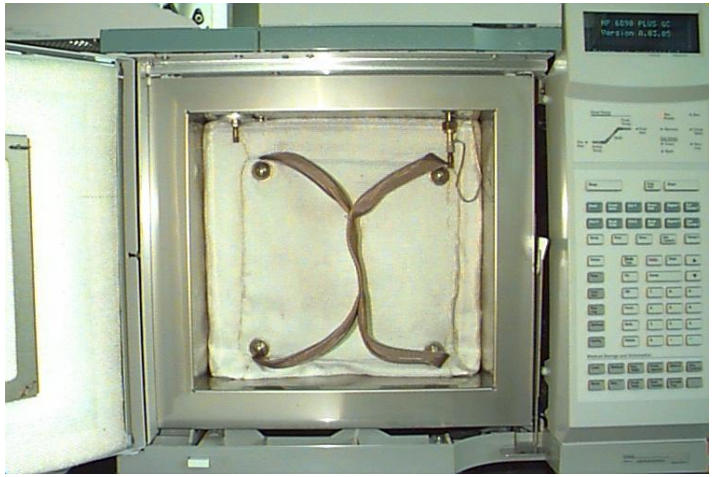


6890/7890 Oven Ramp Rates

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

Oven Insert For The 6890/7890





The insert reduces the 6890/7890 effective oven volume by 50%.

Allows 120V 6890/7890 to achieve ramp rate equal to the 240V.

Allows faster oven cool down over std 6890.

Part No. G2646-60500
(Can't use on 6890/ 5973 MS)

Typical Cooling Times for a LTM Column (Standard Size)

Column Length

°C	2 m	5 m	10 m	15 m	30 m
350->300	3	5	6	7	9
300->250	3	5	7	7	13
250->200	4	7	8	10	17
200->150	4	8	11	13	22
150->100	7	13	17	19	36
100->50	13	27	34	41	75

	Type	Time
350°C → 50°C	LTM (2m Column)	34 seconds (= 3+3+4+4+7+13)
Equilibration		3 seconds
350°C → 50°C	7890 GC	3-4 minutes
Equilibration		2-3 minutes

Some Practical Uses of LTM Rapid Heating/Cooling

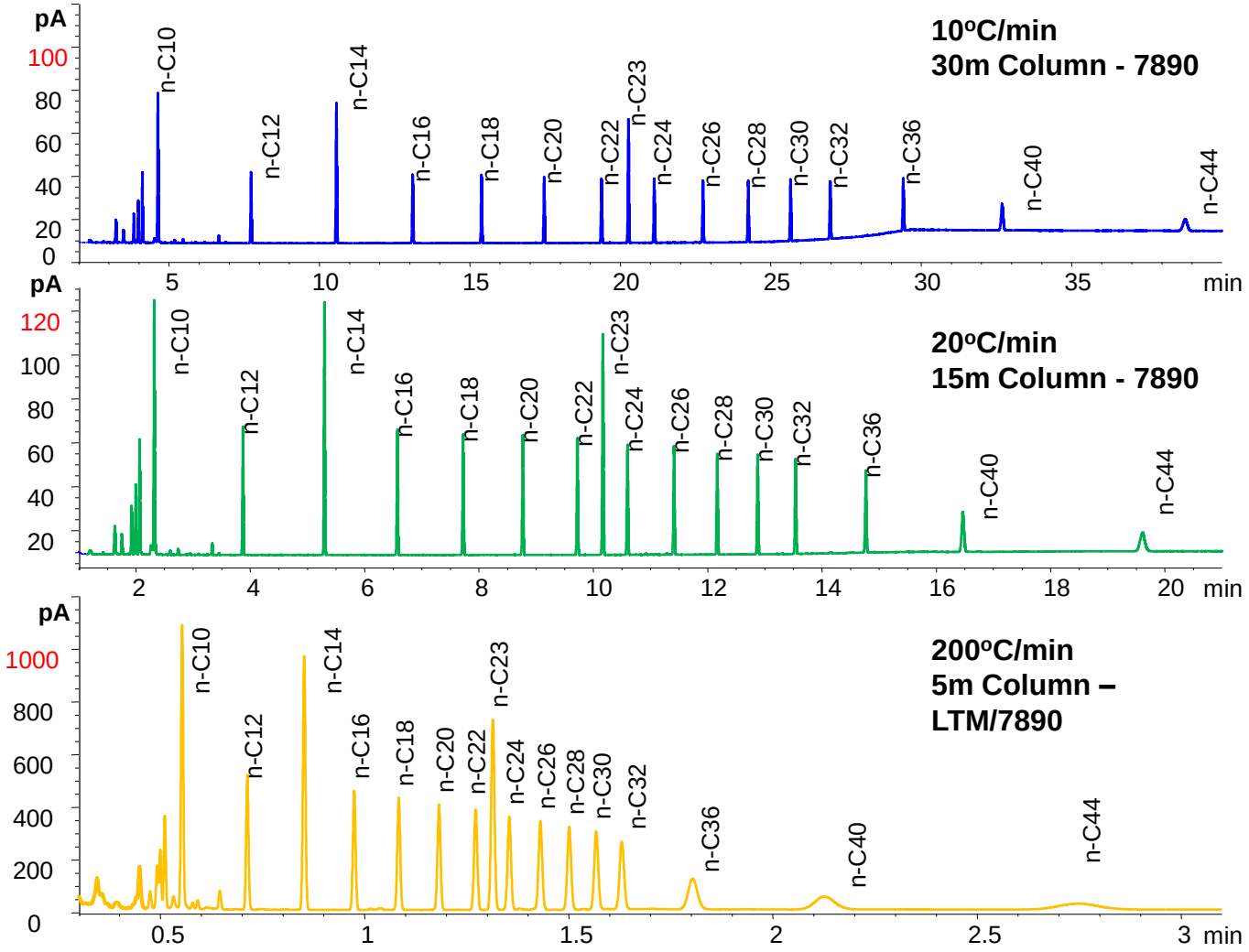
Environmental

Need for high through-put, especially for low margin samples (eg. Total Petroleum Hydrocarbon (TPH)), where analytical cycle times are a critical element in making a profit

Hydrocarbon Processing

Certain process control analyses (eg. Simulated Distillation) lend themselves to batch analysis. Shorter analytical cycle times get data back to operations faster, or allow more samples/shift

TPH Analysis with Faster GC Run Times (C_{10}→C_{44} Standard Shown)

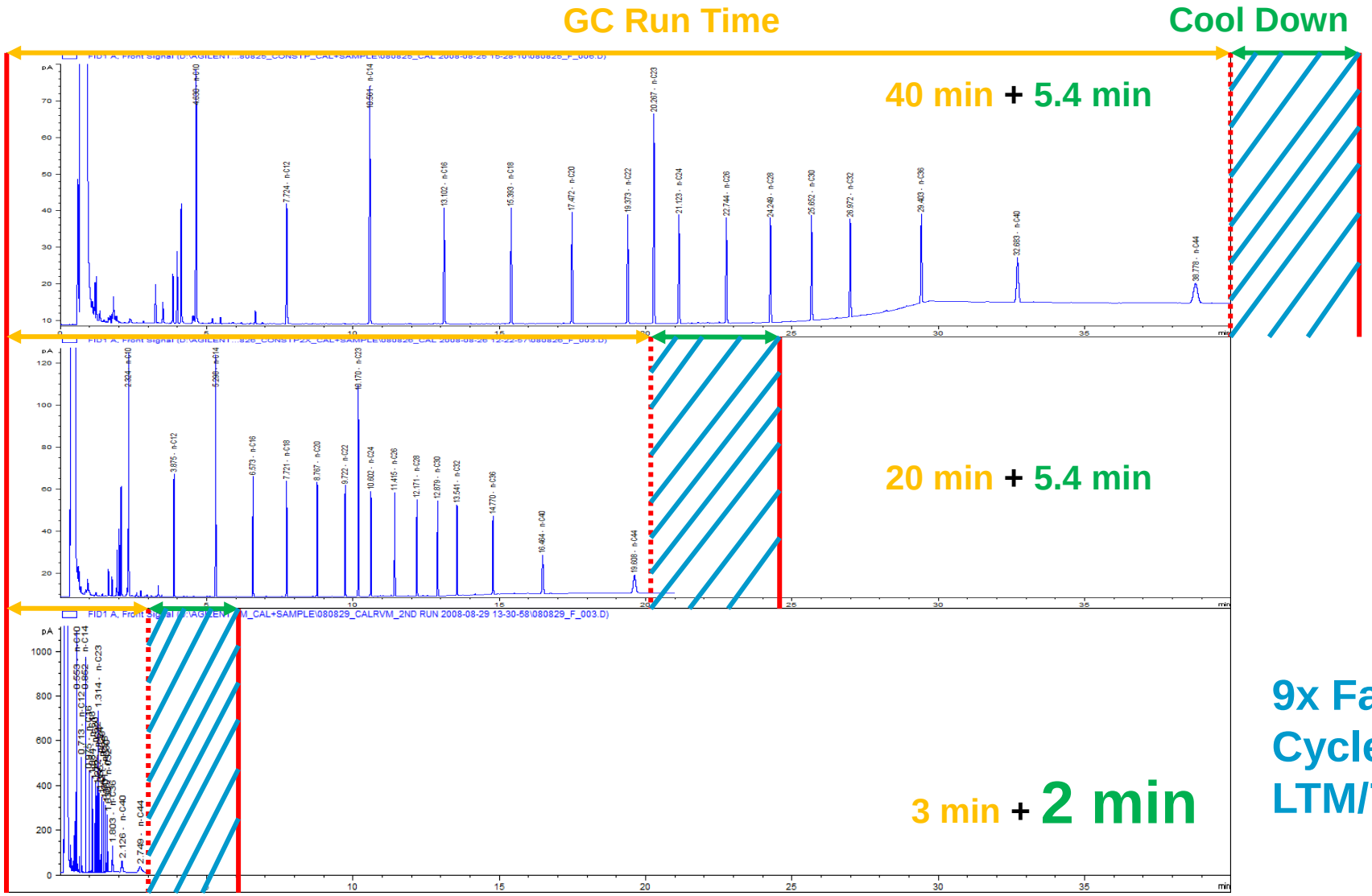


Standard
GC Run Time

Shorter Column,
2x Faster
Ramp Rate

**5m Column,
10x Faster
Ramp Rate
with LTM**

LTM Also Greatly Reduces Cool-Down Times, → 9x Faster Heating/Cooling Cycle Times



9x Faster Cycle Time LTM/7890

Agilent Technologies

CONCLUSIONS

Carrier Gas – Helium can still go fast but Hydrogen has the most advantage at high velocities, Nitrogen might work (GEC)

Diameter – Smaller allows shorter length but has less capacity

Small Change in ID Easier to Translate – Again think capacity

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

Temperature Program – Use MTS to scale temps properly

Method Translation Software – FREE, reliable

Capillary Flow Technology – Backflush instead of Bake Out

Low Thermal Mass GC – Fast Heating, Fast Cooling

ANY QUESTIONS?

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