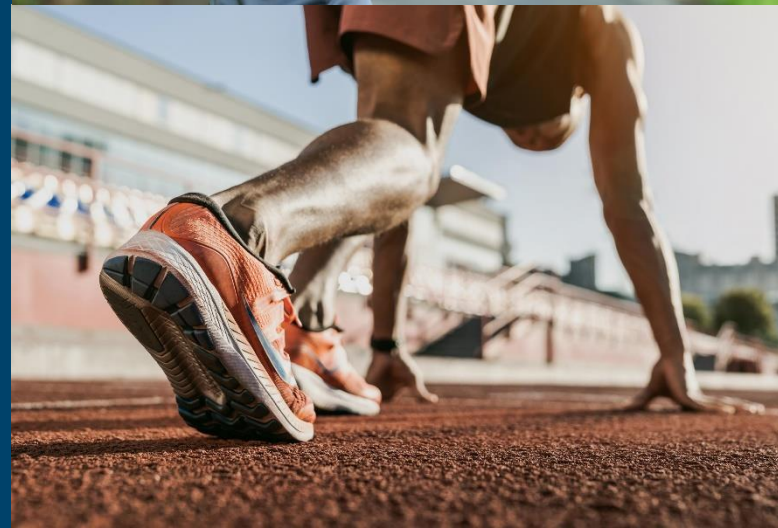


Get Better Resolution for Your New Year's Resolution

GC separation troubleshooting

Alexander Ucci
January 25, 2023



“Everything Was Just Fine... and Then This Happened!”

“How do I troubleshoot?”

Track your actions/keep a logbook of events:

- Changed column, liner, septum, or syringe
- Injected samples, or used another method
- Carried out maintenance, cut column, or inlet flush



Logic
=
**Something changed
(slowly or suddenly)**
=
Something is different

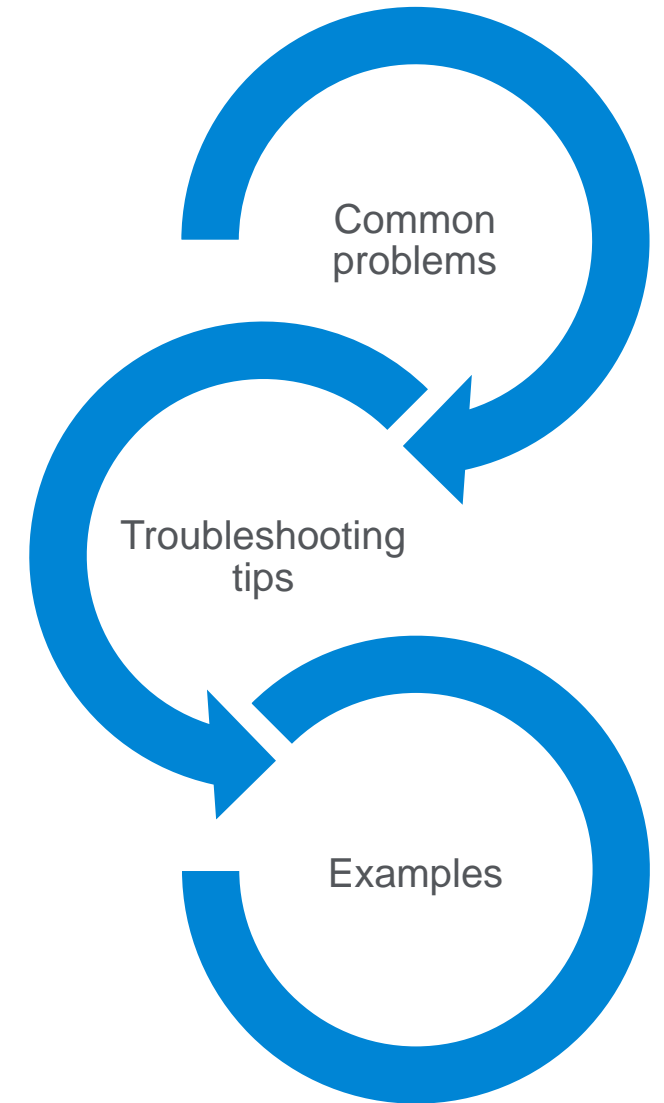
Logical Troubleshooting

Troubleshooting starts with isolating the problem.

- There are five basic areas from where problems can arise:
 - Injector
 - Flow
 - Column
 - Detector
 - Electronics
- Or...
- A combination of these

Knowing what can and cannot cause the symptom is key, and most importantly **DON'T PANIC!**

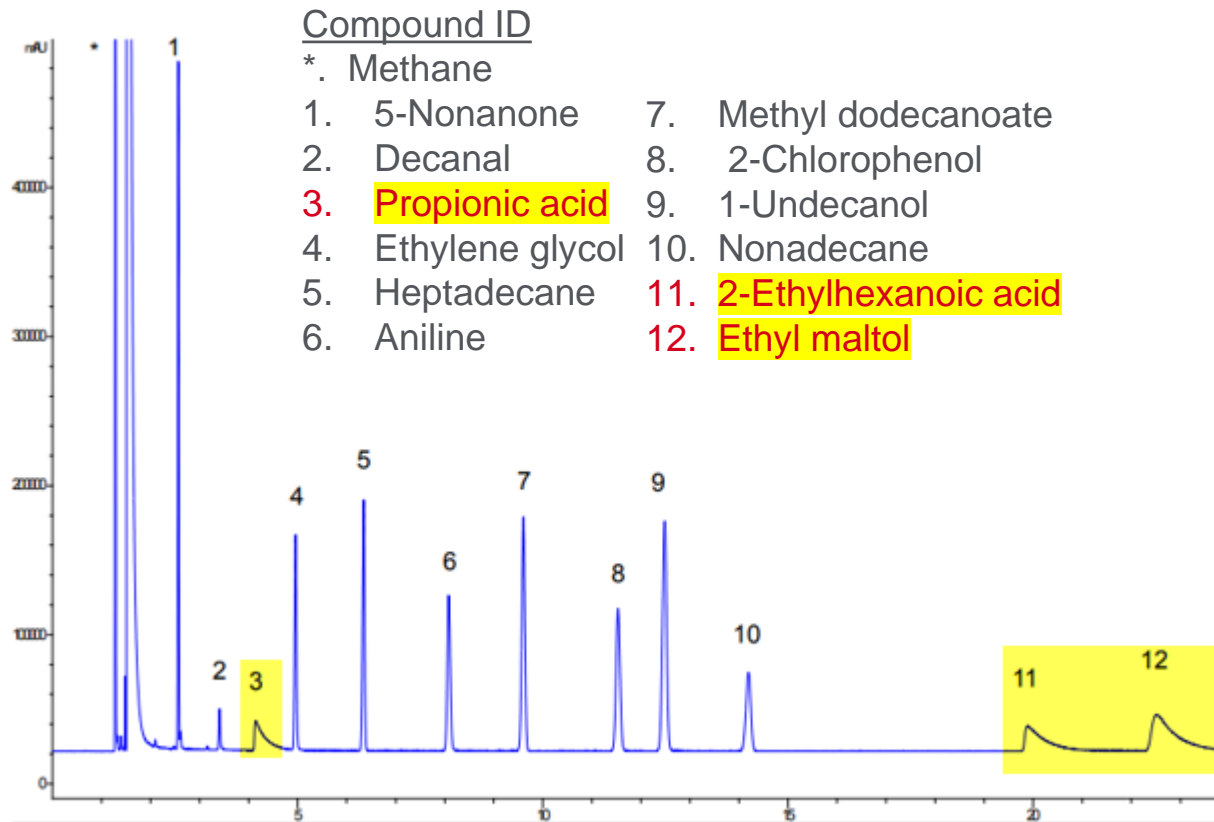
Agenda



Common Peak Shape Issues

- **Peak tailing** – flow path or activity
- **Bonus peaks** – in sample or back flash (carry-over)
- **Split peaks** – injector problems, mixed solvent
- **No peaks** – wasn't introduced, wasn't detected
- **Response changes** – activity, injector discrimination, detector problem
- **Peak fronting** – overload or solubility mismatch, injector problems
- **Shifting retention** – leaks, column aging, contamination, or damage
- **Loss of resolution** – separation decreasing, peak broadening
- **Baseline disturbances** – column bleed, contamination, electronics
- **Noisy or spiking baseline** – electronics or contaminated detector
- **Quantitation problems** – activity, injector, or detector problems
- **Other**

Peak Tailing



Injector or column is active

- Reversible adsorption of active compounds (-OH, -NH, -SH)

Flow problem

- Dead volume, obstruction, poor installation, or severe column contamination

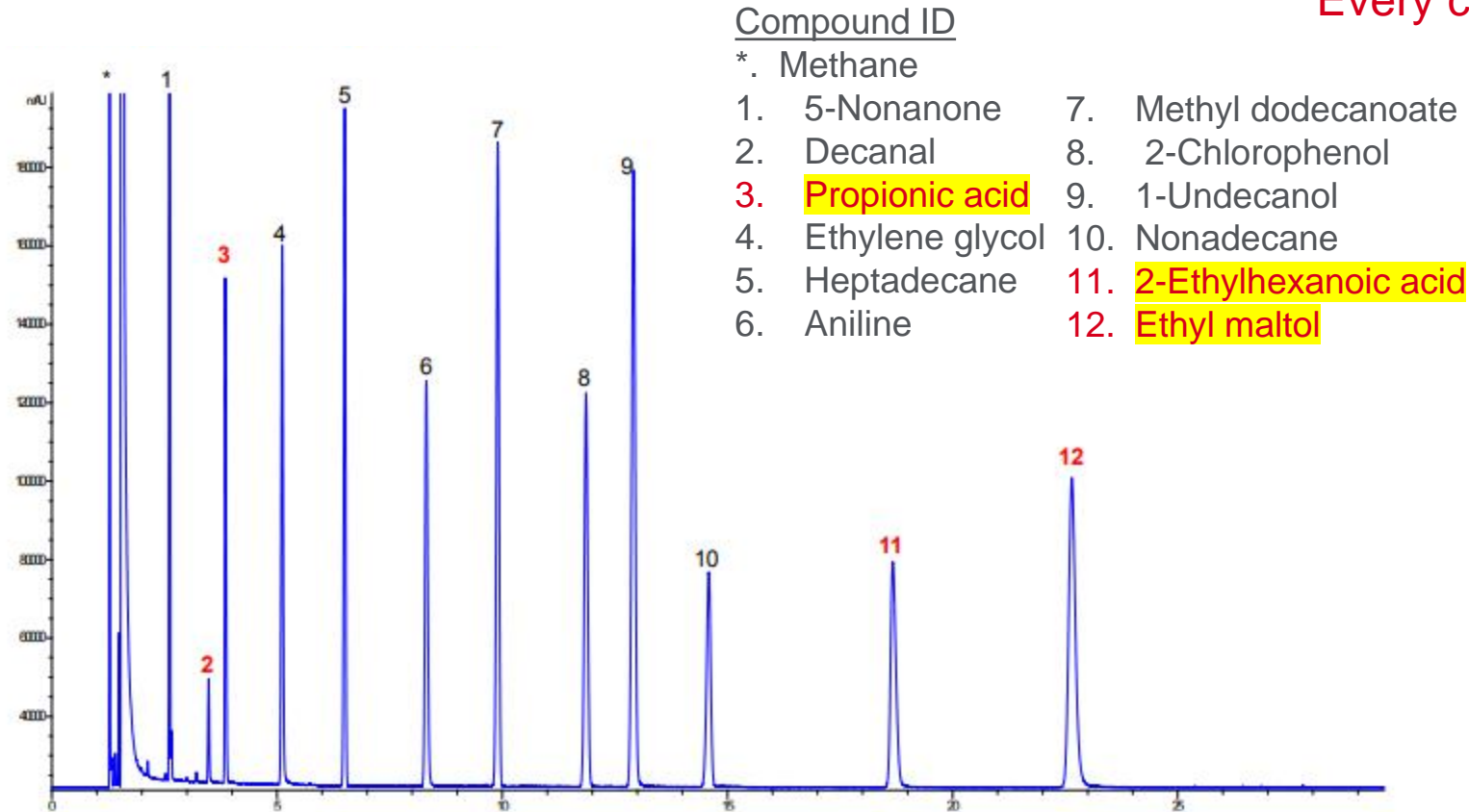
Miscellaneous - overloading of PLOT columns, coelution, polarity mismatch between phase, solute or solvent, and some compounds always tail

***Tip:** Inject a light hydrocarbon. Should not tail unless flow path problem.

Agilent Inert Flow Solution

Modified Agilent J&W DB-WAX UI mix on DB-WAX UI, 122-7032UI

*Every column is tested individually



Brochure 5991-6709EN

Agilent Inert Flow Solution

Agilent UltiMetal Plus inlet weldment, shell, and transfer lines



Agilent Ultra Inert inlet liner



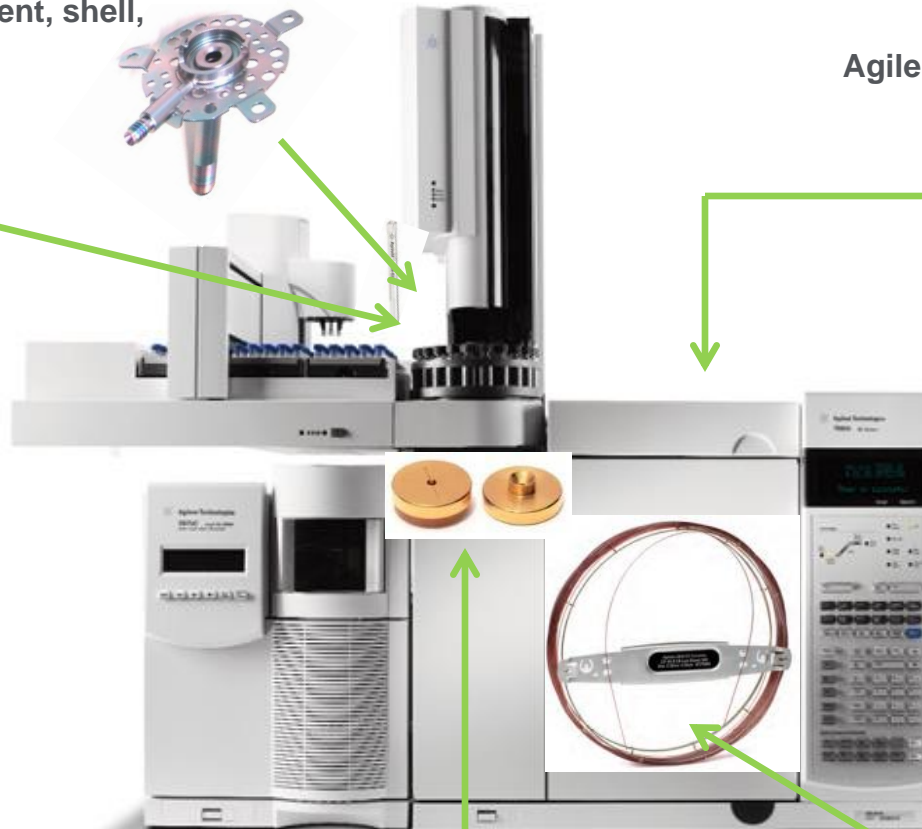
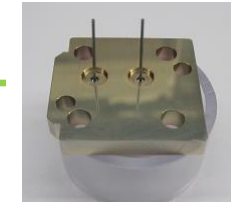
Agilent UltiMetal Plus ferrules



Agilent UltiMetal Capillary Flow Technology Devices, Ultimate union



Agilent UltiMetal Plus- TCD, FPD, NPD/FID jets



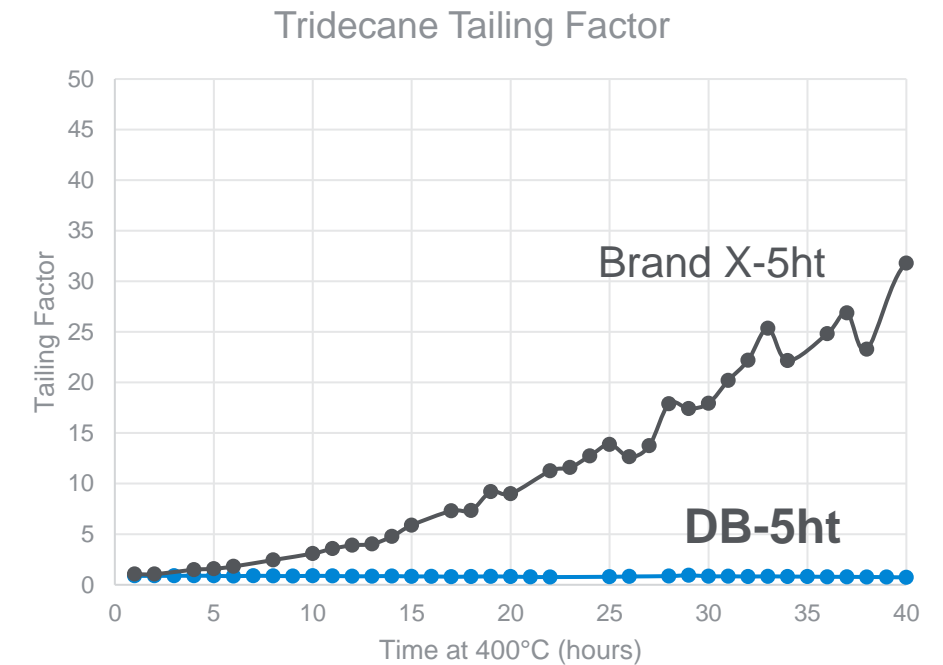
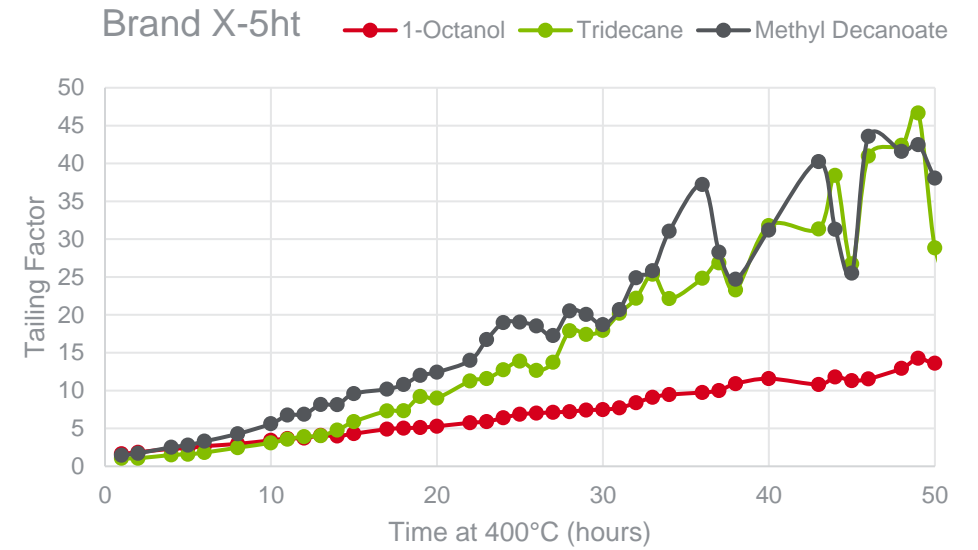
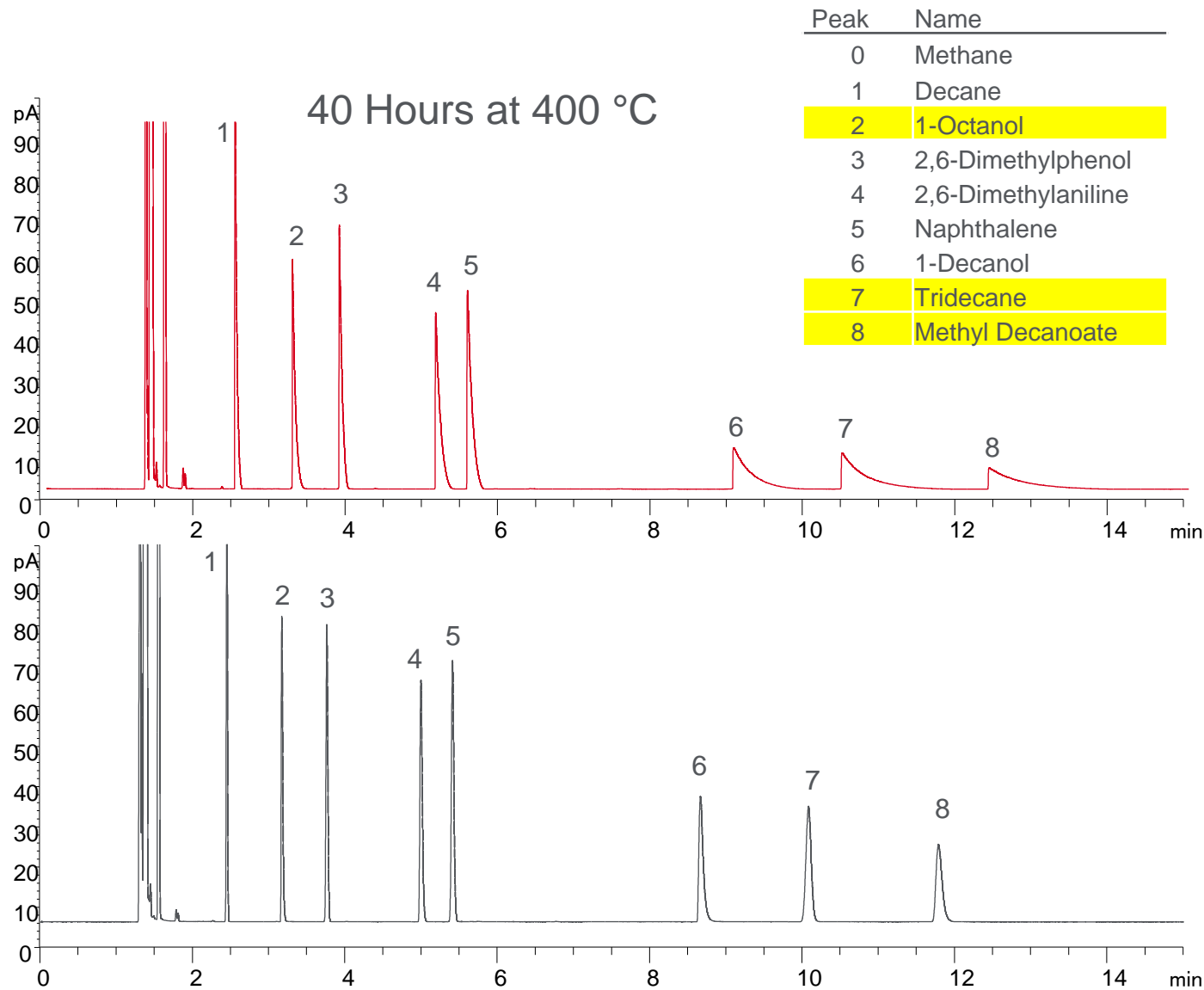
Agilent Ultra Inert gold seal



Agilent J&W Ultra Inert GC column

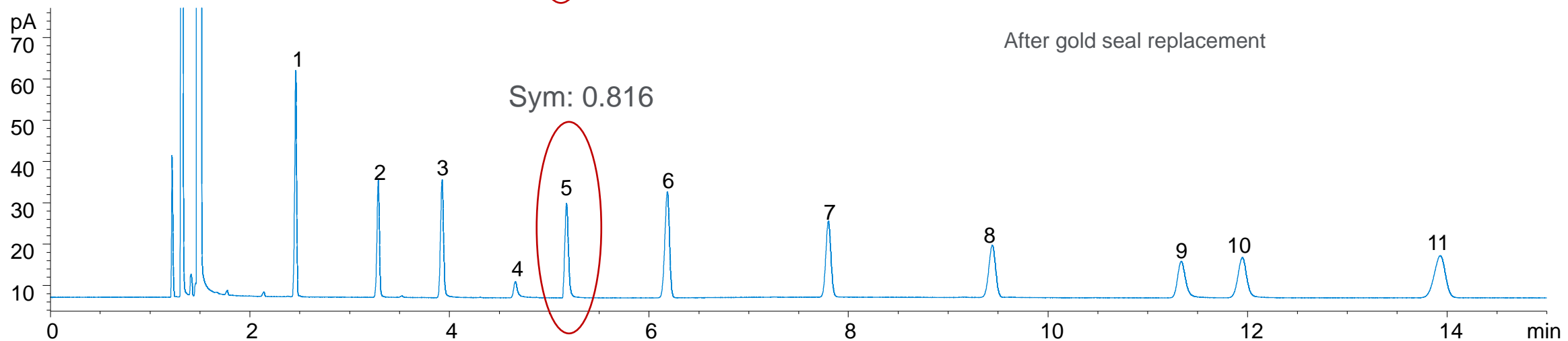
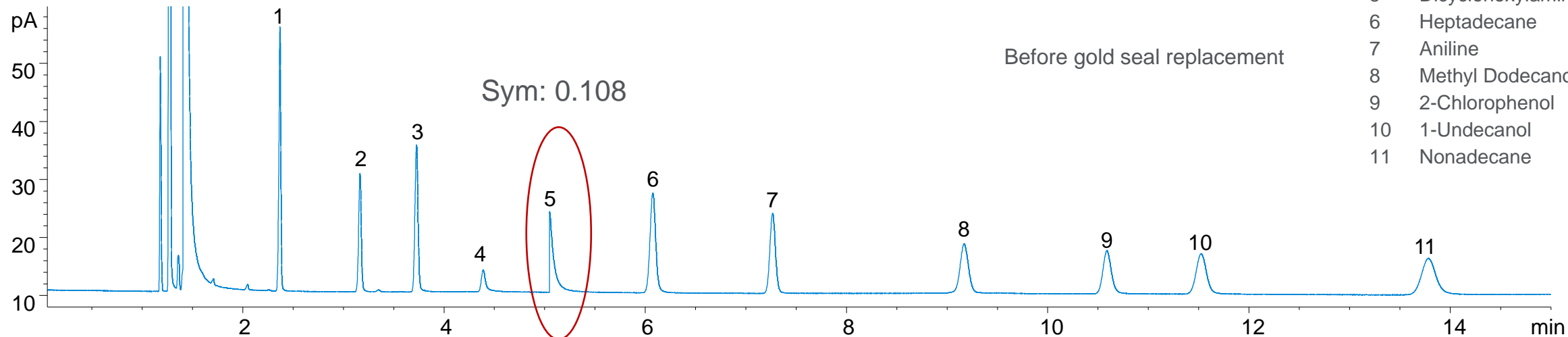
5990-8532EN brochure

Peak Tailing from Thermal Degradation



Peak Tailing from Contaminated Consumables

	Peak
0	Methane
1	2-Nonanone
2	Decanal
3	2,3-Butanediol
4	Ethylene Glycol
5	Dicyclohexylamine
6	Heptadecane
7	Aniline
8	Methyl Dodecanoate
9	2-Chlorophenol
10	1-Undecanol
11	Nonadecane



Self Tightening Nuts: No Leaks, No Downtime, No Frustration



- Spring-driven piston continuously presses against ferrule
- Automatically retightens when ferrule shrinks
- Wing design for finger tightening
- No tools needed
- Works only with graphite/vespel ferrules

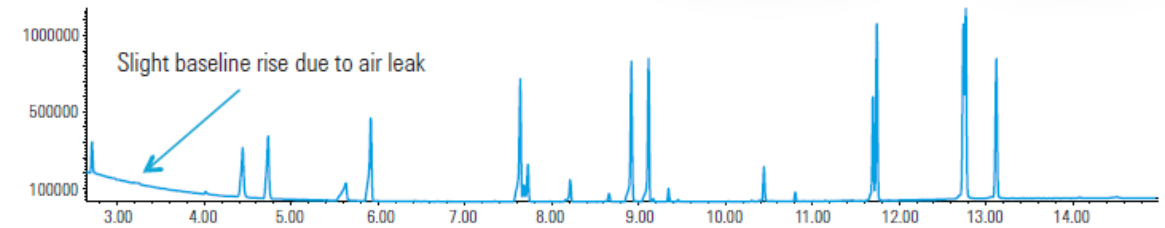
Part Number	Description
G3440-81013	Column Nut, Collared Self-Tightening MSD
G3440-81011	Column nut, Collared Self Tightening Inlet/Detect
G3440-81012	Collar for Self Tightening Nut

<https://www.agilent.com/en/video/gc-supplies-innovation>

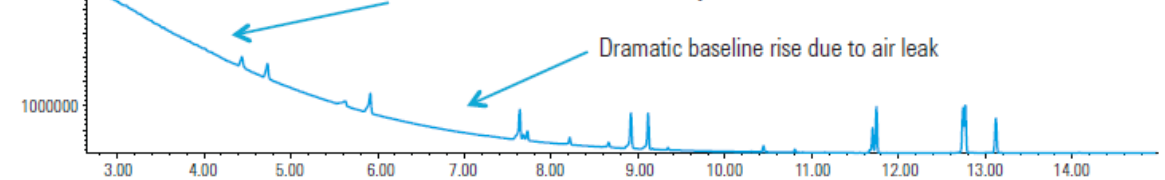
<https://www.agilent.com/en/video/stcn-inlet-detector>

<https://www.agilent.com/en/video/stcn-mass-spec>

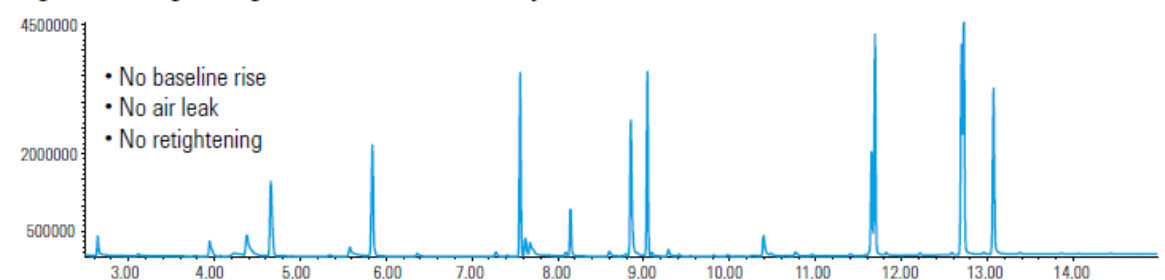
Standard column nuts new fitting



Standard column nuts after 25 injections



Agilent Self Tightening Column Nuts after 400 injections



400 injections

New Agilent Standard Winged Nut and Depth Guide

- Compatible with Agilent/HP style compact ferrules including graphite ferrules
- Winged fastener design for easy engagement and tool free install
- Hollow-body design with low thermal mass mitigates thermal lag during temperature cycling within the GC oven
- Removable locking-collar with soft-PTFE insert to secure column placement during install without damaging the analytical column



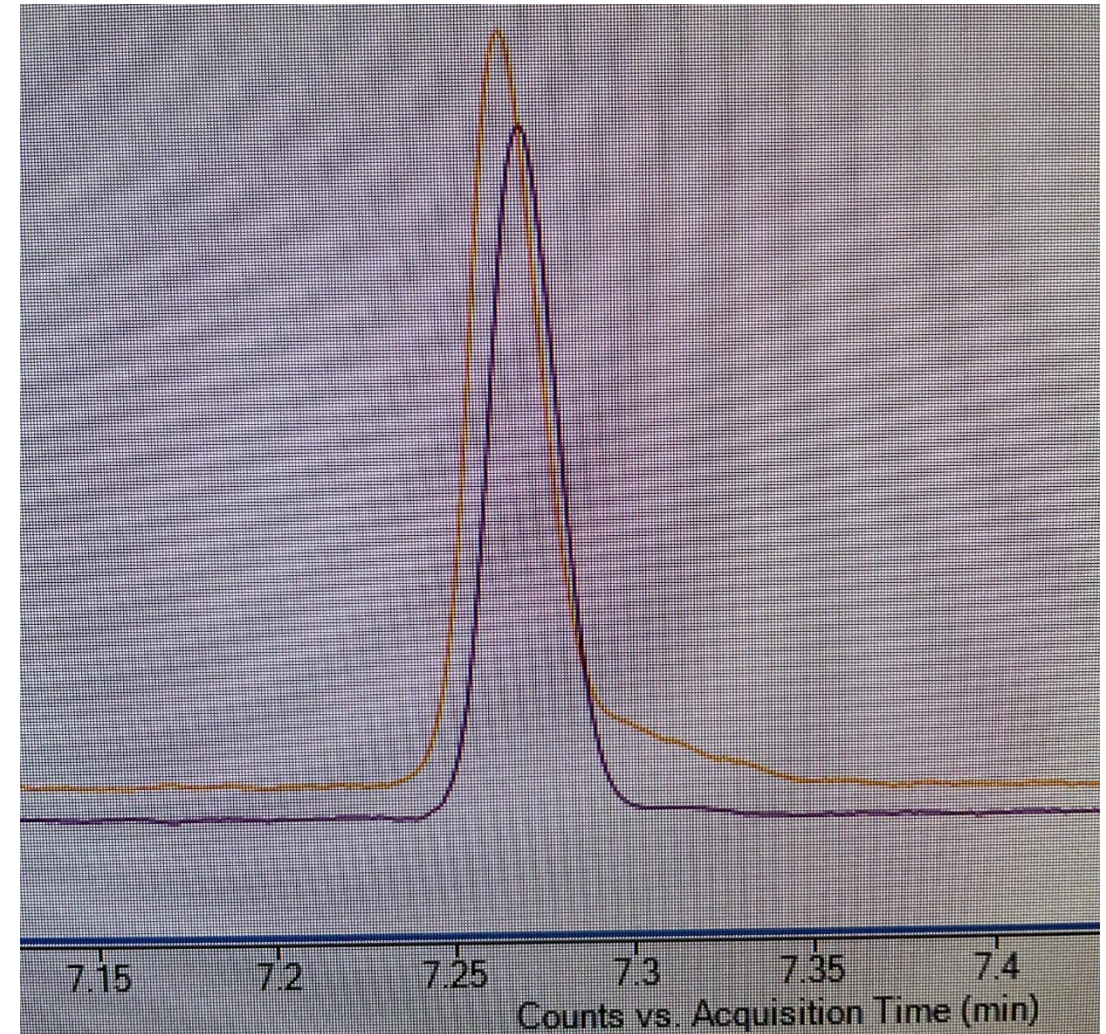
- Easy to use template provides critical capillary column installation for Agilent's most popular GC-configurations
 - SSL, MMI, purge-packed inlets
 - FID, TCD, NPD Detectors
 - EI MSD Source
- Compatible with Agilent's Self Tightening and Winged Column Nuts



Agilent Capillary Column Depth Guide – G3440-88000

Consequences of Improper Column Installation

- Split/splitless inlet used
- Orange trace is 7 mm past the ferrule
- Blue line is 5 mm past the ferrule



Agilent CrossLab CS (Cartridge System)

No peaks from leaks

Features:

- Exchangeable cartridge with ADM Flow Meter
- Automatic Notification of Probe Filter Replacement
- Ergonomic and robust design
- Universal 3AA or USB power
- USB connects to web interface for added functionality and firmware updates
- Easy to view OLED Screen
- Kickstand

Leak detector
cartridge

Handheld



ADM Flow Meter
cartridge

The Cost of Leaks

- Cost of gases
- Contamination from exposure
- Reduced consumable lifetime
- Reduced productivity from downtime
- Detector noise and elevated baselines
- Time in troubleshooting

It is critical that every customer checks for leaks. They should have the best tool for the job!

Check valves, fittings, and traps for leaks after every maintenance, and after thermal cycling as these can loosen some types of fittings.

Assets Available for Launch

- **Agilent.com CrossLab CS Leak Detector**

www.agilent.com/chem/gas-leak-detector

- **Agilent.com – ADM Flow Meter**

<https://www.agilent.com/en/product/gas-purification-gas-management/gas-management/adm-flow-meter>

- **Installation manual**

*Agilent CrossLab CS
Electronic Leak Detector manual*

Part number: G6693-90000

The installation manual is available on Agilent.com.

- **Innovation minute video**

<https://www.agilent.com/en/video/crosslab-cs-innovation-minute>

- **Technical overview**

*Agilent CrossLab Cartridge System
(CS) Electronic Leak Detector*

Publication number: 5994-4262EN

The technical overview is available on Agilent.com

- **Brochure**

*GC Troubleshooting in
the Palm of Your Hand*

Publication number: 5994-3607EN

The brochure is available on Agilent.com

- **Flyer**

*Is a Leak Causing Your
Inaccurate Results?*

Publication number: 5994-4202EN

The flyer is available on Agilent.com

Ordering Guide

One year warranty

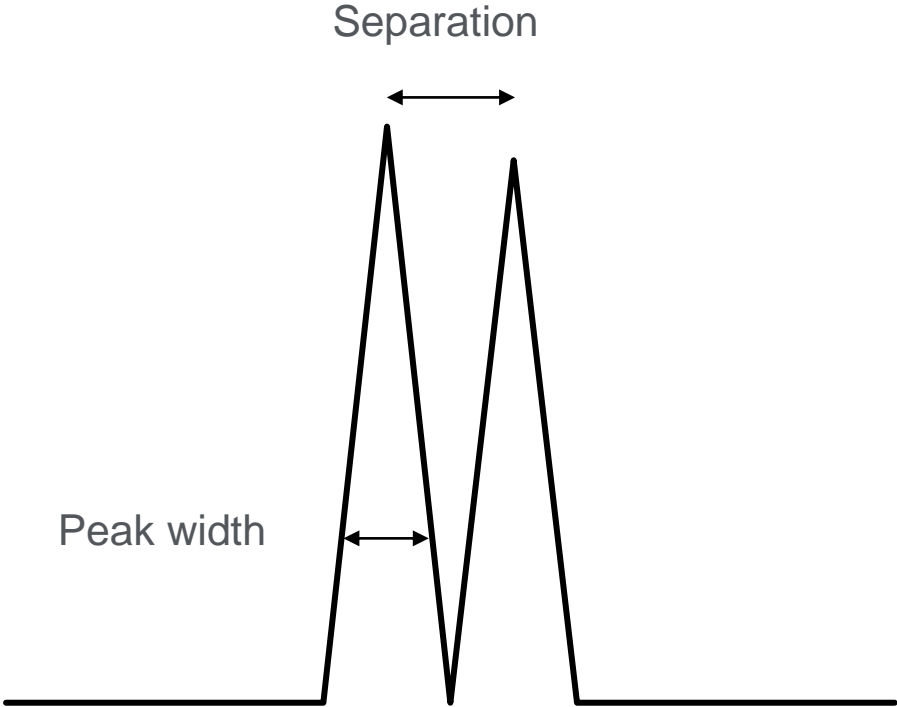
- G6693A – CrossLab CS Electronic Leak Detector
- G6694A – Electronic Leak Detector Cartridge
- G6699A - CrossLab CS Bundle: ADM Flow Meter and Electronic Leak Detector
 - The Bundle will include 1 handheld, 2 cartridges, and a **free** carrying case.
- G6694-60005 – Replacement Probe Filter
- G6691-40500 – Carrying Case



Existing products:

- G6691A – CrossLab CS ADM Flow Meter
- G6692A – ADM Flow Meter Cartridge*
- Note that the ADM Flow Meter cartridge is ordered annually for calibration. The Electronic Leak Detector does not need to be recalibrated!

Loss of Resolution



Resolution is a function of separation and peak width

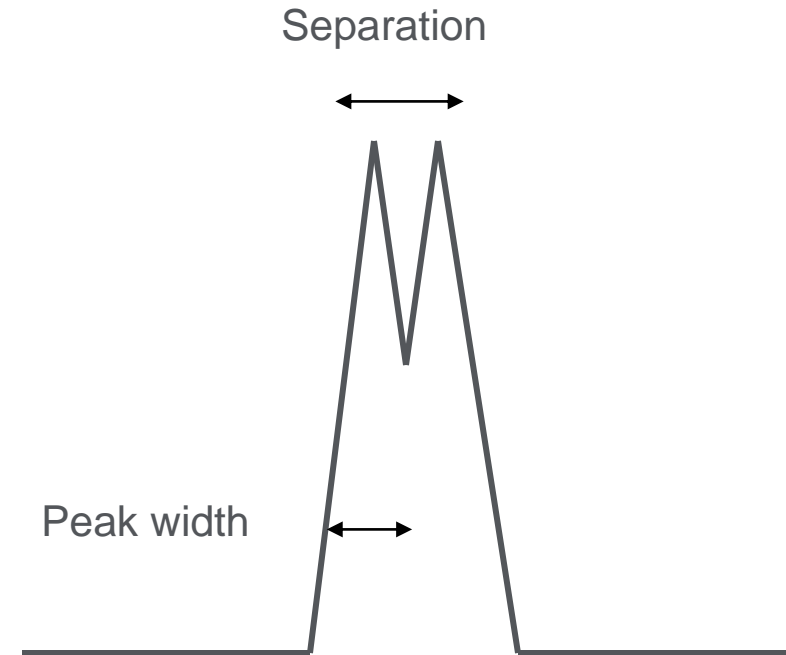
Loss of Resolution - Separation Decrease (Retention Times Changed)

Column

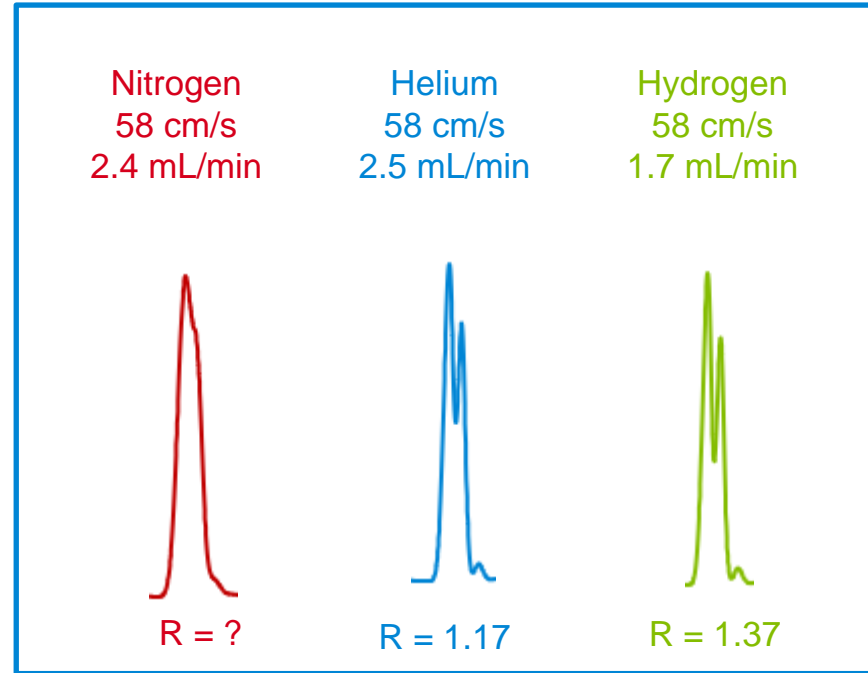
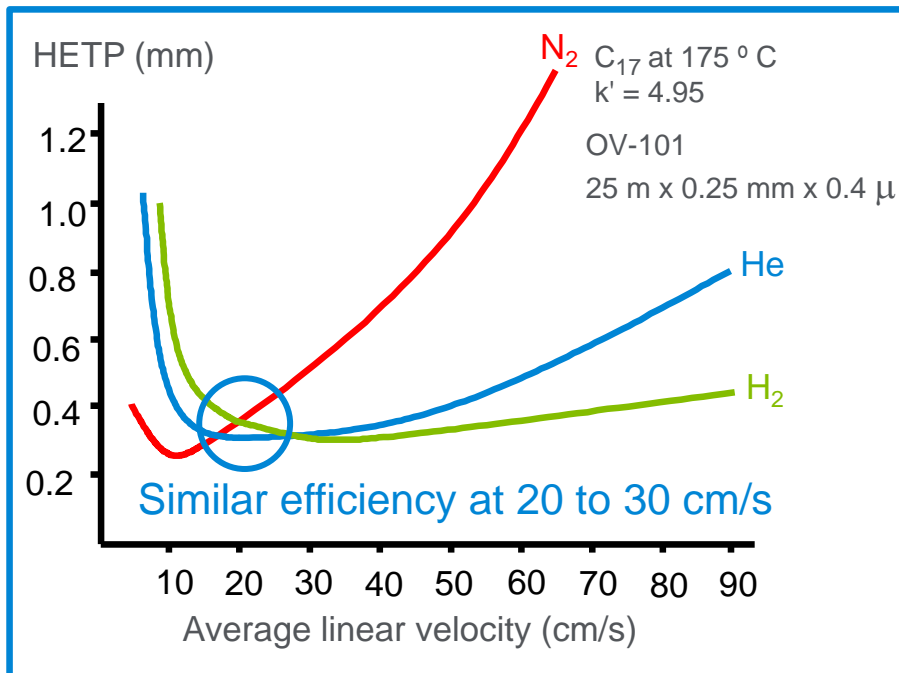
- Different column temperature
- Contamination (more phase?)
- Matrix components coeluting

Flow

- Change in velocity?



Van Deemter Curve



- N_2 actually provides the best efficiency, but at a slower speed
- Most helium methods have too much resolution
 - Lower N_2 efficiency at higher flows can still provide “good enough” resolution
- Most GC methods now use constant flow
- If you change carrier gas, be mindful of these values

Carrier Gas

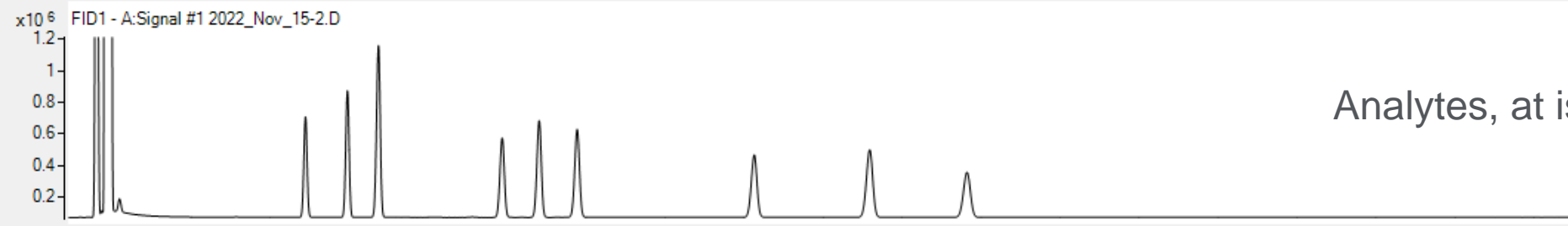
Type	Velocity Range (u_{opt} – OPGV*)
Nitrogen	8–16
Helium	20–40
Hydrogen	30–55

*OPGV = Optimum practical gas velocity

Temperature Optimization



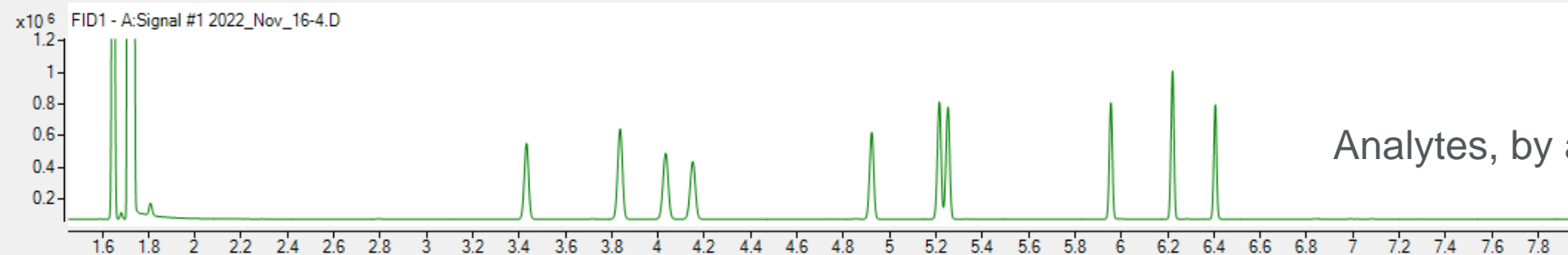
Analytes, at isothermal 165 C



Analytes, at isothermal 135 C



Analytes, at isothermal 125 C



Analytes, by a ramped temperature program

Loss of Resolution - Peak Broadening (Retention Times Unchanged)

Flow

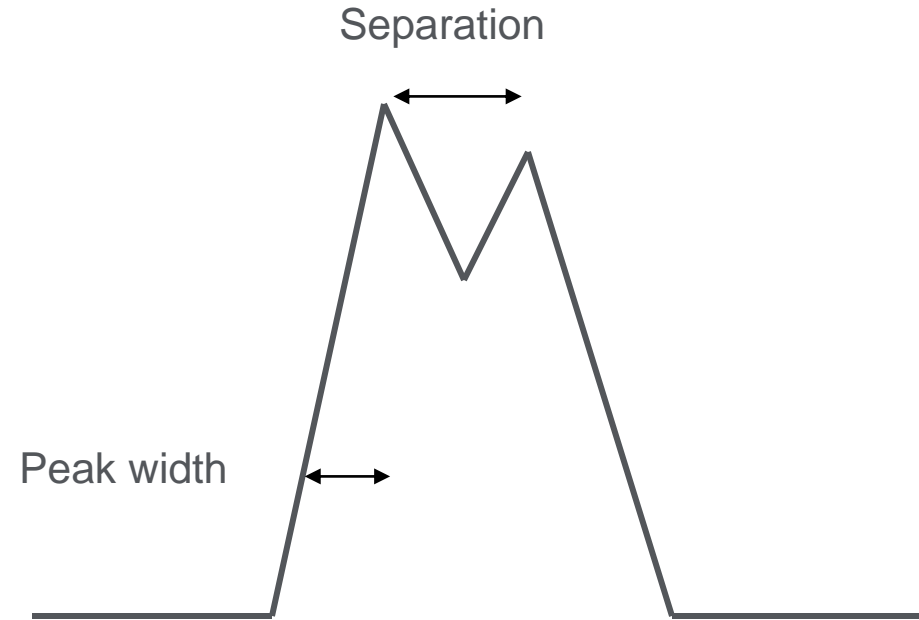
- Make-up gas

Column

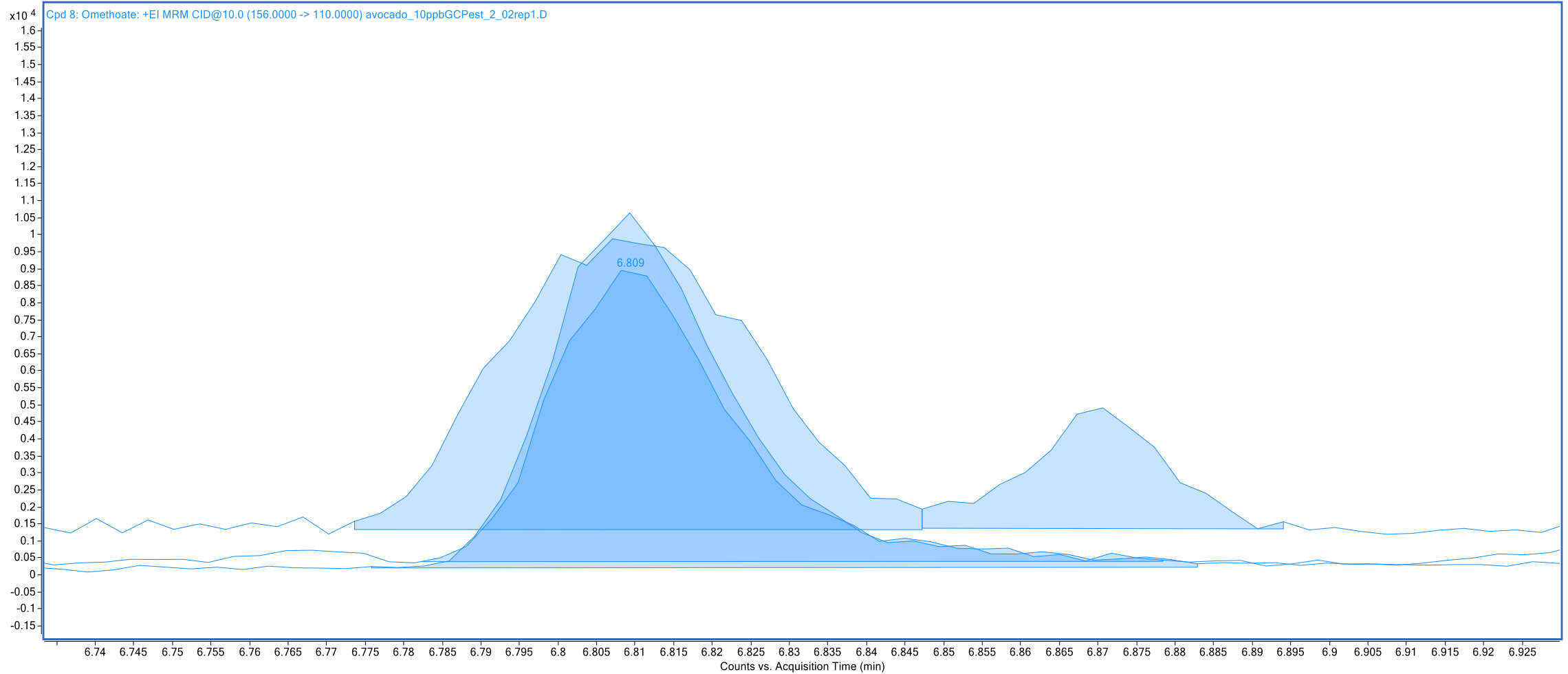
- Contamination
- Phase degradation

Injector (efficiency)

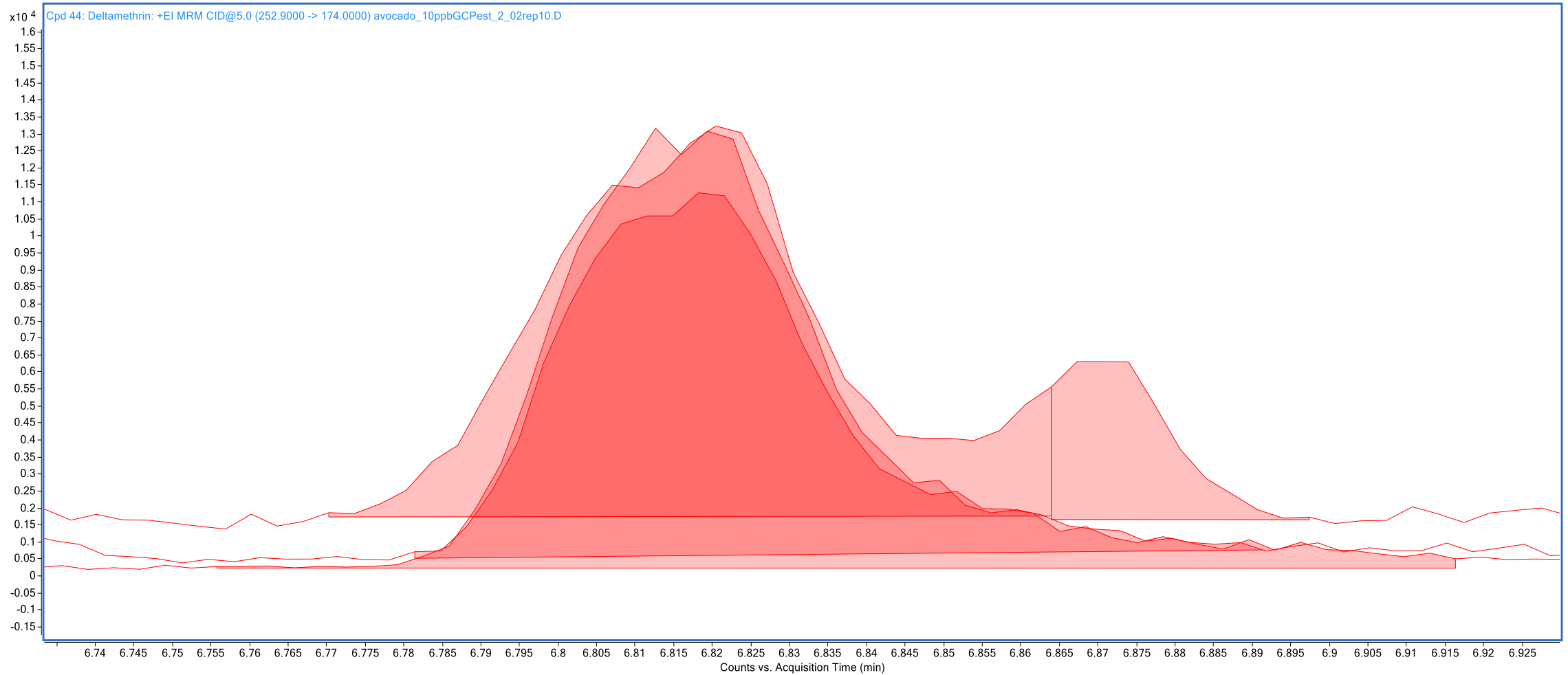
- Settings, liner, installation, etc.



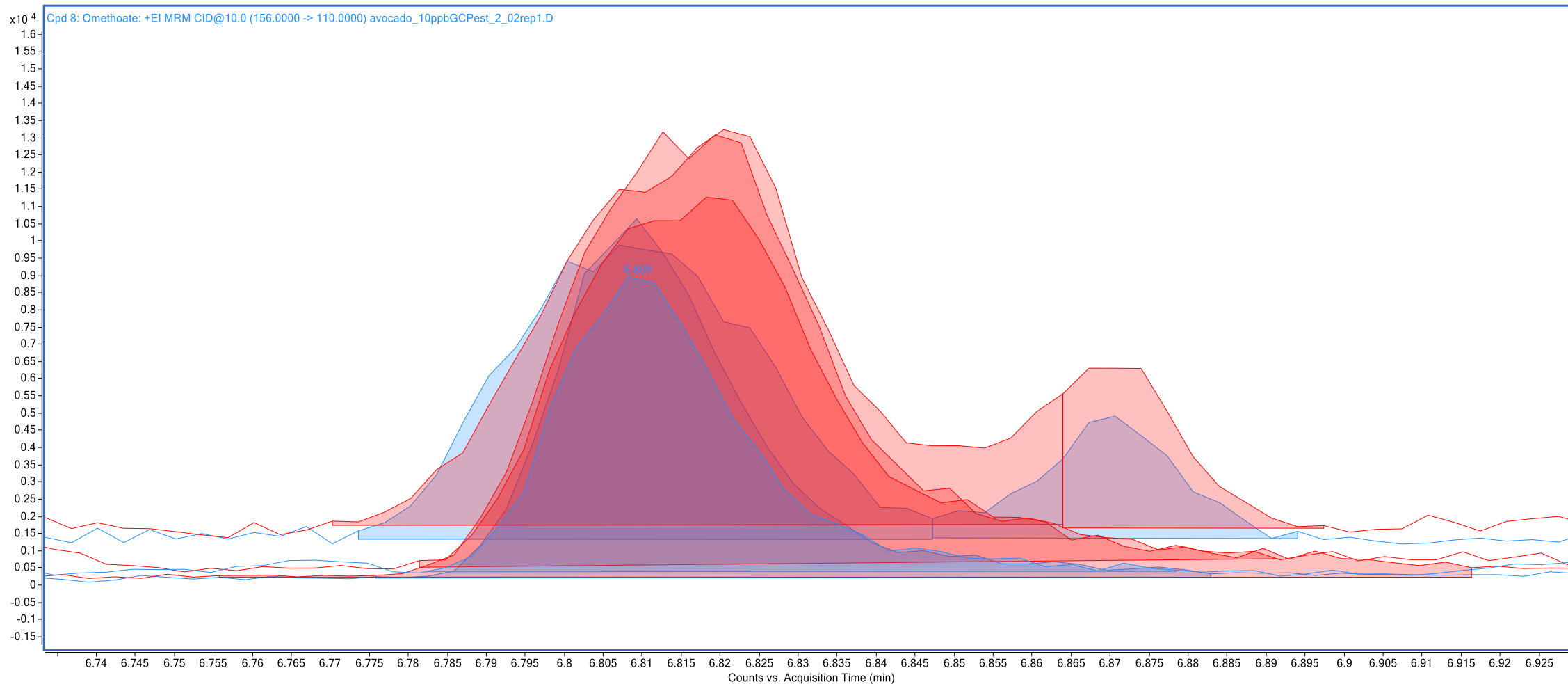
Peak Broadening: Omethoate in Avocado in Run 1



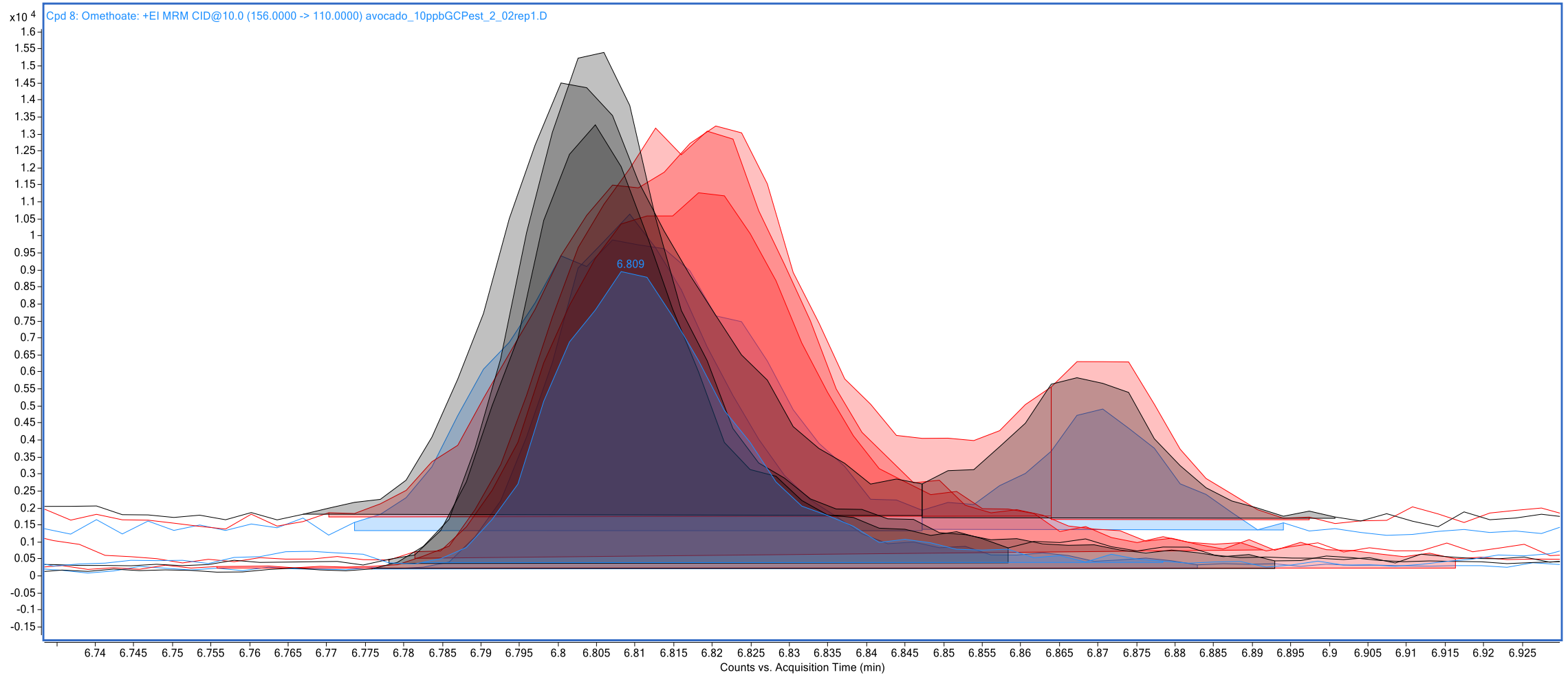
Peak Broadening: Omethoate in Avocado in Run 65



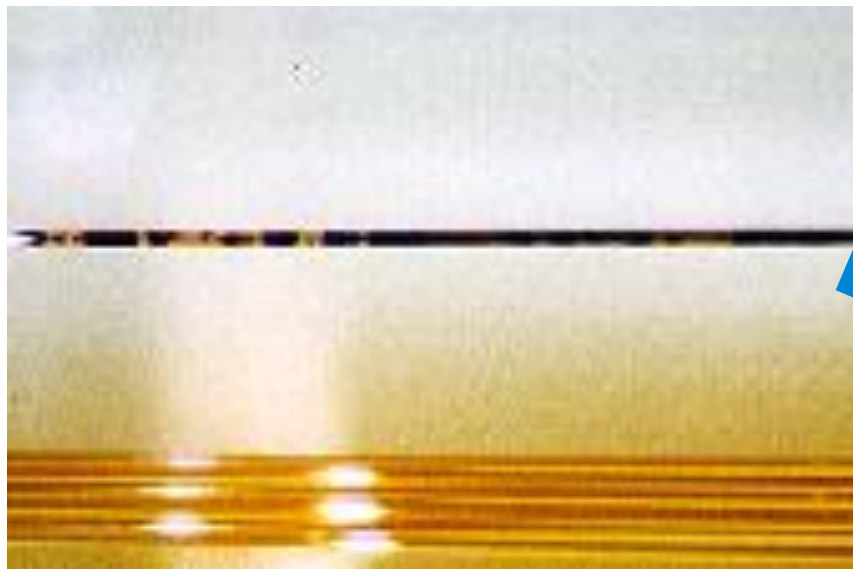
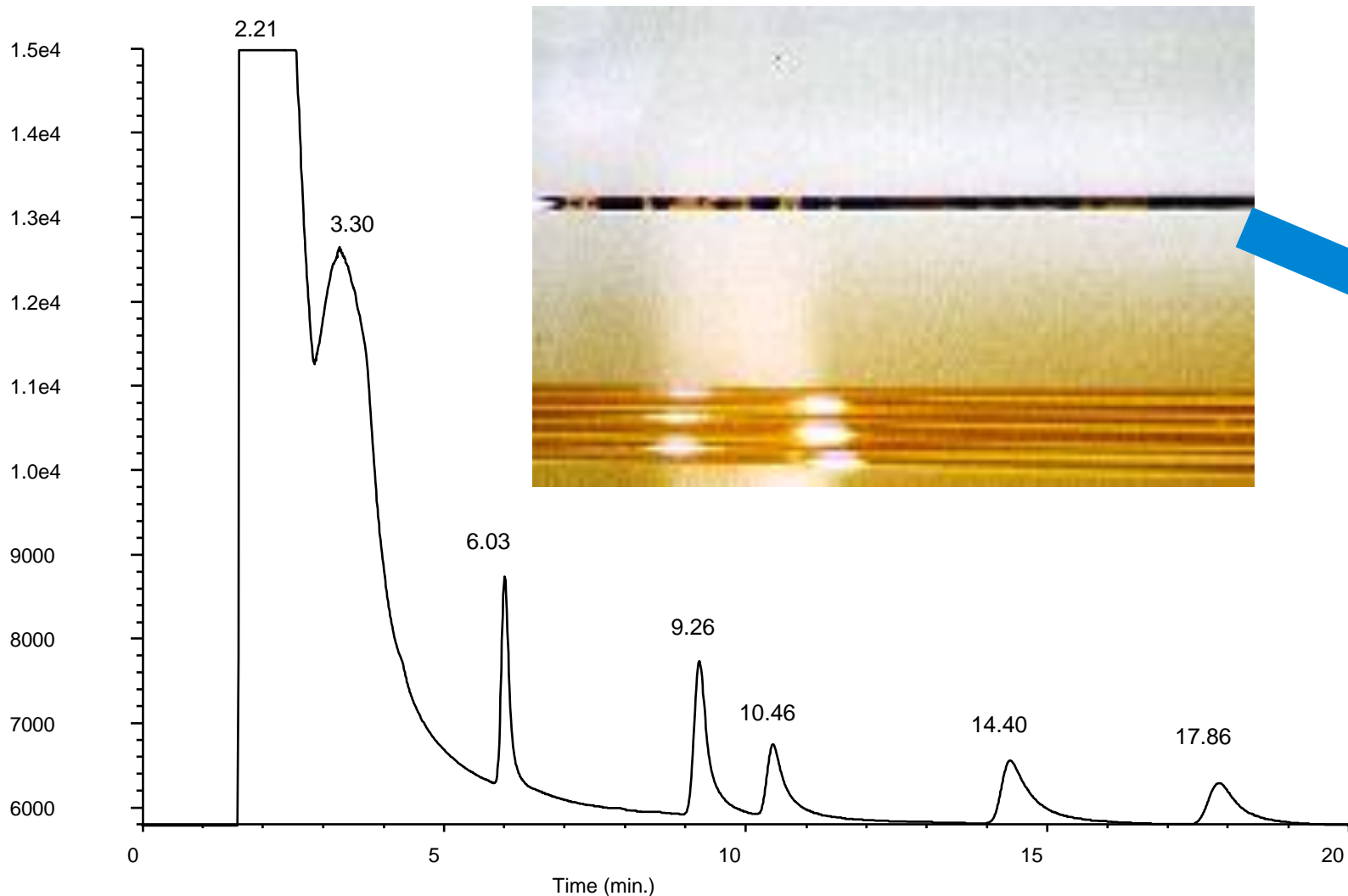
Peak Broadening: Omethoate in Avocado in Run 1 versus Run 65



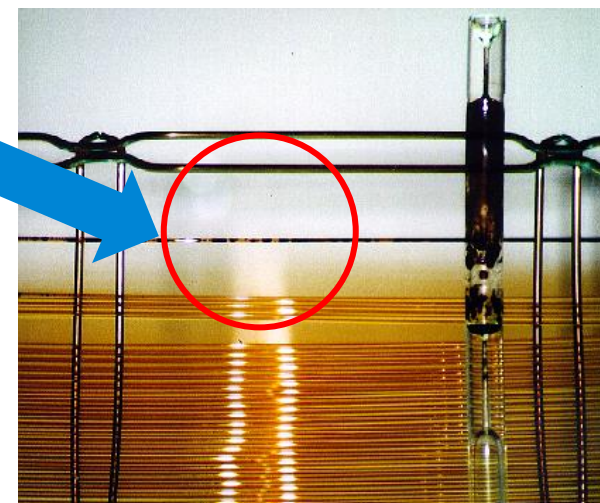
Peak Broadening: Recover Peak Shape with New Liner



Example of Column Contamination and Broad Peaks

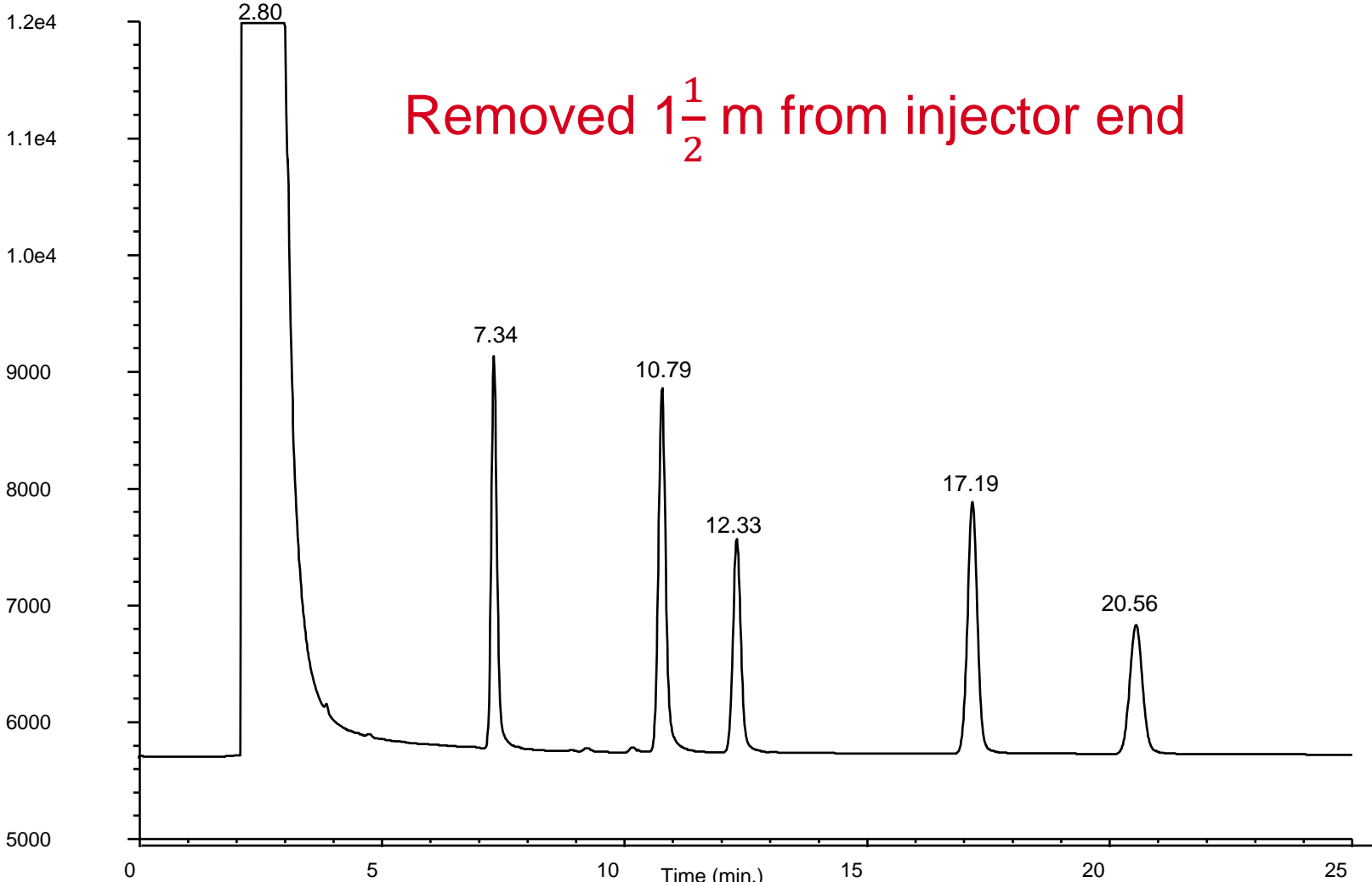


Agilent J&W DB-624 QC Test Mix
After 75 injections of oily sample



***Temperature program// 35 °C hold 1.50 min // 30°/min to 65 °C, hold 10 min**

Example of Column Contamination

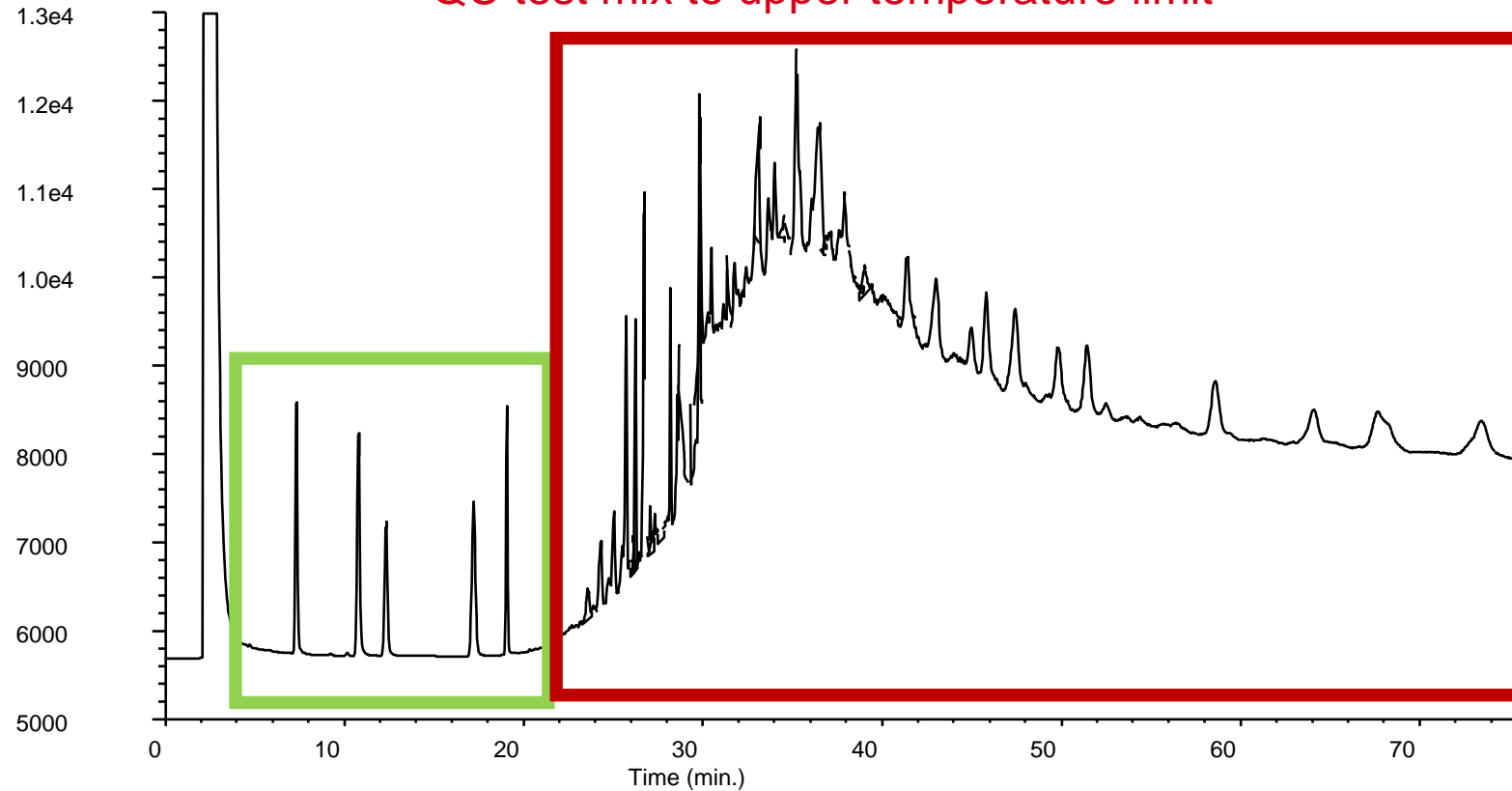


*Before column rinse and bake
Temperature program // 35 °C hold 1.50 min // 30° C/min to 65 °C, hold 10 min

Example of Column Contamination

$1\frac{1}{2}$ m removed*

QC test mix to upper temperature limit



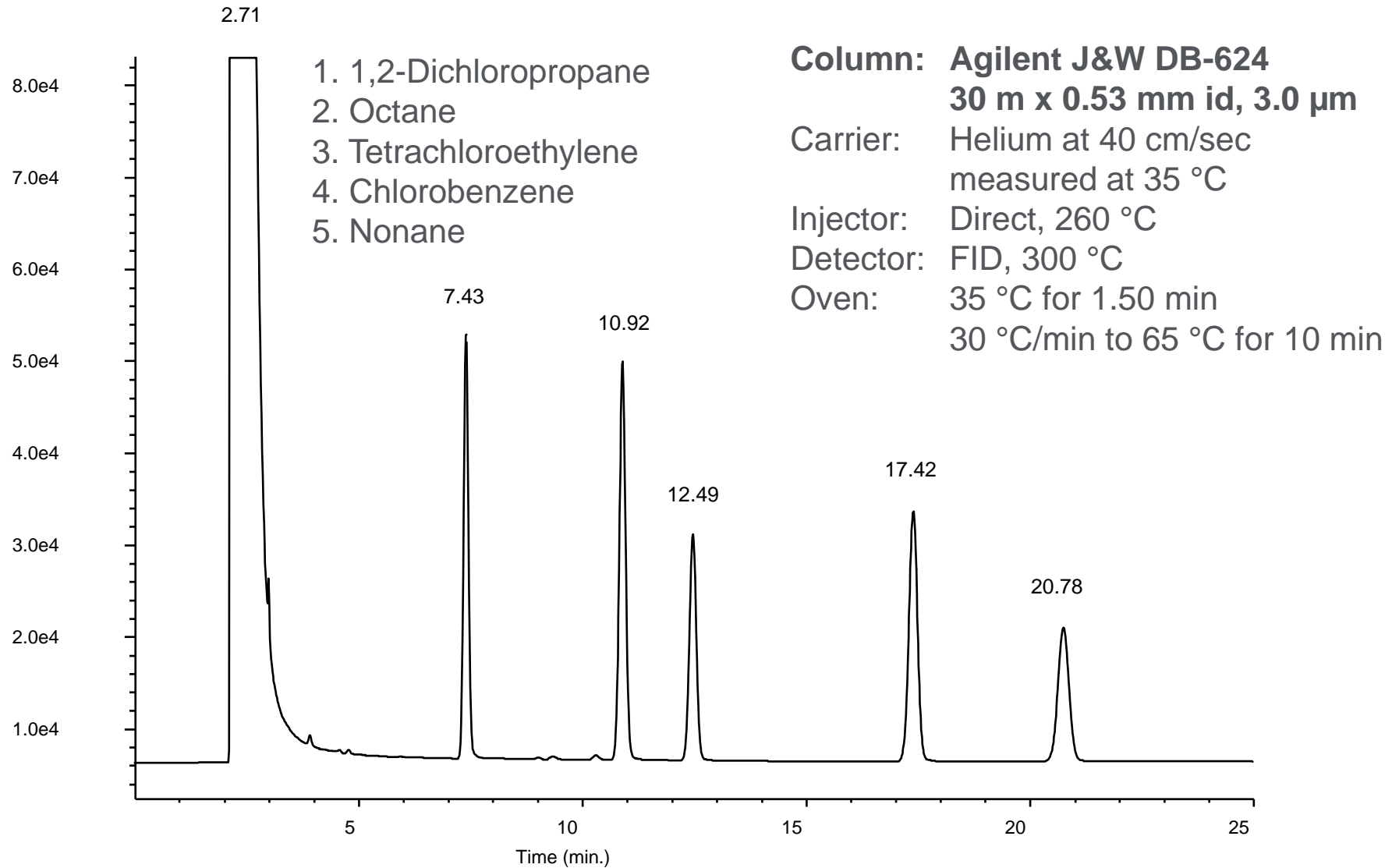
We have more semivolatile contamination!

*Before column bake

Temperature program // 35 °C, hold 1.50 min // 30 °C/min to 65 °C, hold 15 min // 20 °C/min to 260 °C, hold 50 min

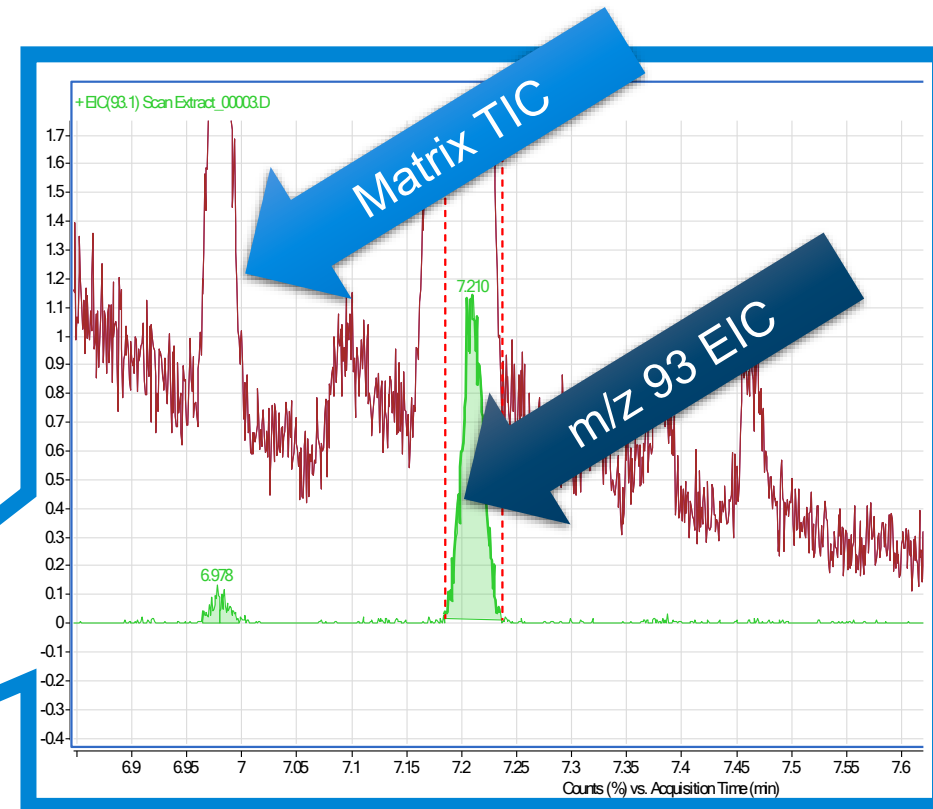
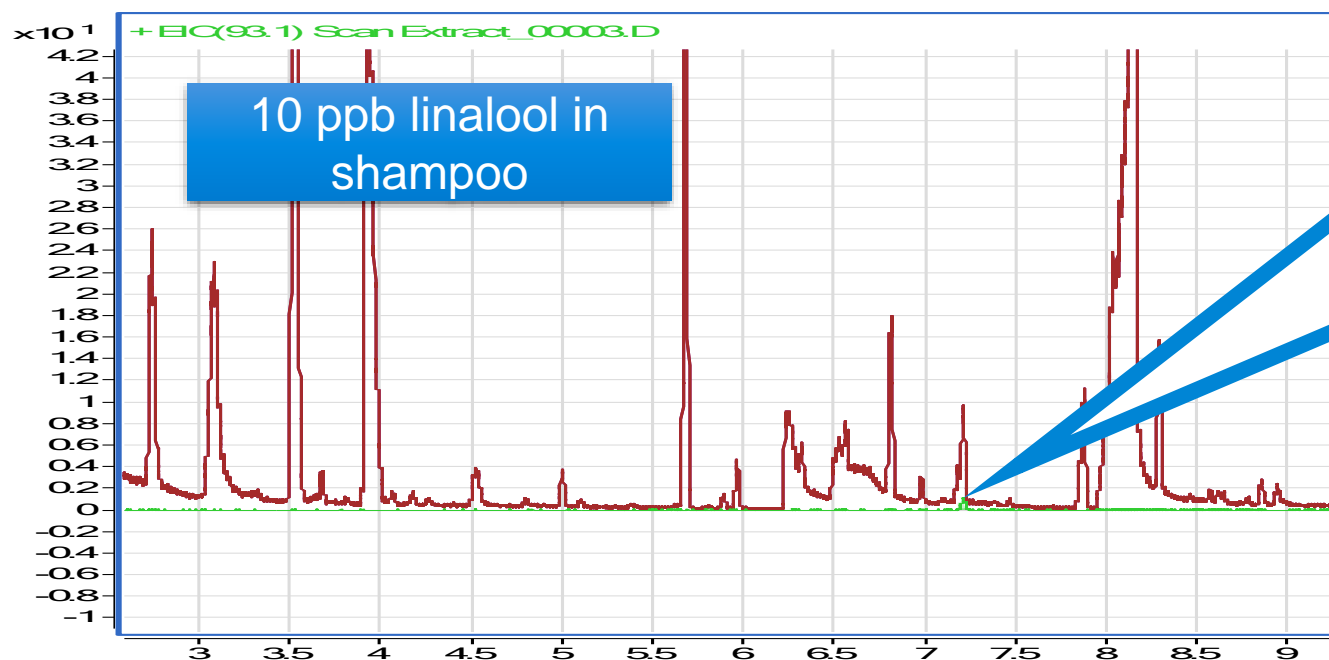
Agilent J&W DB-624 Column

QC Test Mix



The Matrix

If your target ions are buried beneath matrix peaks, it might be time to trim the column or do sample clean-up



...or improve your sample cleanup.

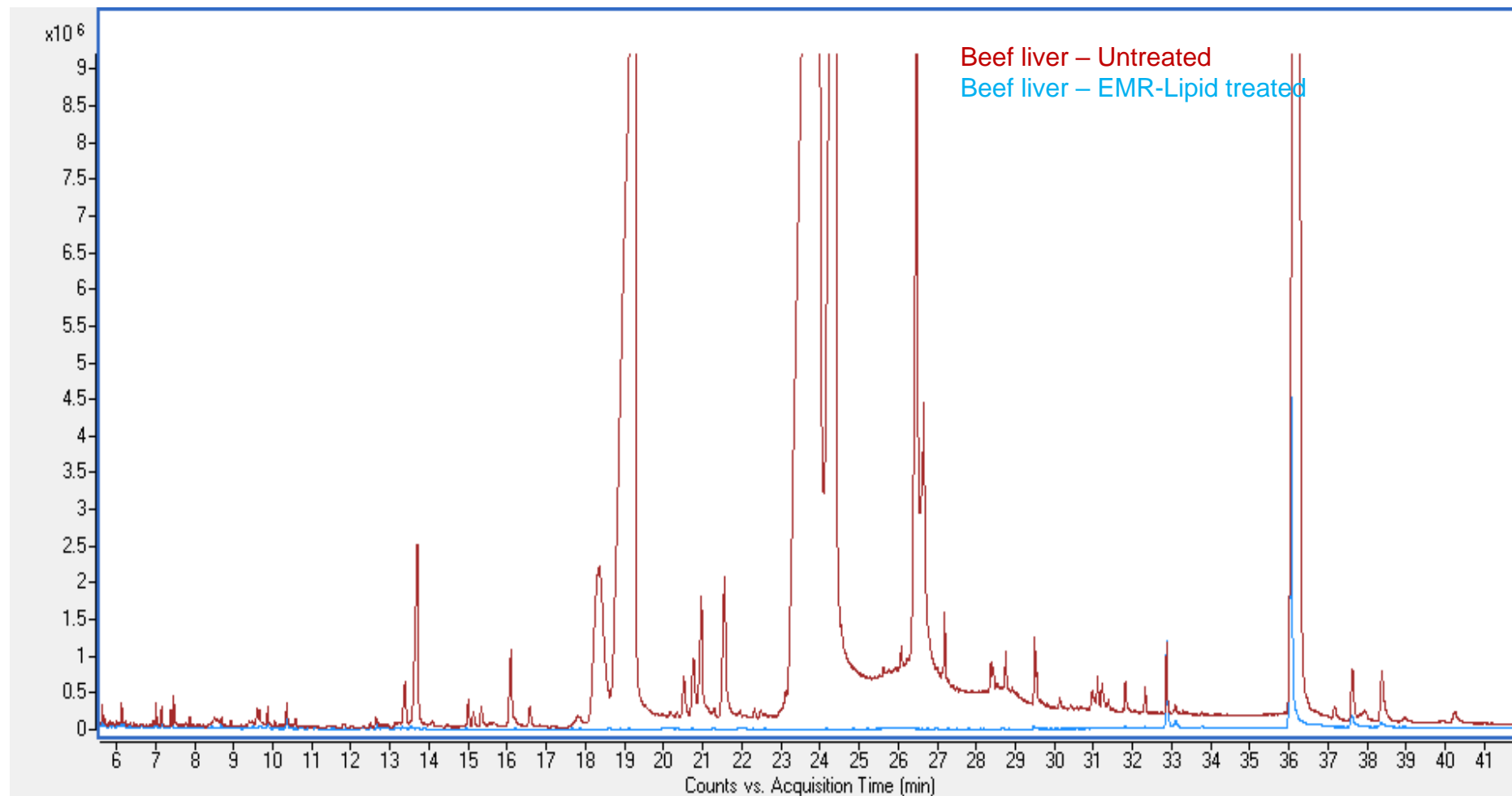
The Importance of Sample Cleanup



50 samples
with cleanup

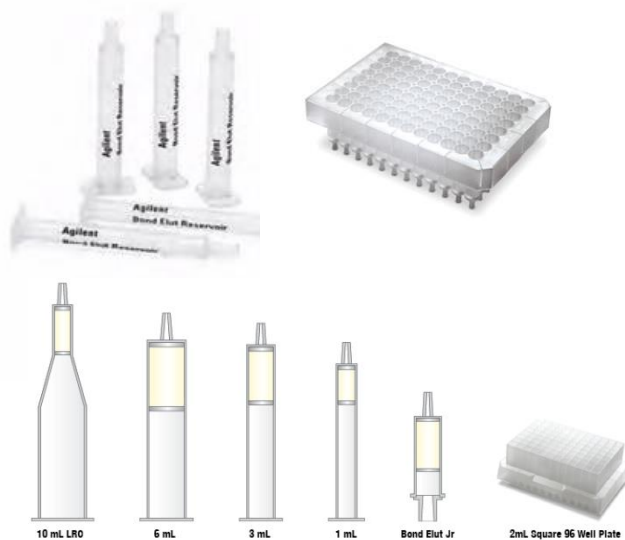


50 samples
without cleanup



Contact us for sample cleanup help: spp-support@agilent.com

Offline Options for Sample Matrix Removal



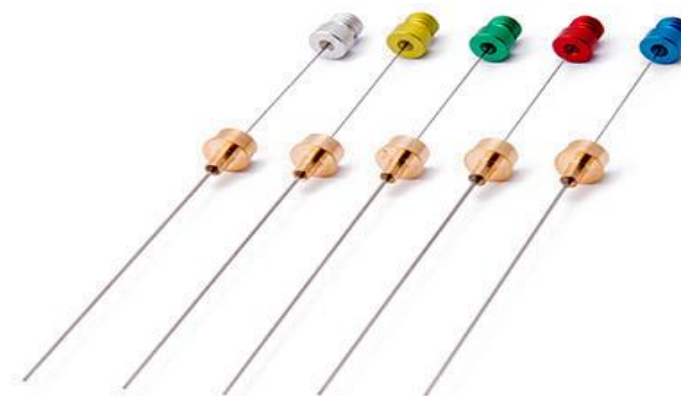
Bond Elut Solid Phase Extraction cartridges and plates



Filter vials



QuEChERS



SPME



Captiva EMR-Lipid filtration cartridges and plates

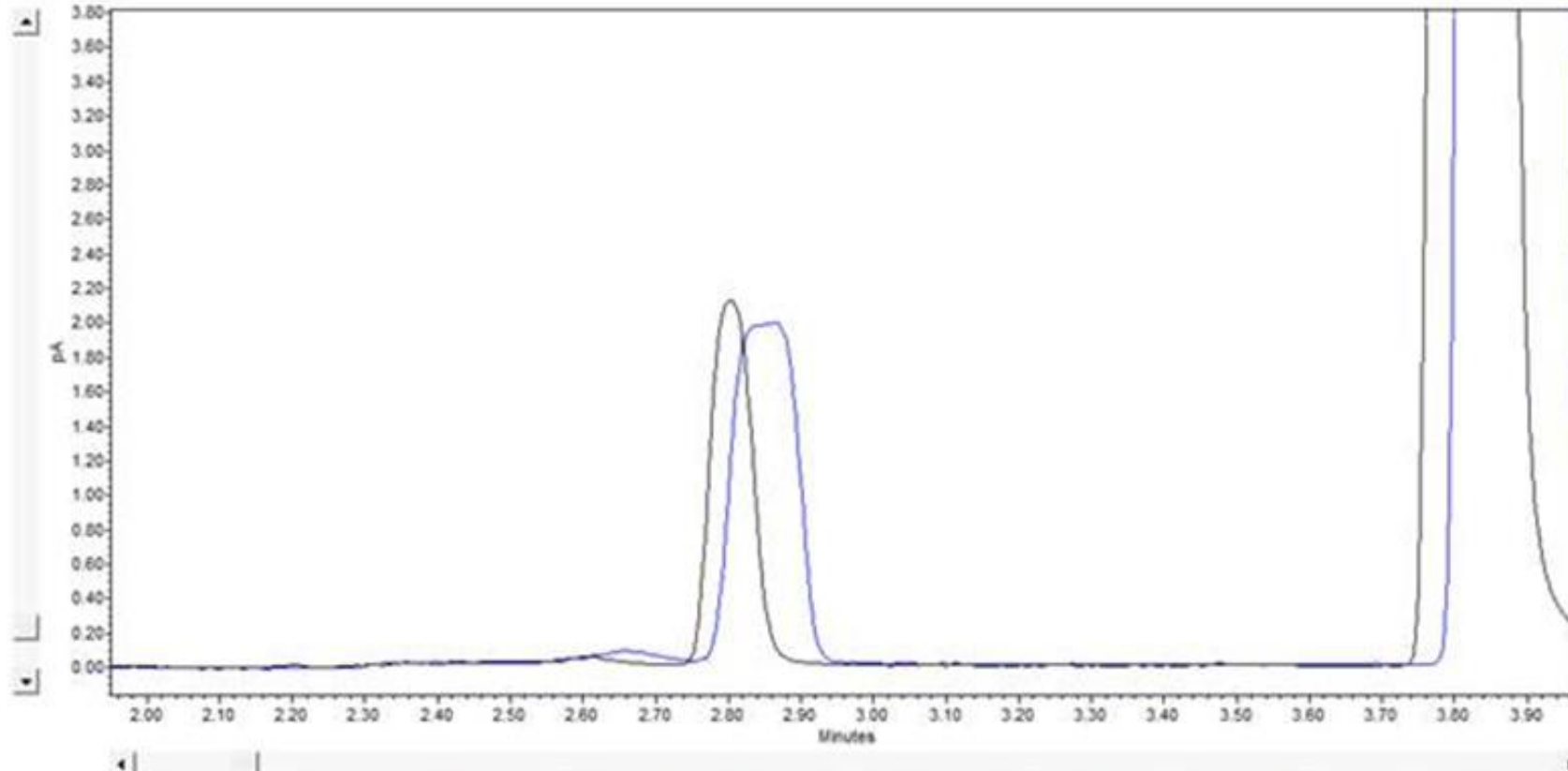


Chem Elut S



Captiva syringe filters

Changing to a Higher Split Ratio Improves Peak Sharpness

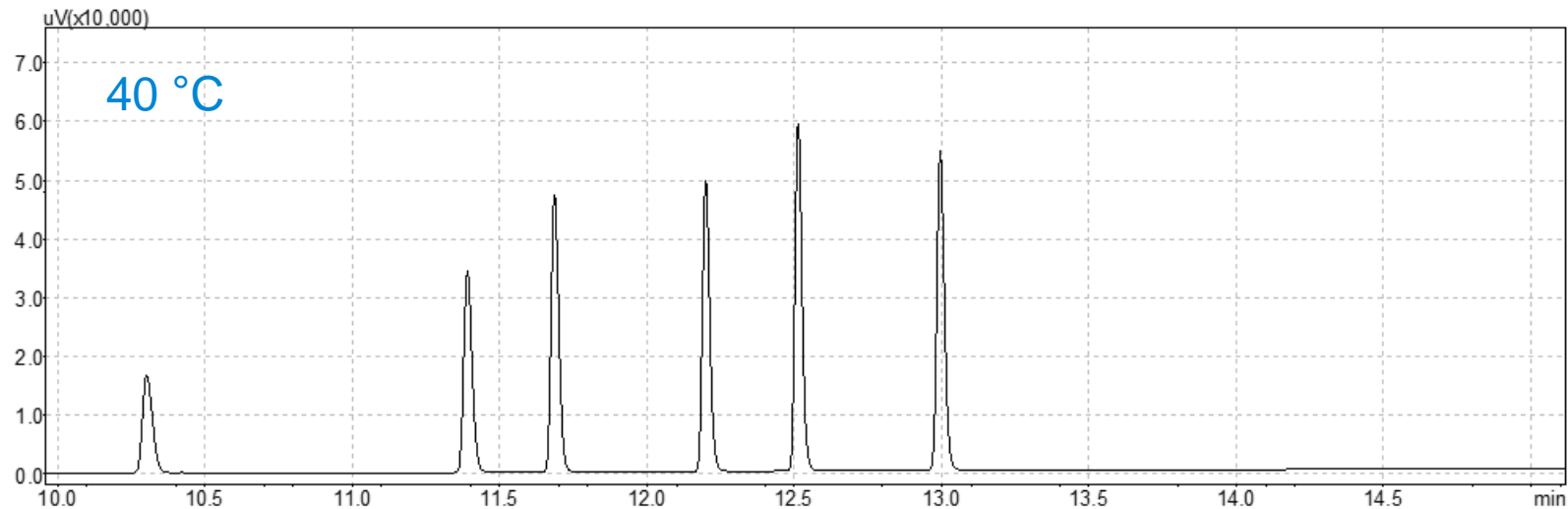
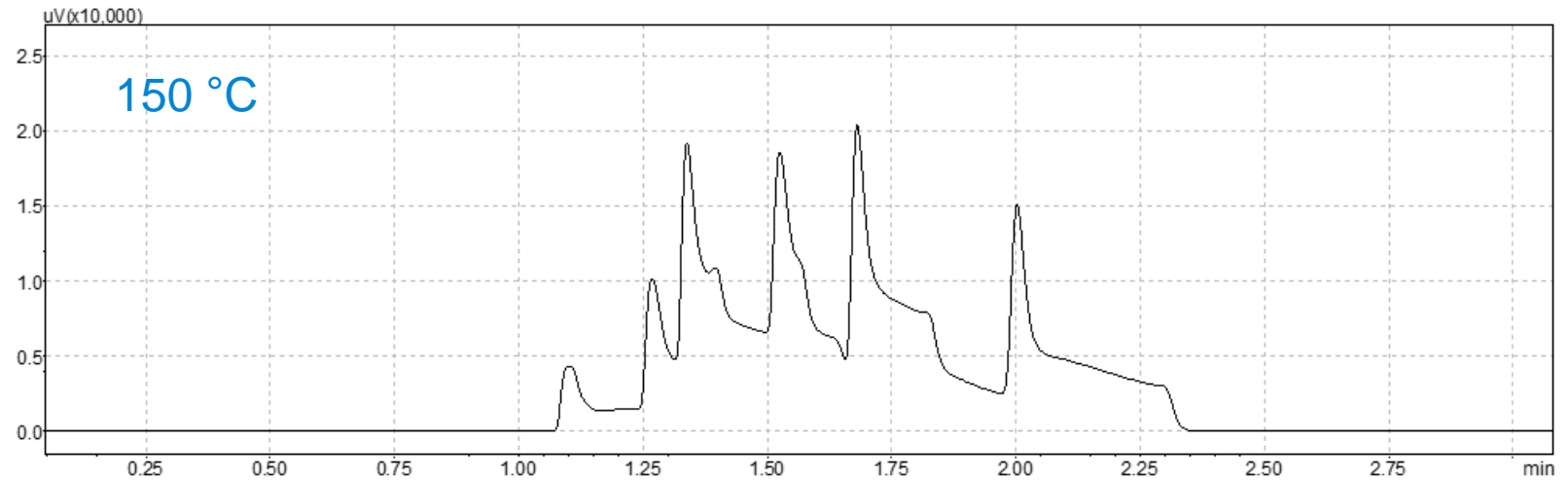


5:1 split ratio

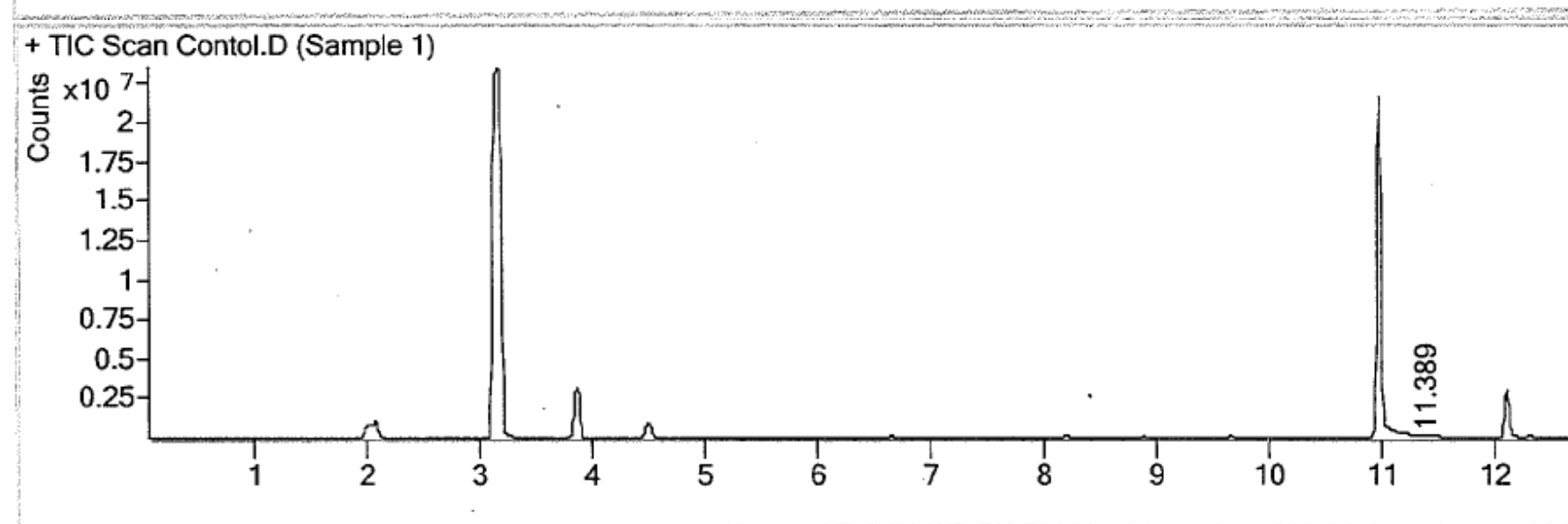
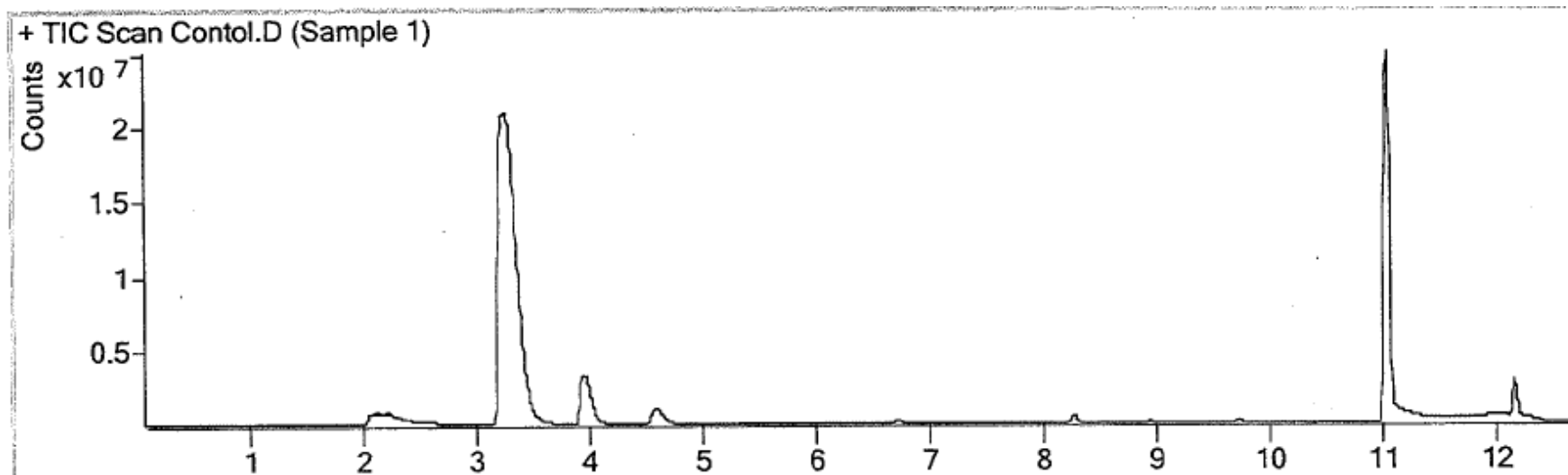
10:1 split ratio

Weird Peak Shape Due to Lack of Analyte Refocusing

Free fatty acids in water on DB-FATWAX UI



Peak Broadening: The Case of the Wrong Liner



Troubleshooting Techniques



Troubleshooting Tools

Bleed profile (non-injection): *baseline problems*

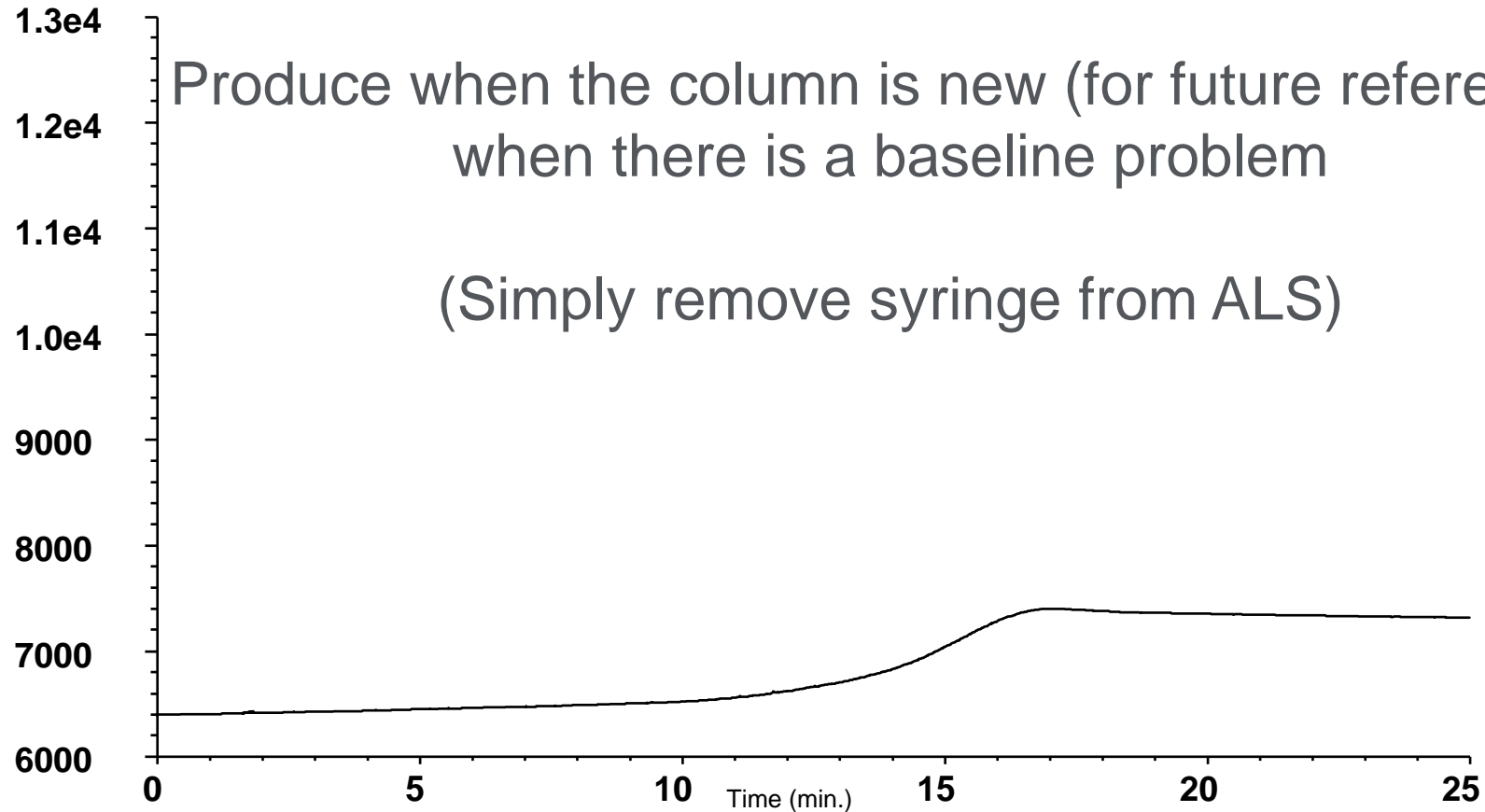
Inject a nonretained peak: *peak shape problems*

Test mix: *all problems*

Isolate the components: *all problems*

Jumper tube test: *baseline problems*

Generating a Bleed Profile

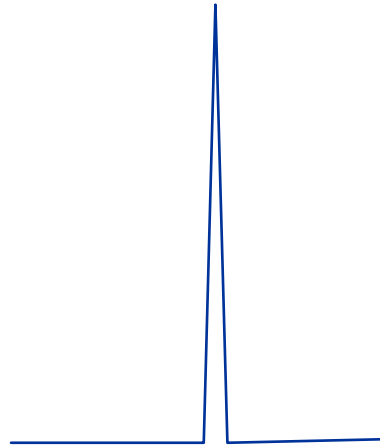


Agilent J&W DB-1, 30 m x 0.32 mm id, 0.25 μ m

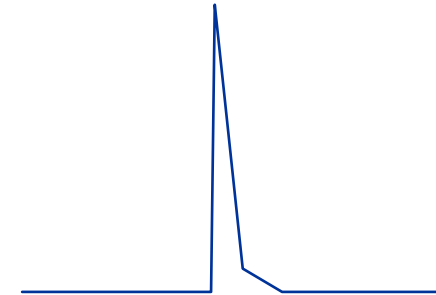
Temperature program // 40 °C, hold 1 min // 20 °C/min to 320 °C, hold 10 min.

Inject a Nonretained Compound to Check Flow Path

Used to check
flow path



Good installation



Improper installation or
injector leak

Potential explanations:

- Injector or septum leak
- Too low of a split ratio
- Liner problem
 - (broken, leaking, misplaced)
- Column position in injector and detector

Test Mix – Make Your Own!

A test mix is used to determine how “good” the column is, or whether the problem is related to the chemical properties of the analytes.

It is simplest to use your own standard.



Compound	Purpose
Hydrocarbons	Efficiency Retention
Alcohols	Activity
FAMEs, PAHs	Retention
Acids	Acidic Character Activity
Bases	Basic Character Activity

Test Conditions	
Inlet:	Split (250 °C)
Detector:	FID(320 °C)
Flow:	37.3 cm/sec (1.8 mL/min)
Carrier gas:	Hydrogen
Holdup compound:	Methane (0.671 min)
Temperature program:	Isothermal (110 °C)

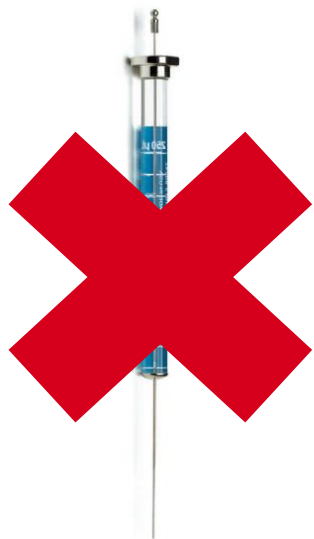
Chemical Standards from Agilent

Agilent ULTRA Chemical Standards have:

- Best in class online search, compare, and ordering capabilities
- Rapid shipping: 99.9% of orders dispatched within 24 to 48 hours (continental US only, as of now)
- Custom standard solutions including our *new* online custom quoting tool, enabling customers to upload recipe formulations to and to modify the recipe before submitting it
 - Tool will allow customers to see the quote pricing instantly and allow them to check quote pricing based on quantity range
 - Check it out at www.agilent.com/en/product/chemical-standards
- Rigorously tested and manufactured under ISO 9001, ISO 17025, and ISO 17034 accreditation
- Sample preparation materials, columns, supplies, instrumentation, and reference materials from a single source



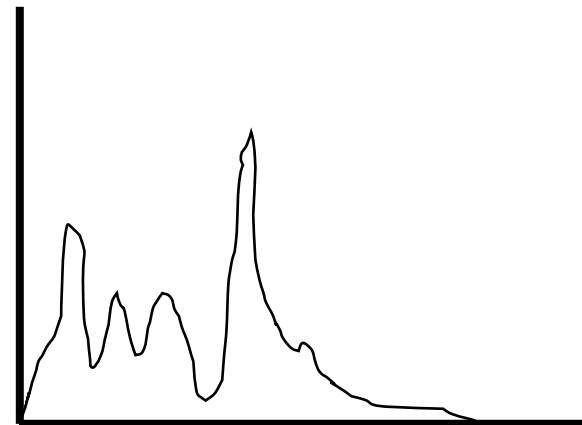
Perform a Noninjection “Blank”



Remove syringe
from autosampler



Run your program



If you see peaks, it is likely
that there is inlet
contamination

Jumper Tube Test

Purpose

- Helps to locate the source of contamination or noise
- Isolates GC components

Jumper Tube Test

Isolate the detector

- Remove column from the detector
- Cap detector and turn on
- Blank run

Jumper Tube Test

Isolation of detector – results:



Detector OK



Detector is the problem



Jumper Tube Test

Isolate the injector

- Connect the injector and detector
 - 1–2 m of deactivated fused silica tubing
- Turn on carrier gas
- Blank run

Jumper Tube Test

Isolate the injector – results:



Injector OK



Injector, lines, or carrier gas contaminated

Jumper Tube Test

Isolate the column

- Reinstall the column
- Set up as before
- Blank run

Jumper Tube Test

Isolate the column – results:

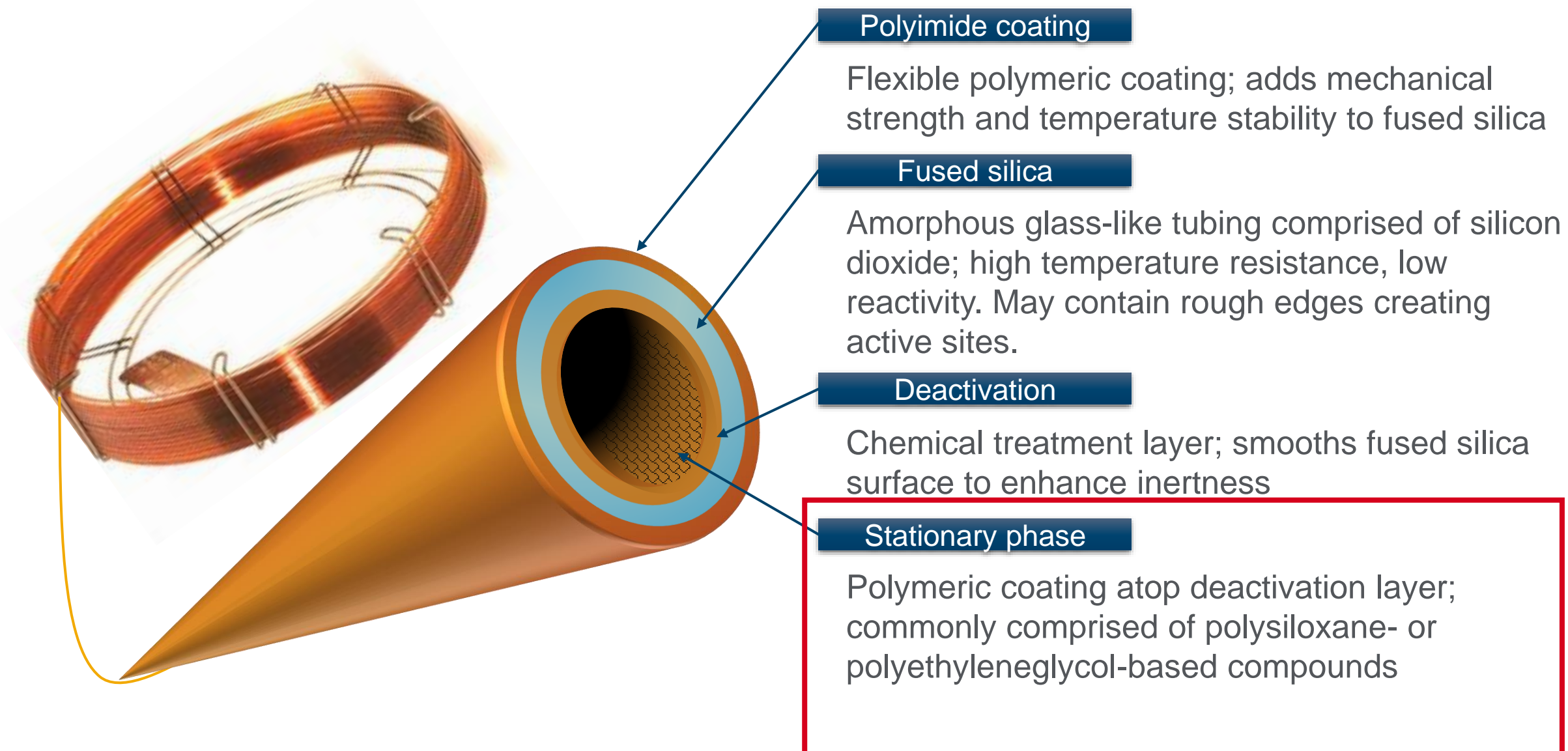
- Problem returns? It's the column
- Problem gone? Previous leak, solid debris, or installation problem

Have a Good Troubleshooting Story? Let Us Know

Call or email us today to share a troubleshooting success story or if you need help troubleshooting!



Column Construction



Polyimide coating

Flexible polymeric coating; adds mechanical strength and temperature stability to fused silica

Fused silica

Amorphous glass-like tubing comprised of silicon dioxide; high temperature resistance, low reactivity. May contain rough edges creating active sites.

Deactivation

Chemical treatment layer; smooths fused silica surface to enhance inertness

Stationary phase

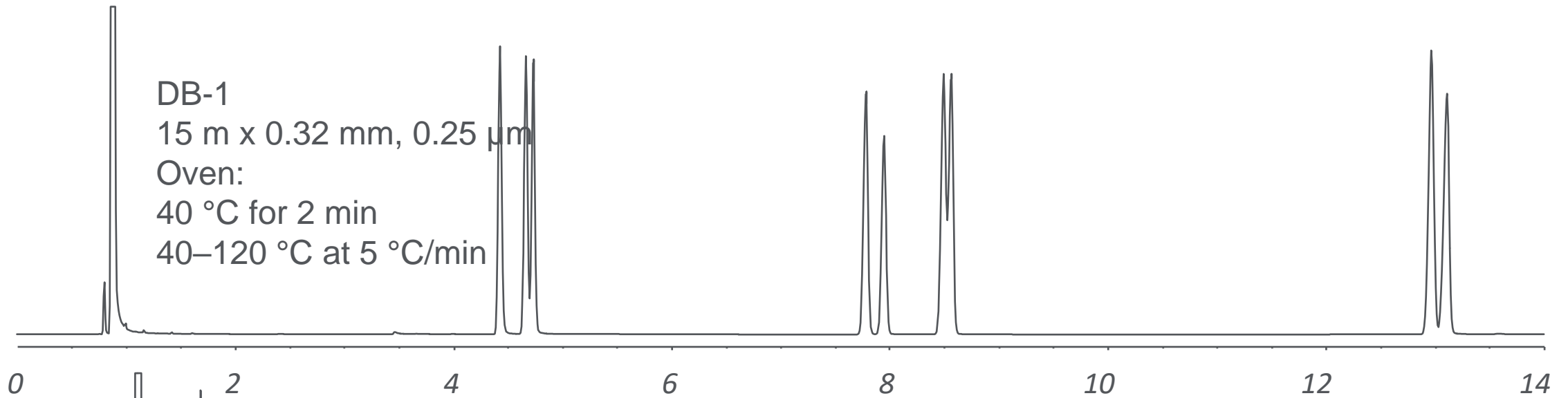
Polymeric coating atop deactivation layer; commonly comprised of polysiloxane- or polyethyleneglycol-based compounds

JW Column Portfolio- DB, HP, CP, VF

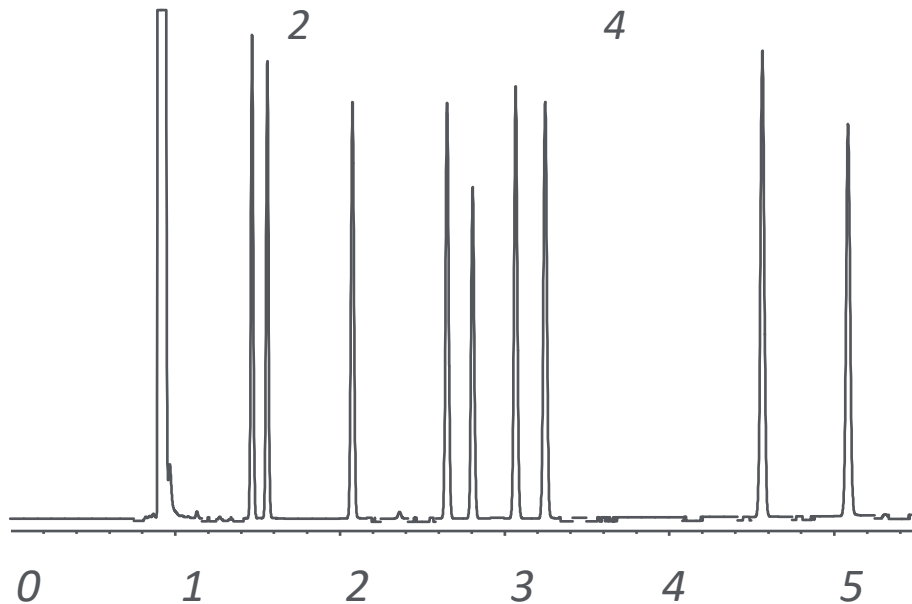
Low Polarity			Mid Polarity			High Polarity		
CP-Sil 2	DB-1ms UI HP-1ms UI	DB & HP-5ms UI	DB-XLB	DB-225ms	DB-ALC1	HP-88	DB-WAX	DB-WAX UI
DB-MTBE	DB-1ms HP-1ms	DB & HP-5ms	VF-Xms	DB-225	DB-Dioxin	CP-Sil 88	DB-WAXetr	DB-HeavyWAX
CP-Select CB MTBE	VF-1ms	VF-5ms	DB-35ms UI	CP-Sil 43 CB	DB-200	DB-23	HP-INNOWax	DB-FATWAX UI
	DB & HP-1	DB & HP-5	DB & VF-35ms	VF-1701ms	VF-200ms	VF-23ms	VF-WAXms	
	CP-Sil 5 CB	CP-Sil 8 CB	DB & HP-35	DB-1701	DB-210		CP-Wax 57 CB	
	Ultra 1	Ultra 2	DB & VF-17ms	CP-Sil 19 CB	DX-4		DB-FFAP HP-FFAP	
	DB-1ht	VF-DA	DB-17	HP-Blood Alcohol			DB-WAX FF	
	DB-2887	DB-5.625	HP-50+	DB-ALC2			CP-FFAP CB	
	DB-Petro/PONA	DB & VF-5ht	DB-17ht	DX-1			CP-WAX 58 FFAP CB	
	CP-Sil PONA CB	CP-Sil PAH CB	DB-608				CP-Wax 52 CB	
	DB-HT SimDis	Select Biodiesel	DB-TPH				CP-WAX 51	
	CP-SimDis	SE-54	DB-502.2				CP-Carbowax 400	
	CP-Volamine		HP-VOC				Carbowax 20M	
	Select Mineral Oil		DB-VRX				HP-20M	
	HP-101		DB-624				CAM	
	SE-30		VF-624ms				CP-TCEP	
			CP-Select 624 CB					
			DB-1301					
			VF-1301ms					
			CP-Sil 13 CB					

Agilent J&W has over 50 different stationary phase offerings

Start with the Right Phase – “like dissolves like”



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



Agilent University

Why training? What can we help with?

Agilent University:

- Trained over 38K students FY19
- 98% customer recommended
- 4.6 out of 5 customer satisfaction
- 94% excellent and very good

Labs who want faster and more efficient learning options to help overcome training challenges

Overtasked staff

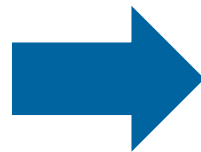
Staff turnover

Pressure to improve quality and productivity

Daily consistency with output and results

Reduce costs associated with lab operations

Flexible and convenient training options when and where you need them:



Virtual training



Virtual instructor led



eLearning self-paced

In-person training



Classroom



On-site or virtual on-site

Trust Agilent for answers leveraging up-to-date knowledge and generally accepted practices for all your training needs

Agilent University

To connect you with the best learning opportunities for you, we might ask:

- What instrument and model numbers are you using (such as GC 7890 or HPLC 1290)?
- Are you interested in on-site training or classroom training?
- What would you like to learn more about?

Troubleshooting Tips

1. Isolate the problem

(blank run, inject unretained compound, jumper tube test)

2. Change only one variable at a time

3. Compare before/after chromatograms

(Peak shape, response, retention, baseline rise, background, look for trends, etc.)

4. Utilize technical support

Remember

Complete system = carrier gas + injector +
column + detector + data system

- Multiple causes and effects
- Do not change too many variables at once



Contact Agilent Chemistries and Supplies Technical Support



1-800-227-9770 Option 3, Option 3:

[Option 1 for GC and GC/MS columns and supplies](#)

Option 2 for LC and LC/MS columns and supplies

Option 3 for sample preparation, filtration, and QuEChERS

Option 4 for spectroscopy supplies

Option 5 for chemical standards

Available in the USA and Canada 8–5, all time zones



gc-column-support@agilent.com

lc-column-support@agilent.com

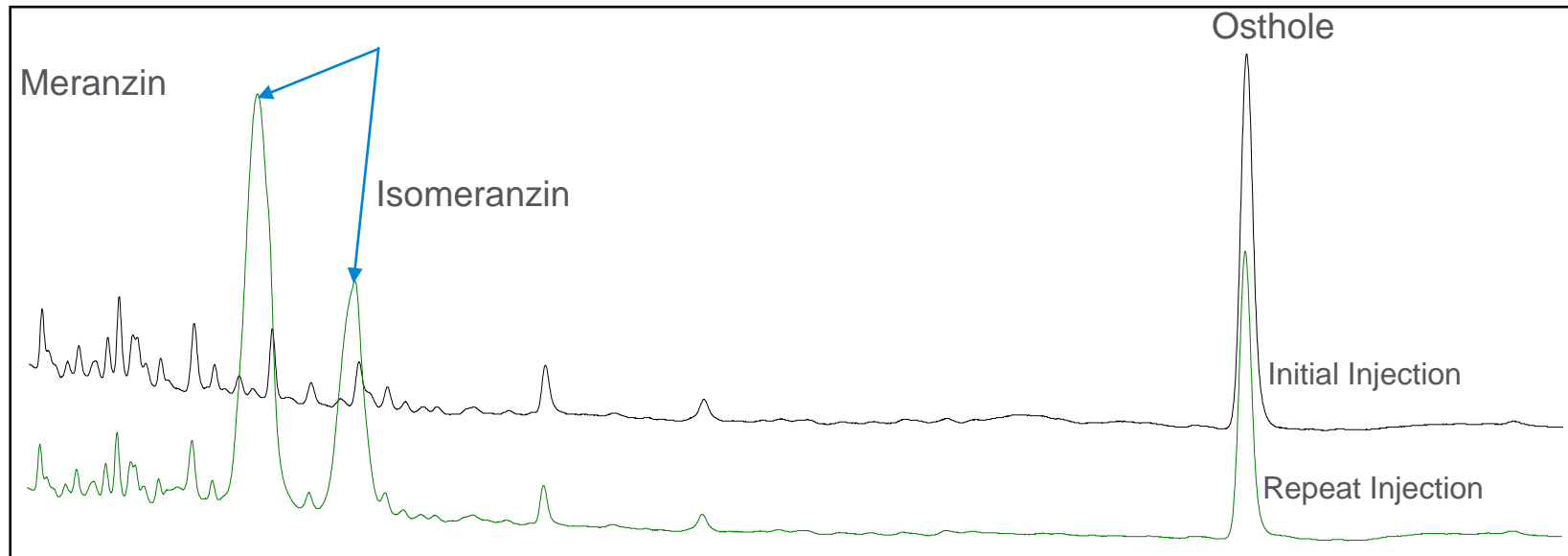
spp-support@agilent.com

spectro-supplies-support@agilent.com

chem-standards-support@agilent.com

Appendix

Bonus or Ghost Peaks



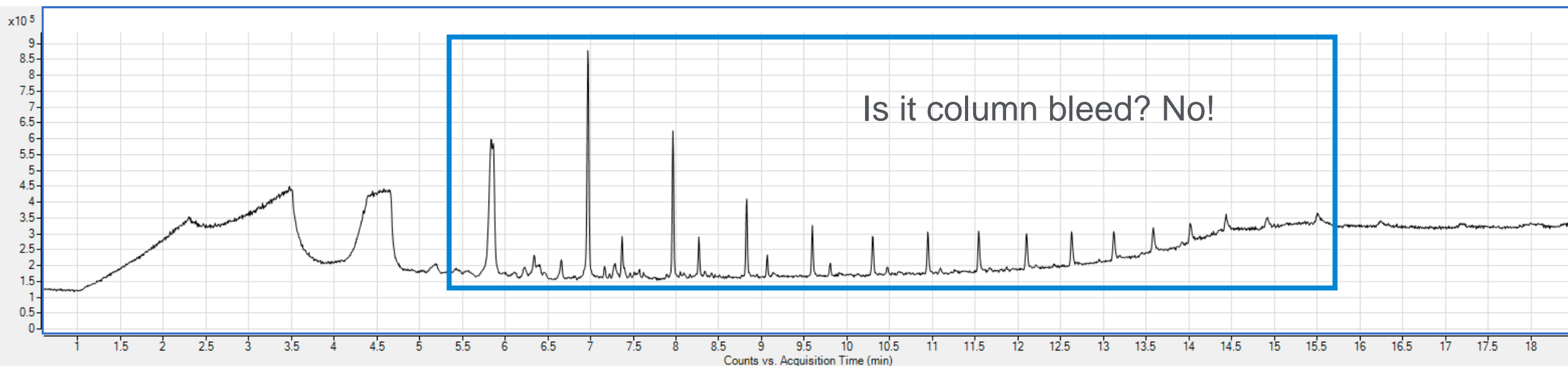
5991-9078EN

Contamination in injector, column, or flow
(carrier gas)

- Carryover from a backflash or previous sample
- Bad tank of gas, or traps have expired
- Septum bleed

Tip: Run a blank run... it should be blank!

What Are These Repeating Peaks?



Common ions for siloxane molecules:

73

147

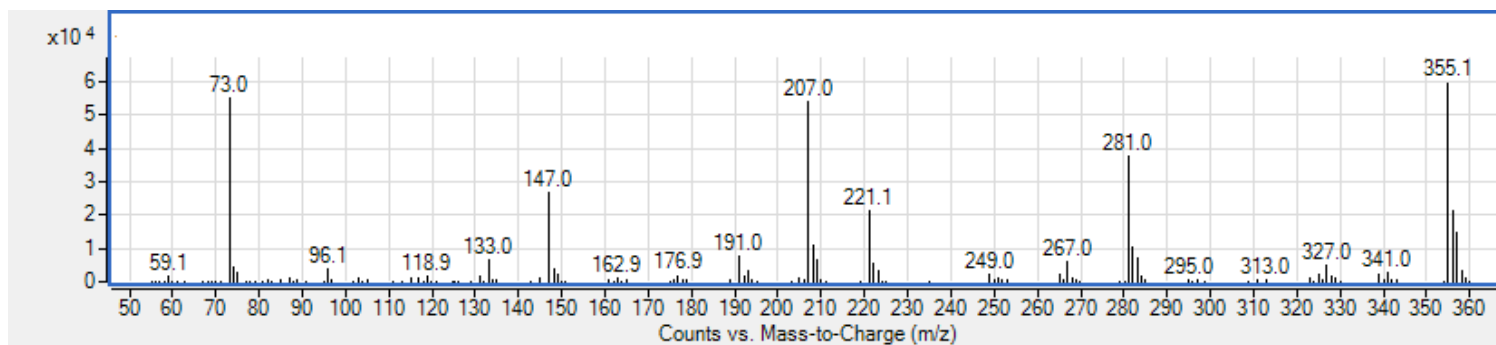
207

281

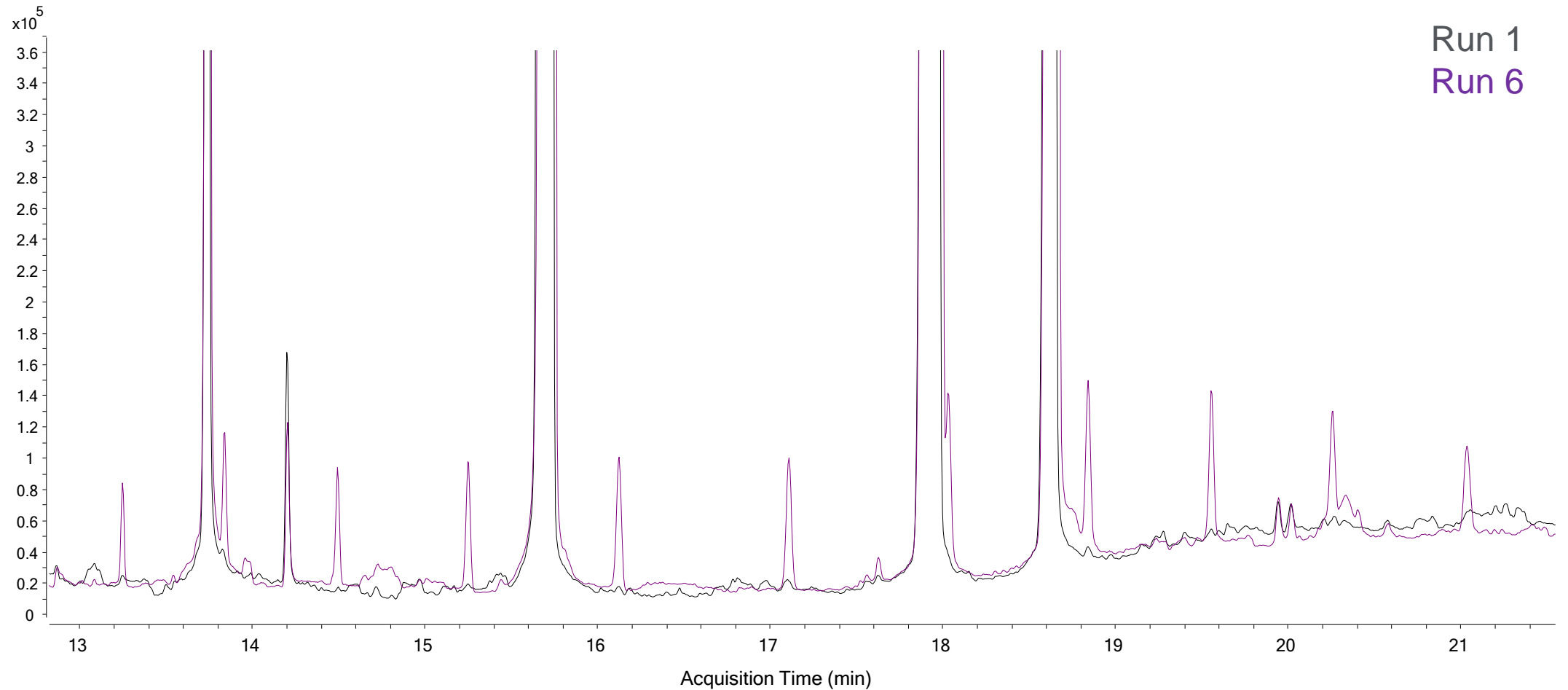
355

Septa contamination in wash vials or inlet liners can be diagnosed by looking for siloxane polymers in your total ion chromatogram. Each peak in the chromatogram corresponds to a cyclized (ring structure) siloxane molecule. These molecules fragment with similar patterns.

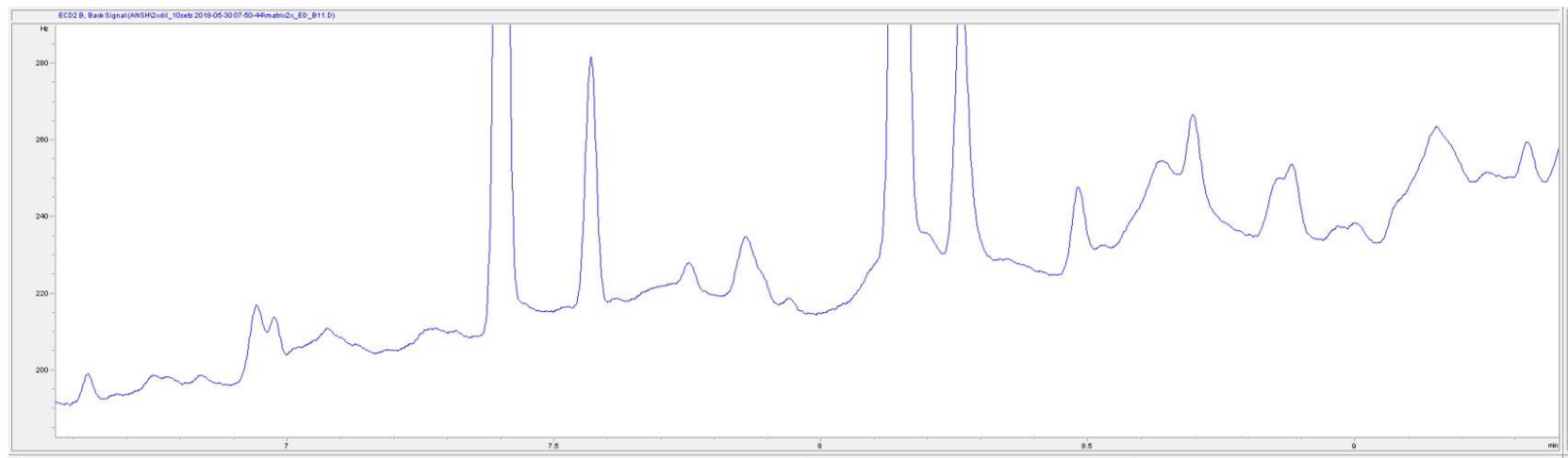
Example spectrum:



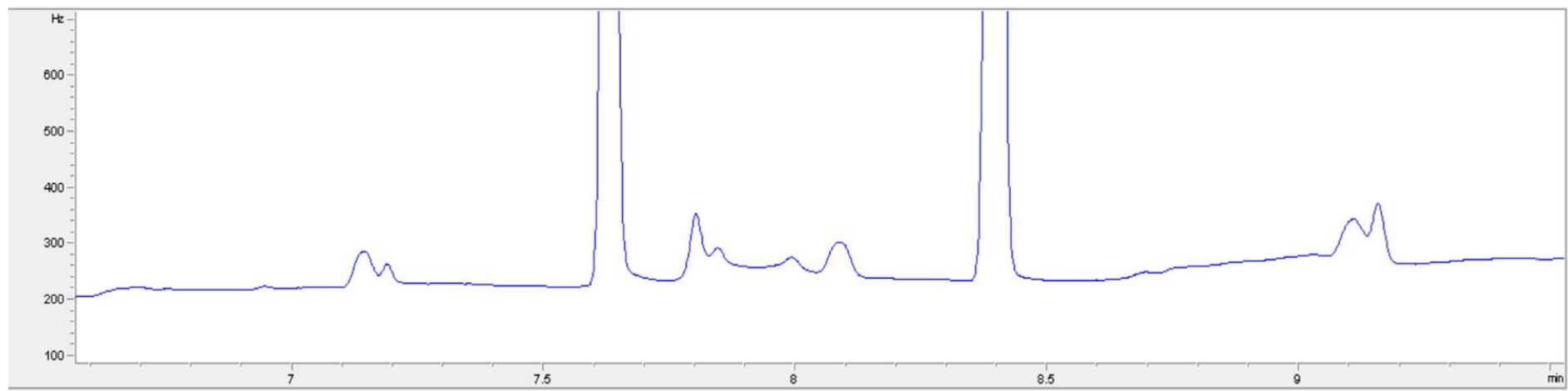
Multiple Injections from the Same Vial: Siloxanes!



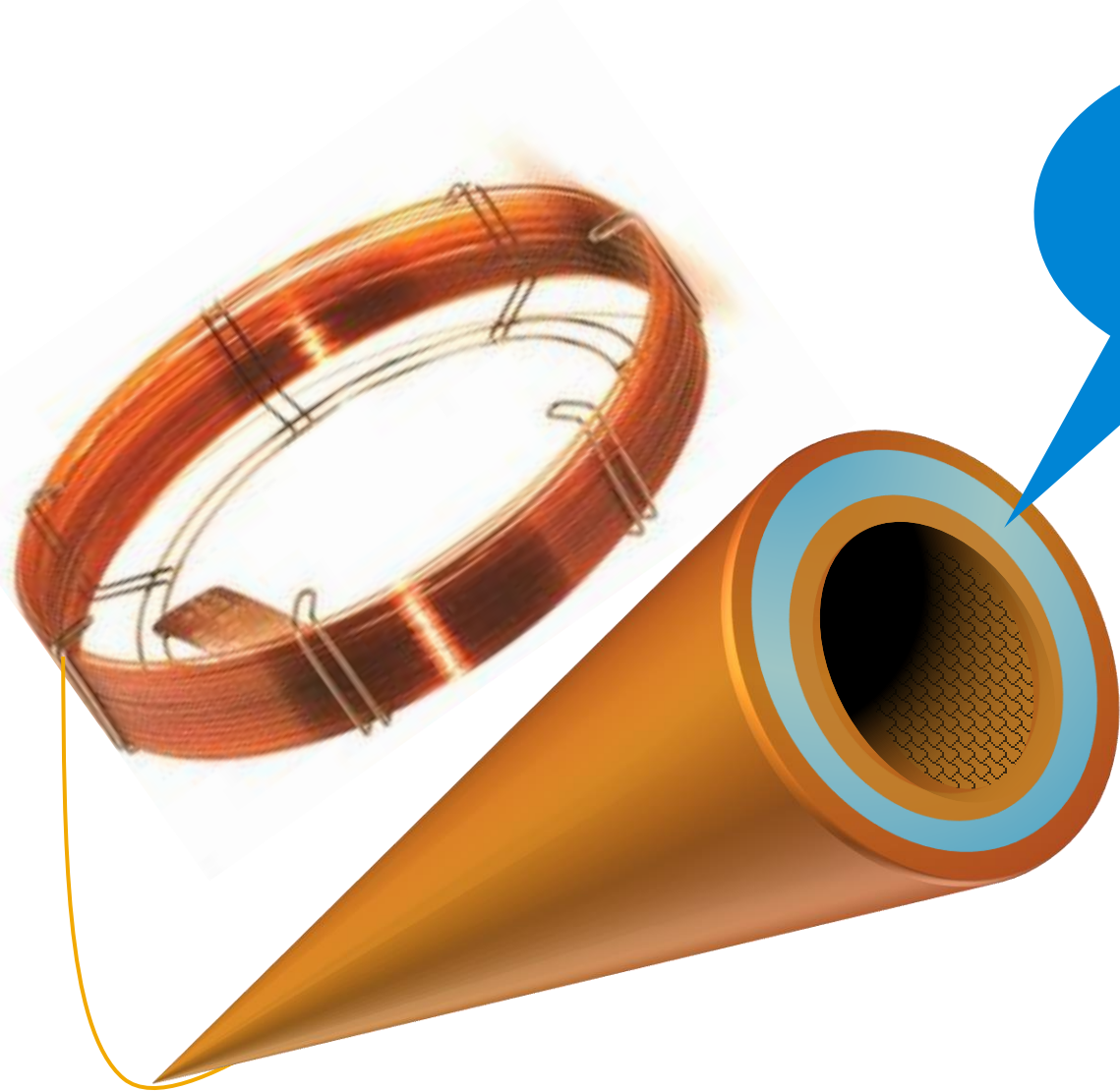
Does Your Baseline Look Like This? Do You See Extra Peaks?



When it *should* look like...



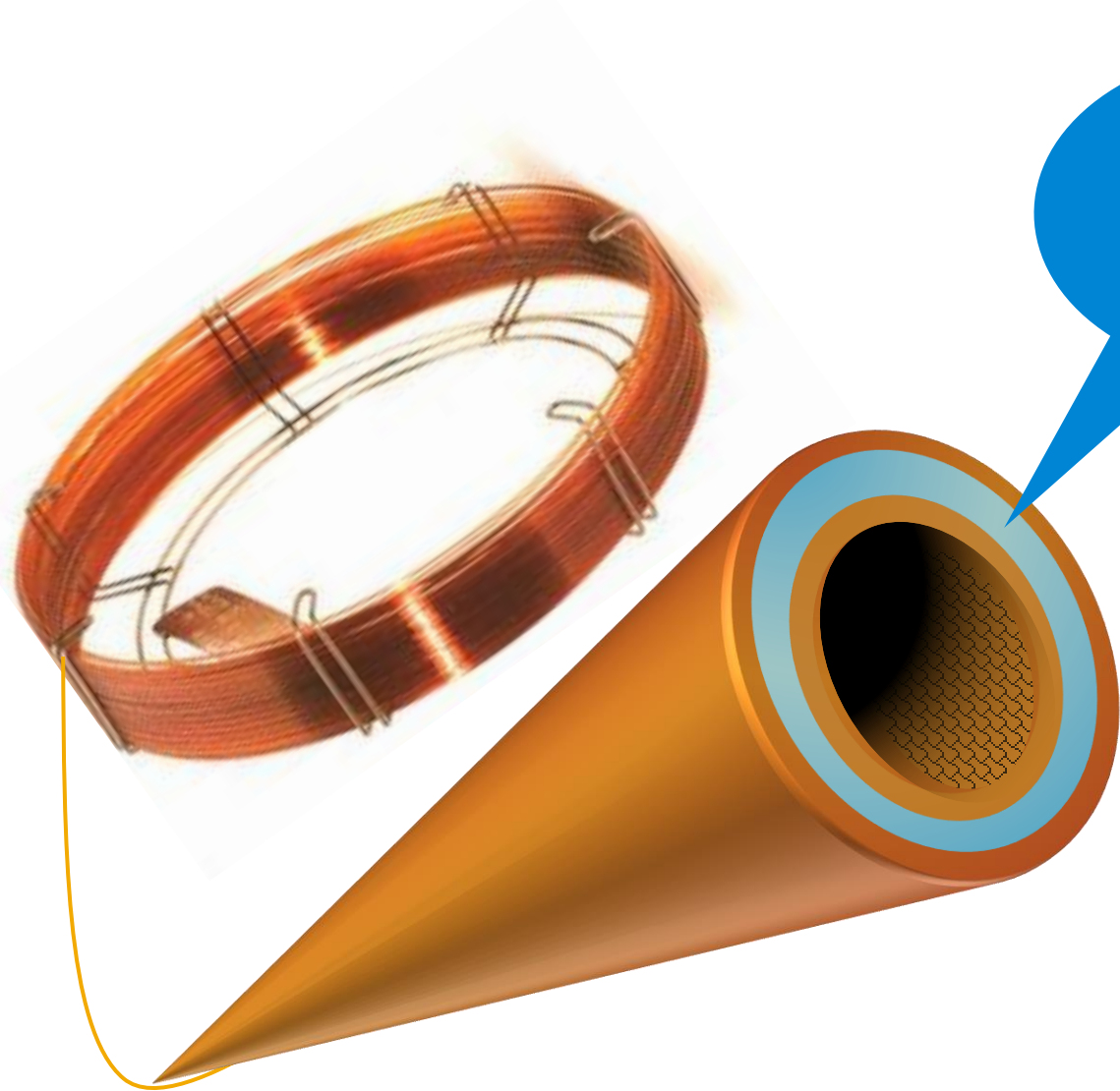
What is Not Caused by a Column?



Not responsible

- Peaks
 - Any reproducible sharp chromatographed peak
- Siloxanes (even though it looks like bleed spectrally)
- Degradation product peaks: Endrin Aldehyde, endrin ketone, DDE, DDD...
- Carryover of sample compounds
- Splitting of peaks

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