

Get Your Peaks into Shape

General GC Column Troubleshooting

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October 5, 2021



“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

It's Peak Season for Great Peak Shapes

DE.2051957599

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:

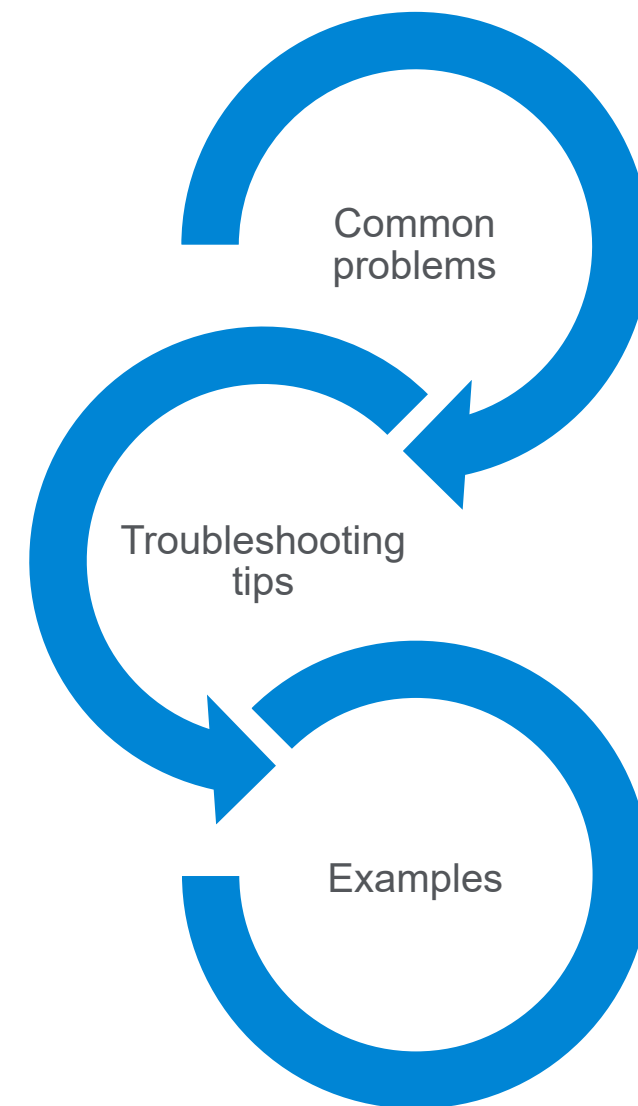
- Injector
- Flow
- Column
- Detector
- Electronics

Or...

- A combination of these

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

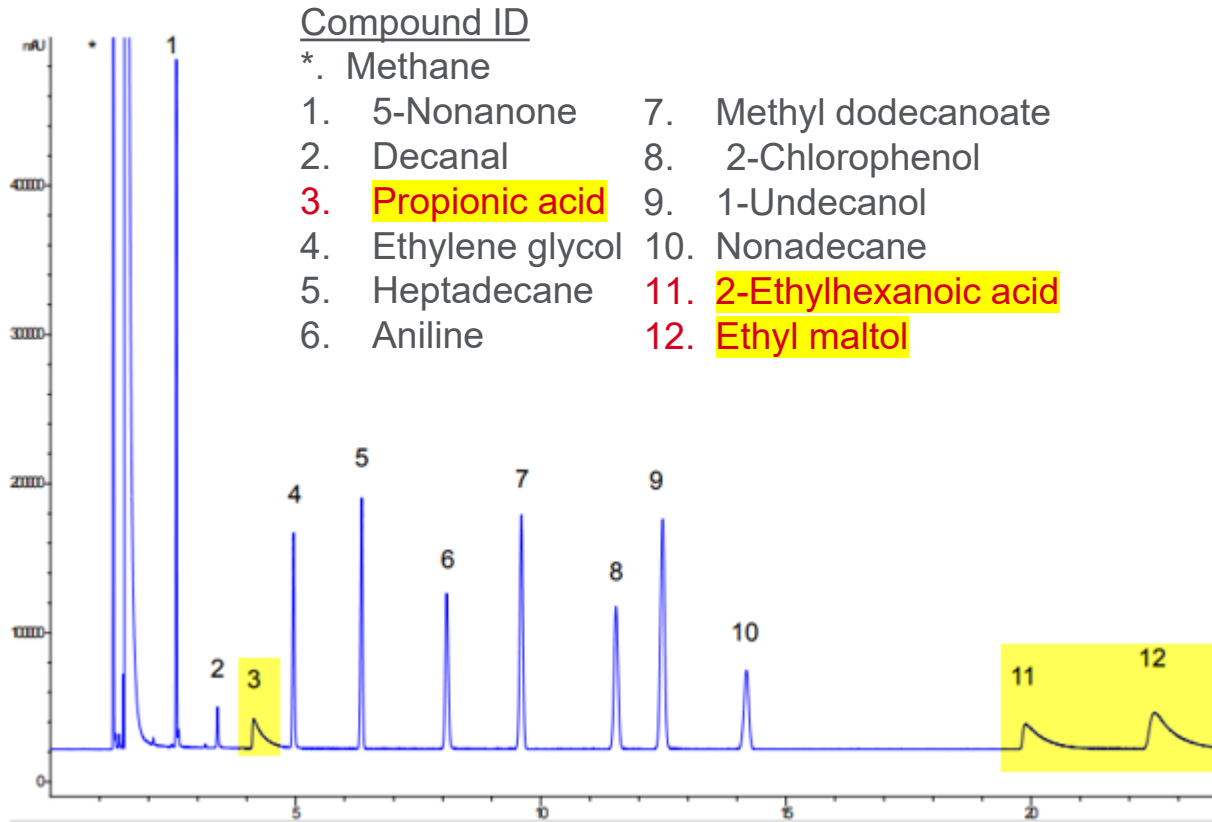
Agenda



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

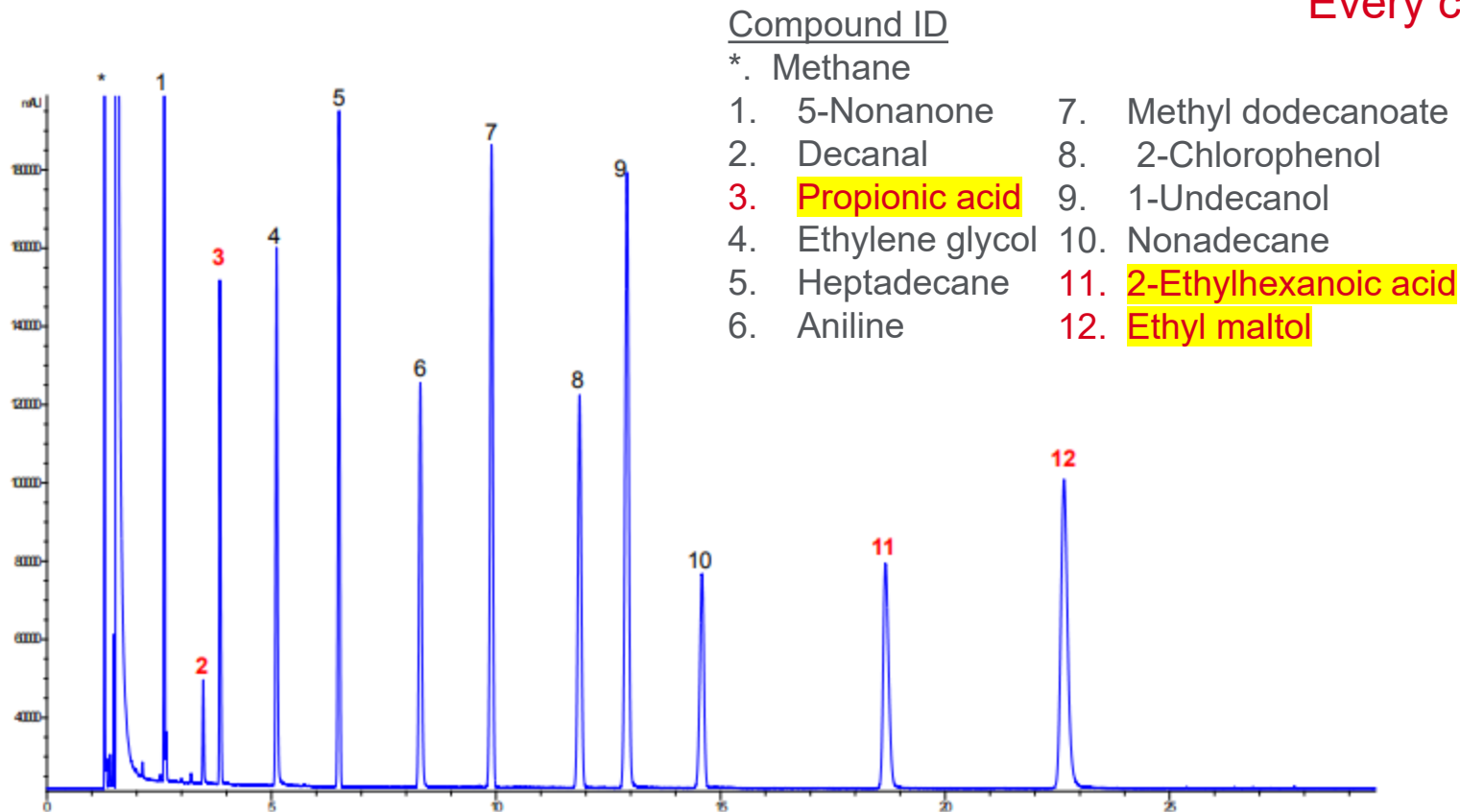
Miscellaneous - overloading of PLOT columns, coelution, polarity mismatch between phase, solute or solvent, and some compounds always tail

***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



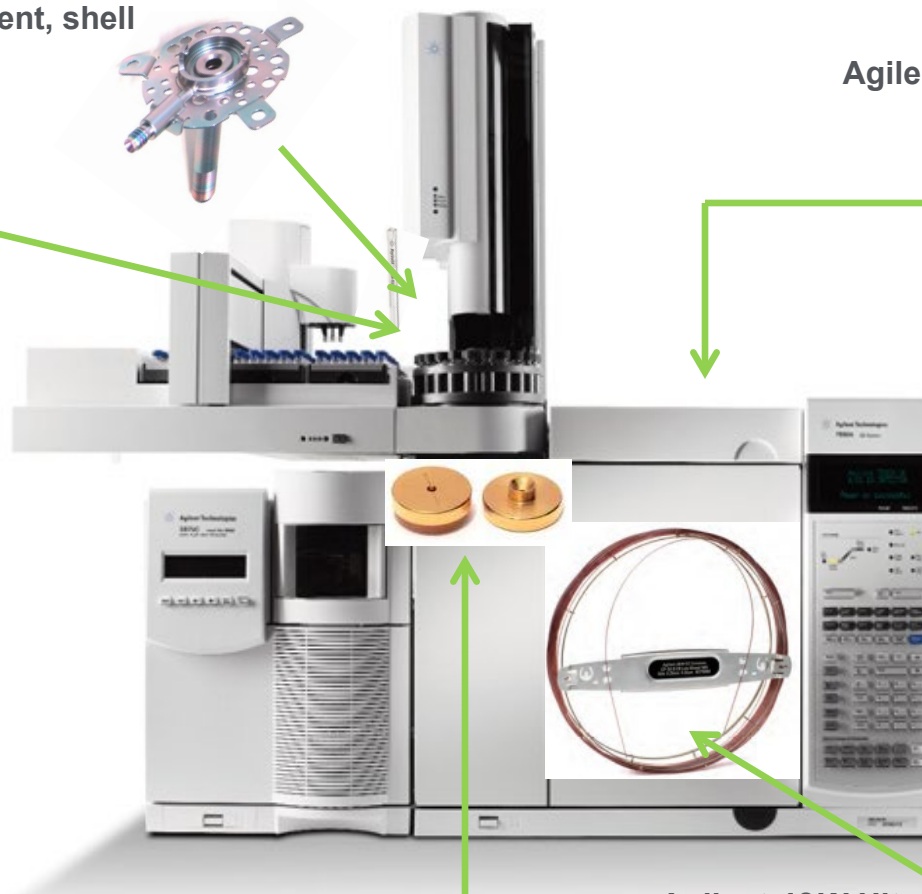
Agilent Ultra Inert inlet liner



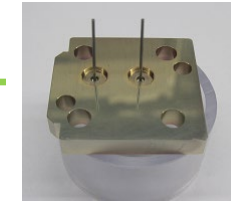
Agilent UltiMetal Plus ferrules



Agilent UltiMetal Capillary Flow Technology Devices, Ultimate union



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



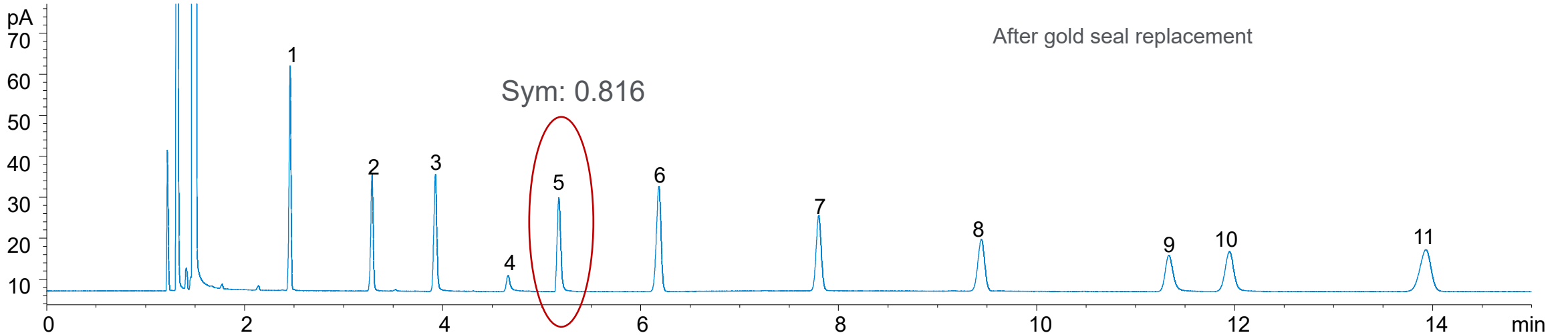
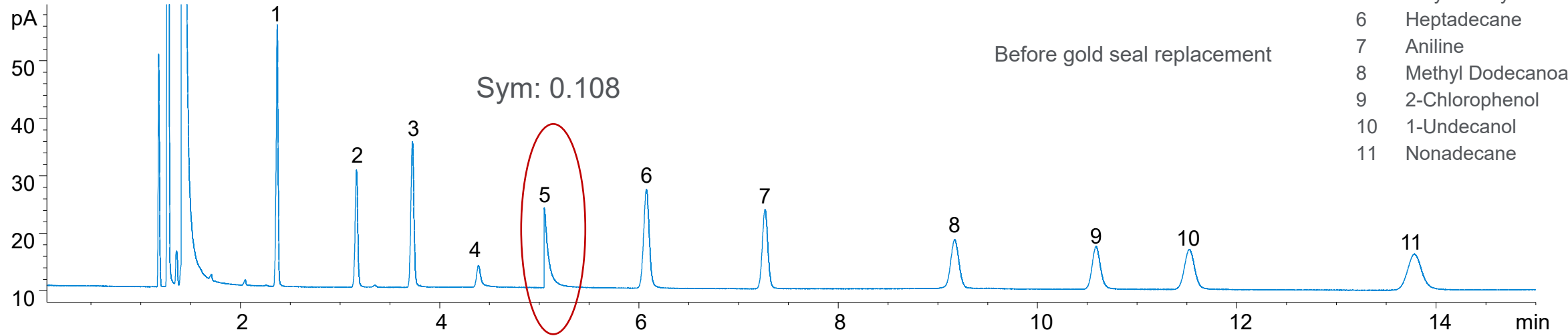
Agilent J&W Ultra Inert GC column

Agilent Ultra Inert gold seal

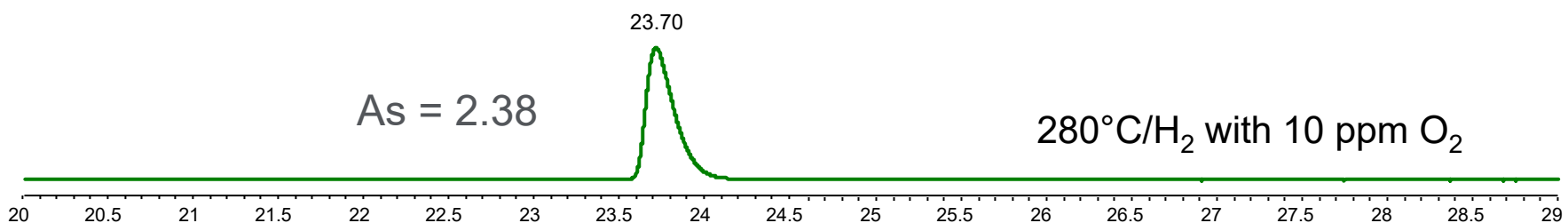
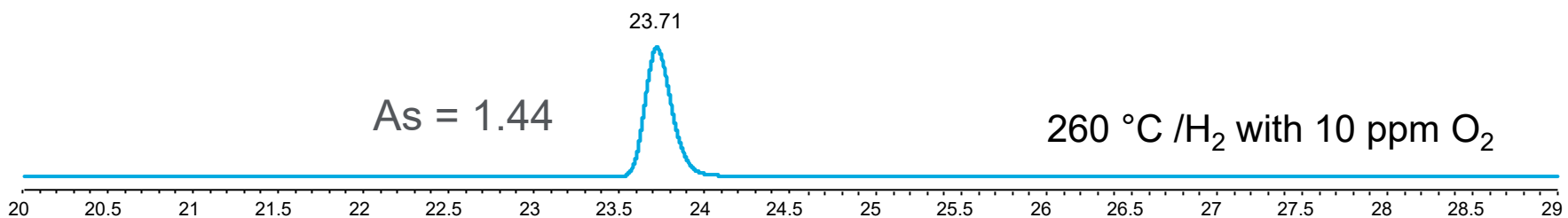
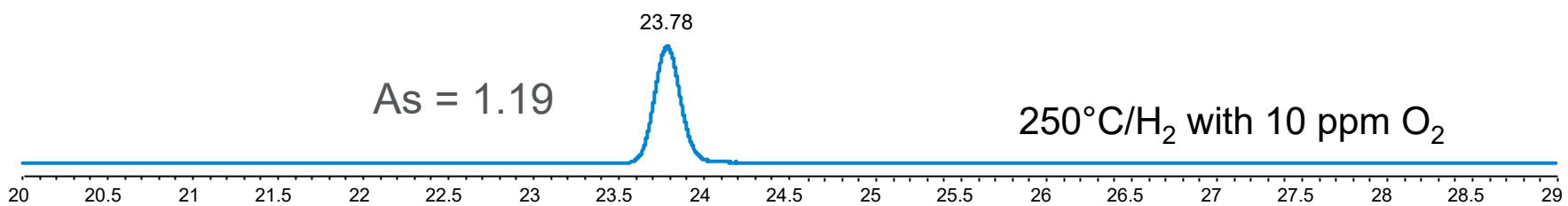
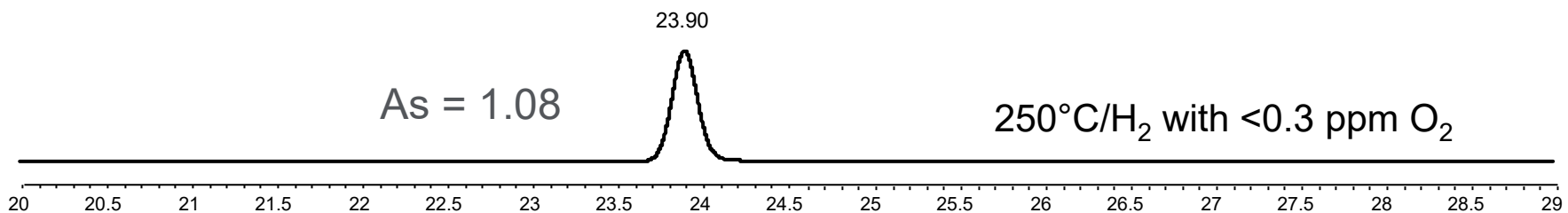
5990-8532EN brochure

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



Effect of Oxygen on Peak Shape of 2-ethylhexanoic Acid



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

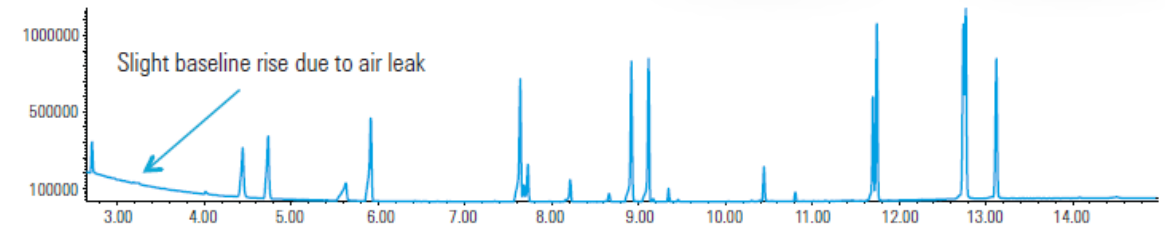
Part Number	Description
G3440-81013	Column Nut, Collared Self-Tightening MSD
G3440-81011	Column nut, Collared Self Tightening Inlet/Detect
G3440-81012	Collar for Self Tightening Nut

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

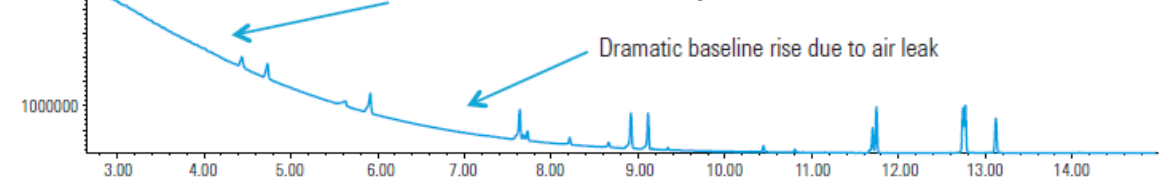
<https://www.agilent.com/en/video/stcn-inlet-detector>

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

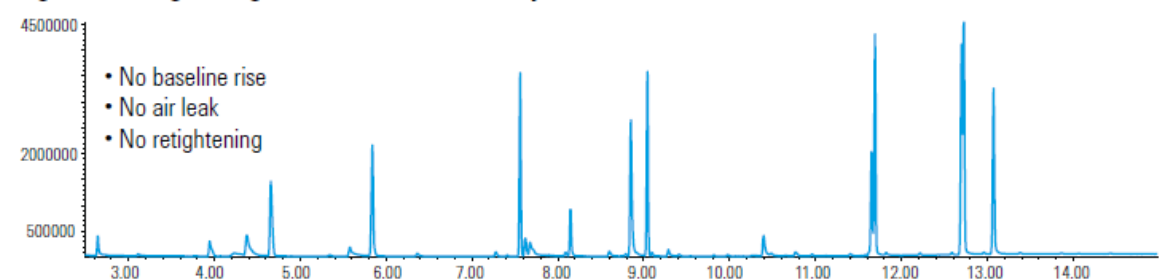
Standard column nuts new fitting



Standard column nuts after 25 injections

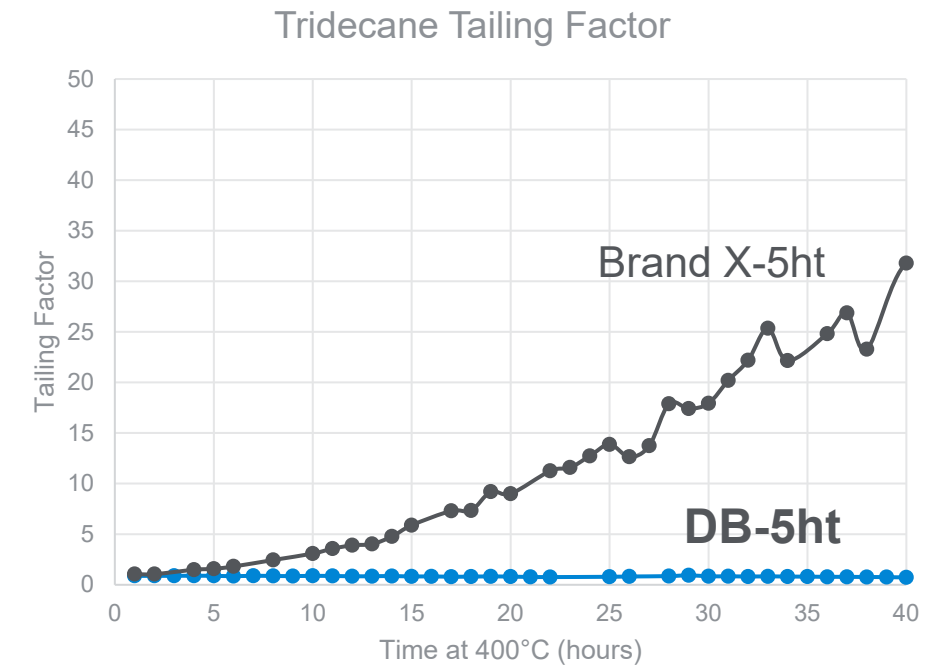
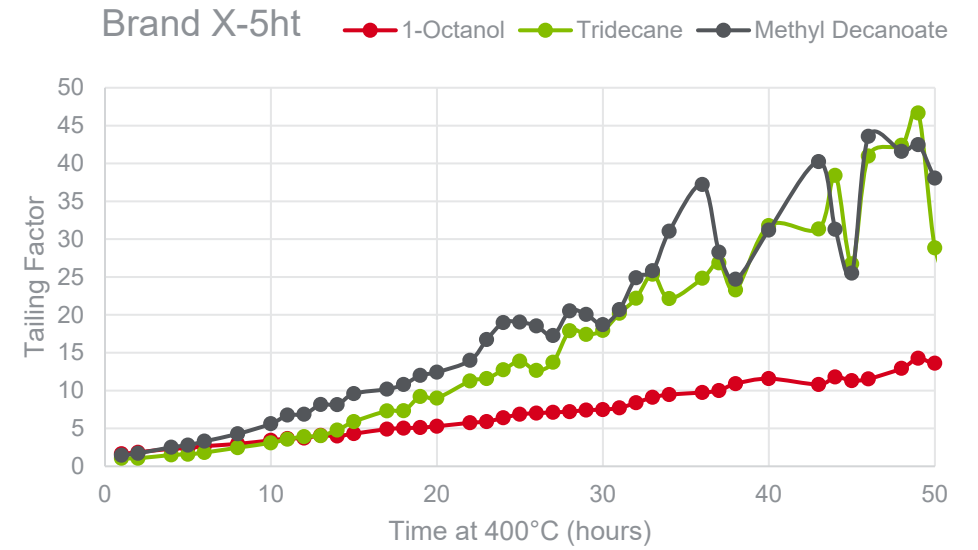
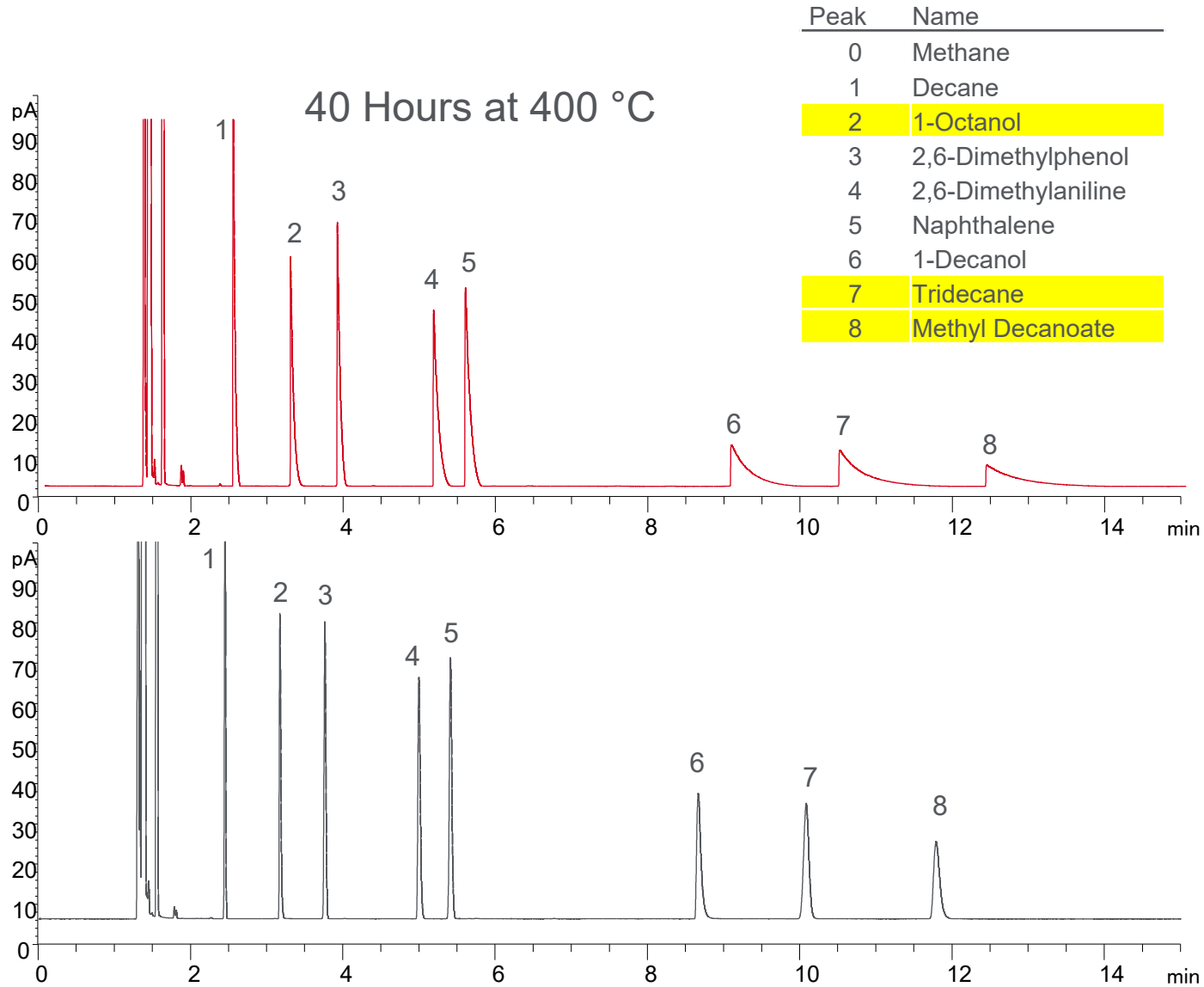


Agilent Self Tightening Column Nuts after 400 injections

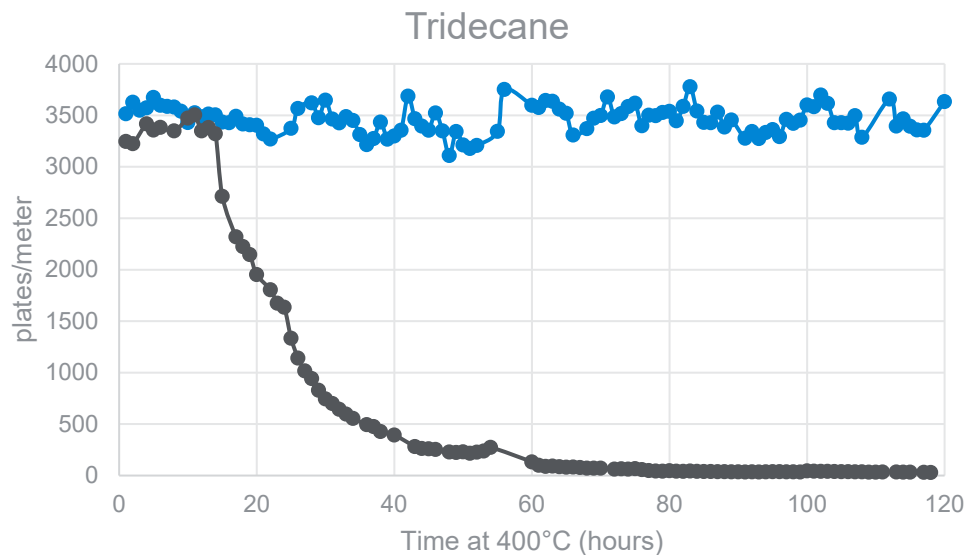


400 injections

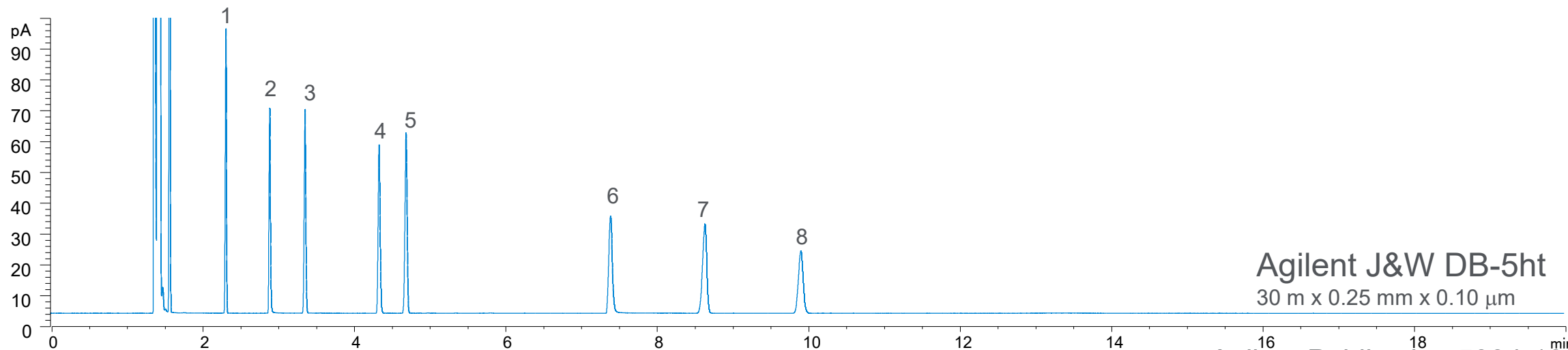
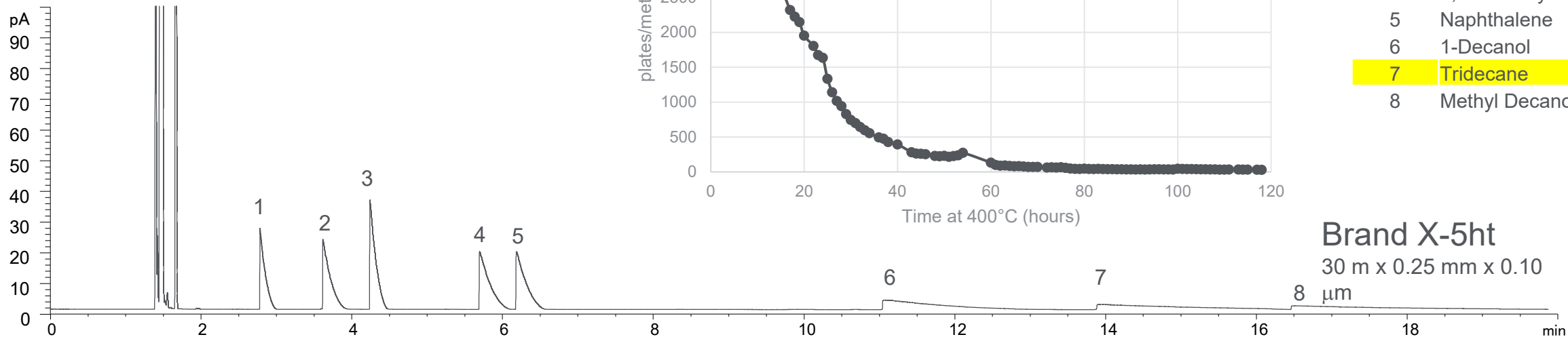
Peak Tailing from Thermal Degradation



Column Efficiency Over 120 Hours at 400 °C

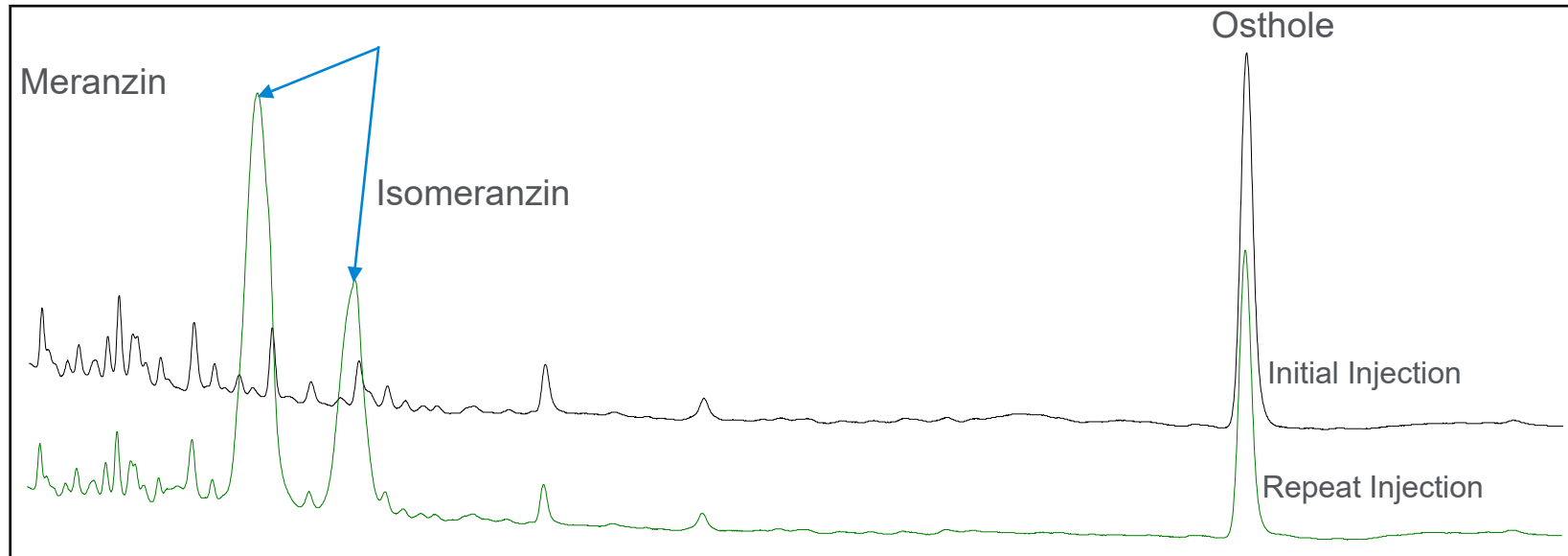


Peak	Name
0	Methane
1	Decane
2	1-Octanol
3	2,6-Dimethylphenol
4	2,6-Dimethylaniline
5	Naphthalene
6	1-Decanol
7	Tridecane
8	Methyl Decanoate



Agilent Publication 5994-1013EN

Bonus or Ghost Peaks



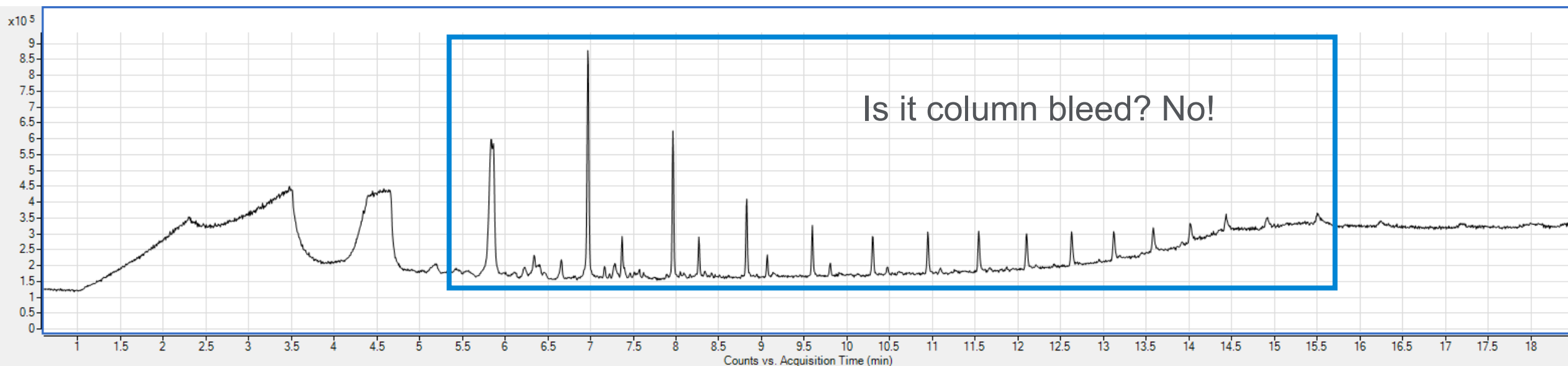
5991-9078EN

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

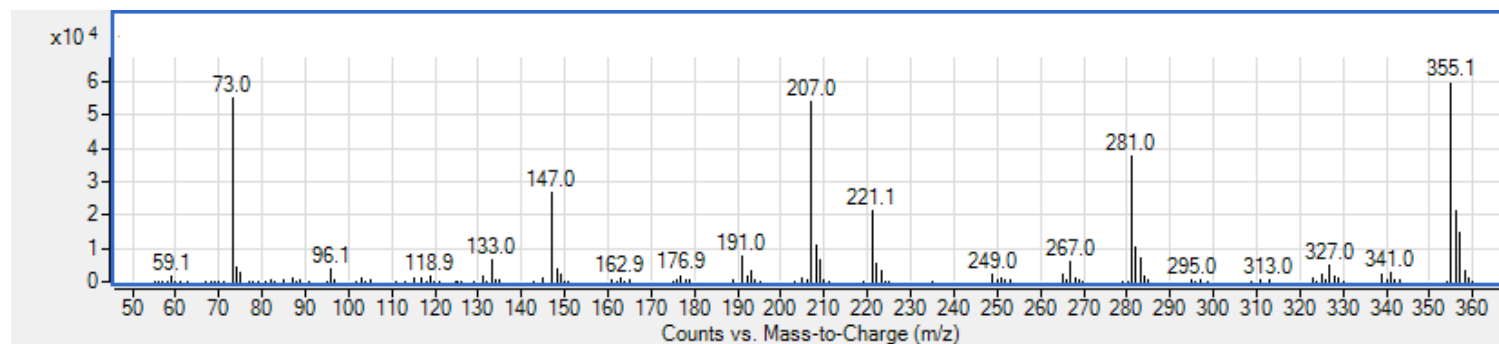
207

281

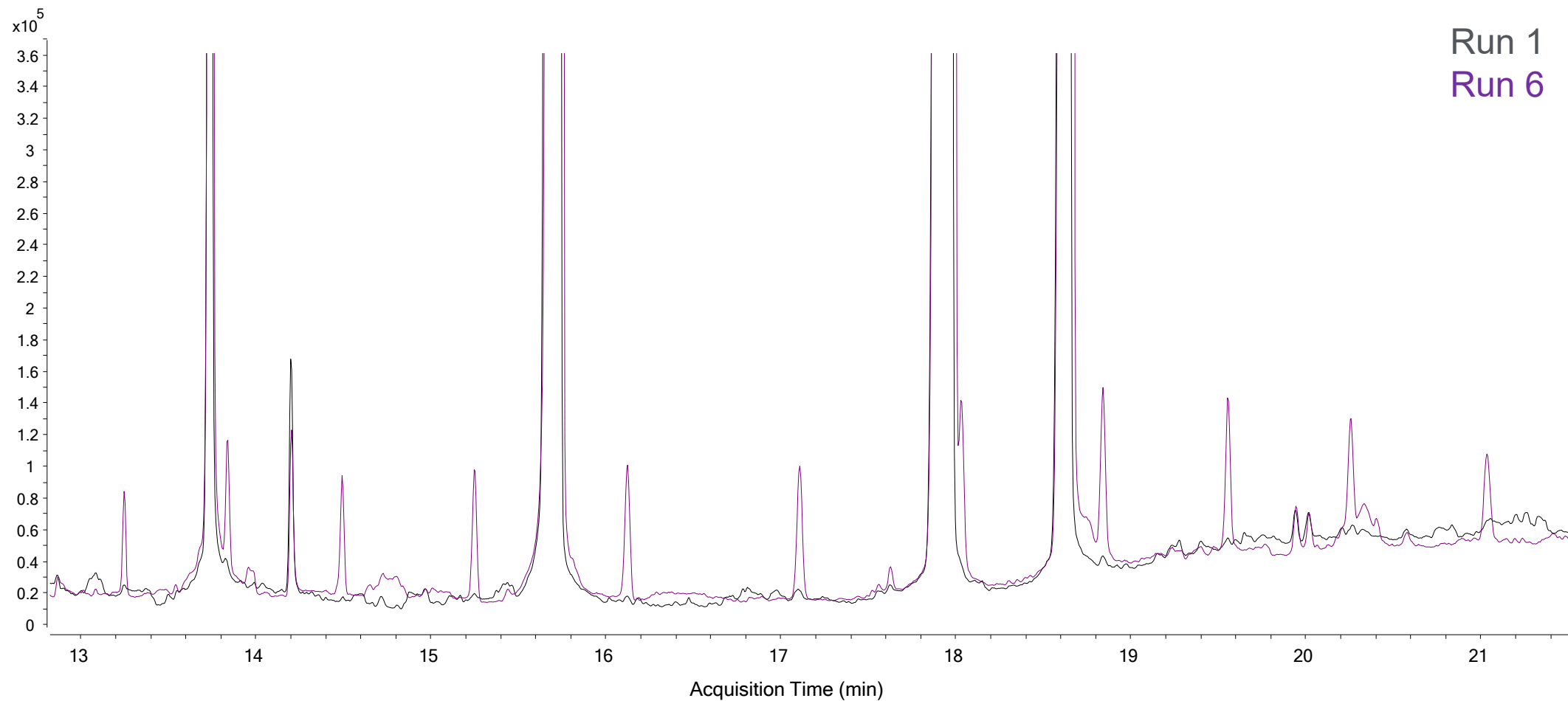
355

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:



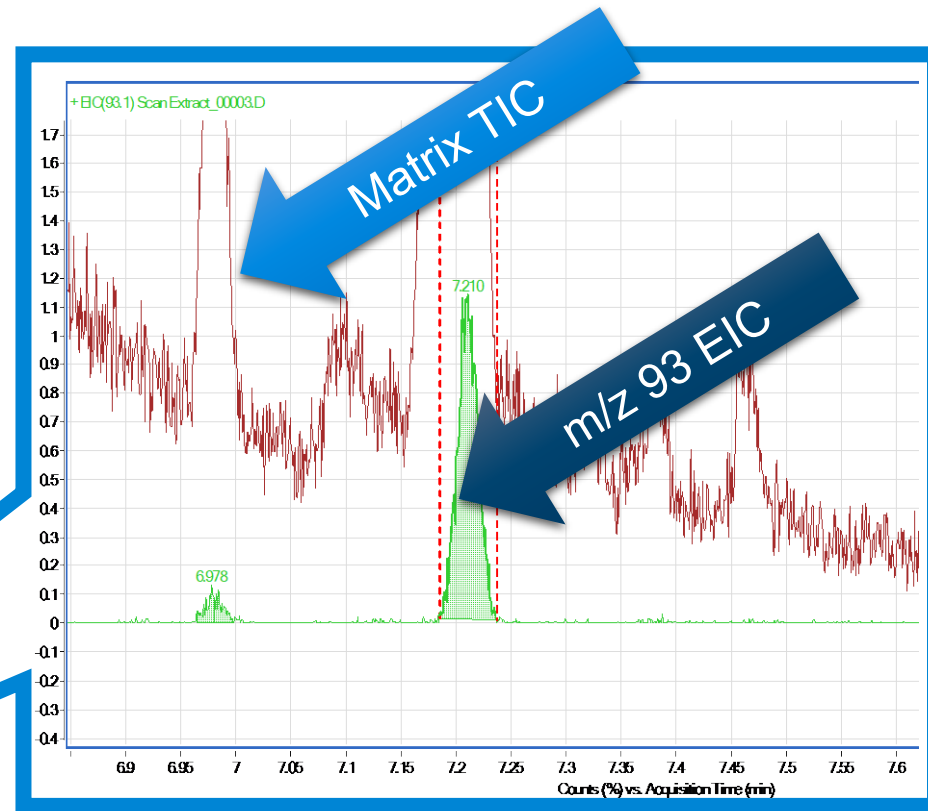
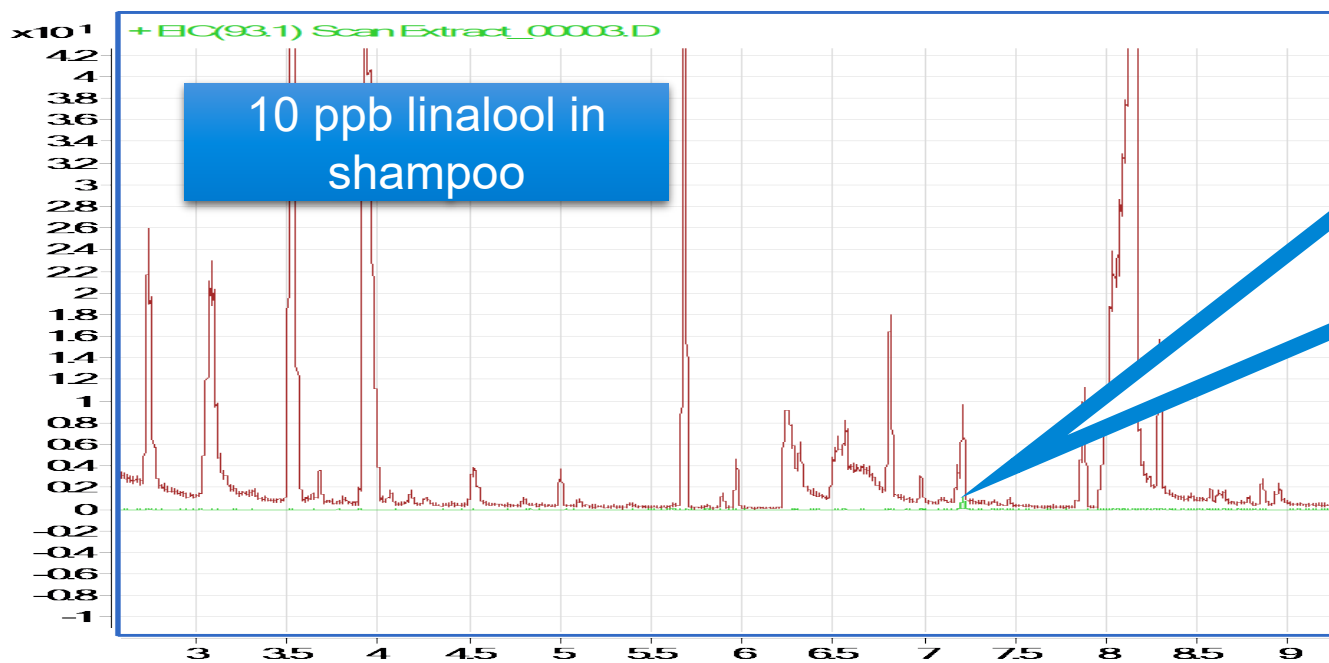
Multiple Injections from the Same Vial: Siloxanes!



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

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)

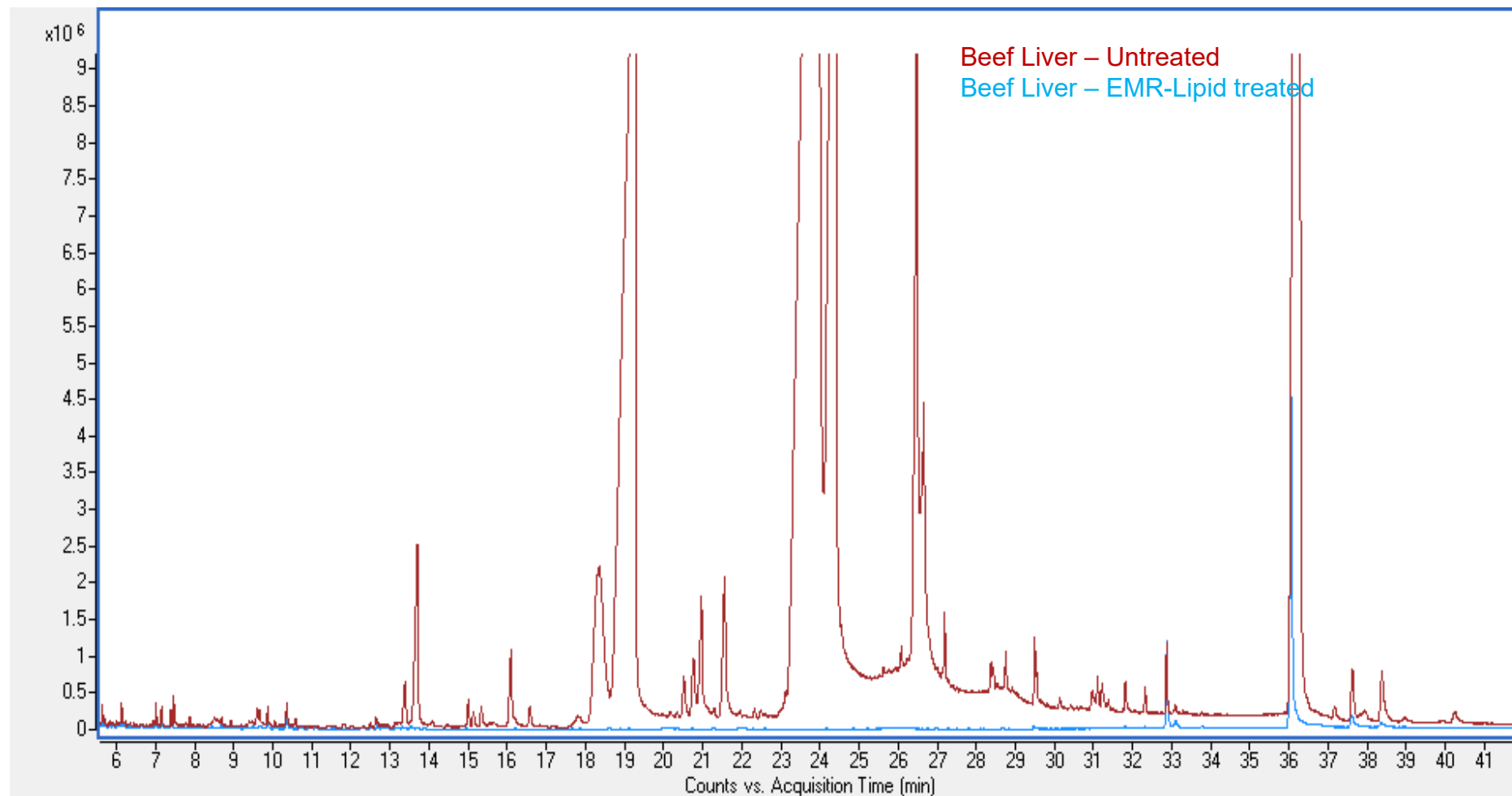
The Importance of Sample Cleanup



50 samples
with cleanup

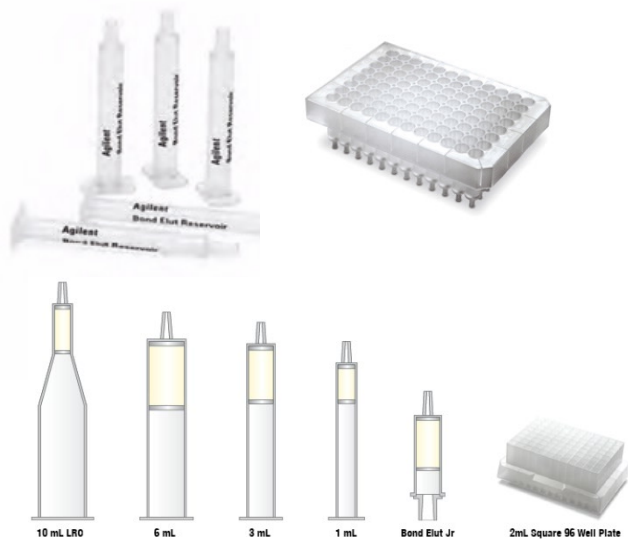


50 samples
without cleanup



For sample cleanup help, please contact us! spp-support@agilent.com

Offline Options for Sample Matrix Removal



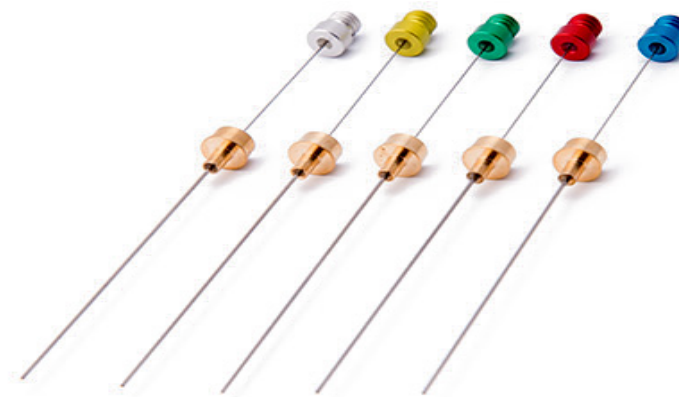
Bond Elut Solid Phase Extraction cartridges and plates



Filter vials



QuEChERS



SPME



Captiva EMR-Lipid filtration cartridges and plates

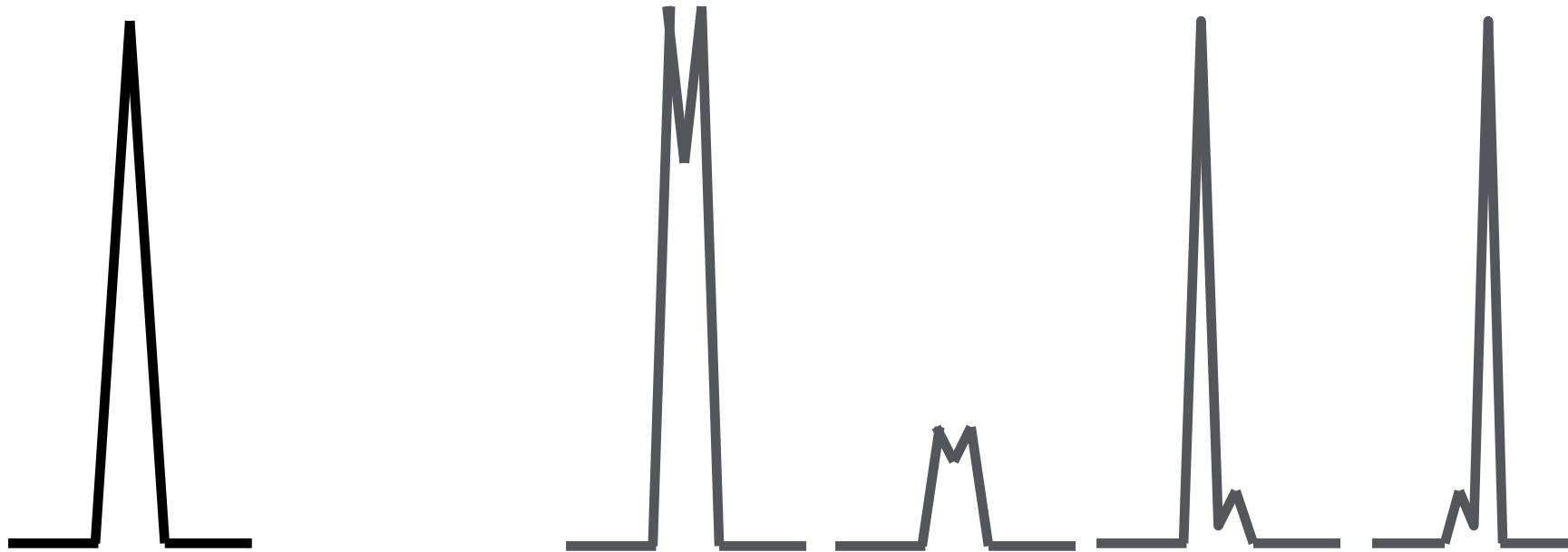


Chem Elut S



Captiva syringe filters

Split Peaks



Injector (poor sample introduction)

- Injecting the sample twice (somehow?)
- Mixed sample solvent (polarity difference)
- Sample in syringe needle (manual inject)

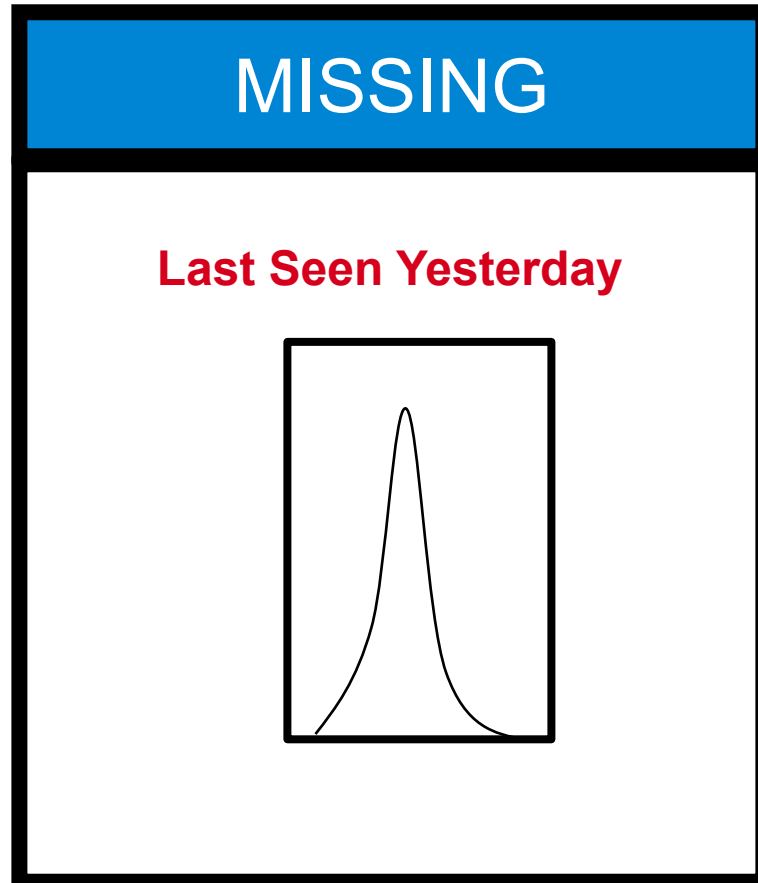
Injector (activity)

- Breakdown (not really a split peak, two peaks)
- Sample degradation in injector

Volatility

- High boilers dropping out on cold spots
- Transfer line temperatures
- Unions or fittings not tracking column temperature

No Peaks



Detector (not on, or not operational)

Injector (not working)

Plugged syringe/plunger not moving

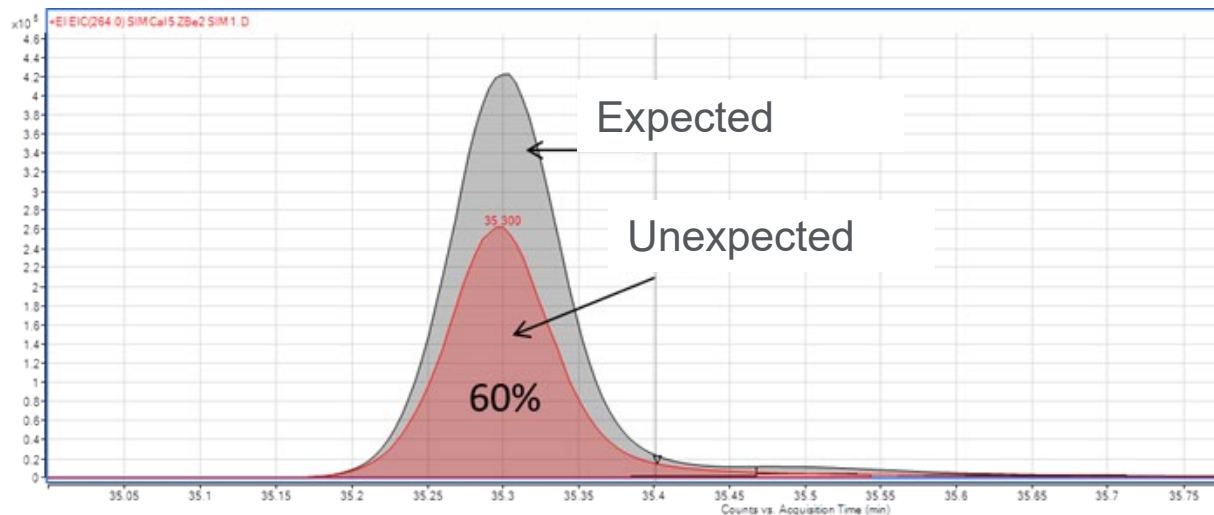
- Wrong injector (or detector)
- Huge leak (older systems)
- No carrier gas flow

Not the column unless...

- Broken column or no column

Peak Response

All change in size



Injector

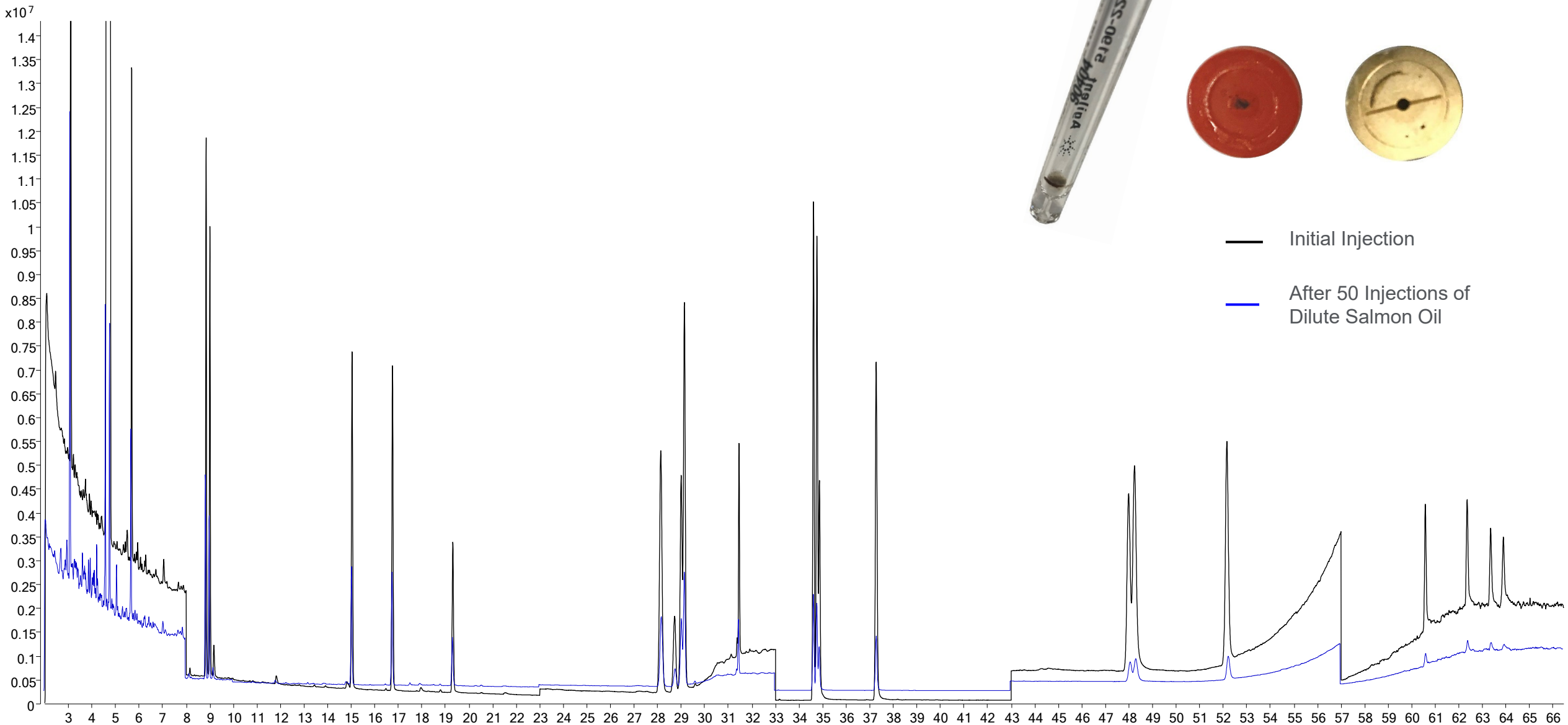
- Leaky syringe
- Split ratio set incorrectly
- Wrong purge activation time
- Septum purge flow too high
- Injector temperature too low*

Detector (response problem)

- Settings or flows changed
- Electronics failing

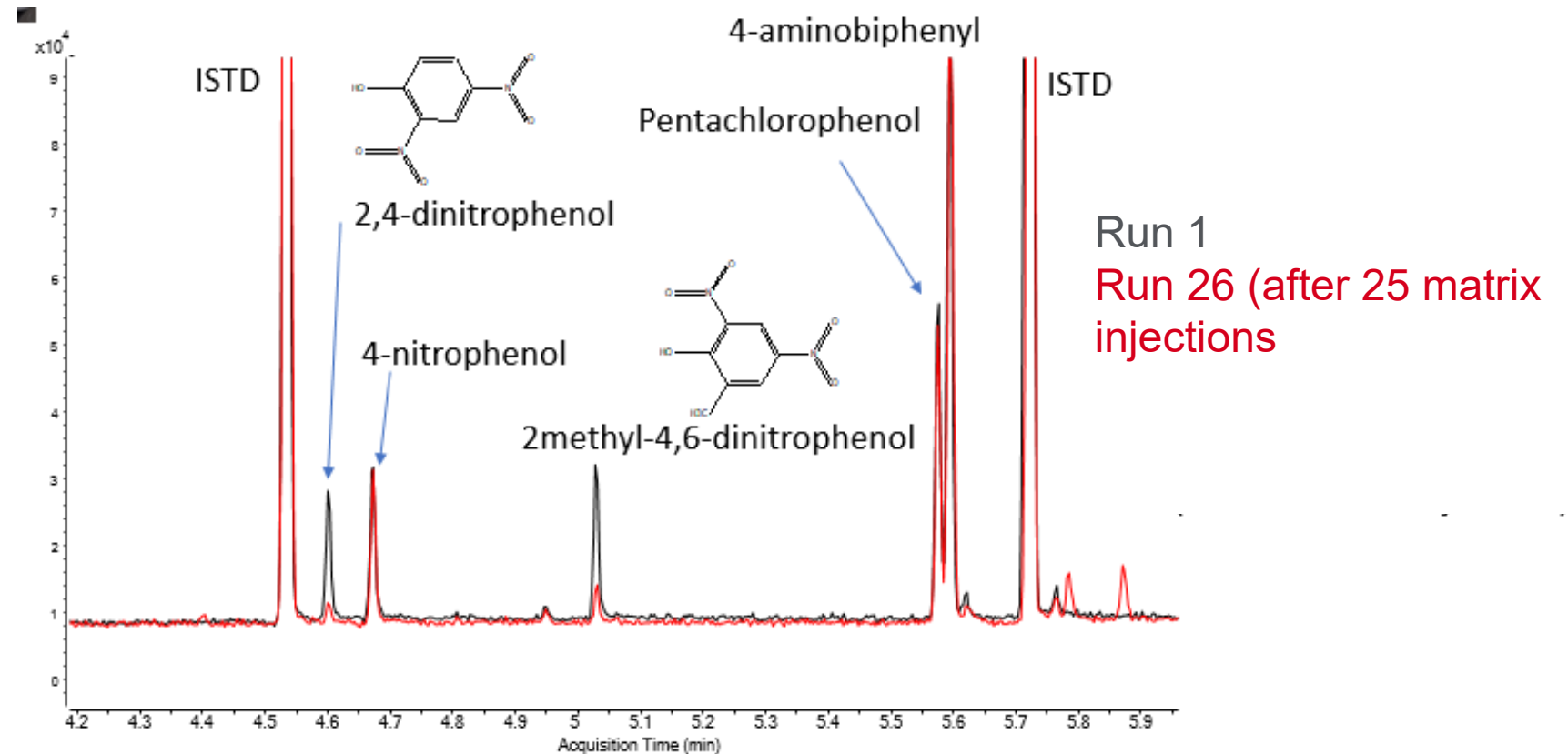
***Tip:** Ask is it all of them or some of them, if all then injector or detector

50 ng/mL before 50 Injections of Salmon Oil



Peak Response

Some change in size



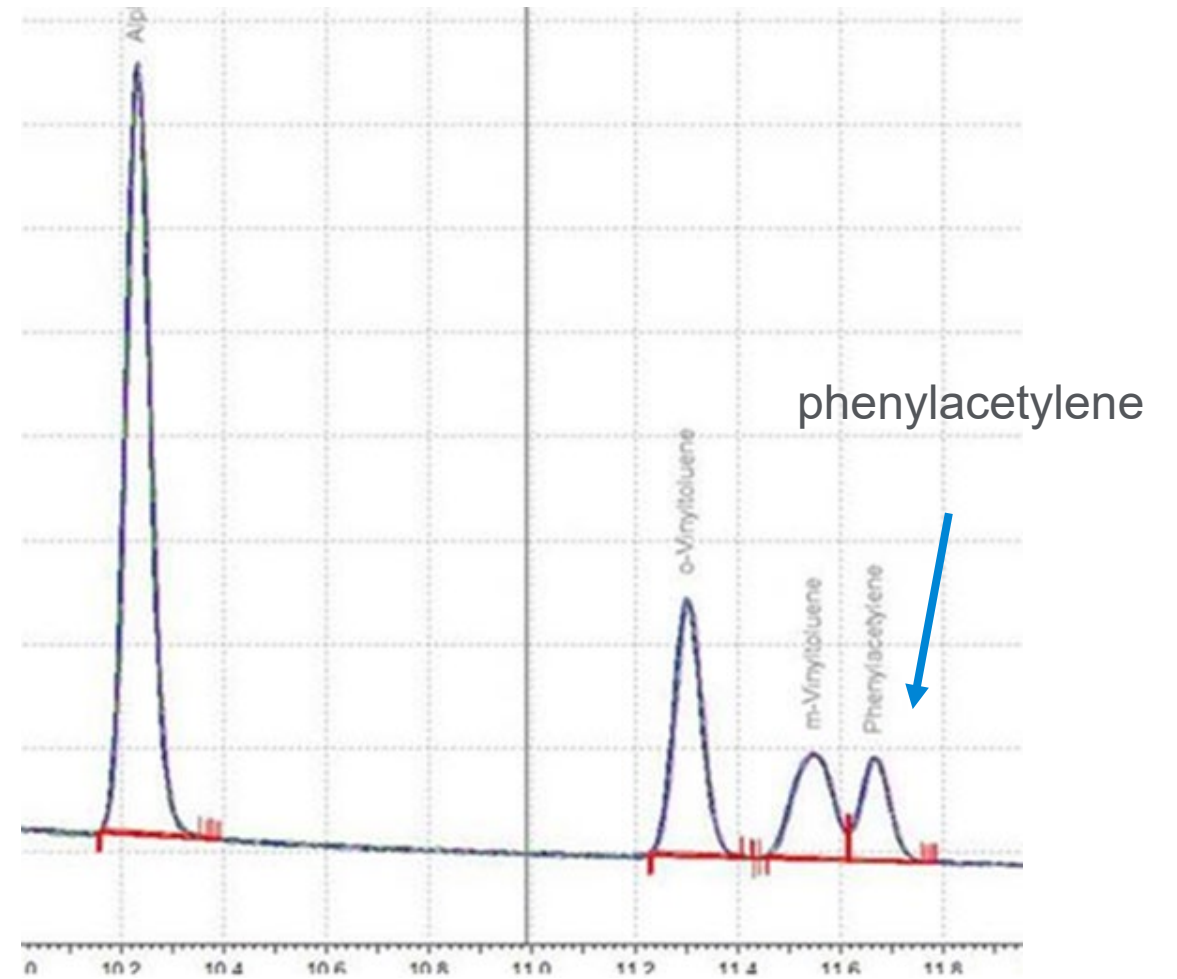
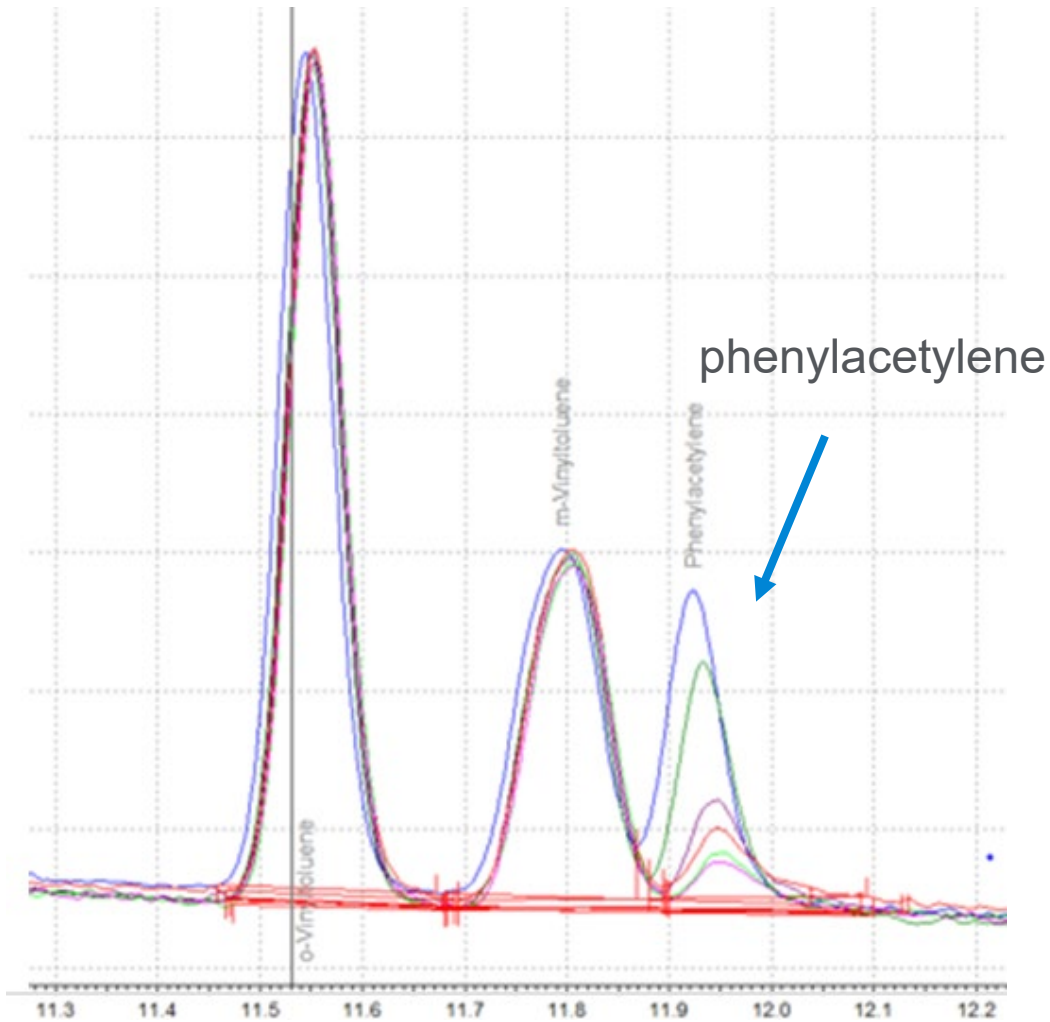
Injector or column is active/contaminated

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

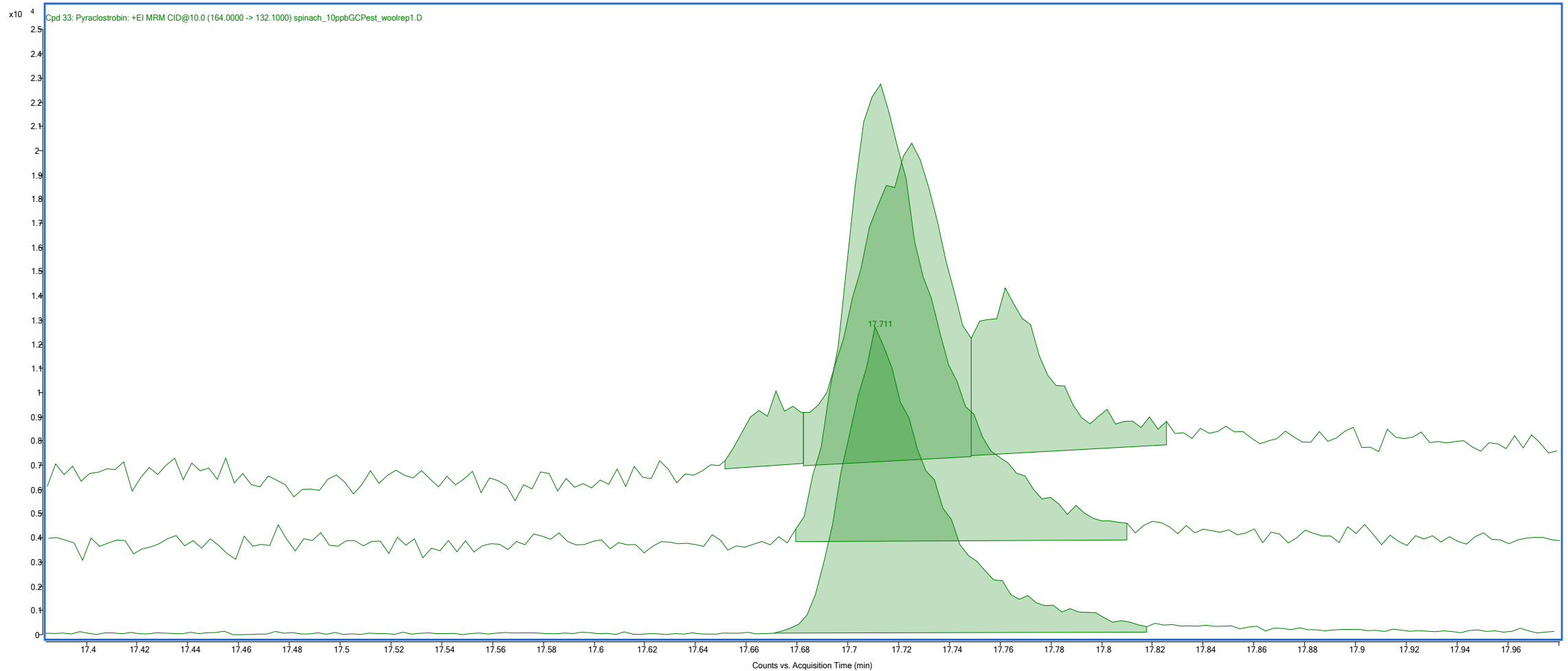
Decomposition of sample

- Temperature change – discrimination
- Evaporation from sample

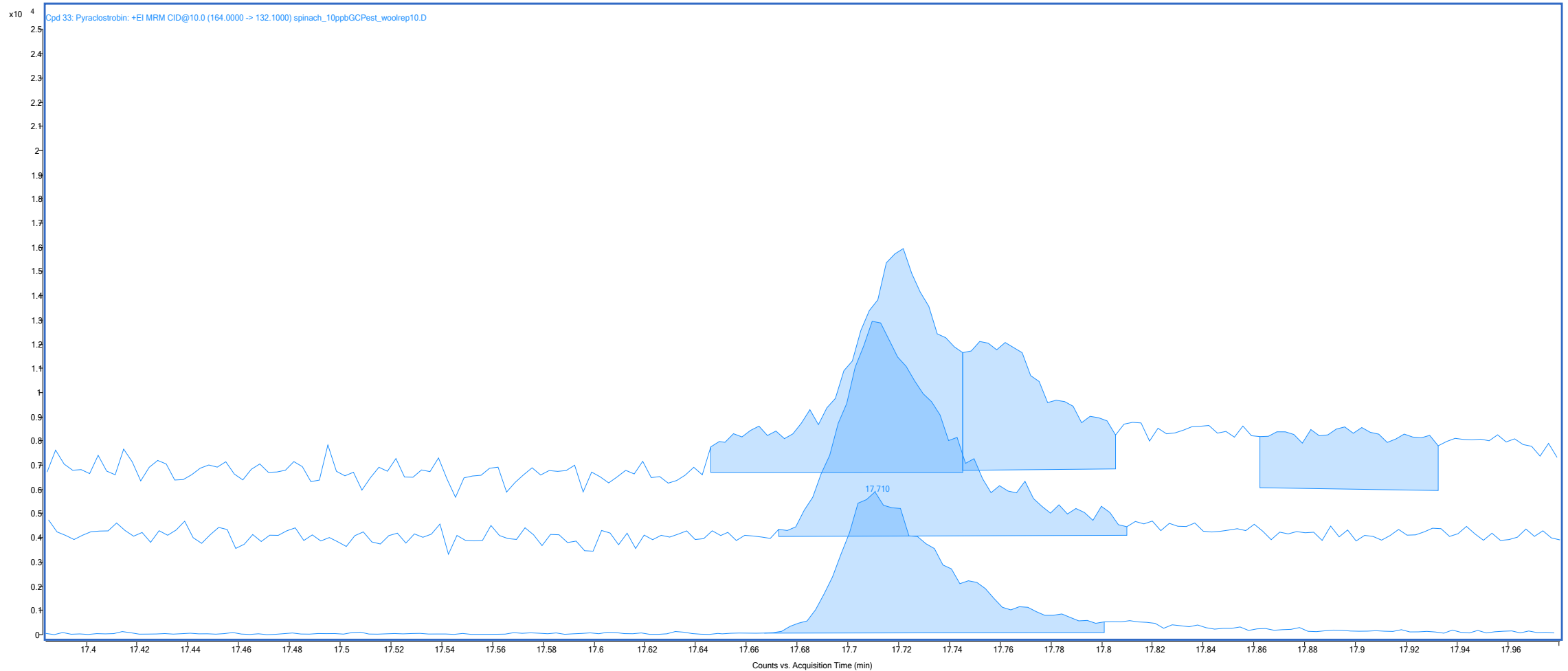
Example of Reduction in Response for One Peak



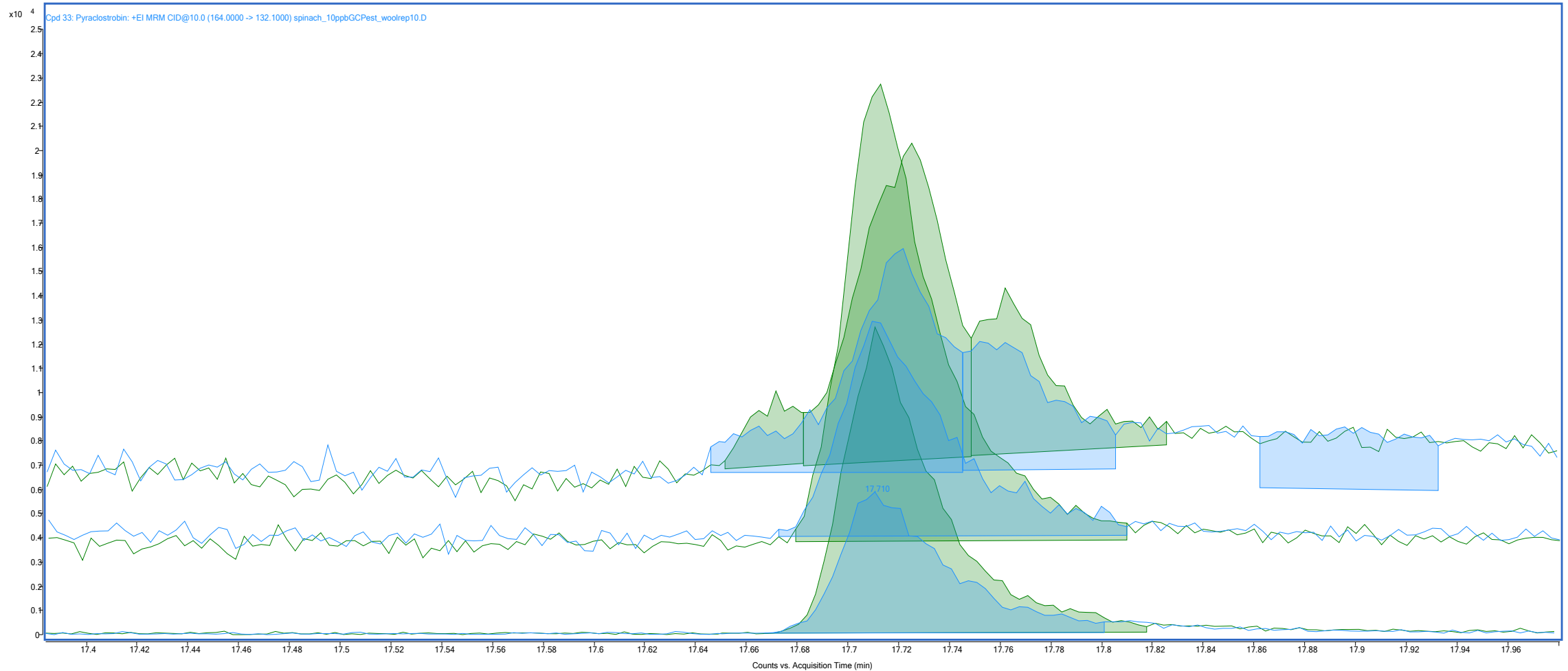
Change in Response: Pyraclostrobin in Spinach on Run 1



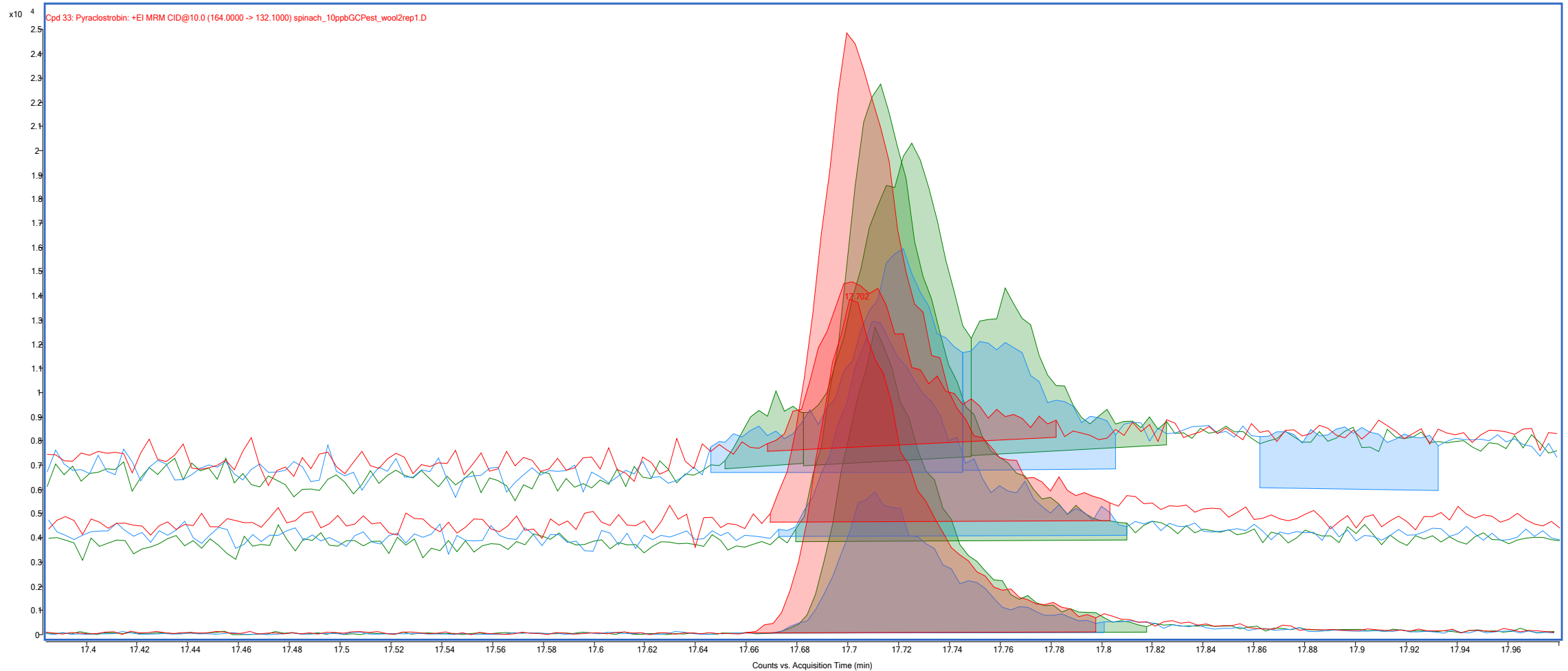
Change in Response: Pyraclostrobin in Spinach on Run 65



Change in Response: Pyraclostrobin in Spinach on Run 1 vs Run 65

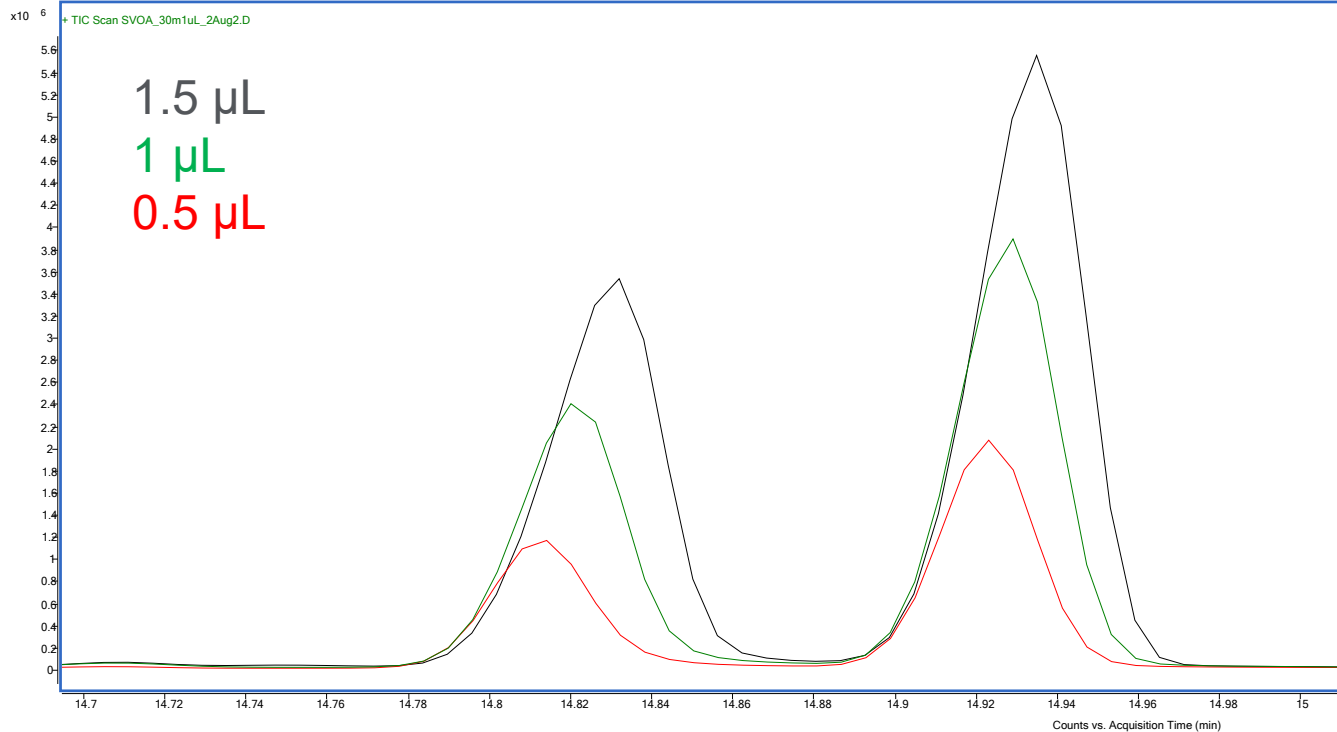


Change in Response: Pyraclostrobin in Spinach with **New Liner**



Peak Fronting

Shark fin-shaped or just slight



Column (contaminated)

- Overload (more pronounced with large solute and phase polarity differences)

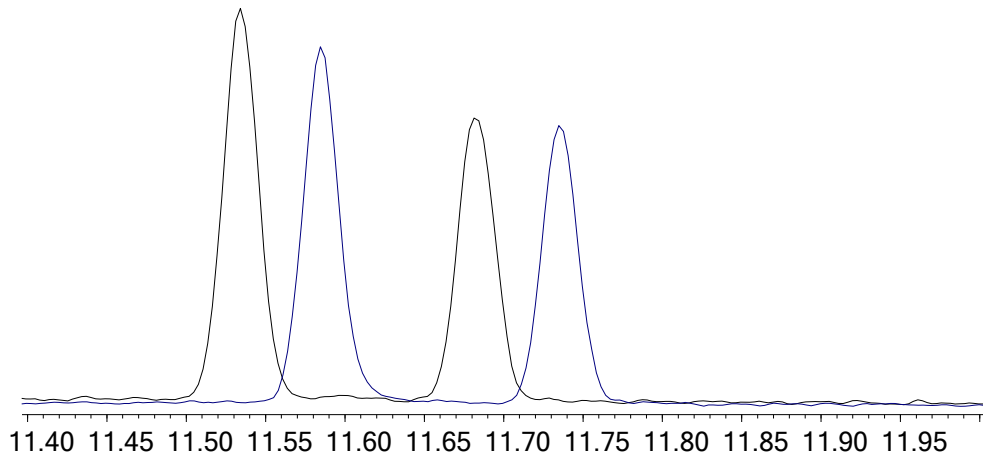
Injector

- Compound soluble in injection solvent (need retention gap)
- Mixed sample solvent

Other

- Coelution
- Breakdown

Retention Time Shift



Injector

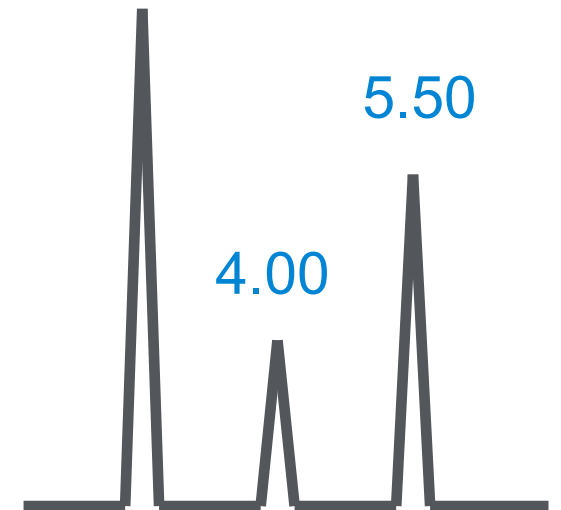
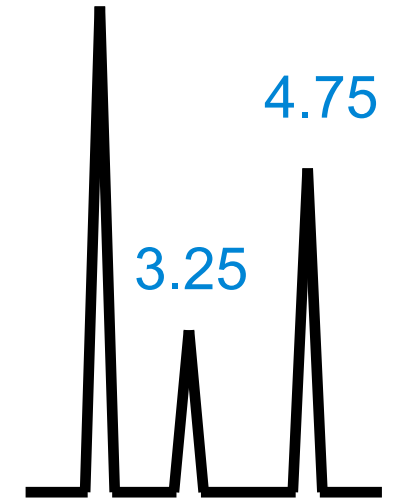
- Leak in the septum
- Change in injection solvent
- Large change in sample concentration

Flow

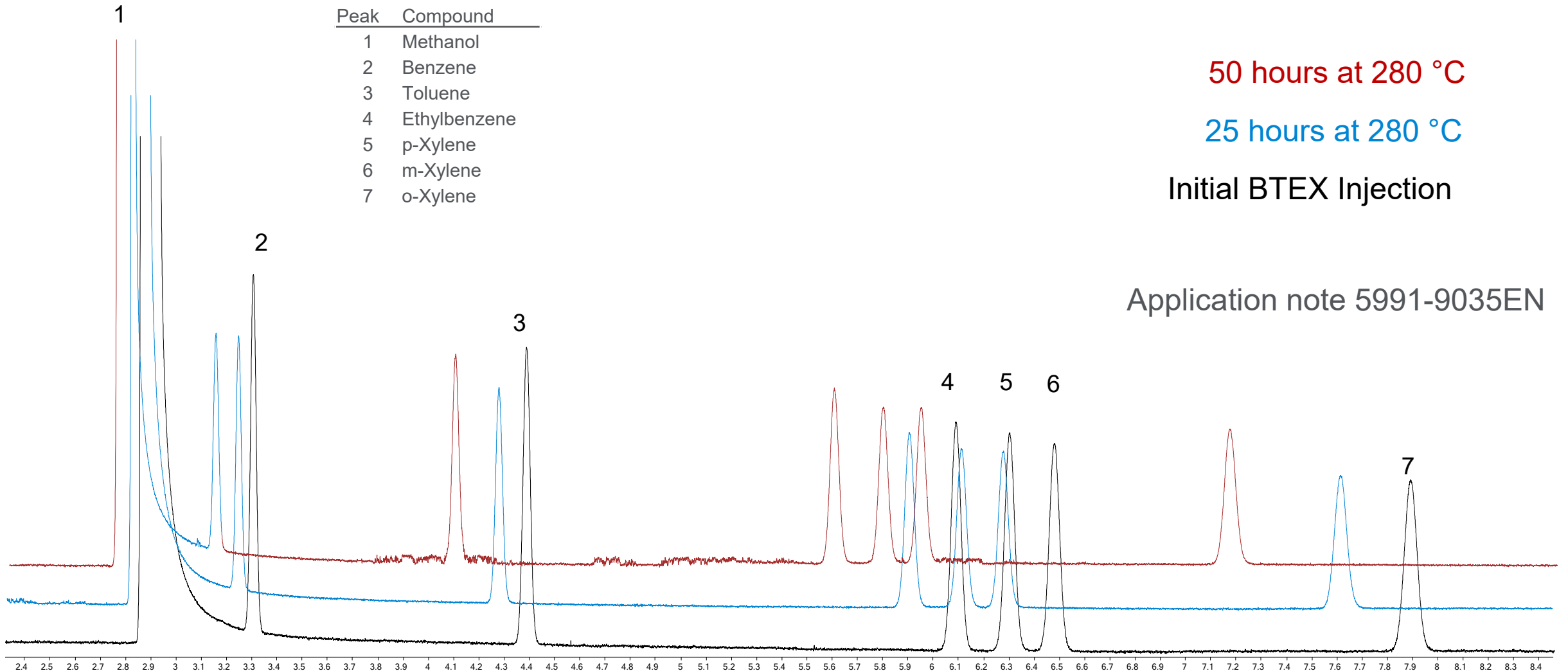
- Change in gas velocity

Column

- Contamination
- Damaged stationary phase
- Loss of stationary phase
- Change in temperature



Thermal Stability and Retention Time Shifting on Standard WAX Column

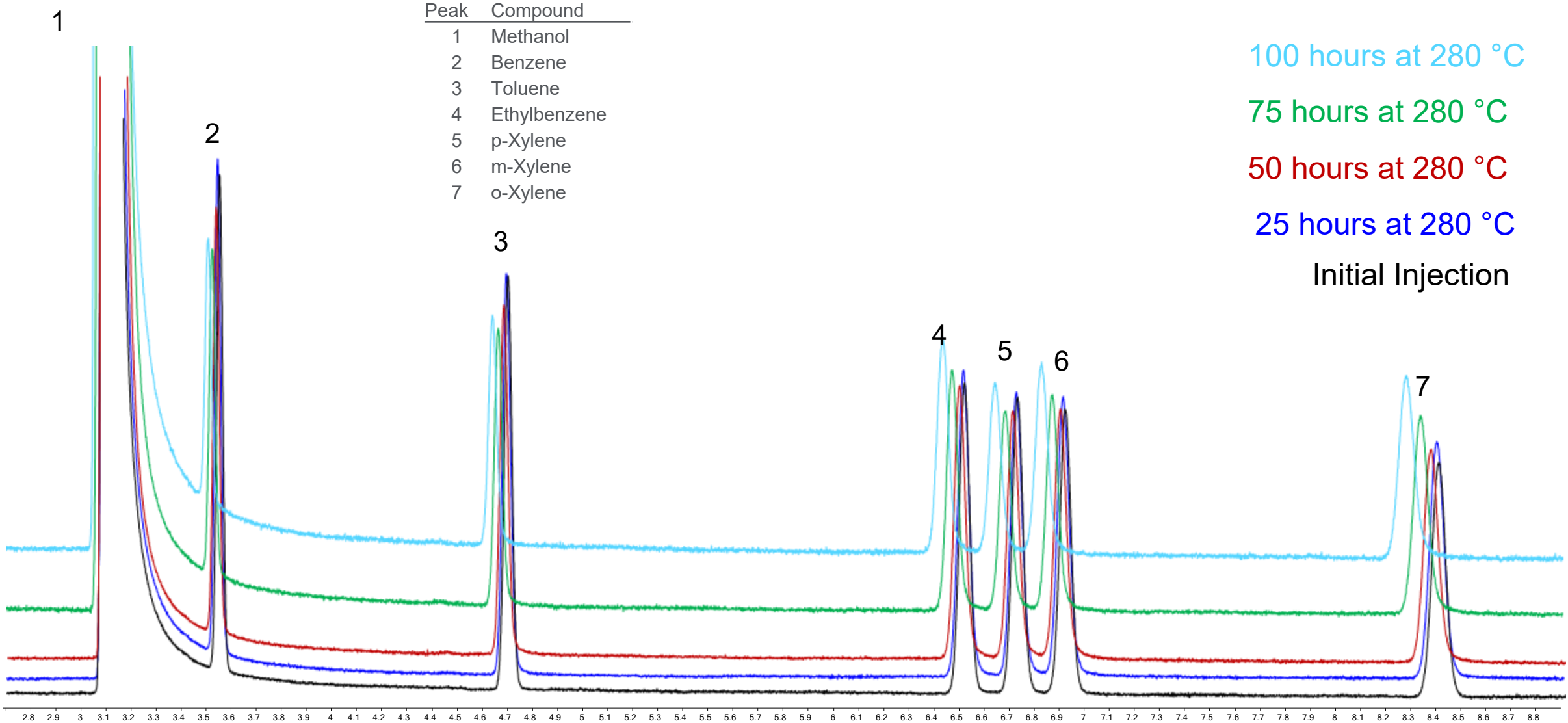


50 hours at 280 °C

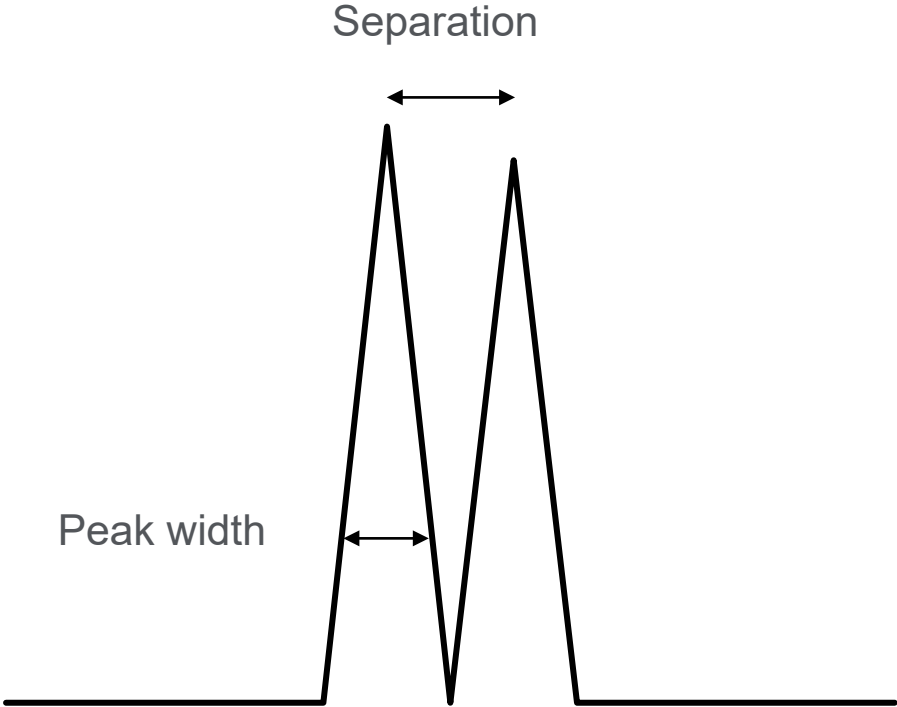
25 hours at 280 °C

Initial BTEX Injection

Application note 5991-9035EN



Loss of Resolution



Resolution is a function of separation and peak width

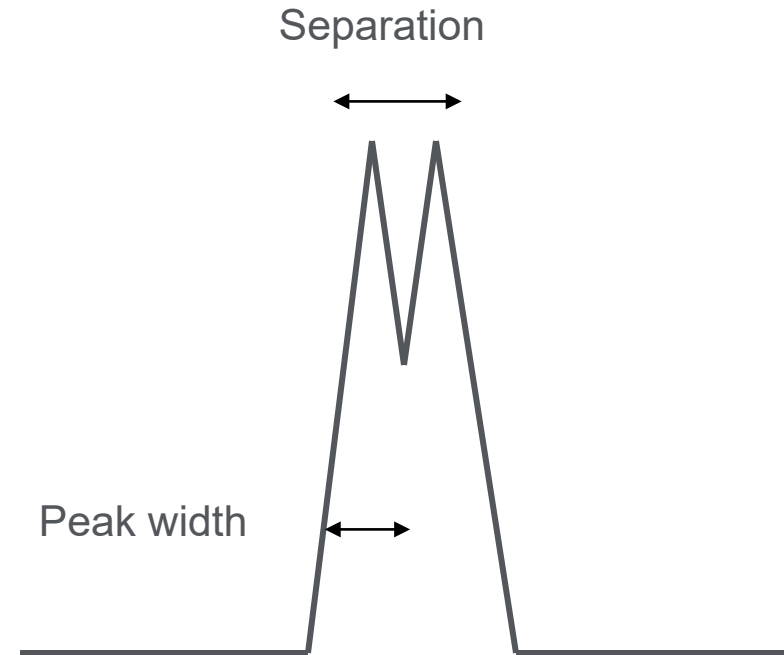
Loss of Resolution - Separation Decrease (Retention Times Changed)

Column

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

Flow

- Change in velocity?



Loss of Resolution - Peak Broadening (Retention Times Unchanged)

Flow

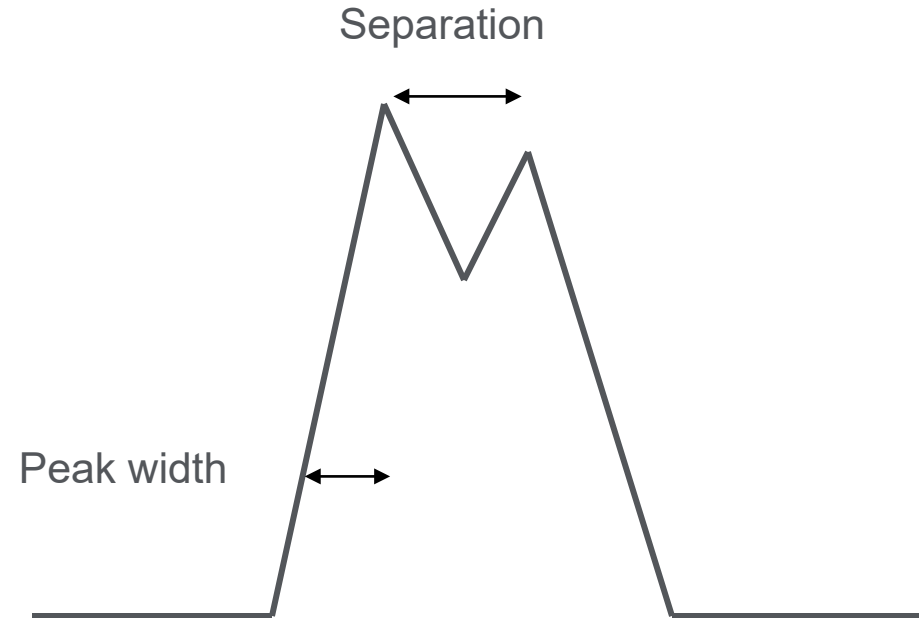
- Make-up gas

Column

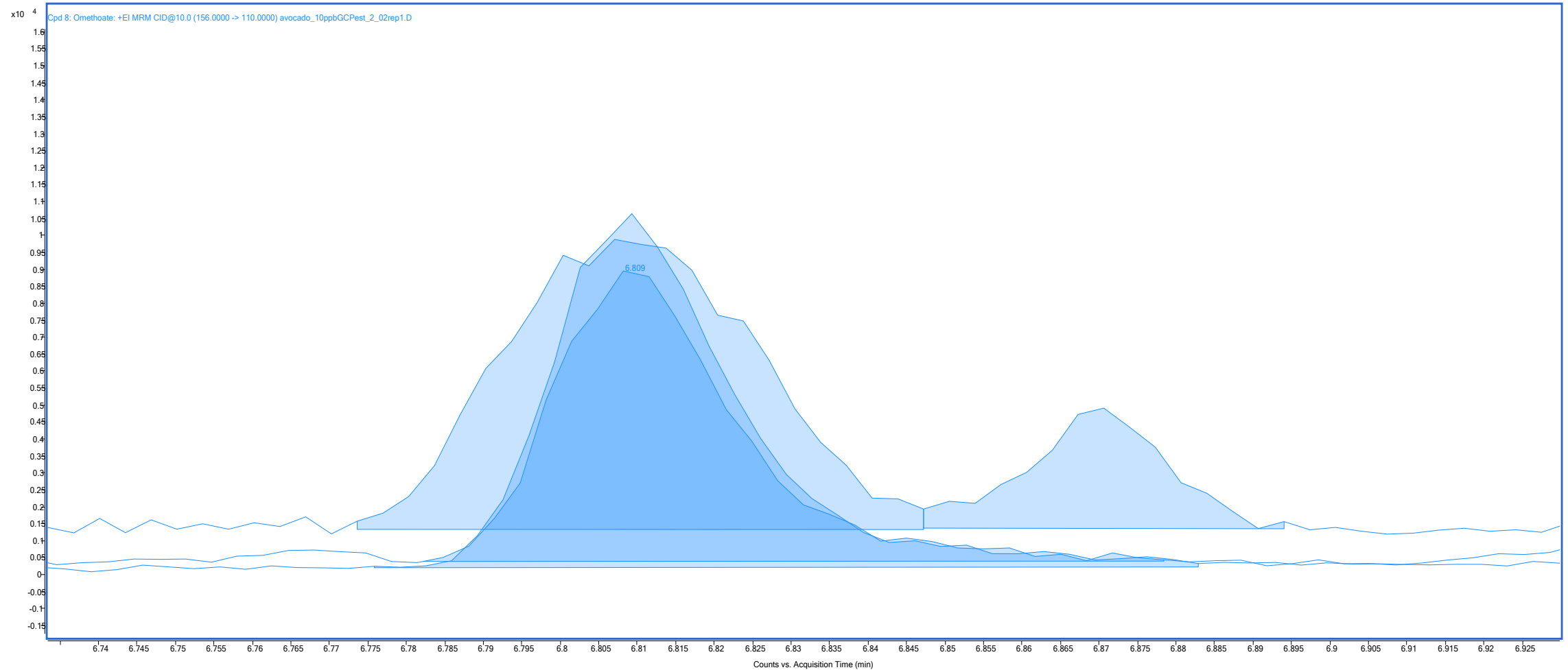
- Contamination
- Phase degradation

Injector (efficiency)

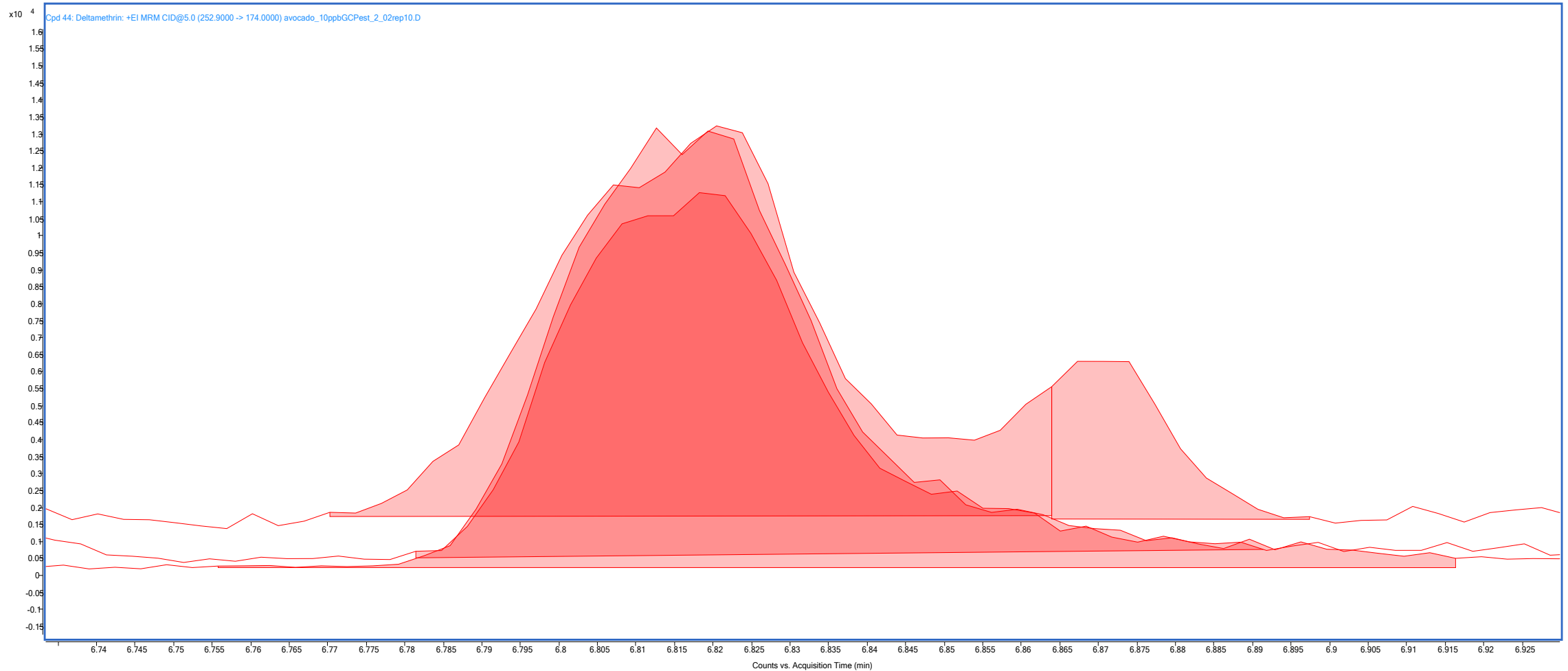
- Settings, liner, installation, etc.



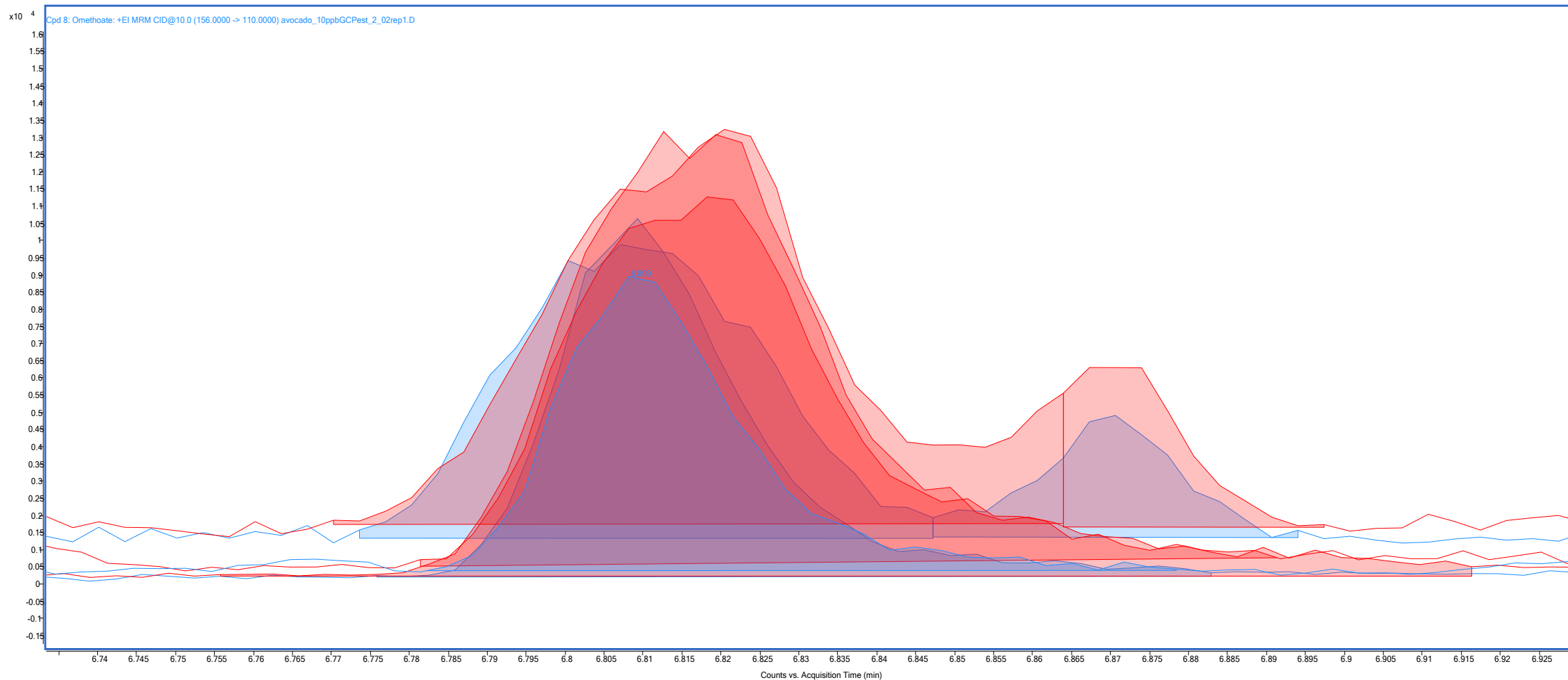
Peak Broadening: Omethoate in Avocado in Run 1



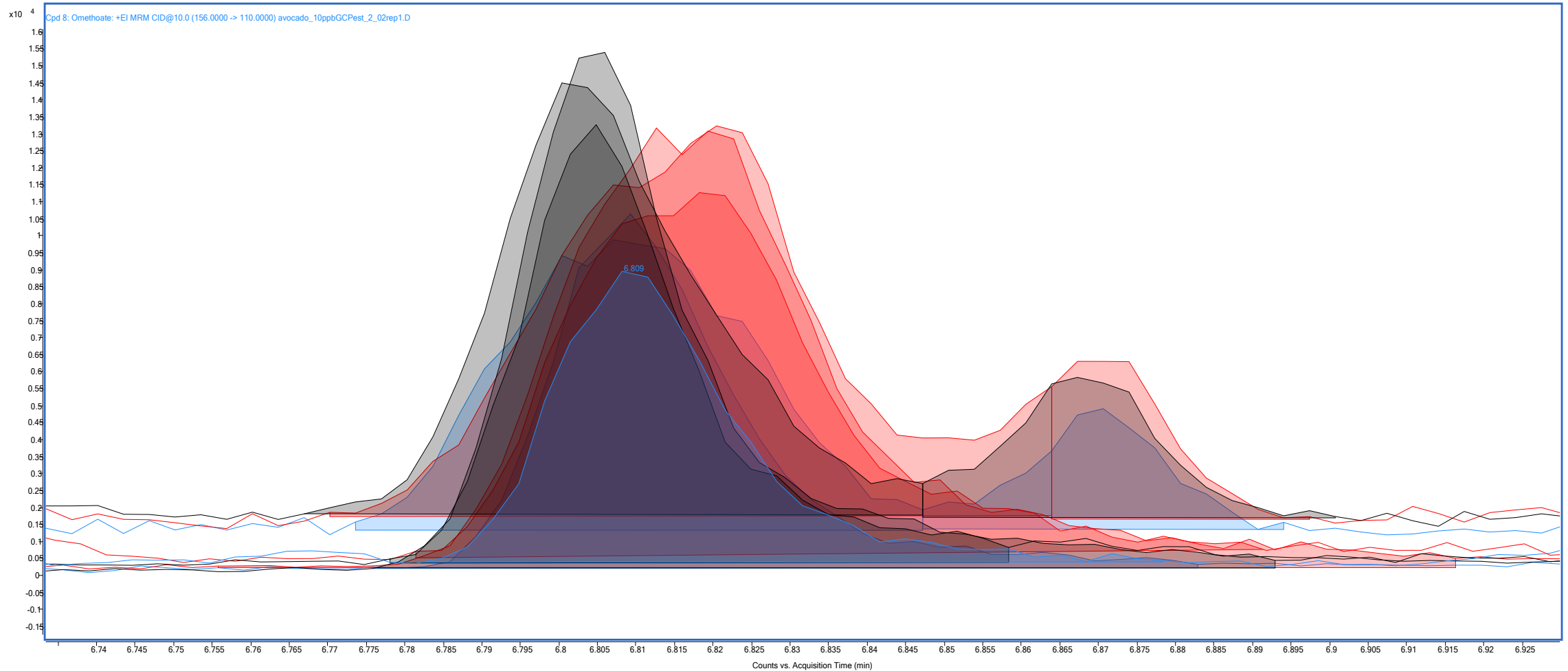
Peak Broadening: Omethoate in Avocado in Run 65



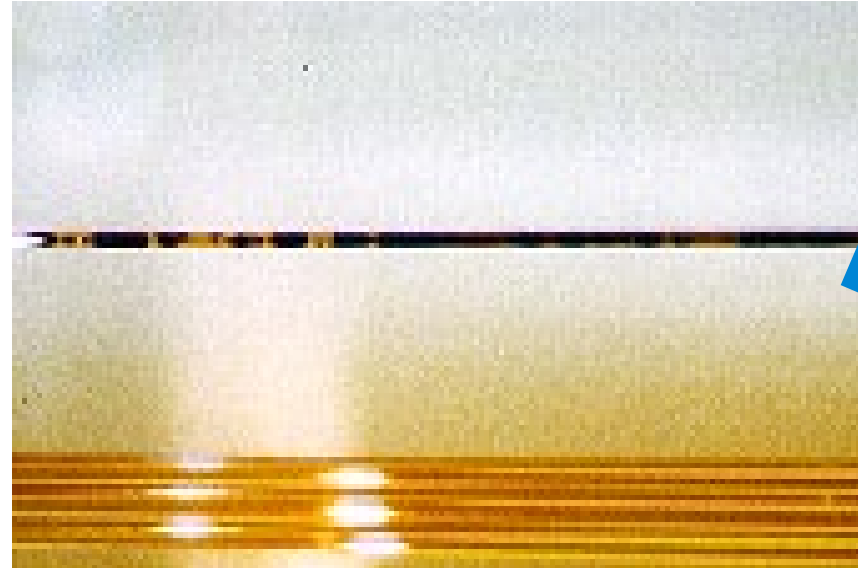
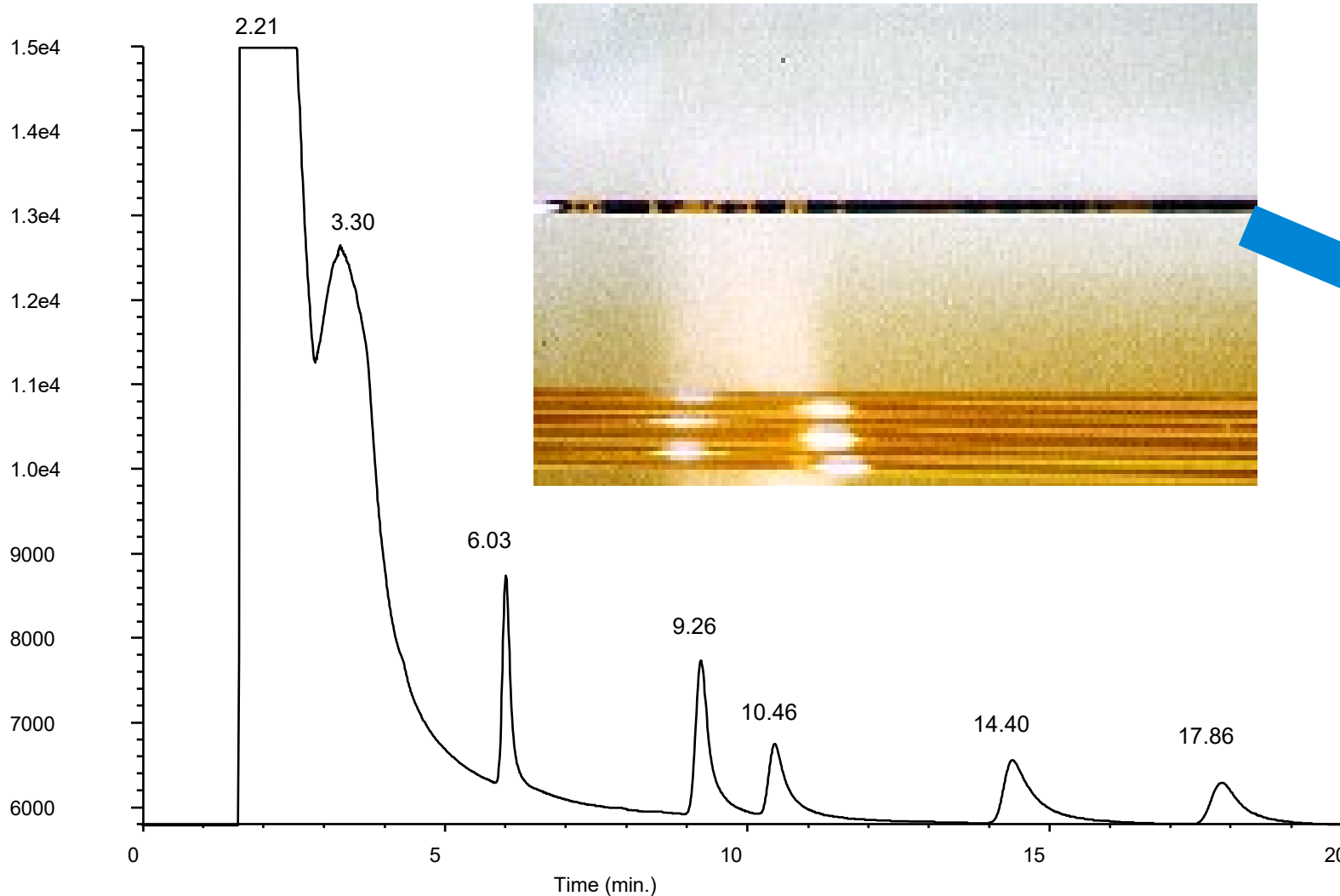
Peak Broadening: Omethoate in Avocado in Run 1 versus Run 65



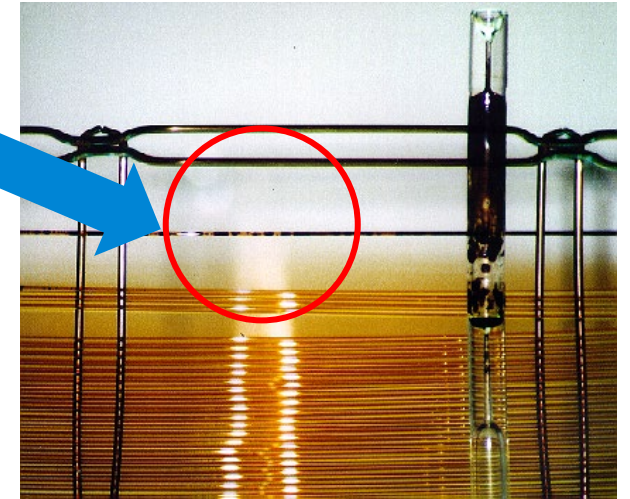
Peak Broadening: Recover Peak Shape with New Liner



Example of Column Contamination and Broad Peaks

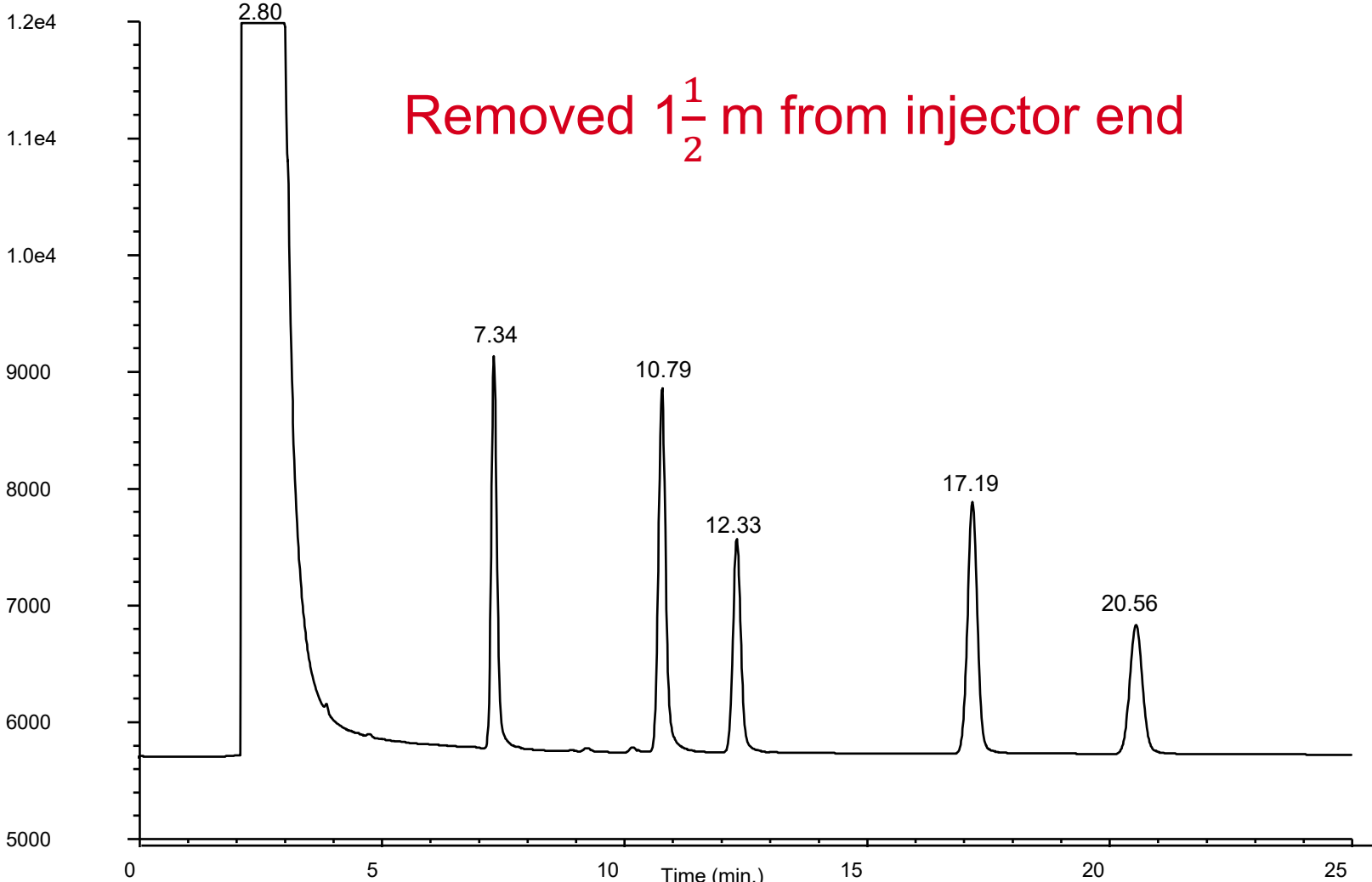


Agilent J&W DB-624 QC Test Mix
After 75 injections of oily sample



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

Example of Column Contamination

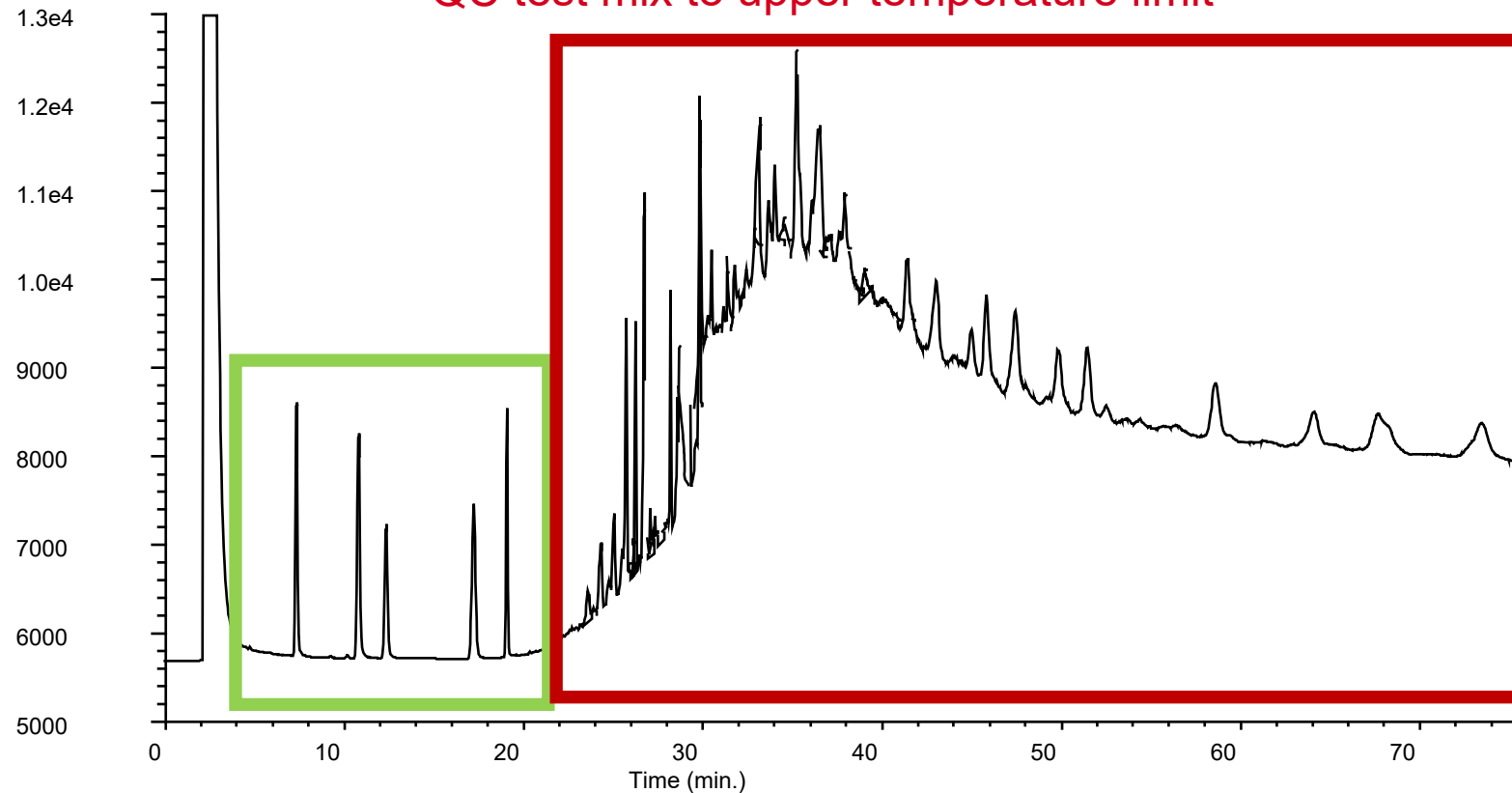


*Before column rinse and bake
Temperature program // 35 °C hold 1.50 min // 30° C/min to 65 °C, hold 10 min

Example of Column Contamination

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

QC test mix to upper temperature limit



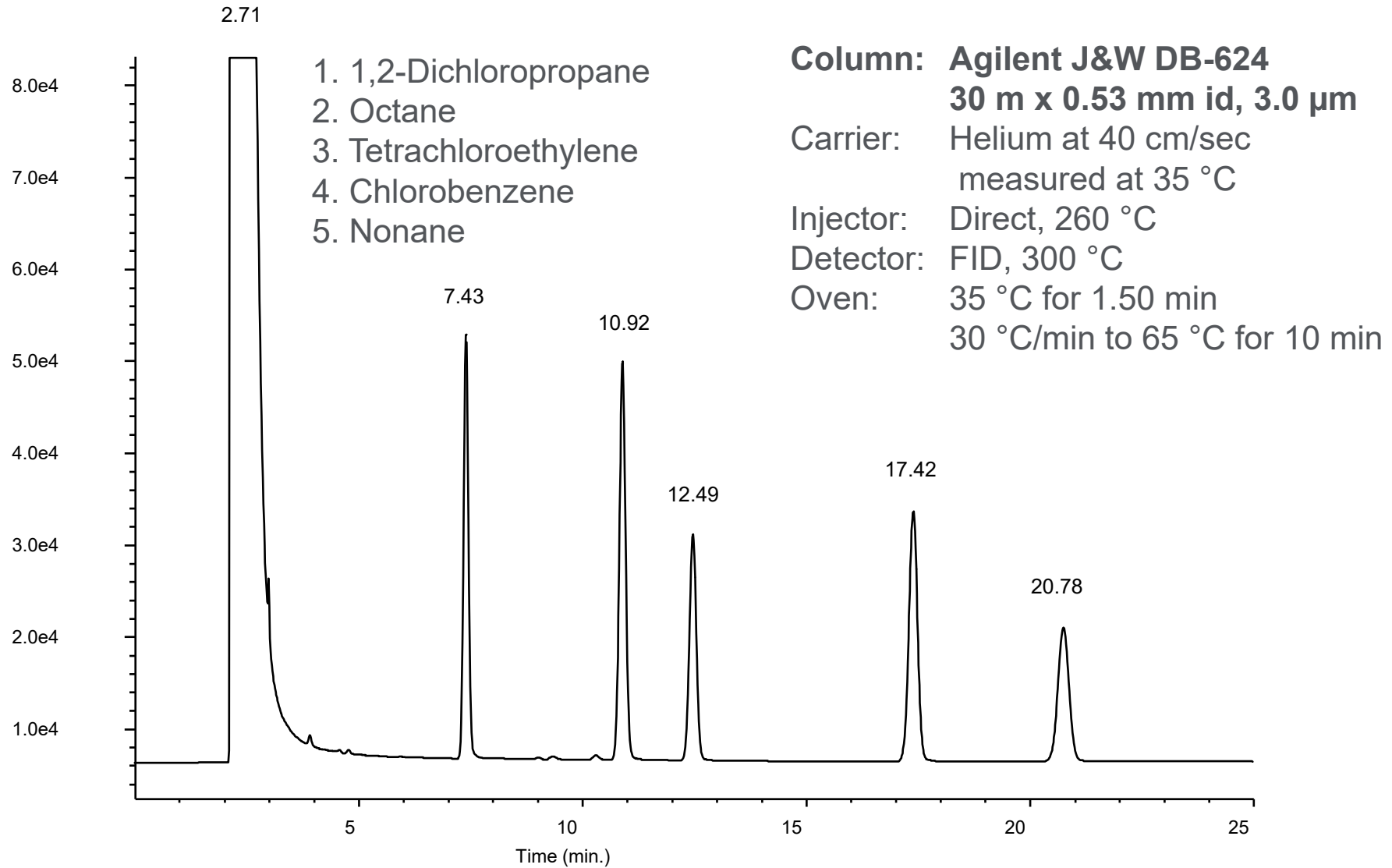
We have more semivolatile contamination!

*Before column bake

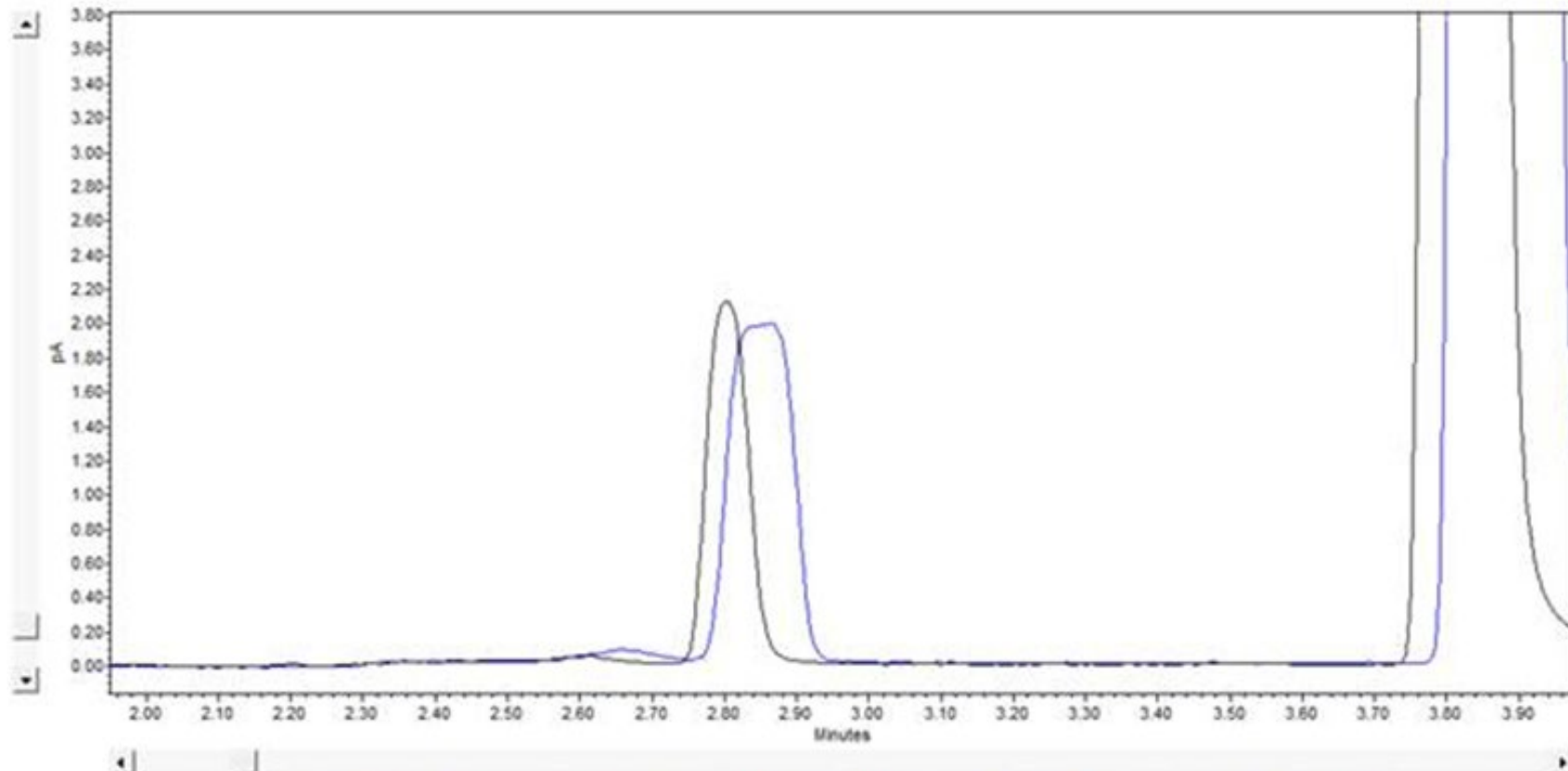
Temperature program // 35 °C, hold 1.50 min // 30 °C/min to 65 °C, hold 15 min // 20 °C/min to 260 °C, hold 50 min

Agilent J&W DB-624 Column

QC Test Mix



Changing to a Higher Split Ratio Improves Peak Sharpness



5:1 Split ratio

10:1 Split ratio

Baseline Disturbances

Sudden changes, wandering, or drifting

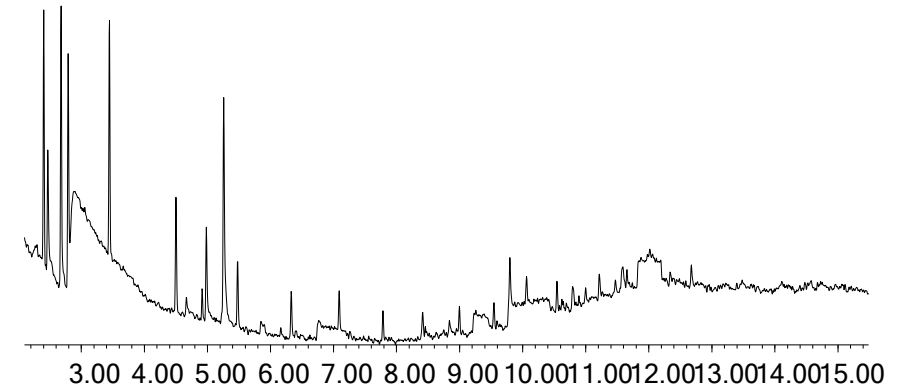
Drifting/wandering/weird disturbances

Column or detector

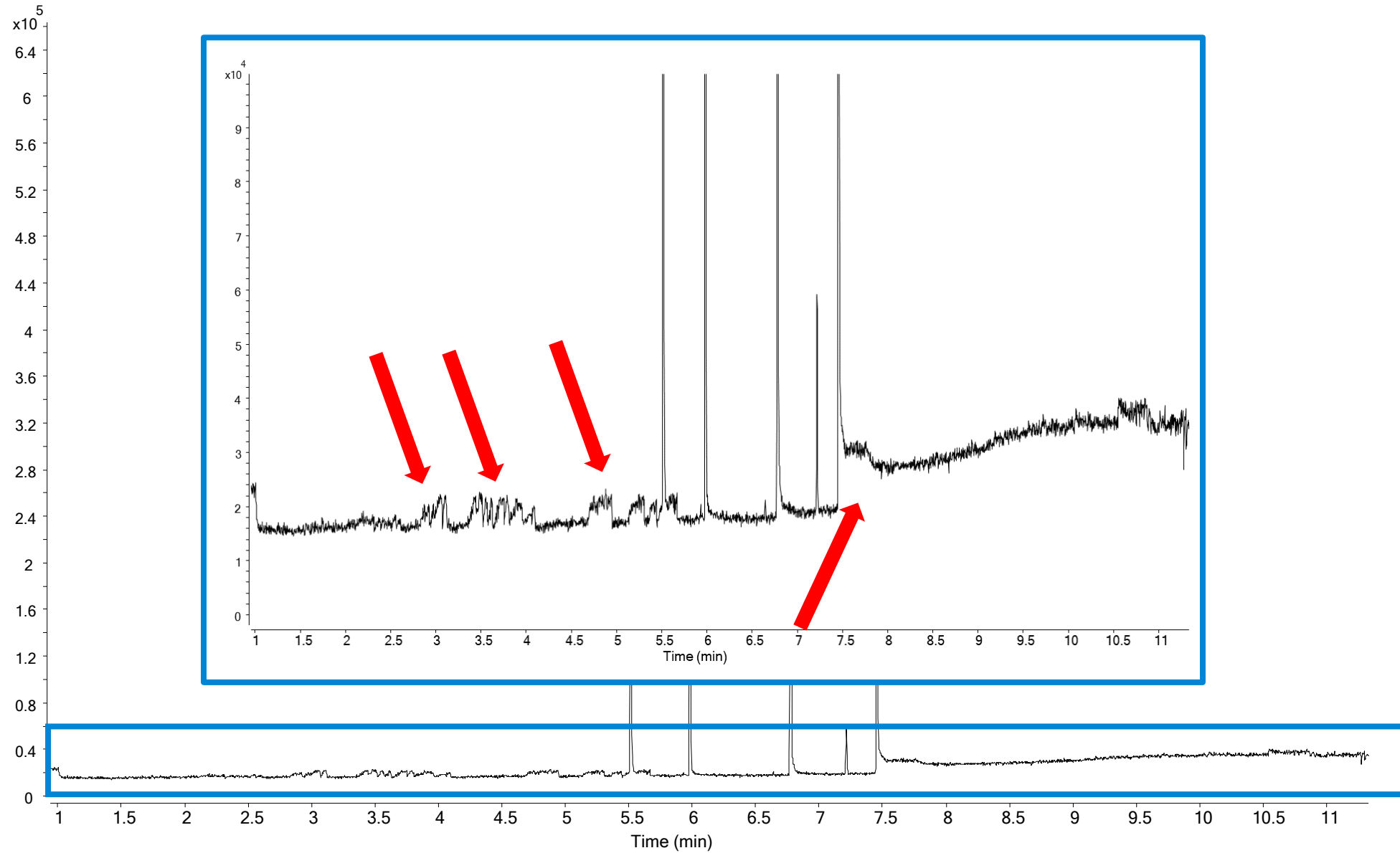
- Not fully conditioned or stabilized (electronics)
- Contamination

Flow

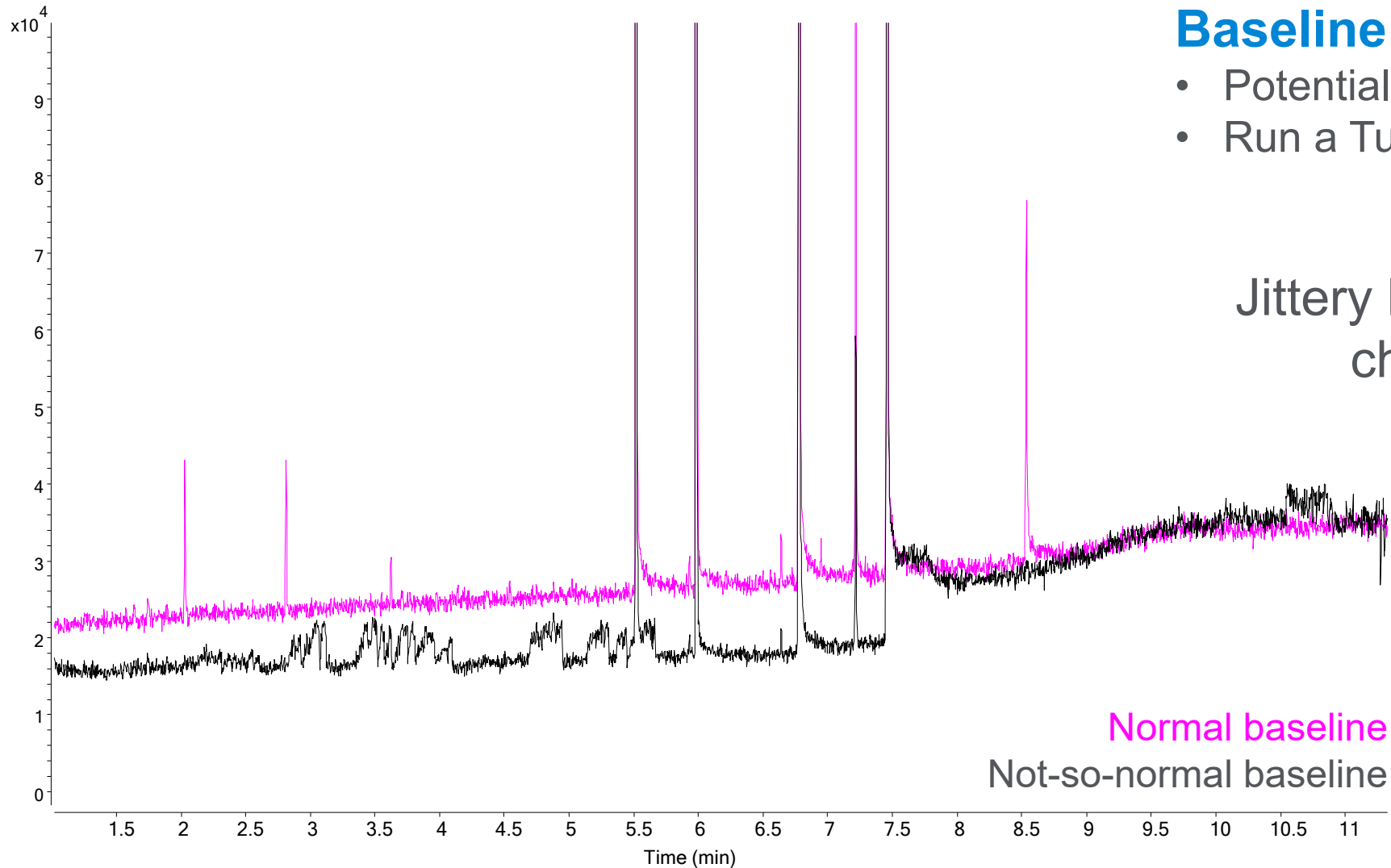
- Changes in carrier and/or detector gas flows
- Valves switching, leaks



Jittery Baseline Example



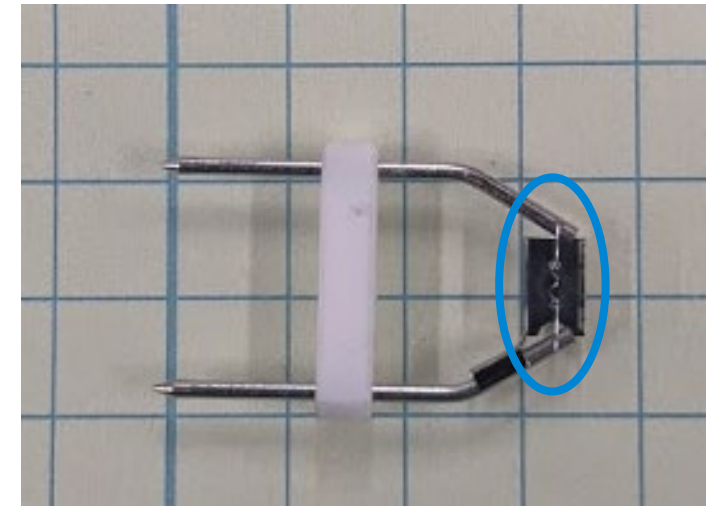
Jittery Baseline Example



Baseline is not normal

- Potential issues with filaments
- Run a Tune Evaluation

Jittery baseline + failed Tune =
check your filaments

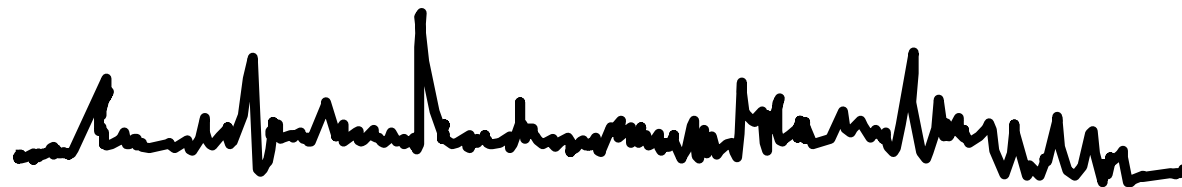


Noisy Baseline

Mild



Severe



Flow

- Contaminated gas
- Incorrect detector settings

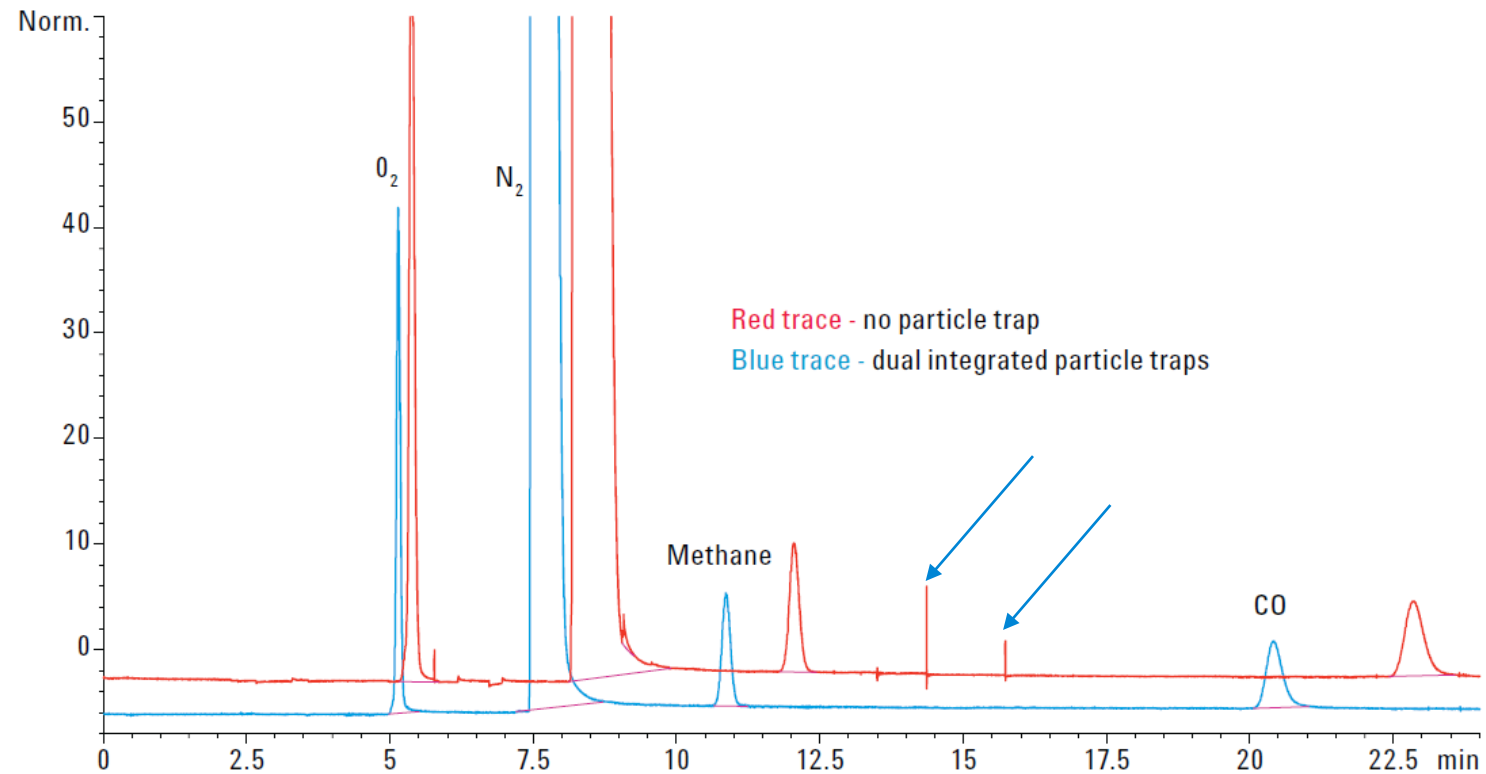
Detector

- Air leak - ECD, TCD
- Electronics malfunction

Column

- Bleed if at high temperature
- In detector flame (poor installation)

Spiking Baseline



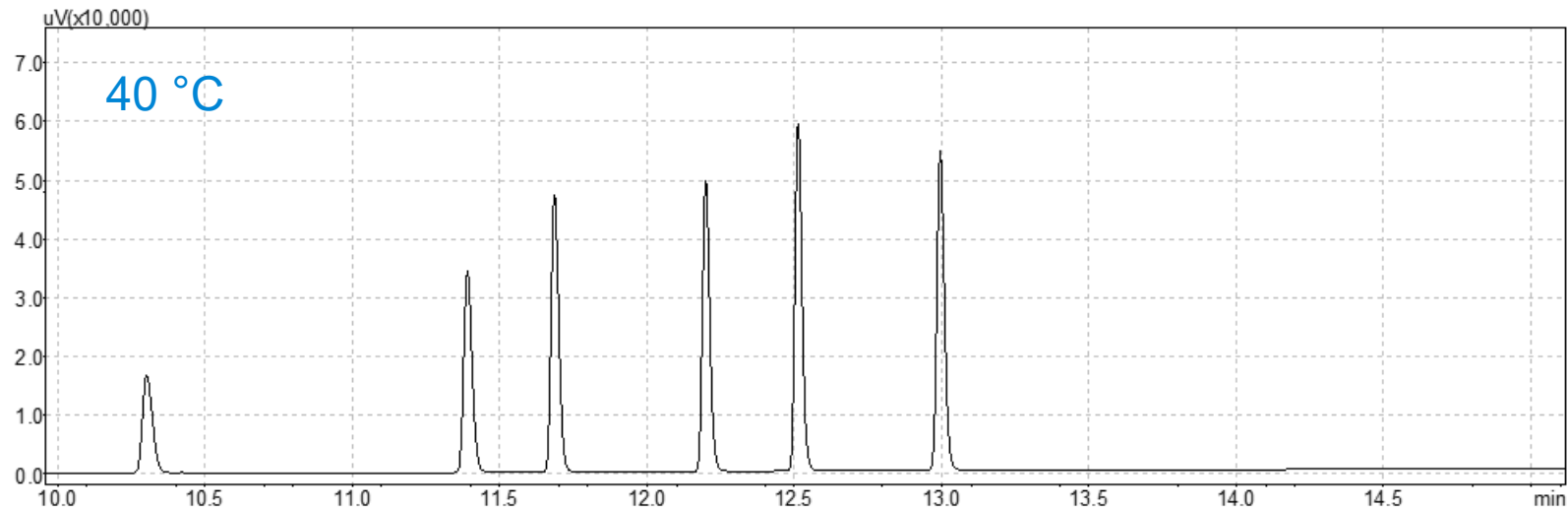
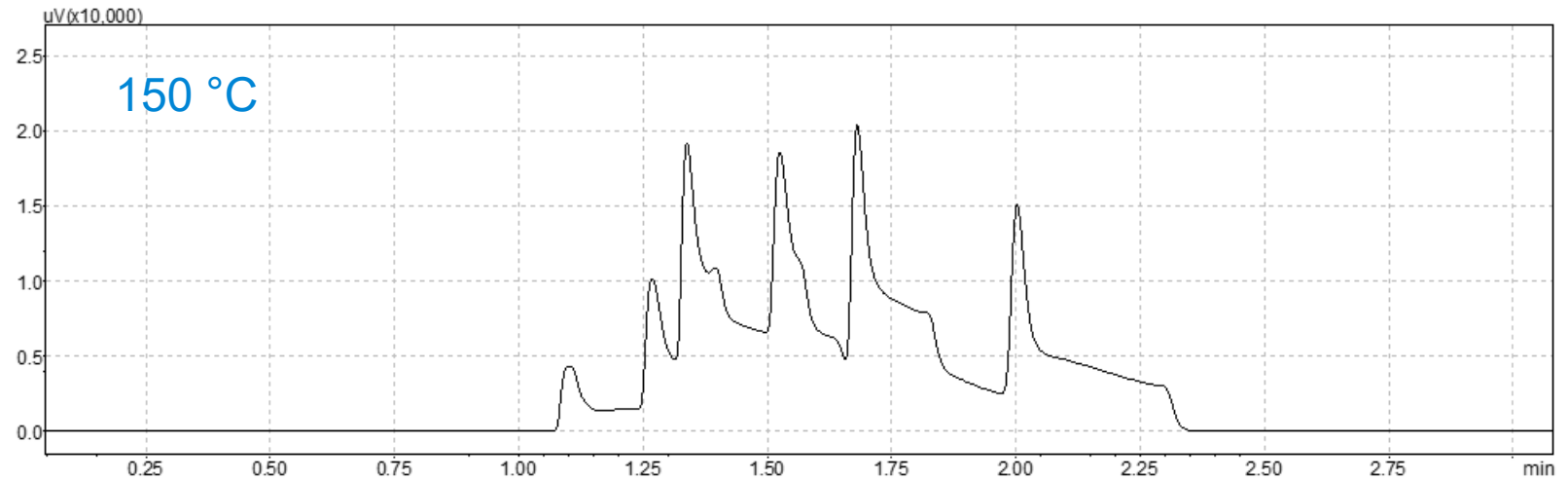
Detector

- Particles entering the detector
- Random: poor connection
- Regular: nearby "cycling" equipment (electronics)

Application note 5991-2975EN

Weird Peak Shape Due to Lack of Analyte Refocusing

Free fatty acids in water on DB-FATWAX UI



Quantitation Problems

Detector

- Poor stability (electronics) or baseline disturbances (contamination)
- Outside detector's linear range or wrong settings
- Integration parameters

Activity (adsorption) in injector or column

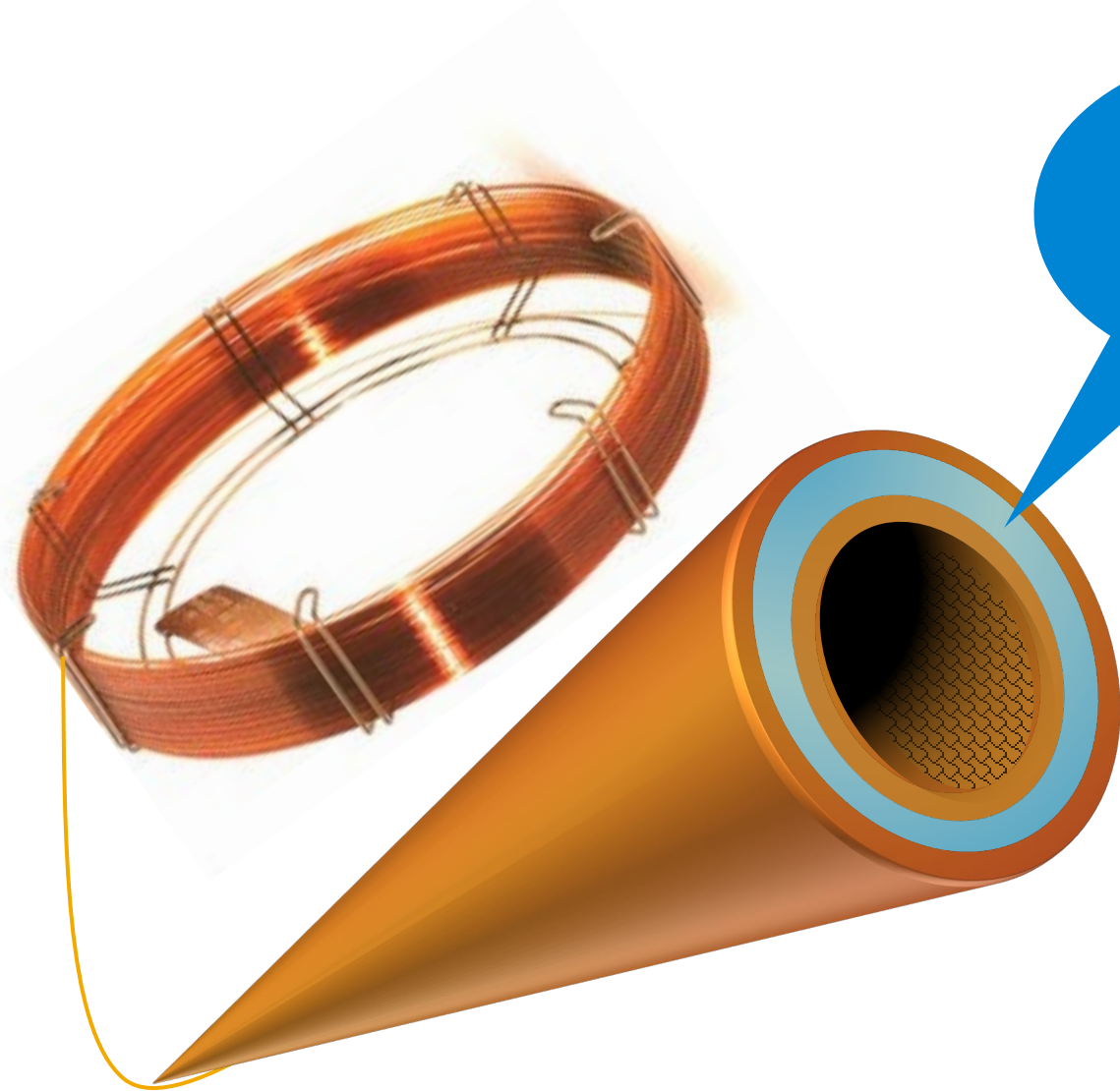
Injector

- Technique, settings, conditions
- Syringe worn

Other

- Coelution
- Matrix effects
- Sample evaporation – leaky vials
- Sample decomposition

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

Troubleshooting Techniques



Troubleshooting Tools

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

Inject a nonretained peak: *peak shape problems*

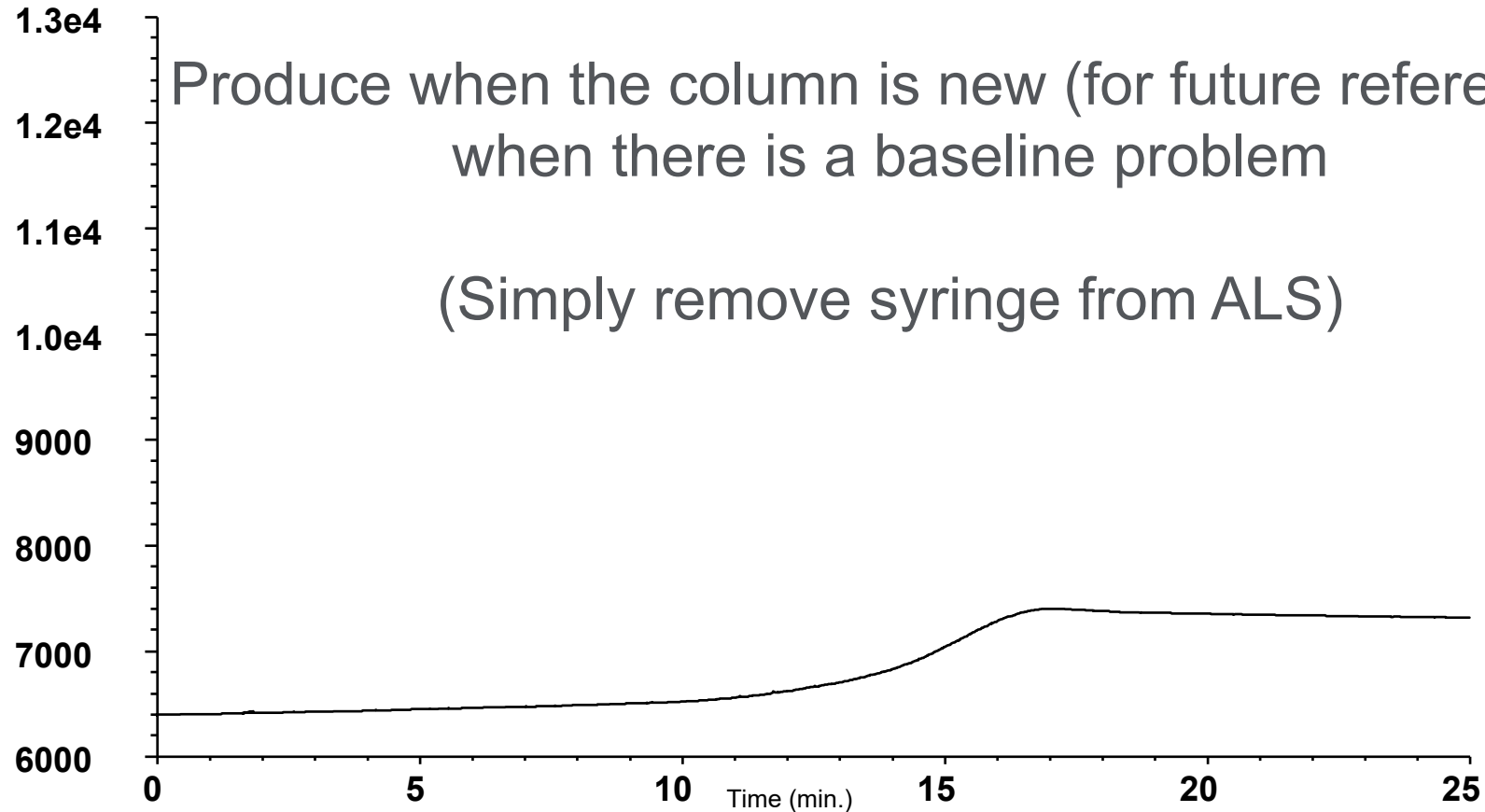
Test mix: *all problems*

Isolate the components: *all problems*

Condensation test: *baseline problems*

Jumper tube test: *baseline problems*

Generating a Bleed Profile

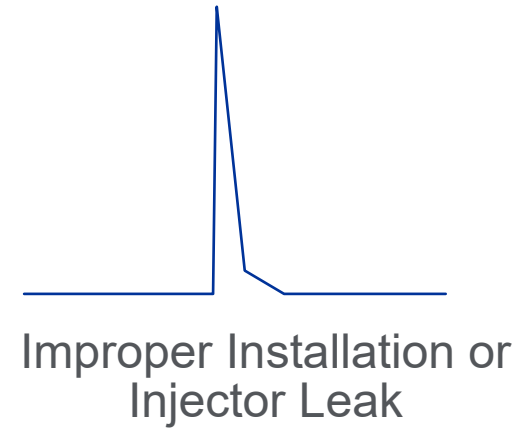
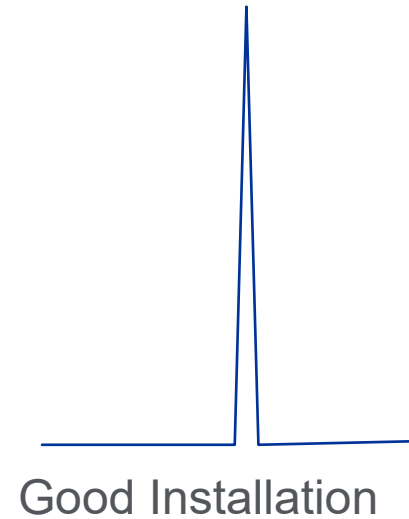


Agilent J&W DB-1, 30 m x 0.32 mm id, 0.25 μ m

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



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)

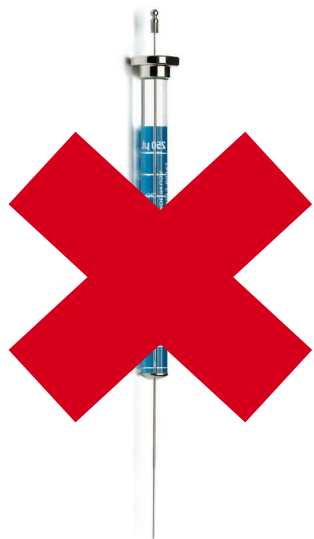
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- Sample preparation materials, columns, supplies, instrumentation, and reference materials from a single source



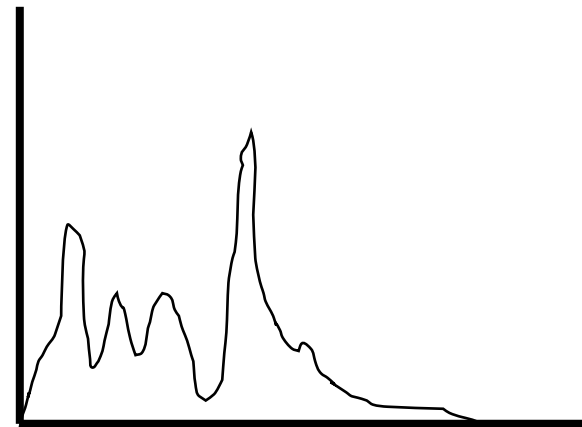
Perform a Noninjection “Blank”



Remove syringe
from autosampler



Run your program



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

Condensation Test

A condensation test is used to isolate the cause of:

- Erratic baselines
- Ghost peaks or carryover

For use when problems are worse after periods of GC nonuse.

Condensation Test

Procedure

- Leave GC at 40–50 °C for > 8 hours
- Blank run
- Repeat a blank run immediately after the first blank run is complete
- Compare the two blank runs

Condensation Test

Results

- First blank run is worse: Contaminants (from injector, lines, traps, traps, or carrier gas) carried into the column.
- Blank runs the same: **Contaminants are not strongly focused on the front of the column.**

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 meters 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!

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



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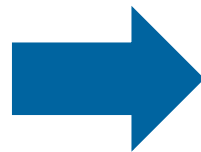
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Troubleshooting Tips

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

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