Peak Perfection: A Guide to GC Troubleshooting

Gas Chromatography

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February 4, 2025

Agilent
Trusted Answers

“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.

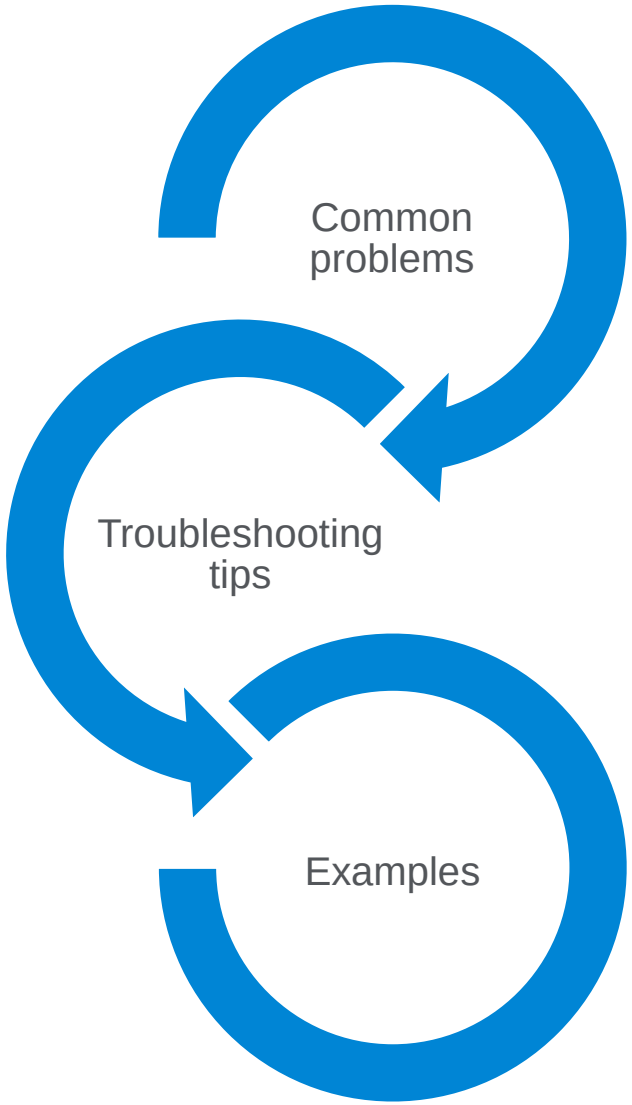
- There are five basic areas where problems can arise:
  - -Injector
  - -Flow
  - -Column
  - -Detector
  - -Electronics

  Or…

  - A combination of these

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

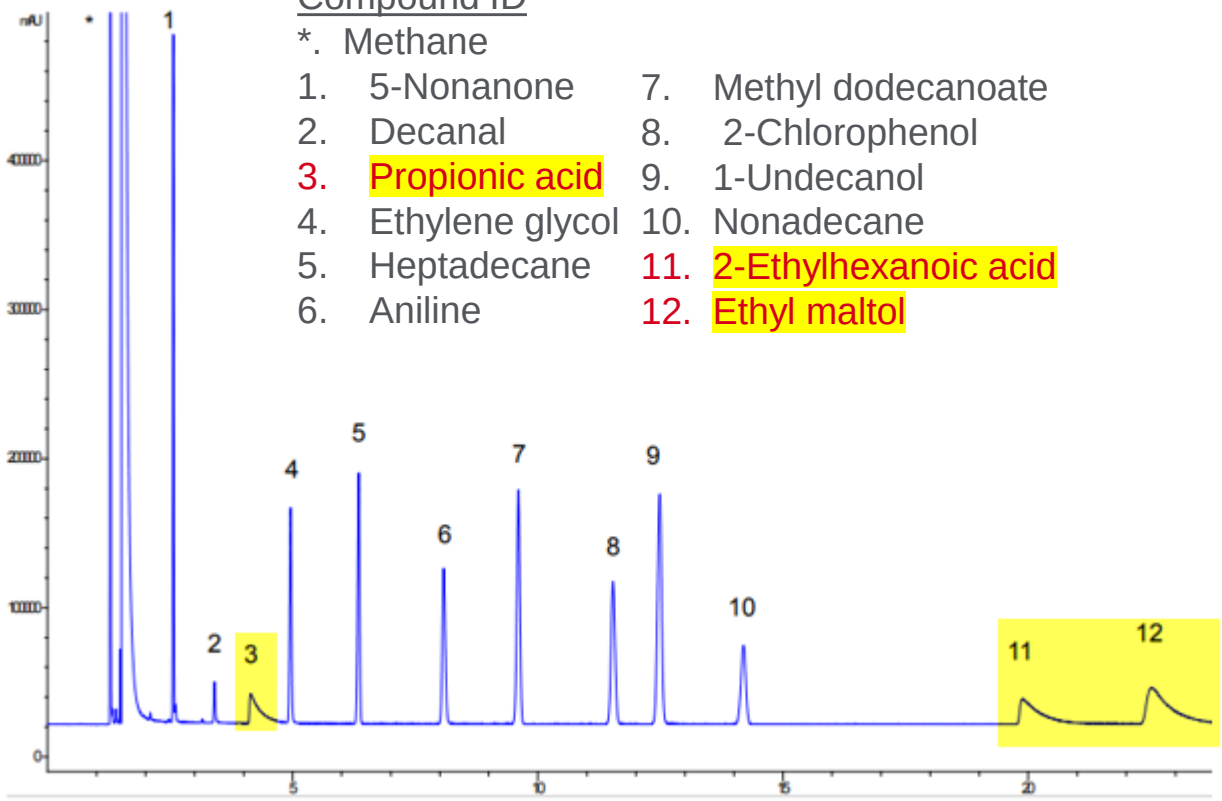
Agenda



Common Peak Shape Issues

- **Peak tailing** – flow path or activity
- **Bonus peaks** – in sample or back flash (carryover)
- **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

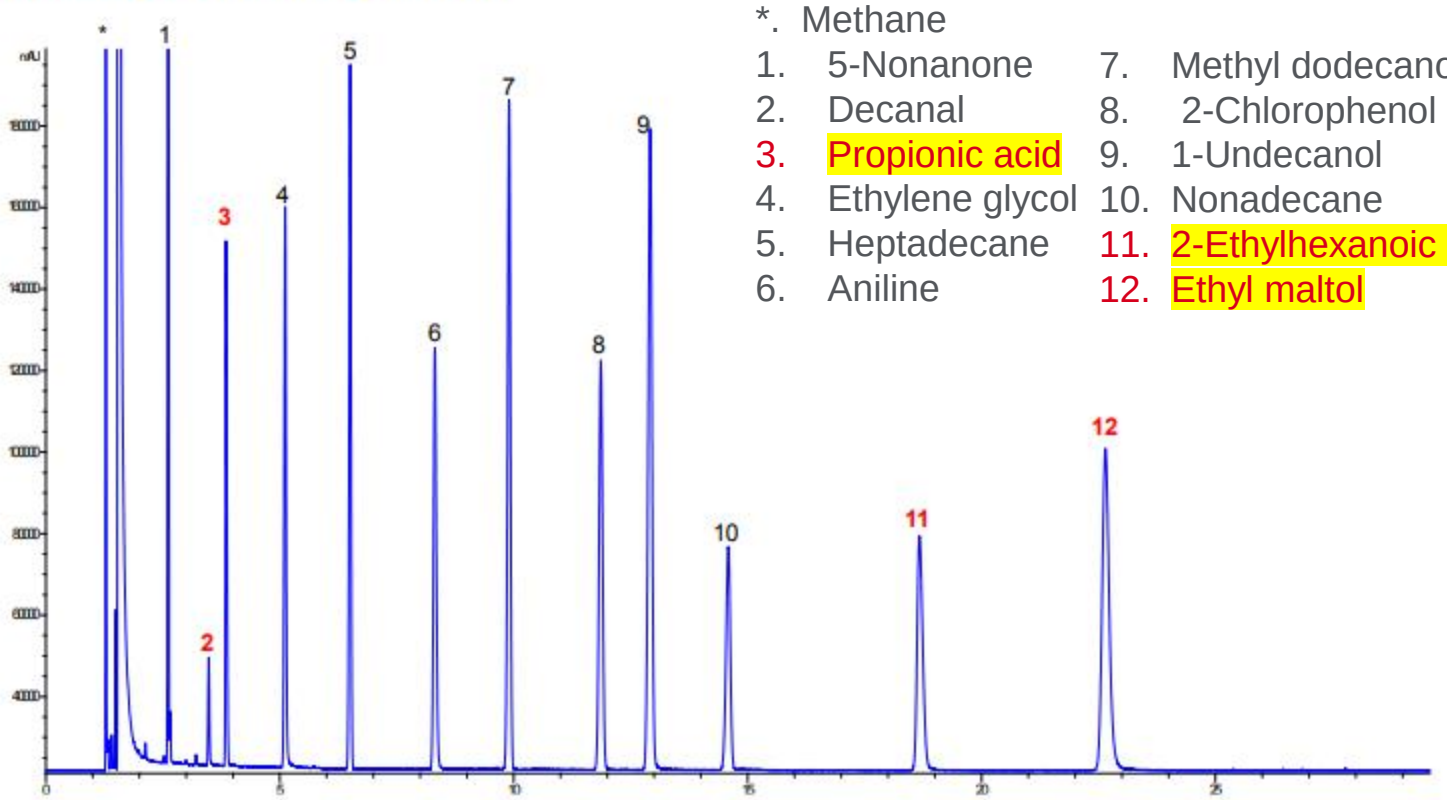
Miscellaneous - overloading of PLOT columns, coelution, polarity mismatch between phase, solute or solvent, and some compounds always tail

***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



Compound ID

*. Methane
1. 5-Nonanone
2. Decanal
3. Propionic acid
4. Ethylene glycol
5. Heptadecane
6. Aniline
7. Methyl dodecanoate
8. 2-Chlorophenol
9. 1-Undecanol
10. Nonadecane
11. 2-Ethylhexanoic acid
12. Ethyl maltol

Agilent publication 5991-6709EN

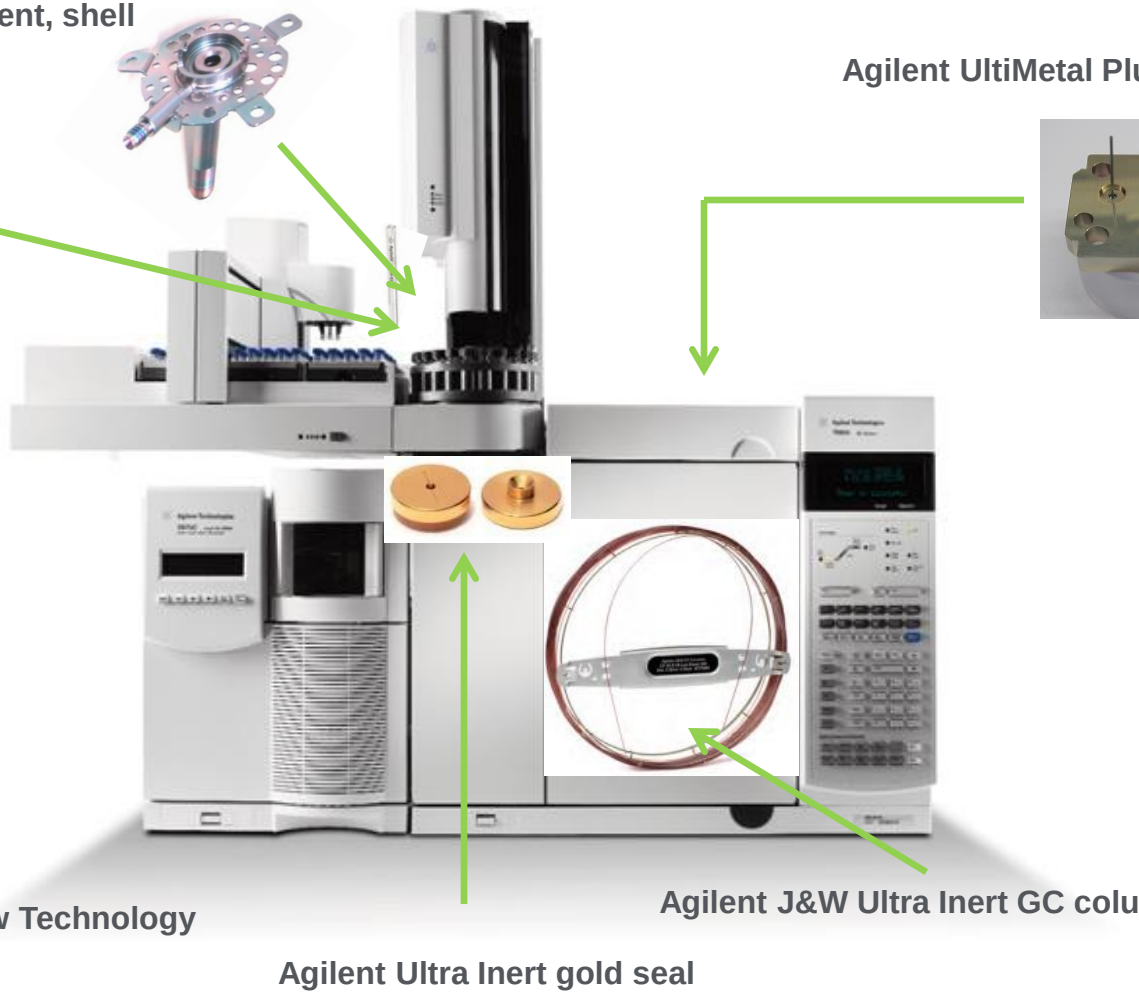
Agilent Inert Flow Path Solution

Agilent UltiMetal Plus inlet weldment, shell and transfer lines

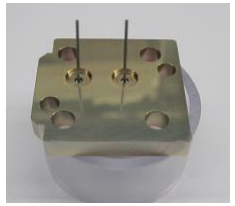
Agilent Ultra Inert inlet liner

Agilent UltiMetal Plus ferrules

Agilent UltiMetal Capillary Flow Technology Devices, Ultimate union



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



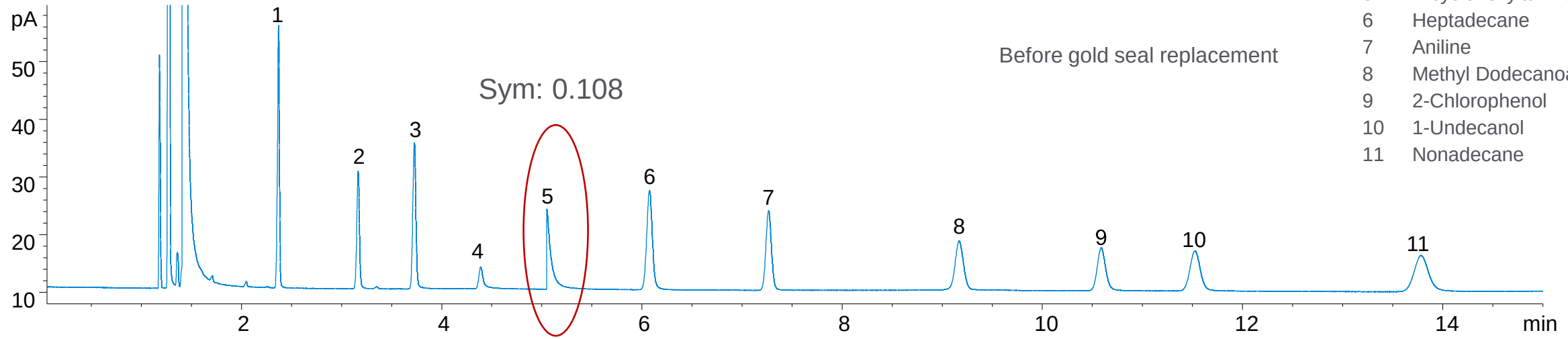
Agilent J&W Ultra Inert GC column

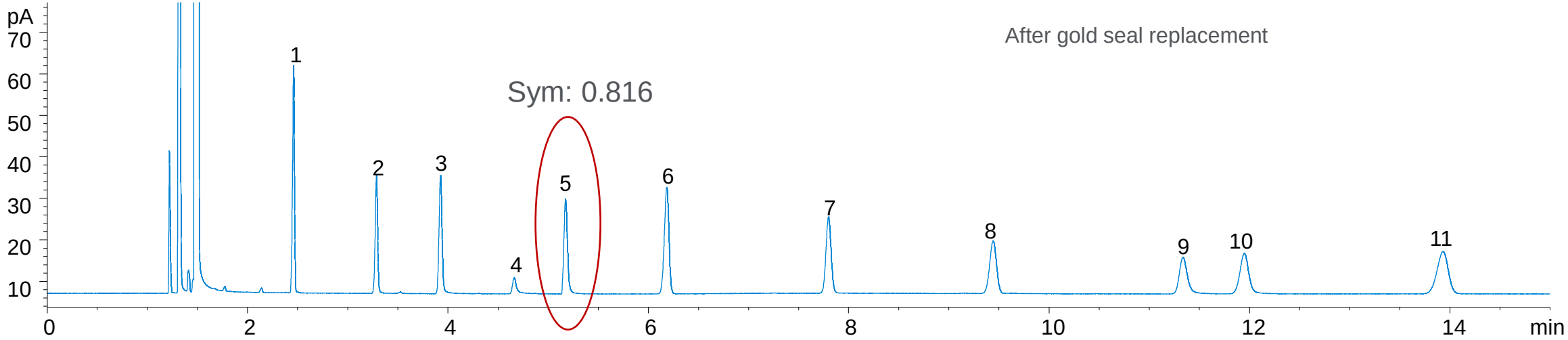
Agilent Ultra Inert gold seal

Agilent publication 5990-8532EN

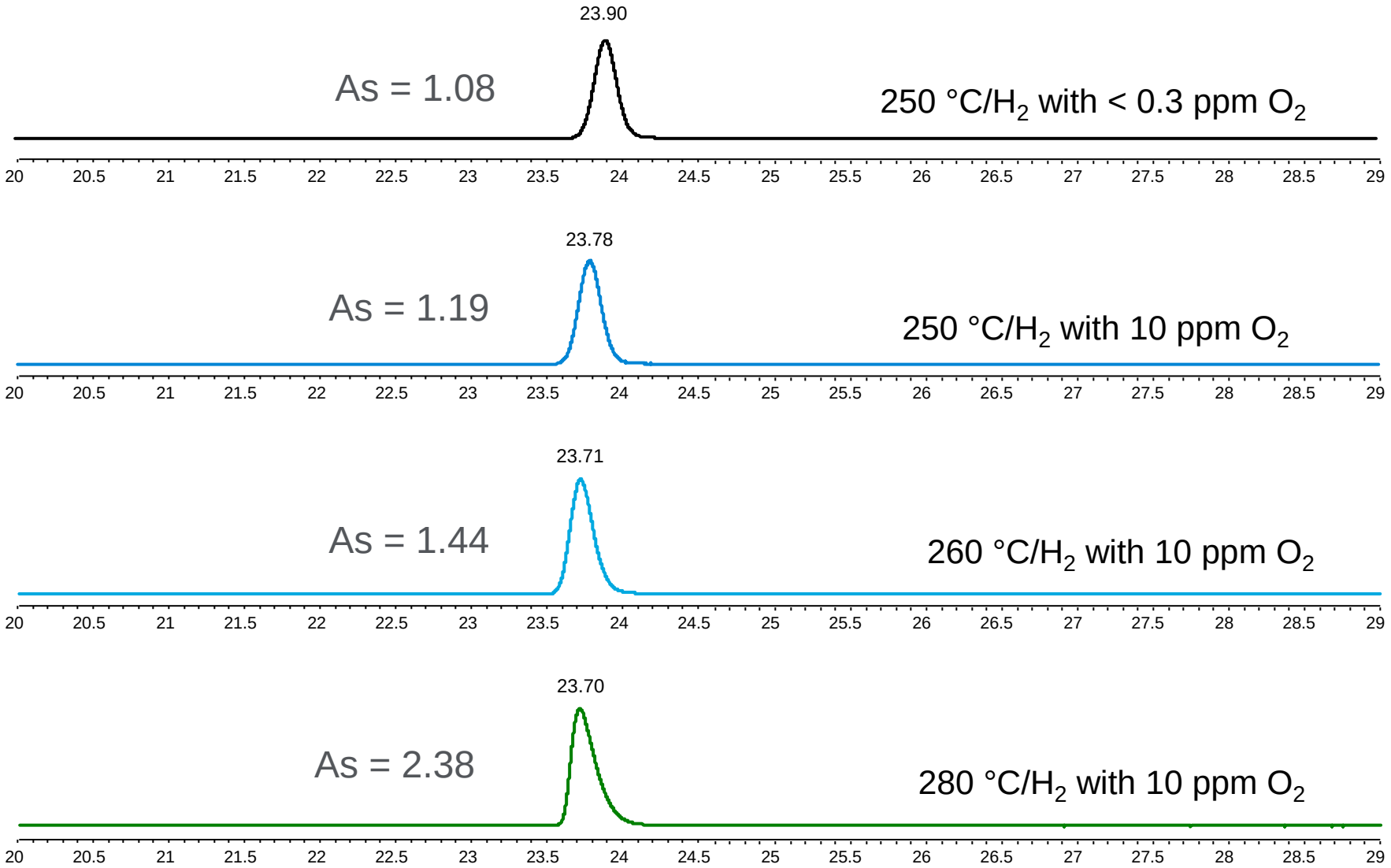
Peak Tailing from Contaminated Consumables

Peak	
0	Methane
1	2-Nonanone
2	Decanal
3	2,3-Butanediol
4	Ethyele 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



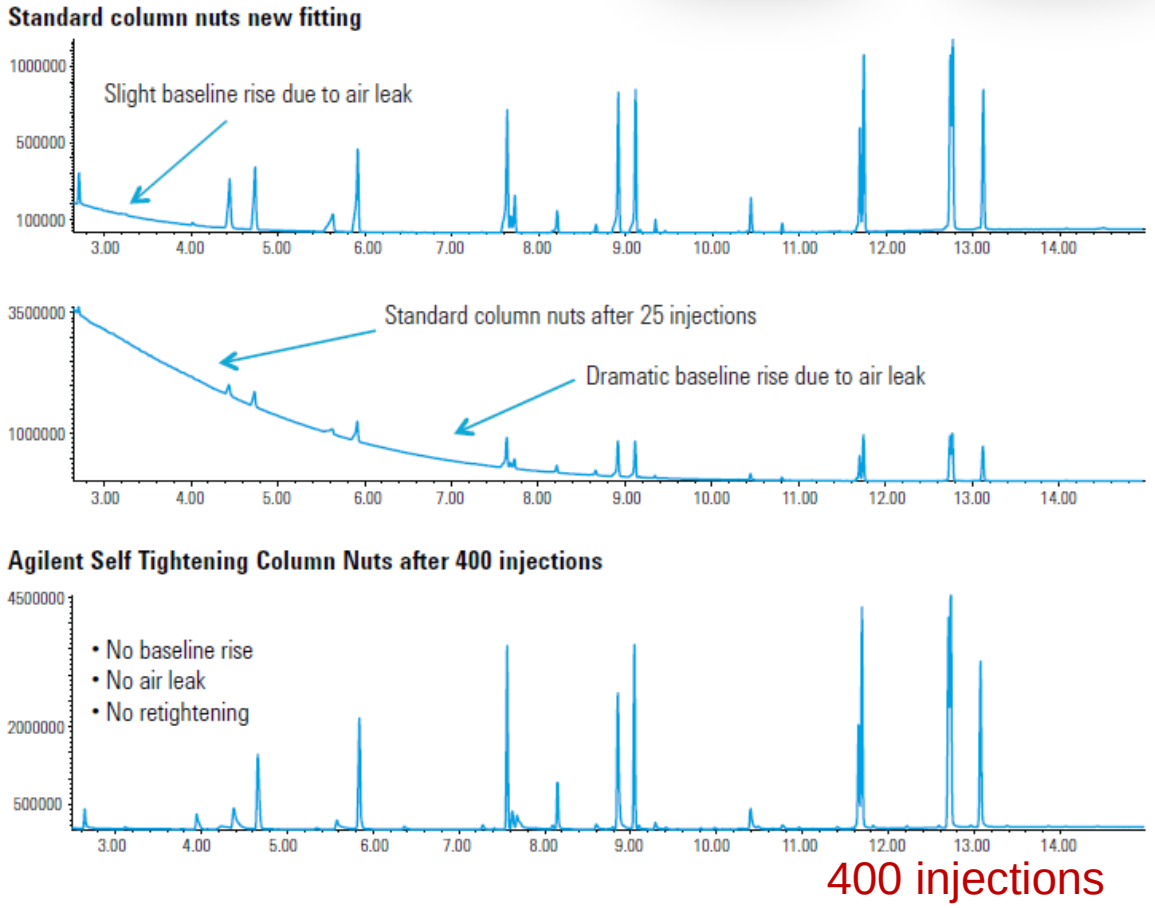
Self Tightening Nuts: No Leaks, No Downtime, No Frustration

- 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/detector
G3440-81012	Collar for self tightening nut

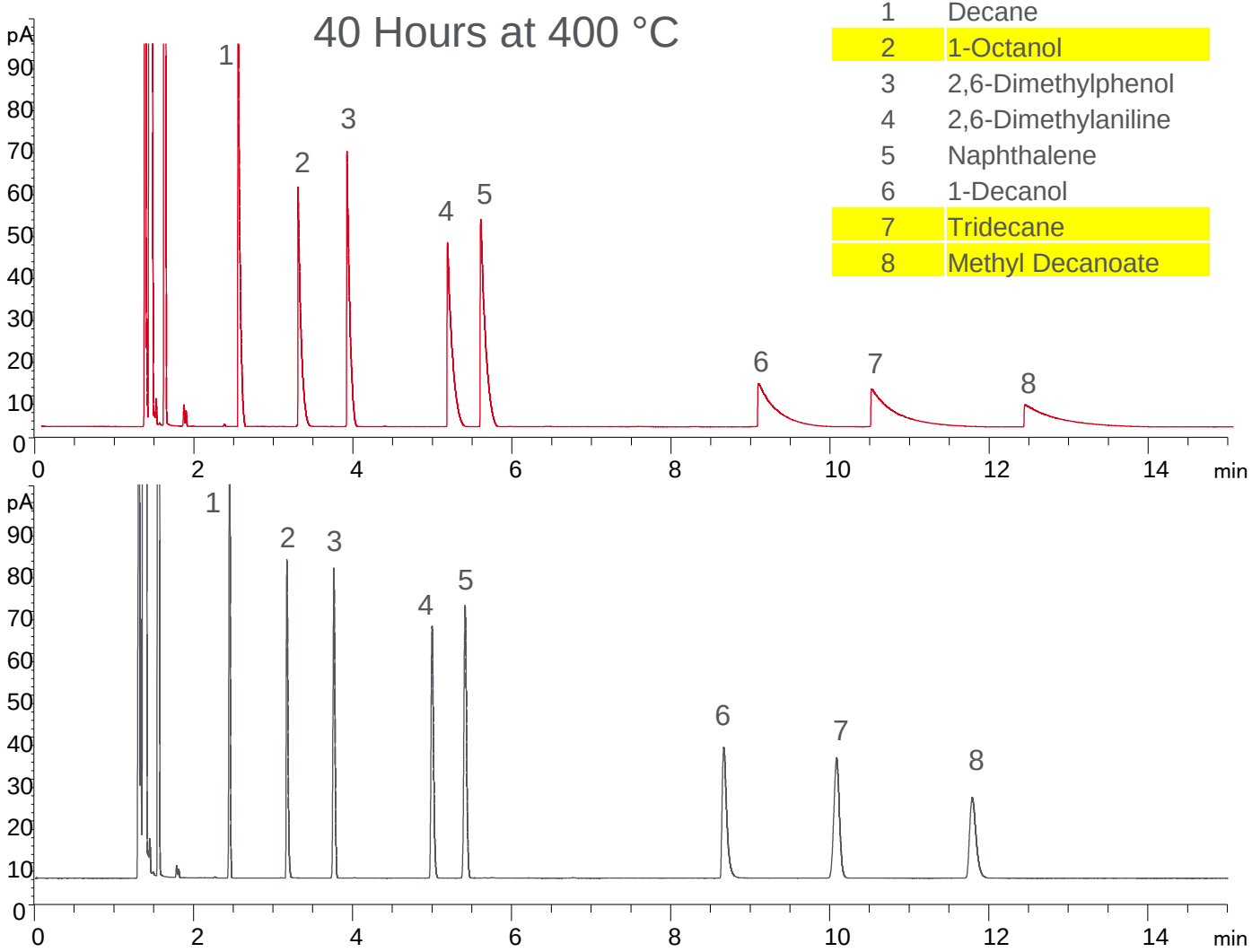
https://www.agilent.com/en/video/gc-supplies-innovation

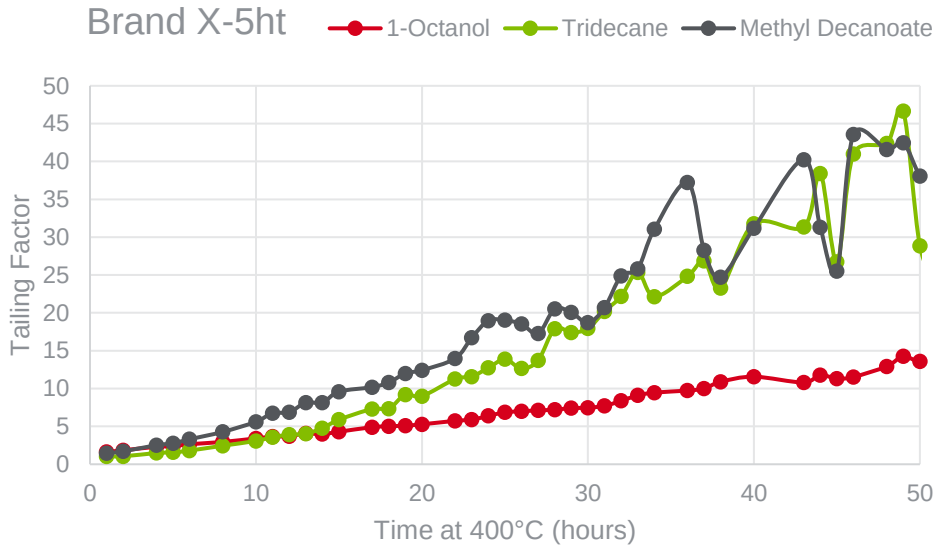
https://www.agilent.com/en/video/stcn-inlet-detector
https://www.agilent.com/en/video/stcn-mass-spec

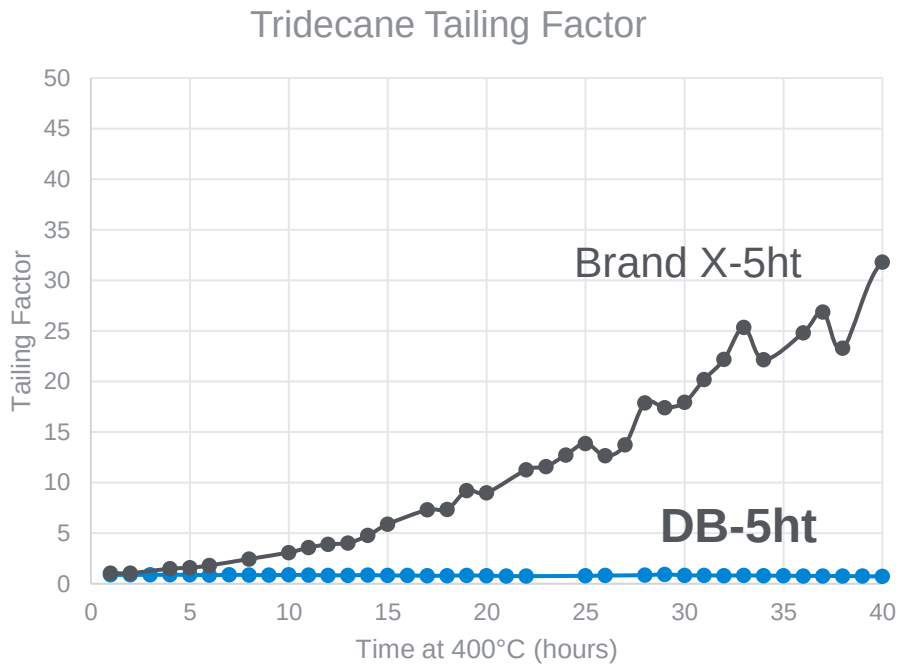


Peak Tailing from Thermal Degradation

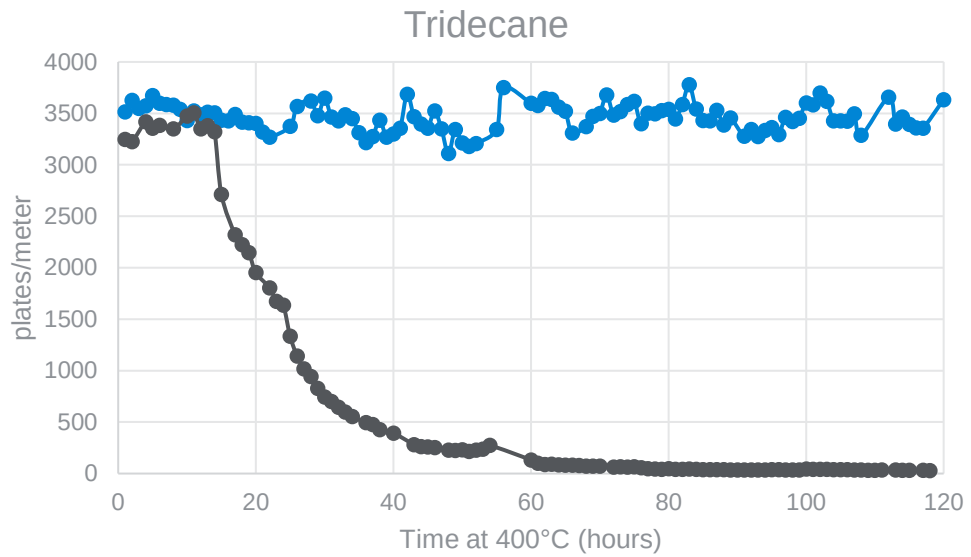
Peak	Name
0	Methane
1	Decane
2	1-Octanol
3	2,6-Dimethylphenol
4	2,6-Dimethylaniline
5	Naphthalene
6	1-Decanol
7	Tridecane
8	Methyl Decanoate







Column Efficiency Over 120 Hours at 400 °C



Peak	Name
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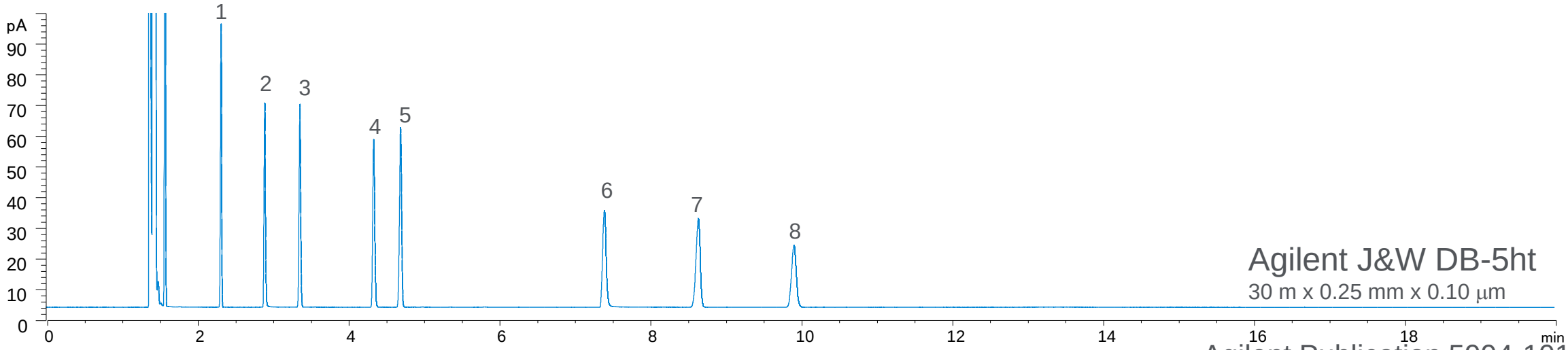
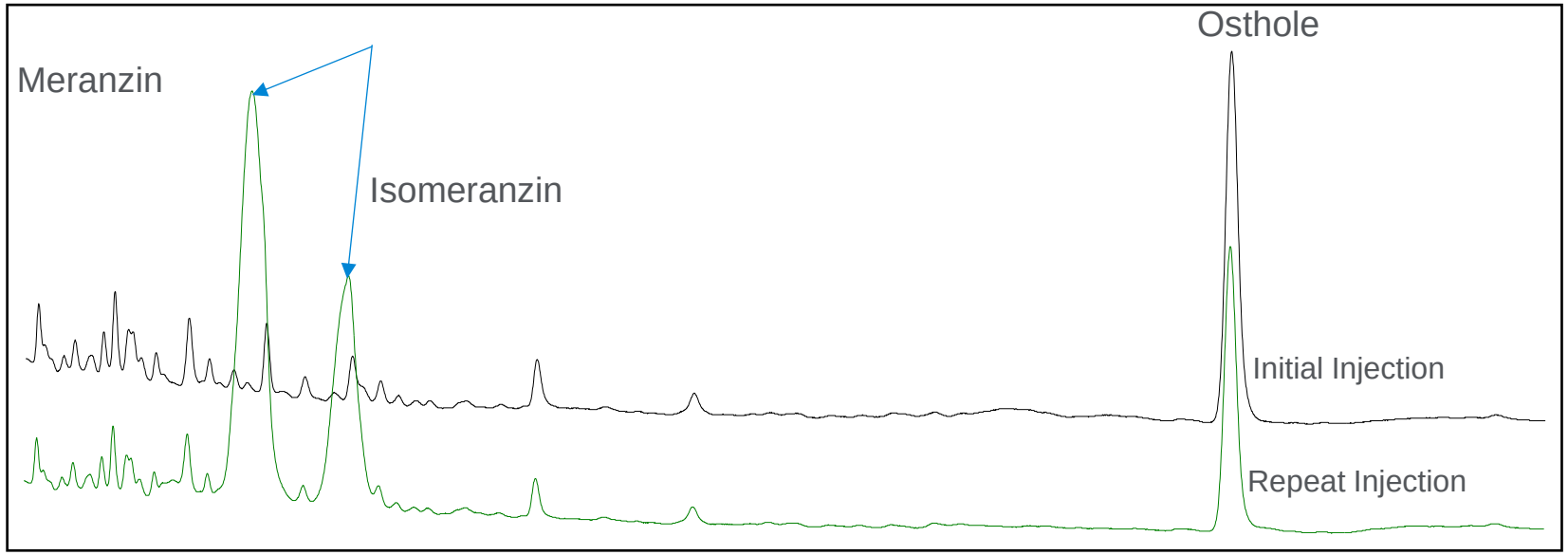
Brand X-5ht
30 m x 0.25 mm x 0.10 µm



Agilent J&W DB-5ht
30 m x 0.25 mm x 0.10 µm

Agilent Publication 5994-1013EN

Bonus or Ghost Peaks



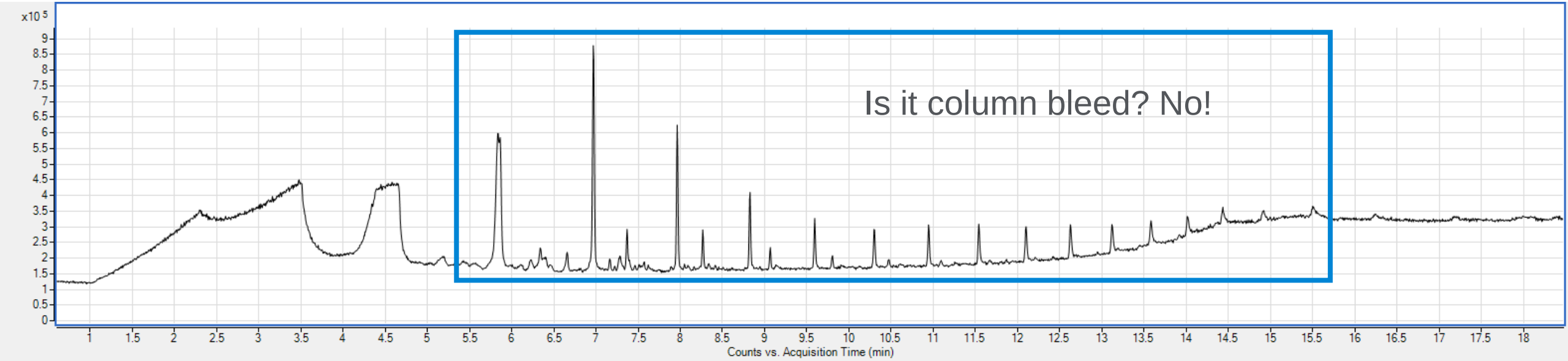
Contamination in injector, column, or flow (carrier gas)

- 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!

Agilent publication 5991-9078EN

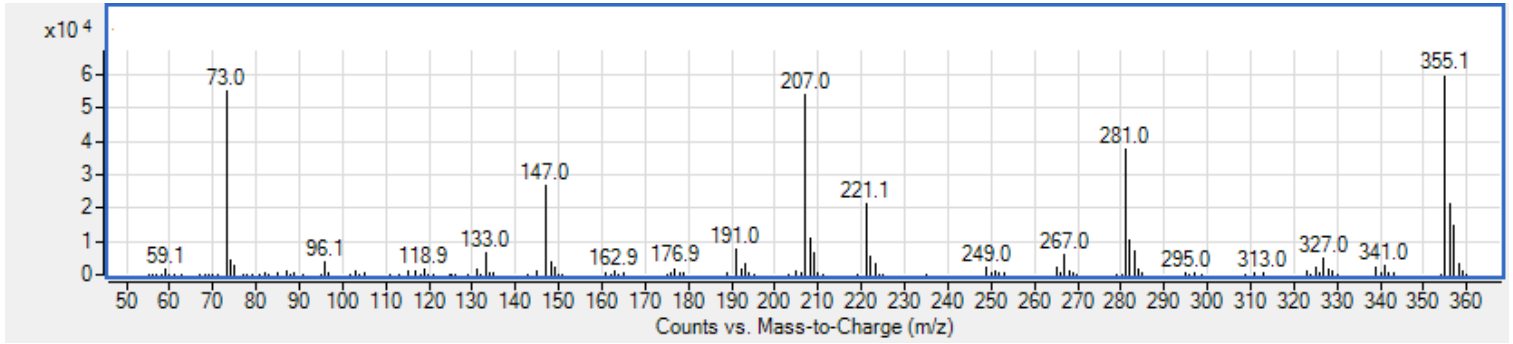
What Are These Repeating Peaks?



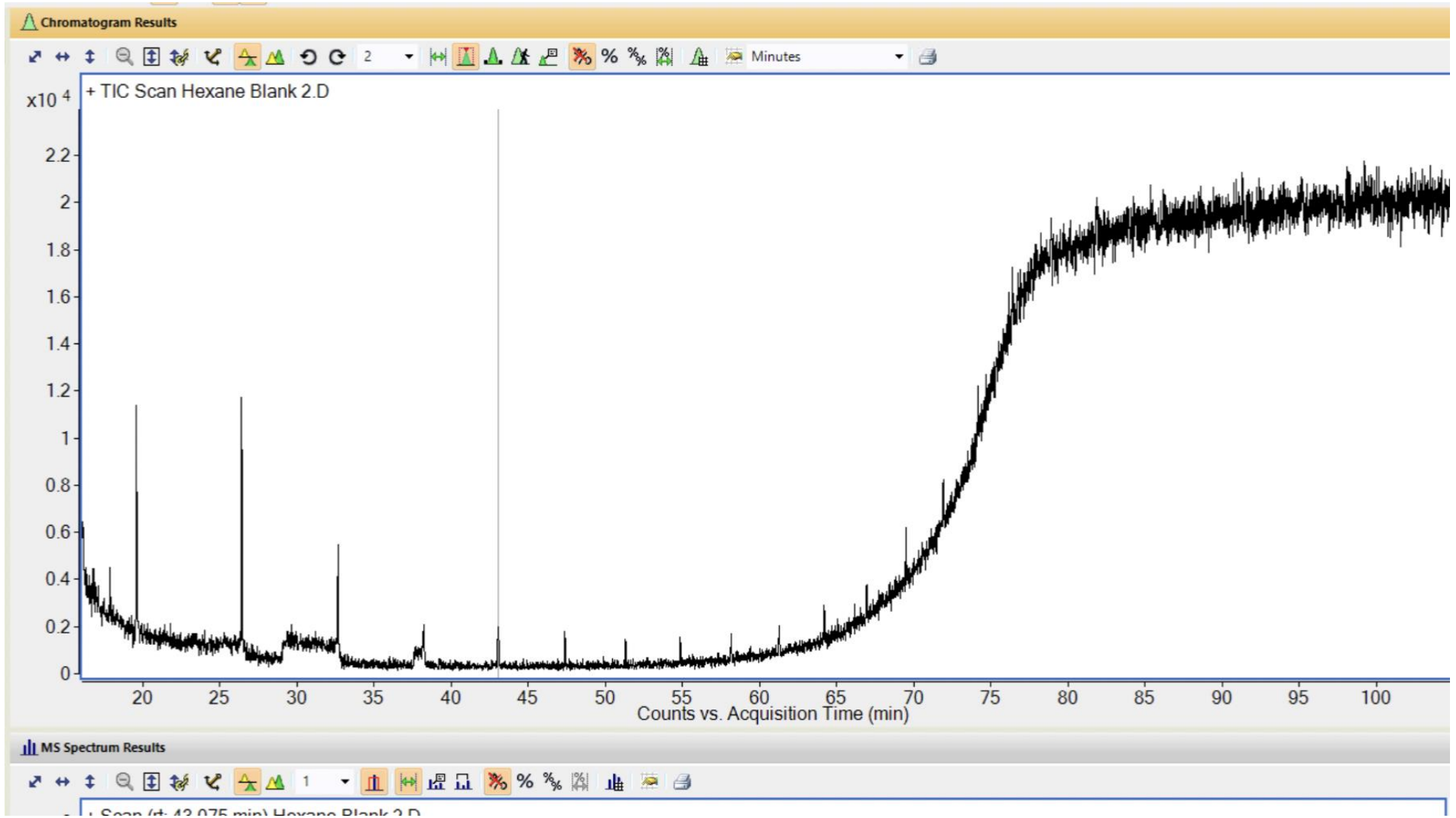
Common ions for siloxane molecules:
73
147
207
281
355

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.

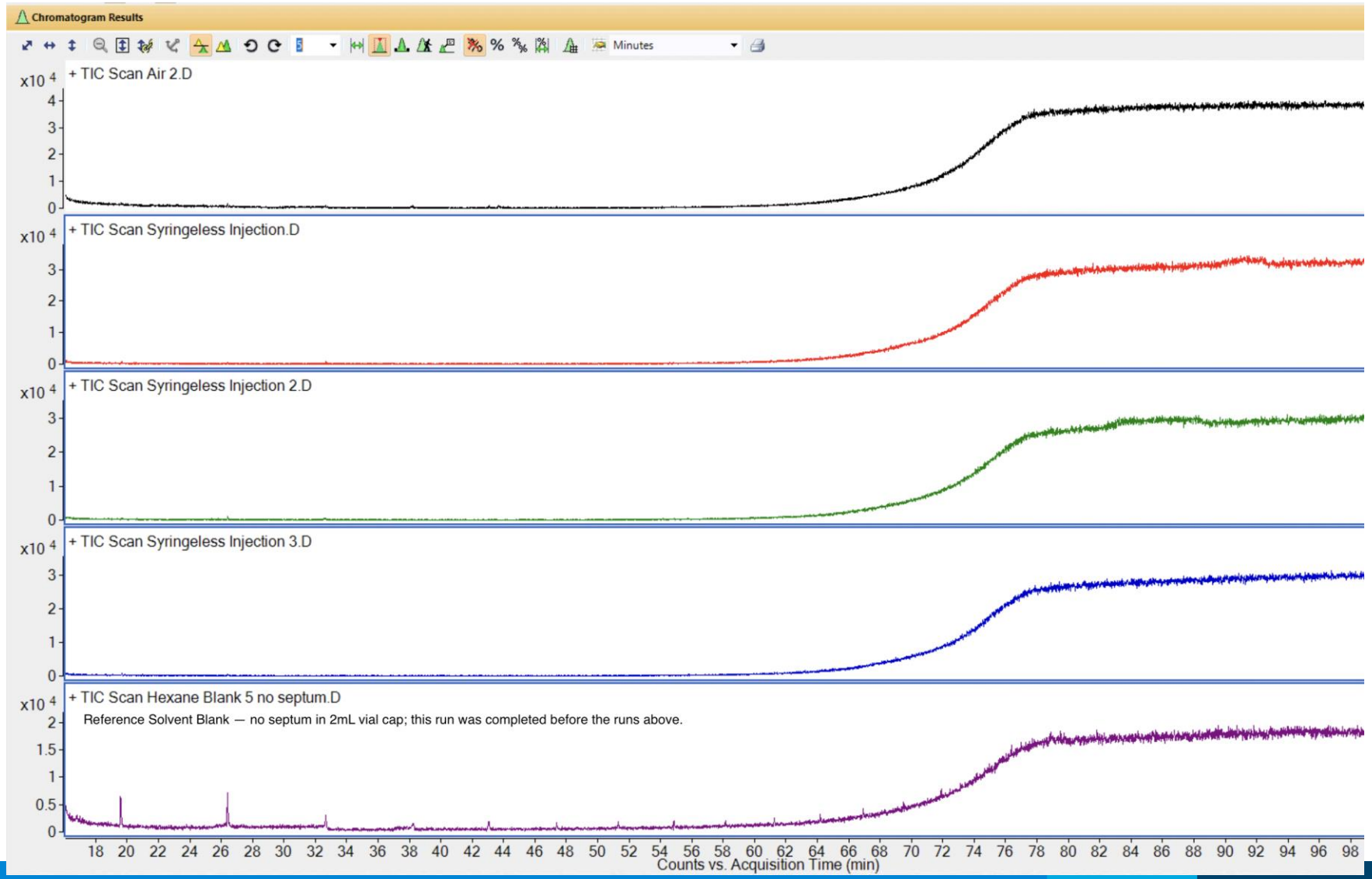
Example spectrum:



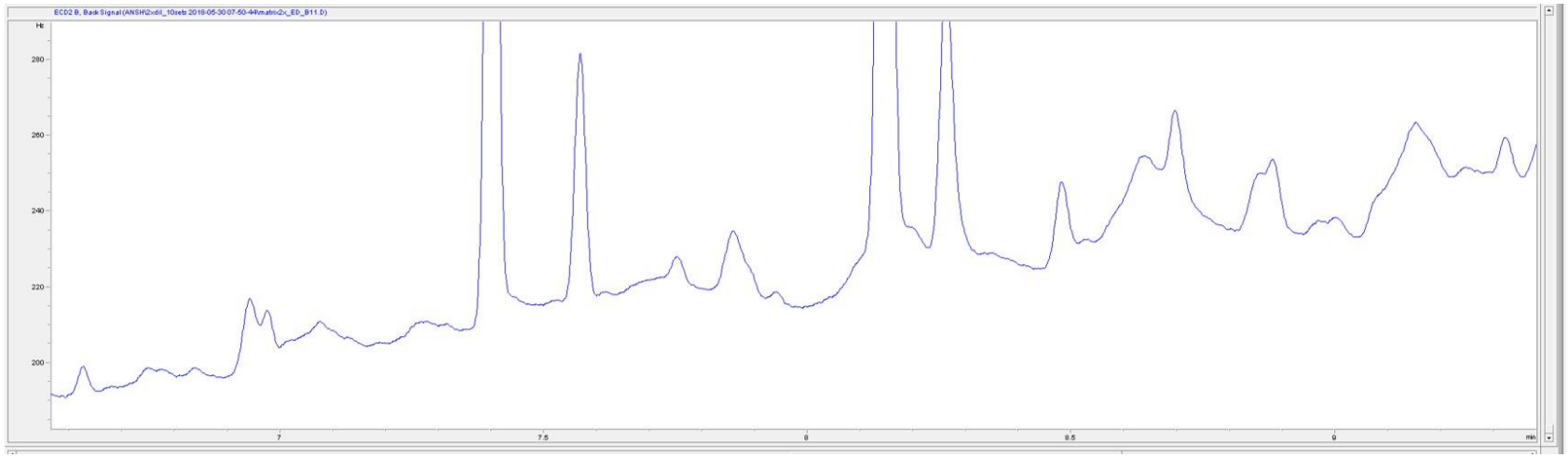
Consistent Siloxane Contamination



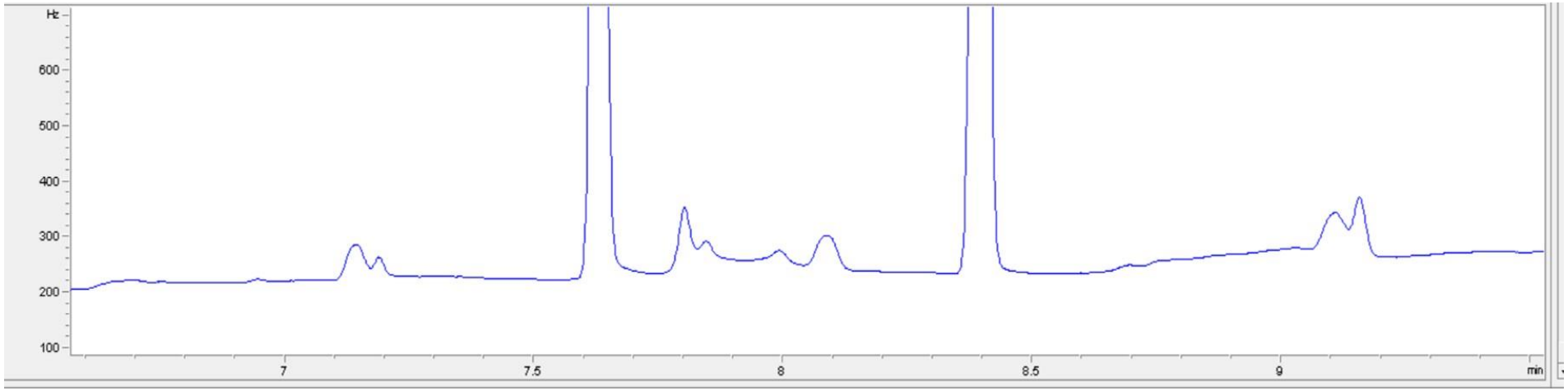
Perform Non-Injections to Determine Root Cause of Siloxane Contamination



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

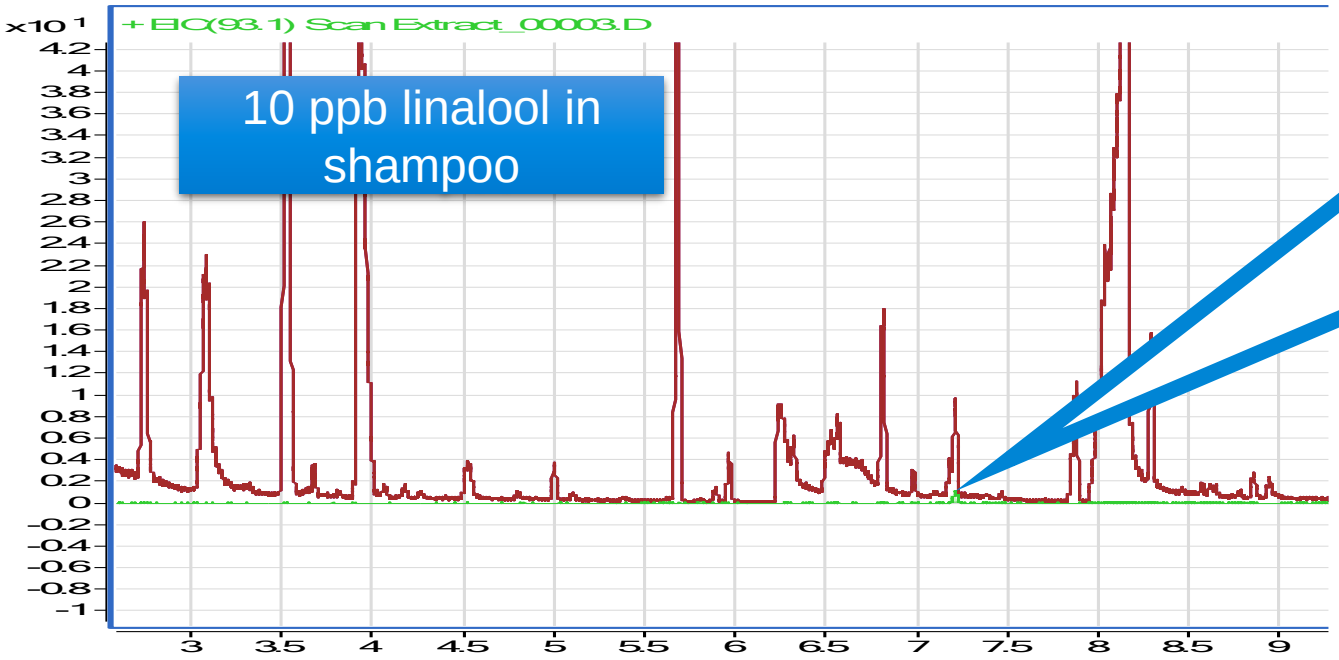


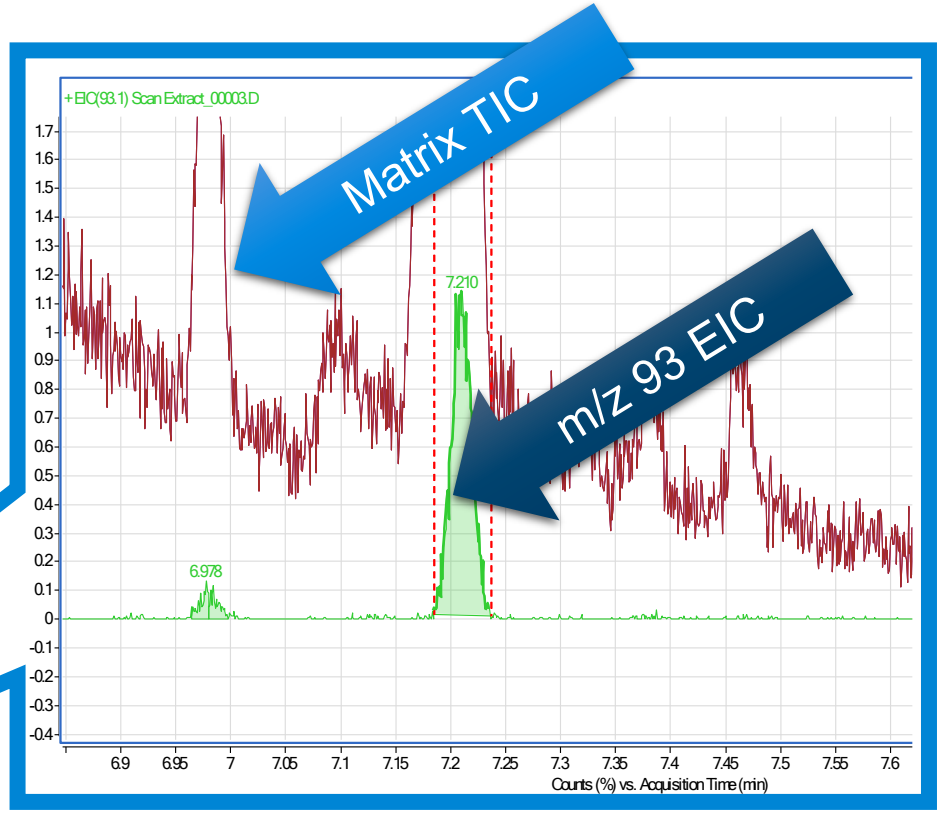
When it *should* look like…



The Matrix

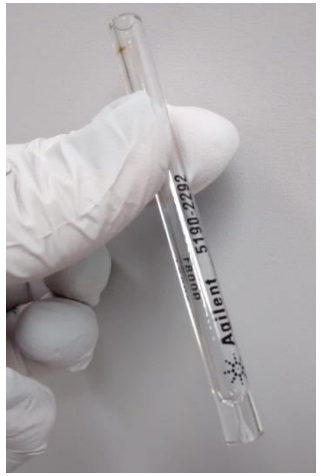
If your target ions are buried beneath matrix peaks, it might be time to trim the column or do sample cleanup



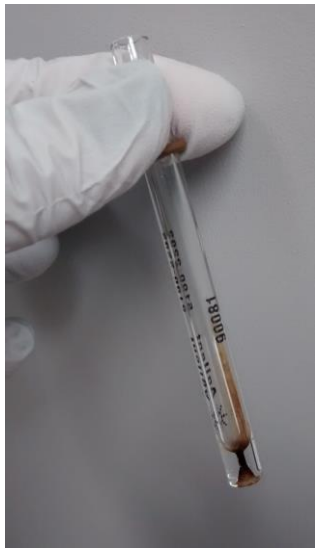


…(or improve your sample cleanup)

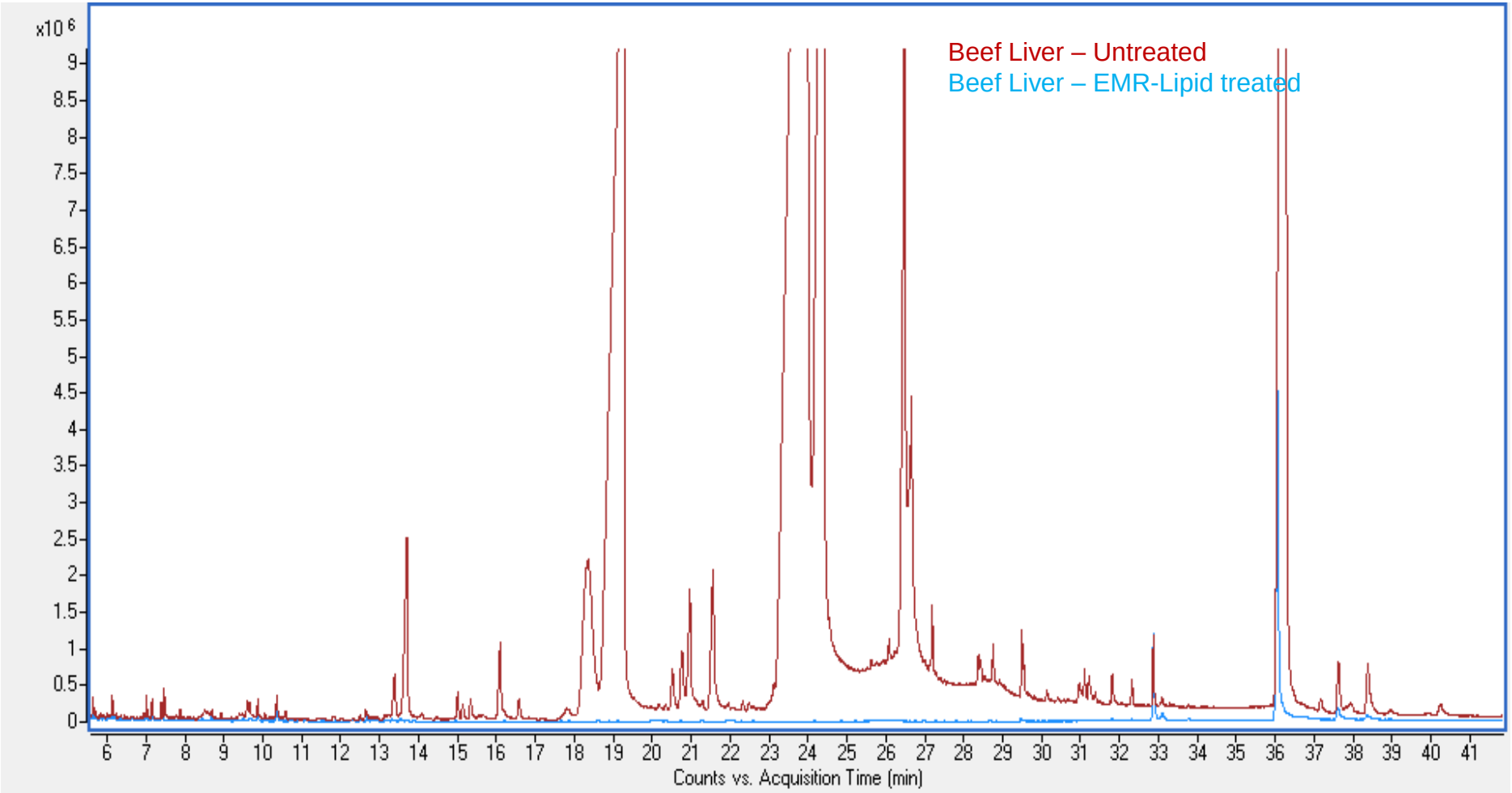
The Importance of Sample Cleanup



50 samples
with cleanup

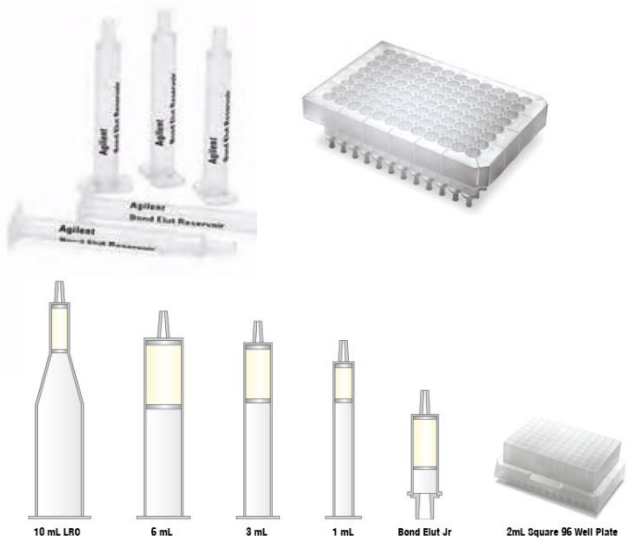


50 samples
without cleanup



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

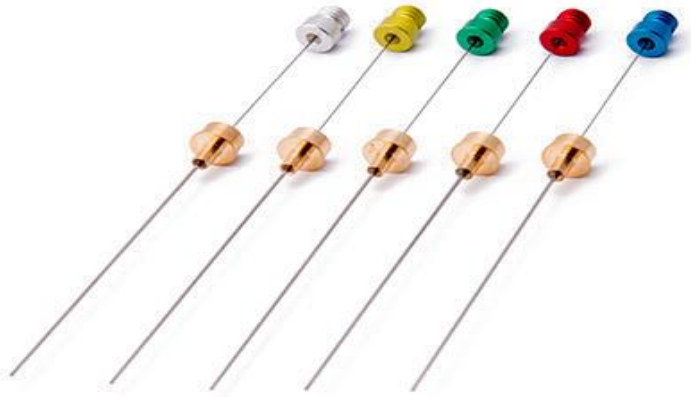
Offline Options for Sample Matrix Removal



Bond Elut Solid Phase Extraction cartridges and plates

Filter vials

QuEChERS



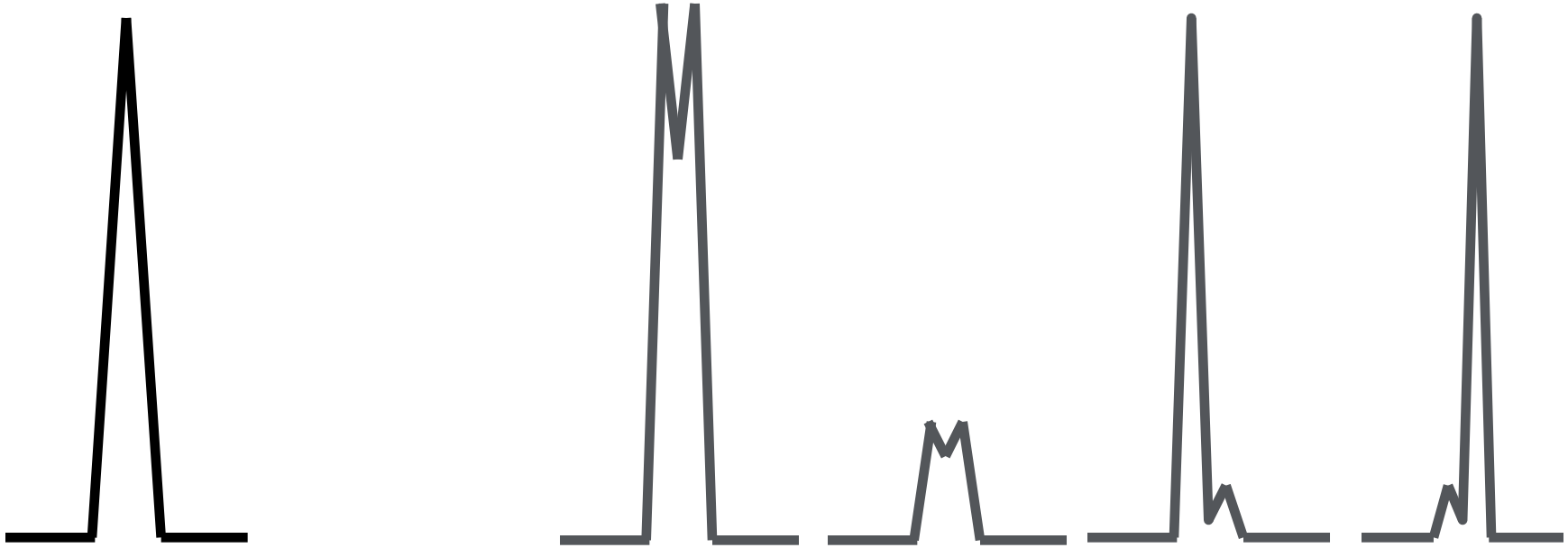
SPME

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)

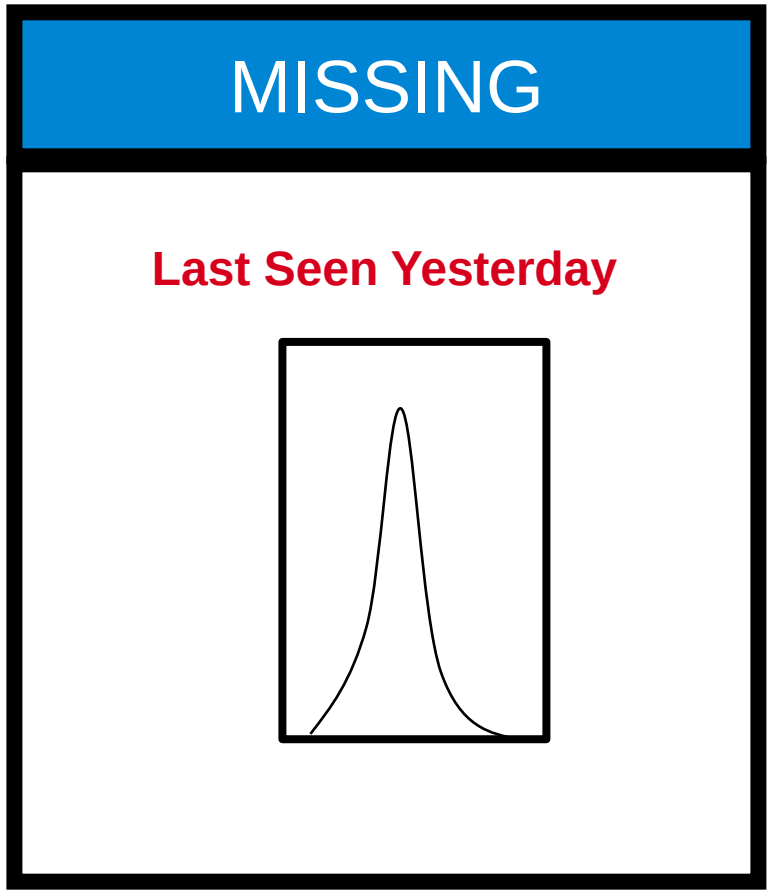
Injector (activity)

- 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

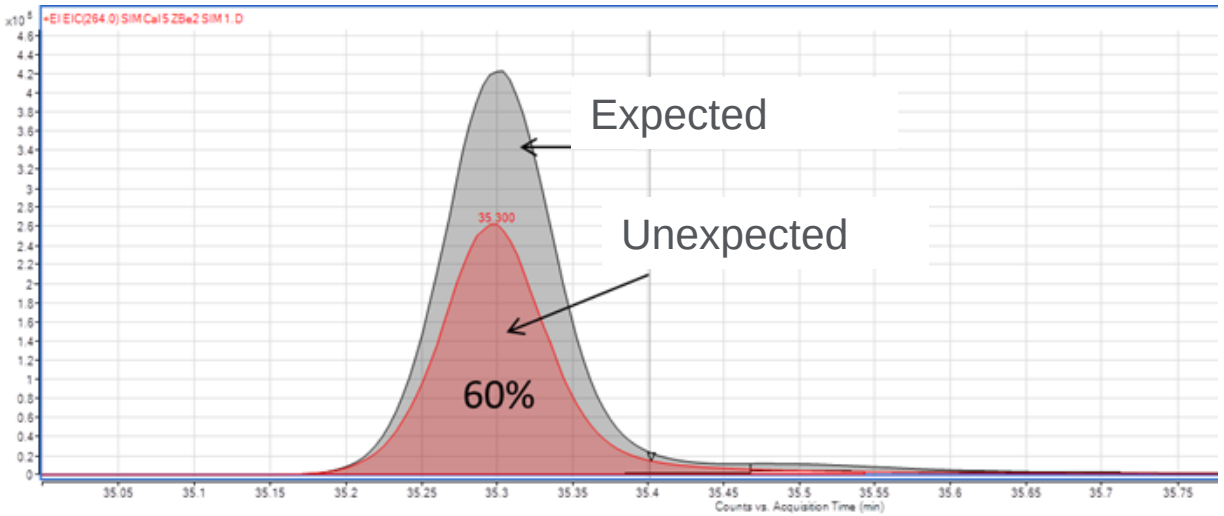
- Wrong injector (or detector)
- Huge leak (older systems)
- No carrier gas flow

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

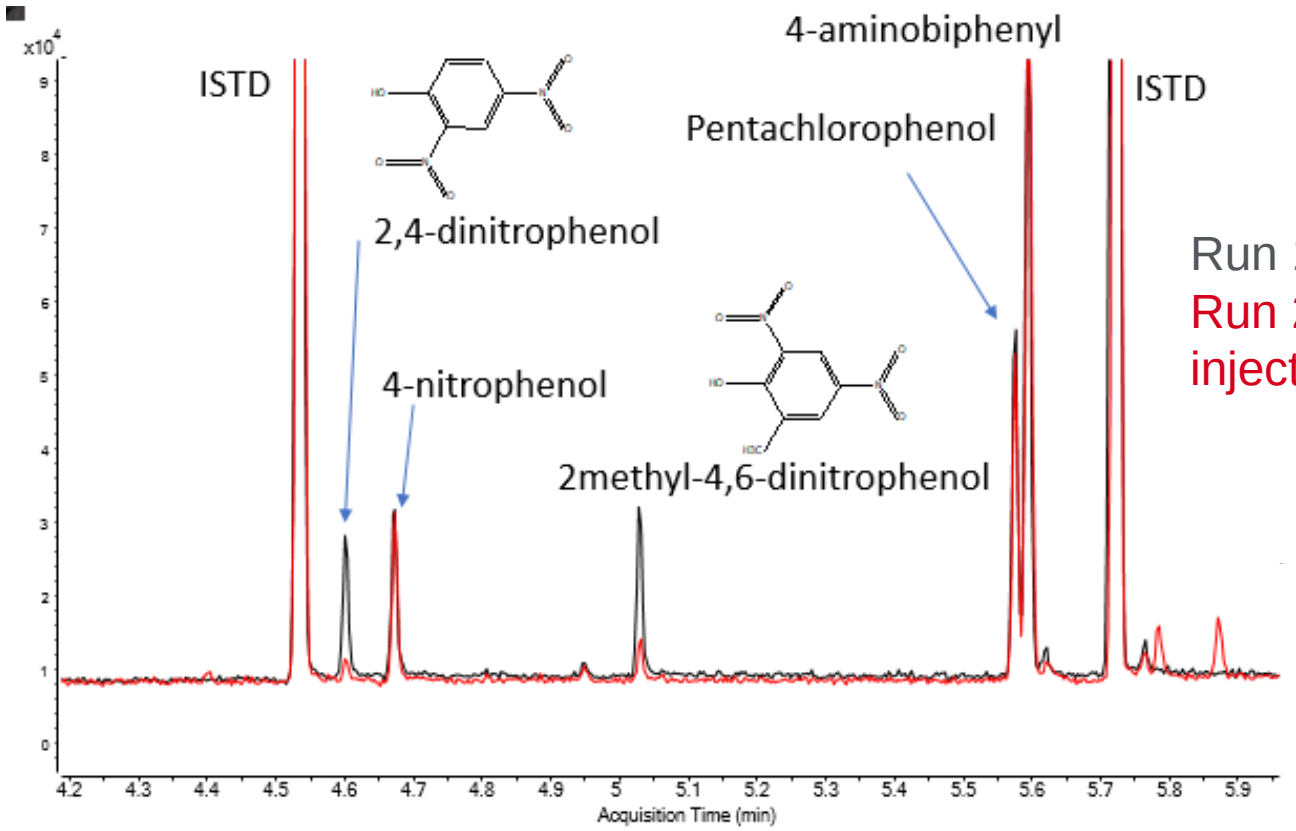
50 ng/mL before 50 Injections of Salmon Oil

Initial Injection

After 50 Injections of Dilute Salmon Oil

Peak Response

Some change in size



Run 1

Run 26 (after 25 matrix injections

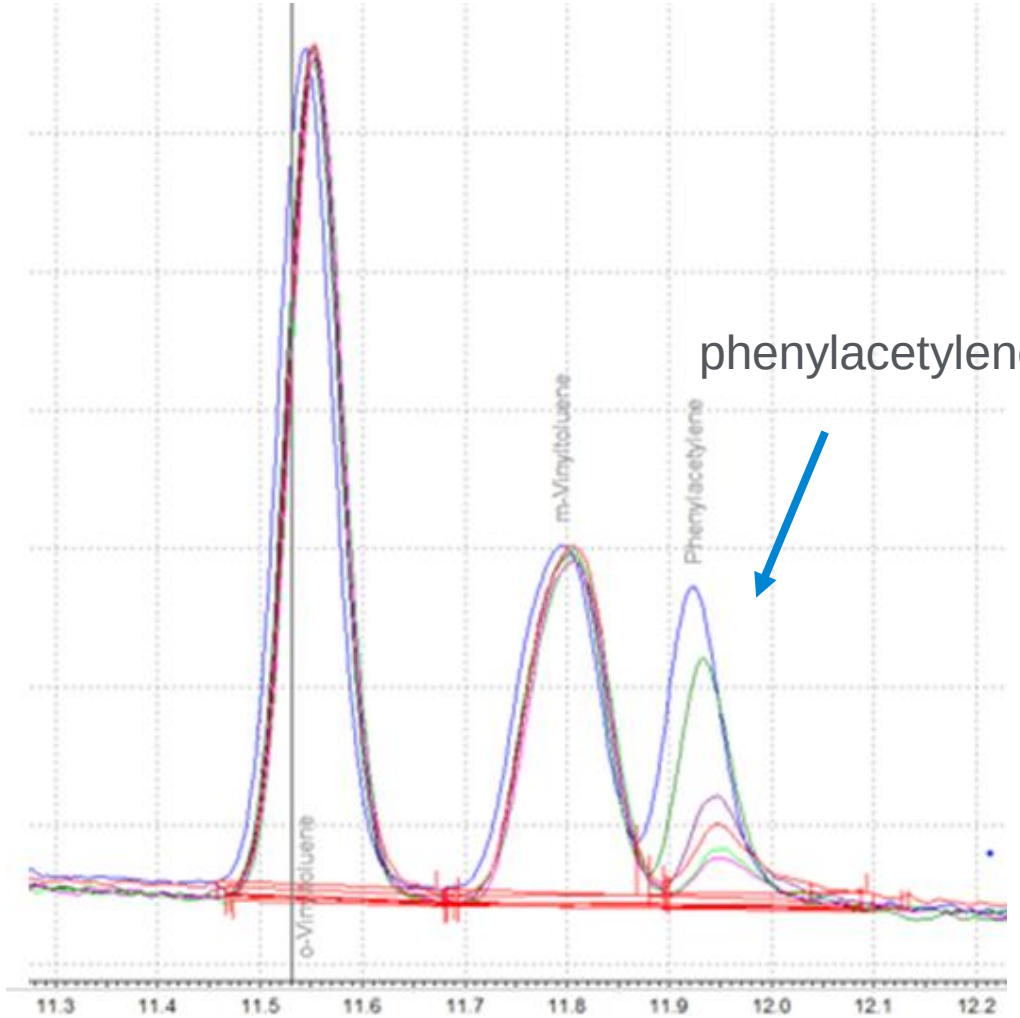
Injector or column is active/contaminated

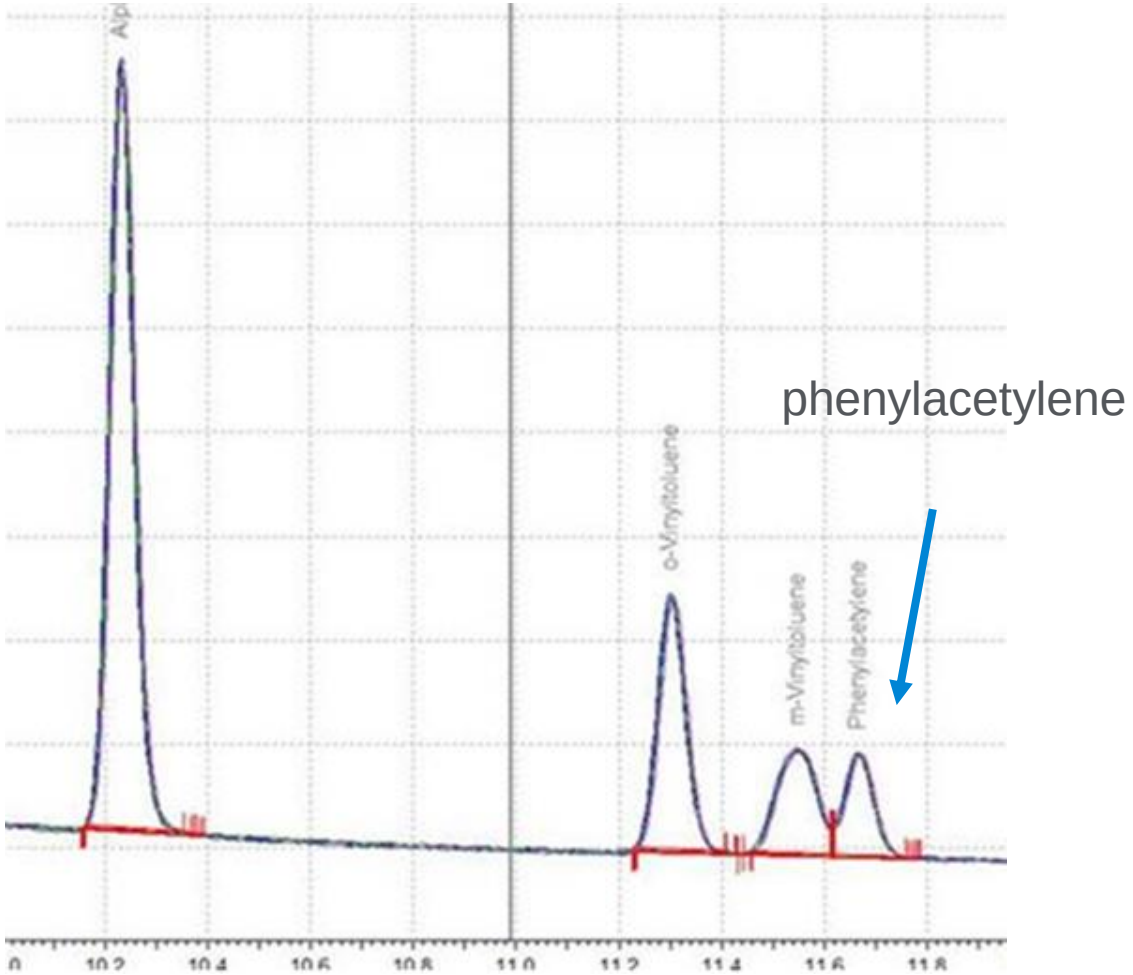
- Irreversible adsorption of active compounds (-OH, -NH, -SH)

Decomposition of sample

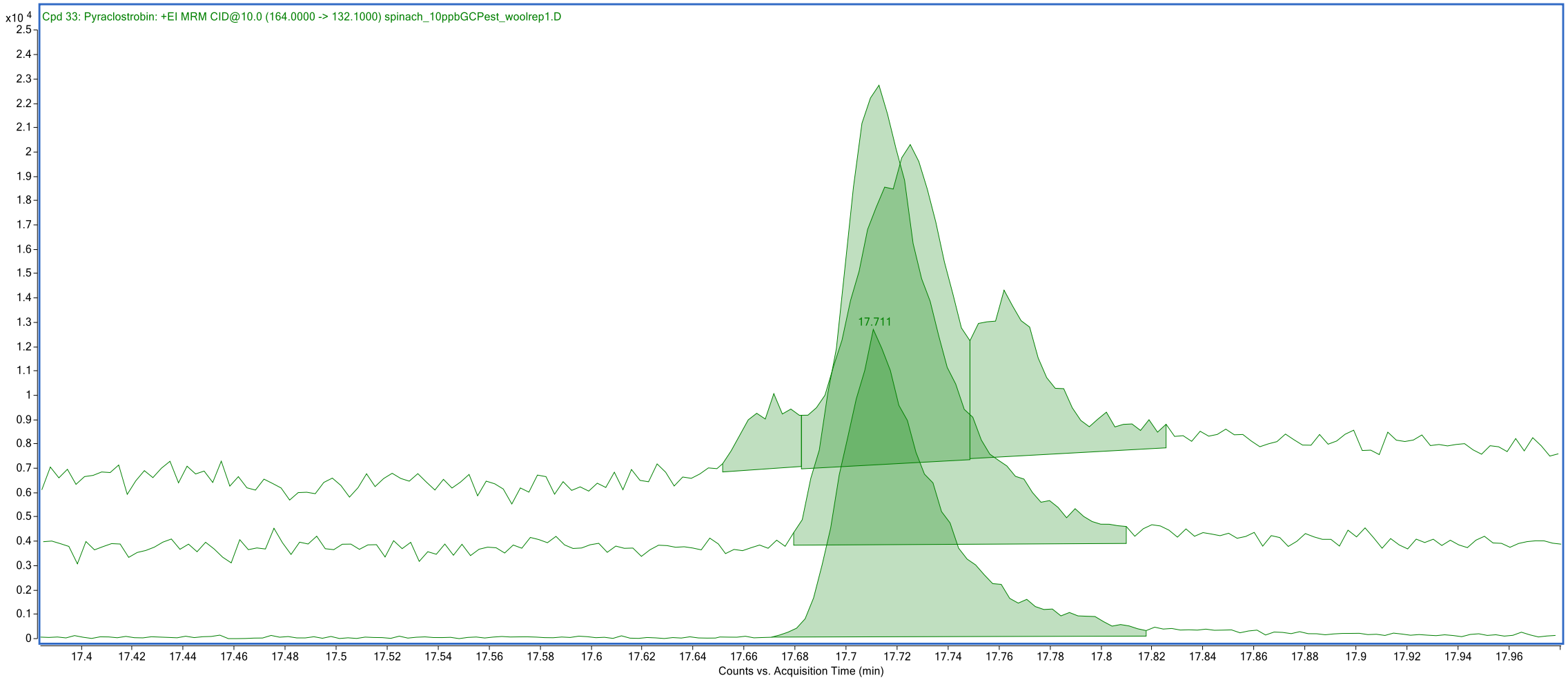
- Temperature change – discrimination
- Evaporation from sample

Example of Reduction in Response for One Peak

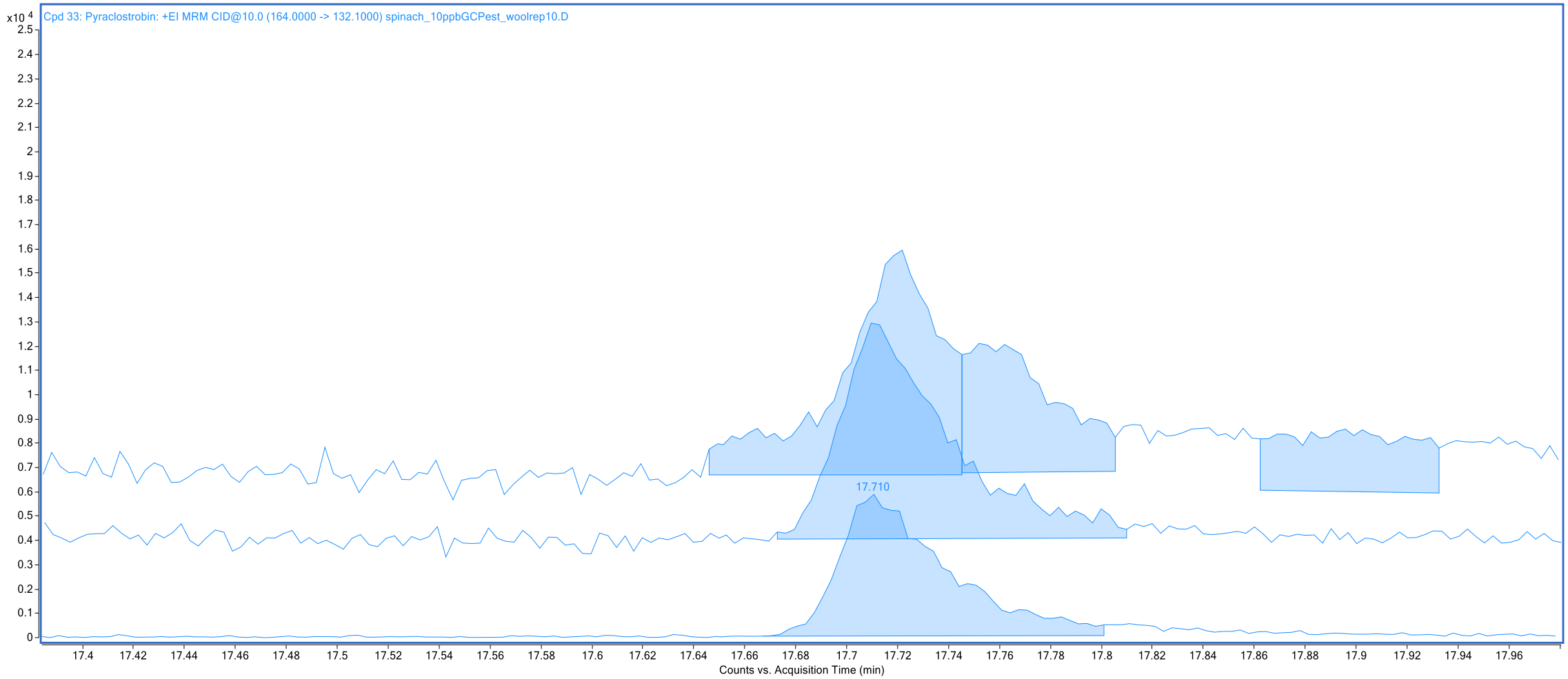




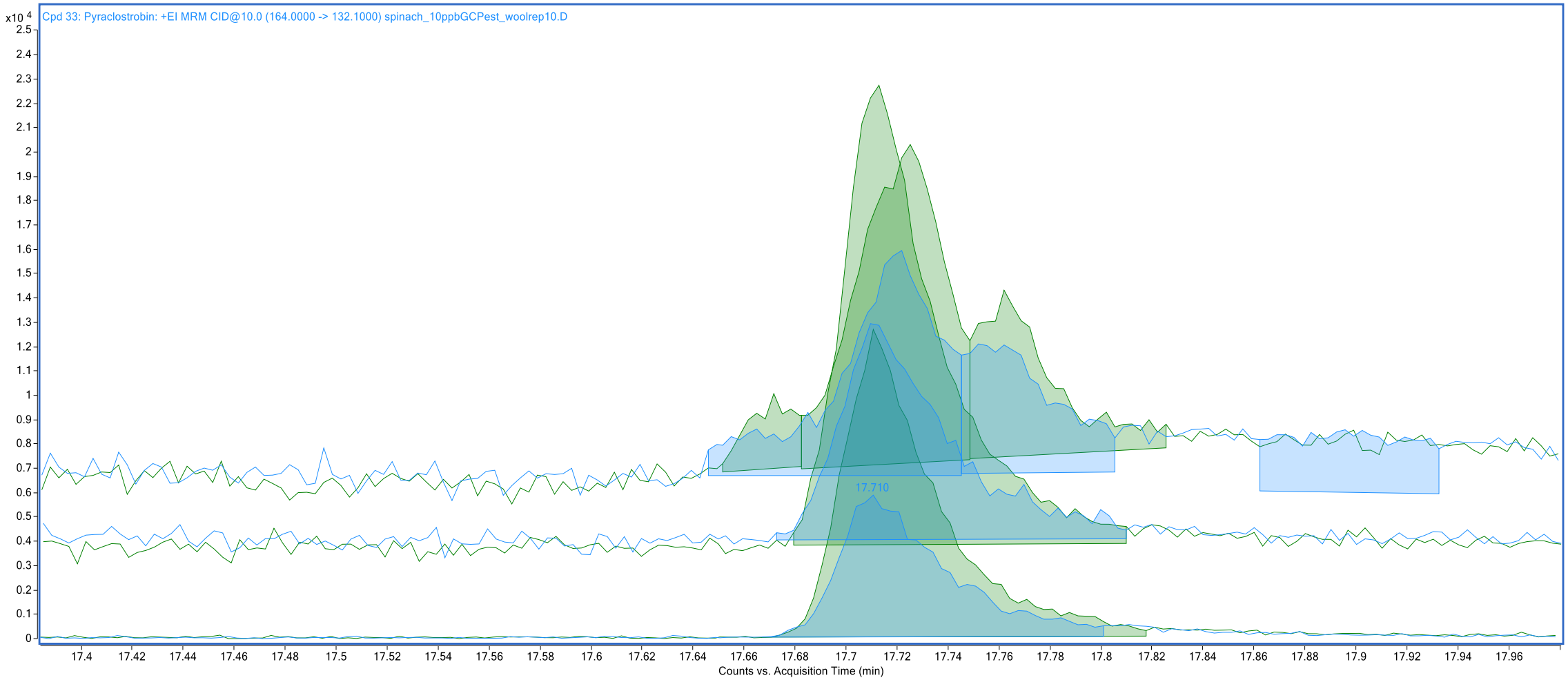
Change in Response: Pyraclostrobin in Spinach on Run 1



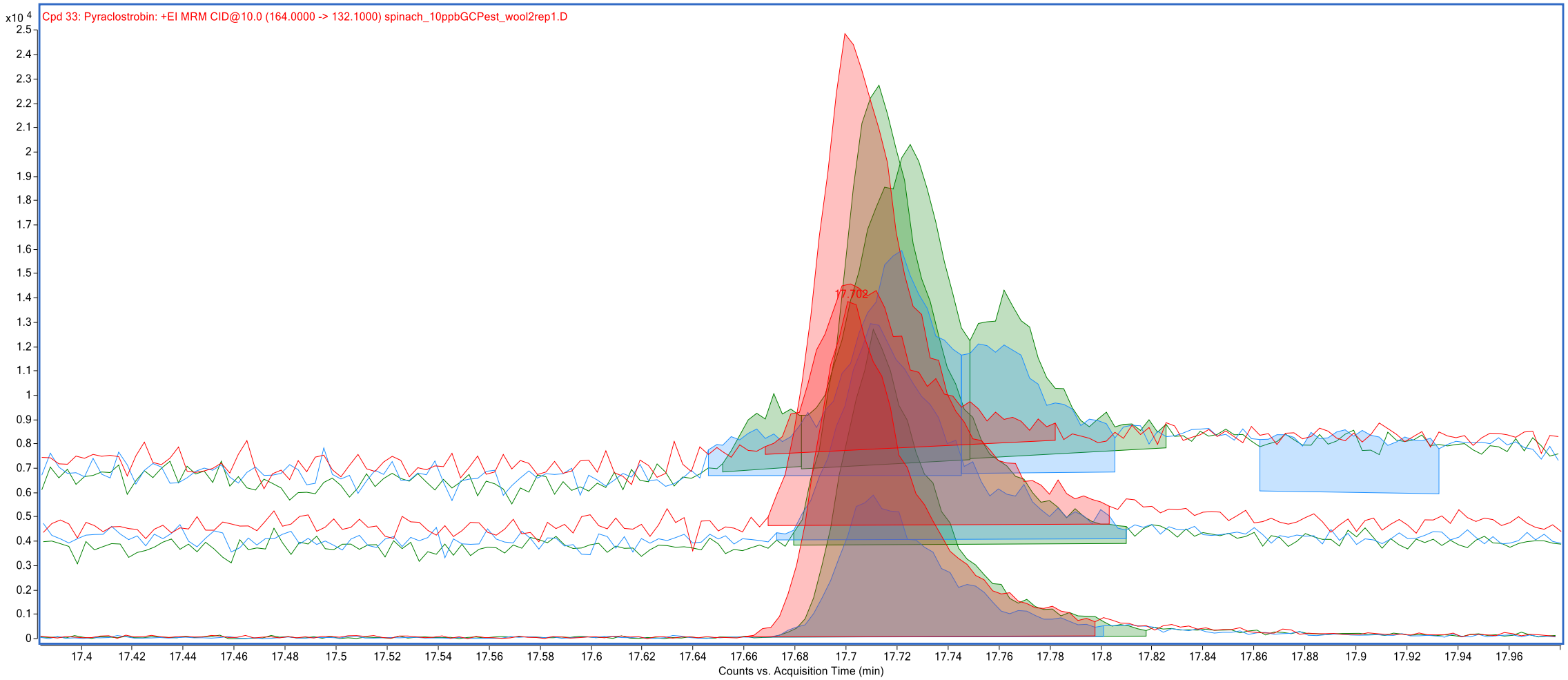
Change in Response: Pyraclostrobin in Spinach on Run 65



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

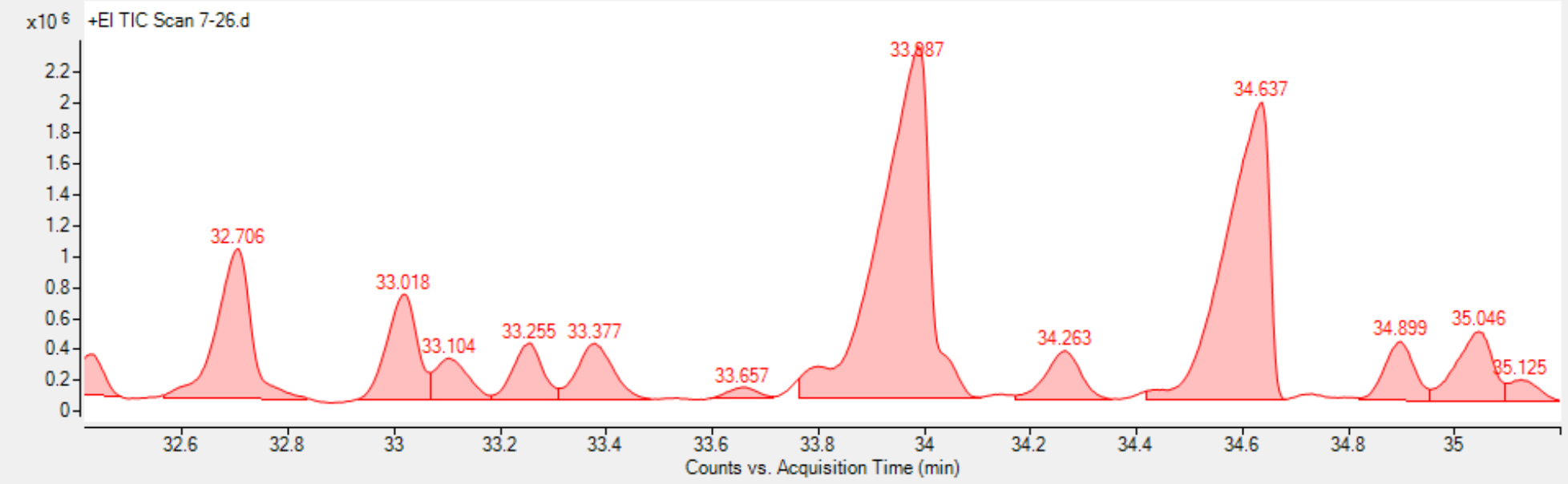


Change in Response: Pyraclostrobin in Spinach with New Liner



Peak Fronting

Shark fin-shaped



Column (contaminated)

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

Injector

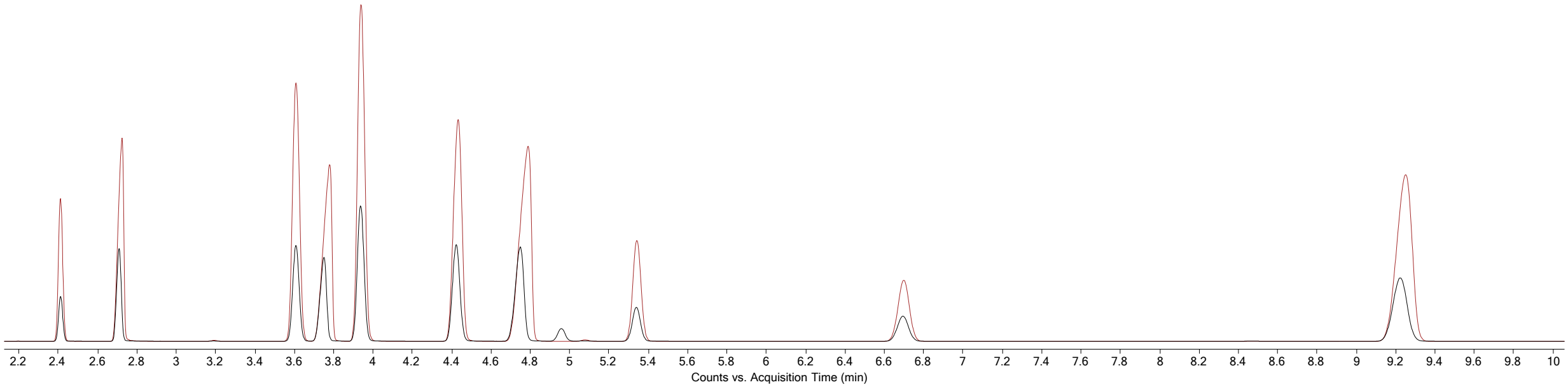
- Compound soluble in injection solvent (need retention gap)
- Mixed sample solvent

Other

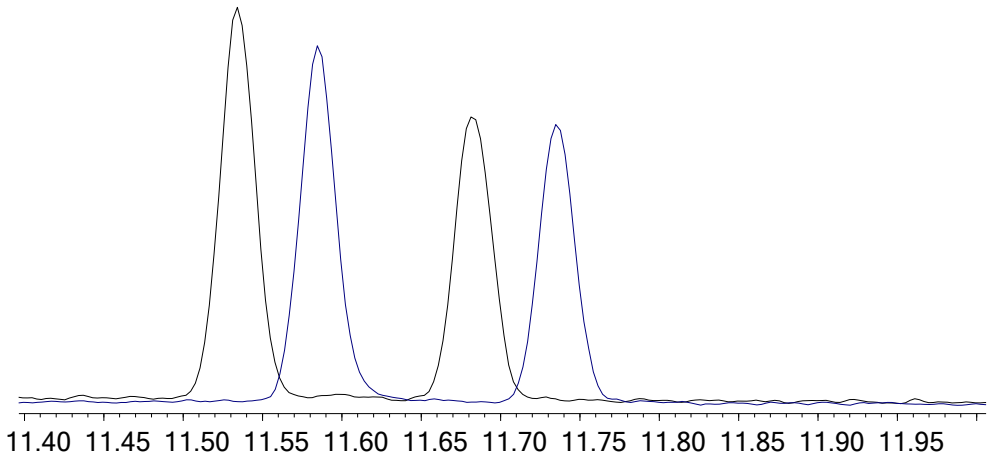
- Coelution
- Breakdown

Column Overload Example

- DB-624 column with analytes all at the same concentration
- Initial injection showed peak overload especially with the last peak (red trace)
- Split ratio and/or concentrations adjusted to address this overload (black trace)



Retention Time Shift



Injector

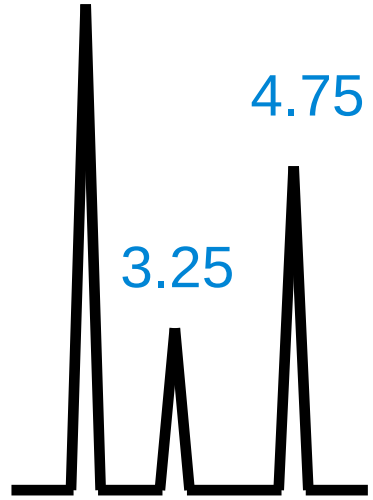
- Leak in the septum
- Change in injection solvent
- Large change in sample concentration

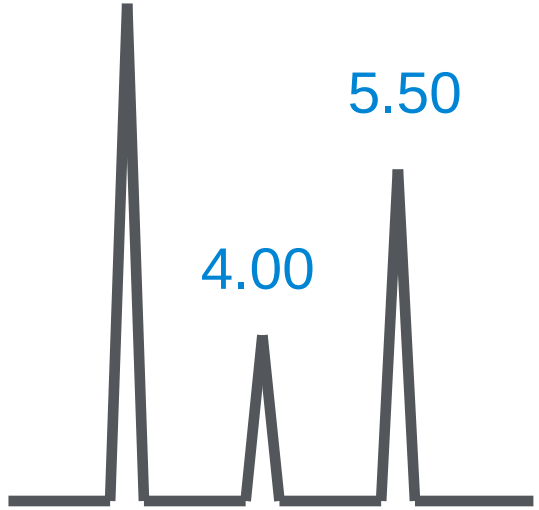
Flow

- 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

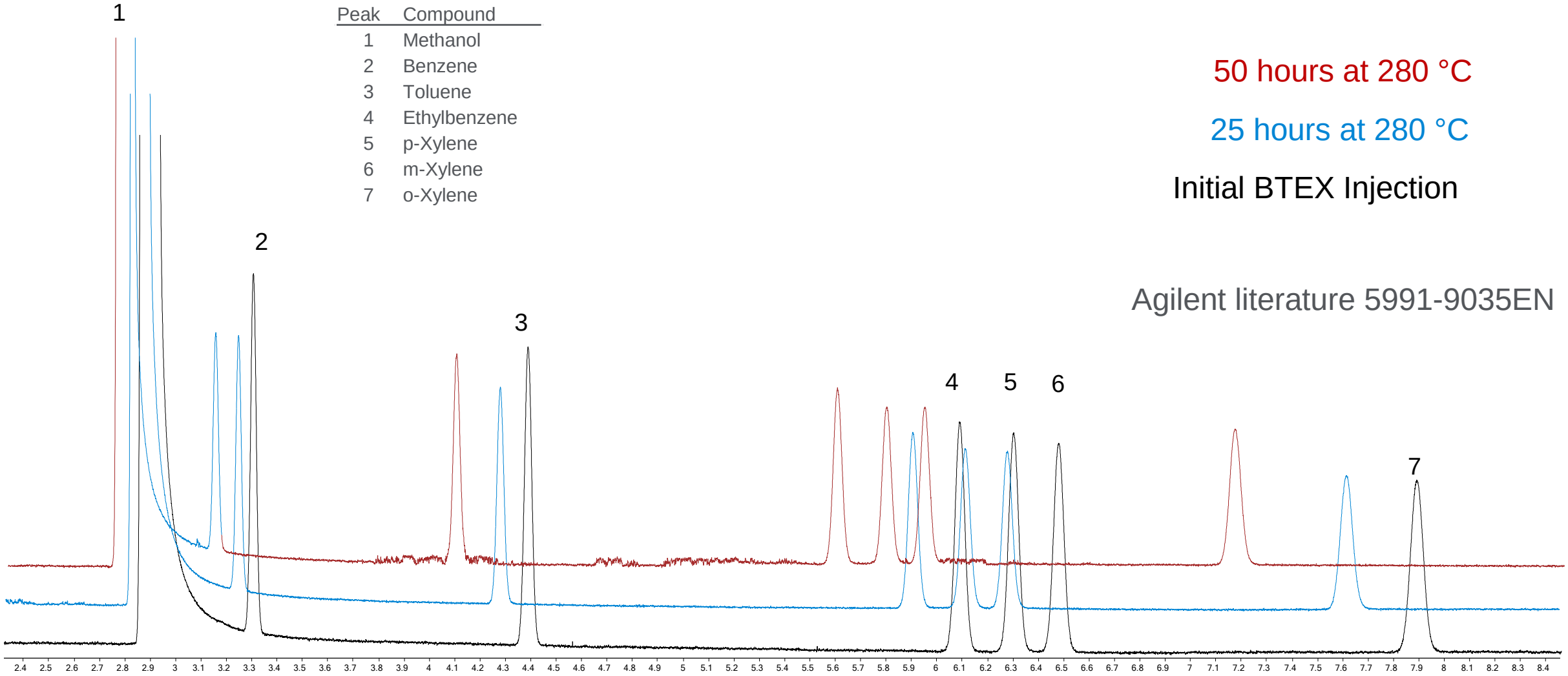
Peak	Compound
1	Methanol
2	Benzene
3	Toluene
4	Ethylbenzene
5	p-Xylene
6	m-Xylene
7	o-Xylene

50 hours at 280 °C

25 hours at 280 °C

Initial BTEX Injection

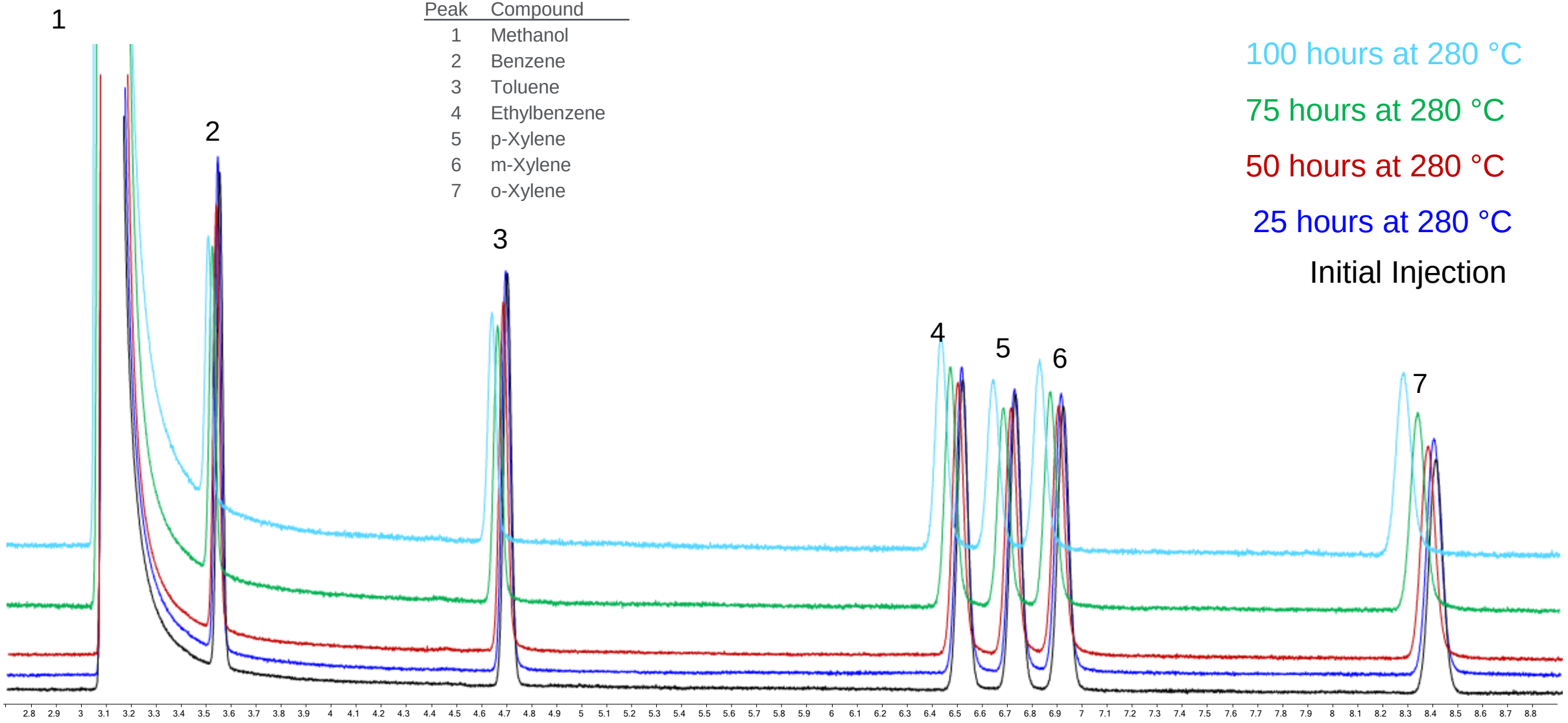
Agilent literature 5991-9035EN



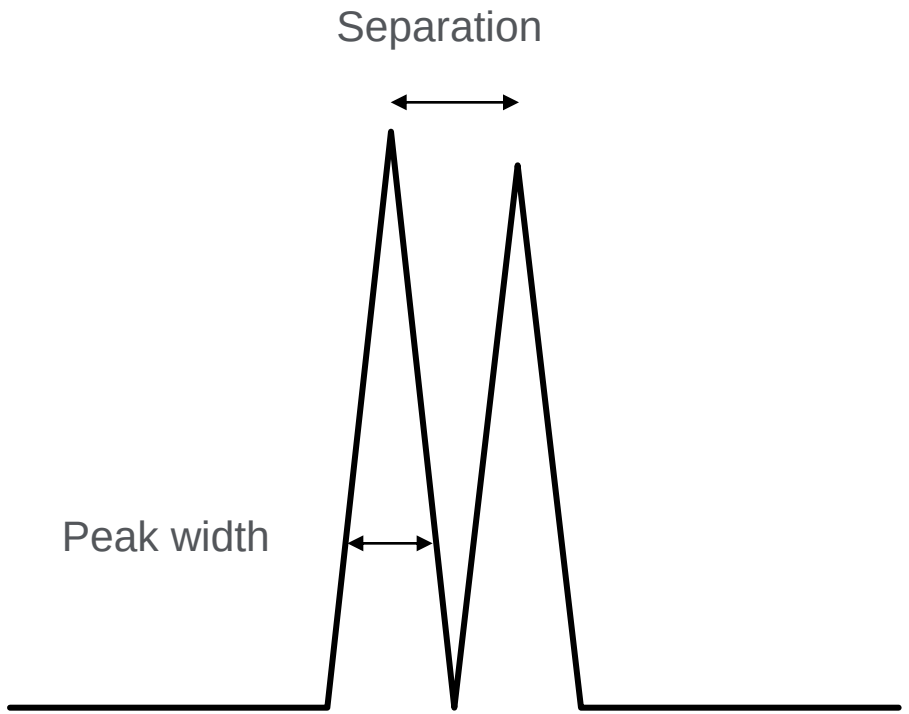
DB-HeavyWAX

Agilent literature 5991-9035EN

Peak	Compound
1	Methanol
2	Benzene
3	Toluene
4	Ethylbenzene
5	p-Xylene
6	m-Xylene
7	o-Xylene



Loss of Resolution



Resolution is a function of separation and peak width

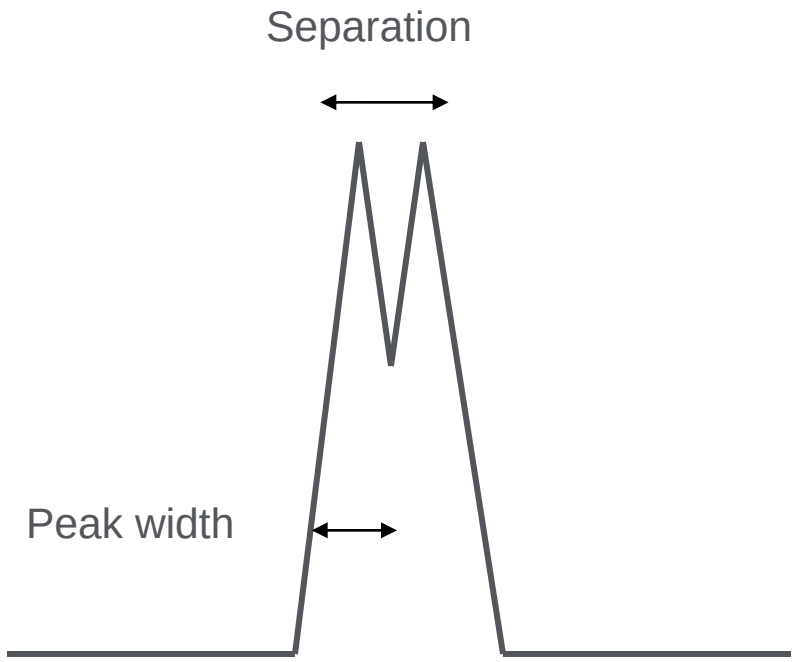
Loss of Resolution - Separation Decrease (Retention Times Changed)

Column

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

Flow

- Change in velocity?



Loss of Resolution - Peak Broadening (Retention Times Unchanged)

Flow

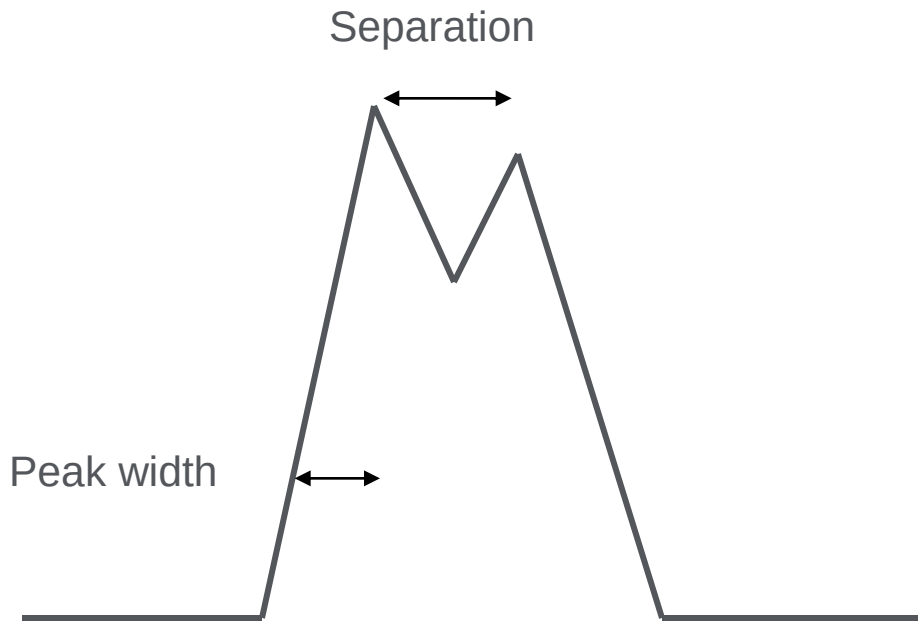
- Make-up gas

Column

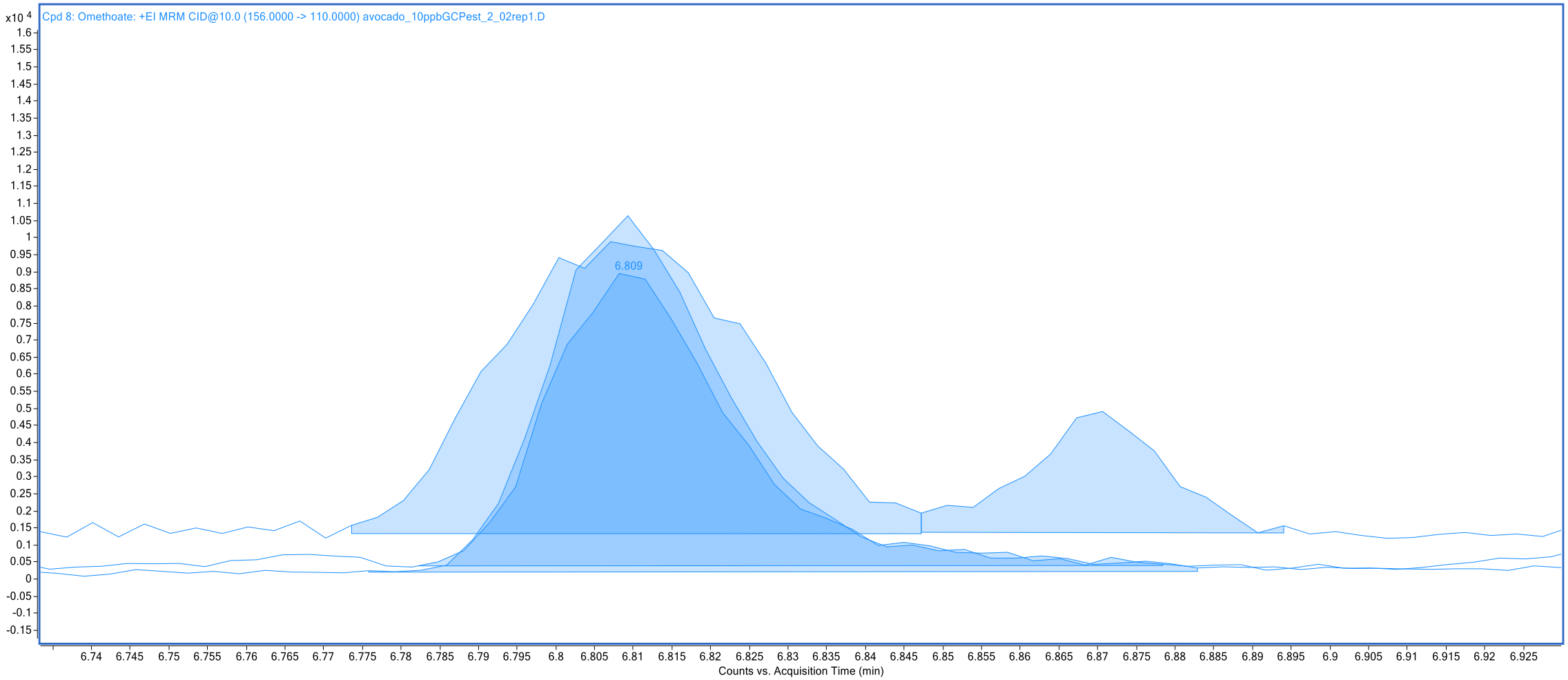
- Contamination
- Phase degradation

Injector (efficiency)

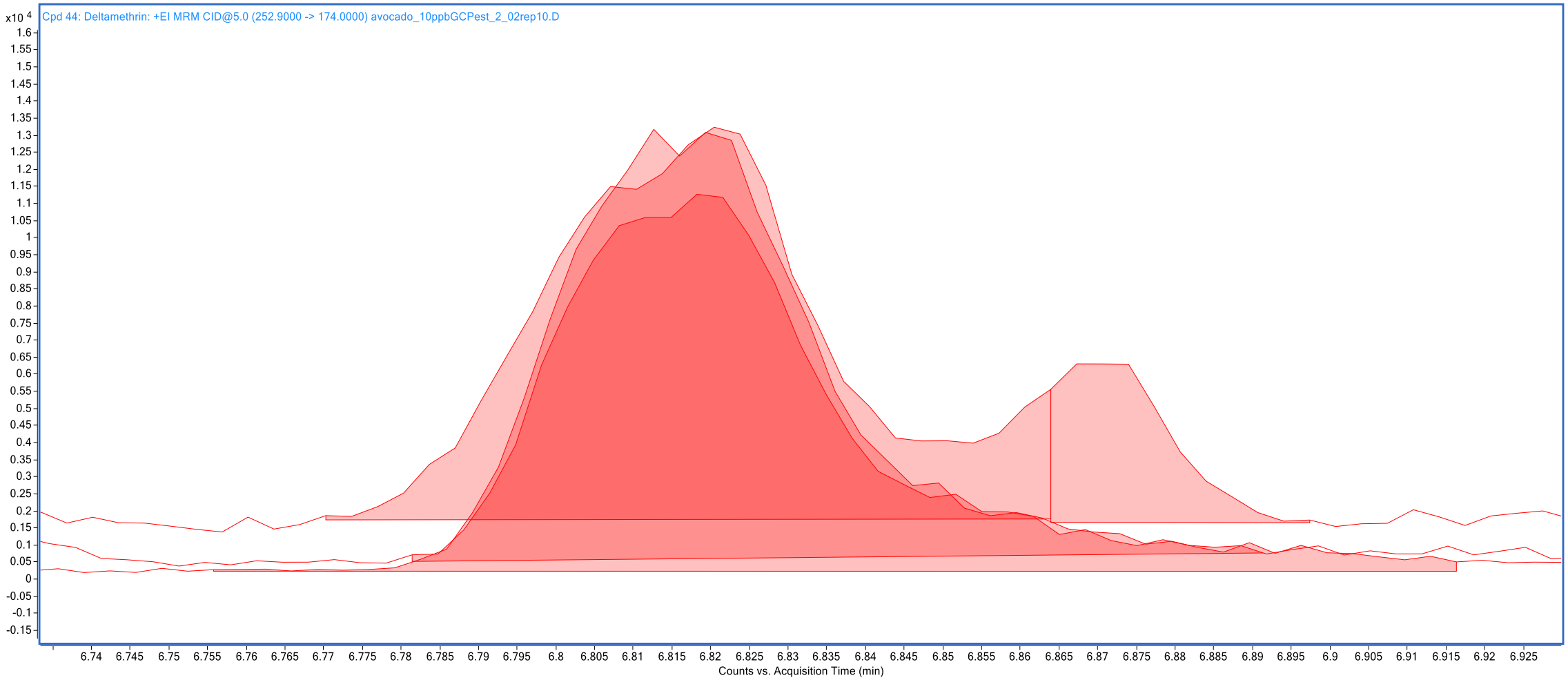
- Settings, liner, installation, etc.



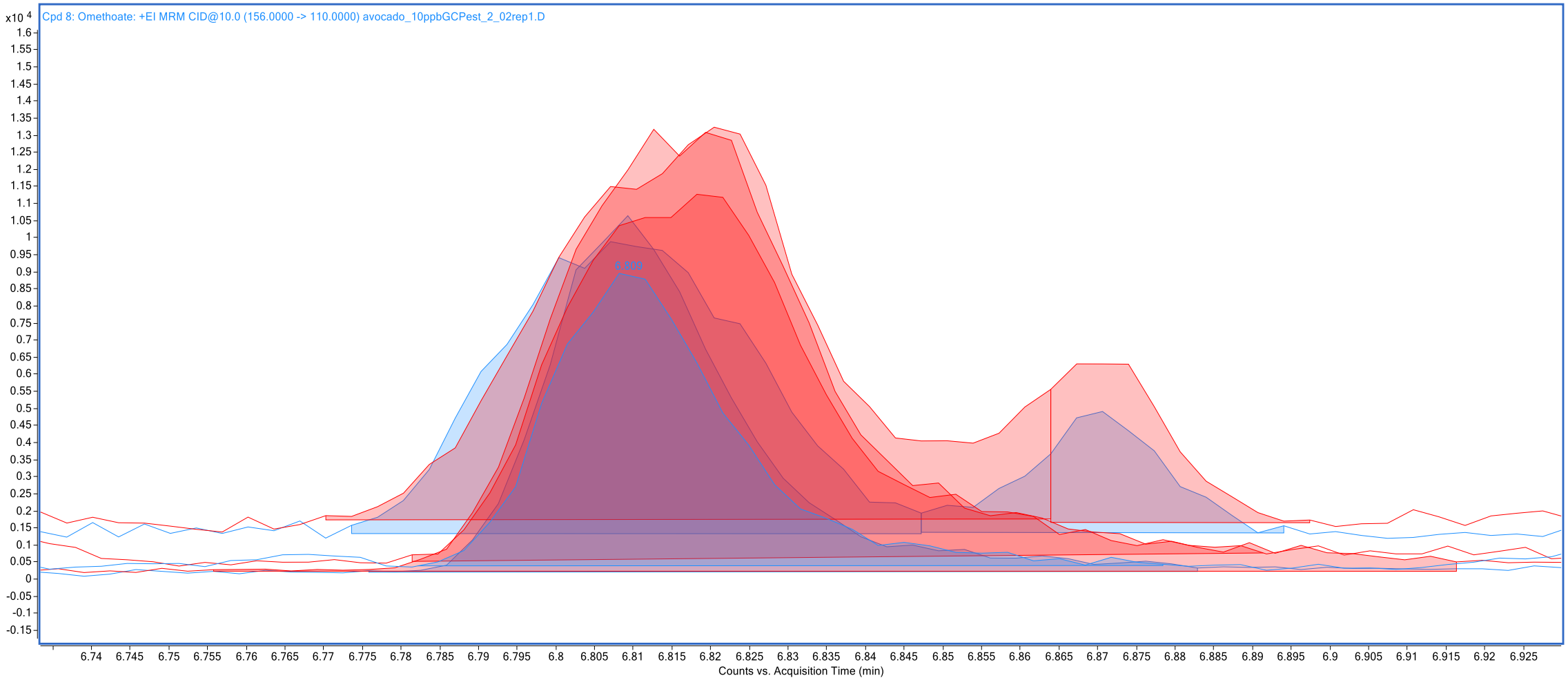
Peak Broadening: Omethoate in Avocado in Run 1



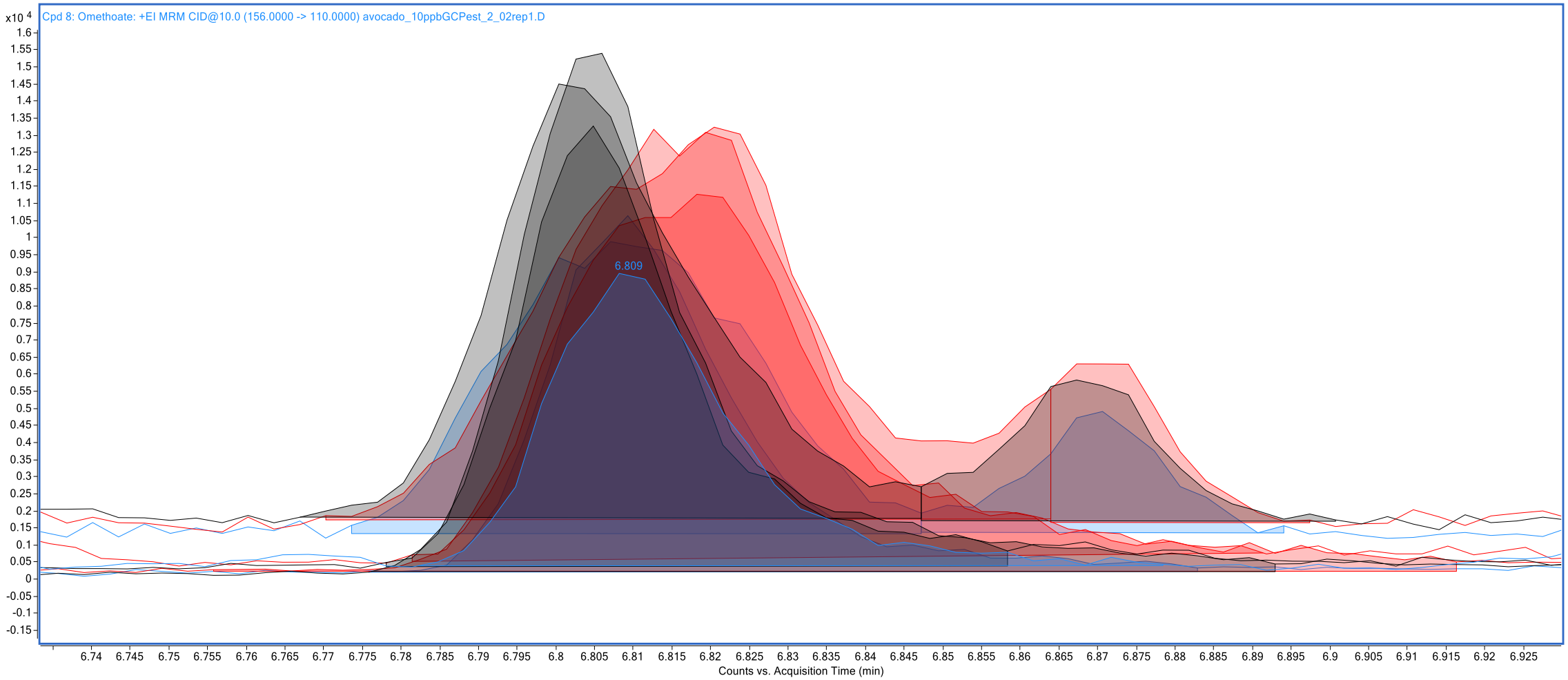
Peak Broadening: Omethoate in Avocado in Run 65



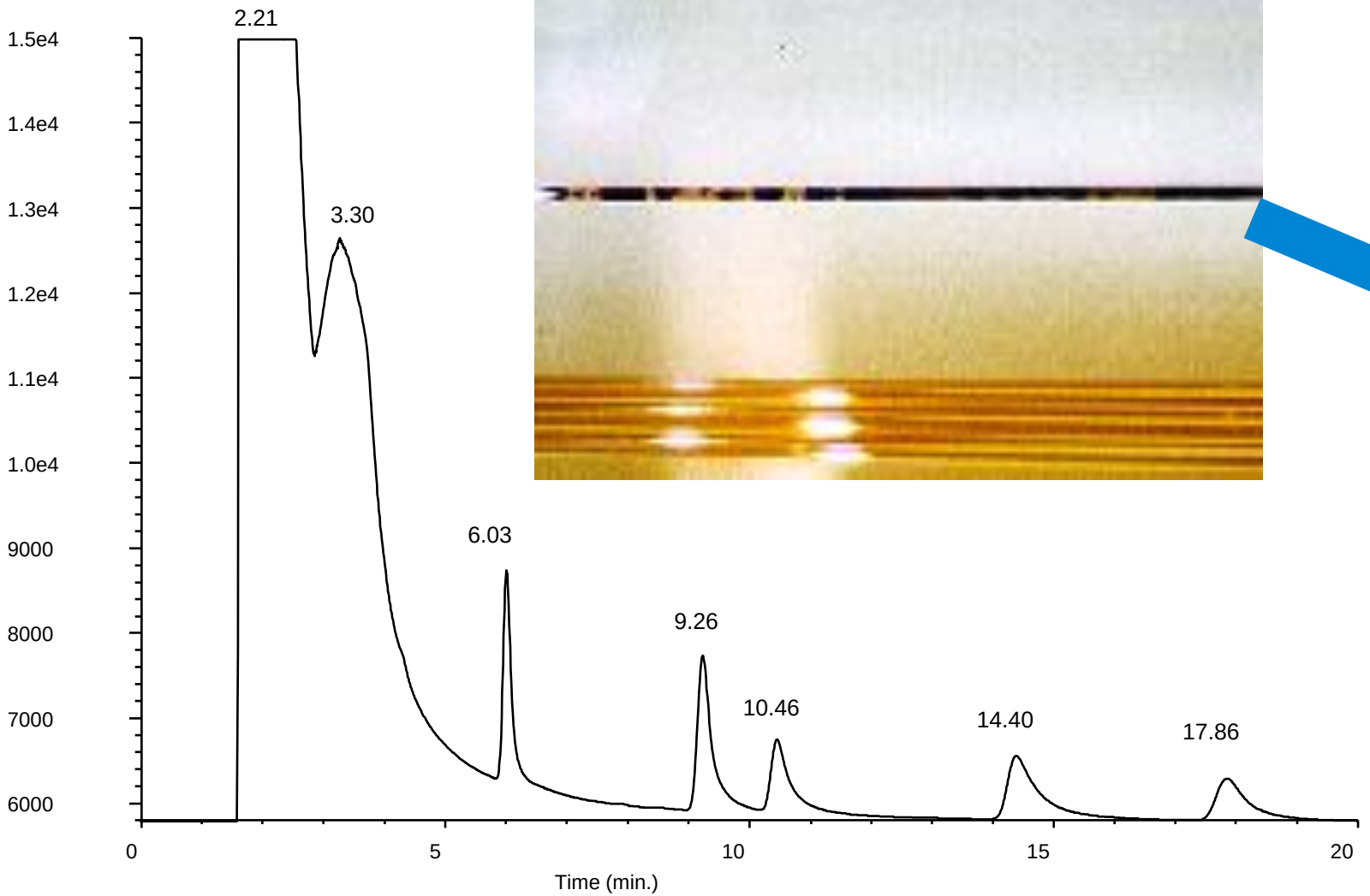
Peak Broadening: Omethoate in Avocado in Run 1 versus Run 65



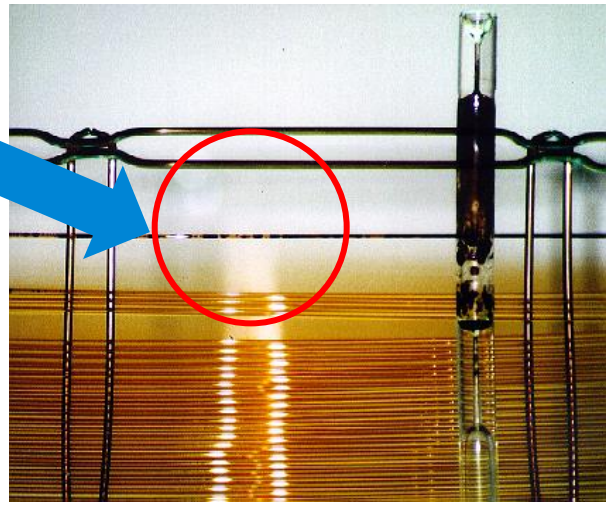
Peak Broadening: Recover Peak Shape with New Liner



Example of Column Contamination and Broad Peaks

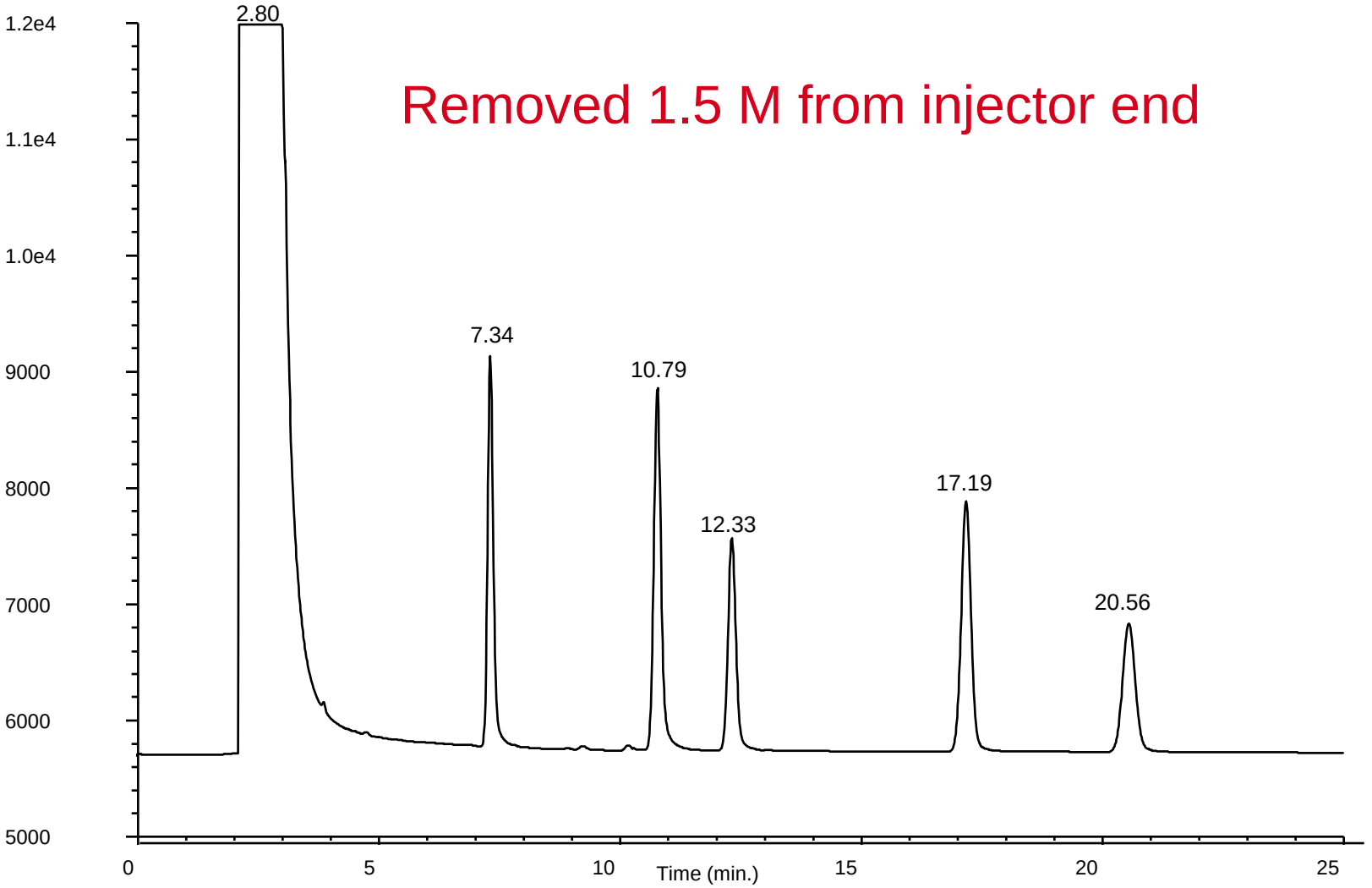


Agilent J&W DB-624 QC Test Mix
After 75 injections of oily sample



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

Example of Column Contamination

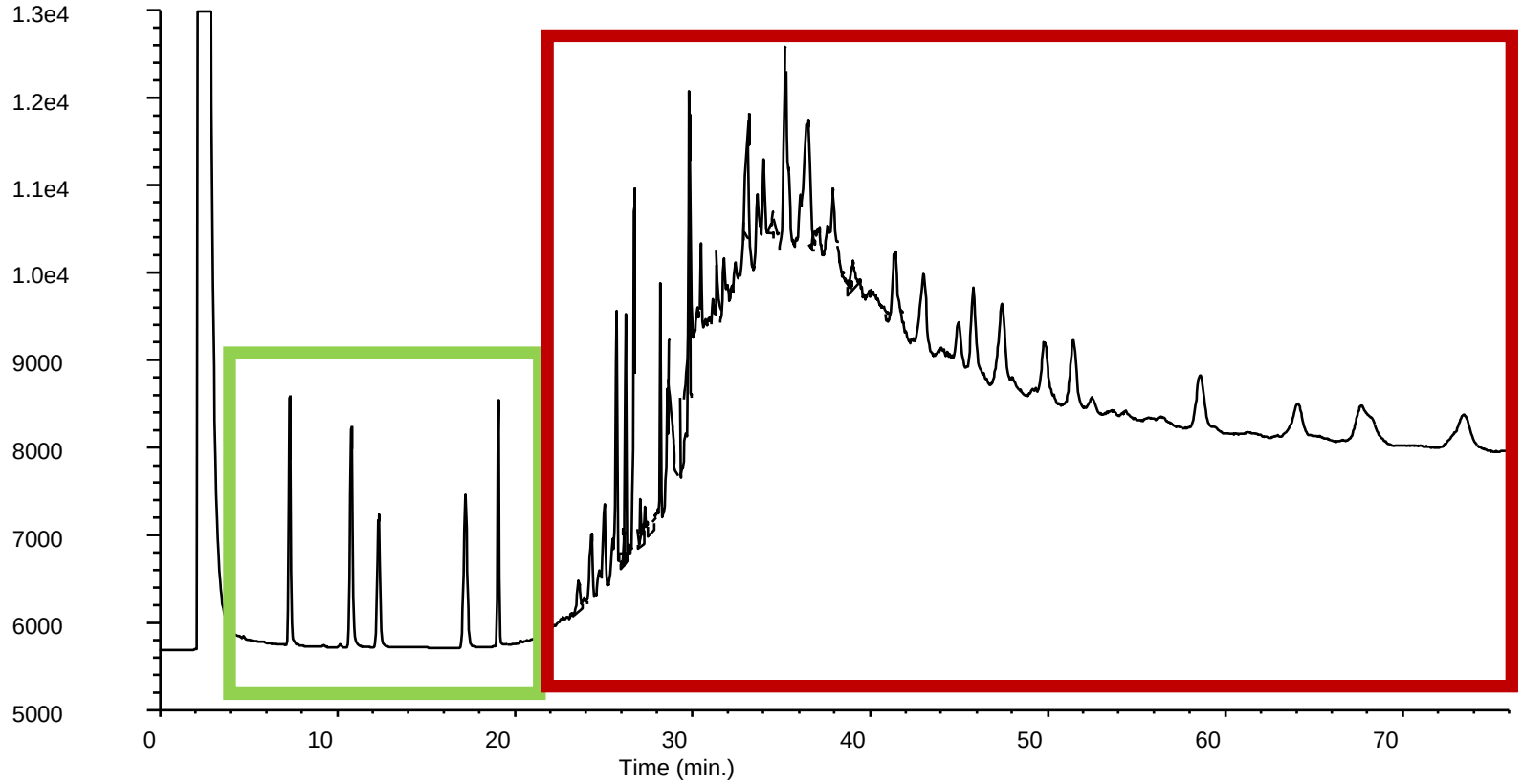


*Before column rinse and bake
Temperature program // 35 °C hold 1.50 min // 30° C/min to 65 °C, hold 10 min

Example of Column Contamination

1.5 M removed*

QC test mix to upper temperature limit



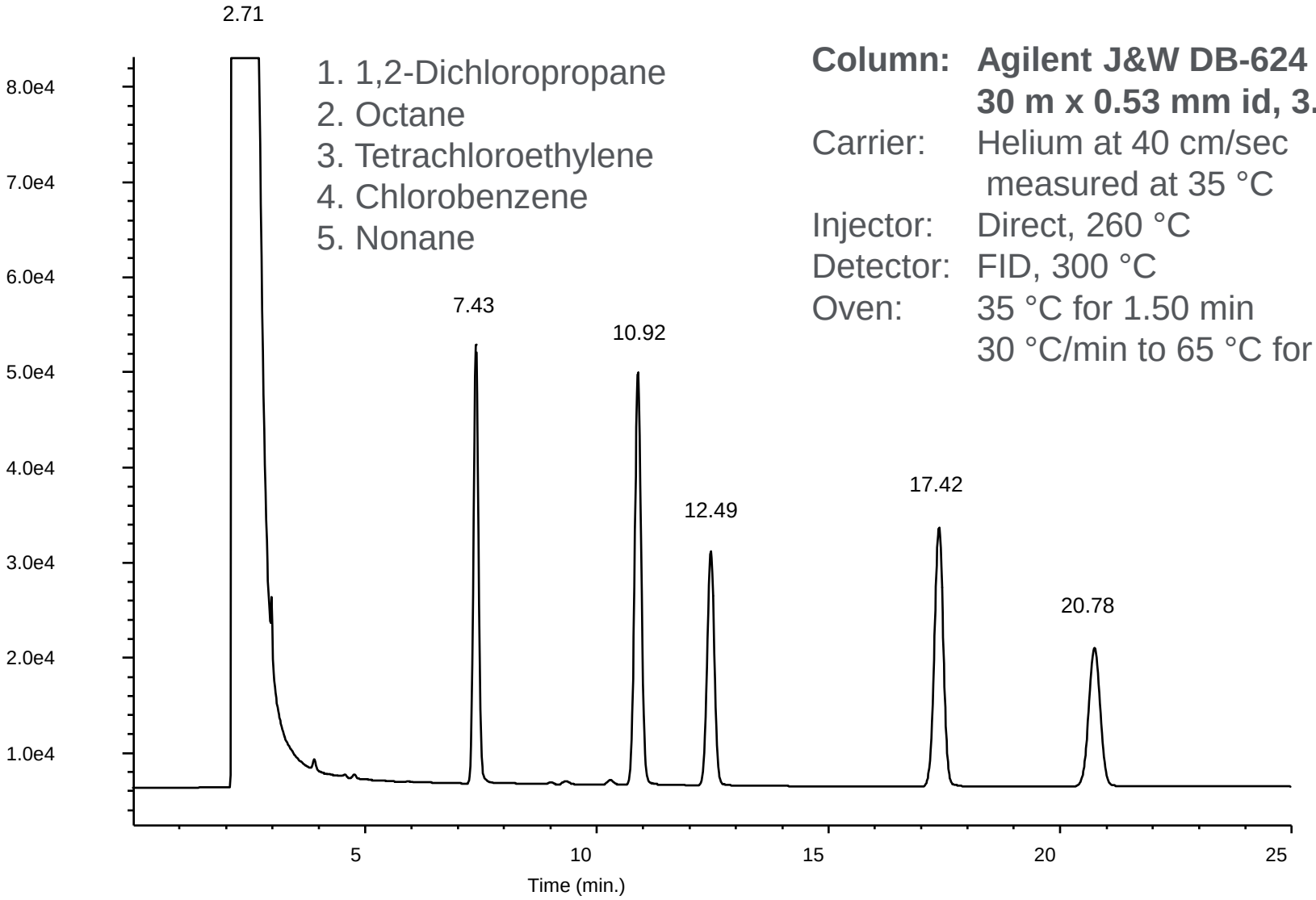
We have more semivolatile contamination!

*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

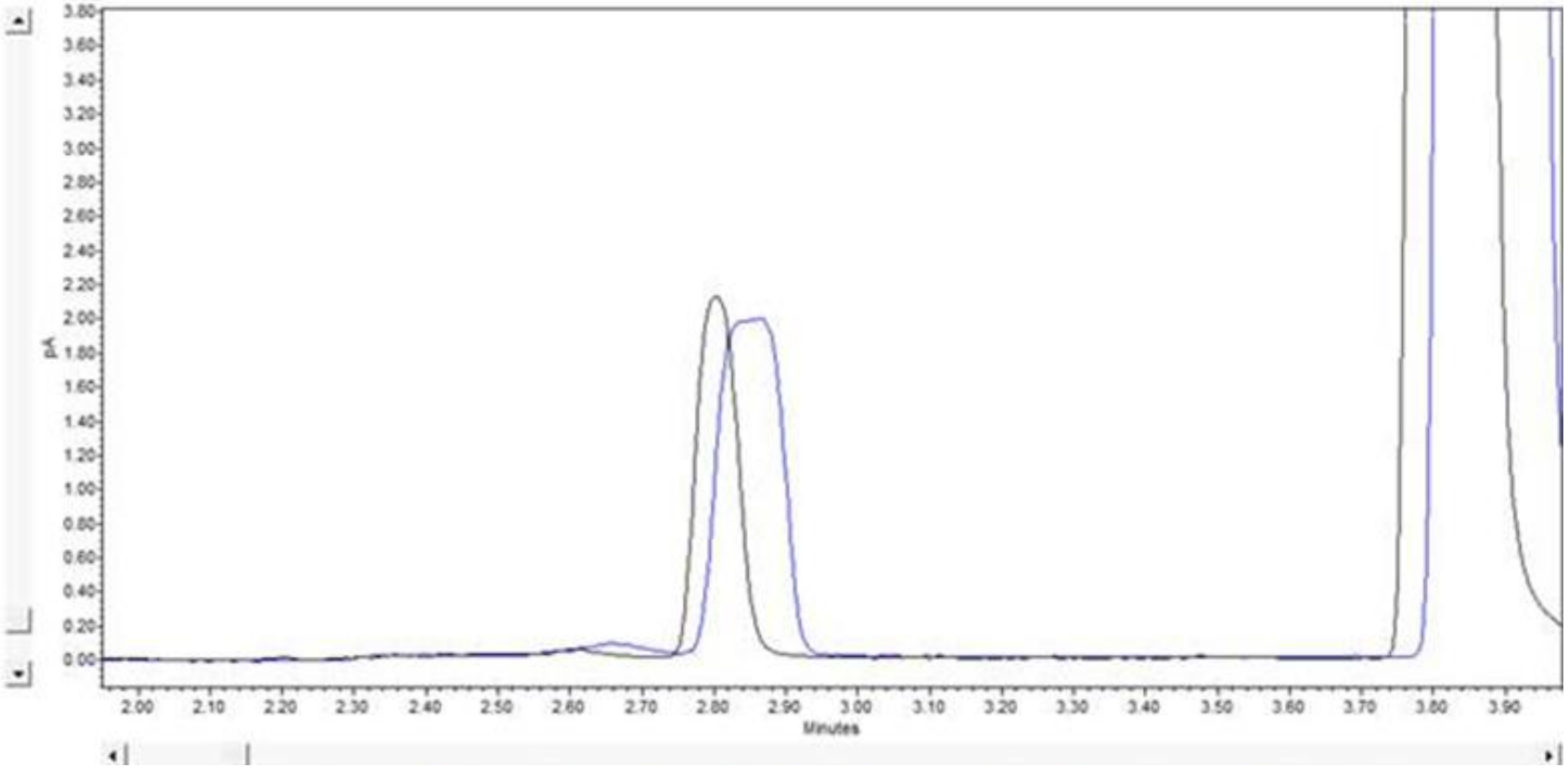
QC Test Mix



1. 1,2-Dichloropropane
2. Octane
3. Tetrachloroethylene
4. Chlorobenzene
5. Nonane

Column: **Agilent J&W DB-624**
30 m x 0.53 mm id, 3.0 µm
Carrier: Helium at 40 cm/sec
measured at 35 °C
Injector: Direct, 260 °C
Detector: FID, 300 °C
Oven: 35 °C for 1.50 min
30 °C/min to 65 °C for 10 min

Changing to a Higher Split Ratio Improves Peak Sharpness



5:1 Split ratio

10:1 Split ratio

Baseline Disturbances

Sudden changes, wandering, or drifting

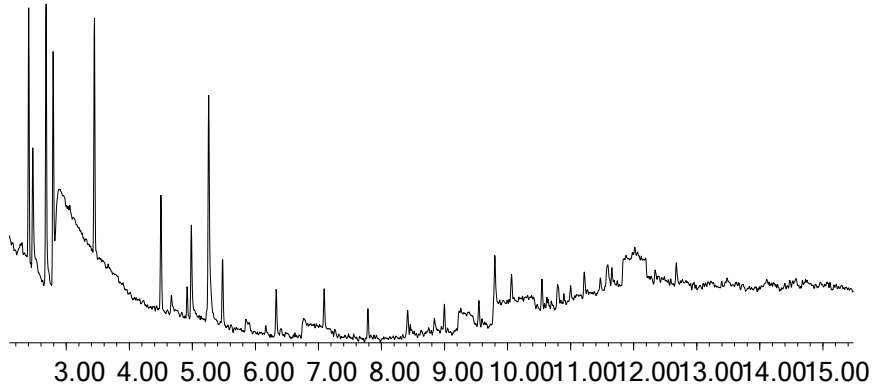
Drifting/wandering/weird disturbances

Column or detector

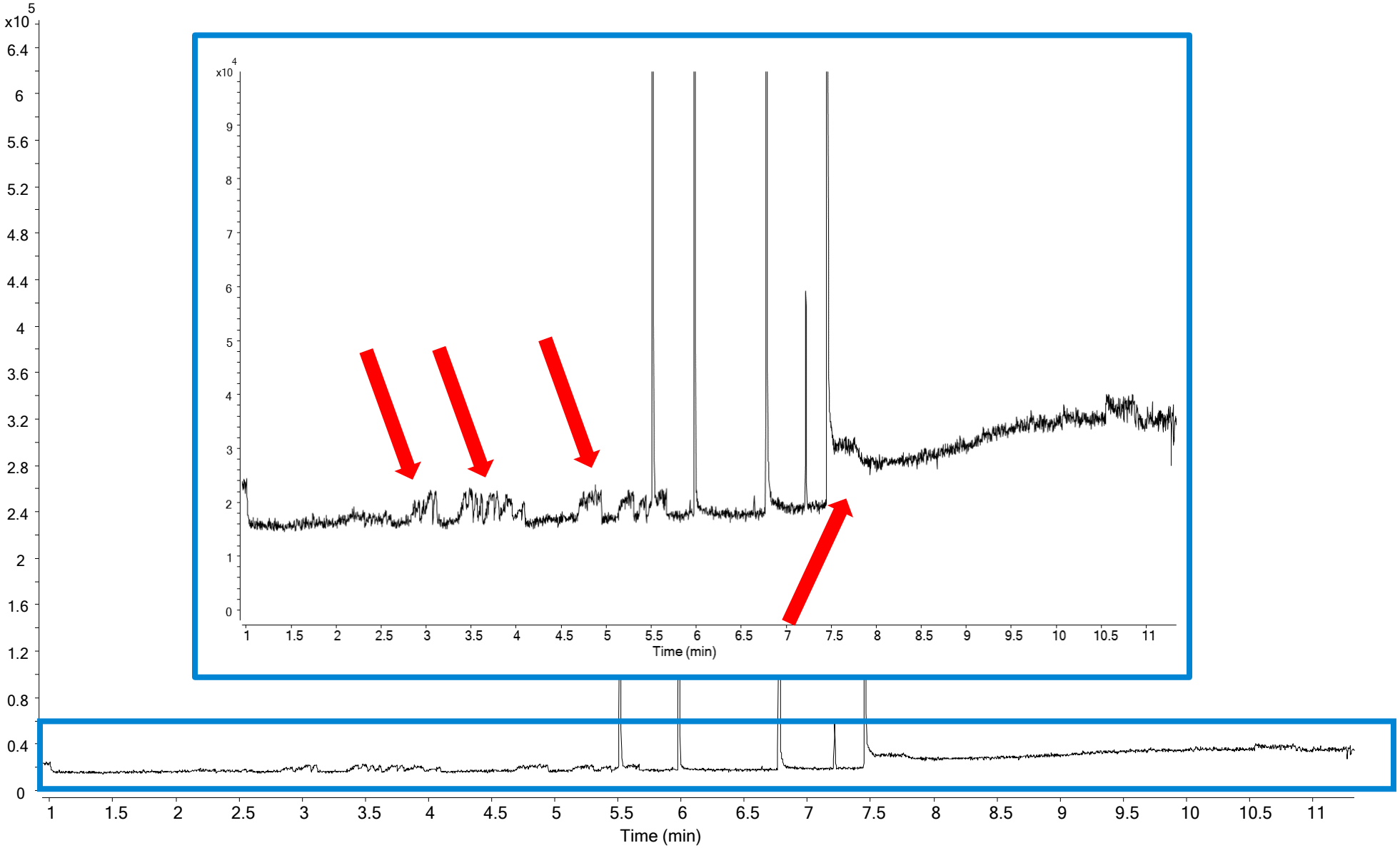
- Not fully conditioned or stabilized (electronics)
- Contamination

Flow

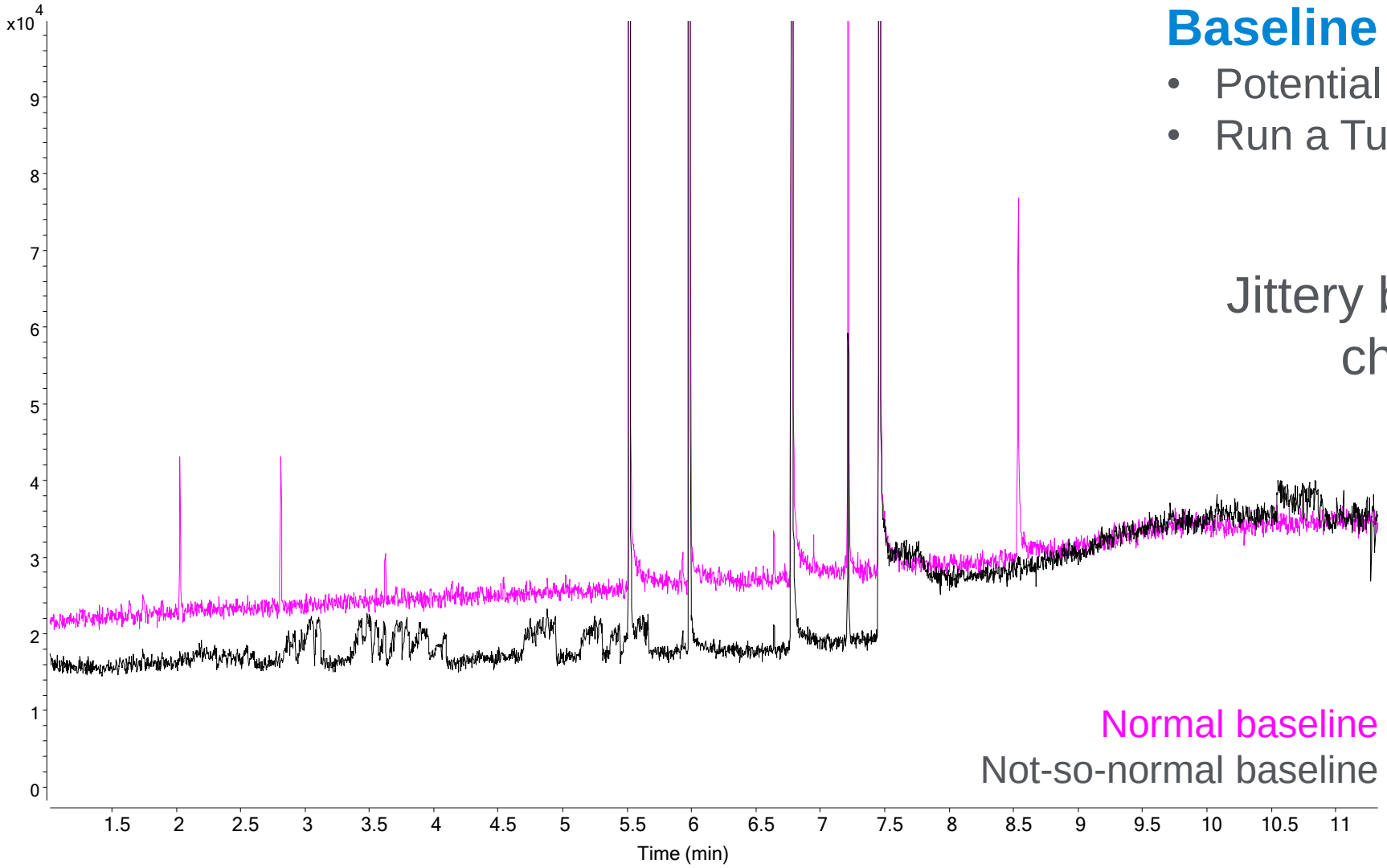
- Changes in carrier and/or detector gas flows
- Valves switching, leaks



Jittery Baseline Example



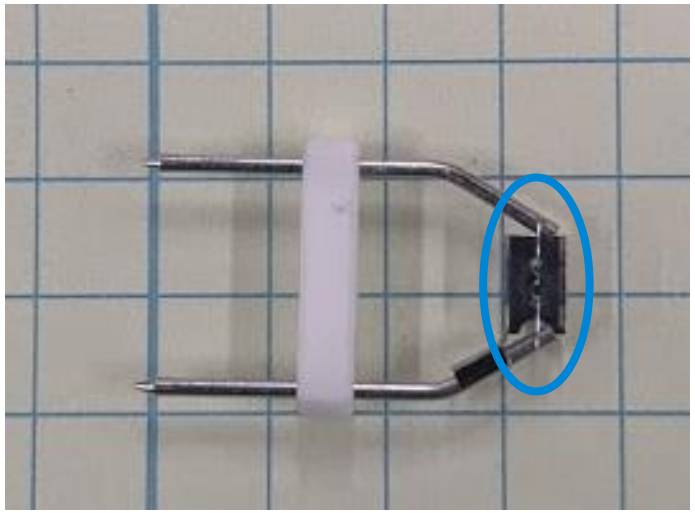
Jittery Baseline Example



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

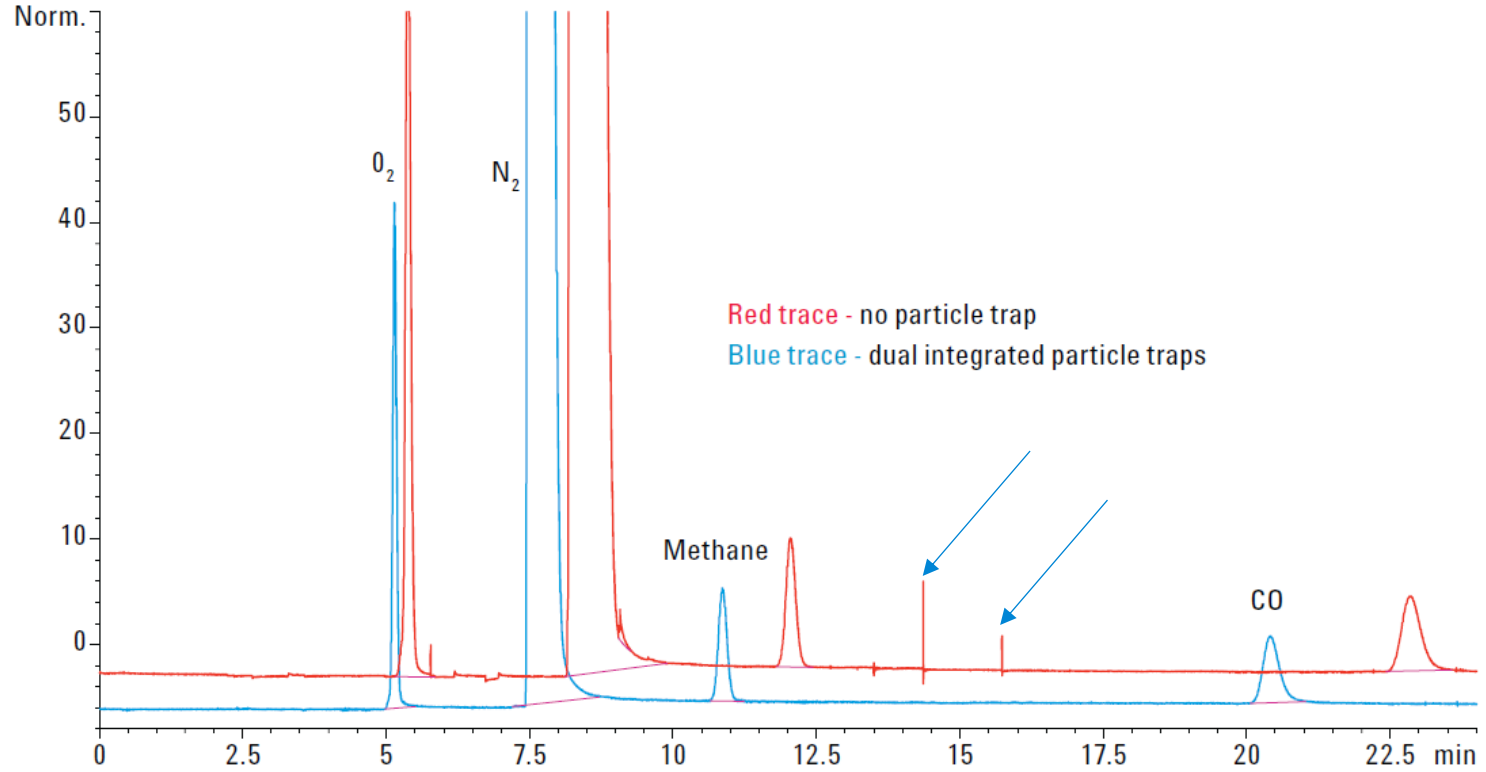
Column

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

Detector

- Air leak - ECD, TCD
- Electronics malfunction

Spiking Baseline



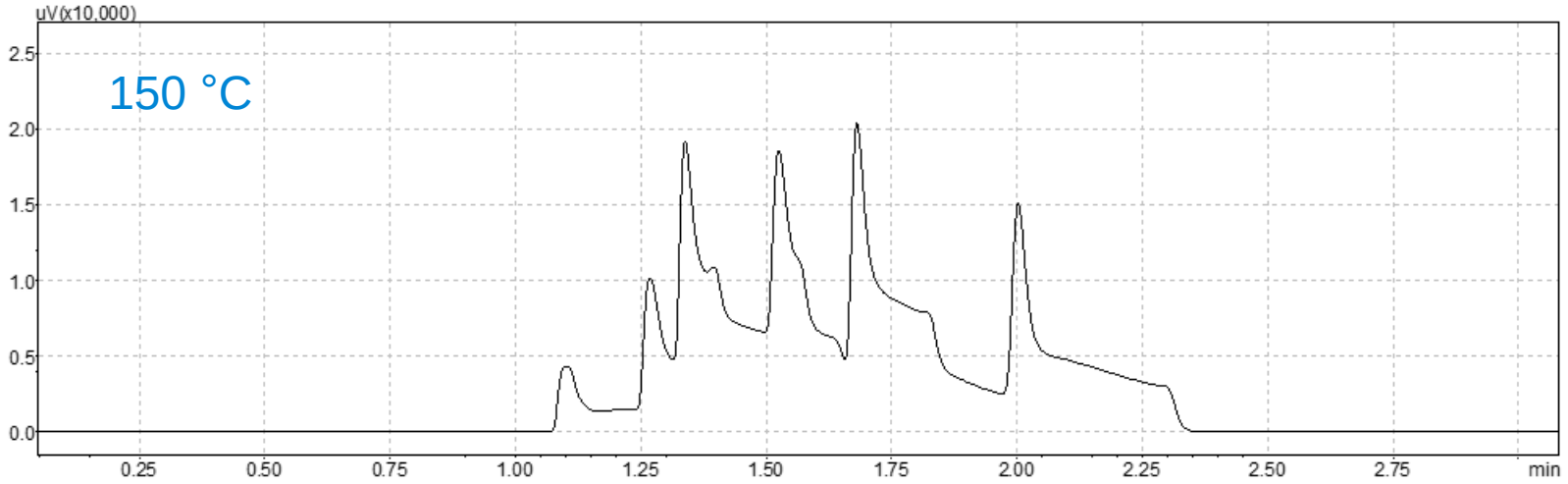
Detector

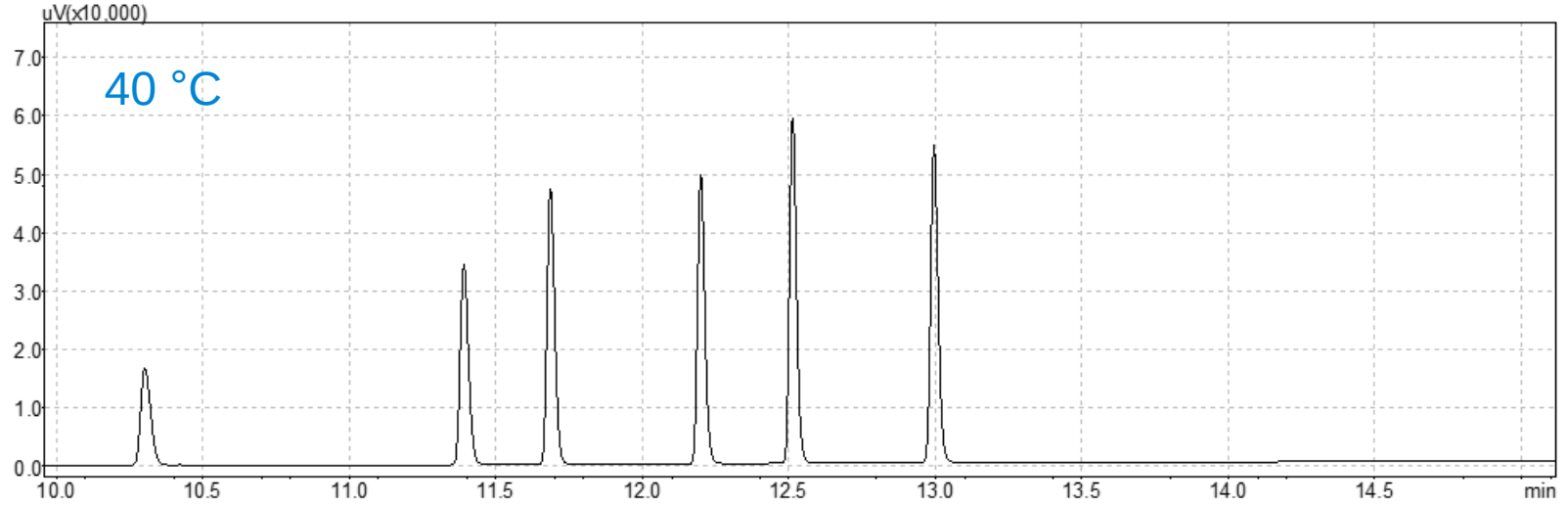
- Particles entering the detector
- Random: poor connection
- Regular: nearby "cycling" equipment (electronics)

Application literature 5991-2975EN

Weird Peak Shape Due to Lack of Analyte Refocusing

Free fatty acids in water on DB-FATWAX UI





Phase Deposition

- Can happen to cyano-phase columns when oven cools down too quickly
- Phase/bleed recondenses on itself
- Can be addressed by cooling the column slowly after a run

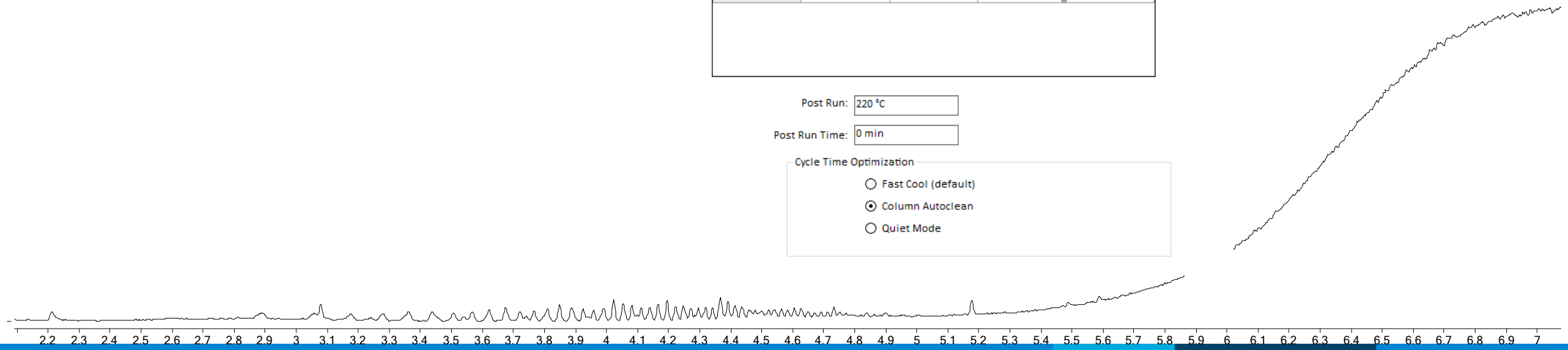
	Rate °C/min	Value °C	Hold Time min	Run Time min
(Initial)		50	1.5	1.5
Ramp 1	40	325	3	11.375
*				

Post Run: 220 °C

Post Run Time: 0 min

Cycle Time Optimization

- ○ Fast Cool (default)
- ◉ Column Autoclean
- ○ Quiet Mode



Quantitation Problems

Detector

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

Activity (adsorption) in injector or column

Injector

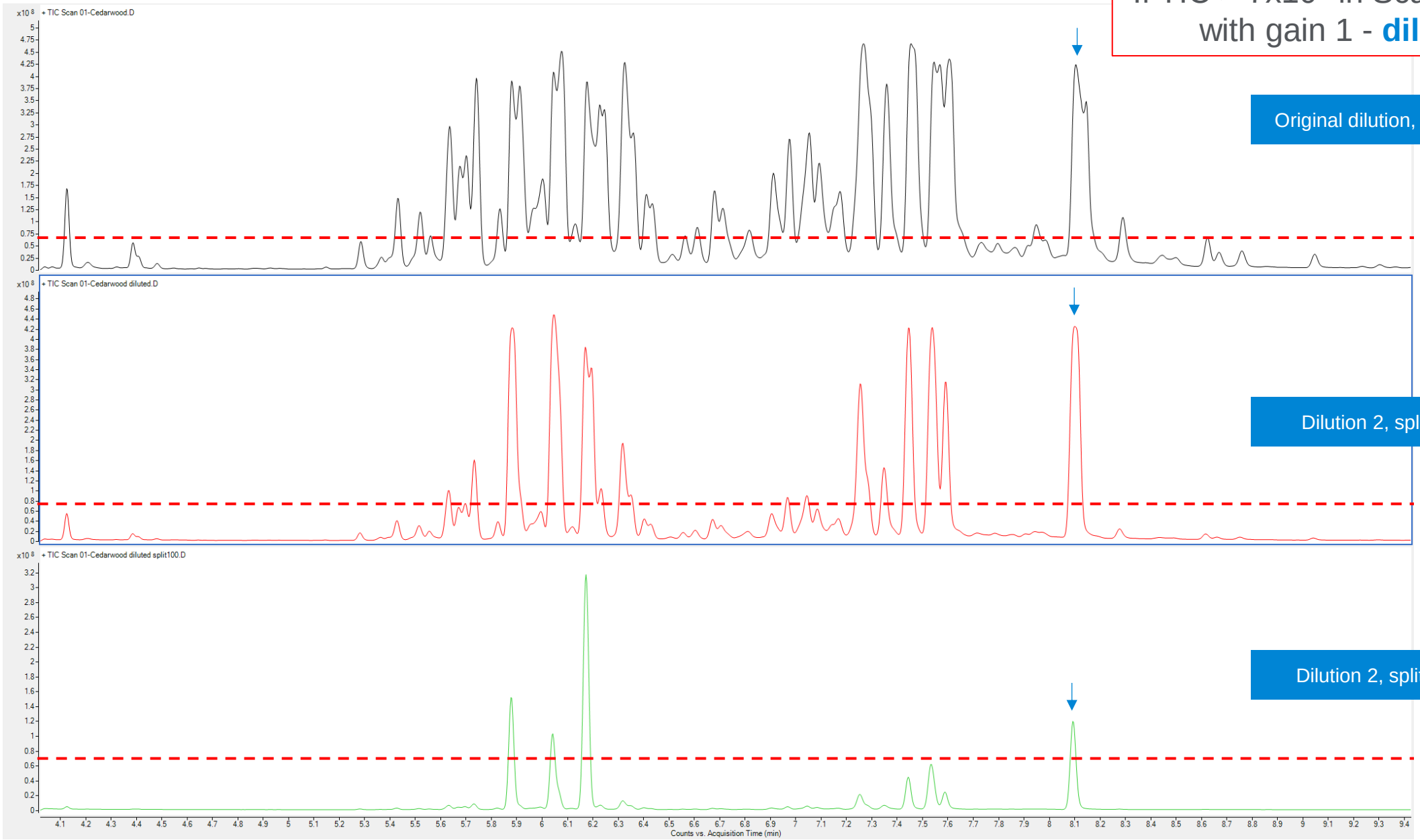
- Technique, settings, conditions
- Syringe worn

Other

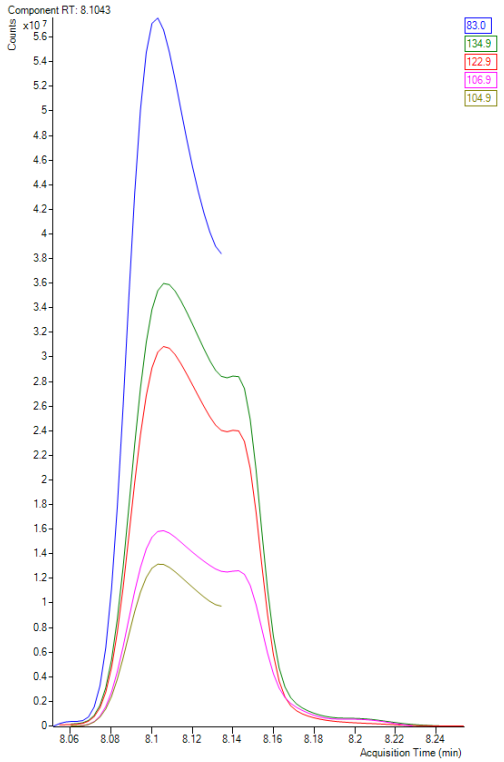
- Coelution
- Matrix effects
- Sample evaporation – leaky vials
- Sample decomposition

Distorted Peak Shape Example- Total Ion Chromatograms

If TIC > $7x10^7$ in Scan mode with gain 1 - **dilute**

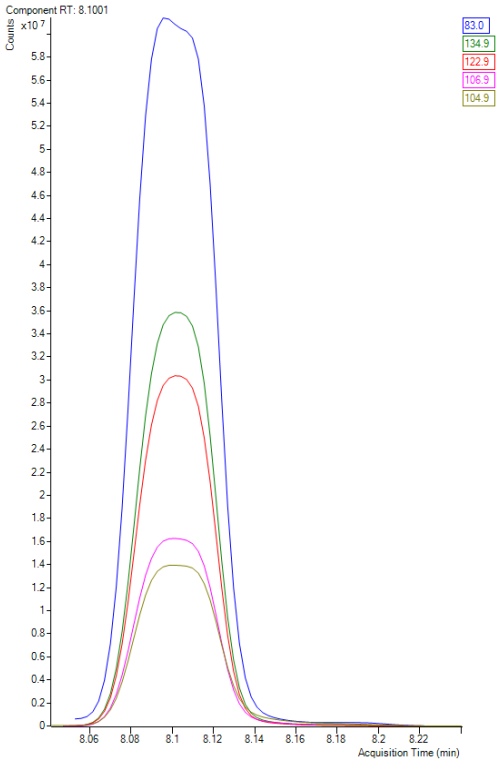


Distorted Peak Shape Example - Deconvoluted Extracted Ion Chromatograms



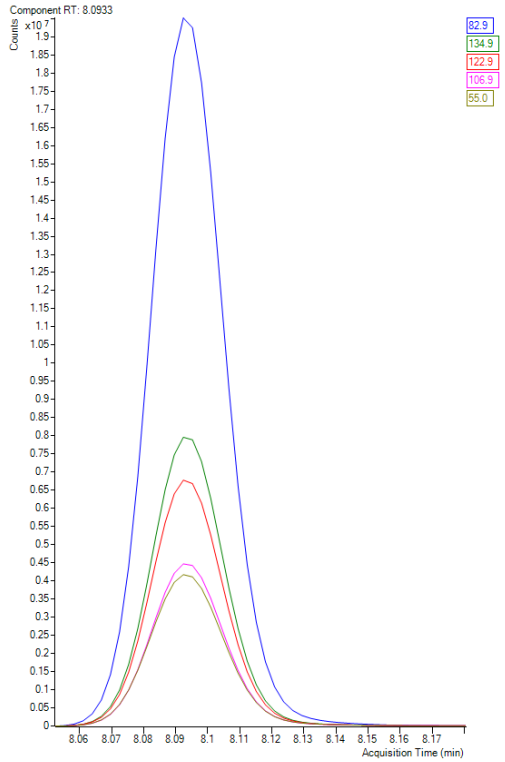
Original dilution, split 10:1

- EIC gaussian shape is lost and deconvolution is struggling to detect end of signal
- Highest abundance in overlay is $5x10^7$ – **too high**.



Dilution 2, split 10:1

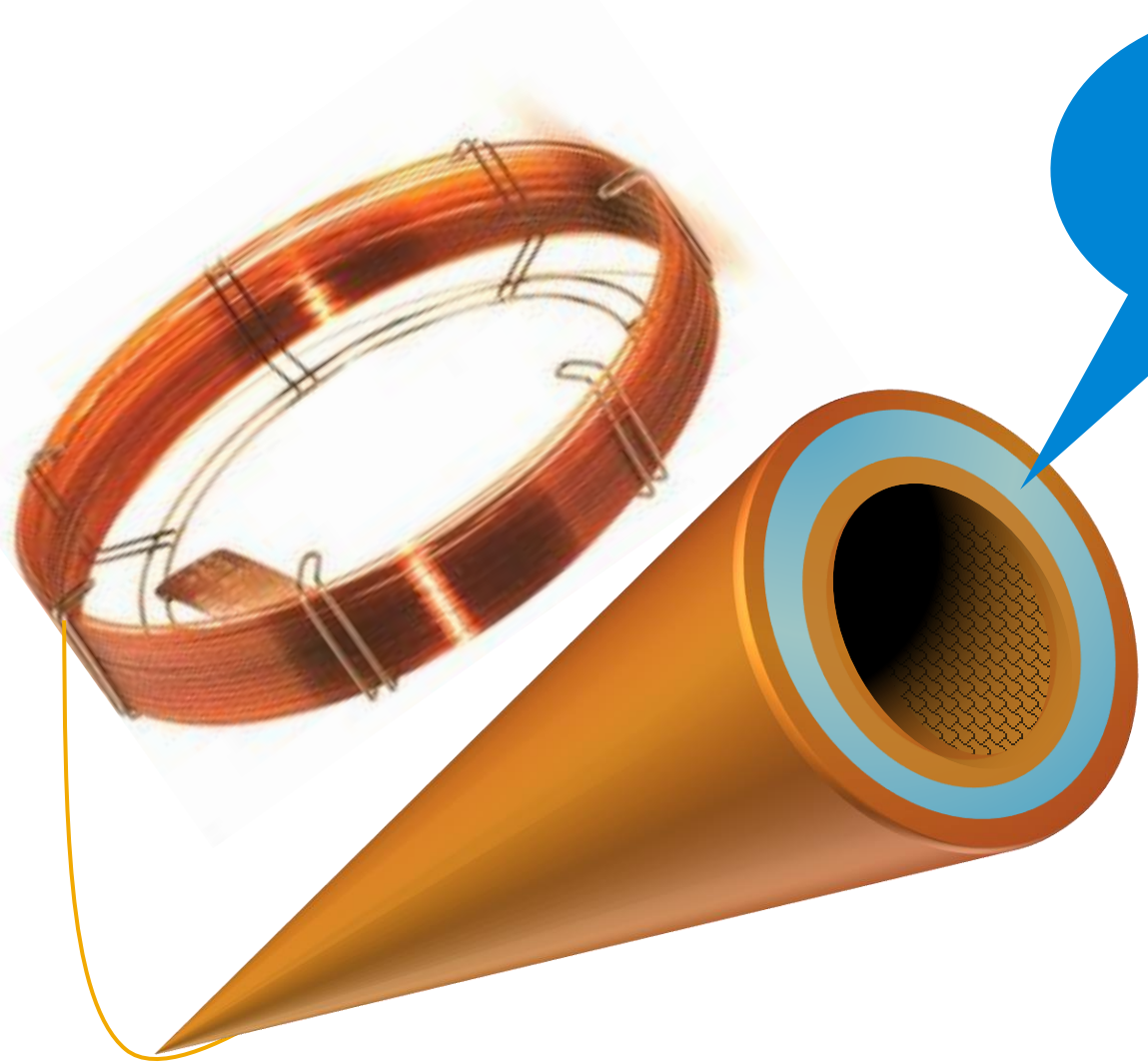
- Peak shape is broad and “rounded” at the top of peaks.
- Better, but still **too high**.



Dilution 2, split 100:1

- EIC gaussian peak shape is acceptable
- EIC abundance is acceptable

What is Not Caused by a Column?



- 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

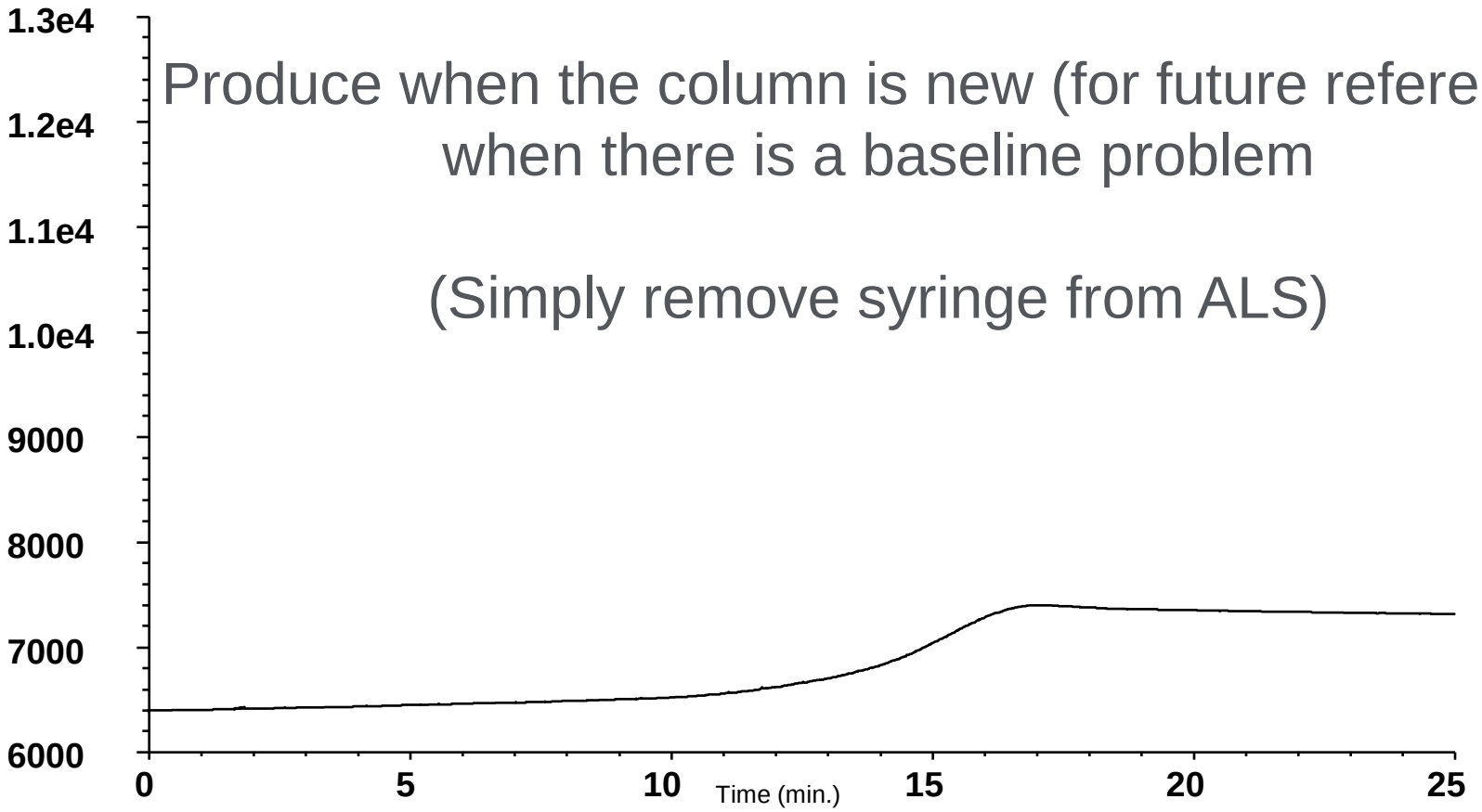
Troubleshooting Techniques

Troubleshooting Tools

Bleed profile (noninjection): *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



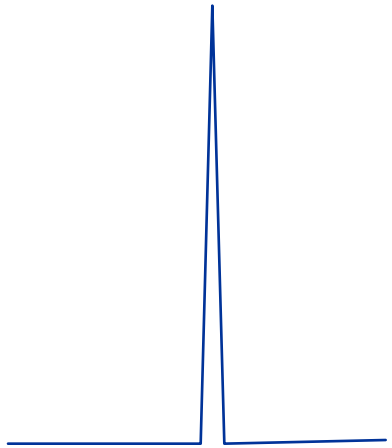
Produce when the column is new (for future reference)
when there is a baseline problem

(Simply remove syringe from ALS)

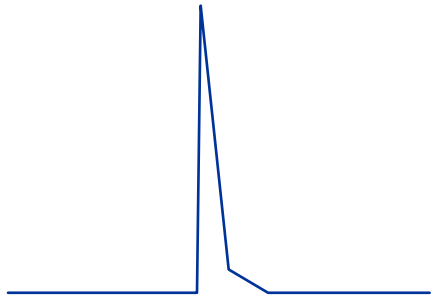
Agilent J&W DB-1, 30 m x 0.32 mm id, 0.25 µm
Temperature program // 40 °C, hold 1 min // 20 °C/min to 320 °C, hold 10 min.

Inject a Nonretained Compound to Check Flow Path

Used to check flow path



Good Installation



Improper Installation or Injector Leak

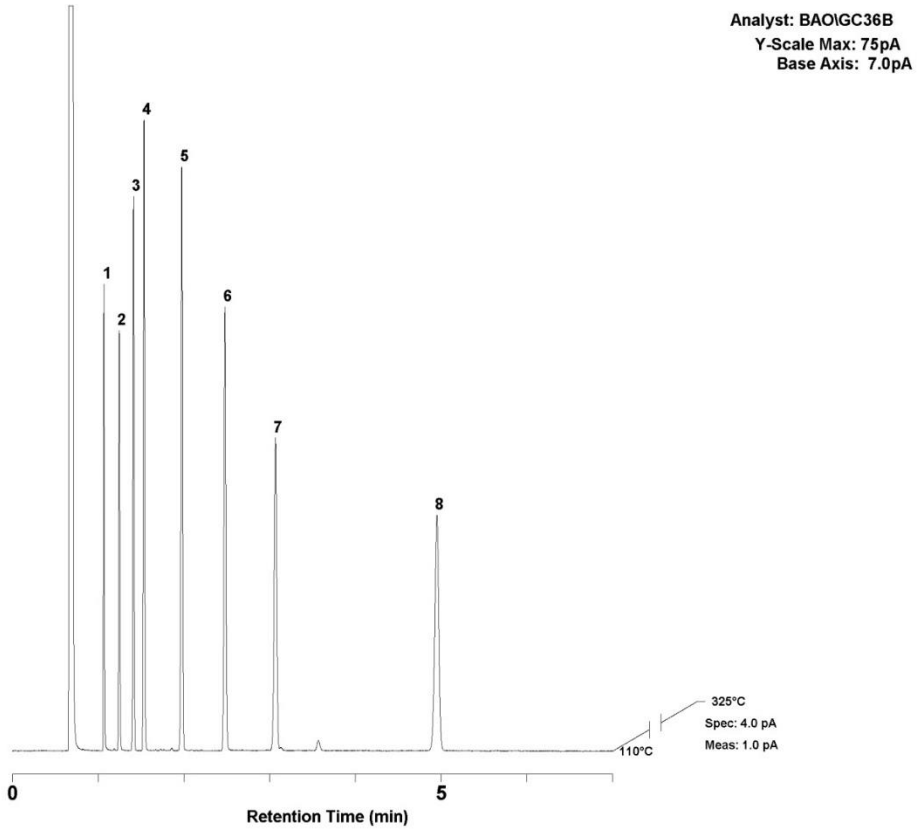
Potential explanations:

- 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)

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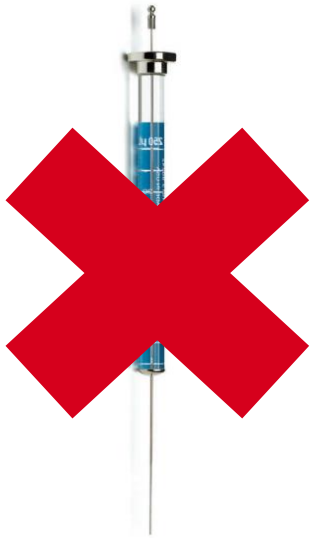
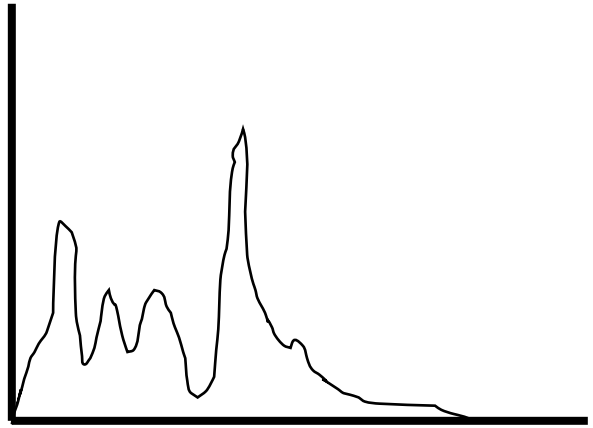
- Rigorously tested and manufactured under ISO 9001, ISO 17025, and ISO 17034 accreditation
- Sample preparation materials, columns, supplies, instrumentation, and reference materials from a single source

Perform a Noninjection “Blank”



Remove syringe from autosampler

Run your program



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

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 to 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, 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 to 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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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

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

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lc-column-support@agilent.com

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