Tips, Tricks, and Troubleshooting for Successful Headspace Analysis

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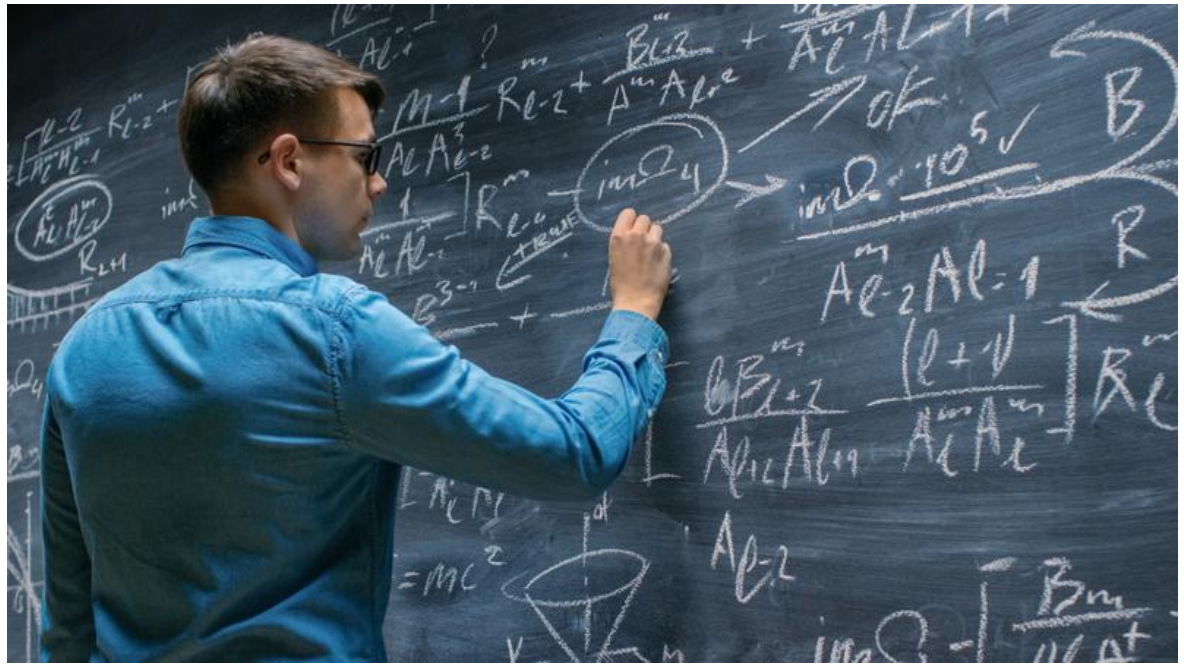
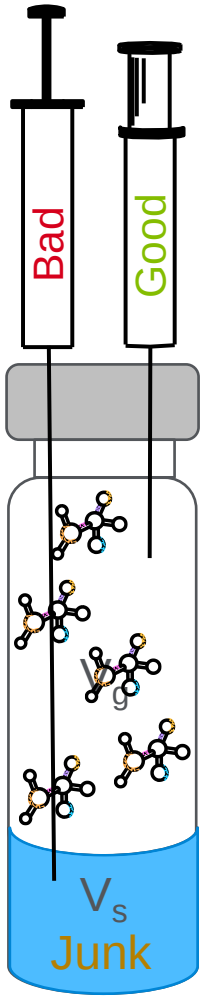
GC Application Scientist
September 17, 2024

Agilent
Trusted Answers

DE-000988

What Is Headspace?





$$K = \frac{C_S}{C_G}$$

$$\beta = \frac{V_G}{V_S}$$

$$C_S = \frac{W_S}{V_S}$$

$$C_G = \frac{W_G}{V_G}$$

$$W_S + W_G = W_0$$

$$C_0 \times V_S = (C_G \times V_G) + (C_S \times V_S) = (C_G \times V_G) + (K \times C_G \times V_S) = C_G \times [K \times V_S + V_G]$$

$$C_0 = C_G\left[\frac{K \times V_S}{V_S} + \frac{V_G}{V_S}\right] = C_G(K + \beta)$$

$$C_G = \frac{C_0}{K + \beta}$$

$$A\ \alpha\ C_G = \frac{C_0}{K + \beta}$$

HS Advanced Operation user guide:

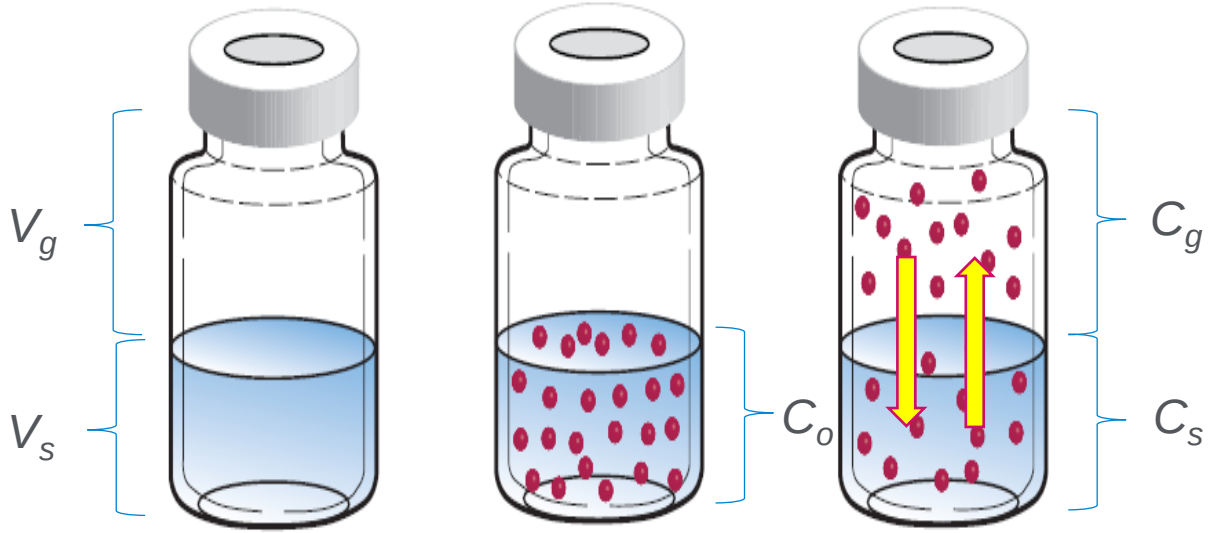
https://www.agilent.com/cs/library/usermanuals/public/G4556-90016.pdf

Why Headspace?

- Offers clean injections into GC systems
  - Less GC maintenance – only the volatile vapors are injected into the system
  - Non-volatiles/semi-volatiles/acids etc. stay in the liquid phase of the HS vial
- Less sample preparation
- Ideal for analysis of volatile analytes in dirty matrices that can’t be directly injected into the GC.

*Not suitable for some applications

Some Math to Make it Fun

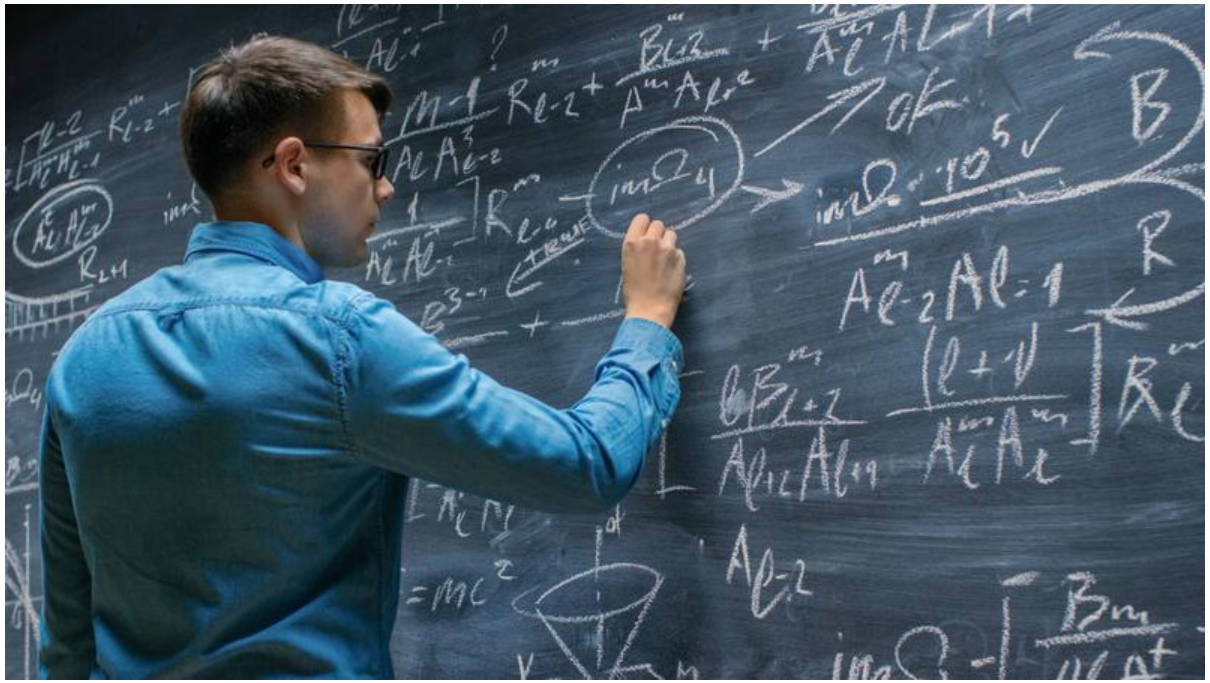


$$CoVs = CgVg + CsVs$$

Partition coefficient: $K = \frac{Cs}{Cg}$

Phase ratio: $\beta = \frac{Vg}{Vs}$

$$Cg = \frac{Co}{(\beta + K)}$$



What Should We Focus On?

Partition coefficient: $K = \frac{Cs}{Cg}$

The smaller the "K", the greater the concentration of the analyte in the gas phase.

Like dissolves like. The greater the solubility or affinity that an analyte has for the matrix, the larger the K.

What drives K?

Temperature:

- Higher temperatures drive K down = better sensitivity

Reduce Solubility = Reduce "K" = Improved response

- Add salt
- Add another solvent to the matrix

What Parameters Drive Success?

- Incubation temperature
  - Typically, 10-20 °C below the solvent BP (need to avoid boiling the solvent!)
- Incubation time
  - Determined experimentally
  - Need to ensure equilibrium is reached
  - Once equilibrium is reached, no need to incubate longer
- Shaking
  - Shortens incubation time
- Efficient transfer of the sample from the vial to the column
- Use of salts

Things to Consider

- You will need to have at least 5 mL of headspace in the vial.
  - 15 ml maximum for 20 mL vials / 10 mL maximum for 10 mL vials
- Keep the incubation temperature 10 to 20 °C below the BP of the solvent/matrix.
- Long incubation times ‘generally’ only delay the first sample.
  - The HS can over-lap samples
- Higher split ratios help get the sample onto the column more efficiently; this results in sharper peaks.
  - Lower splits are ‘OK’ with larger id columns. Higher volumetric flow transfers sample faster.
- Shake, but try to keep the sample from splashing the vial septum.
  - Sample can get into the sample probe and contaminate the loop
- Think about the temperature limitation of vial septa
  - Be considerate of sample/analyte degradation

Headspace Parameters

Temperatures

- Oven
- Sample loop
- Transfer line
- Transfer line interface

Times

- Vial equilibration
- Injection duration
- GC cycle time

Vial and loop

- Vial size
- Shake vials while in oven
- Vial fill mode
- Loop fill mode

Starting Parameters

Temperatures

- Oven 20 °C below the BP of the matrix
- Sample loop Same temperature as the oven or higher (+10 c)
- Transfer line Hot enough not to have anything condense (+ 10 c)
- Transfer line interface Same as the inlet

Times

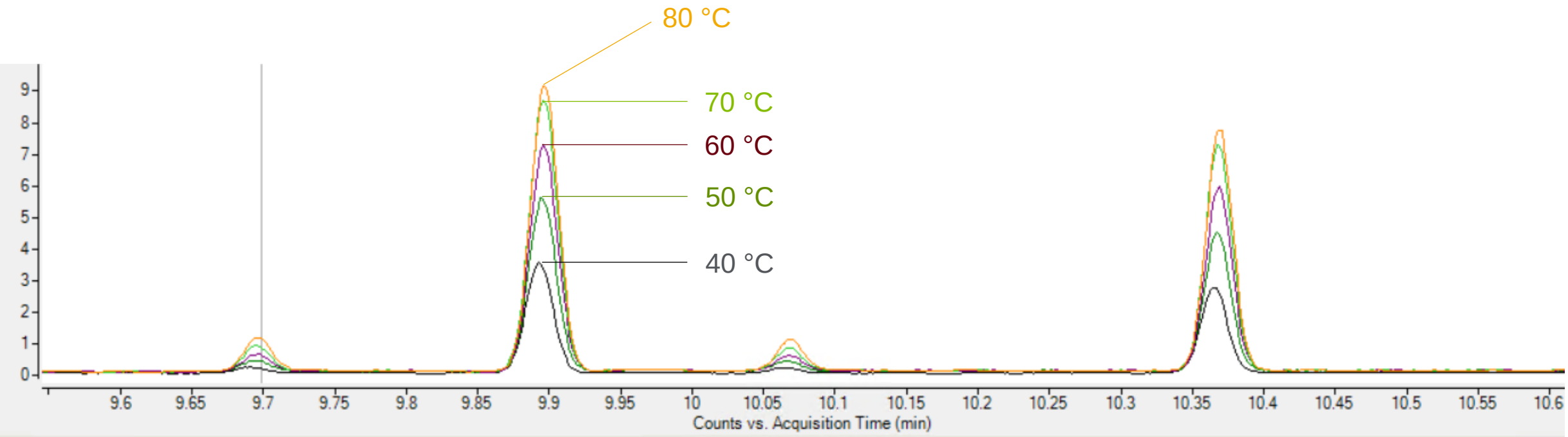
- Vial equilibration 10 minutes, but use method development
- Injection duration 0.5 minutes
- GC cycle time Run time + cool down to ready

Vial and Loop

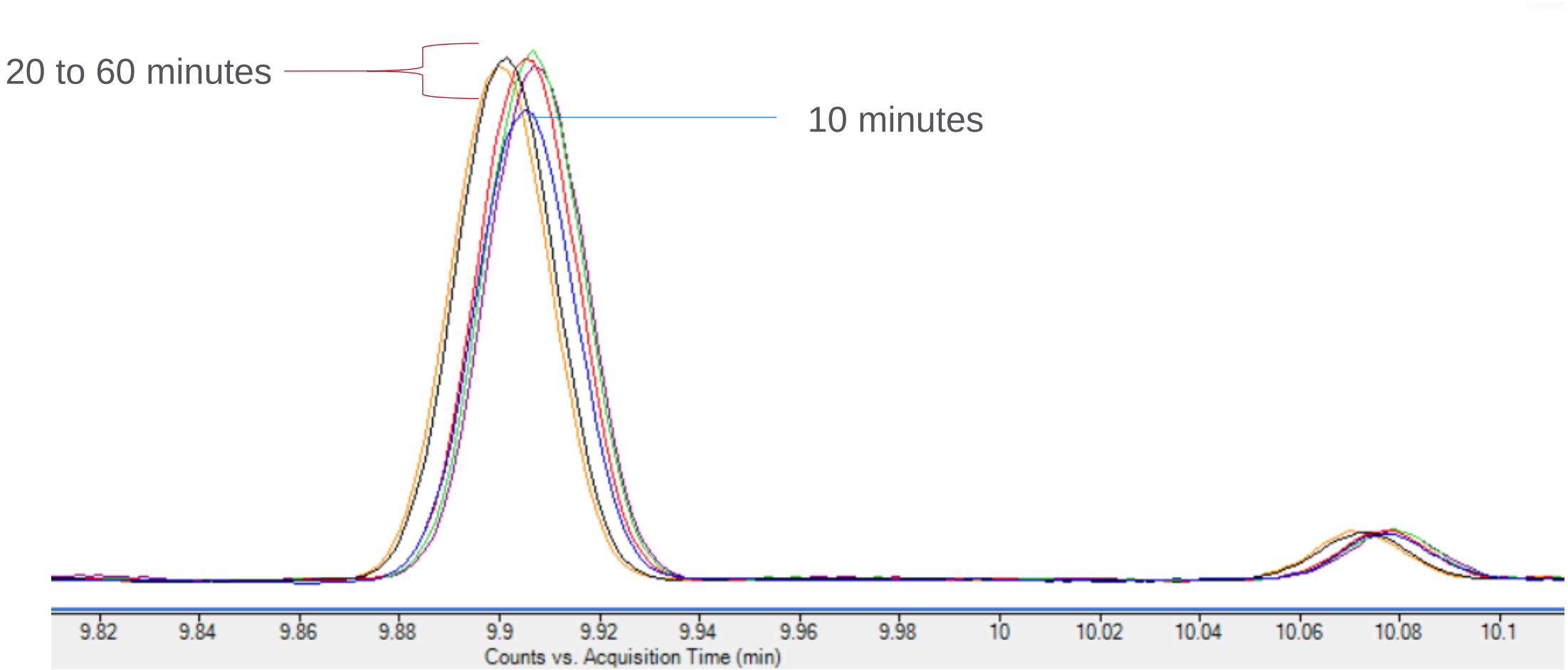
- Vial size 20 mL
- Shake vials while in oven 3 (low)
- Vial fill mode Default 15 psi
- Loop fill mode Default

Incubation Temperature Increase

20 minutes
K decreases with T
Not equal for all analytes



Incubation Time

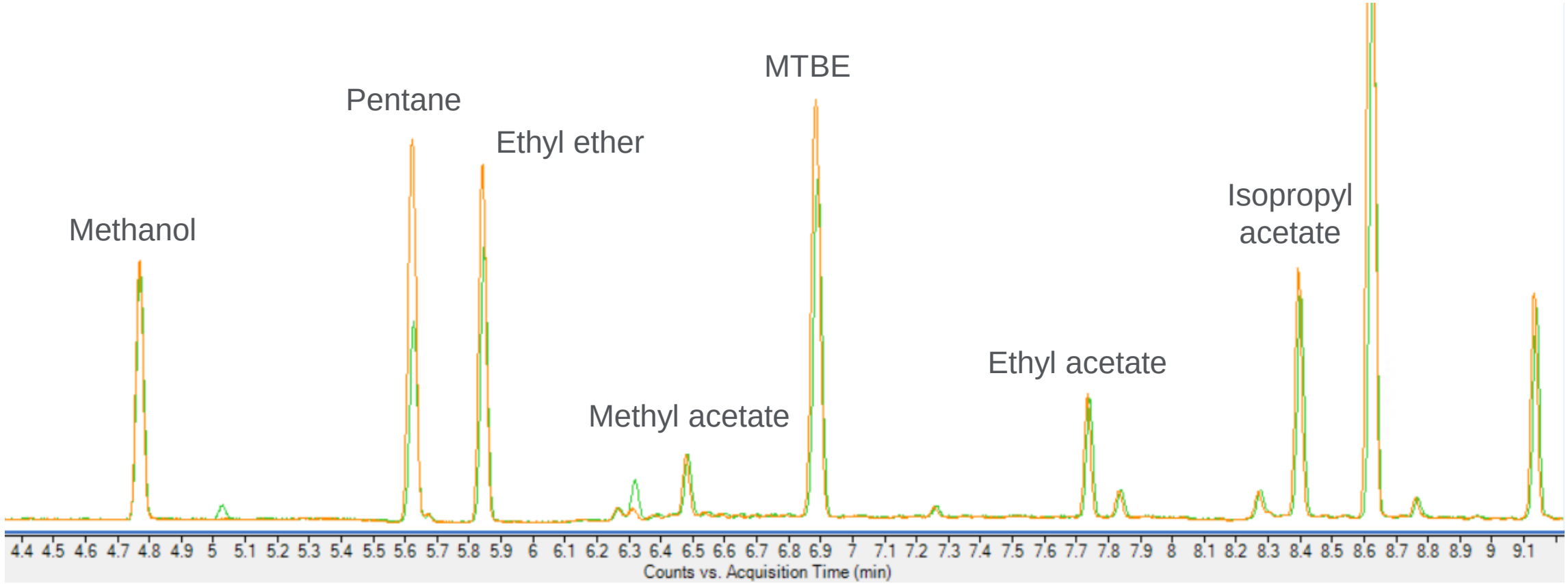


Change in Vial Size

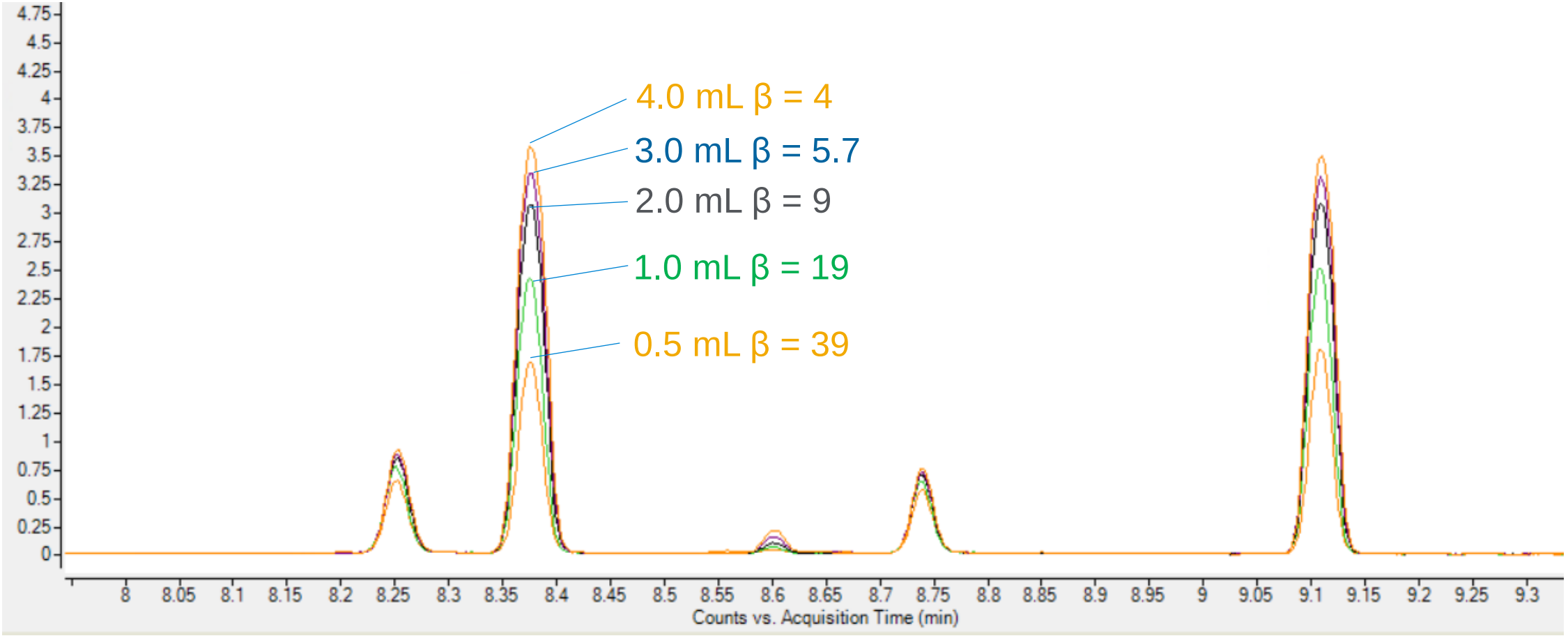
4 mL sample, changing β

10 mL vial β = 1.5

20 mL vial β = 4



Change in Sample Volume in a 20 mL Vial

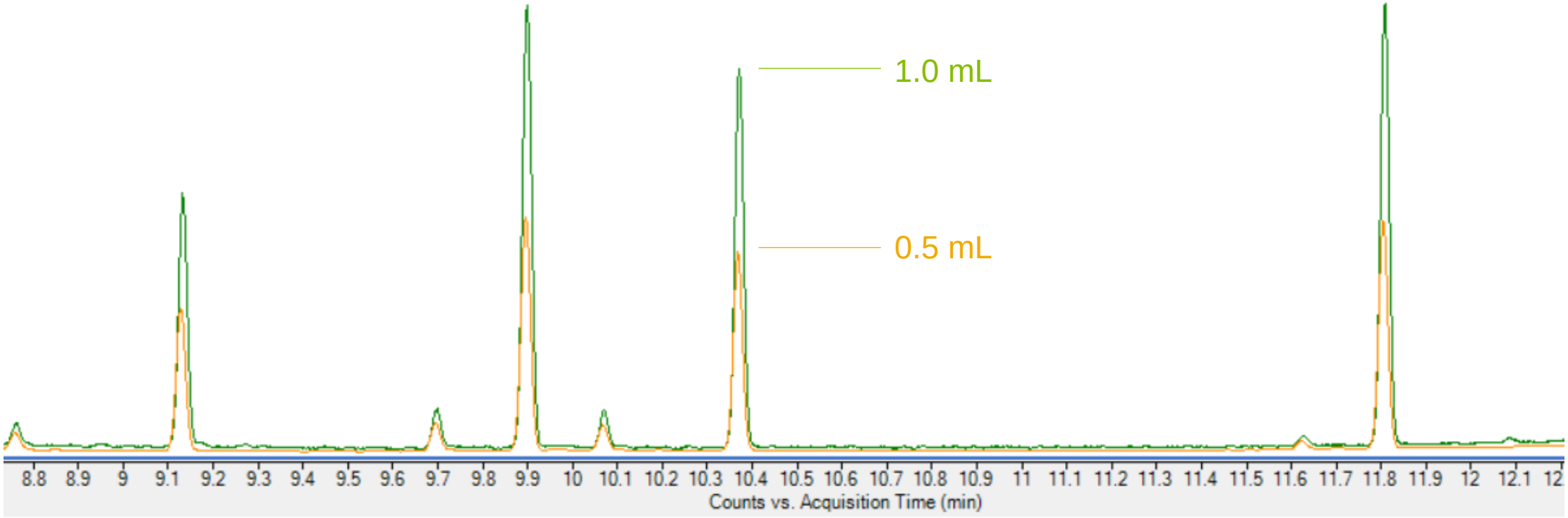


What Else Can Affect Signal?

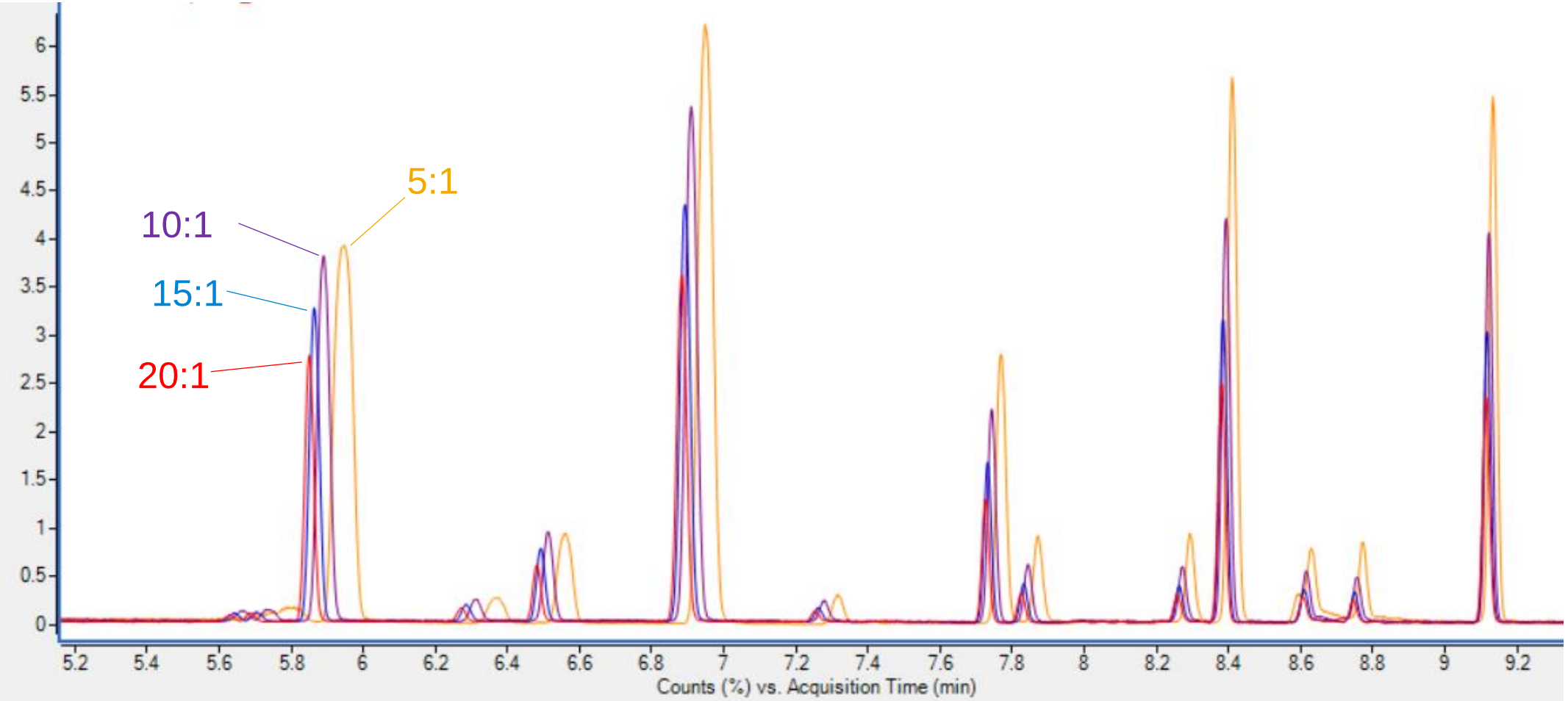
- Loop size
- Split ratio
- Liner type

Change in Loop Size

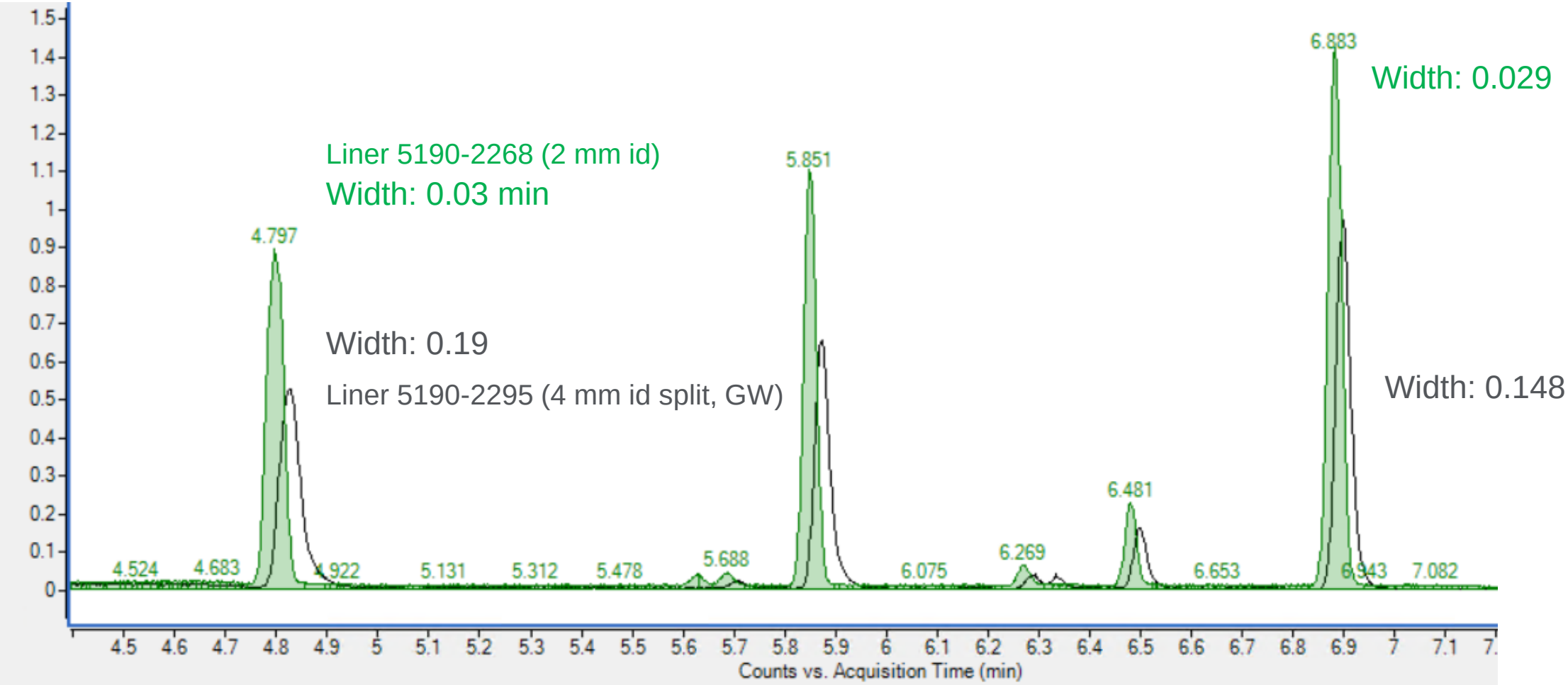
40:1 split (64 mL/min)



Change in Split Ratio



Liner Size and Type



Use of Salts

Decreases the solubility of polar analytes in aqueous samples

Decreases K favoring the gas (headspace) phase

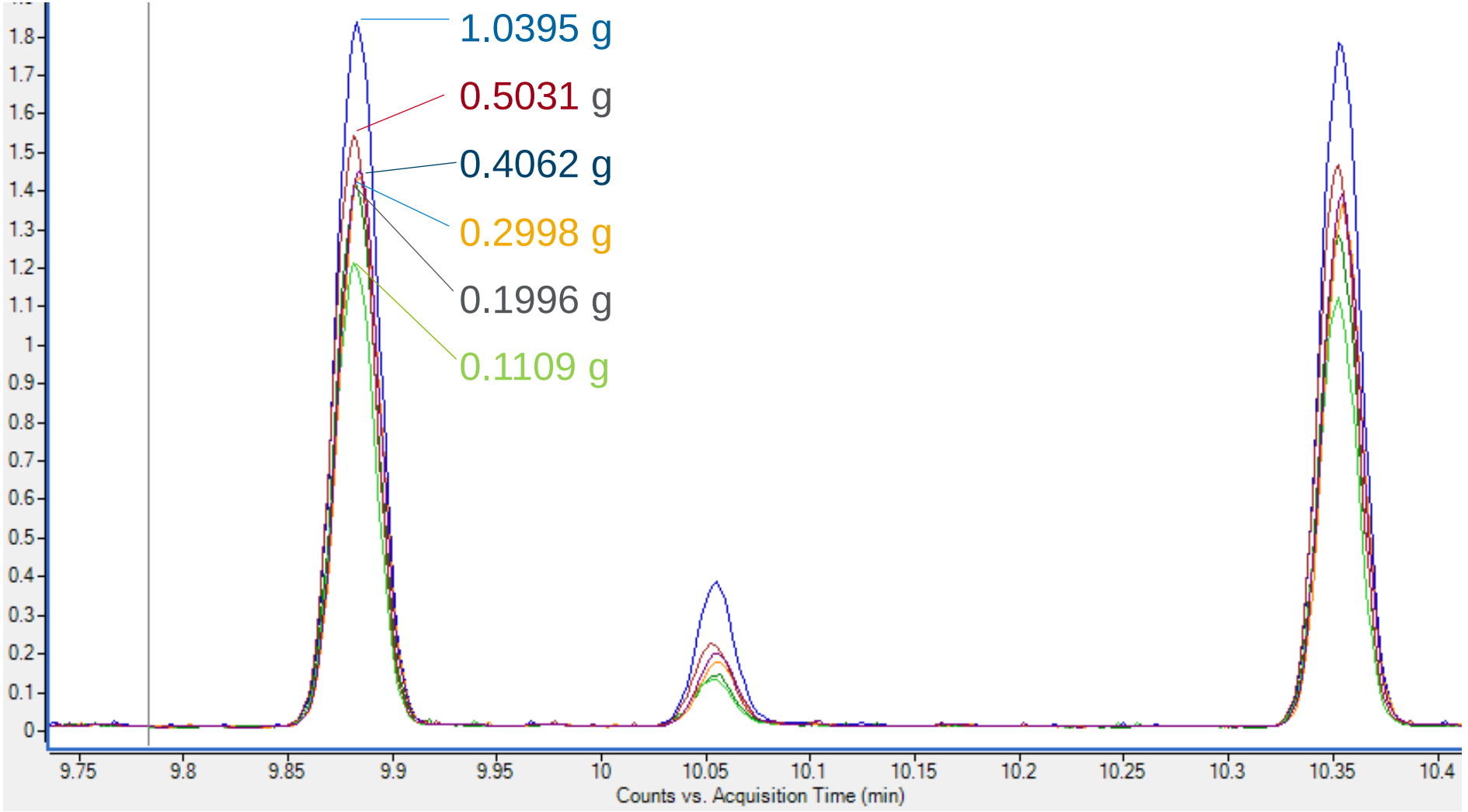
Potassium carbonate (K_2CO_3)
Ammonium chloride (NH_4Cl)
Ammonium sulfate ($(NH4)_2SO_4$)

Sodium chloride ($NaCl$)
Sodium citrate ($Na_3C_6H_5O_7$)
Sodium sulfate (Na_2SO_4)

Use high quality, low impurity salts
Be sure to check blanks with salt for contaminants

Effect of salt

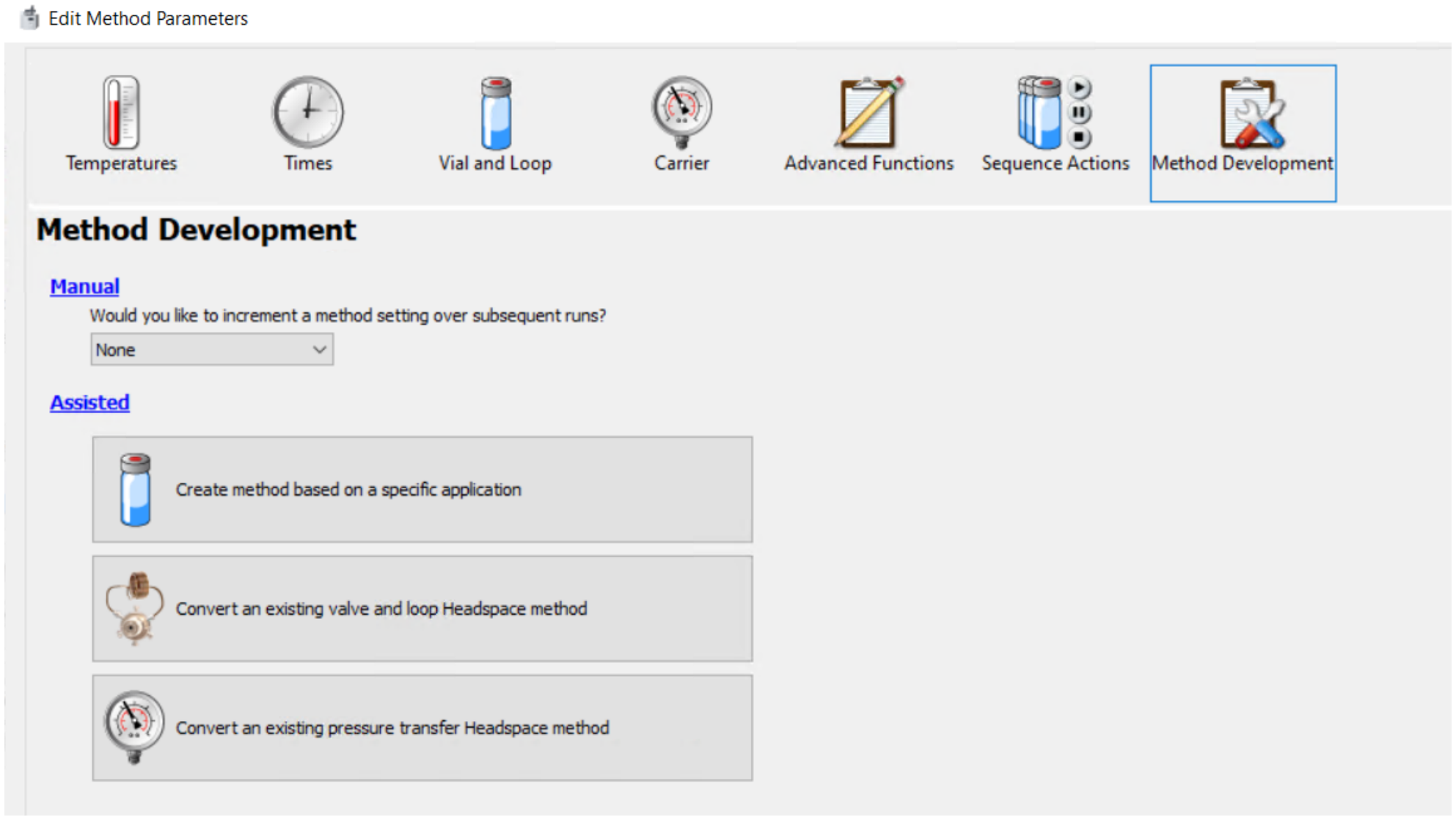
20 mL vial
80 °C oven temperature
20 minute incubation



Can I Inject Multiple Times?

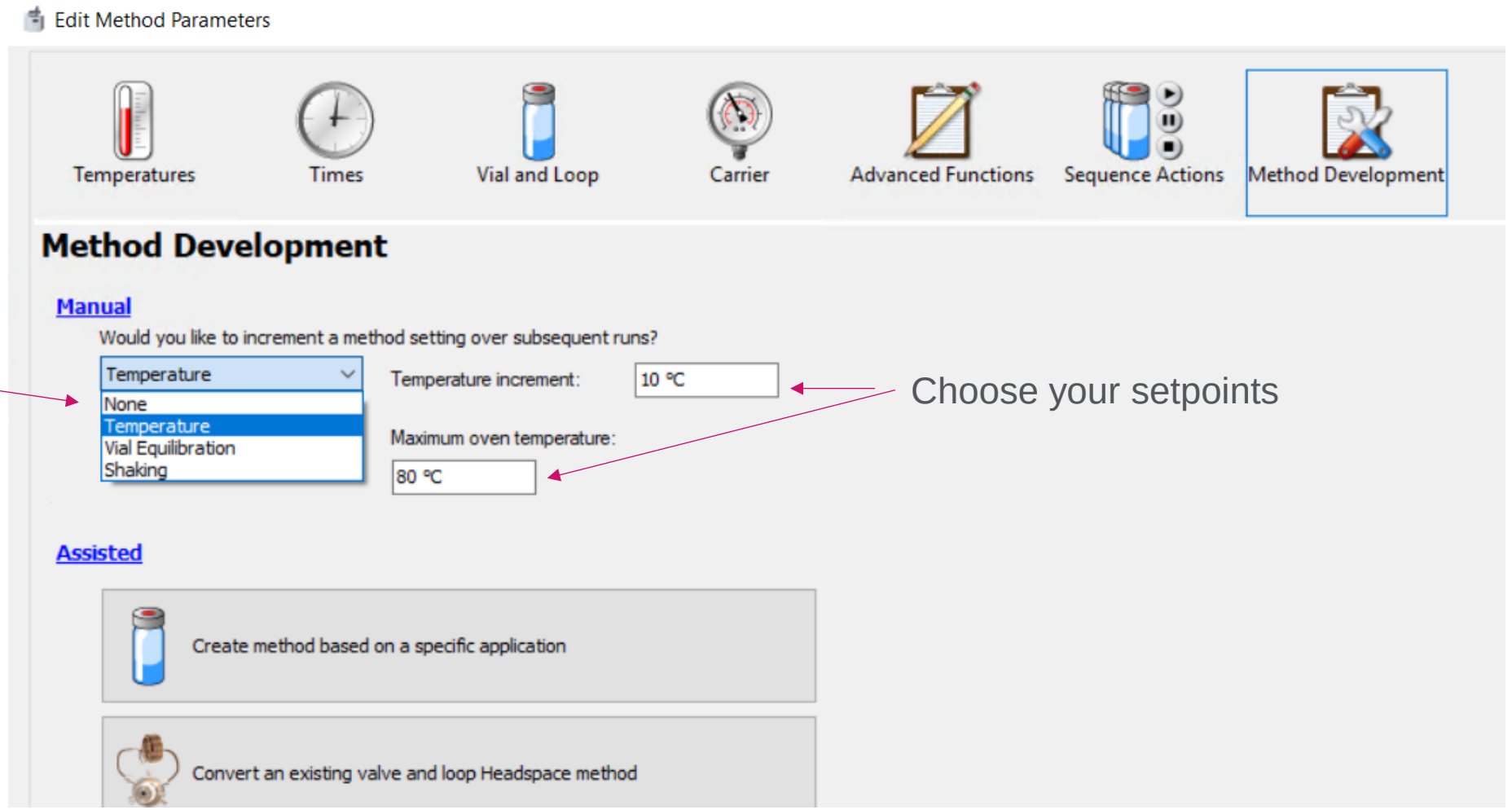
Only for developing a chromatographic method

Method Development Tools



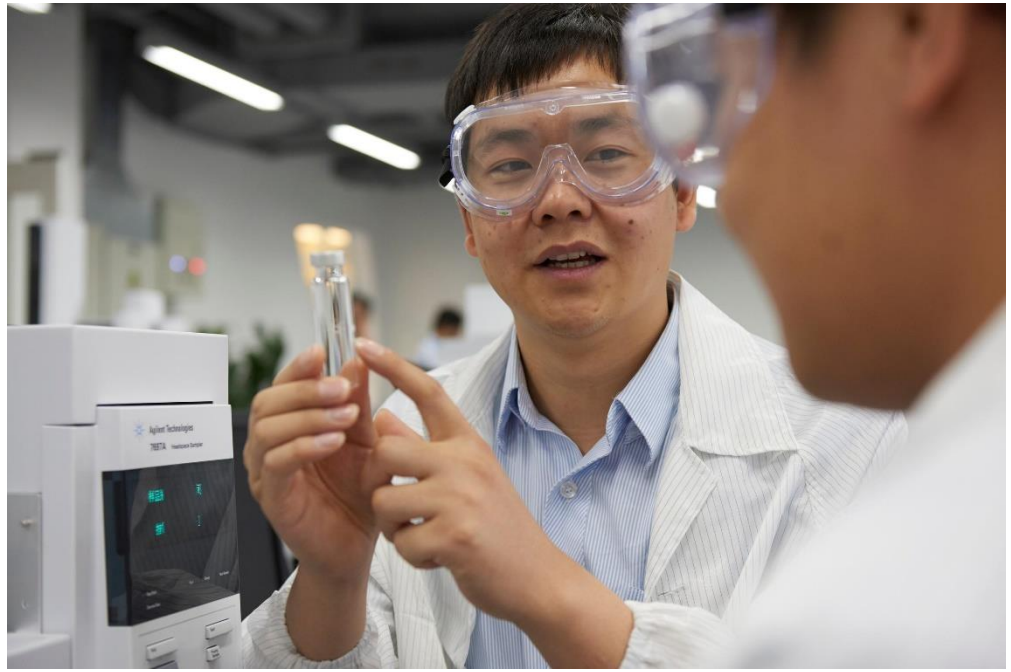
Method Development Tool

Choose what you want to increment



Choose your setpoints

Types of Vials



5182-0837

5188-2753

5067-0226

5182-0838

Consumables

Good for SPME

Max temp 125 °C
Butyl/PTFE

Safety cap
Tears at 45 psi

Max temp 180 °C
Silicone/PTFE

High Performance Septa

Maximum temperature is 300 °C

Reduce siloxane interferences at high temperatures

High-power crimpers are required for steel caps

Publication number: 5990-9385EN

High-Power Crimper

Crimper with 20 mm jaw set
5190-4067
Required when using steel camps

Standard Crimpers

5040-4669

5190-3189

How Tight is Right?

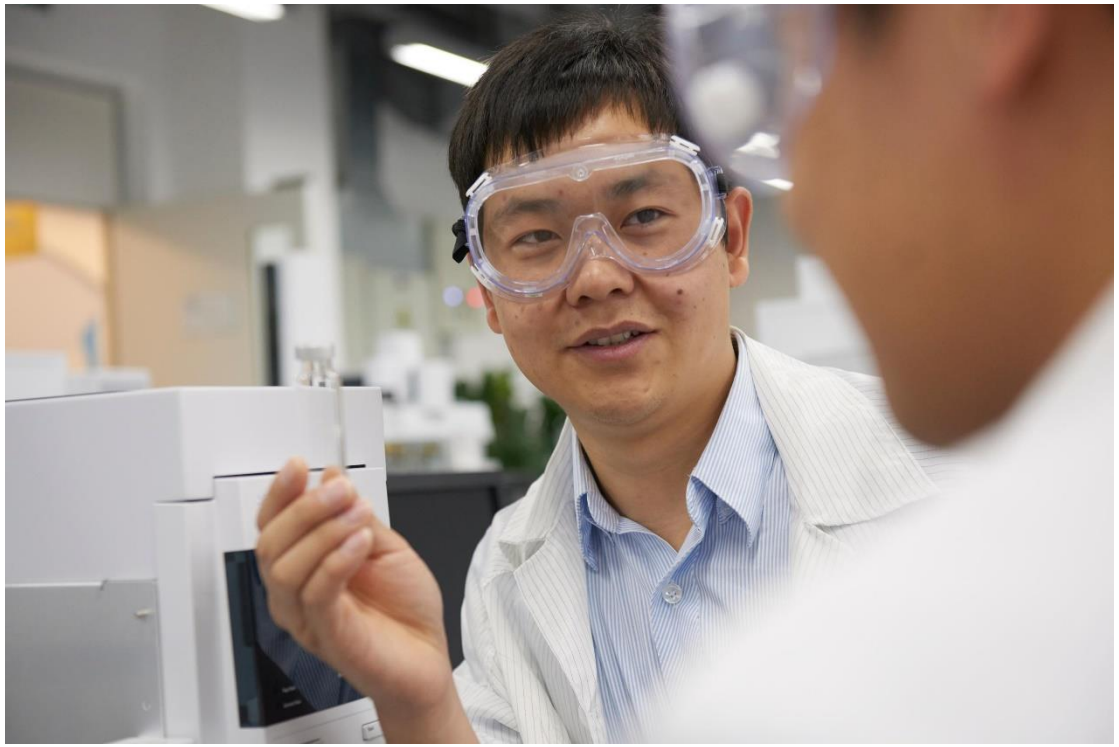
Good crimp

Too tight

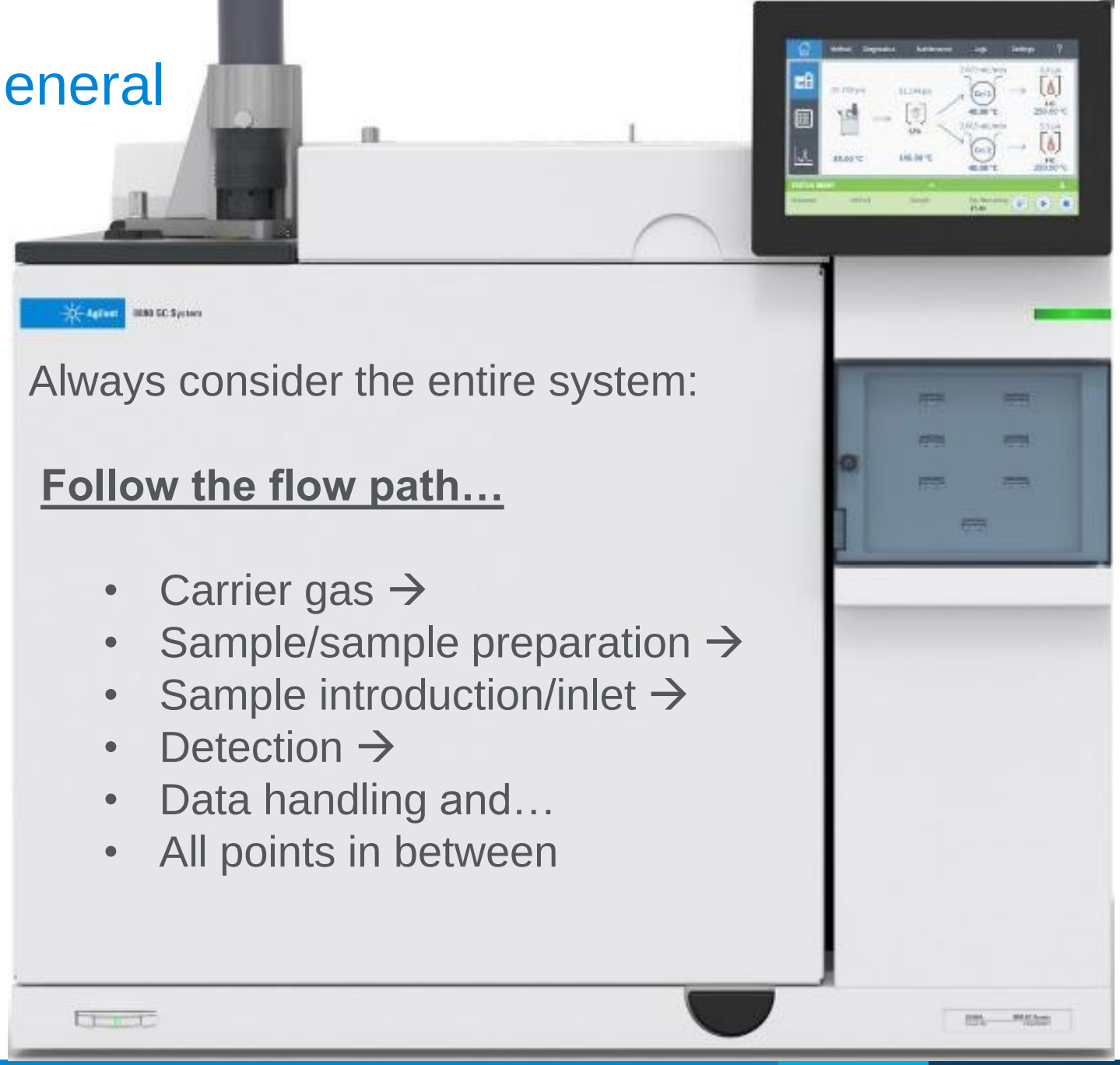
Too loose

Troubleshooting

- No peaks/low peak response
- Retention times not repeatable
- Peak areas not repeatable/poor RSD
- Contamination or carryover



Troubleshooting – General



Always consider the entire system:

Follow the flow path…

- Carrier gas →
- Sample/sample preparation →
- Sample introduction/inlet →
- Detection →
- Data handling and…
- All points in between

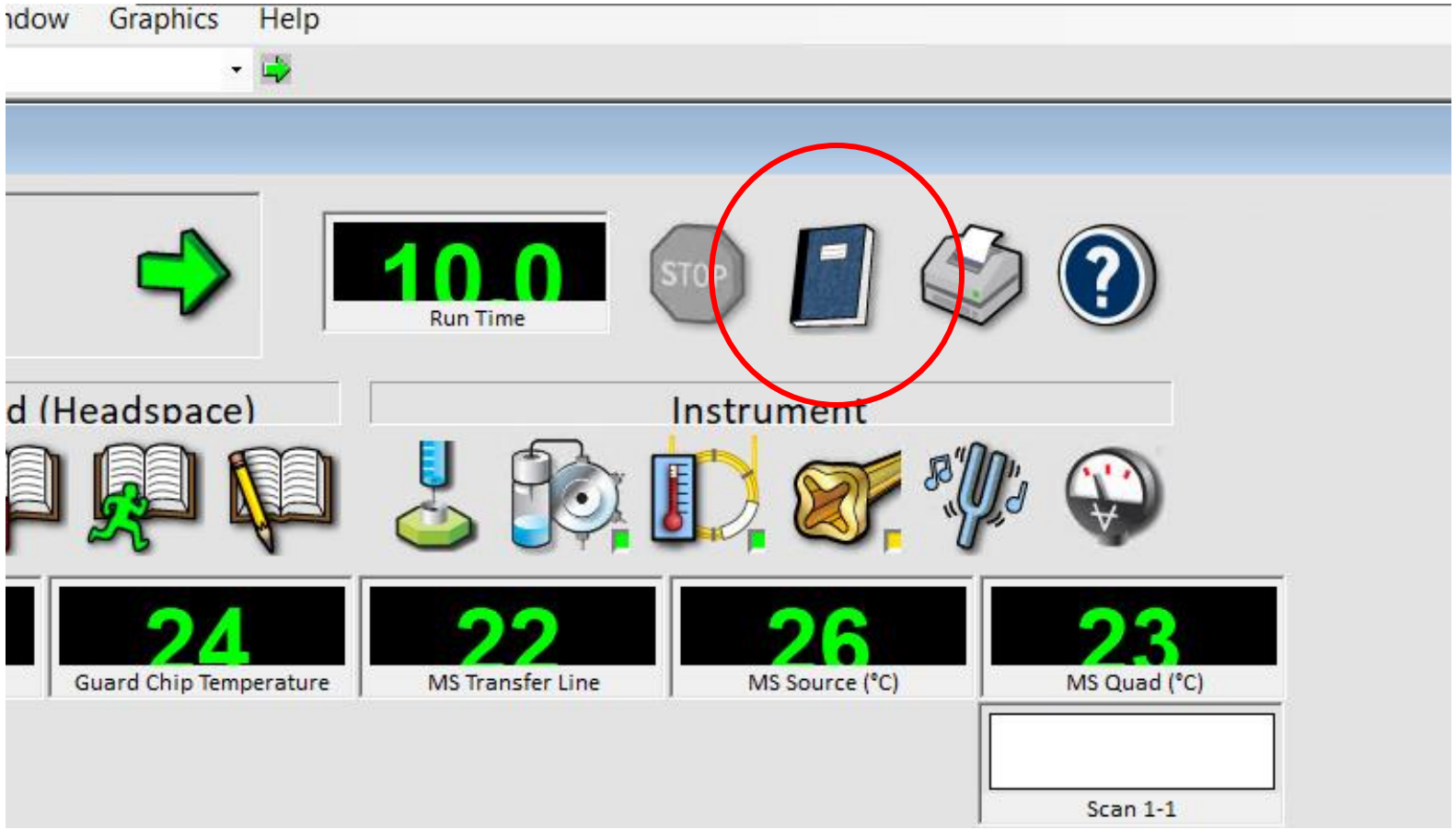
Troubleshooting – General

Always check the logs:

- Does the problem correlate with any recent changes or events?
  - Maintenance
  - Power Failure
- Check HS sequence log
- Check maintenance logs
- Half-split the system
- Check the GC
  - Check error messages/logs
  - If possible, mount an ALS to see if the issue persists
- Run something simpler:
  - System blanks/non-injections
  - Solvent blanks
  - Standards

https://www.agilent.com/cs/library/usermanuals/public/G4556-90018.pdf

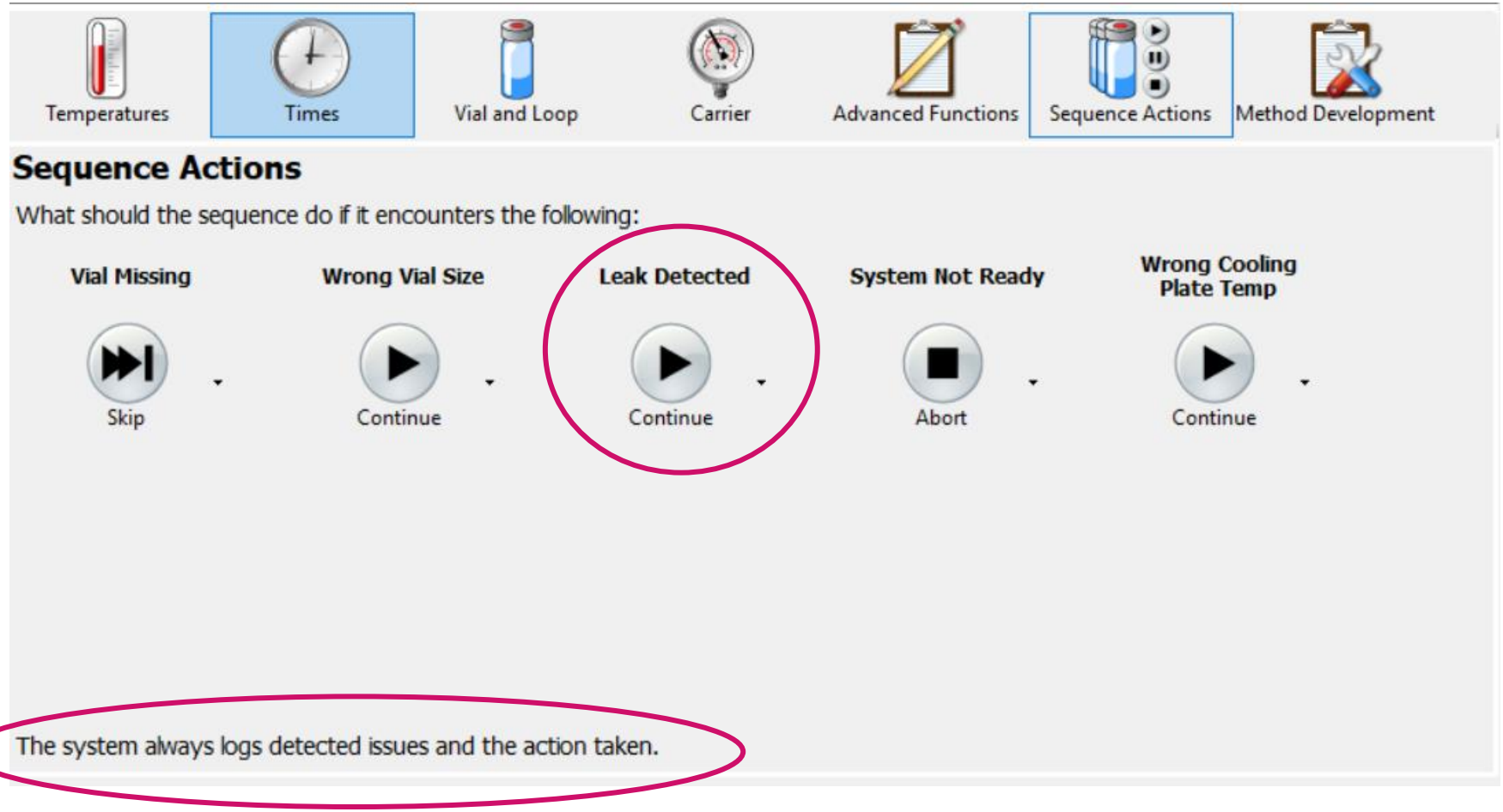
The Logbook Is in the Instrument Control Screen



Troubleshooting – Missing Peaks/Low Peak Response

- Check for proper vial crimp
- Check delivery gas pressures/tanks
  - Delivery pressure should be 20 PSI higher than the highest pressurization setting
- Enable dynamic leak checking
- Check for leaks in HS
  - Transfer line leaks/broken?
  - Probe, valve lines, and fittings

Vial Leaks


Temperatures
Times
Vial and Loop
Carrier
Advanced Functions
Sequence Actions
Method Development
Sequence Actions
What should the sequence do if it encounters the following:
Vial Missing
Skip
Wrong Vial Size
Continue
Leak Detected
Continue
System Not Ready
Abort
Wrong Cooling Plate Temp
Continue
The system always logs detected issues and the action taken.

Troubleshooting – Retention Time Instability

- Check the GC
  - Inlet leaks-septum, liner
  - Gas supply pressure
  - Is the GC given enough time to stabilize between runs?
- Confirm that the column installed matches the one in the method
- Check for leaks in HS
  - Transfer line leaks/broken?
  - Probe, valve lines, and fittings

Troubleshooting – Peak Area Instability

- Check for inconsistencies in sample preparation
- Check for carry-over
- Check for proper vial crimp
- Run standard replicates and calculate RSD
- Enable dynamic leak checking
- Sample not at equilibrium
- Check for leaks in HS
  - Transfer line leaks/broken?
  - Probe, valve lines, and fittings

Troubleshooting – Contamination or Carryover

- Check gas supply/traps
- Check the GC
  - Inlet consumables: septum, liner gold seal, vent trap
  - Check error messages/logs
- Run several instrument blanks
- Run several solvent blanks
  - If carryover does not decay, it probably condensed in the flow path (loop, probe, transfer line)
- Enable dynamic leak checking
- Check HS parameters
  - Loop purge flow/time
  - Enable standby flow
  - Check sample path temps proper: loop/valve, transfer line

Other Common Issues

Carryover/contamination	• Too much sample in the vial — Contaminates the probe and loop • Shaking is set too high • The sample is condensing in the loop
Septum or caps blowing off	• The oven temperature is too high (too much pressure in the vial)
High %RSD	• Vial leaks – check vial crimping; check sequence actions and logbook • Condensation in the flow path • Check temperatures • The vial equilibration time is too short — Can run a leak check
Sequence makes it through first sample only	• GC cycle time is too short; check sequence actions and logbook

Summary

- Stay 10 to 20 °C below the boiling point of the solvent/matrix
- Keep a minimum of 5 mL of headspace in the vial
- Use the Method Development tools
  - Don’t forget to turn off the functions when done!
- Optimize parameters based on compounds with the highest K
  - Not every compound responds/reacts in the same way
- To improve sensitivity:
  - Use 10 ml vials
  - Use salts
  - More sample
  - 2 mm liner
- Be consistent with crimping vials; set the crimper properly so that every user is successful
- When troubleshooting:
  - Think logically about what can/cannot cause problem
  - Half-split the system so you know where to focus your energy
- Contact technical support

Additional Resources

7697A Headspace Sampler Troubleshooting (PDF) G4556-90018

7697A Headspace Sampler Advanced Operation (PDF) G4556-90016

Search for 7697A Headspace Sampler on Agilent.com

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 products, filtration, and QuEChERS

Option 4 for spectroscopy supplies

Available in the U.S., 8-5 all time zones

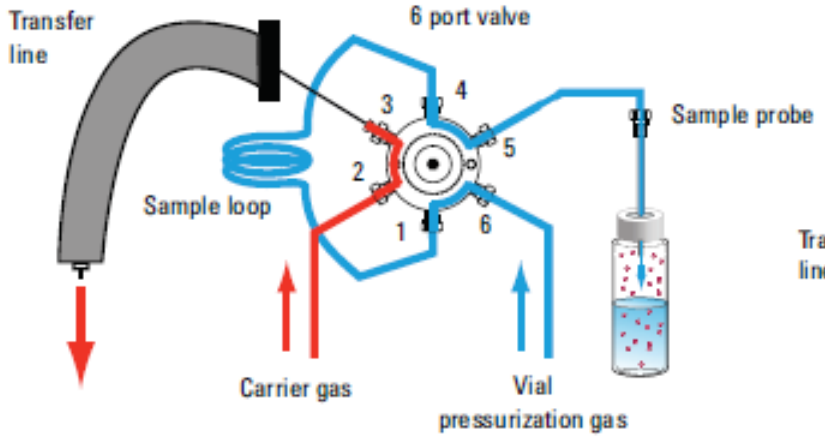
gc-column-support@agilent.com ← GC columns and supplies

lc-column-support@agilent.com

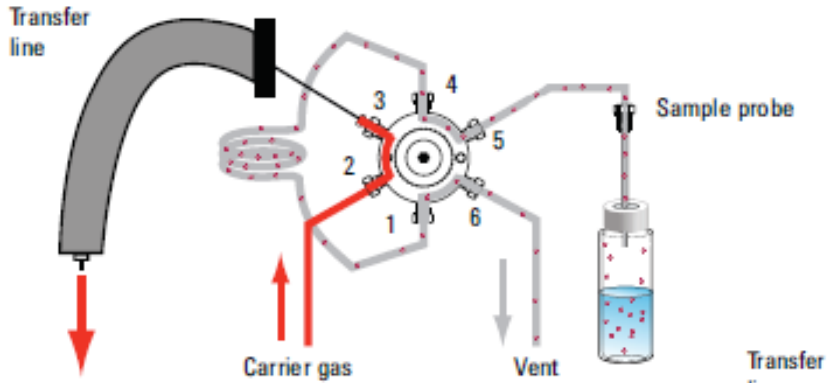
spp-support@agilent.com

spectro-supplies-support@agilent.com

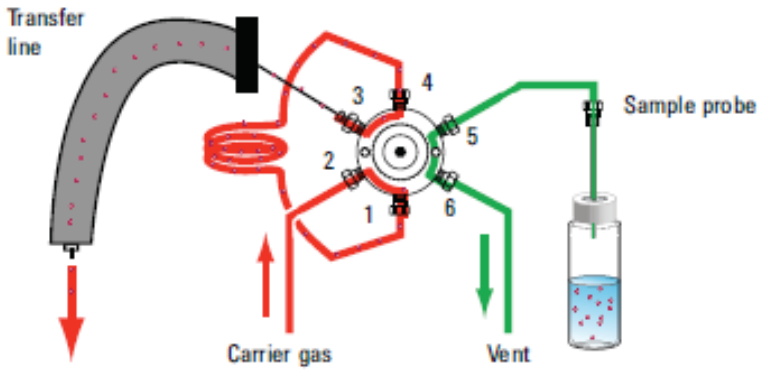
Agilent 7697A/8697 Loop System



Vial pressurization



Loop fill

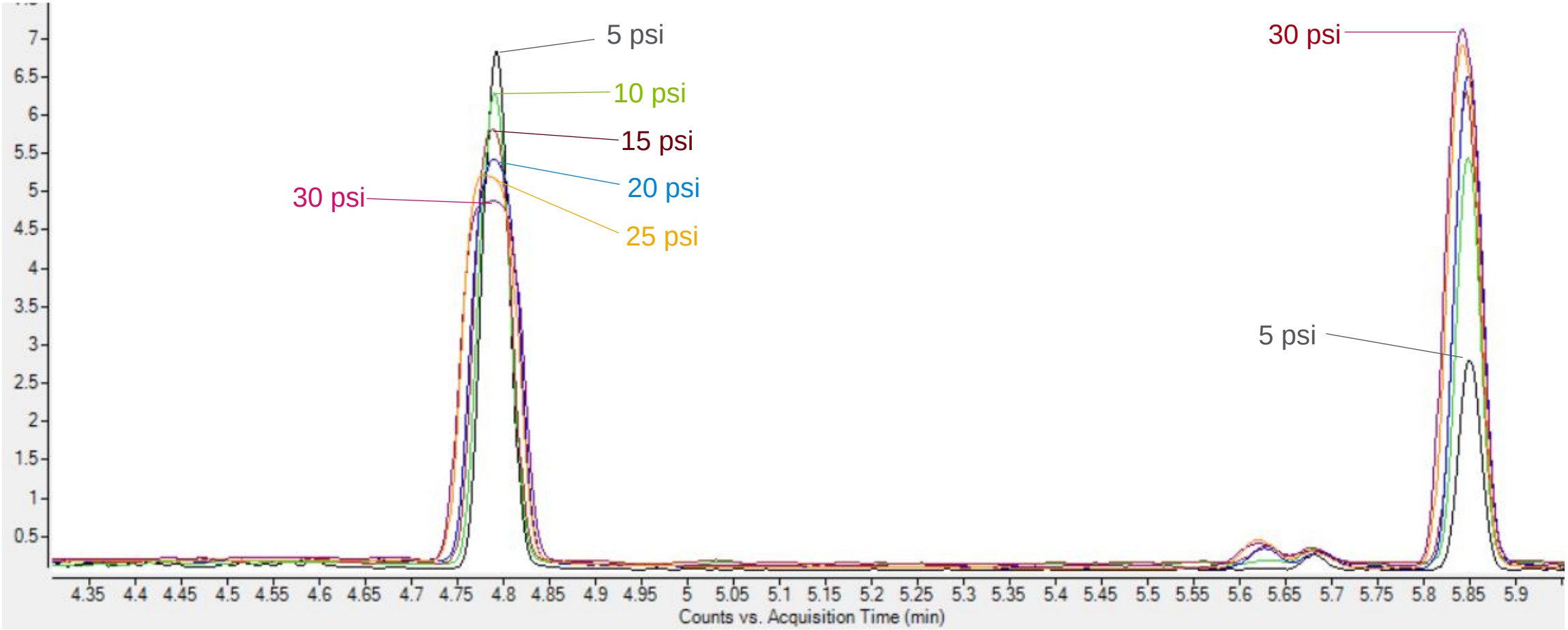


Injection

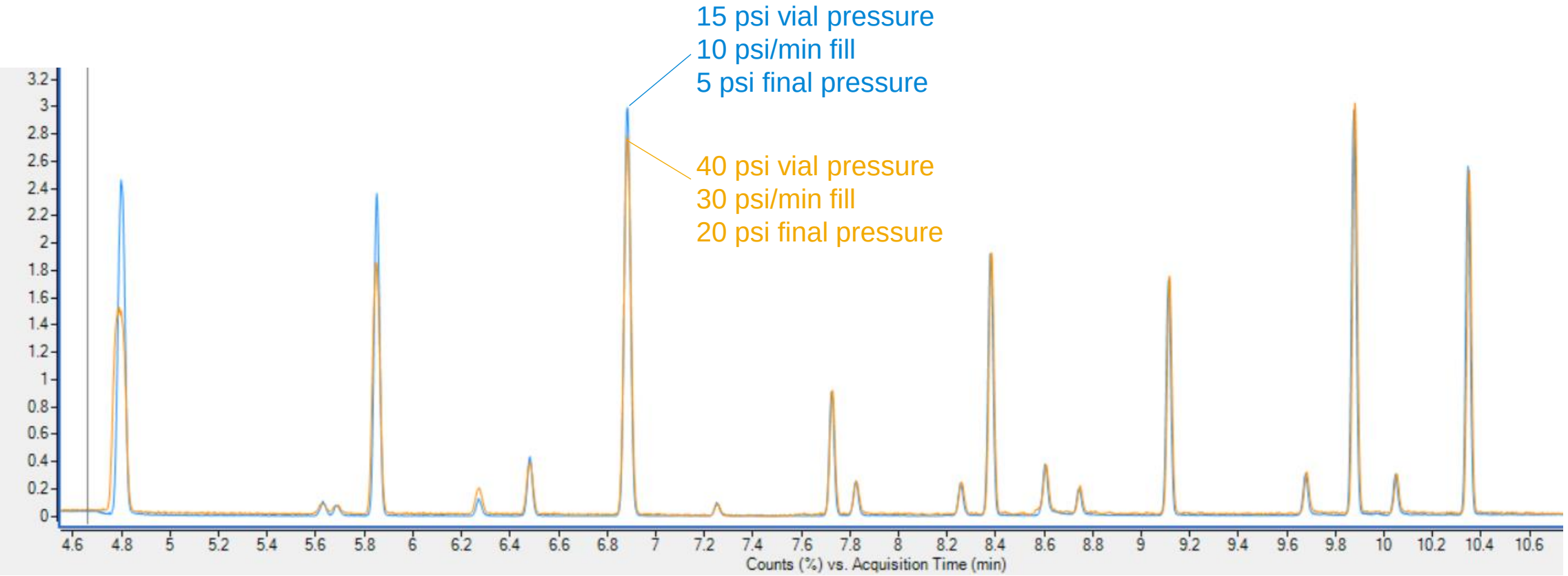
Change in Loop Pressure

First two eluting peaks

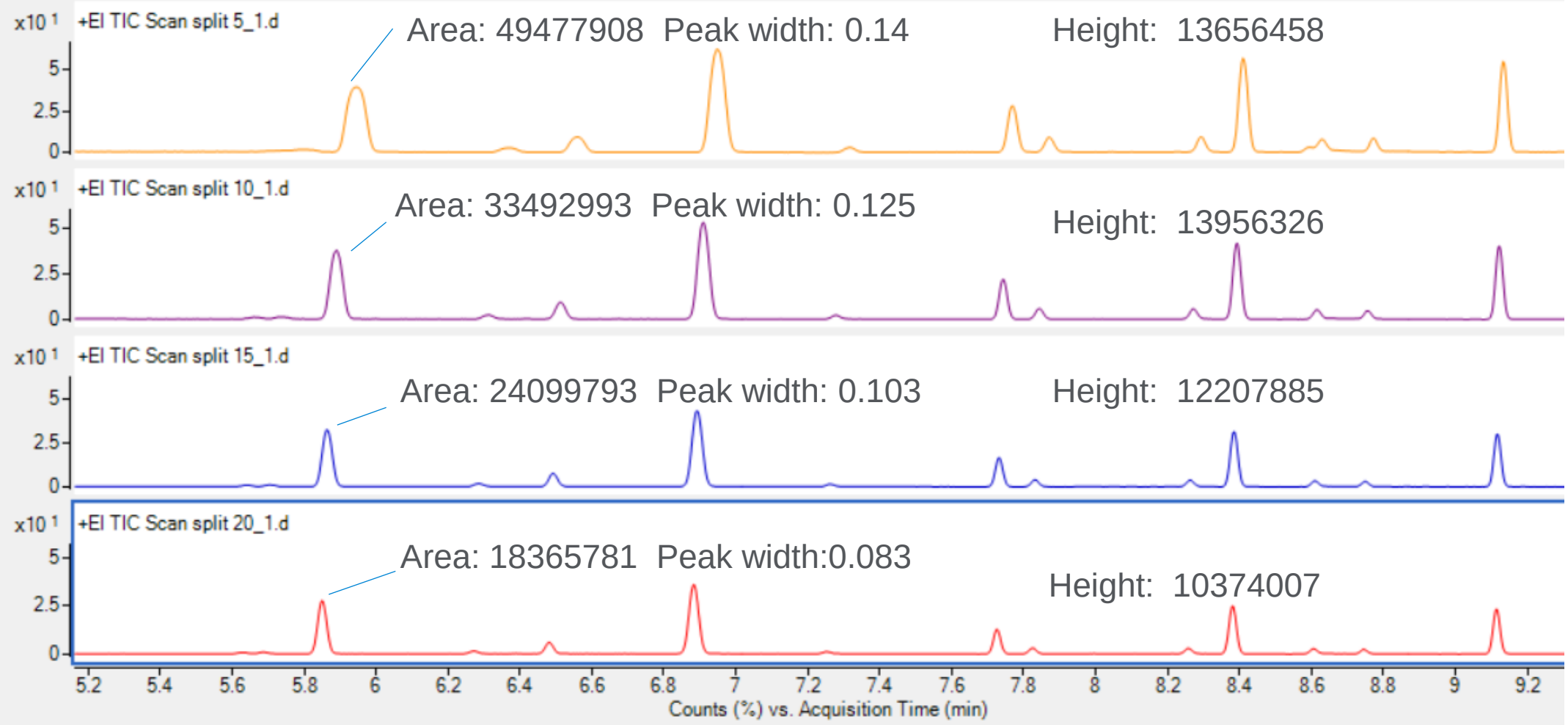
Vial fill pressure: 40 psi
Loop fill rate: 30 psi/min
Inlet pressure: 28.3 psi



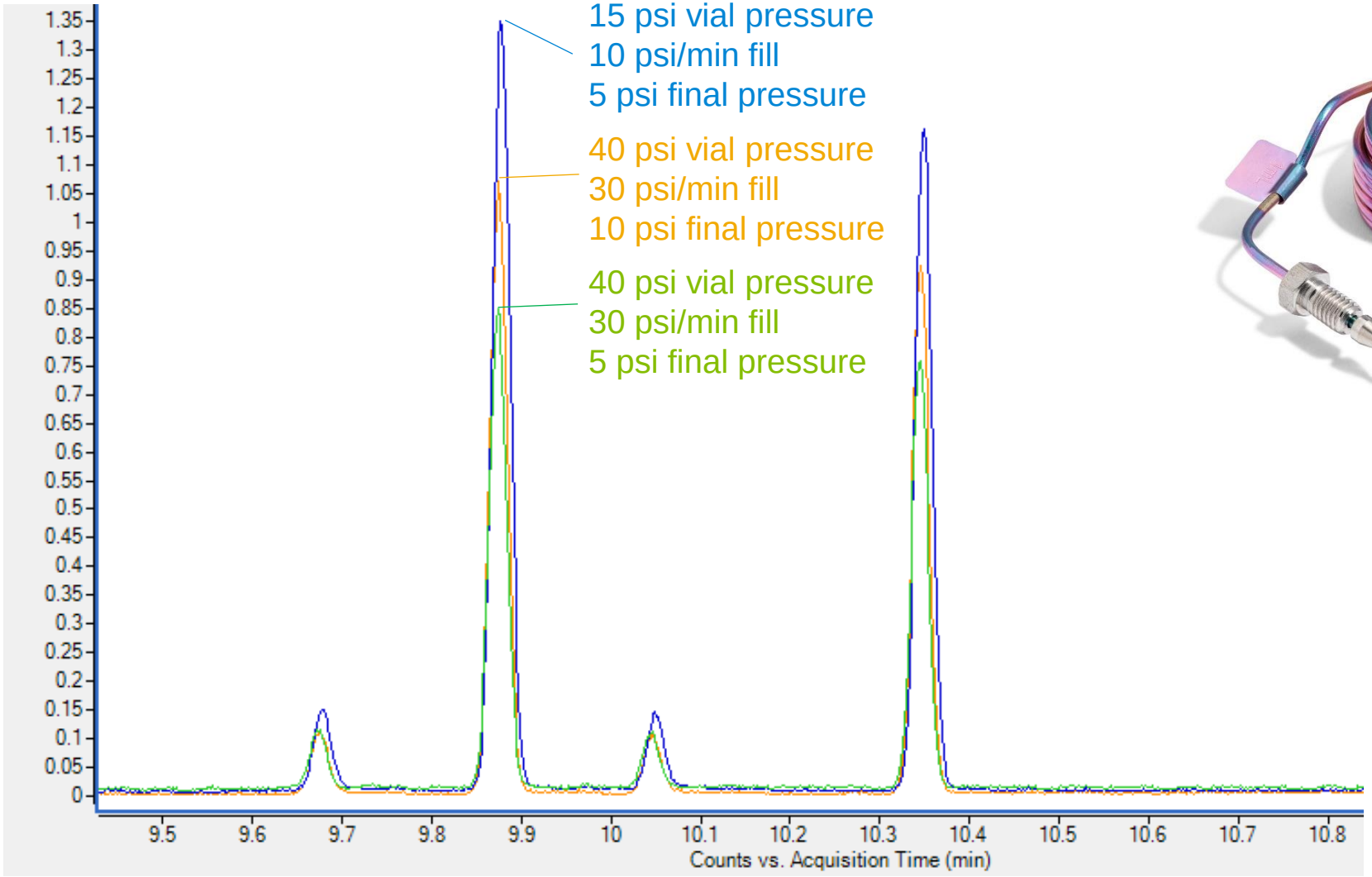
Is That a Good Way to Increase Signal?



Change in Split Ratio



The Effect of Vial Pressure, Loop Pressure, and Fill Rate



Change the Loop Purge Time and Flow

Carryover issues