Scratching Your Head Over Headspace? We'll Help Make Things Simple

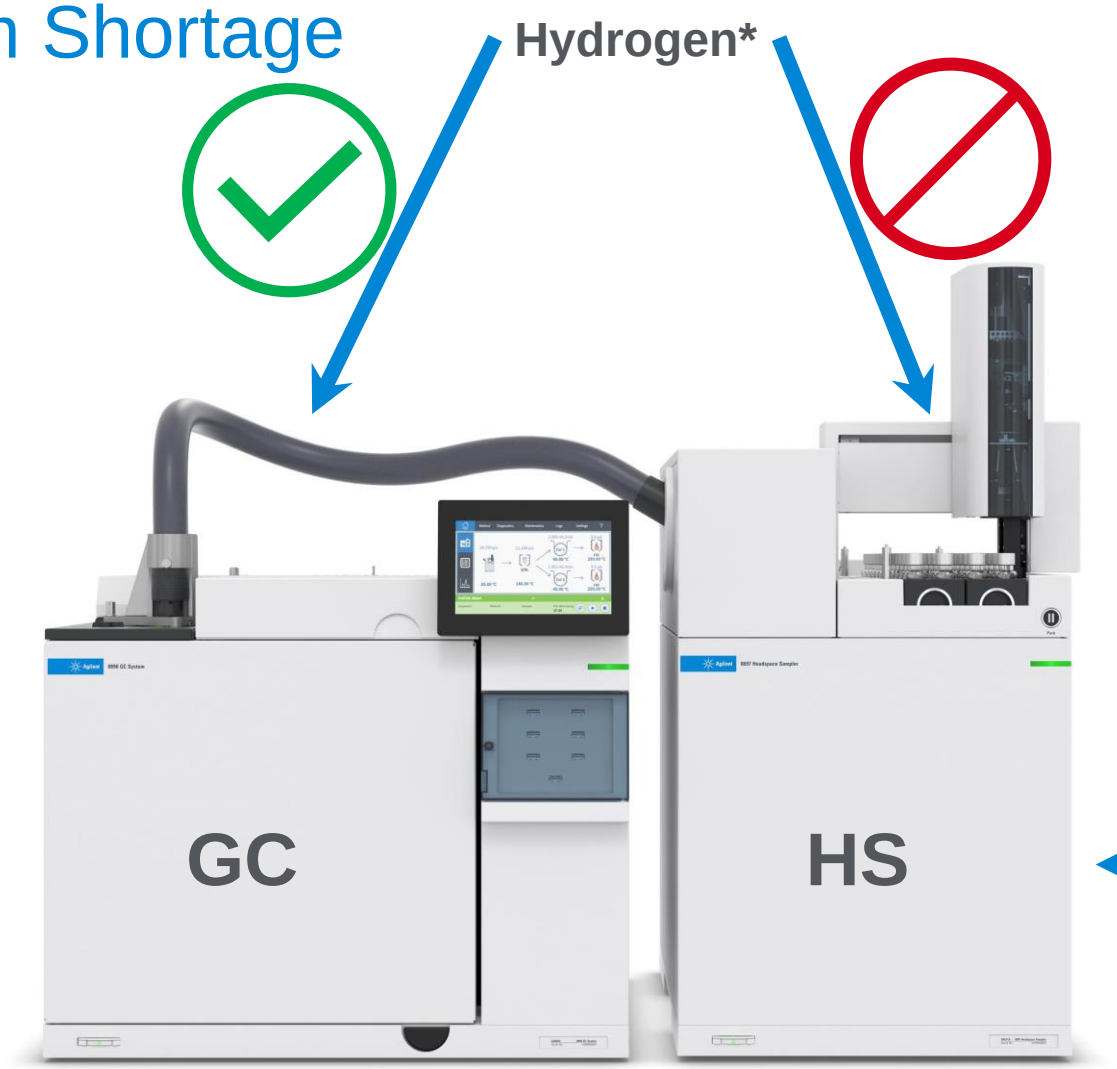
Method development, method optimization, and troubleshooting

Mark Sinnott
GC Application Scientist
22 September 2022

Agilent
Trusted Answers

DE.4178703704

Helium Shortage



*Consult safety guides linked below

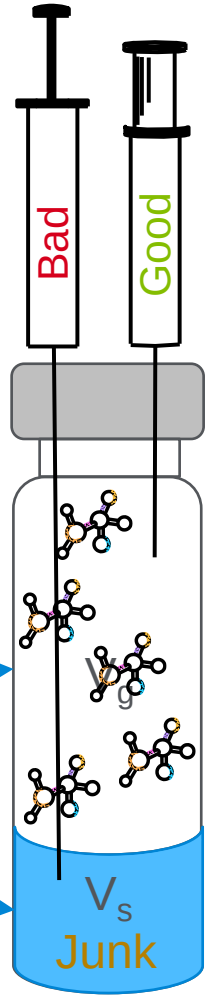
https://www.chem.agilent.com/Library/usermanuals/Public/5955-5398_030756.pdf
https://www.agilent.com/cs/library/usermanuals/public/user-manual-gcms-hydrogen-safety-g7003-90053-en-agilent.pdf

What Is Headspace?

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

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

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



HEAT

Volatiles

Semi-Volatiles / Salts, etc.

$$W_S + W_G = W_0$$

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

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

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

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

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

Types of Headspace

Static versus dynamic

Dynamic – A continuous gas stream is passed through a sample that then elutes the compounds of interest onto a trap, where they are held and concentrated. At some point in the process, the trap is heated to desorb the analytes of interest onto the column to be chromatographed.

- Typically purge and trap
- Headspace trap

Static – The sample is placed into a closed vial, the vial is heated and shaken, and the sample is extracted and injected directly into the GC.

- Loop system
- Syringe
- Pressure balance

Why Headspace?

Offers clean injections into GC systems

- Less maintenance – only the volatile vapors are injected into the system

Less sample preparation

Ideal for analysis of volatile analytes in matrices that can’t be directly injected into the GC.

*Not suitable for some applications

Types of Static Headspace Autosamplers

Gas tight syringes

- Not a ‘true’ closed system. A small amount of sample can be lost as the syringe moves from the vial to the inlet.

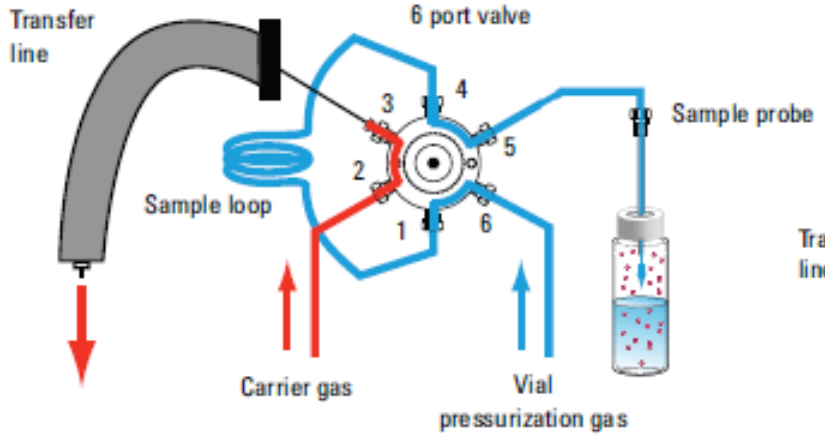
Balanced pressure

- The sample volume injection is regulated by time. Vial pressure is depressurized onto the column. The amount of sample injected is controlled by injection duration.

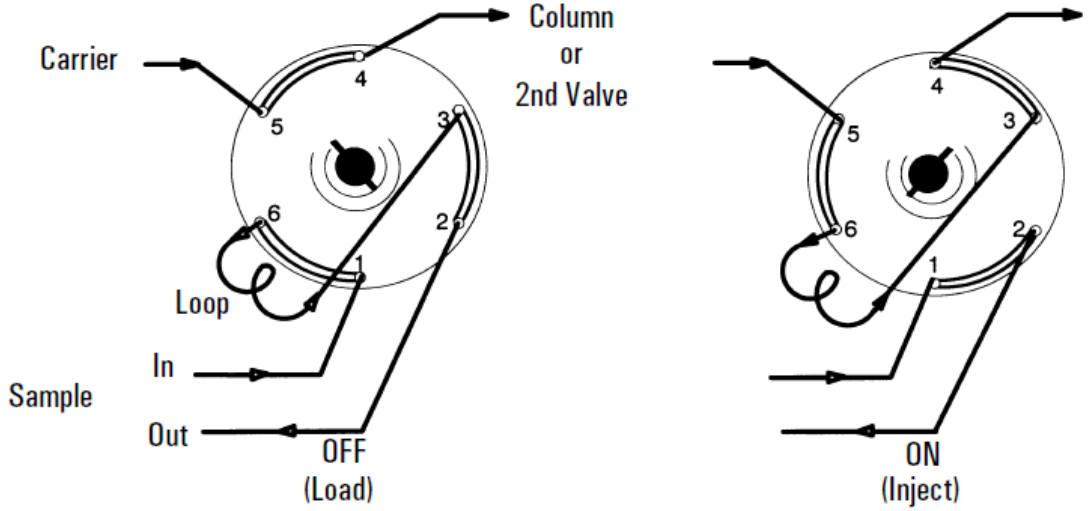
Pressure/loop systems

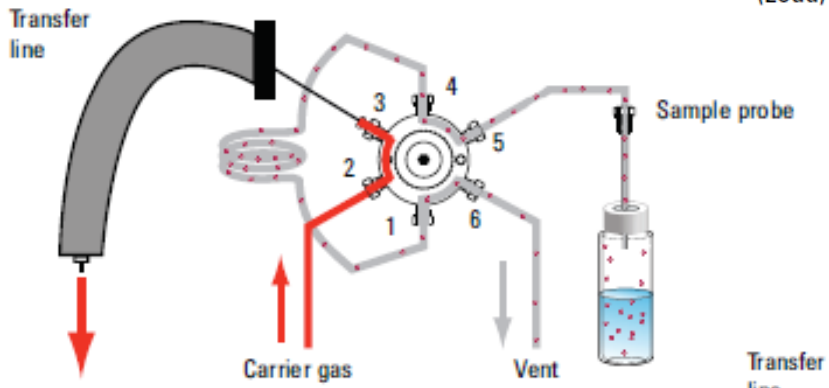
- Fixed loop size determines injected volume. The metal surface area is greater in the loop system.

Agilent 7697A Loop System

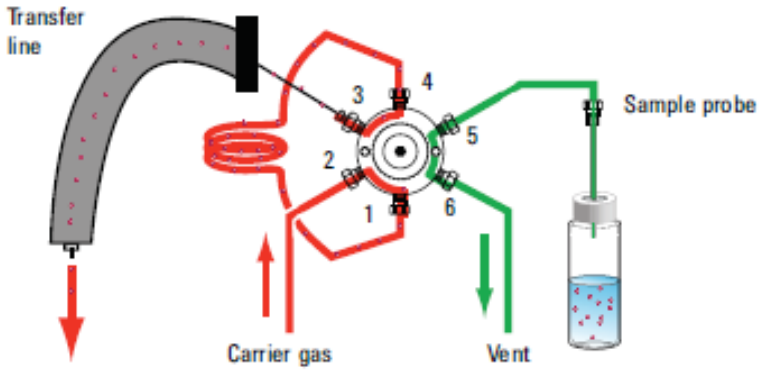


Vial pressurization





Loop fill



Injection

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?

What Drives K?

Temperature:

- Higher temperatures drive K down

Solubility:

- Add salt
- Add another solvent to the matrix

What Parameters Drive Success?

Incubation temperature

- Typically 20 °C below the solvent BP

Incubation time

Shaking

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.
- Keep the incubation temperature 10 to 20 °C below the BP of the solvent/matrix.
- Long incubation times ‘generally’ only delay the first sample.
- 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 touching 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

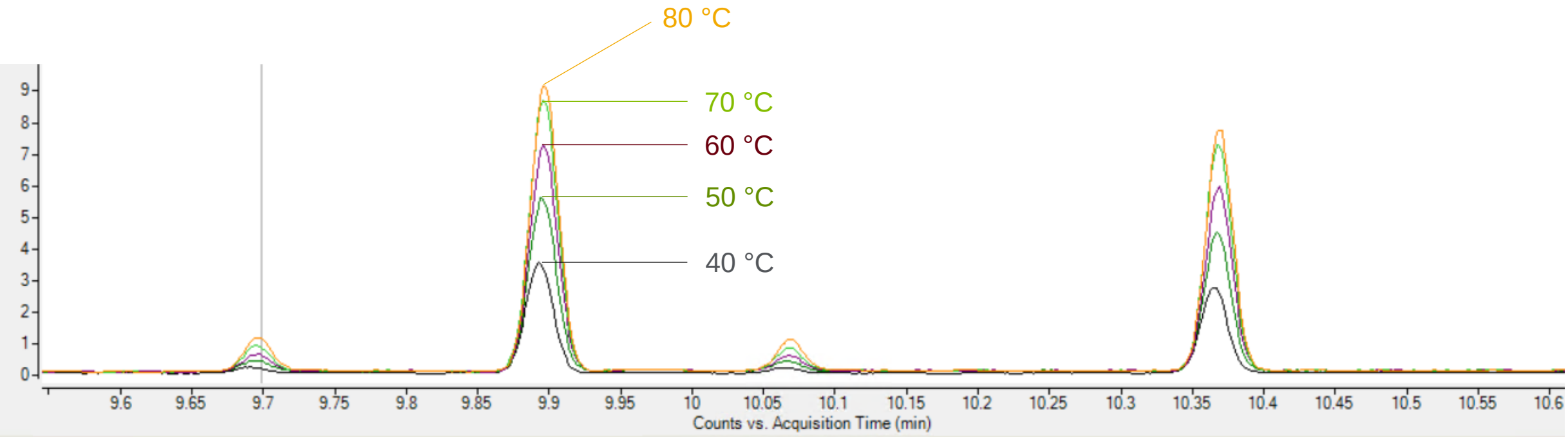
- Vial equilibration
- Injection duration
- GC cycle time

Vial and loop

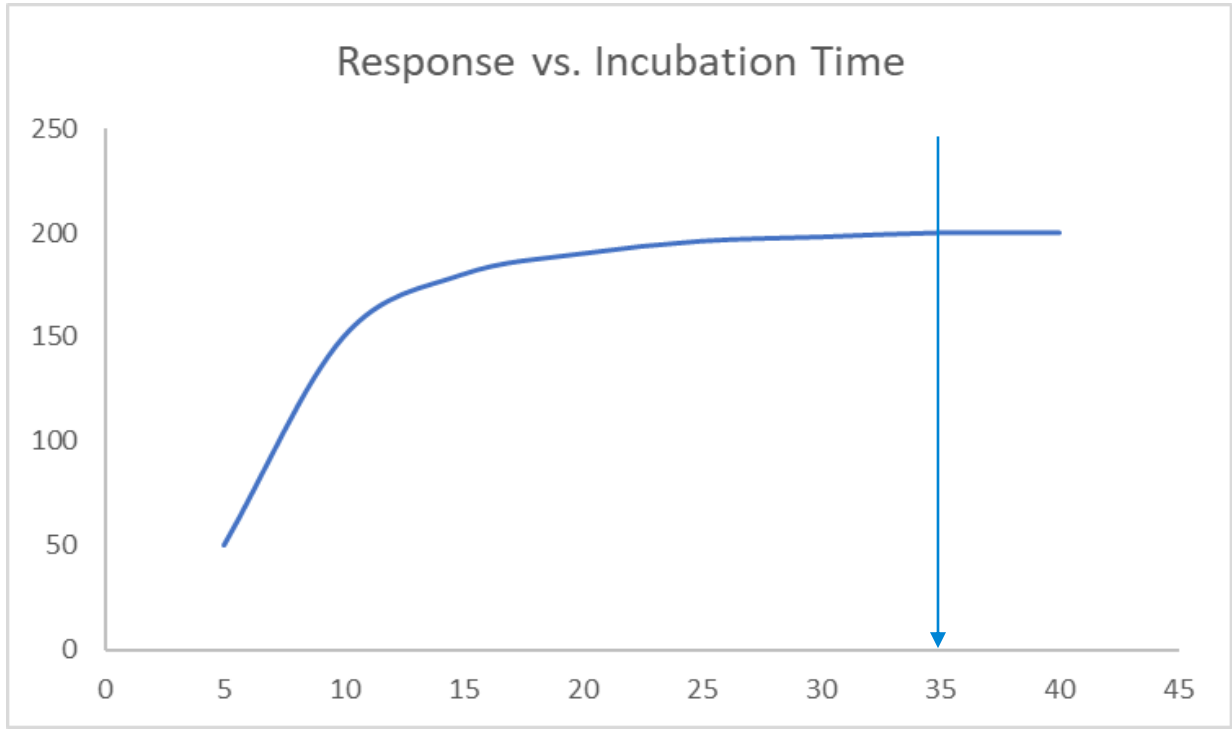
- Vial size
- Shake vials while in oven
- Vial fill mode
- Loop fill mode

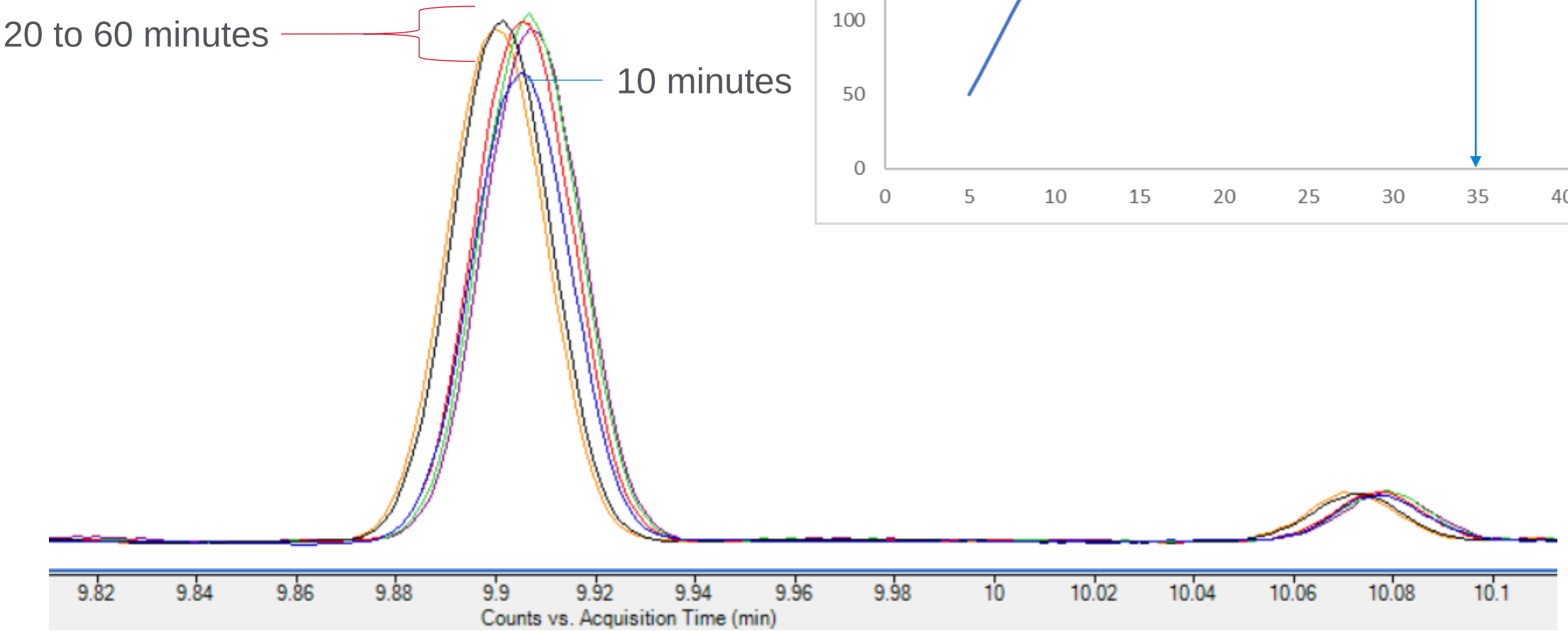
Incubation Temperature Increase

20 minutes
K decreases with *T*
Not equal for all analytes



Incubation Time

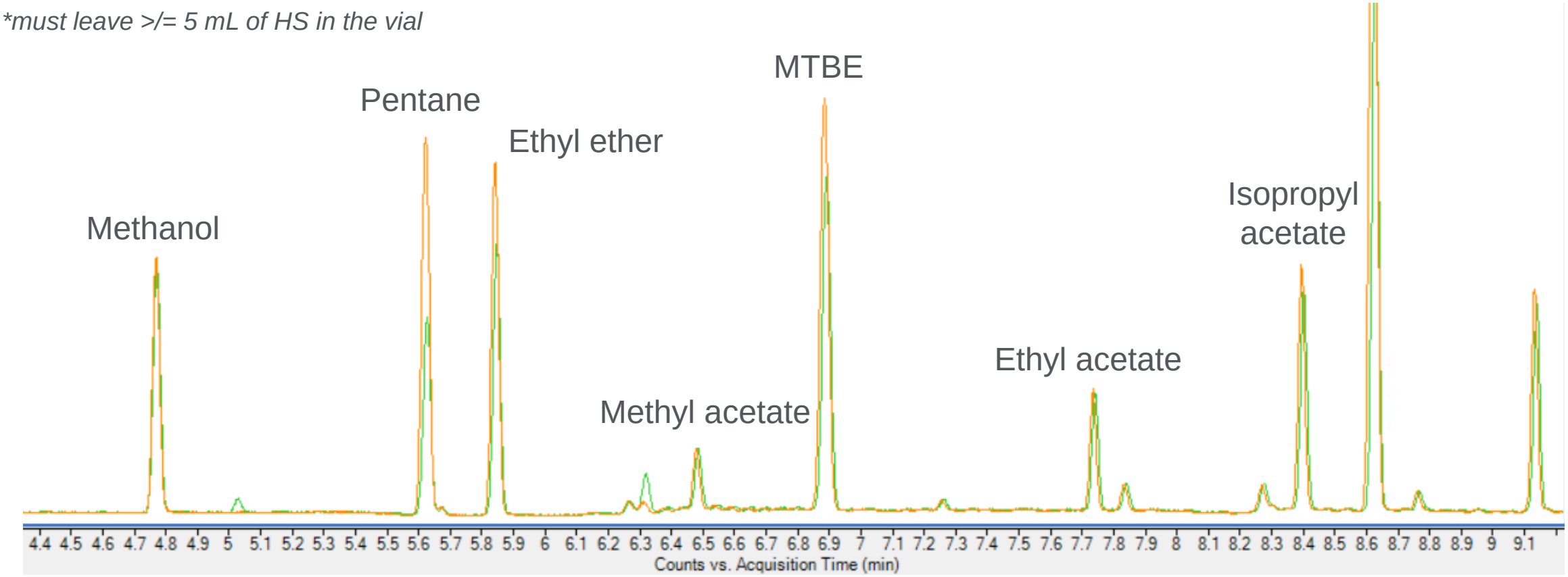




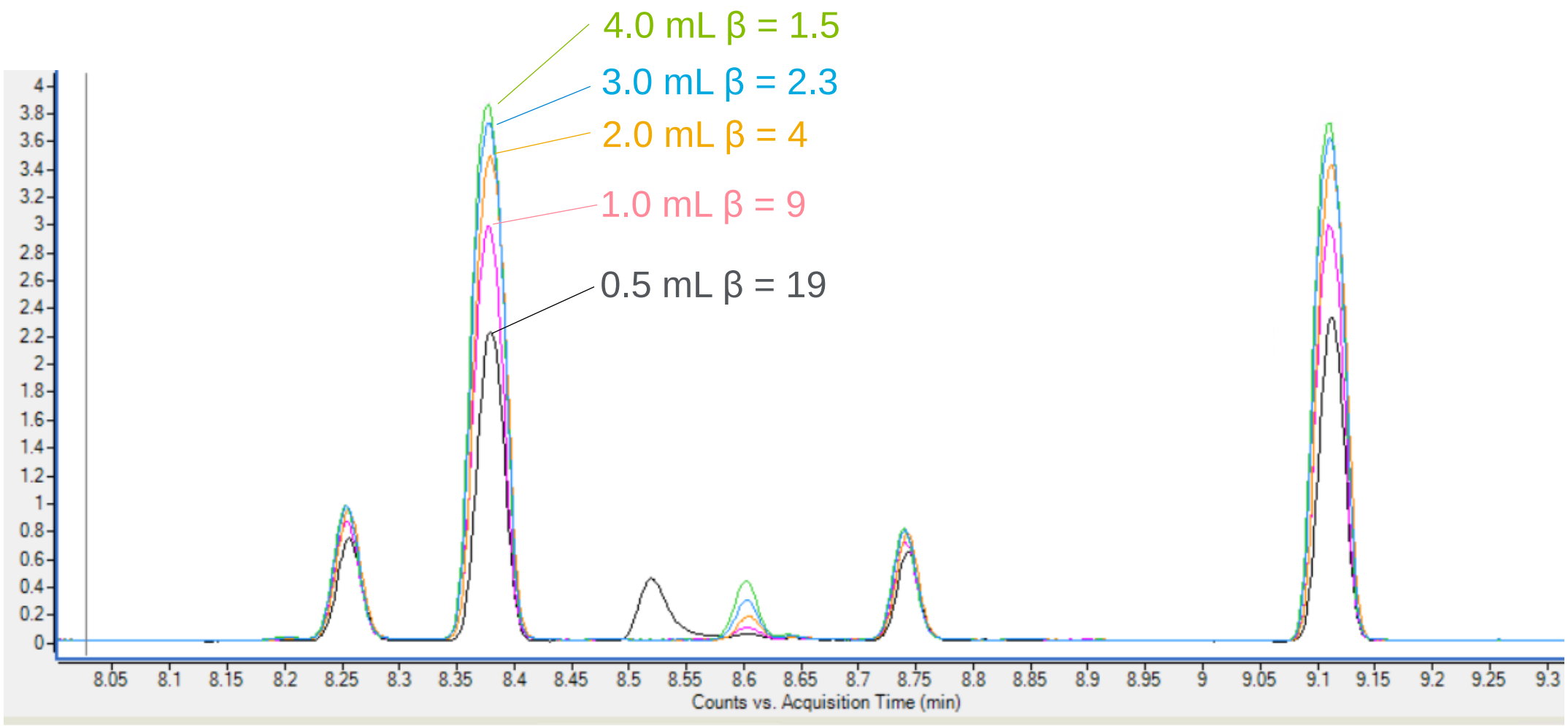
Change in Vial Size

4 mL sample, changing β*
10 mL vial β = 1.5 (6 mL HS)
20 mL vial β = 4 (16 mL HS)

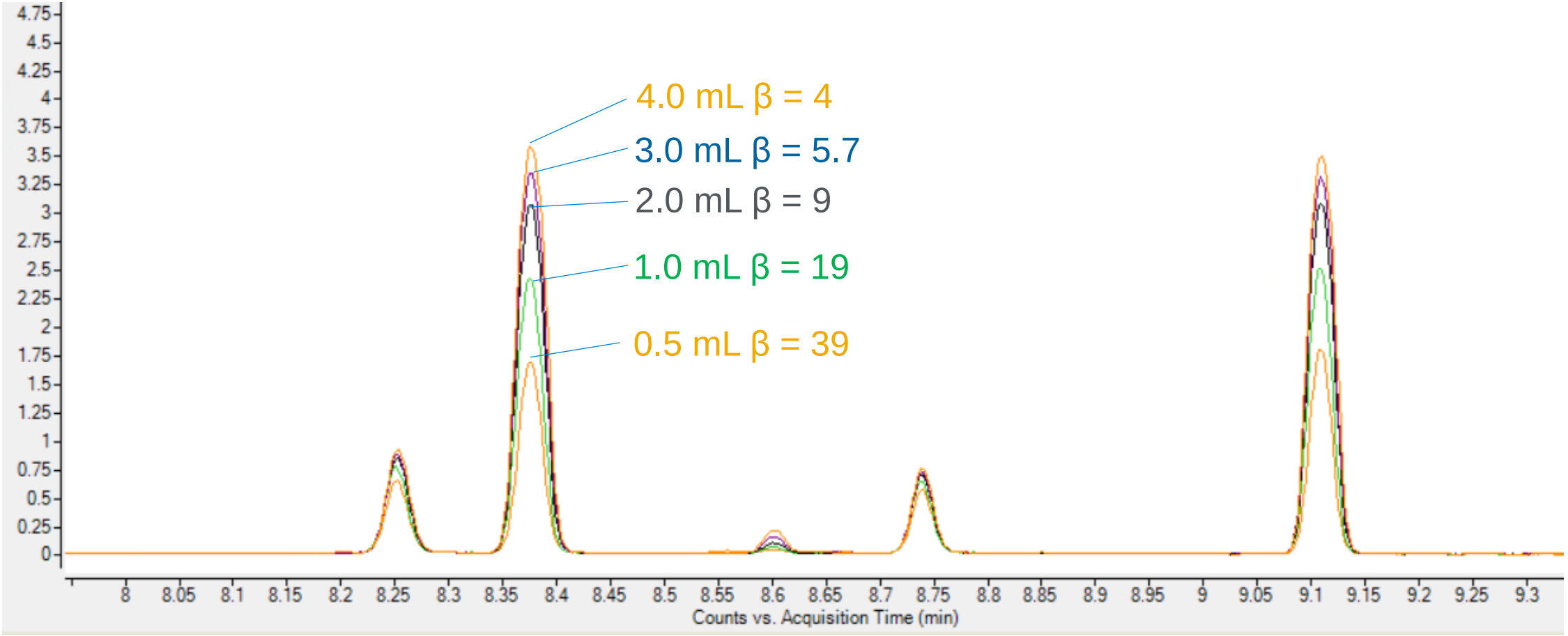
**must leave >/= 5 mL of HS in the vial*



Change in Sample Volume in a 10 mL Vial



Change in Sample Volume in a 20 mL Vial



What Else Can Affect Signal?

Loop size

Loop pressure

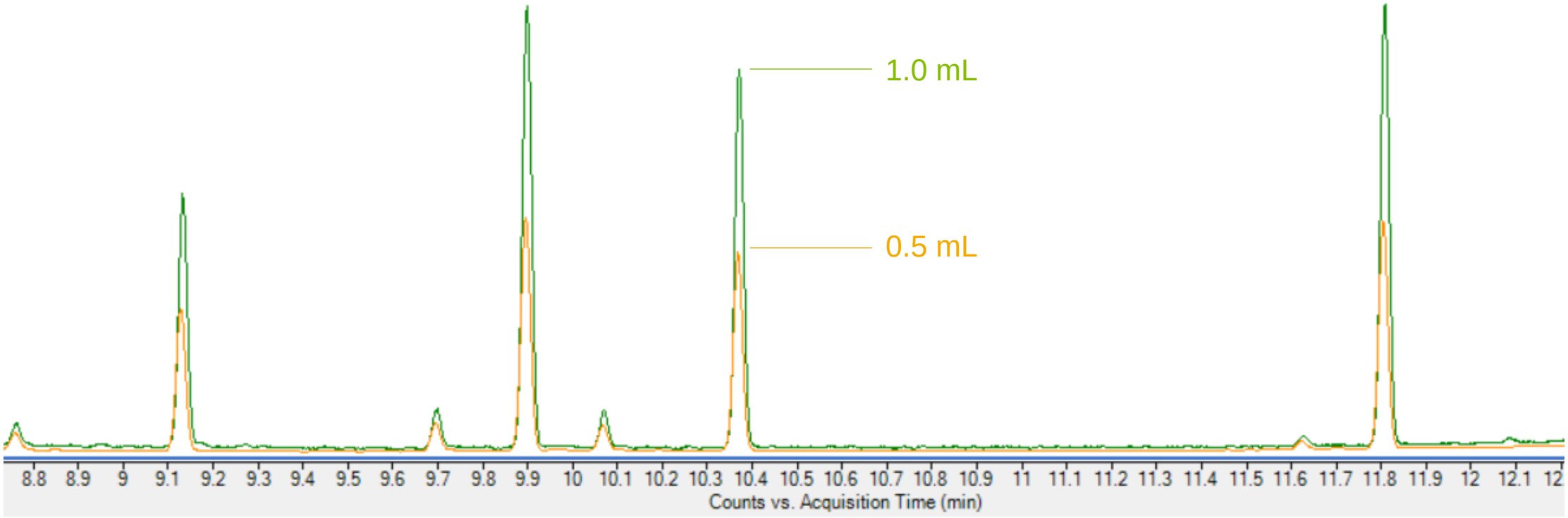
Split ratio

Liner type

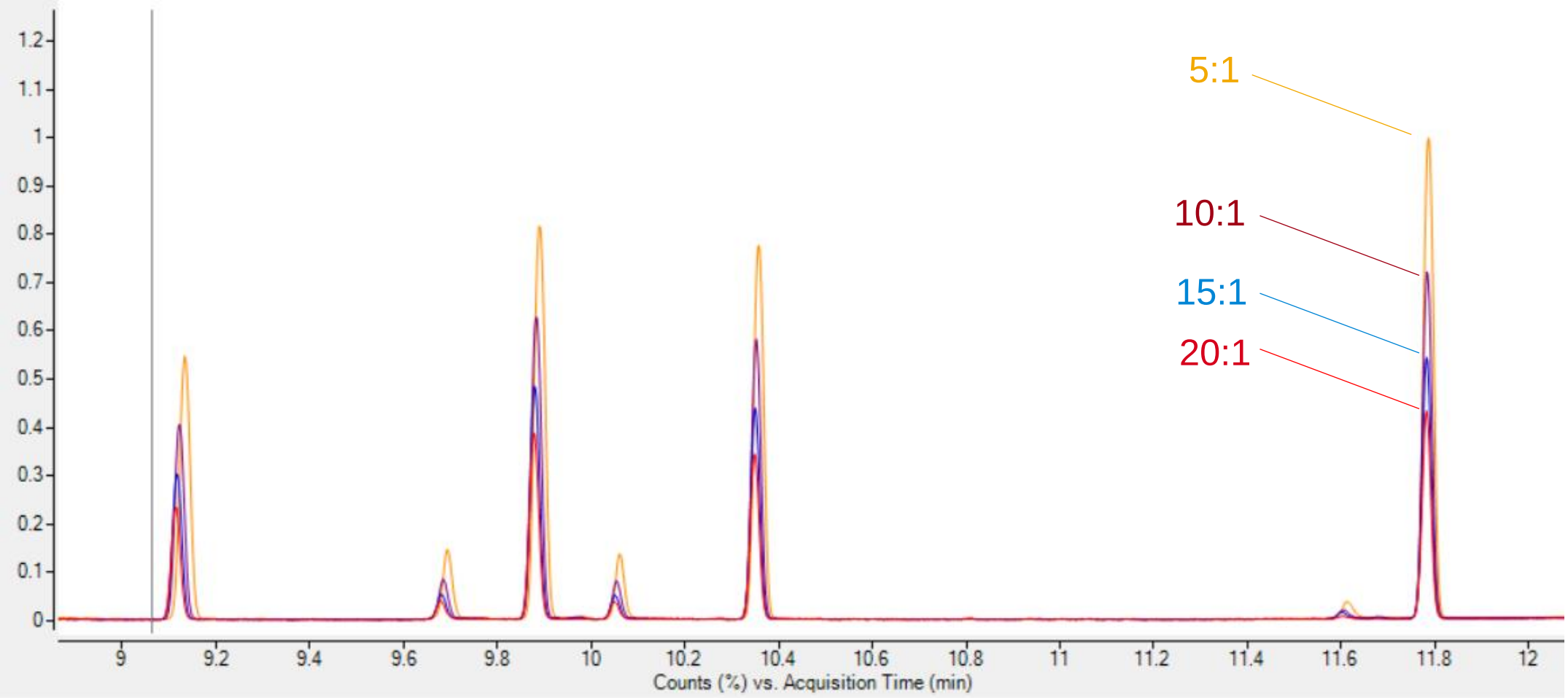
Using salt

Change in Loop Size

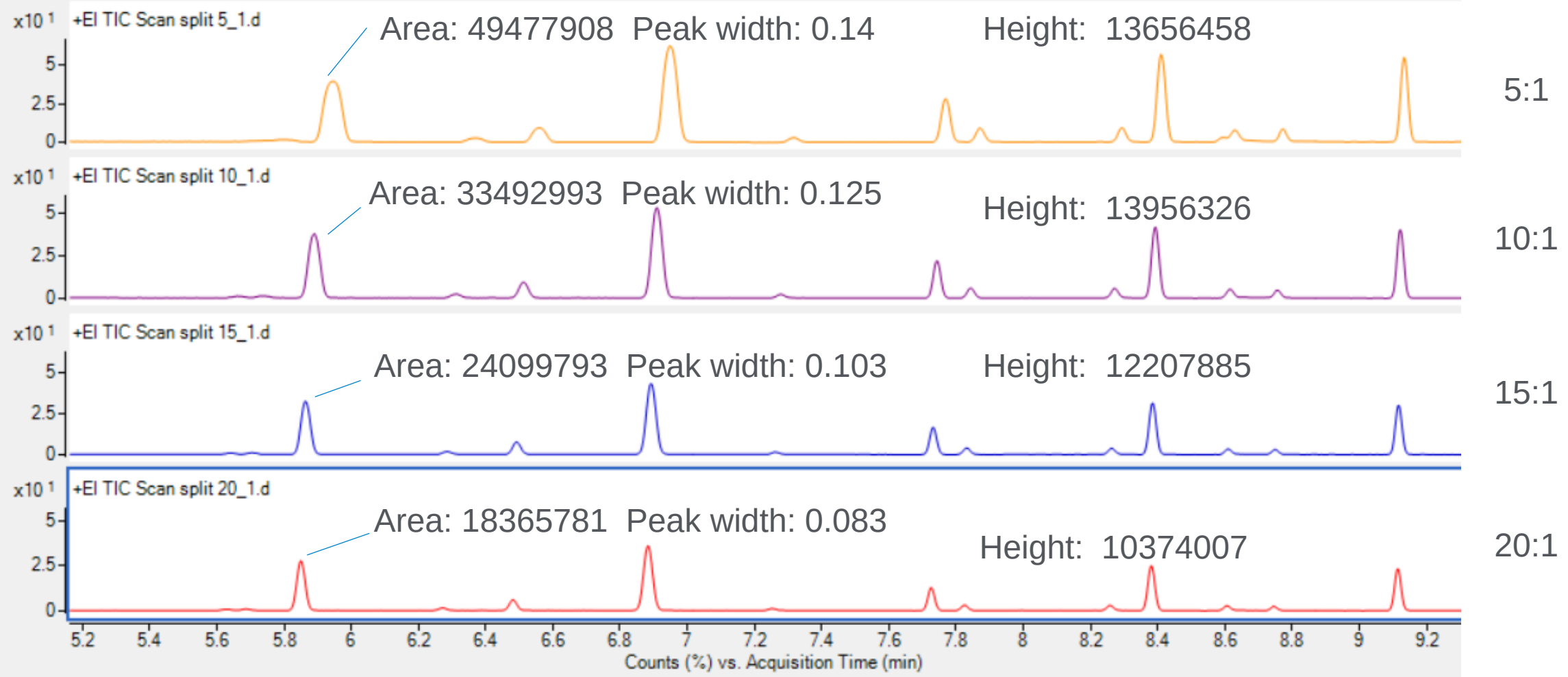
40:1 split (64 mL/min)



Change in Split Ratio



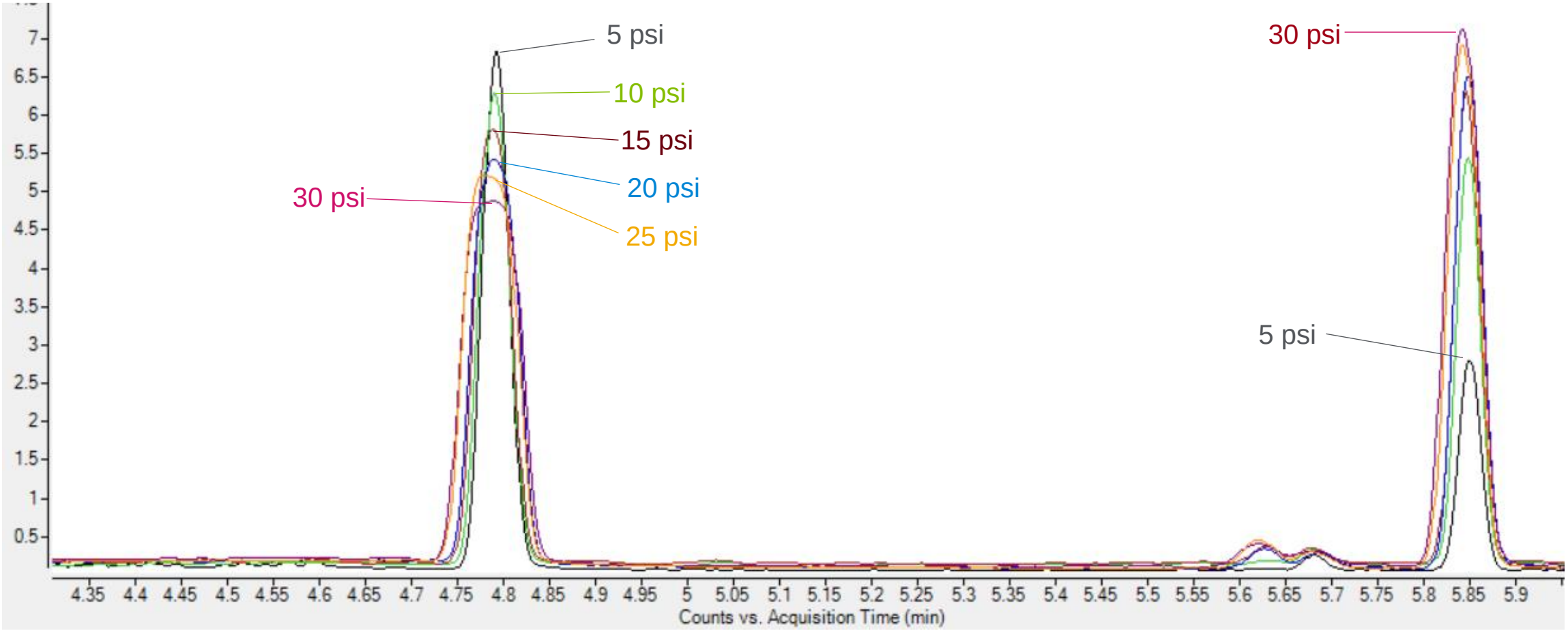
Change in Split Ratio



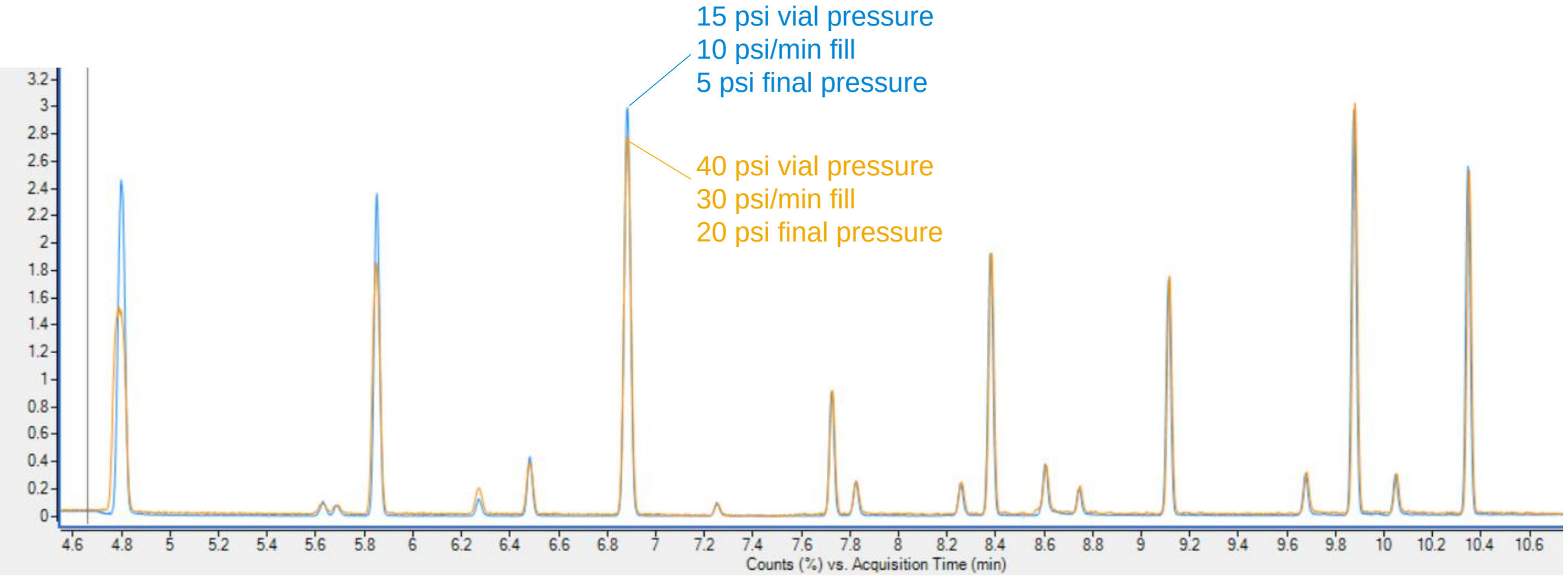
Change in Loop Pressure

First two eluting peaks

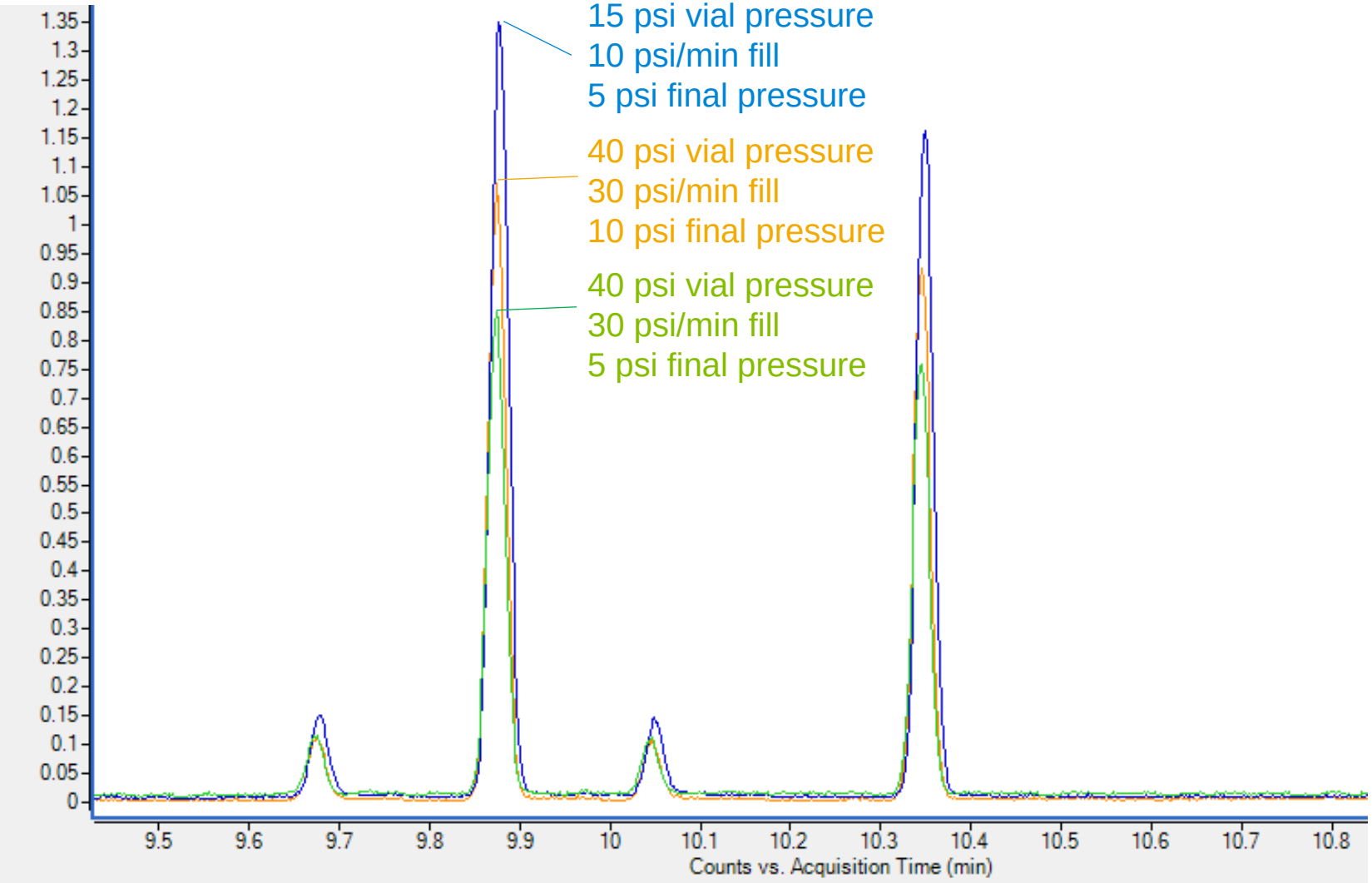
Vial fill pressure: 40 psi
Loop fill rate: 30 psi/min
Inlet pressure: 28.3 psi



Is That a Good Way to Increase Signal?

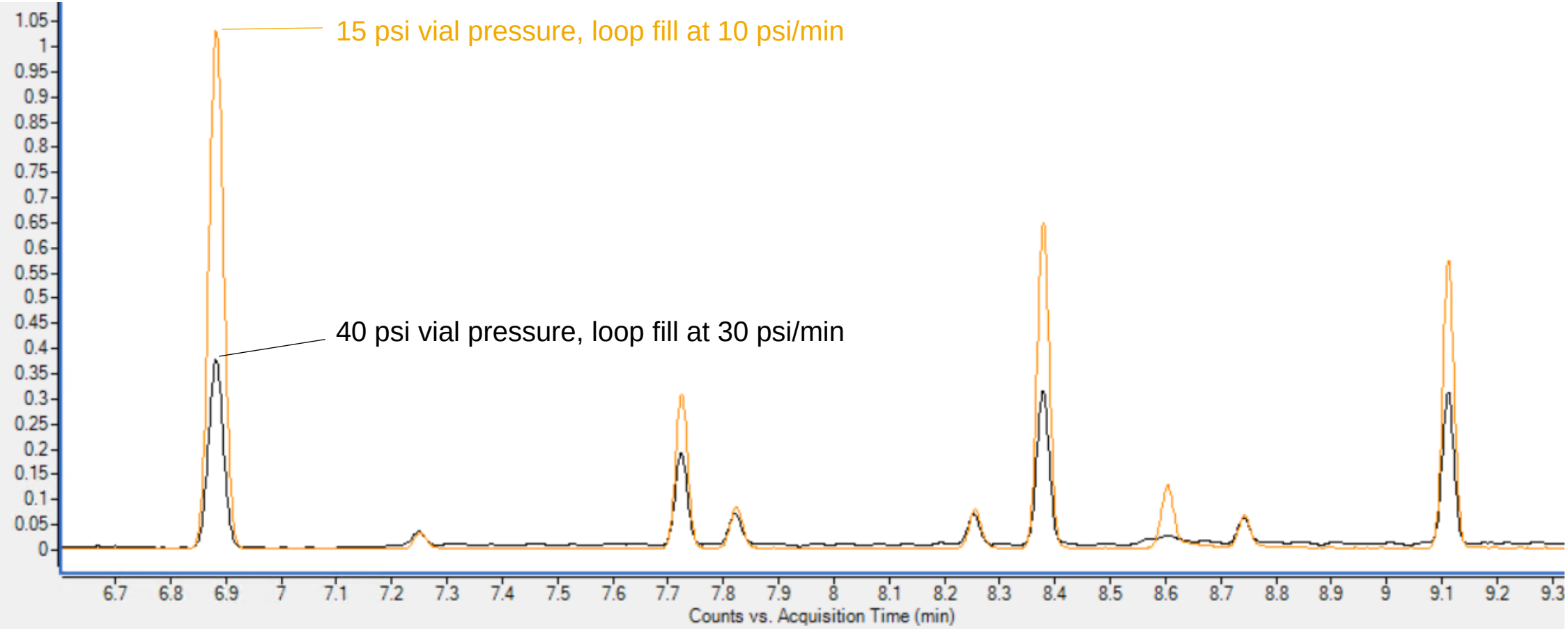


The Effect of Vial Pressure, Loop Pressure, and Fill Rate

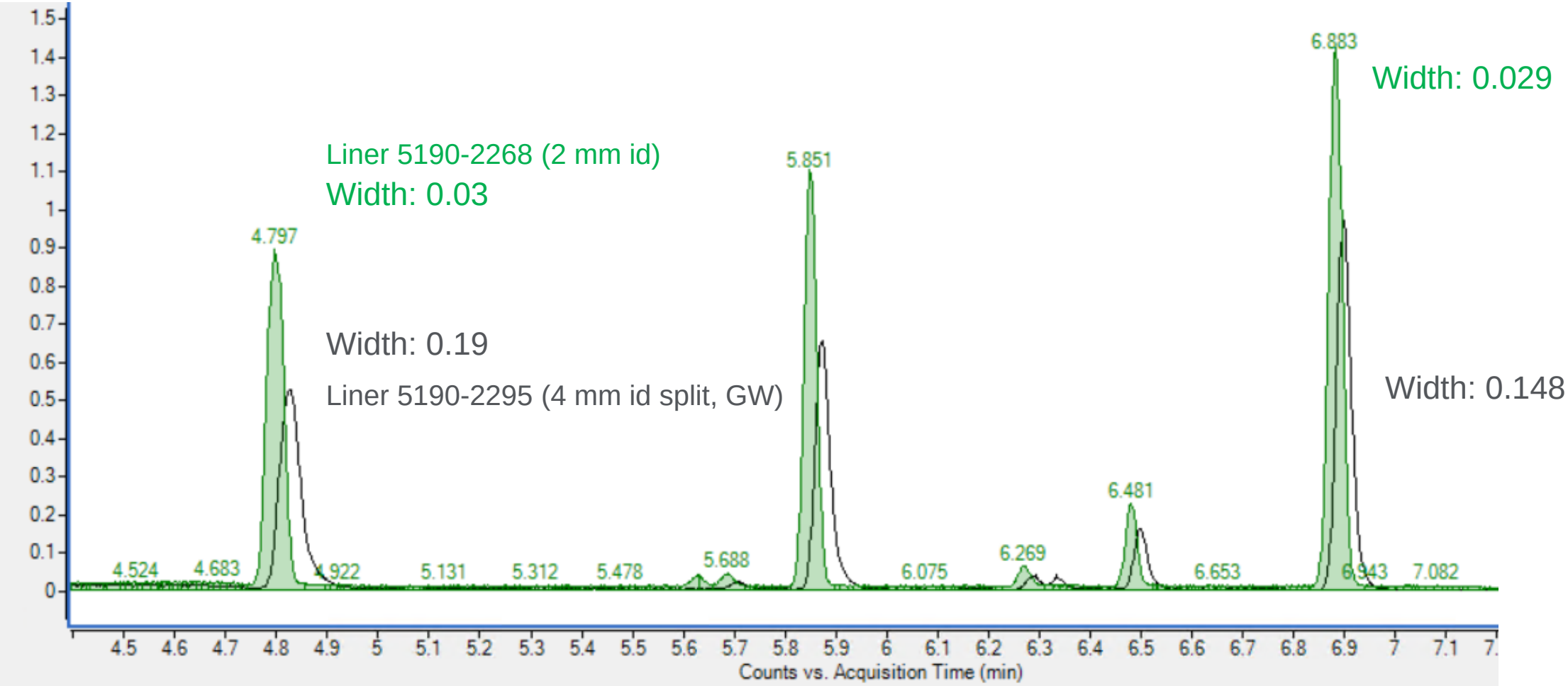


Changing Vial Pressure

5 psi final loop pressure



Liner Size and Type



Use of Salts

Decreases the solubility of polar analytes in aqueous samples

Decreases K, favoring the gas (headspace) phase

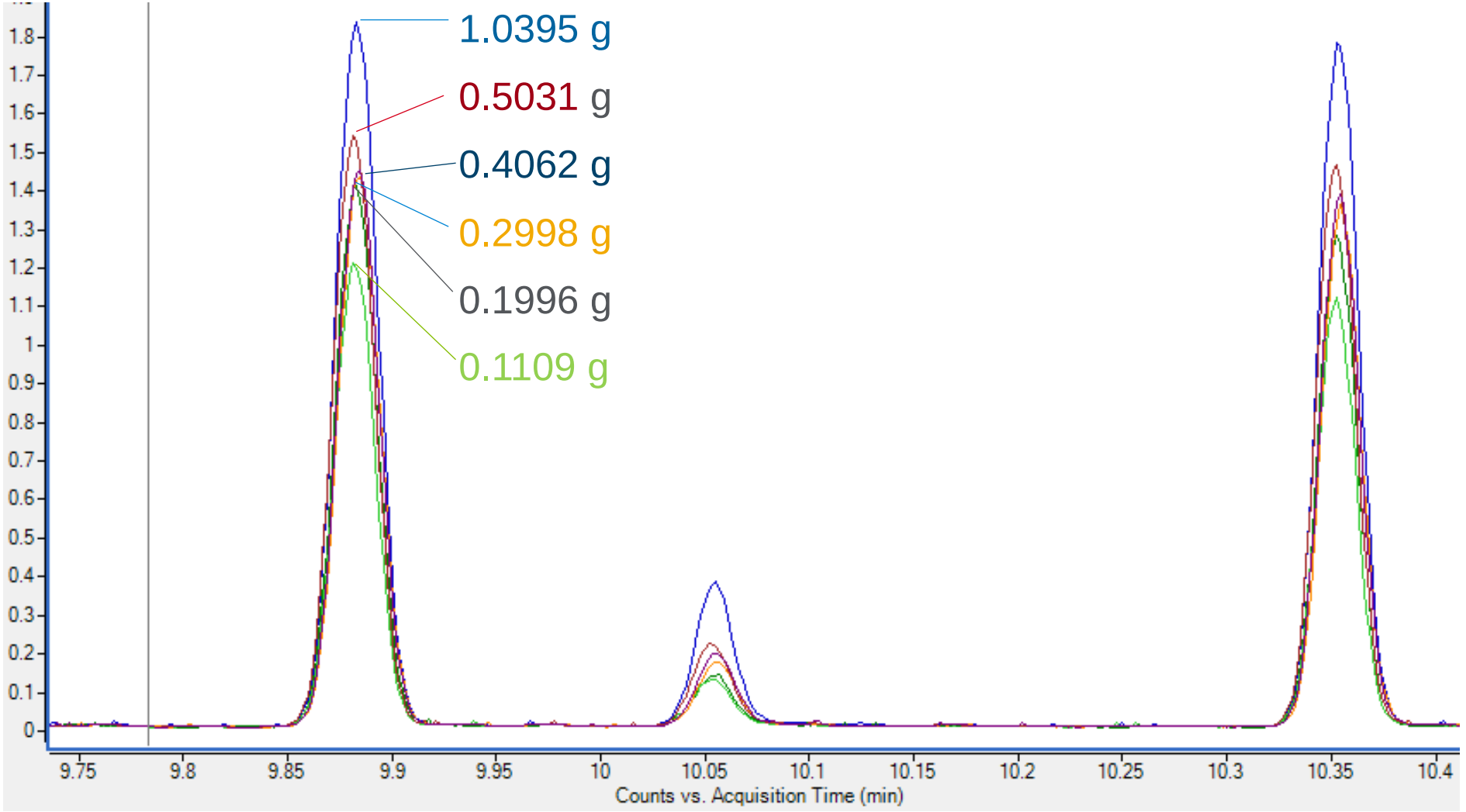
Potassium carbonate (K_2CO_3)
Ammonium chloride (NH_4Cl)
Ammonium sulfate ($(NH4)_2SO_4$)

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

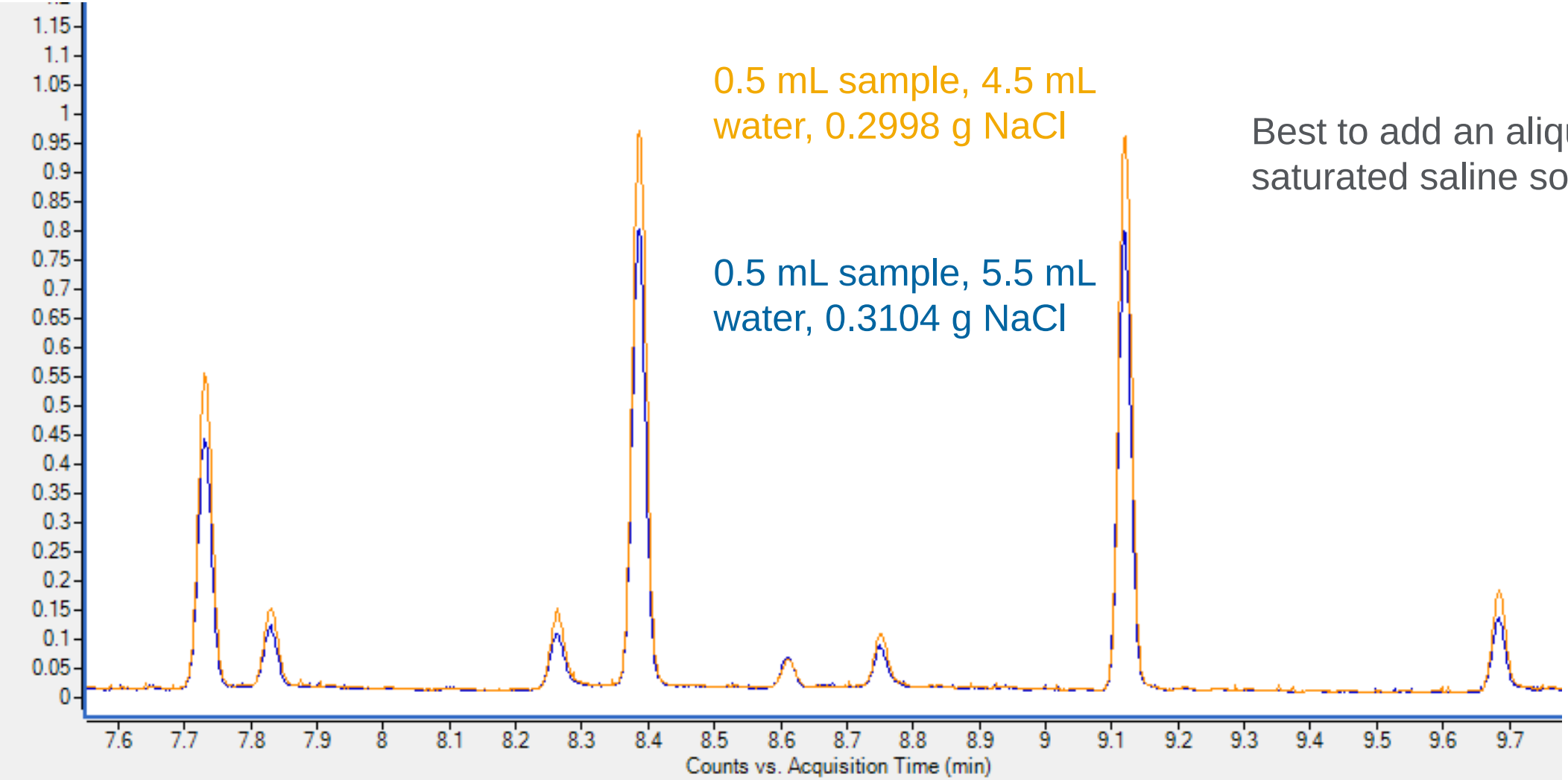
Use high quality, low impurity salts

How Much Salt Do I Add?

20 mL vial
80 °C oven temperature
20-minute incubation



Change in Matrix Volume with Salt

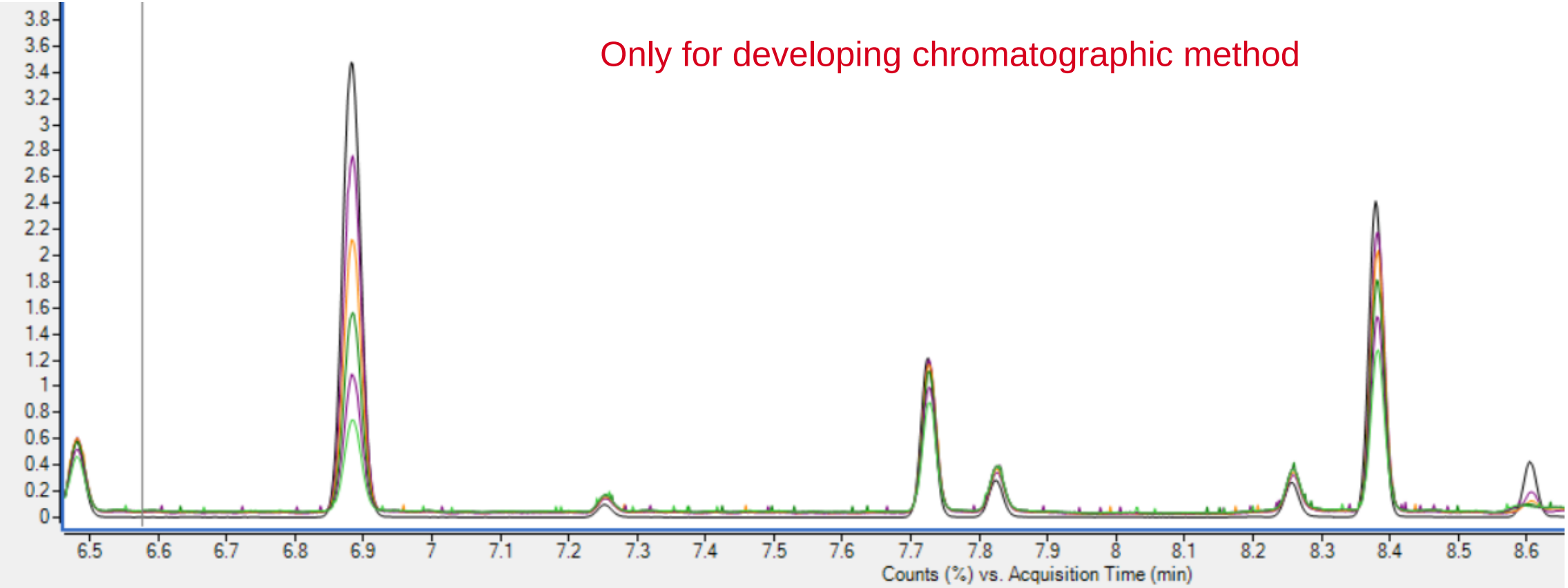


0.5 mL sample, 4.5 mL water, 0.2998 g NaCl

0.5 mL sample, 5.5 mL water, 0.3104 g NaCl

Best to add an aliquot of saturated saline solution

Can I Inject Multiple Times?



Only for developing chromatographic method

Headspace of Solid Matrices

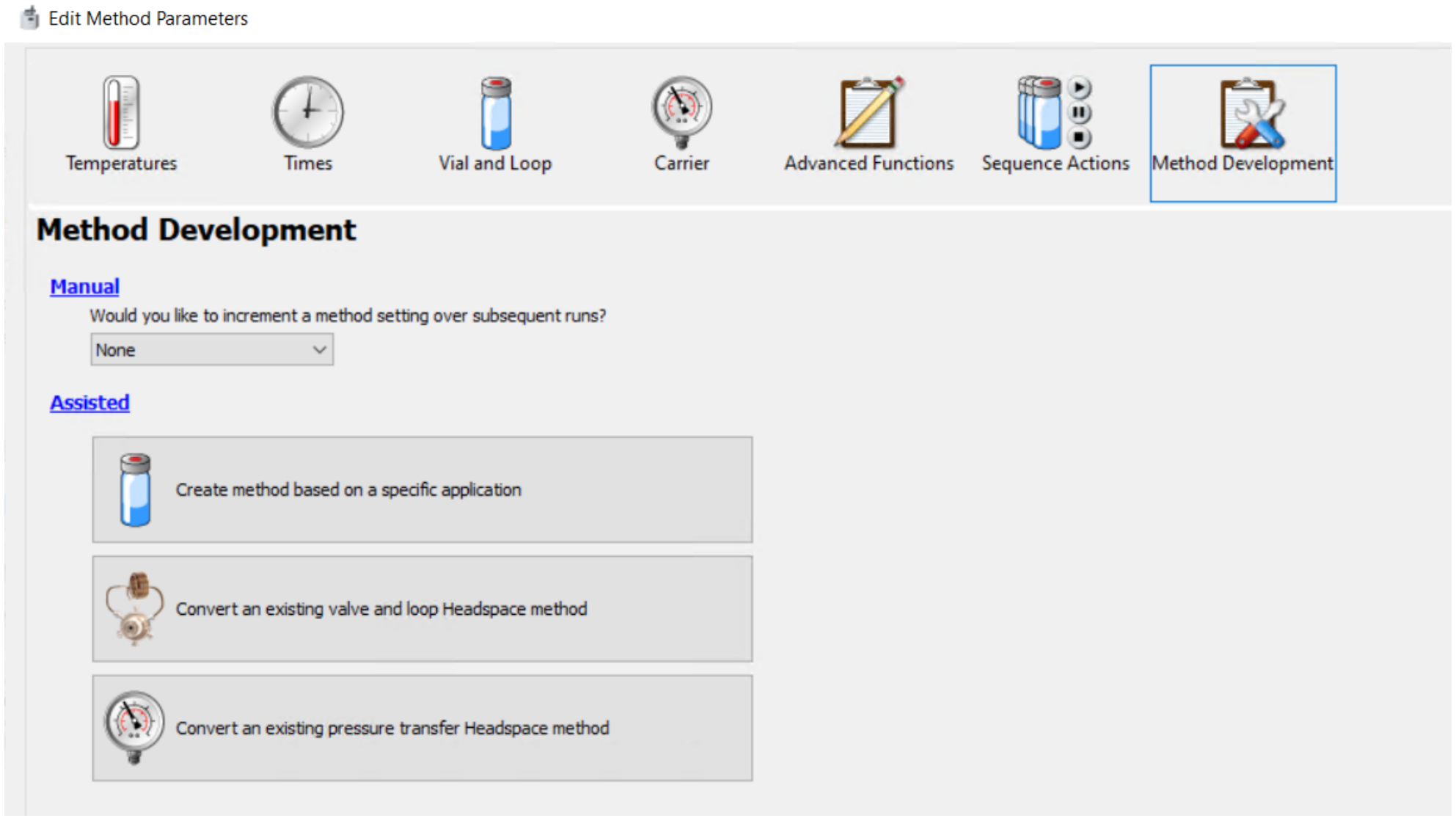
Samples are ground to increase surface area

They are used for solvents in plastics or polymers

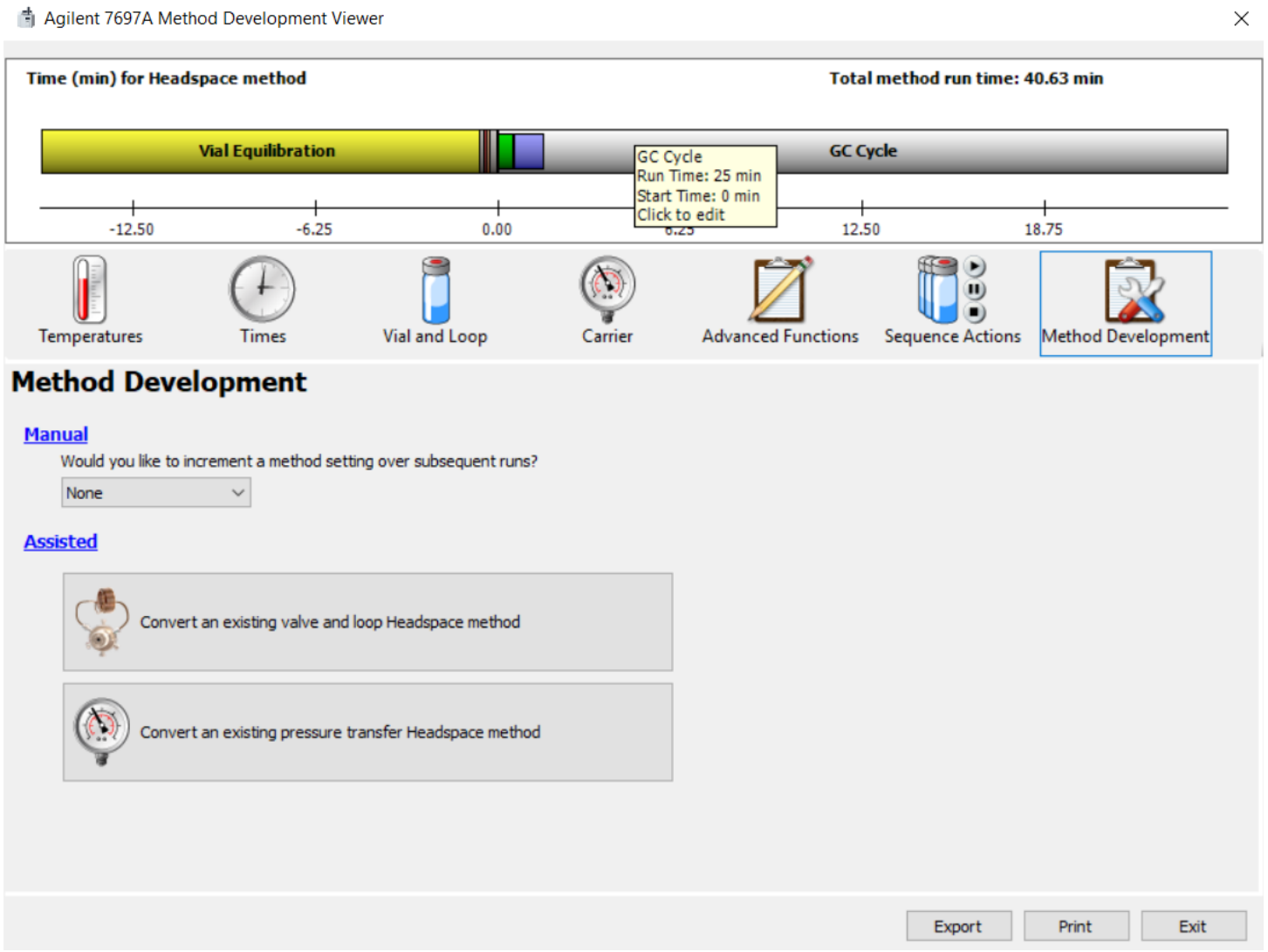
When a matrix match is not available, MHE – “multiple headspace extraction” is used

“Multiple Headspace Extraction for the Quantitative Determination of Residual Monomer and Solvents in Polystyrene” 5991-0974EN

Method Development Tools

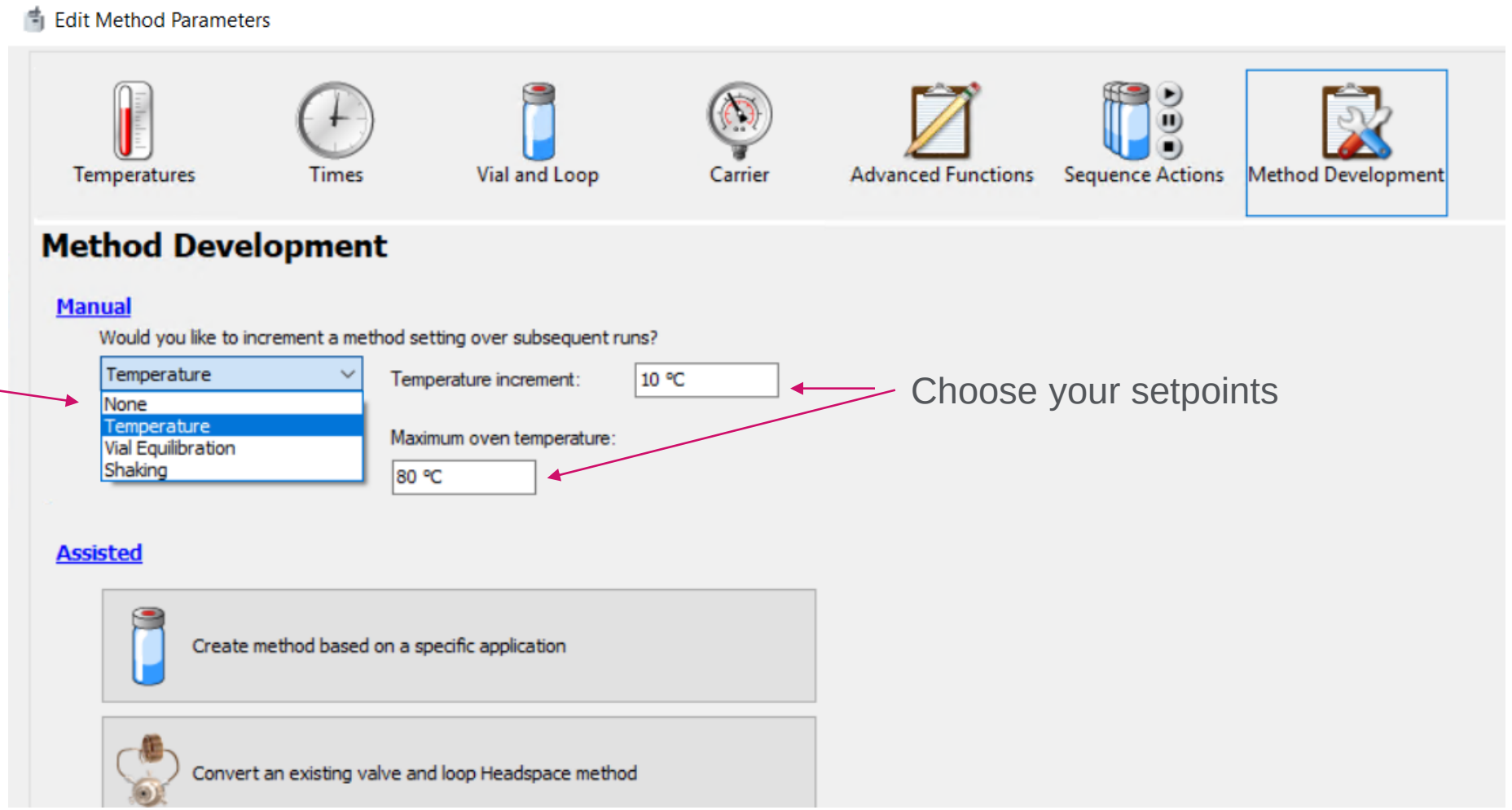


Standalone HS Method Development Viewer



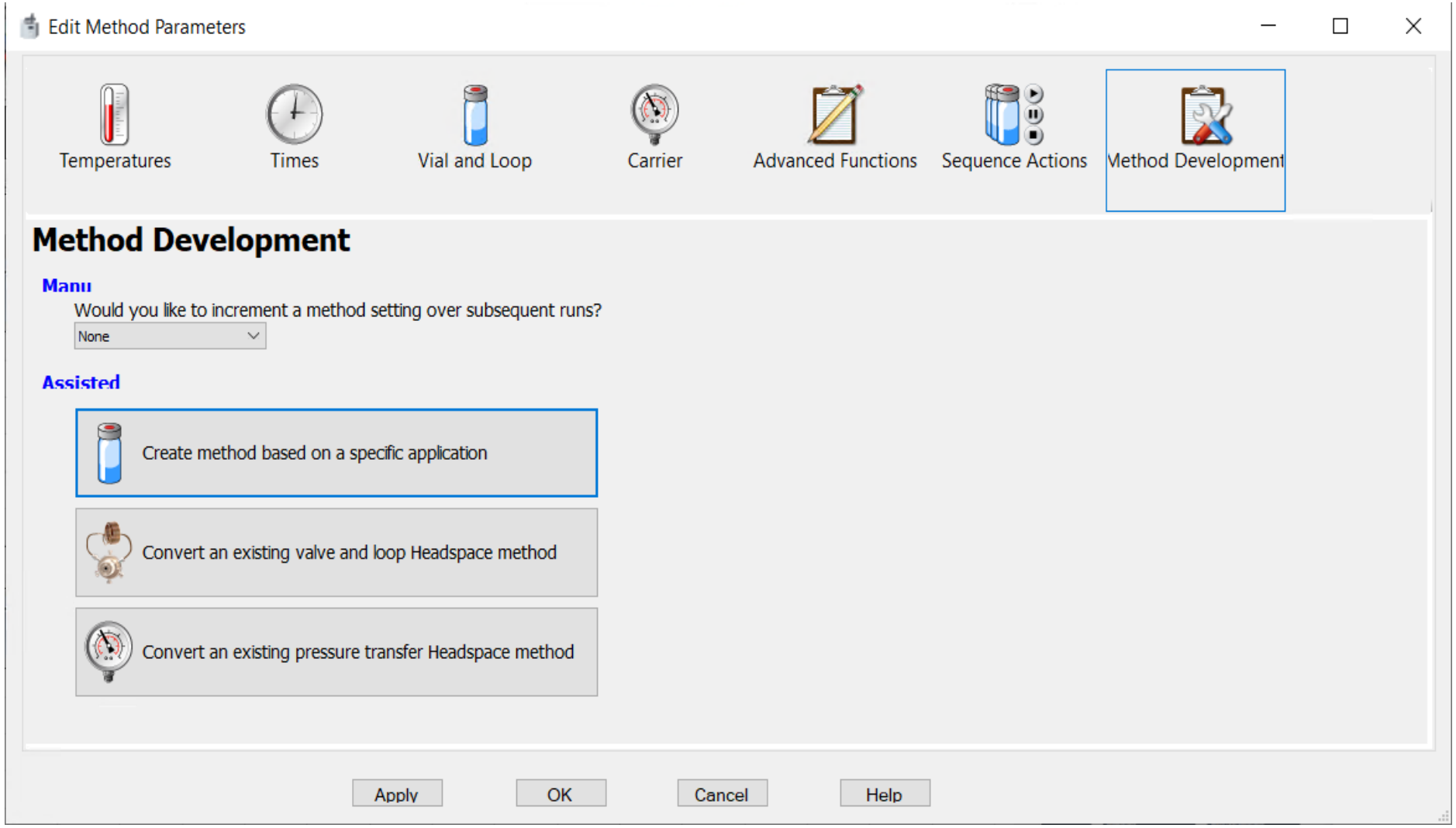
Method Development Tool

Choose what you want to increment

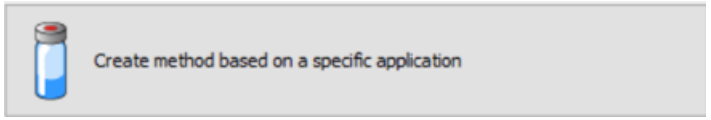


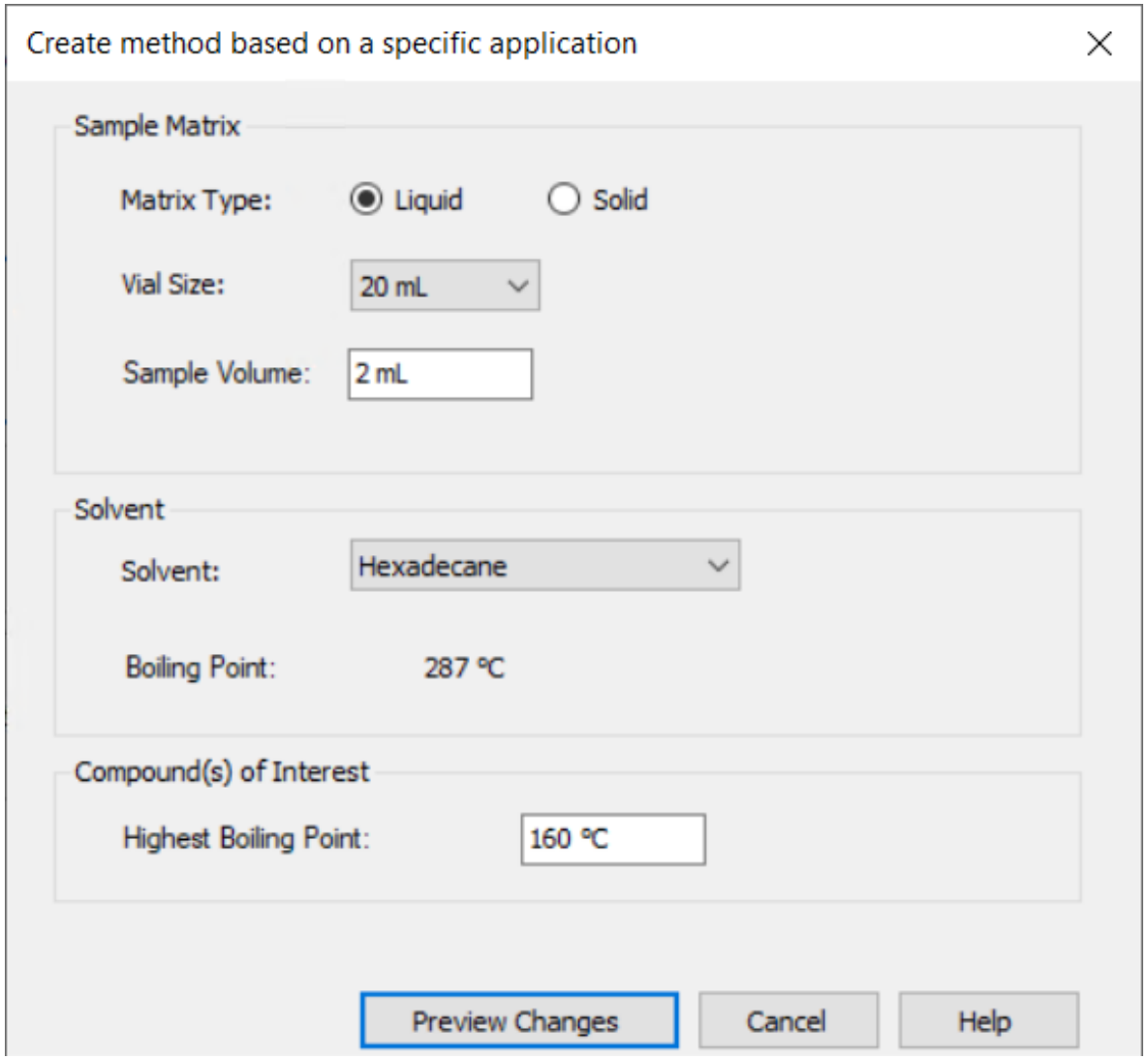
Choose your setpoints

Method Development Tool



Method Development Tools

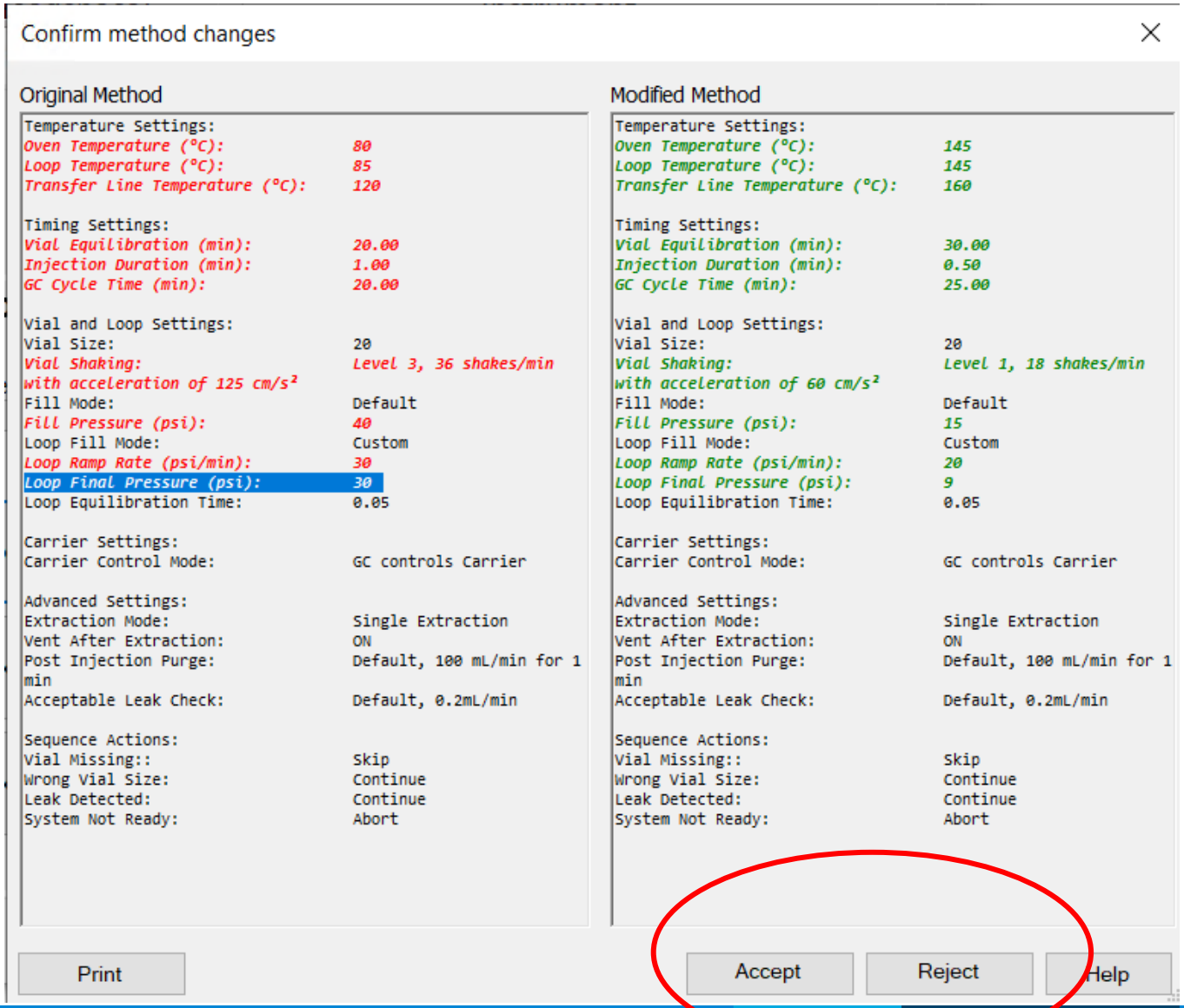




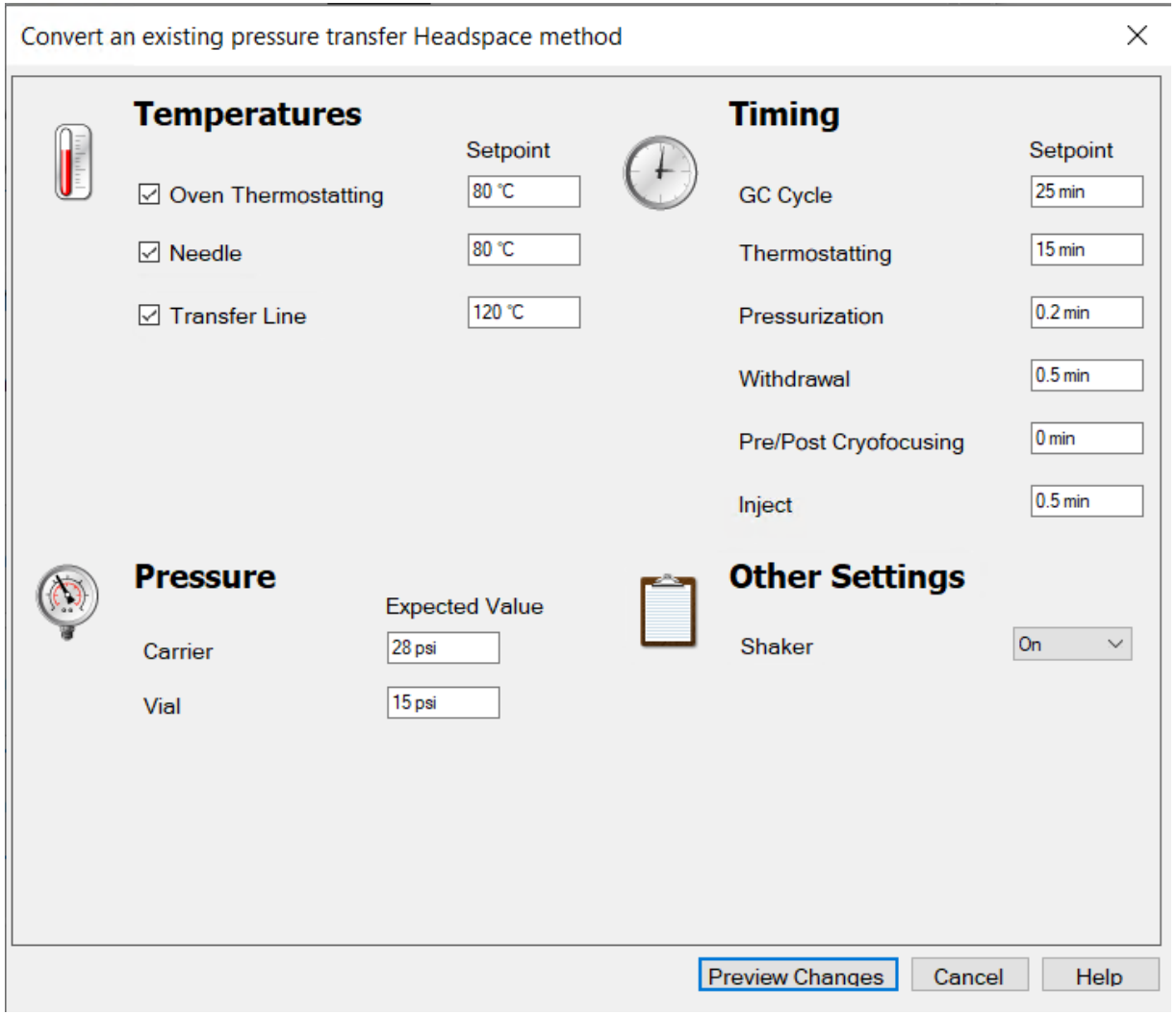
Create Method Based on Specific Application

Red parameters are what will be change from the initial method.

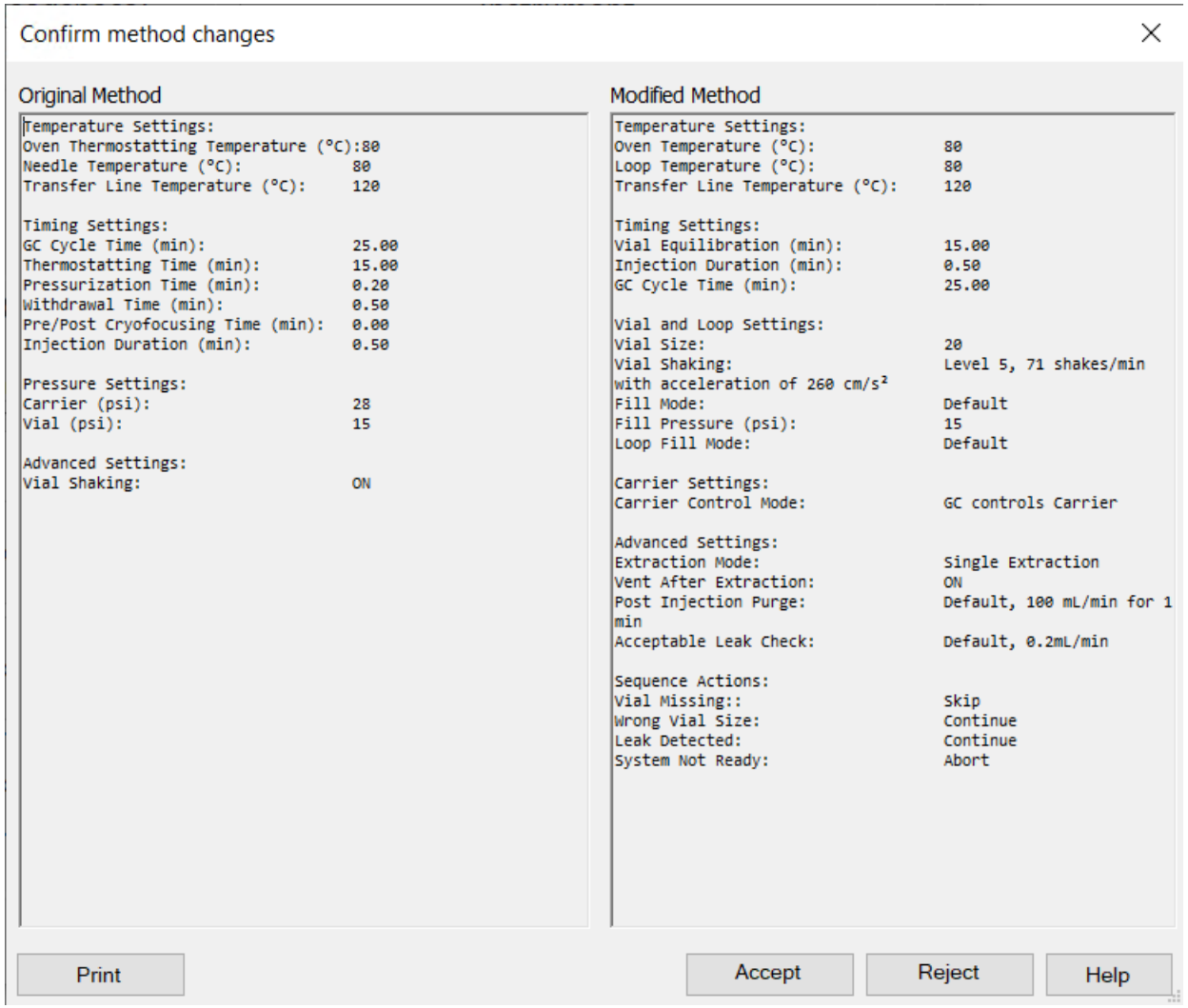
Green parameters are the new settings.



Convert an Existing Pressure Transfer Method



Convert an Existing Pressure Transfer Method

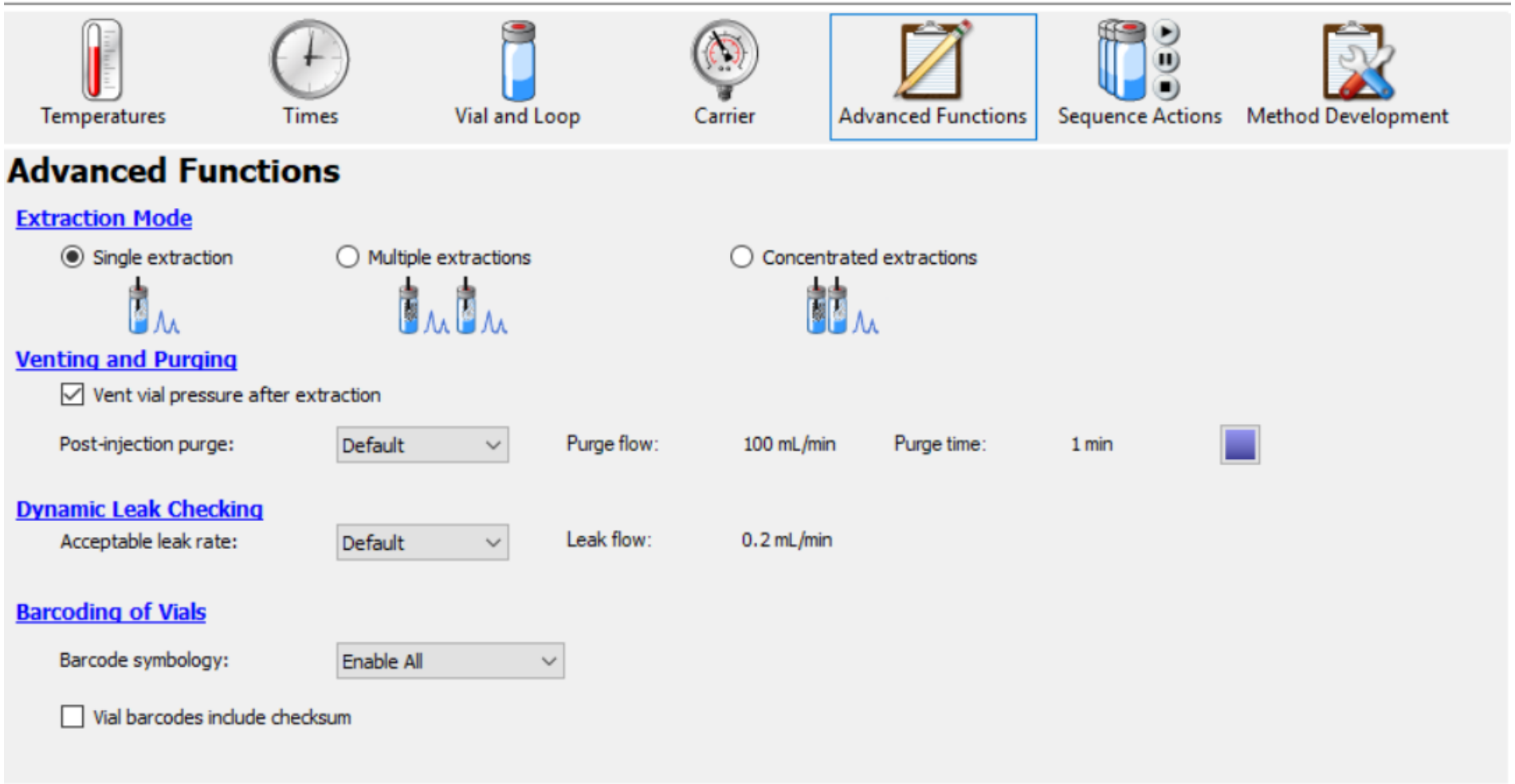


Common Issues

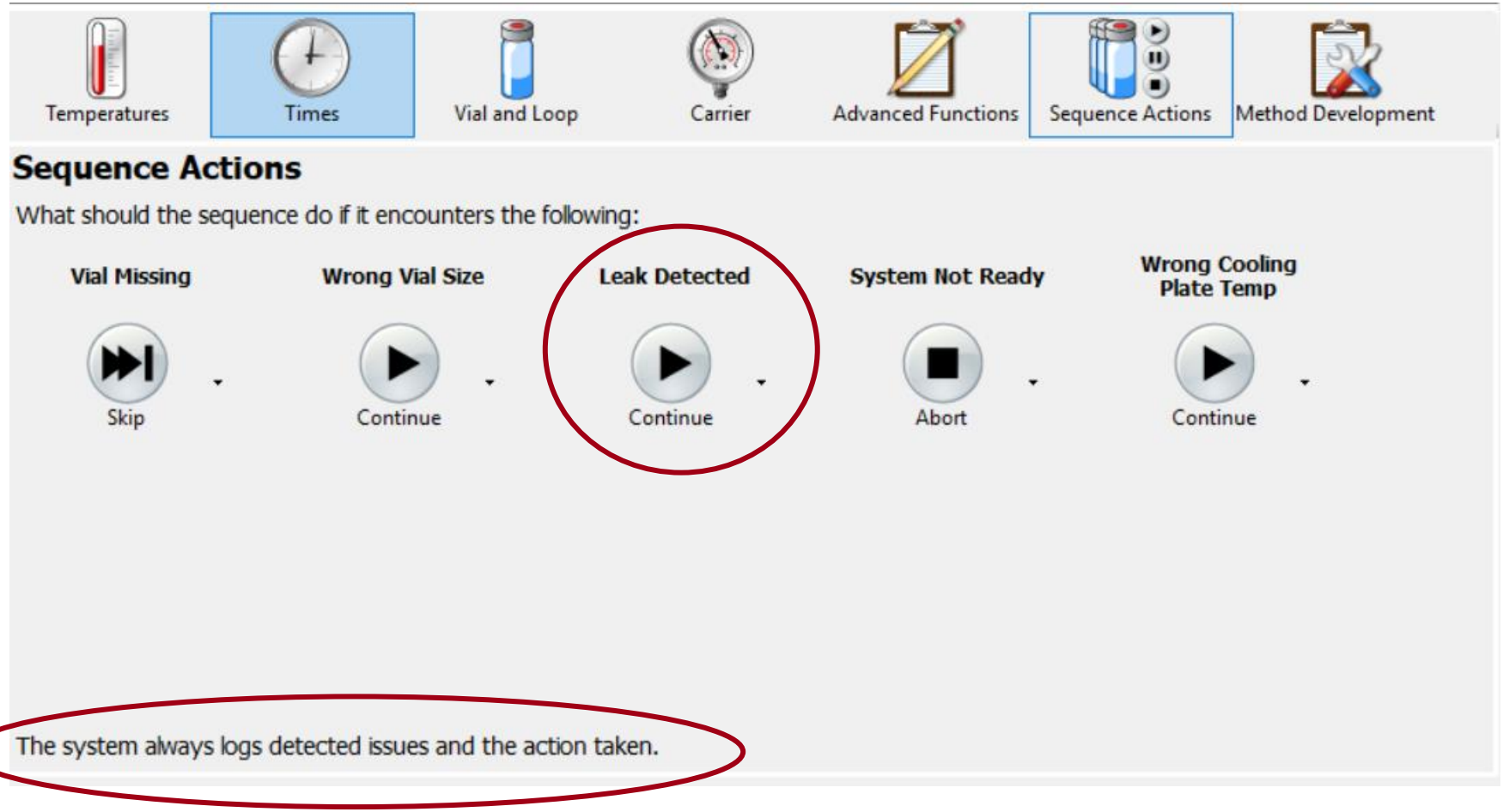
Carryover/contamination	• Too much sample in the vial — Contaminates the probe and loop • Shaking is set too high • Sample condensing in the loop
Septum or caps blowing off	• Oven temperature is too high creating too much pressure in the vial
High %RSD	• Vial leaks. Check vial crimping. Sequence actions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

Change the Loop Purge Time and Flow

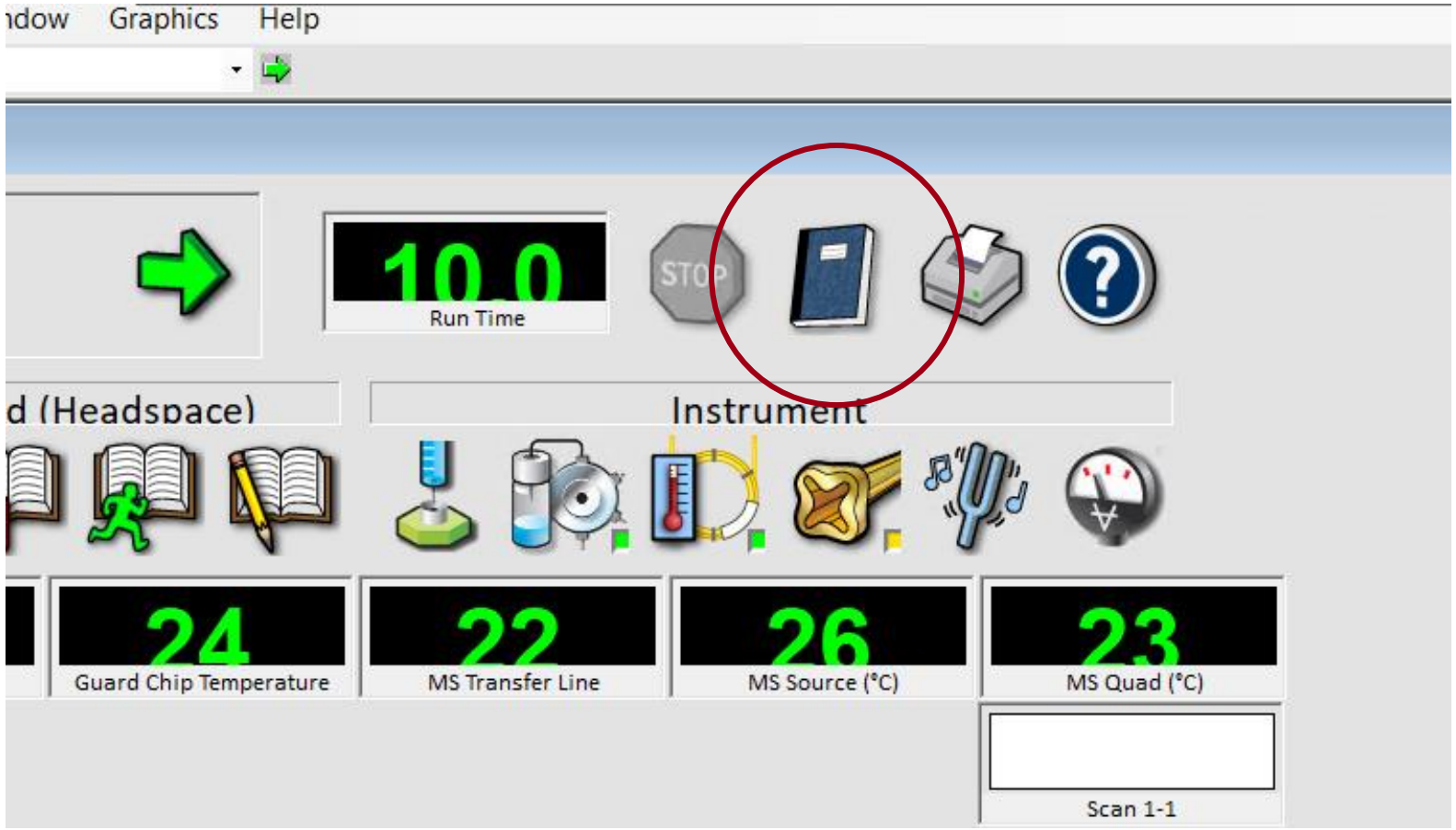
Carryover issues



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.

Logbook is in the Instrument Control Screen



Starting Parameters

Temperatures

- Oven 20 °C below the BP of the matrix
- Sample loop Same temp as oven
- Transfer line Hot enough not to have anything condense
- Transfer line interface Same as 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

Types of Vials

Flat Bottom

Round Bottom

More ideal for certain autosamplers (i.e. CTC/PAL)

5182-0838 5182-0837 5188-2753 5067-0226 5183-4474 5190-2239

Consumables

Good for SPME
8010-0139
(thinner septum)

Safety cap
(5183-4478)
Tears at 45 psi

Max temp 125 °C
Butyl/PTFE (5183-4479)

Max temp 180 °C
silicone/PTFE (5183-4477)

High-Performance Septa

Max temperature 300 °C

Reduced siloxane interferences at high temperature

8010-0428

5190-3987*

*High-power crimpers are required for steel crimp caps

A-line High-Power Crimper

5191-5624	(High Powered crimper with 20 mm jaw set)
5190-4062	(11 mm crimper jaws)
5190-4063	(11 mm de-capper jaws)
5191-5617	(Tool only + power supply; no jaws)

5190-4066 Base

https://www.agilent.com/cs/library/usermanuals/public/manual-A-Line-crimper-high-power-5191-5627-en-agilent.pdf

A-line Crimpers

5191-5615

5040-4669

How Tight is Right?

Good crimp

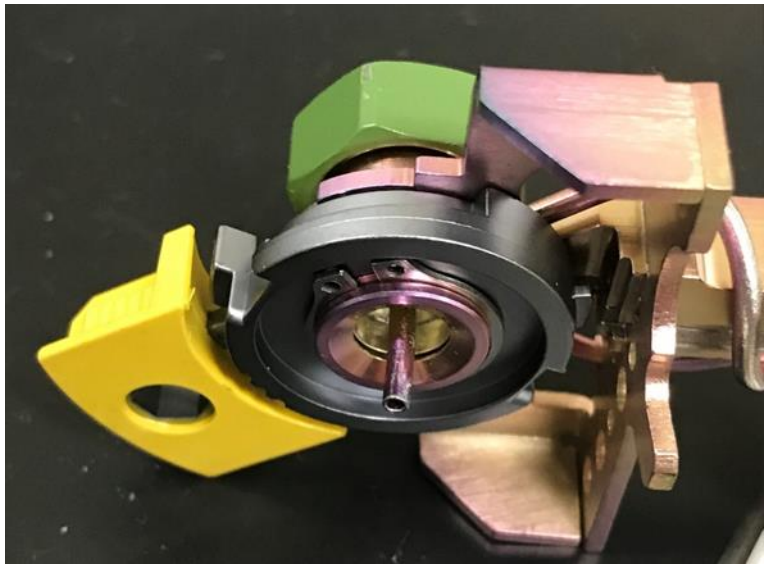
Too tight

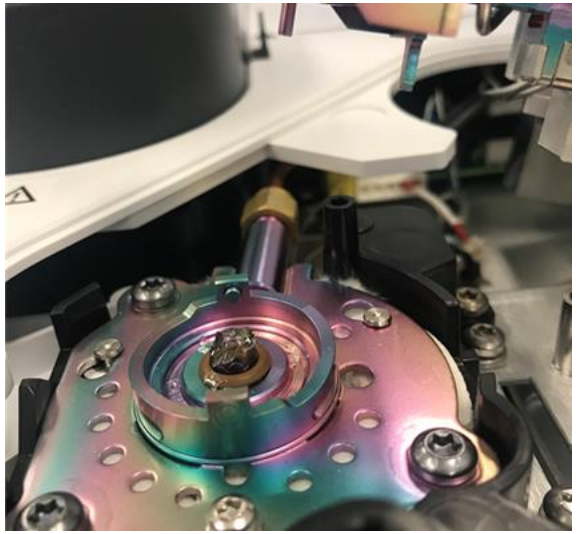
Too loose

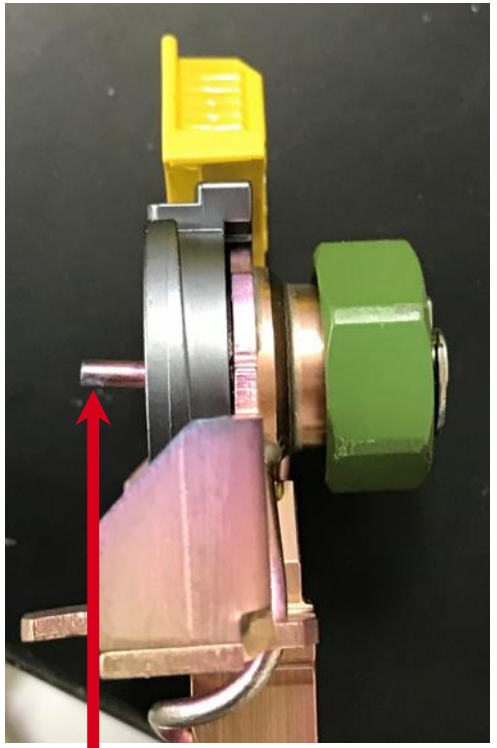
Common Issues

Installation of liner

- 2 mm liner is ideal for HS applications for narrower peaks
- Standard 2 mm liner is too small to accept
- 5190-6168 has slightly large ID, but still a tight fit





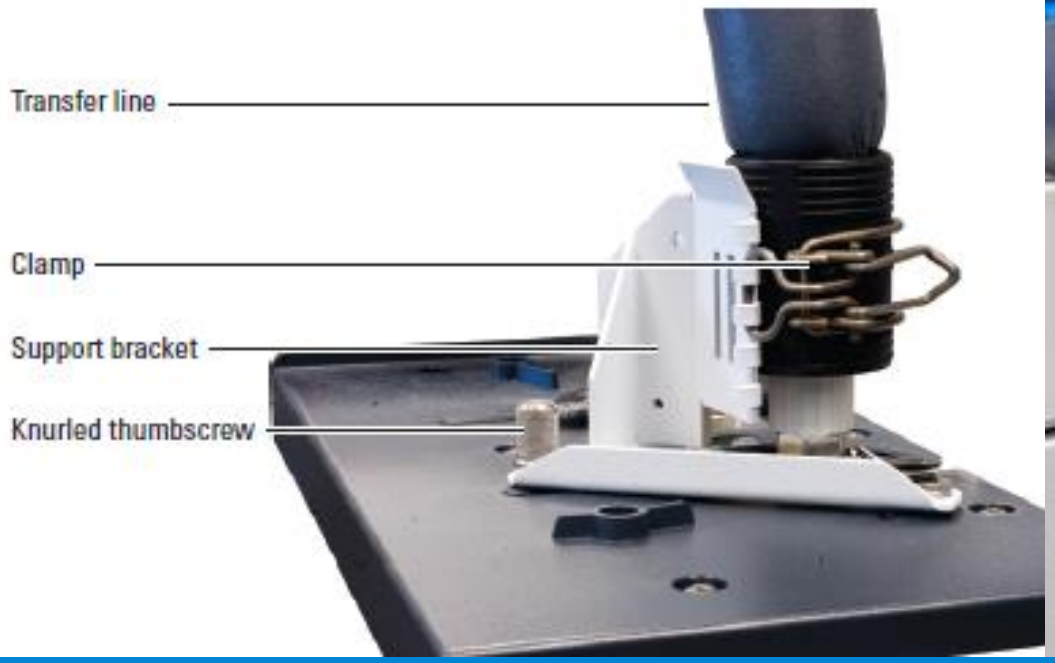


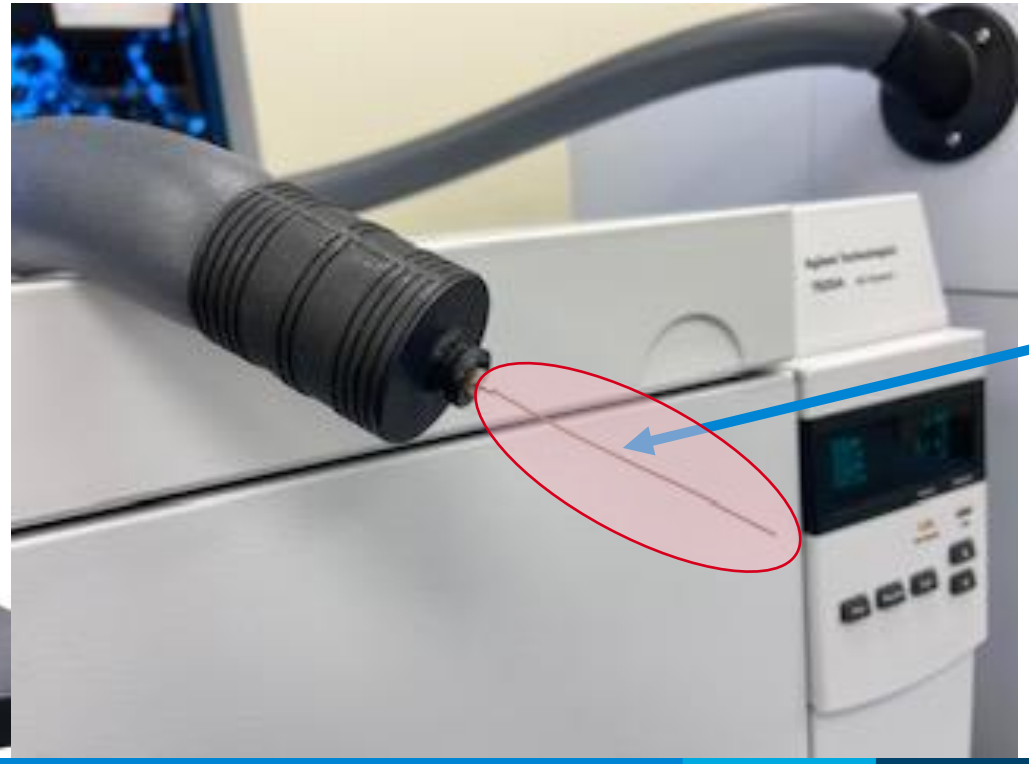
Common Confusion

Terminology

- Sample probe/needle
  - This is on the HS itself and probes the HS vial
- Transfer line “needle”
  - For 7697 and newer transfer line itself is the “needle”
  - No such needle when transfer line is plumbed laterally to the inlet

Figure 79 Sample Probe





This is not a needle but an extension of the fused silica xfer line that is inserted through the inlet septum

Sleeve for Pro-Steel Transfer Line

ProSteel Transfer Line Sleeve (4177-0607)

If you intend to use ProSteel and plan to operate the transfer line at temperatures 200 °C and higher, you must use the ProSteel protective sleeve (4177-0607). Without the protective sleeve, the ProSteel can permanently bind to the internal transfer line tubing.

Common Confusion

Terminology

- Sample probe/needle
  - This is in the HS itself and probes the HS vial
- Transfer line “needle”
  - For 7697 and newer transfer line itself is the “needle”
  - No such needle when transfer line is plumbed laterally to the inlet

Figure 79 Sample Probe

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 function
- Try to maximize parameters based on compounds with highest K
  - Not every compound responds/reacts the same way
- Use 10 mL vials if appropriate
- Be consistent with crimping vials. Set the crimper properly so that every user is successful.
- When troubleshooting, think about what may or may not be causing the issues you are experiencing.
- 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, 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