Agilent

Agilent 8697 Headspace Samplers

Operation

Notices

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CAUTION

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WARNING

A WARNING notice denotes a hazard. It calls attention to an operating procedure, practice, or the like that, if not correctly performed or adhered to, could result in personal injury or death. Do not proceed beyond a WARNING notice until the indicated conditions are fully understood and met.

Contents

1 Introduction

This chapter introduces the Agilent 8697 Headspace Sampler instrument, identifying major components and general headspace sampling techniques.

Introduction

Headspace analysis is a technique for analyzing volatile components of a sample matrix. Headspace analysis samples the ambient volume above a sample matrix, where the volatile compounds exist in gaseous form at predictable levels.

Headspace analysis is useful for situations where:

- The analyte of interest is volatile at temperatures below 300 °C.
- The sample matrix is a solid, paste, or a liquid that is not easy to inject into a GC inlet.
- Sample preparation to allow easy liquid injection is currently difficult.
- Nonvolatile components of the sample are hazardous. (In headspace analysis, the sample only physically touches a disposable sample vial.)

Headspace analysis provides several advantages over traditional injections:

- Simpler sample preparation. The sample does not need to be processed into an injectable liquid.
- Directly analyze a wide range of sample matrices (solids, pastes, liquids, and gases).
- Columns last longer, with less maintenance. The headspace volume above the sample matrix is cleaner than the matrix. By injecting fewer contaminants, the analytical column lasts longer and requires less maintenance (trimming, bakeout, guard column replacement, and so forth).
- High precision.
- Headspace oven temperature can be adjusted to selectively exclude heavier components from the analysis. This allows for faster oven programs, faster oven cooldowns, and longer column life.

Headspace Techniques

At this time, there are three main techniques for performing headspace analysis.

Dynamic headspace sampling: This technique, typically part of a purge and trap system, uses a continuous flow of carrier gas to purge any volatile components from the sample matrix. These analytes are usually trapped in an adsorbant. After a specified time, the trap is heated, releasing the adsorbed compounds, which are swept into the GC inlet.

Static headspace sampling: This technique uses a closed sample container and a sampling system. After placing the sample matrix into the sealed sampling vial, the sample matrix is heated for a specified time, during which the vial can also be agitated (shaken) to help drive volatile compounds from the matrix and into the headspace volume. After a specified time, the vial is punctured, pressurized, and an amount of the headspace vapors are withdrawn and injected into the GC inlet.

Solid Phase Micro Extraction: In this technique, a probe with an adsorbant is placed into a vial that contains the sample matrix. The analytes of interest adsorb into the sample probe. Use of different adsorbants provides flexibility for analyzing different compounds of interest (while ignoring others). After a specified time, the probe is heated to drive off the analytes, which are swept onto the GC column.

Static Headspace Sampling Using a Valve and Loop

There are two main static sampling headspace techniques, *pressure-transfer* and *valve and loop*. (A third technique, performing the injection manually using a gas-tight syringe, does not provide easily reproducible results.)

The valve and loop system, as used in the 8697, also heats and agitates the vial for a specified time. However, the Agilent system uses a sample loop of known volume to collect the sample. The sampling steps for the valve and loop system are:

1 A needle probe punctures the vial.

2 The sampler pressurizes the vial with gas. See **Figure 1**.

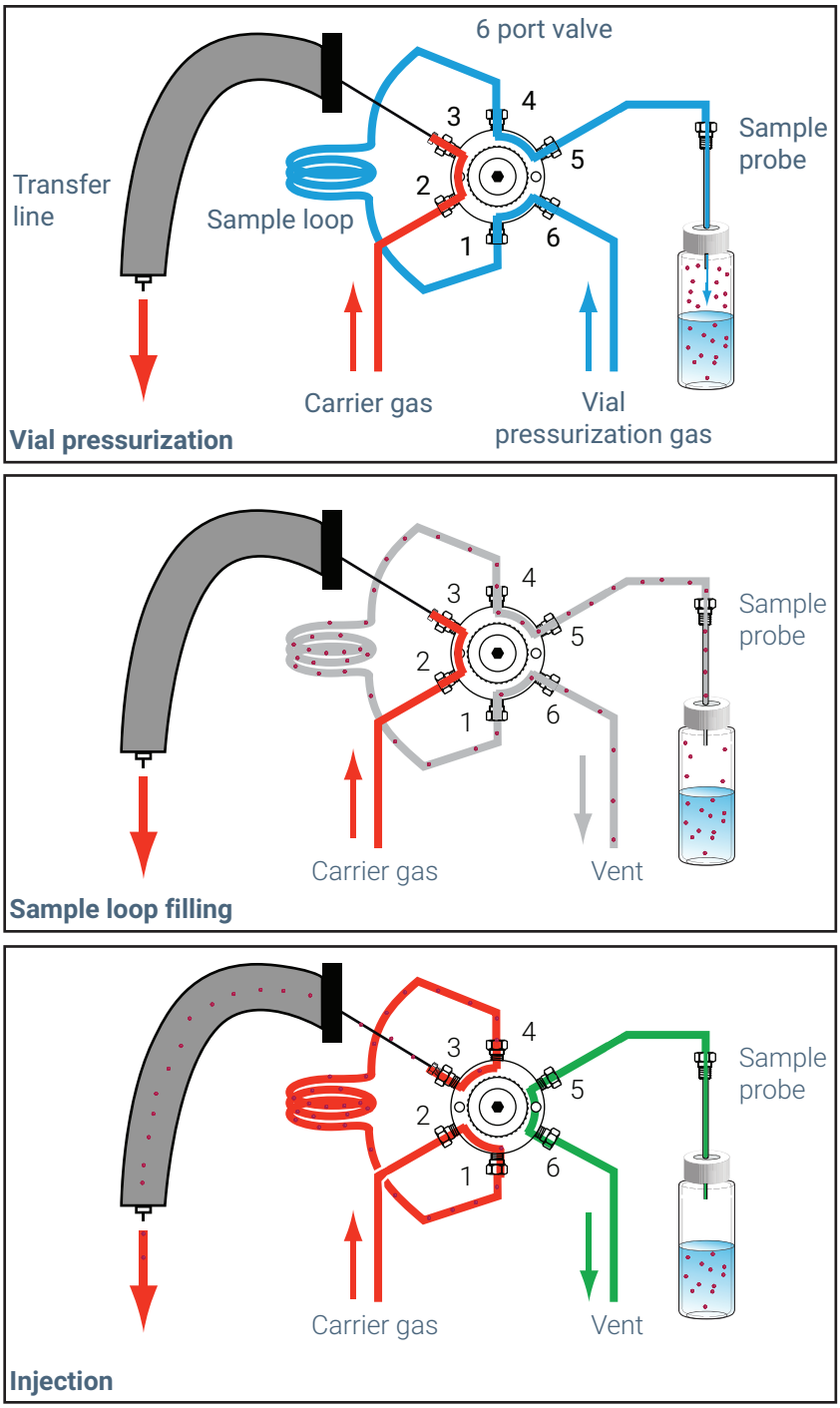


Figure 1. Valve and loop system sampling and injection stages

3 After equilibration at pressure, the pressurized vial gases vent through the sample loop, filling the loop with sample. Note that the vial vents to atmospheric pressure in this case, not to a high column head pressure. Also, the 8697 can control the flow of gas into the sample loop so that the sampling ends before the vial completely depressurizes.

4 After the sample loop equilibrates, the valve switches and the sample loop becomes part of the flow path into the GC inlet. The carrier gas sweeps the known sample amount into the GC inlet for analysis.

The Agilent 8697 Headspace Sampler

The Agilent 8697 Headspace Sampler (HS) is a valve and loop headspace sampling system with a 48-vial capacity or a 120-vial capacity (with XL tray). The HS uses a 12 vial oven for equilibrating samples at temperature. Since the longest hold time in headspace analysis is typically the equilibration time, using a multi-vial oven allows the HS to increase throughput by equilibrating multiple vials at once.

The 8697 HS is controlled through the GC touchscreen, browser interface, or data system connection. It extends the existing GC settings to include the HS method parameters, configuration settings, early maintenance feedback tracking, log entries, current status displays, and so forth. The 8697 HS is an integrated GC component.

To distinguish between GC and HS status entries, the touchscreen and the browser interface status displays will prepend **Headspace** to distinguish the HS entries from the GC entries. So, the touchscreen might display 8697 HS oven temperature as **Headspace Oven Temperature**, and the GC oven temperature will have no prefix or annotation. For example, see the figure below.

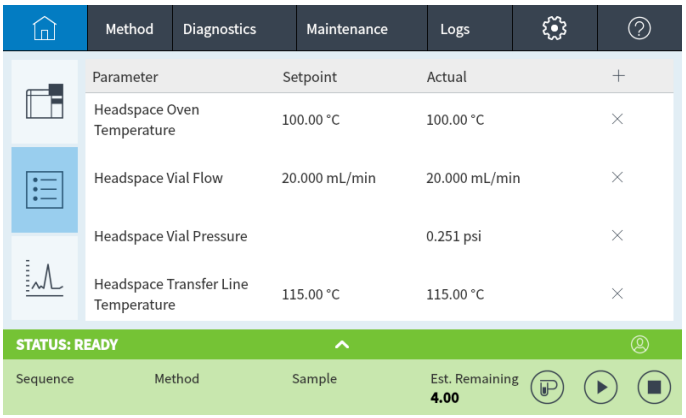


Figure 2. Example Headspace Status items

About This Manual

This manual describes the concepts and tasks needed for routine headspace sampler operation, as well as the information needed to perform more advanced tasks and method development.

Getting Familiar with the Headspace Sampler

Figure 3. Front view

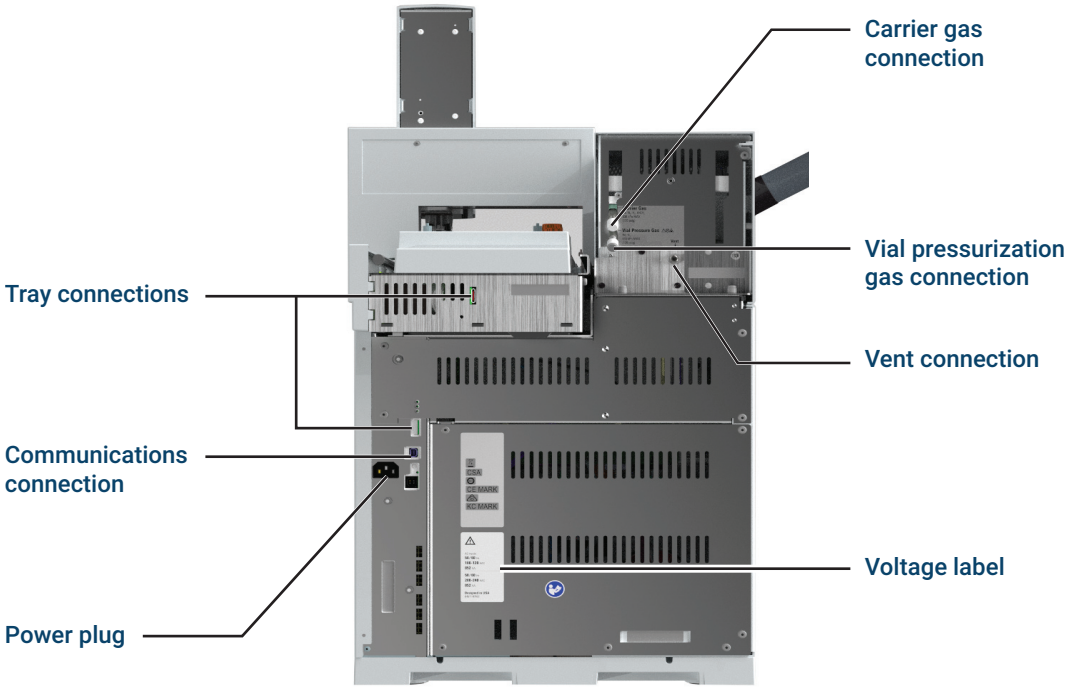


Figure 4. Back view

Status indicator LED

The HS includes a status indicator on the front panel to allow you to quickly determine its general status and readiness. The status indicator changes color depending on the current state of the HS.

- Green: Indicates that HS is ready for operation.
- Yellow: Indicates that the HS is not ready for operation. Power is on and available, but not all parameters have reached operating setpoints. A warning or other message may exist. Check the GC touchscreen for additional information.
- Red: Indicates a fault or other serious condition. A fault or other message may exist. Check the GC touchscreen for additional information. The HS cannot be used until the fault condition is resolved.

In addition to the indicator LED, detailed status information appears on the touch screen of the connected GC, and through the GC's browser interface.

Park button and indicator

The HS park button also includes an indicator light. When lit, the tray is in the park position, and the HS is not ready. To park or unpark the tray, press the **Park** button. See **"Park or Unpark the Tray"** on page 35.

2 The Operation Workflow

This section describes the basic work flow for using the headspace sampler.

Routine Operation Workflow

Figure 5 summarizes the normal operating workflow for headspace analysis. This workflow assumes that the headspace sampler is set up and that the methods and samples are known.

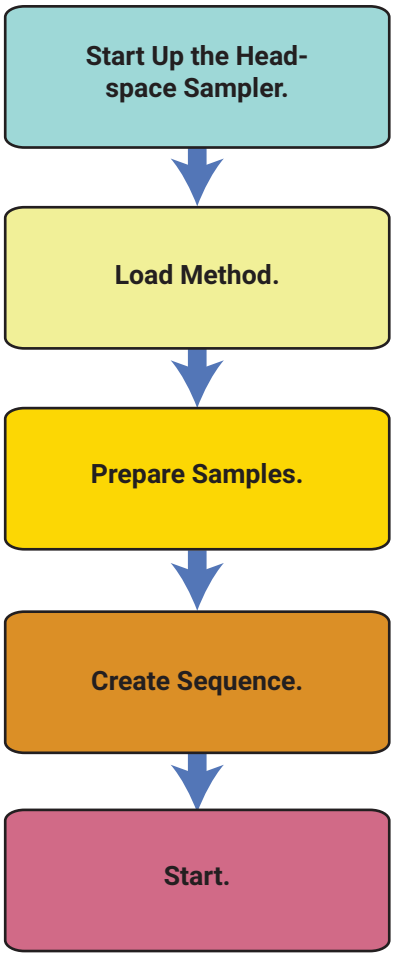


Figure 5. Routine headspace analysis workflow

Method Development Workflow

Figure 6 summarizes the workflow for developing methods. For details about method development, see **"Method Development"** on page 75.

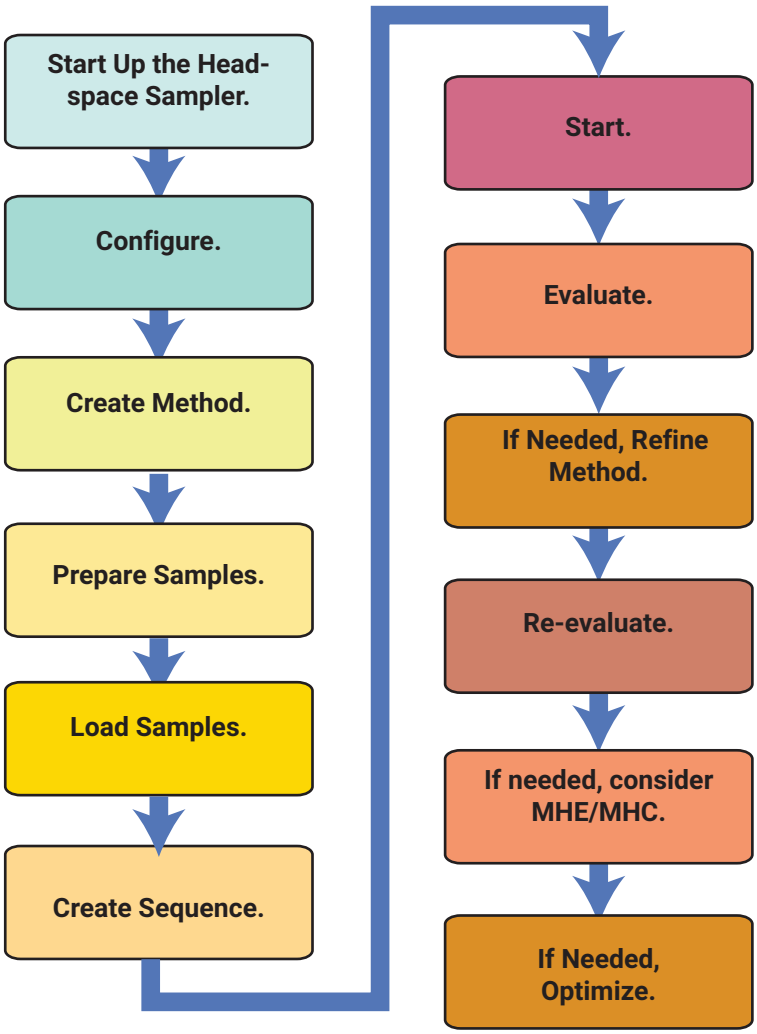


Figure 6. Workflow for method development

3 Consumables

This section lists commonly-used parts, such as vials and sample loops, needed for routine operation of the Agilent 8697 Headspace Sampler. Procedures for replacing these parts can be found in this manual or in the **Maintenance** manual.

Consumables for Headspace Analysis

The following tables list common supplies for the headspace sampler and headspace analysis. For the latest parts available, visit the Agilent website at **www.agilent.com**.

Table 1 Headspace sampler parts and standards

Description	Part number
Leak test kit. Includes: No hole ferrule 11 mm low bleed septa, 5/pk Leak test vial 1/8-in. fitting plug 1/16-in. stainless steel ZDV plug (6 port valve cap)	G4556-67010 5181-7458 5182-3413 G4511-20180 0100-1526 G6600-80039
Tray vial rack, 8697	G4511-60402
Tray vial rack labels Rack 1 labels Rack 2 labels Rack 3 labels Rack 4 labels Rack 5 labels	 G4511-90401 G4511-90402 G4511-90403 G4511-90404 G4511-90405
Replacement Gas Clean Filter, carrier gas (used for vial pressurization gas)	CP17973
Column cutting wafer, ceramic	5181-8836
Sample probe, deactivated	G4556-63825
6-port valve, replacement rotor, WT series, 300 psi, 350 °C	1535-4952
Sample loop retainer clip, 1 each: 1 ea. used with 0.025, 0.05, and 0.10 mL sample loops 2 ea. used with 0.5 and 1.0 mL sample loops 1 ea. used with 3.0 mL sample loops	G4556-20177
Sample loop retainer clip, 1 each: 1 ea. used with 0.025, 0.05, and 0.10 mL sample loops	G4556-20178
Inlet Liner for use with HS Transfer Line Accessory	
Ultra Inert straight 2.0 mm liner	5190-6168
Standards	
Headspace OQ/PV sample	5182-9733

Table 2 Headspace sampler transfer line parts

Description	Part number
Transfer line components	
Transfer line septa (9 mm)	5183-4801
Ferrule, polyimide, graphite, 5/pk	
0.53 mm, 1/32 in. for tubing OD 0.50 x 0.80 mm	0100-2595
0.4 mm id, for columns up to 250 µm od	5190-1437
Septum nut, transfer line, for split/splitless and multimode inlets	G3452-60845
Blanking nut, 1/16-inch stainless steel	01080-83202
Nut and reducing union for 6 port valve and transfer line connection, 1/16-inch to 1/32-inch	0100-2594
Transfer lines	
Deactivated fused silica, 250 µm × 5 m	160-2255-5
Deactivated fused silica, 320 µm × 5 m	160-2325-5
Deactivated fused silica, 450 µm × 5 m	160-2455-5
Deactivated fused silica, 530 µm × 5 m	160-2535-5
ProSteel deactivated stainless steel, 5 m length	160-4535-5
Sleeve for ProSteel tubing, 5 m length	4177-0607
Parts for connection to volatiles interface	
Ferrule, 0.4 mm VG cond .25 col lng 10/pk	5062-3508
Ferrule, 0.5 mm VG cond .32 col lng 10/pk	5062-3506
Ferrule, 0.8 mm VG cond .53 col lng 10/pk	5062-3538

Table 3 Headspace sampler sample loops

Description	Part number
Sample loops, inert	
0.025 mL	G4556-80101
0.05 mL	G4556-80102
0.1 mL	G4556-80103
0.5 mL	G4556-80105
1.0 mL	G4556-80106
1.0 mL, Certified	G4556-80126
2.0 mL	G4556-80107
3.0 mL	G4556-80108
3.0 mL, Certified	G4556-80128
5.0 mL	G4556-80109

Table 4 Headspace vials and caps

Description	Part number
Certified flat bottom vials	
Certified flat bottom headspace vials, 20 mL, 100/pk	5182-0837
Certified flat bottom headspace vials, 10 mL, 100/pk	5182-0838
20 mm Headspace caps, with septa	
Certified headspace Al crimp cap, PTFE/Si septum, 20 mm,100/pk	5183-4477
Headspace vial kits	
Vial kit 20 mL Headspace crimp top, flat bottom vials, silver aluminum one-piece crimp caps with safety feature, PTFE/white silicone septa, 100/pk	5182-0840
Cappers and decappers	
A-Line High Power E-crimper, with power supply, 20 mm jaws	5191-5624
A-Line electronic crimper for 20 mm caps	5191-5615
A-Line electronic decapper for 20 mm cap	5191-5613
Ergonomic manual crimper for 20 mm caps	5040-4669
Ergonomic manual decapper for 20 mm caps	5040-4671

Table 5 Cooling Plate Replacement Parts

Description	Part number
Metal vial rack assembly (5)	G4512-60402
Cooler drip tube	G4522-20540
Secondary drip tray	G4556-40680
Nut and ferrule set, 1/4-in, brass	5080-8752
Nut, 1/4-in, brass	0100-0056
Bulkhead union, 1/4-in	G4522-20500
Clamp, hose, 0.468-0.531-in od, 0.22-in wd	1400-3298

4 Sample Vials

This section discusses sample vial selection, sample preparation, and vial handling with the Agilent 8697 Headspace Sampler.

Sample Vial Types

The headspace sampler accepts 10-mL, 20-mL, or 22-mL sample vials. Set the vial size in the method. The vial size can change with each new method used in a sequence, but not within a method. Using a different vial size than expected by the method causes a run-time exception.

The headspace sampler uses clear or amber glass sample vials with crimp caps, or screw-cap vials. Use amber glass vials for light-sensitive samples. Both types are available with either flat or rounded bottoms. Refer to your Agilent catalog for consumables and supplies for acceptable vial types, or visit the Agilent website at **www.agilent.com**. Incompatible sample vials can cause gripper errors.

Vials must conform to the specifications shown in **Figure 7**.

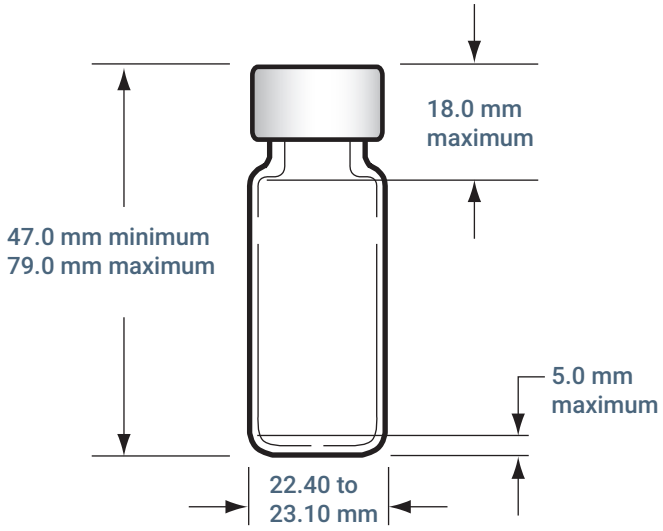


Figure 7. Supported vial dimensions

Avoid reusing vials. Using vials more than once increases their chance of breaking.

Sample Vial Septa and Caps

There are different types of septa used with crimp caps and screw-on caps, each with different resealing characteristics and different resistance to solvents.

Septum material	Compatible with	Incompatible with	Resealability	Maximum temperature*
PTFE/butyl rubber	PTFE resistance until punctured, then septa or liner will have compatibility of rubber (ACN, acetone, DMF, alcohols, diethylamine, DMSO, phenols)	Chlorinated solvents, aromatics, hydrocarbons, carbon disulfide	Good	< 125 °C
PTFE/silicone rubber	PTFE resistance until punctured, then septa will have compatibility of silicone (alcohol, acetone, ether, DMF, DMSO)	ACN, THF, benzene chloroform, pyridine, toluene, hexane, heptane	Average	< 180 °C
High temperature PTFE/silicone	PTFE resistance until punctured, then septa will have compatibility of silicone (alcohol, acetone, ether, DMF, DMSO)	ACN, THF, benzene chloroform, pyridine, toluene, hexane, heptane	Average	< 300 °C

* Approximate. Refer to manufacturer's recommendations.

Vial caps come with or without an internal safety feature that allows the vial to vent if the internal vial pressure exceeds about 310 kPa (45 psi).

In general, do not use crimp caps or septa more than once for headspace analysis.

Refer also to the Agilent website at **www.agilent.com** for acceptable vial types.

Vial Labels

CAUTION

Make sure that any label and ink can withstand the oven heat without degrading.

If using labels, the label needs to conform to the dimensions below. If also using the optional barcode reader (G4527A), the barcode labels must conform to the general dimensions for labels, plus the placement requirements shown.

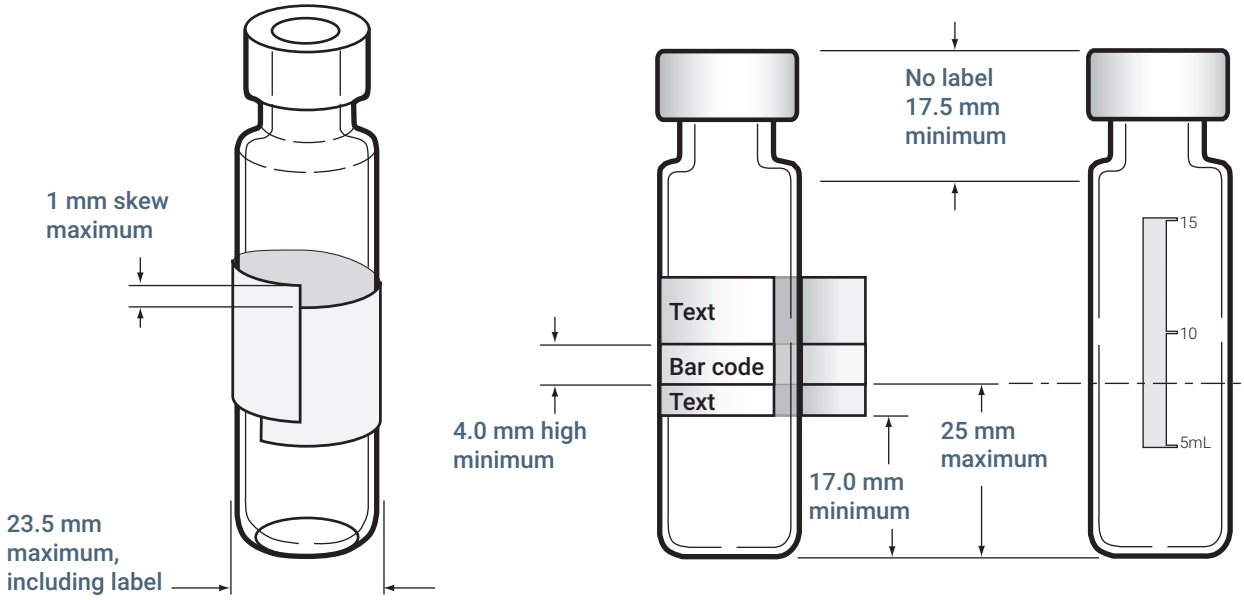


Figure 8. Vial label and barcode specifications (20 mL vial shown)

CAUTION

Correct sample vial dimensions are critical for proper gripper operation. Vials and labels that do not meet these specifications may cause sampler errors. Service calls and repairs found to be due to vials and labels that do not meet these specifications are not covered under warranty or the service contract.

To confirm label placement, place a labeled vial into the barcode reader. Go to **Diagnostics > Headspace > Manual Actions > Read Barcode**. The barcode reader will attempt to read a barcode from the vial.

In addition, barcode labels must:

- Be heat resistant (to avoid degradation or charring when heated)
- Use a matte or other non-glossy finish. Glossy barcode labels can reflect ambient room light, and interfere with the reader.

Supported barcodes

The barcode reader can read any of the following symbologies:

- Code 3 of 9
- Code 128
- Matrix 2 of 5
- Standard 2 of 5
- Interleaved 2 of 5
- UPC-A
- EAN/JAN 13
- EAN/JAN 8
- UPC-E

Filling Sample Vials

In general, fill sample vials half way or less. Although sample amounts can vary depending on the analysis, do not fill vials more than the maximum limits shown in **Figure 9**. Filling the vial correctly ensures that the sampling probe will not contact the matrix during sampling. If you need more sample, use a larger vial or optimize the method to improve results. See **"Method Development"** on page 75 for more information.

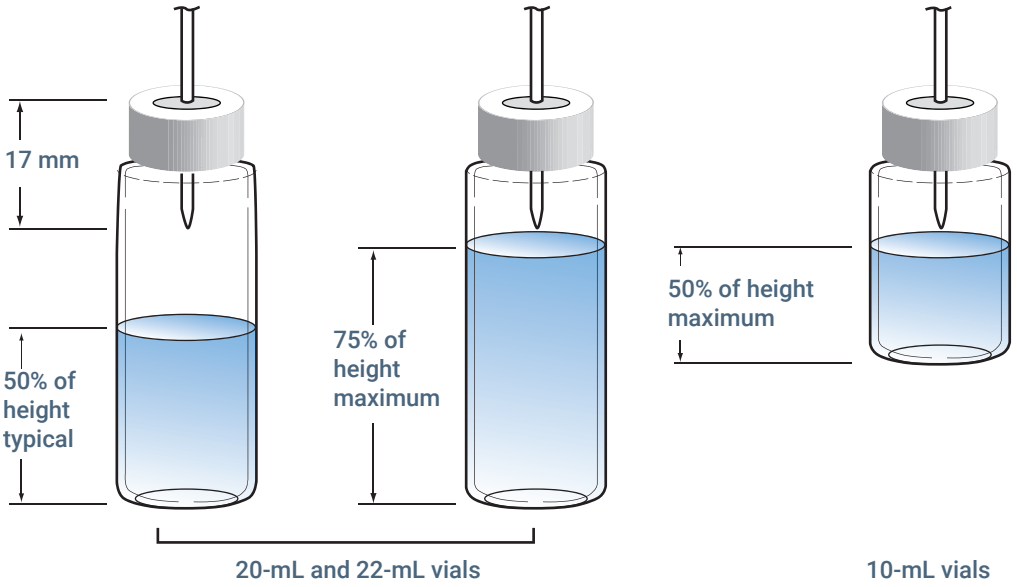


Figure 9. Vial fill limits

Cap a Sample Vial

The vial must be sealed properly to ensure that the headspace gases do not escape prematurely. For crimp top vials, use a crimper designed for headspace vials with 20-mm caps to seal the vials. Screw caps and screw top vials are also available. See **"Consumables for Headspace Analysis"** on page 22.

When capping vials using a crimper:

1. Begin by making a few empty practice vials until the crimps appear acceptable. See **"Cap a sample vial using an electronic crimper"** or **"Cap a sample vial using a manual crimper"**.
2. Prepare five (5) test vials that contain the sample to be analyzed.
3. Use the HS built-in **User Vial Leak Test** to check if the vials are well sealed, and to receive a suggested leak rate threshold for the method. (If you run the test with empty vials, the test cannot suggest a useful leak rate threshold but does evaluate whether the caps are sealed.) See **"Verify proper crimping using the User Vial Leak Test"**.

Cap a sample vial using an electronic crimper

Electronic crimpers provide several advantages over manual crimpers:

- Easy to set and maintain a crimp setting (the crimp setting is usually digital).
- Consistent crimps, independent of operator or hand strength.
- Easily crimp steel vial caps.

To use an electronic crimper, refer to its instructions.

1. Before beginning, clean the inside surfaces of the crimper jaws.
2. If using separate septa and caps, place a septum in a vial cap with the PTFE side facing the vial. Take care not to contaminate the septum.
3. Place the cap upside down on a table.
4. Place the sample in the vial. (Most vials should not be more than 50% full, but some vials can reach 75% full. See **"Filling Sample Vials"**.)
5. Place the septum and cap assembly over the vial opening.
6. Cap the vial as described in the electronic crimper's instructions.
7. Check each vial for proper crimping. See **"Vial crimping visual checks"**.

Cap a sample vial using a manual crimper

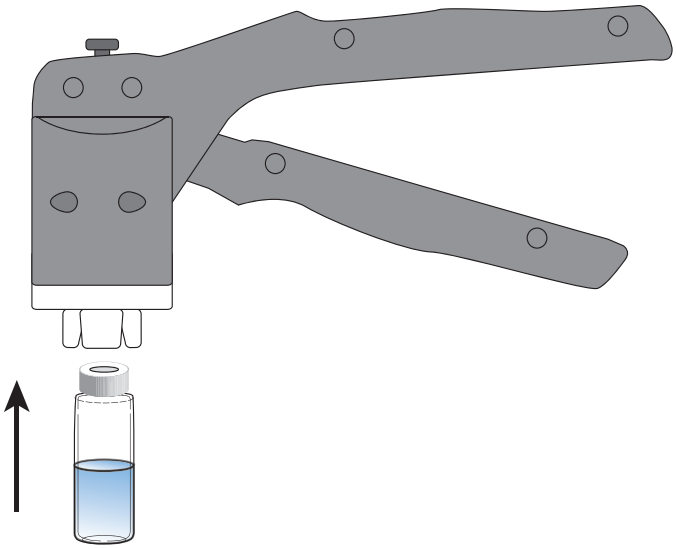
1. Before beginning, clean the inside surfaces of the crimper jaws.
2. If using separate septa and caps, place a septum in a vial cap with the PTFE side facing the vial. Take care not to contaminate the septum.
3. Place the cap upside down on a table.

4 Place the sample in the vial. (Most vials should not be more than 50% full, but some vials can reach 75% full. See **"Filling Sample Vials"**.)

5 Place the septum and cap assembly over the vial opening.

6 Lift the vial into the crimper.

7 With slow and steady pressure, squeeze the crimper handles to seal the vial. (Squeeze the handle until it reaches the adjustment screw.)



8 Check each vial for proper crimping. See **"Vial crimping visual checks"**.

Vial crimping visual checks

Check each vial for proper crimping.

Figure 10 shows proper and improper vial caps.

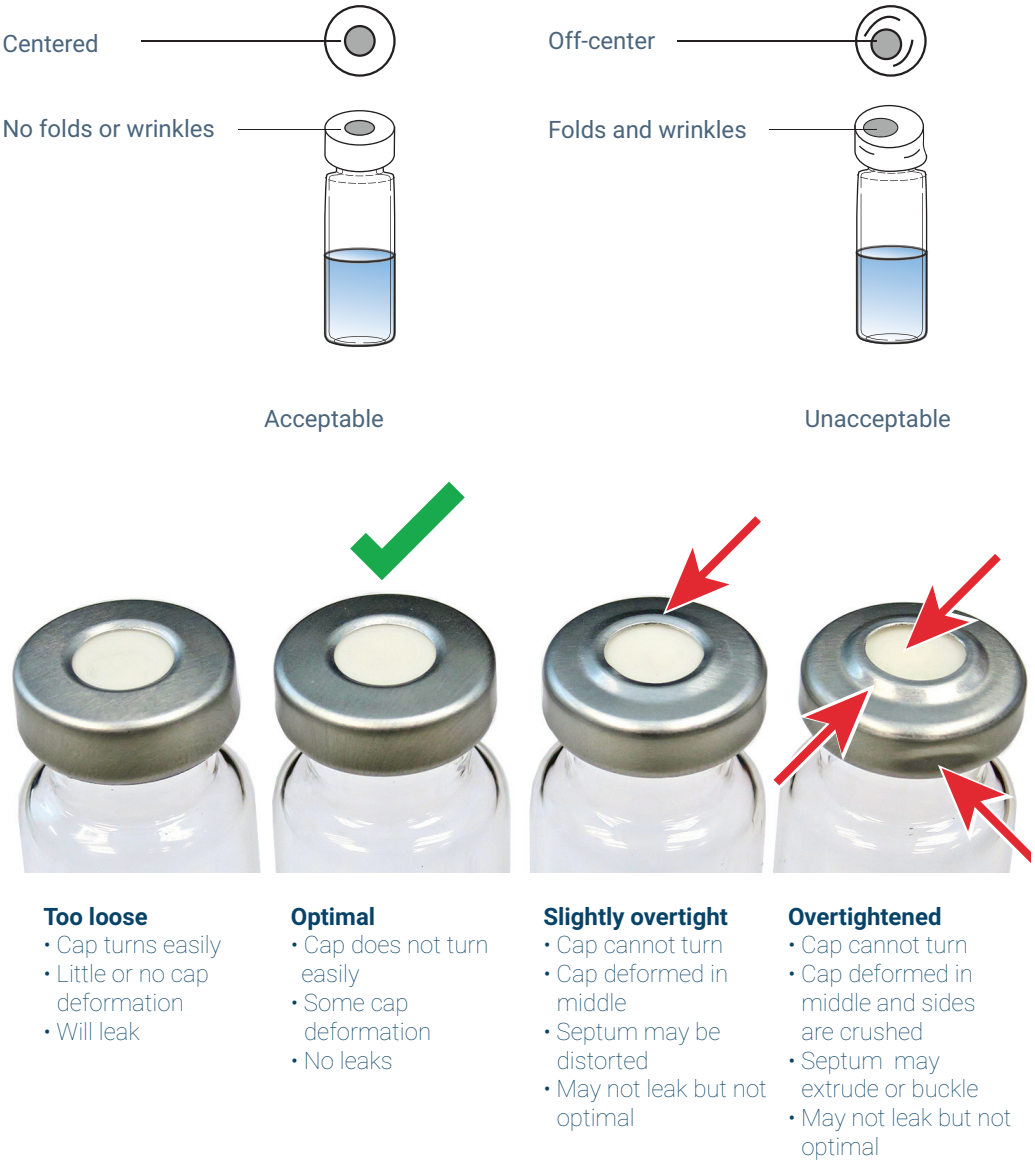


Figure 10. Acceptable and unacceptable vial caps

- Be sure there are no folds or wrinkles on the part of the cap that wraps under the neck of the vial. To remove folds or wrinkles, turn the vial about 10° and crimp it again. Adjust the crimper for a looser crimp by turning the adjusting screw clockwise.

- The cap should be finger-tight. If the cap is loose, adjust the crimper for a tighter crimp by turning the adjusting screw counterclockwise. Crimp the cap again. If the cap is too tight, the septum will distort and the vial may leak.
- Be sure that each cap has a flat septum centered over the top of the vial.
  - If the septum is not flat, remove the cap, turn the crimper adjusting screw clockwise, and try again.
  - If the cap is not centered, remove the cap and make sure the new cap is flat on the top of the vial before you squeeze the crimper.

Note that overcrimping puts additional stress on both the cap and the vial.

Verify proper crimping using the User Vial Leak Test

The best way to determine if the crimp tool is adjusted properly, and that the vials are properly capped, is to use the instrument's built-in test.

1. First, create an empty, practice capped vial as described in **"Cap a sample vial using an electronic crimper"** or **"Cap a sample vial using a manual crimper"**. Inspect it to be sure it looks acceptable. The vial should look like the optimal vial in **Figure 10**. If not, adjust the crimper and create more empty practice vials it until you have a vial that looks optimal.
2. On the GC touchscreen or in the browser interface, go to **Diagnostics > Diagnostic Tests > Headspace > User Vial Leak Test**.
3. Start the test.
4. Follow the prompts to prepare sample vials and run the test. (You will make 5 vials using the sample you plan to analyze.) If the vials pass, then record the setting used to cap the vials, and use this setting for making future sample vials. If the vials fail the leak test, then adjust the crimper and repeat the test with new vials.

   Note that when using test vials that contain sample, the **User Vial Leak Test** will also suggest leak rate threshold for the method. If desired, edit the method to use this suggested leak rate threshold.

If you change crimping tools or experience leaks with a new batch of vials, septa, or caps, re-run this test.

Park or Unpark the Tray

Parking the tray moves the tray gantry to a safe position. When parked, you can load vials into the racks, or install and remove racks from the HS.

Press the park button to park the tray. The park button lights to indicate that the tray is parked.

Press the park button again to unpark the tray and ready it for use.

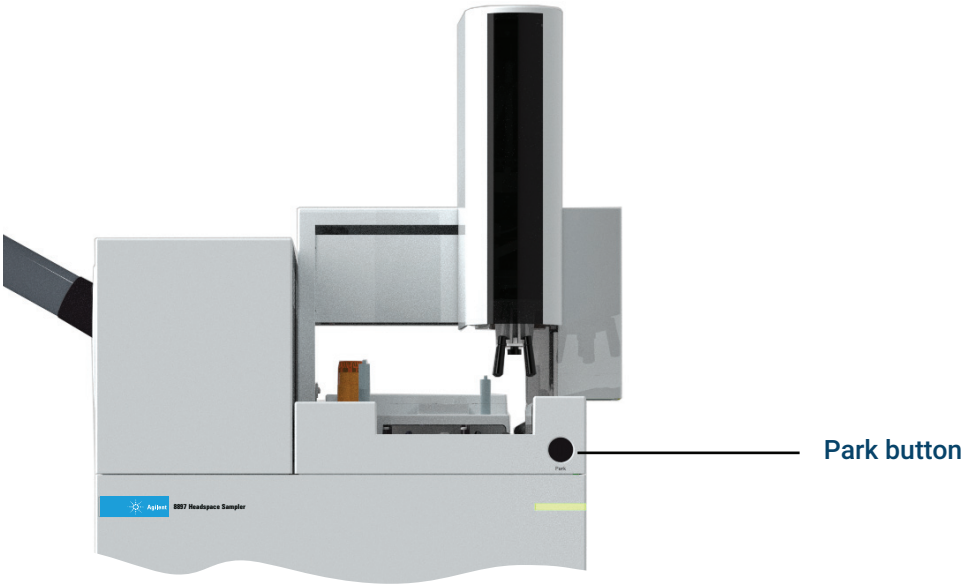


Figure 11. Park button location

You cannot start a sequence if the tray is parked.

Parking the tray during a sequence pauses the sequence. In-process vials continue running normally but vials are unable to enter or leave the oven until the tray is unparked.

Install a Vial Rack

1 Press the tray park button to “park” the tray (move the gantry to a rest position for easy access to the vial rack area). See **Figure 10**.

CAUTION

Avoid excessive motion when handling racks of vials. If the sample coats the septum or coats the vial more than typical, this may change results.

2 While holding up the front end of the rack, slide the rack back and under the mounting clip on the HS top. Then, lower the front of the rack in place.

When installed correctly, a white LED on the front of the tray rack lights.

3 Press the tray park button to prepare the tray for use.

Load a Sample into the Tray

1 Press the park button to “park” the tray (move the gantry to a rest position for easy access to the vial racks).

2 Place the capped sample vials into the tray as desired. See **Figure 12**.

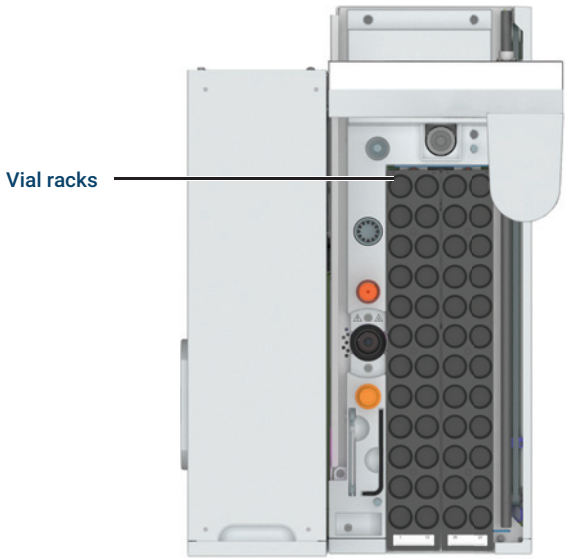


Figure 12. Tray vial positions (48-vial tray shown, 120-vial tray is similar)

3 Press the park button to prepare the tray for use.

5 HS Method Parameters

This chapter describes the method settings available for the HS. Make all method settings using the GC touch screen, browser interface, or in the data system. To learn about HS method development, see **"Method Development"** on page 75.

HS Method Parameters

The 8697 HS adds its method settings and parameters into the method for the GC. Access them like any other GC method setting, using the GC touchscreen, browser interface, or data system.

The HS adds:

- **Temperatures** for the headspace oven, sample loop, and transfer line, plus expected tray temperature (when tray cooling plate is present)
- **Times** for equilibration and injection, plus the GC cycle time (used for sample overlap and throughput calculations)
- **Vial** settings for vial size, filling, shaking, and venting after the injection

Most HS method parameters are accessed through the **Methods** tab on the GC touchscreen or in the browser interface. A few settings are located in different places, however, between the touchscreen and the browser interface. Settings for gas types, the transfer line dimensions, standby vial flow, readiness, and barcode symbologies are found under **Settings** (⚙) **> Configuration > Headspace** for the touchscreen, but are found in **Method > Configuration > Headspace** for the browser interface.

See also **"Settings > Configuration > Headspace"** on page 60. Note that while you set the barcode type in the method or as a configuration setting, the decisions on whether to use barcodes and how to handle barcode problems are made only through a data system. The browser interface does not support barcodes in sequences.

Local user interface

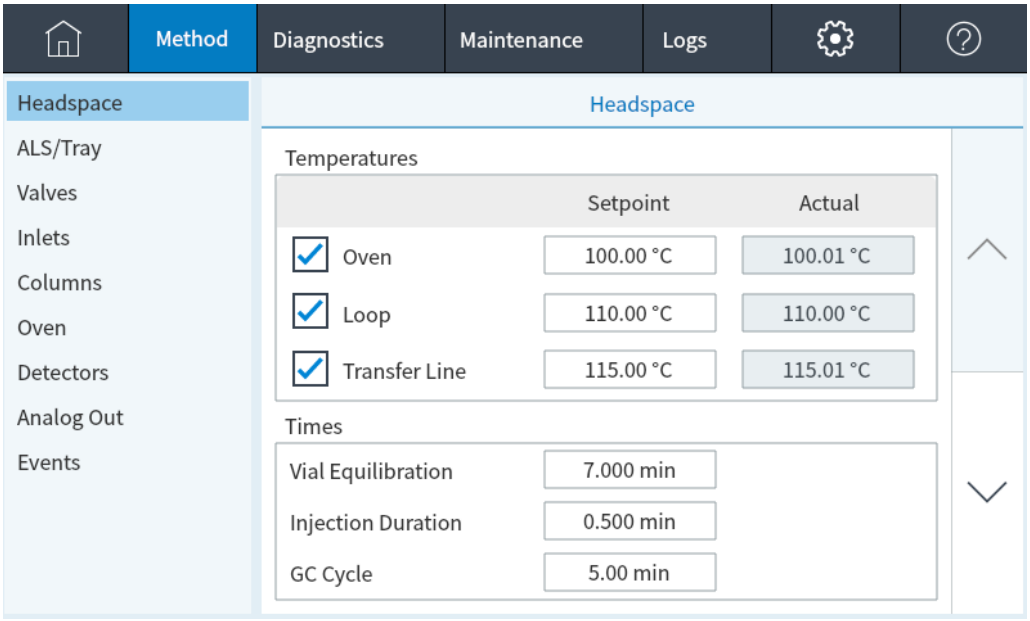


Figure 13. Headspace method parameters shown in the GC local user interface

Settings for transfer line type, sample loop volume, gas type, and similar infrequently changed settings can be found on the touchscreen at **Settings** (⚙) **> Configuration > Headspace**.

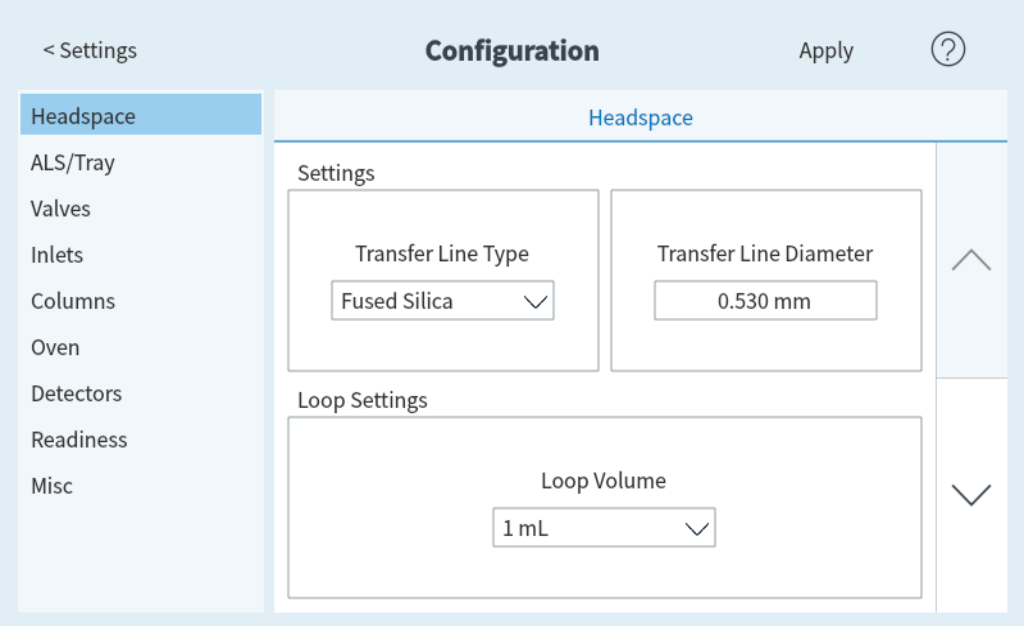


Figure 14. Headspace parameters shown in the GC local user interface (8890 GC)

Browser interface

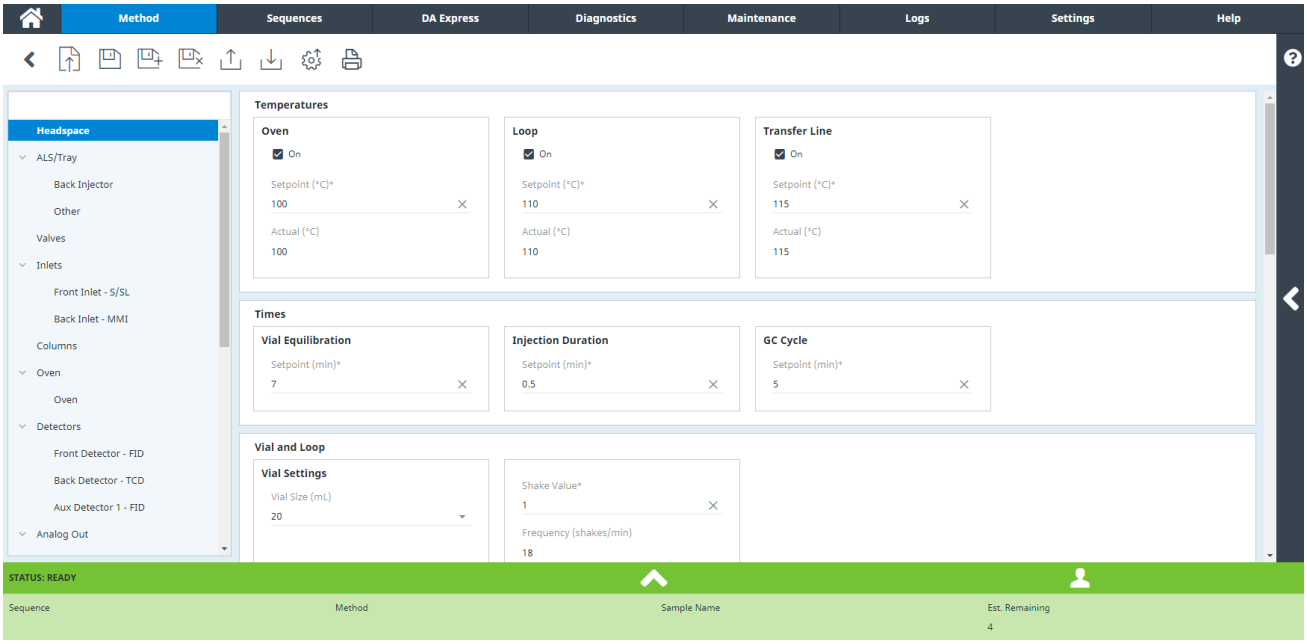


Figure 15. Headspace method parameters shown in the browser interface (8890 GC)

When using the browser interface, note that the method also includes the settings for headspace configuration, such as vial pressurization gas type.

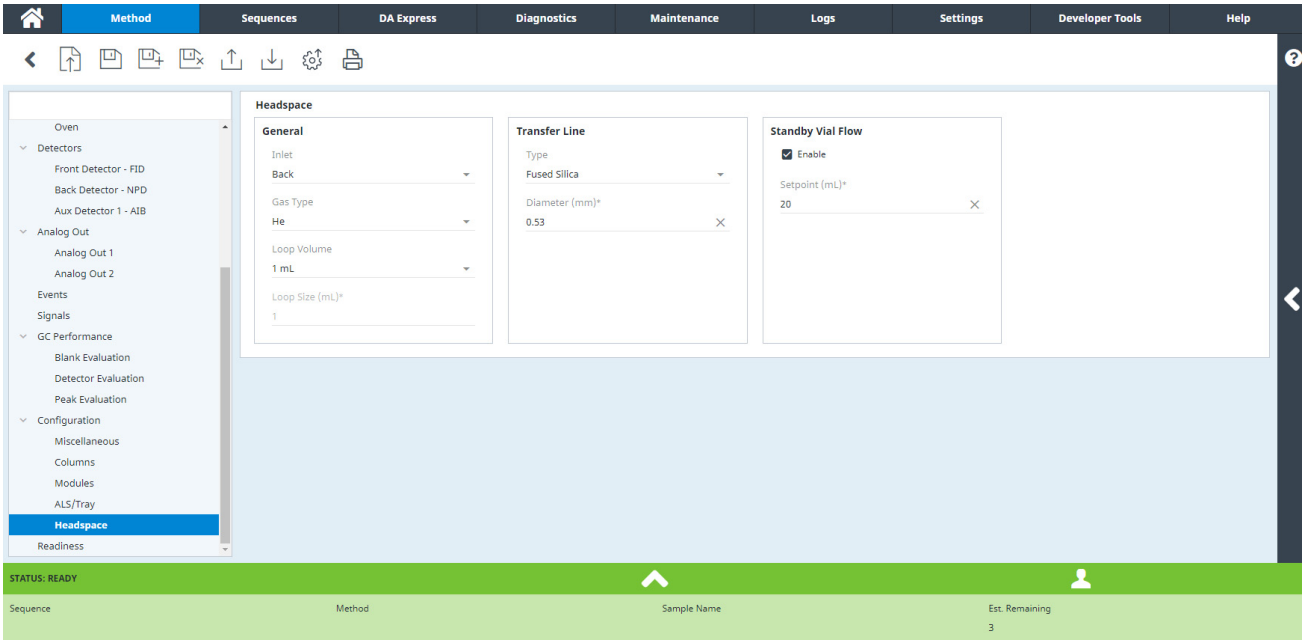


Figure 16. Headspace method configuration parameters shown in the browser interface (8890 GC)

Method Parameter Summary

This section lists method parameters, along with a brief description of each one. For detailed descriptions of the fill modes, see **"Method Development"** on page 75.

Table 6 Common method parameters

Path	Parameter	Description
Method		
Temperatures	Oven	Oven temperature for vial equilibration.
	Loop	Temperature of the sample loop and valve.
	Transfer Line	Temperature of the transfer line.
	Cooling Plate	The expected temperature of the tray, +/- 5°C. The GC will become Ready as long as the tray temperature is Expected Value +/- 5°C. (The HS monitors but does not control the tray temperature.)
Times	Vial Equilibration	Time for the vial to equilibrate in the oven before puncturing.
	Injection Duration	Amount of time to sweep the sample loop vapors into the GC inlet.
	GC Cycle	Time for the GC to complete its run, including the time to cool down and become ready for the next run. See **"Determine the GC Cycle Time"** on page 45.
Vial and Loop	Vial Size (mL)	Select the sample vial size for all vials using this method.
	Shake Value	Set the level of shaking for the sample during equilibration in the oven. Higher values provide more vigorous shaking. The browser interface will also list the frequency and acceleration associated with the selected shaking level.
Vial Fill Mode	Vial Fill Mode	Select how to pressurize the vial. See also **"Pressurizing the vial"** on page 89.
Pressure	Pressure Equilibration Time	Time to allow for the pressure in the vial to stabilize after initial vial pressurization.
	Fill Pressure	Target sample vial final pressure.
Flow to Pressure	Pressure Equilibration Time	Time to allow for the pressure in the vial to stabilize after initial vial pressurization.
	Fill Pressure	Target sample vial final pressure.
	Fill Flow	Flow rate used to pressurize the vial. Default: 50 mL/min.
Constant Volume	Pressure Equilibration Time	Time to allow for the pressure in the vial to stabilize after initial vial pressurization.
	Fill volume, mL	Specific volume of gas with which to pressurize the vial.
Loop Fill Mode		
	Loop Ramp Rate	How quickly to fill the sample loop.
	Final Loop Pressure	Final target pressure for the filled sample loop.
	Loop Equilibration	Time set for the sample loop to stabilize after pressurization.

Table 6 Common method parameters (continued)

Path	Parameter	Description
Extraction Mode	Extraction mode	Set the type of extraction for the method, Single, Multiple, or Concentrated. See also **"Extraction mode"** on page 92.
	Number of extractions	**Concentrated Extractions** Mode only: Enter the number of extractions to concentrate before starting a GC run.
Venting and Purging		
	Vent vial pressure after the last extraction	After the last extraction, and while the sample transfers to the GC, vent residual vial pressure to atmosphere.
	Vent vial pressure between extractions	Vent vial between concentrating extractions. (Multiple or Concentrated extractions only.)
	Purge Flow Mode	
	Purge Flow	Purge sample probe and loop with vial pressurization gas after removing the vial from the probe.
	Purge Time	Length of time to purge the sample probe and loop.
Miscellaneous		
Dynamic Leak Checking	Leak Test Mode	Turn On to check the sample vial for leaks after the vial pressurization. The time spent on the dynamic leak test is equal to the Pressure Equilibration Time + .02 minutes.
	Acceptable Leak Rate	The leak rate considered acceptable for the application. Default is 0.5 mL/min. Use the **User Vial Leak Test** to generate a leak rate threshold for your specific method and sample. See **"Verify proper crimping using the User Vial Leak Test"** on page 34.
Sequence Actions		Set how the HS should handle unexpected sequence issues, such as a missing vial or vial size mismatch.
	Vial Missing	The HS could not find the sample vial in the expected location.
	Wrong Vial Size	The HS determined that the vial being handled by the tray is not the size specified in the method. This could indicate the wrong sample is being processed, or that the wrong method was specified in the sequence.
	Leak Detected	The sample vial failed the dynamic leak check.
	System Not Ready	The HS has processed the sample, made the extraction, and is ready to transfer the sample to the GC inlet, but the GC is not ready to start a run.
Method development		Access parameters to use when developing methods See **"Using parameter increment"** on page 87.
Readiness		HS cooling plate temperature can be considered separately from general HS readiness when the GC checks readiness before starting a run. For normal use with a headspace sampler (HS), require the HS to be ready. Only ignore HS readiness when performing ALS or manual injections. (Because the GC checks HS readiness only at the time of injection, this HS readiness check is unrelated to when the HS places samples into its oven. The headspace sampler will place samples into its oven only if its oven temperature is correct, regardless of the GC's readiness settings. However, if you ignore HS readiness, the HS sample loop and transfer line temperatures might not be ready when the GC starts the run.)

Method > Configuration > Headspace (Browser Interface). See **"Settings > Configuration > Headspace"** on page 60.

Determine the GC Cycle Time

The **GC cycle time** is the time needed for the GC to perform the run, then return to a state ready for the next injection. This includes method runtime, post-run time, cooldown time, and time associated with external components. This value can be estimated but not precisely calculated, therefore it must be measured for a given method and laboratory environment.

The HS relies on a valid **GC cycle time** value to calculate throughput and timing. An accurate **GC cycle time** is crucial for reliable operation and optimal throughput.

If the **GC cycle time** is too long, this can cause:

- Lowered throughput. Vials wait longer than needed before processing.

If the **GC cycle time** is too short, this can cause:

- Sequence faults. Vials may be processed too early and may sit too long while waiting for the GC to become Ready.

It is better to enter a longer time than needed than to enter too short a time and possibly reduce sample quality.

Determine the GC cycle time

To determine the **GC cycle time**:

1. Perform a sequence of five runs that use the HS method and empty vials (capped and sealed but containing nothing). At first, estimate the GC cycle time as the GC oven program time, plus any other known post-run time, plus 10 minutes. This value should be too long.
2. Set the sequence action for System Not Ready to **Skip** or to **Abort**.
3. Run the sequence.
4. After the sequence completes, examine the data system logs. Look in the Activity Log (for OpenLab CDS) or in the Sequence Log (for OpenLab CDS ChemStation Edition) or in the Logbook (for MassHunter) to find the calculated cycle time. There will be 4 cycle times reported that were calculated by the instrument. If using the browser interface, examine the sequence log.
5. A good **GC cycle time** is the average of the cycle times, plus 0.2 to 0.5 minutes.

You can also *estimate* the **GC cycle time** without making a run. By adding the GC oven program duration and the duration of any post-run programs, you can get close to the true cycle time. However, temperature programming and cryogenic operation can make estimation more difficult. Add extra time to account for zone cool down (for example, oven or inlet cool down).

When using an MS, also include any extra time required for any other factors that might impact readiness.

Also consider time for data processing. While in most cases data processing is not a problem, a very busy data system may need extra time between samples.

Validate the GC cycle time

Rerun the sequence of three or four blank vials. There should now be no added wait time between consecutive vials. The HS should be able to start an injection when it is ready, without waiting for the GC to become ready.

Cooling Plate Operation and Specifications

This section describes the features and specifications for the optional cooling plate accessory. This accessory allows for an external water bath to cool the headspace sample vials.

Temperature

All vial positions in the vial racks can be cooled to 4 °C or heated to 80 °C.

The center of each vial location temperature can vary within +1 to -3 °C of the cooling plate sensor reading.

Cooling source

Depending on your lab conditions, you may need to set your cooling source to a lower temperature value than the desired temperature setpoint, as coolant temperature losses can occur between the cooling source and cooling plate.

Coolant

Use only distilled water, ethylene glycol, or propylene glycol as coolant.

Water bath and pump specifications

The water bath and pump system used to control the sample vial temperatures must meet the following specifications:

- The components must meet national standards for safety requirements, be suitable for unattended operation, be suitable for continuous operation, and be controllable for high-temperature protection.
- The recommended coolant temperature range is 4 to 80 °C.
- If you use a built-in pump, it must be suitable for external circulation of liquid and for connection of 1/4-in od (6.35 mm) tubing or larger.
- If you use a pressure pump, it must maintain a pressure from 1.5 to 2.5 psi.
- If you use a suction pump, the pump vacuum cannot exceed –4 psi.
- Typical recirculator cooling power capacity varies from 1000 to 2000 watts.

Condensate and environmental conditions

To avoid excess condensate, keep the ambient humidity level below 65% and the ambient temperature below 23 °C. If either value increases above its limit, excess condensate will form and cause drainage overflow.

Be sure your cooling plate operating temperature remains above 4 °C. Temperatures at 4 °C and lower may cause condensate to freeze and drainage problems may occur.

If operating in a non-air conditioned environment, shut off the cooling plate source or raise its temperature to a value above the expected dew point temperature when not in use.

Occasional excess condensate will not cause permanent damage to your instrument. If the condensate management system overflows, unplug the power source to the headspace as soon as possible and dry the affected areas before use.

6 HS Sequences

Sequences of samples are created and run using the GC's browser interface or an Agilent data system. This chapter describes the special considerations for headspace sequences when using those systems to run samples, and it also describes the sequence-related features provided by the 8697 HS that help optimize throughput.

For information about using the browser interface or data system to create sequences and run samples, please refer to their online help systems.

What Is a HS Sequence?

A sequence for the 8697 Headspace Sampler is an ordered series of sample vials to prepare and inject, including the method needed to prepare each vial.

- A sequence can skip vial locations.
- A sequence can run a vial more than once.
- A sequence does not require any particular vial order. Running vials 1, 23, 5, 2, 3, and 40 is valid.

Sequences, Extraction Modes, and Vial Punctures

In the sequence you can specify the same vial in as many entry lines as desired. How the HS sampler processes the vial depends on the method Extraction mode and the sequence:

- **Extraction Mode** is **Single**.

  Use Single Extraction mode to force the HS to perform one vial puncture, one extraction, and one run per vial. If the same sample vial appears in more than one consecutive line in the sequence, or if the number of injections per vial is > 1, this mode will cause the HS to completely reprocess the vial for each sequence entry or injection.

- **Extraction Mode** is **Multiple**.

  Use Multiple Extractions mode to perform one equilibration cycle, one vial puncture, and one or more extractions per sample vial, where each extraction starts a new run. The vial is punctured only once, regardless of the number of extractions and runs. For each consecutive line in the sequence that uses the same vial, and for the number of injections per vial specified in the sequence, the HS performs an extraction and starts a run. After the last consecutive sequence line for this vial, the vial is returned to the tray. If the same vial appears later in the sequence, it will be equilibrated and punctured again.

- **Extraction mode** is **Concentrated**.

  Use Concentrated Extractions mode to perform one equilibration cycle, one vial puncture, and multiple extractions (and possibly injections) per vial. Typically this mode requires a sample concentrating trap of some kind. (The trap could be an optional external device or an inlet such as the Agilent Multimode inlet.) The HS punctures the vial and performs the number of extractions specified. Each extraction transfers to the GC inlet (or trap), where sample accumulates. After the last extraction, the accumulated sample is injected and the HS starts the GC run.

  If the sequence specifies more than one injection per vial, the vial remains on the sample probe. When the GC run ends, the HS performs the required extractions, then starts the next run. After the last run starts, the vial is returned to the tray.

  If the same vial appears later in the sequence (but not as the next vial), it will be equilibrated and punctured again.

See also **“Sequences and Throughput”**.

Sequences and Throughput

The HS optimizes throughput by checking the methods for the vials specified in the current sequence. When consecutive vials share the same method, the HS will examine the timing parameters for the samples, then calculate the best times to place each vial into the oven. This approach maximizes the number of vials equilibrating at a time.

Vials using different methods will not be handled until the preceding samples leave the oven.

For more information, see **"Optimizing Throughput"** on page 93.

Priority Samples

A *priority sample* is a vial that you want to run as soon as possible, before some of the other vials in the currently-running sequence.

The browser interface and Agilent data system each provide a way to pause and then edit a running sequence to insert a new sample into it. Place the new sample into any unused tray location. Then, pause and edit the sequence to include the new vial. Refer to the browser interface and data system helps for instructions on editing a running sequence.

Note any samples that have begun processing cannot be edited. The HS will continue to process all vials that it already started before it will start processing a new vial. If the new sample uses the same method, it may be placed into the oven concurrently with the other samples are being processed. If it uses different method conditions it might not start until all prior samples have been moved from the oven.

Method Sequence Actions

When the HS encounters certain problems during a sequence, it has the ability to skip a vial, continue anyway, pause the sequence, abort everything, or wait until the system becomes ready. The settings to control HS behaviors during sequence execution are called *sequence actions*. These sequence actions are part of the method, and therefore can change from sample to sample during sequence execution. Use sequence actions to specify what the HS should do when it encounters issues such as a vial size mismatch, missing vial, and similar issues. Sequence Actions provide the flexibility to handle relatively minor issues with the level of attention appropriate for your workflow. You can completely halt sequence processing for some issues, while permitting the sequence to continue for other issues. The GC always logs the issue and the action taken.

Types of sequence issues handled

Sequence Actions provides logical sequence control for the issues listed below. The possible actions are described in **"Available actions"**.

Vial Missing: Control the HS behavior whenever it cannot find a sample vial at the expected location in the tray.

Wrong Vial Size: Control the HS behavior when the HS finds a sample vial, but the size of the vial does not match the size of the vial as defined in the method. A size mismatch can change the analysis results or indicate a misplaced vial, for example. To determine vial size, the HS measures the vial height when the vial is in the gripper. (This means that the HS cannot distinguish between 20 mL and 22 mL vials.)

Leak Detected: Control the HS behavior if the sample vial fails the dynamic leak test. (Only meaningful when dynamic leak checking is enabled.)

System Not Ready: Control the HS behavior when the HS is ready to begin filling the sample loop but the GC is not ready to start a run. When the HS becomes Ready, it checks if the GC is Ready. If the GC is ready, the HS begins filling the sample loop for the injection cycle. If the GC is not ready, the HS follows the specified action. A GC not ready, could indicate a low GC cycle time parameter in the method, normal variances in GC timing, or a GC problem. Note that some data systems may not collect data if the GC is not Ready before the run starts.

Available actions

The actions available for each issue depend on the nature of the sequence issue. (For example, you cannot continue to process a missing vial, but you can skip the vial or abort the sequence.)

- **Continue**: Continue processing the current sample vial and the sequence.
- **Skip**: Skip the current sample vial, then continue processing with the next sample vial in the sequence. The current sample vial is immediately returned to the tray, if appropriate. The system skips all injections for that vial.

- **Pause**: Pause the sequence. Any vials in the oven will continue to be processed, including the current vial, if applicable. No other vials will be moved into the vial oven.

  To recover from a pause: Follow the instructions on the GC touchscreen (or in the Browser Interface).
- **Abort**: Abort the sequence. The HS stops all vial processing, for the current sample vial and all other sample vials. The HS returns all sample vials to the tray, beginning with the sample vial which had the problem. To recover, check the logs to determine which sample vial had the problem. Resolve the problem, then create a new sequence and restart.
- **Wait for Ready**: The HS waits until the GC becomes ready. This setting can increase vial equilibration times for vials in the oven. The HS reports the actual equilibration times in its logs. Note that once the HS begins to fill the sample loop, the HS will start an injection whether or not the GC is ready. Also, if something prevents the GC from becoming ready, the HS waits.

NOTE

Abort stops only the HS. The GC and data system may complete processing for any previously-injected sample.

Note that sequence actions do not override other potential problems, such as a hardware fault, that can interrupt a sequence.

When using an MS

You must include any extra time required for MS solvent delay and other factors in the **GC Cycle time** parameter.

Browser Interface and Data System Sequence Actions

The browser interface and Agilent data systems can provide additional features that can be used to handle unexpected events. These features appear as part of the sequence settings, and vary depending on the data system. For example, the browser interface and many data system provide a setting for handling missing vials in the sequence. In the event of a conflict between the sequence setting and a setting in the HS method, the HS will use the value set in the *HS method* for the specific issues listed in **"Types of sequence issues handled"** on page 54.

The data systems may also provide ways to handle barcode reader errors. Refer to the data system's help for more information.

Stop, Abort, or Pause a Running Sequence

You can interact with a running sequence from either the GC touchscreen stop button or the computer that is running the sequence via the browser interface or a data system.

On the GC touchscreen, press stop (). The GC display prompts to stop the run, stop the sequence, or cancel (do nothing).

- **Stop the run**: Immediately end the current run and move on to the next run in the sequence. The remainder of the sequence finishes normally.
- **Stop the sequence**: Immediately end the current run and abort the sequence. All vials in the oven are returned to the tray through the cooling station and the system returns to an idle state.

The browser interface and a data system provide three options for interacting with a running sequence:

- **Pause sequence:** The HS finishes any samples that have already begun processing, but then waits for further instructions. No new vials will enter the oven. When resumed, the sequence finishes normally.

  Using pause allows the sequence to be edited. During editing, the list of samples that have not yet begun processing can be changed as needed to insert a new sample or to make any other changes. Upon resume, the HS begins processing at whatever is now the next sample in the sequence.
- **Stop the run**: Immediately end the current run and move on to the next run in the sequence. The remainder of the sequence finishes normally.
- **Stop the sequence**: Immediately end the current run and abort the sequence. All vials in the oven are returned to the tray through the cooling station and the system returns to an idle state.

Refer to the help for the GC browser interface and the data system for more details on their sequence features.

Vial Status

Use the GC touchscreen or browser interface status tray to show current status information for the a running sequence. The GC will display:

- Oven temperature
- Loop temperature
- Transfer line temperature
- Vial flow
- Vial pressure
- External carrier pressure
- Vial status. This includes real time monitoring of vial state: equilibrating, pressurizing, extracting, injecting, returning to tray.

Agilent data systems also provide vial status.

7 Settings

This section describes the settings and features available from the GC under Settings.

Headspace Settings

The HS settings available from the **Settings** (⚙) tab apply generally, regardless of the current method. If you make hardware changes, always check these settings and update as needed, for example, after changing the vial pressurization gas type, the transfer line, or the sample loop.

Settings > Configuration > Headspace

⚙ > Configuration > Headspace

The table below lists the HS configuration settings.

Setting	Description
Inlet	Select the inlet connected to the transfer line. (Setting available for GCs with more than one inlet.)
Gas Type	Vial pressurization gas type.
Loop Volume	Internal volume of the installed sample loop.
Transfer Line Type	Select the type of transfer line installed, fused silica or DB-ProSteel.
Transfer Line Diameter	Internal diameter of the transfer line (um).
Standby Vial Flow	Normally leave enabled. The standby **Vial Flow** purges the sample loop and sample probe between extractions and during idle time. If using the GC resource conservation features, this flow can be reduced to conserve vial pressurization gas. Default: 20 mL/min.
Clear Oven at Startup	When enabled, when first turned on the HS will check the vial oven for vials and return all vials found to the tray.
Enable barcode checksum	Available if a barcode reader is present. Certain barcodes can include a checksum value for use in validating whether the barcode is read correctly. Enable this setting when the barcode includes a checksum.
Symbology	Available if a barcode reader is present. Select **All** to let the barcode reader check all available symbologies, or select the specific symbology used on the vial labels. See the full list of supported symbologies below.

The barcode reader can read barcodes of the following types (symbologies):

- 3 of 9
- Code 128
- Matrix 2 of 5
- Standard 2 of 5
- Interleaved 2 of 5
- UPC A
- EAN/JAN 13

- EAN/JAN 8
- UPC E

Settings > Calibration > Headspace

⚙ > Calibration > Headspace

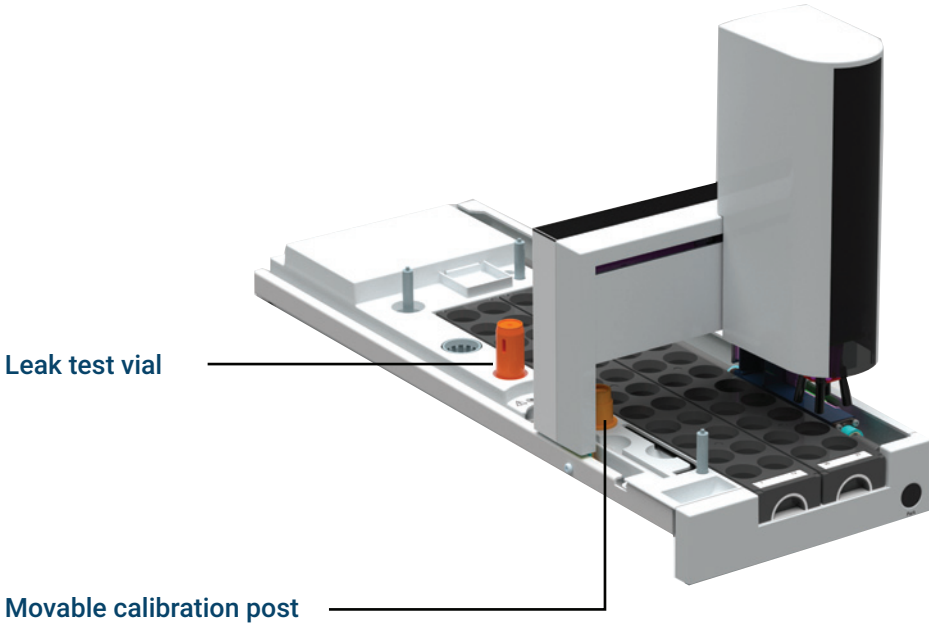
The HS provides a calibration routine for the tray to ensure optimal handling of vials, and a calibration for the gas flow and pressure sensors.

Calibrate the tray and grippers

The tray may require periodic calibration to maintain optimum performance. This calibration ensures the gripper and gantry motions continue to move samples smoothly, without dropped vials. Calibrate the tray after HS installation, after replacing the gripper pads, or when recommended by automated troubleshooting or EMF counters.

1 Before beginning, empty the vial oven and tray of any vials.

2 Verify that the movable calibration post and the leak text vial are located in their dedicated locations.



3 Go to ⚙ **(Settings) > Calibration > Headspace** and select **Start System and Tray Calibration** on the tray calibration settings page.

4 Select **Factory** as the type of calibration. Follow the prompts. A factory calibration calibrates the tray to the mainframe, and calibrates all vials locations on the tray.

Calibrate the grippers

The grippers will automatically be calibrated periodically by the HS. The gripper calibration requires the leak test vial and the movable calibration post.

Calibrate the vial pressurization EPC

The EPC gas control modules contain flow and/or pressure sensors that are calibrated at the factory. Sensitivity (slope of the curve) is quite stable, but zero offset requires periodic updating.

Change the calibration settings or manually calibrate the vial pressurization gas EPC sensors from the GC touchscreen or browser interface:

1 Select ⚙ **(Settings) > Calibration > Headspace** and scroll down to the EPC calibration settings.

2 Select **On** next to the desired sensor to zero it.

3 For the flow sensor: Verify that the gas is connected and flowing (turned on).

4 For the pressure sensor: Disconnect the gas supply line at the back of the HS. Turning it off is not adequate; the valve may leak a little bit.

5 Reconnect any gas line disconnected in the previous step and restore operating flows.

To reset an EPC sensor to its factory calibration, Go to ⚙ **(Settings) > Calibration > Headspace** and under the **EPC** section select **Reset** for that sensor.

Calibrate the aux pressure sensor

The EPC gas control modules contain flow and/or pressure sensors that are calibrated at the factory. Sensitivity (slope of the curve) is quite stable, but zero offset requires periodic updating.

Change the calibration settings or manually calibrate the aux pressure sensor from the GC touchscreen or browser interface:

1 Select ⚙ **(Settings) > Calibration > Headspace** and scroll down to the EPC calibration settings.

2 Select **On** next to the desired sensor to zero it.

3 For the aux pressure sensor: Disconnect the gas supply line at the back of the HS. Turning it off is not adequate; the valve may leak a little bit.

4 Reconnect any gas line disconnected in the previous step and restore operating flows.

To reset this EPC sensor to its factory calibration, Go to ⚙ **(Settings) > Calibration > Headspace** and under the **EPC** section select **Reset** for that sensor.

Leak Rate Calibration Procedure

Though extremely rare, the expansion of some solvents being heated to temperatures above their boiling point can create a dynamic pressure change that is difficult to accurately quantify on the time scale of the typical HS dynamic leak test. Rather than compromising sample throughput by elongating the pressure equilibration time method parameter, the preferred way to account for the solvent expansion is to calibrate the reported leak rate associated with a given set of conditions.

Use the **User Vial Leak Test** (see **"Verify proper crimping using the User Vial Leak Test"** on page 34) to automatically determine an appropriate leak rate threshold for a given method and sample.

A leak rate threshold can also be manually calculated. If a minimum of three vials have been analyzed and report a consistent dynamic leak test leak rate, you can perform the Leak Rate Calibration Procedure below.

1 Verify that your system is leak free.

   Go to **Diagnostics > Diagnostic Tests > Headspace** and select the **Restriction and Pressure Decay-test**. Run the test using the leak test vial (part number G4511-20180) and an Agilent advanced green septum (part number 5183-4759). Make sure that your instrument temperatures are the same as the analytical method setpoints.

   The procedure begins with the system leak test to ensure that no leaks are detected when the system is void of solvent.

2 Calibrate the leak rate.

   a If the Restriction and Pressure Decay test passes, use your desired analytical method to analyze six vials containing the solvent used during analytical runs.

   b Record the leak rate for each of the six vials, then calculate their average and standard deviation. Set the pass/fail leak rate entered into the HS method for the analysis in question at the average leak rate plus three times the standard deviation.

Table 7 displays an example where you should change the analytical method's method leak rate limit to 1.840 mL/min.

Table 7 Example of calculating the method leak rate limit

Vial	Leak rate (mL/min)
1	1.403
2	1.352
3	1.621
4	1.458
5	1.541
6	1.623
Average	1.500
Std dev	0.114
3 * Std dev	0.341
Avg + (3 * Std dev)	1.840

Settings > Service Mode > Headspace

⚙ > Service Mode > Headspace

The headspace service mode lists current, actual values for various configuration, thermal, pneumatic, electronic, and other settings and sensors.

It is also possible to perform a Factory Reset. Normally, do not perform a factory reset unless absolutely necessary. A factory reset erases all custom settings stored in the HS, from flow calibrations to the instrument serial number.

A factory reset will:.

- Clear the maintenance and event logs.
- Clear the firmware update history.
- Clear the current HS configuration and calibrations.
- Clear EMF tracking data and settings.
- Log the factory reset.
- Reboot the HS.

Settings > Scheduler: Resource Conservation

⚙ > Scheduler

The HS uses the GC's resource conservation features, and the GC features for Sleep and Wake methods are extended to include HS method parameters. Because the HS adds many new parameters to the method, some of these can be used to conserve gases and power. Most HS settings, however, are not relevant to sleep methods because they are only used while preparing samples. Consider the following HS parameters when setting a sleep method:

- **Standby Vial Flow**: Reduce if desired. Agilent does not recommend turning this flow off, since this flow protects the sample loop and sample probe from atmospheric contamination.
- Oven, sample loop, and vial oven temperatures can be reduced during periods of inactivity.

8 How the 8697 Headspace Sampler Works

This chapter provides more advanced theory behind the 8697 headspace sampler. This information is intended for use by method developers.

How the HS Processes a Sample Vial

Figure 17 shows the workflow for a vial processed by the HS.

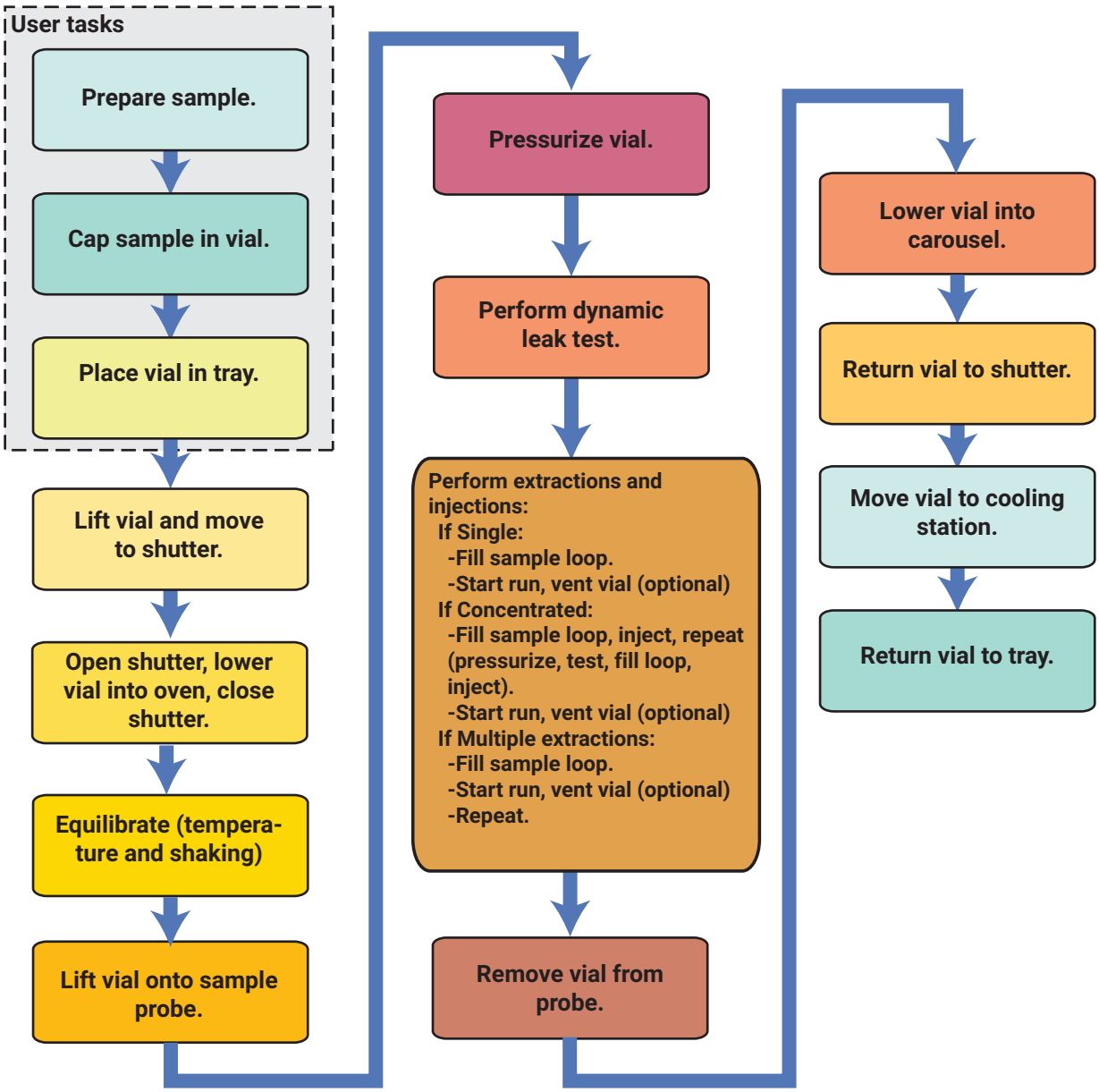


Figure 17. 8697 HS vial process flow

How the HS Equilibrates a Vial

The 8697 HS with tray has a vial oven that can equilibrate up to 12 vials at temperatures up to 300 °C. In addition, the oven can shake the vials at 9 different acceleration levels. As long as sequence vials share the same method, the HS determines when consecutive samples can be loaded into the oven to increase throughput, then automatically loads them. The HS optimizes for throughput regardless of extraction mode, loop fill mode, and so forth.

How the HS Pressurizes a Vial

The HS provides several techniques for pressurizing the sample vial. In addition to simply heating the vial, which may generate enough internal pressure on its own, the HS can provide additional gas to help with extraction. This gas comes from the **Vial Pressure** fitting on the HS back panel, and can be different from the carrier gas used to move the sample onto the column. While the default vial pressurization method is often sufficient, the alternative techniques may be useful in some applications. See **Figure 18** below.

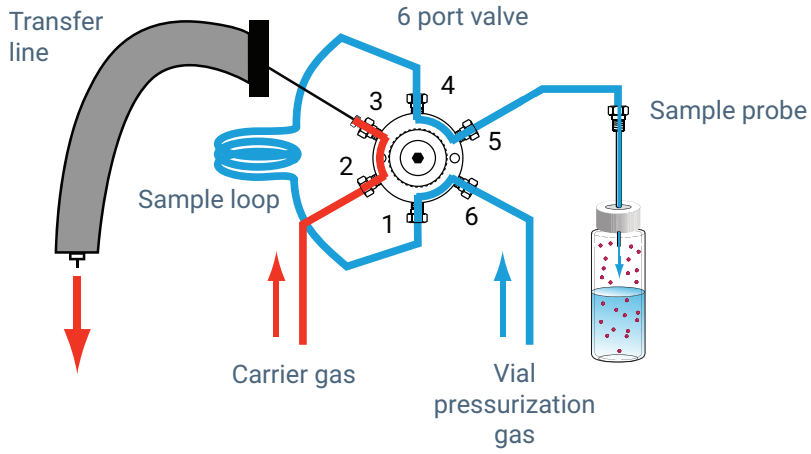


Figure 18. Pressurizing the vial

Flow to pressure

This is the default vial fill mode. In this mode, the HS maintains a specified flow rate of carrier gas into the vial until the pressure inside the vial reaches the fill pressure setpoint. The HS maintains this pressure for the hold time. At the end of the hold time, the sample loop fill begins.

Pressure

In this mode, the HS fills the vial as rapidly as possible to the target fill pressure setpoint, then maintains this pressure for the specified hold time. At the end of the hold time, the sample loop fill begins.

Constant Volume

In this mode, the HS pressurizes the sample vial with a specified volume of carrier gas, then maintains the resultant pressure for the specified hold time. This mode is useful if you need to calculate the exact molar amounts of sample and carrier gas in the vial or sample loop.

Dynamic leak check

By default, the HS performs a leak check after the vial pressurization. While on the probe, the HS can determine if the vial is leaking by checking for pressure decay in the vial. The HS logs the leak test results, and provides a sequence action to allow you to handle (for example, skip or abort) a leaking sample vial.

The time spent on dynamic leak test is equal to Pressure Equilibration Time + .02 minutes.

How the HS Fills the Sample Loop (Extracts a Sample)

After the vial is pressurized and has stabilized, the HS will perform the specified extractions. The six port valve switches, allowing the pressurized sample to vent through the sample loop. After the specified conditions are met, the loop is considered filled. See **Figure 19** below.

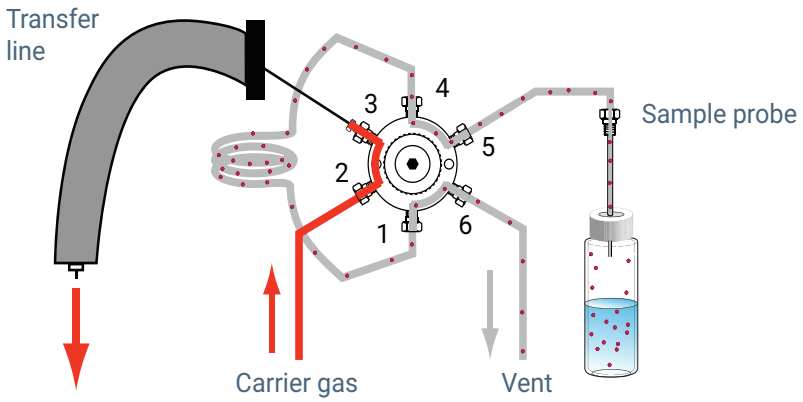


Figure 19. Filling the sample loop

The HS provides two modes for filling the sample loop, **Default** and **Custom**.

Default loop fill mode

In this case, the HS depressurizes the sample vial into the sample loop at a specified rate until the sample vial pressure drops a known amount. The HS calculates the final loop pressure and equilibration time based on current HS configuration and method data.

Custom loop fill mode

In this case, you can specify the loop fill rate, final loop pressure, and equilibration time.

Types of HS Extractions and Injections

The 8697 HS can extract and inject sample once or multiple times per vial. The HS provides a selection for extraction type as an advanced function. **Figure 20** shows the basic flow paths during an injection cycle, where the sample loop is flushed into the GC.

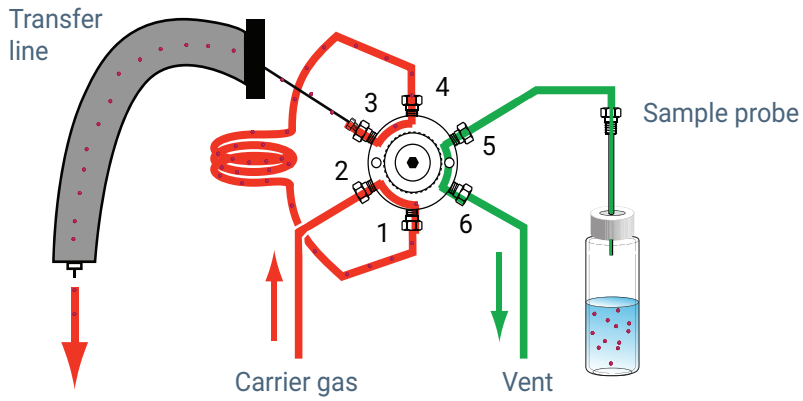


Figure 20. HS injection cycle

Note that the vial pressurization gas flow is always controlled by the HS. The carrier gas flow is always controlled by the GC inlet EPC module.

Refer to **Figure 21** for a diagram of the flow paths within the HS sampler.

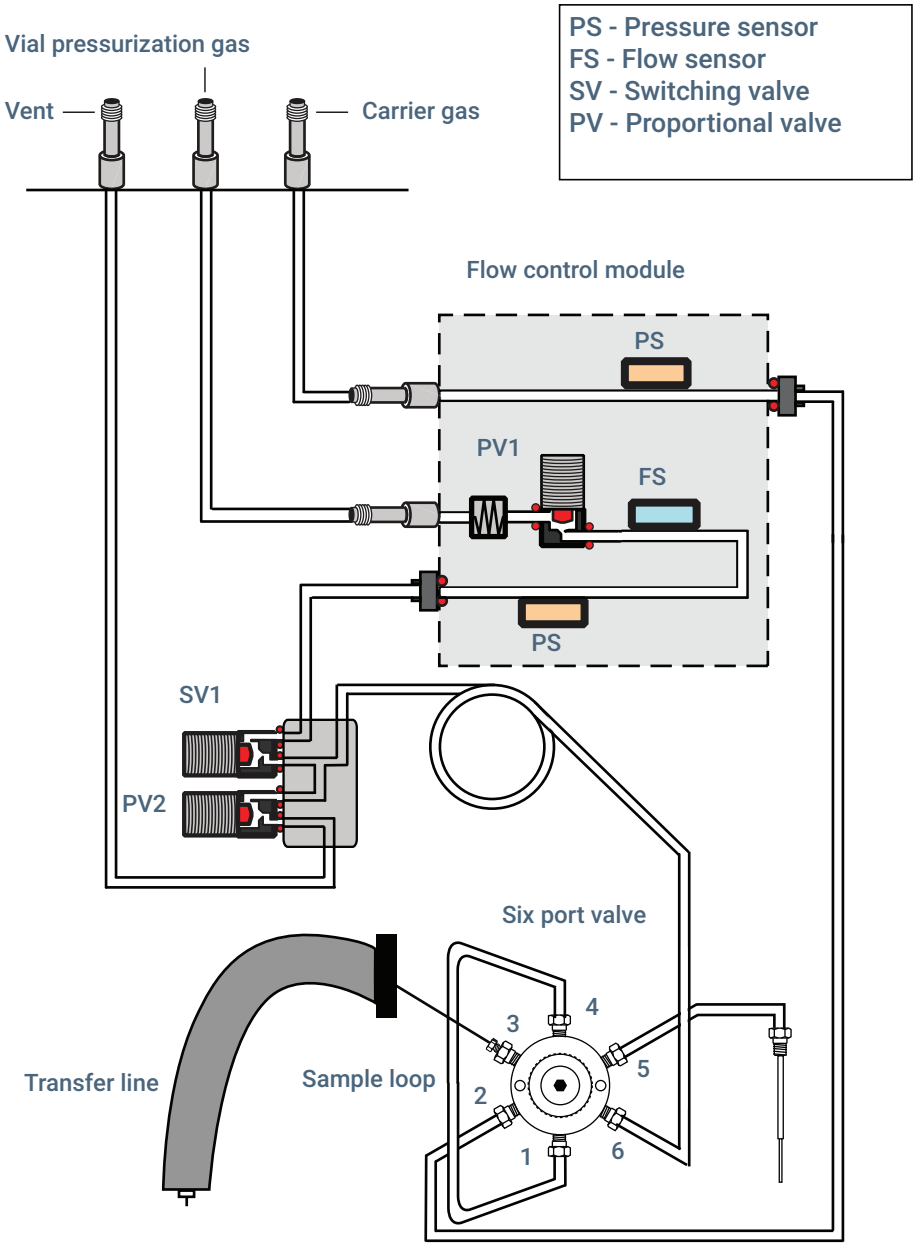


Figure 21. HS sampler flows

Standard extraction

In this mode, the HS performs one extraction and one injection per vial puncture. After the vial equilibrates, the HS checks system readiness. If the system is ready, or if the readiness sequence action is continue, the HS punctures the vial. The HS pressurizes the vial and extracts the sample from it according to the method parameters. See **Figure 18** and **Figure 19**. After any sample loop equilibration, the HS six port valve switches to the inject position, the HS injects the sample, and the HS sends a Start command to the GC. At the same time, the HS

vents residual pressure from the vial (optional). After the inject time elapses, the six port valve returns to its original position. The sample vial is removed from the probe and returned to the carousel and then tray.

Multiple headspace extractions

In this mode, the HS performs multiple extractions and injections using one vial puncture. See **Figure 19** and **Figure 20**. After the vial equilibrates, the HS checks system readiness. If the system is ready, or if the readiness sequence action is continue, the HS punctures the vial. The HS pressurizes the vial and extracts the sample from it according to the method parameters. The sample loop vent closes. The vial remains on the probe. After any sample loop equilibration, the HS six port valve switches to the inject position, the HS injects the sample, and the HS sends a Start command to the GC. At the same time, the HS vents residual pressure from the vial (optional). After the inject time elapses, the six port valve returns to its original position. The vial remains on the probe. When the **GC Cycle** time elapses, the HS again checks the readiness of the system. If the system is ready, or if the readiness sequence action is continue, the HS performs the next pressurization, extraction, injection, and start run. The process repeats until all extractions and injections have been performed.

After the final extraction and injection, the sample vial is removed from the probe and returned to the carousel and then tray.

Concentrated headspace extractions

Use this mode to concentrate sample in the GC. Typically this mode requires a sample concentrating trap of some kind. (The trap could be an optional external device or an inlet such as the Agilent Multimode inlet.) See **Figure 20** and **Figure 21**.

After the vial equilibrates, the HS checks system readiness. If the system is ready, or if the readiness sequence action is continue, the HS punctures the vial. The HS pressurizes the vial and extracts the sample from it according to the method parameters. The vial remains on the probe. After any sample loop equilibration, the HS six port valve switches to the inject position, and the HS injects the sample into the GC. The HS does not send a Start command to the GC. After the inject time elapses, the six port valve returns to its original position. The vial remains on the probe. The vial can be vented (while the injection occurs) or remain pressurized. The HS repeats the pressurization, extraction, injection, and optional vial venting for each of the extractions specified in the method. During the final concentrating injection, the HS sends the start signal to the GC. The HS vents the vial (optional), removes it from the probe, and returns it to the carousel and then tray.

Venting residual vial pressure

Regardless of the type of extraction performed, the HS can vent residual pressure from the used sample vial out of the **Vent** port on the HS back panel. This venting prevents a pressurized vial with potentially noxious contents from being left in the sample tray or in your lab. This venting occurs during the injection time for each current sequence entry. You can disable this feature.

When performing concentrated extractions, you have an additional parameter available: you can vent the vial between concentrating extractions as well as during the final injection.

How the HS Reduces Carryover

The 8697 HS provides two special features to reduce carryover.

- After each vial, the HS purges the sample loop and sample probe with a high flow of vial pressurization gas, as defined in the method. This is called the **Purge** flow, and you control both the flow rate and purge time.
- Between each sequence, the HS purges the sample loop and sample probe with a continuous, low flow of vial pressurization gas. This is called the **Standby** flow. You can control the flow rate.

9 Method Development

This chapter provides details and information about method parameters. This information is intended to help a method developer improve a method's performance using the features of the 8697 headspace sampler.

Overview

Figure 22 shows the typical workflow for developing a headspace sampler method.

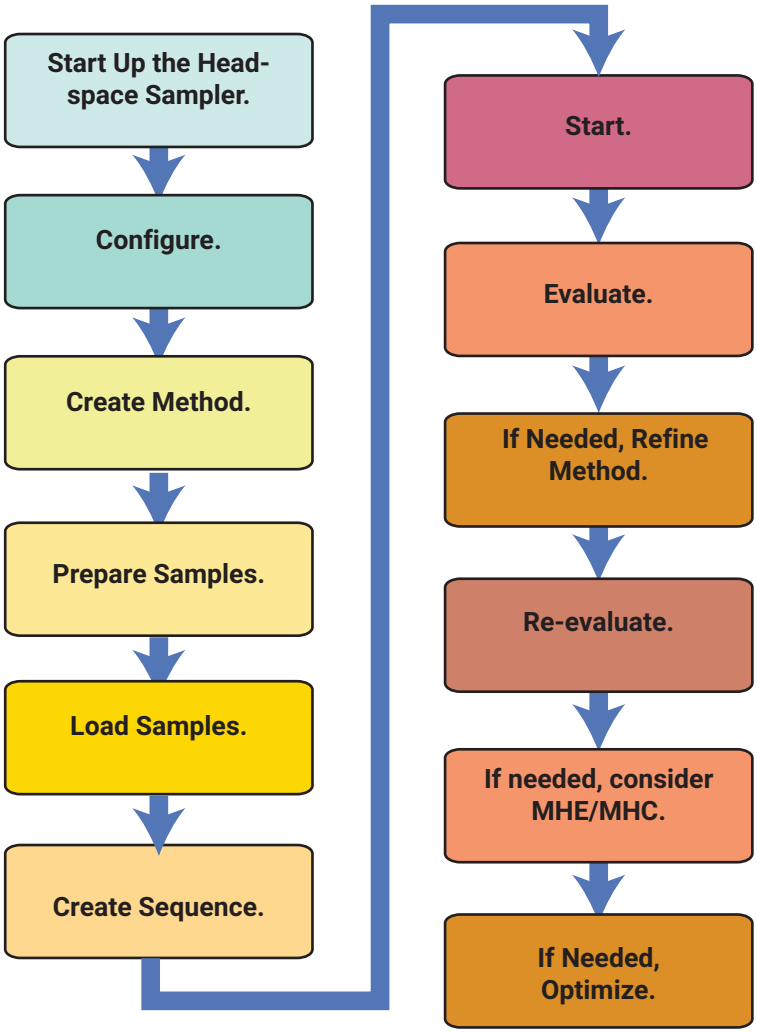


Figure 22. Workflow for method development

This chapter describes techniques to create and refine a method, using the available method parameters and method features of the 8697 HS. It describes all the method parameters available, and discusses how various parameters impact an analysis.

Consider the Sample and Matrix

The first step in developing the method is to understand the sample and matrix.

Theory of headspace analysis

The equations describing headspace theory derive from three physical laws associated with vapor pressure, partial pressures, and the relationship between vapor pressure of an analyte above a solution and the concentration of that analyte in the solution.

Dalton's law of partial pressures states that the total pressure of a mixture of ideas gases is equal to the sum of the partial pressures of each gas in the mixture.

Henry's law for dilute solutions states that at a constant temperature, the amount of a given gas dissolved in a given type and volume of fluid is directly proportional to the partial pressure of that gas in equilibrium with that fluid.

Raoult's law states that the partial pressure of a solute in the headspace volume is proportional to the mole fraction of the solute in solution.

The concentration of sample analyte in the headspace volume is given by mass balance:

$$C_O V_L = C_G V_G + C_L V_L$$

where:

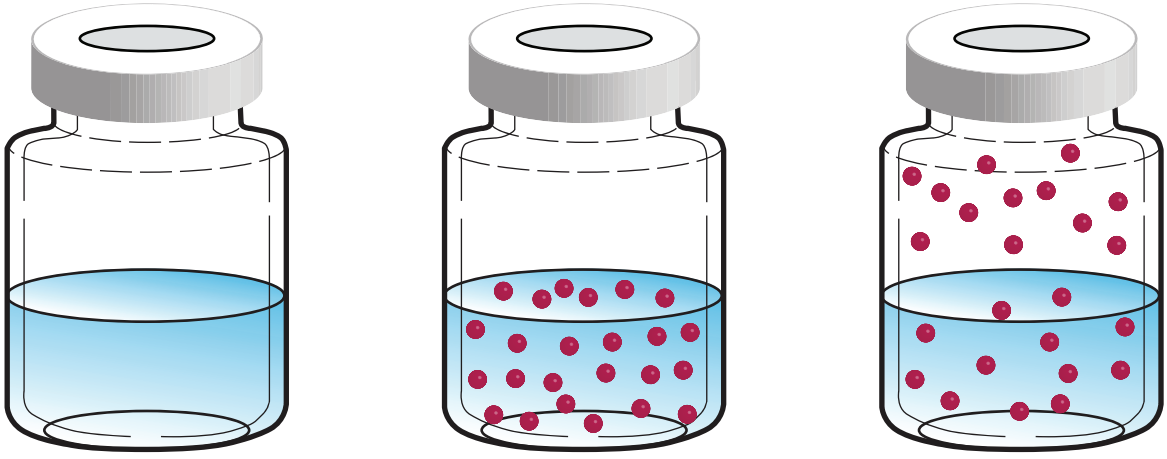
C_G is the concentration of analyte in the headspace

C_O is the concentration of analyte in the original sample

V_G is the volume of gas in the sample vial

V_L is the volume of sample

K is the partition coefficient (or distribution coefficient), C_L/C_G at equilibrium V_G/V_L



Rearranging provides:

$$C_G = \frac{C_O}{\left(K + \frac{V_G}{V_L} \right)}$$

where:

K is the partition coefficient (or distribution coefficient), C_L/C_G at equilibrium

V_G/V_L is also called the phase ratio

The equation shows two important points:

- For consistent results, the ratio V_G/V_L must remain constant. This means that the sample amount and vial size need to be kept the same.
- Minimizing the partition coefficient, K, provides higher concentration of sample vapor in the headspace volume.
- A smaller V_G/V_L ratio yields a greater concentration of volatile of interest in the headspace volume

Impact of K and phase ratio

The concentration of analyte in the headspace volume depends on many factors, including: sample amount, original concentration of analyte in the sample, available headspace volume, temperature, and total pressure in the vial. Some factors are manipulated in the sample and in the matrix, while others can be controlled using the headspace sampler.

Controlling K

When optimizing a headspace analysis, first consider the partition coefficient of the solvent. The table below lists the K values for several common solvents at 25 °C.

Analyte	Solvent	K (25 °C)
Toluene	Decane	~3000
Toluene	Water	~4
Ethanol	Decane	~60
Ethanol	Water	~5000
Ethanol	Water, saturated with Na_2SO_4	~300

At higher temperatures, K will decrease. At 40 °C, the K value for ethanol in water is ~1350. At 80 °C, the K value lowers to ~330.

As can be seen from the table, K also depends on both the analyte and the matrix. Note the change in K for the ethanol-water system compared to the similar system saturated with Na_2SO_4.

Therefore, to improve the concentration of analyte in the headspace volume, heat the sample. If needed, consider changing the solvent (if possible), or consider addition of an inorganic salt to lower the solvent K value.

The other factor to manipulate to increase sensitivity is the phase ratio, V_G/V_L. Recall the vapor phase concentration equation:

$$C_G = \frac{C_O}{\left(K + \frac{V_G}{V_L} \right)}$$

Where K is small, reducing the phase ratio will produce a higher concentration of analyte in the headspace volume. The 8697 can use a variety of sample vials. Select a sample vial and sample amount to create a higher concentration of analyte.

Where K is large, reducing the phase ratio results in less gain.

Controlling the phase ratio

Another factor to manipulate to increase sensitivity is the phase ratio, V_G/V_L. Recall the vapor phase concentration equation:

$$C_G = \frac{C_O}{\left(K + \frac{V_G}{V_L} \right)}$$

Where K is small, reducing the phase ratio will produce a higher concentration of analyte in the headspace volume. The 8697 can use a variety of sample vials. Select a sample vial and sample amount to create a higher concentration of analyte.

Where K is large, reducing the phase ratio results in less gain.

Consider the GC Inlet

Normally, the choice of inlet is determined by the available GC. However, note that for inlet types where the analytical column runs directly into the headspace sampler six port valve, the analytical column is not in the GC oven for its entire length. Peak shapes can change.

With any inlet type, the HS supports only split inlet modes without modification. Splitless inlet modes are supported, but require updated firmware (PID constants) for the inlet EPC module.

Load a Similar Method

When starting a new method, begin with a method for a similar sample type.

If using an Agilent data system, the software provides a new method wizard and conversion wizards. The new method wizard provides safe starting temperatures and other parameters for both liquid and solid matrices, using a list of solvent types (including custom values). The wizard also considers the analyte boiling points.

Edit the New Method

After loading a similar method, edit it as needed for the new sample. This section describes the primary settings, and the following sections describe the extraction modes and other settings.

Temperatures

Go to **Method > Headspace**, scroll to the temperature settings, and enter the desired values for the vial oven, sample loop, and transfer line temperatures.

Table 8 Temperature parameters

Parameter	Comments
Oven	Start with an oven temperature 15 °C below the solvent boiling point.
Loop	Start with this temperature equal to the oven temperature. To prevent condensation of sample, the sample loop and valve should never be lower than the oven temperature.
Transfer Line	Start with a temperature 15 °C higher than the oven temperature. To prevent condensation of sample, the transfer line should never be lower than the sample loop and valve temperature.

Times

Go to **Method > Headspace**, scroll to the time settings, and enter desired values for the timing parameters used by the HS.

Table 9 Time parameters

Parameter	Comments
GC Cycle	The total time required for the GC (or GC/MS) system to return to a ready state after a run. See **To Determine the GC Cycle Time** in the *Operation* guide.
Vial Equilibration	The time the vial spends equilibrating at temperature in the oven, including any shaking. In general, start with a value of at least 15 minutes if an estimated time is unknown.
Injection Duration	The time allotted to sweep the sample from the sample loop, through the transfer line, and into the GC. The default inject time is 0.50 minutes.

The HS uses these parameters when determining throughput. The most important value to a sequence of samples is the **GC Cycle** time. If too short, samples will be prepared before the GC or GC/MS is Ready. Depending on the sequence action settings, this can cause aborted samples or unexpected results. If the **GC cycle** time is too long, throughput may be reduced, but at least the HS maintains sample processing in accordance with the method.

In addition, there are other timings that the HS considers when loading vials into the oven. Among these are:

- A 30 second wait time for all heated zones to stabilize at temperature
- Fixed wait times for actions such as tray moves, carousel moves, and lifter moves
- Fixed wait times for valve switches
- Other internal processing times

The HS considers all of these timings, as well as the sequence of method setpoints, to determine the most efficient schedule for processing the sample vials.

Vial and Loop

Go to **Method > Headspace**, then scroll to the vial and loop settings.

Table 10 Vial and loop parameters

Parameter	Comments
Vial Size	Select the vial size, 10 mL, 20 mL, or 22 mL.
Shake Value	Shaking is available in 9 levels. See **Vial shaking**. Enter the value (1 through 9) directly, or enter 0 to disable. The browser interface will show the frequency (shakes/minute) and acceleration of the vial at each level.

Fill Modes

Go to **Method > Headspace**, then scroll to the fill mode settings. Note that the settings available depend on the fill mode.

Table 11 Fill mode parameters

Parameter	Comments
Vial Fill Mode	• Default: **Flow to Pressure** • The HS determines how to fill the sample loop.) See **"Pressurizing the vial"** for more information.
Vial Fill Pressure	Target sample vial pressure for sampling. • The vial pressure must be high enough to transfer the sample through the sample loop. • For some samples, the pressure developed during equilibration is sufficient for headspace sampling. • Do not exceed any vial pressure limit. • Avoid setting a value below the pressure developed during equilibration. See **"Pressurizing the vial"** for more information.
Vial Fill Flow	Avoid a high flow rate if the change in vial pressure between the natural internal pressure after equilibration and the target pressure is small. See **"Pressurizing the vial"** for more information.
Fill Volume	Used only when the **Fill mode** is set to **Constant Volume**. The specific volume of gas with which to pressurize the vial.
Pressure Equilibration Time	The time allotted for the vial to equilibrate at pressure during vial pressurization. The default time is 0.50 minutes.

Table 11 Fill mode parameters (continued)

Parameter	Comments
Loop Fill Mode	• If using **Default**, the HS picks reasonable values for the other loop parameters. • If using **Custom**, the other loop parameters become enabled for editing. See **"Filling the sample loop"** for more information.
Loop Ramp Rate	If in **Custom** mode, avoid a high fill rate when the difference between vial pressure and loop pressure is small. Default value: 20 psi/min.
Final Loop Pressure	If in **Custom** mode, set the final sample loop pressure. If in **Default** mode, the final pressure is displayed. See **"Filling the sample loop"** for more information.
Loop Equilibration	If in **Custom** mode, default value: 0.05 minutes.

Venting and Purging

Between sample vials, the HS will purge the sample probe, sample loop, and vent. See **Figure 23**. The default purge flow is 100 mL/min for 0.5 minutes.

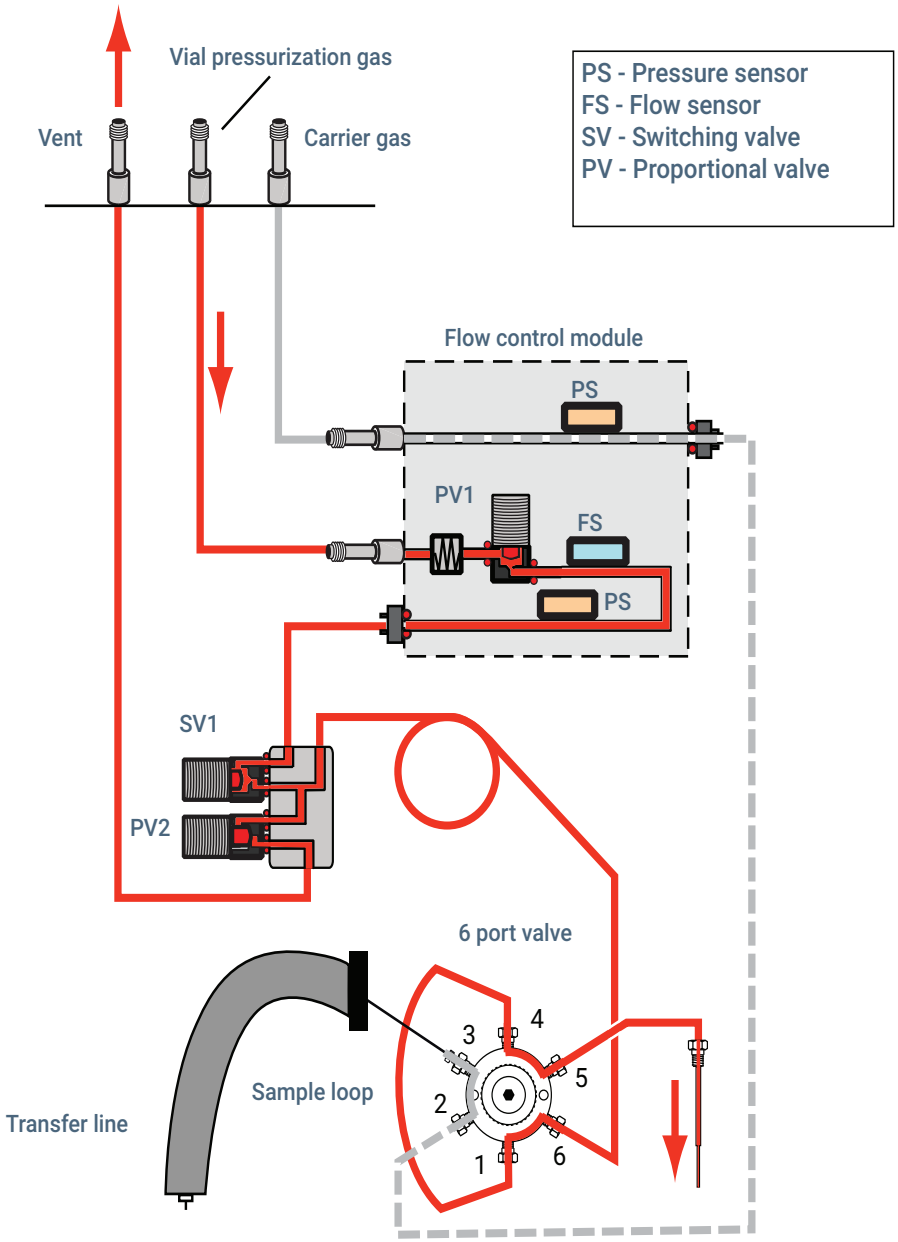


Figure 23. Flow paths during purge time

To set the venting and purging parameters, go to **Method > Headspace**, then scroll to the Venting and Purging settings. These parameters apply only when using an extraction mode other than single. For single extractions, the vial pressure is always vented during the injection cycle.

Table 12 Venting and purging parameters

Parameter	Comments
Vent vial pressure after the last extraction	During an injection cycle that starts a GC run, vent residual vial pressure. The vial is re-pressurized for the next extraction.
Vent vial pressure between extractions	Select to vent the vial pressure between each extraction. The vial is re-pressurized for the next extraction.
Purge Flow Mode	**Default**: The HS purges the sample loop, vent, and sample probe with a 100 mL/min flow of vial pressurization gas for 1 minute. **Custom**: Enter the purge flow rate and time. **Off**: Not recommended. The HS does not purge between samples.
Purge Flow	The time allotted for the vial to equilibrate at pressure during vial pressurization. The default inject time is 0.50 minutes.
Purge Time	The time alloted for the sample probe, loop, and vent to purge.

If experiencing carryover, try increasing the purge flow or purge time to sweep any residual sample vapors from the system.

Note that typically, the HS purges the sample probe (including sample loop) and vent for the first half of the purge time, then closes the vent valve to purge just the sample probe (and sample loop). If the purge time is 0.1 to 0.2 minutes, the first 0.1 minutes purges the vent and sample probe, and the remaining time purges only the probe. If the purge time is less than 0.1 minutes, then the HS purges both the sample probe and vent for the entire time.

Other parameters

In addition to the parameters described above, the remaining headspace sampler method parameters are discussed in the following sections:

Extraction mode

Dynamic leak check

Method Parameter Summary

Method Sequence Actions

Using parameter increment

If using the optional barcode reader, set the types of barcodes used from the touchscreen under **Settings**. See **"Settings > Configuration > Headspace"** on page 60. On the browser interface, these settings appear under **Method > Configuration > Headspace.**

Developing and Improving the Method

This section discusses how to improve a method by using various 8697 HS features. It provides useful tips and background information that will help you develop methods using the HS. It is not a general discussion of headspace chromatography, but rather a collection of information to help you use the 8697 HS to best advantage.

Using parameter increment

The goal of the initial method is to safely get results—*any* results. Once you have determined that a method safely extracts sufficient sample that can be analyzed by the GC (or GC/MS), then next step is typically to empirically determine the equilibration temperature, time, and shaking level that provide the best optimization for your needs.

To do this, use the parameter increment feature of the HS. The parameter increment feature will increase oven temperature, vial equilibration time, or vial shaking level by a set amount in consecutive runs.

To use parameter increment:

1. Open a connection to the GC using the browser interface.
2. Go to the **Method** tab and load the desired method.
3. Scroll to **Miscellaneous (Method Development)**.
4. Enable **Would you like to increment a method setting over subsequent runs?**.
5. Select **Temperature**, **Vial shaking**, or **Vial equilibration hold time**.
6. Enter the appropriate parameters. See **"Oven temperature"**, **"Vial equilibration time"**, or **"Vial shaking level"** below for details.
7. Save the method.
8. Determine the number of sample vials needed.
   - The parameter will increment until it exceeds the specified upper limit. (For an example, see **Table 13**.)
   - Divide the range by the increment and round up.
9. Prepare the sample vials and load them into the tray (or carousel).
10. Create a sequence to run each vial using the parameter increment method.
11. Start the sequence.
    - The HS will start the sequence, running one vial at a time, and will increment the selected parameters with each iteration until it would exceed the specified upper limit on any one parameter.
    - View the current method parameters using the status display. As the HS increments the method parameter for each new vial, the new value is displayed as the setpoint temperature, time, or shaking level.

Oven temperature

When incrementing oven temperature, consider the following:

- Higher temperatures generally improve peak areas.
- Do not exceed the solvent (or analyte) boiling point.
- Incrementing temperature can increase throughput.
- All thermal zones increment at the same rate. If a heated zone reaches (or would exceed) its maximum temperature, it will hold at its maximum temperature for any remaining vials. For example, consider a starting oven temperature of 175 °C, a transfer line temperature of 200 °C, and a sample loop temperature of 190 °C. If incrementing 10 °C, on the fifth run, sample loop temperature should be 230 °C while the oven would be at 215 °C. Since the maximum temperature of the sample loop would be exceeded, instead the temperature holds at 225 °C for the fifth and sixth runs. See the example in **Table 13** below.

Table 13 Example temperatures, in °C, during parameter increment of 10°C per step

Oven	Transfer line	Sample loop
175	200	190
185	210	200
195	220	210
205	230	220
215	240	225
225	250	225

- Vials in this case are run in series. There is no overlap since the oven temperature differs for each vial.
- Do not enter a series that exceeds the number of available vials in the tray.

Vial equilibration time

When incrementing vial equilibration time, consider the following:

- Increment equilibration time if increasing temperature might introduce more solvent than analyte, or would degrade the sample.
- Vials in this case can be overlapped.
- Do not enter a series that exceeds the number of available vials in the tray.

Vial shaking level

When incrementing vial shaking time, consider the following:

- Vials in this case must be run in series, since the shaking level differs for each vial.
- Shaking helps the most with high-K analytes, larger amounts of liquid sample, and more viscous liquid samples.

Vial size

The HS determines the vial size using the gripper or when loading the vial onto the sampling probe.

Vial shaking

The HS can shake vials in the oven at 9 levels. Enter **0** to disable shaking, or enter **1** through **9**, with 9 being the highest shaking.

Higher shaking levels can increase area counts at a given oven temperature.

Sample loop size

Always configure the correct sample loop size. The HS controls certain operational parameters, such as sample loop filling, based on the configured sample loop volume.

Larger loops can help when performing trace analysis at the limits of detection.

Smaller loops may help peak fidelity when connecting directly to the GC column.

Pressurizing the vial

As described in **"Static Headspace Sampling Using a Valve and Loop"** on page 10, the HS pressurizes the vial, then vents the vial to atmosphere through the sampling loop. The HS can control the rate of gas transfer through the loop, as well as the initial head pressure within the vial and the residual pressure left in the vial when sampling ends.

- For more repeatable results, make sure the vial contains sufficient pressure to sweep the sample loop more than once. If the vial develops less than 70 kPa (10 psi) pressure during thermal equilibration, consider adding additional gas to increase that pressure. If the vial pressure is low, it can cause repeatability issues or low peak areas (due to insufficient sample reaching the sample loop).
- The HS can pressurize the vial using 3 different modes. Use a vial pressurization mode appropriate for the sample.
- Set a target vial pressure higher than the pressure developed during thermal equilibration. (Otherwise, you will accidentally vent sample!)

Flow to pressure

This is the default vial pressurization mode, and is suitable for most analyses. The HS uses a fixed flow rate to pressurize the vial to a specified level. This provides less "shock" to the vial.

- Avoid a high flow rate if the change in vial pressure is small.
- Custom sample loop fill options are available when using this mode.

Pressure

In this mode, the HS pressurizes the vial to the target level as rapidly as possible. This mode duplicates the process used on earlier Agilent headspace samplers (G1888 and 7694). Custom sample loop fill options are available when using this mode.

Constant Volume

In this mode, the vial develops its natural internal pressure. The HS sampler then inserts a fixed volume of gas into the vial. In this case, the actual final vial pressure is not known, since it depends on the initial pressure and the compressibility of the added volume of gas.

Because the internal vial pressure is unknown, this mode precludes using advanced sample loop fill options. The HS will determine the best settings for filling the sample loop.

This mode is useful when the exact molar amounts are important.

When using this mode, it is possible to develop insufficient vial pressure. If the final vial pressure after sampling would be < 1 psi (about 7 kPa), the HS will stop sampling when the sample loop/vial pressure reaches 1 psi.

Filling the sample loop

The HS provides two modes for filling the sample loop: **Default** and **Custom**. In the **Custom** mode, you can control the amount of vial pressure used to fill the loop by setting the final residual sample loop (vial) pressure and the ramp rate for filling the sample loop.

Regardless of the mode, you should develop or add sufficient vial pressure before filling the sample loop. Filling the loop relies on the pressure differential between the vial and the loop (which is vented to atmosphere). See **Figure 24**. With a very low initial vial pressure, for example 7 kPa (1 psi), you will rely more on diffusion than on gas flow for transferring the sample to the loop. Results will suffer.

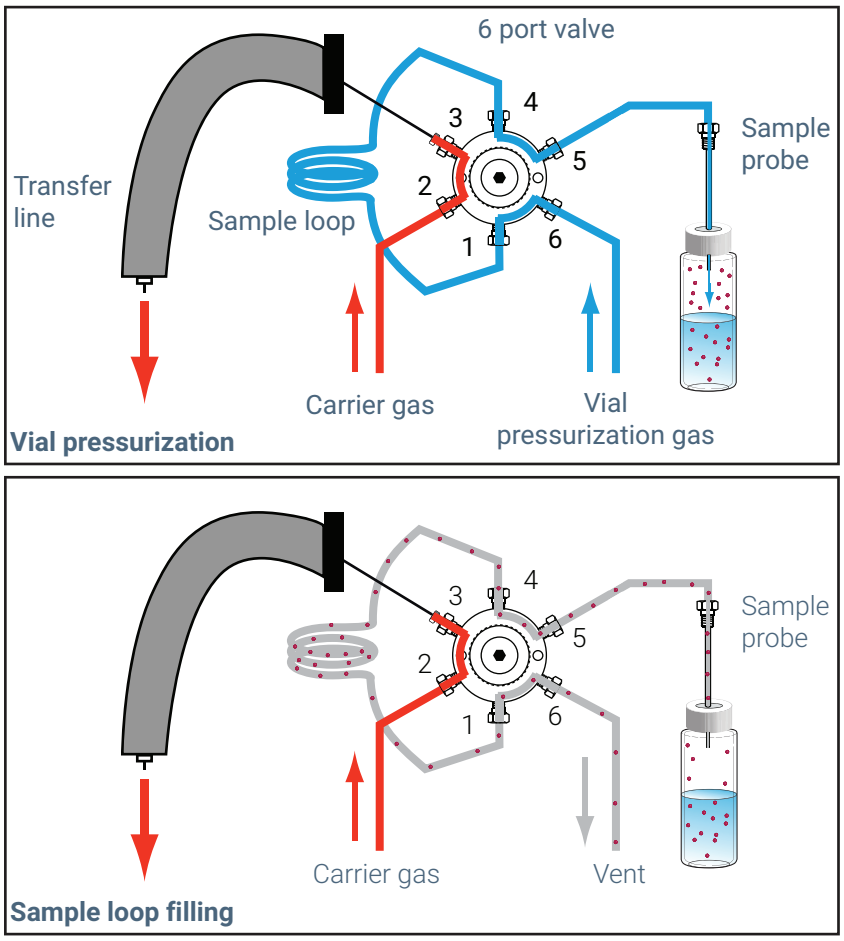


Figure 24. Sample loop filling

For good, repeatable sample transfer to the loop, develop or add sufficient vial pressure.

If starting from a low initial vial pressure (< 70 kPa/10 psi), try increasing the vial pressure. If the results or repeatability improves, there was insufficient pressure to fill the sample loop.

Default

This mode should be sufficient for many analyses. Based on the initial vial pressure (which is known except when using the **Constant Volume** vial pressurization mode), the HS calculates an optimum flow rate and final vial pressure for filling the sample loop. The HS will fill the sample loop from the vial, adjusting the flow rate, until the sample loop is swept at least once with sample.

If the initial vial pressure is low, the HS will make adjustments.

- The final vial pressure cannot be < 1 psi (6.9 kPa) at NTP.
- When using the constant volume vial fill mode, it is possible to develop insufficient vial pressure. If the vial pressure at the start of sampling would result in a final sample loop/vial pressure < 1 psi (~7 kPa), the HS will stop sampling when the sample loop/vial pressure reaches 1 psi.

How the HS calculates the default sample loop fill parameter: The HS takes vial size and atmospheric conditions into account when calculating the default sample loop volume.

Vial Size	Absolute Pressure	Ramp Rate
10 mL	Final Pressure - 2/3 initial pressure	40 psi/min
20 mL	Final Pressure - 5/6 initial pressure	20 psi/min

NTP pressure displayed on the instrument is Absolute Pressure - 1 standard atmosphere.

Custom

In this mode, you can set the rate at which the loop fills, the final sample loop pressure, and a time for the loop to equilibrate after filling. Refer to **Figure 24** as needed.

Loop Ramp Rate: The rate of pressure decay from the vial and through the loop. If you suspect excess sample is being lost during loop fill, lower the flow rate.

Final Loop Pressure: Since the sample loop and vial are connected, this is also the final vial pressure. The HS cannot pull vacuum on a vial.

- In general, set a value > 7 kPa (1 psi).
- The final pressure should provide enough pressure drop from the initial value to make sure the sample loop is filled.
- If set to **0**, the HS will control the sample loop fill until the sample loop (and vial) pressure reaches 1 psi (about 6.9 kPa). Then then vent valve will open completely. The HS does not control the sampling system at this point. When the pressure reaches 0 relative to atmospheric, the vent valve closes. Using this setting may not provide repeatable results.
- If set to a value between 0 and 1 psi (6.89 kPa), a warning appears. The HS will attempt to control the venting to this value, but there may be a loss in repeatability or sample.

Loop Equilibration: Set a time for the sample loop to stabilize after filling.

Possible issues

- If using a small sample loop, and peaks areas are small, you may be oversweeping the loop. If the difference between the initial and final vial pressures is too great given the sample conditions and loop size, too much sample may be flowing through the loop to vent. Try reducing the vial pressure or lowering the difference between the initial and final pressures (which reduces the amount of time the headspace volume sweeps the sample loop).
- If using a large sample loop, and peak areas are small, you may not be sweeping enough sample into the loop. Try increasing the vial pressure or setting a lower loop final pressure (which increases the length of time the headspace volume sweeps into the sample loop).

Extraction mode

There are three (3) extraction modes available, **Single**, **Multiple**, and **Concentrated**. See **"Sequences, Extraction Modes, and Vial Punctures"** on page 51 for detailed descriptions of HS behavior for each mode.

Single extraction

In this mode, the HS equilibrates the vial, punctures it once, fills the sample loop (one "extraction"), then starts a run while injecting the sample onto the GC.

If a vial appears more than once in a sequence, it is completely reprocessed (whether in standalone mode, or if using an Agilent data system).

Multiple extractions

Two typical uses for multiple extraction mode are kinetic studies and calibration.

Note that the vial is punctured only once during the extractions.

Concentrated extractions

This mode can be useful for trace analysis, where the sample can accumulate in the GC inlet or other trap before being swept onto the GC column. This mode requires the use of a multimode inlet or other type of trap.

Optimizing Throughput

The HS automatically manages its timings to maximize the throughput of samples submitted to it for processing. Upon starting a sequence, it compares the methods used for each vial, then determines how and when to place each vial in the oven to minimize any downtime between GC runs. Its analysis depends on:

- The HS timing parameters (wait times, equilibration times, and so forth)
- The accuracy of the entered GC cycle time
- The number of contiguous samples in the sequence that use the same method
- The differences in the HS parameters between each method
- Any differences between the actual GC run time and the entered values for HS parameters such as carrier gas flow or pressure programs

HS throughput analysis does not consider other GC settings, such as GC oven temperature or inlet temperature changes. The HS cannot account for MS solvent wait time or other external events that occur after the GC run completes. You must include these types of timing issues in the **GC Cycle** parameter if any becomes important. For example, suppose you temperature program the inlet. The inlet must cool down before the next run. This will take some amount of time, during which the GC is Not Ready and the HS may have samples in the oven. If the cool down takes too long, the samples would remain in the HS oven too long and trigger the **System Not Ready** sequence action. In this case you may need to consider increasing the **GC Cycle**.

Practices that may increase throughput:

- Group samples that use similar HS oven temperature and shaking.
- Arrange samples to avoid heating, then cooling the HS oven. Analyze samples in order of increasing HS oven temperature.

Practices that may reduce throughput:

- Entering consecutive lines in the sequence that change HS oven or shaking parameters.
- Entering consecutive sequence lines that require HS oven cooling, then heating, then cooling.

Setting Up for a New Method

While the HS can run sequences that include many methods, all methods used during a single HS sequence must have the following in common:

- Same sample loop size
- Same gas types

All other parameters, including vial size, can vary between samples in the sequence.

Any sample which requires a different sample loop size or gas type cannot be run at the same time as samples for that other method. Install the necessary hardware and reconfigure the HS.

Perform Blank Runs

Always perform several blank runs after developing a method. Use the blanks to check for carryover. If carryover is found, resolve it. See the *Troubleshooting* manual.

10 Early Maintenance Feedback

This chapter discusses the Early Maintenance Feedback features of the headspace sampler.

HS Early Maintenance Feedback

The HS adds several counters to the GC's EMF features, found on the touchscreen or browser interface at the **Maintenance > Headspace**. **Table 14** below lists the consumable items tracked by the HS, as well as the type of event the HS uses to track the consumable item. For example, the HS tracks transfer line usage by counting injection cycles.

Table 14 8697 Counters

Item	Counter
Gripper pads	Tray gripper moves
Headspace on time	Instrument uptime
Headspace run count	Injection cycles
Probe	Injection cycles
Sample loop	Injection cycles
Six-port rotor	Injection cycles
Six-port valve	Injection cycles
Transfer line	Injection cycles
Tray calibration	Instrument uptime
Vent tubing	Injection cycles
Vent valve	Injection cycles

Before beginning a sequence, the GC checks the HS EMF counters for available service life. If running the sequence will cause one of the EMF counters to trigger a service warning, the GC will display a warning message but will not prevent the sequence from running.

Set, reset, or disable HS EMFs just like any other EMF on the GC. Refer to the GC help for more information on using EMFs.

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