Agilent 7697A Headspace Sampler

Advanced Operation

Agilent Technologies

Notices

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A CAUTION 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 damage to the product or loss of important data. Do not proceed beyond a CAUTION notice until the indicated conditions are fully understood and met.

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

About This Manual 8

The Keypad 9

Headspace Analysis 11

- Headspace techniques 11
- Static headspace sampling techniques 12

2 How the 7697A Headspace Sampler Works

How the HS Processes a Sample Vial 16

How the HS Equilibrates a Vial 18

How the HS Pressurizes a Vial 19

- Fill at flow to pressure 19
- Fill to pressure 19
- Fill with constant volume 20
- Dynamic leak check 20

How the HS Fills the Sample Loop (Extracts a Sample) 21

- Default loop fill mode 21
- Custom loop fill mode 21

Types of HS Extractions and Injections 22

- Standard extraction 23
- Multiple headspace extractions 24
- Concentrated headspace extractions 24
- Venting residual vial pressure 25

How the HS Reduces Carryover 26

3 Method Development

Overview 28

Consider the Sample and Matrix 29

- Theory of headspace analysis 29
- Impact of K and phase ratio 30

Consider the GC Inlet 33

Load a Similar Method 34

Edit the New Method 35

- Temperatures 35
- Times 36
- Vial 37

Carrier 38
Purge time and flow 41
Other parameters 42

Developing and Improving the Method 43
Using parameter increment 43
Vial size 45
Vial shaking 45
Sample loop size 45
Pressurizing the vial 46
Filling the sample loop 47
Extraction mode 50

Sequence Actions 52
Types of sequence issues handled 52
Available actions 53
Sequence actions and data systems 54

Optimizing Throughput 55

Setting Up for a New Method 57

Perform blank runs 58

4 The Barcode Reader

About the Barcode Reader 60

To Use the Barcode Reader 61

Supported Barcodes 63

Supported Barcode Labels 64

5 Configuration

Configuration 66

Configuration Parameters 67

APG Remote Polarity 69
APG Remote signal electrical specifications 69
APG Remote - Suggested drive circuits 70
APG Remote connector 70
APG Remote signal descriptions 70

Configuring Carrier Gas Control 72
GC Control 72
HS Control 75
GC + HS Control 75

Instrument Schedule (Resource Conservation) 76
Resource conservation when using an Agilent data system 76

To program an instrument schedule 76

6 Options

Calibration 80
To calibrate the atmospheric pressure sensor 80
To calibrate the tray 80
To calibrate the gas sensors 81

Communication 82
To set the LAN address at the keyboard 83
To use a DHCP server 83

Keyboard and Display 84

7 Early Maintenance Feedback

What is Early Maintenance Feedback? 86

To Set Up EMF for Use 87

To Set a Limit for a Counter 88

To Reset a Counter 89

To Disable EMF 90

1
Introduction

About This Manual 8
The Keypad 9
Headspace Analysis 11

This chapter introduces the Agilent 7697A Headspace Sampler and some basic concepts of headspace analysis.

About This Manual

This manual supplements the *Operation* guide. Use this manual as a resource when developing a method. It contains reference information, concepts, and procedures about:

- Headspace theory
- Theory of operation for the headspace sampler
- Advanced functionality
- Method development
- Configuration
- Optional settings

The Keypad

This manual describes the functionality of the Agilent 7697A Headspace Sampler when operating primarily in standalone mode, using the keypad. Most information relates to the parameters available from the instrument keypad, shown in Figure 1 below.

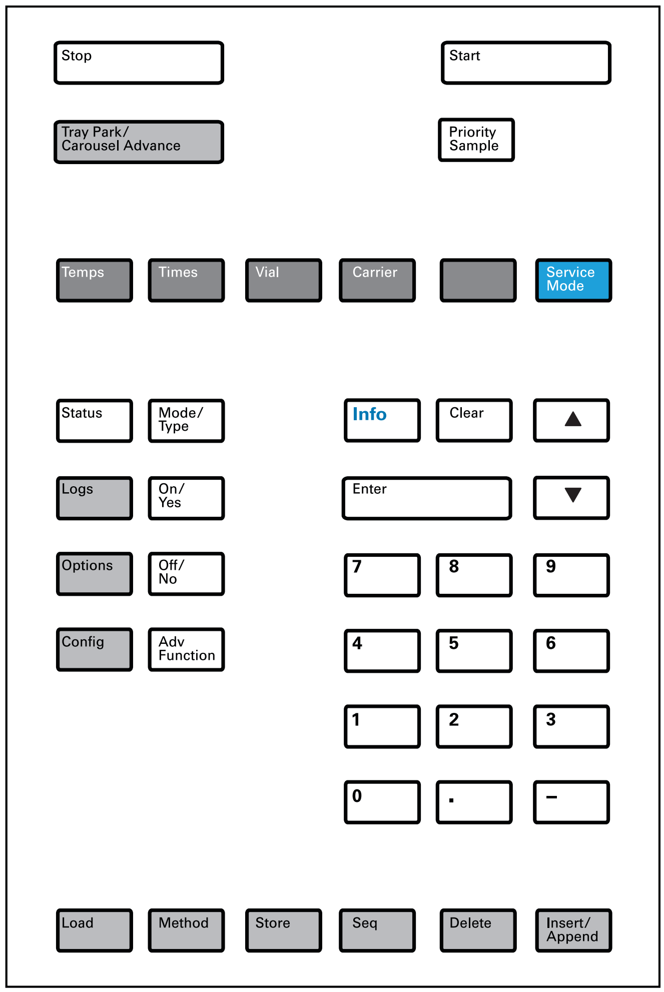


Figure 1 Agilent 7697A HS keypad

If using an Agilent data system with the optional HS control software, more functionality is available:

- Expanded use of the instrument schedule
- Method creation wizard
- Method conversion wizards

- More flexible sequencing

If using a data system, see the data system help for more details. Connect to the HS instrument, open the method editor, and click the help icon ( ) or press F1.

Headspace Analysis

Headspace analysis is a technique for analyzing volatile organic compounds using gas chromatography. 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 285 °C (111 vial model) or 195 °C (12 vial model).
- 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.

Headspace analysis provides several advantages over traditional injections:

- Simpler sample preparation. The sample does not need to be processed until injectable as a liquid.
- Directly analyze a wide range of sample matrices (liquids, solids, and pastes).
- Solvent peak is smaller or nonexistent compared to traditional liquid injection GC techniques.
- Columns last longer, with less maintenance. The headspace volume above the sample matrix is more clean 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 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 techniques

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.)

Pressure transfer systems

The pressure-transfer system uses a specialized needle for vial pressurization and sampling. The vial is heated and agitated for the desired time. Then, the sampling needle punctures the vial, and carrier gas pressurizes the vial. After an equilibration time, the needle allows pressurized gas to flow into the GC inlet for a specified duration. Typically, the sample gas flows into the GC inlet due to the pressure difference between the sample vial and the GC inlet. While the results are repeatable, exact amount of sample gas is unknown.

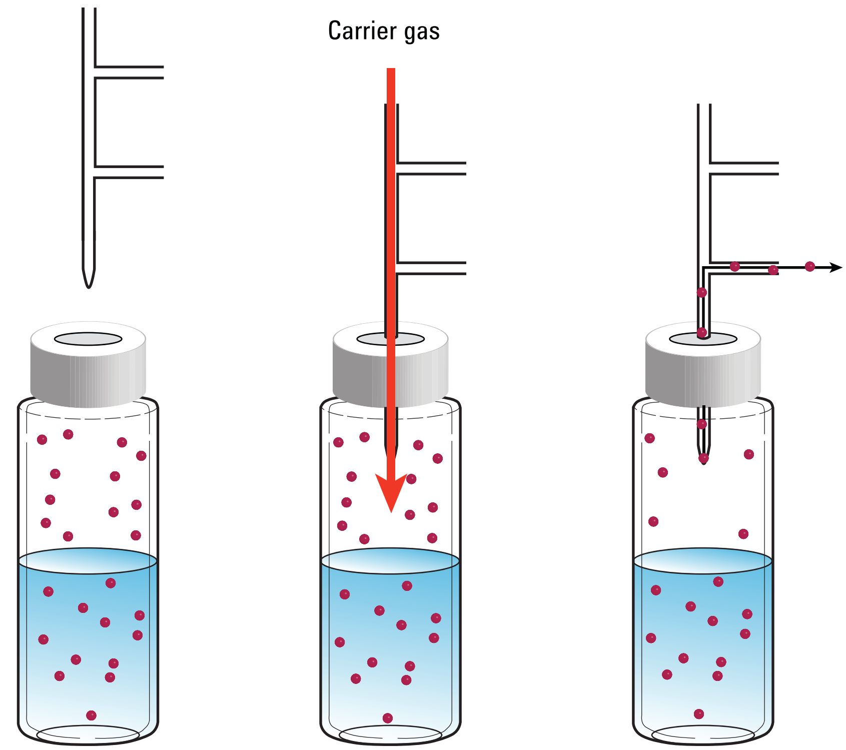


Figure 2 Pressure transfer system

Valve and loop systems

The valve and loop system, as used in the 7697A, also heats and agitates the vial for a specified time. However, the Agilent system uses a sample loop of known size 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 3.
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 7697A 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.

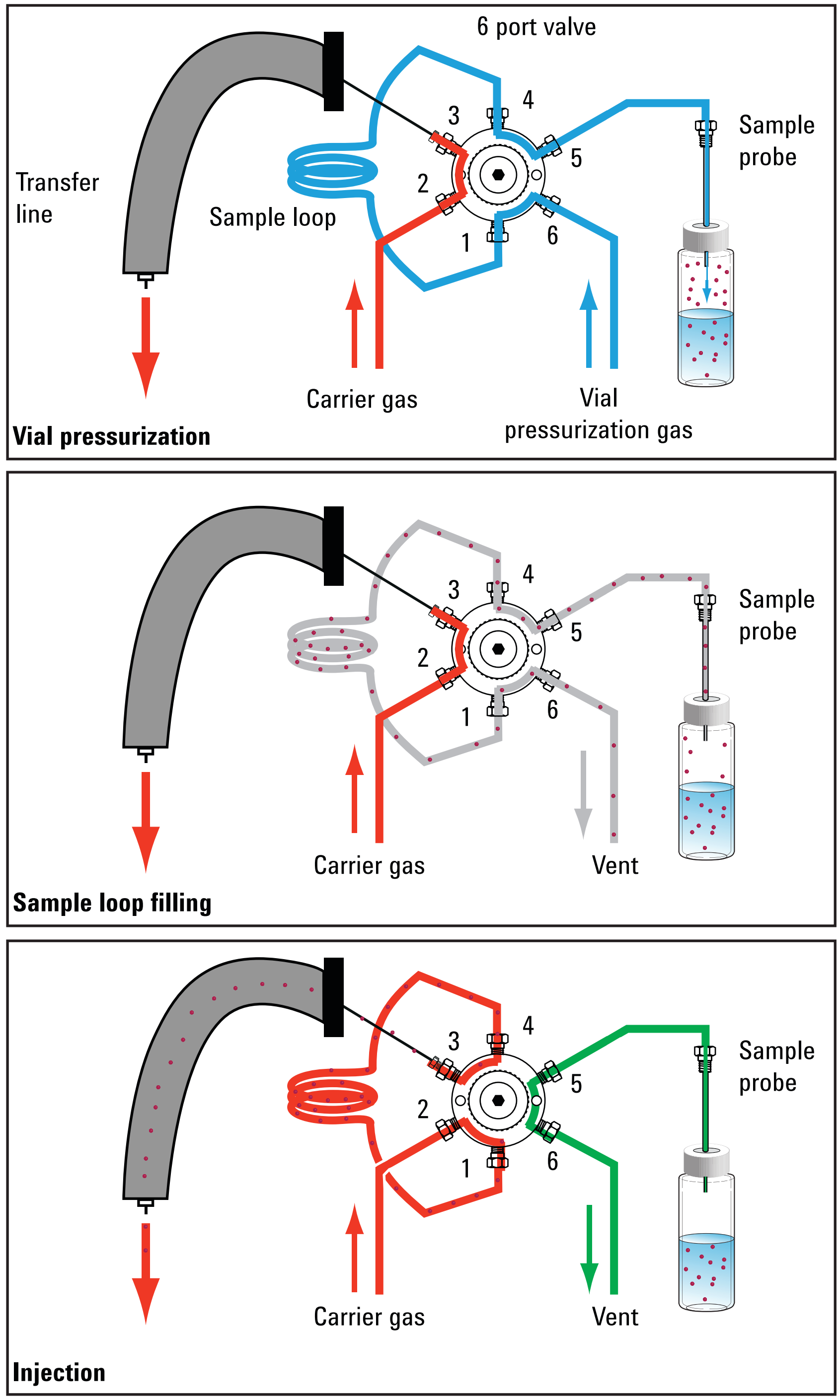


Figure 3 Valve and loop system sampling and injection stages

2
How the 7697A Headspace Sampler Works

How the HS Processes a Sample Vial 16
How the HS Equilibrates a Vial 18
How the HS Pressurizes a Vial 19
How the HS Fills the Sample Loop (Extracts a Sample) 21
Types of HS Extractions and Injections 22
How the HS Reduces Carryover 26

This chapter describes the basic theory behind the 7697A headspace sampler.

How the HS Processes a Sample Vial

Figure 4 shows the workflow for a vial processed by the 12 vial model HS.

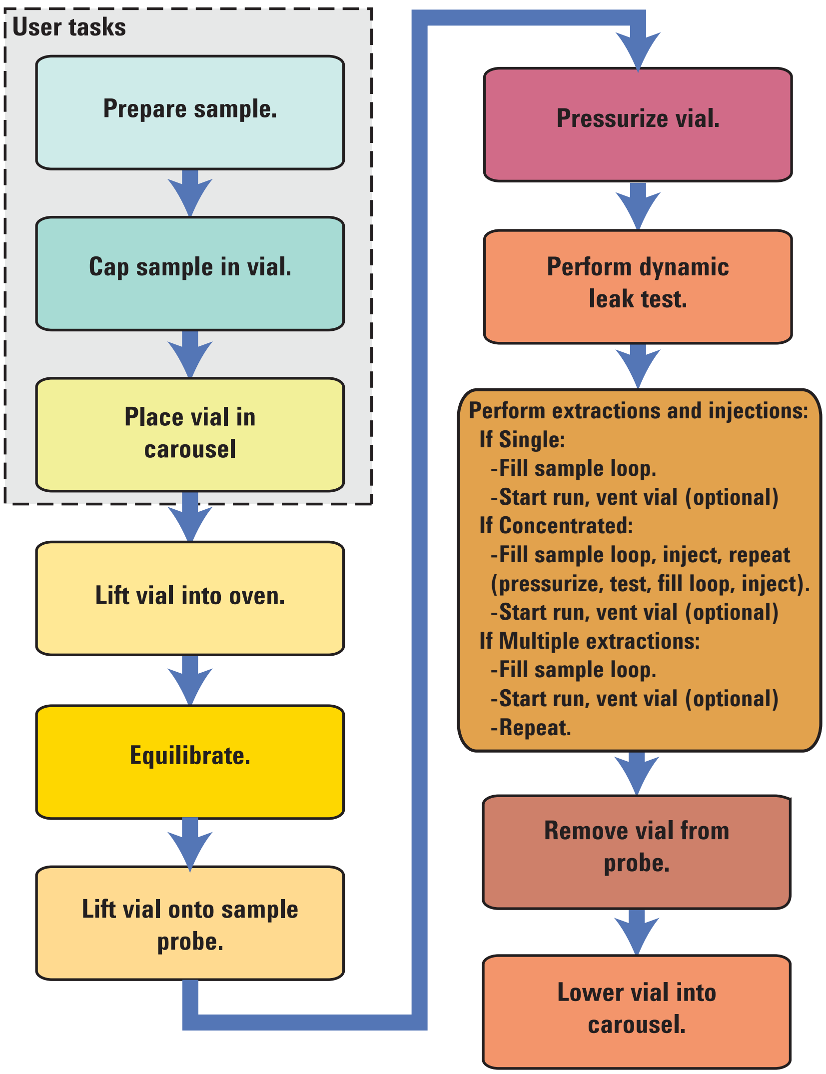


Figure 4 Basic 7697A HS vial process flow, 12 vial model

Figure 5 shows the workflow for a vial processed by the 111 vial model HS (with tray).

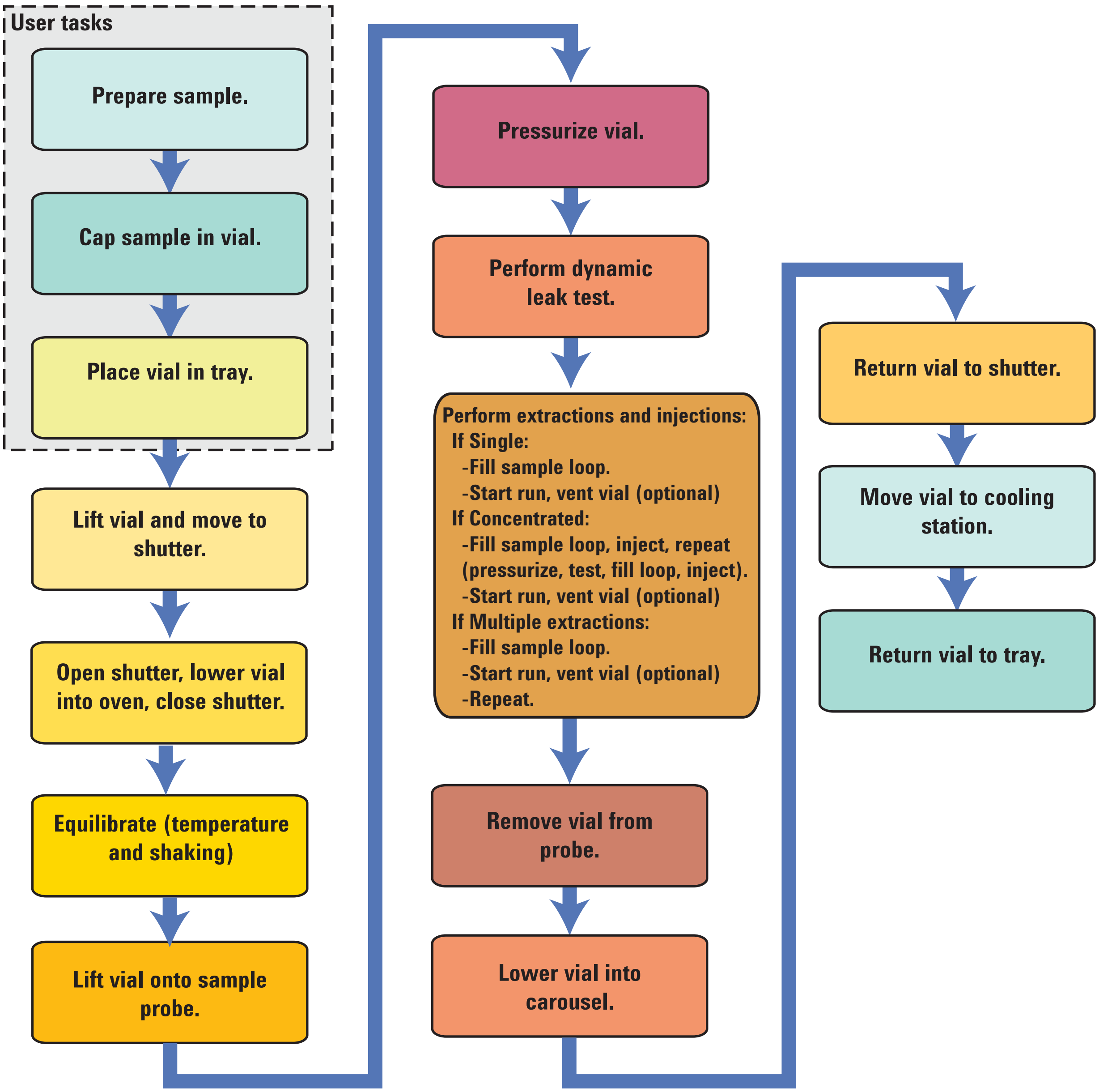


Figure 5 Basic 7697A HS vial process flow, 111 vial model

The major differences in processing between the two models are:

- Tray robotic arm moves vials to and from loading stations
- 111 vial model uses a 12 vial oven that can process more than one vial at a time
- 111 vial model provides shaking

How the HS Equilibrates a Vial

The 7697A HS with tray has a vial oven that can equilibrate up to 12 vials (depending on model) at temperatures from ambient + 5 °C 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 equilibration settings, 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.

The 12 vial model oven can equilibrate a single vial at temperatures from 35 °C up to 210 °C. Shaking is not available.

How the HS Pressurizes a Vial

All 7697A HS provide 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 6 below.

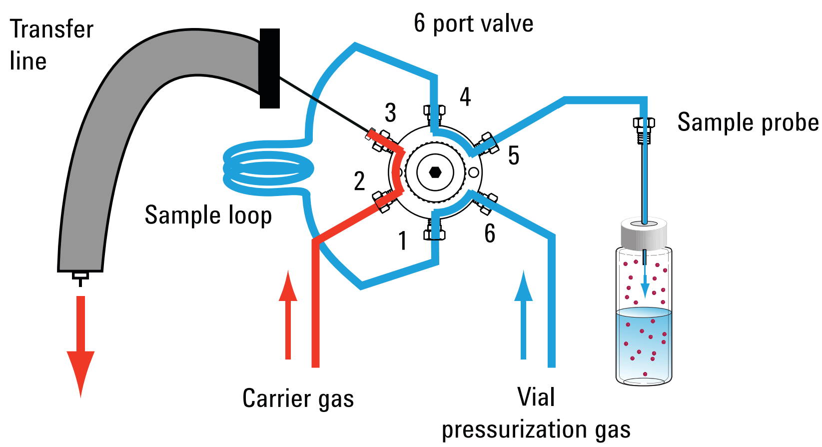


Figure 6 Pressurizing the vial

Fill at 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.

Fill to 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.

Fill with 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. If the HS must continually add gas to maintain the desired pressure in the vial, then the vial is leaking. 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. See "Sequence Actions".

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 7 below.

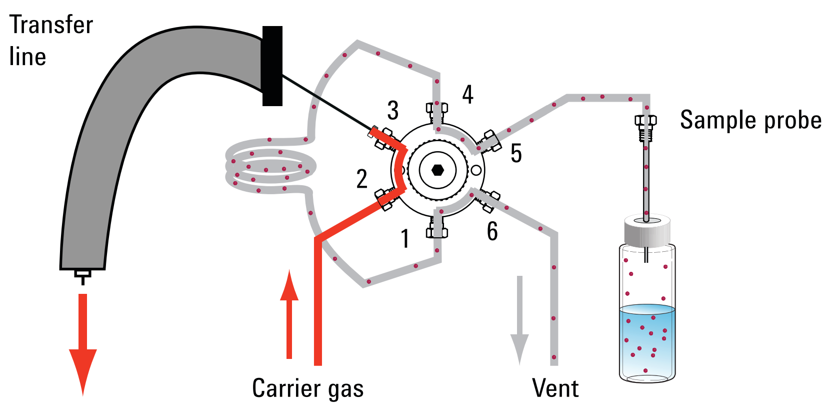


Figure 7 Filling the sample loop

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 7697A 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 8 shows the basic flow paths during an injection cycle, where the sample loop is flushed into the GC.

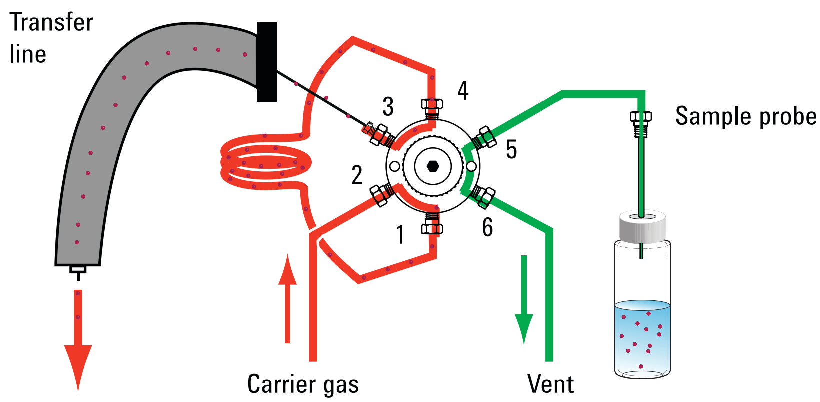


Figure 8 HS injection cycle

Refer to Figure 9 for a diagram of the flow paths within the HS sampler (using GC carrier).

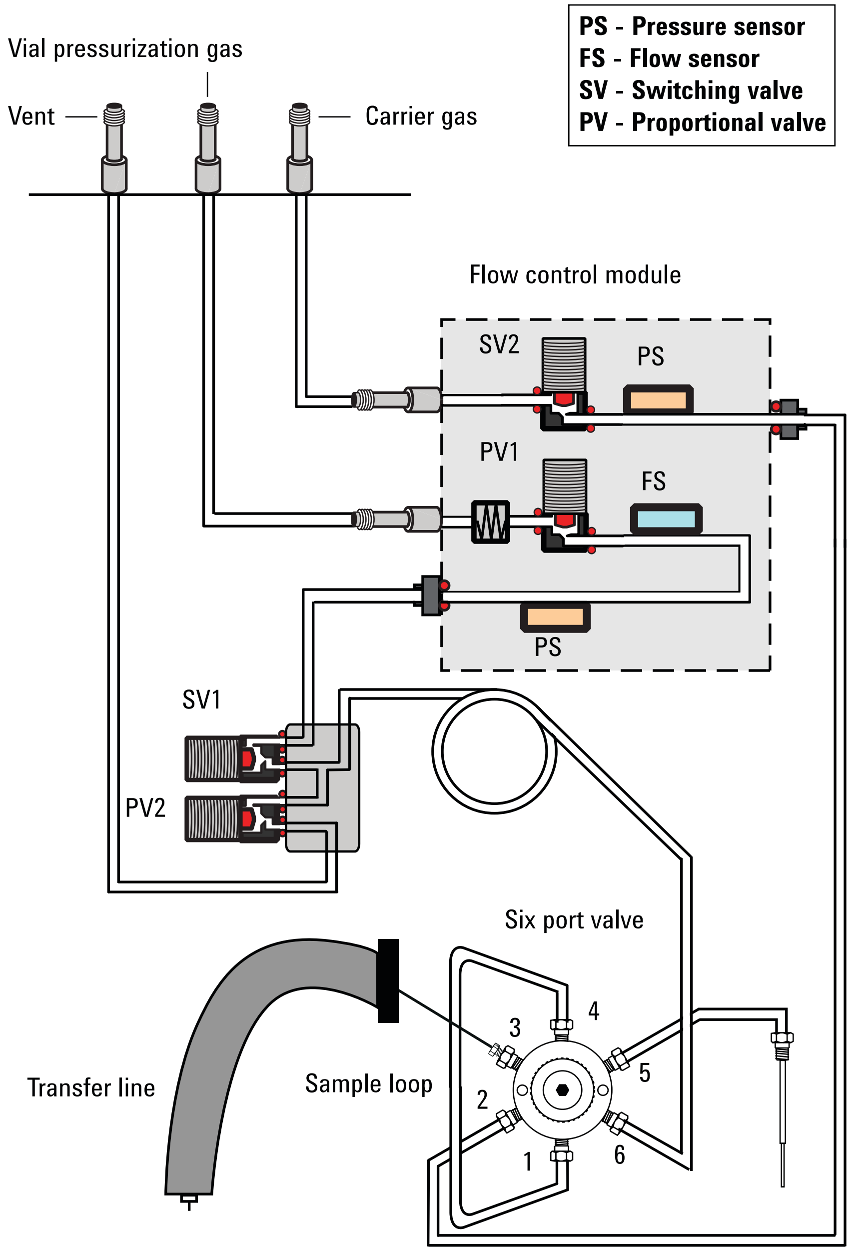


Figure 9 HS sampler flows, GC carrier mode

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 8 and Figure 9. 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 or tray.

Multiple headspace extractions

In this mode, the HS performs multiple extractions and injections using one vial puncture. See Figure 8 and Figure 9. 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 or 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 8 and Figure 9.

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 tray or carousel.

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 7697A 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.

3
Method Development

Overview 28
Consider the Sample and Matrix 29
Consider the GC Inlet 33
Load a Similar Method 34
Edit the New Method 35
Developing and Improving the Method 43
Sequence Actions 52
Optimizing Throughput 55
Setting Up for a New Method 57

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 7697A headspace sampler.

Overview

Figure 10 shows the typical workflow for developing a headspace sampler method.

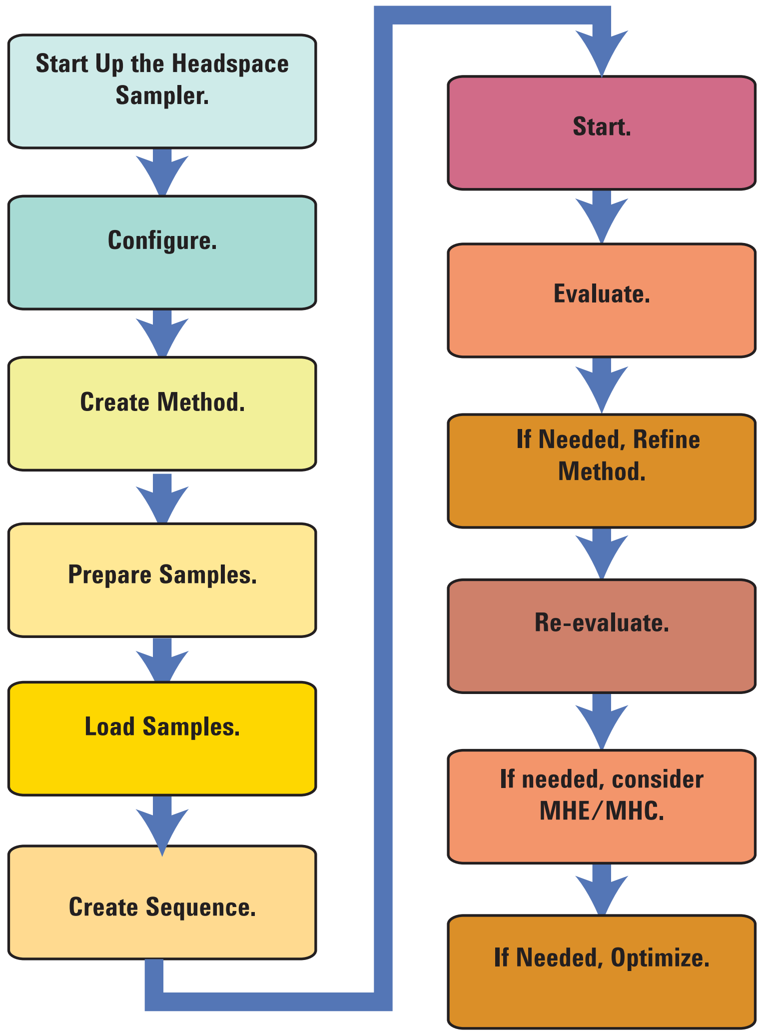


Figure 10 Workflow for method development

This chapter describes techniques to create and refine a method, using the available method parameters and method features of the 7697A HS. It describes all the method parameters available, and discusses how various parameters impact an analysis. This chapter assumes basic familiarity with the HS as described in the *Operation* guide. The *Operation* guide also includes many useful procedures and instructions.

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:

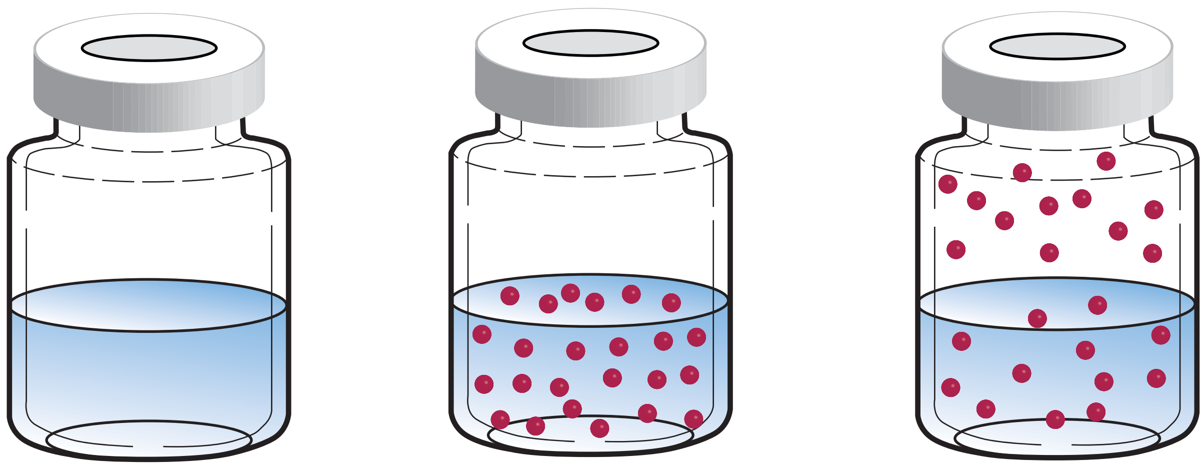
C_G is the concentration of analyte in the headspace

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 7697A 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 7697A 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. Splitless inlet modes are not supported.

Load a Similar Method

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

- The 7697A comes with several built-in methods, one of which may be suitable as a starting point.

  The HS includes the methods listed in Table 1. These methods cannot be edited.

Table 1 Built-in methods

Method name	Comments
Default	
Checkout	Used for the checkout sample, analyte boiling point range of 151 to 210.9 °C in dodecane matrix.
Qualification	Used for Agilent qualification verification.
MeOH in H2O	

- If using the Agilent headspace sampler control software, 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.

NOTE If using the Agilent Control Software for Headspace, you can also start a new method by using one of the wizards provided. Refer to the software's help for details.

Edit the New Method

After loading a similar method, edit it as needed for the new sample. Refer to the *Operation* guide for general information and procedures.

Temperatures

Press [**Temp**] and enter the desired values for the vial oven, sample loop, and transfer line temperatures. If using the optional tray chiller, also set whether or not to use the chiller and the target temperature used on the chiller. Note that the chiller uses an external controller. The HS monitors the vial rack temperature, and will only consider whether the vial temperatures are within the entered setpoint range. Set the actual chiller temperature using its controller.

Table 2 Temperature parameters

Parameter	Comments
Oven	Start with an oven temperature 15 °C below the solvent boiling point.
Loop/Valve	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.
Use Chiller Ready	Available only with optional chiller installed. Turn **On** to enable a sequence action for the vial rack temperature. The sequence action provides a means to control whether or not to run samples if the temperature is out of range.
Chiller temp	Available only when chiller enabled. The target temperature set at the chiller.
Chiller Error-band	Available only when chiller enabled. The allowable temperature range, expressed as Chiller temp +/- Chiller Error-band.

Times

Press [**Time**] and enter desired values for the timing parameters used by the HS.

Table 3 Time parameters

Parameter	Comments
GC cycle time	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 equib time	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.
Pres equib time	The time allotted for the vial to equilibrate at pressure during vial pressurization. The default inject time is 0.50 minutes.
Inject time	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.

For the 111 vial model, 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

Press [**Vial**] and edit the vial parameters.

Table 4 Vial parameters

Parameter	Comments
Fill mode	• Default: **Fill at flow to pressure** • When the **Fill mode** is set to **Constant volume**, the **Loop fill mode** is **Default**. (The HS must determine the appropriate parameters.) • Press [**Mode/Type**] to select the vial fill mode. See "Pressurizing the vial" for more information.
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.
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, mL	Used only when the **Fill mode** is set to **Constant volume**. The specific volume of gas with which to pressurize the vial.
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 fill 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.

Table 4 Vial parameters (continued)

Parameter	Comments
Loop final 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.
Vent after extraction	Default: Yes. During an injection cycle that starts a GC run, vent residual vial pressure.
Vial size	Press [**Mode/Type**] to select.
Shaking	Shaking is available in 9 levels. See Vial shaking. Enter the value (1 through 9) directly, or enter 0 to disable.

Carrier

The method settings for carrier gas change depending on the configured carrier mode.

Table 5 Carrier settings in **GC Control** mode

Parameter	Comments
Pressure	For reference, the HS internal pressure reading for the carrier gas.

Table 6 Carrier settings in **HS Control** mode

Parameter	Comments
Pressure	The current pressure reading. If in pressure mode, also includes the column pressure setpoint.
Flow	The current flow rate. If in flow mode, also includes the column flow setpoint.
Carrier	Press [**Mode/Type**] to select the carrier gas control mode: • **Pressure mode**: Control the carrier gas pressure, whether ramped or constant. • **Flow mode**: Control the carrier gas flow, whether ramped or constant.
Column temp	The initial GC column temperature.

Table 6 Carrier settings in **HS Control** mode (continued)

Parameter	Comments
Column Program time	Displays the time the GC holds the initial column temperature. Set the value in the column temperature program. See Table 8 for parameters.
Edit column temp program?	Select and press [**Enter**] to edit. If the column oven program is not accurate, the HS cannot correctly provide flows. Update as needed if the GC method changes. See Table 8 for parameters.
Edit column flow program? Edit column pressure program?	Select and press [**Enter**] to edit. See Table 9 for parameters.

Table 7 Carrier settings in **GC + HS Control** mode

Parameter	Comments
Pressure	The current pressure reading.
Flow	The current additional flow rate, and setpoint, used to transfer the sample onto the GC column. • The additional flow must be high enough to move the sample through the transfer line and into the GC inlet. Make sure the carrier gas is supplied to the HS with enough pressure to support this flow rate. • The flow is on during the injection duration. • After the injection ends, the added flow rate lowers to the configured **Gas Saver** value. See "Configuration Parameters".

When operating using HS control of carrier gas, the HS requires the GC column temperature program in order to correctly maintain the desired flows. If available, enter the GC column program:

Table 8 GC column temperature program entries

Parameter	Comments
Column temp initial	The GC column oven temperature when the runs starts.
Initial time	The time the GC holds the initial temperature after the run starts.

Table 8 GC column temperature program entries (continued)

Parameter	Comments
Rate 1	The rate, in °C/min, at which the GC heats or cools the oven to **Final temperature 1**.
Final temperature 1	The GC column oven temperature at the end of the ramp period.
Final time 1	The time the GC will hold the final temperature.

Additional ramps are available (rate 2, final temperature 2, and so on). To disable any ramp, enter **0** as the rate. Entering 0 disables that ramp and any further ramps. For example, an isothermal run would have **Rate 1** equal to **0**.

When programming a flow or pressure ramp, enter the parameters as described in Table 9. Programming a flow or pressure ramp is similar to programming a temperature ramp.

Table 9 Flow or pressure program entries

Parameter	Comments
Column flow initial Column press initial	The initial column flow or pressure.
Column flow init time Column press init time	The time the HS holds the initial flow or pressure after the run starts.
Column flow rate 1 Column press rate 1	The rate, in units/min, at which the HS increases or decreases the column flow or pressure to the final flow or pressure for the first ramp.
Column flow final 1 Column press final 1	The final flow or pressure when the ramp ends.
Col flow final time 1 Col press final time 1	The time the HS will hold the final flow or pressure.

Additional ramps are available (rate 2, final flow or pressure 2, and so on). To disable any ramp, enter **0** as the rate. Entering 0 disables that ramp and any further ramps. For example, a constant flow run would have **Rate 1** equal to **0** and an initial time equal to the length of the run.

If using HS carrier control, always keep the GC column configuration entries up to date, since the HS uses these values when providing flows.

Purge time and flow

Between sample vials, the HS will purge the sample probe, sample loop, and vent. See Figure 11. The default purge flow is 100 mL/min for 0.5 minutes.

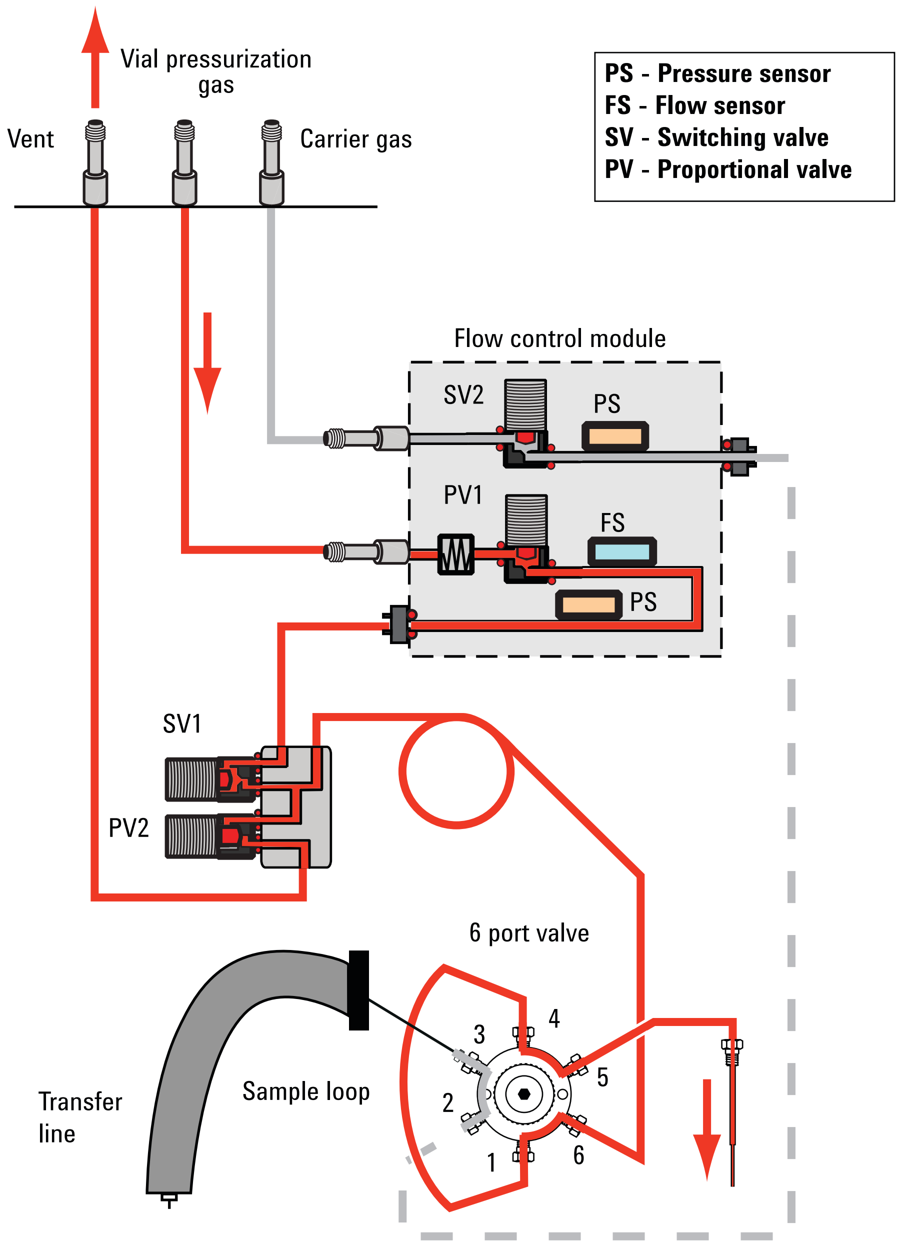


Figure 11 Flow paths during purge time

To set the purge flow:

1 Press [**Adv Function**].
2 Select **Purge flow** and enter the desired flow rate, in mL/min.
3 Select **Purge time** and enter the purge time.

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 can be found using the [**Adv Function**] key. These functions will be discussed in detail in the following sections:

Extraction mode

Sequence Actions

Using parameter increment

The Barcode Reader

Developing and Improving the Method

This section discusses how to improve a method by using various 7697A 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 Agilent 7697A 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. Parameter increment will increase oven temperature, vial equilibration time, or vial shaking level by a set amount in consecutive runs.

To use parameter increment:

1 Load the desired method.
2 Press [**Adv Function**], scroll to **Method development**, then press [**Enter**].
3 With **Parameter increment** selected, press [**Mode/Type**].
4 Select **Temperature**, **Vial shaking**, or **Vial equilibration hold time**.
5 Enter the appropriate parameters. See “Oven temperature”, “Vial equilibration time”, or “Vial shaking level” below for details.
6 Save (store) the method.
7 Determine the number of sample vials needed.
   - The parameter will increment until it exceeds the specified upper limit. (For an example, see Table 10.)
   - Divide the range by the increment and round up.
8 Prepare the sample vials and load them into the tray (or carousel).
9 Create a sequence to run each vial using the parameter increment method.
10 Press [**Start**].

- The HS will start the method, running one vial at a time, until it would exceed the specified upper limit on the parameter.
- View the current method parameters by pressing [**Temp**], [**Time**], or [**Vial**]. As the HS increments the method parameter for each new vial, the new value is displayed.

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 an oven temperature of 250 °C with a transfer line temperature of 275 °C. If incrementing 10 °C, on the third run, transfer line temperature would be 305 °C while the oven would be at 280 °C. The maximum temperature of the transfer line would be exceeded. Instead, the temperature holds at 300 °C. See the example in Table 10 below.

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

Oven	Transfer line	Sample loop
250	275	265
260	285	275
270	295	285
280	300	295
290	300	300
300	300	300

- 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 (or carousel).

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 (or carousel).

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 (111 vial model) or when loading the vial onto the sampling probe (12 vial model).

Vial shaking

111 Vial model only.

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 control 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 Valve and loop systems, 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!)

Fill at 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.

Fill to 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.

Fill with 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 12. 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.

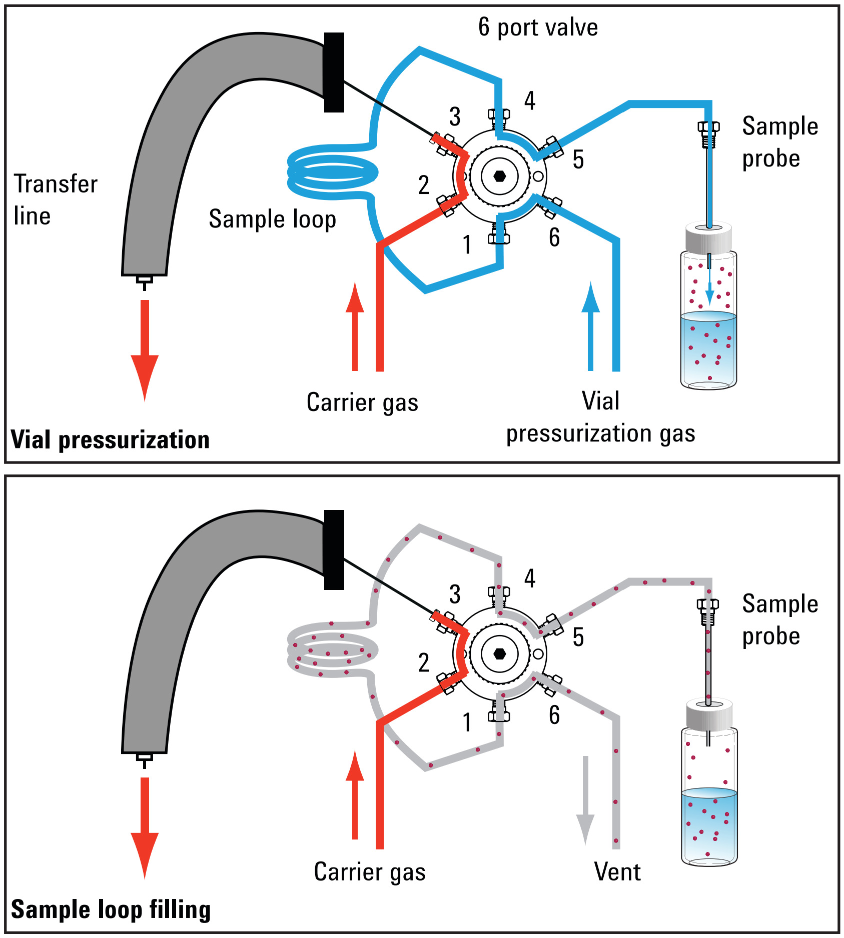


Figure 12 Sample loop filling

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 **Fill with 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 12 as needed.

Loop fill 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.

Loop final 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

Set the extraction mode by pressing the [**Adv Function**] key. There are 3 modes available, **Single**, **Multiple**, and **Concentrated**. See “Types of HS Extractions and Injections” 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.

Sequence Actions

The 7697A HS provides logical control over certain types of HS or GC errors that can occur when handling sample vials for a run or a sequence of runs. This control is provides through the **Sequence action** parameters. These parameters 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 HS 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 available actions are described in “Available actions”.

Vial missing: Control the HS behavior whenever it cannot find a sample vial, for example, if the HS cannot find a vial in the tray. A misplaced vial, a hardware problem, or a problem in the sequence, for example, can cause a missing vial issue.

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. (Note that the HS uses height to determine vial size, so it cannot distinguish between 20 mL and 22 mL vials.) The HS measures the vial height when the vial is in the gripper for the 111 vial model, and when raising the vial onto the sample probe for the 12 vial model.

Check for ready: When the HS becomes Ready, it checks if the GC is Ready. If the GC is not ready for a new injection, the HS follows the specified action. This problem 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. (In this case, do not use **Continue** as the sequence action.)

Wrong chiller temp: Available only if using an optional tray chiller accessory. Control what to do if the tray temperature goes out of range.

Dynamic leak test: Press [**On/Yes**] to enable dynamic leak checking. If enabled, the **Acceptable leak rate** field appears.

Enter the acceptable vial leak rate. The default is 2 mL/min.

Dyn leak test action: Available only when leak detection is enabled. Enter which action to take if a vial fails the dynamic leak test.

In addition, if using a barcode reader additional sequence actions are available. **However, note that data systems typically override any barcode reader actions set in the method.**

Barcode mismatch: Control HS behavior if the barcode value does not match the expected value.

BCR read err action: Control HS behavior if the barcode reader encounters an error while reading the barcode.

BCR invalid checksum: If using a symbology that uses checksum values, select what to do when the checksum does not match the value read from the label.

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. For HS models with a 111 vial tray, no other vials will be moved into the vial oven. For the 12 vial model, the HS processes the current vial, then stops.
  - **To recover from a pause (111 vial model)**: Place missing vial or correct size vial on the shutter. Remove incorrect vial from the tray, if present. Press [**Start**] on the HS keypad.
  - **To recover from a pause (12 vial model)**: The vial was run if present. If missing, place correct vial into the carousel location. Press [**Start**] on the HS keypad.

- **Abort**: Abort the sequence. The HS stops all vial processing, for the current sample vial and all other sample vials. For HS models with a 111 vial tray, 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.

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.

Sequence actions and data systems

The choice of Agilent data system impacts sequence actions. Different data system features make method-based sequence actions unnecessary. Most method sequence actions behave normally when using a data system. The exceptions are listed below.

When using an MS or MSD

If using an MS or MSD, select either **Abort** or **Skip** for the **Check for ready** sequence action. The MS or MSD and the GC/MS Productivity ChemStation will not acquire data unless the entire system is ready when the start command occurs. Using **Continue** can cause lost data. You must include any extra time required for MS or MSD solvent delay and other factors into the **GC Cycle time** parameter.

Barcode reader sequence actions

When using a data system, the data system ignores any *method* barcode reader sequence actions. Instead, the data system controls the barcode reader sequence behavior directly. Make choices about handling barcode reader errors in the data system's sequence.

Optimizing Throughput

The 111 vial model 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 MSD 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 time** 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 **Check for ready** sequence action. In this case you may need to consider increasing the **GC cycle time**.

When using HS carrier gas control, any excess time left in a HS flow or pressure ramp will be honored regardless of GC state. If the GC oven program ends, the run ends, but the HS would continue to execute the flow program until finished. This case may result in reduced throughput.

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 HS carrier configuration (including GC column dimensions when using **HS Control** or **GC + HS Control** for the carrier gas)
- 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, gas type, or HS carrier configuration (including GC column dimensions as noted above) 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.

4
The Barcode Reader

About the Barcode Reader 60
To Use the Barcode Reader 61
Supported Barcodes 63
Supported Barcode Labels 64

This chapter describes the use of the optional barcode reader accessory, as installed on 111 vial 7697A HS model.

About the Barcode Reader

When used with an Agilent data system and the optional headspace control software, the barcode reader provides the data on the vial label to the data system for inclusion in reports. Also, mismatches between the expected barcode value, as entered into the data system sequence, and the barcode actually read will be logged and can trigger specific actions.

Depending on the symbology selected, using the barcode reader provides up to 3 checks on the vial:

- A check for a mismatch between the barcode value entered in the data system sequence and the value read from the vial label.
- A check for the barcode checksum, if supported by the barcode label symbology.
- Whether or not the barcode reader was able to read the vial's barcode label.

The method provides a sequence action to allow you to process each of these types of checks separately. So, you can set the sequence to continue if the checksum fails, but abort if there is a mismatch between the expected and actual values, for example.

To Use the Barcode Reader

To use the barcode reader:

- Select a barcode action.
- Enable the desired barcode symbologies.
- Enable the checksum, if desired.
- Set the barcode reader sequence action.

Barcode reader settings are method parameters. They can change from sample to sample in a sequence by changing the method.

However, most Agilent data systems directly control the sequence behavior for barcodes. *Method* barcode sequence actions are ignored when using an Agilent data system, because the data system automatically replaces them with the correct *sequence* action behaviors. The data system sequence settings override any actions set in the method. If using the HS standalone, then the barcode sequence actions set using the keypad work as expected.

To apply barcode settings for a method:

1 Load the desired method.
2 Press [**Adv Function**].
3 Scroll to **Barcode reader** and press [**Enter**].
4 With **BCR action** selected, press [**Mode/Type**].
5 Select the desired BCR action from the list:
    - **None**: Do not use the barcode reader in this method.
    - **Check read**: For each vial run using this method, read the vial barcode before loading the vial into the vial oven.
    - **Check read before and after**: For each vial run using this method, read the vial barcode before loading the vial into the vial oven, then read the barcode again when retrieving the vial from the oven.
6 Scroll to **Barcode symbology** and press [**Mode/Type**].
7 Select the desired symbology from the list.
    - Select **All** to read any supported barcode type.
    - If you select a specific symbology type, an error occurs if the barcode read is not of that type. This feature can be used to provide a check if you use different barcode label codes for different sample types.

8 With **Enable BCR checksum** selected, press [**On/Yes**] to enable, or [**Off/No**] to disable the checksum.

- Some barcode symbologies (3 of 9 and 2 of 5) support the use of a checksum to verify barcode integrity. If a checksum fails, the HS logs and error and the sequence will follow the barcode sequence action specified in the method.

9 Press [**Clear**] to return to the **Advanced Functions** display.

10 Scroll to **Sequence Actions** and press [**Enter**].

11 Scroll to the barcode reader actions and set the desired actions.

- **Barcode mismatch**: The barcode read does not match the barcode value entered in the data system sequence
- **BCR read err action**: The barcode could not be read from the vial.
- **BCR invalid checksum**: The barcode checksum was not correct or could not be read.

Supported Barcodes

The barcode reader can read any of the following symbologies:

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

Supported Barcode Labels

Dimensions and placement of vial is provided in the *Operation* manual.

Barcode labels must:

- Comply with the dimensions given in the *Operation* manual.
- Be heat resistant (to avoid degradation or charring when heated)
- Be applied within the specifications given in the *Operation* manual.
- Use a matte or other non-glossy finish. Glossy barcode labels can reflect ambient room light, and interfere with the reader.

5
Configuration

Configuration 66
Configuration Parameters 67
APG Remote Polarity 69
Configuring Carrier Gas Control 72
Instrument Schedule (Resource Conservation) 76

This chapter describes the configuration parameters available at the 7697A keypad.

Configuration

Settings which generally apply to all methods, or which usually do not change often, are called *configuration* parameters. A typical example of a configuration parameter is a gas type. Selections for configuration can change the parameters available in methods, or prevent (in some cases) a method from running. For example, the selection for carrier gas control mode, when available, changes the parameters available for all methods used on the HS.

Similarly, the HS changes the available configuration choices based on installed accessories. For example, adding a carrier gas EPC module accessory automatically adds new configuration choices. See Table 11.

Table 11 How installed hardware changes available parameters and choices

Hardware	When installed, find:
G4562A, 7697A Carrier Gas EPC Module Accessory	Choices for carrier gas control. When not installed, only GC carrier gas control is available.
111 vial tray	111 vial positions for a sequence.
12 vial carousel	12 vial positions for a sequence.
G4561A, 7697A Barcode Reader Accessory	Method parameters for barcodes. Barcode sequence actions.
G4563A, 7697A Cooling Plate Accessory	Method parameters for cooling the vial racks.

Configuration Parameters

Depending on the installed hardware, the HS provides the following configuration parameters:

Vial Gas type: Select the gas type used for vial pressurization, helium or nitrogen.

Loop volume (mL): Set the size of the sample loop. Press [**Mode/Type**] to choose from a predefined list of standard Agilent sample loop sizes. If using a custom loop size, enter the size, in mL, directly and press [**Enter**].

Carrier Gas type: Available only if the optional EPC carrier gas module is installed. Select the gas type used for the carrier gas.

Carrier: If the optional 7697A Carrier Gas EPC Module Accessory is not installed, the display reads **GC Control**, and no further setpoints are available. In this case, the GC carrier gas is plumbed to the HS, so that the GC controls carrier gas flow. If the optional EPC module is installed, configure the carrier gas control mode. Press [**Mode/Type**] to select. See “Configuring Carrier Gas Control”.

Gas Saver: (Requires optional EPC module) If in **HS Control** mode, the **Gas Saver** parameter appears. After the injection cycle, the HS can reduce the additive carrier gas flow in order to reduce gas consumption. Enter the desired reduced flow rate, in mL/min, or press [**Off/No**] to disable and keep the flow rate constant at the injection level. In general, maintain sufficient flow to keep the sampling system clean.

If using HS control of carrier gas flow, enter the GC column dimensions. The HS can only calculate flow rates for simple columns. It cannot calculate flow rates through complex columns, such as an Agilent 7890A GC set up for backflushing, or which uses LTM columns or flow splitters.

Column Length (m): Enter the column length, in meters. Use the current actual length if the column has been trimmed significantly.

Column Diameter (u): Enter the nominal column film thickness, in micrometers (µm).

Col Film thickness (u): Enter the column film thickness, in micrometers (µm).

Standby flow: Enter the flow rate of purge gas that flows through the sample loop, sample probe, and vent between sequences. This purge flow keeps the sampling system dry and prevents atmospheric contamination from entering the HS.

- Enter the desired flow rate, in mL/min, then press [**Enter**].
- Select **Off** to turn off the standby flow (not recommended).

Status: Select and press [**Enter**] to change the order of status items displayed.

1. Scroll to the first item to display in the status. Press [**Enter**].
2. Continue selecting items.

   The items will appear in the status display in the order that you selected them.

Clock: Select to set the date and time, or to set the preferred date format.

1. Scroll to **Time zone** and enter the offset from GMT (Greenwich Mean Time), in hours and minutes (hhmm). Press [**Enter**].
2. Scroll to **Time** and enter the current local time, using 24-hour format.
3. Scroll to format. Press [**Mode/Type**] to select the desired format for displaying the date.
4. Scroll to **Date** and enter the date in the current format.

APG Polarity: See “APG Remote Polarity”.

Instrument Schedule: See “Instrument Schedule (Resource Conservation)”.

APG Remote Polarity

The APG Remote start/stop cable is used to synchronize two or more instruments. The cable carries the signals used to monitor system readiness between the connected instruments (HS, GC, and MS/MSD if used) and to send the start command when a device in the system begins a run. Typically, in a HS system, the start command comes from the HS sampler. When the HS is ready for the first injection, it sends a start signal to the other devices connected using the APG Remote cable.

The HS provides two choices for APG Remote Polarity, **Active high** and **Active low**.

- Most Agilent instruments respond to **Active high**. To signal a start, the signal voltage increases.
- If your GC requires a drop in voltage to indicate a start command, select **Active low**.

APG Remote signal electrical specifications

The APG signals are a modified open collector type. The signal levels are generally TTL levels (low voltage is logic zero, high voltage is logic one) but the open circuit voltage will be between 2.5 and 3.7 Volts. The typical voltage is 3 Volts. A voltage over 2.2 Volts will be interpreted as a high logic state while a voltage below 0.4 Volts will be interpreted as a low logic state. These levels provide some margin over the specifications of the devices used.

The pull-up resistance, connected to the open-circuit voltage, is in the range of about 1 K ohms to 1.5 K ohms. For a logic-low state, for a single device on the bus, the minimum current you must be able to sink is 3.3 milliamps. Since devices are connected in parallel, when you have multiple devices this minimum current must be multiplied by the number of devices attached on the bus. The maximum voltage for a low-input state = 0.4 V.

The bus is passively pulled high. Leakage current out of a port must be less than 0.2 milliamps to keep the voltage from being pulled lower than 2.2 Volts. Higher leakage current may cause the state to be interpreted as a low.

Over-voltage protection: APG Remote connections are clamped by a zener diode to 5.6 Volts. Exceeding this voltage will damage the circuit (main board).

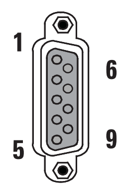
APG Remote - Suggested drive circuits

A signal on the APG bus may be driven by another APG device or by one of the following circuits:

- A relay, with one side connected to ground, when closed will set a logic-low state.
- An NPN transistor, with the emitter connected to ground and the collector connected to the signal line will set a logic-low state if proper base current is supplied.
- An open-collector logic gate will perform this same function.
- A low-side drive IC will also work, but Darlington-type drivers should be avoided as they will not meet the low-side voltage requirement of less than 0.4 V.

APG Remote connector

The signals for each pin on the connector are shown below.



Pin	Function	Logic
1	Digital ground	
2	Not used	
3	Start	LOW true (input)
4	Start relay	
5	Start relay	
6	Not used	
7	Ready	HIGH true (output)
8	Not used	
9	Not used	

APG Remote signal descriptions

Ready (High True): If the ready line is high (> 2.2 VDC) then the system is ready for next analysis. Receiver is any sequence controller.

Start (Low True): Request to start run/timetable. Receiver is any module performing runtime-controlled activities.

Start Relay (Contact Closure): A 120 millisecond contact closure. Used as an isolated output to start another device that is not compatible or connected with APG Remote pin 3.

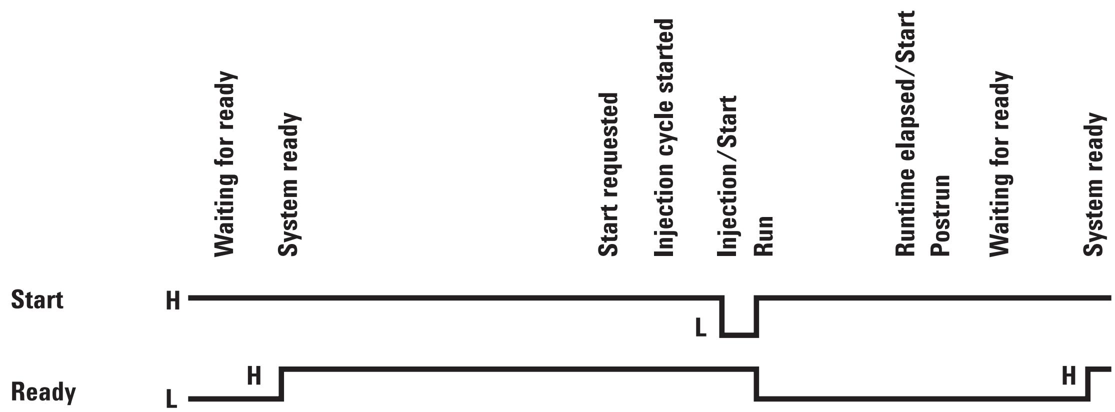


Figure 13 APG Remote timing diagram

Configuring Carrier Gas Control

The 7697A headspace sampler is usually installed so that the GC carrier gas flows through the HS. The GC method parameters completely control the flow of carrier gas through the HS–GC system. However, if using the optional 7697A Carrier Gas EPC Module Accessory, the HS can control the carrier gas flow. Typical uses include connection to a non-Agilent GC.

See also "Carrier".

GC Control

This is the default installation. The GC carrier gas must be plumbed from the GC EPC module to the **Carrier** fitting on the back of the HS. See Figure 14.

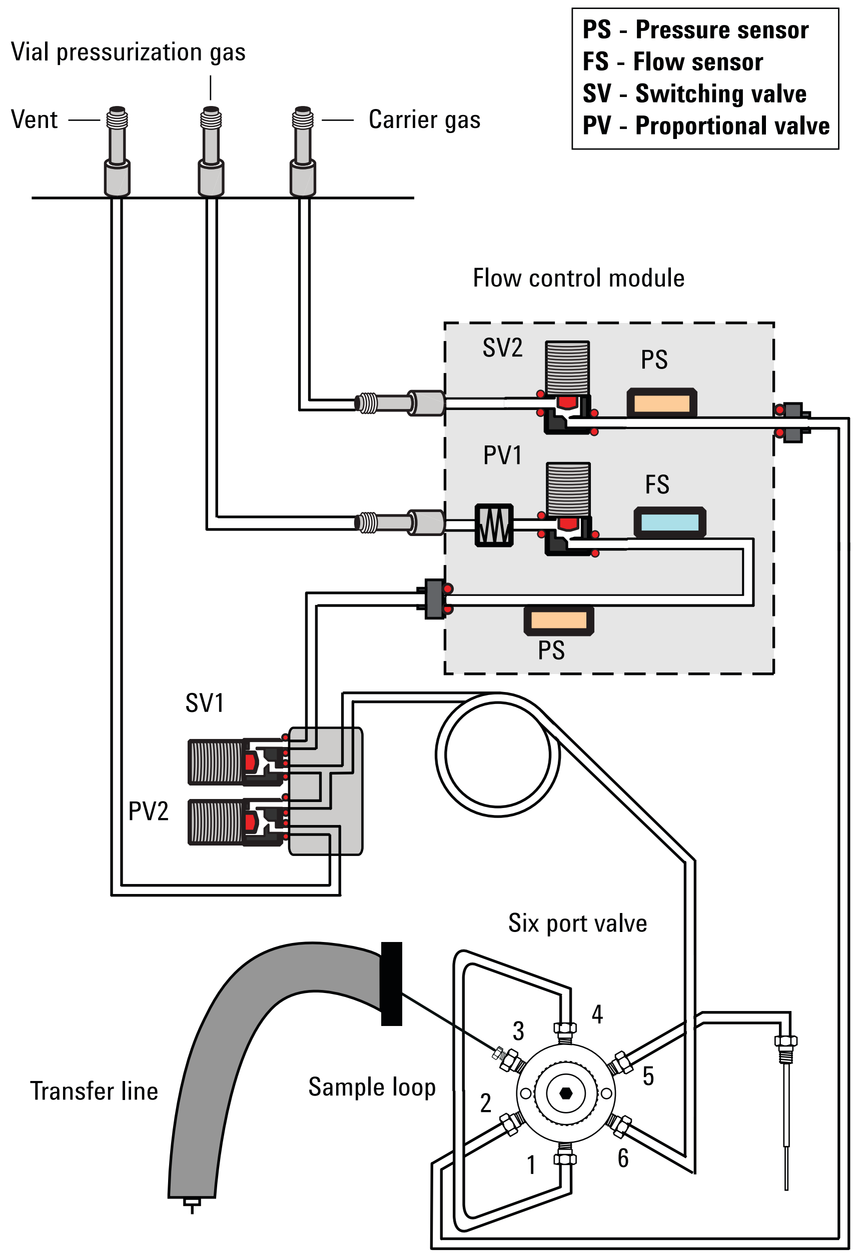


Figure 14 Gas flow paths in the standard configuration

When using **GC Control** for carrier gas, the HS provides no method settings for carrier gas. The sample is injected by switching the sample loop into the carrier gas stream. The HS displays a pressure reading for the carrier gas, but cannot determine a flow rate.

If using the optional 7697A Carrier Gas EPC Module

Accessory, you can select **GC Control** mode only if the carrier gas is plumbed as noted above. In this case, the carrier gas runs through the optional EPC module. The HS can display both flow and pressure data, although it does not provide setpoints. See Figure 15.

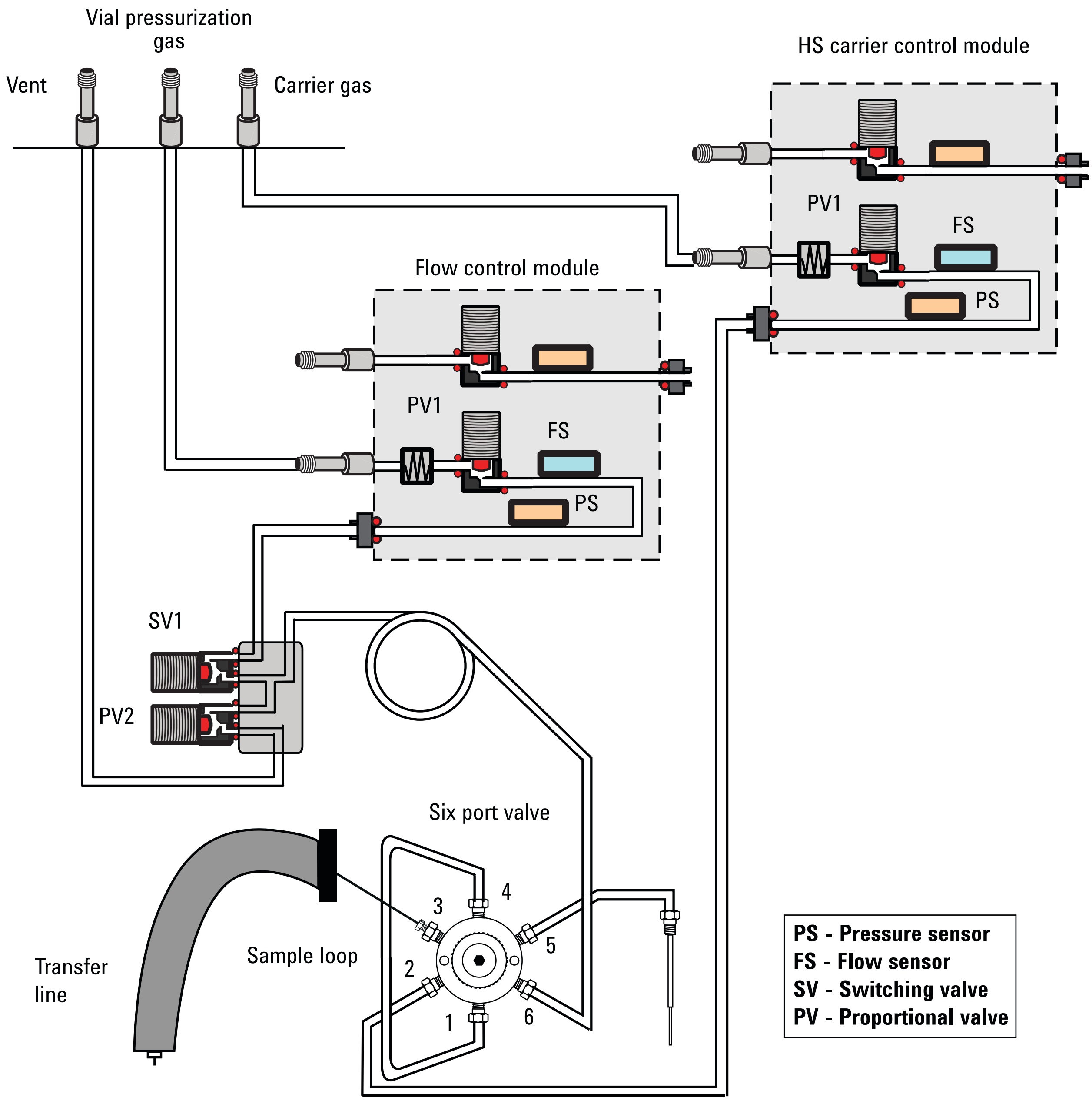


Figure 15 Gas flow paths with the optional 7697A Carrier Gas EPC Module Accessory installed

HS Control

Requires the optional 7697A Carrier Gas EPC Module Accessory.

Select **HS Control** mode to enable HS control of the carrier gas flow. In this installation, a source of carrier gas is plumbed to the HS **Carrier** fitting. See Figure 15. The HS provides all of the carrier gas for the GC.

Any methods used when configured in this mode must include:

- The column flow or pressure program
- GC thermal program information
- A selection for the control mode (flow or pressure)

When in this mode, you must enter the GC column dimensions in the HS so that the HS can provide the correct flows or pressures during GC thermal programming.

GC + HS Control

Requires the optional 7697A Carrier Gas EPC Module Accessory.

Select **GC + HS Control** mode to inject samples using an additive flow. In this case, the GC maintains and uses its own carrier gas supply. The HS uses its own carrier gas supply. To inject the sample, the HS provides an additional flow into the GC inlet.

Any methods used when configured in this mode must include the additive flow rate.

Selecting this mode enables the **Gas Saver** configuration setting for additive flow.

Instrument Schedule (Resource Conservation)

The HS 7697A HS can conserve resources (power and gases) using the instrument schedule.

If enabled, the HS loads the “Sleep” method at the specified time. Program the sleep method to use lower temperatures and gas flows. At the specified “Wake” time, the HS will load the “Wake” method. The wake method can also be the method that was active before the HS loaded the Sleep method. The wake method prepares the HS for use, even if unattended.

A simple use case is a laboratory with working hours from 8 AM to 5 PM, Monday through Friday. Set the HS to load the sleep method at, for example, 6 PM during the week. Set the HS to load the Wake method at 7 AM Monday through Friday. In this example, the HS can heat and stabilize for an hour before employees arrive.

Note the following:

- The HS never loads a sleep or wake method if a sequence is running.
- The HS does not retry loading the wake or sleep method if it skips the schedule due to activity.
- You can load a different method or start a sequence at any time. The instrument schedule does not prevent or delay sequence execution (except for any times required to reach the new setpoints).
- The HS uses its clock, not the clock on the data system computer.

Resource conservation when using an Agilent data system

Set the resource conservation choices using the data system. The data system also provides some simplifications, for example, a 5 day plus weekend schedule.

To program an instrument schedule

1. Press [**Config**], then scroll to **Instrument schedule** and press [**Enter**].
2. Scroll to **Sleep/Wake Enable** and press [**On/Yes**]. More choices and settings appear.
3. Scroll to **WakeUp Method** and press [**Mode/Type**].

4 To use the custom wakeup method, select **Wakeup**. To use the last active method, select **Prior active method**.

5 Set the wakeup and sleep times for each day of the week.

- Press [**Off/No**] to disable wake or sleep for that day. The HS will not load the selected method (wake or sleep).
- Enter the time to load the wakeup or sleep method, using a 24-hour clock. For example, to enter 6 PM, input **1800**, [**Enter**]. To enter 7:45 AM, input **0745**, [**Enter**].

6 Load the sleep method and edit as desired. Save the method.

7 If using the Wakeup method, load it and edit as desired. Save the method.

To turn off the instrument schedule, set **Sleep/Wake Enable** and to **Off**.

6
Options

Calibration 80
Communication 82
Keyboard and Display 84

This chapter describes various options available at the headspace sampler keypad through the [**Options**] key.

Calibration

Use the calibration options to calibrate headspace sampler sensors. To access the calibration parameters, press [**Options**], scroll to **Calibration**, then press [**Enter**].

Table 12 Calibration options

Parameter	Comments
Atmospheric pressure	Select to recalibrate the HS pressure sensor for atmospheric pressure.
Tray	111 Vial model only. Select to calibrate the tray robotic arm (gantry axis movement and other movements).
Vial sensors	Select to calibrate the flow and pressure sensors for the vial pressurization gas.
Carrier sensors	Select to calibrate the flow and pressure sensors for the carrier gas. If the optional carrier gas EPC module is not installed, only a pressure sensor is present.

To calibrate the atmospheric pressure sensor

1 Press [**Options**], scroll to **Calibration**, then press [**Enter**].
2 Select **Atmospheric pressure** then press [**Enter**].

   The last line of the calibration display shows the time and date of the last manual calibration, or **Factory calibration** if using the factory defaults.

   Actual atm pres displays the current reading.
3 Scroll to **Correction**, input the correction, and press [**Enter**]. The new time and date for the calibration is shown.

To delete the calibration, scroll to **Correction** and press [**Delete**], then [**On/Yes**].

To calibrate the tray

If using a 111 vial model, the tray may require periodic calibration. Calibrate the tray as follows:

1 Remove the tray racks.
2 Press [**Options**], scroll to **Calibration**, then press [**Enter**].

3 Select **Tray** then press [**Enter**].

The **Status** line of the calibration display shows the last manual calibration, or **Not calibrated** if using the factory defaults.

Rail axis offset, **Gantry axis offset**, and **Z-axis offset** display the current calibration values.

4 Scroll to **Start calibration**, then press [**Enter**]. The calibration routine starts.

To calibrate the gas sensors

The vial pressurization gas and carrier gas sensors can be calibrated. 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.

- When calibrating a pressure sensor, turn off the gas supply at its source and disconnect from the HS to release any residual backpressure.
- When calibrating a flow sensor, turn off the gas supply at the source, but leave it connected.

1 Press [**Options**], scroll to **Calibration**, then press [**Enter**].

2 Select **Vial sensors** or **Carrier sensors**, then press [**Enter**].

3 Select the desired sensor (if available), flow or pressure.

   - Press [**On/Yes**] to calibrate the sensor.
   - Press [**Off/No**] to restore the factory defaults.

The HS will measure the offset and adjust the sensor.

Communication

Use these settings to set the HS communications parameters. To access them, press [**Options**], then scroll to **Communications** and press [**Enter**].

Table 13 Communications options

Parameter	Comments
IP	Select to enter the IP address for the HS LAN connection.
GW	Select to enter the gateway for the HS LAN connection.
SM	Select to enter the subnet mask for the HS LAN connection.
Enable DHCP	Select to enable or disable DHCP addressing for the HS. Requires a reboot. **DHCP is not supported by all data systems.**
7697 Remote	If the HS is connected to a computer, this line appears and shows the computer name.
Connections	Shows the number of devices communicating with the HS through the LAN port. The HS can host one owner (one data system, for example) with complete control, plus other "read only" connections. • Typically, this number is 1 if using only a data system. • If the number is 2 or more, another computer besides your data system is connected to or trying to connect to the HS. • Agilent Instrument Utilities adds a connection also, but Instrument Utilities does not require instrument control unless performing tasks (for example, updating firmware or running a test).
Reboot instrument	Select to reboot the HS without pressing the power button.
MAC Address	The MAC address for the network interface card (NIC) within the headspace sampler.
Connection timeout	The length of inactivity before the HS assumes a connection to a host (a data system or Agilent Instrument Utilities software, for example) has been lost and drops the connection.

To set the LAN address at the keyboard

1 Press **[Options]**. Scroll to **Communications** and press **[Enter]**.

2 Scroll to **IP**. Enter the numbers of the HS IP address, separated by dots, and press **[Enter]**. A message tells you to power cycle the instrument. Do not power cycle yet. Press **[Clear]**.

3 Scroll to **GW**. Enter the Gateway number and press **[Enter]**. A message tells you to power cycle the instrument. Do not power cycle yet. Press **[Clear]**.

4 Scroll to **SM** and press **[Mode/Type]**. Scroll to the appropriate subnet mask from the list given and press **[Enter]**. A message tells you to power cycle the instrument. Do not power cycle yet. Press **[Clear]**.

5 Scroll to **Reboot instrument**. Press **[On/Yes]** and **[On/Yes]** to power cycle the instrument and apply the LAN setpoints.

To use a DHCP server

Note that DHCP is not supported by all Agilent data systems. Most data systems instead require a fixed address. By using the HS MAC address, however, you can also use DHCP to assign a host name for the HS, and use this host name to configure the HS in the data system.

1 Press **[Options]**. Scroll to **Communications** and press **[Enter]**.

2 Scroll to **Enable DHCP** and press **[On/Yes]**. When prompted, turn the instrument off and then on again.

Keyboard and Display

The HS provides the keyboard options listed in Table 14 below.

Table 14 Keyboard and display options

Parameter	Comments
Keyboard lock	When locked, a local user can use the keyboard to start or stop a sequence, or enter a priority sample (standalone use), but cannot edit method setpoints or sequences.
Hard Configuration lock	**On** prevents keyboard hardware configuration changes (such as installing a new EPC module); **Off** removes lock.
Key click	Click sound when keys are pressed.
Warning beep	Allows you to hear warning beeps.
Method modified beep	Turn on for high pitched beep when a method setpoint is modified.
Pressure units	Press [**Mode/Type**] to select the desired pressure units for the display: • **psi**: pounds per square inch, lb/in^2 • **bar**: absolute unit of pressure, dyne/cm^2 • **kPa**: mks unit of pressure, 10^3 N/m^2
Language	Select [**Mode/Type**] to choose the display language: English or Chinese (中文).
Radix type	Press [**Mode/Type**] to select the radix type. Note that some data systems may require a particular radix, regardless of locale. Match the radix used in the data system for best results.
Display saver	Select **On** or **Off**. When on, the display dims after a period of inactivity.

7
Early Maintenance Feedback

What is Early Maintenance Feedback? 86
To Set Up EMF for Use 87
To Set a Limit for a Counter 88
To Reset a Counter 89
To Disable EMF 90

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

What is Early Maintenance Feedback?

Use the Early Maintenance Feedback (EMF) features of the HS to schedule a reminder to replace a part before it can impact an analysis. EMF provides an alert on the HS display when a consumable item reaches its user-defined lifespan. The HS tracks lifespan using a counter associated with the consumable item. When the counter reaches a user-defined threshold, the HS lights the **Service Due** LED and enters a message in the Maintenance log.

Table 15 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. Note that tray counters appear on the HS display only if a 111 vial tray is installed.

Table 15 7697A Counters

Item	Counter
Transfer line	Injection cycles
Probe	Injection cycles
Vent valve	Injection cycles
6-Port rotor	Injection cycles
6-Port valve	Injection cycles
Sample loop	Injection cycles
Vent tubing	Injection cycles
Gripper pads	Tray gripper moves
Tray calib	Instrument uptime

Agilent's Instrument Utilities software may provide additional EMF features.

To Set Up EMF for Use

To use EMF:

1 After performing maintenance on an item (replacement or calibration, for example), set a limit for its counter. See To Set a Limit for a Counter.

2 The counter will increment as the HS performs injections and runs sequences.

3 When the counter exceeds the limit, the HS will light the **Service Due** indicator and log an entry into the **Event** log.

4 Replace or calibrate the item.

5 Reset the item's counter. See To Reset a Counter.

To Set a Limit for a Counter

Before setting a limit for the counter, determine the point at which the part needs to be changed. For example, you may have determined that the deactivated fused silica transfer line begins to degrade (becomes active) after running a certain number of samples. Set the counter limit slightly below this threshold. A good counter limit will provide a chance to perform maintenance before the chromatography suffers.

To set a limit for a counter:

1 Press [**Service Mode**].
2 Scroll to **Service Reminders**, then press [**Enter**].
3 Scroll to the desired counter.
4 Enter a threshold value, then press [**Enter**].

To Reset a Counter

Resetting a counter restores the counter to zero (0). Reset a the counter for each consumable item after replacing it.

To reset a counter:

1 Press [**Service Mode**].
2 Scroll to **Service Reminders**, then press [**Enter**].
3 Scroll to the desired counter.
4 Enter a threshold value, then press [**Enter**].

The HS logs the reset event.

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To Disable EMF

To disable EMF for one or more counters:

1 Press [**Service Mode**].
2 Scroll to **Service Reminders**, then press [**Enter**].
3 Scroll to the desired counter.
4 Enter **0**, then press [**Enter**].
5 Repeat for each counter to disable.