Agilent

Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion

User Guide

Notices

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Contents

Introduction

Gas chromatograph/mass spectrometer (GC/MS) instruments are used for a wide variety of critical analyses in areas such as food safety, environmental, forensics, and petrochemicals. Historically, helium is the preferred carrier gas for GC/MS. Helium is an inert gas with favorable chromatographic characteristics for high resolution separations that minimize unwanted reactions of analytes in the chromatographic process. Helium is also optimal for use with electron impact (EI) MS in terms of sensitivity. The vast majority of spectra in reference libraries such as NIST are acquired with helium carrier gas.

In recent years, recurring difficulties with the availability and price of helium have resulted in users of GC/MS considering changing to alternative carrier gases. In GC without MS, several different carrier gases have been used successfully. Hydrogen, nitrogen, and argon (with or without methane) have all been used. However, for EI GC/MS, the only practical alternative is hydrogen. Hydrogen has superior chromatographic properties in terms of speed of analysis compared with helium but can have some limitations due to its reactivity. Hydrogen is also compatible with EI MS, although with some drawbacks based on its reactivity and reduced sensitivity.

In general, helium is always a better choice for GC/MS analysis. If helium is available at a reasonable cost, it is clearly preferred. However, if it is not an option, hydrogen can be considered. The purpose of this document is to help users of Agilent EI GC/MS systems determine if hydrogen can be used as a carrier gas for their analyses and what considerations and procedures are necessary to make the transition successful.

Helium Conservation Techniques

Before deciding to convert your methods to hydrogen carrier gas, it is strongly recommended that you first consider helium conservation measures. Many of the conservation techniques can be implemented quickly and may result in substantial reductions in the rate at which helium is used. Even if you are going to pursue conversion to hydrogen, the helium conservation steps can be used during the transition period to save helium while the new hydrogen methods are being developed and validated.

A few of the key conservation measures will be discussed in this guide, but users are encouraged to review the extensive information regarding helium conservation techniques available from **Agilent.com** at the **Alternate Carrier Gas Solutions** website for more details.

CAUTION **Agilent does not recommend turning off the GC gas flow because the GC/MSD vacuum may draw air through the GC inlet and column into the hot source and quadrupole and damage the MS.**

Agilent recommends using one or more of the following approaches for gas flow during conversion.

- **Gas Saver Mode** - Most GC/MS systems use either the split/splitless (SSL) or multimode (MMI) inlets. The column flow is generally very low, typically ~ 1 mL/min. In addition to the column flow, there is the septum purge, which is typically 3 mL/min. The split vent flow defaults to a constant 50 mL/min rate, but can vary widely depending on the application and can be quite high during split injections and at the end of splitless injections. The Gas saver parameter can be used to reduce the split flow to 20 mL/min after the split or splitless injection has been completed. The split flow then remains at 20 mL/min at all times except during the injection. In many cases the total flow used by the GC/MS system can be reduced by 50% or more by simply using Gas saver.
- **Helium Use Audit** - Agilent recommends that laboratories using helium for multiple systems perform a periodic helium use audit and leak check. Record the helium use of each system and calculate the total flow for all systems. Compare this value with the rate at which helium is used from the cylinder that supplies it. For example, if the total flow for all the helium consuming instruments in a laboratory is 500 mL/min and it is supplied by a cylinder that contains 8,000 L of helium (at STP), the cylinder should last approximately 10 to 11 days. If the cylinder requires changing every five days, then the system should be checked for leaks and unknown points of consumption. Laboratories, especially those with large helium distribution manifolds, that have performed an audit often find substantial savings. As an example, Agilent reduced helium consumption at the Wilmington, Delaware site by 40% after performing an audit.
- **Programmable Helium Conservation Module** - Some GC/MS systems are not in constant use and can spend a significant amount of time in standby condition. For these systems, Agilent offers the Programmable Helium Conservation Module. This device is an option for the Agilent 8890 and 7890 GCs. The module provides the capability to automatically switch the inlet subsystem to nitrogen carrier gas for those times when the GC/MS is not in use. When the GC/MS is going to be used, the module then switches back to providing helium as carrier gas. It typically takes 15 to 30 minutes to purge the nitrogen from the system and be ready for use. Switching between gases is time programmable so that, for example, the system can switch to nitrogen on Friday evening and then automatically revert to helium 30 minutes before the GC/MS is needed on Monday morning. This provides a substantial savings in helium consumption while keeping the instrument ready for use upon short notice.

Preparing for Conversion to Hydrogen Carrier Gas

Methods that will generally require less optimization include analytes that are:

- Durable compounds such as PAHs, hydrocarbons, and other low reactivity species
- Analyzed at high concentrations
- Analyzed with split injections
- Derivatized

Methods that will generally require more optimization include analytes that are:

- Fragile compounds
- Compounds that react with hydrogen
- Analyzed at trace concentrations

Regardless of the method to be adapted, there will be at least some changes required. Therefore, it is necessary to allot time for the necessary updates to SOPs and method validation.

It is important to recognize the differences between using hydrogen and helium carrier gas. Time should be allotted for adapting the methods, optimization, and resolving potential problems.

There are several topics to consider when converting from helium to hydrogen carrier for EI GC/MS.

Areas that will need attention are discussed in the following sections and include:

- Hydrogen safety
- Source of hydrogen
- Plumbing for hydrogen
- GC/MSD and GC/TQ hardware changes
- Choosing new chromatographic conditions
- Initial startup with hydrogen
- Potential reduction in signal-to-noise ratio (2 to 5 times or more) due to higher noise
- Changes in spectra and abundance ratios for some compounds
- Activity and reactivity with some analytes

Safety Considerations When Converting to Hydrogen Carrier Gas

Safety is always the first and most important consideration when handling gases. Being an inert gas, helium has relatively few properties of concern. The concerns are mostly related to proper handling of high-pressure cylinders and the possibility of asphyxiation if used in a confined space.

Hydrogen has the added concern of flammability. It is, therefore, necessary to become familiar with the safety aspects of the use of hydrogen with your Agilent GC/MS systems. For detailed safety information see the *Agilent Hydrogen Safety Manual for GC/MS* (part number G7003-90053).

The entire safety manual must be read and understood before connecting and using hydrogen as the carrier gas. Here are some of the key concerns with hydrogen from the document:

- The use of hydrogen as a GC carrier gas, detector fuel gas, or in the optional JetClean system, is potentially dangerous.
- When using hydrogen as the carrier gas or fuel gas, be aware that hydrogen gas can flow into the GC oven and create an explosion hazard. Therefore, be sure that the supply is turned off until all connections are made and ensure that the inlet and detector column fittings are either connected to a column or capped at all times when hydrogen gas is supplied to the instrument.
- Hydrogen is flammable. Leaks, when confined in an enclosed space, may create a fire or explosion hazard. In any application using hydrogen, leak test all connections, lines, and valves before operating the instrument. Always turn off the hydrogen supply at its source before working on the instrument.
- The split vent and septum purge ports for any inlet operated with hydrogen must be connected to a negative flow laboratory vent system to prevent the build up of hydrogen in the laboratory. This is especially important in labs with multiple GCs using hydrogen as the carrier gas.

Hydrogen is potentially explosive and has other dangerous characteristics.

- Hydrogen is combustible over a wide range of concentrations. At atmospheric pressure, hydrogen is combustible at concentrations from 4 to 74.2% by volume.
- Hydrogen has the highest burning velocity of any gas.
- Hydrogen has a very low ignition energy.
- Hydrogen that is allowed to expand rapidly from high pressure can self-ignite.
- Hydrogen burns with a nonluminous flame that can be invisible under bright light.

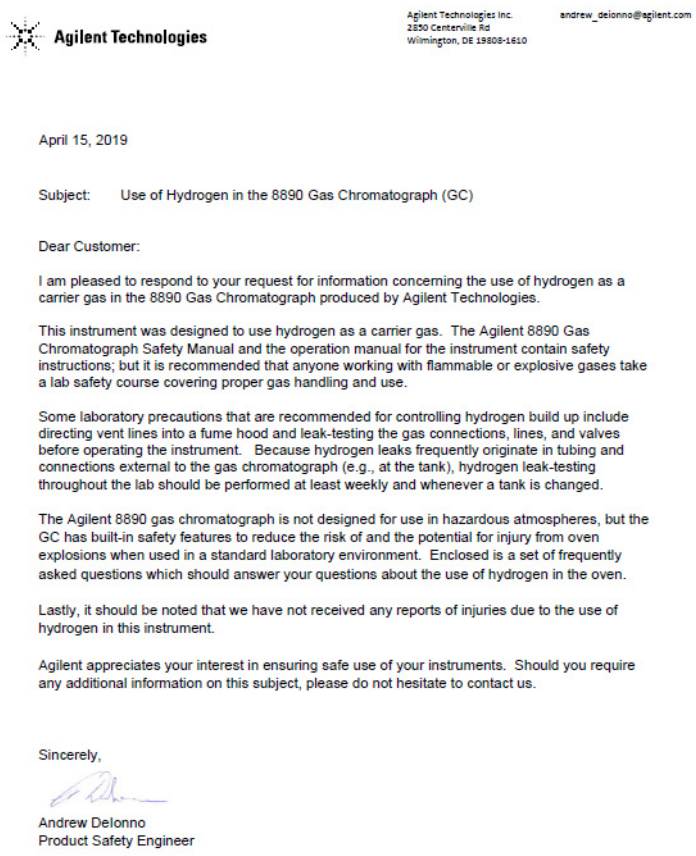
The Hydrogen Safety manual contains specific details for the safe operation of the GC and MS. Following all necessary safety precautions and all necessary operating parameter differences, it has been demonstrated that the Agilent 597Xx, 7000X, and 7010X series GC/MS systems can be operated safely with hydrogen as carrier gas rather than helium.

Figure 1 shows a letter from an Agilent safety engineer. It describes the hydrogen safety features of the Agilent 8890 GC. Letters are also available for the Intuvo 9000 and 7890 GCs. These may be helpful if requested by your facility safety personnel.

Some of the key hydrogen safety features of Agilent 8890 and 7890 GCs and MS systems are:

- **Safety shutdown** - When the gas pressure setpoints are not met, the valve and heater are shut off to prevent explosion
- **Flow limiting frit** - If a valve fails in the open position, an inlet frit limits the flow

- **Oven ON/OFF sequence** - A fan purges the oven before turning on heater to remove any collected hydrogen
- **Explosion test** - The GC and MS are designed to contain parts in case of explosion
- **Hydrogen sensor (optional)** - Agilent offers an optional oven hydrogen sensor accessory for its GCs. The hydrogen sensor will shut down the system if a hydrogen leak is detected in the oven, avoiding a possible hazardous situation. Benefits offered by the sensor include:
  - Integration into gas chromatograph
  - Detect potential leaks early to bring the system to a safe standby
  - Integrated calibration of sensor to ensure long-term reliability



Agilent Technologies

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andrew_delonno@agilent.com

April 15, 2019

Subject: Use of Hydrogen in the 8890 Gas Chromatograph (GC)

Dear Customer:

I am pleased to respond to your request for information concerning the use of hydrogen as a carrier gas in the 8890 Gas Chromatograph produced by Agilent Technologies.

This instrument was designed to use hydrogen as a carrier gas. The Agilent 8890 Gas Chromatograph Safety Manual and the operation manual for the instrument contain safety instructions; but it is recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use.

Some laboratory precautions that are recommended for controlling hydrogen build up include directing vent lines into a fume hood and leak-testing the gas connections, lines, and valves before operating the instrument. Because hydrogen leaks frequently originate in tubing and connections external to the gas chromatograph (e.g., at the tank), hydrogen leak-testing throughout the lab should be performed at least weekly and whenever a tank is changed.

The Agilent 8890 gas chromatograph is not designed for use in hazardous atmospheres, but the GC has built-in safety features to reduce the risk of and the potential for injury from oven explosions when used in a standard laboratory environment. Enclosed is a set of frequently asked questions which should answer your questions about the use of hydrogen in the oven.

Lastly, it should be noted that we have not received any reports of injuries due to the use of hydrogen in this instrument.

Agilent appreciates your interest in ensuring safe use of your instruments. Should you require any additional information on this subject, please do not hesitate to contact us.

Sincerely,

Andrew Delonno
Product Safety Engineer

Figure 1. Letter from Agilent safety engineer regarding suitability of 8890 Gas Chromatograph for use with hydrogen carrier gas.

Sources of Hydrogen for Use as Carrier Gas

As with any carrier gas, it is important to use only ultra-high purity hydrogen. There are several grades of hydrogen available for applications like welding, which are unsuitable for use as carrier gas because of the levels of impurities such as water and oxygen.

There are two main approaches for providing hydrogen for a GC/MS system:

- High pressure gas cylinders
- Hydrogen generators

High pressure cylinders

Cylinders are often less expensive initially. If you are evaluating hydrogen for the first time and are not certain you will be adopting it for routine use, cylinders may offer the simplest way to try hydrogen. Cylinders can be used while developing and testing new hydrogen carrier methods. Once the methods are determined, the hydrogen flow and pressure requirements of the methods can then be used to select a hydrogen generator, if desired.

Make sure to obtain hydrogen with a purity specification of 99.9999% or greater and with low oxygen and water levels. Also, use a cylinder regulator designed for use with high purity hydrogen applications. Consult your gas supplier for selecting an appropriate regulator.

NOTE

There may be restrictions on the use and placement of high pressure hydrogen cylinders in your laboratory, so it is a good idea to check with your facility safety personnel before purchasing any cylinders or regulators.

Hydrogen generators

Hydrogen generators are an alternative way of providing hydrogen carrier gas. They typically have a higher initial cost than cylinders but can be more economical over time.

As with cylinders, there are many different generators available with varying specifications of hydrogen purity. Only those with a purity specification of 99.9999% or greater and with low oxygen and water levels should be considered. When selecting a hydrogen generator, make sure the maximum delivery pressure and flow rate are high enough to meet the needs of your chromatographic methods and all the simultaneously operating instruments that will be supplied by the hydrogen generator.

Hydrogen generators also offer some useful safety features:

- Hydrogen is only generated at the needed pressure (for example 40 psi)
- Maximum flow is limited (for example 250 mL/min)
- Auto-shutdown if the setpoint pressure cannot be maintained
- Minimal stored gas (for example 50 mL at 40 psi) of hydrogen at any one time

Plumbing the Instrument for Hydrogen Carrier Gas

Carrier gas to the GC

Before making any plumbing changes, make sure that the GC and MS are turned off. The plumbing to provide hydrogen to the instrument must be clean and free of leaks. Dirty tubing can cause serious contamination problems. Chromatographic quality stainless steel tubing and fittings are often recommended for hydrogen plumbing and are the best choice if available.

NOTE **You may have to follow local codes or internal company guidelines.**

Copper tubing can also be used during the evaluation of hydrogen for conversion of methods. If copper tubing is used, it should be new 1/8-inch tubing, as old copper tubing becomes brittle and can break. Agilent sells new 1/8-inch copper tubing that has been cleaned for GC use (5180-4196 for 50 feet). If it is determined hydrogen will be used on a permanent basis, the system should be plumbed with stainless steel tubing and fittings.

Once the plumbing is completed, but with the GC turned off, pressurize the system briefly with hydrogen and check all connections with an electronic leak detector such as the Agilent G3388A Leak Detector. This step is necessary because the standard GC/MSD air and water background leak checks will not always find big outgoing hydrogen leaks.

When plumbing a hydrogen generator it is necessary to insert a moisture trap between the output of the generator and the GC. This is required to protect the GC EPC module in the event of water contaminating the hydrogen supplied by the generator.

NOTE **Hydrogen generators require periodic preventative maintenance. It is important that this be performed to prevent problems.**

Measurement of background levels of water, nitrogen, and oxygen levels should be performed later after all plumbing and column installation are completed, the system has been purged, and the GC/MS system pumped down with low temperature settings.

Vent/Exhaust lines

The split vent and septum purge vent for each installed inlet are located on top of the 8890, 8860, and 7890 GC. (**Figure 2**) These vents should be connected to a negative flow laboratory vent system. Use tubing of a large enough inside diameter to assure that no backpressure is built up, as this can cause problems. The septum purge flow is generally very low (3 mL/min) but the split vent flow can be as high as several hundred mL/min.

NOTE **The longer the vent line, the larger the id must be to avoid building pressure. In practice, 1/8-inch od × 1.65 mm id copper tubing works well for the split vent line if it does not exceed 2 m. For longer lengths, consider using larger id tubing.**

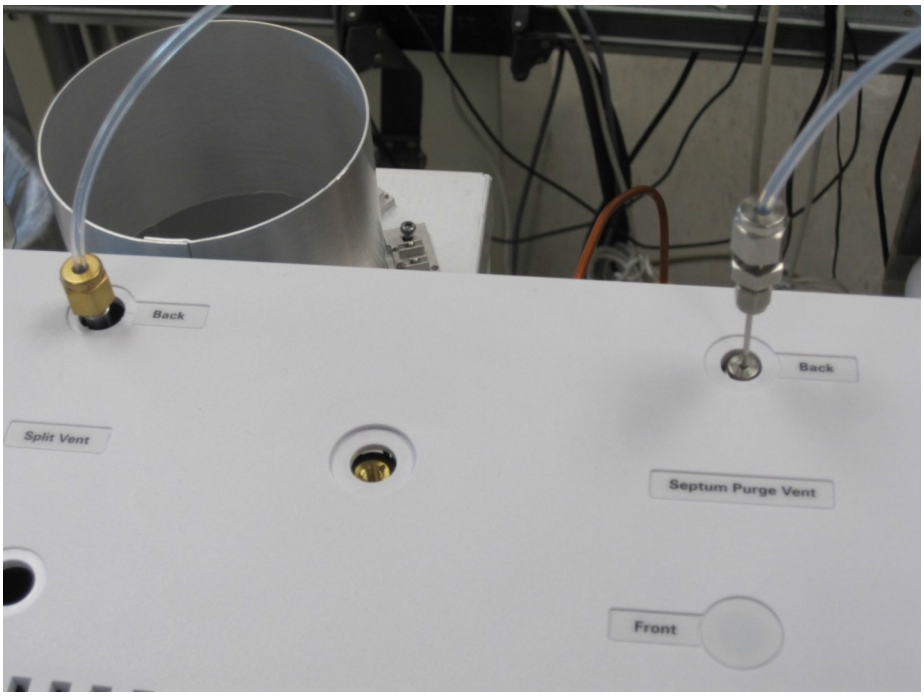

Figure 2. The split vent and septum purge vent for each installed inlet should be connected to a negative flow laboratory vent system.

Foreline pump exhaust

The foreline pump exhaust should be connected to a negative flow laboratory vent system. If the foreline pump is not currently set up this way, purchase a barb fitting, O-ring, and tubing. These can be purchased from Agilent:

- 3/8-inch male NPT to barb fitting, part number G3170-80006
- 20 feet of 1/2-inch tubing, part number G3170-60100
- O-ring for the barb fitting, part number 0905-1193

Additional parts that may be required can be ordered from the Agilent GC and GC/MS Consumables catalog.

When installing the tubing, try not to exceed 20 feet in length and make sure there are:

- No restrictions
- No kinks
- Very few sharp radius bends
- No low spots where oil could pool

Figure 3 shows a diagram of the plumbing for use with hydrogen carrier gas.

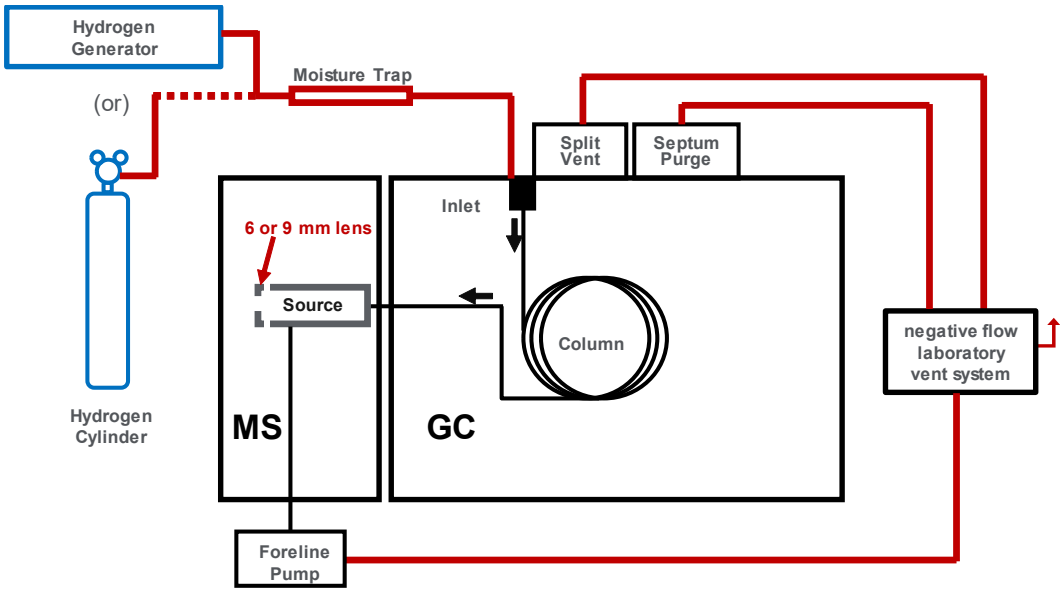

Figure 3. Diagram of the plumbing for use with hydrogen carrier gas.

MS Source Components Required for Conversion

Inert plus (extractor), inert, and stainless steel EI sources

Agilent extractor, inert, and stainless steel EI MS sources all come standard with a 3-mm drawout (inert and stainless steel sources) or 3-mm extractor lens (extractor source). The 3-mm diameter works well with helium carrier gas but can cause problems such as tailing and hydrogenation of analytes in the source when used with hydrogen. It is therefore necessary to replace the 3-mm lens with a larger diameter. Agilent offers both 6- and 9-mm lenses for this purpose. The 9-mm is recommended for most applications with hydrogen carrier gas, as it provides the best overall performance, balancing sensitivity, peak shape, and source reactivity. The 6-mm lens can be used if greater sensitivity is required but it is best to start with the 9-mm first. (**Figure 4**)

In general, hydrogen flows <1.0 mL/min are suitable for 6-mm lens. For hydrogen flows >1.0 mL/min and <1.4-mL/min, the 9-mm lens is required. Higher flows are not recommended for data acquisition.

Table 1 Optional lens part numbers for the extractor, inert, and stainless steel EI sources.

	6-mm	9-mm
Stainless Steel Drawout Lenses	G3163-20530	*
Inert Drawout Lenses	G2589-20045	G3440-20022
Extractor Lenses	G3870-20448	G3870-20449

* A stainless steel 9-mm drawout lens is not available but the 9-mm Inert drawout lens, p/n: G3440-20022, can be used with a stainless steel source.

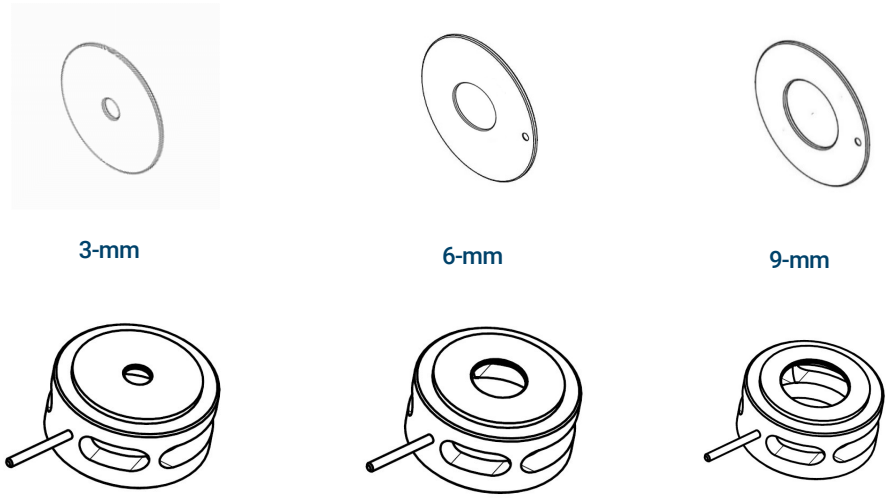

Figure 4. Drawout/extractor lenses for the extractor, inert, and stainless steel EI sources. Only the 6- or 9-mm (preferred) should be used with hydrogen carrier gas.

Additional parts required are can be ordered from the GC and GC/MS Consumables catalog.

Choosing a Column and Method Conditions

MS Hydrogen pumping capacity

The initial step in choosing a column and method conditions for use with hydrogen carrier gas is to determine the flow rate of hydrogen your system can effectively pump. The pumping capacity for hydrogen is approximately 1/2 that of helium. This limits the choice of columns and flows. When choosing a GC/MS system for conversion to hydrogen carrier gas, turbo pumps are preferred over diffusion pumps because their added pumping capacity allows greater flexibility in column flows. **Table 2** lists the optimal, maximum recommended, and maximum flows for hydrogen with Agilent GC/MS systems.

Table 2 Hydrogen flow rate recommendations for Agilent GC/MS systems.

	Optimal flow (mL/min H_2)	Maximum Recommended Flow (mL/min H_2)	Maximum Flow (mL/min H_2)
597Xx diffusion pump	~0.5	0.75	1.00
597Xx turbo pump	0.5 to 1.0	2.0	3.25
7000x/7010x	0.5 to 1.0	2.0	3.25
7200x/7250x	Hydrogen use not permitted		

It is helpful to have an ion gauge on the MS to monitor the vacuum versus column flow. Try to avoid flows that produce pressures higher than 5×10^{-5} Torr. Source performance starts to degrade above this pressure, and you may not get useful data.

Do not exceed the maximum flow into the MS at any time. If your method will use a pressure pulsed injection, verify the maximum column flow during the pulse does not exceed the listed maximum flow.

For methods that will use retention time locking (RTL), do not create the method with the nominal flow at the maximum listed. Since RTL requires changing the flow to match retention times, the locking flow for a different column or system may exceed the maximum flow. Create RTL methods with flow rates at least 30% below the maximum for your system to avoid this problem.

Choosing a Column and Method Conditions

Introduction

There are two major differences with using hydrogen versus helium as a GC carrier gas.

The first is the viscosity of hydrogen is lower than that of helium, meaning that the inlet pressure to obtain the same flow rate with hydrogen is significantly lower. Column dimensions and flow setpoints must be chosen that maintain adequate inlet pressures, preferably 5 psi or greater, to permit precise control of column flow and retention times. Sub-ambient inlet pressures must be strictly avoided as these can cause inlet flow shutdowns and may damage inlet liners and columns due to air being drawn into the system.

The second difference is in chromatographic performance. Hydrogen offers advantages for resolution and speed of analysis over helium. This results mainly from the shape of Van Deemter curve for hydrogen.

To determine appropriate column dimensions for the system, here are some important factors to consider:

1. If possible, use constant flow methods with GC/MS systems. Constant pressure methods with an oven temperature program have a negative impact on MS performance due to the changing flow into the source.
2. Determine the hydrogen pumping capacity of the MS hardware. With diffusion pump systems, try to use flows in the range of 0.5 to 0.7 mL/min and for turbo pump systems, 0.5 to 2 mL/min.
3. Optimal MS sensitivity and performance are obtained with 0.8 to 1.2 mL/min. Try to use a column flow in this range if you have a turbo pump.
4. The inlet pressure should be 5 psi or higher in the temperature range over which the analysis is run. At 25 °C, the inlet pressure should at least be 1 psi to avoid a carrier gas shutdown when the over door is open or when the oven heater is off.
5. The optimum column average velocity range for helium is 20 to 40 cm/sec. For hydrogen, it is 30 to 55 cm/sec. If the flow of helium or hydrogen is too low, peak resolution is lost much faster than if it is too high. Always operate at or above the minimum average linear velocity if possible (see **Figure 5** on page 18).

Simplified Approach to Column Conversion

If the current helium method uses a 30 m × 0.25 mm id × 0.25 µm film thickness capillary column, it may be possible to set up the hydrogen conversion method quickly with the following steps. This is a good starting point that can be optimized later, if necessary:

1. Purchase a 20 m × 0.18 mm id × 0.18 µm film thickness version of the current column with the same stationary phase type (DB-5ms, HP-5ms, etc.). Note, if the 30 m method uses a different film thickness than 0.25 µm, try to find a 0.18 mm id column with a phase ratio closest to the current one.
2. If the MS has a diffusion pump, set the hydrogen flow to 0.6 mL/min constant flow. If the MS has a turbo pump (preferred), set the hydrogen flow to 0.9 mL/min constant flow.
3. Set the new temperature program to the same values as in the current helium method. (This can be optimized later to speed up the method, if desired.)
4. If the helium method uses a pressure pulsed injection, and the MS has a turbo pump, set the pulse pressure of the new method so as not to exceed 3.25 mL/min during the pulse. Pulsed injections are not recommended with diffusion pumps due to insufficient pumping capacity.
5. If the MS has a high vacuum gauge, check to see if the pressure is >5 ×10^{-5} Torr. If it is, reduce the flow until it is less than 5 × 10^{-5} Torr.
6. The solvent elution time will be different, so determine a new solvent delay time for the method.
7. After conditioning the system as described later, run a calibration standard and find the new retention times of the analytes.

The following sections provide more details on parameters that can be adjusted to optimize the converted methods.

Column Dimensions

It is often necessary to change to a column of different dimensions when converting a GC/MS method from helium to hydrogen carrier gas. This is due to hydrogen's viscosity being lower than that of helium, meaning that the inlet pressure to obtain the same flow rate with hydrogen is significantly lower.

For example, 30 m × 0.25 mm id × 0.25 µm film thickness columns are widely used with helium in GC/MS applications. These columns are generally not suitable with hydrogen, because of insufficient inlet pressure as indicated in **Table 3**. **Table 3** lists the inlet pressures required for a flow of 1.0 mL/min for columns of various dimensions at ambient temperature (25 °C) and 100 °C with both helium and hydrogen carrier.

Table 3 Inlet pressures required for a flow of 1.0 mL/min with helium and hydrogen.

Column Dimensions	Inlet Pressure (psi) for He at 25 °C	Inlet Pressure (psi) for He at 100 °C	Inlet Pressure (psi) for H_2 at 25 °C	Inlet Pressure (psi) for H_2 at 100 °C
30 m × 0.25 mm id	6.36	10.75	–0.56	2.40
60 m × 0.25 mm id	15.09	21.29	5.29	9.48
20 m × 0.18 mm id	18.47	25.39	7.57	12.22
40 m × 0.18 mm id	32.21	41.99	16.79	23.37

NOTE **The 30 m × 0.25 mm id column has a low inlet pressure (2.4 psi) with hydrogen at an oven temperature of 100 °C. At ambient, the inlet pressure would be sub-atmospheric and therefore not usable.**

A 60m × 0.25 mm id column would give acceptable inlet pressures, provide better chromatographic separation, and have increased capacity, but would result in longer run times.

The 20 m × 0.18 mm id is a common choice for hydrogen use. It has acceptable inlet pressures with hydrogen and provides similar, and often better, chromatographic resolution than the 30m × 0.25 mm id columns. The sample capacity is about 1/3 of that for the 0.25 mm id column, so the amounts injected may need to be adjusted. These columns are a good starting point for method development.

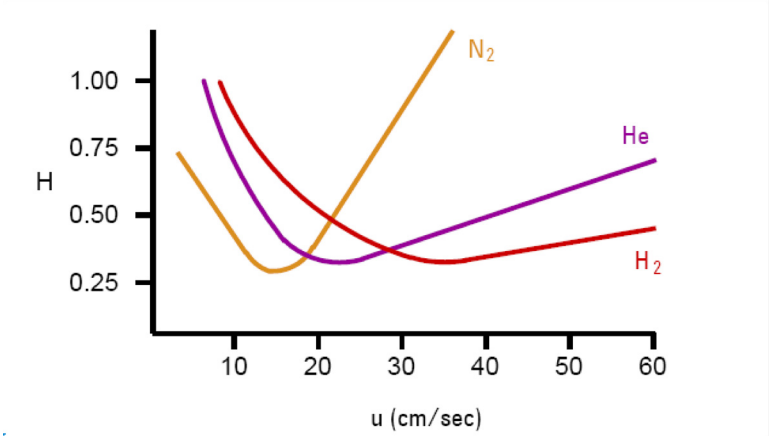

Figure 5. Van Deemter curves for nitrogen, helium, and hydrogen.

The optimum column average velocity range for helium is 20 to 40 cm/sec. For hydrogen, it is 30 to 55 cm/sec. However, since the slope of the Van Deemter curve for hydrogen is relatively flat with linear velocity, only a small amount of resolution lost with increasing average velocity above the optimal value. This is helpful when optimizing the speed of analysis.

NOTE **If the flow of helium or hydrogen is too low, you lose efficiency much faster than if it is too high. Therefore, operating at or above the minimum average velocity is important.**

Flow Calculator Tool

As an aid to developing new GC methods, Agilent offers free downloadable calculators for the GC. Before installing new columns to try with hydrogen, it may be helpful to use the calculators to determine if they would be a good fit. The calculators are available at:

https://www.agilent.com/en-us/support/gas-chromatography/gccalculators

The Pressure Flow Calculator tool is shown in **Figure 6** and **Figure 7**. With the column dimensions, carrier gas type, column outlet pressure, and oven temperature entered, the average velocity can be entered to see what the inlet pressure and flow would be. In **Figure 6** entering an average velocity of 35 (in blue) would give near optimal resolution, but the column flow and inlet pressure are unusably low (in red). In **Figure 7** the inlet pressure is entered as 5.0 psi (in blue) resulting in an acceptable linear velocity of 55.056 cm/s (in green). With this pressure, the outlet flow and inlet pressure are also at acceptable values.

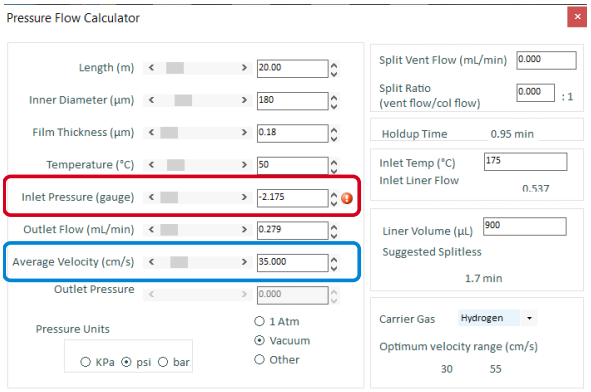

Figure 6. Using Agilent Pressure Flow Calculator to determine chromatographic conditions for 20 m × 0.18 mm id × 0.18 µm film thickness column with average velocity set near optimum 35 cm/sec.

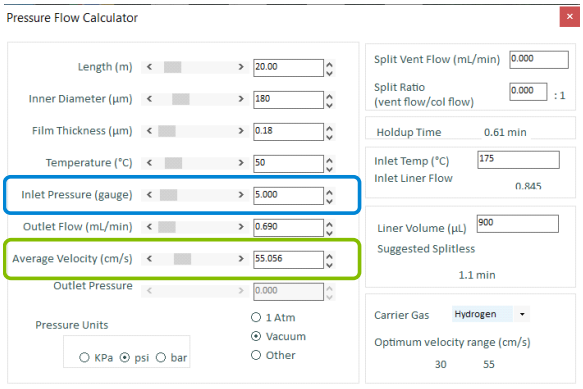

Figure 7. Using Agilent Pressure Flow Calculator to determine chromatographic conditions for 20 m × 0.18 mm id × 0.18 µm film thickness column with inlet pressure entered at 5 psi.

Other useful values provided are the holdup time and a suggested splitless time calculated based on the entered liner volume and inlet liner flow rate.

Another example of the usefulness of the calculator is determining the maximum pressure that can be used for pulsed injections. With the possibility of analytes reacting with hydrogen in the hot inlet, pulsed injections are worth considering. Pulsed injections also aid in transferring analytes from the inlet to a narrower column. **Figure 8** shows the calculation of the pulse pressure (in green) at the maximum allowable flow with a turbo pump system, 3.25 mL/min (in blue).

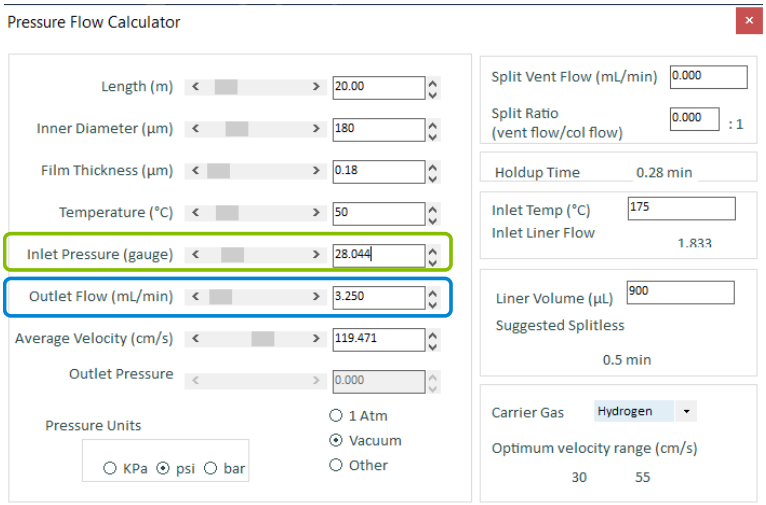

Figure 8. Calculation of the pulse pressure at 3.25 mL/min, the maximum allowable flow with a turbo pump system.

For the conditions used in the example, the calculator indicates that the maximum pulse pressure would be 28 psi. Because the inlet liner flow is higher, the suggested splitless time is lowered by more than two fold.

The Flow Calculator cannot be used for evaluating Intuvo GC flows due to the extra restrictions in the flow path. The Intuvo acquisition software must be used to determine flows.

Method Translator

The Method Translator is useful for optimizing speed improvements when converting from helium to hydrogen. It is designed to evaluate different sets of conditions while maintaining the same elution order and relative elution times.

The method translation tool works best with constant pressure methods in that it accurately predicts the retention times on the new column or same column with different parameters. Since only constant flow methods are recommended for GC/MS, the predicted retention times are not as accurate, and some analytes may reverse elution order. However, the process is still very helpful.

Here are a few things to consider when using the Method Translator:

- If evaluating moving to a different column, the phase chemistry (DB-5, HP-5ms, Innowax etc.) must be the same.
- The process works best with columns of the same phase ratio. If the same phase ratio is not available for the new column, pick one with the closest ratio.
- When increasing the speed of a method, any oven ramps are increased by the factor of the speed gain. Be sure to check if your oven can ramp at the new rate. If not, translate to a lesser speed gain that gives an oven ramp the system can maintain.
- Keep the flow rate in the ranges suggested previously as dictated by the MS pumping system.

Figure 9 shows the Method Translator evaluating moving from a 30 m × 0.25 mm id column with helium to a method with hydrogen carrier gas on the same column, but with a 2x gain in speed (that is, all the retention times on the new method would be approximately 1/2 of those in the original method).

The drawback with this translation is that it requires a relatively high flow, 1.8 mL/min, into the MS source. This is usable if the system has a turbo pump but would result in lower sensitivity. At 1.8 mL/min constant flow, the inlet pressure both during the analysis and with the oven off would also be acceptable.

NOTE **If the MS has an HES (high efficiency source) this flow rate would be too high.**

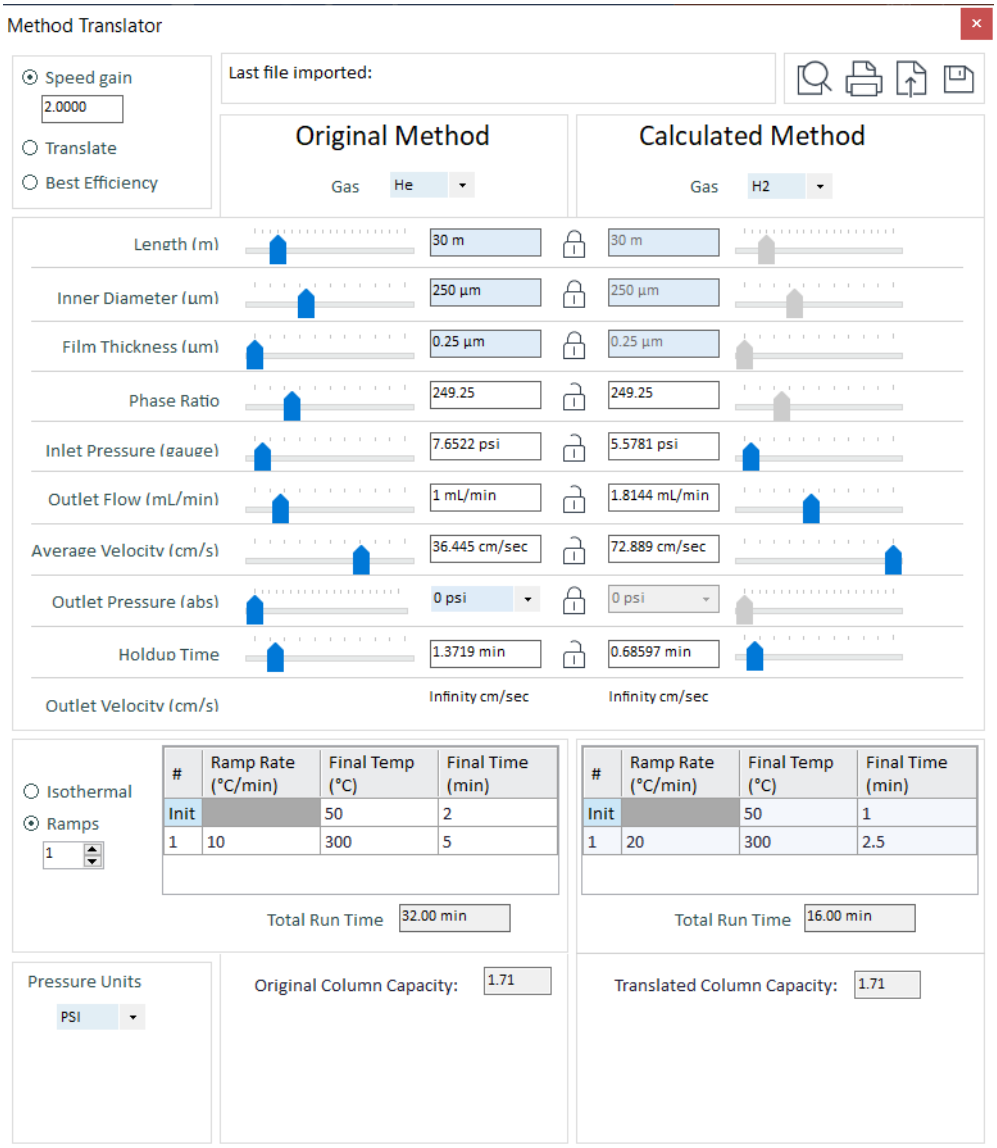

Figure 9. Method translation tool evaluating moving from a 30 m x 0.25 mm id column with helium to a method with hydrogen carrier on the same column with a 2x gain in speed.

Figure 10 shows the translation of the method to a 20 m x 0.18 mm id column with hydrogen carrier gas with a 2.5x gain in speed.

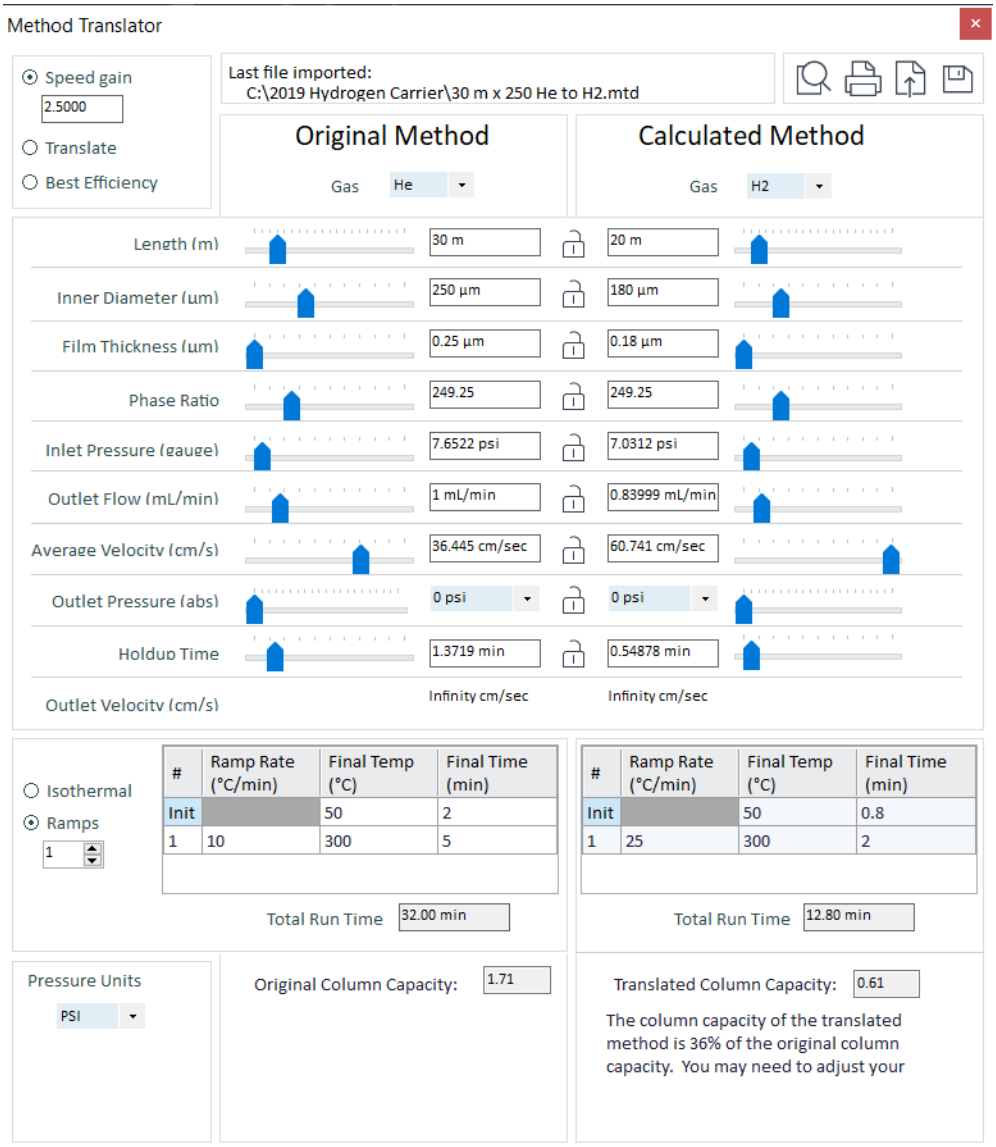

Figure 10. Translation of the method to a 20 m × 0.18 mm id column with hydrogen carrier gas with a 2.5x gain in speed.

With the translation to the 20 m × 0.18 mm id column, a speed gain of 2.5 is achievable with a flow rate in the preferred range. In the bottom right corner, the tool lists the translated column capacity, indicating the new column only has 36% of that with the original column. This method would be a good starting point for the conversion.

If the translation yields a ramp rate that is not attainable with the GC, try using a ramp rate that works (that is, does not cause the oven to go "NOT READY" during the analytical run) and raise the flow to a value in the acceptable range as discussed previously.

As with the Flow Calculator, the Method Translator cannot be used for evaluating Intuvo GC parameters due to the extra restrictions in the flow path. Use the Intuvo acquisition software to determine flows.

Initial Startup with Hydrogen Carrier Gas

After the system is set up with:

- An appropriate supply of hydrogen connected to the instrument and leak checked.
- The source has the correct larger diameter (preferably 9-mm) drawout or extractor lens installed.
- The column is chosen, installed, the appropriate flows set, and leak checked.
- Pumped down for at least one hour with heated zones (inlet, transfer line, source etc.) turned off.
- Heated zones brought to method temperature and allowed to stabilize for one hour.
- MS is tuned.

The system can be started, and testing of the method can begin.

There are typically three problems observed upon initial startup.

- High spectral background with ions at most masses up to about 300 *m/z*.
- Reduced signal-to-noise resulting in a worse MDL.
- Significant tailing for many compounds.

High spectral background

Figure 11 shows a typical background spectrum acquired with hydrogen carrier gas. The spectrum has response at virtually all masses up to 300 *m/z*. The background is very high at first but should drop gradually as the source bakes out. The high background is presumed to result from active hydrogen species cleaning the interior of the source, as is seen with JetClean. A detailed procedure for reducing the background is discussed in a later section.

Reduced signal-to-noise ratio

The high background results in additional baseline noise that reduces the signal-to-noise ratio (SNR) of analytes. As the background drops, the noise drops, and the SNR gradually improves.

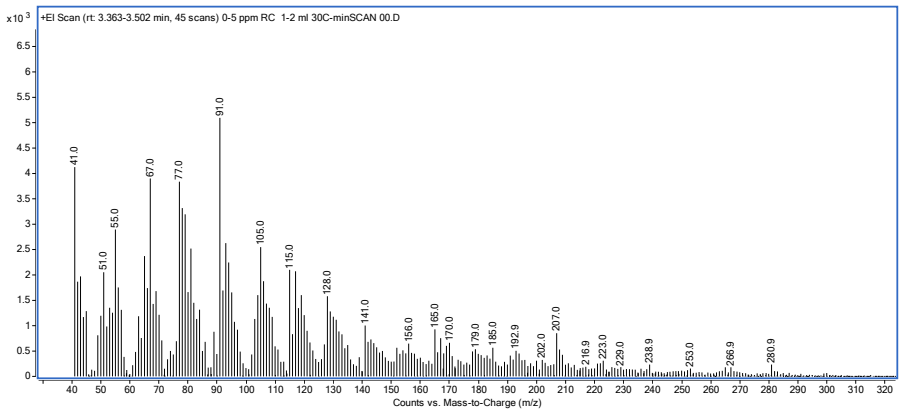

Figure 11. Mass spectrum of background with hydrogen carrier gas.

Severe tailing of some compounds

The third problem, significant tailing for many compounds, is shown in **Figure 12**. The top chromatogram is the TIC of a mixture of underivatized drugs at 5 ng/compound acquired with helium carrier gas. Some of the compounds exhibit tailing due to their polar nature, but most have acceptable peaks shapes.

The bottom chromatogram is the TIC of the same mixture shortly after the carrier gas was switched to hydrogen. The peak shape for phencyclidine (peak 9) is quite good, but the rest of the peaks have become significantly smaller and many exhibit severe tailing.

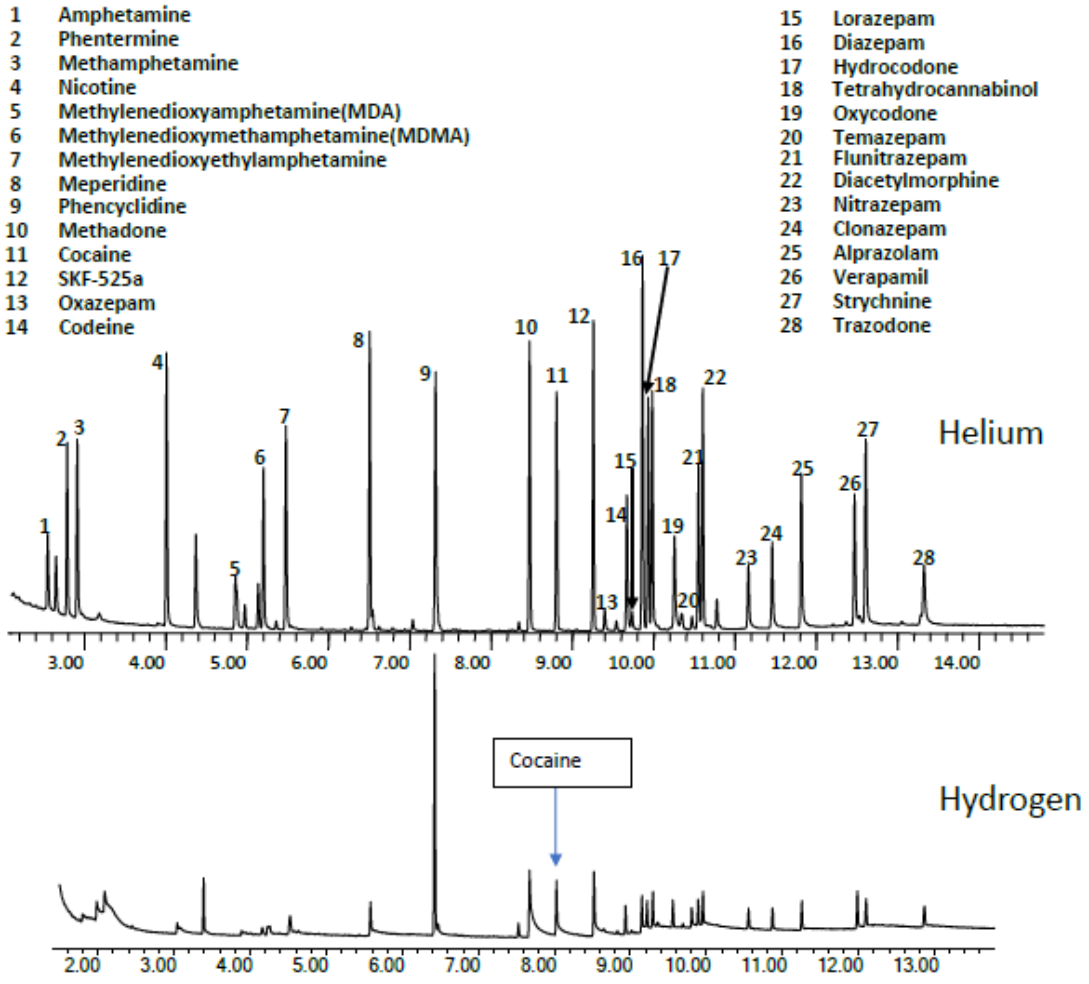

Figure 12. Drug test mix (5 ng/component) run with helium carrier gas (top) and hydrogen carrier gas shortly after initial startup (bottom).

Inspection of the cocaine peak in the TIC of the hydrogen chromatogram shows severe tailing not seen with helium carrier gas. This tailing is not typical chromatographic tailing.

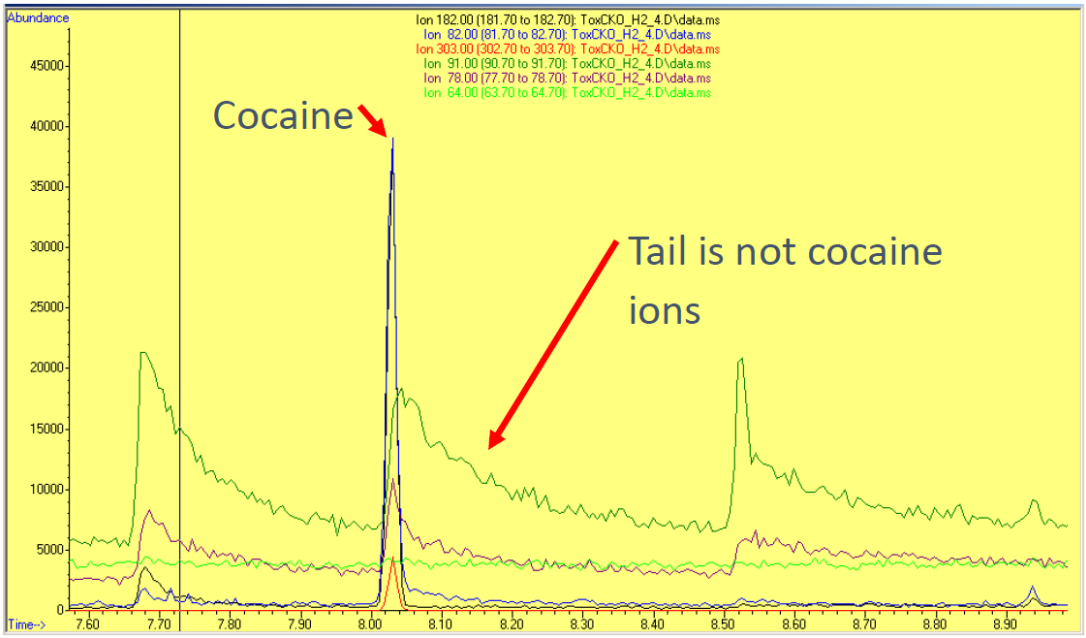

Figure 13. EICs from cocaine peak in **Figure 12** (bottom) with hydrogen carrier gas.

Figure 13 shows the extracted ion chromatograms (EIC) for the principal cocaine ions at *m/z* 182 (black), 82 (blue), and 303 (red). Note they have excellent peak shape. The tails are made up of ions unrelated to cocaine, with *m/z* 91 (green) being the most prominent.

The hydrogen carrier chromatograms in **Figure 12** and **Figure 13** were acquired with the 6-mm extractor lens. This tailing effect is more pronounced with the 6-mm than with the 9-mm lens. The 6-mm was used here to more clearly demonstrate the problem, but the 9-mm is preferred.

Obviously, this performance is unusable. Fortunately, there is a procedure to greatly reduce these problems.

Conditioning the source

The key to reducing the above three problems is to condition the source overnight. The recommended steps are:

1. Have a good source of clean hydrogen such as a >99.9999% purity hydrogen generator.
2. Keep the hydrogen flow limited to a value suitable for your pumping system.
3. Use an optional Hydrogen drawout lens/extractor lens. Start with the 9-mm first. If your maximum sensitivity is insufficient, try the 6-mm.
4. After setup, purging and pump down, go the MS acquisition program and:
   - **a** Set the source to max temp for your source (usually 350 °C, but check).
   - **b** Reduce the EMV to 800 V.
   - **c** Set the program to scan from *m/z* 40 to 300 continuously. This will keep the filament on, which is key to the conditioning process. Leave the FILAMENT ON overnight.
5. Peak shape will be much better, and background will be much lower in the morning.
6. Lower the source temp to method value, retune, and run some samples.

7 Always have extra filaments on hand in case one burns out. Like all GC/MS ion source parts, filaments are normal operator replaceable consumable parts.

The preceeding procedure works well with the 6-mm drawout or extractor lenses. With the 9-mm lens, and a source that is clean, it may not require overnight cleaning. It may be conditioned in 2 to 4 hours as determined by a lower background and improved peak shapes.

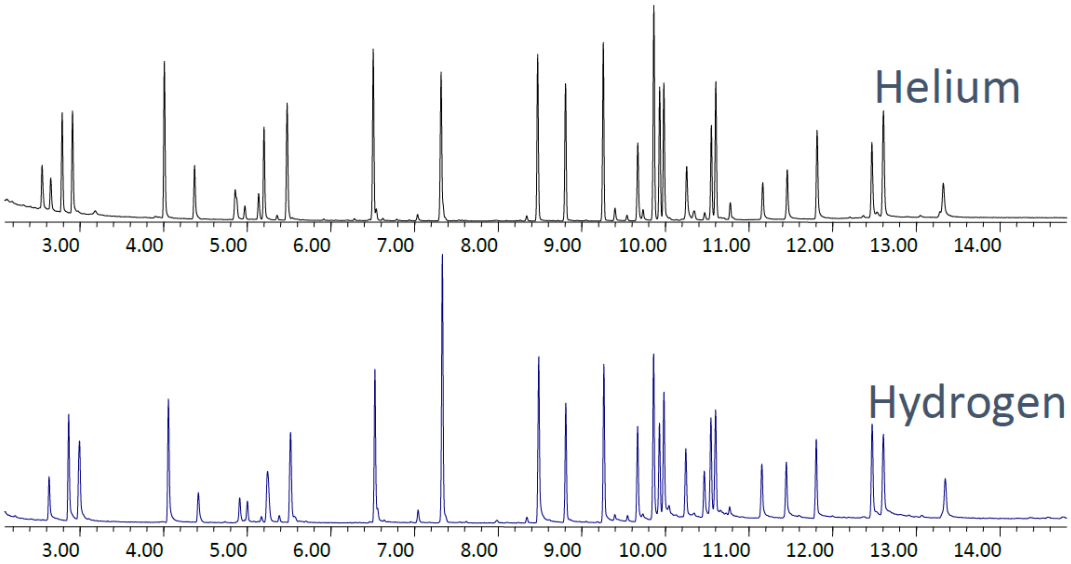

Figure 14. Drug test mix (5 ng/component) runs with helium carrier gas (top) and hydrogen carrier gas (bottom) after conditioning overnight.

Figure 14 shows the dramatic improvement obtained with the overnight conditioning step, greatly reducing all three problems of high background, high noise, and severe tailing.

Performance Expectations

Signal-to-Noise ratio

Signal-to-noise ratio is often worse by about 2 to 5 times or more with hydrogen carrier gas. This varies from compound to compound, so it is important to check all analytes to be determined with the hydrogen method.

Some compounds may disappear at low levels. Examples include: some nitrogen and oxygen containing compounds (alcohols, aldehydes, ketones) such as those found in flavor samples.

Spectral fidelity

While most spectra obtained with hydrogen carrier remain the same as those acquired with helium carrier gas, there are always exceptions. Users should check the reference spectra for important targets to make sure they have not changed

As an example, **Figure 15** shows the chromatograms of a test mixture acquired with both helium and hydrogen carrier gas. The mixture contains a diverse set of compound types to evaluate changes in spectra.

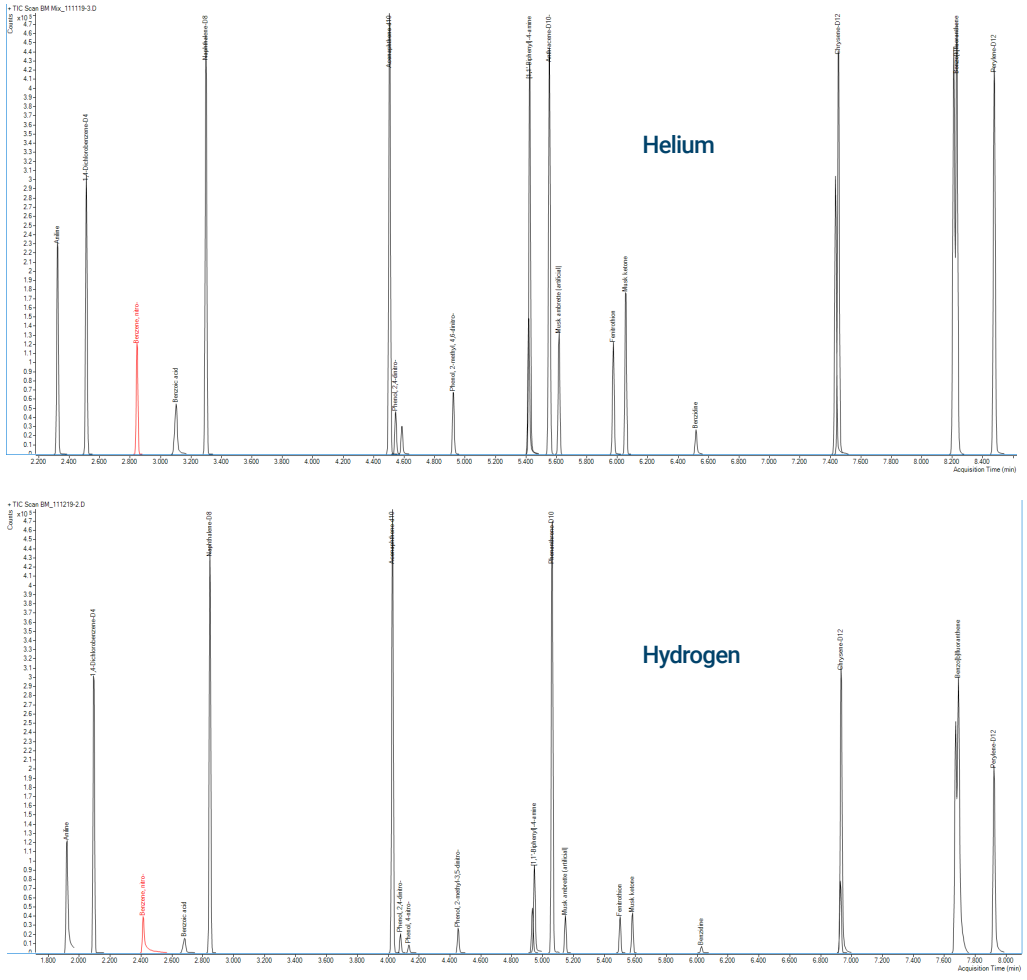

Figure 15. TIC chromatograms of test mixture to compare library match scores against NIST 17 for helium carrier gas (top) and hydrogen carrier gas (bottom). Compounds are listed in **Table 4**.

Table 4 lists the library match scores (LMS) for test mix in **Figure 15**. Spectra were obtained by spectral deconvolution and searched against NIST 17 in MassHunter Unknowns Analysis. For most compounds, the LMS values are comparable between the two carrier gases.

Table 4 Library match scores (LMS) for test mix in Figure 15.

		Library Match Score	
Rt (min)	Compound Name	He carrier	H_2 carrier
2.801	Aniline	98.9	98.2
2.996	1,4-Dichlorobenzene-D4	98.7	98.9
3.334	Benzene, nitro-	97.4	63.3
3.590	Benzoic acid	95.7	95.2
3.798	Naphthalene-D8	97.0	97.4
5.021	Acenaphthene-d10	99.2	98.5
5.050	Phenol, 2,4-dinitro-	92.4	95.4
5.081	Phenol, 4-nitro-	90.2	90.5
5.432	Phenol, 2-methyl, 4,6-dinitro-	96.7	95.2
5.938	[1,1'-Biphenyl]-4-amine	87.4	85.5
6.080	Phenanthrene-D10	97.5	97.1
6.121	Musk ambrette (artificial)	93.3	96.7
6.482	Fenitrothion	92.5	89.0
6.566	Musk ketone	95.3	94.3
7.052	Benzidine	96.5	94.4
8.033	[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dichloro-	99.1	83.5
8.068	Chrysene-D12	97.8	95.8
8.925	Benzo[b]fluoranthene	98.2	95.2
8.949	Benzo[k]fluoranthene	99.3	97.7
9.269	Perylene-D12	93.7	97.7

One notable exception is nitrobenzene, with a substantially lower LMS with hydrogen. This is the result of hydrogenation in the source. **Figure 16** shows the extracted ion profiles and spectra for the nitrobenzene peak.

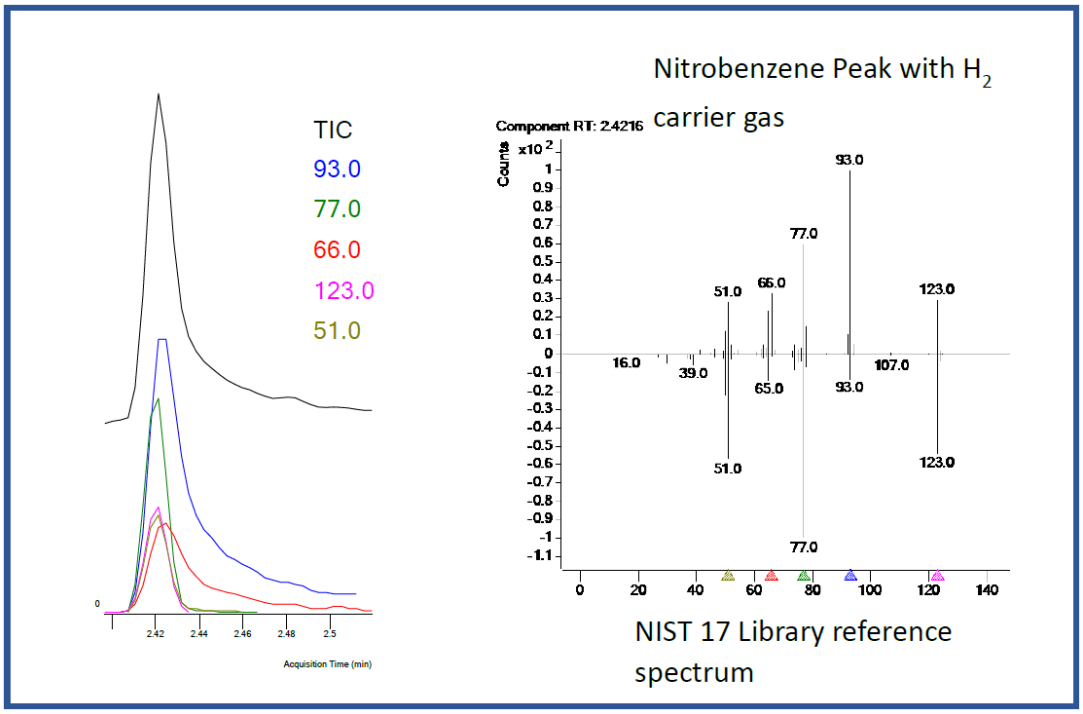

Figure 16. EICs and spectra for the nitrobenzene peak. Reference spectrum is inverted for comparison.

The reason for the lower LMS for nitrobenzene can be seen is **Figure 16**. The ion ratios are substantially different from those in the library reference spectrum.

NOTE

The differences in tailing of the EICs for the ions in nitrobenzene. Ions 51, 123, and 77 *m/z* exhibit no tailing while 66 and 93 *m/z* show substantial tailing, suggesting hydrogenation occurring in the source. In this case, any quantitation of nitrobenzene should use the 77 and 123 ions and avoid 93 and 66.

Other Considerations

Below is a list of items to consider when converting to hydrogen carrier gas:

- Hydrogen is not an inert gas, and therefore inertness problems will still exist or may be worse.
- Use the lowest inlet temp that works (to reduce reactions with hydrogen).
- Use pulsed injection, especially with small bore columns.
- Consider using an MMI in cold splitless mode for fragile compounds.
- Using the optional deactivated split/splitless weldment might help reduce inlet reactions.
- Avoid using methylene chloride as a solvent (especially wet). At higher inlet temperatures (such as, >280 °C), HCl is formed and causes problems.
  - If must be used, use the lowest inlet temp, the optional deactivated SSL weldment, or MMI inlet with the temperature ramped starting at 200 °C.
- Avoid carbon disulfide as a solvent.
- Use liners with a taper at bottom to minimize sample contact with gold seal.
- Install the column high enough in the inlet to minimize sample contact with the gold seal.
- Use Agilent Ultra Inert inlet liners.
- Have extra filaments on hand, as their useful life is usually shorter with hydrogen carrier gas.
- Source cleaning may be needed much less frequently due to the cleaning action of hydrogen.

Summary

For many GC/MS applications, hydrogen can be successfully substituted for helium as the carrier gas. Changes are often required in gas plumbing, instrument hardware, consumables, sample preparation, and method parameters. As discussed in this document, there are several topics that need to be addressed to achieve successful conversion.

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