TECHNICAL NOTE

Gas Chromatography/
Mass Spectrometry

The Use of Hydrogen Carrier Gas for GC/MS

Highlights

- Guidelines that can mitigate dangers and leverage benefits of using hydrogen
- Key safety factors for chemical laboratories
- Practical considerations for GC/MS method development

Introduction

Helium, as a limited natural resource, is increasingly expensive and, in some regions, in limited supply due to rationing. As such, the use of hydrogen as a carrier gas for gas chromatography mass spectrometry (GC/MS) is becoming more and more prevalent. Physical differences between hydrogen and helium give rise to chromatographic differences and the flammable nature of hydrogen increases safety concerns as well. In this document we will demonstrate the effective use of hydrogen with the PerkinElmer® Clarus® SQ 8 GC/MS and provide recommendations for ensuring laboratory safety. While the dangers of using hydrogen in a laboratory can be mitigated, every laboratory faces unique challenges and it is the responsibility of the laboratory manager and safety officer to address these issues to ensure the safety of their laboratory personnel. Extra caution must be taken in the design of both the laboratory and the experimental set-up. The development of safety conscious Standard Operating Procedures (SOP), including a thorough chemical hygiene plan, is a must.

Polycyclic Aromatic Hydrocarbons by GC/MS Using Hydrogen Carrier Gas

The determination of polycyclic aromatic hydrocarbon (PAH) compounds demonstrates the functionality of the PerkinElmer Clarus SQ 8 GC/MS using hydrogen carrier gas. The chromatograms presented in Figure 1 demonstrate the effectiveness of this system using both helium (Figure 1A) and hydrogen (Figure 1B) as carrier gas. A comparison of the two chromatograms clearly illustrates the faster elution times and improved peak sharpness one can expect when switching from helium to hydrogen.

Hydrogen is a flammable gas and when used incorrectly can pose a threat to both life and property. Prior to using hydrogen in a laboratory setting, safety precautions must be developed and subsequently observed to ensure safety.

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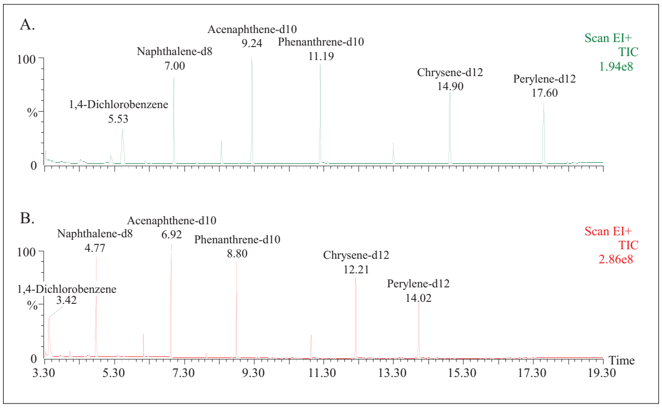

Figure 1. Chromatogram of standard PAH mix using (A) helium and (B) hydrogen as the carrier gas with standards labeled with retention time in minutes and compound name.

Guidelines for Using Hydrogen

The following sections highlight the safety and performance considerations a laboratory will face when electing to use hydrogen as the carrier gas for their GC/MS experiments. The information presented here is provided as a guide only, and especially in the case of hydrogen safety, a full assessment of the dangers and benefits of using hydrogen should be explored prior to initiating any laboratory work.

General Safety Considerations

The main safety concern when using hydrogen in a laboratory is the ever-present danger of explosion stemming from its flammability. Hydrogen is flammable over a wide concentration range, and during the rapid expansion from a high pressure source, can self-ignite. While this is certainly possible when using a compressed gas cylinder as the hydrogen source, the development of a high pressure hydrogen pocket within the instrument is unlikely. The larger threat is the ignition of any accumulated hydrogen from an electrical spark. Carrier gas passes through a number of fittings and the thin-walled and somewhat brittle GC column before passing into the vacuum of the MS. A small leak could develop at any stage resulting in the hydrogen build-up in the GC oven. Accumulation of hydrogen within the MS is predominantly associated with the loss of functionality of the pumping system. While the pumping system is functioning properly all carrier gas that is introduced into the MS will be captured by the turbomolecular pump then vented to the exhaust by the rotary pump. Loss of function, through loss of electrical power or hardware failure, will cause the carrier gas to pool within the vacuum chamber at increasing concentrations resulting in a situation where ignition of hydrogen can occur.

For hydrogen use, as with all procedures performed in the laboratory, a thorough review of local Environmental Health and Safety requirements is essential. Successful safety procedures in lab operations begin with a combination of design and planning, which is supported by a company culture that considers it to be mandatory and of the highest priority. The most effective chemical hygiene plans are ones that are built around a company culture of safety where all personnel strictly adhere to the guidelines and regulations.

Some practical considerations to lessen the danger of hydrogen accumulation include:

- Always vent the roughing pump exhaust and injector vent lines to a fume hood.
- Always leak check the system after changing gas cylinders or installing/repairing the gas lines using a fully functioning hand-held leak sensor suitable for hydrogen applications.
- If you are using compressed gas cylinders always install the Hydrogen Snubber, as shown in Figure 2, and warning label (not shown) that comes with every Clarus GC. The Hydrogen Snubber attaches directly to the exit of the regulator and will prevent a sudden discharge of hydrogen into the lab should a gas line break.
- Consider using a hydrogen generator. Hydrogen generators produce high purity hydrogen at low pressure (relative to compressed gas cylinders), which eliminates the risk of high pressure discharge and subsequent self-ignition.
- Consider using a hydrogen sensor in the GC oven or in the general area the instrument is located.
- It is highly recommended to utilize the optional Nitrogen Purge Vent kit if you are using hydrogen as a carrier gas. The Nitrogen Purge Vent kit will allow nitrogen to be introduced into the mass spectrometer upon venting. This will lower the risk of hydrogen build-up within the vacuum chamber should the carrier gas not be shut off along with the pumping system.
- Always turn off the hydrogen at the cylinder or hydrogen generator every time you shut down the GC or MS.
- Never depressurize a gas cylinder, especially a hydrogen gas cylinder, in the lab. The high pressure venting could result in self-ignition and subsequent explosions.

- After a power failure, the mass spectrometer may have collected hydrogen regardless of whether or not the pumping system was automatically reactivated. It is recommended to utilize the Nitrogen Purge Vent kit function for 30 minutes prior to returning the system to full operation. If the purge kit is not installed the source may be removed to allow the vacuum chamber to vent to atmosphere.

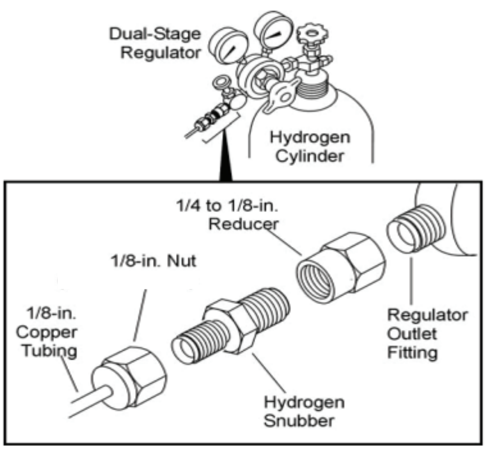

Figure 2. Hydrogen Snubber attached to the exit of the dual-stage stainless steel gas regulator. The installation of a Hydrogen Snubber will prevent the rapid discharge of hydrogen into the laboratory should a gas line break.

Column Compatibility

Because hydrogen has a different viscosity from helium and the maximum column efficiency occurs at a different gas velocity, the applied carrier gas pressure will be different for the two gases when run under optimum conditions. In some instances it may enable or constrain column types when used with an MS detector. Tables 1 and 2 indicate the carrier gas inlet pressure necessary to run under near optimum conditions on columns connected to an MS with a variety of geometries for the two gases respectively. These tables show that most of the commonly used columns are suitable for use with either helium or hydrogen. At the extremes, helium is better with shorter and/or wider-bore columns whereas hydrogen is better with longer and/or narrower-bore columns. When swapping carrier gases, refer to these tables to ensure that the column being used will still work with practical pressures with the new gas.

***Table 1.* Required inlet carrier gas pressures, in psig, for 30 cm/s helium at 50 °C.**

Column i.d. (mm)	Column Length (m) 10	15	30	60	100
0.10	31.6	49.1	>100.0	>100.0	>100.0
0.18	9.1	13.9	29.0	61.9	>100.0
0.25	5.7	7.0	14.4	30.2	52.7
0.32	<5.0	<5.0	8.6	17.8	30.7
0.53	<5.0	<5.0	<5.0	6.3	5.0

***Table 2.* Required inlet carrier gas pressures, in psig, for 40 cm/s hydrogen at 50 °C**

Column i.d. (mm)	Column Length (m) 10	15	30	60	100
0.10	18.5	28.6	60.8	>100.0	>100.0
0.18	5.5	8.3	17.0	35.9	62.8
0.25	<5.0	<5.0	8.6	17.7	30.6
0.32	<5.0	<5.0	<5.0	10.6	18.0
0.53	<5.0	<5.0	<5.0	<5.0	6.3

Experimental Set-up (Configuration, Pressures, and Flows)

Setting up the instrumentation to use hydrogen was quite straightforward. The installation included:

- Ultra high purity hydrogen gas cylinder (99.999%)
- Hydrogen Snubber on the hydrogen gas cylinder (and label)
- Nitrogen Purge Vent kit
- Roughing pump exhaust and injector vent lines vented to the laboratory fume hood

No further modifications of the hardware were necessary to perform this work. Setting up the GC to operate using hydrogen as the carrier gas required the selection of hydrogen on the touch screen of the GC. This was achieved by navigating into the Programmed Pneumatic Control (PPC) configuration window on the touch screen and selecting hydrogen as the "Gas" under the correct Channel tab as illustrated in Figure 3. Selecting a different gas in this window changes the mass-flow calibration parameters used by the firmware. The calibration parameters are traceable to the National Institute of Standards and Technology (NIST®) standards; however, it is prudent to check and recalibrate locally if necessary using a certified flow meter periodically.

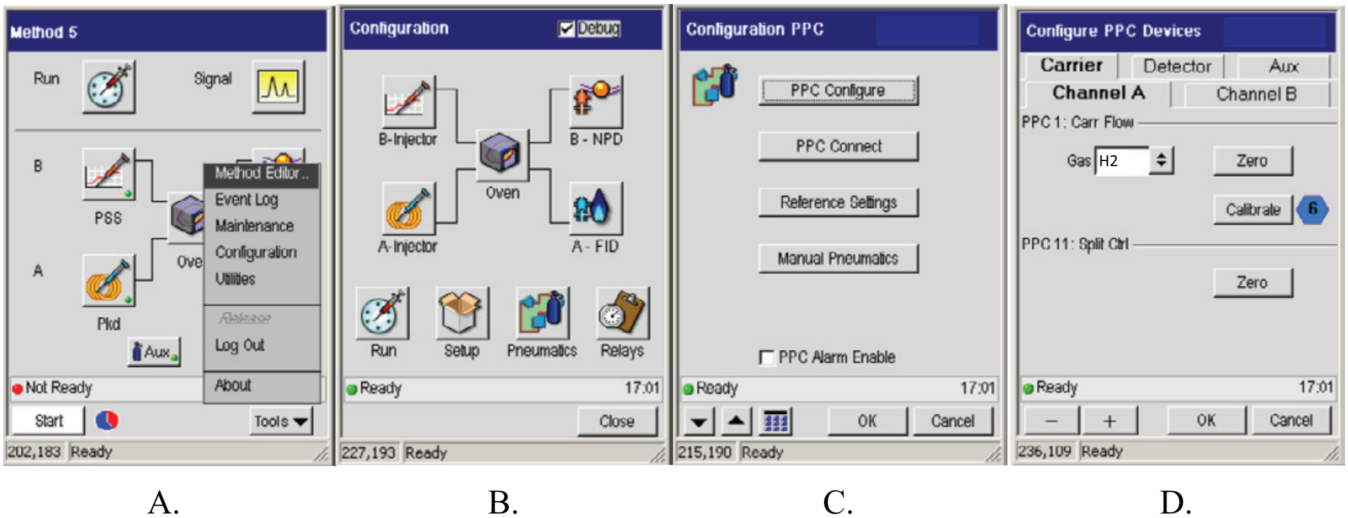

Figure 3. Procedure to change the carrier gas to hydrogen on the GC touchscreen. A) Access the Configuration screen from the Tools menu, B) Select the pneumatics control using the Pneumatics button, C) Choose PPC Configure, D) In the Carrier tab select the proper Channel and select "H2" as the "Gas" and click OK.

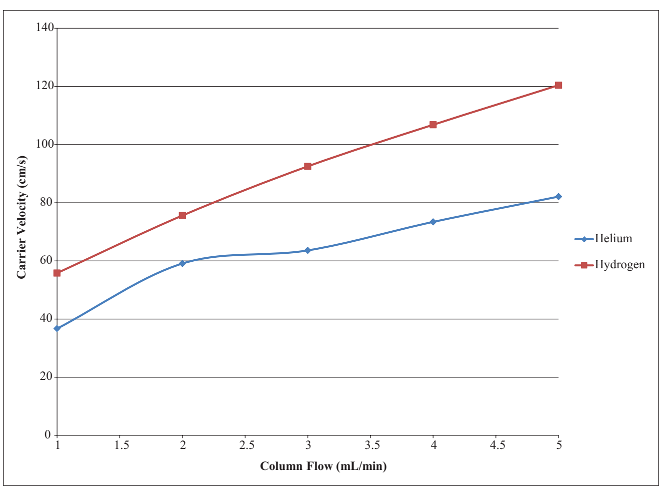

Figure 4. Carrier Velocity vs. Column Flow for hydrogen and helium.

Using a 30 m x 0.25 mm x 0.25 µm column the following carrier velocity versus flow setting was generated (see Figure 4). The velocity numbers were obtained from the GC screen. Hydrogen achieves a much higher carrier velocity and demonstrates more linear behavior over the flow range. This can result in shorter elution times and better chromatography (sharper peaks) however the performance of the mass spectrometer pumping system must also be taken into consideration.

Vacuum System Performance

Two pumping systems are available with Clarus mass spectrometers; the standard "S" model equipped with a 55 L/sec turbomolecular pump and the larger capacity "T" and "C" models equipped with a 255 L/sec turbomolecular pump. The compression of the pumped gas, and thus pumping efficiency, varies according to the square of its molecular mass such that heavier compounds are pumped more efficiently. The resulting compression ratios decrease with molecular weight, see Table 3, and it is recommended to only use the "T" and "C" models if hydrogen is to be used as the carrier gas.

All Clarus mass spectrometers use a single wide range gauge (WRG) that operates using a combined Pirani/inverted magnetron ionization sensor. The pressure reading of the WRG is dependent on the type of gas pumped and is factory set to operate with helium. Converting to hydrogen does not require further actions, however, due to the relative molecular mass (RMM) of hydrogen relative to helium the absolute vacuum reading can be up to a factor of 2 off. In Figure 5 we report vacuum readings relative to flow rate using the same 30 m x 0.25 mm x 0.25 µm column mentioned above. As expected, as more gas is pushed into the mass spectrometer the pressure increases. This effect is more drastic with hydrogen due to the effects previously described. Even when taking up to a factor of 2 difference in the reading, the level of hydrogen raises rapidly relative to helium. Because of this, higher flow rates combined with larger diameter columns are not recommended for use with hydrogen.

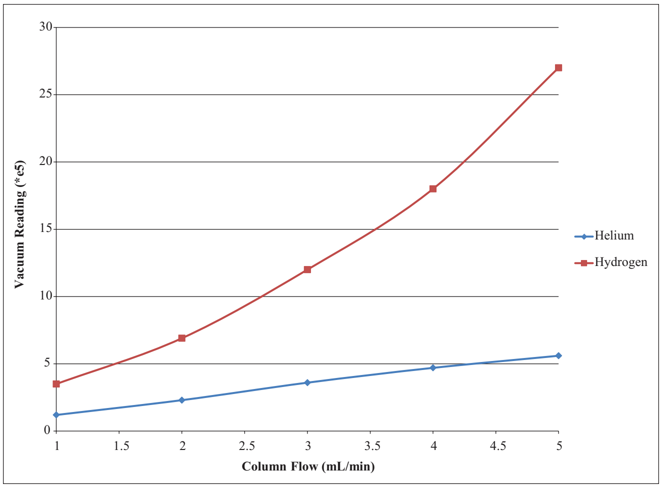

Figure 5. Wide range gauge reading.

***Table 3.* Compression ratios of nitrogen, helium, and hydrogen gas for the large capacity "T" and "C" model turbomolecular pump.**

Compound	Compression ratio
N_2	$>1 \times 10^{11}$
He	3×10^{5}
H_2	1×10^{4}

Sources of Hydrogen

In general, two sources of hydrogen are available – high pressure gas cylinders and hydrogen generators. Both sources have advantages and disadvantages and it falls upon the laboratory manager to select the source most appropriate for their environment. Hydrogen cylinders offer maintenance free operation but can be expensive and in the event of release, can present a safety concern. Hydrogen generators require regular upkeep but operate at low pressures thus improving safety. Additionally, the operation of the unit can be tied to the operation of the GC/MS system so in the event of a loss of electrical power or hardware failure, the generator can be automatically shut off. The initial cost of a hydrogen generator must be weighed against the both improved safety and long term savings versus compressed gas cylinders.

Conclusion

The use of hydrogen as a carrier gas for GC/MS-based experimentation offers many advantages in both cost and performance yet does not come without risks. The flammable nature of hydrogen presents researchers with specific challenges, which when addressed using clear planning and stringent standard operating procedures, can be mitigated such that the safety of both laboratory personnel and property can be reasonably assured. In all cases a regular review of standard operating procedures and a thorough chemical hygiene plan is required. While the dangers of working with hydrogen can never be fully eliminated, many inherently dangerous processes are already commonly performed in lab operations, whose risks are mitigated with the development and observance of well thought out and implemented SOPs and chemical hygiene plans.

Additional information available on the OSHA web site: http://www.osha.gov. Keyword: Hydrogen.

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