Helium to Hydrogen Conversion for GC/MS and GC/MS/MS Analysis of Semi-Volatile, Volatile, and PAH Compounds: A Practical Guide for Environmental Laboratories

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NEMC 2024

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Introduction

In response to the problems laboratories have had with helium shortages, tools and processes are available for predictable transition of GC/MS analysis to hydrogen carrier gas. While helium is the best and most used carrier gas in GC/MS, hydrogen is the best alternative to helium. However, there are several important factors that must be considered to achieve success.

This work provides practical guidance on implementing GC/MS methods with hydrogen carrier gas with the examples of successful implementations, including semivolatiles (SVOCs), volatile organics (VOCs), and polycyclic aromatic hydrocarbons (PAHs).

Preparing for Conversion

Consider Helium Conservation

Strategies to significantly reduce helium usage:

- Helium Conservation Module for GC switches the inlet to nitrogen carrier gas when the GC/MS is not in use and reverts to helium 30 min before use – **up to 85% He savings**
- **Gas Saver Mode** & **Sleep/Wake Methods** reduces the split vent flow from 50 mL/min to 20 mL/min after the injection – **yielding 50% He savings**
- Helium use audit and leak check – comparing the calculated total helium flow for all systems to the rate, at which helium is used. Some laboratories **reduced He consumption by 40%.**

Preparing for Conversion to Hydrogen Carrier Gas

Methods and targets that will require **less optimization**:

- Durable non-reactive compounds like PAHs, hydrocarbons
- Analyzed at high concentrations
- Analyzed with split injections

Methods that might require **more optimization**:

- Fragile and reactive compounds
- Analyzed at trace concentrations

Time should be allotted for adapting the methods, optimization, and resolving potential problems.

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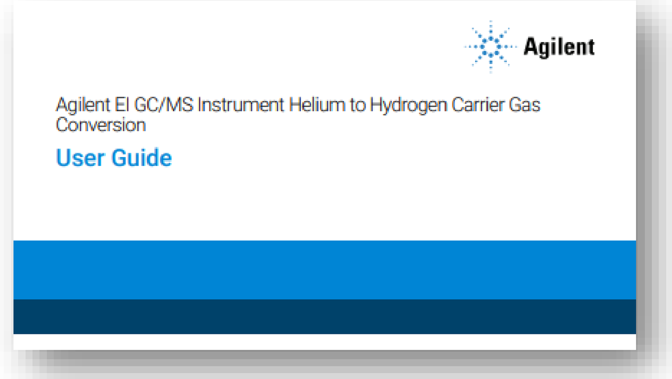
Practical Considerations

User Guide: Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion Guide 5994-2312EN



This user guide [ref. 1] provides in-depth information on converting and using a GC/MS system with hydrogen carrier gas. It is a must-read before converting the instrument and the laboratory to hydrogen.

Sources of Hydrogen:

- Cylinders offer the simplest way to try hydrogen
- Hydrogen generators can be more economical over time and offer safety features but require preventive maintenance
- Hydrogen purity at least 99.9999%

Plumbing the Instrument:

- Chromatographic quality stainless steel tubing is recommended for hydrogen plumbing and is the best choice
- Copper tubing can also be used during evaluation of hydrogen but should be replaced with new 1/8-inch tubing
- A moisture trap is necessary when using a hydrogen generator

Vent/Exhaust Lines:

- The GC split vent and septum purge vent should be connected to a negative flow laboratory vent
- When converting an existing GC, split vent trap needs to be replaced along with other GC preventive maintenance

GC Inlet and Injection:

- When analyzing fragile compounds and/or using chlorinated solvents, consider a temperature-programmable multimode inlet (MMI)
- Consider split or pulsed split injections for minimal residence time in the GC inlet to minimize possible reactions
- For splitless injections, use temperature-programmable mode, pulsed injection, analyte protectants

GC Column:

- It is **not advised** to use s a 30 m × 0.25 mm id × 0.25 µm film thickness capillary column because of low inlet pressure
- Consider a **20 m × 0.18 mm id × 0.18 µm** film thickness version of the column with the same stationary phase type
  - **Speed gain up to 2.5x (!)** with similar chromatographic resolution
  - Note: column capacity will be reduced by 60%
- Alternative column dimensions: 40 m × 0.18 mm id × 0.18 µm, 60 m × 0.25 mm id × 0.25 µm, and other

GC Column Flow:

- Recommended starting column flow is 0.9-1 mL/min
- Maximum recommended flow should not exceed 2 mL/min for MS with a turbo pump and 1 mL/min for diffusion pump

Retention Times and Retention Indices:

- When using *GC Method Translator* to convert from helium to hydrogen:
  - Retention Indices (RIs) remain the same
  - Retention times can remain the same as with helium
  - If analysis speed is increased with hydrogen (speed gain), retention times can be precisely calculated by dividing the original retention times by the speed gain value

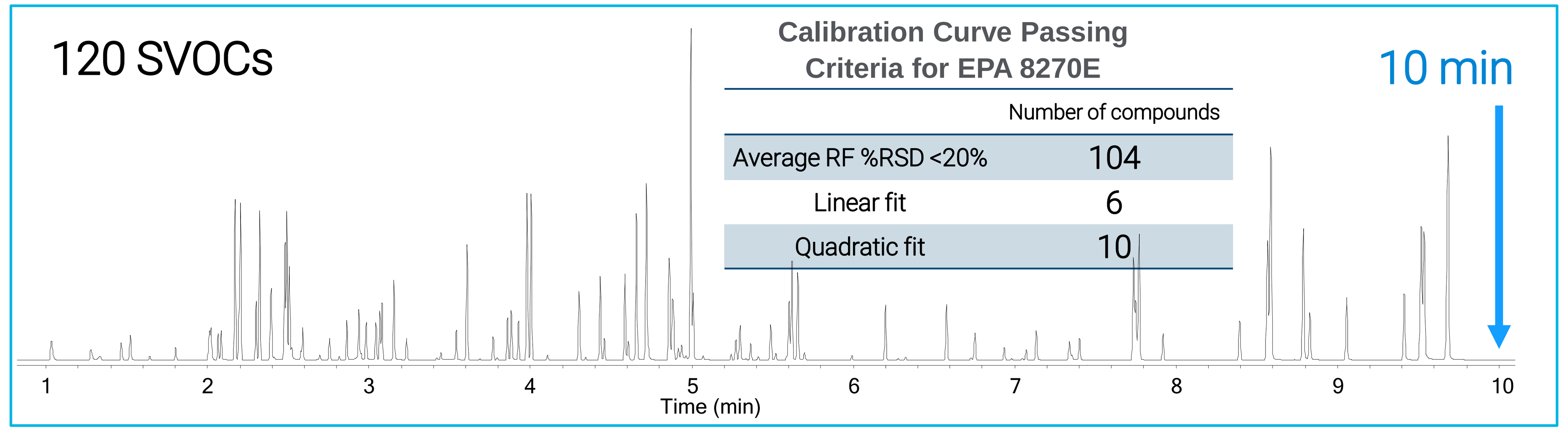
Mass Spectrometer (MS) Hardware:

- When **maintaining the same spectrum** with hydrogen as with helium is important, e.g., analyzing unknowns, – the **HydroInert source** allows for maintaining spectral fidelity with hydrogen even for the reactive compounds
- A **conventional EI source** with a wide **9 mm drawout lens** can be used when evaluating hydrogen. It will decrease but not fully address in-source reactivity with hydrogen carrier gas

Results and Discussion: Successful Conversion of GC/MS Analysis

Semi-volatile Organic Compounds (SVOCs) with EPA 8270E

Fig shows the analysis of **120 target analytes** and surrogates using H_2 carrier gas, the HydroInert source and the 7000E GC/TQ. The use of H_2 carrier and the 0.18 mm id column provided **excellent resolution** and a run time of only **10.5 min**. A 20:1 split injection was used and the MMI inlet was programmed from 250 °C (hold 0.3 min) at 200 °C/min to 350 °C. A calibration range of **0.02-100 µg/mL** was obtained for 82 compounds and 0.1-100 µg/mL for 106 compounds. Note the **excellent peak shape** and resolution in Fig 1. Full details are available in ref [2]. Excellent results were also obtained using the 5977C single quadrupole GC/MSD with H_2 carrier and the HydroInert source. This is detailed in ref [3].



Calibration Curve Passing Criteria for EPA 8270E	Number of compounds
Average RF %RSD <20%	104
Linear fit	6
Quadratic fit	10

Figure 1. TIC of 120 SVOCs in method converted to H_2 carrier using 20m x 0.18 mm id x 0.18 µm DB-5MSUI column.

Volatile Organic Compounds (VOCs) in Drinking Water with Headspace-GC/MS

H_2 carrier allowed the separation of **80 volatile organic compounds** (VOCs) in **7 minutes**. The method used a DB-624 20 m x 0.18mm x 1 µm and a pulsed split injection of 20:1. Complete method details and results are provided in reference [4].

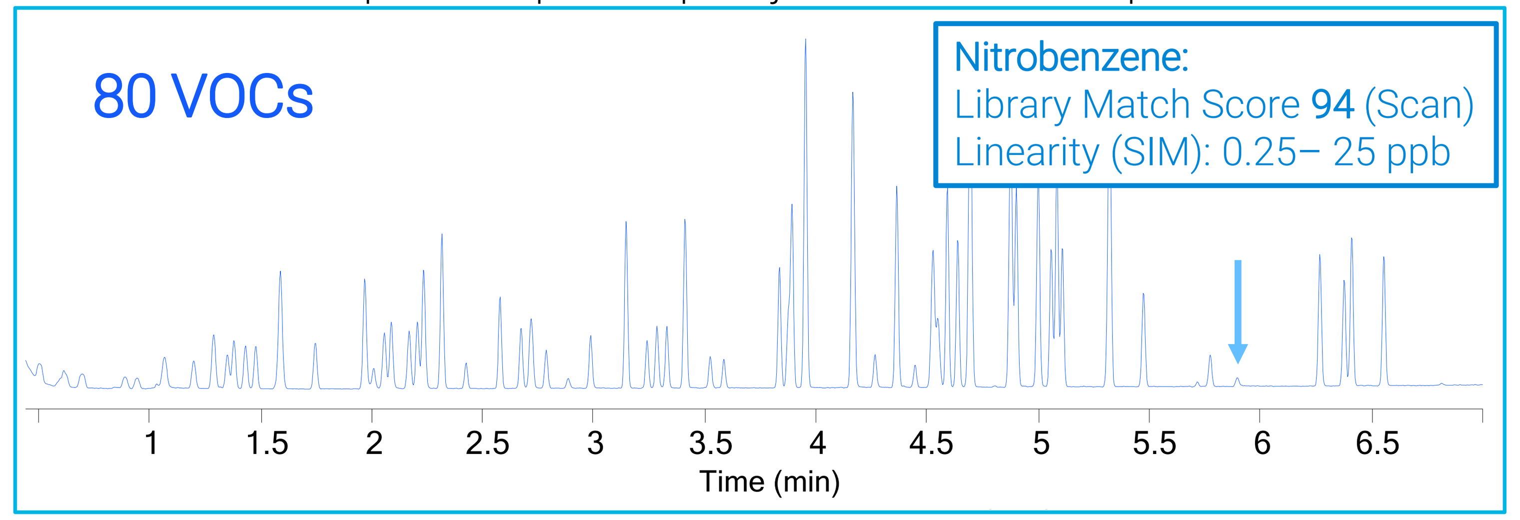


Figure 2. VOCs in water analyzed by headspace/GC/MS.

Scan mode demonstrated **excellent spectral matching** against the NIST20 library (average LMS 94), and **excellent calibration linearity** with an average range of 0.16 to 25 µg/L. In SIM mode, the average range was 0.07 to 25 µg/L, and the average **MDL** for the 80 compounds was **0.026 µg/L**. Fig. 2 shows the chromatogram and highlights the excellent results for nitrobenzene, which is often a problem with H_2 carrier if the HydroInert source is not used.

Polynuclear Aromatic Hydrocarbons (PAHs)

PAHs are durable compounds that tend to tail with He carrier gas. With H_2 carrier and the HydroInert source, **excellent peak shape** with no or little tailing was observed (Fig. 3). The MDL and linearity are comparable to or better than those with He. **Excellent linearity** was observed over the range of **<1 – 1,000 µg/L** with an average RSE = 9.5. The average **MDL** was about **0.1 µg/L**. Full details are available in ref 5. Excellent results were also obtained using the 7000E GC/TQ with H_2 carrier and the HydroInert source. That system was configured with backflushing and response stability was shown over 500 injections with the challenging soil extract. This is detailed in ref. 6.

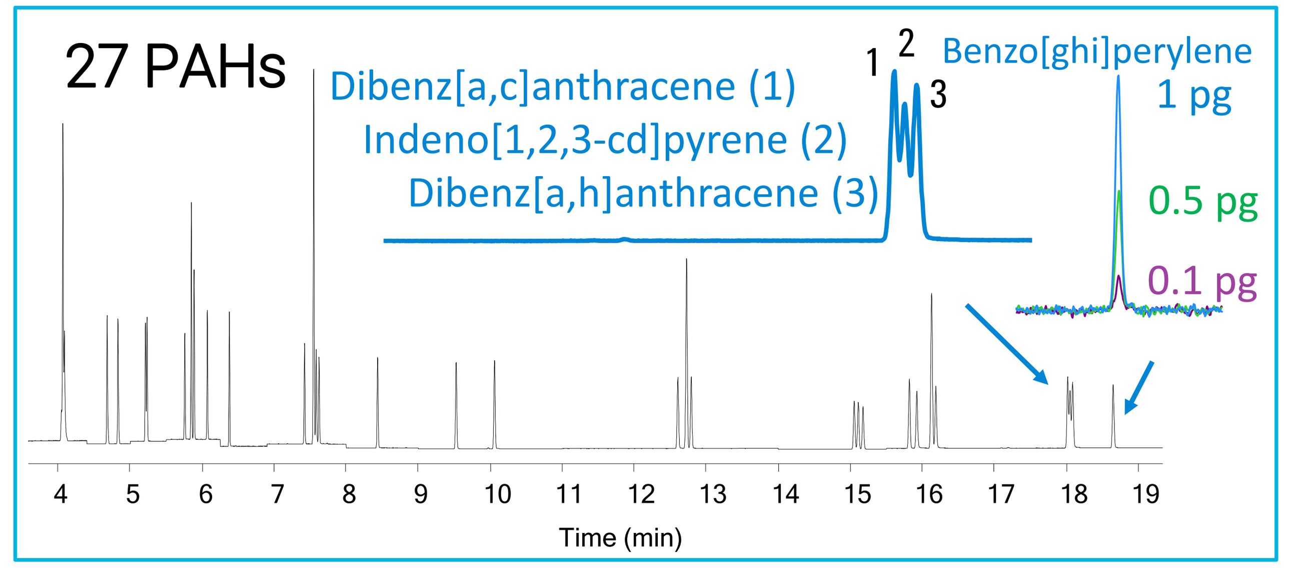


Figure 3. SIM TIC of 27 PAHs (DB-EU PAH 20m x 0.18 mm id x 0.14 µm).

Safety & Other Considerations

Safety

Safety is always the first and most important consideration when handling gases. Key hydrogen safety features:

- Safety shutdown
- Oven ON/OFF sequence
- Flow limiting frit
- Hydrogen sensor
- Explosion test performed by Agilent as a pat of QC

Other Considerations

- Perform preventive maintenance on the GC before switching to hydrogen
- High spectral background will be observed while the source bakes out – allot time for source conditioning
- Sensitivity will be reduced by an average of 2-10 times when switching to hydrogen
- Passing ion ratios for target tunes needs to be verified and is no guaranteed. Some methods, e.g., EPA 8270E allows for the manufacturer's recommended tune
- Use GC Method Translator for successful conversion

Conclusions

If He is available at an acceptable price, it is the preferred carrier for GC/MS and should be used. However, as shown in the examples provided in this poster, H_2 can be used if appropriate adjustments are made to accommodate its use.

Changes are often required in gas plumbing, instrument hardware, consumables, sample preparation, and method parameters. This poster provides an overview of several topics that need to be addressed to achieve successful conversion.

References

[1] Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion. User Guide. 5994-2312EN. 2022.

[2] Analysis of Semivolatile Organic Compounds with Hydrogen Carrier Gas and HydroInert Source by Gas Chromatography/Triple Quadrupole Mass Spectrometry (GC/MS/MS), Agilent, 5994-4891EN, 2022.

[3] Analysis of Semivolatile Organic Compounds Using Hydrogen Carrier Gas and the Agilent HydroInert Source by Gas Chromatography/Mass Spectrometry, Agilent, 5994-4890EN, 2022.

[4] Volatile Organic Compounds Analysis in Drinking Water with Headspace GC/MSD Using Hydrogen Carrier Gas and HydroInert Source, Agilent, 5994-4963EN, 2022.

[5] Analysis of PAHs Using GC/MS with Hydrogen Carrier Gas and the Agilent HydroInert Source, Agilent, 5994-5711EN, 2022.

[6] GC/MS/MS Analysis of PAHs with Hydrogen Carrier Gas, Agilent, 5994-5776EN, 2022.