Poster Reprint

ASMS 2023
Poster number WP 277

Helium to Hydrogen: Explosives & Pesticides & VOAs, Oh My! Successful Transition of GC/MS Analyses

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Introduction

Helium is the best and most used carrier gas in GC/MS. Hydrogen is the second-best alternative to helium. It provides several advantages, including faster analysis times and smaller environmental impact. However, hydrogen is a reactive gas. Hence, every analyte in every method needs to be validated with hydrogen.

This work provides guidance on the GC/MS conditions for the effective transition from helium to hydrogen carrier gas for a variety of applications.

Experimental

HydroInert Source

The HydroInert source is an EI source optimized for use with hydrogen carrier gas. Due to its inert nature, it minimizes undesirable in-source chemical reactions between the analytes and hydrogen. This results in improved library match scores (LMS) vs helium-based libraries and allows using the same target ions in GC/MS and MRM transitions in GC/MS/MS. This makes the transition of methods from helium to hydrogen much easier.

Considerations for GC/MS Method Conversion

The following should be considered when converting from helium to hydrogen.

- Review the document "The EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion Guide" [1] for detailed instructions for method conversion from He to H_2 carrier. This covers all aspects, including H_2 safety, you should consider.
- When targeting fragile analytes like pesticides or explosives, use a temperature programmable inlet like the MMI to minimize possible hydrogenation reactions.
- Use Agilent's Method Translation calculator [1] to pick a column and parameters to obtain the same elution order as with the helium method. Since most helium methods use a 30 m x 0.25 mm id column, the 20 m x 0.18 mm version is a great place to start.
- The increased resolution afforded by hydrogen may allow the development of a faster method.
- For the reasons mentioned above, use the HydroInert source.

Pesticides

Figure 1 compares the chromatograms for 203 pesticides in a spinach QuEChERS extract with He and with the optimized H_2 method. Using Method Translation, the elution order and retention times are the same, greatly simplifying conversion. Note the increased resolution with H_2. This can be further exploited with Method Translation to decrease the run time from 20 min to 10 min [2]. The optimized H_2 method uses the MMI inlet with a temperature programmed Solvent Vent injection of 2 µL. A 2 mm dimpled liner and HP-5MS UI 20m x 20m (0.18mm x 0.18 µm) column set in backflush configuration are also used. With the H_2 optimized method, over 90% of the 203 targets could be quantitated at or below 10 ppb (mg/kg) in spinach extract, which is the default MRL [2].

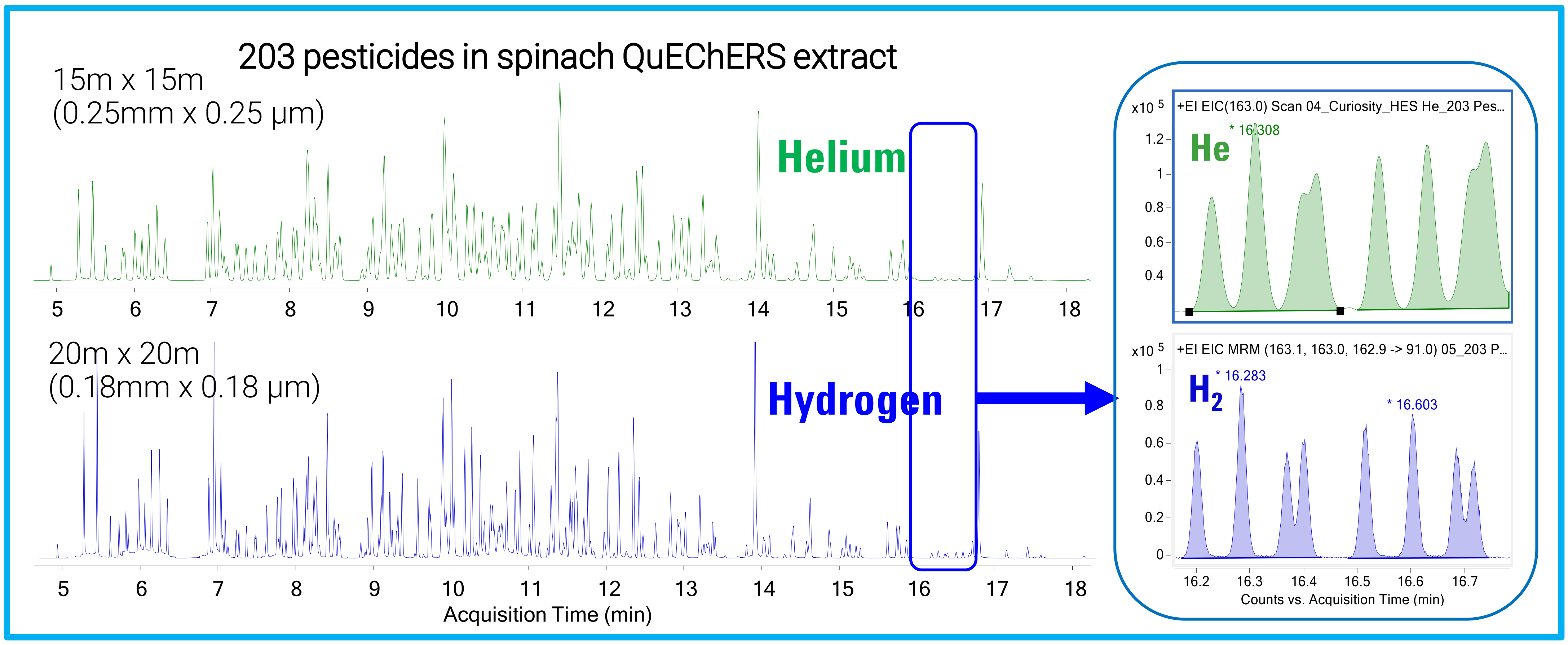


Figure 1. Top: Pesticide method with He carrier. Bottom: Method converted to H_2 carrier using 0.18 mm id column set.

Volatile Organic Compounds 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 20m (0.18mm x 1 µm) and a pulsed split injection of 20:1. Complete method details and results are provided in reference [3]. 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.

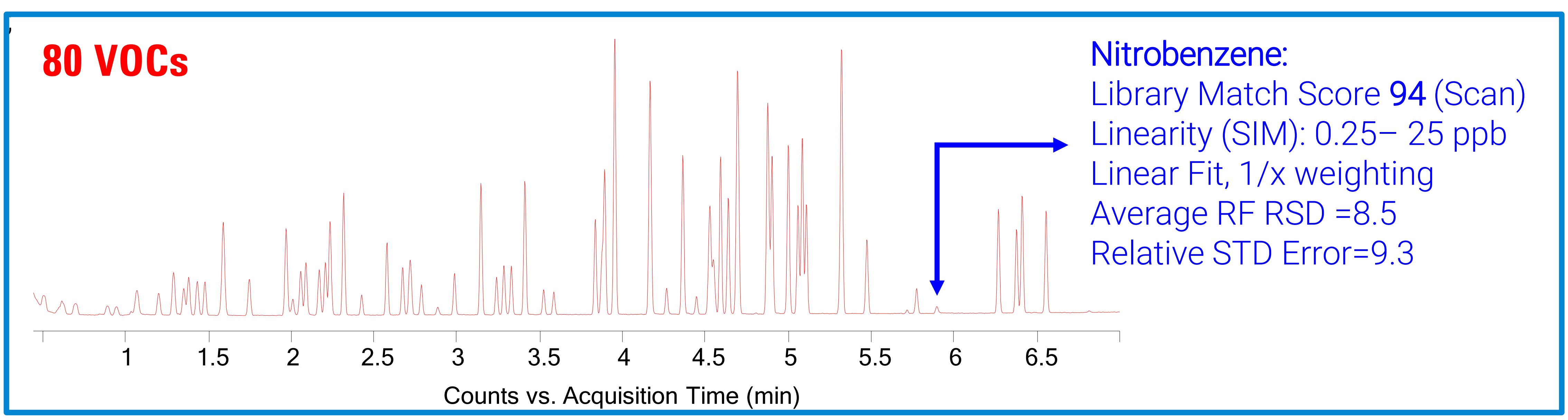
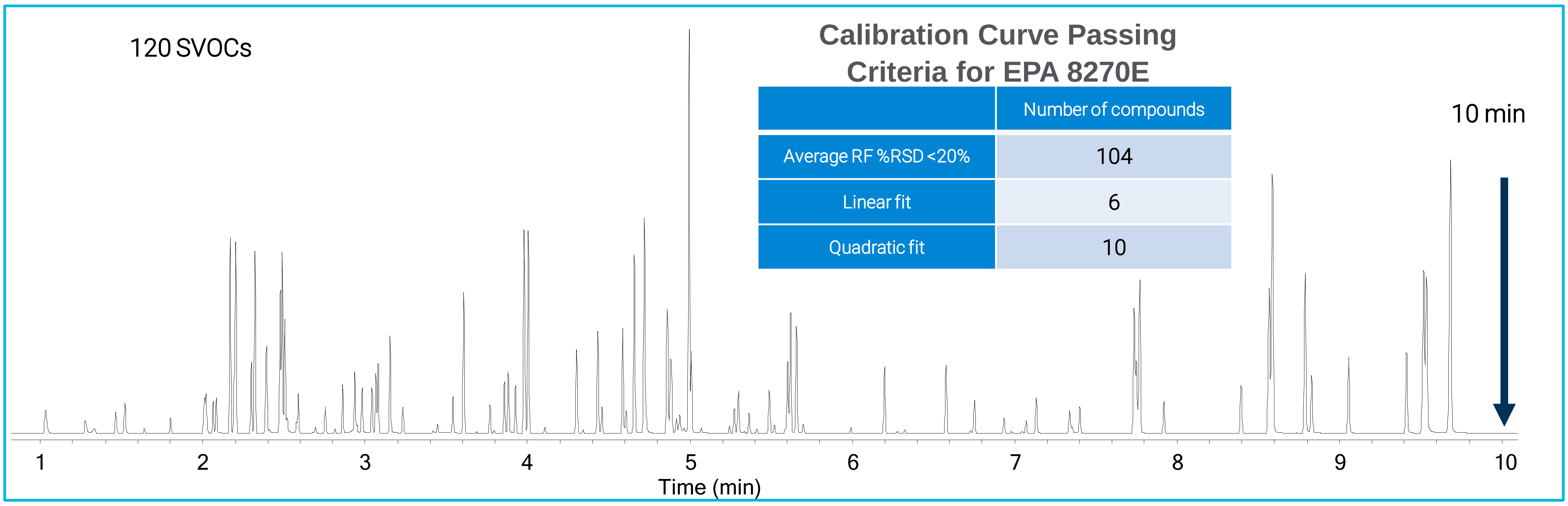


Figure 2. VOCs in water analyzed by headspace/GC/MS.

Results and Discussion

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

Fig 3 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 3. Full details are available in ref [4]. 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 [5].



	Number of compounds
Average RF %RSD <20%	104
Linear fit	6
Quadratic fit	10

Figure 3. 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.

Polynuclear Aromatic Hydrocarbons (PAHs)

PAHs are durable compounds that tend to tail with He carrier gas. With H_2 carrier and the HydroInert source, the peak shape and resolution are significantly improved, as seen in Figs 3. With 5977C GC/MSD, the MDL and linearity are comparable to or better than those with He. Also, the ISTD response was stable across 4 orders of calibration. 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. Due in part to the cleaning action of H_2, response stability was shown over 100 injections of a challenging soil extract with GC/MSD. Full details are available in ref [6]. 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 [7].

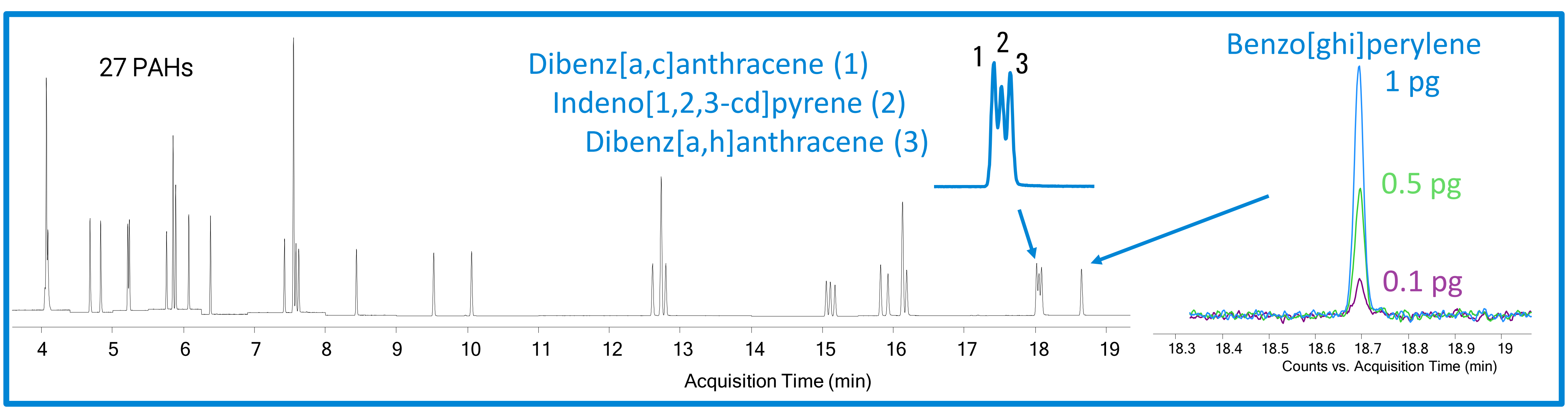


Figure 4. SIM TIC of 27 PAHs in method converted to H_2 carrier using 20m x 0.18 mm id x 0.14 µm DB-EUPAH column.

Explosives

Nitro compounds used in explosives are highly prone to hydrogenation, leading to poor library match scores (LMS) with H_2 carrier and traditional EI sources. A group of nitroaromatics commonly encountered in explosives were analyzed using a 50:1 temperature ramped split injection, a 20 m x 180 µm x 0.18 µm DB-5MSUI column, and the HydroInert source with H_2 carrier gas in the 5977C GC/MSD. As seen in Fig 5, excellent LMS values were obtained, indicating minimal hydrogenation.

Peak #	Compound	LMS
1	nitrobenzene	95
2	1-methyl-2-nitrobenzene	96
3	1-methyl-4-nitrobenzene	94
4	1,3-dinitrobenzene	95
5	2-methyl-1,3-dinitrobenzene	97
6	1-methyl-2,4-dinitrobenzene	94

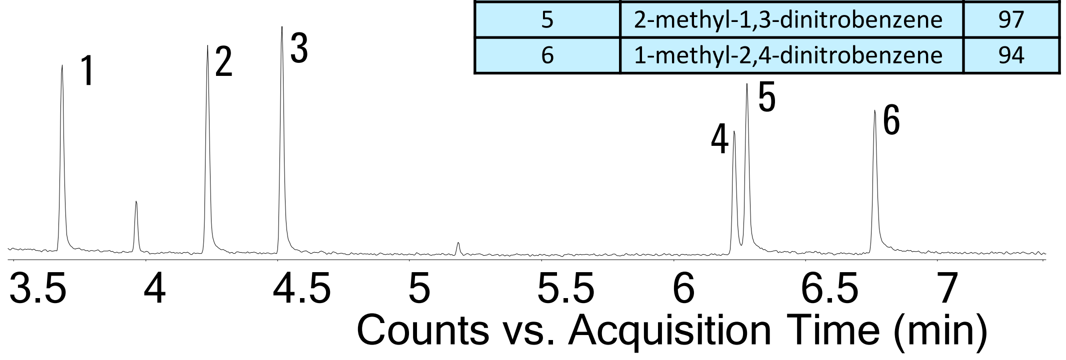


Figure 5. TIC of nitroaromatic compounds.

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 this overview of several converted methods, H_2 can be used if appropriate adjustments are made to accommodate its use.

References

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

[2]Achieving the MRLs with Hydrogen Carrier Gas: GC/MS/MS Analysis of 200 Pesticides in Produce. ASMS Poster MP 225 ASMS 2023.

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

[4]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.

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

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

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Published in USA, May 31,2023