Improved Performance with Hydrogen Carrier Gas Methods for SVOC and Organochlorine Pesticides Analysis by GC/MS/MS

Is there a Helium Shortage?

- World Demand Increasing Past 20 Years
  - Electric vehicle manufacturing
  - Semi-conductor manufacturing
  - Medical device cooling

- World Supply Decreasing Over Past 20 Years
  - Geopolitical concerns
  - Sale of US Strategic Reserves and Enrichment

- Significant Increase in Cost
  - Doubled in past 5 Years
  - Increased more than 600% in past 20 years

Sources of Helium

- Helium cannot be effectively manufactured artificially
- Two sources of Helium
  - Nuclear fusion reactions in stars (the Sun)
  - Decay of radioactive elements in the Earth's crust
- World supply of helium today comes from mining and enriching helium from the earths crust

Sources of Helium

US Enrichment Plant
Amarillo, TX

Sources of Helium

Sources of Helium

Environmental Analytical Concerns

- Critical Carrier Gas for GCMS Applications
- Continued Supply-Chain Issues
- Significantly Increasing Cost
- Single Quadrupole Mass Spectrometers have not historically allowed other carrier gasses due to ionization and reaction issues
- Significant Increase in Cost
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Experimental Approach

- GC/TQ method adapted from current helium-based method to hydrogen using method translation tools.

- This work defined the use of hydrogen as carrier gas
- based on four parameters:
  - Calibration linearity and dynamic range
  - Reactivity as measured by DDT and Endrin breakdown in an injection of a standard containing each compound at 100 ug/L
  - Chromatographic separation measured by separation of benzo(b)fluoranthene and benzo(k)fluoranthene from a 100 ug/L standard
  - The evaluation of peak shape determined from pentachlorophenol and benzidine tailing factors.

Instrument Settings

Parameter	Value
MS	Agilent 7010D GC/TQ
Column	Agilent J&W DB-5ms UI, 20 m, 0.18 mm, 0.18 µm
Inlet	Split/Splitless Inlet Ultra Inert, universal mid-frit liner
Injection volume	2 µL Splitless
Injection mode	Pulsed splitless (0.7 min, pulse @40 psi for 0.7 min)
	Pulsed split 40:1 (pulse @30 psi for 0.5 min)
Inlet temperature program	280 °C
Oven temperature program	40 °C for 1 min; 25 °C/min to 260 °C, 5 °C/min to 280 °C; 25 °C/min to 320 °C, 1.6 min hold
Carrier gas	Hydrogen
Column flow	0.9 mL/min constant flow
Transfer line temperature	320 °C
Quadrupole temperature	150 °C
Source temperature	300 °C

Chromatographic performance

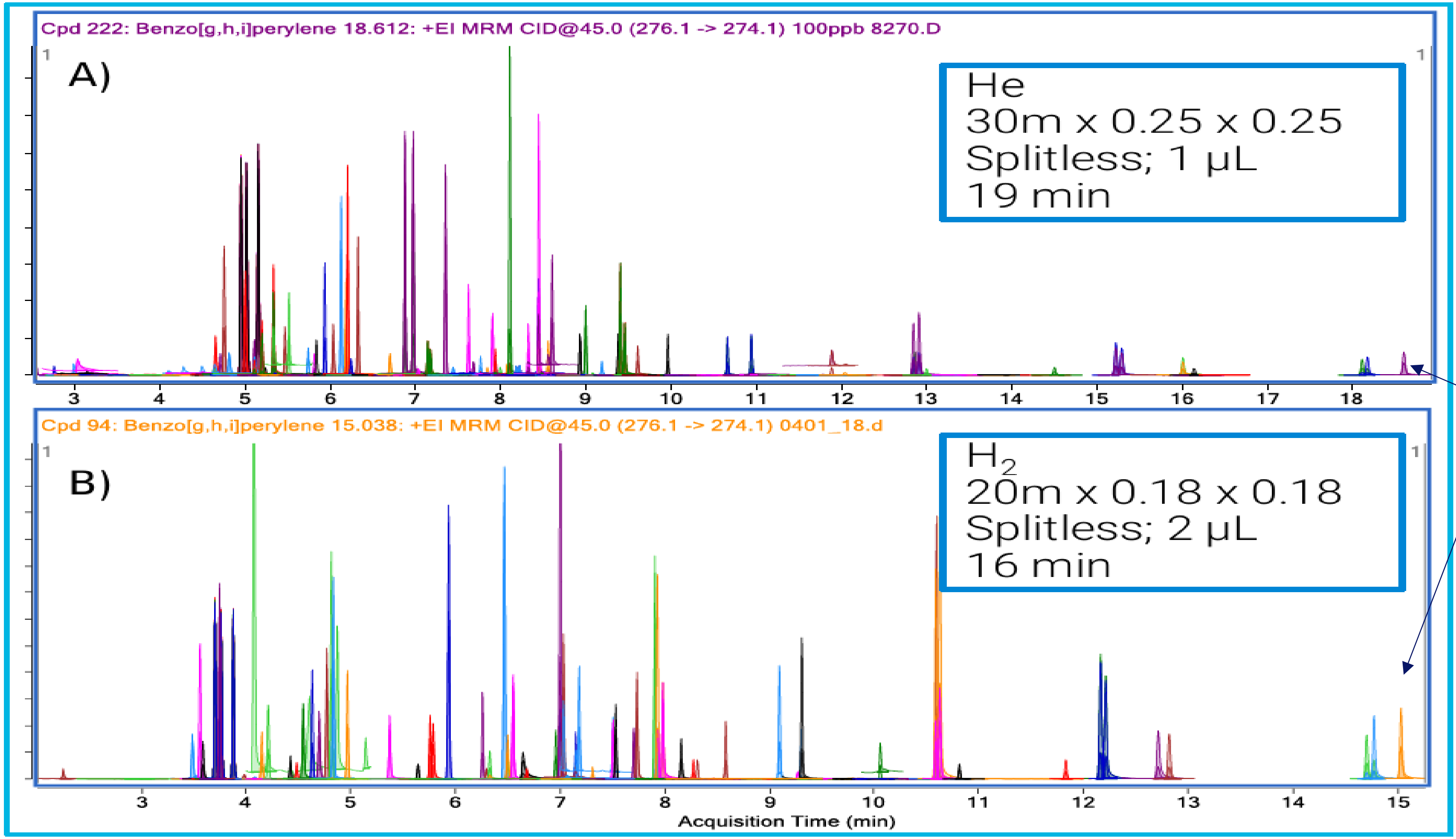

Figure 2. MRM chromatograms with (A) Helium; (B) Hydrogen carrier gasses at the mid-level 100 ppb calibration standard.

Improved Discrimination With Hydrogen

Results: Calibration Linearity

Carrier Gas	Helium	Hydrogen Low-to-Mid-Concentrations	Hydrogen Mid-to-High Concentrations
Injection	Splitless, 1 µL	Pulsed Splitless, 2 µL	Pulsed Split 40:1, 1 µL
Calibration Range	0.5-1000 ug/L	1-500 ug/L	100-10000 ug/L
On-column loading	0.5 pg - 1 ng	2 pg - 1 ng	2.5 pg - 250 pg
No. Analytes with Average RF RSD < 20	52	54	58
No. Analytes with Linear Cal. Fit	5	2	1
No. Analytes with Quadratic Cal. Fit	6	7	4

Results: Reactivity

DDT Area Count	DDE Area Count	DDD Area Count	% Breakdown DDT	Method Limit (%)
1736665	10554	13377	1.4	15
Endrin Area Count	Endrin Ketone Area Count	Endrin Aldehyde Area Count	% Breakdown Endrin	Method Limit (%)
74952	1455	1390	3.7	15

Results: Peak Shape

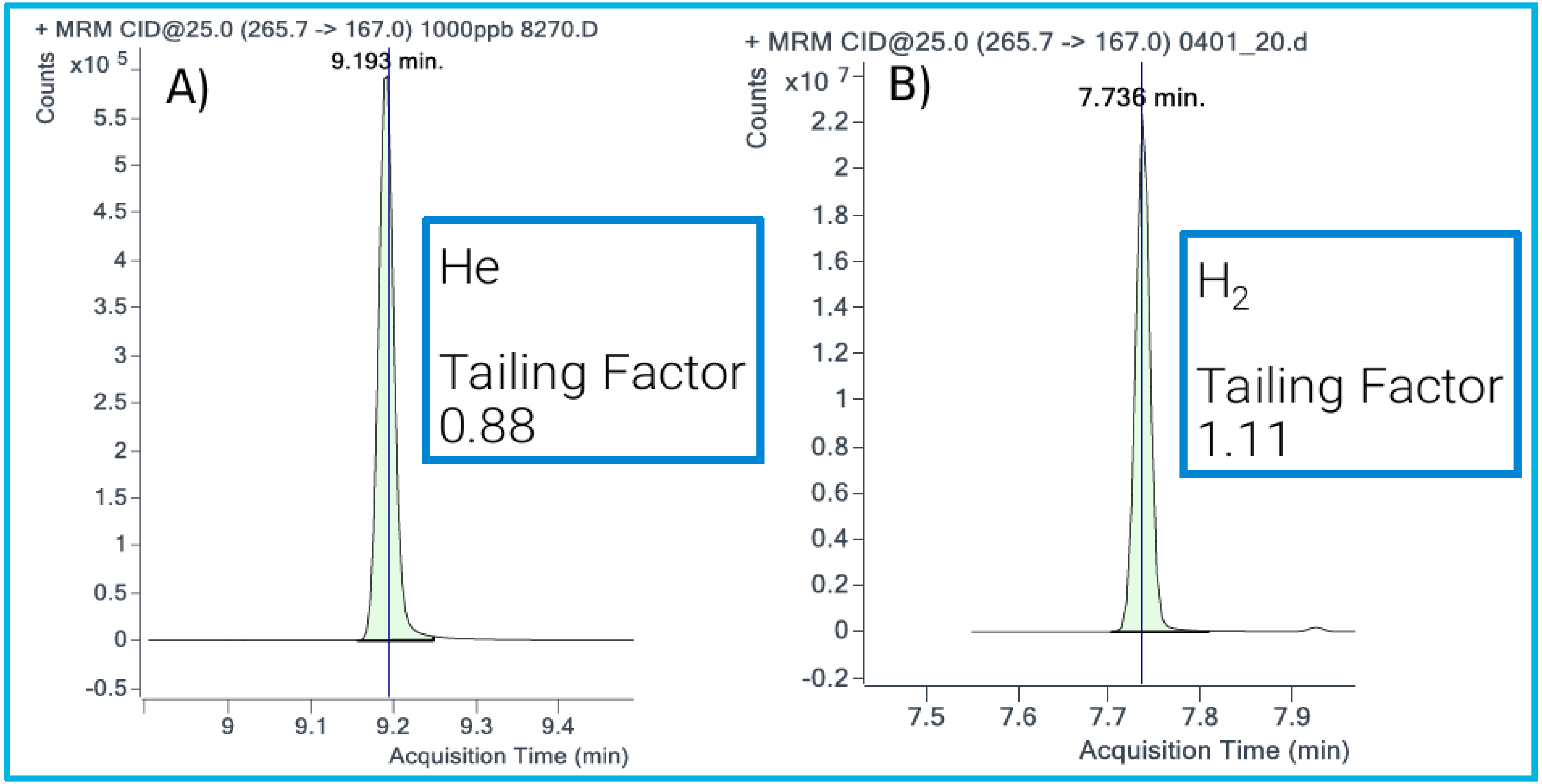

Figure 3. MRM chromatograms for pentachlorophenol at the highest calibration levels with (A) helium, 1000 ppb and (B) hydrogen, 500 ppb.

Results: Separation

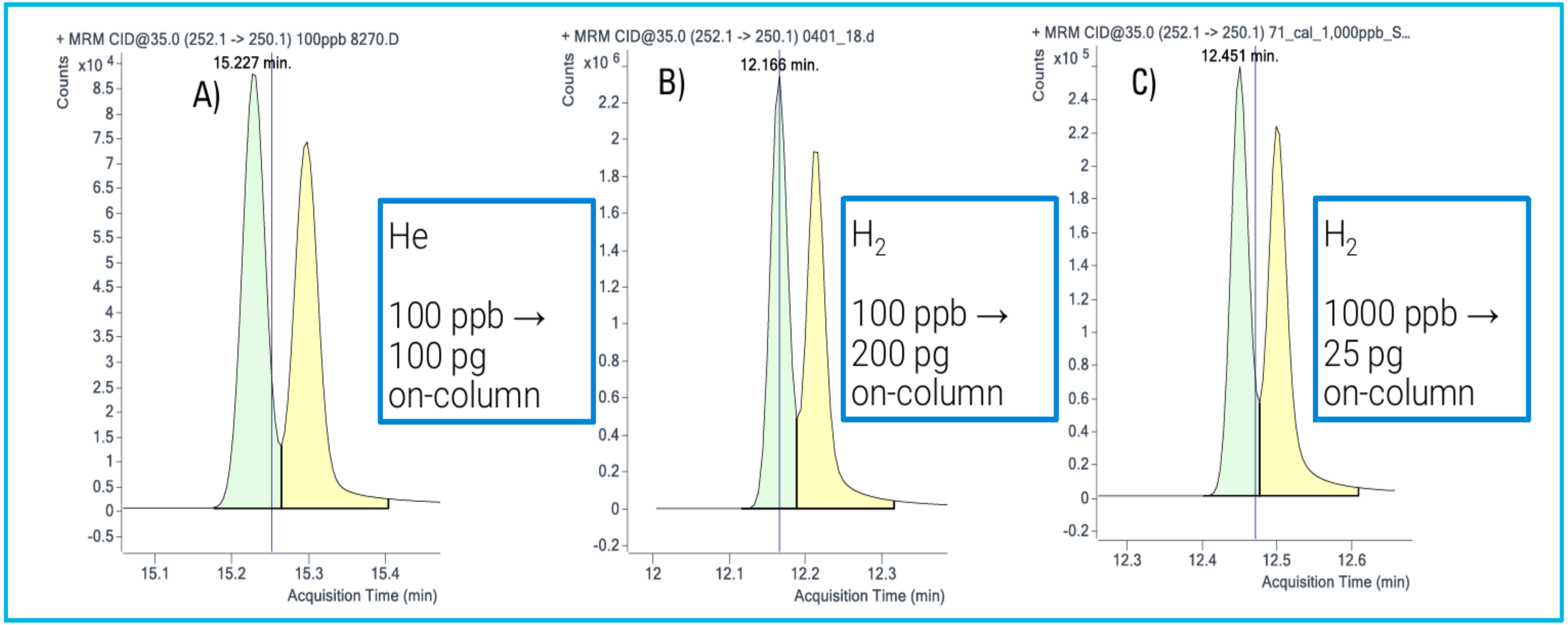

Figure 4. MRM chromatograms for Benzo(b)fluoranthene and Benzo(k)fluoranthene at the midpoint calibration level with (A) helium 100 ppb splitless; (B) hydrogen 100 ppb splitless; (C) hydrogen 1 ppm split 40:1.

Disadvantages of Hydrogen as an alternative to Helium for mass spectroscopy

- Potential reactivity with column or system components
- Potential reactivity with certain analytes of interest
- Highly flammable gas may pose increased safety concerns

Advantages of Hydrogen as an alternative to Helium for mass spectroscopy

- Improved chromatographic discrimination on heavier analytes
- Degradation / breakdown of analytes equivalent or superior to Helium
- Equivalent to superior peak shape and peak tailing
- Equivalent or superior peak separation

Advantages of Hydrogen as an alternative to Helium for mass spectroscopy

- Reduced cost of analysis
- Increased certainty of supply
- Availability of hydrogen generators to generate supply on-site at the laboratory
  - Operational efficiency – continuous supply
  - Cost efficiency – no cylinder purchase costs
  - Enhanced safety – no storage or handling of high pressure cylinders

Questions?

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