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

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Introduction

GC Single Quadrupole MS (GC/SQ) has long been a standard for analyzing semi-volatile organic compounds (SVOCs) in environmental samples, but Triple Quadrupole (GC/TQ) is emerging as a more powerful alternative due to its enhanced sensitivity and selectivity.

Using Multiple Reaction Monitoring (MRM) in GC/TQ, increases sensitivity allowing for smaller sample extraction volumes and reducing costs for solvents, sample preparation, and waste disposal.

MRM also reduces matrix interferences, enabling the analysis of more compounds, faster batch reviews, and greater confidence compared to GC/SQ in SIM or Scan modes.

Additionally, with helium shortages, hydrogen has become a viable carrier gas alternative.
Hydrogen offers the following benefits:

- reduced GC/MS source cleaning
- increased chromatographic resolution
- minimized peak tailing
- improved internal standard stability.

This study discusses the successful adaptation of hydrogen as the carrier gas in GC/TQ for SVOC analysis.

Figure 1. Agilent 8890/7010D GC/TQ.

Experimental

The GC/TQ method was adapted from a helium-based method to hydrogen using method translation tools.

This work defined the use of hydrogen as carrier gas based on three parameters:

- reactivity with target analytes as measured by DDT and Endrin breakdown in an injection of a standard containing each compound at 100 ug/L
- chromatographic separation of analytes measured by separation of benzo(b)fluoranthene and benzo(k)fluoranthene determined from a 100 ug/L standard
- the evaluation of peak shape determined from pentachlorophenol and benzidine tailing factors.

Method criteria from USEPA method 8081B was used to define the DDT and endrin breakdown limits, and method 8270E was used to measure acceptance of chromatographic separation and tailing.

Two hydrogen-optimized methods are presented:

1. Pulsed splitless injection for low-to-mid concentration samples: 1-500 ppb
2. Pulsed split injection with split ratio 40:1 for mid-to-high-concentration samples: 100 ppb-1ppm.

Parameter	Value
MS	Agilent 7010D GC/TQ
Column	Agilent J&W DB-5ms UI, 20 m, 0.18 mm, 0.18 µm (p/n 121-5522UI)
Inlet	Split/Splitless Inlet Ultra Inert, universal mid-frit liner (part number 5190-5105)
Injection volume	2 µL with Pulsed Splitless 1 µL with Pulsed Split
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
TQ mode	dMRM

Table 1. GC/MS method parameters

Initial Calibration with Helium and Hydrogen Carrier Gasses

Figure 2 shows full MRM chromatograms at the midpoint calibration level with helium carrier gas (Fig. 2A) and with hydrogen carrier gas
(Fig. 2B) using splitless injection. The analysis with hydrogen carrier gas resulted in faster analysis time: 16 min vs. 19 min while providing enhanced chromatographic resolution.

Table 2 provides the summary of the initial calibration performance with helium carrier gas, and with hydrogen using splitless and split injection.

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 ppb	1–500 ppb	100 ppb–10 ppm
On-column loading	0.5 pg–1 ng	2 pg–1 ng	2.5 pg–250 pg
Average RF RSD < 20	52	54	58
Linear Cal. Fit	13	2	1
Quadratic Cal. Fit	12	7	4

Table 2. Initial calibration for SVOC with He and H_2 carrier gasses

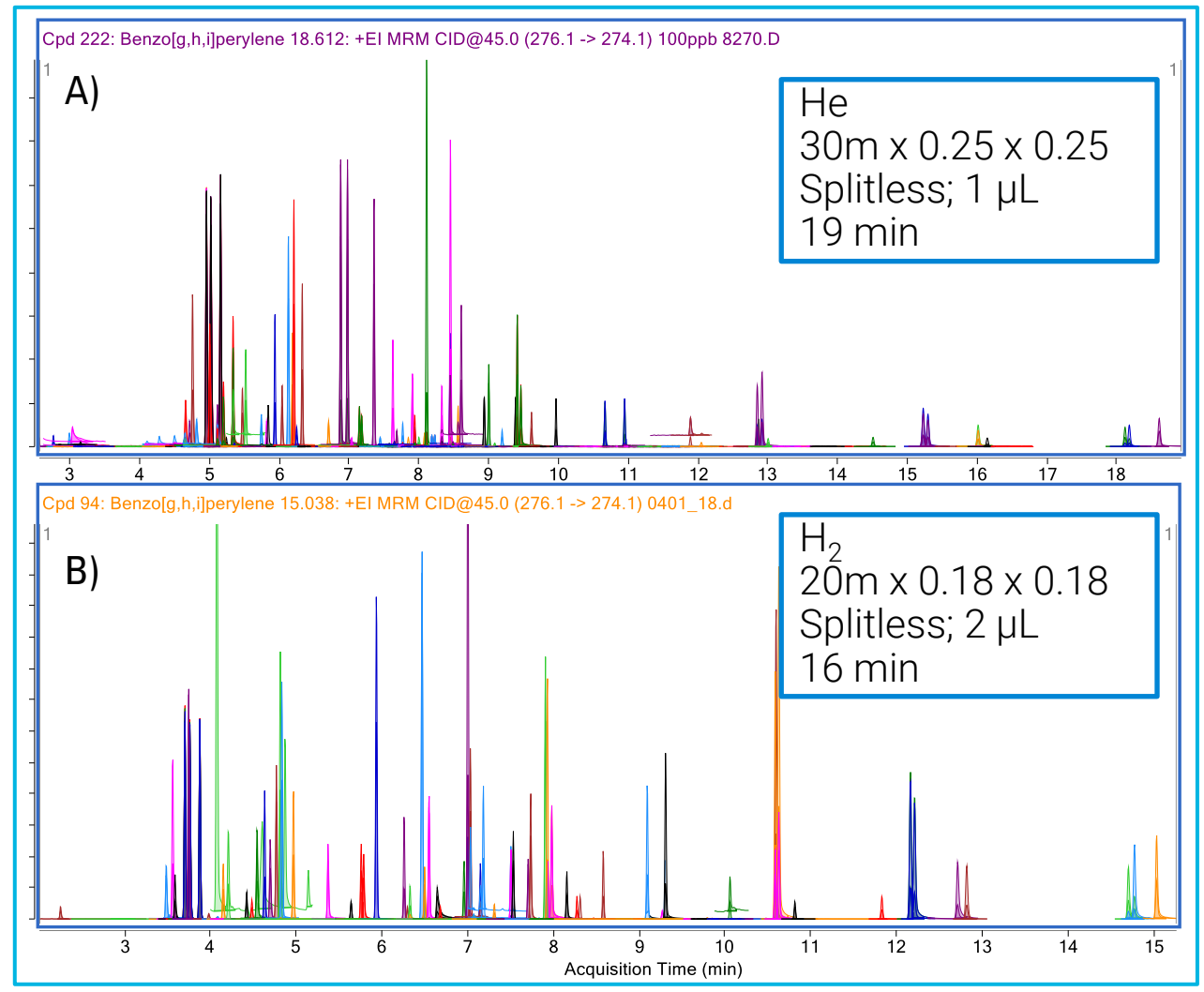


Figure 2. MRM chromatograms with (A) Helium; (B) Hydrogen carrier gasses at the mid-level 100 ppb calibration standard.

Results of Reactivity to Target Analytes with Hydrogen Carrier Gas

The % breakdown of DDT and Endrin were measured using the following formulas from USEPA SW846 8081B:

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD+DDE)}}{\text{sum of all peak areas (DDT+DDD+DDE)} \times 100}$$

$$\%\ \text{breakdown of Endrin} = \frac{\text{sum of degradation peak areas (Aldehyde+Ketone)}}{\text{sum of all peak areas (Endrin+Aldehyde+Ketone)} \times 100}$$

As shown in Table 3, breakdown of these active compounds were less than 15 % each as required by the target method for analysis.

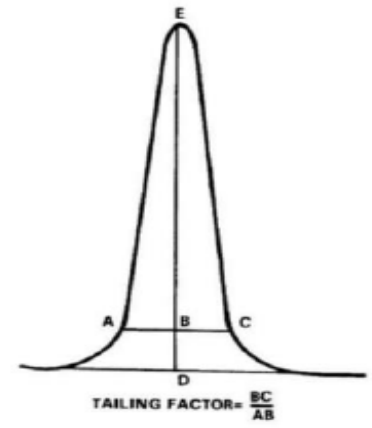
DDT	DDE	DDD	% Breakdown of DDT
1,736,665	10,554	13,377	**1.4%**
Endrin	Endrin Ket	Endrin Ald	**% Breakdown of Endrin**
74,952	1,455	1,390	**3.7%**

Table 3. Endrin and DDT % breakdown

Results of Tailing Evaluation of Pentachlorophenol and Benzidine

Pentachlorophenol and Benzidine tailing factors calculated by the formula provided in USEPA method 8270E. Peak shape for both reactive compounds were within the guidelines of the EPA method.

Tailing factor = BC/AB



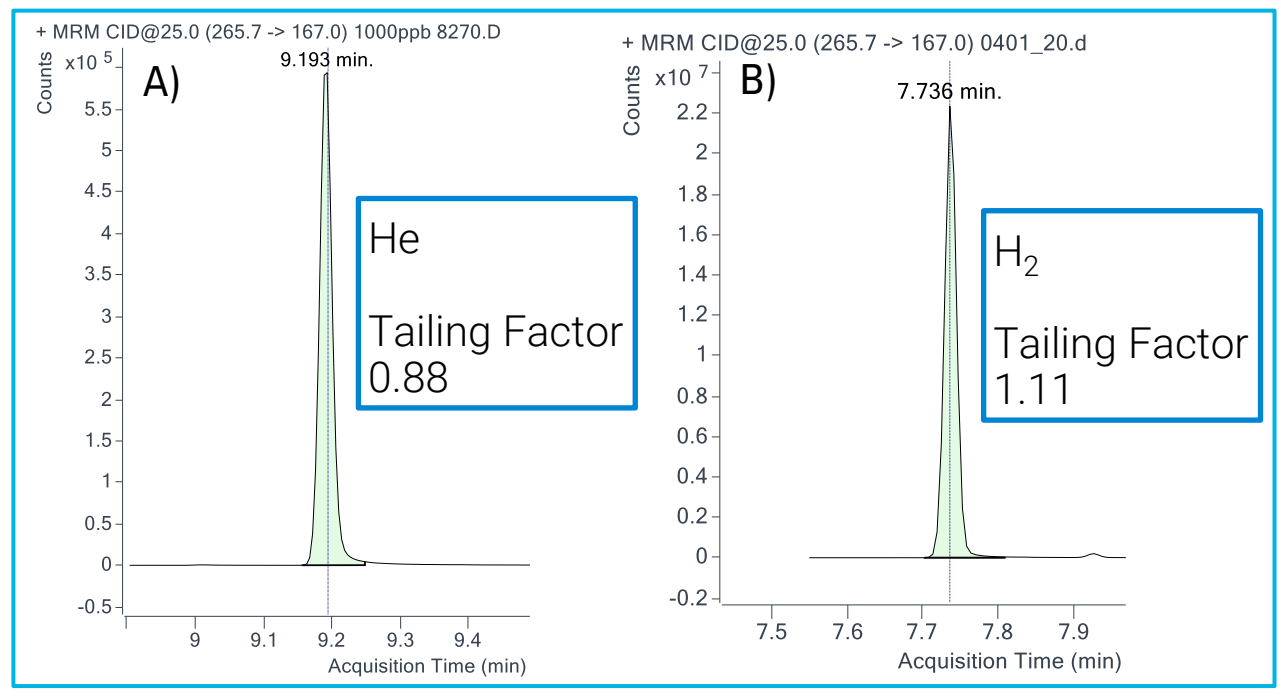


Figure 3. MRM chromatograms for pentachlorophenol at the highest calibration levels with (A) helium, 1000 ppb and (B) hydrogen, 500 ppb

Results and Discussion

Chromatographic Separation of Structural isomers

Benzo(b)fluoranthene and Benzo(k)fluoranthene were evaluated for separation using hydrogen carrier as per the requirements in method 8270E. Isomers are considered resolved if the peaks are at least 50% resolved (i.e., the height of the valley between two isomer peaks is ≤ 50% of the average of the two peak heights, or 1−[valley height]/[average peak height] is ≥50%). The resolution should be verified on the midpoint concentration of the ICAL.

Figure 4 below documents that separation of the structural isomers benzo(b)fluoranthene and benzo(k)fluoranthene at the midpoint of the initial calibration curve exceeds the minimum separation requirement as stated in method SW846 8270E.

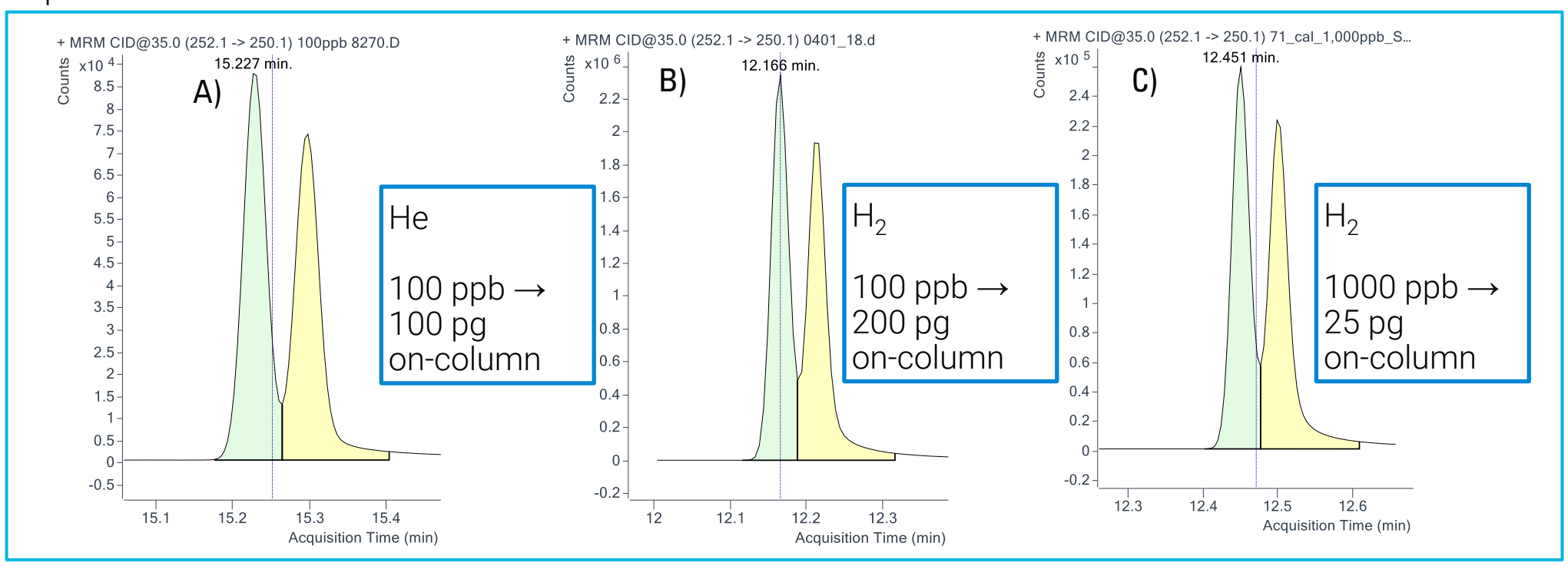


Figure 4. MRM chromatograms for Benzo(b)fluoranthene and Benzo(k)fluoranthene at the midpoint calibration level with (A) helium 100 ppb splitless; (B) hydrogen 100 ppb splitless; (C) hydrogen 1 ppm split 40:1.

Conclusions

Using hydrogen as the carrier gas, the system achieved comparable or superior results to as compared to helium. The analysis of the 179 MRMs for over 80 target compounds showed acceptable chromatographic characteristics with degradation and reactivity behaviors well within limits currently used to validate performance with helium carrier gas.

With increasing cost and reduced availability of helium in the market, the results of this study validate the viability of substituting hydrogen as the carrier gas for environmental analysis of extractable organics using GC/MS/MS technology.

References

Method 8081B, Revision 2, Update IV to the Third Edition of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846, 2/2007.

Method 8270E, Revision 6, Update VI to the Third Edition of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846, 6/2018.

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