

Pesticide Analysis using GC×GC-TOFMS & Hydrogen Carrier Gas A Proof-of-Concept Study



Lena Dubois; Sebastiano Panto; Nick Jones
LECO European Application & Technology Center, Berlin (Germany)

INTRODUCTION

Analysis of pesticides in foodstuffs is a routine, yet often complex analytical requirement, particularly in foodstuffs, containing significant levels of interfering matrix components, which can adversely affect the identification and quantification of numerous pesticides with satisfactory confidence.

One approach, using comprehensive two-dimensional gas chromatography (GC×GC) coupled to Time-of-Flight mass spectrometry (TOFMS), allows the impact of interferences from complex food matrices to be resolved, by a combination of significantly enhanced separation capacity together with fast acquisition, un-skewed, full mass range data collection. This results in far superior chromatographic resolution of pesticides and allows effective use of mass spectral deconvolution, therefore improving the detection and quantification confidence.

Currently, due to significant issues with helium (He) supplies, both in terms of availability and increasing costs, much attention is focused on the use of hydrogen (H₂) as an alternative carrier gas, due to the ease of using generators to source it abundantly and at high purity. Historically, issues with using certain MS instrumentation with H₂ carrier gas, concerning mass spectral quality, sensitivity and robustness, deterred many analysts from transferring their methods.

Here, we summarise a proof-of-concept evaluation of the analysis of various pesticide chemistries with H₂ carrier gas, using GC×GC and a uniquely designed TOFMS technology. Comparisons of mass spectral fragmentation, dynamic range, sensitivity, robustness, chromatographic resolution and run times, obtained with both He and H₂, were performed. The results demonstrated both carrier gases gave very similar mass spectral fragmentation and similarity for NIST MS library matching, similar sensitivity and dynamic range and, also the possibility to reduce analysis time using H₂.



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- Industry Leading Deconvolution & Non-Target Detection
- ChromaTOF® – A Single Software for Hardware Control and Data Processing
- Benchtop Footprint

SAMPLES

A standard mixture containing >100 individual pesticides was used for calibration purposes. A 6-level calibration curve ranging from 1 to 500 ng/mL was established for both He and H₂ supplied methods to check linearity, dynamic range and sensitivity. A close focus on H₂-sensitive components (e.g., halogenated pesticides) was performed to evaluate their behavior when using H₂ carrier gas. An *n*-alkanes mixture (C7-C30) was used for Linear Retention Index (RI) calculation.

METHODS

Table 1 displays the GC×GC-TOFMS parameters selected for the purpose of this study. Some of the conditions are shared between the He and H₂ supplied methods. The oven temperature ramps were optimized according to [1]. A splitless liner was used for all applications (Restek # 23303).

Table 1. GC×GC-TOFMS parameters for He and H₂ supplied methods

GC (Agilent 8890 GC)	Helium	Hydrogen
Injection	1 μL Splitless 250 °C	1 μL Splitless 250 °C
Carrier gas	1.4 mL/min	1 mL/min
Primary Column (D ₁)	Rxi-5MS 30 m x 0.25 mm ID x 0.25 μm coating	
Secondary Column (D ₂)	Rxi-17SilMS 0.75 m x 0.15 mm ID x 0.15 μm coating	
Oven Program	75 °C (1 min), 7 °C/min to 320 °C (2 min)	75 °C (1 min), 6 °C/min to 320 °C (2 min)
Secondary Oven	+ 5 °C with respect to the primary oven	
Modulator	+ 15 °C with respect to the secondary oven	
Transfer line	250 °C	
MS	LECO Pegasus BT4D	
Ion source temp	250 °C	
Mass range	40 – 500 m/z	
Acquisition rate	200 spectra/s	

RESULTS

The transition from He to H₂ supplied GC(×GC)-MS methods, particularly for 1 dimensional analyses, often requires reducing the primary column's internal diameter to adjust to the reduced viscosity of H₂ and obtain optimum inlet pressures. This also yields increased chromatographic efficiency and the ability to reduce analysis times.

For this 2 dimensional study, instead, we decided to stay with a conventional 1D column (i.e., 0.25 mm ID) taking advantage of the restriction determined by the ID of 2D column (i.e., 0.15 mm ID). Ultimately, this configuration enabled a starting head pressure of ~ 5 psi at 75 °C (a value within the inlet head pressure requirements) and, very similar sample capacities for the two methods. Furthermore, it made conversion of an existing He-supplied GC×GC-TOFMS method into a H₂ supplied one, very easy, as no hardware changes were required.

Figure 1 shows a comparison between the He- and H₂-supplied GC×GC-TOFMS methods. As expected, even though the same column setup was used for both experiments, the H₂ method resulted in faster analysis times (~15%), compared with He. This was calculated based on the R.T. of the last pesticide residue monitored for this analysis (i.e., dimethomorph CAS: 110488-70-5). Moreover, looking into a zoomed area (orange rectangle), the chromatographic resolution, both in 1D and 2D between the two methods was fully comparable, despite the different oven program rates and overall faster run time.

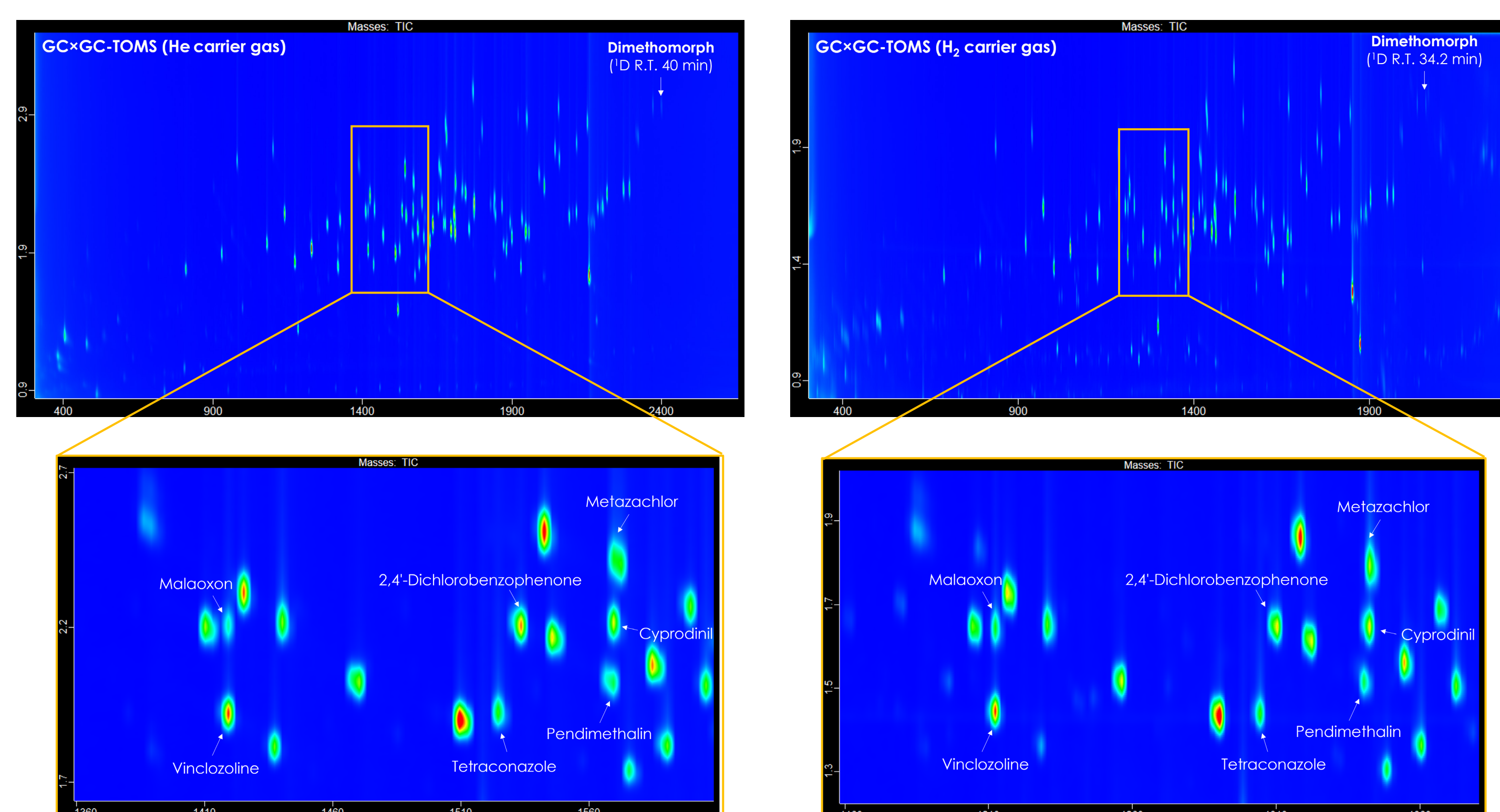


Figure 1. Comparison between the He- and H₂-supplied GC×GC-TOFMS methods based on the whole contour plots and a zoomed area of interest with many pesticide residues nicely resolved thanks to the separation in the 2D column.

Figure 2 shows a comparison between the TOFMS spectra obtained for the same pesticide residues (i.e., benzene, hexachloro and chlorpyrifos methyl) with both He and H₂ carrier gas. This has often been a concern using various MS technologies, as H₂ carrier gas may produce spectra with higher background m/z fragments and/or significantly variable fragmentation, not searchable with conventional MS libraries (i.e., NIST). No substantial differences were observed in this respect, as both spectra resulted in high and comparable similarity score values.

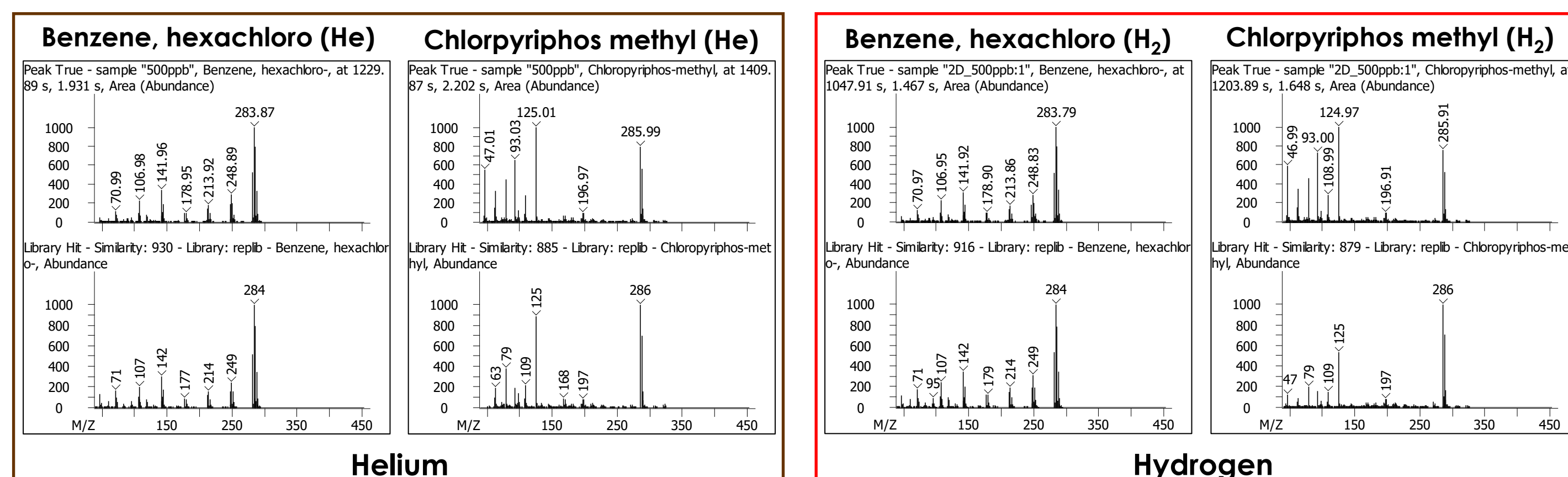


Figure 2. Comparison between He and H₂ MS spectra for two selected pesticide residues.

Table 2 reports the list of pesticides we selected for this study along with the information regarding their R.T.s, library similarity scores, correlation coefficients (R²) obtained from the calibration as well as the S/Ns calculated at the lowest level calibrated (i.e., 1 ng/mL). The results are showed for both the He and H₂ GC×GC-TOMS methods.

Table 2. Overall comparison between He and H₂ GC×GC-TOFMS methods. Information about spectral quality, sensitivity and linearity are reported for 10 selected pesticide residues.

Name	Helium					Hydrogen				
	1D RT	2D RT	Similarity Score*	R ²	S/N (1ng/mL)	1D RT	2D RT	Similarity Score*	R ²	S/N (1ng/mL)
Etridiazole	929.924	1.89	910	0.99582	31	791.941	1.425	888	0.99908	33
Chlorpropham	1172.9	1.835	741	0.99762	94	1001.92	1.38	811	0.99332	25
Pyrimethanil	1325.88	2.135	923	0.99169	73	1129.9	1.6	927	0.99876	154
Tolclofos-methyl	1424.86	2.31	885	0.99401	27	1215.89	1.72	874	0.99926	76
Heptachlor epoxide	1583.85	2.085	897	0.99532	83	1353.87	1.555	887	0.99967	22**
Quinalphos	1598.84	2.265	876	0.98749	17	1365.87	1.685	870	0.9978	26
p,p'-DDE	1634.84	2.1	916	0.99963	480	1449.86	1.54	914	0.99674	380
Chlorobenzilate	1754.83	2.075	868	0.98616	17	1503.86	1.53	888	0.99857	42
p,p'-DDD	1772.82	2.26	890	0.99566	63	1517.85	1.665	893	0.99919	59
Tebuconazole	1865.81	2.23	845	0.98968	20	791.941	1.425	888	0.99908	33

*calculated at 100 ng/mL calibration level

** at 2 ng/mL level

CONCLUSIONS

This study demonstrated that using LECO's Pegasus BT4D, results obtained using H₂ carrier gas compared closely to those generated when using He, with no significant performance differences. In particular, when focusing on fragmentation quality and sensitivity, the H₂-supplied method showed very comparable results, indicating that LECO's StayClean Ion source is highly suitable when H₂ is selected as the carrier gas of choice. This ultimately translates into easy-convertible GC×GC methods.

Furthermore, no sensitivity losses were observed due to the lower vacuum pump capacity. This allowed the same injection volumes to be maintained, thus avoiding overloading the system with unnecessary matrix.

[1] Blumberg L. M., Klee M., J Micro Sep 12: 508–514, 2000