Utilising unique TOF-MS technology and hydrogen carrier gas for fast GC-MS to produce robust, high quality, library comparable mass spectral data

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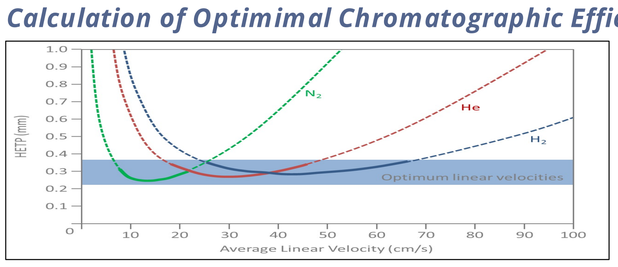
Introduction

Helium is an increasingly limited and expensive natural resource. Utilising hydrogen as a carrier gas in GC applications is becoming more desirable. In addition to safety concerns, mass spectral quality & fragmentation obtained when using hydrogen, in comparison with helium, as well system sensitivity, robustness and acquisition rates are important factors which can differ and negatively affect results. In this study we have investigated the use of a particular type of GC-TOF-MS technology with regards to overcoming these issues whilst taking effectively leveraging the benefits of hydrogen carrier gas.

Calculation of Optimimal Chromatographic Efficiency – Van Deemter Curves



Operating in the optimal plate height (blue shaded) region allows the best chromatographic resolution and efficiency to be achieved – using helium, transfer to narrower ID columns can enable some speed benefits whilst maintaining resolution. Using hydrogen widens this operational range, allowing additonal speed to be achieved with less compromise on resolution.

Practical Considerations

A GC-FID uses many times more flow than a GC-MS so any lab setup for GC-FID is already well on the way to using hydrogen carrier gas. The use of a hydrogen generator mitigates many safety concerns and reduces the ongoing costs to that of electricity – far cheaper than the ever-increasing cost of helium.

Instrumentation suitability is key to success. The vacuum pump must be capable of operating with the reduced pressure associate with hydrogen. The detector must be fast enough to cope with the higher speeds, not just of detecting the peaks but with enough data point to deconvolute and quantify. Additionally, the ion source design must mitigate the issues created by hydrogen "scrubbing" and provide fragmentation comparable with libraries created using helium carrier gas.

Method

A stepwise method transfer process was performed starting with a standard 30m x 0.25mm column (column A) and helium carrier gas. This was changed to a 20m x 0.18mm column (column B) with helium before switching to hydrogen carrier gas using the same column and finally swapping to a 15m x 0.15mm column (column C) with hydrogen. RTX-5 column phase was in all cases and the phase ratio kept at 1 throughout.

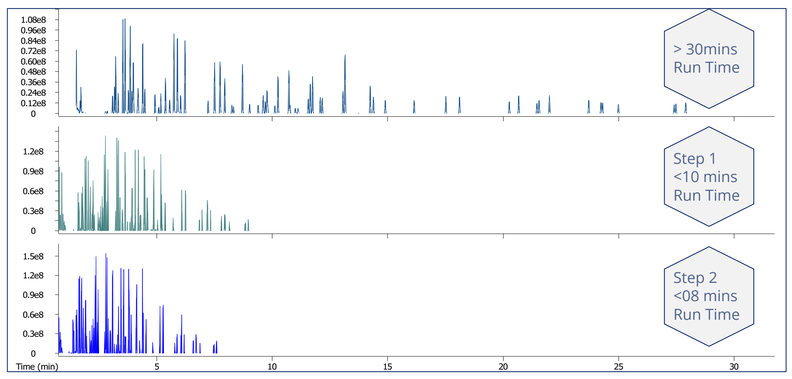
Pressure/flow/temperature calculations were executed to test performance criteria at a) optimum plate height, calculated for direct chromatographic resolution transfer between the phases and b) applicability of additional chromatographic speed. The free online EZGC Method Translator (Restek) was used for the calculations.

Tests were performed using EPA 8270 standard and extracts of waste, river and drinking waters.

Performance criteria evaluated were chromatographic resolution, speed & precision and mass spectral data quality, including spectral fragmentation, signal precision, sensitivity and dynamic range for different chemical classes.

Results

Results from the calculations and analysis of EPA 8270 standard mix showed increased analysis speeds by a factor of 3.67 whilst maintaining chromatographic resolution and by 4.53 with only a small loss in resolution.



Overall Translation

Columns A to C
Helium to Hydrogen

Step 1: Resolution maintained with increased speed

Step 2: Speed increased further

Repeatability tests showed retention time precision in the range of 4-6 %RSD for both helium and hydrogen.

	Start	Column A		Column B		Column C	
Optimisation		**Resolution**	**Speed**	**Resolution**	**Speed**	**Resolution**	**Speed**
Time improvement	**x1.00**	x1.55	x1.86	x2.59	x3.12	x3.67	**x4.53**
Resolution	**1.66**	1.72	1.61	1.63	1.54	1.58	**1.51**

Resolution calculated using 2,3,5- & 2,3,6- trichlorophenol

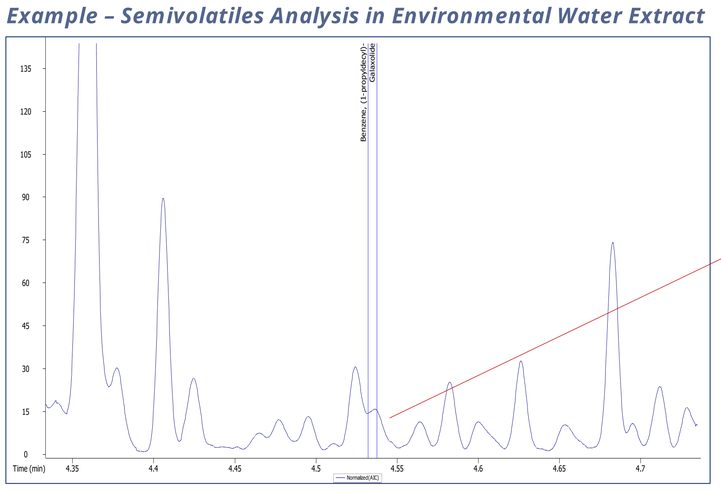
MS Performance – Sensitivity & Quantification

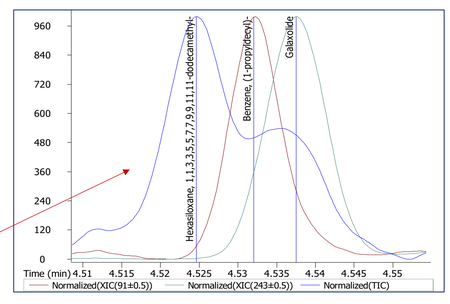
Signal to noise comparisons (1pg analyte on column) showed similar or increased sensitivity when using hydrogen. R^2 values of 0.997-0.999 were observed for calibration plots in the range of 1 to 1000 ppb.

Analyte	CAS	Helium 20m x 0.18mm		Hydrogen 20m x 0.18mm	
		R^2	S/N @ 1pg/µL	R^2	S/N @ 1pg/µL
Benzene, 1,2,4-trichloro-	120-82-1	0.9992	25	0.99786	27
Hexachlorbutadiene	87-68-3	0.99929	44	0.99811	37
Naphthalene, 2-methyl-	91-57-6	0.99882	37	0.998	31
Benzene, hexachloro-	118-74-1	0.99903	43	0.99781	104
Phenanthrene	85-01-8	0.99836	37	0.9978	104
Di-n-octyl phthalate	117-84-0	0.99906	11	0.99786	7
Indeno[1,2,3-cd]fluoranthene	193-43-1	0.99816	25	0.99848	60
Dibenz[a,h]anthracene	53-70-3	0.99775	31	0.99902	60

Examples of signal to noise ratios at 1pg/µL and R^2 values with helium compared with hydrogen using the same column and direct method transfer conditions

Example – Semivolatiles Analysis in Environmental Water Extract

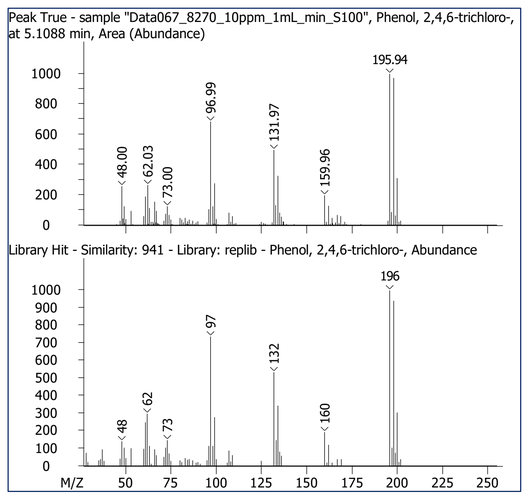


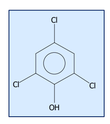


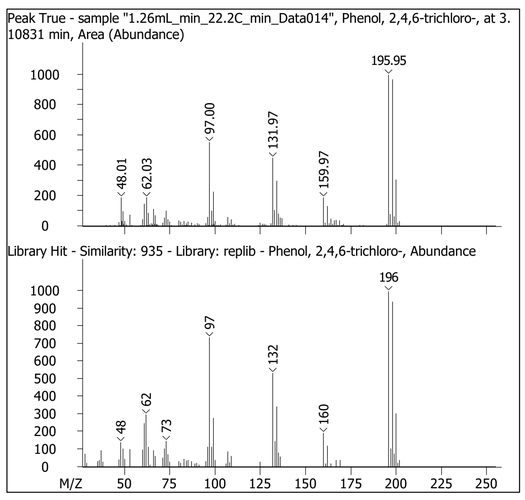
Waste water shows co-elutions in very high matrix load. TOF-MS acquisitions speeds with full range spectra allow 3 peaks coelluting in 0.7 seconds to be identified and quantified.

MS Performance – Spectral Quality

Fragmentation patterns observed were highly comparable with helium and NIST Library entries.





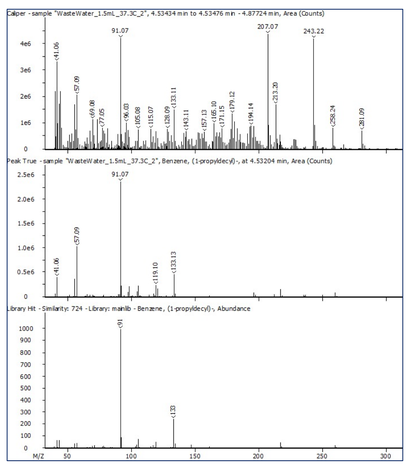


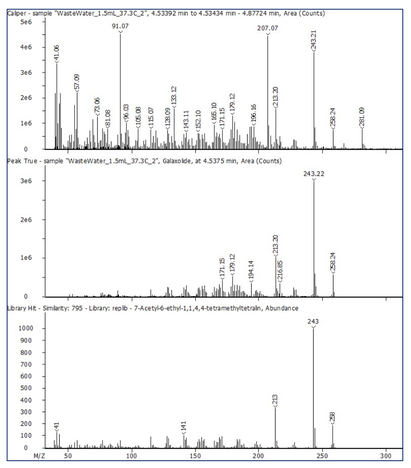
Helium Match = 941

Hydrogen Match = 935

Analyte	Similarity		Analyte	Similarity	
	He	H_2		He	H_2
Aniline	946	945	m-Nitroaniline	879	855
Phenol, 2-chloro-	923	921	Dibenzofuran	897	885
Benzyl alcohol	903	828	Phenol, 2,3,4,6-tetrachloro-	926	917
Benzene, 1,2,4-trichloro-	941	928	Diethyl Phthalate	893	859
p-Chloroaniline	918	933	Diphenylamine	940	924
Hexachlorobutadiene	939	920	Benzene, 1-bromo-4-phenoxy-	852	851
Naphthalene, 2-methyl-	915	896	Benzene, hexachloro-	933	901
Phenol, 2,4,5-trichloro-	931	920	Phenanthrene	934	909
Naphthalene, 2-chloro-	934	907	Indeno[1,2,3-cd]fluoranthene	912	912
Acenaphthylene	950	940	Dibenz[a,h]anthracene	865	865

Additional mass spectral similarity comparisons of helium vs hydrogen (calculated in comparison with NIST library entries): very similar mass spectral fragmentation is observed.





Waste Water deconvolution example

Galaxolide mass spectrum is deconvoluted from Benzene, (1-propyldecyl) and from siloxane contamination

Left: Benzene,(1-propyldecyl)
Right: Galaxolide

Top: caliper spectrum (average)

Middle: deconvoluted spectrum

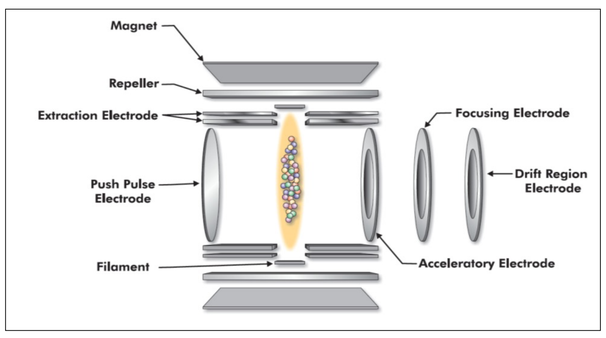
Bottom: Library matches

Discussion

Complex samples, such as environmental water, create complex coelutions. To deconvolute and quantify the analytes a fast detector producing wide mass spectral data is required. Additionally, hydrogen has a scrubbing effect on metal surfaces, creating issues within MS sources and producing fragmentation patters dissimilar to those from helium. A source without sides is the ideal solution, such as an open ion source. This study has demonstrated how well an open ion source works with hydrogen when compared to helium.

Time of Flight Mass Spectrometer (TOF-MS)

- TOF-MS allows fast data acquisition speeds
- Full mass range, unskewed data is collected at all acquisition rates
- These features combined are ideal for deconvoluting fast GC data in complex samples



Stay-Clean® Open Ion Source Design

- Open ion source design which minimises interaction of sample ions with surfaces and thus eliminates the need for cleaning – especially important with hydrogen carrier gas
- The open design also ensures that spectral fragmentation is very similar with hydrogen to that observed when using helium – vital for MS library matching

Conclusions

Safety considerations for working with H2 are clear and can be handled easily

Costs savings can be achieved over the short-medium term

The chromatographic method transfer process can be managed nicely and easily by following a systematic calculation approach

Analysis throughput is improved significantly, whilst maintaining chromatographic resolution

Using suitable instrumentation is important, especially for obtaining good sensitivity, robust, high quality MS data and comparable MS spectral fragmentation for identification purposes (TOF-MS and open ion source design)

Acknowledgements

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Learn more: Pegasus BT® StayClean® Ion Source

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