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Application Note 155

TD–GC–MS analysis of VOCs in air using hydrogen carrier gas

Summary

This application note demonstrates how a Markes Multi-Gas thermal desorber can operate with hydrogen carrier gas as well as it does with helium to meet all the performance criteria cited in US EPA Method TO-17, including linearity, reproducibility and method detection limits (MDLs).

This application note focuses on the impact of switching regulated TD–GC(–MS) air monitoring methods to hydrogen carrier gas using a 10-ppb gas standard comprising a challenging, extended suite of US EPA Method TO-17 ‘air toxics’ compounds as an example.

Figure 1: The TD100-xr Multi-Gas instrument for 100-tube automation with helium, nitrogen or hydrogen carrier gas.

Introduction

Helium is a finite resource that is increasingly expensive and difficult to source as a gas chromatography (GC) carrier gas. Also, it has to be extracted and stored before being shipped around the world, giving it a high carbon footprint. Hydrogen is simple to generate using water and electricity so seems to be the obvious environmentally-friendly alternative. Securing against helium shortages in the long term and offering immediate cost and operational savings, hydrogen also promises shorter analytical cycle times and faster sample throughput.

Several of Markes’ world-leading xr-range thermal desorption (TD) systems are now certified for safe operation with hydrogen carrier gas and can be connected to any hydrogen-ready gas chromatograph and mass spectrometer. These are:

- **UNITY-xr™** – optimum two-stage TD performance for single sorbent tubes.
- **TD100-xr™** – the world’s leading automated thermal desorber with capacity for 100 tubes (Figure 1).
- **UNITY–ULTRA-xr™** – 100-tube TD system with versatile upgrade routes.
- **UNITY–ULTRA-xr Pro™** – 199-tube automation of thermal desorption, re-collection and repeat analysis.

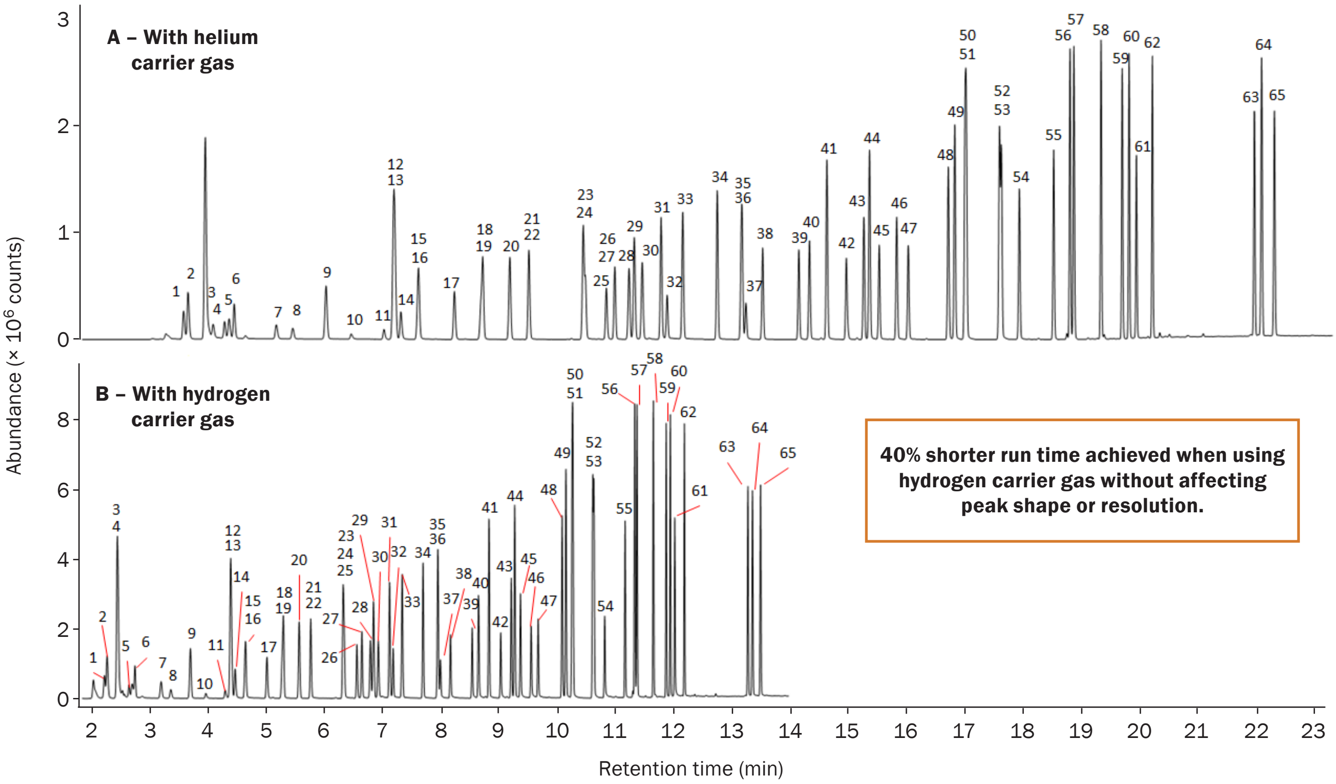
In this new family of Markes systems, no TD features or functions are compromised by using hydrogen, and all hydrogen-ready thermal desorbers can also be used with helium or nitrogen carrier gas without changing system hardware.

Method development and optimisation

Aliquots of ‘air toxics’ standard (10-ppb level) were loaded into conditioned ‘Universal’ tubes (Markes International part number C3-CAXX-5266) at atmospheric pressure using the Calibration Solution Loading Rig™ (part number C-CSLR) and a 10-ml gas syringe. The rig was set up with a 50 mL/min flow of pure nitrogen to sweep the injected analytes through the sampling end of the tube and onto the sorbent. After purging for 1 minute, the loaded tubes were removed and sealed. The volumes of gas standard introduced were adjusted such that the mass of each analyte equated to the levels that would be retained when sampling 1 L of air at component concentrations ranging from 0.5 ppb to 10 ppb.

First, the TD–GC–MS system was benchmarked using conventional helium carrier gas and the existing US EPA Method TO-17 parameters to provide a reference before the system and method were translated over to the use of hydrogen carrier gas for comparison. The same TD–GC–MS instruments and capillary column were used in each case. Example total ion chromatograms obtained using helium and hydrogen carrier gas are shown in Figure 2.

A free software tool for GC method translation was used initially to adjust the GC program for operation with hydrogen carrier gas. A visual inspection of the chromatograms revealed similar profiles, but the run was completed in under 14 minutes with hydrogen compared to 23 minutes using helium. This will have a major effect on analytical productivity and sample throughput (Figure 3).



40% shorter run time achieved when using hydrogen carrier gas without affecting peak shape or resolution.

Figure 2: Total ion chromatogram obtained from the equivalent of 1000 mL of a 10-ppb ‘air toxics’ standard: (**A**) Analysed using a hydrogen-ready TD100-xr configured to a GC with quad-MS and using helium carrier gas; (**B**) Analysed using hydrogen carrier gas.

1 Propene
2 Dichlorodifluoromethane
3 Dichlorotetrafluoroethane
4 Chloromethane
5 Vinyl chloride
6 Butadiene
7 Bromomethane
8 Chloroethane
9 Trichlorofluoromethane
10 Ethanol
11 Acrolein
12 1,1-Dichloroethene
13 1,1,2-Trichloro-1,2,2-trifluoroethane
14 Acetone
15 Isopropanol
16 Carbon disulfide
17 Dichloromethane
18 1,2-Dichloroethene
19 *tert*-Butyl methyl ether
20 Hexane
21 1,1-Dichloroethane
22 Vinyl acetate
23 Methyl ethyl ketone
24 *trans*-1,2-Dichloroethene
25 Ethyl acetate
26 Tetrahydrofuran
27 Trichloromethane (Chloroform)
28 1,1,1-Trichloroethane
29 Cyclohexane
30 Tetrachloromethane
31 1,2-Dichloroethane
32 Benzene
33 Heptane
34 Trichloroethene
35 1,2-Dichloropropane
36 Methyl methacrylate
37 1,4-Dioxane
38 Bromodichloromethane
39 *cis*-1,3-Dichloropropene
40 4-Methylpentan-2-one
41 Toluene
42 *trans*-1,3-Dichloropropene
43 1,1,2-Trichloroethane
44 Tetrachloroethene
45 Methyl n-butyl ketone
46 Dibromochloromethane
47 1,2-Dibromoethane
48 Chlorobenzene
49 Ethylbenzene
50 *m*-Xylene
51 *p*-Xylene
52 *o*-Xylene
53 Styrene
54 Tribromomethane (Bromoform)
55 1,1,2,2-Tetrachloroethane
56 Benzyl chloride
57 4-Ethyltoluene
58 1,3,5-Trimethylbenzene
59 1,2,4-Trimethylbenzene
60 1,2-Dichlorobenzene
61 1,4-Dichlorobenzene
62 1,3-Dichlorobenzene
63 1,2,4-Trichlorobenzene
64 Hexachlorobutadiene
65 Naphthalene

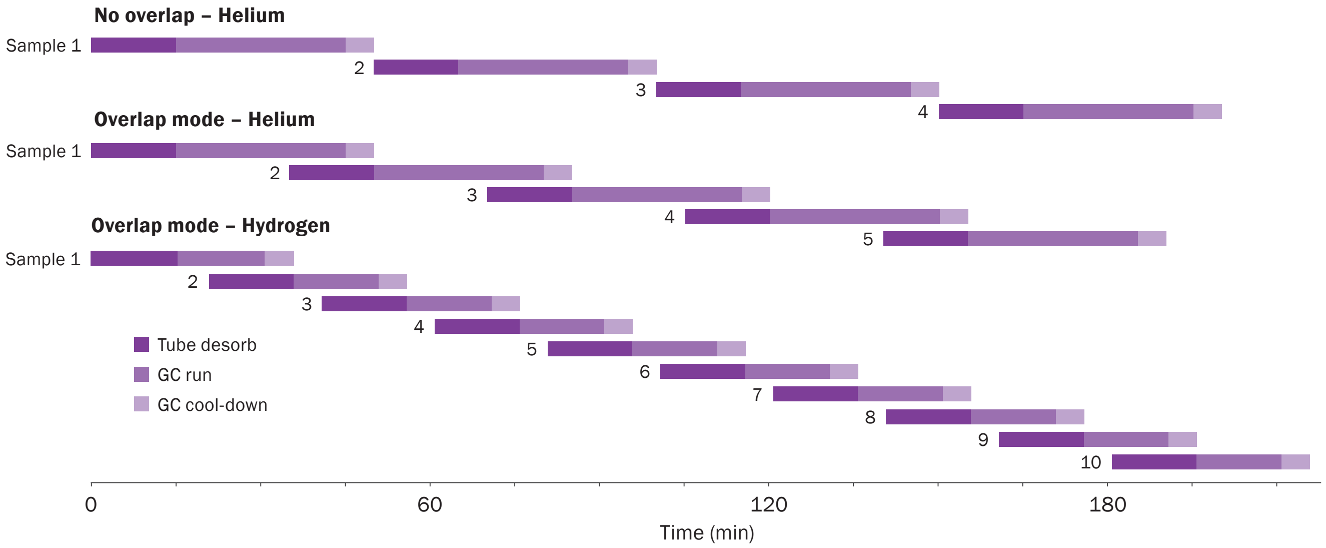
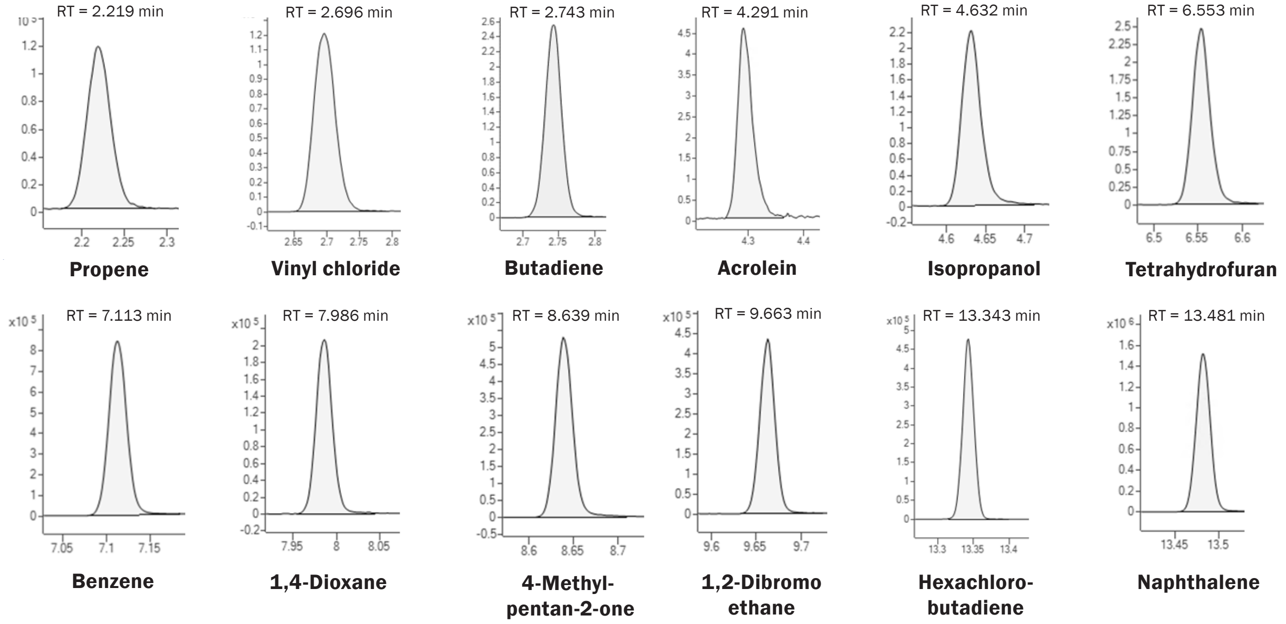


Figure 3: Markes’ overlap mode, with reduced GC cycle times, improves analytical productivity, especially when compared with instruments without sample overlap. Productivity is further improved when using hydrogen carrier gas.



Propene **Vinyl chloride** **Butadiene** **Acrolein** **Isopropanol** **Tetrahydrofuran**

Benzene **1,4-Dioxane** **4-Methyl-pentan-2-one** **1,2-Dibromo ethane** **Hexachloro-butadiene** **Naphthalene**

Figure 4: Extracted ion chromatograms of specified compounds at 10 ppb using hydrogen carrier gas.

A closer inspection of individual components in the hydrogen chromatogram (Figure 4) shows the excellent peak shape obtained, even for polar compounds such as acrolein, isopropanol and 1,4-dioxane.

Meeting TO-17 method performance criteria

1. Method detection limits (MDLs)

Although the use of hydrogen carrier gas is often considered to reduce GC–MS sensitivity slightly, this effect has not been observed in our studies.

Seven replicate injections of the lowest-level standard (equating to 0.25 ppb in 1 L of air) were used to calculate MDLs for both helium and hydrogen carrier gas using the recommended US EPA procedure.[1]

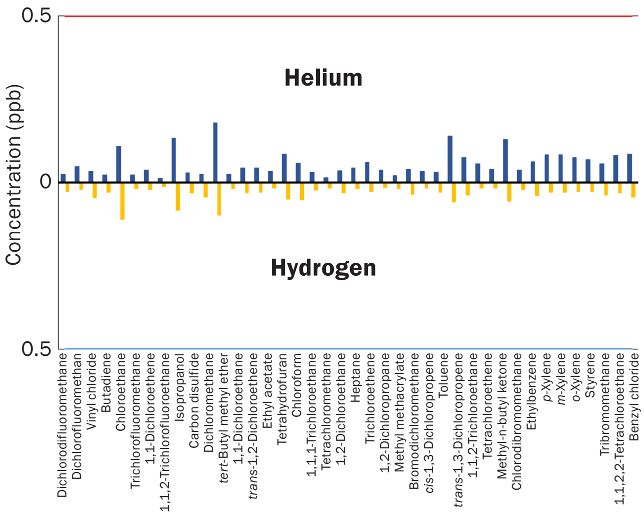


Figure 5: A comparison of MDLs for selected air toxics compounds using helium and hydrogen carrier gas.

In practice, this study showed that the impact of hydrogen on sensitivity was small and the detection limits of many compounds using hydrogen carrier gas were actually comparable to conventional helium (Figure 5 and Table 1).

In any event, the key finding was that all 65 air toxics components in these tests were comfortably below the 0.5-ppb TO-17 performance criteria for MDLs using both helium and hydrogen as a carrier gas.

Compound	Helium	Hydrogen
Dichlorodifluoromethane	0.026	0.027
Vinyl chloride	0.033	0.046
Butadiene	0.023	0.029
Chloroethane	0.108	0.111
Trichlorofluoromethane	0.024	0.020
1,1,2-Trichlorofluoroethane	0.013	0.014
Isopropanol	0.134	0.083
Carbon disulfide	0.030	0.031
Dichloromethane	0.026	0.045
Vinyl acetate	0.044	0.032
Tetrahydrofuran	0.058	0.052
Tetrachloromethane	0.036	0.033
Heptane	0.060	0.027
Methyl methacrylate	0.041	0.037
Bromodichloromethane	0.034	0.018
cis-1,3-Dichloropropene	0.031	0.029
Methyl-n-butyl ketone	0.129	0.058
Ethylbenzene	0.062	0.039
p-Xylene	0.084	0.031
Styrene	0.070	0.028
1,1,2,2-Tetrachloroethane	0.081	0.033
Benzyl chloride	0.085	0.044

Table 1: MDL data (in ppb) for selected air toxics compounds using helium and hydrogen carrier gas as seen in Figure 4.

2. Linearity

Linearity was evaluated using the system with helium carrier gas and then again with hydrogen carrier gas using six standards equating to a range 0.5 to 10 ppb in 1 L air sample volumes. Examples of some of the most challenging components in the TO-17 test mix are shown in Figure 6.

Again, all components in the test mix were found to comfortably exceed the US EPA performance criteria for R^2 (>0.99) using both helium and hydrogen as a carrier gas.

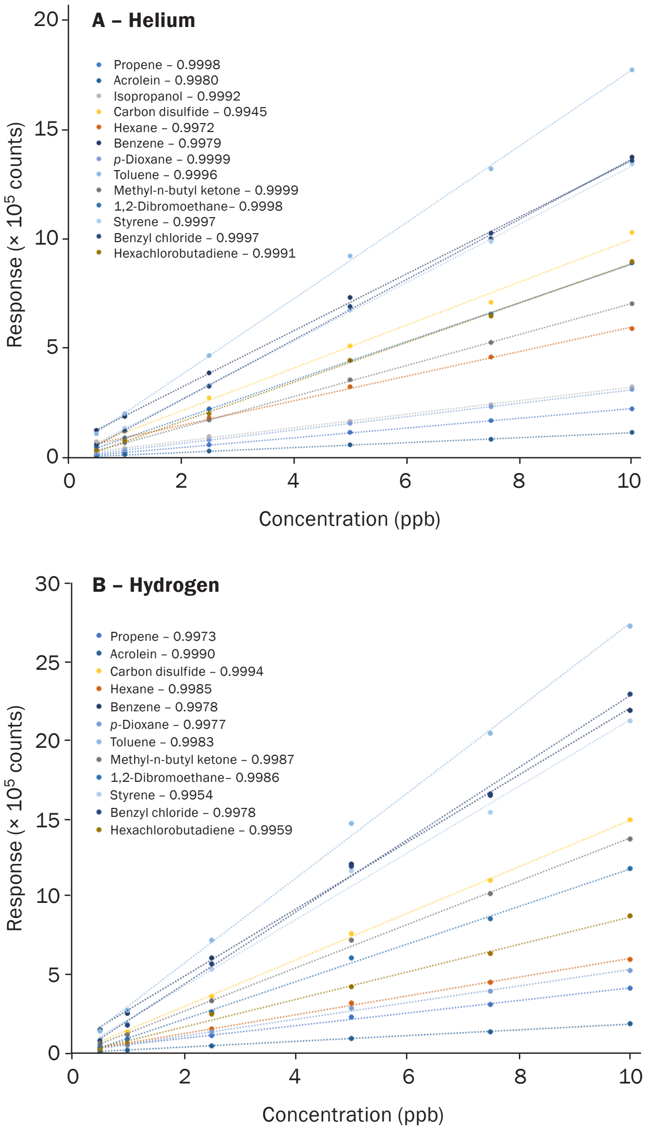


Figure 6: Linearity plots for a wide range of VOCs with (**A**) helium and (**B**) hydrogen.

3. Reproducibility

Method reproducibility was evaluated using 10 replicate injections of the 5-ppb standard, using hydrogen as a carrier gas. The results are shown in Table 2 for the reproducibility of the response, relative response factors and retention time stability. Again, system performance was found to be comfortably within US EPA requirements for TO-17.

Compound	%RSD area (n = 10)	%RSD RRF	%RSD retention time (n = 50)
Propene	5.0	22.2	0.16
Acrolein	4.9	13.9	0.07
Isopropanol	5.0	4.60	0.05
Carbon disulfide	3.8	7.6	0.06
Hexane	2.0	2.5	0.09
Benzene	2.5	18.8	0.04
p-Dioxane	2.9	2.6	0.02
Toluene	2.4	4.6	0.02
Methyl-n-butyl ketone	2.5	8.6	0.02
1,2-Dibromoethane	2.9	16.8	0.01
Styrene	2.3	8.9	0.01
Benzyl chloride	3.5	15.1	0.01
Hexachlorobutadiene	4.4	16.5	0.01
Average across full range of target VOCs	**3.8**	**10**	**0.11**
Criteria	**<20**	**<30**	**<1**

Table 2: TD–GC–MS reproducibility evaluated using the 5-ppb air toxics standard with hydrogen carrier gase.

4. Other important system performance checks

While not required for method compliance, the impact of hydrogen on two other important practical aspects of VOC air monitoring were evaluated during this study.

(a) Dry-purging for water management: TO-17 air toxics include some very volatile and polar target analytes that require the inclusion of a strong carbon molecular-sieve-type sorbent in the sampling tube. Such sorbents are not hydrophobic, and a significant mass of water (several milligrams) can be retained when sampling 1 or 2 L air volumes in humid environments. This means that many ambient air samples require dry-purging before desorption to selectively remove retained water while retaining all target analytes, including the most volatile and polar compounds.

Dry-purging can be carried out off-line before analysis using Markes' TC-20™ system to purge up to 20 tubes simultaneously using any dry clean gas – typically nitrogen – flowing in the sampling direction. All Markes' automated TD systems offer the option to run a dry-purge step as an integral part of the automated TD process: a controlled flow of carrier gas is automatically passed through each ambient temperature tube, in the sampling direction, after the leak test and immediately before primary (tube) desorption. The water is directed to vent, eliminating interference in the subsequent analysis.

(b) Checking for hydrogenation: Hydrogen is not as inert as helium and there could be concerns regarding the possibility of hydrogenation of compounds of interest when it is used as a GC carrier gas.

The internal sample flow path of every Markes thermal desorber is inert, uniformly heated and narrow-bore, reducing the risk of any form of chemical activity, including hydrogenation. However, it is not possible to rule out the risk completely for every conceivable TD application.

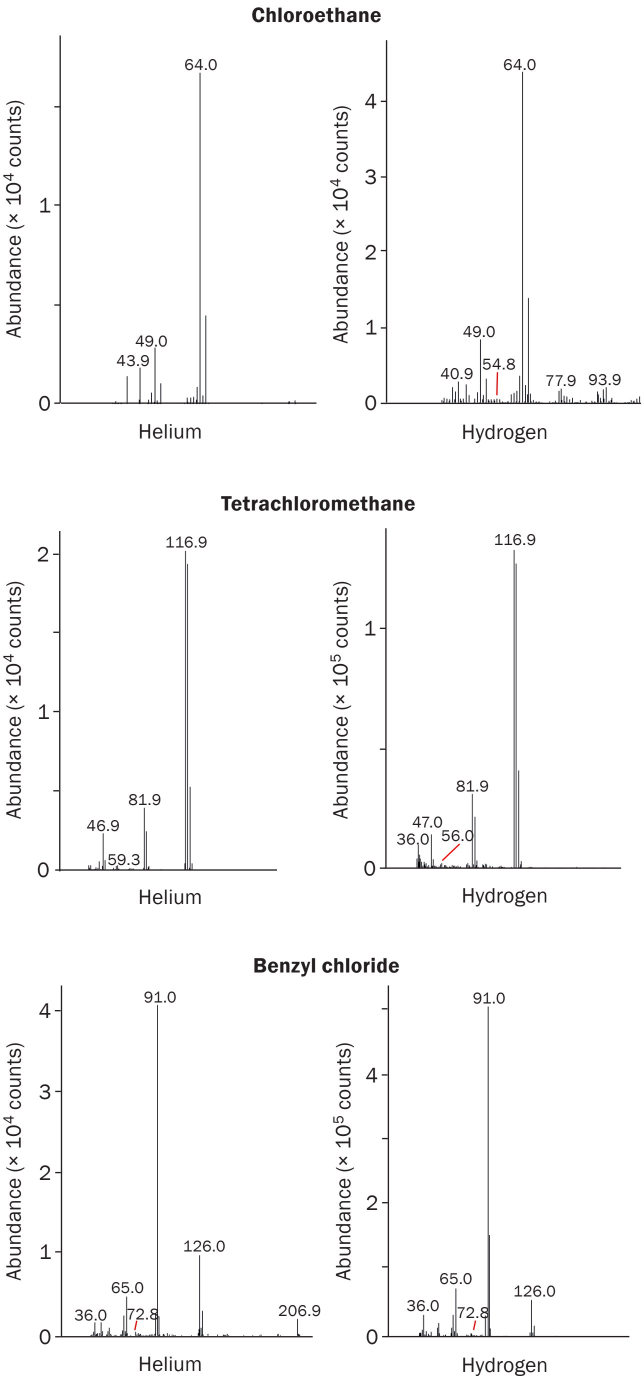


Figure 7: Example spectra for challenging compounds shown for both helium and hydrogen displaying minimal changes – major ions remain the same and with comparable ratios to qualifier ions.

If chemical activity does occur during GC analysis, it typically results in poor precision and linearity for affected compounds and this often becomes apparent during calibration. Compound losses (poor recovery) may also be evidenced by artefact formation. The results shown in this application (Figure 7) show no evidence of hydrogenation or spectral distortion.

Moreover, Markes' TD systems feature quantitative sample re-collection for repeat analysis, which is one of the simplest and most efficient ways of validating analyte recovery through the entire TD–GC process, as described in international standard methods.[2,3]

The function works by quantitatively transferring any and all sample split flow to a clean sorbent tube for re-collection, allowing a sequence of repeat analyses to be carried out on a single standard or sample. Whether it is caused by absorption/condensation, reactivity (*e.g.*, hydrogenation) or thermal degradation, any analyte losses that do occur quickly become apparent from a selective reduction in signal for the affected compound, relative to the split ratio and/or to more stable compounds in the run (see Application Note 024 for more information).

Automated sample re-collection and repeat analysis were used to test the recovery of the air toxic compounds through TD–GC–MS analysis using hydrogen carrier gas (Figure 8). The masses determined in each repeat analysis were as predicted from the split ratio, confirming no hydrogenation or any other sample losses.

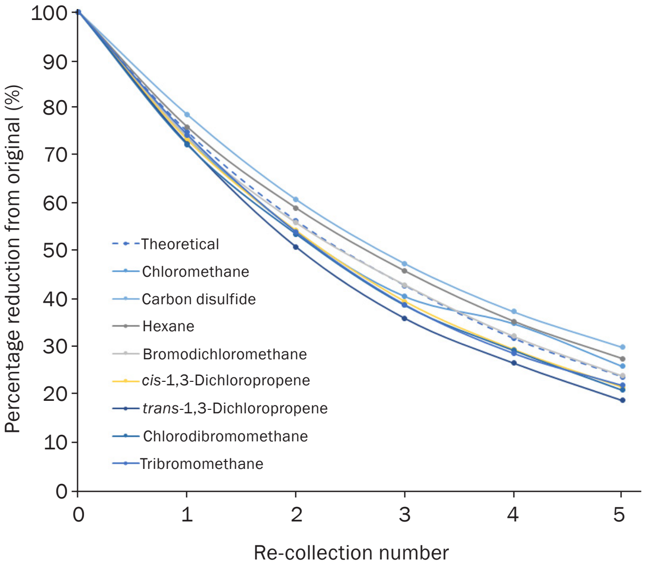


Figure 8: Results from a sequence of repeat TD–GC–MS analyses for a representative selection of air toxics.

The implementation of quantitative sample re-collection as a standard function of commercial TD systems was pioneered by Markes International and remains a powerful advantage of Markes' technology.

Details vary depending on the system configuration chosen, but every Markes desorber allows some form of quantitative re-collection of split flow (manual or automated) to enable repeat analysis and validation of analyte recovery.

Furthermore, most configurations feature the further proprietary advantage of allowing automated repeat analysis of re-collected samples, either outlet-split only or full double (inlet and outlet) split.

Note that, as shown in Figure 8, re-collection works equally well on a Markes Multi-Gas thermal desorber using hydrogen carrier gas as it does with helium.

Conclusion

This work has demonstrated that all the performance criteria cited in US EPA Method TO-17, including linearity, MDLs and reproducibility, can be comfortably met using a hydrogen-ready thermal desorber from Markes International, operating with either helium or hydrogen carrier gas. Furthermore, this study found no obvious negative impacts with using hydrogen – no significant reduction in sensitivity nor evidence for analyte hydrogenation – even across the varied compound groups present in the air toxics standard.

The investigation also showed how switching to hydrogen carrier gas resulted in a dramatic improvement in productivity by delivering approximately one extra sample to be processed each hour (Figure 3).

This is a major enhancement. It means at least 24 more billable samples can be processed every 24 hours on each hydrogen-ready TD100-xr. Depending on price, this adds up to over $12,000 extra revenue each week or >$480,000 per system per year, not including any additional savings on carrier gas costs.

References

1. Definition and procedure for the determination of the method detection limit, revision 2, US EPA, 2016, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2; December 2016 (epa.gov).
2. ISO 16000-6:2011, Indoor air — Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID, https://www.iso.org/standard/52213.html.
3. ASTM D6196 - 15e1, Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air, https://www.astm.org/Standards/D6196.htm.

Acknowledgements

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