White Paper 054
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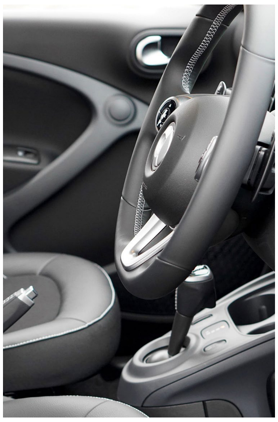
Analysis of odours and emissions from automotive textiles and trimmings by thermal desorption with GC×GC–TOF MS



This study demonstrates the use of direct desorption of various textiles and trimmings prior to analysis by thermal desorption (TD) and comprehensive two-dimensional gas chromatography with BenchTOF2™ time-of-flight mass spectrometry (GC×GC–TOF MS) to identify malodours and compounds of potential concern.

Introduction

The release of volatile and semi-volatile organic compounds (VOCs and SVOCs) from products and materials has been the subject of various mandatory regulations and 'green codes' for many years. US building codes, the European Construction Product Regulation (CPR) and Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)[1] are key examples of regulatory developments that increase the need for chemical emissions testing as part of product labelling.

The analysis of vehicle trim materials (including plastics, polyurethane, foam, wood, carpets, textiles and adhesives) has also been a major focus for emissions testing, in response to health concerns and off-odour complaints.

Markes International, a company of the Schauenburg Analytics Ltd group alongside SepSolve Analytical, has a well-deserved reputation for work on indoor air analysis, emissions from materials and vehicle interior air quality (VIAQ). The company's thermal desorption (TD) instrumentation is widely used to carry out standard methods, such as those stipulated in VIAQ regulations.[2]

However, the sample and matrix complexity, as well as an ever-expanding list of odorous compounds of concern, makes it a challenge for those responsible for performing sampling and analysis of target and non-target compounds. This has led to a need for innovative new methods for complete emissions characterisation.

Additionally, the recent global push towards a circular economy has meant that manufacturers are being urged to improve the sustainability of their operations by increasing the use of recycled or renewable materials, such as innovative plant-derived plastics. However, robust quality control is essential to ensure the final products will not produce volatile emissions that could be considered harmful or cause malodours.[3]

Here, we combine thermal desorption with comprehensive two-dimensional gas chromatography and BenchTOF2 time-of-flight mass spectrometry (TD–GC×GC–TOF MS) for versatile sampling, enhanced separation and confident screening of target and non-target compounds.

In this study, small sections of automotive textiles and trimmings were placed within empty TD tubes to allow volatile emissions to be directly desorbed onto the GC×GC–TOF MS, in a future-proofed system capable of going beyond current regulations and to help accelerate research and development of new materials.

Experimental

A schematic of the workflow used in this study is provided in Figure 1.

Samples: Eight different textiles and trimmings were analysed (Table 1). Each sample was carefully cut into small sections (weighing between 15–350 mg) and placed within empty inert-coated stainless steel tubes for direct desorption.

TD: UNITY–ULTRA-xr™ automated thermal desorber (Markes International); Desorbed at 100°C onto a ‘Material Emissions’ focusing trap (Markes International, part no. U-T12ME-2S).

GC×GC: INSIGHT® flow modulator (SepSolve Analytical); Modulation period (P_M) = 3.0 s

TOF MS: BenchTOF2 mass spectrometer (SepSolve Analytical); Mass range: m/z = 35–400; Ionisation energy: Tandem Ionisation at 70 eV and 14 eV.

Software: ChromSpace® software (SepSolve Analytical) for full instrument control and processing.

Please contact SepSolve for full analytical parameters.

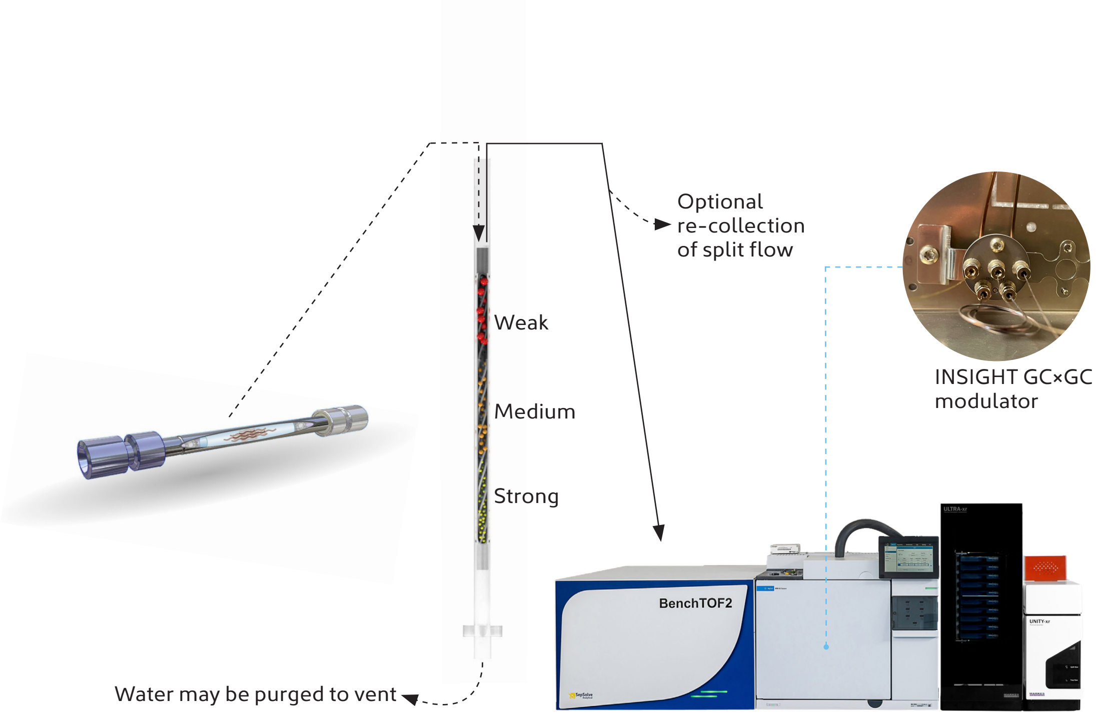


Figure 1

Overview of the analytical workflow used in this study.

1. Simple direct desorption of textiles and trimmings within an empty TD tube.
2. Electrically-cooled focusing trap with backflush operation for compatibility with multi-bed sorbents and wide analyte range.
3. Automated analysis by TD–GC×GC–TOF MS with full instrument control and data processing by ChromSpace software.

Table 1

List of samples analysed in this study.

Sample ID	Sample type	Sample weight (mg)
A	Composite foam	97.9
B	Vinyl upholstery (PVC leather)	15.0
C	Felt carpet	93.6
D	Rubber sealing strip	348.6
E	Polypropylene (PP) plastic	301.9
F	Sponge	52.3
G	Sound insulation cotton	45.0
H	Textile	70.2

Results and discussion

Figure 2 shows the comparison of chromatograms for direct desorption of a composite foam analysed by both GC–MS and GC×GC–TOF MS, with multiple peaks separated that would have co-eluted in 1D GC analysis.

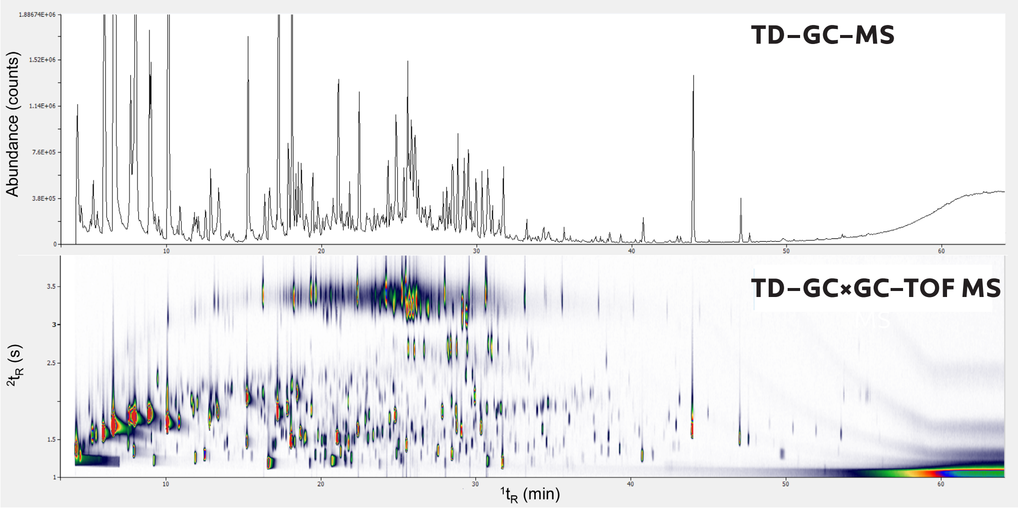


Figure 2

Comparison of chromatograms obtained from direct desorption coupled with 1D GC–MS and 2D GC×GC–TOF MS for the analysis of a composite foam.

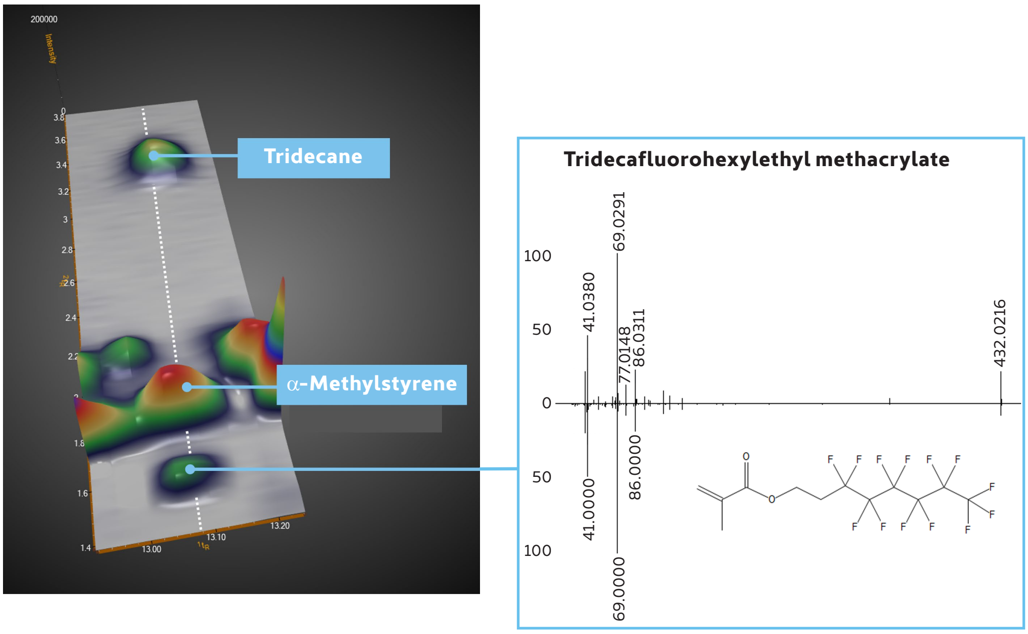


Figure 3

Enhanced region of the composite foam sample showing the improved separation capacity of GC×GC–TOF MS, enabling confident identification of a fluorotelomer acrylate, which would have been masked in 1D GC–MS.

It is possible that deconvolution could uncover some co-eluting species, but the more co-elutions that are present and the more ions that the co-eluting compounds have in common, the more difficult it becomes to deconvolve their spectra. It is clear from the complexity shown in the chromatogram in Figure 2 that deconvolution would struggle to resolve all of the components.

Figure 3 shows an enhanced region of the chromatogram, highlighting three components by GC×GC–TOF MS that would have co-eluted in 1D GC–MS. Interestingly, one of the peaks in this example is a fluorotelomer acrylate belonging to the per-/polyfluoroalkyl substances (PFAS) family. PFAS have received much attention in recent years, due to their adverse health effects, widespread use and persistence in the environment. It is likely that in 1D GC–MS, this trace fluorotelomer acrylate would have been overlooked, due to co-elutions with multiple analytes. On the other hand, with TD–GC×GC–TOF MS, the analytes are physically separated for cleaner spectra and confident identification (Figure 3). In this case, a polar column has been used in the first dimension, with a non-polar column in the second dimension, meaning that non-polar analytes (e.g. tridecane) are more highly-retained by the secondary column and therefore elute later in the second dimension.

It is important to note that the described TD–GC×GC–TOF MS system provides sampling, separation and identification of wide-ranging analytes – including volatiles, semi-volatiles and thermally-labile species. Figure 4 shows examples of a volatile sulfur species and a larger phenolic compound, both modulated efficiently by the INSIGHT flow modulator, as demonstrated by the excellent peak shape.

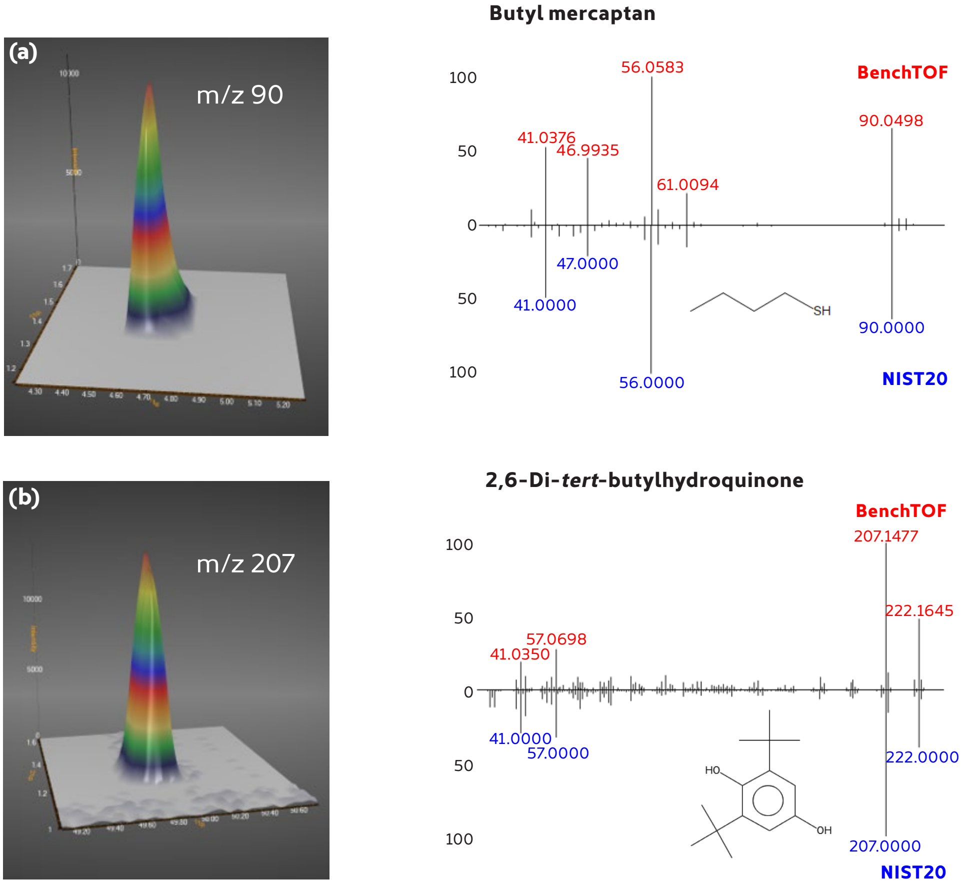
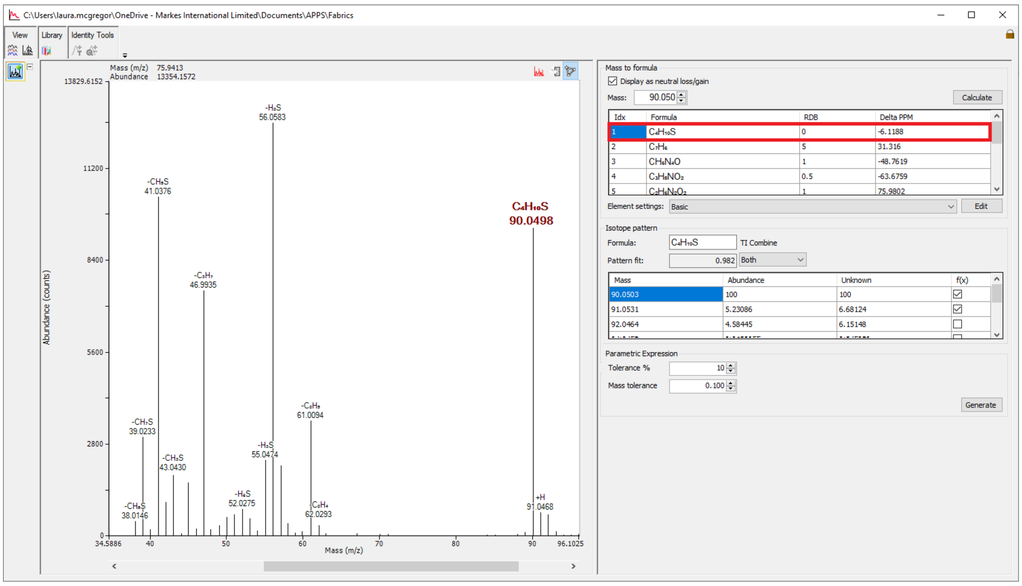


Figure 4

Examples showing a volatile and semi-volatile compound from the rubber sealing strip, efficiently modulated using the INSIGHT flow modulator.

Additionally, the BenchTOF2 mass spectrometer adds confidence in the identification of these analytes, through reference-quality spectra, accurate isotope abundances and powerful mass accuracy (<50 ppm), as shown in Figure 4. The mass-to-formula calculator in ChromSpace harnesses this improved mass accuracy to reduce the number of possible formulae and simplify identification (Figure 5).



C:\Users\laura.mcgregor\OneDrive - Markes International Limited\Documents\APPS\Fabrics

Mass (m/z) 75.9413
Abundance 13354.1572

Mass to formula
☑ Display as neutral loss/gain
Mass: 90.050

Idx	Formula	RDB	Delta PPM
1	$C_4H_{10}S$	0	-6.1188
2	C_7H_6	5	31.316
3	CH_6N_4O	1	-48.7619
4	$C_3H_8NO_2$	0.5	-63.6759
5	$C_2H_6N_2O_2$	1	75.9802

Element settings: Basic

Isotope pattern
Formula: $C_4H_{10}S$ TI Combine
Pattern fit: 0.982 Both

Mass	Abundance	Unknown	f(x)
90.0503	100	100	☑
91.0531	5.23086	6.68124	☑
92.0464	4.58445	6.15148	☐

Parametric Expression
Tolerance % 10
Mass tolerance 0.100

Figure 5

Mass-to-formula calculator in ChromSpace software helps to confirm compound identity. Here, $C_4H_{10}S$ is displayed as the top match (with a mass accuracy of <10 ppm), confirming butyl mercaptan as the peak identity.

The ability of the system to identify such compounds confidently and with high sensitivity is imperative in odour and emissions studies. For example, the butyl mercaptan highlighted in Figure 4(a) has an unpleasant sulfurous, garlic-like odour[4] and an extremely low odour threshold value, thought to be in the range of 0.001–0.0001 ppm.[5] It is therefore important to be able to detect it at trace levels in materials to ensure it will not negatively impact consumers, e.g., by causing an off-odour in vehicle cabins.

Figure 6 provides a comparison of the chromatograms obtained for each sample type, showing the huge complexity of the various textiles and trimmings analysed in this study. A wide range of odorous or potentially harmful compounds were identified by automated searching against commercial libraries (NIST20 and Wiley) in ChromSpace software. A target method was prepared using a selection of these compounds of concern, allowing their relative abundances to be compared across all samples (Table 2).

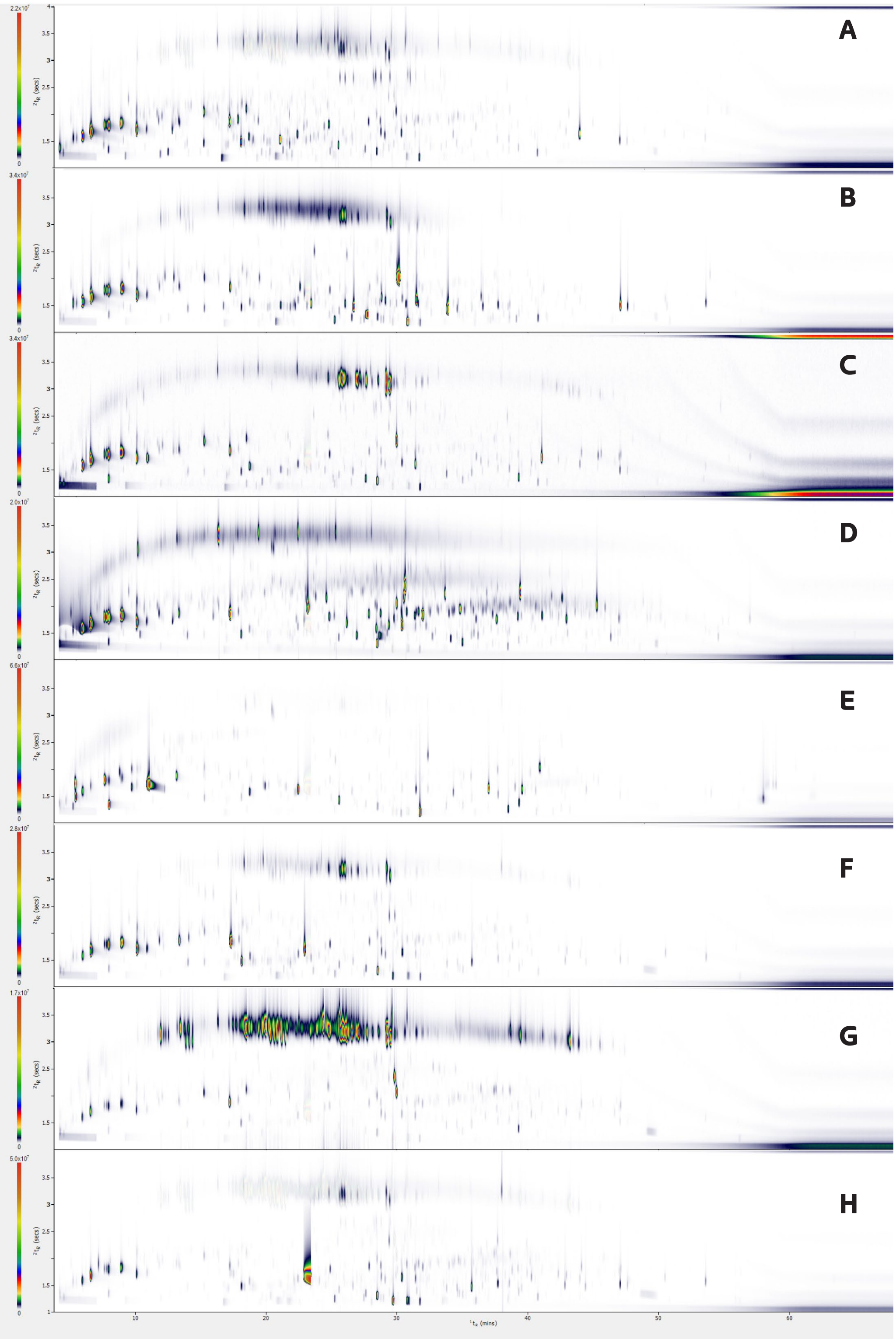
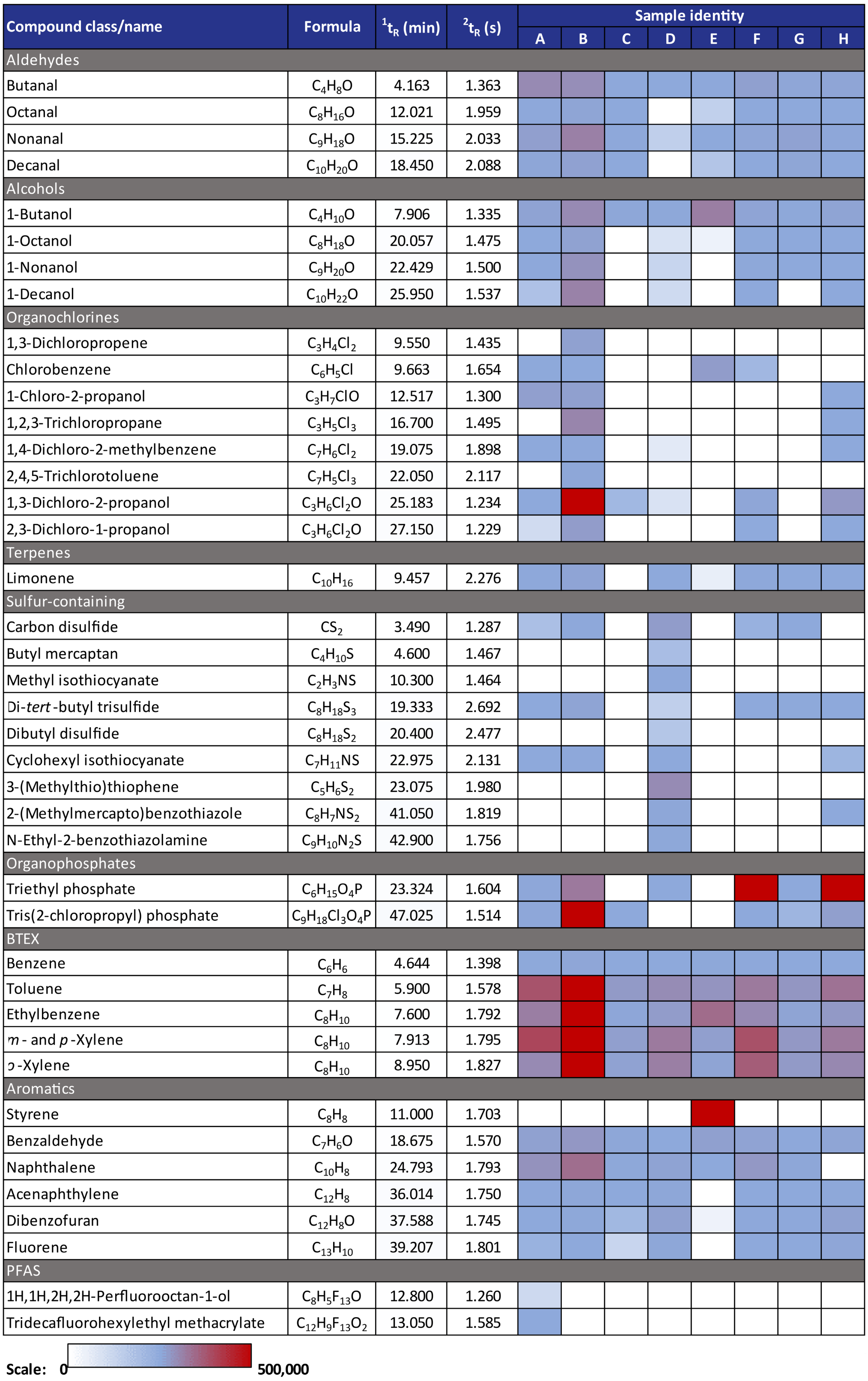


Figure 6

TD–GC×GC–TOF MS chromatograms for all samples analysed in this study. Labels correspond to the sample identities provided in Table 1.

Table 2

A selection of some compounds of interest identified in the textile and trimming samples. Heatmap scale represents the peak area (normalised by sample weight).



Compound class/name	Formula	^1t_R (min)	^2t_R (s)	Sample identity							
				A	B	C	D	E	F	G	H
Aldehydes											
Butanal	C_4H_8O	4.163	1.363	🟪	🟪	🟦	🟦	🟦	🟦	🟦	🟦
Octanal	$C_8H_{16}O$	12.021	1.959	🟦	🟦	🟦	⬜	🟦	🟦	🟦	🟦
Nonanal	$C_9H_{18}O$	15.225	2.033	🟦	🟪	🟦	🟦	🟦	🟦	🟦	🟦
Decanal	$C_{10}H_{20}O$	18.450	2.088	🟦	🟦	🟦	⬜	🟦	🟦	🟦	🟦
Alcohols											
1-Butanol	$C_4H_{10}O$	7.906	1.335	🟦	🟪	🟦	🟦	🟪	🟦	🟦	🟦
1-Octanol	$C_8H_{18}O$	20.057	1.475	🟦	🟦	⬜	🟦	🟦	🟦	🟦	🟦
1-Nonanol	$C_9H_{20}O$	22.429	1.500	🟦	🟪	⬜	🟦	⬜	🟦	🟦	🟦
1-Decanol	$C_{10}H_{22}O$	25.950	1.537	🟦	🟪	⬜	🟦	⬜	🟦	⬜	🟦
Organochlorines											
1,3-Dichloropropene	$C_3H_4Cl_2$	9.550	1.435	⬜	🟦	⬜	⬜	⬜	⬜	⬜	⬜
Chlorobenzene	C_6H_5Cl	9.663	1.654	🟦	🟦	⬜	⬜	🟦	🟦	⬜	⬜
1-Chloro-2-propanol	C_3H_7ClO	12.517	1.300	🟦	🟦	⬜	⬜	⬜	⬜	⬜	🟦
1,2,3-Trichloropropane	$C_3H_5Cl_3$	16.700	1.495	⬜	🟪	⬜	⬜	⬜	⬜	⬜	🟦
1,4-Dichloro-2-methylbenzene	$C_7H_6Cl_2$	19.075	1.898	🟦	🟦	⬜	🟦	⬜	⬜	⬜	🟦
2,4,5-Trichlorotoluene	$C_7H_5Cl_3$	22.050	2.117	⬜	🟦	⬜	⬜	⬜	⬜	⬜	⬜
1,3-Dichloro-2-propanol	$C_3H_6Cl_2O$	25.183	1.234	🟦	🟥	🟦	🟦	⬜	🟦	⬜	🟦
2,3-Dichloro-1-propanol	$C_3H_6Cl_2O$	27.150	1.229	🟦	🟦	⬜	⬜	⬜	🟦	⬜	🟦
Terpenes											
Limonene	$C_{10}H_{16}$	9.457	2.276	🟦	🟦	⬜	🟦	🟦	🟦	🟦	🟦
Sulfur-containing											
Carbon disulfide	CS_2	3.490	1.287	🟦	🟦	⬜	🟦	⬜	🟦	🟦	⬜
Butyl mercaptan	$C_4H_{10}S$	4.600	1.467	⬜	⬜	⬜	🟦	⬜	⬜	⬜	⬜
Methyl isothiocyanate	C_2H_3NS	10.300	1.464	⬜	⬜	⬜	🟦	⬜	⬜	⬜	⬜
Di-*tert*-butyl trisulfide	$C_8H_{18}S_3$	19.333	2.692	🟦	🟦	⬜	🟦	⬜	🟦	🟦	🟦
Dibutyl disulfide	$C_8H_{18}S_2$	20.400	2.477	⬜	⬜	⬜	🟦	⬜	⬜	⬜	⬜
Cyclohexyl isothiocyanate	$C_7H_{11}NS$	22.975	2.131	🟦	🟦	⬜	🟦	⬜	⬜	⬜	🟦
3-(Methylthio)thiophene	$C_5H_6S_2$	23.075	1.980	⬜	⬜	⬜	🟪	⬜	⬜	⬜	⬜
2-(Methylmercapto)benzothiazole	$C_8H_7NS_2$	41.050	1.819	⬜	⬜	⬜	🟦	⬜	⬜	⬜	🟦
N-Ethyl-2-benzothiazolamine	$C_9H_{10}N_2S$	42.900	1.756	⬜	⬜	⬜	🟦	⬜	⬜	⬜	⬜
Organophosphates											
Triethyl phosphate	$C_6H_{15}O_4P$	23.324	1.604	🟦	🟪	⬜	🟦	⬜	🟥	🟦	🟥
Tris(2-chloropropyl) phosphate	$C_9H_{18}Cl_3O_4P$	47.025	1.514	🟦	🟥	🟦	⬜	⬜	🟦	🟦	🟦
BTEX											
Benzene	C_6H_6	4.644	1.398	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Toluene	C_7H_8	5.900	1.578	🟥	🟥	🟦	🟪	🟦	🟪	🟦	🟪
Ethylbenzene	C_8H_{10}	7.600	1.792	🟪	🟥	🟦	🟦	🟪	🟪	🟦	🟦
m- and *p*-Xylene	C_8H_{10}	7.913	1.795	🟥	🟥	🟦	🟪	🟦	🟥	🟦	🟪
o-Xylene	C_8H_{10}	8.950	1.827	🟪	🟥	🟦	🟪	🟦	🟥	🟦	🟪
Aromatics											
Styrene	C_8H_8	11.000	1.703	⬜	⬜	⬜	⬜	🟥	⬜	⬜	⬜
Benzaldehyde	C_7H_6O	18.675	1.570	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Naphthalene	$C_{10}H_8$	24.793	1.793	🟪	🟪	🟦	🟦	🟦	🟦	🟦	⬜
Acenaphthylene	$C_{12}H_8$	36.014	1.750	🟦	🟦	🟦	🟦	⬜	🟦	🟦	🟦
Dibenzofuran	$C_{12}H_8O$	37.588	1.745	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Fluorene	$C_{13}H_{10}$	39.207	1.801	🟦	🟦	🟦	🟦	⬜	🟦	🟦	🟦
PFAS											
1H,1H,2H,2H-Perfluorooctan-1-ol	$C_8H_5F_{13}O$	12.800	1.260	🟦	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Tridecafluorohexylethyl methacrylate	$C_{12}H_9F_{13}O_2$	13.050	1.585	🟦	⬜	⬜	⬜	⬜	⬜	⬜	⬜

Scale: 0 500,000

Interestingly, the BTEX compounds (which are commonly targeted in standard methods, such as VDA 278 for vehicle interior air quality) were found to be present in significant amounts in all samples, while other odorous and potentially harmful compounds were found to vary considerably.

Most notably:

- The rubber sealing strip (sample D) was found to contain increased levels of all sulfur-containing compounds, such as the potent butyl mercaptan (as mentioned earlier), dibutyl disulfide and methyl isothiocyanate, which all contribute unpleasant sulfurous odours.[4]
- Two PFAS compounds were only detected in the composite foam (sample A). The release of PFAS into indoor air is of great concern due to their bioaccumulation potential and prevalence in consumer products.
- 1-Butanol was increased in the polypropylene plastic and is likely to contribute a fermented, fusel odour.[4]
- Organophosphates were increased in the upholstery, sponge and textile samples, likely due to their flame-retardant properties.
- 1,3-Dichloro-2-propanol was increased in the vinyl upholstery (sample B) and is classed as a Group 2B carcinogen meaning ‘possibly carcinogenic to humans’. It is also known to be a thermal degradation product of the flame retardant tris (1,3-dichloroisopropyl)phosphate (TDCPP), which was also detected within sample B.

Table 2 provides just a small selection of the many hundreds of compounds separated and identified within each sample, but importantly, many of these compounds would have been masked by co-eluting peaks in a 1D GC–MS separation, meaning that (despite their potent odour or potential toxicity) they may have been overlooked.

For example, Figure 7 shows the peak for 1-butanol in the rubber sealing strip (sample D), which would have been masked by the higher-responding xylenes in a 1D separation, meaning it may have been overlooked completely. It is also worth noting that the reverse fill/flush flow modulation used by the INSIGHT device enables efficient modulation of volatiles $<C_5$ (such as 1-butanol). This would be a difficult or impossible task for thermal modulation, which works based on trapping analytes via a cold jet.

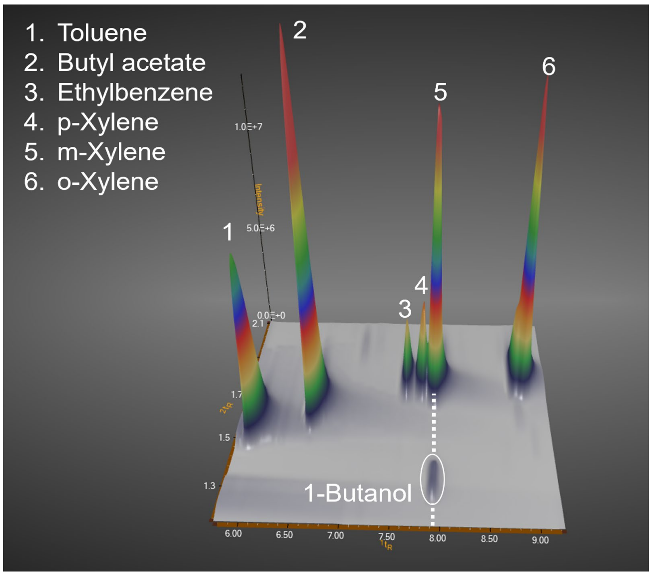


Figure 7

Expanded region of the TD–GC×GC–TOF MS chromatogram for the rubber sealing strip, showing the separation of 1-butanol from the higher loading xylenes.

Conclusions

This study has shown that TD in conjunction with GC×GC–TOF MS provides:

- Sampling, separation and identification of wide-ranging analytes – including VOCs, SVOCs and thermally-labile species.
- Enhanced separation by GC×GC ensures robust screening of both targets and non-targets for improved discovery of odorous or 'hidden' compounds.
- Low running costs through cryogen-free sampling and analysis via an electrically-cooled focusing trap within the TD and INSIGHT flow-modulated GC×GC, respectively.
- Confident identification using the reference-quality spectra and powerful mass accuracy of BenchTOF2 mass spectrometers.
- A future-proof system capable of going beyond current regulations and to help accelerate research and development of new materials.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

References

[1] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/4, Official Journal of the European Union, 2007, 3–280.

[2] Markes International Application Note 131: The development of standard methods relating to vehicle interior air quality (VIAQ) and how to comply with them, https://markes.com/content-hub/application-notes/application-note-131.

[3] SepSolve Analytical White Paper 048: Improved characterisation of malodours in recycled plastics using TD–GC×GC with BenchTOF2 MS, https://www.sepsolve.com/white-papers/odours-emissions/improved-characterisation-of-malodours-in-recycled-plastics-using-tdgcgc-with.aspx.

[4] The Good Scents Company Information System (search facility), www.thegoodscentscompany.com/search2.html (accessed on 13th July 2022).

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[6] International Agency for Research on Cancer, List of Classifications, https://monographs.iarc.who.int/list-of-classifications/ (accessed on 13th July 2022).

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