New car smell: Improved identification of odours in vehicle interior air

This study demonstrates the discovery of odour compounds using thermal desorption (TD) with GC×GC–TOF MS. This solution provides target and non-target screening of car trim components on a single platform, for advanced analysis of vehicle interior air quality (VIAQ).

Introduction

VIAQ has been a topic of interest since the late 1970s, when concern over the effect of volatile and semi-volatile organic compounds (VOCs and SVOCs) on the indoor environment began to be replicated in the automotive industry.

The release of VOCs and SVOCs from vehicle trim materials (including plastics, polyurethane, foam, wood, carpets, textiles and adhesives) is the major factor causing poor VIAQ, and the consequent negative effect on health is the primary driver for regulations in this area. Additional concerns relate to consumers' dislike of off-odours in vehicle cabins, which has risen to be the most complained-about quality issue in China.[1]

The advent of the mandatory Chinese regulation GB/T 27630 "Guideline for air quality assessment of passenger car"[2] further increases the pressure on manufacturers and the related suppliers to carry out VIAQ and material screening. Typically, the standard methods and associated regulations focus on targeted lists of compounds of concern.[3] However, the increased focus on off-odours in the car cabin has meant an increase in olfactory testing on materials. These methods give a somewhat subjective response to the strength and nature of the odour.

The sample complexity and 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 to be created and validated to respond to the pressures being placed on manufacturers, suppliers, researchers and test laboratories alike.

Here, we describe a discovery platform utilising TD with GC×GC–TOF MS to uncover 'hidden' odorous compounds, as well as other potentially harmful components, which could be overlooked using conventional GC–MS techniques.

Experimental

Samples: A steering wheel cover and leather sample, cut into ~1 cm sections.

Dynamic headspace: Cut sections of the samples were placed in a sealed chamber for dynamic headspace/emissions testing combined with subsequent focusing and TD. Relevant methods include ISO 12219-series and ISO 16000-series standards.

TD: Instrument: xr-series thermal desorber (Markes International). Focusing trap 'Material Emissions' (U-T12ME); Trapping temperature: 25°C; Desorption temperature: 280°C; Trap heating rate: Max.

GC×GC: Modulator: INSIGHT® (SepSolve Analytical); Modulation period (P_M): 5 s.

TOF MS: Instrument: BenchTOF-Select™; Mass range: m/z 45–500; Acquisition rate: 100 Hz in Tandem Ionisation® mode at 70 eV and 14 eV.

Software: Full instrument control and data processing by ChromSpace®.

Please contact SepSolve for full analytical parameters.

Results

Figure 1 shows the TD–GC×GC–TOF MS colour plot for a section of the steering wheel cover with the typical target compounds – from regulated methods such as GB/T 27630 – annotated on the plot. It can be seen that many of these target components would have co-eluted with numerous other compounds in the equivalent 1D separation, meaning that concentrations would likely be overestimated, or the target compounds could be missed completely.
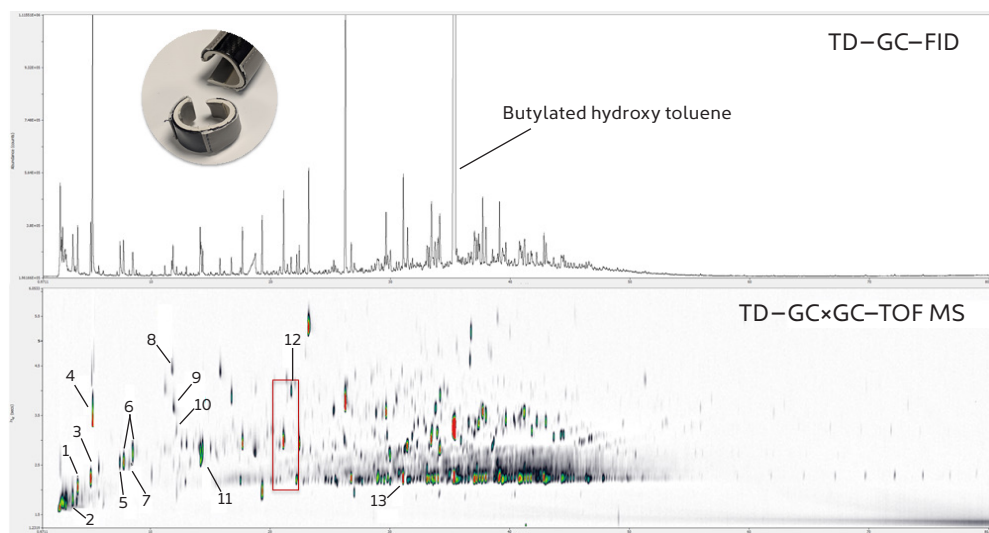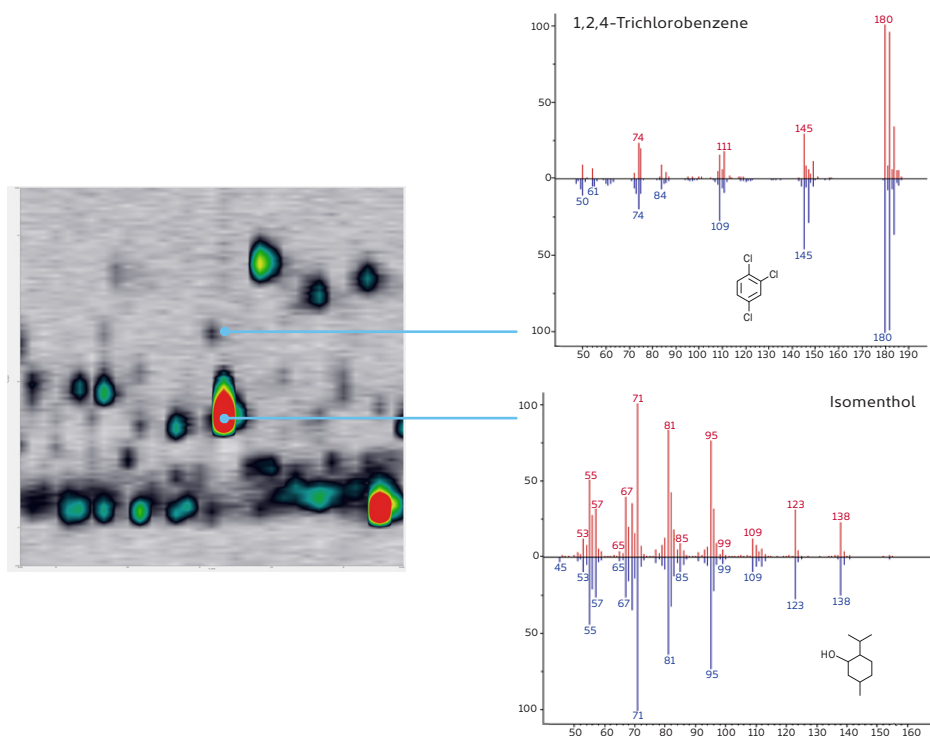
1. 1,2-Dichloropropane (potential carcinogen)
2. Benzene
3. Toluene
4. *N,N*-Dimethylformamide (industrial solvent)
5. Ethylbenzene
6. Xylenes
7. Styrene
8. Aniline (odorant)
9. Phenol
10. *p*-Dichlorobenzene
11. Limonene (fragrance allergen)
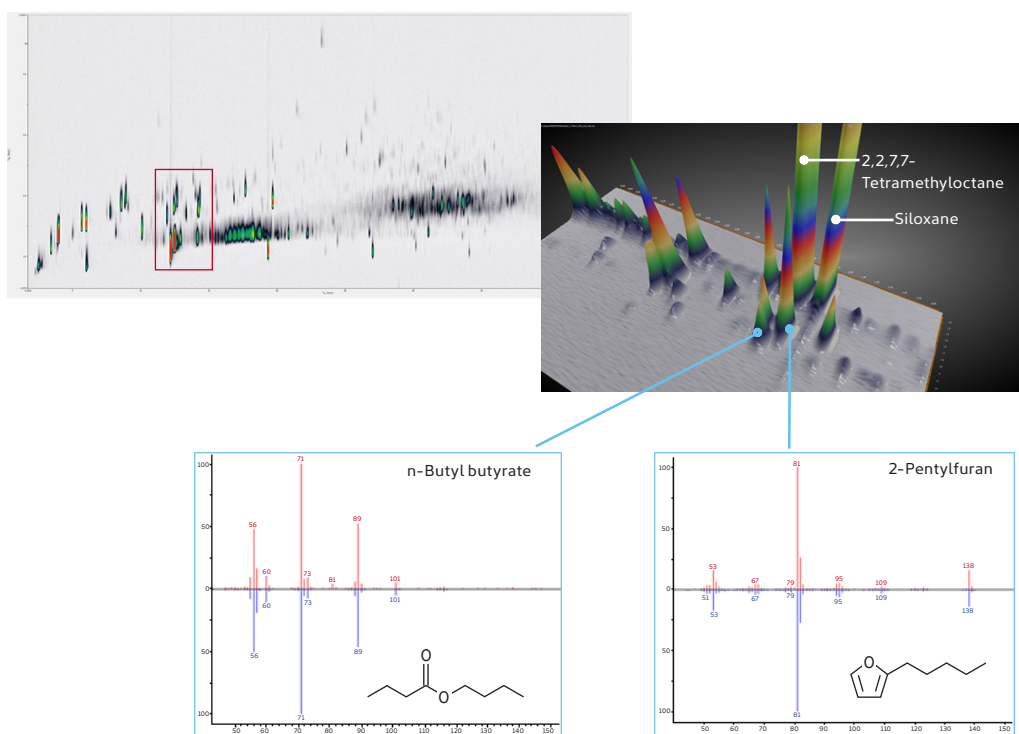12. Naphthalene
13. Tetradecane

The enhanced separation of GC×GC also means that not only can the target components be confidently identified and quantified, in adherence to regulated methods, the sample can be screened for non-targets too. For example, in the steering wheel cover, a number of compounds that may be harmful to health were identified, such as 1,2-dichloropropane, as well as potential odorants, such as aniline (known to cause an undesirable 'fishy' odour[4]).

The coupling of BenchTOF MS with GC×GC ensures that these components can be identified confidently, using simple screening against commercial libraries, such as NIST and Wiley. The expanded region in Figure 2 illustrates this point – where a trace peak is well-separated from the higher-loading isomenthol, and can be confidently identified as 1,2,4-trichlorobenzene.

Figure 3 shows the TD–GC×GC–TOF MS colour plot for the analysis of a section of leather. Here, n-butyl butyrate and 2-pentylfuran are confidently identified using BenchTOF spectra. The surface chart shows that both of these compounds would have been masked by higher-loading components. This enhanced discovery ensures that the method is not only capable of adhering to current methods, but provides future-proofing in case of expansion of target lists. Table 1 lists other potentially harmful compounds and odorants identified in the leather sample.

Compound	^1t_R (min)	^2t_R (s)	Peak area
Benzene	3.4661	1.5734	9.53E+04
2-Ethoxyethanol	3.9750	1.8015	3.06E+07
Toluene	5.0186	1.8815	9.72E+05
Butyl acetate	6.0000	2.0215	1.21E+07
Ethylbenzene	7.5322	2.2338	4.71E+05
m- + p-Xylene	7.7604	2.2215	3.17E+06
n-Butyl ether	8.1536	1.9015	1.45E+06
o-Xylene	8.5000	2.3615	1.74E+06
Butyl acrylate	8.5678	2.3303	6.99E+06
2-Butoxyethanol	8.8918	2.4376	6.49E+06
n-Butyl propionate	9.1041	2.3364	8.29E+05
α-Pinene	10.0950	1.9499	7.99E+06
Camphene	10.7500	2.0815	9.79E+04
Benzaldehyde	11.2500	3.7415	1.29E+05
Mesitylene	11.6050	2.4615	7.13E+05
β-Pinene	11.9287	2.1673	3.61E+06
2-Pentylfuran	12.4081	2.2995	8.04E+06
Isobutyl butyrate	12.6770	2.4064	4.29E+06

Table 1

Some compounds of interest identified by the TD–GCxGC–TOF MS of leather.

Compound	^1t_R (min)	^2t_R (s)	Peak area
3-δ-Carene	13.3457	2.1985	2.11E+06
Limonene	14.2770	2.3262	1.09E+07
Terpinolene	16.8463	2.4584	1.17E+06
2-Hexylfuran	17.0833	2.4015	1.33E+05
Nonanal	17.6861	2.5862	5.17E+06
2-Ethylhexyl acetate	19.6667	2.3815	1.08E+07
Naphthalene	21.4562	3.9025	3.87E+05
2-Methylnaphthalene	26.5219	3.7710	2.47E+05
1-Methylnaphthalene	27.1318	3.9698	3.16E+05
p-n-Butylacetophenone	28.4167	2.8215	1.42E+05

The enhanced separation of GC×GC, combined with highly sensitive, confident identification by BenchTOF, provides sensitive and objective analysis of odours within interior cabins. However, if human olfactory testing is also required, an odour port can simply be connected by using a splitter prior to the modulator. This allows human evaluation of the odours, while the second separation enables the source compound to be separated and identified correctly.

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.

► Flexible sampling options – from chambers, bags or sorbent tubes.

► Enhanced separation by GC×GC ensures robust screening of both targets and non-targets for improved discovery of odorous or 'hidden' compounds.

► Cryogen-free sampling and analysis for low running costs.

► Confident identification using the reference-quality spectra of BenchTOF.

► Future-proofing in case of expansion of target lists.

Markes International, SepSolve Analytical's sister company, has a well-deserved reputation on work in the VIAQ area. The company's thermal desorption instrumentation is widely used to carry out standard methods and those stipulated in VIAQ regulations. Combining Markes instruments with SepSolve's

GC×GC–TOF MS results in a future-proof system capable of going beyond current regulations. Markes International and SepSolve Analytical are companies of the Schauenburg Analytics Ltd group.

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

References

[1]   J.D. Power and Associates, China Initial Quality Study, 2016, www.jdpower.com/business/press-releases/2016-china-initial-quality-study-iqs. 'Unpleasant odour' was the cause of 16.0 reported problems per 100 new vehicles in the first 90 days after purchase, well above the next most common complaint, 'Excessive road noise', with a rating of 5.9.

[2]   GB/T 27630-2011, National Standard Of The People's Republic Of China, Guideline for Air Quality Assessment of Passenger Car, 2011.

[3]   Markes International Application Note 131: The development of standard methods relating to vehicle interior air quality (VIAQ) and how to comply with them.

[4]   The Good Scents Company Information System (search facility), www.thegoodscentscompany.com/search2.html (accessed on 20th Nov 2019).

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