TDTS 59

Direct desorption of car trim materials for VOC and SVOC analysis in accordance with VDA Method 278

Summary

In this Application Note, we demonstrate the suitability of Markes' ULTRA-UNITY™ automated thermal desorption system for performing the analysis of volatile and semi-volatile organic chemicals (VOCs and SVOCs) in three types of automotive trim materials (polypropylene, artificial leather and foam) in accordance with VDA Method 278.

Introduction

The German Association of the Automotive Industry (VDA) consists of automobile manufacturers, their development partners and their suppliers. VDA promotes the interests of the entire German motor trade by participating in the development of economic, transport and environmental policy, and setting appropriate technical standards. Given the international nature of the automotive industry, the actions of VDA also have an impact outside Germany, for example on subsidiaries and suppliers based in other countries.

Concern is growing worldwide over the quality of air in vehicle cabins. Many people, including vulnerable groups such as children and the elderly, spend a significant proportion of their time in cars and are at risk of being exposed to any odorous or toxic organic chemicals that may be emitted from car interior trim components. The levels of volatile and semi-volatile organic compounds (VOCs and SVOCs) found in car cabin air can be several times higher than normal ambient air levels (indoor or outdoor) – see Application Note TDTS 33.

In response to such concerns, VDA developed a series of methods for assessing (S)VOC emissions from car trim components such as upholstery, carpets, glues, sealing compounds, plastics, foam, leather, coatings and paint. One such test, known as VDA Method 278, requires the assessment of two groups of compounds:

- The 'VOC value' – the sum of the VOCs and SVOCs up to n-C_{20} emitted under one set of specified analytical conditions
- The 'FOG value' – the sum of the SVOCs (from n-C_{16} to n-C_{32}) emitted under a different set of specified test conditions

VDA Method 278 specifies direct thermal desorption (using heat and a flow of inert gas) of small samples of relatively homogeneous materials used in car trim components (leather, plastic, *etc.*). VOCs and SVOCs are extracted from the sample into the gas stream and are then re-focused onto a secondary focusing trap prior to injection into a GC/MS or GC/FID system for analysis.

VDA Method 278 comprises two extraction stages:

1. **VOC-analysis:** This involves desorbing the sample at 90°C for 30 minutes to extract compounds with volatilities up to n-C_{20}. This is followed by semi-quantitative analysis of each compound as micrograms of toluene equivalents per gram of sample.
2. **FOG-analysis:** This involves desorbing the sample to 120°C for 60 minutes to extract compounds ranging in volatility from n-C_{16} to n-C_{32}. This is followed by semi-quantitative analysis of each compound as micrograms of n-hexadecane equivalents per gram of sample.

Experimental

Samples:
Polypropylene: 30 ± 5 mg; leather: 10 ± 3 mg; foam: 15 ± 5 mg. All samples were weighed directly into an empty unfritted glass sample tube.

Step 1: Determination of VOC-value:
Instrument: ULTRA-UNITY (Markes International)
Desorption temp.: 90 °C
Desorption time: 30 min
Focusing trap: General-purpose hydrophobic (Tenax®–graphitised carbon black)
Focusing trap low: –30 °C
Focusing trap high: 300 °C
Focusing trap hold: 3 min
Flow path temp.: 200 °C
Trap flow: 20 mL/min
Split flow (inlet and outlet): 20 mL/min
Carrier gas flow: 1.3 mL/min (constant flow)
Temp. program: 40 °C (2 min), then 3 °C/min to 92 °C, then 5 °C/min to 160 °C, then 10 °C/min to 280 °C (10 min)
Mass range: 29–280 amu
Aux. temp: 280 °C

Step 2: Determination of FOG-value
Instrument: ULTRA-UNITY (Markes International)
Desorption temp.: 120 °C
Desorption time: 60 min
Focusing trap: General-purpose hydrophobic (Tenax–graphitised carbon black)
Focusing trap low: –30 °C
Focusing trap high: 300 °C
Focusing trap hold: 5 min
Flow path temp.: 200 °C
Trap flow: 20 mL/min
Split flow (inlet and outlet): 20 mL/min
Temp. program: 50 °C (2 min), then 25 °C/min to 160 °C, then 10 °C/min to 310 °C (30 min)
Mass range: 29–370 amu
Aux. temp: 280 °C

A calibration solution of toluene and hexadecane in methanol at a concentration of 500 ng/µL was introduced onto the sampling end of a sample tube packed with 200 mg Tenax sorbent, in a stream of pure inert gas.

All chromatograms displayed in this report have been reprocessed with ClearView™ software. ClearView software uses sophisticated Dynamic Background Compensation (DBC) algorithms to distinguish between chromatographic peaks and background/baseline anomalies. It reprocesses stored GC/MS data files, eliminating background ions from the total ion chromatogram (TIC) and improving both spectral purity and peak integration. Original (un-reprocessed) data files are retained for comparative purposes.

Results

VOC and FOG analyses

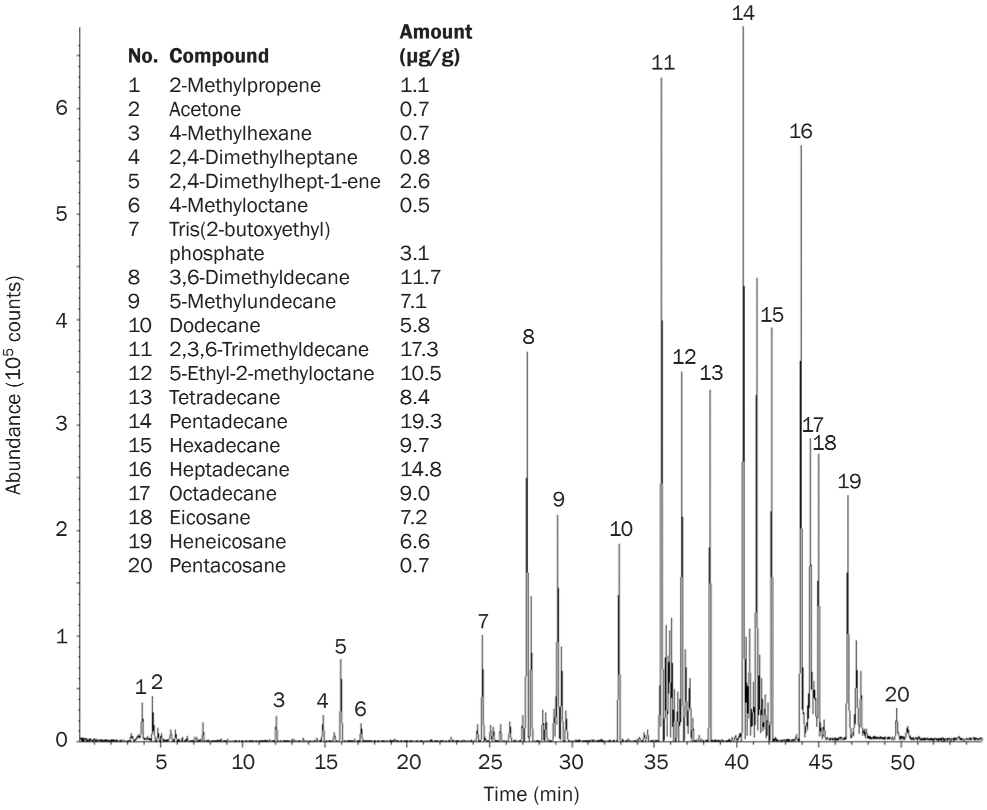
Results of the VOC and FOG analyses for samples of polypropylene, artificial leather and foam, using Markes' ULTRA-UNITY automated thermal desorber, are presented in Figures 1–6.

System inertness and recovery of active compounds

To demonstrate system suitability (inertness) for polar species, an activity test mix containing 18 different compounds was prepared at a concentration of 0.4 µg/µL ± 0.1 µg/µL. The standard solution contains non-polar, polar, alkaline and acid components, as listed in Table 1.

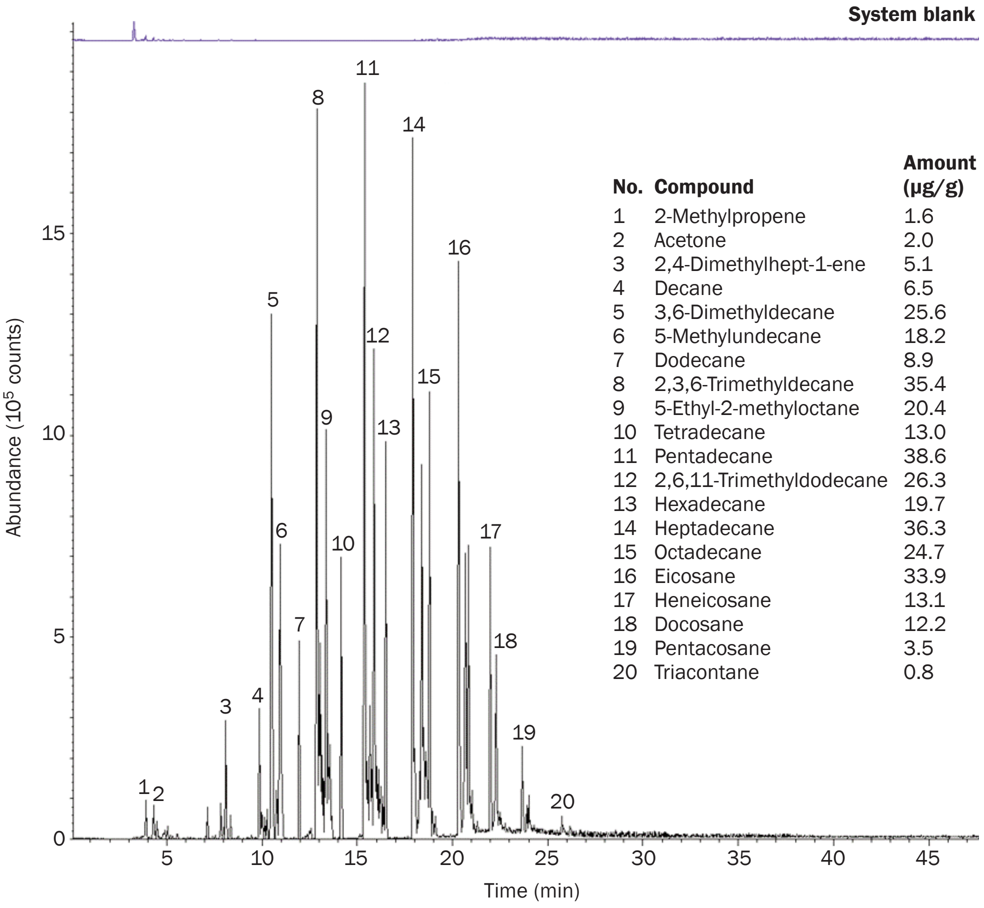
No.	Compound	Concentration (µg/µL)
1	Benzene	0.44
2	n-Heptane	0.35
3	Toluene	0.43
4	n-Octane	0.30
5	*p*-Xylene	0.43
6	*o*-Xylene	0.44
7	n-Nonane	0.36
8	n-Decane	0.37
9	2-Ethylhexan-1-ol	0.42
10	n-Undecane	0.37
11	2,6-Dimethylphenol	0.45
12	n-Dodecane	0.38
13	n-Tridecane	0.38
14	n-Tetradecane	0.38
15	Dicyclohexylamine	0.45
16	n-Pentadecane	0.38
17	n-Hexadecane	0.39
18	Bis(2-ethylhexyl) adipate	0.46

Table 1: Activity test mix and associated component concentration levels.



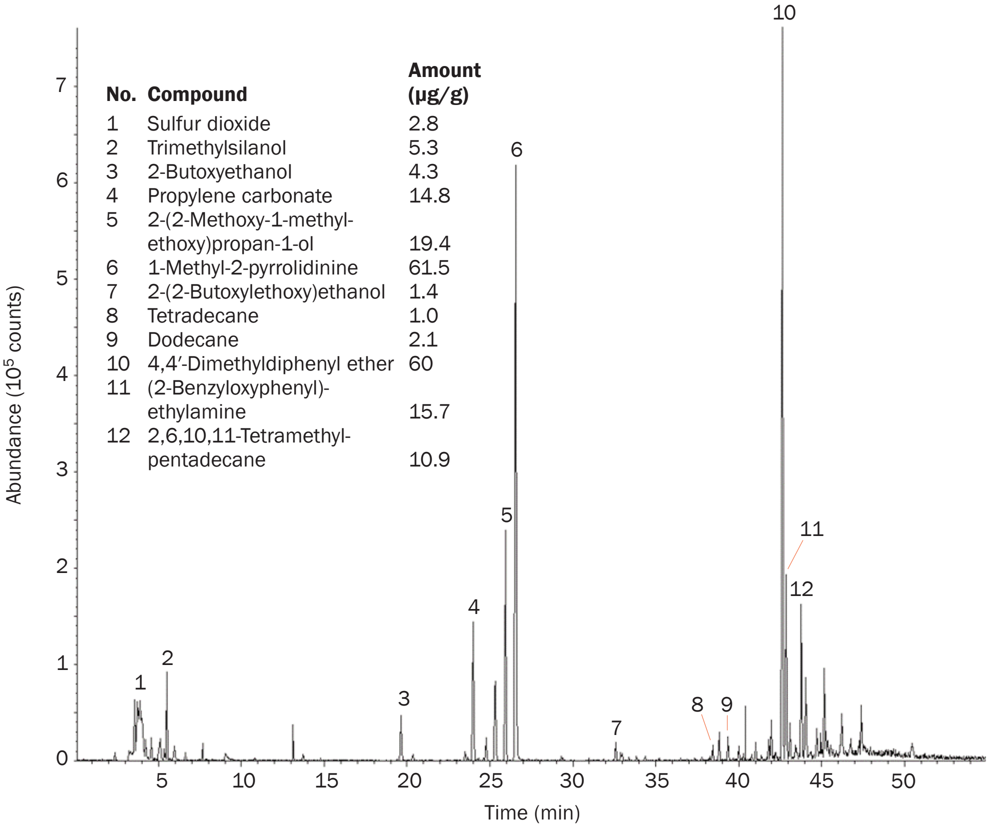
No.	Compound	Amount (µg/g)
1	2-Methylpropene	1.1
2	Acetone	0.7
3	4-Methylhexane	0.7
4	2,4-Dimethylheptane	0.8
5	2,4-Dimethylhept-1-ene	2.6
6	4-Methyloctane	0.5
7	Tris(2-butoxyethyl) phosphate	3.1
8	3,6-Dimethyldecane	11.7
9	5-Methylundecane	7.1
10	Dodecane	5.8
11	2,3,6-Trimethyldecane	17.3
12	5-Ethyl-2-methyloctane	10.5
13	Tetradecane	8.4
14	Pentadecane	19.3
15	Hexadecane	9.7
16	Heptadecane	14.8
17	Octadecane	9.0
18	Eicosane	7.2
19	Heneicosane	6.6
20	Pentacosane	0.7

Figure 1: VOC analysis of a 31.4 mg sample of polypropylene.



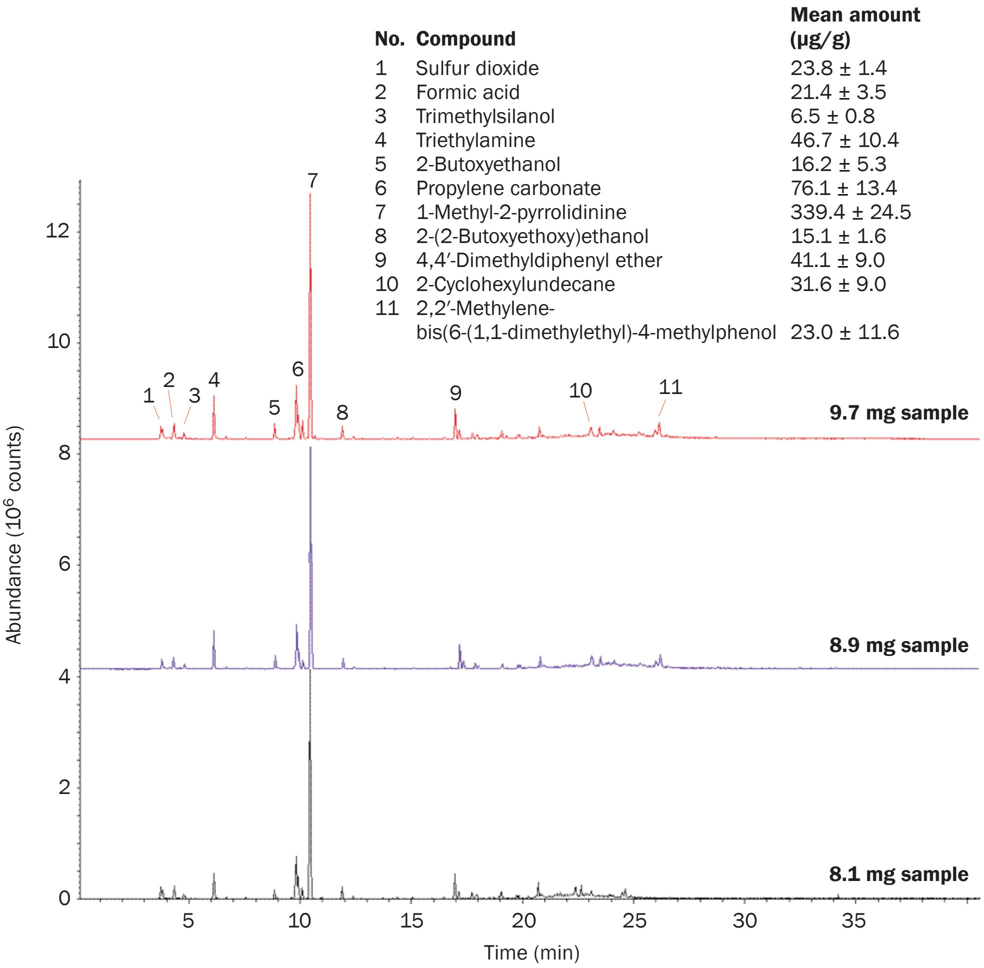
No.	Compound	Amount (µg/g)
1	2-Methylpropene	1.6
2	Acetone	2.0
3	2,4-Dimethylhept-1-ene	5.1
4	Decane	6.5
5	3,6-Dimethyldecane	25.6
6	5-Methylundecane	18.2
7	Dodecane	8.9
8	2,3,6-Trimethyldecane	35.4
9	5-Ethyl-2-methyloctane	20.4
10	Tetradecane	13.0
11	Pentadecane	38.6
12	2,6,11-Trimethyldodecane	26.3
13	Hexadecane	19.7
14	Heptadecane	36.3
15	Octadecane	24.7
16	Eicosane	33.9
17	Heneicosane	13.1
18	Docosane	12.2
19	Pentacosane	3.5
20	Triacontane	0.8

Figure 2: FOG analysis of a sample of polypropylene, followed by a system blank, showing no carryover of high-boiling compounds.



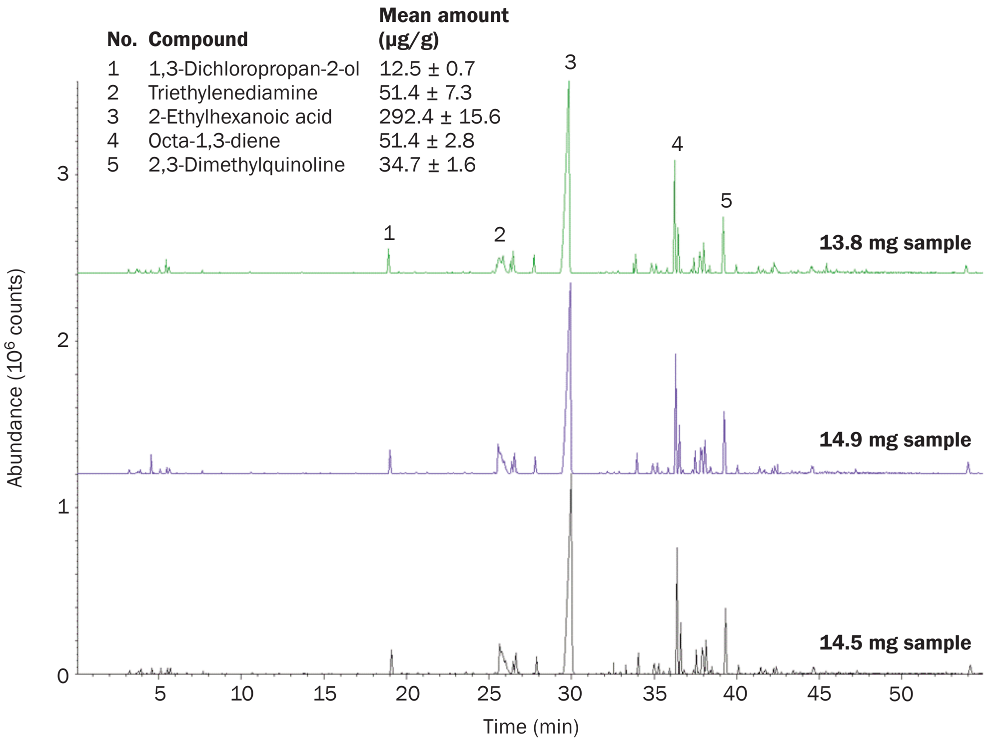
No.	Compound	Amount (μg/g)
1	Sulfur dioxide	2.8
2	Trimethylsilanol	5.3
3	2-Butoxyethanol	4.3
4	Propylene carbonate	14.8
5	2-(2-Methoxy-1-methylethoxy)propan-1-ol	19.4
6	1-Methyl-2-pyrrolidinine	61.5
7	2-(2-Butoxylethoxy)ethanol	1.4
8	Tetradecane	1.0
9	Dodecane	2.1
10	4,4′-Dimethyldiphenyl ether	60
11	(2-Benzyloxyphenyl)-ethylamine	15.7
12	2,6,10,11-Tetramethyl-pentadecane	10.9

Figure 3: VOC analysis of a 12.5 mg sample of artificial leather.



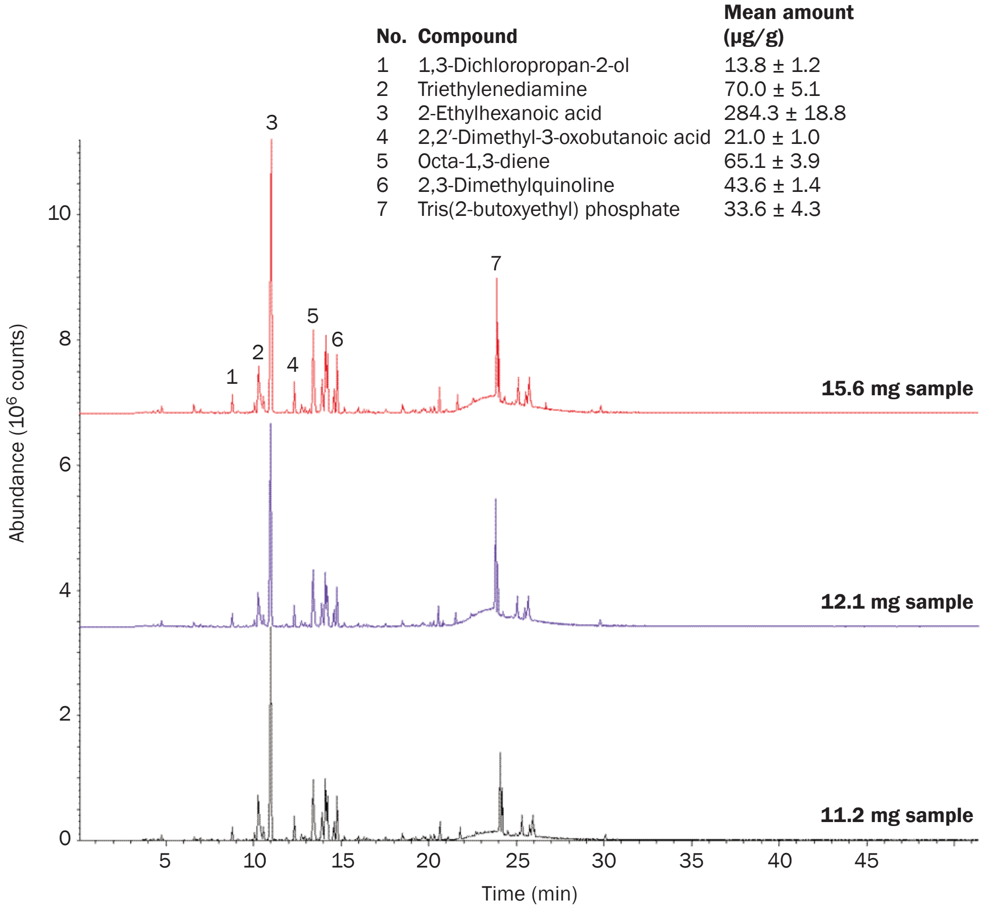
No.	Compound	Mean amount (μg/g)
1	Sulfur dioxide	23.8 ± 1.4
2	Formic acid	21.4 ± 3.5
3	Trimethylsilanol	6.5 ± 0.8
4	Triethylamine	46.7 ± 10.4
5	2-Butoxyethanol	16.2 ± 5.3
6	Propylene carbonate	76.1 ± 13.4
7	1-Methyl-2-pyrrolidinine	339.4 ± 24.5
8	2-(2-Butoxyethoxy)ethanol	15.1 ± 1.6
9	4,4′-Dimethyldiphenyl ether	41.1 ± 9.0
10	2-Cyclohexylundecane	31.6 ± 9.0
11	2,2′-Methylene-bis(6-(1,1-dimethylethyl)-4-methylphenol	23.0 ± 11.6

Figure 4: FOG analysis of three samples of artificial leather.



No.	Compound	Mean amount (µg/g)
1	1,3-Dichloropropan-2-ol	12.5 ± 0.7
2	Triethylenediamine	51.4 ± 7.3
3	2-Ethylhexanoic acid	292.4 ± 15.6
4	Octa-1,3-diene	51.4 ± 2.8
5	2,3-Dimethylquinoline	34.7 ± 1.6

Figure 5: VOC analysis of three samples of foam.



No.	Compound	Mean amount (µg/g)
1	1,3-Dichloropropan-2-ol	13.8 ± 1.2
2	Triethylenediamine	70.0 ± 5.1
3	2-Ethylhexanoic acid	284.3 ± 18.8
4	2,2′-Dimethyl-3-oxobutanoic acid	21.0 ± 1.0
5	Octa-1,3-diene	65.1 ± 3.9
6	2,3-Dimethylquinoline	43.6 ± 1.4
7	Tris(2-butoxyethyl) phosphate	33.6 ± 4.3

Figure 6: FOG analysis of three samples of foam.

1	Benzene	7	n-Nonane	13	n-Tridecane
2	n-Heptane	8	n-Decane	14	n-Tetradecane
3	Toluene	9	2-Ethylhexan-1-ol	15	Dicyclohexylamine
4	n-Octane	10	n-Undecane	16	n-Pentadecane
5	*p*-Xylene	11	2,6-Dimethylphenol	17	n-Hexadecane
6	*o*-Xylene	12	n-Dodecane	18	Bis-(2-ethylhexyl)adipate

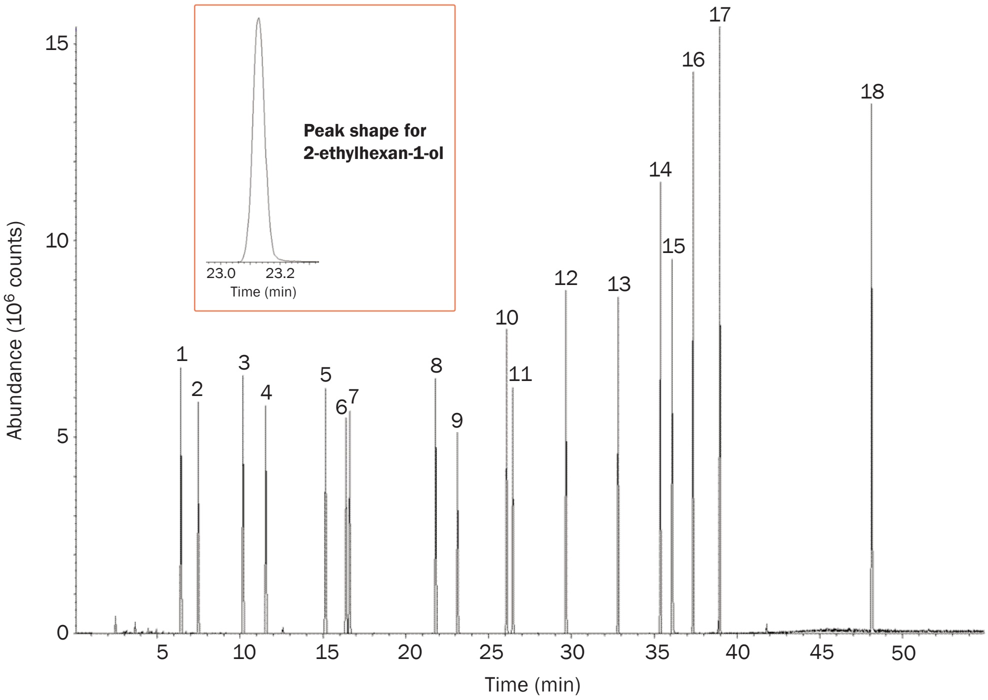


Figure 7: Analysis of 0.4 µg/µL activity test mix spiked onto a Tenax tube.

1 µL of the activity mix was injected onto the sampling end of a conditioned Tenax tube in a stream of inert gas using Markes' Calibration Solution Loading Rig (CSLR™). During analysis, the split portion of the sample was re-collected onto a second conditioned Tenax tube. Figure 7 shows the chromatogram obtained from analysis of a Tenax tube loaded with 1 µL of activity test mix and desorbed using the VOC analysis conditions. This procedure was repeated a second time, giving three analyses from the one sample (Figure 8).

The lack of bias between the three chromatograms shows there are no losses in the system, thus validating recovery of all analytes.

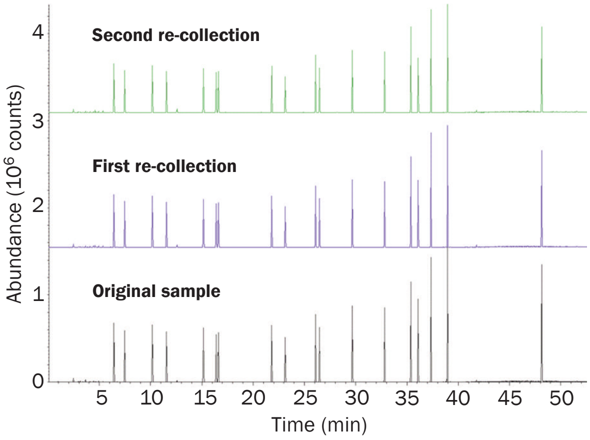


Figure 8: Repeated analyses of the activity test mix.

Repeatability of toluene analysis

0.5 µg of toluene was injected onto 20 tubes packed with Tenax TA. These 20 samples were then analysed over a one-week period. The following values were produced:

Average recovery:	100%
Standard deviation:	5%
Minimum recovery:	92% (80%)
Maximum recovery:	110% (120%)

These were found to be within the limits outlined in VDA Method 278 (bracketed).

Linearity and limit of determination/detection

System linearity was demonstrated over the range 0.01–5 µg by preparing a range of liquid standards of toluene and eicosane (n-C_{20}) in methanol, and dotriacontane (n-C_{32}) in n-hexane. These were introduced onto the sampling end of conditioned Tenax tubes in a stream of clean inert gas.

Detection and determination limits were determined in accordance with the procedure described in VDA Method 278. Split and GC conditions used correspond with the VOC and FOG method parameters respectively. All tubes were desorbed at a temperature of 320 °C to ensure complete recovery of the standard solutions from the Tenax sorbent.

Plots showing the linearity of the system for toluene, eicosane and dotriacontane are shown in Figures 9–11.

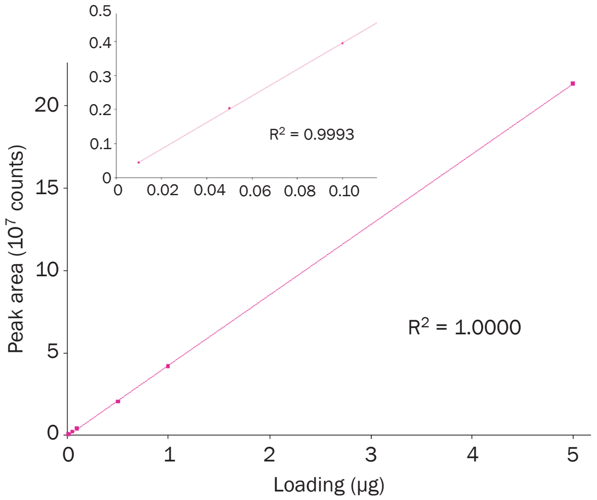


Figure 9: Linearity of toluene over the loading range 0.01–5 µg and (inset) over the range 0.01–0.10 µg.

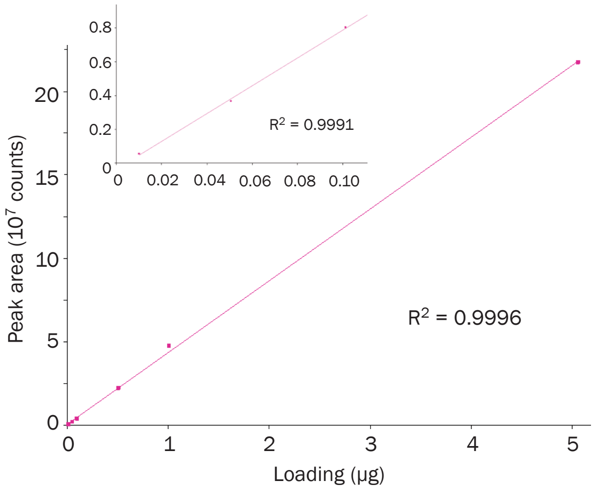


Figure 10: Linearity of eicosane over the loading range 0.01–5 µg and (inset) over the range 0.01–0.10 µg.

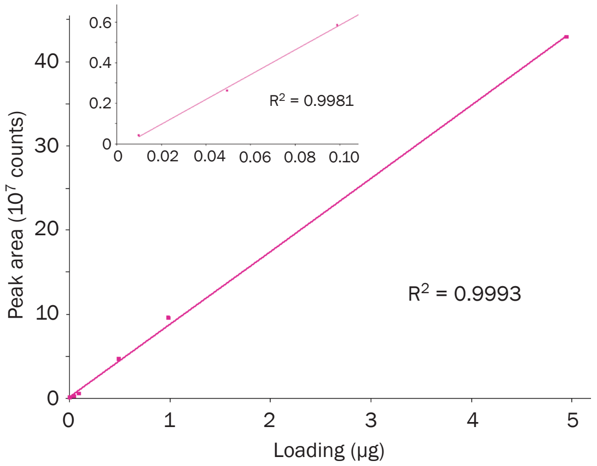


Figure 11: Linearity of dotriacontane over the loading range 0.01–5 µg and (inset) over the range 0.01–0.10 µg.

In each case, LOD and LOQ values were determined using the 0.01–0.10 µg loading ranges (see Table 2).

Compound	LOD [a]	LOQ
Toluene	0.006 µg (<0.04 µg)	0.017 µg
Eicosane	0.006 µg (<0.06 µg)	0.02 µg
Dotriacontane	0.009 µg (<0.06 µg)	0.02 µg

Table 2: Values for limit of detection (LOD) and limit of determination (LOQ) for the three compounds investigated over the loading range 0.01–0.10 µg.
[a] The limit cited in VDA Method 278 is given in parentheses.

Conclusions

The suitability of Markes' ULTRA-UNITY thermal desorber for performing the analysis of automotive trim materials in accordance with VDA Method 278 has been demonstrated.

Analyses of a variety of typical trim materials/standard solutions on the demonstrated:

- Excellent linearity
- Low detection/determination levels
- Excellent peak shape for reactive (polar) compounds (demonstrating good system inertness)
- Repeatable results even for very high-boiling compounds.

Key features of the ULTRA-UNITY system which are essential for VDA Method 278 include:

- Leak-testing of each tube prior to analysis to ensure data integrity
- Effective sealing of all sample tubes loaded onto the ULTRA 2 autosampler – before and after analysis – to prevent contamination and loss of volatiles
- Inert flow path for compatibility with reactive species
- Backflushed and electrically-cooled (cryogen-free) focusing (cold) trap for efficient trapping and desorption of compounds from C_2 to n-C_{40}
- Full EPC control of carrier gas through the TD system for optimum retention time stability and improved qualitative identification of minor compounds
- Quantitative re-collection for repeat analysis or method validation (SecureTD-Q™ technology), to demonstrate quantitative recovery through the system and allow method validation.

Trademarks

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