

## Application Note 059

# 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' TD100 automated thermal desorption system for performing the analysis of volatile and semi-volatile organic compounds (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 033](#).

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 values:

- **The 'VOC value':** the sum of the VOCs and SVOCs up to n-C<sub>25</sub> emitted under one set of specified analytical conditions.
- **The 'FOG value':** the sum of the SVOCs (from n-C<sub>14</sub> to n-C<sub>32</sub>) 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<sub>25</sub>. 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 at 120°C for 60 minutes to extract compounds ranging in volatility from n-C<sub>14</sub> to n-C<sub>32</sub>. 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, with restrictions at either 15 mm or 30 mm depending on sample material.

### Step 1: Determination of VOC value:

Instrument: TD100™ (Markes International)  
 Desorption temp.: 90°C  
 Desorption time: 30 min  
 Focusing trap: General-purpose hydrophobic (Tenax® TA–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: 42 mL/min  
 Split flow (inlet and outlet): 42 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: m/z 29–280  
 Aux. temp: 280°C

### Step 2: Determination of FOG value

Instrument: TD100 (Markes International)  
 Desorption temp.: 120°C  
 Desorption time: 60 min  
 Focusing trap: General-purpose hydrophobic (Tenax TA–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: 42 mL/min  
 Split flow (inlet and outlet): 42 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: m/z 29–370  
 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 TA sorbent, in a stream of pure inert gas.

## Results

### VOC and FOG analyses

Results of the VOC and FOG analyses for samples of polypropylene, artificial leather and foam, using Markes' TD100 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 compounds was prepared at a concentration of 0.4 μg/μL ± 0.1 μg/μL (see 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.

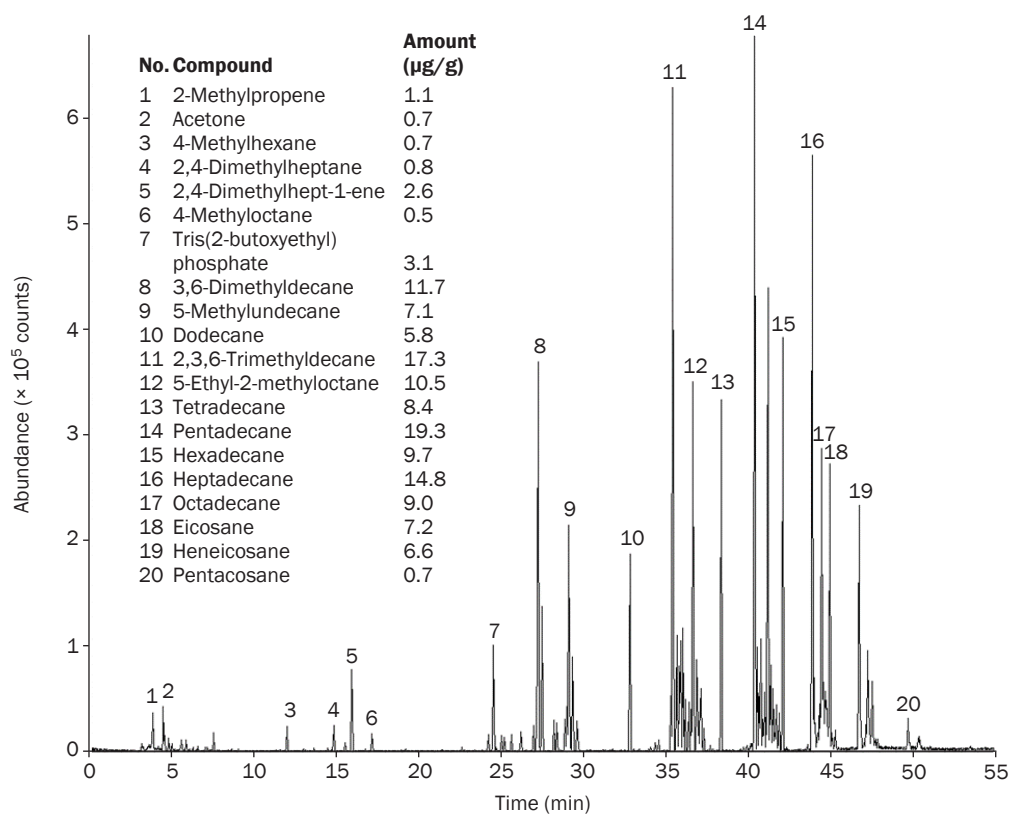


Figure 1: VOC analysis of a 31.4 mg sample of polypropylene.

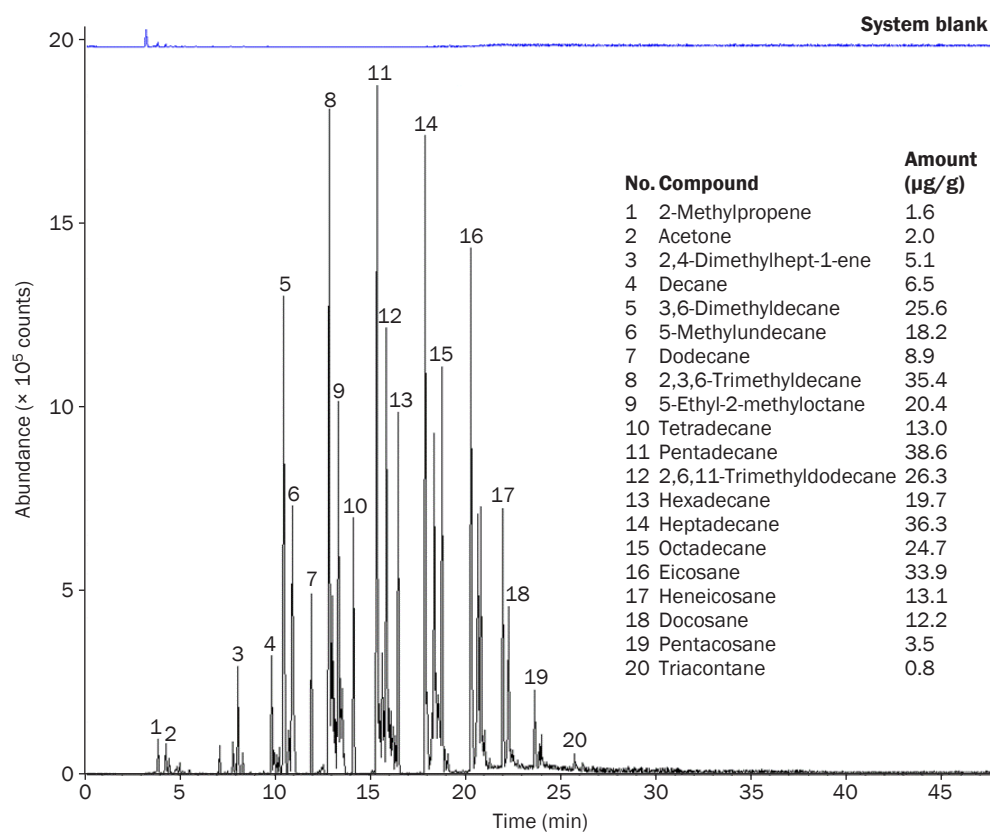


Figure 2: FOG analysis of a sample of polypropylene, followed by a system blank, showing no carryover of high-boiling compounds.

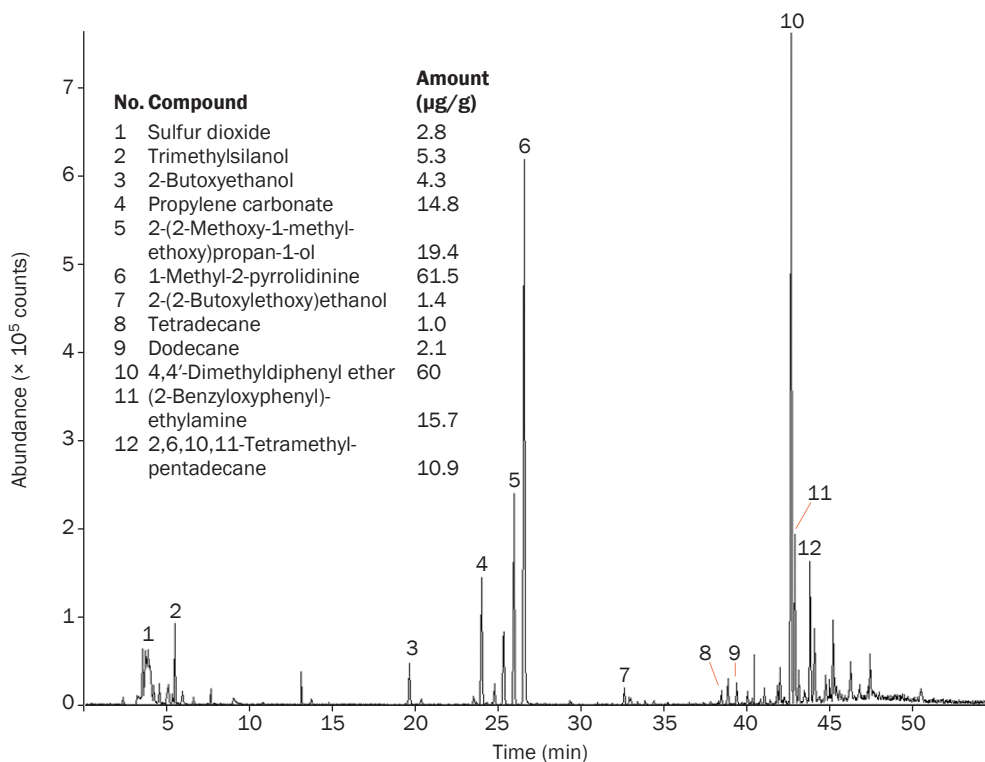


Figure 3: VOC analysis of a 12.5 mg sample of artificial leather.

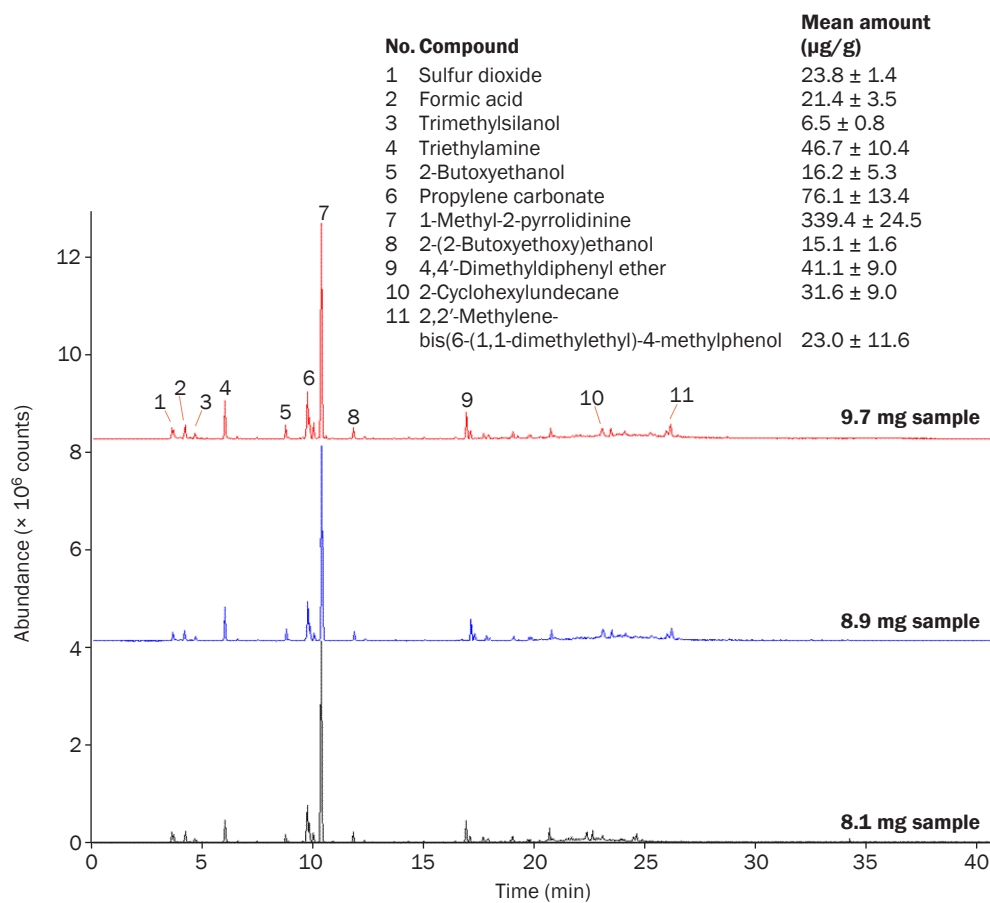


Figure 4: FOG analysis of three samples of artificial leather.

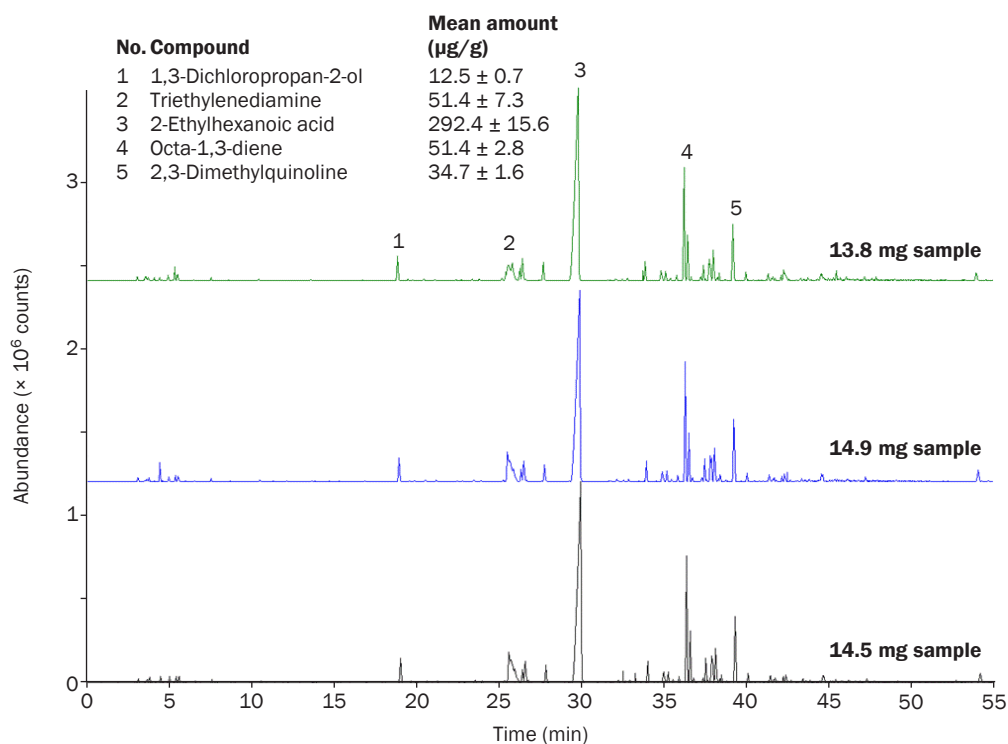


Figure 5: VOC analysis of three samples of foam.

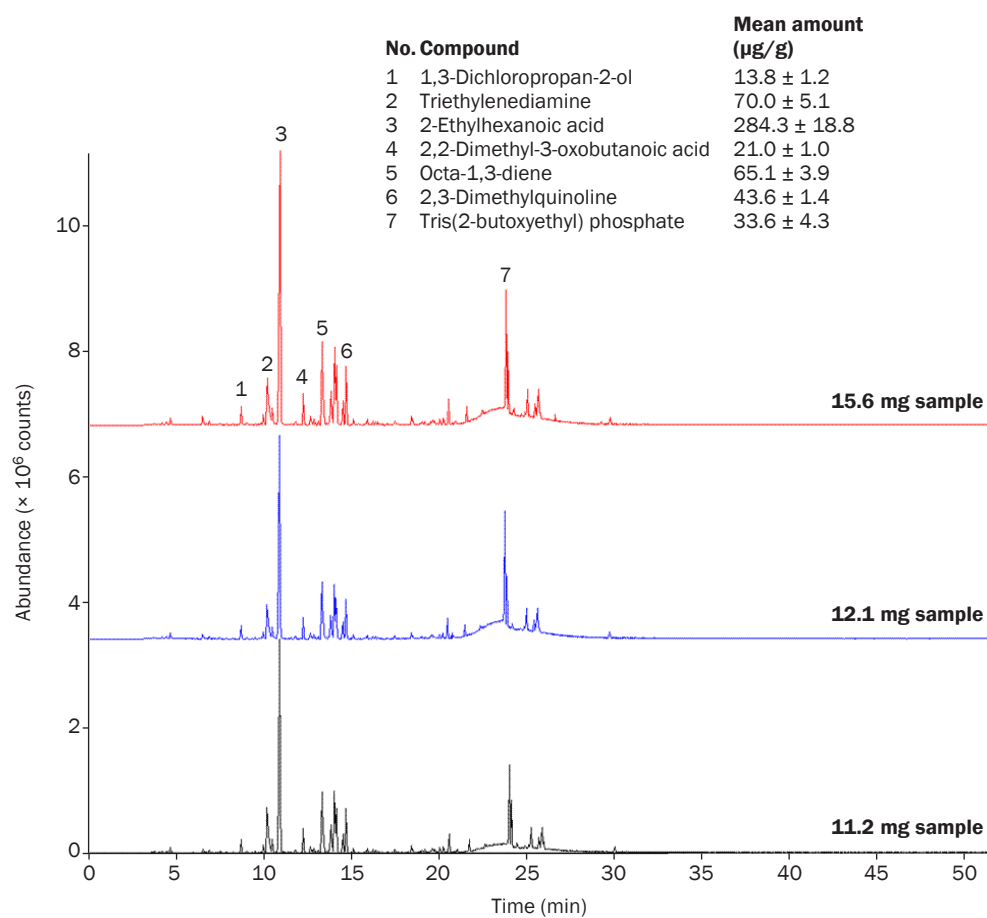
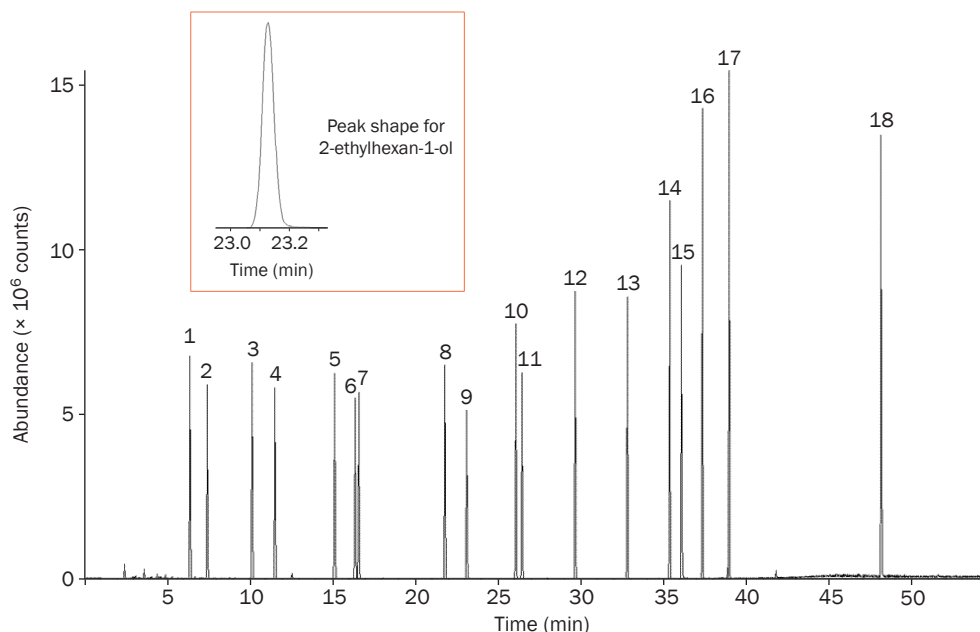


Figure 6: FOG analysis of three samples of foam.

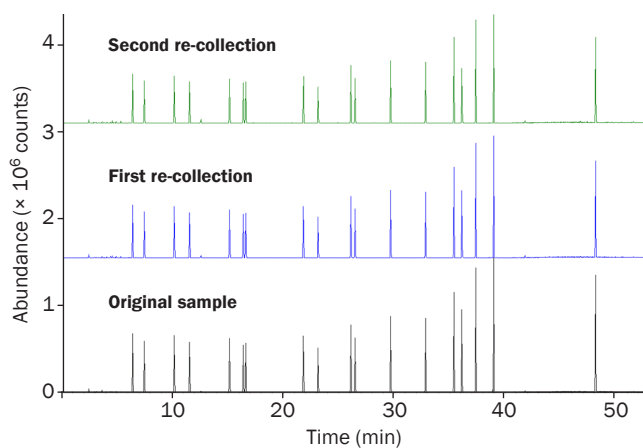
1 Benzene	6 o-Xylene	11 2,6-Dimethylphenol	16 n-Pentadecane
2 n-Heptane	7 n-Nonane	12 n-Dodecane	17 n-Hexadecane
3 Toluene	8 n-Decane	13 n-Tridecane	18 Bis(2-ethylhexyl) adipate
4 n-Octane	9 2-Ethylhexan-1-ol	14 n-Tetradecane	
5 p-Xylene	10 n-Undecane	15 Dicyclohexylamine	



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

1 µL of the activity mix was injected onto the sampling end of a conditioned Tenax TA 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 TA tube. Figure 7 shows the chromatogram obtained from analysis of a Tenax TA 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).

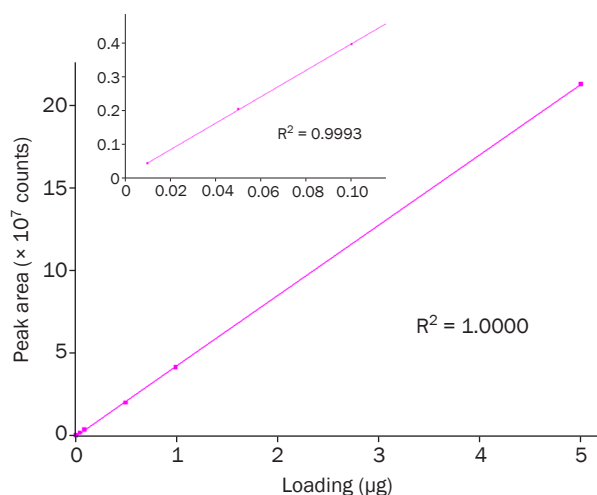
#### Linearity and limit of determination/detection

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

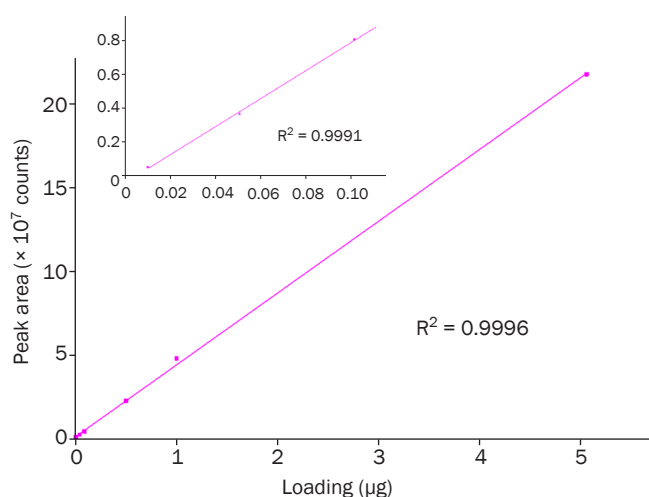
Detection and determination limits were determined in accordance with the procedure described in VDA Method 278. Split and GC conditions used correspond with the VOC and FOG method parameters respectively. All tubes were desorbed at a temperature of 320 °C to ensure complete recovery of the standard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

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

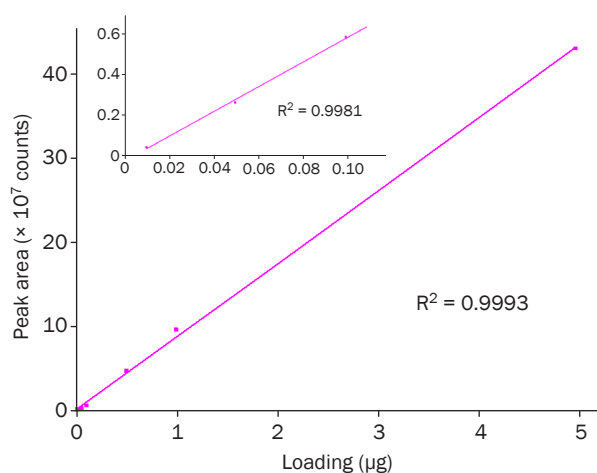
In each case, LOD and LOQ values were determined using the 0.01–0.10 µg loading ranges (see Table 2).



**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.

Compound	LOD <sup>a</sup>	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.

<sup>a</sup> The limit cited in VDA Method 278 is given in parentheses.

## Conclusions

The suitability of Markes' TD100 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 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 TD100 system that 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 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 trap for efficient trapping and desorption of compounds from C<sub>2</sub> to n-C<sub>44</sub>.
- 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, to demonstrate quantitative recovery through the system and allow method validation.

## Trademarks

CSLR™ and TD100™ are trademarks of Markes International.

Tenax® is a registered trademark of Buchem B.V.

*Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.*

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