

TDTS 33

Analysis of the interior atmosphere of a passenger car by TD-GC/MS

Summary

This Application Note describes the use of thermal desorption (TD) in conjunction with GC/MS for the analysis of potentially harmful volatile organic compounds in the air of two recently acquired 'compact' passenger cars.



Introduction

Many of the fittings used in car interiors are known to emit volatile organic compounds (VOCs), which may cause odour problems as well as being hazardous to health.

The range of compounds used in interior fittings can include alkanes, aromatic hydrocarbons, nitrogen compounds, terpenes and sulfur compounds. High temperatures and humidities can also increase the concentrations of some pollutants.

There has long been concern over exposure to such compounds whilst driving, and this has been reflected in the development of methods to determine levels of VOCs and SVOCs in car interiors¹. In this Application Note we show how TD-GC/MS can be applied to the problem of analysing compounds spanning a wide range of volatilities and concentrations.

Experimental

The cars used in these experiments were new standard 'compact' models with the windows and doors kept closed. As material emissions increase with rising temperature, the cars were sampled at both ambient temperature and 40°C – to simulate the temperature reached inside a parked car in full sun. In all cases, 2 L of air from inside the cars was pumped at a rate of 50 mL/min onto sorbent tubes packed with Tenax™ TA and Carbograph™ 1TD. Samples were then analysed using a UNITY™ thermal desorber (Markes International) linked to an Agilent 6890 gas chromatograph with a 5973 mass selective detector.

TD:

Prepurge time:	1 min
Primary desorb:	275°C for 6 min (split on)
Trap low temp.:	30°C
Trap desorb:	300°C for 3 min (split on)
Trap:	Two-bed Tenax and Carboxpack™ B
Flow path temp:	200°C
Carrier gas pressure:	10 psi
Desorb flow:	20 mL/min
Split flow:	30 mL/min
Split ratio:	75:1

GC:

Column flow:	~1 mL/min
Start temp.:	40°C for 5 min
End temp.:	200°C for 1 min
Temp. increase:	10°C/min
Column:	30 m × 0.32 mm × 1.0 µm DB1 equivalent (non-polar) phase

MS:

Source temp.:	230°C
Quadrupole temp.:	150°C
MSD transfer line:	280°C
Mass scan range:	45–350 amu

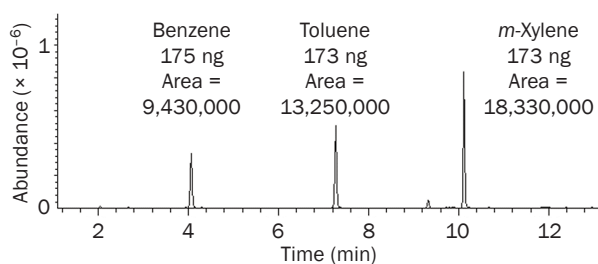


Figure 1: Analysis of a standard solution of benzene, toluene and *m*-xylene.

Results

The analytical system was calibrated using a 2 μ L injection of a benzene, toluene and *m*-xylene standard in methanol (Figure 1). The standard solution was introduced onto a Tenax tube in a stream of carrier gas using the Calibration Standard Loading Rig (CSLR™, Markes International). Using the response for toluene as a convenient average, a peak area of 11 million counts equates to approximately 20 ppb in the vehicle atmosphere.

Analyses were carried out for the following vehicles:

- **A** – Standard upholstery, at 20°C (Figure 2) and 40°C (Figure 3)
- **B** – Identical to **A** but with leather upholstery, at 20°C (Figure 4)
- **C** – A different model from **A** and **B**, at 20°C (Figure 5).

Area counts are presented for every identified component in Table 1. The sum of all the peak areas and the equivalent total VOC (TVOC) concentrations are also shown.

A major component all all four profiles is toluene (#11).

Considering Vehicle **A**, there is an approximate three-fold increase TVOC (in toluene equivalents) on raising the internal temperature from ambient to 40°C, with a shift in emphasis from the more volatile to the less volatile components.

The change from standard to leather upholstery in Vehicle **B** appears to be responsible for the appearance of several new analytes – the most significant being tetrachloroethene (#14, a dry-cleaning agent) and propylene glycol diacetate (#24, a high-boiling solvent/finishing agent).

The overall VOC profile of the air taken from Vehicle **C** is quite different from **A** and **B**, with a decrease in TVOC, but the appearance of several lower-volatility hydrocarbons.

No.	Compound name	Peak area			
		A (20°C)	A (40°C)	B (20°C)	C (20°C)
1	Trimethylsilanol	–	–	–	9.1
2	Methyl ethyl ketone	3.3	–	10.9	–
3	Ethyl acetate	–	–	2.8	–
4	n-Hexane	3.0	–	–	–
5	Benzene	3.3	–	2.9	4.0
6	Cyclohexane	4.6	–	17.9	–
7	Isoheptane	–	–	6.5	–
8	n-Heptane	5.7	–	7.6	9.2
9	Methylcyclohexane	12.0	9.6	15.4	19.3
10	<i>N,N</i> -Dimethylformamide	7.3	19.2	6.0	–
11	Toluene	74.8	93.4	112.4	38.6
12	Isooctane	7.0	–	7.0	15.8
13	n-Octane	7.2	–	–	16.1
14	Tetrachloroethene	–	–	27.4	–
15	Methoxybutanol	–	–	2.8	–
16	4-Hydroxy-4-methyl-pentan-2-one	–	–	2.4	–
17	Ethylbenzene	9.9	18.1	8.4	8.1
18	<i>m/p</i> -Xylene	36.5	57.2	30.0	22.1
19	Styrene	9.5	14.5	10.7	8.4
20	<i>o</i> -Xylene	13.3	19.2	11.2	9.7
21	n-Nonane	7.4	8.6	–	–
22	Ethyltoluene	6.4	–	–	–
23	Trimethylbenzene	26.0	46.0	–	15.4
24	Propylene glycol diacetate	–	–	45.2	–
25	n-Decane	37.7	124.3	44.1	42.8
26	Dimethylbenzylamine	70.0	194.3	–	36.5
27	$C_{11/12}$ isomer	65.0	124.1	72.3	–
28	<i>trans</i> -Decalin	–	–	–	21.2
29	$C_{11/12}$ isomer	69.7	110.1	64.0	–
30	C_{12} isomer	50.4	94.9	37.1	–
31	C_{13} isomer	44.3	–	–	–
32	n-Undecane	–	–	–	98.0
33	Methyldecalin isomer	–	–	–	31.0
34	Methyldecalin isomer	–	–	–	24.1
35	2-(2-Butoxyethoxy)-ethanol	5.5	56.9	9.4	–
36	n-Dodecane	–	28.0	–	66.9
37	C_{13} isomer	–	–	–	18.6
38	C_{14} isomer	–	–	–	13.9
39	n-Tridecane	6.4	48.5	6.3	27.5
40	Cubebene/Copaene	7.8	28.5	–	–
41	n-Tetradecane	–	44.1	3.3	5.7
42	Butylated hydroxy toluene	–	42.0	–	2.8
Total peak area		2038	5349	1893	1480
Total organics in 2 L air		26.6 μ g	9.7 μ g	24.7 μ g	19.3 μ g
TVOC (as toluene equiv.)		3.7 ppm	9.7 ppm	3.4 ppm	2.7 ppm

Table 1: Results of the analysis for each of the three saloon cars (A, standard upholstery; B, leather upholstery; C, different model). Peak areas are all divided by 10^6 .

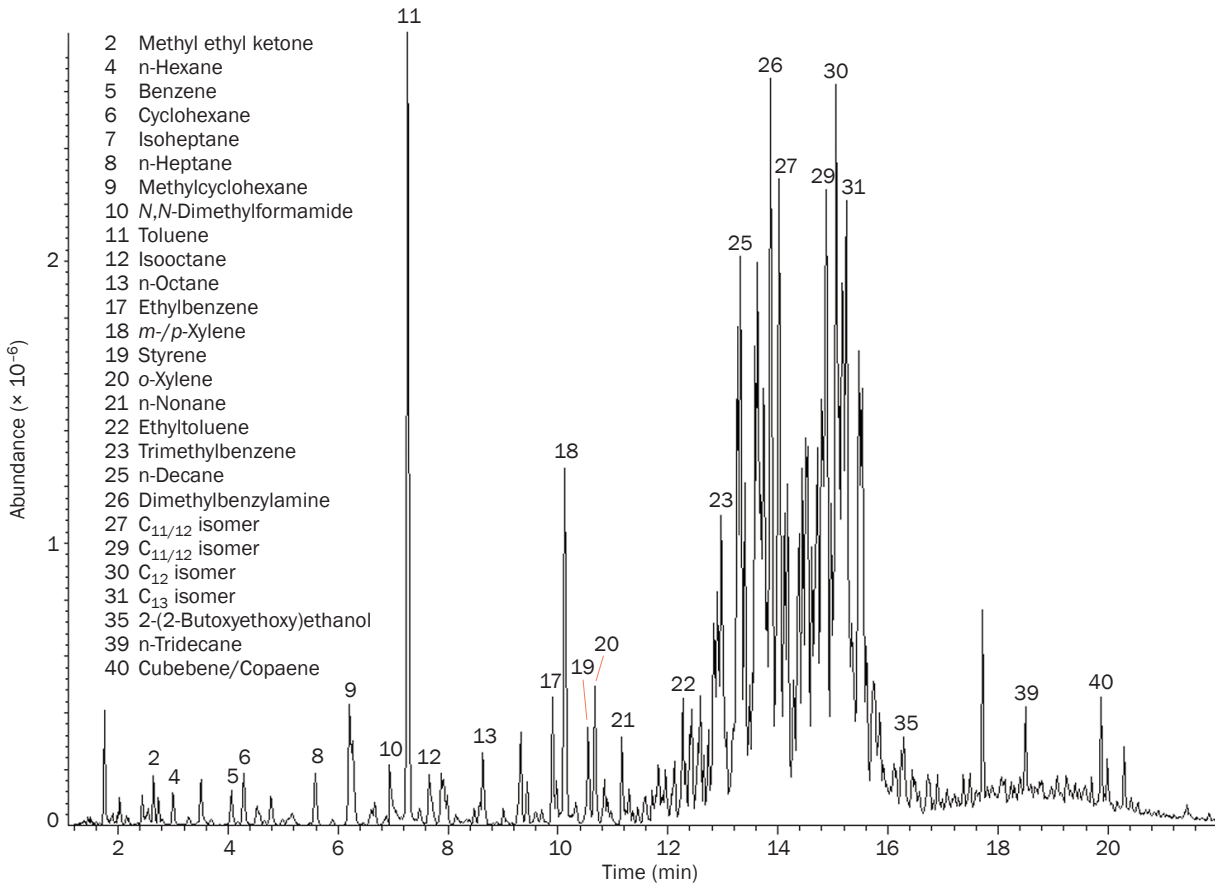


Figure 2: Analysis of air taken from Vehicle A (with standard upholstery), at 20°C.

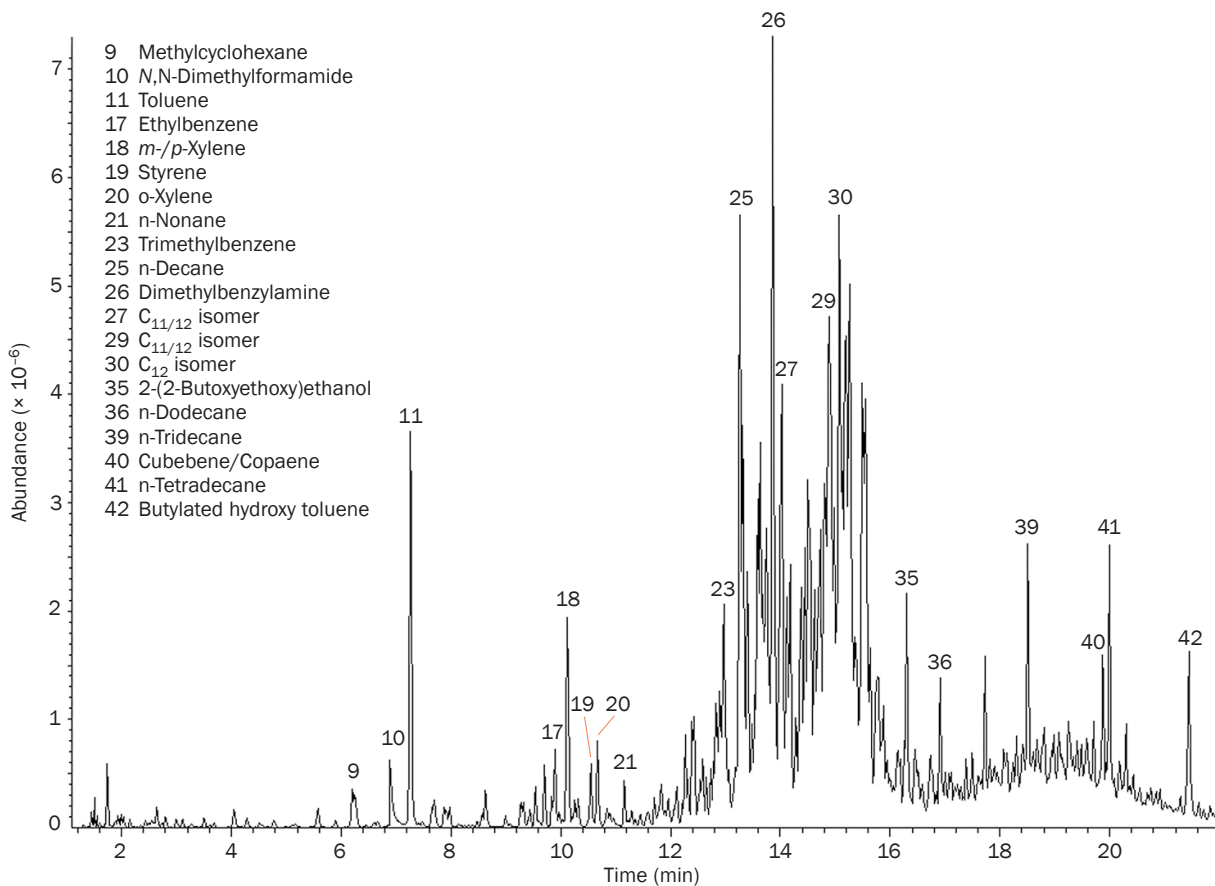


Figure 3: Analysis of air taken from Vehicle A (with standard upholstery), at 40°C.

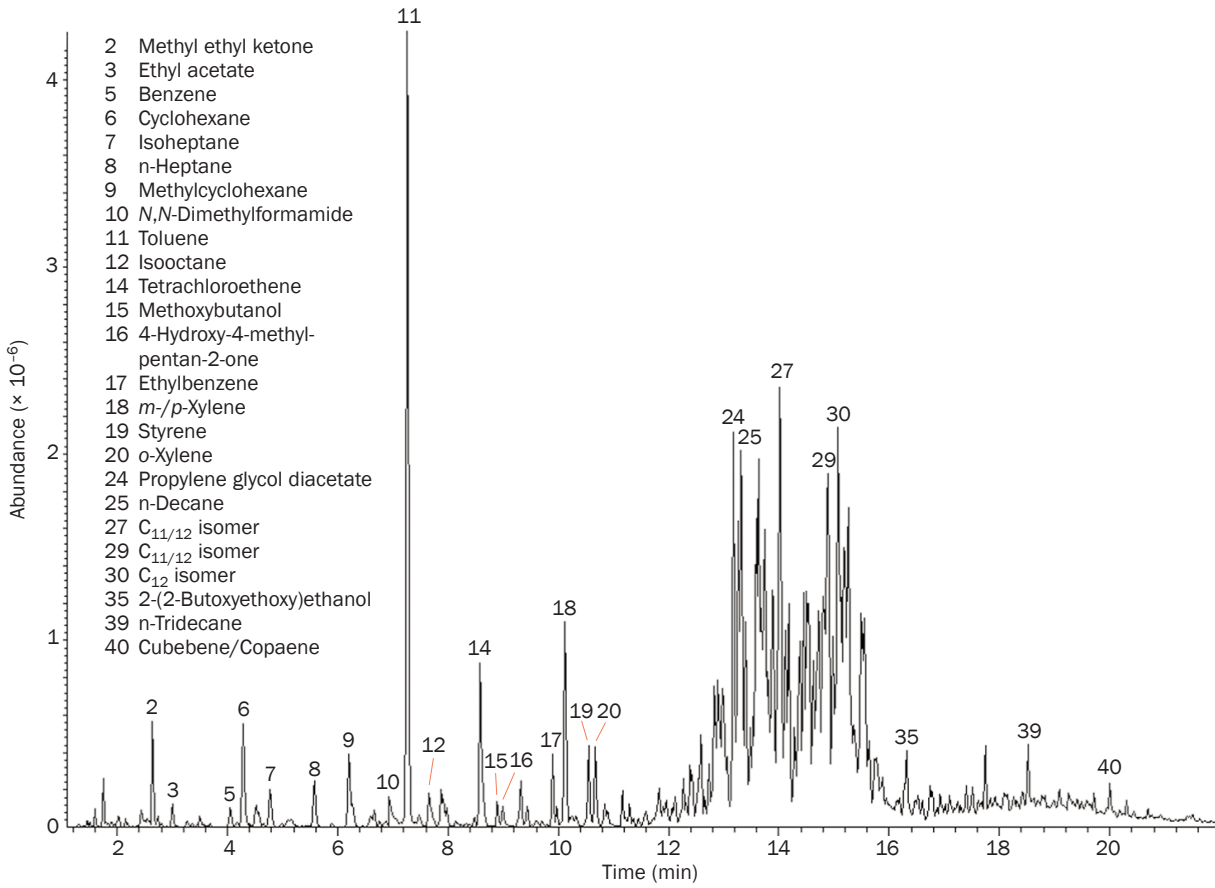


Figure 4: Analysis of air taken from Vehicle B (identical to A but with leather upholstery), at 20°C.

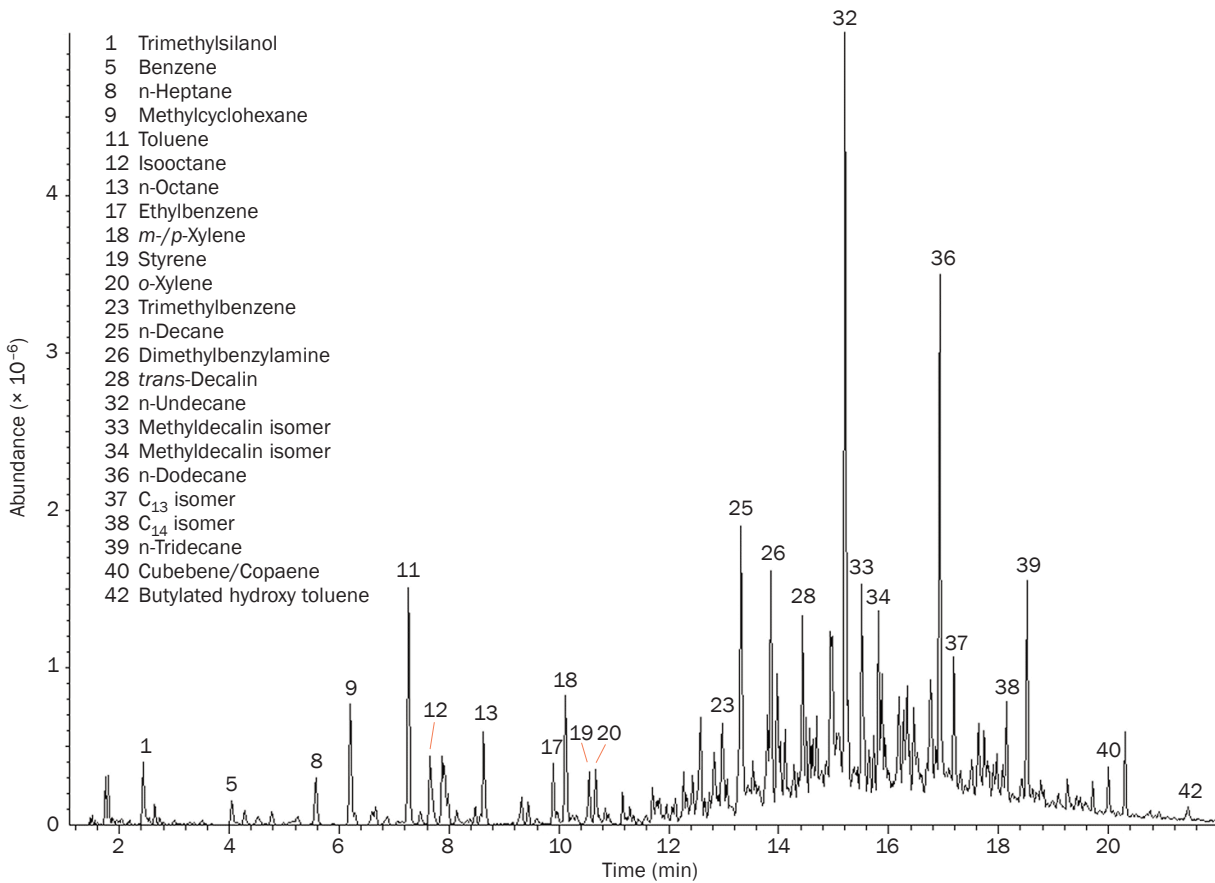


Figure 5: Analysis of air taken from Vehicle C (a different model from A and B), at 20°C.

Conclusions

Pumped sampling in conjunction with TD–GC/MS has been shown to be a useful method for the analysis of VOCs and SVOCs in car cabin air. A wide range of compounds can be screened, and comparison made between different models, allowing information to be obtained about the source of individual components.

Reference

1. M. Wensing, Standard test methods for the determination of VOCs and SVOCs in automobile interiors, in: *Organic Indoor Air Pollutants*, ed. T. Salthammer, Wiley-VCH, 2009, pp. 147–161.

Trademarks

UNITY™ is a trademark of Markes International Ltd, UK.

Carbograph™ is a trademark of LARA s.r.l., Italy.

Carbopack™ is a trademark of Supelco Inc., USA.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

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