Application Note 10363

Determination of Volatile Compounds in Automotive Interior Materials by Thermal Desorption GC-MS

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Introduction

The new car smell is for many families the enchanting scent of a long-planned and eagerly awaited delight. This typical odor comes from the variety of polymer materials found in new automobiles. But despite the popularity and attraction of new cars, owners are increasingly concerned about the air quality inside of a new car if the emitted chemicals pose a potential health risk.

Studies show that the indoor air of new vehicles carries a high amount of volatile organic compounds (VOCs) that are released from new vehicle interiors. The total VOC concentration (TVOC) within the interior of a minivan was determined to be as high as 7,500 µg/m^3 of inside air on the second day after delivery, which is approximately two orders of magnitude higher than regular outdoor TVOC concentrations. This study identified more than sixty chemicals inside the interior of vehicles that were released from different materials such as carpets, pedals, seat covers, door linings, and others [1].

In China, the overall automotive interior air quality discussion has attracted government departments, agencies, automobile inspectors, and decorative materials manufacturers with the first release of the "passenger air quality assessment guidelines" on March 1st, 2012 [2].

These new international regulations mandate that the organic materials used for automobile interiors be screened at the manufacturer and the raw material

suppliers for VOC and semi-volatile (SVOC or FOG) release to ensure the quality of the air inside the car. The reference method for the determination of VOCs and FOG in automotive interior materials is the VDA278 standard (or GMW15634) using a thermal desorption gas chromatography-mass spectrometry method [3,4]. VDA stands for the German Quality Management System (QMS) of the automobile industry (Verband der Automobilindustrie, Germany). The VDA278 is part of the delivery specifications of the car manufacturers Daimler, BMW, Porsche, and Volkswagen. GM/Opel uses the corresponding GM Engineering Standards GMW15634. The VDA278 analysis procedure determines the emissions from non-metallic materials that are used for interior parts in motor vehicles such as textiles, carpets, adhesives, scaling compounds, foam materials, leathers, plastic parts, foils, lacquers, or combinations of different materials.

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The complete VDA278 procedure comprises the determination of volatiles (VOCs) and semi-volatile analysis (SVOCs, FOG) in two analysis steps from one and the same sample. Included are quality control runs with calibrations with the application of a control mix in different concentrations before the sample is applied.

In this application, the focus is on the first part of the VDA278 method with the determination of the volatile organic compounds (VOC) from polymer materials by means of a sample thermal desorption followed by gas chromatographic separation and detection with a mass spectrometer (ATD-GC/MS). The setup and methodology used in this application follows the VDA278 standard in its status of 2002. Later versions of the method incorporate certain amendments as commented.
The analysis of SVOCs is documented in a separate application report.

Sample Preparation

Samples were taken directly into a glass adsorption tube, which is then analyzed by ATD-GC-MS.
Specific sampling requirements apply according to the investigated materials. For ABS, PVC, leather, and other plastic parts about 30 mg ± 5 mg are used, cut into pieces approximately 4 cm by 3 mm.

Experimental Conditions

The VOCs are determined using thermal desorption at 90 °C for 30 minutes. The emitted compounds are analyzed and calibrated using a toluene standard, so that the VOC concentration is expressed as toluene equivalent.
All analyses were performed using the Markes™ TD-100™ thermal desorption instrument connected to the Thermo Scientific™ TRACE™ 1310 GC and the Thermo Scientific™ ISQ™ LT single quadrupole GC-MS system as shown in Fig.1. Markes glass sorbent tubes were used for samples, see Fig. 2. Tenax™ TA internal sorbent tube material was used. The application parameters can be found in Tables 1–3.

Table 1. Thermal desorption parameter settings.

Desorption parameters:	
Desorption tubes	Deactivated glass, empty tubes for samples, Tenax TA filled tubes for calibration
Desorption temperature	90 °C for VOCs
	300 °C for calibration and control standards
Desorption time	30 min for VOCs
	10 min for calibration and control standards
Desorption flow	50 mL/min
Split Flow	Splitless
Transfer line temperature	200 °C
Pre-purge	3 min
	Bypass 20 mL/min
Focusing cold trap parameters:	
Initial temperature	-30 °C
Desorption temperature	300 °C
Heating rate	100 °C/s
Hold time	3 min for VOCs
	10 min for calibration and control standards
Cold trap desorption flow	Split flow 20 mL/min

Fig. 1. Automated thermal desorption system with GC-MS detection for VDA 278 analysis , comprised of a Thermo Scientific TRACE 1310 GC, a Thermo Scientific ISQ LT single Quadrupole MS and a Markes TD100 Thermal Desorber

Fig.2. Thermal desorption glass tubes used for VDA 278 analysis with a prepared sample.

Table 2. GC conditions.

Column type	Thermo Scientific™ TraceGOLD TG-5MS
Column dimensions	60.0 m × 0.25 mm × 0.25 µm (p/n 26098-1540)
Carrier gas, pressure	Helium (99.999% purity), 29 psi constant pressure
Oven program	40 °C, 2 min
	20 °C/min to 80 °C, 2 min
	10 °C/min to 160 °C, 5 min
	20 °C/min up to 320 °C, 15 min
Transfer line temperature	280 °C

Table 3. MS conditions

Ionization	EI, 70 eV
Scan mode, range	full scan, scan range 29-450 Da
Acquisition rate	300 ms/scan
Ion source temperature	280 °C

Fig. 3. Detail of the automated thermal desorption system loaded with sample tube trays (Markes TD-100).

Sample Measurements

BTEX Testing

A series of standards with concentrations of 10, 50, 100, 200, 500, and 1000 ng/µL in methanol was prepared as the working standards used for calibration. The calibration solutions have been applied directly into Tenax-filled desorption tubes and analyzed using the above described method for TD-GC-MS measurements. The chromatogram of the VOC compounds as the total ion current is shown in Figure 4. In Table 4, the BTEX compounds analyzed are listed with retention times and the specific ions used for selective quantification, also showing the resulting R^2 values giving the precision of the quantitative calibration.

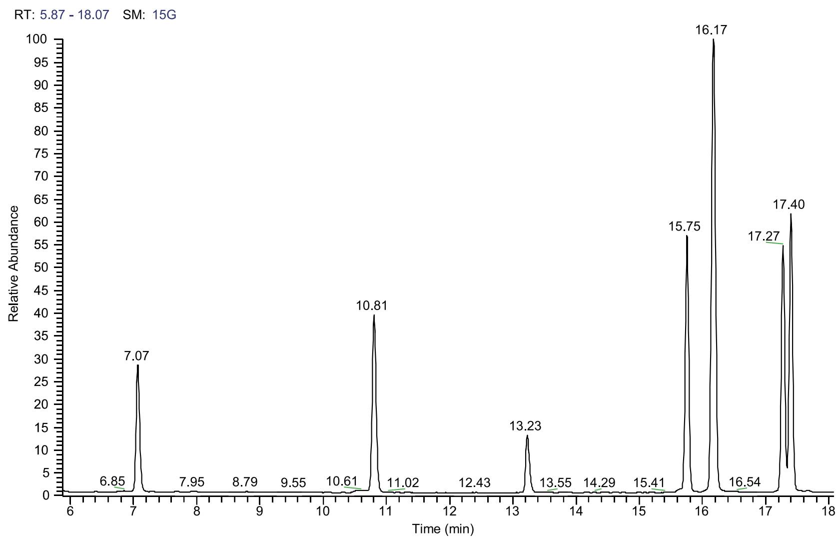

Figure 4. TD-GC-MS total ion chromatogram (TIC) of the volatile organic standard.

Table 4. VOCs of the BTEX test with retention times and quantitative precision.

Compounds	Retention time [min]	Quantitation ion [*m/z*]	Linearity R^2
Benzene	7.07	78	0.9991
Toluene	10.81	91	0.9999
Ethylbenzene	15.75	91	0.9990
p/m-Xylene	16.17	91	0.9998
Styrene	17.27	91	0.9993
o-Xylene	17.40	91	0.9994

TVOC Testing

The TVOC value of a sample is determined by the integration of the chromatographic peak area between C6–C16 with 100 ng total integrated area toluene peak comparison calculated. The two standards, hexane and n-hexadecane, determine the retention time position of the C6 and C16 peaks (see Figure 5). Recent amendments to the VDA278 methodology require the TVOC to be measured from the start of the chromatogram to C25. For the test samples, the peak area between the calibrated retention times of n-hexane and n-hexadecane is determined as a total peak area. The TVOC concentration of the sample is then calculated according to the following formula:

$$C_s = \frac{100 \times A}{A_T \times m_s}$$

A = Sample, C6-C16 chromatographic total peak area integration [area cts]

A_T = Toluene reference, 100 ng injection, chromatographic peak area integration [area cts/100 ng]

m_s = Sample volume [mg]

C_s = The TVOC concentration in the sample [ng/mg]

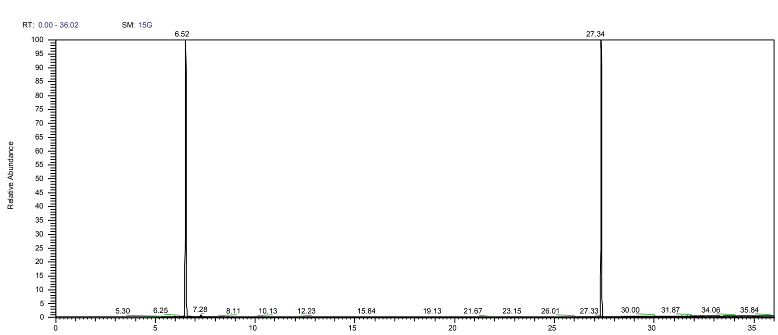

Figure 5. C6 and C16 retention time to determine the total ion current.

Sample Measurements

Typical car interior materials and accessories have been bought in the local market and prepared using the above method for test samples for BTEX and TVOC analysis. Leather samples and sponge samples are shown with the total ion current in Figures 6 and 7. Table 5 contains the results of the BTEX and TVOC measurements from the analyses in Figures 6 and 7.

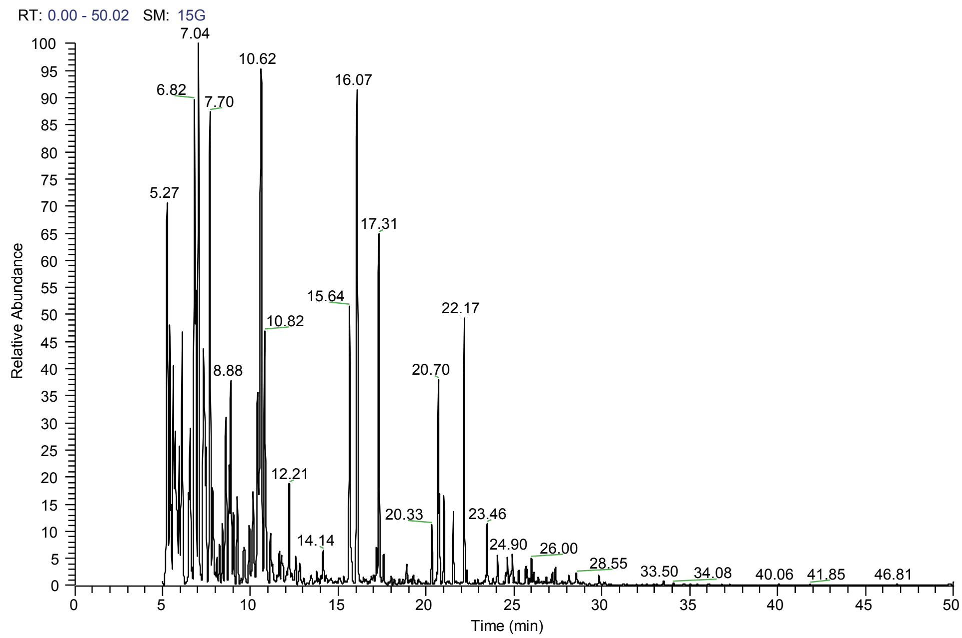

Figure 6. A leather sample TD-GC-MS analysis (total ion current).

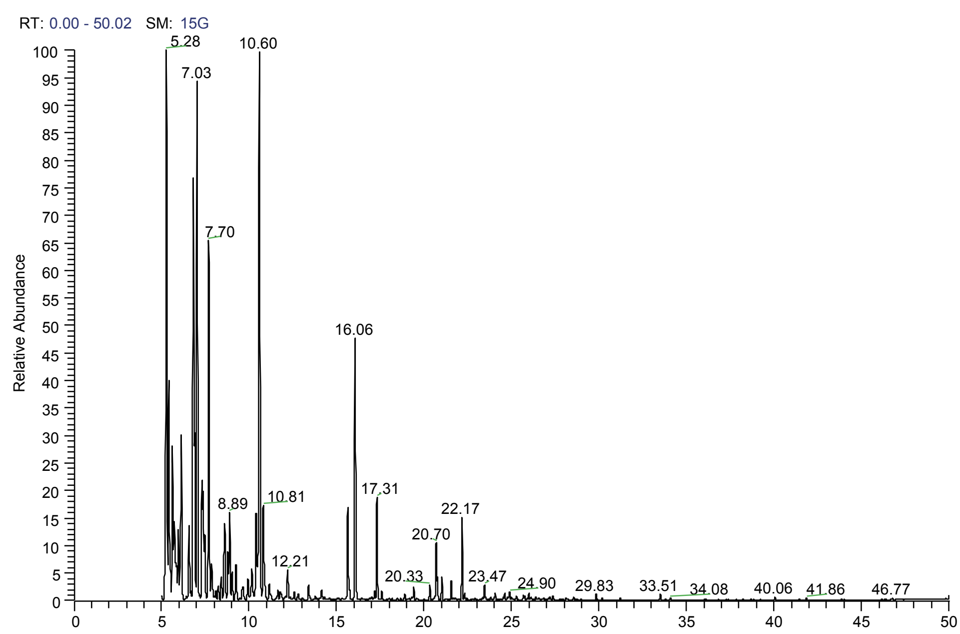

Figure 7. A sponge sample TD-GC-MS analysis (total ion current).

Table 5. Results of the BTEX and TVOC measurements from Fig.6/7 analyses.

Compounds	Leather [µg/g]	Sponge [µg/g]
Benzene	5.23	1.52
Toluene	16.24	7.99
Ethylbenzene	5.50	0.83
p/m-Xylene	9.22	2.33
Styrene	0.65	0.06
o-Xylene	5.17	0.79
TVOC	185.70	76.45

Conclusions

This application demonstrates the use of the Markes thermal desorber unit combined with a TRACE 1310 GC and the ISQ single quadrupole MS for the analysis of VOCs and TVOCs in automotive interior materials.

The analytical method follows the international recognized method VDA 278 for the analysis of volatiles for the automotive industry. The described application provides the standard analytical solution for testing automotive interior materials for VOC and TVOC data.

The sample preparation is simple, and the measurement can be run fully automated. The combined Markes and Thermo Scientific instrumentation provides high sensitivity and a wide linear range.

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References

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