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Application News

No. SCA_280_099

Gas Chromatography Mass Spectrometry

Analysis of VOC and FOG emissions of Non-Metallic components from automobiles according to VDA 278

▪ Introduction

The automobile industry is producing more than 84 million passenger cars worldwide.

To ensure a high-quality car, implemented control standards are mandatory for the supply chain of a vehicle.
The German Association of the Automotive Industry (VDA) recommends to standardize certain control standard analyses, which have to be followed by suppliers for VDA members and the car manufacturers themselves.

Such a guideline for analyzing organic emissions of non-metallic materials used in automobiles based on thermal desorption techniques, is stated in the VDA 278. This guideline is the basis for this application.

The VDA 278 recommends to distinguish between two classes of compounds: highly and medium volatile substances (VOC) up to C25 and those of low volatility (FOG) in the range of C14 up to C32.

In this application Polypropylene (PP)-Granules, a raw material for moulded automobile interior parts as well as synthetic leather have been analyzed according to VDA 278 regarding their organic emissions.

▪ Analytical conditions

Measurements were carried out using the TD-30R thermal desorption unit combined with the GCMS-QP2020 NX. The applied analytical parameters are listed in Table 1.

Table 1: Analytical conditions

TD-30R	
Desorption temp.: (VOC/FOG/Cal)	90 °C / 120 °C / 280 °C
Desorption time: (VOC/FOG/Cal)	30 min / 60 min / 20 min
Desorption flow:	82 mL/min
Trap cool temp.:	-20 °C
Line temp.:	280 °C
Interface temp:	280 °C
GC	
Oven program:	
VOC + Cal:	40 °C, 3 min → 10 °C/min to 300 °C, 13.5min
FOG:	50 °C, 2 min → 25 °C/min to 160 °C, 0 min → 10 °C/min to 280 °C, 30 min
Column:	SH-Rxi-5Sil MS 60 m x 0.25 mm x 0.25 µm (P/N: 227-36036-02)
Flow Control Mode:	Constant pressure at 200 kPa
Split:	100:1
MS	
Interface temp.:	280 °C
Ion Source temp.:	240 °C
Acquisition Mode:	EI, 70 eV, emission current 20 µA, Scan (Range: *m/z* 29-450)

Workflow

According to VDA 278 the workflow shown in Figure 1 has to be followed

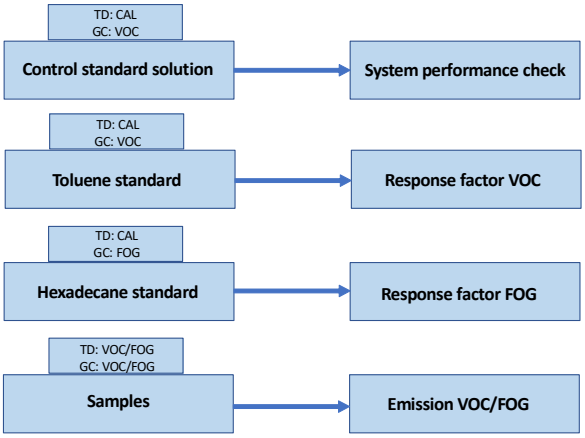

Figure 1: Workflow according to VDA 278

A control standard solution of 18 compounds including alkanes and typical VOCs in concentrations of approximately 0.11 µg/µL (Restek, P/N: 574003), must be checked to ensure instrument performance followed by the measurement of two standards as calibration substances.

In case of VOC runs, Toluene is used to determine the response factor (Rf) whereas for FOG runs Hexadecane is used.

The corresponding Rfs are then used for calculating the Total Organic Emissions of the samples.
For that, the area-sum of all peaks above the baseline, up to C25 for VOC, and between C14 and C32 for FOG is used in combination with the Rfs to determine the emission based on the formulas displayed in Figure 2.

$$R_f = \frac{\mu g\ Toluene, C16}{Peak\ area}\ x\ 1000000$$

$$Emission\left[\frac{\mu g}{g}\right] = R_f\ (Toluene, C16)\ x\ \frac{\sum peak\ areas}{1000\ x\ sample\ weight\ [mg]}$$

Figure 2: Formulas for the calculation of Response factors(Rf) (VOC: Toluene, FOG: C16) and the emission of the sample

The VOC-Emission of a material has to be measured twice: One sample is used for a VOC analysis only, the second one is measured under VOC conditions subsequently followed by FOG analysis.

For the calibration, standard solutions were spiked on tubes filled with Tenax® TA (P/N: 980-24308). The solvent was evaporated after injection, under a continuous flow of nitrogen gas (5 min at 100 mL/min).

For sample measurements a material amount of approximately 30 mg was placed into empty TD tubes as shown in Figure 2.

Figure 2: Synthetic leather sample placed into the TD tube

For smaller sample parts a fixation with deactivated glass wool was realized.

Results and discussion

The chromatogram of the control standard solution which displays sufficient peak separation is shown in Figure 3.

VDA 278 requires a “nearly baseline separation” of o-Xylene and n-Nonane. This criteria is fulfilled with a peak resolution of 1.6 in this application.

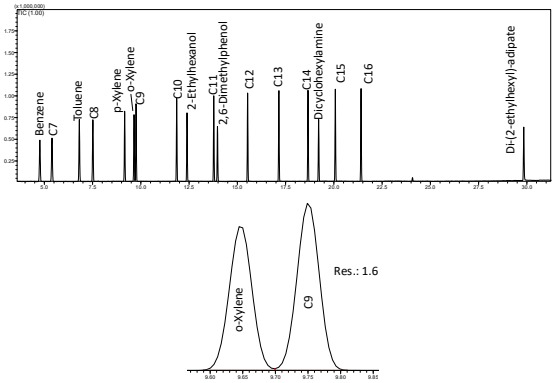

Figure 3: Chromatogram of the control standard and the separation of o-Xylene and C9.

Recovery rates for the compounds checked were well within the limits of 60 – 140% which are displayed in Table 2.

Table 2: Recovery rates of the control sample

Component	Recovery ratio [%]
Benzene	77.7
n-Heptane	82.9
Toluene	98.0
n-Octane	99.2
p-Xylene	98.1
o-Xylene	93.9
n-Nonane	106.9
n-Decane	111.5
2-Ethylhexanol-1	93.2
n-Undecane	114.6
2,6-Dimethylphenol	75.2
n-Dodecane	118.2
n-Tridecane	119.5
n-Tetradecane	122.0
Dicylohexylamine	87.4
n-Pentadecane	126.7
n-Hexadecane	126.3
Di-(2-ethylhexyl)-adipate	78.5

For toluene, an average recovery of 98% was determined which passed the given criteria with a range of 80 – 120%.

It was also possible to surpass the required decision limits for Toluene (<0.04 µg) and the n-alkane C20 (<0.06 µg) under VOC- as well as for C32 (<0.2 µg) under FOG-conditions.
A significant difference between the blank and half the amount of the claimed decision limit was observed (see Figure 4).

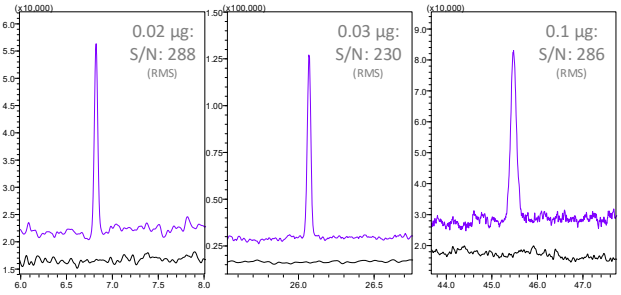

Figure 4: Sensitivity test with 50% of the claimed decision limit amount. **Purple**: Standard, **Black**: Blank

Example chromatograms of VOC and FOG measurements of synthetic leather are displayed in Figure 5, as well as the corresponding emissions in Table 3.

Table 3: VOC and FOG-Emission from PP-Granules and synthetic leather

PP-Granules:		**Synthetic leather:**	
Emission VOC 1:	189 µg/g	Emission VOC 1:	232 µg/g
Emission VOC 2:	183 µg/g	Emission VOC 2:	216 µg/g
Emission FOG:	258 µg/g	Emission FOG:	516 µg/g

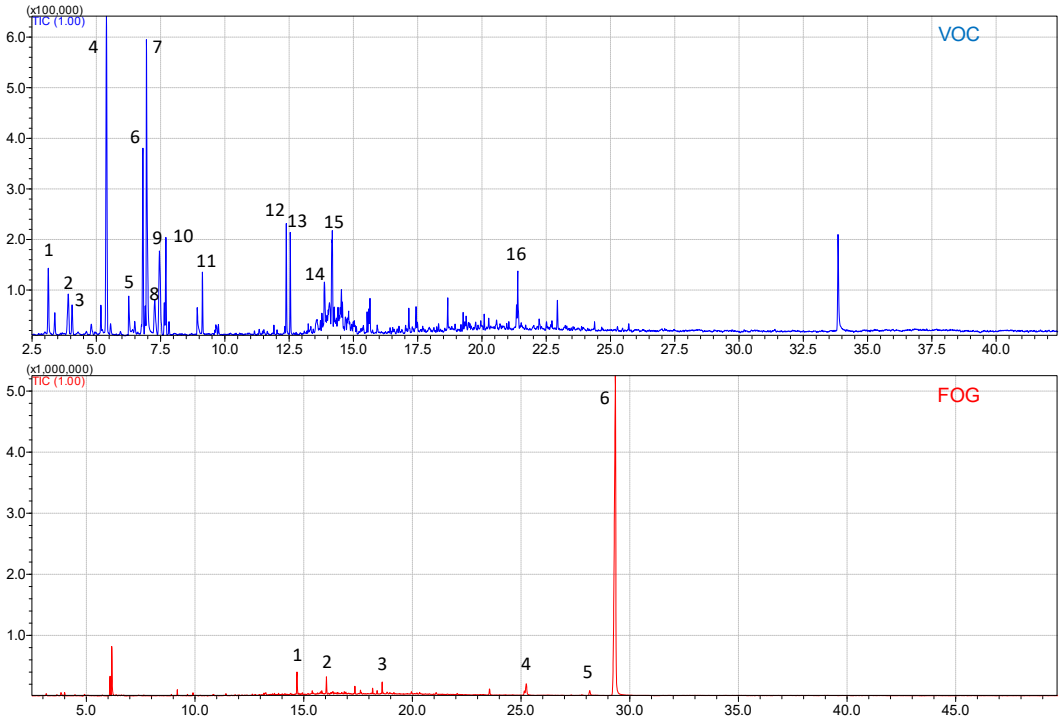

Figure 5: Chromatograms of synthetic leather measured under VOC (**blue**) and FOG conditions (**red**)

Every peak that corresponds to an emission ≥1 µg/g in the sample was identified using the NIST 17 Mass Spectral Library (P/N: 980-24517) and the Shimadzu Polymer Additives Library (P/N: 225-31990-92).
As an example, a list of identified compounds in synthetic leather is listed in Table 4.

Table 4: VOC and FOG compounds with emissions ≥1 µg/g from synthetic leather

VOC (>1 µg/g)				FOG (>1 µg/g)	
1	Acetone	9	3-Methyl-3-heptene	1	Diethyl phthalate (DEP)
2	2-Butanone	10	3-Methyl-2-heptene	2	2-Ethylhexyl benzoate
3	Ethyl acetate	11	1,3-Dimethylbenzene	3	Dibutyl phthalate (DBP)
4	n-Heptane	12	2-Ethylhexanol	4	Bis(2-ethylhexyl)phthalate (DEHP)
5	Pyridine	13	D-Limonene	5	Bis(2-ethylhexyl)isophthalate (DOIP)
6	Toluene	14	Nonanal	6	Bis(2-ethylhexyl)terephthalate (DEHT)
7	N,N-Dimethylformamide	15	3,6-Dimethyldecane		
8	2-Octene	16	2-Ethylhexyl 2-ethylhexanoate		

▪ Conclusion

The QP2020NX in combination with the TD-30R fulfills all the criteria of VDA 278 and represents a reliable setup for the emission-analysis of non-metallic components by thermo desorption from car interior.
The VDA requirements concerning the resolution of o-Xylene and n-Nonane as well as the corresponding decision limits for VOC and FOG were achieved and even surpassed.

The recovery rates were within the postulated range between 60 – 140% for the control substances and between 80 – 120% for Toluene.
Based on these settings, the emission of synthetic leather and PP-granules was measured and the substances with an emission ≥1 µg/g were successfully identified by the NIST and Shimadzu Polymer Additives Library.

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