

## VDA 277: Analysis of Volatile Contaminants from Polymers

Modern vehicle interiors contain a multitude of different polymers. The car manufacturers' constant strive for an increase in product quality leads to the implementation of softer polymers, e.g. in the dash panel. Such softer materials offer an increased grip feeling and overall quality impression to the customer. Especially these softer formulations and blends containing multiple polymers at various fractions are prone to emit volatile contaminants. The latter can be inhaled by customers, leading to adverse effects on health. Emitted concentrations increase further, when polymers are subjected to higher temperatures. A typical example would be vehicles in summer under the influence of direct sunlight. The evaporated contaminants such as phthalates are frequently misunderstood as "new car smell" by customers, resulting in an underestimation of the associated risks.



Figure 1: Polymer samples in headspace vials

### ■ Analytical methods: quality assurance

In order to avoid potential health risks for customers, car manufacturers implement various quality control procedures for estimating the contaminant emissions of individual materials. One of these procedures is described in VDA 277 [1]. This procedure uses gas chromatographic analysis with headspace sampling after thermal incubation of polymer samples in gas-tight flasks. The present study uses the GC-2010 Plus gas chromatograph with the HS-20 automated headspace sampler.

### ■ Experimental work

Instrument calibration is carried out via calibration solutions that contain acetone in - butanol with the following concentrations: 0.1, 0.5, 1, 5, 10, 50 and 100 g/L. Individual 20 mL sample vials are spiked with 4  $\mu$ L of these solutions and are immediately sealed with gas-tight screw caps that are outfitted with silicone/PTFE septa. Polymer samples are disintegrated into pieces of 10-25 mg. 2 g of these pieces are weighted into each 20 mL sample vial as shown in Figure 1.

First step of the measurement is an incubation of the samples at 120°C, either for 1 hour (calibration samples) or for 5 hours (polymer samples). During this time, the polymer samples equilibrate with their headspace (Figure 2), which denotes the gas volume that is contained inside the sample flasks alongside the solid polymer samples.

The overlapping routines of the HS-20 automated headspace sampler increase time-efficacy over the course of such long incubations by simultaneous processing of up to 12 samples. Afterwards, 1 mL of the equilibrated sample headspace gas is abstracted from the sample flask by the headspace sampler and introduced into the gas chromatograph. This is carried out via pressurized and heated flow lines and a sample loop, in which the headspace gas is precisely gauged.

Gas chromatographic separation of analytes is realized on a Restek Rtx®-Wax column (polyethyleneglycol) with an internal diameter of 0.25 mm, a coating thickness of 0.25 µm and a length of 30 m. The oven program starts at 50 °C for 3 min, proceeds to 200 °C at 12 K/min and concludes at 200°C for 4 min. Two sample chromatograms are shown in Figure 3. Peak separation is of secondary importance, since specific compounds are not analyzed individually but only altogether as a sum parameter. This makes the method very straightforward to use and improves time-efficiency in the laboratory.

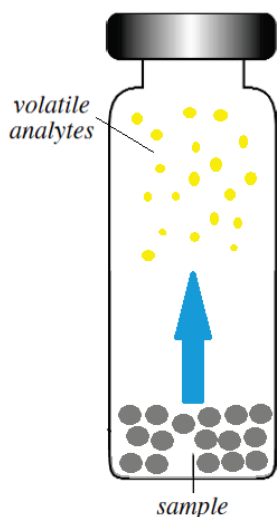


Figure 2: Polymer sample headspace equilibration

Instrument	GC-2010 Plus & HS-20
Incubation temperature	120 °C
Incubation time	5 h for samples
Agitation strength	2 (of 5)
Vial pressurization	90 kPa (relative)
Sample line temperature	200 °C
Sample volume	1 mL
Injector temperature	200 °C
Split ratio	1:20
Gas & flow speed	Helium at 27 cm/sec
Oven program time	19.5 min
Detection	Flame ionization (FID)
Detector temperature	250 °C

Table 1: Instruments and Analytical Conditions

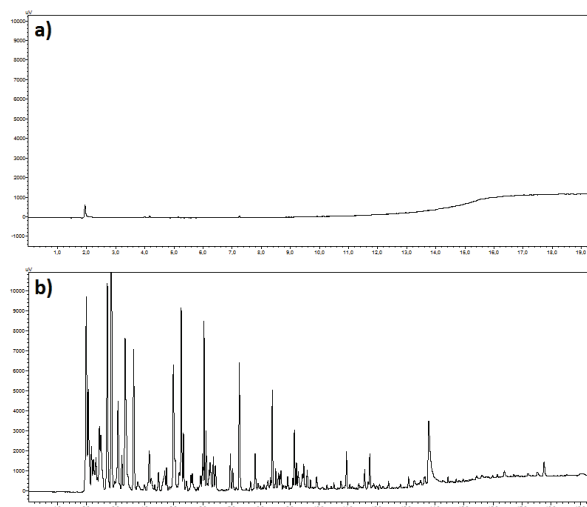


Figure 3: Chromatograms for an inconspicuous (a) (PC/ABS) and a potentially problematic sample (b) (PBT/GF) with clearly visible emissions

Further instrumental details are presented in Table 1. The resulting peak areas of the volatile contaminants are summarized and quantified into µg C per g of initial sample via the preliminary calibration. This permits a straightforward comparison of the outgassing potential of each type of polymer as shown in Figure 4. With the obtained results, potentially problematic polymers can easily be identified.

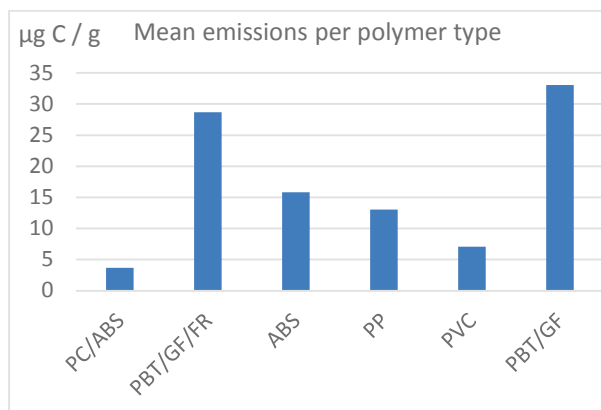


Figure 4: Results for exemplary polymer samples

### ■ Conclusion

GC-2010 Plus equipped with the HS-20 automated headspace sampler is an ideal combination for the assessment of potential outgassing of volatile contaminants from polymer materials in accordance to VDA 277. Sample preparation and analysis process are user-friendly, reliable and reproducible. The quantification of the final results is straightforward and can easily be implemented into quality control mechanisms of the manufacturers. The exemplary measurements showed two potentially problematic PBT/GF polymers blends.

Further method optimization according to the user demands holds potential for additional improvements in time efficiency e.g. by implementation of fast-GC separation columns. Identification of specific, problematic compounds is possible as well and may enable backtracking of contaminations into the production process.

### ■ References

[1] Verband der Automobilindustrie e.V. – VDA 277 (1995)