



Studies on the emission behavior of polypropylene by gas chromatography/mass spectrometry with static headspace or thermodesorption

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ARTICLE INFO

Article history:

Available online 18 November 2010

Keywords:

Polyolefins
Surface dependence
Fogging
Sample-introduction techniques
Volatiles (VOC)

ABSTRACT

Emissions from polypropylene (PP) may cause undesired smell, be harmful, or lead to so-called fogging which prohibits its use for car interiors. Thus, qualitative as well as quantitative emission studies are necessary. Thermodesorption (TDS) and static headspace (sHS) with subsequent GC–MS analysis are two powerful tools for analyzing the emission behavior of polymers with a minimum of sample handling. In this work we investigated the emission behavior of PP with TDS and sHS coupled to GC–MS paying special attention to quantitative considerations and to the relevance of emitted substances for fogging phenomena. After extraction for 30 min and incubation for 2 h, TDS–GC–MS and sHS–GC–MS results were satisfyingly repeatable (with relative standard deviations up to 5%). TDS allowed to introduce substances up to higher boiling points into the GC–MS system, but required to control sample geometry, as emission depended rather on sample surface than on sample mass. In sHS, emission was governed by partitioning between the gas and the sample phase rather than by full evaporation of the analytes. Above a certain analyte-dependent amount, peak area became independent of the sample amount. However, if the sample amount was kept constant, peak areas of emitted substances showed a linear dependence upon concentration of volatiles. Therefore, accurate quantitation was still possible. Typically alkanes, alkenes and dialkenes dominate TDS–GC–MS and sHS–GC–MS chromatograms of PP. They only contributed to fogging if they had a chain length higher than C16. These substances were only detectable when TDS was used for sample introduction, but not with sHS. sHS–GC–MS is thus not useful for judging fogging behavior.

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1. Introduction

Polypropylene (PP) takes a key position in various sectors of industry such as packaging, automotive, mechanical engineering and electronics, as it exhibits an excellent cost–performance ratio and material properties superior to those of other polyolefins [1]. Progress in catalyst development and innovative processing technologies promise that PP is going to gain even more importance in the future.

Not only material testing, but also analytical chemistry plays an important role in the PP industry. The molecular-weight distribution is determined with high-temperature GPC, fillers can be identified with X-ray fluorescence, and the content of stabilizers is mostly assessed with HPLC. Furthermore, the emission behavior of PP is controlled.

Especially the automotive industry strongly promoted that polymer producers integrated the determination of volatiles in

their quality management. They had to cope with the problem that volatiles from the interior parts of cars condensed on the car windows, resulting in a sticky and greasy film which impaired the driver's sight. This highly undesired phenomenon is called 'fogging' and can only be averted by avoiding highly emitting materials for car interior. Furthermore, some monomers or low-molecular-weight compounds from the polymer may be harmful or may cause an undesirable smell. Therefore, various standard procedures to characterize emission behavior were developed. In fogging tests, standardized sample bodies are exposed to elevated temperature, and volatile substances subsequently condense on a cooled aluminum or glass plate. The amount of emitted substances is then determined either gravimetrically (e.g. DIN 75201-B, ISO 17071 or PV 3015) or optically (e.g. DIN 75201-A, ISO 6452 or PV 3920). The smell of PP pellets is determined by a human panel (e.g. PV 3900, VDA 270 or FLTM BN 131-01) and formaldehyde is derivatized and determined photometrically (e.g. E DIN EN ISO 27587, PV 3925 or VDA 275).

Furthermore, organic emitted substances can be characterized by GC with MS detection. For GC–MS, different sample introduction systems allow to reduce sample handling to a minimum. In static headspace (sHS) examinations, a gaseous sample is directly

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taken out from the headspace of a vial after equilibration at a certain temperature. In thermodesorption (TDS), analytes are stripped off by a continuous stream of gas and focussed by adsorption or condensation (achieved via cryofocussing). Therefore, analytes can be exhaustively extracted from the sample if TDS parameters are chosen in an appropriate way. Alternatively, analytes released into the gas phase can be collected with a fibre coated with a polymeric coating (e.g. polydimethylsiloxane, polyacrylate). This technique is known as solid phase microextraction (SPME) and is useful for trace analysis of selected analytes. In TDS as well as in SPME, substances are released into the GC system after the enrichment step by raising the temperature. While sHS and TDS allow a representative analysis of all the substances in the gas phase, selectivity differences of the SPME fibre for the various analytes may lead to discrimination respectively overestimation of some components. Therefore, sHS and TDS promise to be the more appropriate techniques for an overall-analysis of substances emitted from PP and are used in several standard procedures (e.g. PV 3341 or VDA 277 for sHS-GC and PB VWL 709 or VDA 278 for TDS-GC). SPME is often utilized as a sample-introduction system to measure the emission of specific analytes from polymers (e.g. [2–4]).

In the field of polyolefin analysis, degradation products from unstabilized as well as from stabilized PP were identified with sHS-GC-MS, TDS-GC-MS, and SPME-GC-MS. Typically, methylated alkanes and alkenes were emitted [5–7]. They were considered to be products of shear and heat induced degradation occurring during extrusion, as pyrolysis of PP yielded similar products (more precisely methylated alkenes, alkanes and dialkenes) [8–11]. They were formed by main-chain cleavage, intramolecular radical transfer (called “backbiting”), and β -scission [8]. After thermal or photooxidation, many more oxygen-containing substances were emitted [12–15]. Later studies carried out with differently C^{13} labeled grades of PP [16,17] represent the state-of-the-art as far as volatile degradation products generated in the presence of oxygen are concerned. These examinations allowed to exactly locate which bonds had been cleaved.

Examining industrial grades of PP, a broader range of substances was observed. sHS-GC with flame ionization detection (FID) was used to detect organic solvents (namely ethyl acetate and ethanol) adsorbed in PP film used for food packaging [18]. Furthermore the appearance of substances such as di-tert-butylphenol, di-tert-butyl-p-cresol, and di-tert-butyl-benzoquinone [6,7] was documented. Their structures are related to those of phenolic antioxidants, which makes it likely that they are their degradation products.

The multitude of emitted substances suggests that distinguishing different grades of PP according to their characteristic emission pattern is possible. This fingerprinting approach is a promising tool for batch and vendor identification, etc. and was thoroughly evaluated by Willoughby et al. [5].

Obviously, scientific work published so far concentrated on qualitative information on the emission from PP and reaction pathways which could be derived from it. Information on quantitative aspects such as repeatability, linearity, and potential influence of sample geometry on emission could not be found. Therefore, it was decided to thoroughly examine the potential of sHS-GC and TDS-GC methods for the analysis of emissions from PP paying special attention to quantitative considerations. Investigated parameters were detectable analytes, establishment of the equilibrium respectively the progress of extraction with time, and repeatability. The impact of sample geometry was evaluated for TDS. For sHS, we examined the increase in peak area both for increasing sample amount at constant concentration of volatiles and for increasing concentration of volatiles at constant sample amount. Furthermore, we evaluated the relevance of the different emitted substances for fogging phenomena. For this purpose, the residue from a gravimetric fog-

ging test was dissolved and subsequently examined with GC-MS. Emissions observed in the sHS-GC-MS and the TDS-GC-MS were compared to the substances contained in the residue from the fogging test.

2. Experimental

2.1. Instrumentation

TDS-GC-MS and sHS-GC-MS were carried out with an Agilent GC 6890N coupled to a 5975C mass spectrometer (with electron impact (EI) ionization), both from Agilent Technologies, Waldbronn, Switzerland. The system was equipped with an MPS2 multi-purpose sampler for headspace injection, a KAS 4 cold-injection system (CIS) and a TDS 3 TDS system with a TDS A2 autosampler (all from Gerstel, Mühlheim, Germany). Separations were achieved with a HP-5MS column (30 m, 0.25 mm inner diameter, 0.25 μ m film thickness) from Agilent.

Liquid-injection GC-MS measurements were done with a GC 6890N coupled to a 5973 MSD (EI), also from Agilent, equipped with a MPS2 multi-purpose sampler for liquid injection from Gerstel. Substances were separated on an Rxi-5ms column (30 m, 0.25 mm inner diameter, 0.25 μ m film thickness) from Restek (Bad Homburg, Germany).

2.2. Samples and reagents

An overview on examined PP samples is given in Table 1. An aluminum foil with residues from a gravimetric fogging test (according to DIN 75201-B) was provided by Borealis.

A boiling-point calibration mix (part number 5080-8768) was purchased from Agilent. Dichloromethane (p.a.) was obtained from Merck (Darmstadt, Germany). n-Pentane (puriss. p.a.; 99.5%) was purchased from Fluka (Buchs, Switzerland).

2.3. Analytical procedures

For the liquid-injection experiments, the fogging residue from about 50% of the aluminum foil was dissolved in 10 mL of dichloromethane. Subsequently this solution was concentrated to about 2 mL by evaporating the solvent at room temperature and analyzed with GC-MS by injecting 1 μ L in splitless mode (inlet temperature 280 °C).

Sample amounts for PP were about 20 mg for TDS (corresponding to one pellet in case of granulate) and 1 g for sHS. Deviant amounts are explicitly mentioned in Section 3. Pieces of about 2 mm² and 3 cm² respectively were cut from the aluminum foil were directly placed into TDS tubes and sHS vials. Trace amounts of the boiling point calibration mix (less than 1 μ L) were directly put into a TDS tube.

TDS and sHS temperatures were chosen similarly to VDA 277 and VDA 278 – FOG. In sHS, samples were incubated at 115 °C for 120 min. After incubation, 1 mL was injected in split mode (split ratio 1:25, inlet temperature 150 °C). The temperature program of the TDS oven started at 20 °C and went up to 120 °C at a rate of 60 °C/min. This final temperature was held for 30 min. The gas flow during TDS was 100 mL/min He. Substances were cryofocussed between – 100 °C and – 150 °C, subsequently the trapped compounds were released by heating at a rate of 12 °C/s up to 280 °C (held for 5 min). The split ratio when releasing substances from the CIS was 1:50. Only when the aluminum foil with the fogging residue on it was measured, substances were transferred in splitless mode to the GC column. As the available amount of aluminum foil with fogging residue on it was limited we wanted to keep the necessary sample amount as low as possible.

Table 1
Different grades of PP used in this study.

Material no.	Shape	Obtained from	Comment	Used for the investigation of
1	Granulate	Borealis Polyolefine GmbH (Linz, Austria)	–	Range of detectable substances (TDS and sHS), sensitivity (TDS and sHS), extraction time (TDS), equilibration time (sHS), repeatability (sHS), linearity (sHS)
2	Powder	Borealis Polyolefine GmbH	–	Linearity (TDS), repeatability (TDS)
3	Cylindrical sample bodies with different heights	Commercial yoghurt beaker	Punched out at positions of differing wall thickness	Linearity (TDS)
4	Granulate (emission-reduced)	Prepared from material 1	Heated in a flask up to about 90 °C while pumping off emitted volatiles with a vacuum pump for 32 h	Linearity (sHS)
5	Disc	Borealis Polyolefine GmbH	The same material as the fogging test had been performed with	Fogging

All materials except material 2 (unstabilized) and material 3 (unknown stabilization) were stabilized with 0.1% ADK Stab AO-60 (phenolic antioxidant) and 0.1% Everfos 168 (phosphite processing stabilizer).

In GC–MS (after liquid injection as well as after TDS and sHS), the mobile phase was helium with 1.0 mL/min constant flow. The different temperature gradients are given in Table 2. For the examination of substances relevant for fogging, a somewhat steeper temperature gradient was chosen. The detected mass range was 35–550 *m/z*. In case of liquid injection, a solvent-delay step of 4 min was introduced for the MS.

These parameters were used for all measurements unless otherwise mentioned in the text.

3. Results and discussion

In this work, the emission behavior of PP was characterized with TDS–GC–MS and sHS–GC–MS concerning the range of detectable substances, sensitivity, extraction respectively equilibration time, repeatability, and linearity. Table 1 summarizes which examination was carried out with which material. The constituents of a fogging-residue were compared to emitted substances in order to identify volatiles causing fogging.

Throughout the entire work, fundamental comparative studies on the emission behavior of PP were carried out; however, no absolute values were determined. Attributing absolute numbers to emissions from polymers in TDS–GC–MS and sHS–GC–MS can be quite challenging. One approach is to calibrate via liquid injection. Using this sample-introduction system for calibration seems risky to us, as slightly differing flow characteristics in the different inlets (i.e. the TDS and sHS inlet on the one hand and the liquid-injection inlet on the other hand) may result in differing discrimination effects. This jeopardizes the calibration via liquid injection. Introducing calibration solutions using the TDS and the sHS systems, one faces the problem that very small volumes of calibration solutions have to be transferred into TDS tubes and sHS

vials. This implies dosage problems. To sort them out an internal standard can be used [19]. However, in order to add the internal standard to the sHS vial containing the polymeric sample the septum is usually pierced. In this way, leakage cannot be excluded. To use bigger volumes of highly diluted analyte-solutions is not an alternative; the solvent might clog the cryofocussing system and disturb the equilibrium in sHS. Furthermore, the risk that analytes evaporate while preparing the calibration samples is high, especially for highly volatile analytes. Immobilizing the analytes on adsorptive material facilitates the dosage of small analyte amounts and reduces the risk of analyte loss without introducing big amounts of solvent into the sample-introduction system. However, if analytes are not fully desorbed inaccurate calibration curves will be acquired. In view of these difficulties we only performed comparative studies within this work. Nevertheless, future studies will focus on the task of absolute quantification too.

3.1. Range of detectable substances, sensitivity, equilibration and extraction time, and repeatability in TDS and sHS–GC–MS

Typical TDS–GC–MS and sHS–GC–MS chromatograms of PP are shown in Fig. 1. Emitted substances are mainly methylated alkanes, alkenes, and dialkenes. If TDS is used as sample introduction technique, substances with much higher boiling points can be analyzed than with sHS–GC–MS. This difference is easily understandable if one considers the different mechanisms of TDS and sHS. While in

Table 2
GC temperature gradients.

General studies on emission behavior		Studies on fogging behavior	
Rate (°C/min)	Target temperature (°C)	Rate (°C/min)	Target temperature (°C)
–	40 (held for 8 min)	–	35 (held for 4 min)
2	100	10	280 (held for 20 min)
4	275 (held for 25 min)		

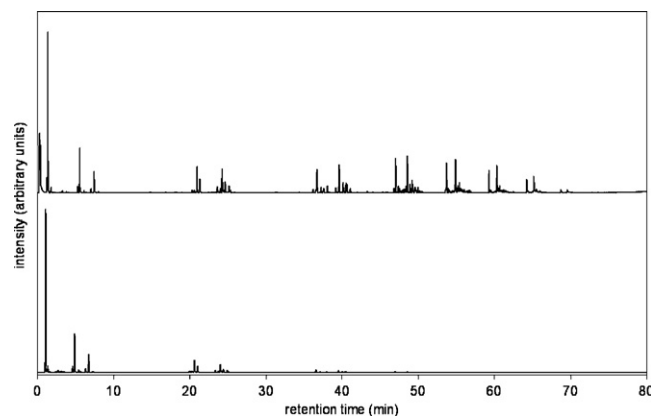


Fig. 1. GC–MS chromatograms obtained by sHS (lower line) or TDS (upper line) for emissions from PP (material 1).

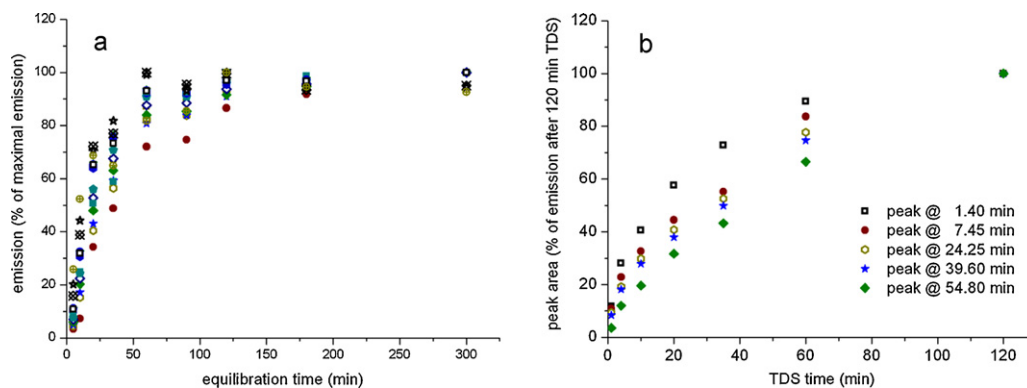


Fig. 2. Influence of (a) equilibration time in sHS and (b) extraction time in TDS on peak areas in GC-MS measurements of emissions from PP (material 1).

sHS a static equilibrium is established, volatile analytes are immediately stripped off by a constant gas stream in TDS. They are removed from the equilibrium, which makes TDS (if carried out long enough) an exhaustive extraction technique. In TDS-GC-MS, the amount per analyte which can be transferred into the chromatographic system is bigger than in sHS-GC-MS. This renders TDS-GC-MS far more sensitive than sHS-GC-MS.

Equilibration time for sHS-GC-MS was examined from 5 to 300 min. The equilibrium established within a similar time window for all detected substances (see Fig. 2a). For further experiments, the sHS incubation time was set to 120 min. In TDS-GC-MS, the extraction time was investigated from 1 to 120 min. Even for the earliest-eluting substances, exhaustive extraction was not reached within this time domain (compare Fig. 2b). For early eluting substances, extraction proceeded faster than for later eluting substances.

Substances with low retention times are highly volatile. Hence, these analytes are extracted faster than those with higher boiling points (i.e. higher retention times), for which the fraction in the gas phase is much lower. For these later-eluting substances, emission increases almost linearly with TDS time demonstrating that – although substances are constantly removed – the concentration on the surface of the pellet is barely decreasing. However, as a compromise between TDS time (and therefore also consumption of liquid nitrogen, as the CIS has to be operated constantly during TDS) and extracted sample amount, further measurements were carried out with a TDS step of 30 min.

If samples with a constant surface-to-mass ratio were measured (PP powder in the case of TDS and PP granulate in sHS-GC-MS), both TDS and sHS-GC-MS gave a good repeatability with a relative standard deviation of under 5%. With increasing retention time the

relative standard deviation tended to increase. This was probably due to integration problems because of decreasing peak size.

3.2. Linearity in TDS-GC-MS – influence of sample geometry

For a PP powder, the emission of the different substances increased linearly with sample amount from 10 to 50 mg sample amount. This behavior was expected for a set of samples with constant surface-to-mass ratio.

However, TDS-GC-MS is so sensitive that a sample amount of a few milligrams PP – corresponding to one single pellet – is sufficient. The surface/mass ratio may differ between pellets. If the diffusion coefficient of analytes within the pellet is sufficiently high, this does not have to be taken into account for quantification. According to literature [20], this applies to equilibration temperatures above the glass-transition temperature (T_g). For PP this condition definitely is fulfilled as its T_g is about -10°C [1]. If diffusion coefficients should nevertheless be quite small, only substances on or very close to the surface of the polymer particles could become volatile and therefore be detected with TDS-GC-MS. In this case, emission would be dependent on sample surface rather than on sample mass.

This aspect was examined with a set of sample bodies with a differing surface-to-mass ratio (with a sample weight from 3.2 mg up to 16.4 mg). When their emission was plotted against sample mass, the emission did not approach zero upon extrapolation to a sample amount of 0 mg (see Fig. 3a). Plotting peak areas against sample surface rather than against sample mass, emission approached zero for a sample amount of 0 mg (see Fig. 3b). Therefore, emission evidently depended on sample surface. With this knowledge, the plot of emission vs. sample mass shown in Fig. 3a could be reinterpreted.

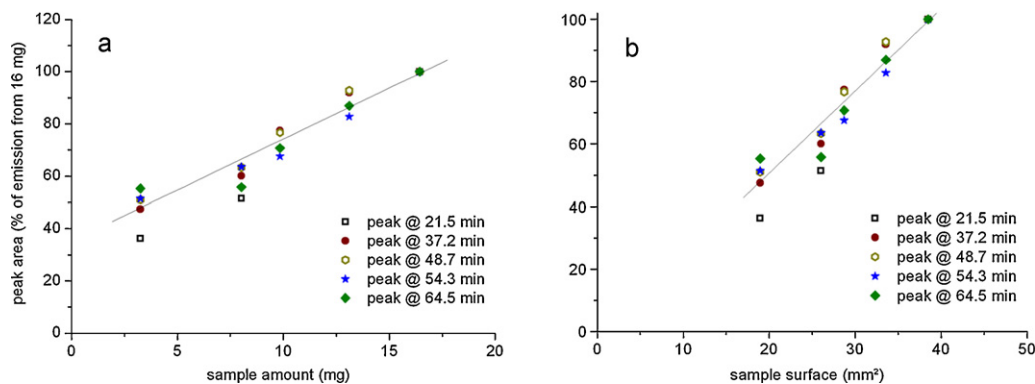


Fig. 3. Dependence of peak areas on (a) sample amount and (b) sample surface for TDS-GC-MS measurements of emissions from cylindrical PP sample bodies with constant diameter but differing height (resulting in different surface-to-mass ratios; material 3).

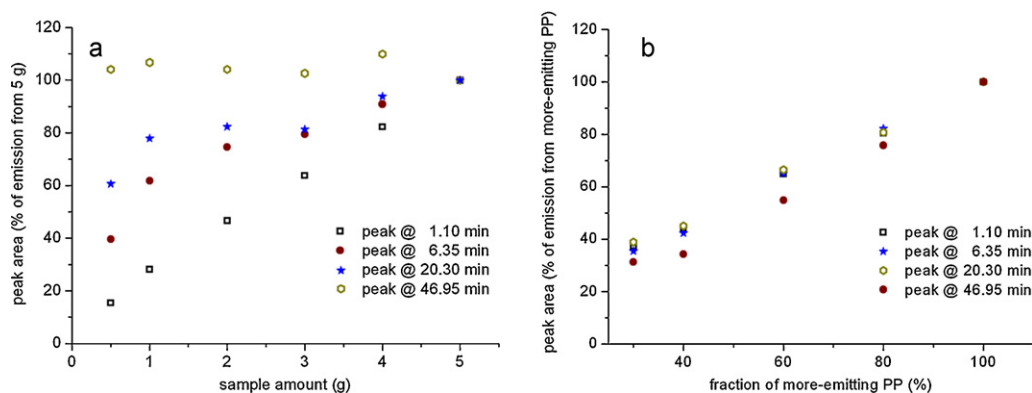


Fig. 4. Dependence of peak area on (a) sample amount at constant concentration of volatiles (material 1) and on (b) concentration of volatiles at constant sample amount obtained by sHS-GC-MS (mixtures of material 1 and material 4).

Due to the geometric shape of the cylindrical sample bodies, the surface area of the bottom and the top was constant, while only the lateral area changed. Hence, the intercept on the y axis in Fig. 3a corresponded to the emission from the bottom and top areas of the sample bodies, while the increase in emission was caused by growing lateral area. For the biggest sample body (with 16.4 mg respectively 38.5 mm² sample surface), the top and bottom area of the cylinder accounted for 36.7% of the total sample surface and in case of the smallest sample body (of 3.2 mg respectively 19.0 mm²) for 74.6%. The intercept on the y-axis when extrapolated to a sample amount of 0 mg (i.e. the emission from the bottom and top area of the cylinder) corresponded to 35.2% respectively 68.7% of the total emission from these sample bodies, which nicely coincided with the expected 36.7% and 74.6%.

3.3. Linearity in sHS-GC-MS – impact of sample amount and concentration of volatiles on peak area

In sHS-GC-MS sample amount was varied from 0.5 until 5 g. Here, a significantly different behavior was observed. Only the peak area of the earliest-eluting substance increased linearly with rising sample amount (see Fig. 4a). If the amount of less-volatile substances (i.e. higher retention times and boiling points) in the vial increased, their concentration in the gas phase did not rise to the same extent.

This observation illustrates that analytes distribute in sHS according to a partitioning system which has to be understood either (analogous to retention in GC) as a liquid–gas distribution [20] if the diffusion coefficients are sufficiently high, or otherwise as an adsorption–desorption distribution. An equilibrium constant K describes the distribution of the analytes in the gas phase (where the concentration of the analyte is c_g) and the sample phase (with the concentration c_s) [20].

$$K = \frac{c_s}{c_g} \quad (1)$$

Furthermore, the phase ratio β (i.e. the ratio of gas-phase volume V_g and sample volume in the vial V_s) characterizes a sHS system [20].

$$\beta = \frac{V_g}{V_s} \quad (2)$$

The relation of c_g , K , and β is given by

$$c_g = \frac{c_0}{K + \beta} \quad (3)$$

where c_0 is the original concentration in the sample [20].

Only very early eluting substances (with very low boiling points) had a small K -value so that they evaporated (nearly) completely.

In this case c_g was directly proportional to the sample amount in the vial and linear curves were obtained. Substances with higher retention times were less present in the gas phase, and β lost its importance. Therefore, c_g became independent from the sample amount in the vial, so that the calibration curve flattened and approached a plateau. In this way, emission in sHS became at a certain (analyte-dependent) sample amount independent of the surface-to-mass ratio of the sample. This was in contrast to observations in TDS (compare Section 3.2).

However, competition in the gas phase could further influence the equilibrium. An increasing amount of highly volatile substances in the vial may push less-volatile substances back into the condensed phase. To investigate whether competition effects were present, a constant amount of PP pellets was spiked with different amounts of n-pentane (up to 8 μ L added to 2 g of PP in a 20 mL vial). n-Pentane did not influence the emission of other substances, which excluded the presence of competition effects.

Furthermore it should be checked, whether linear calibration curves were obtained when the sample amount was kept constant. By mixing a less-emitting PP grade with untreated PP (resulting in a total sample amount of 2 g), different concentrations were achieved. Linear calibration curves were obtained for early-eluting as well as for later eluting analytes (compare Fig. 4b).

3.4. Relevance of emitted substances for the fogging behavior

TDS-GC-MS chromatograms of the aluminum foil with the fogging residue on it and liquid-injection GC-MS chromatograms of the dissolved fogging residue (Fig. 5, lowest line) showed the same substances. This proved that during the solvent delay of the liquid injection no analytes were lost and that all substances contained in the fogging residue could be analyzed with TDS as sample-introduction technique. Substances were identified with the MS library. At early retention times, low-molecular-weight substances with structures related to polyethylene glycol eluted (e.g. (1) diethylene glycol, (2) 2,1,3-dimethyl-2-propanol, 3 triethylene glycol methylether, (4) triethylene glycol, (5) tetraethylene glycol, and (6) pentaethylene glycol in Fig. 5, lowest line). These substances were most likely contaminations from the polyethylene glycol used for temperature control during the fogging test. Peak (7) was identified as di-tert-butylphenol which corresponded to a degradation product of a phenolic antioxidant. Its appearance was already documented in the scientific literature [6,7,21]. For alkanes and alkenes (peaks (8)–(14)) the identification with the MS library was not definite. In fact, peaks eluting at significantly different retention times were assigned to the same substance by the software. However, comparing the chromatogram of the boiling-point calibration mix allowed estimating the size of the emitted alkanes and alkenes.

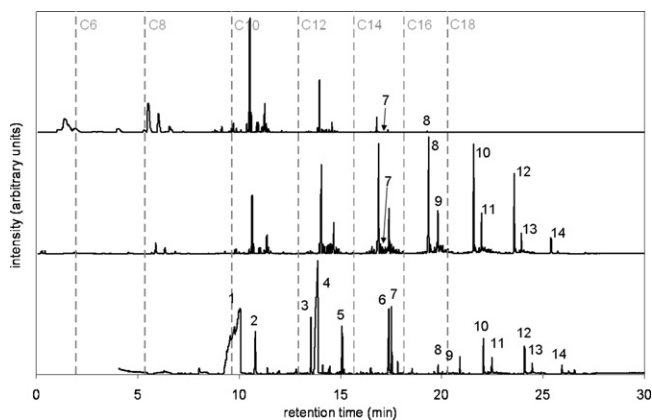


Fig. 5. Comparison of sHS-GC-MS (upper line) and TDS-GC-MS measurements (middle line) of the emissions from PP (material 5) with liquid-injection GC-MS of the fogging residue of the same PP material deposited on aluminium foil (lowest line). For peak identification see Section 3.4.

Only alkanes and alkenes with a chain length higher than C16 were present in the fogging residue. Hydrocarbons with a shorter chain length were obviously not causing any fogging problems.

In sHS-GC-MS as well as in TDS-GC-MS, chromatograms of the emissions from the PP disc used for the fogging test were dominated by methylated alkanes and alkenes (Fig. 5, upper and middle line). Their appearance is already well-documented in the literature (e.g. [5–7]). As can be seen in Fig. 5, the sHS-GC-MS chromatogram of the emissions from the PP disc only showed peaks for compounds up to C17. This implies that sHS-GC-MS could not detect the main substances responsible for the fogging behavior of PP. TDS-GC-MS though allowed the analysis of substances up to the relevant boiling points. It was important to notice that emitted hydrocarbons with a chain length shorter than C16 did not cause any fogging. Therefore, their presence does not prohibit the use of PP for car interior.

4. Conclusions

Both TDS and sHS-GC-MS are powerful techniques for the high-throughput analysis of the emission from PP. Both techniques have a satisfying repeatability with relative standard deviations typically lower than 5%. The equilibrium in sHS was established after 2 h, a reasonable extraction time in TDS was 30 min.

Due to its dynamic character, TDS is able to detect substances up to higher boiling points than sHS-GC-MS. However, in TDS emission depended rather on sample surface than on sample mass. This was somewhat surprising as literature predicted sufficiently high diffusion coefficients for polymers as soon as T_g was exceeded. As TDS was carried out at 120 °C (T_g for PP < 0 °C) this should have definitely been the case. This surface-dependence of emission makes it crucial to control the surface-to-mass ratio for accurate quantification in TDS.

In sHS, c_g increased linearly with sample amount only for the most volatile compounds. Substances with lower vapor pressures preferred the condensed phase with increasing sample amount. This behavior could be attributed to partitioning, while competition effects were excluded. If the sample amount was kept constant but the concentration of volatiles varied, linear calibration curves were obtained for the different analytes. Accurate quantification of the emitted substances is therefore indeed possible if the sample amount is kept constant. Furthermore, the influence of surface on emission can be excluded by increasing the sample amount so that c_g is primarily determined by K rather than by β .

GC-MS of the dissolved residue from the fogging test allowed identifying the main responsible substances. Compounds at early retention times turned out to be contaminations from the liquid used for thermostating during the fogging test. Furthermore, a degradation product of a processing stabilizer significantly contributed to fogging. Alkanes, alkenes and dialkenes were only important if they had a chain length higher than C16. This was already beyond the detectable range of the sHS-GC-MS analysis. The results show that sHS-GC-MS is not a useful technique for judging fogging behavior. TDS-GC-MS chromatograms can be used as a criterion for fogging, however, attention must be paid that only relevant substances (i.e. substances at relevant retention times) are taken into account.

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