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Comparison of Different Analytical Methods for Volatile and Odour-Active Substances in Polyolefins

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Summary: Emissions of volatiles of polymeric materials are an important parameter for materials characterisation, and gain more and more importance either by their odour activity or by other undesired behaviour. Currently, numerous methods are applied for the determination of volatiles, but all of them use gas chromatography (GC) with different detectors. The information gained by flame ionisation detection (FID) is the total emitted volatiles expressed as a sum value, but no further deeper information is provided. Additionally, due to different sample amounts, preparation, way of sampling and GC parameters, results cannot be compared to each other. Also, determination of single sum values by integrating the total area of volatiles is of little help for material development due to the lack of detailed information about chemical composition, and other methods have to be applied. Other compounds of interest such as odour-active ones turn up in only very small amounts and cannot be detected by these methods as an extensive analytical sample preparation is necessary. We compare results obtained by different sample preparation techniques used in industrial standards (VDA 277 and VDA278) to scientific alternatives such as Solid Phase Microextraction (SPME) coupled to GC with mass spectrometry (MS) and Simultaneous Distillation/Extraction SDE coupled to GC-MS to demonstrate capabilities and applicability of each method.

Keywords: gas chromatography (GC); odour-active compounds; polyolefins; solid phase microextraction (SPME); volatiles

Introduction

The use of polymeric materials in application such as packaging, automotive interior and water piping is an important economic factor all around the world nowadays. Polymers which are used for these applications are polyolefins, namely polyethylene (PE) and polypropylene (PP).

Apart from mechanical properties such as Young's modulus, elongation at break, long-term-stability, crack growth resistance and tensile strength these materials have to fulfil, other parameters such as processability and certain chemical behaviour as well. One more and more importance gaining requirement especially for applications in direct contact with foods, beverages or humans is that of the amount of total organic compounds (VOCs) and the odour.

In the Directive 2004/42/CE of the European Parliament "v*olatile organic compound (VOC) means any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa*". Nevertheless, much more detailed definitions are in use depending on the application.

For plastics in the automotive interior numerous standards from the German Car Manufacturer (VDA) are in use. Determi-

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nation of VOCs is facilitated by numerous industrial standards with varying sample amount, way of sampling, way of detection and analysis, but all methods use gas chromatography (GC) for separation of analytes.

According to VDA 278 [1] the ''...*VOC-value is the sum of high to middle volatiles determined as toluene equivalent. With this method substances in the boiling and elution range up to eicosane (C20) can be analysed*''. This area should cover all compounds which can be determined by analysing the automotive interior air.

For the VDA 277 [2] ''... *the emission of organic compounds from non-metallic materials are determined, which are directly and indirectly subject to the reach of the passenger cabin of automotives expressed as total carbon emission amount with acetone as reference*''.

A further differentiation in the VDA 278 is carried out as with this standard both VOCs and ''fogging'' are determined. The so called Fog-value ''... *is the sum of low volatiles eluting from the retention time of n-hexadecane. It is calculated as hexadecane equivalent. Substances in the boiling range of n-alkanes between C16 to C32 are taken into account*.'' These compounds condense easily at room temperature and contribute significantly to fogging on the automotive wind screen.

One special area in the field of volatiles and emissions is that of odour-active compounds. To speak of an odorous compound it has to be (a) volatile at standard pressure in order to reach the upper nasal cavity where odour perception occurs and (b) be present in a concentration which is above its sensory threshold, i.e. that concentration when a given compound is able to stimulate the human odour receptors.

In practise these requirements also have a huge impact on odour analysis as (i) high volatility also bears the problem of evaporation before analysis and (ii) sensory thresholds can sometimes be below detection limits of analytical instrumentation e.g. in the sub-nanogram per litre water range.

In polyolefins, most odour-active compounds derive from oxidation during thermal compounding and processing and include carboxylic acids, aldehydes and ketones.[3–7] Due to the similar mass spectrometry (MS) fragmentation pattern of carbonyls compared to alkanes and alkenes, analysis of odour-active carbonyls in polyolefins can be tricky as the vast majority of volatiles present in PE and PP consists of linear and branched alkanes and alkenes. In practise three ways to solve this analytical problem are thinkable:

(a) the use of a selective detector such as oxygen selective flame ionisation detector (OFID) or atomic emission detector (AED) which for aldehydes do not show the needed sensitivity.
(b) a GC separation which separates interfering substances from the analytes which is not working due to the huge amount of interferences compared to the analytes.
(c) the separation of interfering compounds from the analytes prior to the GC analysis as e.g. by the use of SPE fractionation.

In this work we applied fractionation on solid phase extraction (SPE) to separate interfering non-polar alkanes and alkenes from the mid-polar carbonyls.

In this work we compared results from VDA 277 and 278 measurements as the most used standards to one obtained by the use of Solid Phase Microextraction (SPME) as an solvent-free extraction/sampling device as well as to results from simultaneous steam distillation/extraction (SDE) with subsequent fractionation on silica SPE.

SPME was invented by J. Pawliszyn in 1990[8] as a solvent-free extraction device. In principal, it is a combination of a headspace syringe coated with a purge-and-trap adsorbent, where a coated fused silica fibre working as the adsorbent/absorbent is attached to a septum piercing needle necessary for mechanical support and fibre protection.[9] Different fibre materials are available to enable analyte-specific extraction from a sample. Once the analytes are extracted on the fibre, the SPME device can be directly transferred into the gas chromatography (GC) injector where analytes are thermally desorbed and transferred to the GC column and subsequently analysed. SPME has been applied to the analysis of VOCs and odour-active compounds in various plastics by several authors e.g. ref. [10–13].

SDE is as old as analytic chemistry and is still in use due to its advantages such as extracting target volatiles from a sample matrix. In the case of polymers water is used and therefore no additional non-volatile compounds are extracted from the matrix such as plasticizer. The used apparatus according to Veith[14] was developed for pesticide extraction but is also applied for the analysis of volatiles from polymers.[15] Major drawbacks for SDE such as thermal artefact generation is for polymers no issue as polymer pellets or parts have been exposed to much higher temperatures during processing and compounding. In this work we used SDE in combination with fractionation on silica gel solid phase extraction cartridges to separate non-polar, non-odorous volatiles from mid-polar, odour-active volatiles as previously described in ref. [16].

Materials

One PE-HD and one PP were gift samples from Borealis Polyolefine GmbH. All used solvents were of pesticide purity from LGC Standards, Wesel, Germany. SPE cartridges were obtained from Phenomenex, Aschaffenburg, Germany. All SPME fibres (2cm StableFlex 50/30 μm Divinylbenzene/Carboxen/Polydimethyl siloxane (DVB/CAR/PDMS)) were purchased from Supelco, Vienna, Austria. All used GC gases were of 5.0 purity. The measurements of VDA 277 and VDA 278 were done at Borealis Polyolefine GmbH, Linz, Austria according to the standard. All GC methods used apolar 5% Phenyl methyl siloxane/95% Polydimethyl siloxane capillary columns.

Methods

A comparison of these methods shown in Table 1 is difficult as they use dramatically different sample amounts ranging from 30 mg for the thermodesorption (TD) up to 500 g for the SDE method. For the two headspace (HS) methods the volatile distribution between the sample matrix and the headspace above the sample makes an estimation of sample injected into the GC difficult. For the calculation we assumed a complete transfer of the volatiles into the headspace. For SPME also a concentration of the volatiles by the fibre material has to be considered. The two remaining methods use the whole sample amount, where the SDE-fractionation method injects the sample equivalent of 150 mg per μl due to the high concentration factor as described in.[16] This is necessary to achieve sufficient

Table 1.
Summary of testing conditions for determination of VOCs used in this study.

	VDA 277	VDA 278	SPME	SDE + fractionation
Sampling	HS	TD	HS-SPME	Liquid injection
Injection amount	400 ng/4 μl a)	30 mg	- b)	150 mg/μl
Temperature	120 °C	VOC: 90 °C/Fog:120 °C	50 °C c)	100 °C
Duration of sampling	300 min	VOC: 30 min/Fog: 90 min	20 min	240 min + fractionation
Results	μg C/g sample (ref. Acetone)	μg Emission/g sample (ref. VOC toluene, Fog n-C16) + MS spectra	MS spectra	MS spectra; separation of carbonyls

a)Calculation based on assumption that all volatiles are transferred to the HS;b)cannot be calculated due to concentration factor of SPME fibre;c)this temperature gave best extraction results in pre-tests after 5 min thermostatisation of the sample.

concentrations of the aldehydes detectable by the GC-MS system.

For the measurements of the SPME and SDE-fractionation samples a 5890 HP series II GC with a 5972 quadrupole MS system was used.

For the SPME samples a HP-5MS GC column with 30 m × 0.25 mm ID × 1 μm film thickness was applied, while for the SDE-fractionation samples the same configuration but with 0.25 μm film thickness was used. The oven program for the SPME samples started at −10 °C using liquid nitrogen for the cooling with a hold of 1 min followed by a temperature ramp of 12 °C/min up to 280 °C and held there for 5 min. Injection was done at 270 °C in splitless mode (split valve opened after 2 min) using a special SPME liner with a 0.75 mm inner diameter to obtain sharper peaks (Sigma Aldrich, Vienna, Austria).

For the SDE-fractionation aliquots of 1 μl were injected splitless (split valve opened after 1 min) with an injection port temperature of 250 °C. The oven program started at 35 °C with a hold of 1 min, ramped with 5.3 °C/min to 280 °C and held there for 5 min.

In all GC-MS measurements helium 5.0 was the carrier gas applying a constant flow with a linear velocity of 33 cm/s for both methods. For all measurements the transfer line for the MS was held at 280 °C and the mass spectra were recorded between 20 and 300 m/z with 3 scans per second. Fragmentation was made by electronic impact ionization at 70 eV. Peaks were assigned using the NIST (National Institute of Standards and Technology) GC-MS mass spectra library and by comparison of the spectra and the retention times with pure reference compounds (purity of 97% and more; all obtained from Sigma-Aldrich, Vienna, Austria).

Results and Discussion

In Figure 1a–d chromatograms obtained by VDA 277, VDA 278 and HS-SPME for the two samples are shown.

With VDA 277 only major emission contributors such as alkanes, alkenes and other compounds present in high concentrations are detected. By comparison of the PE and the PP sample differences in the emission pattern can be seen as for the PP the number of peaks is larger than for the PE due to the chemical structure. With VDA 277 it is possible to detect volatiles from methane up to a boiling area of n-hexadecane.

For the VDA 278-1st VOC results the same trend can be observed but due to higher sensitivity of the analysis method the number of compounds is increased. For the PP a typical pattern is observed between two subsequent even-numbered n-alkanes with methyl-branched alkanes eluting shortly after each other. For the VDA 278 VOC measurements volatiles from n-hexane up to the boiling area of n-docosane are detected. For the VDA 278 Fog measurements a similar picture as for the VOC method can be found. Again the typical PP pattern of mono- and dimethyl-branched alkanes and alkenes can be found. This method detects volatiles from n-octane up to the boiling range of n-pentacosane.

With HS-SPME optimised for the extraction of volatiles in an odour-relevant area between n-C6 to n-C16 similar trends can be observed. However, with none of these methods detection of saturated aldehydes is possible e.g. by ion extraction of the relevant m/z 44. Extraction of other, more unique m/z for the saturated aldehydes such as 100 or 110 for the n-octanal was not successful due to their low abundances.

Detection of saturated aldehydes as one major group of odour-active compounds in polyolefins is possible by SDE followed by fractionation on SPE as shown in Figure 2. As on the used GC-column saturated aldehydes co-elute with n-alkanes with two C-atoms more, a method is needed to separate these compounds from each other.

By SDE much more volatiles can be sampled and therefore also the needed concentration of odour-active compounds can be achieved.

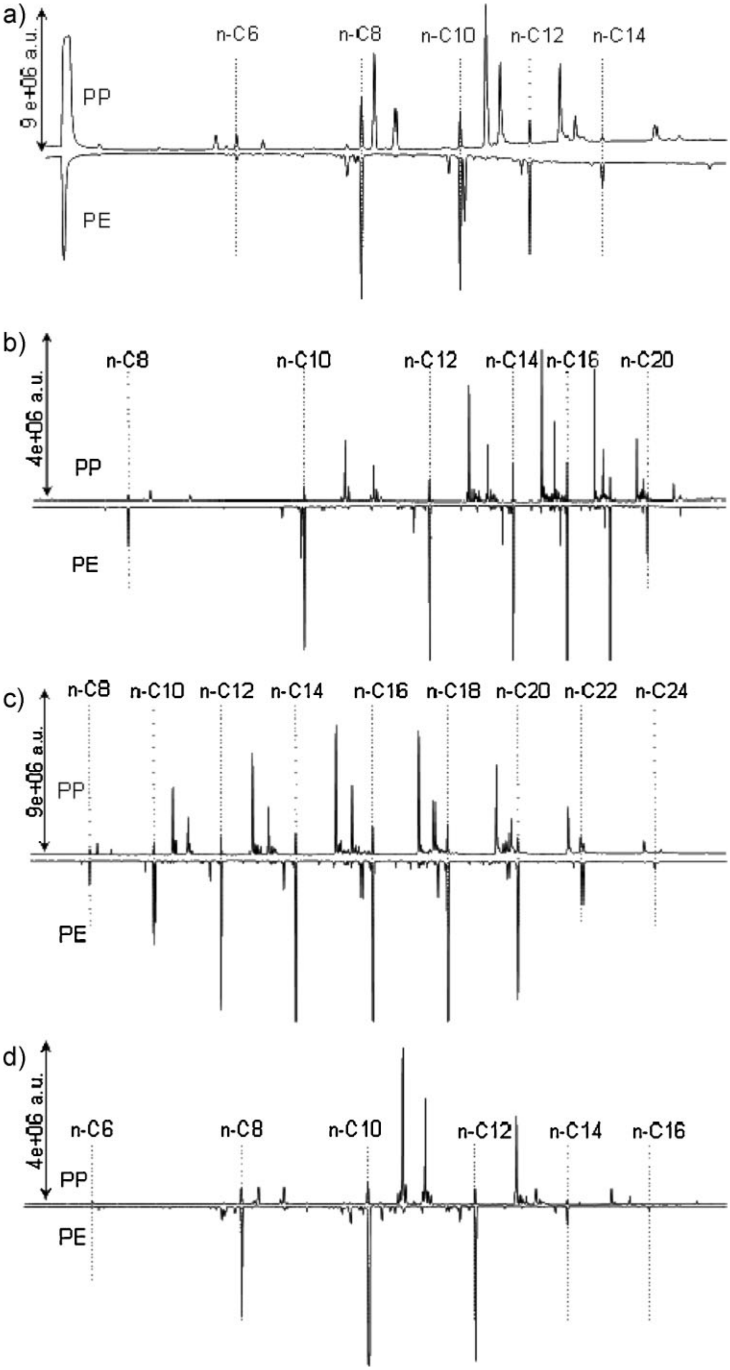

Figure 1.
Chromatograms of the PE (bottom) and PP (top) sample obtained by (a) VDA 277, (b) VDA 278-1st VOC, (c) VDA 278-Fog and (d) HS-SPME.

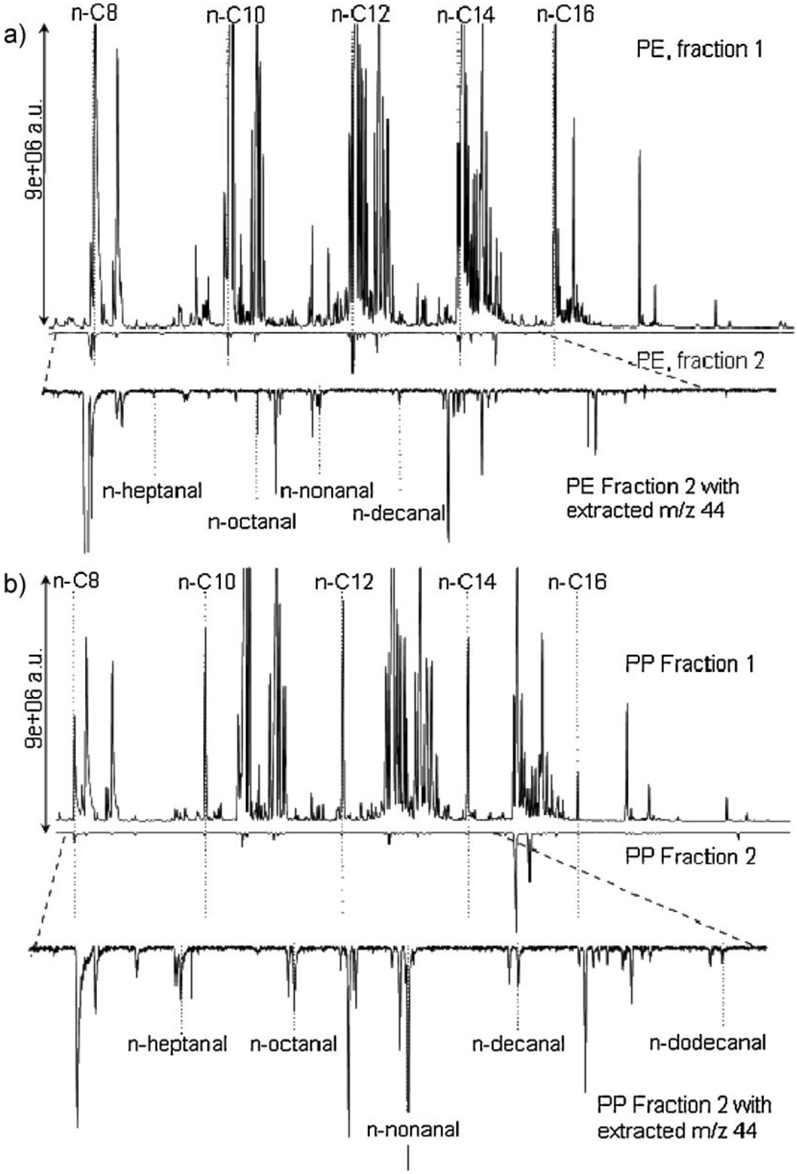

Figure 2.
Chromatograms of PE (a) and PP (b) samples obtained by SDE and subsequent fractionation showing fraction 1 on top (un-polar alkanes and alkenes), fraction 2 in the middle (mid-polar compounds) and extracted m/z 44 from fraction 2 at the bottom (linear aldehydes).

Sensory thresholds of saturated aldehydes in a polyolefin-like matrix were determined in the range of 1.9 to 2.1 μg/kg (data submitted for publication). By comparison of the PE and the PP sample it can be seen that the PP has higher amounts of saturated aldehydes, and while in the PE sample the n-octanal shows the highest concentration, in the PP sample the n-nonanal is present in a two- to three-fold higher amount. In both samples the amounts of the aldehydes are above their sensory thresholds.

Conclusion

Various analytical methods are currently used for determination of volatiles of plastics. In the automotive industry, the standards according to VDA 277 and VDA 278 are the mostly used ones as they are rather simple and do not require special emission chambers.

However, with VDA 277 which uses a headspace technique for sampling analytes, only major volatiles can be detected. Additional, no information about structure is provided due to the use of an FID instead of an MS.

With VDA 278 which uses thermal desorption, much more information can be obtained as the sensitivity is increased, but representativeness of the 30 mg sample amount for analysis (i.e. approx. 3 pellets) can be questioned. Also, the use of a MS provides additional information for the identification of unknown compounds. The combined measurement of VOCs followed by higher boiling substances relevant for fogging-relevant compounds provides a more detailed view of the tested material.

A similar method to the VDA 278 is facilitated by the use of SPME instead of TD. Depending of the analytes of interest, various fibre coatings, temperatures and extraction times can be applied. All above mentioned methods require minimum sample preparation and amount and can be automated for increased sample throughput. So they are excellent tools for quality control measurements in a routine laboratory. Several publications already demonstrated the use of SPME as a sampling tool for VOCs and odour-active compounds in plastics.[10–13] SPME also proves lower detection limits compared to normal headspace methods due to the concentration of the volatiles on the ab-/adsorbing fibre material as shown e.g. by ref. [17].

Nevertheless, for material development e.g. for less-odorous polyolefins these methods face one major problem: they cannot separate the non-odorous alkanes and alkenes from the odour-active compounds such as carbonyls and acids, especially for the polyolefins where the major part of the emitting substances are alkanes and alkenes.

Only a time-consuming and intensive sample preparation using a SDE with subsequent fractionation on SPE is able to deliver information about odour-active compounds and their relation to various process parameters such as polymer technology, additivation or processing.

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