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Journal of Chromatography A, 1052 (2004) 151–159
JOURNAL OF CHROMATOGRAPHY A
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Correlation between emitted and total amount of 2-cyclopentyl-cyclopentanone in polyamide 6.6 allows rapid assessment by HS and HS-SPME under non-equilibrium conditions

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Received 18 June 2004; received in revised form 23 July 2004; accepted 25 August 2004

Abstract

A correlation was found between the emitted and total amount of 2-cyclopentyl-cyclopentanone in polyamide 6.6. The emitted amounts were measured by GC–MS after headspace (HS) or headspace solid-phase microextraction (HS-SPME) and the total content was determined after microwave-assisted extraction (MAE). The correlation was valid also under non-equilibrium conditions, which allows rapid assessment of 2-cyclopentyl-cyclopentanone content in polyamide 6.6 by headspace techniques. The incubation time needed for non-equilibrium headspace analysis could be reduced from 5 h to 45 min if the PA66 granules were milled to powder prior to extraction. However, to reach equilibrium between the analyte in the solid sample and the headspace still required 12 h of incubation at 80 °C. The long incubation time is explained by slow diffusion rate due to the strong hydrogen bonding between analyte and matrix and the relatively high crystallinity of polyamide 6.6. The headspace extraction profile showed several equilibrium-like patterns that are easily mistaken for the real equilibrium.

Keywords: Polyamide; Solid-phase microextraction; Headspace; Volatiles; Polymers; Emission

1. Introduction

The increasing environmental awareness has drawn attention to the influence of low molecular mass compounds emitted from polymeric products on human health and environment. These low molecular mass compounds include additives, residual monomers, degradation-products, side-products formed during polymerisation and others. Low molecular mass compounds in polymers are traditionally extracted and identified by static or dynamic HS–GC [1–6], although also other techniques, e.g. supercritical fluid extraction (SFE) and dissolution of the polymer prior to HS-extraction and GC–MS analysis have been employed [7–9]. Additives and other extractable compounds in polymers are also studied using solvent-based extraction-techniques, e.g. microwave-assisted extraction (MAE) and Soxhlet-extraction. These techniques are thoroughly described in excellent reviews by Eskilsson et al. [10] and Vandenburg et al. [11]. Solvent based extraction techniques all suffer from being rather time-, labour- and solvent-consuming. For example, Soxhlet extraction may take several days to complete and can consume up to 500 ml of solvent in one extraction. In addition, the risks of losing volatile analytes, or masking them by the solvent peak in subsequent chromatographic analysis, are rather high using solvent based extractions and volatiles are thus preferably analysed using solvent-free headspace extraction techniques.

Although headspace analysis is a well-established and rather straightforward technique, there are certain limitations in the quantitative analysis of volatiles in solid matrices by headspace techniques. The use of external or internal cali-

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doi:10.1016/j.chroma.2004.08.110

bration for quantitation of volatiles in solid matrices requires that standards are produced by spiking the matrix with known amount of analyte. Such standards are basically impossible to produce for polymer matrices as volatile compounds are lost at the high temperatures required to melt the polymers. Thus, when headspace techniques and external calibration are applied for analysis of volatiles in polymers, the emitted amounts rather than the absolute amount of volatiles are measured. The theory of headspace extraction, along with different areas of application, has been thoroughly discussed in the literature [12–14]. More recently, solid-phase microextraction has emerged as an effective technique to extract volatile compounds from a variety of matrices, including polymers. HS-SPME has been shown to provide better sensitivity than traditional static HS for extraction of e.g. low molecular mass degradation products in polyethylene [15] and flavour compounds in milk [16]. It has also been applied for quality control of polymeric materials [17], analysis of volatile organics in styrene [18,19] and to study the migration of low molecular mass compounds from poly(vinyl chloride) (PVC) blends [20,21]. The advantages and limitations of headspace techniques in the analysis of volatiles and semi-volatiles in polymers are discussed in a review by Bart [22].

Also the plastic compounding- and processing-industry routinely estimates the content of volatile organic compounds (VOC) in polymeric materials to quality control their products. After production, polymers are devolatilized to remove low molecular mass compounds that otherwise could migrate out of the plastics during their service life [23]. After devolatilization, a standardised HS–GC method is generally used to estimate the remaining volatile content. In a common standard method, plastic granules or pieces are thermostated for 5 h at 120 °C prior to sampling and analysis. The total volatile organic content (TVOC) is estimated by comparing the sum of all peak areas in the chromatogram to a calibration with acetone as a standard and the TVOC is reported in μg C/g. This measurement does not give the absolute content, as it is performed under non-equilibrium conditions, and no compensation is made for sample volume, matrix effects or differences in volatility between analytes and the used standard. However, the obtained values are associated with threshold values that restrict the use of the materials in certain applications. For use of polymeric materials in, e.g. vehicle interiors some major vehicle producers accept emissions of 50 μg C/g, although in the near future the restrictions will be lowered to 30 μg C/g.

We have earlier by HS-SPME–GC–MS identified 2-cyclopentyl-cyclopentanone as one of the major volatile compounds in polyamide 6.6 [24]. The content of 2-cyclopentyl-cyclopentanone was higher in virgin than in recycled polyamide 6.6 and the content was reduced upon repeated processing. The content of cyclopentanone and other low molecular mass cyclopentanones, e.g. 2-pentyl-cyclopentanone and 2-ethyl-cyclopentanone were found to increase during processing, indicating that 2-cyclopentyl-cyclopentanone is formed already during the polymerisation of polyamide 6.6 and degrades then into lower molecular mass cyclopentanones when polyamide 6.6 is processed [25]. 2-Cyclopentyl-cyclopentanone has also been identified after thermal degradation of polyamide 6.6 in inert atmosphere at 200 °C [26], 305 °C [27] and 600–800 °C [28]. These studies do not, however, mention if the low molecular mass compounds were analysed prior to degradation, which means that the 2-cyclopentyl-cyclopentanone may have been present in the materials already before the thermal aging. Allen and Harrison found that 2-cyclopentyl-cyclopentanone was one of the most abundant compounds in the 2-propanol extracts of polyamide 6.6 films and chips [29]. SotoValdez et al. [30] used a dynamic headspace system to quantify the amount of volatiles in polyamide 6.6 “microwave and roasting bags” (MBR). They found that 17.4 mg 2-cyclopentyl-cyclopentanone was emitted from each bag during heating for 2 h at 200 °C under nitrogen, corresponding to 3.6 mg/g polyamide 6.6. Due to the presumably exhaustive extraction by the dynamic headspace extraction, this was considered as the total amount of 2-cyclopentyl-cyclopentanone in the bags. In a following study, Gramshaw and SotoValdez [31] measured the amount 2-cyclopentyl-cyclopentanone in chicken after cooking using MBR. The study showed that 2.9 μg 2-cyclopentyl-cyclopentanone/g polyamide 6.6 MBR migrated into chicken during cooking. This corresponds to only 0.08% of the amount initially present in the MBR. This was recognised as a rather low amount as generally 0.3–3% of the low molecular mass compounds initially present in ovenable materials migrate into heated foods during cooking.

The quantitative determination of volatiles in polymers demands time- and/or solvent-consuming extractions. Qualitative analysis of volatiles emitted from polymers can, however, be performed using solvent-free headspace techniques. In the present study, HS-SPME–GC–MS and traditional HS–GC–MS were applied to determine the emission of 2-cyclopentyl-cyclopentanone from PA66. The emitted amounts measured by HS–GC–MS and HS-SPME–GC–MS were compared to the 2-cyclopentyl-cyclopentanone content in the polyamide samples determined by MAE. The aim was to investigate if a correlation could be found between the emitted and total amounts, which would allow rapid assessment of 2-cyclopentyl-cyclopentanone content in different polyamide 6.6 samples by headspace techniques.

2. Experimental

2.1. Materials

Five different grades of polyamide 6.6 were used: unstabilised but lubricated Zytel 101L from DuPont (Stockholm, Sweden), unstabilised laboratory grade polyamide from Sigma-Aldrich (Aldrich Chemicals, Milwaukee, WI, USA), unstabilised industrial grade polyamide Domamid 33ABH from Domo (Leuna, Germany), recovered in-plant polyamide waste collected and grinded for reuse in new

nylon compounds and, lastly, a commercial 30 wt.% glass-fibre reinforced grade containing 47% of the recovered waste and 20% of the industrial grade polyamide. The commercial compound also contained some additives. The five materials will hereafter be designated Zytel, Aldrich, Base, Recovered and Compound, respectively. The Base, Recovered and Compound materials were generously supplied by Polykemi (Ystad, Sweden), a major Swedish producer of plastic compounds. The polyamide 6.6 granules were milled into a fine powder using a Retsch (Hann, Germany) ZM1 centrifugal mill with a screen of 1.0 mm diameter holes. Prior to milling, the polymer granules were immersed in liquid nitrogen for 10 min to prevent melting of polymer and loss of analyte due to the heat evolved during milling. Additional liquid nitrogen was dripped into the mill during milling.

2.2. SPME-fibres and chemicals

The capacities of five different SPME fibres to extract 2-cyclopentyl-cyclopentanone were evaluated: 85 μm StableFlex Carboxen/Polydimethylsiloxane (CAR/PDMS), 70 μm StableFlex Carbowax/Divinylbenzene, 85 μm Polyacrylate (PA), 100 μm Polydimethylsiloxane (PDMS) and 65 μm StableFlex Polydimethylsiloxane/Divinylbenzene (PDMS/DVB). All fibres were purchased from Supelco (Bellafonte, PA, USA). Quantitation was done against calibration curves made of 2-cyclopentyl-cyclopentanone (>99%) from Lancaster (Lancashire, UK) in methanol (≥99.9%) from Fluka (Buchs, Germany). In microwave-assisted extractions cyclohexanone (≥99.9%) from PolyScience (Niles, IL, USA) was used as internal standard and the previously mentioned methanol and chloroform (>99.8%) from LabScan Ltd. (Dublin, Ireland) as solvents.

2.3. Gas chromatography–mass spectrometry (GC–MS)

Chromatographic separation and mass spectrometric detection was performed using a ThermoFinnigan (San José, CA, USA) GCQ GC–MS system. A Gerstel (Mülheim and der Ruhr, Germany) MPS2 autosampler was used for HS-sampling, HS-SPME and injection of extracts from MAE. The GC was equipped with a 30 m WCOT Varian (Lake Forest, CA, USA) CP-Sil-8 column with 0.25 mm inner diameter and a 0.25 μm thick stationary phase. The GC was programmed to start at 40 °C, hold the temperature for 1 min and then increase the temperature by 10 °C/min to 180 °C. This temperature was held for 1 min and lastly all high boiling compounds were eluted by heating the column to 270 °C at 30 °C/min and keeping it at 270 °C for 15 min. Helium of 99.9999% purity from AGA (Stockholm, Sweden) was used as carrier gas at a constant average linear velocity of 40 cm/s maintained by the electronic pressure control (EPC) of the GC. Temperature of the injector was 250 °C. The injector operated in splitless mode when SPME and MAE samples were analysed. A split ratio of 1:100 (118 ml/min split flow) was applied for HS-extractions. A narrow bore liner with 2 mm inner diameter was used for SPME and HS-samples whereas a 4 mm inner diameter liner was used for liquid injections from MAE samples. The temperatures of the transfer line and ion source were 275 °C and 180 °C, respectively. The mass spectrometer scanned in the range of 35–400 *m/z* with a scan time of 0.43 s. Data was evaluated using the Xcalibur 1.2 software. In extractions from the Compound 2-cyclopentyl-cyclopentanone co-eluted with another product and quantitation was made from reconstructed ion chromatograms (RIC) plotting the 2-cyclopentyl-cyclopentanone base peak of m/z = 84. For all the other materials the peak areas were calculated by integrating the total ion current (TIC).

2.4. Extraction of polyamide samples

For both HS and HS-SPME extractions 20 ml clear glass vials (Supelco) sealed with magnetic silicone/PTFE crimp caps (Varian) were used. Samples were equilibrated and extracted in the autosampler agitator with the agitator working in cycles of 5 s with agitation at 500 rpm followed by 2 s without agitation.

2.4.1. Headspace (HS)

2.000 g of granules and 1.000 g of powder were equilibrated at 120 °C or 80 °C in closed vials. After the equilibrium time 500 μl of the gaseous phase was removed from the headspace above the polyamide 6.6 by a 2.5 ml gastight syringe heated to the same temperature as the sample and then injected into the GC–MS. The syringe was flushed three times with sample prior to injection and cleaned between extractions by flushing it for 20 s with helium. The five calibration solutions of 2-cyclopentyl-cyclopentanone in methanol used for preparation of calibration curves were of concentrations 0.1, 0.5, 1.0, 5.0 and 10.0 μg/μl, respectively. One microliter of each calibration solution was extracted under conditions identical to the extraction of samples to construct the calibration-curve. No compensation was made for the differences in headspace volume between vials containing samples and standard-solutions. Standards were analysed three times and samples four times. The headspace sampling was performed in accordance with a procedure commonly employed by the plastics compounding industry for estimation of TVOC in polymers.

2.4.2. Headspace-solid phase microextraction (HS-SPME)

10 to 100 mg powdered samples were used for HS-SPME. The amounts used for the different samples were adjusted to give approximately equal peak areas, within the linear range of the SPME-fibre, for all samples. The fibres were exposed to the headspace approximately 6 cm above the polyamide 6.6 sample. This rather large distance between the sample and the SPME fibre was used to prevent fibre breakage due to the agitation of the sample vial during extraction. After completed extraction the SPME fibre was allowed to desorb the extracted analytes for 5 min in the injector of the GC–MS.

Blanks were run between some of the samples and no carry-over between samples could be observed. The amount of 2-cyclopentyl-cyclopentanone in the samples was determined by external calibration from solutions of 0.96, 9.6, 28.8, 48.0, 72.0 and 96.0 ng 2-cyclopentyl-cyclopentanone/μl MeOH. To construct the calibration-curve 1 ul of each standard solution was extracted under conditions identical to the conditions used to extract the samples. As the sample volumes were only 0.1–1.0% of the vial volume no compensation for reduced headspace volume using, e.g. inert glass beads was made. All standards were analysed three times and all the samples were analysed four times.

2.4.3. Microwave-assisted extraction (MAE)

A MES 1000 microwave extraction system from CEM (Matthews, NC, USA) was used to extract 2-cyclopentyl-cyclopentanone from the different polyamide 6.6 samples. 1.000 g of powdered polyamide 6.6 was placed in a lined extraction vessel and 10 ml MeOH containing 5 μg cyclohexanone was added to the vessel. Cyclohexanone was used as internal standard to compensate for possible losses of analyte during extraction and handling. For each material four samples were extracted simultaneously. The samples were heated from ambient temperature to 90 °C in 10 min. After completed extraction the samples were allowed to cool to room temperature and the extract was then filtered through 0.45 μm Cameo PTFE-filters (GE Waters Technologies, Trevose, PA, USA) into 2 ml screw top vials (Supelco). Pre-concentration was not necessary and the samples were analysed directly by GC–MS in the splitless mode without further preparation. Quantitation was done by constructing calibration curves at seven concentration levels: 1.01, 10.1, 101.0, 505.0, 1010.0, 1520.0 and 2020.0 pg/μl. Each standard solution contained 0.5 ng cyclohexanone per microliter and was analysed in triplicate.

3. Results and discussion

3.1. Optimisation of headspace extraction variables

3.1.1. SPME fibre selection

Five different SPME-fibres were evaluated for the extraction of 2-cyclopentyl-cyclopentanone. Fig. 1 shows the relative peak areas after triplicate extractions from 100 ng 2-cyclopentyl-cyclopentanone for each type of fibre. The extraction time was 30 min at 80 °C. The CAR/PDMS-fibre showed the highest recovery, but it also showed the lowest repeatability, with a relative standard deviation (R.S.D.) of 18%. In addition, the 2-cyclopentyl-cyclopentanone peak showed excessive tailing when extracted with the CAR/PDMS-fibre. The peak symmetry could not be improved by increasing the injector temperature as tailing was still observed at injector temperatures of 270 °C and 300 °C. For the following extractions it was decided to use the PDMS/DVB fibre, which showed excellent R.S.D. of 3% and

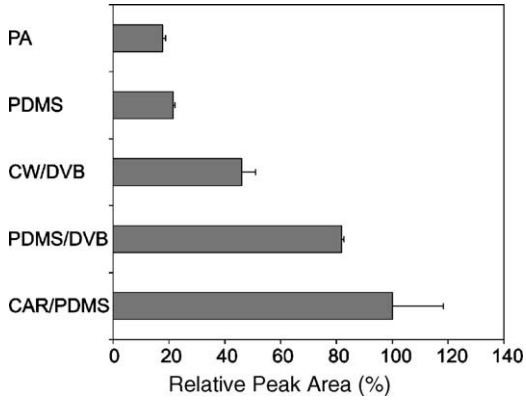

Fig. 1. Relative peak areas and standard deviations after triplicate extractions from 100 ng 2-cyclopentyl-cyclopentanone. Extraction time was 30 min at 80 °C. PA: polyacrylate; PDMS: polydimethylsiloxane; CW/DVB: carbowax/divinylbenzene; PDMS/DVB: polydimethylsiloxane/divinylbenzene; CAR/PDMS: carboxen/polydimethylsiloxane.

the second best recovery, i.e. 80% of the CAR/PDMS recovery. The PDMS/DVB fibre also gave good peak symmetry.

3.1.2. The equilibrium time for 2-cyclopentyl-cyclopentanone in the absence of polyamide matrix

The equilibrium time between the headspace and the fibre coating for free 2-cyclopentyl-cyclopentanone, i.e. 2-cyclopentyl-cyclopentanone in the absence of a polymer matrix, was studied by extraction from 10 ng of 2-cyclopentyl-cyclopentanone for 10–60 min at 80 °C. The extraction profile is shown in Fig. 2 and it clearly shows that when extracting 2-cyclopentyl-cyclopentanone in the absence of sample matrix at 80 °C, optimal recovery is found after 20 min of extraction. It should, however, be noticed that the recovery decreases upon prolonged heating. Headspace equilibrium is usually established in less than 30 min and the drop in recovery on prolonged heating is probably due to warming up of the SPME fibre, which is known to reduce the amount of analyte extracted. The standard deviation is rather large at

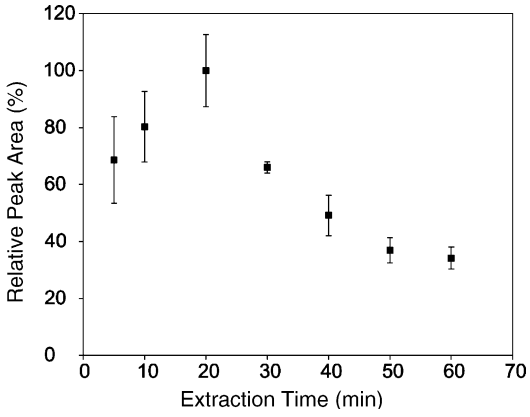

Fig. 2. Extraction profile after triplicate extractions of 10 ng 2-cyclopentyl-cyclopentanone in 1 μl methanol. A PDMS/DVB fibre was used for the extractions and extraction time was varied from 5 to 60 min at 80 °C.

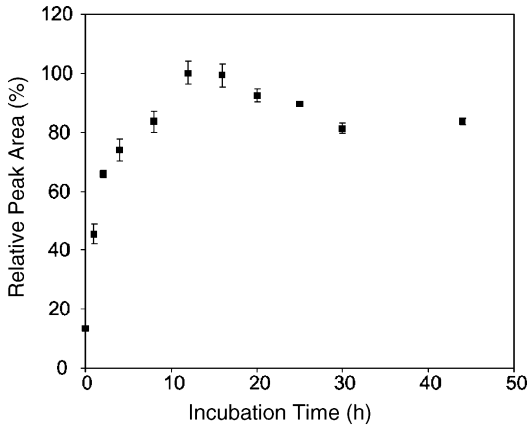

Fig. 3. Recovery profile after extraction from 25 mg powdered Zytel. Extraction time was 30 min at 80 °C. The samples were incubated at 80 °C for 0–44 h prior to extraction.

the optimal recovery but decreases at extraction times over 40 min. The large standard deviation is explained by changing fibre temperature due to warming up of the fibre during the first 40 min of extraction.

3.1.3. The equilibrium time for 2-cyclopentyl-cyclopentanone in powdered samples

The time required for reaching equilibrium between the analyte in the samples and in the headspace was studied by incubating 25 mg of powdered Zytel at 80 °C for 0–44 h followed by extraction for 30 min. The extraction profile is shown in Fig. 3 and it clearly shows that equilibrium is found after 12 h of incubation at 80 °C. The long time required for reaching the equilibrium is most likely caused by strong hydrogen bonding between the analyte and the polymer matrix. The high degree of crystallinity (approximately 50%) of polyamide 6.6 may also contribute to the slow diffusion rate. This long equilibrium time reflects the need for rapid methods to estimate the 2-cyclopentyl-cyclopentanone content under non-equilibrium conditions.

In addition to the real equilibrium reached after 12 h of incubation, two equilibrium-like states were observed during the first 60 min of extraction. The extraction profiles of 2-cyclopentyl-cyclopentanone from powdered Zytel during 60 min of extraction at 50 °C and 80 °C are shown in Fig. 4a. At both temperatures the recovery increased dramatically after 30–40 min of extraction. When extracting at 80 °C, the extraction profile flattens out after 40 min and the recovery does not vary with extraction time, i.e. the extraction seems to have reached equilibrium. Fig. 4b shows the extraction profile at the two temperatures within the first 30 min of extraction. As can be seen from the figure, equilibrium-like conditions were reached also after 20 min at 80 °C and after 30 min at 50 °C. It is proposed that the equilibrium-like shape of the extraction profile, found during the first 30 min of extraction, represents the equilibrium between the readily available "free" 2-cyclopentyl-cyclopentanone on the surface of the polyamide 6.6 powder, the headspace and the SPME-

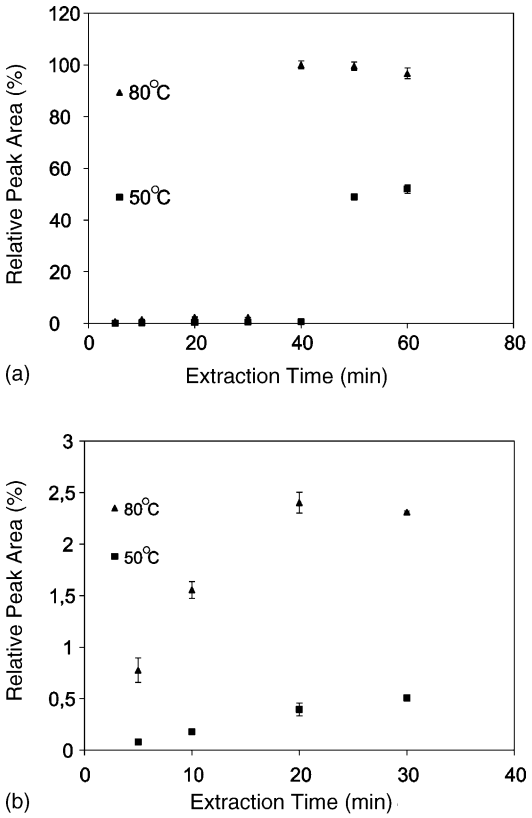

Fig. 4. Extraction profile after triplicate extractions from 1.00 g powdered Zytel at 80 °C and 50 °C using a PDMS/DVB fibre. Extraction times varied from (a) 5 to 60 min and (b) 5 to 30 min.

fibre. The second equilibrium-like state probably represents equilibrium for the 2-cyclopentyl-cyclopentanone originally present inside the polyamide 6.6 powder, at a close distance to the outer surface. For the following studies 45 min at 80 °C was chosen as the optimum extraction time as the recovery then was adequate and the extractions showed good reproducibility. In addition, after 45 min the temperature of the SPME fibre was stabilised, which gave better reproducibility.

Figs. 2 and 4a and b show that the recovery decreases if the extraction time is extended from the optimum extraction time. The drop in recovery is not as large when extracting from a polymer matrix as when extracting free 2-cyclopentyl-cyclopentanone, i.e. the relative drop in recovery is larger in Fig. 2 than in Fig. 4a and b. This is explained by the continuous migration of analyte from the sample matrix during the extraction. If true equilibrium has not been established, additional analyte will migrate from the sample during extraction, thus counteracting the drop in extraction efficiency due to heating of the SPME fibre, i.e. the solid sample acts as a reservoir of analyte, which continues to be released from the matrix. The results reflect the difficulties in finding true equilibrium conditions for the headspace analysis of volatiles in solid sample matrices. The equilibrium-like shape of the recovery profile may lead to erroneous selection of extraction conditions, which in turn gives erroneous quantitation.

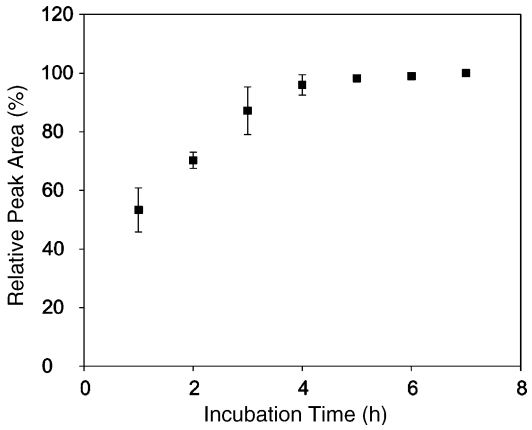

Fig. 5. Relative peak areas after triplicate extractions for 20 min at 80 °C from 1.000 g Zytel granules using a PDMS/DVB fibre. The samples were incubated between 1 and 7 h at 80 °C prior to extraction.

3.1.4. Extraction of 2-cyclopentyl-cyclopentanone from the granules

Fig. 5 shows the relative peak areas of 2-cyclopentyl-cyclopentanone after solid-phase microextraction for 20 min at 80 °C of 1.00 g Zytel granules that were incubated for 1–7 h at 80 °C prior to extraction. The figure clearly shows that after 5 h of incubation at 80 °C, equilibrium-like conditions are established between the 2-cyclopentyl-cyclopentanone in the solid and gaseous phase. A small increase in recovery is, however, noticed upon prolonged heating, confirming that true equilibrium is not established. The sample size strongly affects the time required to reach conditions where the recovery varies only little with time, which is desirable for reproducible extractions. As expected, milling the granules into powder considerably shortens the extraction time. For powdered polyamide 6.6 it is enough to extract for 45 min, whereas polyamide 6.6 granules required 5 h of incubation at 80 °C.

3.1.5. Comparison of HS and HS-SPME performance

Table 1 shows that the calibration curve correlation coefficients obtained at 120 °C were acceptable for both HS and HS-SPME with values of 0.995 or higher. However, when extraction was performed at 80 °C the correlation coefficients were not as good: 0.993 for HS and 0.986 for HS-SPME. The better correlation coefficients at higher temperature speak in the favour of extracting at 120 °C, however, at this temperature the rubber caps of the vials degraded and already after 20 min of extraction at 120 °C the resulting chromatograms consisted mainly of very large peaks representing siloxane compounds formed as a result of silicone rubber degradation. HS-extractions showed a linear relationship over a larger range of analyte concentration than HS-SPME extractions, which in the present study was linear only up to approximately 112 ng. The limit of quantitation (LOQ) was estimated by extrapolating the linear regression lines of signal-to-noise ratios versus concentration for the calibration curves used for quantitation to S/N = 10. The LOQ was considerably higher

Table 1
Measured amount of 2-cyclopentyl-cyclopentanone in the five different polyamide 6.6 samples at 80 °C and 120 °C using HS-SPME and traditional HS-extraction

$n = 4$	HS						HS-SPME			
	Granules		Powder				Powder			
	120 °C, 5 h ($r^2 = 1.000$)		120 °C, 45 min ($r^2 = 0.995$)		80 °C, 45 min ($r^2 = 0.993$)		120 °C, 45 min ($r^2 = 0.995$)		80 °C, 45 min ($r^2 = 0.986$)	
	Mean (ng/g)	STD (R.S.D.)	Mean (ng/g)	STD (R.S.D.)	Mean (ng/g)	STD (R.S.D.)	Mean (ng/g)	STD (R.S.D.)	Mean (ng/g)	STD (R.S.D.)
Zytel	343.6	13.0 (3.8)	911.2	22.6 (2.5)	136.9	4.5 (3.3)	5144.4	255.4 (5.0)	606.6	86.7 (14.3)
Aldrich	293.2	11.3 (3.8)	922.1	33.2 (3.6)	180.8	25.3 (14.0)	2998.2	457.8 (15.3)	570.0	80.0 (14.0)
Base	6.2	1.4 (23.2)	55.9	17.5 (31.3)	20.8	8.8 (42.2)	250.7	25.9 (10.3)	44.7	0.6 (1.4)
Recovered	154.0	7.4 (4.8)	522.7	23.3 (4.5)	65.4	8.3 (12.7)	923.4	42.7 (4.6)	219.2	32.0 (14.6)
Compound	56.0	2.3 (4.1)	161.3	28.0 (17.3)	15.6	0.5 (3.3)	300.7	33.7 (11.2)	92.3	8.2 (8.9)

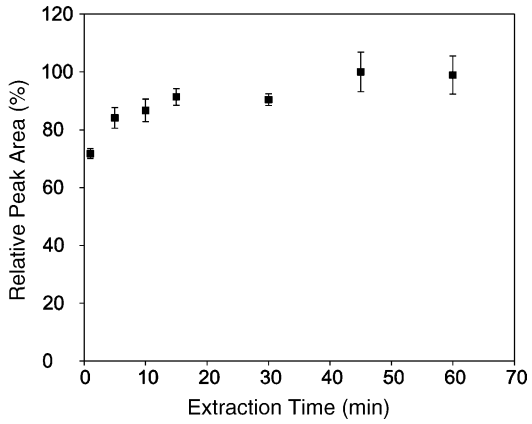

Fig. 6. Relative peak areas after MAE of 1.000 g Base material in 10 ml methanol. The lined extraction vessel was heated to 90 °C in 10 min and then maintained for 45 min to complete the extraction.

for HS-extractions, 3.91 ng at 80 °C (r^2 = 0.993) and 3.75 ng at 120 °C (r^2 = 0.871), than for HS-SPME which could quantify at levels as low as 0.16 ng at 80 °C (r^2 = 0.958) and 0.81 ng at 120 °C (r^2 = 0.978). HS generally showed better precision, with most R.S.D.s less than 5%, while R.S.D.s for HS-SPME were generally around 10%.

3.2. Optimisation of microwave-assisted extraction (MAE)

The microwave-assisted extraction was optimised with respect to the type of solvent, extraction temperature, extraction time and sample-to-solvent ratio. Chloroform and methanol were evaluated as extracting solvents. After extraction at 90 °C for 30 min highest recovery was achieved using methanol as a solvent. This is attributed to the better compatibility between polar polyamide 6.6 and polar methanol compared to polar polyamide 6.6 and non-polar chloroform. Good compatibility gives good swelling of the polyamide 6.6 matrix and more effective analyte extraction. The difference between the two solvents was, however, not very large and the amount extracted using chloroform as a solvent was approximately 90% of the amount extracted using methanol. When methanol was used as the extraction solvent, the maximum extraction temperature was 90 °C due to fusing of polyamide 6.6 at 100 °C.

The effect of extraction time on the recovery of 2-cyclopentyl-cyclopentanone was studied by extracting 1.000 g Base material in 10 ml methanol for different times varying from 5 to 60 min. The resulting extraction profile is shown in Fig. 6. The figure shows that 2-cyclopentyl-cyclopentanone rather rapidly migrates to methanol. The maximum recovery was achieved first after 45 min, but already after 1 min of extraction approximately 75% of the maximum recovery is achieved. This means that most of the 2-cyclopentyl-cyclopentanone in polyamide 6.6 migrates into the extraction solvent already during heating of the extraction vessel. A tendency to equilibrium was found after 15 min of extraction but higher recovery was found after 30 min of additional heating, i.e. after 45 min. To ensure that the high extraction temperature and long extraction time does not cause degradation of 2-cyclopentyl-cyclopentanone, 2-cyclopentyl-cyclopentanone was heated in methanol at 90 °C for 45 min. GC–MS analysis showed that the amount of 2-cyclopentyl-cyclopentanone in the solution was the same before and after the heating and hence no analyte degradation took place. In addition, no 2-cyclopentyl-cyclopentanone degradation products could be observed in the solution after the heating. Some samples were also extracted with 5 and 15 ml of methanol. Changing the sample-to-solvent volume did not, however, affect the extracted amount.

3.3. The amount of 2-cyclopentyl-cyclopentanone emitted from the different polyamide samples

Table 1 shows the amount of 2-cyclopentyl-cyclopentanone extracted from the five polyamide 6.6 samples using traditional HS extraction and HS-SPME at 80 °C and 120 °C. Under non-equilibrium conditions, sample size and extraction temperature strongly affected the amount of 2-cyclopentyl-cyclopentanone emitted from polyamide 6.6. Due to non-equilibrium conditions during the extraction the measured amount also depended on the used extraction method: the amount measured after HS-SPME was for all the samples two to five times higher than the amount measured after HS. This is explained by the differences in sampling time between the two methods. Traditional HS sampling removes a selected portion of the gas-phase in a few seconds. HS-SPME sampling, however, requires longer time, in the present study 45 min, as the gaseous analyte also has to equilibrate with the SPME fibre coating. Hence, during HS-SPME sampling there is time for the system to compensate for the amount of analyte removed by the SPME-fibre by releasing more analyte into the gas-phase, which gives larger amounts measured by HS-SPME than with traditional HS. This also explains the higher sensitivity of SPME compared to HS under equilibrium conditions.

The temperature obviously affects the amount of 2-cyclopentyl-cyclopentanone emitted from polyamide 6.6. Both HS and HS-SPME showed that the amounts emitted at 120 °C are approximately 3–10 times higher than the amounts emitted at 80 °C. This is a natural consequence of increased temperature and is described by Henry's law. The amount of 2-cyclopentyl-cyclopentanone that had migrated from the granules after 5 h of incubation at 120 °C was lower than the amount that had migrated from the powder after only 45 min of incubation at 120 °C. This shows the large effect of sample size on the migration rate and equilibrium time. It also confirms that true equilibrium between polyamide 6.6 granules and their headspace had not been reached after 5 h of incubation at 120 °C. This is also seen from the extraction profile presented in Fig. 5 as slow increase in the amount of 2-cyclopentyl-cyclopentanone is observed even after 5 h of incubation. The analyte, thus, continues to migrate

from the matrix but at a much lower rate. The diffusion of 2-cyclopentyl-cyclopentanone seems to proceed in two different stages with the second stage being considerably slower than the first. The analysis time can, however, be considerably shortened if the polyamide 6.6 granules are milled to powder prior to testing.

2-Cyclopentyl-cyclopentanone was the single most abundant compound in the chromatograms after HS and SPME extractions from the Aldrich, Zytel and Base materials and represented more than 95% of the total peak area. In the extractions from Compound, however, 2,4-di-*tert*-butylphenol was the most abundant compound and its peak area was more than 125 times larger than the 2-cyclopentyl-cyclopentanone peak area. This compound is most likely formed due to degradation of the additive tris(2,4-di-*tert*-butylphenyl)phosphite which is known under trade names like Irgafos 168, Nauguard 524 and Ultranox 626. In the extractions from the Recovered material large amount of compounds with typical alkane and alkene mass spectra were found. In these chromatograms the 2-cyclopentyl-cyclopentanone peak area represented less than 10% of the total peak area. The presence of aliphatic compounds indicates that the Recovered polyamide 6.6 may contain lubricants or be contaminated by polyolefins. After MAE extractions the cyclic polyamide 6.6 repeating unit with molecular mass 226 g/mol was the most abundant compound in all the chromatograms. However, in the MAE extracts of the Compound 2,4-di-*tert*-butylphenol was also detected.

The Base material emitted very low amounts of 2-cyclopentyl-cyclopentanone. As the Compound material consisted of 47% Recovered material, 20% Base material, 30% glass-fibres and 3% additives, this means that the amount of 2-cyclopentyl-cyclopentanone emitted from the compound should be approximately half of the amount emitted from the Recovered material. The measured amounts are, however, only 25–40% of the amount emitted from the Recovered material. This is explained by degradation of 2-cyclopentyl-cyclopentanone during compounding and is in agreement with our earlier results that showed degradation of 2-cyclopentyl-cyclopentanone during repeated processing [25].

3.4. Correlation between headspace measurements and the amounts measured by MAE

Multiple headspace solid phase microextraction (MHS-SPME) showed that the recovery of 2-cyclopentyl-cyclopentanone by the developed MAE method was approximately 80% [32]. The amounts measured after MAE were, however, in the present study used as an approximation of the total content. Table 2 shows the amount of 2-cyclopentyl-cyclopentanone in the five polyamide samples determined after MAE. These MAE results are in good agreement with the emitted amounts measured by the two headspace techniques, i.e. the amount of 2-cyclopentyl-cyclopentanone extracted from Zytel and Aldrich was 5–10 times higher than the amount extracted from the other samples. Furthermore, the lowest amount was extracted from the Base material and less than half of the amount extracted from the Recovered material was extracted from the Compound.

Table 2
Amount 2-cyclopentyl-cyclopentanone in the five polyamide 6.6 samples measured after MAE

Material	Mean (μg/g)	STD (μg/g)	R.S.D. (%)
Zytel	13.18	0.44	3.3
Aldrich	13.30	0.28	2.1
Base	0.48	0.09	18.8
Recovered	4.95	0.11	2.2
Compound	1.33	0.10	7.5

1.000 g sample was extracted by 10 ml methanol at 90 °C for 45 min. Cyclohexane was used as internal standard at 0.5 ng/μl. The calibration curve correlation coefficient (r^2) was 0.996.

The emitted amount of 2-cyclopentyl-cyclopentanone measured by HS and HS-SPME was correlated to the total amount measured after MAE. The time for HS thermostating and HS-SPME extractions was 45 min, i.e. the analysis was performed under non-equilibrium conditions. Fig. 7 shows the relationship between HS and MAE extractions and Fig. 8 shows the correlation between HS-SPME and MAE extractions. The amount 2-cyclopentyl-cyclopentanone emitted from the samples measured by the developed non-equilibrium headspace methods was found to be in rather good correlation with the total amount in the samples measured by MAE. This shows that it is possible to estimate the amount of 2-cyclopentyl-cyclopentanone in polyamide 6.6 using headspace measurement without establishing true equilibrium and without compensating for volume or matrix effects. The headspace techniques could, thus, be applied to rapidly compare or quality control different samples with respect to their 2-

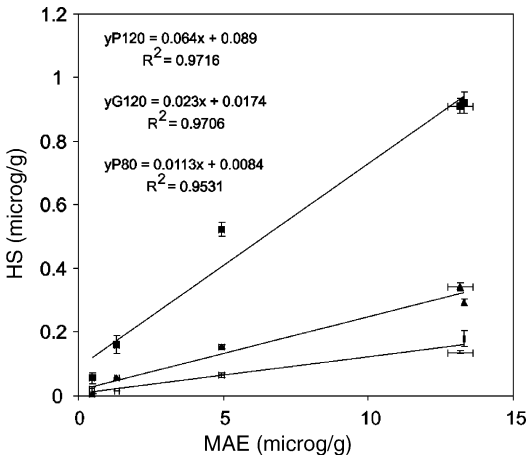

Fig. 7. Correlation between 2-cyclopentyl-cyclopentanone content measured by traditional HS-extraction and after MAE. P120: powder 120 °C; G120: granules 120 °C; and P80: powder 80 °C.

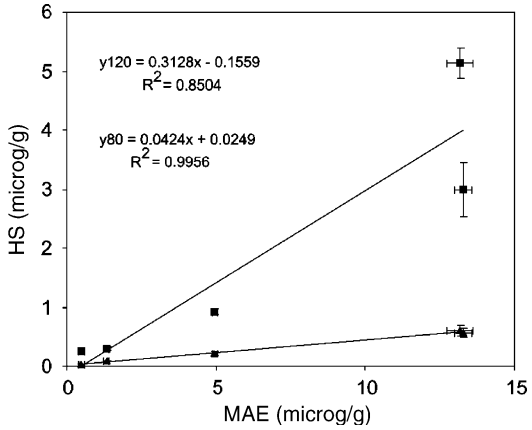

Fig. 8. Correlation between 2-cyclopentyl-cyclopentanone content measured after HS-SPME and after MAE. y120: powder 120 °C and y80: powder 80 °C.

cyclopentyl-cyclopentanone or other volatile contents. When HS-extraction was used the correlation was better at 120 °C than at 80 °C but when HS-SPME was used the correlation was best at 80 °C. The measurement is hence preferably made with HS at 120 °C or with HS-SPME at 80 °C.

4. Conclusions

A correlation was found between the amount 2-cyclopentyl-cyclopentanone emitted from polyamide 6.6 measured by HS and HS-SPME and the content measured by MAE. This correlation was valid also under non-equilibrium conditions and shows that both HS and HS-SPME and simple external calibration are applicable to rapidly assess the amount of 2-cyclopentyl-cyclopentanone in polyamide 6.6. Traditional HS-extraction gave better precision, with R.S.D. generally around 5%, while R.S.D. for HS-SPME was approximately 10%. However, the limit of quantitation was more than four times lower for HS-SPME (approximately 0.2–1.0 ng) than for traditional HS-extraction (approximately 4.0 ng). Milling the granules into powder reduces the incubation time and improves the sensitivity. Establishment of true equilibrium between 2-cyclopentyl-cyclopentanone in polyamide 6.6 and the headspace required 12 h of incubation at 80 °C. The long equilibrium time is explained by the relatively high crystallinity of polyamide 6.6 and hydrogen bonding between the analyte and the polymer matrix. Emission of 2-cyclopentyl-cyclopentanone in polyamide 6.6 proceeded step-wise giving an extraction profile with several equilibrium-like patterns that should not be mistaken for true equilibrium.

Acknowledgement

Professor Ann-Christine Albertsson is acknowledged for valuable discussions and inspiration throughout this work.

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