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Multiple headspace solid-phase microextraction of 2-cyclopentyl-cyclopentanone in polyamide 6.6: possibilities and limitations in the headspace analysis of solid hydrogen-bonding matrices

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Abstract

The interactions between a polar analyte, 2-cyclopentyl-cyclopentanone, and a solid polar matrix, polyamide 6.6, during multiple headspace solid-phase microextraction (MHS-SPME) were studied. Strong hydrogen bonding between the analyte and the matrix was observed and shown to cause slow migration and adsorption of the analyte. These matrix effects led to erroneous quantitation despite the use of multiple headspace extraction. Addition of water disrupted the hydrogen bonding between the analyte and the matrix and a valid quantitation was achieved. The addition of water also increased the sensitivity and allowed the identification of 2,5-bis(cyclopentyl)-1-cyclopentanone. The amount of 2-cyclopentyl-cyclopentanone in five different polyamide 6.6 samples was measured using the developed multiple headspace solid-phase microextraction method with water-displacer. The measured concentrations were in the range of 1.44–15.61 μg/g. These concentrations were up to 30% higher than the concentrations measured after microwave-assisted extraction (MAE), which indicates incomplete recovery by MAE. The use of water as a displacer eliminated the matrix effects and complete recovery of the analyte was achieved by MHS-SPME.

Keywords: Multiple headspace extraction; Solid-phase microextraction; SPME; Microwave-assisted extraction; Polyamide; Volatiles

1. Introduction

Additives, side-products from polymerisation, degradation products and residual monomers are some of the low molecular mass compounds frequently present in plastic products. In most of the plastic applications, it is highly important to know the identity and amount of these low molecular mass compounds, as they will eventually migrate from the products into the surrounding environment. If plastics are used for implants in the body, as packaging materials or in vehicle interiors, this information is required for toxicological reasons. The polymer producing and processing industry measures the amount of additives, residual monomer or side-products to quality control their products.

The identification and quantitation of low molecular mass compounds in solid matrices is an important analytical challenge. Traditionally, solvent-based techniques such as microwave-assisted extraction (MAE) or Soxhlet extraction are used. They are limited by being rather time, solvent and labour consuming [1–5]. Solvent-based techniques also involve a risk of losing volatiles during sample preparation, extraction and clean-up. In addition, volatile analytes may be masked by the solvent peak in the subsequent chromatographic analysis. Due to these limitations, headspace (HS) extraction, i.e. sampling the gaseous analytes with a syringe from the headspace above the heated sample, is the favoured technique to extract volatiles from solid matrices [6–11]. More recently, headspace solid-phase microextraction (HS-SPME) has emerged as a rapid and efficient alternative [12–20]. The principles of headspace extraction and some of its applications in analysis of low molecular mass

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compounds in polymers are discussed in a review by Bart [21]. Quantitative analysis of volatiles in solids is a difficult task regardless if solvent based- or headspace techniques are used. This is mainly due to the difficulties in preparing spiked samples for calibration as it is often impossible to properly mix solid matrices with volatiles. In addition, many solid matrices exert strong matrix effects that must be eliminated for valid quantitation. Multiple headspace extraction (MHE) involves consecutive headspace sampling from the same sample vial. The theory considers the extractions to be carried out ad infinitum, i.e. until all analyte is removed from the sample. The evident advantages of MHE are hence the complete recovery of analyte and the elimination of matrix effects. In practice, a limited number of extractions are carried out and the peak area corresponding to the total amount is obtained by extrapolation. MHE was developed in the 1970's by Kolb and is described in several papers [22–25] and a book [26]. MHS-SPME has been applied for determination of volatiles in multilayer packaging [27–30] and BTEX in soil [31]. MHE with traditional HS has, e.g. been applied for determination of volatiles in cellulose-based packaging [32–34].

2-Cyclopentyl-cyclopentanone has earlier been identified as one of the major volatile compounds in polyamide 6.6 [35–42]. We have previously studied the emission of 2-cyclopentyl-cyclopentanone from polyamide 6.6 by HS-SPME and external calibration [43]. The aim of the present study was to investigate the interactions between polar analytes and solid polar matrices and the effect of these interactions on the MHS-SPME analysis. Understanding these effects ensures correct quantitation and allows the use of MHE in the quantitative determination of polar analytes in solid polar matrices. 2-Cyclopentyl-cyclopentanone and polyamide 6.6 were selected as model analyte and matrix and a multiple headspace microextraction method for quantitative analysis of 2-cyclopentyl-cyclopentanone in polyamide 6.6 was developed.

2. Experimental

2.1. Materials

Five different polyamide 6.6 grades were used: unstabilised but lubricated Zytel 101 L from DuPont (Stockholm, Sweden), unstabilised laboratory grade polyamide from Sigma–Aldrich (Aldrich, Milwaukee, WI, USA), unstabilised industrial grade polyamide Domamid 33ABH from Domo (Leuna, Germany), recovered in-plant polyamide waste 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 the milling.

2.2. SPME-fibre and chemicals

A 65 μm StableFlex polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre from Supelco (Bellafonte, PA, USA) was used for SPME. Quantitation was done by preparing calibration solutions of 2-cyclopentyl-cyclopentanone (>99%) from Lancaster (Lancashire, UK) dissolved in methanol (≥99.9%) from Fluka (Buchs, Germany). In some samples, chromatography-grade water (Merck, Darmstadt, Germany) was used as a displacer. In the microwave-assisted extractions cyclohexanone (≥99.9%) from Poly-Science (Niles, IL, USA) was used as an internal standard and the previously mentioned methanol as a solvent.

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 both for HS-SPME and for the injection of extracts from MAE. The GC was equipped with a 30 m WCOT Varian (Lake Forest, CA, USA) CP-Wax 52 CB 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 any 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 a carrier gas at a constant average linear velocity of 40 cm/s maintained by the electronic pressure control (EPC) of the GC. The injector operated in splitless mode at 250 °C. A narrow bore liner with 2 mm inner diameter was used for SPME 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 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 the extractions from the Compound 2-cyclopentyl-cyclopentanone co-eluted with another product and the quantitation was made from reconstructed ion chromatograms (RIC) by 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. Headspace-solid phase microextraction (HS-SPME)

Samples were extracted in 20 ml clear glass vials (Supelco, Bellafonte, PA, USA) sealed with magnetic silicone/PTFE crimp caps (Varian, Lake Forest, CA, USA). The vials 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. 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. The extracted analytes were desorbed for 5 min in the injector of the GC–MS. Blanks were run between some of the samples and no carry-over could be observed.

2.5. Microwave-assisted extraction

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. The development of the MAE method is described in a previous paper [43]. 1.000 g of powdered polyamide 6.6 was placed in a lined extraction vessel and 10 ml MeOH containing 5 μg of cyclohexanone was added to the vessel. Cyclohexanone was used as an internal standard to compensate for possible losses of analyte during the extraction and handling. For each material, four samples were extracted simultaneously. The samples were heated from ambient temperature to 90 °C in 10 min and the temperature was then maintained at 90 °C for 45 min. After completed extractions, the samples were allowed to cool to room temperature and the extracts were filtered through 0.45 μm Cameo PTFE-filters (GE Waters Technologies, Trevose, PA, USA) into 2 ml screw top vials (Supelco, Bellafonte, PA, USA). 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 seven point calibration curves. The concentrations for the calibration solutions were 1.01, 10.1, 101.0, 505.0, 1010.0, 1520.0 and 2020.0 pg/μl. Each standard solution also contained 0.5 ng cyclohexanone per microliter as an internal standard and was analysed in triplicate.

3. Results and discussion

3.1. Linear range of the SPME-fibre

The first parameter to study during the development of a MHS-SPME method is the linear dynamic range of the SPME fibre. If the linear dynamic range is exceeded, the amount of analyte extracted in successive extractions will not decay exponentially. Fig. 1 shows the normalised peak areas for the extractions from 1 to 1000 mg of polyamide 6.6 (Zytel). The extraction time and temperature were 45 min and 80 °C. The figure shows that under the given conditions the dynamic range of the PDMS/DVB fibre is linear for the extractions from 1 to 100 mg of Zytel, The correlation coefficient was 0.9977. It was decided to use 75 mg of sample for the extraction of 2-cyclopentyl-cyclopentanone from Zytel at 80 °C, as this gave a clear peak in the chromatograms and was within the linear dynamic range of the fibre. To make sure that the linear dynamic range of the fibre was never exceeded, the peak area after the 45 min extraction from 75 mg Zytel at 80 °C was used as a reference. The amount of all the other samples was adjusted to obtain initial peak areas close to the reference peak area.

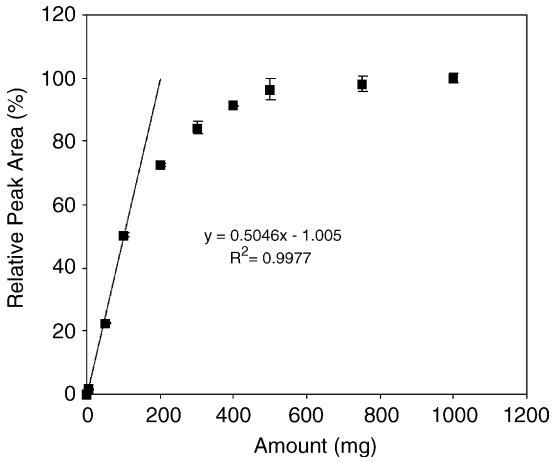

Fig. 1. The 45 min extractions of 2-cyclopentyl-cyclopentanone from 1 to 1000 mg polyamide 6.6 at 80 °C using a PDMS/DVB fibre. The dynamic range was linear when the sample size was between 1 and 100 mg.

3.2. Extraction profiles

Quantitation by MHS-SPME can be done under non-equilibrium conditions. Although the extraction can be stopped before the equilibrium is reached, it is desirable to continue the extraction until the extraction profile shows little variation in extracted amount with extraction time, as this improves the reproducibility. Fig. 2 shows the extraction profiles for 25 mg of Zytel extracted for 30 min at 80 °C (circles) and for 30 mg of Zytel extracted for 20 min at 90 °C (squares). Two hundred and fifty microliters of water was added to the sample extracted at 90 °C. The samples were incubated between 0 and 25 h at 80 °C or between 0 and 10 h at 90 °C before the extraction. Different fibres were used to construct the curves and they should hence not be compared to each other with respect to absolute peak areas. The curves are shown normalised with respect to their maximum recovery and they primarily aim to point out the significant reduction in time required to optimal recovery when incubating at higher temperature and in the presence of a displacer. At 80 °C, the extracted amount increased dramatically with time during the first 10 h of extraction. However, after approximately 10 h of extraction the curve flattened

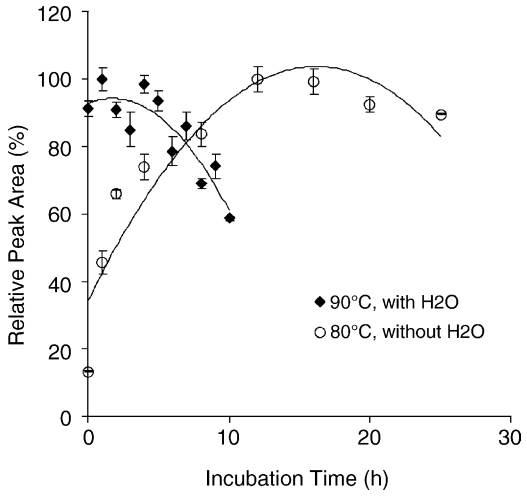

Fig. 2. The extraction profiles of 25 mg Zytel extracted for 30 min at 80 °C (circles) and 30 mg Zytel extracted for 20 min at 90 °C together with 250 μl water as a displacer (squares). The samples were incubated for up to 25 h prior to extraction.

out. The long time required to reach the optimal recovery is probably due the strong hydrogen bonding between the analyte and the polar polyamide 6.6 matrix, which caused slow migration of the analyte. When water was added as a displacer, and the extraction was performed at 90 °C, the extraction profile showed little variance with respect to extraction time. The significantly shorter time required for reaching the optimal recovery is a result of the increased temperature, which increases the migration rate, and the addition of water, which shows higher affinity than the analyte towards the polar hydrogen-bonding sites of the matrix and thus releases the analyte from the polymer matrix. Hence, the optimal recovery is achieved 10 times faster if the temperature is increased from 80 to 90 °C and water is added as a displacer.

3.3. Optimisation of extraction parameters

The regression line for the plot of logarithms of the peak areas obtained in consecutive multiple headspace extractions versus the extractions should have a correlation coefficient of at least 0.998 to show that the matrix effects are truly absent. However, the repeatability of SPME is lower than the repeatability of conventional HS, and somewhat lower correlation coefficients can hence be accepted. For MHS-SPME, the correlation coefficient should be examined together with the shape of the extraction plot and a clear linear trend should be observed in the extraction plot to ensure the absence of matrix effects. The effect of sample amount, extraction temperature, incubation time and addition of a displacer on the measured amount of 2-cyclopentyl-cyclopentanone in Zytel and the characteristics of the corresponding linear regression lines are shown in Table 1. The 75 mg Zytel sample extracted at 80 °C appears several times in the table to clarify the effect of studied variables and to allow easier comparison between the samples. There was no significant difference between the concentrations measured at 80 °C from the 50 and 75 mg samples. In both cases, the measured concentration of 2-cyclopentyl-cyclopentanone was approximately 3.9 μg/g.

The extraction temperature, however, strongly influenced the measured concentrations. After MHS-SPME at 50 °C, the measured concentration of 2-cyclopentyl-cyclopentanone was 0.47 μg/g. At 80 and 120 °C, the measured concentrations were 3.90 and 96.07 μg/g, respectively. The very low correlation coefficient of 0.686 obtained at 120 °C immediately tells that the measurement is invalid. At 50 and 80 °C, the correlation coefficients were 0.936 and 0.975, respectively. However, a close examination of the two extraction plots shows that both measurements are invalid. Fig. 3A shows the extraction plot obtained after six consecutive extractions from 75 mg Zytel at 50 °C versus the extractions. The extraction plot is approximately linear from the second to the fifth extraction. However, the extraction plot flattens

Table 1
The amount of 2-cyclopentyl-cyclopentanone measured in Zytel using MHE-SPME under various conditions

$n = 3$	Amount (μg/g)	Equation		Correlation
	Mean ± S.D.	Slope	Intercept	r^2 ± S.D.
Amount sample (80 °C)				
50 mg	3.97 ± 0.08	−0.29 ± 0.01	17.58 ± 0.07	0.995 ± 0.002
75 mg	3.90 ± 0.53	−0.21 ± 0.03	17.36 ± 0.02	0.975 ± 0.019
Temperature				
50 °C, 75 mg	0.47 ± 0.00	−0.39 ± 0.04	16.03 ± 0.09	0.936 ± 0.029
80 °C, 75 mg	3.90 ± 0.53	−0.21 ± 0.03	17.36 ± 0.02	0.975 ± 0.019
120 °C, 25 mg	96.07 ± 17.57	−0.04 ± 0.01	15.22 ± 0.04	0.686 ± 0.020
Incubation (80 °C)				
0 h, 75 mg	3.90 ± 0.53	−0.21 ± 0.03	17.36 ± 0.02	0.975 ± 0.019
25 h, 10 mg	2.08 ± 0.15	−0.81 ± 0.10	15.05 ± 0.14	0.968 ± 0.025
With modifier (90°)				
30 mg	15.61 ± 1.22	−0.20 ± 0.03	16.63 ± 0.28	0.991 ± 0.021

Each value is an average of three measurements. The extraction was performed for 45 min.

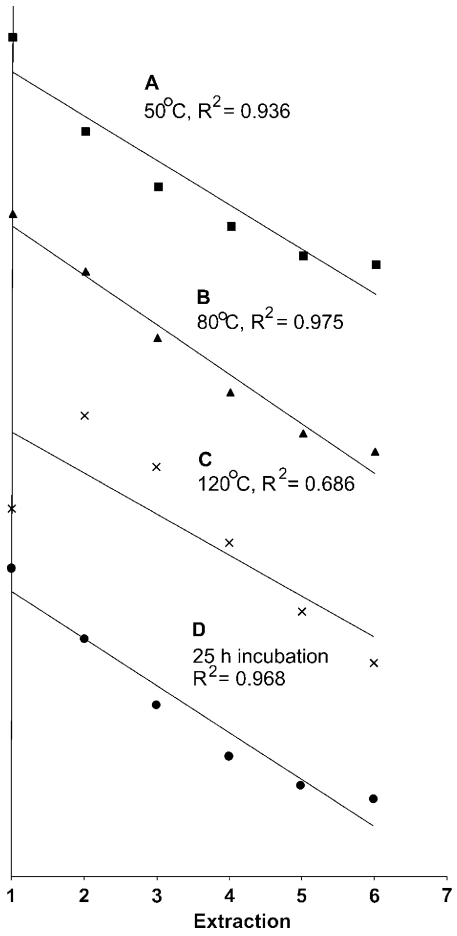

Fig. 3. The extraction plots of six consecutive 45 min extractions from: (A) 75 mg Zytel at 50 °C; (B) 75 mg Zytel at 80 °C; (C) 75 mg Zytel at 120 °C; and (D) 10 mg Zytel at 80 °C. The 10 mg samples were incubated for 25 h at 80 °C prior to extraction.

out between the fifth and the sixth extractions. In addition, the difference in the relative peak area between the first and second extraction is larger than the difference in the relative peak areas between the following extractions. These deviations from linearity in the beginning and at the end of the extraction plot result in a rather poor average correlation coefficient of 0.936. The two parts of the extraction plot deviating from linearity, i.e. the beginning and the end, are concluded to represent two different phenomena which are together responsible for the erroneous measurement at 50 °C. The relatively larger difference in the peak area between the first and second extraction, compared to the difference between the following extractions, reflects the slow migration of analyte from the sample at the low temperature used for the extraction. In the first extraction, the readily available analyte is extracted from the sample. In the second extraction, the analyte has not had time to migrate from inside the polyamide 6.6 powder to replace the analyte removed in the first extraction. In the third extraction, the sample has been heated for a total of 2 h and 15 min and the analyte has, thus, had time to migrate to the headspace of the powder, giving the linear part of the extraction plot. Between the fifth and sixth extraction, the extraction plot flattens out, which is concluded to be due to the adsorption of the analyte to the polar surface of the polyamide 6.6 powder. In the extraction plot, the adsorption is observed only after several extractions when the amount of not hydrogen-bonded analyte in relation to the hydrogen-bonded analyte has decreased.

The shape of the extraction plot for the extraction at 80 °C is shown in Fig. 3B. Again the extraction plot flattens out between the fifth and the sixth extraction, showing the adsorption of analyte by the matrix also at this temperature. At 80 °C, the average correlation coefficient is higher, i.e. 0.975, compared to 0.936 at 50 °C. This is largely due to the faster migration rate at the higher temperature. This can be seen in Fig. 3B, as the extraction profile is linear already from the beginning of the extraction, i.e. the difference in peak areas between the first and second extraction is not larger than the difference between the following extractions. At 80 °C, the migration rate is high enough to compensate for the amount of analyte removed by the SPME-fibre in the first extraction and a linear relationship was obtained in the first part of the extraction plot. At 80 °C, the 2-cyclopentyl-cyclopentanone concentration was measured to be 3.90 μg/g. This considerably higher value also reflects the faster migration rate at the higher temperature. However, due to the adsorption of the analyte, shown by the flattening of the extraction plot, this value is also considered erroneous.

At higher temperature, the faster migration rate may release more analyte into the headspace than what is removed by the SPME-fibre in the first extraction, giving an extraction plot with a positive slope between the first and the second extraction. This is seen in Fig. 3C, which shows the 45 min extractions of 25 mg powdered Zytel at 120 °C. A small tendency to adsorption of analyte may be noticed as the extraction plot flattens out slightly between the fifth and sixth extractions. The concentration measured at 120 °C was 96.07 μg/g, but again the very poor average correlation coefficient of 0.686, together with the non-linear extraction plot, indicates erroneous results.

To overcome the problem of slow diffusion of analyte in the solid matrix, 10 mg samples of powdered Zytel were incubated for 25 h at 80 °C prior to the 45 min extraction at 80 °C. The resulting extraction plot is shown in Fig. 3D. The average slope of the regression line is quite high: −0.83, showing that large amounts of analyte are removed by the SPME-fibre in each extraction step. Hence, larger amount of analyte has been made available by migration from the sample to the headspace during incubation. The plot shows rather good linearity during the first four extractions. However, the analyte is still adsorbed by the matrix as the extraction plot flattens out after the fourth extraction. The concentration of 2-cyclopentyl-cyclopentanone in Zytel was measured to be 2.08 μg/g when samples were incubated for 25 h at 80 °C prior to extraction. Although the correlation coefficient of 0.968 is quite high, the shape of the extraction plot tells that the measurement was still not valid.

Table 2
The amount of 2-cyclopentyl-cyclopentanone measured in five different polyamide 6.6 samples using MAE and standard addition (SA)

Material	MAE (n = 4)	SA (n = 3)	
	Mean (μg/g) ± S.D.	Mean (μg/g) ± S.D.	r^2
Zytel	13.18 ± 0.44	3.58 ± 0.11	0.985 ± 0.003
Aldrich	13.30 ± 0.28	3.65 ± 0.12	0.993 ± 0.002
Base	0.48 ± 0.09	0.17 ± 0.01	0.989 ± 0.009
Recovered	4.95 ± 0.11	0.87 ± 0.22	0.984 ± 0.008
Compound	1.33 ± 0.10	0.49 ± 0.09	0.968 ± 0.027

3.4. Standard addition to verify adsorption of analyte

Adsorption of the analyte to the matrix was verified by multiple additions of 2-cyclopentyl-cyclopentanone to five different polyamide 6.6 samples followed by HS-SPME. To each sample, six different amounts in the range of 0–48 ng were added. The samples were stored for 24 h in room temperature to allow equilibrium between the solid sample and the added analyte prior to extraction for 45 min at 80 °C. The amount of 2-cyclopentyl-cyclopentanone in the samples was calculated by extrapolating the linear regression line to the intercept with the x-axis, which corresponds to the concentration of 2-cyclopentyl-cyclopentanone in the samples. The results from the standard addition measurements, i.e. the measured amounts and average regression line coefficients are shown in Table 2. The concentrations obtained after MAE are also shown for comparison. Table 2 shows that for all the samples standard addition gives approximately 20–40% of the concentration measured by MAE. The 24 h equilibrium time should be enough for the solid sample to adsorb the added standard on its surface. The lower amount measured results from the slow migration of the analyte, which makes the peak area corresponding to the sample without additional analyte too small. Higher amounts would probably have been measured if the samples had been incubated for a sufficiently long time to reach true headspace equilibrium before standard was added. This would have shifted the regression line to larger peak areas and made it cross the x-axis at higher amounts.

3.5. Extraction in the presence of displacer

The strong hydrogen bonding between 2-cyclopentyl-cyclopentanone and the polar polyamide 6.6 is responsible for the previously discussed adsorption of analyte by the matrix. These matrix effects cause a significant error in the quantitative measurement of 2-cyclopentyl-cyclopentanone by MHS-SPME. Although the slow migration rate may be overcome by incubating the samples prior to extraction, the problem of adsorption of analyte by the matrix still remains. The adsorption of analyte may be suppressed by adding a compound with higher affinity than the analyte to the adsorption sites of the matrix. In the present study, water was selected as a displacer primarily as it is known to be easily adsorbed by polyamide 6.6 and it is, thus, expected to be an efficient displacer. The volume of water was adjusted to completely cover the powdered sample, which for 25 mg of powder corresponded to 250 μl. When 50 mg samples, containing lower amounts of 2-cyclopentyl-cyclopentanone, were used, they required the addition of 300 μl of water. A constant volume of displacer should always be used as it affects the headspace volume and, consequently, the sensitivity of the extraction. The sensitivity is also reduced if the analyte is soluble in the displacer. Larger volume of displacer solvates larger amount of analyte and reduces the sensitivity even more. 2-Cyclopentyl-cyclopentanone is not soluble in water and it aids in increasing the headspace concentration of 2-cyclopentyl-cyclopentanone by excluding it from the adsorption sites of the matrix. The use of water as a displacer also allowed the identification of 2,5-bis(cyclopentyl)-1-cyclopentanone among the volatile compounds in the polyamide 6.6 samples. In the HS-SPME chromatograms from the Compound, the peak corresponding to 2,5-bis(cyclopentyl)-1-cyclopentanone co-eluted with a large peak corresponding to 2,4-di-tert-butylphenol, a degradation product from the additive tris(2,4-di-tert-butylphenyl)phosphite, and could not be detected in the total ion current chromatograms. 2,5-bis(Cyclopentyl)-1-cyclopentanone could, however, easily be identified in the extractions from the other samples and was found in relative abundances of 1:3:3:2 in the Base:Aldrich:Zytel:Recovered samples, respectively. 2,5-bis(Cyclopentyl)-1-cyclopentanone was not detected in the chromatograms after MAE.

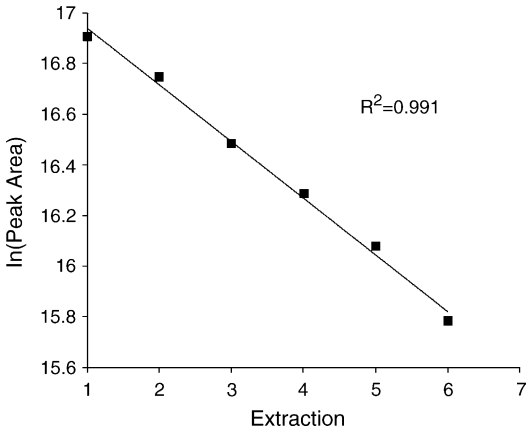

Fig. 4. The extraction plot of six consecutive 30 min extractions from 25 mg Zytel at 90 °C in the presence of 250 μl water. The water acted as a displacer and eliminated the matrix effects.

Fig. 4 shows the extraction profile of 25 mg powdered Zytel extracted at 90 °C for 30 min in the presence of 250 μl water. The extraction profile shows good linearity with an average correlation coefficient of 0.991, which for MHE-SPME is considered satisfactory. The extraction plot is linear throughout the multiple extractions and no tendency to adsorption can be noticed. Although there is some spreading of the individual data points relative to the linear regression line,

Table 3
The measured concentrations of 2-cyclopentyl-cyclopentanone in five different polyamide 6.6 samples after MHS-SPME with water-displacer and MAE

Material	MAE (n = 4)	MHS-SPME (n = 3)		MHS-SPME/MAE
	Mean (μg/g) ± S.D. (R.S.D. %)	Mean (μg/g) ± S.D. (R.S.D. %)	r^2	
Zytel	13.18 ± 0.44 (3.3)	15.61 ± 1.22 (7.8)	0.991 ± 0.02	1.184
Aldrich	13.30 ± 0.28 (2.1)	15.30 ± 2.11 (13.8)	0.995 ± 0.00	1.150
Base	0.48 ± 0.09 (18.8)	1.44 ± 0.39 (27.1)	0.980 ± 0.00	3.000
Recovered	4.95 ± 0.11 (2.2)	4.87 ± 0.37 (7.6)	0.989 ± 0.02	0.984
Compound	1.33 ± 0.10 (7.5)	1.76 ± 0.06 (3.4)	0.993 ± 0.01	1.301

The ratios between the concentrations measured after MHS-SPME and MAE are also given.

the variation is random and caused by the poorer reproducibility of HS-SPME. It is hence concluded that the measurement is valid and that the added water acted as a good displacer and replaced the analyte at the binding sites of the matrix. Using the given conditions for MHS-SPME, the concentration of 2-cyclopentyl-cyclopentanone in Zytel was measured to be 15.61 μg/g.

3.6. Validation of MHS-SPME method

To validate the developed MHS-SPME method, the concentrations of 2-cyclopentyl-cyclopentanone in five different polyamide 6.6 samples as measured by MHS-SPME, were compared to the concentrations measured after MAE. The measured concentrations and the ratios between the measured concentrations after MHS-SPME and MAE are shown in Table 3. Table 3 shows that MHS-SPME and MAE give rather comparable results for all the samples but one, i.e. the Base material, for which MHS-SPME measured a three times higher concentration than MAE. In general, the concentrations measured after MHS-SPME were up to 30% higher than the concentrations measured after MAE. As it was shown that the developed MHS-SPME method eliminated the matrix effects and MAE rarely gives 100% complete extraction, the concentrations measured using MHS-SPME were considered to be the true concentrations. The recovery of the MAE was, thus, around 70–85%.

The total analysis time for MHS-SPME is considerably longer than the analysis time for MAE. If six consecutive extractions are performed, the total analysis time for one sample and a standard is approximately 6 h. In MAE, the extraction is performed in approximately 1 h, including cooling and filtering of the solution. However, if the linearity of the MHS-SPME plot under the given conditions has been verified, the number of extractions can be reduced to two, which reduces the total analysis time to 2 h. Other advantages of MHS-SPME compared to MAE are, e.g. its higher sensitivity, the small sample amount required, solvent free nature and if an autosampler is used a low demand of labour time. In addition, as matrix effects are absent, the recovery will always be 100%. This is very valuable compared to other techniques for extraction of volatiles in polymers in which the recovery should be calculated from extraction of spiked samples, which are practically impossible, to produce.

4. Conclusions

Addition of water as a displacer eliminated the matrix effects and allowed quantitative measurement of 2-cyclopentyl-cyclopentanone in polyamide 6.6 by MHS-SPME. Without the addition of water, matrix effects, caused by hydrogen bonding between the analyte and the polyamide matrix, caused slow migration and adsorption of analyte, which ultimately led to invalid quantitation. The use of water as a displacer also increased the sensitivity of HS-SPME and allowed the identification of 2,5-bis(cyclopentyl)-1-cyclopentanone among the volatile compounds. During the development of a MHS-SPME method, several consecutive extractions have to be performed to ensure that there are no disturbing matrix effects present.

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References

[1] C.S. Eskilsson, E. Björklund, J. Chromatogr. A 902 (2000) 227.
[2] H.J. Vandenburg, A.A. Clifford, K.D. Bartle, J. Carroll, I. Newton, L.M. Garden, J.R. Dean, C.T. Costley, Analyst 122 (1997) R101.
[3] M.D. Luque de Castro, L.E. Garcia-Ayuso, Anal. Chim. Acta 369 (1998) 1.
[4] X.W. Lou, H.G. Janssen, C.A. Cramers, Anal. Chem. 69 (1997) 1598.
[5] H.J. Vandenburg, A.A. Clifford, K.D. Bartle, J. Carroll, I.D. Newton, Analyst 124 (1999) 1707.
[6] S.J. Romano, J.A. Renner, P.M. Leitner, Anal. Chem. 45 (1973) 2327.
[7] L.S. Ettre, in: Rouseff, Cadwaller (Eds.), Headspace Analysis of Food and Flavours: Theory and Practice, Kluwer Academic/Plenum Publishers, New York, 2001, p. 9.
[8] R. Meininghaus, F. Fuhrmann, T. Salthammer, Fresenius J. Anal. Chem. 356 (1996) 344.
[9] S.C. Hodgson, M.J. O'Connor, R.J. Casey, S.W. Bigger, J. Agric. Food Chem. 46 (1998) 1397.
[10] R.A. Shanks, Scan (Cambridge, UK) 6 (1975) 20.
[11] X.S. Chai, Q.X. Hou, F.J. Schork, J. Chromatogr. A 1040 (2004) 163.
[12] P. Kusch, G. Knupp, J. Polym. Environ. 12 (2004) 83.
[13] P. Kusch, G. Knupp, J. Sep. Sci. 25 (2002) 539.

[14] O. Ezquerro, B. Pons, M.T. Tena, J. Chromatogr. A 963 (2002) 381.
[15] M. Eriksson, J. Faldt, G. Dalhammar, A.K. Borg-Karlson, Chemosphere 44 (2001) 1641.
[16] T.J. Clark, J.E. Bunch, J. Agric. Food Chem. 45 (1997) 844.
[17] M. Hakkarainen, A.-C. Albertsson, S. Karlsson, J. Environ. Polym. Degrad. 5 (1997) 67.
[18] M. Hakkarainen, M. Gröning, A.-C. Albertsson, J. Appl. Polym. Sci. 89 (2003) 867.
[19] M. Hakkarainen, Polym. Degrad. Stabil. 80 (2003) 451.
[20] M. Hakkarainen, J. Chromatogr. A 1010 (2003) 9.
[21] J.C.J. Bart, Polym. Test. 20 (2001) 729.
[22] B. Kolb, P. Pospisil, Chromatographia 10 (1977) 705.
[23] B. Kolb, Chromatographia 15 (1982) 587.
[24] B. Kolb, P. Pospisil, M. Auer, Chromatographia 19 (1984) 113.
[25] B. Kolb, L.S. Ettre, Chromatographia 32 (1991) 505.
[26] B. Kolb, L.S. Ettre, Static Headspace–Gas Chromatography: Theory and Practice, Wiley-VCH, New York, 1997.
[27] O. Ezquerro, B. Pons, M.T. Tena, J. Chromatogr. A 985 (2003) 247.
[28] O. Ezquerro, B. Pons, M.T. Tena, J. Chromatogr. A 999 (2003) 155.
[29] O. Ezquerro, B. Pons, M.T. Tena, J. Chromatogr. A 1020 (2003) 189.
[30] O. Ezquerro, B. Pons, M.T. Tena, J. Chromatogr. A 1008 (2003) 123.
[31] O. Ezquerro, G. Ortiz, B. Pons, M.T. Tena, J. Chromatogr. A 1035 (2004) 17.
[32] T. Wenzl, E.P. Lankmayr, J. Chromatogr. A 897 (2000) 269.
[33] T. Wenzl, E.P. Lankmayr, J. Sep. Sci. 24 (2001) 885.
[34] T. Wenzl, E.P. Lankmayr, Anal. Bioanal. Chem. 372 (2002) 649.
[35] M. Gröning, M. Hakkarainen, J. Chromatogr. A 932 (2001) 1.
[36] M. Gröning, M. Hakkarainen, J. Appl. Polym. Sci. 86 (2002) 3396.
[37] N.S. Allen, M.J. Harrison, Eur. Polym. J. 21 (1985) 517.
[38] D.H. Mackerron, R.P. Gordon, Polym. Degrad. Stabil. 12 (1985) 277.
[39] L.H. Peebles Jr., M.W. Huffman, J. Polym. Sci. Part A 9 (1971) 1807.
[40] J.W. Gramshaw, H. Soto-Valdez, Food Addit. Contam. 15 (1998) 329.
[41] H. Soto-Valdez, J.W. Gramshaw, J. Mater. Sci. Lett. 19 (2000) 823.
[42] H. Soto Valdez, J.W. Gramshaw, H.J. Vandenburg, Food Addit. Contam. 14 (1997) 309.
[43] M. Gröning, M. Hakkarainen, J. Chromatogr. A (2004) in press.