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# Migration from polycarbonate packaging to food simulants during microwave heating

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ABSTRACT

The interactions between polycarbonate (PC) packaging and different food simulants during microwave heating were evaluated by identifying the compounds migrating into aqueous, alcoholic and fatty food simulants. The migration of compounds, such as 9,9-dimethylxanthene and m-tert-butyl-phenol, from the PC package to ethanol and isooctane increased significantly during microwave heating as compared to conventional heating. The increase in migration can be explained by degradation caused by microwave heating and/or stronger food simulant interactions. Depending on the food simulant the migrants were quantified either by multiple headspace – solid-phase micro-extraction (MHS–SPME) or direct injection in combination with gas chromatography–mass spectrometry. A partial least squares (PLS) regression model was developed to predict the extraction efficiency for headspace – solid-phase micro-extraction (HS-SPME) of food package migrants from the analyte properties. The most significant property for prediction of the enrichment factors was the octanol-water partition coefficient (log $K_{ow}$). Polydimethylsiloxane (PDMS) and polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibres were compared for the extraction of the migrants. High correlation was found between the PDMS and PDMS/DVB enrichment factors ($R^2 = 0.98$), but the extraction by PDMS/DVB fibre was much more efficient compared to the extraction by PDMS fibre. The detection limits after SPME extraction by PDMS/DVB fibre were 1, 0.1 and 3 ng/L for 4-ethoxy-ethyl-benzoate, 2,4-di-tert-butyl-phenol and benzophenone, respectively.



## 1. Introduction

Plastic food packaging materials contain additives and other low molecular weight compounds, which could migrate into the food, especially during microwave heating or other processing of the food inside the plastic packaging [1,2]. Establishing techniques to detect and quantify any migrating compounds, even at low concentrations, is therefore essential to ensure the safe use of packaging materials. Solid-phase micro-extraction (SPME) presents an attractive choice due to the rapidity, repeatability and easiness of the method preparation. SPME can also be automated to further decrease the preparation time and to improve precision. SPME was introduced by Arthur and Pawliszyn in 1990 [3] and is an extraction technique where a fused-silica fibre coated with a polymeric stationary phase is held in the liquid or headspace of a solution to extract and adsorb the analytes to the fibre. The SPME technique is commonly used to extract and pre-concentrate analytes before the GC–MS analysis and have previously been applied for extraction of e.g. thermo-oxidation [4] and hydrolysis products from polymers [5].

In migration determinations, headspace (HS) techniques are often preferable over direct immersion techniques, because of the possibility to use the same techniques on real food samples where immersion is not always possible due to the high viscosity, fat content and/or solid dispersions that will de-attach or destroy the SPME fibre during agitation. SPME extraction by immersion mode was used to extract migrants such as styrene, phenol and benzophenone from crosslinked polyethylene pipes in water with a detection limit of around 5 μg/L. The simultaneous extraction of several compounds from solution decreased the relative yield of each individual compound compared to extraction from solutions containing single analytes, a potential drawback of the SPME technique. A polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre was found to be the most efficient for the analysed compounds. Temperature of extraction was 60 °C and time 30 min [6]. Butylated hydroxytoluene (BHT), a common antioxidant in plastic materials, together with some other commonly occurring migrants, such as phthalates, have been extracted with immersion-SDME from water, 3% acetic acid and 15% ethanol [7]. BHT had detection limits of 0.05 μg/L and 0.09 μg/L in water and 10% ethanol,

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respectively. The analysis of various volatile aliphatic and aromatic ethers, aldehydes and amides from multilayer PA-6 films in food simulants water and 95% ethanol has also been investigated and the efficiencies of polydimethylsiloxane (PDMS), PDMS/DVB and carbowax/divinylbenzene (CW/DVB) fibres were compared. In that study BHT had a detection limit of 0.2 ng/L in water. The optimum fibre was PDMS. However, PDMS/DVB fibre also gave similar peak areas for the analytes. The optimum extraction conditions were 20 min at 80 °C at 225 rpm stirring rate [8].

Polycarbonate (PC) is a clear and transparent, hard and ductile material which is widely used in for example reusable food packaging and in water and baby bottles. Most migration studies concerned the migration of bisphenol A (BPA) from polycarbonate materials and information on other potential migrants is lacking. An exception is a study by Nerin et al where several additives and other compounds in a commercial PC container, for example phenol, bisphenol A, 2,4-di-tert-butyl-phenol (2,4-bis(1,1-dimethylethyl)-phenol), Cyasorb UV5411, bis(2-ethylhexylphthalate), Irganox 1076, and Irgafos 168 were identified [9]. Headspace micro-extraction techniques such as SPME are commonly used to extract phenolic compounds from aqueous matrices [6,10].

Due to the increasing use of microwavable packaging by consumers, a better understanding of the food/package interactions during microwave heating and identification of package degradation and/or compounds migrating during heating by microwaves is desirable. It is also important to develop analytical methods and general guidelines concerning the choice of extraction methods for the analysis of low molecular weight compounds migrating to food simulants during heating. In this study an SPME method for quantification of volatile substances migrating to food simulants is developed and used to determine the migration from a commercial microwavable PC package to food simulants during microwave heating. A partial least squares (PLS) model will be constructed to identify the most important parameters that govern the extraction efficiencies of the different migrants from different food simulants.

## 2. Material and methods

### 2.1. Materials

Water (LC-MS grade), chloroform (100% HPLC grade) and methanol (99.9% LC-MS grade) were obtained from Fisher. Ethanol (99.9% chromatography grade), isooctane (2,2,4-trimethylpentane) (99.0% LC grade) and 1-methylnaphthalene (>98%) were obtained from Merck. 2,4-bis(1,1-dimethylethyl)-phenol (97%), 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (98%) and m-tert-butyl-phenol (99%) were obtained from Acros. 9,9-dimethylxanthene (96%), 4-ethoxy-benzoic acid ethyl ester (98%) and 1,1′(1,3-propanediyl)bis-benzene (100%) were obtained from Alfa. Acetophenone was obtained from Polyscience (Niles, IL). Benzophenone (>99.9%) was obtained from Fluka. Bisphenol A (99.0%) was obtained from Aldrich. The plastic food container of polycarbonate (PC) was a new reusable commercial food storage box suitable for microwave oven and purchased from local supermarket. It was wrapped in a cardboard package. The PC package had a thickness of approximately 1.7 mm.

### 2.2. Standard preparation

#### 2.2.1. Ethanol standard solution for direct injection

A standard solution was prepared by dissolving standard compounds in ethanol to a concentration approximately within one order of magnitude to the concentration in the samples. It was used for the quantification by direct injection of the analytes that migrated to the food simulants ethanol and isooctane.

#### 2.2.2. Water and 10% ethanol standard solutions for SPME

A 10% ethanol standard solution for SPME extraction was prepared by weighing in and dissolving small amounts of compounds in ethanol, adding an amount of that solution to a 20 ml headspace vial and then diluting with water until a 10% ethanol solution was obtained. A standard solution in water was prepared by adding 10 ml of water to a 20 ml headspace vial and then injecting 1 μL of a chloroform solution containing all the analytes directly into the water. The vial was shaken lightly to dissolve the drop. The concentrations of the standard compounds were in the range from 1 to 20 μg/L.

### 2.3. Migration studies

#### 2.3.1. Microwave heating

A sample of the polymer package was cut into a small piece weighing approximately 0.5 g and put into the Teflon vessel of a Microwave Assisted Extraction (MAE) device. The MAE device was a CEM MES-1000, a multimode type microwave solvent extraction system with a rotating turntable with a maximum effect of 950W. 10 ml of food simulant (FS) was added to the vessel containing the sample and closed gastight. The temperature was automatically held constant at 80 °C by the MAE device using a temperature probe measuring the food simulant temperature. Blank samples of pure food simulants without any polymer samples were also heated for the same durations and temperatures as the samples with polymer. Samples were heated with an effect of 50% for the water and ethanol food simulants, because a higher effect caused a too rapid temperature increase making a stable temperature impossible to hold by the device. Pure isooctane cannot be heated with microwaves due to lack of polarity, therefore 10% ethanol had to be added to the isooctane samples. Because of this small amount of ethanol, the effect setting on the MAE device had to be 100% on 90:10 isooctane/ethanol samples for the temperature to reach 80 °C. After the 1 h heating time, the samples were allowed to slowly cool down to below 30 °C. The vessels were opened and the FS was withdrawn and put into 20 ml glass vials, sealed and stored for later analysis. The determinations were carried out in duplicate.

#### 2.3.2. Conventional heating

Sample pieces of the PC package were as a comparison heated conventionally on a heating plate. Approximately 0.5 g of a polymer sample was put into a 20 ml headspace glass vial, 10 ml of food simulant was added and the vial was closed and sealed with a PTFE/Silicone septum. The vial was then immersed in a preheated silicone oil bath on a heating plate. The temperature of the oil was held constant at 80 °C using an electronic temperature regulator. Blank samples of pure food simulants without any polymer samples added were also heated for 1h at 80 °C. After the heating time the sample vials were removed from the oil bath, allowed to slowly cool to room temperature and then the vials were opened and the polymer samples were removed. The vials containing only the food simulant were re-sealed and stored for later GC–MS analysis. The determinations were carried out in duplicate.

### 2.4. Dissolution-precipitation

To identify and quantify low molecular weight compounds present originally in the PC package approximately 0.3 g piece of the PC package was added to a small glass vial and 3 ml of chloroform was added. The vial was sealed and shaken for a couple of minutes to dissolve the sample. The dissolved sample was then

**Table 1**
Retention times, LODs, LOQs, repeatability (relative standard deviation) and linear range for different standard compounds after SPME (PDMS/DVB) extraction of 10% ethanol and water standard solutions.

| Compound | RT (min) | 10% ethanol | | | Linear range (μg/L) | Water | | | Linear range (μg/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | LOD (μg/L) | LOQ (μg/L) | Repeatability (%) | | LOD (μg/L) | LOQ (μg/L) | Repeatability (%) | |
| Acetophenone[a] | 8.4 | 0.3 | 0.8 | 21 | 6–18 | 0.005 | 0.02 | 11 | 0.6–6 |
| m-tert-butyl-phenol[a] | 11.8 | 0.03 | 0.09 | 28 | 1.2–4.8 | 0.0004 | 0.001 | 4 | 0.12–1.2 |
| 1-methylnaphthalene[a,b] | 12.2 | 0.0009 | 0.003 | 4 | – | 0.0003 | 0.001 | 3 | – |
| 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione | 14.1 | 0.01 | 0.03 | 18 | 3.2–6.4 | 0.004 | 0.01 | 18 | 0.32–3.2 |
| 2,4-bis(1,1-dimethylethyl)-phenol | 14.6 | 0.002 | 0.006 | 19 | 1.3–5.2 | 0.0001 | 0.0004 | 24 | 0.13–1.3 |
| 4-ethoxy-benzoic acid ethyl ester[a] | 14.9 | 0.01 | 0.04 | 13 | 6.3–19 | 0.001 | 0.005 | 2 | 0.63–3.2 |
| Benzophenone[a] | 16.3 | 0.02 | 0.07 | 15 | 4.3–17 | 0.003 | 0.009 | 3 | 0.43–4.3 |
| 1,1′(1,3-propanediyl)bis-benzene[a,b] | 16.5 | 0.002 | 0.006 | 17 | – | 0.002 | 0.008 | 4 | – |
| 9,9-dimethylxanthene[a] | 17.0 | 0.009 | 0.03 | 31 | 2.1–4.2 | 0.0009 | 0.003 | 38 | 0.21–2.1 |

[a] Found migrating from the PC package.
[b] Not quantified, peak areas in samples close to detection limit.

re-precipitated by adding 1 ml of methanol, stored for 1 night in a refrigerator and filtrated through a 0.45 μm filter tip using a glass syringe. This sample was then filtrated through a 0.45 μm filter tip and injected directly into the GC–MS system. The dissolution-precipitation was carried out in triplicate.

### 2.5. Gas chromatography–mass spectrometry (GC–MS)

The isooctane, ethanol and water food simulants and standards were analysed on a Finnigan MAT GCQ system (San José, CA, USA) with a Gerstel MPS2 autosampler (Mülheim an der Ruhr, Germany). A wall coated open tubular (WCOT) CP-SIL 8 CB low bleed/MS 0.25 mm × 0.25 μm × 30 m column from Varian was used with helium (99.9999% purity) carrier gas at a constant linear velocity of 40 cm/s. The column oven was programmed as: 40 °C for 1 min, thereafter heated with a constant rate of 10 °C/min up to 270 °C and finally held at 270 °C for 15 min. MS detector mass scan range was set to 35–400 ($m/z$) and electron ionization (EI) mode was used with 70 eV acceleration energy. The isooctane and ethanol food simulant extracts were injected into the GC–MS directly after filtration through a 0.45 μm filter and the injection volume was 1 μL. Peak integration was carried out on the most intense mass fragment ($m/z$) ion detector response for respective compound (reconstructed ion chromatograms using base peak). The analytes that migrated to the water food simulant from the sample were quantified by using multiple headspace-solid-phase micro-extraction (see Section 2.5.2). Positive identification of compounds in samples was made if the standard and sample compound's mass spectra were identical and the retention time of the sample compound was equal to the retention time of the corresponding standard compound.

#### 2.5.1. Solid-phase micro-extraction (SPME)

The SPME fibres used were a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre and a 100 μm polydimethylsiloxane (PDMS) fibre from SUPELCO (Bellefonte, PA USA). The fibres were conditioned in the injector port according to the manufacturer's description before use. 10 ml of the sample and standard solutions were added to 20 ml headspace vials which were then capped with crimp seals with PTFE/Silicone septa. The extraction was carried out by pre-heating the vials for 1 min at 80 °C and thereafter penetrating the septum with the fibre needle and exposing the fibre to the headspace above the solution under constant agitation for 30 min at 80 °C. After the extraction, the fibre needle was withdrawn from the vial and immediately injected into the GC injection port which was held at 250 °C. The fibre was left in the injection port for a desorption time of 5 min. The extraction procedure was performed automatically by the Gerstel MPS2 autosampler of the GC–MS system.

#### 2.5.2. Multiple headspace–solid-phase micro-extraction (MHS–SPME)

The multiple headspace quantification technique was originally developed for ordinary headspace analysis by Kolb and Pospisil in 1977 [11]. It has the advantage of elimination of matrix effects and is therefore suitable for real liquid or solid samples as well as on

**Table 2**
Concentration of compounds in 10% ethanol standard solution and MHS-SPME parameters: slopes ($q'$), peak area sums ($A_s$) and regression coefficients ($R^2$) of ln $A$ vs extraction number.

| Compound | CAS nr | Concentration (μg/L) | $R^2$ | Slope ($q'$) | $A_s$ |
|---|---|---|---|---|---|
| Acetophenone | 98-86-2 | 6 | 0.943 | −0.15 ± 0.04 | 813,000 ± 17% |
| m-tert-butyl-phenol | 585-34-2 | 1 | 0.981 | −0.15 ± 0.06 | 4,430,000 ± 40% |
| 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione | 719-22-2 | 3.2 | 0.960 | −1.08 ± 0.11 | 3,760,000 ± 14% |
| 2,4-bis(1,1-dimethylethyl)-phenol | 96-76-4 | 1.3 | 0.983 | −0.28 ± 0.01 | 27,100,000 ± 3% |
| 4-ethoxy-benzoic acid ethyl ester | 23676-09-7 | 6.3 | 0.972 | −0.23 ± 0.04 | 7,530,000 ± 16% |
| Benzophenone | 119-61-9 | 4.3 | 0.995 | −0.17 ± 0.01 | 5,140,000 ± 7% |
| 9,9-dimethylxanthene | 19814-75-6 | 2.1 | 0.995 | −0.34 ± 0.004 | 110,000,000 ± 1% |

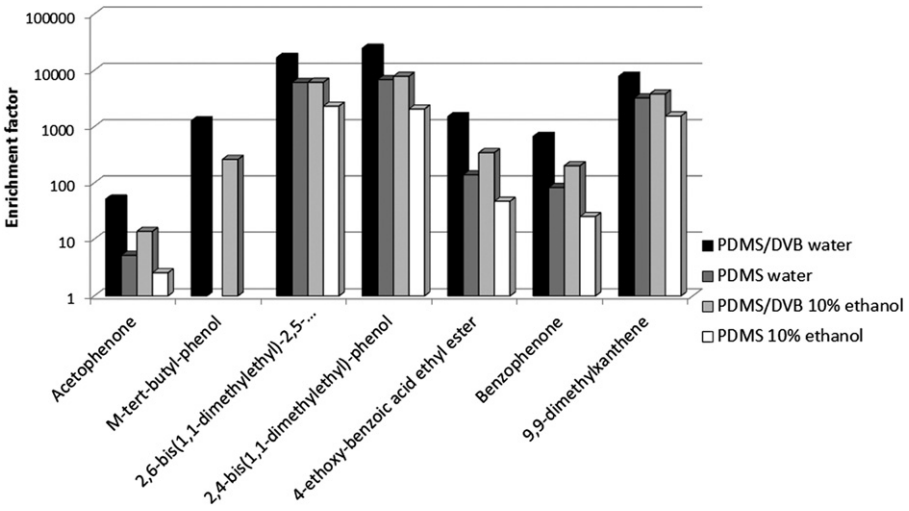



**Fig. 1.** Comparison of enrichment factors for SPME (PDMS/DVB and PDMS) of water and 10% ethanol standard solutions.

food simulants. This technique has for instance earlier been used to quantify 2-cyclopentylcyclopentanone in polyamide using SPME [12] and volatile phenols from wine [13]. The method also works during non-equilibrium conditions [14]. The sample and standard vials were extracted by SPME and the analytes were injected into GC–MS four consecutive times according to the procedure explained above. The peak areas showed an exponential decline with each consecutive extraction according to the theory and could therefore be fitted to a linear regression equation (log (peak area) against extraction number) and the slopes for each compound, $q'$, could be obtained. The area sums, corresponding to the total amounts of analytes in the sample, could then be calculated by summation of the individual areas, according to the equation [11]:

$$A_s = \sum_{i=1}^{\infty} A_i = \frac{A_1}{1 - e^{q'}} \quad (1)$$

where $A_1$ is the area for the first extraction and $A_i$ the area for the i:th extraction. The migrated amounts were then calculated by

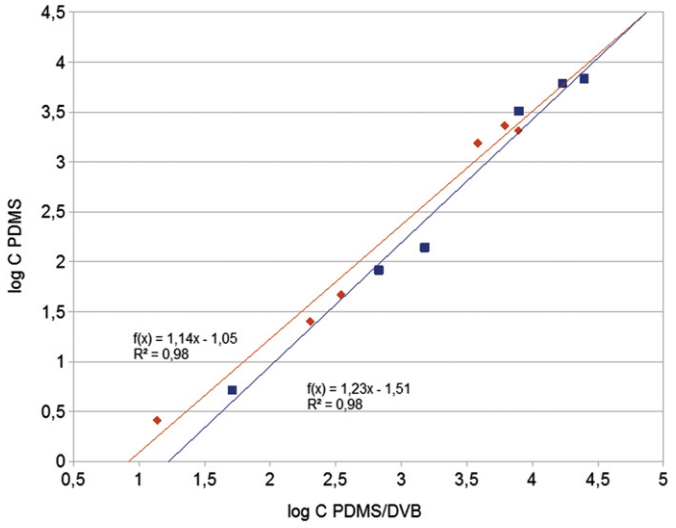



**Fig. 2.** Correlation between PDMS and PDMS/DVB extraction enrichment factors (log C) for extraction of compounds from 10% ethanol (◆) and water (■) standard solutions.

$$m_{\text{sample}} = \frac{A_{s,\text{sample}}}{A_{s,\text{standard}}} \times C_{\text{standard}} V_{\text{standard}} \quad (2)$$

where $m_{\text{sample}}$ is the mass of migrated analyte, $A_{s,\text{sample}}$ and $A_{s,\text{standard}}$ the area sums of the sample and standard, $C_{\text{standard}}$ the standard analyte concentration and $V_{\text{standard}}$ the standard solution volume. The standard solution was analysed in triplicate. The mean value of the three areas in the parallel standard extractions was used when determining the standard area sums. The migrated amounts in each duplicate FS sample were determined individually and averaged later.

## 3. Results and discussion

PC samples were heated by microwaves and conventionally in water, ethanol or isooctane to identify migrants and to evaluate the effect of microwave heating. To extract the analytes from the aqueous food simulants, the samples were subjected to headspace SPME before the GC–MS analysis. The identified migrants were also used as model compounds for partial least squares (PLS) analysis with the aim to find correlations between the extraction efficiency and analyte properties.

### 3.1. Compounds migrating from the PC container during microwave heating

A large number of compounds migrated from the PC samples during microwave heating in water, ethanol and isooctane. These compounds were identified and are listed in Table 1. Some of the listed compounds are known constituents of plastics that have been given specific migration limits (SML) by the EU [15]. Benzophenone is frequently found in packaging materials as it is a common photo-initiator for curing inks sometimes used in the printing of labels or stickers in contact with the packages. This might have come from the printed cardboard package the container was originally wrapped in M-tert-butyl-phenol has earlier been found after thermal degradation of PC [16]. 9,9-dimethylxanthene is a known impurity of commercial bisphenol A [17]. This compound has been shown to be influential in the yellowing of PC, and could be formed from the PC polymer by a Fries chain rearrangement reaction [18]. 2,4-bis(1,1-dimethylethyl)-phenol and 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione are degradation products from antioxidants Irgafos 168 and Irganox 1010 antioxidants [2] and were

**Table 3**
PLS model results and predictor properties. Property values were obtained from the Scifinder database.

| | | | | |
|---|---|---|---|---|
| R2Y(cum) | 0.94 | | | |
| Q2(cum) | 0.85 | | | |
| Predictors | log $K_{ow}$ | $M_w$ | Vapour pressure | Water solubility |
| Range | 1.67–4.64 | 120–220 g/mol | 0.08–40 Pa | 0.002–2.4 g/L |
| Coefficient values | | | | |
| PDMS/DVB water | 0.78[a] | 0.59[a] | 0.41 | 0.04 |
| PDMS/DVB 10% ethanol | 0.72[a] | 0.55[a] | 0.32 | 0.00 |
| PDMS water | 0.67[a] | 0.52[a] | 0.30 | 0.00 |
| PDMS 10% ethanol | 0.66[a] | 0.51[a] | 0.29 | 0.00 |

[a] Significant factor.

included in this method development due to their common occurrence in plastics.

### 3.2. Method development

Table 1 shows the limits of detection (LOD) and limits of quantification (LOQ) and other values of interest that were determined after SPME of standard water and 10% ethanol solutions. The LOD and LOQ values were established at 3 and 10 times the *S*/*N* values, respectively. Repeatability values were established as the relative standard deviations of the areas (%) obtained from consecutively extracting three identical samples. Quite low detection limits were obtained, especially in the water solutions. For example, a detection limit for benzophenone was 3 ng/L, 4-ethoxybenzoic acid ethyl ester 1 ng/L and for 2,4-bis(1,1-dimethylethyl)-phenol 0.1 ng/L. The 10% ethanol standard solution had higher LOD's and LOQ's due to the increased solubility of the standards due to the presence of ethanol in the water. A similar trend of increasing detection limits was observed earlier for various pesticides as a function of increasing ethanol content in water [19].

Table 2 lists the concentrations of standard compounds in the solutions and the parameters (slopes, regression coefficients and area sums) that were obtained from the standard MHS-SPME extractions. The area sums of the integrated MS peaks were calculated by Equation (1), individually from each of the triplicate measurements and the mean values together with relative standard deviations are given in the table. For most compounds high $R^2$ values were obtained and in most cases the standard deviations in the slopes and area sums were relatively small.

To evaluate the efficiency of the SPME extraction technique, enrichment factors were calculated by the equation $S/E^*1/100$ where $S$ is the peak area obtained for the SPME extracted compounds and $E$ is the area obtained for the compounds by directly injecting 1 μL of a 100-fold more concentrated ethanol solution. An enrichment factor of 1 therefore means that the amount adsorbed in the SPME fibre would be equal to that in the drop of a directly injected solution having the same concentration of analytes. Although the extractions were not taken to full equilibrium, the factors should also correspond to the gas phase-fibre partition coefficients, but the relationship is more complex since the separation in this case is also governed by the gas–liquid distribution. Enrichment factors for the SPME extraction of standards from water and 10% ethanol can be seen in Fig. 1. They were in most cases very high, for example 25,000 for 2,4-bis(1,1-dimethylethyl)-phenol and 17,000 for 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione extracted from water by PDMS/DVB. The PDMS/DVB fibre gave higher values than the PDMS fibre for all the analytes. Fig. 1 shows that the enrichment factor's selectivity was similar between PDMS and PDMS/DVB and between water and 10% ethanol extractions, a relationship which is more clearly seen in Fig. 2 showing the correlation between the PDMS and PDMS/DVB enrichment factors for water and 10% ethanol extractions plotted in a log–log diagram. Correlation coefficients ($R^2$) of 0.98 for both water and 10% ethanol extraction were obtained.

#### 3.2.1. Partial least squares (PLS) regression analysis

To evaluate which property/properties of the analytes that were influential on the extraction efficiency, PLS regression analysis was conducted to find a model of the Y data (enrichment factors for SPME extracted standards) explained by the available X data; octanol-water partition coefficient (log $K_{ow}$), vapour pressure, molecular weight and water solubility of the migrant, using a 2-component model. The analysis was performed using the computer software SIMCA-P+ v. 12.0.1.0 by Umetrics AB. The data

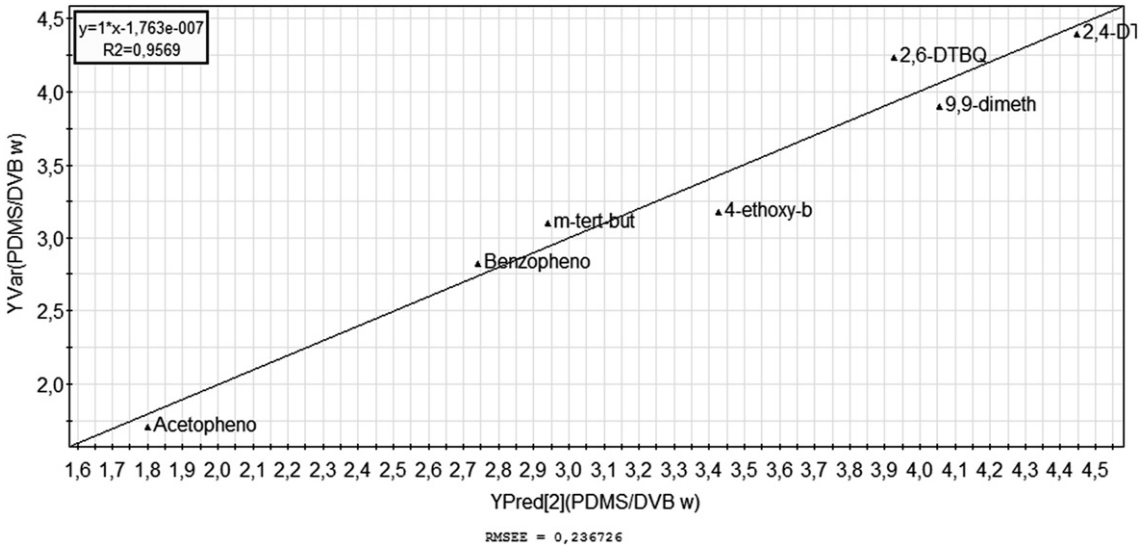



**Fig. 3.** Example of PLS model results for the enrichment factors after PDMS/DVB extraction of water. The observed values (vertical axis) are plotted against the predicted values (horizontal axis). Abbreviations: 2,4-DTB – 2,4-bis(1,1-dimethylethyl)-phenol, 2,6-DTBQ: 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione.

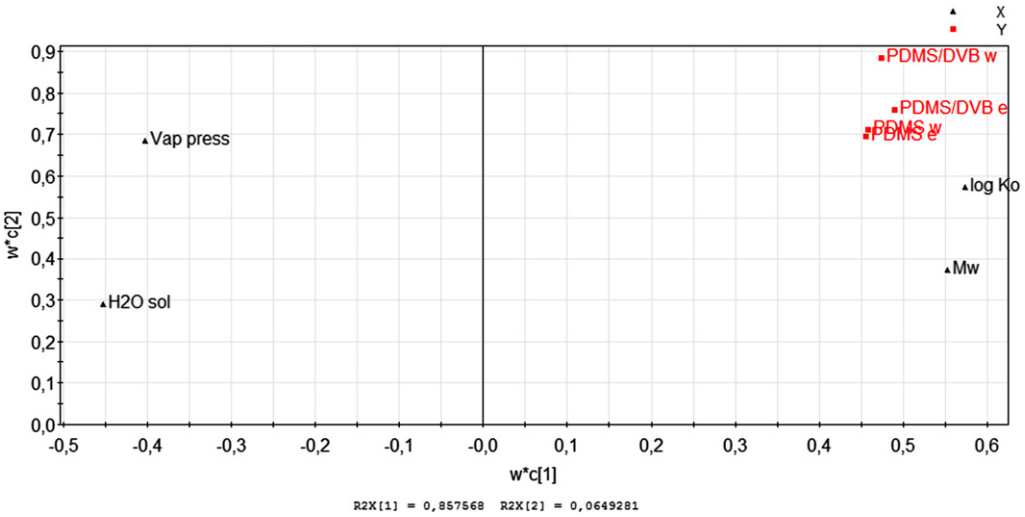



**Fig. 4.** PLS loading scatter plot showing the predictor weights of the first, most significant, component (horizontal axis) and the second component (vertical axis). Y variables are the enrichment factors for SPME (PDMS, PDMS/DVB) from water (w) and 10% ethanol (e).

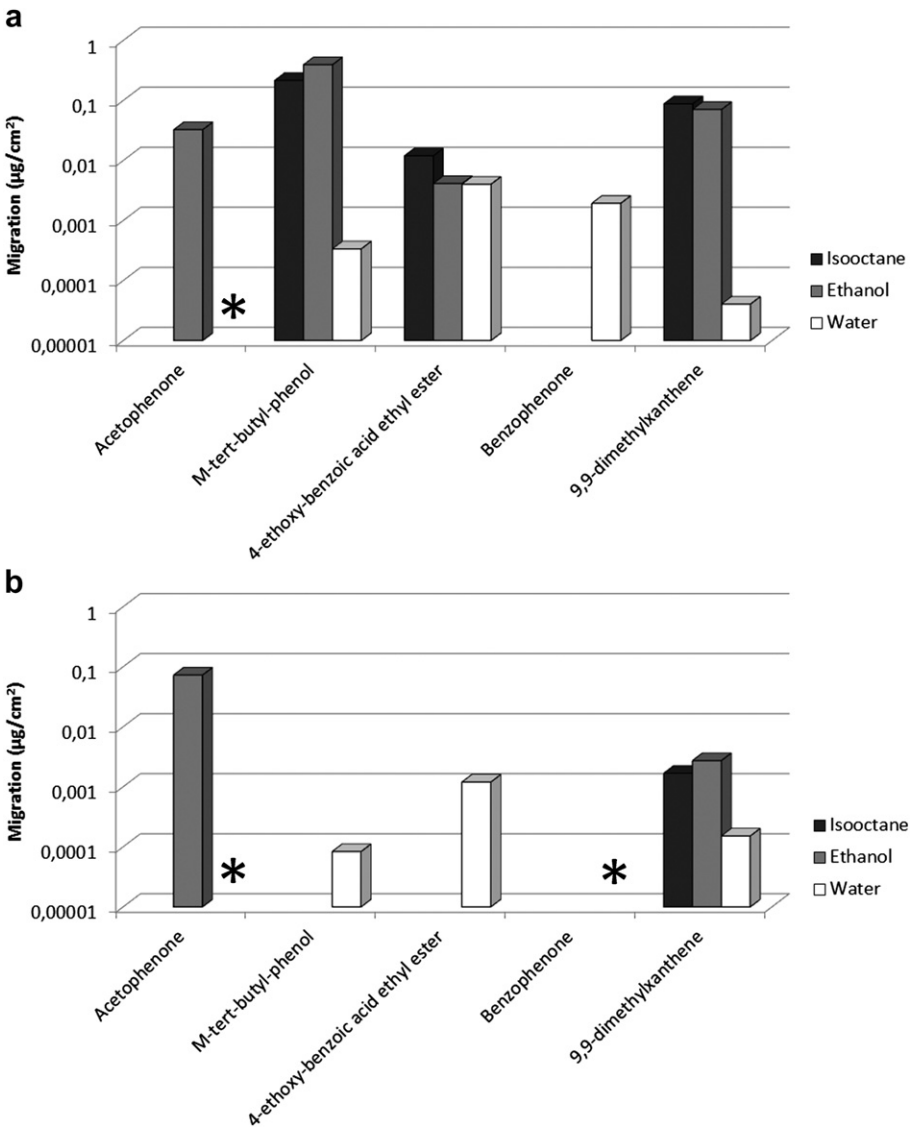



**Fig. 5.** Migration from PC to food simulants during (a) microwave and (b) conventional heating. $R^2$ range for MHS-SPME extraction from water samples: 0.92–1.00. (*) detected but not quantified due to low linearity of ln *A* vs extraction number.

was scaled and centred and the vapour pressure and water solubility was further log-transformed before fitting. The R2Y(cum) and Q2(cum) values of the resulting model and other parameters of interest can be seen in Table 3. The high R2Y(cum) and Q2(cum) indicate that the model was good. Both these values are a measure of fit and the R2Y(cum) shows how much of the Y data is explained by the model and the Q2(cum) shows how well the X and Y data correlate, that is how well the Y data could be predicted from the X data by the model. Both of these should be high for a good model.

The rather good correlation between the predicted and measured values for SPME extraction using PDMS/DVB fibre on water standard can be seen in Fig. 3. The figure looked similar for the other SPME fibre types for water and 10% ethanol. The relative weights of the input variables on the two resulting loading components 1 and 2 are shown in the loading scatter plot (Fig. 4) with component 1 (most significant) on the horizontal axis and component 2 on the vertical axis. It shows that the enrichment factors for the SPME fibre extractions and the log $K_{ow}$ are positively correlated in both components. The relative weights (coefficients) of the input variables and their significances with respect to extraction technique can also be seen in Table 3. In the model, the most significant variable predicting the SPME enrichment factors was log $K_{ow}$ as shown by the highest coefficient values. Other studies have found strong correlation between analyte liquid phase/fibre partition coefficients and log $K_{ow}$ values during immersion-SPME using for example PDMS and PA (polyacrylate) fibres [20,21]. The high coefficient values for log $K_{ow}$ during SPME extractions together with the good correlation between measured and predicted values shows that the correlation is strong even for headspace SPME. Vapour pressure also correlated positively with the SPME enrichment factors as seen in Table 3 but the coefficients were not significant. A model validation using 20 random permutations of the order of compounds in the original Y matrix while keeping the X matrix intact yielded in most cases much lower Q2(cum) values, indicating that the model was valid for the SPME extractions.

### 3.3. Low molecular weight compounds present in PC package before microwaving

Only one compound, 9,9-dimethylxanthene at the concentration of 11.3 ± 3.4 μg/g, was detected in the original PC package. No residual bisphenol A was detected, which means that the amount was lower than the detection limit of 0.4 μg/g. Other studies have found bisphenol A in commercial PC containers at levels ranging from 7 to 58 μg/g [22] or 10–177 μg/g [23].

### 3.4. Migration from PC samples to food simulants during microwave and conventional heating

The migration from PC samples during microwave- and conventional heating for 1 h at 80 °C showed that the compound found originally in the polymer, 9,9-dimethylxanthene and several other volatile aromatic substances migrated to the food simulants, isooctane, ethanol and water. The migrated amounts can be seen in Fig. 5. Fig. 6 shows a chromatogram obtained after SPME of PC migrants from water. During microwave heating the migration of individual compounds was in most cases larger than during conventional heating. Benzophenone was not detected after conventional heating but was found in the water after microwaving. 4-ethoxy-benzoic acid ethyl ester was detected in ethanol and isooctane after microwave heating but not after conventional heating in these food simulants. Migration of 9,9-dimethylxanthene was found both after microwave- and conventional heating but the migration during microwave heating was higher by a factor of almost 100. It should be noted that the migrated amount of 9,9-dimethylxanthene into ethanol and isooctane during conventional heating (around 0.001 μg/cm$^2$) was only a small fraction (1/1000) of the amount that was measured in the sample.

The migration into isooctane and ethanol was in most cases much larger than the migration into water, as expected from the analyte's relatively high hydrophobicities. When comparing the two fatty food simulants isooctane and ethanol, the migration of most compounds into both of them was similar. Acetophenone which migrated into ethanol but was not detected in isooctane was an exception. Sorption of the food simulant could also be influential on the migration, therefore the sorption was determined as the weight increases (% of the original weight) of the PC samples after the 1 h heating. The sorption values of isooctane, ethanol and water was 0.42, 0.48 and 0.29% after microwave heating and 0.22, 0.79 and 0.29 after conventional heating. These values are all quite low and would thus probably not explain the large differences in migration levels between microwave and conventionally heated samples. Benzophenone has an SML of 0.6 mg/kg (1 μg/cm$^2$) and 4-ethoxy-benzoic acid ethyl ester 3.6 mg/kg (6 μg/cm$^2$), specified as the highest amount allowed per kg of food in contact with the plastic under worst case or severe usage conditions. These SML values were converted to μg/cm$^2$ units from a valid conversion factor [15] (assuming 1 kg of food has contact with 6 dm$^2$ of plastic surface). The migration of these compounds was always much less than the SML values. Microwave heating of polycarbonate packaging in contact with food simulants, thus, considerably increased

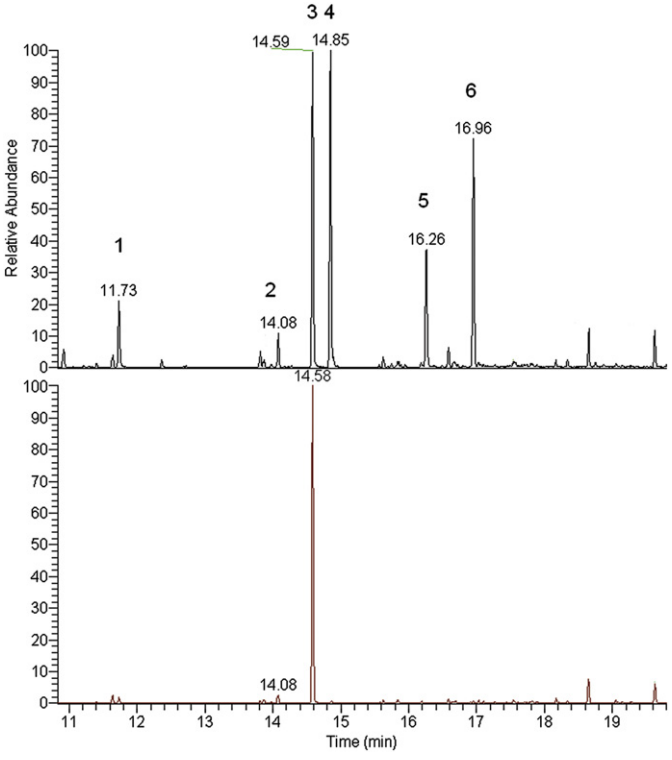
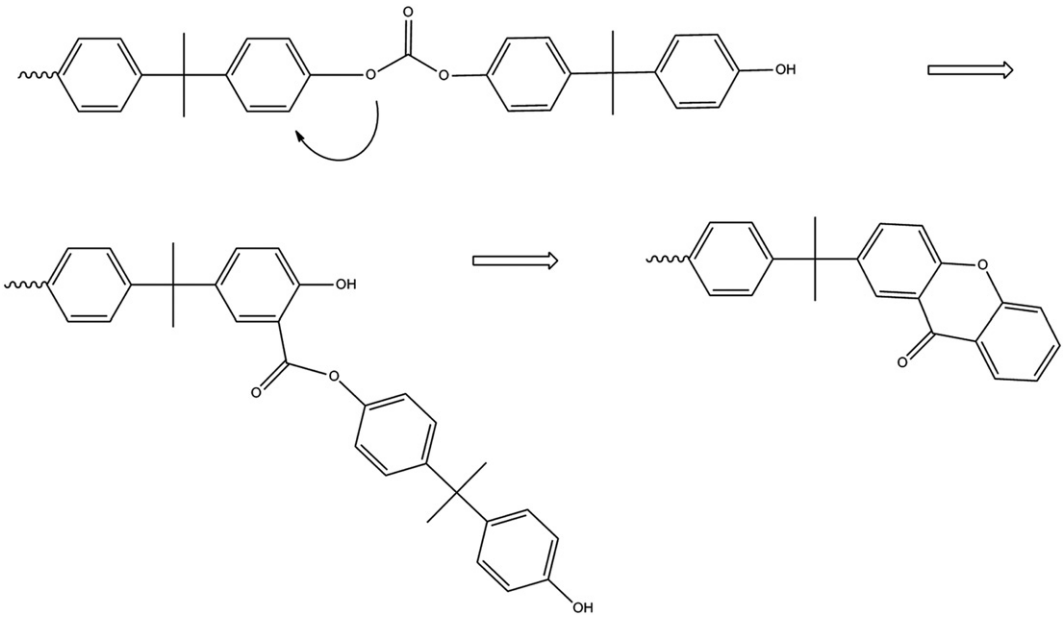



**Fig. 6.** Chromatogram (reconstructed base peak) showing the SPME extracted compounds that were detected in water after microwave heating with the immersed PC sample: 1: m-tert-butyl-phenol, 2: 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione, 3: 2,4-bis(1,1-dimethylethyl)-phenol, 4: 4-ethoxy-benzoic acid ethyl ester, 5: benzophenone, 6: 9,9-dimethylxanthene. Below is a chromatogram from a microwave heated blank water sample.




**Scheme 1.** 9,9-dimethylxanthene formation from Fries chain rearrangement reaction [18].

the migration of low molecular weight compounds from packaging to food simulants.

The diffusion coefficient for 9,9-dimethylxanthene in PC can also be determined using the expression $m/A = 2^{*}x_0{}^{*}\rho^{*}\sqrt{(Dt/\pi)}$ assuming high solubility of the migrant in the food simulant, where $m/A$ is the migration into the food simulant, expressed as migrated mass/area unit, $x_0$ is the initial weight fraction migrant, $\rho$ is the density of the PC sample, $D$ is the diffusion coefficient and $t$ is the migration time [24]. The diffusion coefficient for 9,9-dimethylxanthene during conventional heating using the expression above was calculated to be $1 \times 10^{-12}$ cm$^2$/s at 80 °C. The corresponding diffusion coefficient calculated with respect to the migrated amount of 9,9-dimethylxanthene during microwave heating was calculated to be $9 \times 10^{-9}$ cm$^2$/s, showing an increase by a factor of 9000 during microwave heating. This is an unrealistically large difference to be explained only by enhanced diffusion by the microwaves. For example, earlier work by Antonio et al. showed that the diffusion coefficient of cyclopentanone in an epoxy resin only approximately doubled during microwave heating [25]. One possible explanation to the larger migrated amount could instead be that degradation of the polymer chain by a Fries chain arrangement reaction (Scheme 1) [18] produced more 9,9-dimethylxanthene and resulted in the seemingly higher calculated diffusion coefficient. This explanation seems plausible, since we earlier observed that antioxidant additives degraded in polypropylene during microwave heating and not during conventional heating to the same temperature [2] showing that degradation reactions also can be induced or accelerated by microwaves in polymeric packaging.

## 4. Conclusions

The developed headspace SPME method enabled extraction and identification of low molecular weight compounds migrating from PC containers during microwave heating in different food simulants. The migrants could be detected at low detection limits and all the compounds could be simultaneously quantified by using MHS-SPME or direct injection depending on the food simulant used. As an example 4-ethoxy-benzoic acid ethyl ester, 2,4-bis(1,1-dimethylethyl)-phenol and benzophenone had detection limits of 1, 0.1 and 3 ng/L respectively in water when extracted by the PDMS/DVB fibre. The migration of 9,9-dimethylxanthene and m-tert-butyl-phenol increased significantly during microwave heating in ethanol and isooctane as compared to conventional heating at the same temperature, possibly due to polymer degradation. The SPME extraction efficiency for food package migrants could be predicted from the analyte properties by using the partial least squares (PLS) regression model. Log $K_{ow}$ was shown to be the most significant property for the extraction efficiency of headspace SPME from aqueous food simulants by PDMS and PDMS/DVB fibres. For most compounds this value can be easily obtained from the literature. The 65 μm PDMS/DVB fibre proved to be much more efficient than the 100 μm PDMS fibre, but both fibres showed similar adsorption selectivity with respect to migrant with high correlation between PDMS and PDMS/DVB enrichment factors ($R^2 = 0.98$ for both water and 10% ethanol extractions).

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