



# Emission pattern of semi-volatile organic compounds from recycled styrenic polymers using headspace solid-phase microextraction gas chromatography–mass spectrometry

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## ABSTRACT

The emission of low molecular weight compounds from recycled high-impact polystyrene (HIPS) has been investigated using headspace solid-phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS). Four released target analytes (styrene, benzaldehyde, acetophenone, and 2-phenylpropanal) were selected for the optimisation of the HS-SPME sampling procedure, by analysing operating parameters such as type of SPME fibre (polarity and operating mechanism), particle size, extraction temperature and time. 26 different compounds were identified to be released at different temperatures from recycled HIPS, including residues of polymerisation, oxidated derivatives of styrene, and additives. The type of SPME fibre employed in the sampling procedure affected the detection of emitted components. An adsorptive fibre such as carbowax/polydimethylsiloxane (CAR/PDMS fibre) offered good selectivity for both non-polar and polar volatile compounds at lower temperatures; higher temperatures result in interferences from less-volatile released compounds. An absorptive fibre as polydimethylsiloxane (PDMS) fibre is suitable for the detection of less-volatile non-polar molecules at higher temperatures. The nature and relative amount of the emitted compounds increased with higher exposure temperature and smaller polymeric particle size. HS-SPME proves to be a suitable technique for screening the emission of semi-volatile organic compounds (SVOCs) from polymeric materials; reliable quantification of the content of target analytes in recycled HIPS is however difficult due to the complex mass-transfer processes involved, matrix effects, and the difficulties in equilibrating the analytical system.

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## 1. Introduction

Emission of volatile (VOCs) and semi-volatile organic compounds (SVOCs) from polymeric materials is a matter of increasing concern, in terms of their environmental hazard and their possible impact on indoor air quality and human health. These emissions may occur under every step of the life cycle of the polymer product, including processing of the plastic material at high temperatures, during their service life in the application they were intended for, or during further waste management processes. Polymers may retain in their structure a wide range of low molecular weight compounds, either as residues from the synthesis process (residues of polymerisation, traces of initiators, catalysts, and solvents) or intentionally introduced in the manufacturing process (e.g. additives such as antioxidants, stabilisers, plasticisers, and flame retardants). Other organic compounds may be formed during degradation processes of the polymeric matrix and the additives under the life cycle of

the plastic materials. In the case of recycled plastics, low molecular weight compounds may even be absorbed from the surrounding environment during the previous life [1,2]. The presence and emission of contaminants and other small molecules in recycled plastics is a matter of fundamental importance, which hinders the application of recyclates in new applications (e.g. food contact applications). This is one of the key parameters that have been identified for the quality assessment and the improved use of recycled plastics [3,4]. It is therefore of great importance to develop fast analytical methods to detect the possible release of these volatile compounds from recycled plastics and to understand under which conditions these compounds are emitted.

The emission of VOCs during the processing operations of a wide range of plastic materials, including polyolefins and engineering plastics has been widely studied [5]. Emission of more than 500 different nitrogen-containing VOCs and SVOCs under thermal degradation of different plastics at relatively low temperatures has been recently reported [6]. Increased concern has arisen in the recent years for the bioaccumulation of polymeric additives as brominated flame retardants in the environment and human tissue [7]; interesting results about the emissions of these addi-

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tives in recycling plants of electronic waste have been provided by Thuresson et al. [8,9].

Different analytical procedures have been reported for the monitoring of volatile emissions from plastics. These techniques normally involve a sampling step, which is carried out by headspace extraction, prior to chromatographic determination. Solid-phase microextraction (SPME) is a relatively new extraction technique introduced by Arthur and Pawliszyn [10] in the early 1990s that has gained further attention for its capability to extract a wide variety of analytes from diverse matrices. Headspace solid-phase microextraction (HS-SPME) has been recently applied for the extraction of low molecular weight compounds released from polymeric matrices [3,10–23]. Identification of VOCs in multilayer packaging materials using headspace solid-phase microextraction gas chromatography–mass spectrometry (HS-SPME–GC–MS) was proposed by Ezquerro et al. early in 2002 [22]; a method for the quantification of the release of these compounds in polymeric multilayer packaging was as well proposed by the same research group using multiple HS-SPME [23]. Different VOCs released from expanded polystyrene have been screened using this technique [19,20]. Odorous compounds emitted from biofibre–polymeric composites [11] and magnetic tape coatings [17] have been identified. HS-SPME has also proven to be a valuable tool for monitoring degradation processes in polymeric materials [12,21] and for the quality control of recycled plastics [3,16]. However, HS-SPME determination of volatiles released from polymeric materials is a very complex analytical process, which requires optimisation of the different operational procedures for successful quantitative application. Polymeric matrixes are not inert solid matrixes and their diffusive and structural properties may vary with different operational parameters such as extraction temperature and particle size.

In a previous study, different low molecular weight compounds were detected in recycled high-impact polystyrene (HIPS), including residues of polymerisation (styrene monomer, dimers, and trimers) and degradation products (oxidated derivatives of styrene) [4]. This article aims to offer a deeper knowledge about the emitting pattern of VOCs and SVOCs from recycled HIPS under various conditions using HS-SPME prior to GC–MS detection. The influence of operational parameters (type of fibre, extraction temperature and time, particle size) has been investigated for the determination of four selected target analytes (styrene, benzaldehyde, acetophenone, and 2-phenylpropanal) that were previously reported to be present in recycled HIPS [4]; these target analytes are interesting for quality purposes in recycled HIPS because they are related to the presence of residues of polymerisation (styrene monomer) and the degree of degradation (benzaldehyde, acetophenone, and 2-phenylpropanal). This study will cast some light on the complex mechanistic mass-transfer processes involved during the release and HS-SPME detection of low molecular weight compounds from polymeric materials.

## 2. Experimental

### 2.1. Materials and sample preparation

Styrene (analytical standard, purity 99.8%, CAS number 100-42-5) purchased from Riedel-de Haën (Seelze, Germany), benzaldehyde (puriss., p.a., purity 99.5%, CAS number 100-52-7), acetophenone (puriss., p.a., standard for GC, purity 99.5%, CAS number 98-86-2) both provided by Fluka (Buchs, Switzerland), and 2-phenylpropanal (also known as 2-phenylpropionaldehyde, purity 98%, CAS number 93-53-8) purchased from Aldrich (Stockholm, Sweden) were chosen as target analytes for the determination of SVOCs in recycled styrenic polymers. Table 1 shows the physical properties of the selected target analytes, which will

influence their recovery during HS-SPME. 4-Methylstyrene (purity 99%) from Fluka was used as internal standard. Seasand (SiO<sub>2</sub>, suitable for chromatography, CAS number 14808-60-7) provided by Sigma–Aldrich (Stockholm, Sweden) was employed as inert solid media for method development.

Spiked seasand with standard solutions of the target analytes and the internal standard were employed for SPME fibre selection and development of the HS-SPME–GC–MS method. HS-SPME vials containing 10 g of seasand were spiked with 10 mL of a standard solution containing the target analytes (1 µL/mL of styrene, 0.2 µL/mL of acetophenone, 0.2 µL/mL of benzaldehyde and 0.2 µL/mL of 2-phenylpropanal) in methanol (HPLC grade) from Fisher Scientifics (Pittsburgh, PA, USA) and 100 µL of an internal standard solution (0.2 µL/mL in methanol). The vials were then sealed with 20 mm magnetic caps, 8 mm centre hole with silicone blue/PTFE white obtained from Supelco (Bellefonte, PA, USA) and then kept refrigerated until use.

Recycled high-impact polystyrene (HIPS) from yoghurt packaging applications in granules, provided from Acteco (Alcoy, Spain), was employed for the method optimisation in recycled styrenic polymeric samples. To analyse the influence of particle size on the emission of volatiles from recycled HIPS using HS-SPME, the polymeric granules (5 mm average size) were further grinded under cryogenic conditions into powder (1 µm average size) using a rotary mill with liquid nitrogen. HS-SPME vials were prepared with 9 g of seasand spiked with 100 µL of internal standard solution (0.2 µL/mL in methanol) and 1 g of recycled HIPS (either in granule or powder form). The vials were sealed with 20 mm magnetic caps and then kept refrigerated until use.

### 2.2. HS-SPME

HS-SPME sampling was performed using a multipurpose sampler MPS 2 for GC purchased from Gerstel (Mülheim an der Ruhr, Germany). Three different fibres for autosampler holder, purchased from Supelco (Bellefonte, PA, USA), were used: 100 µm polydimethylsiloxane (PDMS), 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and 75 µm carbowax/polydimethylsiloxane (CAR/PDMS). PDMS and PDMS/DVB fibres were conditioned at 250 °C for 30 min and CAR/PDMS was conditioned at 300 °C for 90 min before use. The extraction protocol was as follows: the vials were pre-conditioned at the extraction temperature for 1 min; the extraction was performed at selected times and temperatures under agitation; finally, the fibres were desorbed in the GC injector during 5 min. Each sample extraction was carried out in triplicate, to diminish the possible experimental errors and to analyse the deviation in the results.

For fibre selection and the development of the HS-SPME–GC–MS method, spiked seasand with standard solution of the target analytes and internal standard were analysed for different extraction times (5, 10, 20, and 30 min), extraction temperatures (30, 45, and 60 °C) and types of fibre coating (PDMS, PDMS/DVB, and CAR/PDMS). CAR/PDMS and PDMS gave the highest recoveries for all the target analytes, and they were thus selected for the extraction of volatiles from recycled HIPS.

To analyse the emitting pattern of low molecular weight from recycled styrenic polymers using HS-SPME, vials containing seasand with internal solution and recycled HIPS (either in granules or powder) were extracted using CAR/PDMS and PDMS fibres for different times (10, 20, 30, and 45 min) and extraction temperatures (60, 75, and 90 °C).

### 2.3. GC–MS

The GC–MS analyses of the HS-SPME extracts were performed on a FinniganMAT GCQ (Thermo, San Jose, CA, USA) equipped with

**Table 1**  
Physical properties of the target analytes.

	Styrene	Benzaldehyde	Acetophenone	2-Phenylpropanal
CAS-nr.	100-42-5	100-52-7	98-86-2	93-53-8
Molecular weight (g/mol)	104,14	106,13	120,16	134,18
Boiling point (°C)	145,2	179,0	201,7	205,0
Melting point (°C)	-30,6	-26,0	19,7	< -60
Polarity	-	-	+	++

a wall-coated fused silica, low bleed CP-sil 5CB column (dimensions 0.25 mm × 30 m × 0.25 μm) from Varian (Lake Forest, CA, USA). The injection temperature was held at 200 °C. The chromatographic separation in the column was achieved using a temperature program as follows during a total time of 25 min: hold at 40 °C during 2 min; increase until 250 °C at 10 °C/min; and final isothermal step during 2 min. The Helium (scientific grade purity) from AGA Gas AB (Lidingö, Sweden) at a constant flow of 0.8 mL min<sup>-1</sup> was employed as carrier gas. The detection was carried out by ion-trap mass spectrometry. Electron ionisation was employed with an ion source temperature of 280 °C. Mass spectra were collected in the full scan mode (35–500 *m/z* at a scan rate of 2 spectra s<sup>-1</sup>). Compound identification was performed either by injection of analytical standards and by comparison of the obtained spectra with the NIST MS search 2.0 database.

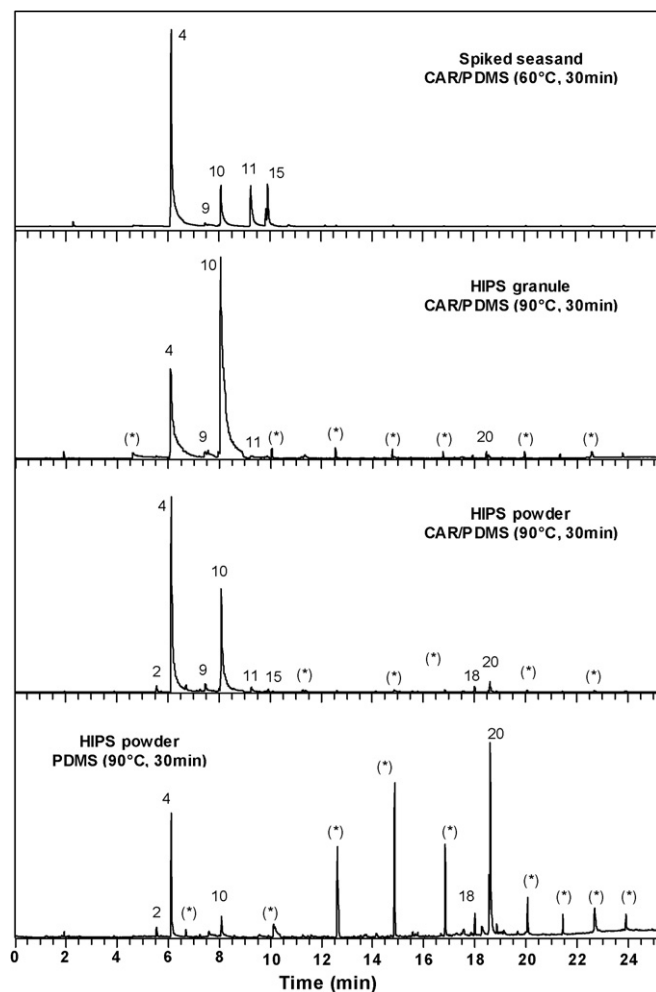
### 3. Results and discussion

#### 3.1. Initial optimisation of HS-SPME parameters for the analysis of target analytes in static headspace

Prior to the analysis of volatiles and semi-volatiles emitted from recycled polymers, optimisation of different SPME parameters was performed for the extraction of the target analytes (styrene, benzaldehyde, acetophenone, and 2-phenylpropanal) from spiked seasand; Fig. 1 shows a chromatogram of the extracted target analytes from the spiked samples. The identified peaks have been numbered in order of elution and displayed in Table 2; the peaks marked with asterisks correspond with cyclic oligomeric derivatives of dimethylsiloxane, formed by thermal degradation of the septa from the extraction vial, which do not interfere with the extracted analytes. Three different SPME fibres were considered according to the volatility and polarity of the analytes: PDMS (100 μm), PDMS/DVB (65 μm), and CAR/PDMS (75 μm). The main parameters that determine the affinity between fibres and analytes are the fibre coating polarity (polar, non-polar, or bi-polar) and the mechanism of analyte retention in the fibre coating (adsorption and/or absorption). PDMS fibre has a non-polar coating and its main extraction mechanism is absorption. On the other hand, both CAR/PDMS and PDMS/DVB have mixed polar/non-polar coatings, which extract analytes primarily via adsorption mechanisms. Different extraction temperatures (30, 45, and 60 °C) and extraction times (5, 10, 20, and 30 min) were also evaluated for optimisation.

The equilibrium curves for the target analytes using the different fibres and extraction temperatures are shown in Fig. 2. CAR/PDMS fibre provided larger extracted amounts compared to PDMS and PDMS/DVB for the target analytes at almost each extraction conditions. However, tailing of the chromatographic peaks obtained by CAR/PDMS extraction was observed for all the analytes (Fig. 1), due to hindered desorption of the analytes from the fibre in the injector. In general, the PDMS/DVB fibre gave the lowest extraction values for the analytes due to their relatively low volatility and polarity. The influence of temperature on the extraction amounts is different depending on the type of analyte and the type of fibre. Higher temperatures enhance the transport of analytes into the headspace phase, increasing their concen-

tration in that phase. On the other hand, the coating/headspace distribution coefficient for the analyte decreases by increasing temperature, especially at high temperature [24]. For absorption fibres (e.g. PDMS), the extracted amount of all the target analytes increases proportionally to their concentration in the headspace phase, as it can be observed for the four target analytes (styrene, benzaldehyde, acetophenone and 2-phenylpropanal). However, the target analytes showed different behaviour with temperature when extracted with CAR/PDMS fibre; styrene and benzaldehyde showed a decrease in the amount of extracted analyte, whereas for acetophenone and 2-phenylpropanal an increase in the extraction temperature led to an increase of the extracted analyte. This



**Fig. 1.** Chromatographic pattern of the extracted analytes using HS-SPME: (a) spiked seasand using CAR/PDMS fibre at 60 °C during 30 min; (b) recycled HIPS granules using CAR/PDMS fibre at 90 °C during 30 min; (c) recycled HIPS powder using CAR/PDMS fibre at 90 °C during 30 min; (d) recycled HIPS powder using PDMS fibre at 90 °C during 30 min. Note: Identified peaks have been labelled in order of elution according to Table 2. Peaks with asterisk (\*) correspond with cyclic oligomeric derivatives of dimethylsiloxane formed by thermal degradation of the septa from the extraction vial that do not interfere with the analytes.

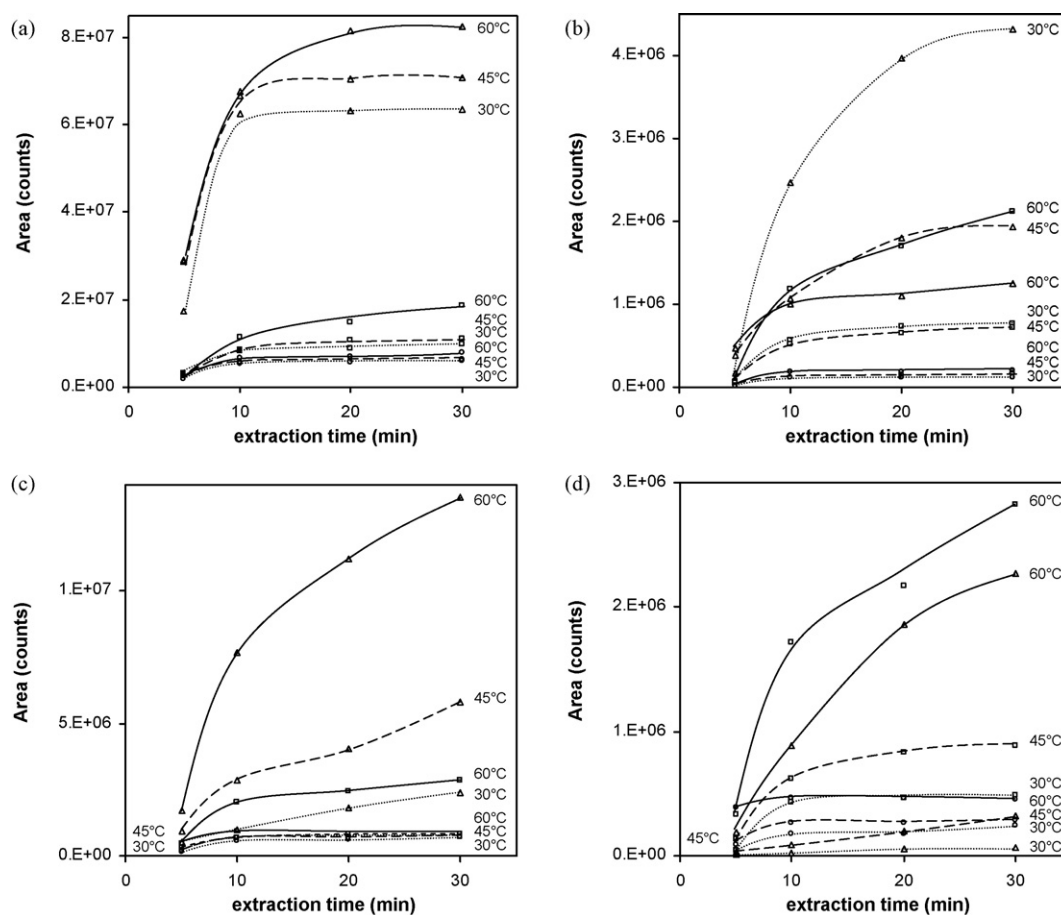
**Table 2**  
Identification of the released low molecular weight compounds from recycled HIPS using HS-SPME under different conditions.

Peak nr.	Proposed compound	R.T. (min)	Area counts ( $\times 10^3$ )															
			CAR/PDMS fibre									PDMS fibre						
			HIPS granules					HIPS powder				HIPS granules			HIPS powder			
			30 °C	45 °C	60 °C	75 °C	90 °C	30 °C	45 °C	60 °C	75 °C	90 °C	60 °C	75 °C	90 °C	60 °C	75 °C	90 °C
1	Toluene <sup>b</sup>	3.90	4	4	3	6	9	50	53	51	311	84	–	–	–	5	6	7
2	Ethylbenzene <sup>b</sup>	5.55	–	–	10	30	49	187	188	92	1646	601	–	–	–	34	38	50
3	Xylene <sup>b</sup>	5.71	–	–	–	15	33	–	–	85	406	146	–	–	–	5	6	6
4	Styrene <sup>a</sup>	6.13	2726	3039	5307	9843	9146	16190	16505	15145	88057	32934	111	170	218	537	719	819
5	Cumene <sup>b</sup>	6.70	–	–	–	–	–	–	–	–	998	235	–	7	11	25	31	36
6	Prop-1-en-2-ylbenzene <sup>b</sup>	7.11	–	–	–	–	–	–	–	–	304	67	–	–	–	–	–	3
7	Propylbenzene <sup>b</sup>	7.24	–	–	–	–	–	–	–	–	730	207	–	–	–	7	9	13
8	1-Ethyl-4-methyl-benzene <sup>b</sup>	7.36	–	–	–	–	–	–	–	–	167	42	–	–	–	–	–	2
9	Benzaldehyde <sup>a</sup>	7.45	49	59	82	194	212	651	724	763	2430	829	–	–	–	–	6	5
10	1-Ethenyl-4-methyl-benzene <sup>a</sup>	8.09	Internal standard (I.S.)															
11	Acetophenone <sup>a</sup>	9.26	4	16	21	68	90	216	24	35	826	558	–	–	–	–	–	1
12	1-Phenylethanol <sup>b</sup>	9.57	–	–	–	–	–	–	–	–	–	39	–	–	–	–	–	–
13	1,3-Diethylbenzene <sup>b</sup>	9.76	–	–	–	–	–	–	–	–	43	21	–	–	–	–	–	–
14	2-(4-Methylphenyl)propan-1-ol <sup>b</sup>	9.84	–	–	–	–	26	–	–	–	40	49	–	–	–	–	–	–
15	2-Phenylpropanal <sup>a</sup>	9.91	–	–	11	14	47	38	19	30	311	234	–	–	–	–	5	2
16	2,6-Ditert-butylcyclohexa-2,5-diene-1,4-dione <sup>b</sup>	15.03	–	–	–	–	–	–	–	–	35	53	–	–	–	–	10	8
17	4-Methyl-2,6-ditert-butylphenol <sup>b</sup>	15.53	–	–	–	7	13	–	–	–	64	63	12	12	13	12	34	30
18	(2-Phenylcyclobutyl)benzene (cis-) <sup>b,c</sup>	17.96	–	–	–	3	36	–	–	–	56	288	18	45	51	25	84	140
19	3-Phenylpropylbenzene <sup>b</sup>	18.24	–	–	–	–	–	–	–	–	–	–	5	22	74	7	71	200
20	(2-Phenylcyclobutyl)benzene (trans-) <sup>b,c</sup>	18.56	–	–	–	1	84	–	–	–	119	673	124	398	669	159	738	1627
21	1-Phenyltetralin <sup>b</sup>	18.81	–	–	–	–	5	–	–	–	12	56	7	17	32	7	35	78
22	1,2-Dihydro-1-phenylnaphthalene <sup>b,c</sup>	19.08	–	–	–	–	–	–	–	–	–	–	–	–	–	–	9	30
23	1-Phenyl-4-(1-phenylethyl)-tetralin diastereomers <sup>c</sup>	21.63	–	–	–	–	–	–	–	–	–	–	–	–	59	–	30	123
24		22.06	–	–	–	–	–	–	–	–	–	–	–	–	112	–	38	172
25		22.16	–	–	–	–	–	–	–	–	–	–	–	–	19	–	8	38
26		22.45	–	–	–	–	–	–	–	–	–	–	–	–	17	–	16	67

<sup>a</sup> Identification by injection of standard substances.

<sup>b</sup> Proposed identification by comparison to the NIST database.

<sup>c</sup> Proposed identification through Ref. [35].



**Fig. 2.** Equilibration curves from the static HS-SPME extraction of the target analytes from spiked seasand. Influence of different operational parameters. Type of SPME fibre: (Δ) PDMS; (□) CAR/PDMS; (○) PDMS/DVB. Temperatures: (○) 30°C; (□) 45°C; (Δ) 60°C. Target analytes: (a) styrene; (b) benzaldehyde; (c) acetophenone; (d) 2-phenylpropanal.

can be explained by the different extraction mechanism for porous fibres such as CAR/PDMS, which operate by an adsorption-based mechanism; at higher temperatures, the more volatile analytes (e.g. styrene and benzaldehyde) have to compete with the less-volatile analytes (e.g. acetophenone and 2-phenylpropanal) due to limited adsorptive surface, leading to the displacement of the more volatile analytes by the less-volatile analytes as their concentration increases, in agreement with the classical adsorption mechanism theory [25]. The time required to reach equilibrium for the different analytes depends on the type of fibre and the extraction temperature. Both PDMS and PDMS/DVB fibre reach equilibrium faster than CAR/PDMS; theoretically equilibrium cannot be reached in carbowax fibres, due to the small pore size that causes capillary condensation to occur [25]. The extraction temperature also affects reproducibility; higher extraction temperatures result in less reproducible results, especially for adsorptive fibres as CAR/PDMS. In general, CAR/PDMS fibre offers the best extraction rates for the most volatile analytes with moderate extraction temperatures, whereas when trying to extract non-polar semi-volatile compounds in the headspace, the use of an absorptive fibre coating at higher temperatures such as PDMS gives rise to better results.

### 3.2. HS-SPME method development for the determination of volatiles emitted from recycled HIPS

Diffusion of low molecular compounds from polymeric materials is a complex phenomenon, due to the complex interrelations between solute mobility and polymeric macromolecular relax-

ations. Material morphology and architecture, e.g. whether the polymer is elastomeric, crosslinked, amorphous, or semicrystalline, plays an important role on their transport properties [26,27]. A basic kinetic model for the emission of low molecular weight compounds from polymers into the environment involves three consecutive steps: (i) diffusion of the analytes from the core of polymer particles to their surface; (ii) transfer of the analytes from the polymer surface to the solvent boundary layer; (iii) mass transfer of the analytes into the surrounding environment. This complex diffusion processes must be considered in addition to the mechanisms involved in HS-SPME for the identification of volatile organic compounds evolved from recycled styrenic polymers. Fig. 3 summarises graphically the different steps involved in this analytical problem.

PDMS and CAR/PDMS fibres were selected for the detection of low molecular weight compounds emitted from recycled HIPS at different temperatures and times, using the experience obtained from the initial study of SPME extraction of the target analytes from spiked seasand. The influence of the polymeric particle size on the emission and detection of volatiles was also taken into account; polymer granules (5 mm average size) and polymer powder (1 μm average size) were thus analysed. A wide range of organic low molecular weight compounds emitted from recycled HIPS have been extracted and identified using HS-SPME coupled with GC-MS under different conditions. As an example, Fig. 1 shows the chromatograms of the compounds emitted from recycled HIPS in granule and powder form after 30 min extraction at 90°C using CAR/PDMS and

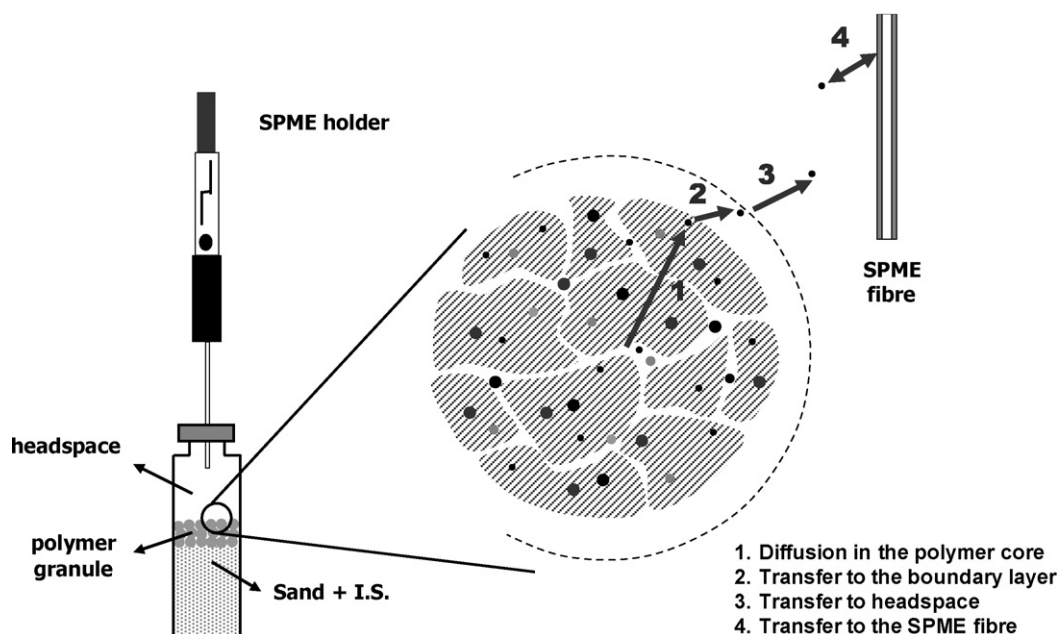


Fig. 3. Basic kinetic steps involved in the emission of low molecular weight compounds from polymers into the environment and their detection using SPME.

PDMS fibres. Styrene monomer (peak 4), as expected, proves to be the most prominent compound emitted from HIPS. Other aromatic volatile compounds such as toluene, ethylbenzene, xylenes, prop-1-en-2-ylbenzene (also known as  $\alpha$ -methylstyrene), 1-ethyl-2-methyl-benzene, propylbenzene 1,3-diethylbenzene, 1-methylethylbenzene are as well released from recycled HIPS at different temperatures; these compounds have been reported to be present as residues of polymerisation and/or released from polystyrene and other styrenic plastics [4,19,20,28–31]. Different oxidated derivatives from styrene such as benzaldehyde, acetophenone, 2-phenylpropanal, and 1-phenylethanol, have been as well identified using HS-SPME-GC-MS. These compounds have been reported to be present in recycled HIPS in a previous work [4];

their formation has been attributed to the oxidation of polystyrene [32,33], suggesting the fact that recycled HIPS has been subjected to degradative processes during its previous life. Different released compounds from HIPS may proceed from different additives incorporated in the plastic materials; 4-methyl-2,6-ditert-butyl-phenol (also known as butylated hydroxytoluene or BHT) is a commonly employed antioxidant in styrenic polymers [4,34] and 2,6-ditert-butylcyclohexa-2,5-diene-1,4-dione (also known as 2,6-di-tert-butyl-p-benzoquinone) is an oxidation product from different phenolic antioxidants [34,35]. Semi-volatile compounds, such as diverse styrenic dimers, have been also identified to be released from recycled HIPS, mainly at higher temperatures; compounds such as cis- and trans-(2-phenylcyclobutyl)benzene

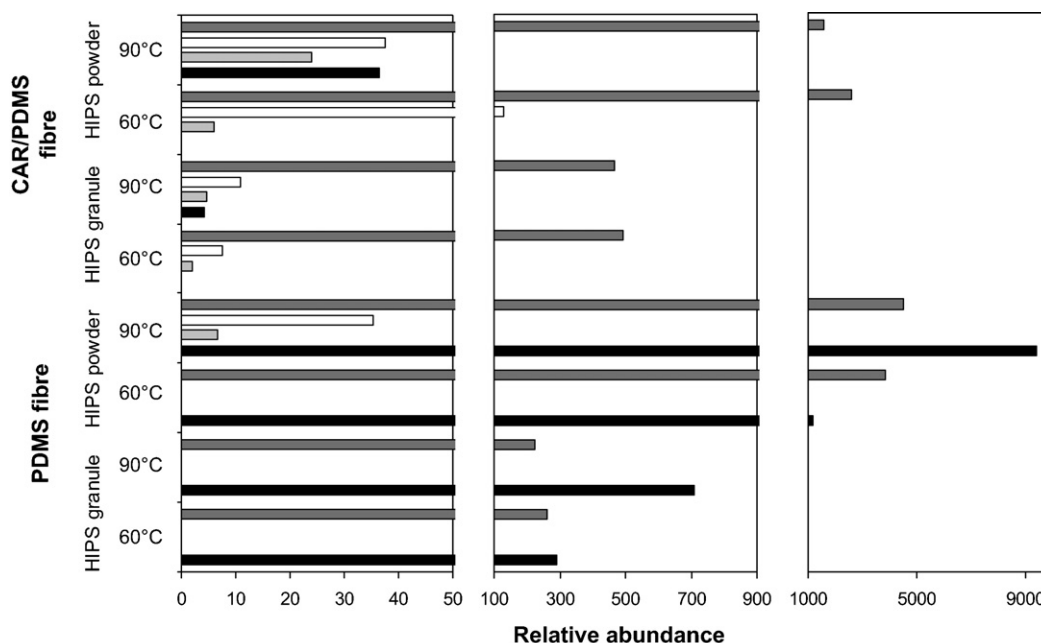


Fig. 4. Comparison of SPME extraction efficiency of released low molecular weight compounds from recycled HIPS using CAR/PDMS and PDMS fibres at different conditions: (■) styrene; (□) benzaldehyde; (▒) acetophenone; (■) styrene dimer (trans (2-phenylcyclobutyl)benzene).

isomers, and 1-phenyltetralin have been reported to be produced by side reactions during the thermal polymerisation process of styrene [36–39], so their presence in recycled HIPS may be due to the fact that they are retained in the polymeric matrix as polymerisation residues. The nature and relative abundance of the identified emitted compounds from recycled HIPS differed depending on the type of fibre and the temperature. Table 2 lists the relative abundance of the identified compounds released from granule and powder recycled HIPS at different temperatures, using CAR/PDMS and PDMS fibres; the influence of the type of fibre, the temperature, and the polymeric structure and particle size on the emitting pattern will be discussed in the following sections.

### 3.2.1. Influence of type of fibre on the detection of emitted SVOCs from recycled HIPS

Fig. 4 compares the extraction efficiency of PDMS and CAR/PDMS fibres for 4 different released compounds from granule and powder HIPS with different polarity and volatility (styrene, benzaldehyde, acetophenone, and a styrene dimer—*trans* (2-phenylcyclobutyl)benzene—) under different temperatures. In general, CAR/PDMS fibre gives the highest signal for a wide range of emitted compounds from recycled HIPS with different polarity and volatility at the different temperatures, due to its combination of absorptive and adsorptive coating materials. However, for non-polar less-volatile analytes such as styrene dimers, PDMS offers better extraction efficiency. CAR/PDMS fibre was able to detect some non-polar volatile at lower extraction temperatures of 30 and 45 °C. PDMS fibre was tested at these low temperatures, but no satisfactory results were obtained. At moderate extraction temperatures of 60–75 °C, CAR/PDMS fibre offers excellent sensitivity for both non-polar and more polar volatile compounds. However, at higher extraction temperatures (90 °C), the signal for volatile compounds as styrene, ethylbenzene, toluene, or xylene decreases significantly when compared to the same emitting pattern at 75 °C (Table 2). This distorting effect may be caused by the release of bigger molecules from the polymer, such as different styrene dimers, which adsorb preferentially in the small pores of the CAR/PDMS fibre, and thus displacing smaller volatile molecules. This effect may give problems when quantification of the different released compounds may be attempted, due to the fact that porous fibres such as CAR/PDMS are especially sensitive to matrix composition interferences and the concentration linearity range can be easily surpassed [25]. PDMS fibre shows, on the other hand, better results for the detection of less-volatile non-polar molecules at higher temperatures, including bigger molecules as styrene dimers (especially *trans* (2-phenylcyclobutyl)benzene) and additives such as butylated hydroxytoluene (BHT) (Fig. 4, Table 2). In addition, different styrene trimers such as the 4 diastereomers of 1-phenyl-4-(1-phenylethyl)-tetralin, could be only detected with PDMS fibre. PDMS gives, however, extremely low response for more polar compounds such as oxidated derivatives of styrene containing carbonyl or hydroxyl moieties, due to the non-polar nature of the silicone coating; CAR/PDMS is the fibre of choice in this specific case.

### 3.2.2. Influence of extraction temperature on the emission pattern

Temperature has a large influence on the release of low molecular weight compounds from recycled HIPS and their extraction using HS-SPME. Every step of the mass-transfer process for the emission of low molecular compounds from polymers and their absorption/adsorption in the SPME fibre is affected by temperature. Polymeric morphology and chain mobility is affected by temperature; HIPS is an amorphous polymer that exhibits a glass transition relaxation of the polystyrene phase at around 90 °C (previously measured using differential scanning calorimetry [40]), so higher temperature is supposed to favour polymer mobility and the release of low molecular weight compounds retained in its

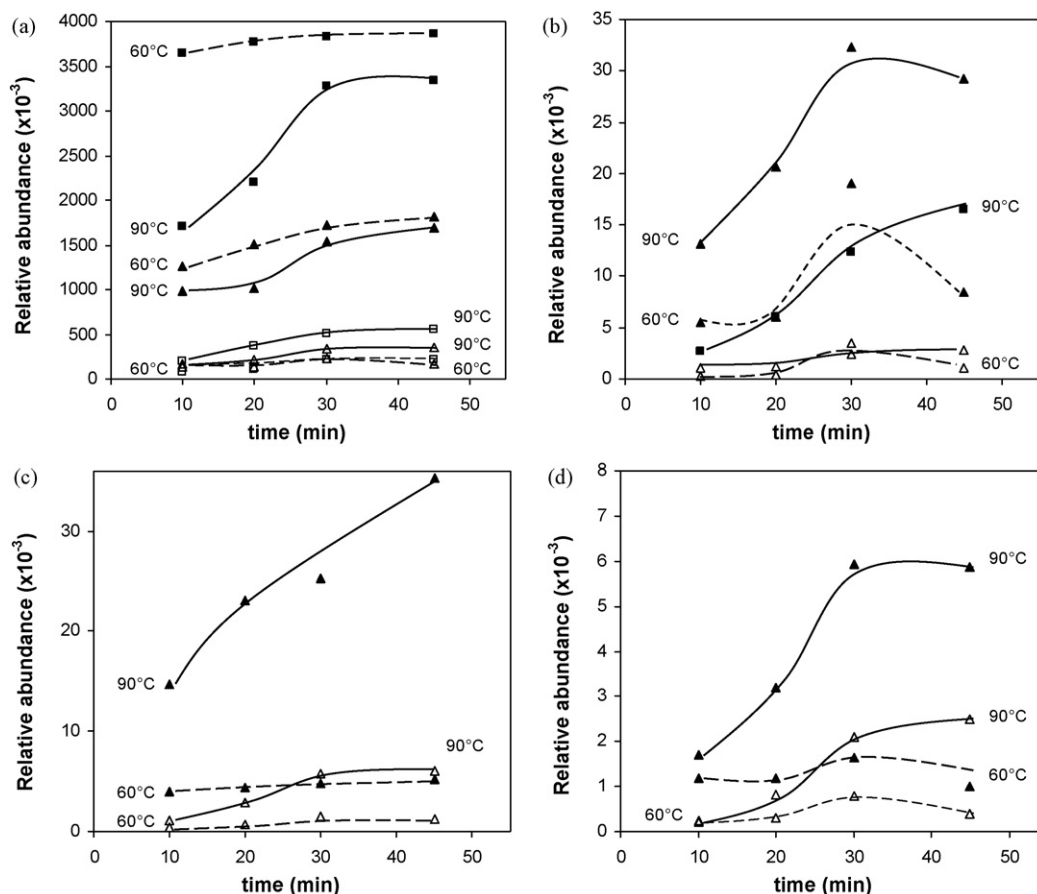
bulk structure. Higher temperatures also enhance the diffusion of small molecules in the polymeric core, and enhance the transfer of these compounds into the headspace phase. Finally, temperature influences the equilibrium between the headspace and the fibre coatings, and the kinetics of the SPME extraction process, showing different mechanisms for absorbing fibres [24] (e.g. PDMS fibre) and for adsorbing fibres [25] (e.g. CAR/PDMS). Increasing temperature results therefore in the release of higher amounts of a wide range of organic compounds from recycled HIPS in granule and powder form, as detected by both PDMS and CAR/PDMS fibres (Table 2). At lower extraction temperatures (30–45 °C), minor quantities of volatile compounds such as toluene, ethylbenzene, styrene, or benzaldehyde are detected, using specifically CAR/PDMS fibre. At higher extraction temperatures, the pattern of organic compounds released from the polymeric matrix broadens. A broad range of aromatic compounds, including benzene derivatives and oxidated aromatic compounds, can be specifically detected using CAR/PDMS fibre. Different styrene dimers and trimers, originally present in the polymeric material as residues of the thermal polymerisation of polystyrene, are also emitted at higher temperatures and have been detected using PDMS fibre. The significant increase in the emission of low molecular weight compounds at 90 °C can be related to structural parameters of HIPS. Polystyrene presents its glass transition temperature ( $T_g$ ) at around 90 °C, which results in the transition from the glassy state to the rubbery state, with increased mobility of the polymeric segments. This enhanced mobility is expected to facilitate dramatically the migration of low molecular weight compounds from the polymeric core and their transfer to the headspace phase. This fact may explain the release of molecules with lower volatility such as styrene dimers and trimers at elevated temperatures.

### 3.2.3. Influence of particle size on the emission pattern

The influence of polymeric particle size on the emission of organic compounds from recycled HIPS was analysed by the comparison of the release pattern from polymer granules (5 mm) and polymer powder (1 μm). Smaller particle size results in the emission of a wider range of organic compounds, with significantly higher intensities (Fig. 1 and Table 2). This fact proves the importance of analyte diffusion in the polymeric core in the release and detection of volatiles using SPME. This remarkable increase in the amount and variety of molecules with smaller particle size indicates that the molecular diffusion in the polymeric core may be the crucial step in the emission process, controlling the overall extraction process. As predicted, an increase in the extraction temperature enhances the release of volatiles both in granule and powder form; temperature has an important influence in both the diffusion coefficient and structural parameters controlling polymeric mobility.

### 3.2.4. Influence of extraction time. Equilibration curves

The effect of extraction time on the release of low molecular weight compounds from recycled HIPS was studied by obtaining the equilibration curves for the selected target analytes (styrene, benzaldehyde, acetophenone, and 2-phenylpropanal) under the different conditions (Fig. 5). The signals of the different compounds were normalised towards the area of the internal standard (4-methylstyrene), to obtain comprehensive information about the relative sensitivity of each fibre to detect the released target compounds. Styrene equilibration curves from powder and granule HIPS could be obtained at 60 and 90 °C using both PDMS and CAR/PDMS fibres. However, the low detection provided by PDMS fibre for the oxidated derivatives of benzene made it impossible to obtain their equilibration curves at both temperatures. PDMS fibre gives better sensitivity for styrene when related to the internal standard than CAR/PDMS, especially at lower temperatures. For



**Fig. 5.** Influence of different operational parameters on the equilibration curves from the HS-SPME extraction of the target analytes from recycled HIPS. Type of SPME fibre: (Δ) PDMS; (□) CAR/PDMS. Temperatures: (—) 60°C; (---) 90°C. Particle size: (◆) HIPS powder; (◇) HIPS granule. Target analytes: (a) styrene; (b) benzaldehyde; (c) acetophenone; (d) 2-phenylpropanal.

the oxidated derivatives of styrene with higher polarity, CAR/PDMS offers better extraction, as detailed earlier. The equilibration curves for benzaldehyde, acetophenone, and 2-phenylpropanal released from powder HIPS show, however, anomalous shapes for higher temperatures and particularly with CAR/PDMS fibre. These facts prove again the limitation of CAR/PDMS to detect compounds in complex matrixes operating at high temperatures.

The complexity for HS-SPME equilibration when studying the release of low molecular weight compounds from polymers is clearly observed for the target analytes (Fig. 5) when compared with the equilibration curves for the same compounds in the initial study without the presence of the polymeric matrix (Fig. 2). Dynamic diffusion of the analytes from the polymeric core into the headspace hinders the establishment of the thermodynamic equilibrium and therefore controls the overall HS-SPME extraction process. Previous stabilisation of the volatile release from the polymer core into the headspace by sample conditioning could enable the successful quantification of the released compounds using HS-SPME. Moreover, the influence of matrix interferences of other released compounds from HIPS in the equilibration curves for the target analytes is particularly evident in the case of CAR/PDMS fibre at higher temperatures and times. Bigger molecules with lower volatility released from the polymeric matrix at higher temperatures may interfere with the adsorption of smaller molecules and therefore cause impossibility to equilibrate the system. This fact proves the difficulty of SPME with porous fibres for obtaining verifiable quantification data for the release of volatiles released from polymeric materials.

#### 4. Conclusions

The emission pattern of low molecular weight compounds from recycled HIPS has been investigated using HS-SPME and further analysis with GC-MS. A wide range of compounds have been identified, including aromatic compounds, residues of polymerisation (styrene monomer, different styrene dimers and trimers), oxidated degradation products of polystyrene (benzaldehyde, acetophenone, and 2-phenylpropanal), and fragments of additives (butylated hydroxytoluene). The nature and relative amounts of the released compounds determined using HS-SPME varied according to the temperature, HIPS particle size, and type of SPME fibre detected. SPME fibre gave better response to non-polar compounds with lower volatility (styrene dimers and trimers) at high temperatures, whereas CAR/PDMS was the fibre of choice for more polar volatile compounds (oxidated derivatives of benzene) at lower temperatures. Increased temperature and smaller particle size result in a higher amount and variety of released compounds. The optimisation of SPME parameters was carried out for 4 target compounds (styrene, benzaldehyde, acetophenone, and 2-phenylpropanal). The comparison of the HS-SPME equilibration curves for the analytes with and without polymeric matrix indicates the complex nature of the processes involved in extraction of low molecular weight compounds from polymeric matrices using SPME, especially for porous fibres as CAR/PDMS. The limitations of HS-SPME-GC-MS for the effective quantification of volatile compounds in polymeric matrices have been pointed out, due to matrix effects and the difficulties in equilibration the whole analytical system.



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