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Determination of volatile organic compounds in recycled polyethylene terephthalate and high-density polyethylene by headspace solid phase microextraction gas chromatography mass spectrometry to evaluate the efficiency of recycling processes

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ABSTRACT

A method for the determination of volatile organic compounds (VOCs) in recycled polyethylene terephthalate and high-density polyethylene using headspace sampling by solid-phase microextraction and gas chromatography coupled to mass spectrometry detection is presented. This method was used to evaluate the efficiency of cleaning processes for VOC removal from recycled PET. In addition, the method was also employed to evaluate the level of VOC contamination in multilayer packaging material containing recycled HDPE material. The optimisation of the extraction procedure for volatile compounds was performed and the best extraction conditions were found using a 75 μm carboxen-polydimethylsiloxane (CAR-PDMS) fibre for 20 min at 60 °C. The validation parameters for the established method were linear range, linearity, sensitivity, precision (repeatability), accuracy (recovery) and detection and quantification limits. The results indicated that the method could easily be used in quality control for the production of recycled PET and HDPE.

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1. Introduction

Food packaging is a rapidly growing market. As a consequence, the demand for recycled post-consumer packaging materials continues to grow. However, the recycling of post-consumer plastics into materials for direct food contact applications requires detailed knowledge of contamination in order to assess the risk to consumers' health [1].

The most promising post-consumer polymer for use as a food-packaging material is polyethylene terephthalate (PET), due to low diffusivity of contaminants within the polymer. In general, this characteristic allows only small amounts of contamination into the material even when used in non-food applications. On the other hand, polymers with higher diffusion and sorption characteristics, such as high-density polyethylene (HDPE), have also been considered and received so-called "no objection" letters from the FDA for certain well-defined uses [2,3]. In Brazil, the use of PET post-consumer materials for direct food contact was recently approved [4].

For packaging recycling, two main processes are currently applied: (a) conventional PET recycling, involving sorting, grinding, washing, drying and extrusion. The use of the resulting material for direct food contact should be avoided or be used in conjunction with an appropriate food contact barrier layer. Risk for human health caused from contaminant migration into food would be expected to be negligible, provided that the recycled resin is separated from the food by an effective barrier constructed from virgin resin or other appropriate material; and (b) "super clean" PET recycling, which is conventional PET recycling with an additional deep cleansing process, such as solid state post-condensation. The resulting material is expected to be suitable for direct food contact applications [5]. However, if the procedures for cleaning and decontamination (super clean) are not effective, post-consumer substances or compounds absorbed by the polymer due to the possible misuse of PET and HDPE, such as for the storage of household chemicals, may migrate into the foodstuff. These substances include a variety of low molecular weight compounds, many of unknown toxicological properties, posing a possible risk to human

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health [6,7]. In addition, some of the migrants can cause undesirable changes in sensorial properties of the packaged food [8].

Consequently, it is important to evaluate the chemical quality of recycled materials [9,10], and thus there is a need to develop and apply analytical methods for the determination of contaminants coming from virgin and recycled packaging to help manage consumer health risks. Since the measurement of contaminants in every packaging material is impossible, challenge tests have been developed in which surrogate chemicals are artificially introduced into a recycling process. As a safety parameter or as a criterion for cleaning efficiency, a migration limit of 10 $\mu g\,L^{-1}$ surrogate into food from a packaging material produced in a challenged recycling process has been generally accepted [3,11–13].

The analysis of volatile contaminants in recycled PET and HDPE material involves some type of extraction facilitated by solvent strength, supercritical fluid state and/or temperature. Recycled samples have been traditionally solvent extracted by Soxhlet extraction [14,15], total dissolution [5,13,15–20], microwave-assisted extraction (MAE) [21], static headspace, supercritical fluid extraction (SFE) [22] and dynamic headspace [2,23,24] techniques. Other contaminants and additives in recycled PET have been analysed by the migration test [25] and supercritical fluid extraction [26]. These techniques are either time consuming or use large quantities of solvents, and/or due to the requirement of a post-extraction concentration step, they are only applicable to the analysis of semivolatile compounds. Solid phase micro extraction (SPME) is a technique that allows direct analysis of the volatile compounds in solid samples, thus avoiding the use of solvents [27]. SPME has specifically been reported for the analysis of volatile organic compounds (VOCs) in packaging material [28,29]. MHE-SPME is a modification of SPME developed for quantitative analysis that avoids possible matrix effects based on an exhaustive analyte extraction from the sample and broadens the applicability of SPME to quantitative determination of analytes in solid matrixes.

The aim of this work was to develop and validate a simple and high-throughput method for the determination of VOCs in PET and HDPE materials by means of SPME. The resulting method was used to evaluate the efficiency of cleaning processes for the removal of VOCs from recycled PET. In addition, the method was also employed to evaluate the level of VOC contamination in multilayer packaging materials containing recycled HDPE material.

2. Experimental

2.1. Reagents and materials

Analytical standards of alpha-terpinene (purity 95.0%), benzaldehyde (purity 99.0%) and styrene (purity 99.0%) were supplied from Fluka. Limonene (97.0%), bornyl acetate (95.0%), chlorobenzene (purity 99.5%), toluene (99.5%), diisobutyl phthalate (DBP, 99.0%), naphthalene (99.0+%), 2,4-di-tert-butylphenol (99.0%), 2,6-di-tert-butyl-4-methylphenol (BHT, purity 99.0%), alpha-pinene (98.0%), diethyl phthalate (DEP, 99.5%) and linalool (97.0%) standards were supplied by Sigma-Aldrich (St Louis, MO, USA). Benzophenone (purity 99.0%) was obtained from Merck and hexane and isooctane (analytical grade) were from Scharlau (Barcelona, Spain).

Stock solutions of pure compounds were prepared in hexane at a nominal concentration of 2.0 $mg\,g^{-1}$. Working standard solutions of all volatile organic compounds at a nominal concentration of 0.05 $mg\,g^{-1}$ were prepared by diluting the stock solution in hexane. For SPME analysis, standard solutions with nominal concentrations of 60.0, 170.0, 600.0, 990.0, 3090.0, 5300.0, 7210.0 and 10510.0 $ng\,g^{-1}$ were prepared, and 20 μL of each standard solution was added to a 20 mL vial.

Table 1
PET and HDPE samples.

Sample	Material	Type of process
S1	PET flakes	Conventional cleaning: flake washed with water
S2	PET flakes	Conventional followed by super clean[a]
S3	PET amorphous pellets	Conventional and deep cleaning, extrusion
S4	PET pellets	Conventional and super clean[a], extrusion and SSP (solid state pos condensation)
S5cc	PET flakes	Conventional cleaning
S6cc	PET flakes	Conventional cleaning
S7cc	PET flakes	Conventional cleaning
S5dc	PET flakes	Deep cleaning: hot caustic washing with detergent, friction washing and drying
S6dc	PET flakes	Deep cleaning: hot caustic washing with detergent, friction washing and drying
S7dc	PET flakes	Deep cleaning: hot caustic washing with detergent, friction washing and drying
PET-V1	PET pellets	Virgin
PET-V2	PET flakes	Virgin bottle
PET-R1	PET pellets	Recycled conventional cleaning
PET-R2	PET pellets	Recycled conventional cleaning
HDPE-R	HDPE pellets	Recycled unknown recycling process
HDPE-3	HDPE multilayer packaging	Layers: polyethylene/polyethylene with maleic acid + post consumer recycled polyethylene/polyethylene
HDPE-5	HDPE multilayer packaging	Layers: polyethylene/polyethylene with maleic acid + post consumer recycled polyethylene/EVOH/polyethylene with maleic acid + post consumer recycled polyethylene/polyethylene

[a] Super clean: hot water and additives.

An SPME holder (Supelco, Bellefonte, PA, USA) was used to perform the experiments for extraction optimisation. The following SPME fibres were purchased from Supelco: 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane–divinylbenzene (PDMS/DVB) and 75 μm carboxen–polydimethylsiloxane (CAR/PDMS).

2.2. Samples

All the samples were supplied by Brazilian packaging and recycling companies. The PET post consumer flakes and pellets were obtained after cleaning, recycling and in some cases, extrusion processes (Table 1). The PET samples were ground in a Marconi Mill, Model MA580 (Belo Horizonte, Minas Gerais, Brazil), in order to increase the surface area and thus improve the extraction efficiency. HDPE multilayer packaging containing recycled HDPE was cut in slices of 4.0 cm × 3.0 cm.

2.3. Method optimisation

2.3.1. HS-SPME – manual – extraction of volatile organic compounds

A random sample (1.0, 4.0 and 7.0 g) of pellets of amorphous PET (blank sample) was placed into a vial (20 mL) and fortified with 1000 $ng\,g^{-1}$ of each volatile organic compound. The vials were transferred to a hot plate and, after 10 min, the fibre was exposed to the vapour phase. After this period of time, the fibre was inserted into the needle and subsequently introduced into the injection port of the GC. The desorption of the analytes from the fibre coating was performed at 300 °C for 60 min.

2.3.2. Apparatus

A Varian CP-3800 gas chromatograph interfaced with a mass spectrometer (MS Saturn 2000, Varian) was used in this research. The chromatographic separations were carried out with a 30 m × 0.25 mm × 0.25 μm BPX5 capillary column (SGE, Scientific Instrument Services, NJ, USA). The GC operating conditions were as follows: injector temperature 280 °C (splitless mode); oven temperature was held at 40 °C for 5 min, then heated to 130 °C at 3 °C min^{-1}, then heated to 250 °C at 6 °C min^{-1}, then to 320 °C at 20 °C min^{-1} and kept at this temperature for 1 min. The carrier gas was helium at a constant flow rate of 1.0 mL min^{-1}. The mass spectrometer was scanned from *m*/*z* 40 to 650; the ionisation was performed by electronic impact and the ion trap temperature was 200 °C; and the electron multiplier voltage was 1600 V. Compounds were identified by matching their mass spectra to the US National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) commercial library (matching criterion >85%).

2.3.3. Experimental design

A central face-centred composite design was carried out to distinguish the significant parameters affecting the SPME procedure. The experimental design consisted of a model with 37 experiments plus 3 repetitions in the centre. Two optimisation criteria were independently considered: the first was maximisation of the sum of the chromatographic peak areas of the 15 selected compounds (alpha-terpinene, alpha-pinene, benzaldehyde, styrene, limonene, bornyl acetate, chlorobenzene, toluene, diisobutyl phthalate (DBP), naphthalene, 2,4-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol (BHT), benzophenone, diethyl phthalate (DEP) and linalool), while the second was maximisation of individual areas for some compounds of interest. Table 2 shows the experimental matrix with detailed conditions for all of the experiments. All statistical calculations were carried out with the software package Modde 6.0 from Umetrics (Umeå, Sweden).

2.3.4. HS-SPME–GC–MS conditions

A random sample (1.0 g) of the PET powdered flakes and pellets, as well as slices of the HDPE multilayer packaging and HDPE recycled pellets, were put into a vial (20 mL). To quantify the spiked samples, calibration curves were then prepared by placing the same amount of PET or HDPE samples in 20 mL vials and adding 20 μL of the standard solution containing a mixture of the surrogates (alpha-terpinene, benzaldehyde, styrene, limonene, bornyl acetate, chlorobenzene, toluene, DBP, naphthalene, 2,4-di-tert-butylphenol, BHT, alpha-pinene, DEP, linalool and benzophenone) in hexane at different concentration levels. After 10 min of exposure, the samples were analysed by HS-SPME–GC–MS.

A CTC Analytics CombiPal autosampler from Agilent (Palo Alto, CA, USA) was used during the experiments. The pre-incubation time was 60 s at 60 °C. The extraction time was 20 min and the desorption time was 1 min. After injection, the fibre was conditioned for 5 min. The autosampler was coupled to an Agilent 6890 gas chromatograph system interfaced to a 5973 mass spectrometer. Analytes were separated with a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column. The carrier gas was He and the column flow was maintained at 1.5 mL min^{-1}. The initial oven temperature was held at 40 °C for 5 min, then increased to 130 °C at 3 °C min^{-1}, increased to 250 °C at 6 °C min^{-1}, increased to 320 °C at 20 °C min^{-1}, and then held at 320 °C for 1 min. Injection was carried out in the splitless mode (280 °C). The mass spectrometer was operated under the following conditions: 70 eV electron energy, 230 °C ion source temperature and a mass range from 45 to 650 amu. Each chromatographic peak was then assigned using a GC–MS mass spectra library (US National Institute of Standards and Technology, NIST).

Table 2
Matrix of the experimental design.

Experiment	Temperature (°C)	Time (min)	Sample amount (g)	Fibre
N1	60.0	5.0	1.0	100 μm PDMS
N2	100.0	20.0	1.0	100 μm PDMS
N3	100.0	5.0	7.0	100 μm PDMS
N4	60.0	20.0	7.0	100 μm PDMS
N5	100.0	5.0	1.0	100 μm PDMS
N6	60.0	20.0	1.0	100 μm PDMS
N7	100.0	20.0	7.0	100 μm PDMS
N8	60.0	5.0	7.0	100 μm PDMS
N9	60.0	5.0	4.0	100 μm PDMS
N10	60.0	12.5	7.0	100 μm PDMS
N11	80.0	5.0	7.0	100 μm PDMS
N12	80.0	20.0	4.0	100 μm PDMS
N13	80.0	12.5	1.0	100 μm PDMS
N14	100.0	5.0	1.0	65 μm PDMS/DVB
N15	60.0	20.0	1.0	65 μm PDMS/DVB
N16	60.0	5.0	7.0	65 μm PDMS/DVB
N17	100.0	20.0	7.0	65 μm PDMS/DVB
N18	100.0	20.0	1.0	65 μm PDMS/DVB
N19	100.0	5.0	7.0	65 μm PDMS/DVB
N20	60.0	20.0	7.0	65 μm PDMS/DVB
N21	60.0	5.0	1.0	65 μm PDMS/DVB
N22	60.0	5.0	4.0	65 μm PDMS/DVB
N23	60.0	12.5	1.0	65 μm PDMS/DVB
N24	80.0	5.0	1.0	65 μm PDMS/DVB
N25	100.0	12.5	4.0	65 μm PDMS/DVB
N26	80.0	12.5	4.0	65 μm PDMS/DVB
N27	100.0	5.0	1.0	75 μm CAR/PDMS
N28	60.0	20.0	1.0	75 μm CAR/PDMS
N29	60.0	5.0	7.0	75 μm CAR/PDMS
N30	100.0	20.0	7.0	75 μm CAR/PDMS
N31	60.0	5.0	1.0	75 μm CAR/PDMS
N32	100.0	20.0	1.0	75 μm CAR/PDMS
N33	100.0	5.0	7.0	75 μm CAR/PDMS
N34	60.0	20.0	7.0	75 μm CAR/PDMS
N35	80.0	12.5	4.0	75 μm CAR/PDMS
N36	80.0	12.5	4.0	75 μm CAR/PDMS
N37	80.0	12.5	4.0	75 μm CAR/PDMS

2.4. Migration test for HDPE multilayer packaging

VOCs in the HDPE multilayer packaging were extracted in a migration test by placing 4.0 cm × 3.0 cm slices of each package in the simulant (isooctane) in 20 mL vials with Teflon® caps, closing the vials, and then incubating in an oven at 20 °C for 2 days. The HDPE samples were then removed and the obtained extracts were stored at 4 °C while awaiting analysis. Several vials were prepared as blank samples (without plastic samples) via the same migration procedure. Following the treatment described above, 1.0 μL of extract was then injected in split mode (20:1) into the Agilent 6890 gas chromatograph system interfaced to a 5973 mass spectrometer.

3. Results and discussion

3.1. Choice of VOC surrogates

The FDA recommends that recyclers use materials that have a variety of chemical and physical properties to simulate consumer misuse. In particular, the FDA recommends that the surrogate contaminants represent "common" materials accessible to the consumer and include a volatile polar organic substance, a volatile non-polar organic substance, a non-volatile polar organic substance and a non-volatile non-polar organic substance [3]. The volatile organic compound (VOC) surrogates for this study were chosen according to the results from previous studies (Table 3).

Table 3
Volatile organic compounds applied for the screening analytical method.

Compounds	CAS	Reference
Benzophenone	119-61-9	[3]
Limonene	5989-27-5	[3]
Chlorobenzene	108-90-7	[3]
Naphthalene	91-20-3	[15]
BHT	128-37-0	[16]
DEP	84-66-2	[16]
DBP	84-74-2	[16]
2,4-Di-tert-butylphenol	96-76-4	[17]
Benzaldehyde	100-52-7	[17]
Styrene	100-42-5	[17]
Alpha-pinene	80-56-8	[17]
Alpha-terpinene	99-86-5	[17]
Toluene	108-88-3	[18]
Bornyl acetate	5655-61-8	
Linalool	78-70-6	

3.2. Optimisation of HS-SPME–GC–MS method

A large number of variables are involved in the SPME extraction procedure. The most important include the nature of the fibre, the sample volume, the extraction time and the temperature [30]. Experimental design was then used for the extraction procedure optimisation with surrogates (about 1000 ng g^{-1} each VOC compound). Briefly, the surrogates were extracted by HS-SPME according to the conditions shown in Table 2 and analysed by GC–MS. Peak areas were processed in two ways: either sum of all the areas or sum of individual peak areas. The statistical model used was fitted with PSL (Partial Least Square) and all responses were analysed simultaneously.

Fig. 1 shows the summary of fit, where R^2 is the percent of the variation of the response explained by the model (i.e., how well the model fits the data), Q^2 is the percent of the variation of response predicted by the model according to cross validation, Model Validity is a measure of validity of the model and Reproducibility is a variation of the response under the same conditions (pure error), often at the centre points, compared to the total variation of the response.

A larger R^2 is a necessary condition for a good model, but it is not sufficient, as it is necessary to evaluate the reproducibility and Model Validity. In this case, the R^2 is larger for all compounds. In addition, a useful model should have a large Q^2. In this case, a poor Q^2 despite a good R^2 showed moderate model validity, and a design with many degrees of freedom for the residuals was due to insignificant terms in the model.

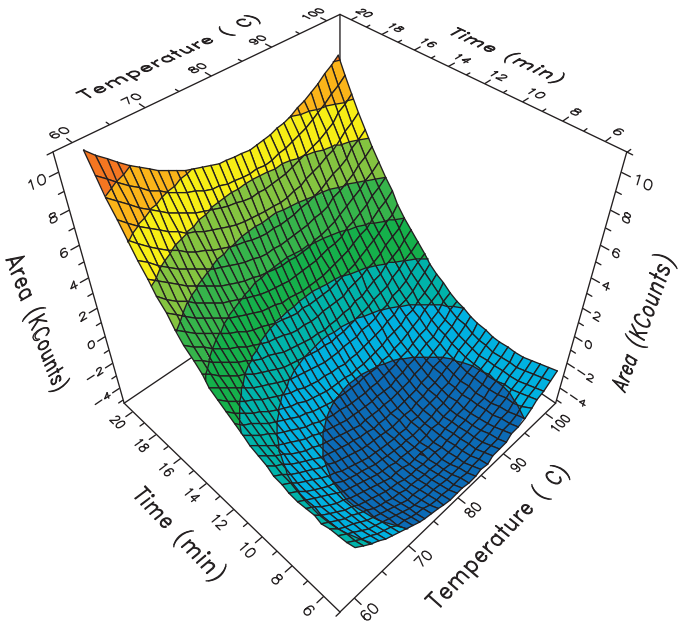

Fig. 2. Surface contour plots from the optimisation experimental set-up: effect of time and temperature of extraction over the total area counts.

The obtained results showed good reproducibility for all of the VOCs except toluene, chlorobenzene and 2,4-di-tert-butylphenol. In addition, the fit with PSL for the model was valid for all VOCs except limonene, a-pinene and benzophenone because there was significant lack of fit and the model error was significantly larger than the pure error for these three compounds.

Following the summary fit, the effects of variables were evaluated and significant effects were deemed to be those where the confidence interval included zero. According to this definition, effects from interactions between variables and the sample amount were not significant. Time extraction and temperature, as well as the coating material of the fibre, however, were significant. To find the best coating material three fibres were evaluated: 100 μm PDMS, 65 μm PDMS/DVB and 75 μm CAR/PDMS. According to the

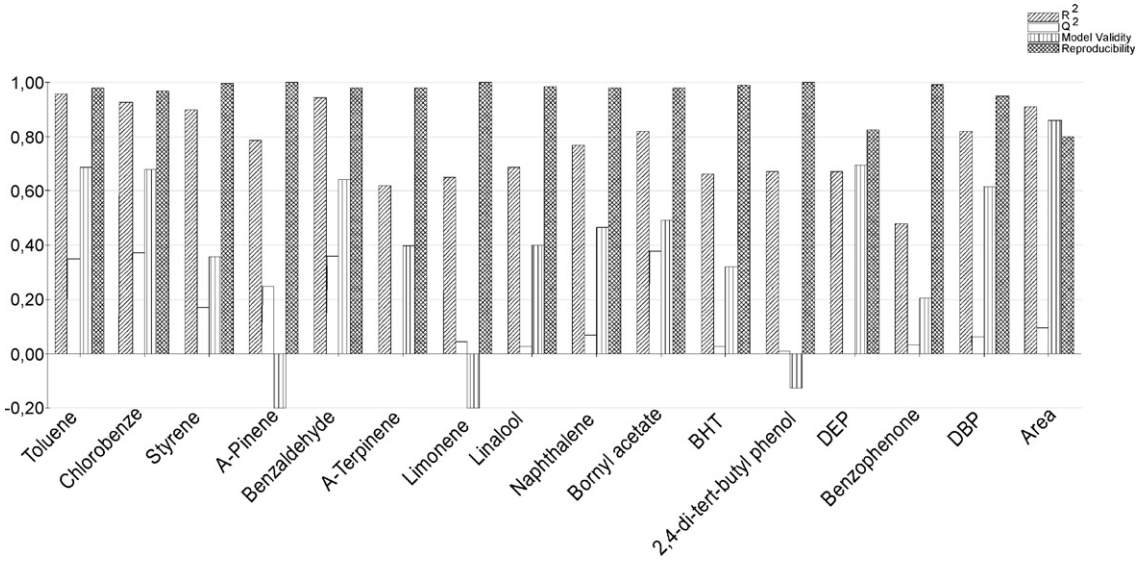

Fig. 1. Summary of the fit obtained with PSL.

Table 4
Parameters of validation HS-SPME–GC–MS.

Parameters	Benzaldehyde			Limonene			2,4-Di-tert-butylphenol		
Linear range (ng g^{-1})	63–11,749			66–12,387			50–9312		
Linearity (R^2)[a]	0.9648			0.9732			0.7297		
Sensitivity (u.a. ng^{-1})	1697.57			832.99			8996.42		
Fortification level (ng g^{-1})	5928	8059	11,749	6250	8496	12,387	4699	6387	9312
Recovery (%) (±s)	66 ± 4.85	93 ± 4.20	81 ± 5.57	84 ± 19.43	106 ± 4.60	88 ± 4.77	93 ± 9.49	77 ± 4.99	78 ± 4.01
Fortification level (ng g^{-1})	3448	8059	11,749	3636	8496	12,387	2733	6387	9312
Intra-assay precision RSD[b] % (n = 3, 95%)	6	11	16	6	4	5	3	9	6
Inter-assay precision RSD[b] % (n = 3, 95%)	48	7	8	35	17	16	10	5	6
LOD[c] (ng g^{-1})	21			22			17		
LOQ[d] (ng g^{-1})	63			66			50		

Parameters	2,6-Di-tert-butyl-4-methylphenol (BHT)			Styrene			Chlorobenzene		
Linear range (ng g^{-1})	57–10,676			48–9051			47–8906		
Linearity (R^2)[a]	0.9246			0.9854			0.9903		
Sensitivity (u.a. ng^{-1})	1504.60			3646.37			2422.10		
Fortification level (ng g^{-1})	5387	7322	10,676	4567	6208	9051	4494	6109	8906
Recovery (%) (±s)	108 ± 13.68	126 ± 37.67	102 ± 2.21	77 ± 4.91	101 ± 5.31	87 ± 6.29	98 ± 5.77	124 ± 6.09	113 ± 0.33
Fortification level (ng g^{-1})	3133	7322	10,676	2656	6208	9051	2614	6109	8906
Intra-assay precision RSD % (n = 3, 95%)	19	9	2	14	6	6	11	5	0.30
Inter-assay precision RSD % (n = 3, 95%)	0.77	0.05	3	37	8	8	49	26	20
LOD[c] (ng g^{-1})	19			16			16		
LOQ[d] (ng g^{-1})	57			48			47		

Parameters	Benzophenone			Naphthalene			Diethyl phthalate (DEP)		
Linear range (ng g^{-1})	48–9051			51–9660			92–17,348		
Linearity (R^2)[a]	0.9797			0.9781			0.8604		
Sensitivity (u.a. ng^{-1})	84.64			2442.58			94.29		
Fortification level (ng g^{-1})	4567	6208	9051	4874	6626	9660	8753	11,899	17,348
Recovery (%) (±s)	137 ± 2.49	98 ± 19.87	106 ± 10.42	89 ± 8.96	107 ± 11.57	98 ± 2.18	15 ± 1.40	7 ± 0.72	4 ± 0.51
Fortification level (ng g^{-1})	2656	6208	9051	2835	6626	9660	5091	11,899	17,348
Intra-assay precision RSD % (n = 3, 95%)	1	17	2	10	13	7	23	25	10
Inter-assay precision RSD % (n = 3, 95%)	20	7	4	8	1	2	2	13	21
LOD[c] (ng g^{-1})	16			17			31		
LOQ[d] (ng g^{-1})	48			51			92		

[a] Linearity is expressed as the linear correlation coefficient obtained through the calibration graph.
[b] RSD is relative standard deviation.
[c] LOD is limit of detection.
[d] LOQ is limit of quantification.

statistical parameters from the model fit to PSL, the fibre chosen was 75 μm CAR/PDMS. Similar results were also reported in the scientific literature where CAR/PDMS fibre provided the best results in terms of amount of compounds extracted. Besides, this fibre provided the best results for low molecular mass compounds, as reported by Ezquerro et al. [28] and Cho et al. [31].

The next step was the ANOVA statistical test and generation of response surfaces for all substances except styrene, bornyl acetate and linalool because for these compounds ANOVA was not considered valid. The 75 μm CAR/PDMS fibre with 1.0 g of sample was selected to evaluate the response surface.

To establish the optimum conditions for the simultaneous HS-SPME extraction of the surrogates from the samples, it was necessary to consider the maximum extraction achievable for each VOC, as well as the suitability of the analysis time. Fig. 2 shows the 3-D response surface plots of the total peak area considering temperature and time of extraction as independent variables for 1.0 g sample of PET pellets using 75 μm CAR/PDMS fibre. The results indicated that optimum conditions were achieved at an extraction time of 20 min and a temperature of 60 °C. These conditions were then used in the validation of the HS-SPME method for the determination of VOCs in PET.

3.3. Validation parameters for HS-SPME–GC–MS

Having established the experimental conditions for the HS-SPME VOC extraction from recycled PET, the method was validated in-house according to the following performance criteria: linear range and linearity, sensitivity, accuracy, intra- and inter-assay precision and limits of detection and quantification. The results are shown in Table 4.

The linear range, linearity, and sensitivity were obtained from the calibration curve using pellets of amorphous PET (blank samples) fortified with all of the volatile organic compounds of interest at five fortification levels from 60 to 10,000 ng g^{-1}, with triplicate analyses. Although limonene, benzophenone and styrene were excluded from the optimisation experimental design, they were included in this step of method validation because these substances were detected in the screening step of several model samples.

The method developed presented R^2 values higher than 0.92 for all VOCs except 2,4-di-tert-butylphenol, which had an R^2 of 0.73. Furthermore, the approach employed to evaluate the accuracy of the method was based on the recovery of known amounts of each VOC spiked into the blank samples at three fortification levels (approximately 5500, 7300 and 10,700 ng g^{-1}). The results for recovery were in the range of 66–137%, with the exception of DEP, which presented recoveries in the range of 4–15%. The lower values for R^2 obtained for some of the studied compounds suggested competition among substances for the active sites of the fibre and could be related to several factors, such as molecular weight and polarity.

The precision of the method was evaluated over one day of operation under the same conditions (intra-assay) and for three days (inter-assay precision). The intra- and inter-assay precisions were expressed as relative standard deviations (RSD %) and were lower than 19 and 26% for intra- and inter-assay, respectively (Table 4). The exception was DEP, which presented an intra-assay precision of 25%. For inter-assay precision, chlorobenzene, benzaldehyde, limonene and styrene presented 49, 48, 35 and 37%, respectively.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to Miller and Miller [32], using the following expressions: $LOD = 3s_{y/x}/m$ and $LOQ = 10s_{y/x}/m$, where $s_{y/x}$ is the standard deviation and m the slope of the analytical curve, respectively.

Based on these results, the HS-SPME–GC–MS method is a rapid, versatile, solventless and economical method with adequate detection in the determination of volatile organic compounds in recycled PET. The analytical method presented is therefore reliable for the assessment of safety in recycled PET.

3.4. Sample analysis by HS-SPME–GC–MS

Although the optimisation of the analytical procedure, mainly the separation of the analytes, sorption and desorption steps from the SPME fibre and extraction time was carried out with PET, it could be assumed that similar conditions could be applied to HDPE. It is worth to emphasize that standard addition procedure was applied using PET and HDPE for calibration plots for the analysis of PET or HDPE, respectively. Thus, the validated method was applied to the determination of VOCs in recycled PET and HDPE samples. The method was used to evaluate similarities and differences among different decontamination processes of PET for the removal of VOCs. The level of VOC contamination in multilayer packaging material containing HDPE recycled material was also evaluated.

Initially, the established extraction procedure (HS-SPME) was used for the tentative identification of the VOCs present in the PET and HDPE samples by GC–MS. The identified compounds included aliphatic and aromatic aldehydes, ethers, esters, aliphatic acids, aromatic compounds, alkanes, alkenes, ketones and alcohols (Table 5).

As reported by Dzieciol and Trzeszczynski [33], PET is subjected to temperatures in the range from 200 to 300 °C under vacuum, nitrogen, or air in its production, processing and recycling. These conditions result in degradation reactions that generate changes in the properties of the polymers (for example, reduction in the molecular mass and intrinsic viscosity and yellowing) and the emission of volatile substances. These substances, produced during the heat degradation of PET, include aldehydes (benzaldehyde), aromatic hydrocarbons (styrene) and acetophenone. At low temperatures, the concentrations of aromatic and aliphatic hydrocarbons increase with temperature [34]. Thus, some of the compounds identified in the present study could have been formed during PET degradation reactions. This phenomenon is even more important for HDPE.

In addition to degradation, other sources of contamination should also be considered. Recently, Widén et al. [35] identified substances they believed could have come from recycled packaging material. The authors suggested three possible sources of this contamination: (1) misuse of the package by the consumer, (2) food products (fermented and fortified alcoholic beverages), and (3) non-food products (petroleum products, detergents and cleaning products, compounds containing ethers and unknown products). These sources were listed apart from other compounds resulting from the deterioration of the original product from storage in an inappropriate place.

Limonene, a non polar aroma compound, is frequently found in post-consumer PET and originates from prolonged contact with soft drinks or fruit juices [12,22]. Although some authors have reported that the absorption of limonene by the package causes no relevant sensory changes in food products, for example in orange juice [36], several studies on the transport mechanisms have been conducted. Hernandez-Muñoz et al. [37] determined the partition coefficient (K) of aroma compounds (including D-limonene) diluted in several fatty food simulants, in contact with several food packaging materials, PET among them. The authors evaluated the equilibrium environment/package/food system. For PET it was verified that K values for D-limonene were inferior to 1 for all the simulants indicating that this aroma preferred the simulant to the polymer. Nevertheless, when the polarity of the simulant increases, limonene K values also increases. Consequently, for PET, it would be expected higher sorption of this compound in the polymer in aqueous media when compared to fatty media.

Other investigations have pointed out that the presence of limonene could affect the properties of plastic materials and facilitate the loss of other volatile compounds of greater relevance to the shelf-life of the product because of its plasticising effect on the structure of the package wall [38]. Nonetheless, considering recycling aspects, determination limonene in PET could be used in some instances to guarantee that post-consumer recycled material is free of contaminants [39,40].

Fayoux et al. [38] showed that the majority of the terpenes absorbed by PET were not removed even after the severest of washing treatments, and thus off-flavours could appear in the next product introduced into the package. In addition, naphthalene contamination resulted from a polluted environment (e.g., from lacquer, paint and mothballs) [15,17]. It should be mentioned here that the majority of the contaminants identified in the samples analysed in the present study had already been identified in recycled PET by other authors [10,15,19,22,35,41].

A comparison of the results obtained for material from the suppliers who applied conventional cleaning showed that o-xylene, nonanal, 2,6-dimethyl-octadecane, heneicosane, dodecane, tritetracontane, tetratetracontane and isobutyl octadecyl ester phthalic acid were removed after deep cleaning in all of the PET samples. By comparison, 1-R-alpha-pinene, camphene, o-cymene, 10-methyl nonadecane, alpha-isomethyl ionone, 3,7-dimethyl-6-octenal (citronelal), diphenyl ether, 1,4-bis(1-methylethyl)benzene, pentyl ester 2-hidroxy benzoic acid, alpha-trichloromethyl benzenemethanol acetate, 9-butyl anthracene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene, 1-pentylheptyl-benzene and 2-phenyl-methylene-octanal were removed from the HDPE multilayer packaging after cleaning.

GC–MS chromatograms showed, as expected, a larger number of peaks for recycled PET in comparison with virgin PET samples.

Samples submitted to deep cleaning, due to the effectiveness of this process in removing contaminants, showed lower numbers of peaks compared to samples conventionally washed.

Table 5
List of volatile organic compounds identified in recycled PET and HDPE.

RT (min)	Number	Identified volatile organic compounds	CAS	MW	S1	S2	S3	S4	S5cc	S6cc	S7cc	S5dp	S6dp	S7dp	PET-V1	PET-V2	PET-R1	PET-R2	HDPE-R	HDPE-3	HDPE-5
3.399	1	Toluene	108-88-3	92.14	X	X	X	X		X	X	X	X	X		X	X	X	X	X	X
6.913	2	p-Xylene	106-42-3	106.16	X	X	X	X				X	X	X		X	X	X			
8.585	3	Styrene	100-42-5	104.06							X										
11.110	4	o-Xylene	95-47-6	106.16					X	X	X								X	X	X
12.649	5	Benzaldehyde	100-52-7	106.12	X	X	X	X				X	X	X		X	X	X			
13.903	6	1-R-alpha-pinene	80-56-8	136.23															X		
14.364	7	4-Ethyl-1,2-dimethylbenzene	934-80-5	134.22	X		X	X				X	X				X	X			
14.367	8	2-Ethyl-1,3-dimethylbenzene	2870-04-4	134.22	X	X	X	X				X	X	X		X	X	X			
14.435	9	4-Ethyl-1,2-dimethylbenzene	934-80-5	134.22		X						X				X					
14.750	10	Camphene	79-92-5	136.23															X		
17.863	11	Acetophenone	98-86-2	120.15	X	X	X					X	X	X		X					
19.231	12	Limonene	5989-54-8	136.23					X	X									X	X	X
21.948	13	2,6-Dimethyl-7-octen-2-ol	18479-58-8	156.15															X		
22.473	14	Heptyl hexyl ether	7289-40-9	200.21		X	X	X				X	X	X		X	X	X			
22.486	15	Dodecane	112-40-3	170.20									X				X			X	
22.775	16	o-Cymene	7399-49-7	132.20															X		
23.104	17	Naphthalene	91-20-3	128.17	X	X	X	X				X		X		X	X	X			
24.137	18	Nonanal	124-19-6	142.24					X	X	X									X	X
25.348	19	10-Methylnonadecane	56862-62-5	282.55	X	X	X	X				X	X	X			X	X	X		
25.535	20	2-Methyl decane	6975-98-0	156.31		X	X	X				X	X			X	X	X			
25.610	21	7-Methyl hexadecane	26730-20-1	240.47	X		X	X					X	X		X	X	X			
26.032	22	3,7-Dimethyl-6-octenal (citronelal)	106-23-0	154.25															X		
26.169	23	3-Methyl-undecane	1002-43-3	170.20																	X
26.901	24	Tridecane	629-50-5	184.22	X	X		X				X	X	X		X			X	X	X
26.904	25	Tritetracontane	7098-21-7	605.16	X	X	X	X				X	X	X		X	X	X			
27.530	26	10-Methylnonadecane	56862-62-5	282.55										X							
27.599	27	(Z)-2-dodecene	7206-26-0	168.32																X	
27.613	28	Tetratetracontane	7098-22-8	619.18	X	X	X	X				X	X	X		X	X	X			
27.943	29	1-Chlorooctadecane	3386-33-2	288.94	X	X	X	X	X			X	X	X		X	X	X			
27.951	30	Dodecane	112-40-3	170.20															X		X
28.080	31	Heptacosane	593-49-7	380.73	X	X	X	X				X	X	X		X	X	X		X	
28.112	32	Pentadecane	629-62-9	212.42												X			X		X
28.864	33	Decane	124-18-5	142.28	X	X	X	X				X	X	X		X	X	X	X		
29.008	34	Hexadecane	544-76-3	226.44	X	X	X	X				X	X	X		X	X	X			
29.132	35	Nonadecane	629-92-5	268.31	X	X	X	X				X	X	X		X	X	X			X
29.583	36	10-Methyleicosane	54833-23-7	29.657	X	X	X	X				X	X	X		X	X	X			
29.875	37	3,8-Dimethyldecane	17312-55-9	170.33	X		X	X					X	X		X	X	X			
29.983	38	2,6,10-Trimethyldodecane (farnesan)	3891-98-3	212.41	X	X	X	X				X	X	X		X	X	X			
30.827	39	1,1′-Oxybis-dodecane	4542-57-8	354.65				X				X	X	X		X	X	X			
31.116	40	2,6-Dimethyl-octadecane	75163-97-2	282.33					X	X	X										
31.144	41	4-[1,1-Dimethylethyl]-benzeethanal	109347-45-7	176.12															X		
31.258	42	Tetradecane	629-59-4	198.39																	X
31.260	43	2,6,10,14-Tetramethyl heptadecane	18344-37-1	296.57																X	
32.039	44	Isobornyl acetate	5655-61-8	196.29															X	X	X
32.514	45	Diphenyl ether	101-84-8	170.07									X				X		X		
33.236	46	1,1′-Oxybis-decane	2456-28-2	298.55	X	X	X	X				X	X	X		X	X	X			
33.456	47	1,4-Bis(1-methylethyl)-benzene	100-18-5	162.27															X		
33.718	48	Tetratriacontane	14167-59-0	478.92	X	X	X					X	X	X		X	X	X			

Table 5 (*Continued*)

RT (min)	Number	Identified volatile organic compounds	CAS	MW	S1	S2	S3	S4	S5cc	S6cc	S7cc	S5dp	S6dp	S7dp	PET-V1	PET-V2	PET-R1	PET-R2	HDPE-R	HDPE-3	HDPE-5
34.134	49	4-tert-Butylcyclohexyl acetate	32210-23-4	198.16															X	X	X
34.797	50	(+)-4-Carene	29050-33-7	136.23															X	X	
35.180	51	Nonadecane	629-92-6	268.52									X				X				
35.630	52	4-tert-Butylcyclohexyl acetate	32210-23-5	198.16															X	X	X
35.740	53	Heneicosane	629-94-7	296.57					X	X	X		X						X	X	
35.963	54	2,6-Di-tert-butyl-4-methylphenol (BHT)	128-37-0	220.35	X	X	X	X				X	X	X		X		X			
36.793	55	Tetradecane	629-59-4	198.24															X	X	X
36.795	56	Dodecane	112-40-3	170.2					X	X	X								X		X
37.397	57	Dodecyl ester trichloroacetic acid	74339-50-7	330.00																X	
37.418	58	9-Thiabicyclo(3.3.1)nonane-2,6-dione	37918-35-7	170.04																	X
37.787	59	Trycyclo[4.2.4.1(2,5)]dec-3-en-9-ol, stereoisomer	70220-93-8	150.10																X	
37.811	60	3a,4,7,7a-Tetrahydro-4,7-methano-1H-indene	77-73-6	132.09															X		X
38.361	61	Tritetracontane	7098-21-7	605.16					X	X	X										
38.709	62	Tetratetracontane	7098-22-8	619.18					X	X	X										
39.157	63	Alpha-isomethyl ionone	127-51-5	206.32															X		
39.320	64	Diethyl phthalate (DEP)	84-66-2	222.24													X		X	X	X
39.470	65	Tricyclo[4.4.0.0(2,8)]decane	49700-59-6	136.13															X		
39.697	66	N-methyl-N-phenyl-acetamide	579-10-2	149.08															X		
39.960	67	1-Chlorooctadecane	3386-33-2	288.26																X	
40.286	68	2,5-Bis(1,1-dimethylethyl) phenol	5875-45-6	206.32															X	X	X
40.438	69	1-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-1-penten-3-one	7779-30-8	206.17															X		
40.551	70	Benzophenone	119-61-9	182.22	X	X	X	X				X	X	X		X	X	X			
40.681	71	Trycyclo[4.2.4.1(2,5)]dec-7-en-9-ol	1000191-01-9	150.10																	X
40.966	72	Lilial	80-54-6	204.31															X	X	X
41.099	73	Pentyl ester 2-hydroxy-benzoic acid	2050-08-0	208.25															X		
41.375	74	Alpha-trichloromethyl-benzenemethanol acetate	90-17-5	267.53															X		
43.930	75	9-Butyl-anthracene	1498-69-7	234.33															X		
43.958	76	11,12-Dihydroxysychellane	055823-65-9	238.19																X	
43.972	77	4-Allyl-5-furan-2-yl-2,4-dihydro-[1,2,4]triazole-3-thione	1000300-01-3	207.05																	X
44.642	78	Allyl ester 3-methylphenyl-carbamic acid	1000314-77-3	191.10															X		
44.767	79	Dibutyl phthalate (DBP)	84-74-2	278.34	X	X	X	X				X	X	X		X	X	X			X
45.005	80	2,3-Dihydro-1,1,3-trimethyl-3-phenyl-1H-indene	3910-35-8	236.35															X		
45.149	81	1-Pentylheptyl-benzene	2719-62-2	246.43															X		
45.839	82	2-Phenyl-methylene-octanal	101-86-0	216.32															X		
47.547	83	Galaxolide 1	1000285-26-6	258.20															X	X	X
47.988	84	Isobutyl octadecyl ester phthalic acid	1000309-06-1	474.37					X	X	X				X				X	X	X
55.713	85	Bis(2-ethylhexyl) ester hexanedioic acid	103-23-1	370.00					X		X				X						

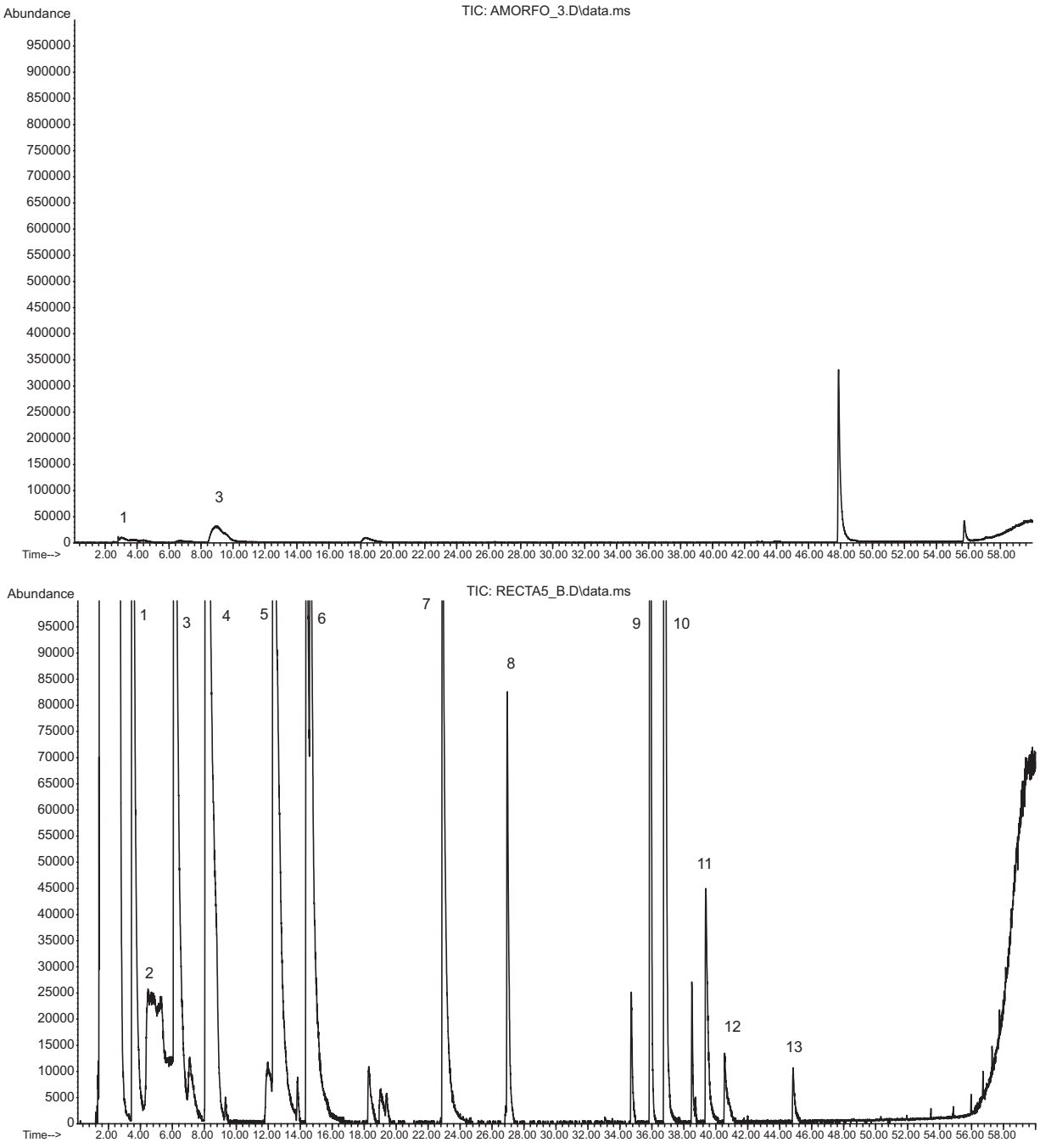

Fig. 3. GC–MS chromatogram from blank (top) and fortified (5000 ng g^{-1}) PET amorphous pellet samples (bottom) extracted by HS-SPME. Peaks identity is as follows: (1) toluene, (2) hexamethyl cyclotrisiloxane, (3) chlorobenzene, (4) styrene, (5) benzaldehyde, (6) limonene, (7) naphthalene, (8) isobornyl acetate, (9) BHT, (10) 2,4-di-tert-butylphenol, (11) DEP, (12) benzophenone and (13) DBP.

Comparing the four steps applied in the PET super cleaning process, it was observed that the number of peaks in the chromatogram decreased after each subsequent step. However, little difference could be observed between the extruded sample (S3) and the sample from SSP (S4).

The multilayer (3 and 5 layers) packaging containing recycled HDPE showed a quite similar chromatographic profile among them. Nevertheless, both of them showed smaller peak areas and lower number of peaks when compared to the recycled HDPE pellets. These results suggested a lower concentration of the same VOCs in the multilayer packaging compared to the recycled HDPE. In addition, the co-extrusion process employed for the packaging manufacture could eliminate most of the volatile compounds from the recycled HDPE. On the other hand, it was important to consider the formation and/or introduction of other contaminants, such as 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-1-penten-3-one, tricyclo[4.2.4.1(2,5)]dec-3-en-9-ol and 2,6,10,14-tetramethyl heptadecane, due to the influence of the transformation process on the other polymers that constituted the whole packaging.

After their identification, some of the VOCs were quantified by the validated HS-SPME–GC–MS method using analytical curves. Characteristic chromatograms of a sample and a fortified sample (5000 ng g^{-1}) are presented in Fig. 3 .

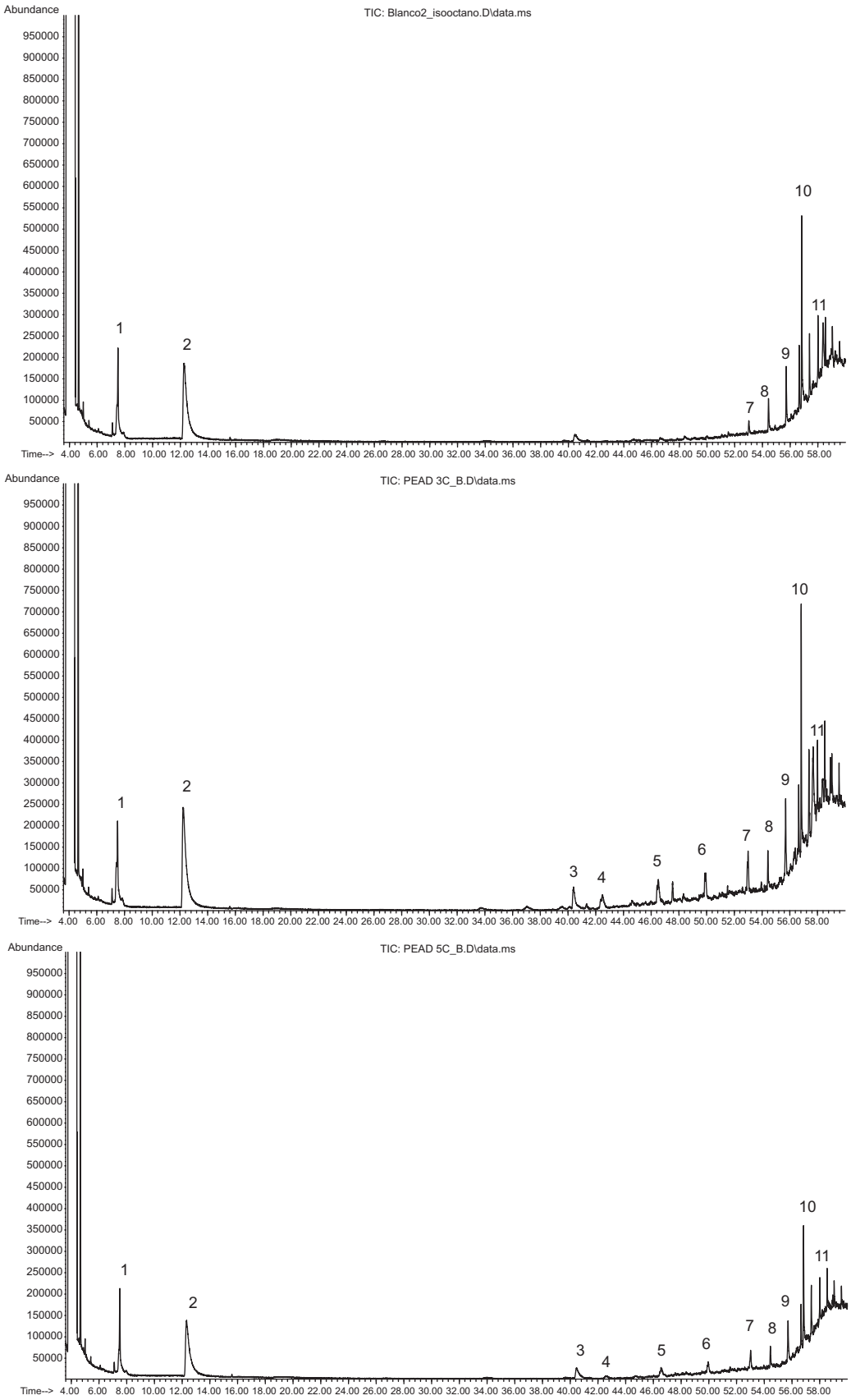

Fig. 4. GC–MS chromatogram from a blank sample (top) and HDPE packaging multilayer samples with either 3 layers (middle) or 5 layers (bottom). Peaks identity is as follows: (1) octane; (2) nonane; (3) 2,4-di-tert-butylphenol; (4) tritetracontane; (5) tetratriacontane; (6) butyl tetradecyl ester sulphurous acid; (7) docosane; (8) tetratriacontane; (9) tetratetracontane; (10) 2,2′-methylenebis[6-(1,1-dimethylethyl)-4-ethyl-phenol]; (11) 9-methyl nonadecane.

Table 6
Quantification of some compounds in PET and HDPE samples by HS-SPME–GC–MS ($n = 3$).

Samples	Benzaldehyde	Concentration (ng g^{-1}) 2,4-di-tert-butylphenol	BHT	Limonene
S1	859.87 ± 37.00	1490.81 ± 3.14	440.75 ± 4.69	
S2	764.75 ± 41.47	1490.84 ± 14.03	485.91 ± 26.34	
S3	1055.85 ± 25.99	1490.82 ± 4.54	467.00 ± 4.98	
S4	850.79 ± 53.97	1490.71 ± 11.39	481.39 ± 34.01	
S5cc	931.08 ± 32.69			
S6cc	915.77 ± 66.46			
S7cc	802.44 ± 27.42			
PET-V1	528.94 ± 30.40			
PET-V2	740.73 ± 20.53			
PET-R1	661.47 ± 23.00	1517.61 ± 0.33		
PET-R2	1527.14 ± 7.20		476.72 ± 13.72	
HDPE-R		1607.08 ± 30.66		
HDPE-3		1720.42 ± 59.86		441.06 ± 37.46
HDPE-5				1558.89 ± 31.15

According to the US FDA model for assessing the efficiency of a recycling process, the maximum acceptable level of a residual contaminant in a polymer that corresponds to an estimated daily rate of 1.5 μg/person/day depends on the density of the polymer, its thickness and the consumption factor. Based on this, a maximum value for residues of 220 ng g^{-1} was proposed for recycled PET (with a density of 1.4 g cm^{-3}), assuming the conservative supposition that all types of foods use packages made with this polymer and that the final item consisted of 100% recycled PET. For recycled HDPE polyolefins (with a density of 0.965 g cm^{-3}), the maximum value for residues was 320 ng g^{-1} [3].

The results obtained in the current study (Table 6) indicated that, even after conventional and super clean cleaning processes, benzaldehyde was present at levels above the limit of 220 ng g^{-1} in recycled PET samples. After deep cleaning, however, these contaminants were completely removed. In addition, 2,4-di-tert-butylphenol and BHT were quantified in samples obtained from super clean treated and recycled PET. The presence of high levels of some contaminants could be attributed to the misuse of post-consumer PET material and a lack of control in the collection of this material. This could also have occurred due to recontamination in the recycling system or even by external contamination. In the HDPE samples, 2,4-di-tert-butylphenol, BHT and limonene presented values above 320 ng g^{-1}.

Welle [2] previously explained the presence of 2,4-di-tert-butylphenol in the recycled HDPE samples. The explanation was that this compound was generated during the recycling process and could have been the degradation product of the additive Irgafos 168, which is commonly used as an antioxidant in polyolefins.

3.5. Migration test for HDPE multilayer packaging

HDPE multilayer packaging was exposed to a fatty food simulant, isooctane, in order to determine the migration level of VOCs. The results can be seen in Fig. 4, which shows the chromatograms obtained for blank simulant (without sample) and for the simulant exposed to the packaging. The migration tests did not show the presence of contaminants in the simulant exposed to both samples of multilayer HDPE, and the compounds found in the blank samples of the HDPE multilayer packaging and the compounds found in the blank simulant were the same as those analysed in the extracts of the packaging samples after the migration test. These results indicate that VOCs do not migrate to the fatty food simulant under the tested condition employed.

4. Conclusion

The HS-SPME–GC–MS method presented in this report was shown to be rapid, sensitive, economical, and ecologically sensitive, as it used a reduced amount of organic solvents. The method presented adequate selectivity and detection capability for the determination of VOCs in post-consumer PET and HDPE. In addition, the method could easily be used for quality control in the production of recycled PET and HDPE. Furthermore, the study demonstrated the efficiency of the deep cleaning process for PET samples. Such oversight, however, would require adequate monitoring of post-consumer PET material using a reliable analytical method, such as the one presented and validated here. Moreover, the results obtained with a fatty food simulant (isooctane) for HDPE multilayer packaging confirmed that no migration of VOCs occurred.

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