Migration of volatile substances from recycled high density polyethylene to milk products

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ABSTRACT

Plastic recycling is the main solution to reduce the plastic waste. High-density polyethylene has not been recycled yet successfully as food contact material due to the amount of chemicals present in post-consumer material together with its high chemical sorption capacity. The migration of two post-consumer recycled HDPE milk bottles were studied to both 50 % ethanol as food simulant and real food (one type skimmed milk and two plant base beverages (soy milk and horchata). Firstly, a headspace-solid phase extraction-gas chromatography mass spectrometry method was developed and optimized to analyze these milky samples. After exposure, 53 compounds were identified and among them several additives, NIAS such as 2,5-cyclohexadiene-1,4-dione, 2,6-bis (1,1-dimethylethyl), 2,4-di-tert-butylphenol and 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione, degradation products of antioxidant compounds as well as several residues from cleaning products, detergents and flavoring agents were found. Finally, the risk assessment was applied and it was found that five compounds did not comply after migration to 50 % ethanol.

1. Introduction

Nowadays, there is a growing concern about the huge plastic accumulation found in our environment, in oceans as well as in natural landscapes. This problem is closely related to two facts; the great consumption of these materials and their no-degradable nature. The global production of plastic in Europe was 55 million tones in 2020, PlasticsEurope (2020) of which about 40.5 % was dedicated to food packaging materials due to their suitable properties as optimum cost/benefit ratios, lightness and good processability.

To tackle increasingly prominent environmental issues, the European Union agreed that a circular economy is the main solution to mitigate this problem, being recycling as the first option for the plastic that has been used, thrown away, collected, cleaned, reprocessed and remade into new product, the so called post-consumer plastic packaging waste.

The concept of circular economy is a great driving force for food companies and food contact materials manufacturers and represents as well a big challenge. In the case of recycled packaging materials the challenge gets even more complex by the possible increase of chemical migration with respect to virgin materials. In recycled materials the

accumulation of additives and their degradation products, the increase of compounds coming from for example; printing inks as benzophenone, polymeric benzophenone and polymeric ITX or 2-butoxyethanol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol 10 (TMDD) and TMDD ethoxylates found in acrylic adhesives or benzene 4–cyanocyclohexene and benzene isothiocyanate in rubber adhesives (Aparicio & Elizalde, 2015; Canellas, Vera, & Nerin, 2017; Galbiati, Jacxsens, & De Meulenaer, 2021; Nerin et al., 2013). Also compound found in labels or multilayers as the appearance of oligomers (diacid and monoglycol monomers as well as diglycol monomers) in polyethylene naphthalate and polybutylene terephthalate or also cyclic co-oligomers found in EVA plastics or cyclic PET and PTB oligomers (Hoppe, de Voogt, & Franz, 2021; Nerin et al., 2022; Vera, Canellas, Nerin, Dreolin, & Goshawk, 2022; Xu et al., 2021) could occur. Therefore, the effort of manufacturing safe recycled materials might be aggravated.

To guarantee the safety, both virgin and recycled materials in contact with food must fulfill the Regulation (EC) Nº 1935/2004 (Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food), the Commission Regulation (EU) 10/2011 (Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials

and articles intended to come into contact with food) and the recently published regulation on recycled plastics for food contact (Commission Regulation (EU) 2022/1616 on recycled plastic materials and articles intended to come into contact with foods will enter into force on 10 October 2022), where specific migration limits (SML) and conditions of the migration tests are detailed.

It is worth emphasizing that polyolefin like polypropylene (PP) and high/low density polyethylene (HDPE and LDPE) account for 49.7 % (PlasticsEurope, 2020) of the plastic production for food packaging. These materials offer, besides the characteristic described above, a great versatility in their uses, organoleptic and chemical properties, moisture barrier, thermal and rupture resistance (Vera, Canellas, & Nerin, 2018; Vera, Canellas, Barknowitz, Goshawk, & Nerin, 2019). However, they have not been successfully recycled yet as food contact materials due to their high chemical diffusion potential and the lack of technology properly designed for these materials. Compared to polyethylene terephthalate (PET), which is almost the unique plastic successfully recycled as food contact material, polyolefins have higher chemical sorption capacity, a faster diffusion of organic compounds through the matrix and higher migration potential than PET. Consequently, cleaning procedures used for PET cannot be simply and directly applied to polyolefins. New researches, developments and investments are required to satisfy the high quality demands of industry (Strangl, Ortner, & Buettner, 2019). The crucial step for this achievement is to get a previous knowledge about the chemical compositions in post-consumer polyolefins and to design innovative and efficient recycling systems with enough capabilities to remove most of additives and NIAS from this kind of samples (Welle, 2005).

As far as we know, study about migration from recycled polyolefins, in particular recycled HDPE, as food contact materials is rare. Some researches focused their studies on odorants found in postconsumer bags and films of HDPE (Cabanes, Strangl, Ortner, Fullana, & Buettner, 2020; Strangl, Ortner, Fell, Ginzinger, & Buettner, 2020; Strangl, Schlummer, Maeurer, & Buettner, 2018). Also, several migration studies from different recycled HDPE were investigated (Devlieghere, De Meulenaer, Demyttenaere, & Huygherbaert, 1998; Dutra et al., 2014; Welle, 2005) and recently, some untargeted studies about migration from pellets and flakes were done to investigate potential risks coming from these materials under worse-case scenario in our laboratory (Su, Vera, Nerin, Lin, & Zhong, 2021; Su, Vera, Salafranca, & Nerin, 2021).

The main objectives of this work was to identify the migrant compounds coming from containers made of recycled post-consumer HDPE milk bottles and to determine the migration to food simulant and to the real food.

This work was divided in different tasks: (1) to optimize a method based on solid phase microextraction (SPME) gas chromatography mass spectrometry (GC-MS) to study the migration from plastic to food; (2) to carry out an untargeted study of migration to the food simulant 50 % ethanol as well as to different real milk products; (3) to quantify the migrants and perform the risk assessment of these migrants in both simulant and milk food products.

2. Materials and methods

2.1. Reagents

The standards alpha-Terpinene (CAS: 99-86-5), naphthalene (CAS: 91-20-3), 1-dodecene (CAS: 112-41-4), dodecane,1-chloro- (CAS: 112-52-7), naphthalene,1-methyl (CAS: 90-12-0), 1-tetradecene (CAS: 1120-36-1), diphenyl ether (CAS: 101-84-8), 2,6-Bis(2-methyl-2-propanyl)-1,4-benzoquinone (CAS: 719-22-2), butylated hydroxytoluene (CAS: 128-37-0), 2,4-Di-tert-butylphenol (CAS: 96-76-4), diethyl phthalate (CAS: 84-66-2), ethyl dodecanoate (CAS: 106-33-2), 1,2-benzenedicarboxylic acid, bis (2-methyl-propyl) ester (CAS: 84-69-5), 7,9-di-terc-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione (CAS: 82304-66-3), octocrylene (CAS: 6197-30-4), cinamaldehyde (CAS: 104-55-2),

cyclohexylmethacrylate (CAS:101-43-9), 1-hexadecanol (CAS: 36653-82-4), benzophenone (CAS: 119-61-9), 1-hexadecene (CAS: 629-73-2), -Phenyl-2-butanone (CAS: 1007-32-5), 2-ethylhexyl salicylate (CAS: 118-60-5), isopropyl myristate (CAS: 110-27-0), dibutilphthalate (CAS: 84-74-2), isopropyl palmitate (CAS: 142–91–6) and hexanedioic acid, bis(2-ethylhexyl) ester) (CAS: 103-23-1) were purchased from Sigma-Aldrich Química S.A (Madrid, Spain). All of them were of analytical quality. Ethanol and water of HPLC grade were supplied by Scharlau Chemie S.A (Sentmenat, Spain).

2.2. Samples

2.2.1. Plastic containers

Two kinds of plastic containers made of different flakes coming from post-consumer HDPE milk bottles were studied. These flakes were provided by two European plastic recycling companies where HDPE milk bottles were kerbside collected and separated from other plastics in their sorting plants. After that, they were cut up and washed with water to attain both flake samples. Finally, they were extra decontaminated with a non-destructive deodorization process by heating; no more details of these extra decontamination processes are available for confidential reasons.

After that, the flakes supplied by these companies were pelletized separately by means of Collin ZK-50 twin screw extruder, screws diameter 50 mm, at 50 rpm and 230ºC. This machine was capable to manufacture the pellets, which were re-extruded to manufacture these kinds of containers under study, Fig. 1a.

The small containers used were made up of a body and its corresponding lid and their geometry corresponds to the diagrams shown in Fig. 1b.

The molds corresponding to lid and body are two small molds, 75 × 75 × 93 mm for the body and 75 × 75 × 73 mm for the lid, made of 1.2344 steel. The lid mold has a central gate and the piece is ejected with a single central pin. In the case of the body, it is a central injection mold in which the part is ejected by means of a ring that pushes around the entire perimeter of the part's mouth. Fig. 1c shows both molds open and with advanced ejection.

All parts were produced by injection in a Babyplast machine (Babyplast 6/10, fabricada en 2005 por Cronoplast S.L. en LHospitalet (Barcelona), España), with a piston diameter of 14 mm, the process conditions were: material Temperature (°C) 230 and 220 °C, Injection time (s) 2 and 3.7, maximum pressure on the material (kg/cm^2) 1100 and 700 and cooling time (s) 2 and 5 all conditions in the body and in the lid respectively.

2.2.2. Food products

Three classes of milk products (skimmed milk, soy milk and horchata) were studied. Skimmed milk was used to optimize the conditions of SPME-GC-MS and the migration analysis. Its composition was as follows; 34Kcal energy value, 0.3 g of fats, 0.2 g of saturated fats, 4.7 g of carbohydrate, 4.7 g of sugar, 3.2 g proteins, 0.1 g of salts and 120 mg of Calcium as mean values in 100 mL. Besides, soy milk with 36Kcal energy value, 1.8 g of fats, 0.3 g of saturated fats acids, 1 g of carbohydrate, 0.6 g of sugar, 3.6 g proteins, 0.5 g of dietary fiber and 1.5 g of polyunsaturated fatty acids and horchata with 31 kcal energy value, 1.7 g of fats, 0.3 g of saturated fats acids, 0.6 g of carbohydrate, 0.6 g of sugar, 3.1 g proteins, 0.4 g of dietary fiber and 1 g of polyunsaturated fatty acids also as mean values in 100 mL were used for migration tests. All real foods were contained in plastic bottles of 1 L of capacity and stored at room temperature in the supermarket. They were purchased in a supermarket from Zaragoza (Spain).
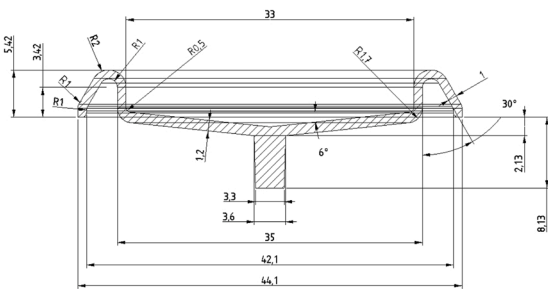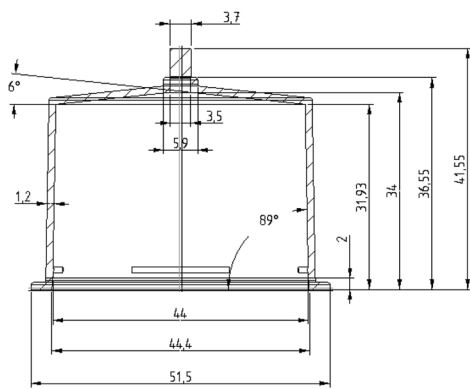
2.3. SPME-GC-MS conditions

2.3.1. Optimization of SPME conditions with skimmed milk

SPME method was optimized before studying the migration from

Fig. 1. a: Samples of recycled HDPE studied. b: Sketch of the body (left), and of the lid (right) (Dimensions in mm). c: Lid (left) and body (right) molds.

recycled HDPE to milk and vegetable beverages products. For this purpose, firstly a search of compounds in bibliography was carried out in order to choose several additives as well as NIAS commonly found in this kind of recycled HDPE samples. The only indispensable requirement was that these compounds should have been detected previously by GC-MS methodology (Cabanes et al., 2020; Strangl et al., 2018; Su, Vera, Nerin, et al., 2021; Vera, Canellas, & Nerin, 2020).

15 compounds (Table 1) were chosen as common compounds coming from previous studies of recycled HDPE. These compounds were added

to skimmed milk in order to optimize the best conditions for SPME-GC-MS analysis. For this purpose, one mixed solution of 1 ug/g, which contained all these compounds, was prepared in milliQ water and used to spike with different volumes the skimmed milk to obtain a final concentration of 10 ng/g. Finally, these spiked skimmed milks were analyzed by SPME-GC-MS in order to optimize the parameters as follows: head-space or immersion as extraction conditions, fiber type, matrix effect, extraction temperature and time.

The first set of parameters to optimize was the extraction type;

Table 1

Compounds selected for SPME optimization with their CAS numbers, retention times (Rt), masses for SIM method. Optimization results expressed as ratio of areas between different fibers, HS or immersion method, dilutions 1:5 or 1:10 of spiked milk product.

Compounds	CAS	Rt	Masses	Fiber DVD/CAR/PDMS /Fiber PDMS		Recovery % HS/Immersion and dilution 1:5/1:10			
				HS	Immersion	HS and dil1:5	HS and dil1:10	Immersion and dil 1:5	Immersion and dil 1:10
alpha-Terpinene	99-86-5	6.7	93.1/136.1/77	0.59	0.61	64.2	64.2	78.1	98.3
Naphthalene	91-20-3	9.45	128.1	21.7	21.6	81.6	98.9	97.6	95.8
1-dodecene	112-41-4	9.6	55.1/69.1/83.1	1.84	1.36	88.6	98.8	44.4	0.21
Dodecane,1-chloro-	112-52-7	11.3	91.1/55.1/69	17.1	16.7	50.7	99.9	68.2	76.6
Naphthalene,1-methyl	90-12-0	12.6	142/115	1.76	2.37	63.9	93.4	57.3	94.9
1-tetradecene	1120-36-1	14.85	55.1/69.1/83.1	8.14	6.08	65.6	99.9	64.6	79.0
Diphenyl ether	101-84-8	15.15	170.1/141.1	3.02	2.17	49.4	86.2	43.8	99.9
2,6-Bis(2-methyl-2-propanyl)-1,4-benzoquinone	719-22-2	16.5	177.2/220.2/205.2	0.98	1.09	71.0	70.5	52.8	95.6
Butylated hydroxytoluene	128-37-0	17.32	205.2/191.2/220.2	0.04	2.29	69.9	86.3	74.5	96.5
2,4-Di-tert-butylphenol	96-76-4	17.41	191.2/206.2	6.86	8.85	37.3	98.2	96.9	99.8
Diethyl phtalate	84-66-2	18.85	149/177.1	1.60	1.52	45.4	94.9	31.8	46.9
Ethyl dodecanoate	106-33-2	18.91	88/101	2.03	2.29	21.0	99.9	42.8	68.9
1,2-benzenedicarboxylic acid, bis (2-methylpropyl) ester	84-69-5	24.59	149/223	1.95	3.51	14.7	54.6	81.6	98.8
7,9-di-terc-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione	82304-66-3	24.4	205.2/217.2/175.1	0.56	0.97	0.00	6.09	41.2	98.7
Octocrylene	6197-30-4	33	204.1/249.1/232	0.59	0.61	64.2	64.2	78.1	98.3

Red values highlighted showing the highest values comparing HS dil 1:5 against HS dil 1:10 and inmersion dil 1:5 against inmersion dil 1:10.

headspace or immersion, fiber type and matrix effect (diluting 5 or 10 times the milk).

The optimization design was based on a total of 16 experiments, half of which were done with PDMS fiber (100 μm) and the other half with DVB/CAR/PDMS fiber (50/30 μm). Within these 8 experiments with each type of fiber, 4 were analyzed by the HS method and 4 by immersion. And finally, among each method one was prepared with the 1/5 dilution, another with 1/10, one blank of water and the last one at concentration of 10 ng/g of mix solution in water without milk, to compare and calculate the recovery in order to study the matrix effect of the milk. These assays were prepared and studied by duplicate.

To carry out these experiments, other criteria were chosen; the vials should have a total sample capacity of 5 mL to be analyzed with HS method and a capacity of 18 mL for the immersion method. As previously described, for HS method 1 g or 0.5 g of milk were diluted with 5 g with water for the 1/5 and 1/10 dilution respectively. Both solutions were spiked with 50 μl of mixed solution to get a final concentration of 10 ppb. On the other hand, for immersion method (18 mL capacity) and 1/5 dilution or 1/10 dilution, 3.6 g or 1.8 g of milk respectively, were filled up with 18 g of water and spiked with 180 μl of mixed solution to get a final concentration of 10 ppb.

All experiments were analyzed by GC-MS. The criterion for selecting the best fiber was based on the signal intensity of the peaks detected when comparing both fibers. The choice of the other two parameters (method and dilution) was based on the comparison of the signal versus the same analysis but using 10 ng/g of mix solution in water and their recoveries were calculated.

Secondly, an experimental design was used to optimize the best conditions of temperature and extraction time parameters. It was carried out by response surface methodology (RSM) with the software MODDE v6.0 (Umetrics AB). 14 experiments were designed, where the temperature was studied from 50 to 80 °C and extraction time from 15 to 40 min. For this purpose, 0.5 g of milk were diluted 10 times with water and spiked with 50 μL of mixed solution, placed into 20 mL vials and analyzed by HS-SPME-GC-MS with the fiber DVD/CAR/PDMS. The RSM and all statistical analyses across the study were processed by the open-source R programming.

Finally, the optimized conditions for milk analysis were as follows;

HS-SPME extraction, DVD/CAR/PDMS fiber, dilution 1:10, 80 °C of extraction temperature and 40 min of extraction time.

2.3.2. Gas chromatography–mass spectrometry GC-MS

To perform chromatographic separation Agilent Technologies 7820A gas chromatograph coupled to a series mass detector (5977B MSN) from Agilent Technologies (Madrid, Spain) was used. The capillary column HP-5MS (30 m × 0.25 μm × 250 μm) from Agilent Technologies (Madrid, Spain) was used. The injection type was splitless and the helium flow was 1.0 mL/min. The injector temperature was 250 °C. The acquisition was done in electron impact ionization (EI).

For the optimization assays the oven temperature program was from 80 °C (5 min), a ramp of 10 °C/min to 120 °C, 2 °C/min to 130 °C, 10 °C/min to 170 °C, 2 °C/min to 180 °C, 10 °C/min to final temperature of 300 °C (35 min of analysis). Acquisition was carried out in SIM (selected ion monitoring) mode where the masses chosen are shown in Table 1.

The oven temperature program used for specific migration analysis was from 50 °C (5 min), a ramp of temperature of 10 °C/min to 300 °C maintained for 5 min. Acquisition was done in SCAN mode (50–450 *m/z*) for both screening and quantification migration analysis.

2.4. Migration assays

The migration studies were carried out according to Commission Regulation (EU) 10/2011 (Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food), which indicates the application of 50 % ethanol as the proper simulant to milk products (simulating the migration of skimmed milk under study) and also for cloudy drinks: juices and nectars and soft drinks containing fruit pulp, musts containing fruit pulp, liquid chocolate (simulating the vegetable beverages such as soy milk and horchata under study). Besides skimmed milk, soy milk and horchata as real foods were tested, because the analyzed rHDPE containers were intended to be in contact with this kind of foods.

For the migration assays, both recycled high density polyethylene (rHDPE) containers were filled in with 3.5 mL of simulant and/or real foods (applying a surface to volume ratio of 6 dm^2 per kg of food). Then,

the containers with 50 % ethanol as simulant were kept in the oven at 60 °C for 10 days, simulating the storage conditions of milk and vegetable beverages products in a HDPE bottle, usually stored for about 3–6 months at room temperature according to Commission Regulation (EU) 10/2011(Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food), where the contact times above 30 days (long term) at room temperature and below, shall be tested in accelerated test conditions at elevated temperature for a maximum of 10 days at 60 °C. However, the containers with real food were placed during the same time but in the fridge at 6ºC to avoid their spoiling. Three replicates of each assay and each sample were prepared.

In addition, three replicates with 3.5 mL of 50 % ethanol and the real foods were prepared in vials of 20 mL and kept at the same migration conditions (50 % ethanol in the oven at 60 °C during 10 days and real foods in the fridge at 6 °C during 10 days) in order to use them as blanks of the migration assays.

After the exposure, 1 g of simulant diluted with 4 g of water and 0.5 g of real food diluted with 4.5 g of water were placed in 18 mL vials and analyzed by HS-SPME-GC-MS with the method previously optimized.

2.5. Identification of migrant compounds from simulant and real food

Different steps were carried out to determine and identify the migrant compounds coming from 50 % ethanol and real foods. Initially, the migration chromatograms of both containers after migration assays were compared to their respective blanks. Then, only the compounds present in the samples and absent in the blanks were taken into account as markers. Once the markers were chosen for each container and simulant or real food, their identifications were carried out using the NIST v.17 and WILEY v.275 mass spectra libraries. Only the markers with a match factor higher than 80 were chosen as potential candidates.

To refine the identification, Kovatx indexes (KI) of all markers were calculated in order to improve the reliability of the identification as well as to facilitate the literature search of candidates, where their fragments obtained and these KI calculated were compared to the compounds used in the manufacture of polyolefin materials.

Finally, to confirm the identification, the standards found were injected under the same chromatographic conditions (HS-SPME-GC-MS), matching their retention times and mass spectra.

2.6. Migration quantification and risk assessment

After confirming the identification of all migrant compounds, their concentration was quantified in order to check the potential human risks. For this purpose, fresh calibrated curves were prepared by standard addition by spiking each sample with 10 μl of standard solution which contained six standards with increasing concentrations. Each calibration curve had a final concentration in the range of 0.1 ng/kg to 100 ng (of compound) /kg (of simulant or real food). All calibration curves were prepared in the different matrices (10 % ethanol and skimmed milk, soy milk and horchata diluted 10 times in water) and analyzed by HS-SPME-GC-MS. Their LODs were calculated as the concentration that had a signal-to-noise ratio (S/N) of 3 using the least concentration detected. In case of lack of standards, the migrant compounds were quantified with other standards with similar chemical structure. These migration values were compared to their respective SML found in the Regulation positive list Commission Regulation (EU) 10/2011 (Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food).

When the compounds were not authorized in the legislation, they were classified into three Cramer categories: Class I, low toxicity, class II medium toxicity and class III high toxicity, depending on their structures, according to software Toxtree®. Then, their migration was compared to the maximum values of human daily intake recommended by Cramer that corresponded to 1.8, 0.54 and 0.09 mg/Kg food for class I, II and III respectively (Threshold of toxicological concern TTC, 2005; Risk assessment of non-listed substances (NLS) and not-intentionally added substances (NIAS) under article 19. PlasticsEurope).

3. Results and discussion

3.1. Optimization SPME-GC-MS conditions to work with milk products

The compounds selected for the optimization of SPME conditions are shown in Table 1 together with their retention times and their characteristic masses used for SIM acquisition.

3.1.1. Fiber type, extraction method and effect matrix

The highest areas for most of the compounds were obtained with the DVD/CAR/PDMS fiber and are shown in Table 1. The ratio between the areas obtained for each fiber, DVD/CAR/PDMS over PDMS fiber, and each compound was calculated. This process was applied for HS as well as immersion method. As shown, in most of the cases, these ratios are higher than 1, which means that the extraction was better using DVD/CAR/PDMS fiber.

Table 1 also lists the extraction recoveries with the DVD/CAR/PDMS fiber using HS and immersion modes, when the dilutions were 1:5 or 1:10. As these results show, the best areas were obtained for dilution 1/10 compared to dilution 1/5 in both immersion and HS method. However, comparing both methods, for some compounds such as 1-dodecene, dodecane,1-chloro-, 1 tetradecene. ethyl dodecanoate and diethyl phthalate, HS method was clearly better, while for alpha-Terpinene, 2,6-Bis(2-methyl-2-propanyl)-1,4-benzoquinone, 1.2-benzenedicarboxylic acid. bis (2methylpropyl) ester, 7,9-di-terc-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione and octocrylene immersion method was the best one, as expected, based on the volatility of the compounds. Therefore, the selection would be a compromise solution, finally opting for HS method due to the fact that working with milk products the immersion mode could damage the SPME fiber earlier.

3.1.2. Temperature and extraction time

To study the effect of both parameters, one central composite on face as design of experiments was selected. A good fit for this model was obtained with a fraction of the variation of the response (R2) and a fraction of the variation of the response predicted by the model (Q2) closed to 1 for all compounds. The response surface plots for some compounds are shown in Fig. 2, where Fig. 2a shows the response surface for the sum of all areas of all compounds. It can be seen that the total response increases when extraction time and temperature increase. Therefore, the best conditions were 80ºC and 40 min of extraction, namely, the highest limits chosen for both parameters. Most of the compounds individually studied had a similar tendency and their areas increased with the time and temperature, as for example 2,4-Di-tert-butylphenol, Fig. 2b. Other compounds such as naphthalene,1-methyl, diphenyl ether, 2,6-Bis(2-methyl-2-propanyl)-1,4-benzoquinone, butylated hydroxytoluene, diethyl phthalate, ethyl dodecanoate, 1,2-benzenedicarboxylic acid, bis (2methylpropyl) ester and 7,9-di-terc-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione had also similar response, although their slopes could slightly change.

Fig. 2c shows dodecane,1-chloro- response, where a slight concave curvature in the temperature can be observed, with a maximum between 70 and 75 °C. The same response was found for naphthalene and octocrylene, the last compound with the highest area at 70 °C. However, a convex curvature was obtained in Fig. 2d for 1-tetradecene compound, where the highest area was found for the shortest time and lowest temperature (15 min and 50 °C). The same tendency was found for 1-dodecene. Finally, Fig. 2e. shows the response for alpha-Terpinene, where the maximum area was found for the longest time (40 min) and lowest temperature (50 °C).
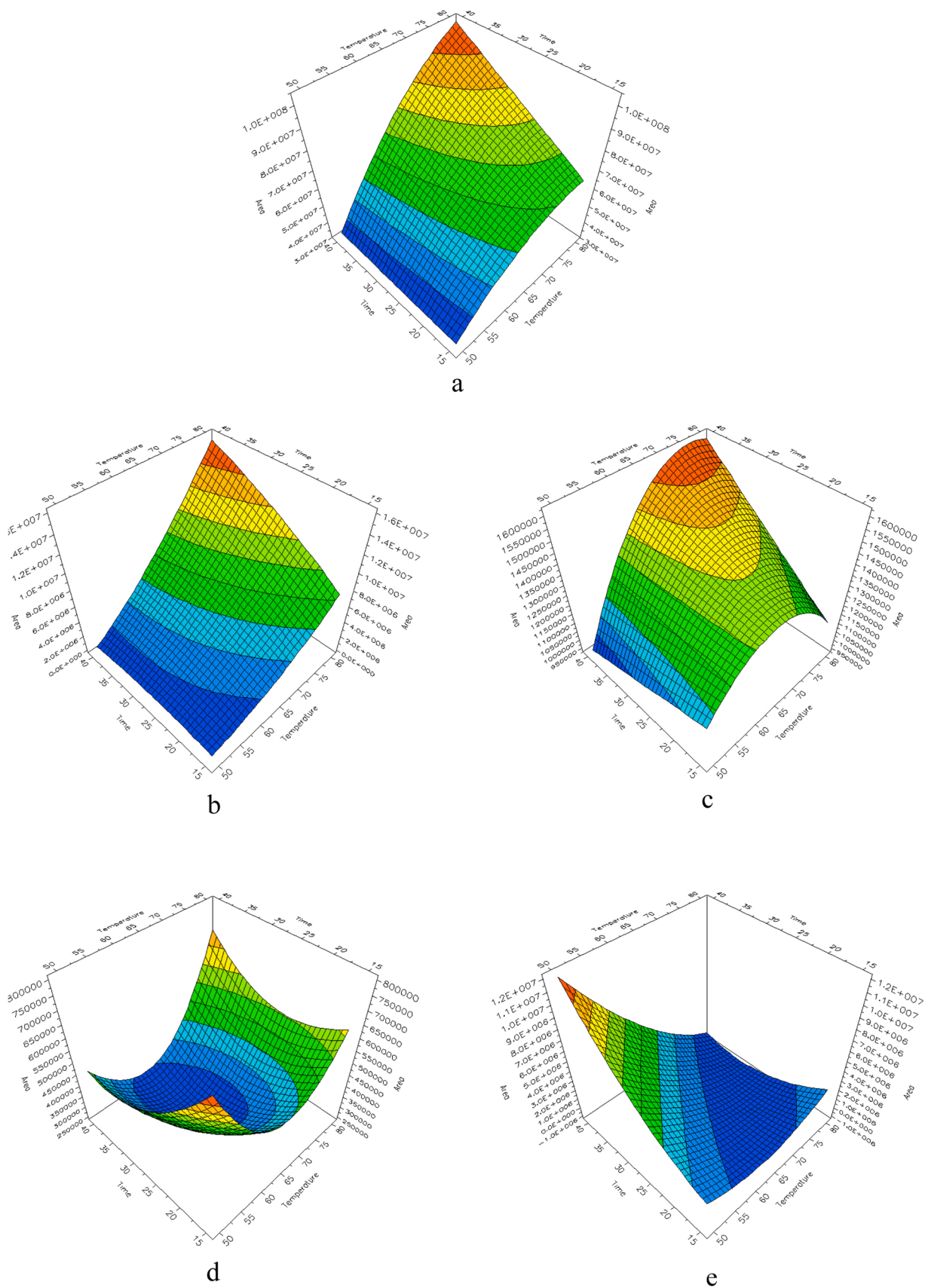
Fig. 2. Response surface plot expressed in area with respect to the time and temperature extraction. a. Response surface plot of the sum of area of all compounds. b. Response surface plot of 2,4-Di-tert-butylphenol. c. Response surface plot of dodecane,1-chloro-. d. Response surface plot of 1-tetradecene. e. Response surface plot of alpha-Terpinene.

Thus, taking into account these results, the optimized conditions were a compromise situation. As most of the compounds showed the same pattern, that means the highest areas for the highest temperature (80 °C) and the longest time (40 min), these were the conditions chosen after all.

3.2. Identification of migrants

Fifty three compounds were detected and are listed in Table 2. Most of the compounds were found in both containers, only four different compounds were detected in one container (compound 40 in the container 1 and compounds 51, 52 and 53 in the container 2). Sixteen compounds were identified and corroborated with their standards.

Table 2
Compounds identified after migration studies with their retention times (Rt), their matches in case of the lack of standard (match), their Kovats index (IK) and their CAS and their more abundant masses (*m/z*).

Nº	Rt	Match	IK	Compound	Container 1	Container 2	CAS	Masses (m/z)
1	13.98		1193	1-Dodecene	x	x	112-41-4	55.1; 69.1; 83.1; 97.1
2	14.32		1266	Cinnamaldehyde, (E)-	x	x	14371-10-9	131; 103; 78
3	14.87		1322	Ni	x	x		147; 91; 162.1
4	15.1	78.55	1346	4-Tert-butylcyclohexyl acetate	x	x	32210-23-4	57.2; 97.1; 83.1
5	15.98		1393	1-Tetradecene	x	x	1120-36-1	83.1; 69.1; 55.1; 97.1
6	16.1		1396	Diphenyl ether	x	x	101-84-8	170.1; 141.1; 115.1
7	16.66	76.2	1426	1-(4-tert-Butylphenyl)propan-2-one	x	x	81561-77-5	147.1; 175.2; 190.1
8	16.79	72	1433	Naphthalene, 2-methoxy-	x	x	93-04-9	115; 158
9	16.82		1461	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	x	x	719-22-2	177; 220.2
10	17.34		1504	Butylated Hydroxytoluene	x	x	128-37-0	205.1; 220.2
11	17.41		1515	2,4-Di-tert-butylphenol	x	x	96-76-4	191.1; 206.2
12	17.51	74.7	1517	1-Penten-3-one, 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-	x	x	7779-30-8	121.1; 93.1; 135.1
13	17.58		1518	Ni	x	x		66; 138; 117
14	17.68		1519	Ni	x	x	14852-31-4	57.2; 97.1; 83.1
15	17.71	82.7	1520	Naphthalene. 2-ethoxy-	x	x	93-18-5	144.1; 115; 172.1
16	17.75	84.5	1534	Amyl salicytate	x	x	2050-08-0	120; 138; 208.1
17	18.24	72.7	1557	Isoamyl salicylate	x	x	87-20-7	120; 138; 208.
18	18.28		1592	1-Hexadecene	x	x	629-73-2	83.1; 97.1; 69.1
19	18.34		1596	Dodecanoic acid. ethyl ester	x	x	106-33-2	88; 101.1; 71.1
20	18.45		1601	Ni	x	x		57.2; 97.1; 83.1
21	18.5		1603	Ni	x	x		57.2; 97.1; 83.1
22	18.6		1607	Ni	x	x		57.2; 97.1; 83.1
23	18.96		1623	Benzophenone	x	x	119-61-9	182.1; 105; 77.1; 51.1
24	19.08	80	1645	Cinnamaldehyde. α-pentyl-	x	x	122-40-7	129; 115.1; 202.1; 91
25	19.2		1655	Ni	x	x		191.2; 119.1; 91.1
26	19.3		1664	Ni	x	x		191.2; 119.1; 91.1;
27	19.46	79.5	1678	n-Hexyl salicylate	x	x	6259-76-3	120; 138; 222.1
28	19.67		1698	Ni	x	x		191.2; 135.1;
29	19.81		1711	Ni	x	x		57.2; 97.1; 83.1
30	20.03		1732	Ni	x	x		57.2; 97.1; 83.1
31	20.22	96.6	1750	Cinnamaldehyde. α-hexyl	x	x	101-86-0	129.1; 115.1; 216.1; 91.1
32	20.27	70.2	1753	Benzene. 1,1'-(1.2-cyclobutanediyl) bis-. trans-	x	x	20071-09-4	104.1; 78
33	20.45	70.4	1778	Cinnamaldehyde. α-hexyl	x	x	101-86-0	129.1; 115.1; 91.1
34	20.5	75.2	1785	Ethanone. 1-(2.3.4.7.8.8a-hexahydro-3.6.8.8-tetramethyl-1H-3a.7-methanoazulen-5-yl)-		x	68039-35-0	161.1; 231.1; 105.1
35	20.52		1795	1-Octadecene	x	x	112-88-9	83.1; 97.1; 69.1
36	20.78		1807	2-Ethylhexyl salicylate	x	x	118-60-5	120; 138; 250.1
37	20.88		1812	Isopropyl myristate	x	x	110-27-0	228.2; 211.1
38	21.25	75	1850	Cyclopenta[g]-2-benzopyran. 1.3.4.6.7.8-hexahydro-4.6.6.7.8.8-hexamethyl	x	x	1222-05-5	243.2; 258.1; 213.2
39	21.31	77.7	1851	7-Acetyl-6-ethyl-1.1.4.4-tetramethyltetralin	x	x	88-29-9	243.1; 258.1; 213.1
40	21.56		1875	Ni	x			91.1; 228.1; 243.1; 65
41	21.62		1887	Ni	x	x		243.2; 258.1; 213.1
42	21.66	82.5	1904	Homosalate	x	x	118-56-9	138; 120; 109.1; 355
43	21.77		1910	Ni	x	x		243.1; 258.1; 213.1
44	22.05		1916	7.9-Di-tert-butyl-1-oxaspiro(4.5)deca-6.9-diene-2.8-dione	x	x	82304-66-3	205; 281.1; 217.1; 175.1
45	22.17		1921	Ni	x	x		57.2; 97.1; 83.1
46	22.29		1924	Dibutyl phthalate	x	x	84-74-2	149; 57; 71.1
47	22.63		1993	Benzenepropanoic acid. 3.5-bis(1.1-dimethylethyl)-4-hydroxy-. methyl ester	x	x	6386-38-5	277.1; 292.1; 147
48	22.8	90.7	2027	Isopropyl palmitate	x	x	142-91-6	256.1; 239.1; 102.1
49	22.89		2032	Ni	x	x		57.2; 97.1; 83.1
50	26.06		2393	Hexanedioic acid. bis(2-ethylhexyl) ester	x	x	103-23-1	129; 147; 112; 57.1
51	26.65		2482	Ni (sulfur compound)		x		91;129.1;194.1
52	27.39		2536	Ni (sulfur compound)		x		91;129.1;194.1
53	27.49		2578	Ni (sulfur compound)		x		91;129.1;194.1;

Ni: no identified.
The highlighted masses were common in different compounds.

Among them there were several common additives used in the manufacture of plastics: butylated hydroxytoluene (compound 10) and benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy- methyl ester as antioxidants (compound 47) (Vera et al., 2018), 2-ethylhexyl salicylate (compound 36) and benzophenone (compound 23) were UV-filter and photoinitiator in UV (Sapozhnikova & Hoh, 2019) respectively, a plasticizer as dibutyl phthalate (compound 46) and diphenyl ether (compound 6) used as solvent for successive solution fractionation of high-density polyethylene (Stephenne, Bailly, Berghmans, Daoust, & Godard, 2009), fatty acids like dodecanoic acid, ethyl ester and hexanedioic acid, bis(2-ethylhexyl) ester (compounds 19 and 50 respectively) and several alkenes coming from production of this kind of polymer (HDPE) (compounds 1, 5, 18 and 35). Besides, several NIAS as 2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl), 2,4-Di-tert-butylphenol (compounds 9 and 11) degradation products of Irgafos 168 (Kato & Conte, 2021) and 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6, 9-diene-2,8-dione from irganox 1010 or irganox 1076 (compounds 44) (Graino, Sendon, Hernandez, & de Quiros, 2018; Murat, Puttaswamy, Ferret, Cosledan, & Simon, 2020).

Cinnamaldehyde (E) was also identified, which may be a residue coming from its previous use as additive in food or also as active antimicrobial compound in active packaging (Nerín, Vera, & Canellas, 2017).

On the other hand, seventeen compounds were identified with a high

match over 70, but they were not confirmed due to the lack of standard. For example, some residues related to cleaning products such as 4-tert-Butylcyclohexyl acetate (compound 4) and amyl or isoamyl salicylate, that are (compound 16 and 18) fragrance ingredients used in cosmetics and personal care products and also in washing and cleaning products (Bhatia, Jones, Letizia, & Api, 2008; Lapczynski, Jones, McGinty, Bhatia, Letizia, & Api, 2007); naphthalene, 2-methoxy- (compound 8) that is used as fragrance in cleaning agents and detergents found in PET samples (Widen, Leufven, & Nielsen, 2005) and naphthalene, 2-ethoxy (compound 15) used for detergent and soap flavor (Fukuda, Sakurai, & Yamahara).

Besides, some of these compounds were associated with flavoring agents for food; cinnamaldehyde, α-pentyl and α-hexyl, n-hexyl salicylate and isopropyl palmitate (compounds 24, 31 or 33, 27 and 48 respectively) (Onghena et al., 2016), the last one has already been found in plastic materials (Sapozhnikova & Hoh, 2019).

The compounds benzene, 1,1′-(1,2-cyclobutanediyl)bis-, trans (compound 32) could be an extractable residue associated with polystyrene materials (Murat et al., 2020) and homosalate (compound 42) a UV-absorber (Sapozhnikova & Hoh, 2019).

And finally, eight compounds (numbers 14, 20, 21, 22, 29, 30, 45 and 49) whose rupture masses were 57; 97; 83 *m/z* were classified as non-identified compounds. Also, three compounds (numbers 25, 26 and 28) were not identified with match below than 70, all of them had the

Table 3
Migration from post-consumer HDPE containers to 50 % ethanol (simulant) expressed as ng of compound/g simulant, their SML and their Cramer classification.

No.	Compounds	Quantified with other standard	Migration container 1 ng/g	Migration container 2 ng/g	SML EU/10/ 2011 ng/g	Cramer toxicity
1	1-dodecene		**615 ± 36**	**2630 ± 382**	50	
2	Cinnamaldehyde, (*E*)-	Cinnamaldehyde	**1830 ± 146**	**3450 ± 143**		I
4	4-tert-Butylcyclohexyl acetate	Cyclohexylmethacrylate	44.6 ± 3.5	121 ± 24		II
5	1 Tetradecene		< LOQ = 4.2	24.6 ± 2.3	50	
6	Diphenyl ether		22.5 ± 1.8	57.3 ± 4.9		III
7	1-(4-tert-Butylphenyl)propan-2-one	Cinnamaldehyde	615 ± 49	946 ± 142		I
8	Naphthalene, 2-methoxy-	Naphthalene, 1-methyl	< LOQ = 1.67	3.63 ± 0.27		III
9	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-		26.3 ± 1.8	27.1 ± 4.1		II
10	Butylated Hydroxytoluene		15.3 ± 1.2	25.9 ± 2.5	3000	
11	2,4-Di-tert-butylphenol		42.5 ± 3.4	62.4 ± 6.8		I
12	1-Penten-3-one, 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-	2,5-Cyclohexadiene-1,4-dione, 2,6-bis (1,1-dimethylethyl)-	11.6 ± 0.6	12.5 ± 1.4		I
15	Naphthalene, 2-ethoxy-	Naphthalene, 1-methyl	< LOQ = 1.67	1.88 ± 0.11		III
16	Amyl salicytate	2-ethylhexyl salicylate	103 ± 7	201 ± 18		I
17	Isoamyl salicylate	2-ethylhexyl salicylate	224 ± 18	505 ± 33		I
18	1-Hexadecene		103 ± 7.9	219 ± 19		I
19	Dodecanoic acid, ethyl ester		4.61 ± 0.36	6.20 ± 0.37		I
23	Benzophenone		104 ± 8.3	205 ± 13	600	
24	Cinnamaldehyde, α-pentyl-	Cinnamaldehyde	1615 ± 113	**7340 ± 500**		I
27	n-Hexyl salicylate	2-ethylhexyl salicylate	715 ± 58	1760 ± 80		I
31	Cinnamaldehyde, α-hexyl-	Cinnamaldehyde	651 ± 52	706 ± 41		I
32	Benzene, 1,1′-(1,2-cyclobutanediyl)bis-, trans-	Naphthalene, 1-methyl	3.22 ± 0.16	9.93 ± 0.54		III
33	Cinnamaldehyde, α-hexyl-	Cinnamaldehyde	20.8 ± 3.4	43.7 ± 6.6		I
34	Ethanone, 1-(2,3,4,7,8,8a-hexahydro-3,6,8,8-tetramethyl-1 H-3a,7-methanoazulen-5-yl)-	1-fenil-2-butanona	< LOD = 0.7	28.1 ± 1.8		III
35	1-Octadecene		52.8 ± 2.7	82.1 ± 8.3		I
36	2-Ethylhexyl salicylate		33.7 ± 2.7	127 ± 7		I
37	Isopropyl myristate		48.9 ± 4.5	101 ± 2		I
38	Cyclopenta[*g*]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-	Benzophenone	**2120 ± 179**	**3990 ± 336**		III
39	7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin	Benzophenone	322 ± 25	**716 ± 47**		II
42	Homosalate	Benzophenone	99.6 ± 9.6	223 ± 15		I
44	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione		< LOD = 2.5	< LOQ = 8.4		III
46	Dibutilftalato		90.2 ± 7.1	93.1 ± 8.0	300	
47	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester		20.2 ± 1.8	23.9 ± 0.8		II
48	Isopropyl palmitate	Methyl palmitate	38.6 ± 3.9	13.2 ± 1.6		I
50	Hexanedioic acid, bis(2-ethylhexyl) ester		22.4 ± 3.5	38.9 ± 6.2	18,000	

LOQ: Limit of quantification and LOD: Limit of detection.

common masses 191.2, 119.1 and 91.1 *m/z*. The last three compounds (numbers 51, 52 and 53), which were found only in the container 2, had common masses (91, 129.1 and 194.1 *m/z*), all their candidates had sulfur in their structures, but with matches bellow 70 therefore they were classified as non- identified compounds.

3.3. Migration compounds to 50 % ethanol and milk and vegetable beverages products and its risk assessment

The concentrations of the migrating compounds were subsequently determined from calibration curves prepared in 10 % ethanol and skimmed milk (diluted 10 times in water). Table 3 shows the migration values expressed as ng of compound/g simulant for both containers to 50 % ethanol as simulant. Their SML and Toxtree classes when the compound was not legislated are also shown.

Comparing the migration values between both containers, the migration values were higher in container 2 than in container 1, except for isopropyl palmitate. This fact could be attributed to the washed and extra decontaminating heating process previously applied to the flakes by the company that supplied them to manufacture the container 1.

Surprisingly, only six compounds, alkenes (1-dodecene and 1-tetra-decene), the antioxidant BHT, benzophenone, dibutyl phthalate and hexanedioic acid, bis(2-ethylhexyl) ester were included in the Commission Regulation (EU) 10/2011 (Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food). Their migration values were below their SMLs, except for 1-dodecene, whose migration values were much higher than 50 ng/g for both containers, specifically 615 ± 36 and 2630 ± 382 ng/g respectively.

The toxicity of the rest of the compounds (86 % of the set found) was classified according to Cramer classes. Seven compounds had class III of toxicity, likely due to the presence of several aromatic rings in their chemical structure. For example, the compound cyclopenta[g]-2-ben-zopyran,1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl, had migration values much higher than 90 ng/g recommended by Cramer for class III and 716 ± 47 ng/g were found for 7-Acetyl-6-ethyl-1,1,4,4-tetramethyl-tetralin (Class II), higher than 540 ng/g recommended by Cramer for sample 2. Although most of the compounds found were classified as class I of toxicity, both compounds cinnamaldehyde (E) for both containers and cinnamaldehyde α-pentyl- for sample 2 were also above the values recommended by Cramer (1800 ng/g, class I).

Thus, after applying the risk assessment, it could be concluded that both containers did not comply with the Commission Regulation (EU) 10/2011 (Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food) and the recommendations of the maximum values of human daily intake (Risk assessment of non-listed substances (NLS) and not-intentionally added substances (NIAS) under article 19. PlasticsEurope). Therefore, these containers were not recommended for packaging milk products not even for cloudy drinks as juices and nectars and soft drinks containing fruit pulp, musts containing fruit pulp and liquid

chocolate for all periods of prolonged storage above 30 days (long term) at room temperature.

Finally, Table 4 shows the migration values for both containers to skimmed milk and vegetable beverage products. Only seven compounds were detected in these real foods. All of them were below their SML or recommended values by Cramer. Therefore, these containers were recommended for packaging milk products and cloudy drinks for periods of time less than 30 days at refrigerated temperature.

The difference found between the migration to 50 % ethanol as simulant and real milk or vegetable beverages products could be related to the temperature used for both migration assays. Temperature of 60 °C for 10 days was chosen for the simulant following the legislation, to represent the worst scenario, for all periods of prolonged storage above 30 days (long term) at room temperature covering the milk and vegetable beverage bottles storage, usually about 3–6 months at room temperature before consumption. However in the case of real food migration assays, it was impossible to reach and reproduce these assays at this temperature. For this reason the migration assays were kept in a fridge at 6 °C avoiding the microbiological contamination of milk products.

4. Conclusion

The migration from two different containers of recycled post-consume HDPE coming from different recycling companies, potentially used to package milk or vegetable milky beverages, has been evaluated. The study was focused on migration to 50 % ethanol as food simulant and to different kind of real foods as a skimmed milk products and two vegetable beverages, soy milk and horchata.

The optimized method of SPME-GC-MS has demonstrated to be a fast and efficient one for the analysis of migrants in both ethanol 50 % as food simulant and in several milk products, with recoveries over 90 % in most of the cases and without prior complex and time consuming sample treatment.

Fifty three compounds were detected in 50 % ethanol simulant and among them several common additives such as antioxidants (BHT and benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy- methyl ester), UV-filters and photoinitiators (2-ethylhexyl salicylate, benzophenone and homosalate), plasticizer (dibutyl phthalate), solvent (diphenyl ether) as well as several NIAS coming from breakage of large antioxidants as Irgafos 168, irganox 1010 and irganox 1076, residues related to cleaning products as 4-tert-Butylcyclohexyl acetate, amyl or isoamyl salicylate naphthalene, 2-methoxy- and naphthalene, 2-ethoxy and several compounds associated with flavoring agents. However, only eight compounds were detected after migration to milk and vegetable beverage products.

Besides, their risk assessment was evaluated, where the compound 1-dodecene exceed its SML. Four compounds were above the migration values recommended by Cramer in the simulant 50 % ethanol, but this was not the case in milk and vegetable beverages products, where the migration values were much lower showing that the temperature strongly affected migration, as expected.

Table 4
Migration from post-consumer HDPE containers to real food like skimmed milk, soy milk and horchata expressed as ng of compound/g food.

No.	Compound	Migration to skimmed milk ng/g		Migration to soy milk ng/g		Migration to horchata ng/g		SML EU/10/2011 ng/g	Cramer toxicity
		Container 1	Container 2	Container 1	Container 2	Container 1	Container 2		
6	Diphenyl ether	0.18 ± 0.02	0.16 ± 0.04	0.12 ± 0.01	0.58 ± 0.15	0.20 ± 0.03	0.07 ± 0.01		III
8	Naphthalene, 2-methoxy-	< LOQ = 2.76	< LOQ = 2.76	< LOD = 0.78	< LOD = 0.78	< LOD = 0.78	< LOD = 0.78		III
9	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	0.26 ± 0.01	< LOQ = 0.24	< LOQ = 0.66	< LOQ= 0.66	< LOQ = 0.82	< LOQ = 0.82		II
10	Butylated Hydroxytoluene	0.26 ± 0.02	0.26 ± 0.02	<LOQ= 0.22	0.24 ± 0.02	< LOQ = 0.36	< LOQ = 0.36	3000	
11	2,4-Di-tert-butylphenol	< LOQ = 0.25	0.35 ± 0.04	<LOQ= 0.50	<LOQ= 0.50	< LOQ = 0.55	< LOQ = 0.55		I
19	Dodecanoic acid, ethyl ester	< LOQ = 0.25	< LOQ = 0.25	<LOQ= <0.65	1.72 ± 0.21	< LOQ = 0.65	< LOQ = 0.65		I
27	n-Hexyl salicylate	< LOQ = 1.18	< LOQ = 1.18	5.36 ± 0.32	18.8 ± 2.0	< LOQ = 3.85	< LOQ = =3.85		I

These results emphasize the importance of new researches, developments and investments for this kind of recycled materials. It is clear that the cleaning technology of postconsumer HDPE requires extra-decontamination process to reduce the amount of migrants and to reach a high quality recycled materials, completely safe inside this circular economy.

CRediT authorship contribution statement

Paula Vera: Conceptualization, Methodology, Validation, Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Elena Canellas:** Conceptualization, Validation, Data curation, Writing – original draft, Writing – review & editing. **Qi-Zhi Su:** Conceptualization, Methodology. **Daniel Mercado:** design and manufacture of samples under study. **Cristina Nerín:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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