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Evaluation of new safety decontamination approaches at lab scale for recycled highdensity polyethylene (rHDPE) intended for food contact

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ABSTRACT

Background: The increasing use of plastic packaging materials generates concerns related to the environmental problem generated by their waste. As a result, the search for new recycling methodologies to extend the lifecycle of plastic packaging is becoming more important, without forgetting to ensure the safety of these materials. Currently, the use of recycled polyolefins as food contact materials is not widespread yet. This is because the decontamination processes currently available are insufficient to produce clean, safe materials suitable for such applications. This work is focused on the evaluation of the safety of recycled high-density polyethylene (rHDPE), and the search for strategies to achieve its decontamination.

Results: To this end, three batches of flakes and three batches of pellets of rHDPE coming from the mechanical recycling of post-consumer milk bottles were analyzed. The analysis of the volatile and semi-volatile compounds present in the samples was carried out using gas chromatography-mass spectrometry (GC–MS), finding a total of 67 compounds. The strategy to achieve the decontamination of flakes and pellets of this material has been based on the application of high temperature and vacuum at lab scale, obtaining a clear decrease in volatile compounds, below 50% of the initial value in most cases when applying 120 °C during 5 h. The migration test performed in the samples (treated and untreated) to different food simulants (10 % ethanol and 3 % acetic acid, 95 % ethanol) revealed also a clear decrease of concentrations of volatiles.

Significance: The findings are highly encouraging, demonstrating substantial progress toward the safe and effective use of rHDPE in specific food packaging applications. This indicates a significant step forward in the potential uses of rHDPE. Nevertheless, the lack of toxicity data for many migrants necessitates additional toxicological testing to obtain a more precise risk assessment.

1. Introduction

Over the last few years, the development of plastic materials has increased substantially, with plastic packaging being one of the main contributors to this increase. This sector accounted for 39 % of plastic demand in 2021 in Europe and 44 % worldwide [1]. The use of plastic in packaging involves some environmental concerns due to the high volume of production, its slow degradation and the problems related to waste management. In view of this, recycling appears to be a great measure to reduce food packaging waste and therefore the overall impact of plastic packaging on the environment [2]. However, only recycled polyethylene terephthalate (PET) has been successfully recycled and used as food contact material, mainly due to its low additives content, if any, and its little capacity to absorb contaminants [2] . In contrast, polyolefins, that are the most important group of polymers used for food packaging (70 %) [3] have a low percentage of recycling: 10 % of HDPE, 5 % of LDPE and <1 % of PP [4] and nearly none of them are used for food contact applications. This fact is mainly due totheir reduced thermal stability as well as to their high absorption and diffusion capacity, linked to a higher chemical migration from these recycled materials to the food compared to other polymers [5]. European Regulation EU/10/2011 for plastic materials intended for food contact [6] established a positive list of substances that may be used for the manufacture of these materials, which are named as *Intentionally Added Substances*, IAS. Among these compounds stand out monomers, antioxidants, plasticizers or adhesives [7]. However, food contamination can also occur through the transfer of non-intentionally added substances, NIAS, which can be formed by degradation of the polymer matrix and its additives during synthesis, processing or polymer life cycle, and can also come from impurities or reaction products when contacting material

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and food [8–10]. As a consequence of this, it is crucial to have methodologies to identify the composition of postconsumer polyolefins but also to study appropriate recycling systems to ensure de safety of recycled polyolefins intended for food contact. There are some studies in regard to the analysis and quantification of volatile NIAS and IAS in post-consumer polyolefins (mainly by SPME-GC–MS) and safety issues related to their use [11–13], as well as certain methods to remove volatile organic compounds (VOCs) from plastic waste [14,15]. The decontamination procedures compiled in the studies showed good results in eliminating VOCs present in different polyolefins, such as steam stripping, supercritical fluid extractions or high temperatures combined with reduced pressure, but, in general, decontamination efficiency decreased as the molecular weight increased. However, migration from recycled polyolefins has been studied to a lesser degree. In the study performed by Su et al. (Su et al. 2021), 475 migrants were detected in various recycled polyolefins, 39.2 % of them were related to food and 36.2 % to cosmetics. Additionally, the study showed that 21.4% of the compounds identified were saturated hydrocarbons, fatty acyls or prenol lipids.

This study seeks to assess the viability of employing rHDPE for food-contact purposes, with a focus on safety considerations and to explore new decontamination techniques that reduce the NIAS content of rHDPE. For this purpose, in first place an untargeted screening of volatile and semivolatile compounds from both flakes and pellets of post-consumer polyolefin was performed by head space-solid-phase microextraction gas chromatography mass spectrometry (HS-SPME-GC–MS). Afterwards, decontamination process consisting in the application of temperature and pressure was tested at different times in order to find the optimal conditions of treatment. The analysis of decontaminated flakes and pellets at these conditions was compared with the results obtained in the screening of untreated materials. Principal component analysis was performed in order to reduce the dimensionality of decontamination processes data and identify patterns, thus increasing interpretability and minimizing information loss. Finally, both the untreated and the decontaminated samples were submitted to migration test with 3 different food simulants (3 % acetic acid, 10 % ethanol and 95 % ethanol) and under the conditions established in the European Directive EU/10/2011. The same analytical technique was performed in order to identify volatile and semi-volatile compounds migrating from both types of samples into these three simulants. Potential sources of their origins were explored, and quantification of migrants was conducted when possible.

2. Material and methods

2.1. Samples

Three batches of flakes and three batches of pellets of mechanically recycled high-density polyethylene were studied (rHDPE). Flakes were cut-offs of post-consumer milk bottles that had been submitted to several cleansing processes. They were irregular fragments with different shapes and thicknesses. Pellets came from the extrusion of the latter flakes and showed a cylindrical shape (diameter=5 mm; height=2 mm; density=971 Kg m^{-3}). Both were provided by a recycling company.

2.2. Reagents and SPME fibers

Ethanol (HPLC-MS quality) and glacial acetic acid (pharma grade), both from PanReac AppliChem (Barcelona, España), and ultrapure water obtained from a Wasserlab Ultramatic equipment were used.

The standards used were all analytical quality: α-Terpineol (CAS No: 98–55–5), 1-chlorododecane (CAS No: 112–52–7), 1-dodecanol (CAS No: 112–53–8), 1-methylnaphthalene (CAS No: 90–12–0), 1-tetradecene (CAS No: 1120–36–1), 2,4-di-ter-butylphenol (CAS No: 96–76–4), 4-propylbenzaldehyde (CAS No: 28,785–06–0), bornyl acetate (CAS No: 76–49–3), benzophenone (CAS No: 119–61–9), butylated hydroxytoluene (CAS No: 128–37–0), dodecane (CAS No: 112–40–3), phenol (CAS No: 108–95–2), ethyl laurate (CAS No: 106–33–2), limonene (CAS No: 138–86–3), menthol (CAS No: 89–78–1), isopropyl myristate (CAS No: 110–27–0), methyl palmitate (CAS No: 112–39–0), 2-ethylhexyl salicylate (CAS No: 118–60–5), cyclohexanol (CAS No: 108–93–0), 2-ethylhexyl acetate (CAS No: 103–09–3), benzocyclobutene (CAS No: 694–87–1), allyl benzoate (CAS No: 583–04–0), α-ionone (CAS No: 127–41–3), 2,6-diisopropylnaphthalene (CAS No: 24,157–81–1) and undecane (CAS No: 1120–21–4) . They were bought to Sigma-Aldrich (Barcelona, Spain).

SPME fibers (PDMS 100 μm, DVD/CAR/PDMS 50/30 μm) were provided by Supelco (Bellefonte, PA, USA).

2.3. Analysis of volatile and semi-volatile compounds in rHDPE by HS-SPME-GC–MS

Initially, 1.2 g of flakes or 2.3 g of pellets, were weighed and placed in 20 mL glass vials hermetically closed prior to be analyzed by HS-SPME-GC–MS. All the experiments were performed in triplicate. The samples were first equilibrated at 80 °C during 5 min and then, extracted at 80 °C for 40 min. The samples were heated in the heater module of a PAL RSI 85 autosampler from Agilent. SPME fiber was desorbed at 250 °C for 2 min in splitless mode. For the analysis, a gas chromatograph 7820A GC system coupled to a mass spectrometer 5977C MSD from Agilent Technologies (Santa Clara, CA, USA) was used. The column was a HP-5MS Ultra Inert (30 m x 25 mm x 0.25 μm film thickness) from Agilent. The oven temperature ramp was as follows: initially 50 °C for 3 min, 10 °C min^{-1} to 150 °C, then 5 °C min^{-1} to 200 and held at 300 °C for 2 min. MS analysis was performed in SCAN mode from m/z 45 to 450.

The identification of a detected compound was initially performed by comparison of its mass spectrum with those reported in NIST library. A candidate was considered confirmed by NIST when the match value between the mass spectrum of the compound and the proposed candidate (matching values from 0 to 1000) was above 700. The retention index (RI) of the detected compound was also calculated, injecting a solution of alkanes from C7 to C40 under the same conditions as the sample. A candidate was confirmed by RI when the relative difference between its calculated RI value (RI_{exp}) and RI value from the bibliography (RI_{bib}) was <5 %. Finally, when the standard of the compound was available, it was injected, and the retention time and mass spectra were compared with those of the sample. A candidate was considered confirmed by the standard when a good match was obtained.

2.4. Optimization of rHDPE decontamination treatment

For conducting the rHDPE decontamination process, a vacuum drying oven Vaciotem TV 4001490 from P.Selecta was used. This oven allowed the application of temperatures from 35 °C to 200 °C and a minimum pressure of 1 mBar.

A set of experiments, at 120 °C (the most extreme possible conditions without exceeding the melting point of the polyolefin [16]), were performed at different rising times: 1, 2, 3, 5 and 10 h and under vacuum conditions.

In order to estimate the optimal treatment conditions for the decontaminating process of rHDPE, both flakes and pellets at the different treatment times as well as in the untreated samples were analyzed by GC–MS. The analysis methodology is described in Section 2.3.

In order to verify that vacuum conditions improved the decontamination process, samples were also decontaminated at 120 °C under atmospheric pressure during the optimal treatment time.

Final rHDPE decontamination treatment was as follows: In the case of flakes, final decontamination protocol consisted in 3 h of treatment at 120 °C, and, while in the case of pellets the optimal conditions were 5 h of treatment at 120 °C. In both cases under vacuum conditions.

2.5. Migration from rHDPE pellets before and after the decontamination protocol

2.5.1. Migration assays

Based on the Regulation EU/10/2011, the following food simulants were used: ethanol 10 % v/v (simulant A), acetic acid 3% w/v (simulant B) and ethanol 95 % v/v (simulant D2 substitute). The use of these simulants covers any kind of packaged food. 2.3 g of pellet (with an estimated surface area of 0.657 cm^2/pellet) were used for the total immersion migration test (18 mL food simulant). Resultswere re-calculated based on the ratio of 6 dm^2 surface area in contact with 1 kg of food, as stipulated in the legislation. Even though pellets are not the final food contact material, migration results can be extrapolated to migration from final packaging. Migration tests were carried out in the oven at 60 °C for 10 days to mimic long-time storage (> 6 months) at room temperature. Blanks of each simulant were also simultaneously submitted to the same time-temperature conditions.

Once the migration vials were cooled at room temperature, an aliquot of 6 mL of each simulant solution was introduced in a 20 mL vial in the case of simulants A and B for being analyzed. In the case of 95 % ethanol, prior to the analysis, 1 mL of the simulant was diluted with 5 mL of MilliQ water to avoid damage on the SPME fiber. Then, the analysis was performed by HS-SPME-GC–MS, under the conditions as described in 2.3. All the analyses were done in triplicate.

2.5.2. Identification and quantification of migrants

When determining the migrants present in the different simulants, chromatograms of migration solutions and migration blanks were overlaid and visually compared, in order to check the presence of those peaks only present in the samples. Once the migrants were identified in all samples, a quantification by external calibration method was performed, using the reference standard when available, or alternatively, a standard with similar chemical structure, thus performing a semi-quantification. Calibration curves were prepared in A and B simulants. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the smallest concentration of the analyte that provided a signal (heigh) three times and ten times the blank, respectively. The migration results for initial rHDPE and decontaminated rHDPE were compared for each simulant.

2.5.3. Statistical analysis

Principal component analysis (PCA) was carried out with the software Unscrambler X 10.3. Before performing the PCA all the areas were normalized by subtracting their average value and dividing by the standard deviation.

For the calculation of *t*-test statistics, Excel data analysis tools were used.

3. Results and discussion

3.1. Identification of volatile and semivolatile compounds in rHDPE and pattern recognition

In total, 67 compounds were identified by HS-SPME-GC–MS in the rHDPE flakes and pellets. Three of these compounds were only present in pellets, but at low levels of intensity (Table 1). These results showed that the extrusion process did not modify in a relevant way the composition in volatiles and semi-volatiles of the original flakes, even though the intensity of some compounds was altered during the process. (Supplementary Material 1)

According to their functional groups, ClassyFire application [17] classified the identified compounds in 15 classes of chemicals, being benzene and substituted derivatives the most relevant class (20.9%) in terms of abundance, followed by saturated hydrocarbons (14.9%) and fatty acids (11.9%). Families like lactones, carboxylic acids and derivatives or phenols were among the least relevant ones (1.5%), as seen in Supplementary Material 2.

The compounds found include polyethylene oligomers, mainly alkanes and alkenes such as 1-dodecene, tetradecane and hexadecane. These compounds are derived from the polymer structure itself and can come from both the manufacture of polyolefins and their degradation during recycling operations. Also, several additives intentionally added to the polymer, during the manufacture or the recycling process, to improve its properties were detected, such as butylated hydroxytoluene (BHT), which is added as an antioxidant to prevent aging [12]; diethyl phthalate, used as a plasticizer; 1-dodecanol and 1-hexadecanol, also used as plasticizers; or benzophenone, used as a stabilizer or UV absorber to prevent photo-oxidation of polymers as well as photo-initiator of UV curing printing inks. Even though some of these additives, such as phthalates or fatty alcohols, are not commonly used in HDPE they could come from cross-contamination with other polymers during the recycling process. Compounds coming from the degradation of common plastic additives were also detected, such as 2,4-di-tert-butylphenol, originated from Irgafos 168, a widely used antioxidant; and 7, 9-di-tert-butyl-1-oxaspiro[4,18]deca-6,9-diene-2,8-dione, degradation product of Irganox 1010 [19]. Besides that, a series of monoterpenoids such as limonene, eucalyptol, camphor or terpineol were found. These compounds probably come from previous applications of plastics, since they are used as flavorings in food or aromatics (Geueke et al. 2018). Other compounds present in the analyzed polyolefins might also come from previous use of the plastics. For example, isopropyl myristate and isopropyl palmitate, drugs present in some cosmetics for skin protection but also used as lubricants when processing plastics; homosalate, which is used in sunscreens as it absorbs UV radiation [20]; and 2,3-dichloro benzenamine, used as intermediate in different products such as pesticides or dyes [21].

3.2. Effect of temperature and vacuum application on the volatile compound profile of flakes and pellets

Once the initial profile of the volatile compounds in rHDPE was known, the effect of the application of temperature and vacuum was studied at different treatment times. For this purpose, the samples were analyzed following the protocol described in 2.3. and the area of the 67 compounds was measured. The aim was finding out which would be the optimum conditions for decontamination of recycled polyolefins. The experiment was performed over flakes and pellets to evaluate the effect of materials shape on the decontamination times and rates.

In order to reduce the dimensionality of data and verify if there was a statistical grouping of samples, a principal component analysis was carried out with the areas of the 67 detected compounds at the different decontamination times. The explained variance achieved for the first 2 principal components was about 85 % for both flakes and pellets. In the first place, PCA of flakes (Fig. 1a) showed that samples were grouped according to their treatment time, and time 3 h and time 5 h were grouped together as they were similar. In the case of pellets (Fig. 1b), the samples were also grouped depending on their treatment time, but in this case, it was clearly seen that samples treated 5 h were far apart from samples treated during shorter times. The fact that the flakes required less time to decontaminate than pellets might be attributed to its higher specific surface area. Although times longer than 5 h were tested, it was observed that samples were merged, thus impeding the analysis, so it was discarded as a possible treatment time.

In view of this results, 15 different compounds with varying intensities, functional groups and distributed along the chromatogram were selected and their relative areas (A_r) related to the area of the original rHDPE samples, were calculated at the different treatment times (t_x) using Eq. (1):

$$A_r(t_x) = \frac{100\ x\ A(t_x)}{A(t_0)} \quad (1)$$

Table 1
Identified volatile and semi-volatile compounds in both flakes (F) and pellets (P). Retention time (t_R), bibliographic and experimental retention indexes (RI_{bib} and RI_{epx}) and compounds signal intensity (Int) being L = low (<1 E6), M = medium (1 E6 – 5 E6) and H = high (> 5 E6).

N°	t_R (min)	Compound	Formula	CAS	RI_{bib}	RI_{epx}	Int. (F)	Int. (P)
1	7.38	Phenol	C_6H_6O	108–95–2	981	996	nd	M
2	8.29	D-Limonene	$C_{10}H_{16}$	5989–27–5	1031	1033	L	L
3	8.35	Eucalyptol	$C_{10}H_{18}O$	470–82–6	1032	1036	L	L
4	9.04	7-Octen-2-ol, 2,6-dimethyl-	$C_{10}H_{20}O$	18,479–58–8	1064	1074	L	L
5	9.37	p-cymene	$C_{10}H_{12}$	1195–32–0	1090	1092	L	L
6	9.49	Undecane	$C_{11}H_{24}$	1120–21–4	1100	1100	L	L
7	10.32	Camphor	$C_{10}H_{16}O$	76–22–2	1145	1151	L	L
8	10.78	Benzenamine, 4-methoxy-	C_7H_9NO	104–94–9	1187	1181	nd	L
9	10.95	1-Dodecene	$C_{12}H_{24}$	112–41–4	1185	1191	L	L
10	11.02	α-Terpineol	$C_{10}H_{18}O$	98–55–5	1189	1196	L	L
11	11.08	Dodecane	$C_{12}H_{26}$	112–40–3	1200	1200	M	M
12	11.3	1-Heptanol, 2-propyl-	$C_{10}H_{22}O$	10,042–59–8	1206	1215	L	L
13	11.43	Ethanol, 2-phenoxy-	$C_8H_{10}O_2$	122–99–6	1225	1224	M	M
14	12.47	Bornyl acetate	$C_{12}H_{20}O_2$	76–49–3	1285	1295	M	M
15	12.55	Cyclohexanol, 2-(1,1-dimethylethyl)-	$C_{10}H_{20}O$	13,491–79–7	1300	1301	M	M
16	12.59	Naphthalene, 2-methyl-	$C_{11}H_{10}$	90–12–0	1307	1311	M	M
17	12.84	Naphtalene, 1-methyl-	$C_{11}H_{10}$	91–57–6	1317	1320	L	M
18	13.08	Benzenamine, 2,3-dichloro-	$C_6H_5Cl_2N$	608–27–5	1351	1338	nd	M
19	13.6	4-tert-Butylcyclohexyl acetate	$C_{12}H_{22}O_2$	32,210–23–4	1368	1374	M	M
20	13.86	1-Tetradecene	$C_{14}H_{28}$	1120–36–1	1392	1393	M	M
21	13.98	Tetradecane	$C_{14}H_{30}$	629–59–4	1400	1401	H	H
22	14.04	3-Tetradecene, (E)-	$C_{14}H_{28}$	41,446–68–8	1385	1405	L	L
23	14.13	Diphenyl ether	$C_{12}H_{10}O$	101–84–8	1405	1415	H	H
24	14.19	Naphthalene, 1,3-dimethyl-	$C_{12}H_{12}$	575–41–7	1417	1415	L	M
25	14.43	Indan-1,3-diol monoacetate	$C_{11}H_{12}O_3$	–	–	1431	M	M
26	14.79	1-(4-tert-Butylphenyl) propan-2-one	$C_{13}H_{18}O$	81,561–77–5	1426	1455	M	M
27	14.87	Naphthalene, 2-methoxy-	$C_{11}H_{10}O$	93–04–9	1458	1460	M	M
28	15.1	1-Dodecanol	$C_{12}H_{26}O$	112–53–8	1473	1477	M	M
29	15.29	α Isomethyl ionone	$C_{14}H_{22}O$	127–51–5	1480	1481	L	M
30	15.47	Pentadecane	$C_{15}H_{32}$	629–62–9	1500	1498	L	M
31	15.72	2,4-Di-tert-butylphenol	$C_{14}H_{22}O$	96–76–4	1514	1515	M	H
32	15.81	Butylated Hydroxytoluene	$C_{15}H_{24}O$	128–37–0	1513	1517	L	M
33	15.84	2-Phenoxyethyl butyrate	$C_{12}H_{16}O_3$	23,511–70–8	1521	1527	M	M
34	15.88	Dodecanoic acid, methyl ester	$C_{13}H_{26}O_2$	111–82–0	1526	1524	nd	L
35	15.93	N-Methyl ionone	$C_{14}H_{22}O$	7779–30–8	1524	1526	M	M
36	16.04	Naphthalene, 2-ethoxy-	$C_{12}H_{12}O$	93–18–5	1530	1533	M	M
37	16.16	Isoamyl salicylate	$C_{12}H_{16}O_3$	87–20–7	1538	1540	M	M
38	16.83	Benzoic acid, 2-hydroxy-, pentyl ester	$C_{12}H_{16}O_3$	2050–08–0	1552	1542	H	M
39	17.04	Cetene	$C_{16}H_{32}$	629–73–2	1592	1592	H	M
40	17.15	Diethyl Phthalate	$C_{12}H_{14}O_4$	84–66–2	1594	1600	nd	H
41	17.17	Hexadecane	$C_{16}H_{34}$	544–76–3	1600	1600	H	H
42	17.6	Isopropyl laurate	$C_{15}H_{30}O_2$	10,233–13–3	1618	1625	nd	L
43	17.8	Benzophenone	$C_{13}H_{10}O$	119–61–9	1635	1637	M	M
44	17.98	Benzene, (1-propyloctyl)-	$C_{17}H_{28}$	4536–86–1	1643	1647	M	L
45	18.08	Cinnamaldehyde, α-pentyl-	$C_{14}H_{18}O$	122–40–7	1654	1653	L	L
46	18.16	Hedione	$C_{13}H_{22}O_3$	24,851–98–7	1657	1654	M	M
47	18.26	Octyl ether	$C_{16}H_{34}O$	629–82–3	1659	1663	M	L
48	18.46	Amberonne	$C_{16}H_{26}O$	–	1664	1671	M	M
49	18.61	n-Hexyl salicylate	$C_{13}H_{18}O_3$	6259–76–3	1683	1686	H	H
50	18.87	Heptadecane	$C_{17}H_{36}$	629–78–7	1700	1698	L	H
51	19.21	Myristyl monoethoxylate	$C_{14}H_{30}O_2$	4536–30–5	1719	1717	L	L
52	19.85	Cinnamaldehyde, α-hexyl-	$C_{15}H_{20}O$	101–86–0	1750	1752	M	M
53	20.38	Acetyl cedrene	$C_{17}H_{26}O$	68,039–35–0	1780	1782	M	M
54	20.58	1-Octadecene	$C_{18}H_{36}$	112–88–9	1793	1790	M	M
55	20.7	Octadecane	$C_{18}H_{38}$	593–45–3	1800	1796	M	M
56	20.91	2-Ethylhexyl salicylate	$C_{15}H_{22}O_3$	118–60–5	1811	1807	M	M
57	21.16	Isopropyl myristate	$C_{17}H_{34}O_2$	110–27–0	1827	1821	L	L
58	21.81	Versalide	$C_{18}H_{26}O$	88–29–9	–	1849	M	M
59	22.14	1-Hexadecanol	$C_{16}H_{34}O$	36,653–82–4	1880	1878	L	L
60	22.39	Homosalate	$C_{16}H_{22}O_3$	118–56–9	1897	1891	L	L
61	22.99	7,9-Di-tert-butyl-1-oxaspiro(4,5) deca-6,9-diene-2,8-dione	$C_{17}H_{24}O_3$	82,304–66–3	1923	1913	L	L
62	24.11	1-Eicosene	$C_{19}H_{38}$	18,435–45–5	1994	1991	L	L
63	24.19	Eicosane	$C2_0H_{42}$	112–95–8	2000	1999	L	L
64	24.58	Isopropyl palmitate	$C_{19}H_{38}O_2$	142–91–6	2023	2023	L	L
65	25.59	Heneicosane	$C_{21}H_{44}$	629–94–7	–	2097	L	L
66	26.74	1-Docosene	$C_{22}H_{44}$	1599–67–3	2194	2194	L	L
67	26.81	Docosane	$C_{22}H_{46}$	629–97–0	2200	2200	L	L

nd: non detected.

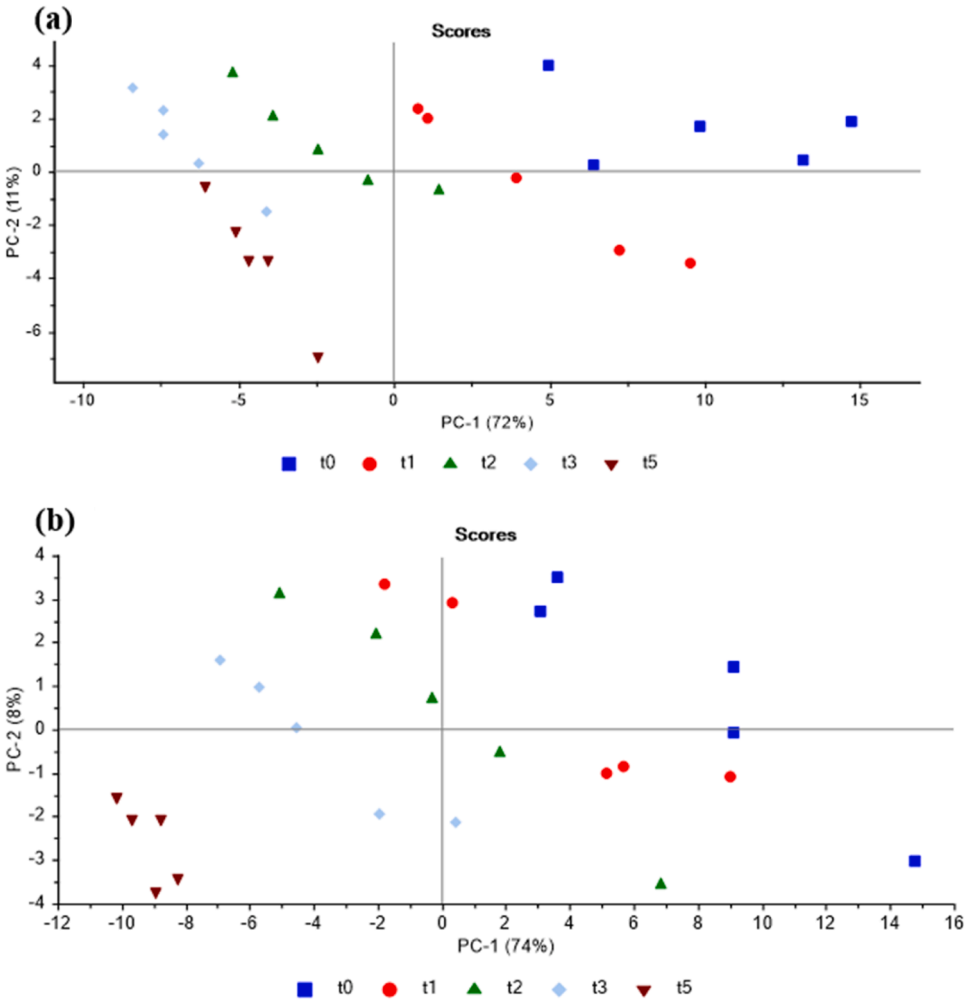

Fig. 1. Principal Components Analysis score plot for flakes (a) and pellets (b) at different treatment times under vacuum conditions at 120 °C.

being A (t_0) the initial area ($t = 0$ h) and A (t_x) the area after the successive vacuum heat treatments at different times ($t = 1$, 2, 3 and 5 h). The aim was to check the decrease profile of volatiles during the decontamination process and evaluate the magnitude of the differences between times.

The results are plotted in Fig. 2a and b. In flakes, a decrease in the area (and therefore concentration) of the 15 compounds was observed as the treatment time increased, up to 3 h. This decrease was more pronounced for the first compounds, which corresponded to the most volatile compounds, while the peaks corresponding to compounds with higher molecular weight (compounds n° 10 to 15) needed more time of treatment to show a clear decrease. At time = 5 h, in turn, a slight increase in areas was observed only in some compounds. After applying a *t*-test for independent samples to each compound between 3 h and 5 h, it was found that there were no significant differences (at 95 % confidence) for 9 of the 15 compounds represented. In four of the remaining compounds, the areas obtained at 5 h were significantly higher than those at 3 h, probably because these compounds could be generated from thermal degradation processes. Therefore, the optimum time for decontamination of flakes at 120 °C and vacuum conditions would be 3 h. The results obtained from a Pearson correlation test showed that the percentage of decrease of the volatiles after the decontamination protocol was negatively correlated with the molecular weight of the molecule (−0.71) and the retention time (−0.85), while no correlation was observed versus other physic-chemical parameters such as log P or vapor pressure (Supplementary Material 3).

In the case of pellets, Fig. 2b shows that in most cases, the area decreased progressively as the treatment time increased, reaching the minimum values at $t = 5$ h. After applying the corresponding t-statistics, for most of the compounds, it was found that at 5 h the areas were significantly smaller than at 3 h ($p < 0.05$). This way, decontamination of the rHDPE pellets improved significantly when the treatment time was 5 h and at 120 °C of temperature with the application of vacuum. As happened with flakes, the first peaks, showed a faster decrease than the heavier ones, probably due to the fact that the application of temperature had a higher effect to the most volatile compounds. Eighteen of the compounds showed a decrease greater than 90 %, 24 between 50 and 90% and 15 between 20 and 50 % (Supplementary Material 4). In this case, the results obtained from the Pearson correlation test also showed a negative correlation between the percentage of decrease of the volatiles with the molecular weight (−0.84) and the retention time (−0.85), and no correlation log P or vapor pressure (Supplementary Material 5).

Finally, to evaluate the effect of applying vacuum on the overall pellet decontamination treatment, the same thermal treatment was carried out, but at atmospheric pressure for both 1 and 5 h. PCA was performed, and the results showed that samples were grouped according to their treatment time and pressure conditions. As seen in Fig. 3, samples treated for 1 hour were grouped together and the same occurs in the case of samples treated for 5 h. At the same time, samples decontaminated under atmospheric pressure were clearly differentiated from those treated under vacuum.

The compound areas of samples treated under vacuum conditions were compared to those treated at atmospheric pressure. It was observed

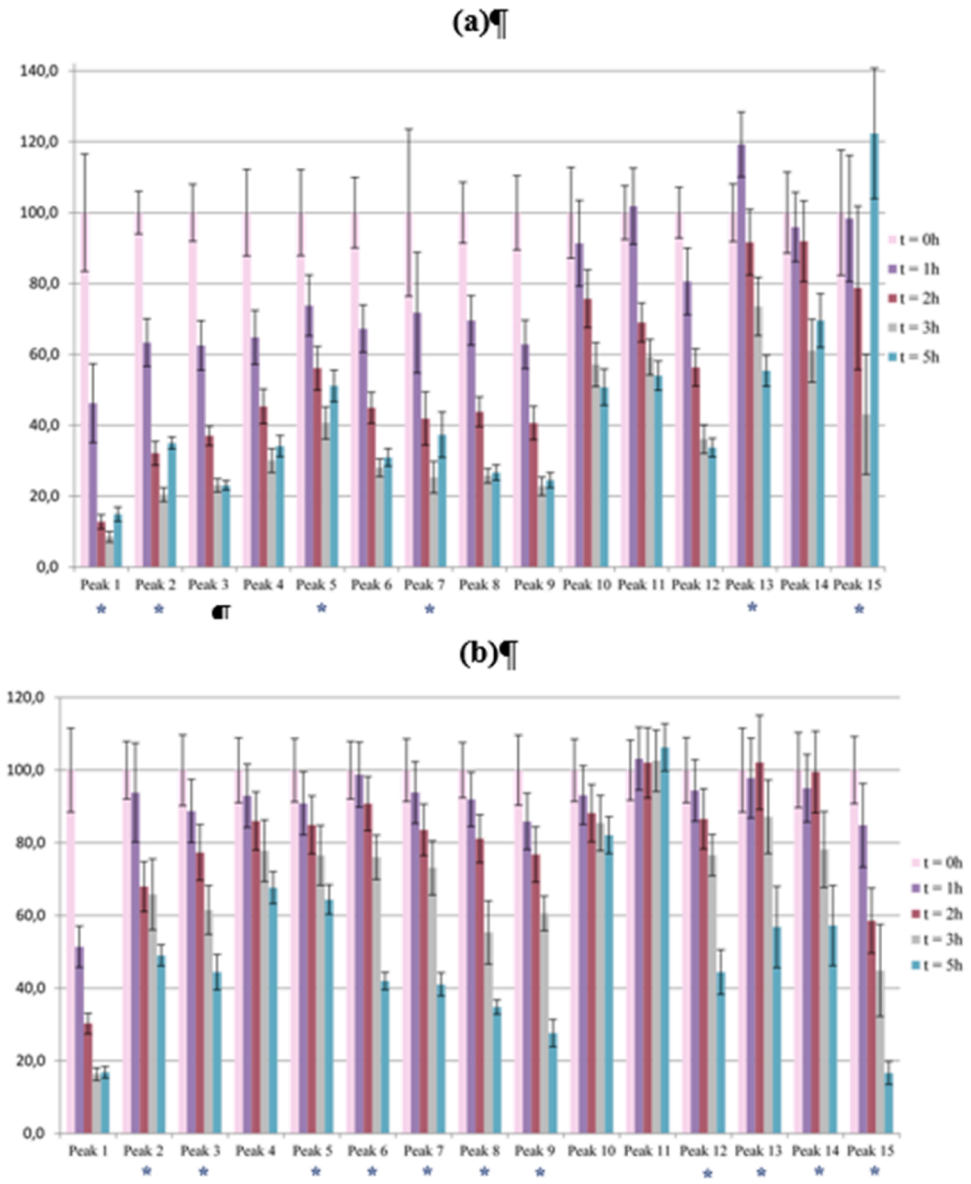

Fig. 2. Graphical representation of the relative areas at the different treatment times (time: 0, 1, 2, 3 and 5 h), related to the area in the original rHDPE samples, of the 15 selected compounds in flakes (a) and pellets (b). Those compounds with statistically significant differences in their areas during the 3 and 5 hour treatments are marked with an asterisk.

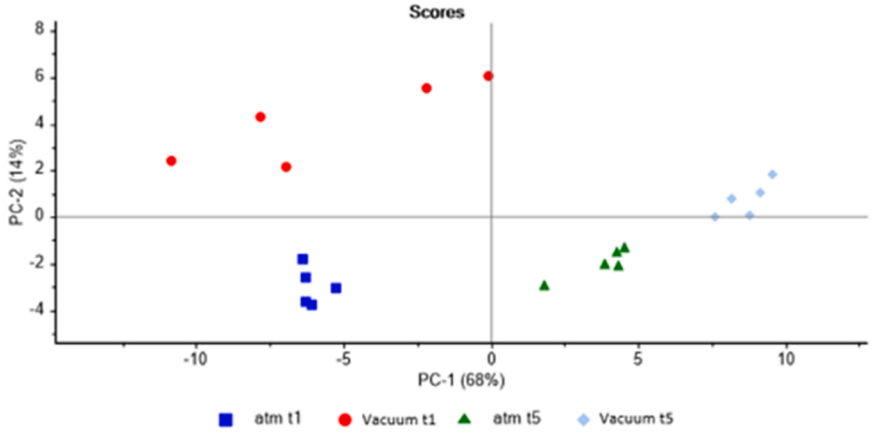

Fig. 3. Principal Components Analysis score plot for pellets treated under atmospheric pressure (atm) or vacuum conditions (vacuum), at 1 and 5 h of treatment at 120 °C (t1 and t5).

that after 5 h of treatment, 57 compounds of the 67 identified, provided smaller areas in the vacuum-treated samples, with decreases ranging from 8.8 % to 100 %. In addition, a *t*-test was performed to check if the differences were significant. The results indicated that 38 compounds showed significant differences ($p < 0.05$). This pattern was also observed in samples treated for 1 hour. This way, the decontamination treatment performed under vacuum proved to be the most effective.

Besides that, a cluster analysis was performed using the normalized areas of the compounds at different treatment times. The purpose was to organize all compounds into groups based on how closely associated they were. As shown in (Supplementary Material6), compounds with lower molecular weight were grouped, thus indicating that they had similar response to thermal treatment compared to the heavier ones.

3.3. Migration assays

Migration tests were performed in triplicate for not decontaminated rHDPE pellets ($t = 0$ h) and for rHDPE pellets after 5 h at 120 °C under vacuum ($t = 5$ h), that corresponded to the optimal decontamination conditions. Quantification of migrants was conducted by external calibration, and the analytical parameters for the quantification by HS-SPME-GC–MS are shown in Table 2. Table 3 shows the migration results for the three food simulants, acetic acid 3 %, ethanol 10 % and ethanol 95 % and Fig. 4 shows the chromatograms of migration samples.

A total of 83 different volatile migrants were found in migration samples. For 3% acetic acid migration, a total of 67 compounds were identified, 42 of them had been previously detected in pellets screening. For some of them, migration was noteworthy due to their presence at high concentration levels such as 3,4-dimethylbenzaldehyde (65.8 μg/kg), used as food flavoring, indan-1,3-diol-monoacetate (36.73 μg/kg),

Table 2
Analytical parameters for the quantification of volatile migrants by HS-SPME-GC–MS in 3 % acetic acid (HAc) and 10 % ethanol (EtOH).

Compound		Matrix	*m/z*	R^2	Linear Range (μg kg^{-1})	LOD (μg kg^{-1})	LOQ (μg kg^{-1})
Q1	Limonene	3 % HAc	68	0.994	0.78–38.3	0.23	0.78
		10 % EtOH		0.997	0.58–38.65	0.17	0.58
Q2	Undecane	3 % HAc	57	0.998	4.9–50.5	1.47	4.9
		10 % EtOH		0.997	4.4–105.7	1.32	4.4
Q3	Menthol	3 % HAc	71	0.998	0.43- 50	0.13	0.43
		10 % EtOH		0.999	1.19- 200.2	0.35	1.19
Q4	α-Terpineol	3 % HAc	59	0.996	0.37–54.8	0.11	0.37
		10 % EtOH		0.996	0.2–59.2	0.06	0.2
Q5	Dodecane	3 % HAc	57	0.998	1.24–101.2	0.37	1.24
		10 % EtOH		0.997	0.44–98.6	0.13	0.44
Q6	Dodecane. 1-chloro-	3 % HAc	91	0.995	1.04–102.1	0.31	1.04
		10 % EtOH		0.997	0.91–107.4	0.27	0.91
Q7	Benzaldehyde. 4-propyl-	3 % HAc	91	0.995	0.84–200.2	0.25	0.84
		10 % EtOH		0.999	0.29–210.6	0.09	0.29
Q8	Bornyl acetate	3 % HAc	95	0.995	0.15–96.7	0.05	0.15
		10 % EtOH		0.995	0.19–104.3	0.05	0.19
Q9	Naphthalene. 1-methyl-	3 % HAc	142	0.999	0.03–29.3	0.01	0.03
		10 % EtOH		0.997	0.05–29.22	0.01	0.05
Q10	1-Tetradecene	3 % HAc	55	0.991	0.27–199.9	0.08	0.27
		10 % EtOH		0.986	0.03–26.38	0.01	0.03
Q11	Diphenyl ether	3 % HAc	170	0.991	0.15–98.7	0.05	0.15
		10 % EtOH		0.995	0.015–28.6	0.004	0.015
Q12	1-Dodecanol	3 % HAc	55	0.995	0.33–120.3	0.10	0.33
		10 % EtOH		0.992	0.03–107.8	0.01	0.03
Q13	Butylated hydroxytoluene	3 % HAc	205	0.994	0.06–105.3	0.02	0.06
		10 % EtOH		0.994	0.023–95.4	0.007	0.023
Q14	Ethyl laurate	3 % HAc	88	0.996	0.13–99.8	0.04	0.13
		10 % EtOH		0.997	0.04–203.3	0.01	0.04
Q15	Diethyl Phthalate	3 % HAc	149	0.996	0.58–283.4	0.14	0.58
		10 % EtOH		0.998	0.68–255.1	0.2	0.68
Q16	Benzophenone	3 % HAc	105	0.999	0.29–201.2	0.09	0.29
		10 % EtOH		0.997	0.44–205.2	0.13	0.44
Q17	Dibutyl adipate	3 % HAc	185	0.995	0.56–200.3	0.14	0.56
		10 % EtOH		0.997	0.11–58.8	0.03	0.11
Q18	2-Ethylhexyl salicylate	3 % HAc	120	0.996	0.03–242.4	0.01	0.03
		10 % EtOH		0.997	0.02–182.9	0.01	0.02
Q19	Isopropyl myristate	3 % HAc	102	0.989	0.06–113.8	0.02	0.06
		10 % EtOH		0.998	0.06–100.2	0.02	0.06
Q20	Methyl palmitate	3 % HAc	74	0.991	0.02–105.1	0.006	0.02
		10 % EtOH		0.997	0.04–200.8	0.01	0.04
Q21	Isopropyl palmitate	3 % HAc	102	0.988	0.09–106.2	0.03	0.09
		10 % EtOH		0.993	0.06–101.7	0.02	0.06
Q22	2-Ethylhexyl acetate	3 % HAc	70	–	–	–	–
		10 % EtOH		0.999	0.08–115.10	0.02	0.08
Q23	Benzocyclobutene	3 % HAc	104	0.999	0.24–87.44	0.07	0.24
		10 % EtOH		0.999	0.06–100.24	0.02	0.06
Q24	Allyl benzoate	3 % HAc	105	0.995	0.37–133.70	0.11	0.37
		10 % EtOH		0.999	1.82–249.02	0.54	1.82
Q25	α-Ionone	3 % HAc	121	0.999	0.043–55.56	0.013	0.043
		10 % EtOH		0.997	0.06–107.86	0.02	0.06
Q26	2,6-Diisopropylnaphthalene	3 % HAc	197	0.998	0.03–188.91	0.008	0.03
		10 % EtOH		0.998	0.10–280.25	0.03	0.10
Q27	2,4-Di-tert-butylphenol	3 % HAc	191	0.998	0.039–46.45	0.012	0.039
		10 % EtOH		0.997	0.01–152.30	0.004	0.01

Table 3
Migration values in all three food simulants: 3 % acetic acid (HAc), 10 % ethanol (EtOH) and 95 % ethanol (EtOH), for untreated ($t = 0$ h) and decontaminated ($t = 5$ h) rHDPE pellets; and specific migration limits on EU/10/2011 regulation (SML) or Cramer Class (I, II or III).

						3 % HAc (μg/kg)		10 % EtOH (μg/kg)		95 % EtOH (μg/kg)		SML (μg Kg^{-1})/ Cramer Class
N°	t_R (min)	Compound	Formula	CAS	QS*	$t = 0$h	$t = 5$h	$t = 0$h	$t = 5$h	$t = 0$h	$t = 5$h	
1	8.29	D-Limonene	$C_{10}H_{16}$	5989–27–5	Q1	10.93 ± 0.63	4.60 ± 0.28	2.945 ± 0.035	1.100 ± 0.021	101.50 ± 2.75	23.5 ± 1.9	I
2	8.35	Eucalyptol	$C_{10}H_{18}O$	470–82–6	Q3	5.08 ± 0.35	0.533 ± 0.087	10.88 ± 0.55	<LOQ	<LOD	<LOD	III
3	9.02	2,6-Dimethyl-7-octen-2-ol	$C_{10}H_{20}O$	18,479–58–8	Q12	1.83 ± 0.13	<LOQ	0.891 ± 0.020	<LOQ	<LOD	<LOD	III
4	9.37	p-cymene	C10H12	1195–32–0	Q3	3.78 ± 0.50	0.97 ± 0.13	<LOD	<LOD	<LOD	<LOD	I
5	9.46	3-Octanol, 3,7-dimethyl-	C10H22O	78–69–3	Q12	1.409 ± 0.088	<LOQ	5.34 ± 0.29	0.212 ± 0.005	<LOD	<LOD	I
6 −22–2	10.32 Q4	Camphor 10.40 ± 0.65	C10H16O 1.495 ± 0.093	76 <LOD	<LOD	<LOD	<LOD	no SML				
7	10.71	Menthol	C10H20O	1490–04–6	Q3	3.55 ± 0.20	<LOQ	5.11 ± 0.10	<LOQ	<LOD	<LOD	I
8	10.92	3-Methylacetophenone	C9H10O	90–04–0	Q16	2.47 ± 0.12	0.408 ± 0.048	<LOQ	<LOQ	<LOD	<LOD	I
9	10.95	1-Dodecene	$C_{12}H_{24}$	112–41–4	Q10	<LOD	<LOD	<LOD	<LOD	36.3 ± 1.1	0.12 ± 0.01	600
10	11.02	α-Terpineol	$C_{10}H_{18}O$	98–55–5	Q4	8.78 ± 0.65	0.649 ± 0.099	32.78 ± 0.65	3.50 ± 0.23	<LOD	<LOD	III
11	11.08	Dodecane	$C_{12}H_{26}$	112–40–3	Q5	<LOD	<LOD	<LOD	<LOD	8085 ± 161	1106 ± 33	I
12	11.3	1-Heptanol, 2-propyl-	$C_{10}H_{22}O$	10,042–59–8	Q12	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOD	I
13	11.43	Benzaldehyde, 3,4-dimethyl-	$C_9H_{10}O$	98–52–2	Q7	65.8 ± 2.5	77.5 ± 4.8	12.4 ± 1.2	12.15 ± 0.28	<LOD	<LOD	I
14	11.68	o-Chloroacetophenone	C_8H_7ClO	122–99–6	Q16	0.695 ± 0.053	0.580 ± 0.060	0.889 ± 0.018	0.823 ± 0.025	<LOD	<LOD	III
15	11.76	Cumaldehyde	$C_{10}H_{12}O$	5779–94–2	Q7	8.90 ± 0.13	<LOQ	2.71 ± 0.11	0.855 ± 0.023	<LOD	<LOD	I
16	12.15	1-Decanol	$C_{10}H_{22}O$	98–53–3	Q12	0.384 ± 0.005	<LOQ	<LOQ	<LOQ	<LOD	<LOD	I
17	12.23	Benzaldehyde, 4-propyl-	$C_{10}H_{12}O$	2142–68–9	Q7	4.01 ± 0.07	4.85 ± 0.38			<LOD	<LOD	I
18	12.47	Bornyl acetate	$C_{12}H_{20}O_2$	122–03–2	Q8	11.13 ± 0.65	2.27 ± 0.14	19.78 ± 0.15	4.04 ± 0.17	278.98 ± 0.83	66.3 ± 3.5	I
19	12,55	Cyclohexanol, 2-(1,1-dimethylethyl)	C10H20O	470,666–82–1	Q12	6.05 ± 0.44	0.70 ± 0.05	4.59 ± 0.01	0.34 ± 0.02	288 ± 15	58.44 ± 0.27	I
20	12.59	Naphthalene, 1-methyl-	$C_{11}H_{10}$	512–85–6	Q9	0.46 ± 0.06	<LOQ	0.628 ± 0.021	0.118 ± 0.014	35.5 ± 2.5	9.45 ± 0.58	III
21	12.77	4-tert-Butylbenzaldehyde	$C_{11}H_{14}O$	112–05–0	Q7	<LOD	<LOD	26.10 ± 0.55	13.51 ± 0.19	<LOD	<LOD	I
22	12.84	Naphthalene, 2-methyl-	$C_{11}H_{10}$	112–30–1	Q9	<LOQ	<LOQ	0.406 ± 0.009	0.075 ± 0.005	21.10 ± 0.45	5.220 ± 0.068	III
23	13,6	4-tert-Butylcyclohexyl acetate	$C_{12}H_{22}O_2$	32,210–23–4	Q22	20.2 ± 1.5	4.96 ± 0.27	16.08 ± 0.44	4.24 ± 0.20	177.5 ± 1.7	51.2 ± 1.5	II
24	13.86	1-Tetradecene	$C_{14}H_{28}$	1120–36–1	Q10	<LOD	<LOD	<LOD	<LOD	290.5 ± 7.0	100.7 ± 2.2	600
25	13.98	Tetradecane	$C_{14}H_{30}$	629–59–4	Q5	<LOD	<LOD	<LOD	<LOD	32,114 ± 2347	12,447 ± 522	I
26	14.04	3-Tetradecene, (E)-	$C_{14}H_{28}$	41,446–68–8	Q10	<LOD	<LOD	<LOD	<LOD	34.73 ± 0.88	8.40 ± 0.70	I
27	14.13	Diphenyl ether	$C_{12}H_{10}O$	101–84–8	Q11	5.53 ± 0.53	1.23 ± 0.10	6.00 ± 0.13	2.02 ± 0.12	216 ± 3	72.3 ± 1.4	III
28	14.18	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$	575–37–1	Q9	<LOD	<LOD	<LOD	<LOD	28.0 ± 2.8	12.17 ± 0.23	III
29	14.19	1-Heptanol, 2-propyl-	$C_{10}H_{22}O$	10,042–59–8	Q12	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOD	I
30	14.37	Dodecane, 1-methoxy	$C_{13}H_{28}O$	3482–63–1	Q5	<LOD	<LOD	<LOD	<LOD	16,949 ± 718	5881 ± 345	I

(*continued on next page*)

Table 3 (*continued*)

N°	t_R (min)	Compound	Formula	CAS	QS*	3 % HAc (μg/kg)		10 % EtOH (μg/kg)		95 % EtOH (μg/kg)		SML (μg Kg^{-1})/ Cramer Class
						t = 0h	*t* = 5h	*t* = 0h	*t* = 5h	*t* = 0h	*t* = 5h	
31	14,4	Indan-1,3-diol monoacetate	$C_{11}H_{12}O_3$	–	Q23							
	36.7 ± 1.3	10.84 ± 0.44	26.18 ± 0.44	8.06 ± 0.16	<LOD	<LOD	I					
32	14.41	Naphthalene, 1,4-dimethyl-	$C_{12}H_{12}$	571–58–4	Q9	<LOD	<LOD	<LOD	<LOD	28.1 ± 1.0	10.5 ± 3.5	III
33	14.47	Naphthalene, 2,6-dimethyl-	$C_{12}H_{12}$	581–42–0	Q9	<LOD	<LOD	<LOD	<LOD	13.63 ± 0.80	5.53 ± 0.05	III
34	14.5	1,2-Dodecanediol	$C_{12}H_{26}O_2$	1119–87–5	Q12	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOD	II
35	14.87	Naphthalene, 2-methoxy-	$C_{11}H_{10}O$	81,561–77–5	Q9	0.07 ± 0.10	0.303 ± 0.07	0.850 ± 0.088	0.358 ± 0.028	8.7 ± 1.3	3.76 ± 0.06	III
36	15.07	Dodecane, 1-chloro-	$C_{12}H_{25}Cl$	112–52–7	Q6	<LOD	<LOD	<LOD	<LOD	1632 ± 57	742 ± 45	III
37	15.1	1-Dodecanol	$C_{12}H_{26}O$	112–53–8	Q12	2.85 ± 0.28	0.829 ± 0.045	5.54 ± 0.18	0.978 ± 0.080	480 ± 23	188 ± 13	I
38	15.47	Pentadecane	$C_{15}H_{32}$	629–62–9	Q5	<LOD	<LOD	<LOD	<LOD	7025 ± 910	3472 ± 302	I
39	15.72	2,4-Di-tert-butylphenol	$C_{14}H_{22}O$	96–76–4	Q9	15.13 ± 0.47	6.13± 0.30	2.25 ± 0.06	0.863 ± 0.006	303 ± 19	96.8 ± 6.0	I
40	15.81	Butylated Hydroxytoluene	$C_{15}H_{24}O$	128–37–0	Q13	<LOQ	<LOQ	<LOQ	<LOQ	76.1 ± 1.4	39.5 ± 1.9	II
41	15,93	N-Methyl ionone	$C_{14}H_{22}O$	1335–46–2	Q25	2.96 ± 0.12	1.21 ± 0.06	5.47 ± 0.14	2.61 ± 0.05	<LOD	<LOD	I
42	16.04	Naphthalene, 2-ethoxy-	$C_{12}H_{12}O$	93–18–5	Q9	<LOQ	<LOQ	0.460 ± 0.045	0.221 ± 0.013	13.6 ± 2.2	8.18 ± 0.15	III
43	16.16	Isoamyl salicylate	$C_{12}H_{16}O_3$	87–20–7	Q18	<LOQ	<LOQ	<LOQ	<LOQ	71.0 ± 2.5	23.50 ± 0.75	I
44	16.29	Decane, 4-phenyl-	$C_{16}H_{26}$	06–12–4537	Q2	<LOD	<LOD	<LOD	<LOD	38,200 ± 712	25,532 ± 966	I
45	16.43	Naphthalene, 2,3,6-trimethyl-	$C_{13}H_{14}$	829–26–5	Q9	<LOD	<LOD	<LOD	<LOD	7.8 ± 1.1	5.43 ± 0.11	III
46	16.61	Decane, 3-phenyl-	$C_{16}H_{26}$	4621–36–7	Q2	<LOD	<LOD	<LOD	<LOD	46,063 ± 1010	31,123 ± 1198	I
47	16,83	Benzoic acid, 2-hydroxy-, pentyl ester	$C_{12}H_{16}O_3$	2050–08–0	Q24	9.9 ± 1.2	5.18 ± 0.48	31.4 ± 1.3	16.7 ± 1.1	4128 ± 253	326 ± 21	I
48	17,04	Cetene	$C_{16}H_{32}$	629–73–2	Q10	<LOD	<LOD	<LOD	<LOD	486 ± 52	326 ± 22	I
49	17.15	Diethyl Phthalate	$C_{12}H_{14}O_4$	84–66–2	Q15	69.2 ± 2.7	29.5 ± 1.4	80.5 ± 3.5	35.68 ± 0.60	<LOD	<LOD	I
50	17.17	Hexadecane	$C_{16}H_{34}$	544–76–3	Q5	<LOD	<LOD	<LOD	<LOD	31,212 ± 4444	19,406 ± 2366	I
51	17.64	Isopropyl laurate	$C_{15}H_{30}O_2$	4537–13–7	Q14	<LOD	<LOD	<LOD	<LOD	146.8 ± 4.5	99.1 ± 2.3	I
52	17.78	Benzophenone	$C_{13}H_{10}O$	119–61–9	Q16	8.85 ± 0.93	4.04 ± 0.23					500
53	17.83	Undecane, 5-phenyl-	$C_{17}H_{28}$	4537–15–9	Q2	<LOD	<LOD	<LOD	<LOD	89,567 ± 2406	75,076 ± 1884	I
54	18.39	Undecane, 3-phenyl	$C_{17}H_{28}$	4536–86–1	Q2	<LOD	<LOD	<LOD	<LOD	91,302 ± 2063	75,863 ± 1153	I
55	18,46	Amberonne	$C_{16}H_{26}O$	54,464–57–2	Q26	1.46 ± 0.13	1.06 ± 0.07	2.09 ± 0.08	1.76 ± 0.12	156.4 ± 6.3	133.5 ± 5.4	III
56	18.57	1-Tetradecanol	$C_{14}H_{30}O$	122–40–7	Q12	<LOD	<LOD	<LOD	<LOD	412 ± 57	304 ± 24	I
57	18.61	n-Hexyl salicylate	$C_{13}H_{18}O_3$	6259–76–3	Q18	0.63 ± 0.10	0.156 ± 0.017	0.820 ± 0.030	0.14 ± 0.01	718 ± 62	555 ± 21	I
58	18.87	Heptadecane	$C_{17}H_{36}$	629–78–7	Q5	<LOD	<LOD	<LOD	<LOD	7659 ± 1414	5385 ± 764	I
59	19.04	Undecane, 2-phenyl-	$C_{17}H_{28}$	4536–88–3	Q2	<LOD	<LOD	<LOD	<LOD	197,028 ± 7595	169,517 ± 3260	I
60	19.36	Methyl myristate	$C_{15}H_{30}O_2$	4536–30–5	Q21	<LOD	<LOD	<LOD	<LOD	208 ± 11	165.0 ± 3.0	I
61	19.47	Dodecane, 6-phenyl-	$C_{18}H_{30}$	124–10–7	Q5	<LOD	<LOD	<LOD	<LOD	10,893 ± 798	10,120 ± 370	I
62	19.58	Dodecane, 5-phenyl-	$C_{18}H_{30}$	2719–62–2	Q5	<LOD	<LOD	<LOD	<LOD	11,214 ± 726	10,594 ± 347	I
63	20.09	Dibutyl adipate	$C_{14}H_{26}O_4$	105–99–7	Q17	1.97 ± 0.16	1.24 ± 0.01	8.33 ± 0.90	5.430 ± 0.035	<LOD	<LOD	I
64	20.18	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	$C_{15}H_{22}O_2$	1620–98–0	Q7	13.7 ± 1.0	13.60 ± 0.52	20.4 ± 1.9	16.45 ± 0.65	<LOD	<LOD	II

(*continued on next page*)

Table 3 (*continued*)

N°	t_R (min)	Compound	Formula	CAS	QS*	3 % HAc (μg/kg)		10 % EtOH (μg/kg)		95 % EtOH (μg/kg)		SML (μg Kg^{-1})/ Cramer Class
						$t = 0h$	$t = 5h$	$t = 0h$	$t = 5h$	$t = 0h$	$t = 5h$	
65	20.19	Dodecane, 3-phenyl-	$C_{18}H_{30}$	2400–00–2	Q5	<LOD	<LOD	<LOD	<LOD	10,439.5 ± 867	9673 ± 353	I
66	20.58	1-Octadecene	$C_{18}H_{36}$	101–86–0	Q10	<LOD	<LOD	<LOD	<LOD	488.75 ± 100	361 ± 58	I
67	20.7	Octadecane	$C_{18}H_{38}$	68,039–35–0	Q5	<LOD	<LOD	<LOD	<LOD	27,515 ± 5093	20,105 ± 3490	I
68	20.91	2-Ethylhexyl salicylate	$C_{15}H_{22}O_3$	118–60–5	Q18	<LOQ	<LOQ	<LOQ	<LOQ	420 ± 40	384 ± 20	I
69	21.16	Isopropyl myristate	$C_{17}H_{34}O_2$	110–27–0	Q19	<LOQ	<LOQ	0.066 ± 0.007	<LOQ	990 ± 101	887 ± 34	I
70	22.21	1-Hexadecanol	$C_{16}H_{34}O$	36,653–82–4	Q12	<LOD	<LOD	<LOD	<LOD	782 ± 156	748 ± 103	no SML
71	22,46	Homosalate	$C_{16}H_{22}O_3$	118–56–9	Q24	<LOD	<LOD	<LOD	<LOD	1302 ± 160	1360 ± 86	I
72	22,99	7,9-Di-tert-butyl-1-oxaspiro(4,5) deca-6,9-diene-2,8-dione	$C_{17}H_{24}O_3$	82,304–66–3	Q27	5.21 ± 0.70	4.55 ± 0.31	2.82 ± 0.41	2.76 ± 0.50	<LOD	<LOD	III
73	23.02	Methyl palmitate	$C_{17}H_{34}O_2$	118–56–9	Q20	<LOD	<LOD	<LOD	<LOD	1284 ± 175	1241 ± 82	I
74	24.11	1Eicosene	$C_{19}H_{38}$		Q10	<LOD	<LOD	<LOD	<LOD	374 ± 75	311 ± 51	I
75	24.19	Eicosane	$C_{20}H_{42}$	112–39–0	Q5	<LOD	<LOD	<LOD	<LOD	13,659 ± 2376	10,931 ± 2019	I
76	24.58	Isopropyl palmitate	$C_{19}H_{38}O_2$	57–10–3	Q21	1.10 ± 0.38	1.40 ± 0.13	1.14 ± 0.10	0.58 ± 0.03	708 ± 143	660 ± 55	I
77	25.38	1-Octadecanol	$C_{18}H_{38}O$	18,435–45–5	Q12	<LOQ	<LOQ	<LOQ	<LOQ	213 ± 18	202 ± 30	I
78	25.65	Methyl 8-octadecenoate	$C_{19}H_{36}O_2$	112–95–8	Q21	<LOD	<LOD	<LOD	<LOD	235 ± 64	229 ± 16	I
79	25.96	Methyl stearate	$C_{19}H_{38}O_2$	142–91–6	Q21	<LOD	<LOD	<LOD	<LOD	141 ± 40	149 ± 14	I
80	26.47	Ethyl Oleate	$C_{20}H_{38}O_2$	112–92–5	Q21	<LOD	<LOD	<LOD	<LOD	81 ± 26	85.3 ± 8.3	I
81	26.76	Ethyl stearate	$C_{20}H_{40}O_2$	2345–29–1	Q21	<LOD	<LOD	<LOD	<LOD	88 ± 21	98.3 ± 7.8	I
82	26.81	Docosane	$C_{22}H_{46}$	112–61–8	Q5	<LOD	<LOD	<LOD	<LOD	3050 ± 422	2825 ± 391	I
83	28.78	Tetracosane	$C_{24}H_{50}$	111–62–6	Q5	<LOD	<LOD	<LOD	<LOD	701 ± 287	867 ± 114	I

Represented in bold are those compounds that exceeded the maximum recommended migration values; Those compounds whose concentration after treatment decreased above 90 % are colored in dark grey and those that decreased between 50 and 90 % in light grey.

* QS: Quantification Standards codes are explained in Table 2; LOQ: limit of quantification; LOD: limit of detection.

2,4-di-tert-butylphenol (30.45 μg/kg) and diethyl phthalate (69.25 μg/kg). In second place, 69 compounds were detected in migration to 10 % ethanol, most of them being common to those detected in acetic acid and at similar concentration levels. Finally, in the case of 95 % ethanol, 82 compounds were identified, many of them were also present in previous migrations to 3 % acetic acid or 10 % ethanol. New compounds were also found in 95 % ethanol, such as: longifolene, belonging to the terpenes group and used in cosmetics and oils; methyl and ethyl stearates, used as non-ionic surfactants and emulsifiers; or ethyl oleate, used in pharmaceuticals, cosmetics and food, but also as a plasticizer and lubricant. Migration of these new compounds might be due to the greater capacity of extraction of lipophilic substances of this simulant, compared to the two previous ones. In addition to increasing the number of detected compounds, higher concentrations levels were also observed for 95 % ethanol migration, reaching mg kg^{-1} for 18 migrants being alkylbenzenes (phenylundecane isomers and phenyldecane isomers) the migrants with the highest values. This group of alkylbenzenes may belong to breakdown products produced by the degradation of alkylbenzene sulfonates, widely used as anionic surfactants in detergents and cleaning agents [22].

According to their functional groups, the migration compounds were distributed by ClassyFire in 9 classes of chemicals, being benzene and substituted derivatives the most relevant class (25.7%) in terms of abundance, and oxanes and organochlorines the least relevant ones (1.4%), as seen in (Supplementary Material 7), this classification being similar to pellets.

When comparing the migration to all simulants of untreated versus decontaminated rHDPE pellets, high percentages of area decrease were observed for the most volatile compounds, being greater than 80 % for compounds such as eucalyptol, 3-octanol, 3,7-dimethyl, α-terpineol or naphthalene, 1-methyl in the case of 3 % acetic acid and 10 % ethanol migrations; and 1-dodecene, dodecane and benzoic acid, 2-hydroxy-pentyl ester in the case of 95 % ethanol. Compounds with the highest retention time did not show significant area reductions, as expected due to their lower volatility.

Finally, in order to assess the safety of rHDPE food contact materials, the concentration values obtained at $t = 5$ h for the different compounds in all simulants should be compared with the specific migration limits (SMLs) listed in Regulation (EU) 10/2011, as far as the compounds are included therein. Among the migrants quantified, only benzophenone, 1-dodecene and 1-tetradecene had SML in the legislation, being their values 600 μg/kg for the first compound and 500 μg/kg for the other two. These limits were not exceeded in any simulant. Other migrants such as camphor or 1-hexadecanol were also listed in the regulation, but with no SML value. In the case that the migrant is not listed in EU/10/2011, its migration value should be <10 μg/kg, as long as they are not CMR (Carcinogenic, Mutagenic, Reprotoxic). However, the protocol followed in these cases is to carry out a bibliographic search for toxicity values that allow estimating a maximum migration, such as no-observed-adverse-effect level (NOAEL) or low-observed-adverse-effect level (LOAEL), and if these are not available, a theoretical estimate of its toxicity using theoretical approach based on chemical structure, such as the Threshold of Toxicological Concern (TTC) based on Cramer rules, which classify the toxicity of a compound according to its molecular

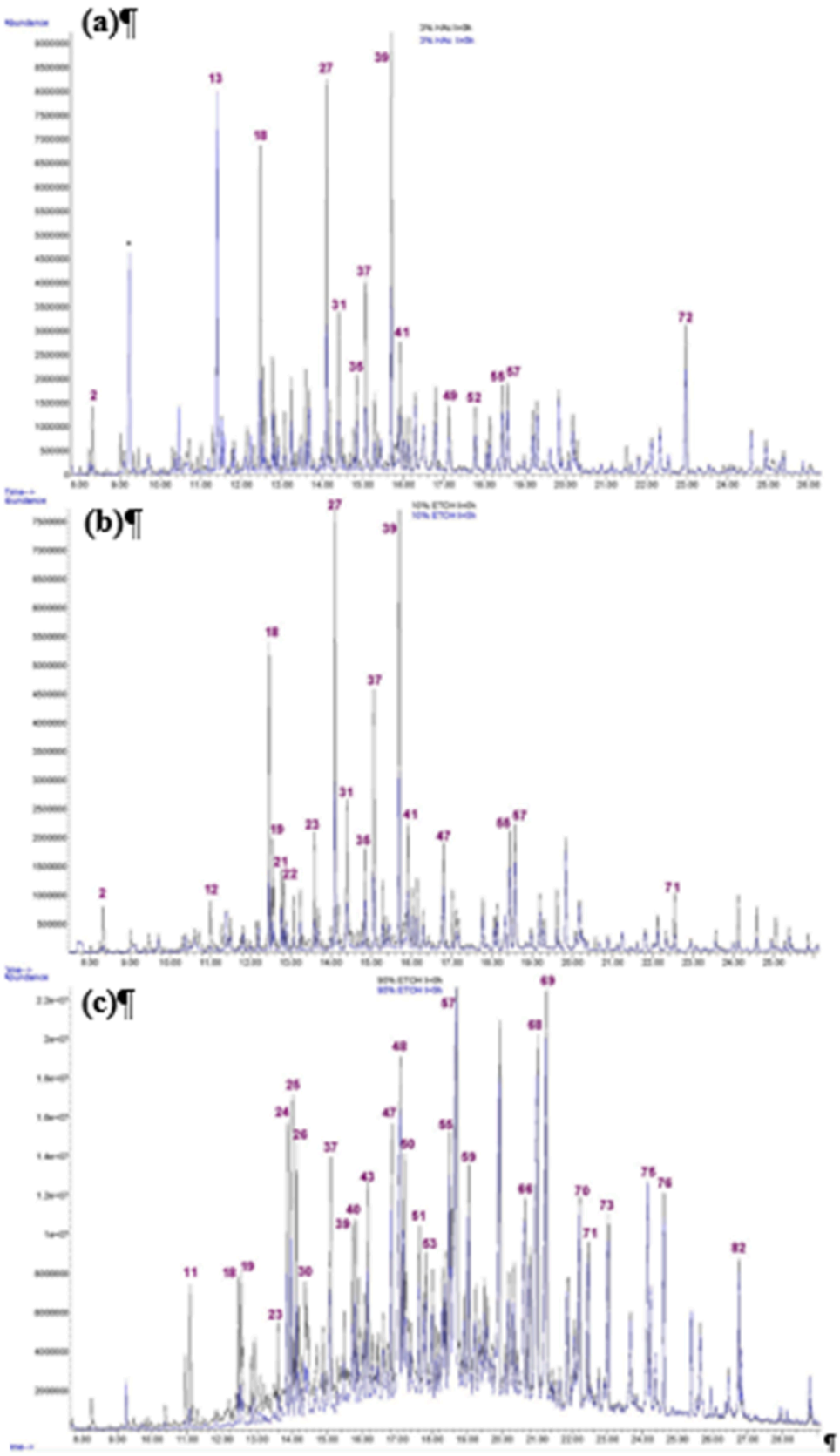

Fig. 4. Chromatograms of migration samples in 3 % acetic acid (a), 10% ethanol (b) and 95% ethanol (c) at both 0 (black) and 5 (blue) hours of decontamination treatment. (Numbers coded on Table 3, * corresponded to a siloxane).

structure. For this purpose, Toxtree software version 3.1.0.1851 was used. Organic chemicals are classified into one of three classes: Class *I* = low toxicity, Class II = intermediate toxicity and Class III = high toxicity. Each Cramer class corresponds to a maximum recommended daily intake: 30 μg/kg bodyweight-day for Class I, 9 μg/kg bodyweight-day for Class II and 1.5 μg/ kg bodyweight-day for Class III. Assuming, according to EFSA [23], an average weight of 70 kg for the European adult population and an average daily food intake of 1 kg, migration values should not exceed 2100 μg kg^{-1} for Class I, 630 μg kg^{-1} for Class II and 105 μg kg^{-1} for Class III. Among all migrants, 61 were assigned to class I, 4 to class II and 18 to class III.

None of the migrants exceeded the recommended values in 3 % acetic acid or 10% ethanol. However, the migration experiments conducted in 95 % ethanol yielded to highest migration values, potentially due to its increased capacity of extraction and, as can be seen in Table 3, and some of them exceeded the TTC recommended values (compounds marked in bold). As mentioned before, alkylbenzenes reached high concentrations, thus exceeding TTC values, but migration of some alkanes such as heptadecane or eicosane was also above this value. These compounds are considered HDPE oligomers.

4. Conclusions

A total of 67 compounds were identified in the analysis of both rHDPE flakes and pellets, including additives, degradation compounds and residues from previous uses. After the application of different decontamination conditions, it was concluded that the optimal treatment for pellets involved thermal drying at 120 °C under vacuum conditions for 5 h. Even though the decontamination over flakes was quicker, it did not show highest decontamination ratios. This method resulted in a reduction of volatile content by over 50 % for 42 out of the 67 compounds, demonstrating its effectiveness as a decontamination strategy. For both, flakes and pellets, the efficiency of the decontamination was negatively correlated with the molecular weight of the molecule and its chromatographic retention time.

To assess the effectiveness of this decontamination approach, migration tests were conducted on both untreated samples and samples treated under optimal conditions. The results revealed a generalized reduction in concentration values for the decontaminated material. When comparing the results across different food simulants, similar migration values were observed for 3 % acetic acid and 10% ethanol, with concentrations in the μg/kg range. However, a larger number of compounds and higher migration values were observed in ethanol 95 %. Since this simulant is associated with lipophilic foods, using rHDPE for packaging fatty foods may require careful consideration to ensure consumer safety. The absence of toxicity data for many migrants makes necessary further toxicological tests to achieve a more accurate toxicity assessment. Despite this, the findings are very promising, indicating significant progress towards the safe use of rHDPE in certain food packaging applications.

CRediT authorship contribution statement

Estela Pérez-Bondía: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Celia Domeño:** Writing – review & editing, Conceptualization. **Cristina Nerín:** Writing – review & editing, Resources, Funding acquisition. **Margarita Aznar:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2024.465348.

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