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Identification of volatile and semi-volatile components in food contact bioplastics based on GC–MS non-targeted screening

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ABSTRACT

Bio-based and/or biodegradable materials recently used as a sustainable alternative to conventional petroleum-based materials for food packaging applications may transfer residual monomers, additives as well as non-intentionally added substances (NIAS) into the food. The identification of potential migrating substances is the first and essential step that should be addressed to evaluate the chemical safety of packaging materials.

In this work an analytical strategy based on Purge & Trap (P&T)-GC-LRMS and GC—HRMS has been applied to investigate extractable compounds from bioplastics. Under the optimized conditions, P&T-GC-LRMS method allowed tentatively identifying 100 volatile compounds including, monomers, other starting substances, additives, solvent residues, degradation products, and so on using mass spectral libraries.

GC—HRMS was used to investigate semi-volatile compounds after extraction with acetonitrile, enabling the identification of NIAS, including oligoesters and lactic acid oligomers.

Both analytical techniques have proven to be complementary, providing comprehensive information on the volatile and semi-volatile components of the polymeric materials. The identification of extractable compounds, and consequently potential migrating substances, from the packaging materials is the first step that needs to be addressed in a global risk assessment process.

1. Introduction

Food packaging protects the food from physical damage and microbial spoilage and makes easy its transport and storage. It is historically made of conventional plastics derived from petroleum due to their excellent properties and low cost. However, due to its non-biodegradable nature, it causes environmental pollution. Consequently, it is being replaced by bioplastics, which are more sustainable alternatives made of bio-based and/or biodegradable polymers [1]. Bio-based polymers are derived from renewable sources (biomass), although this term does not imply biodegradability [2]. Polymers may be considered compostable if they are biodegradable and disintegrable in a short time, in a way that all compostable polymers are biodegradable, but not conversely [2]. The production of such environmentally friendly materials is expected to continue growing this decade (European Bioplastics, 2024) [3].

An overview of the various bioplastics used as food contact materials has been reported elsewhere [2]. Polylactic acid (PLA), a thermoplastic polyester that is both bio-based and biodegradable, is the most used biopolymer in the manufacture of food packaging [3,4]. Cellulose-based polymers and polyhydroxyalkanoates (PHA) are other bio-based and biodegradable materials with food contact applications. Bio-based but non-biodegradable polymers include bio-polyethylene, bio-polypropylene and polyethylene furanoate (PEF). Petroleum-based biodegradable polymers include polybutylene succinate (PBS), polycaprolactone (PCL) and polyvinyl alcohol (PVOH).

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Chemically, bio-based materials contain complex mixtures of substances [5], which are not only intentionally added substances (IAS) such as plasticizers, antioxidants or slip agents, but are also non-intentionally added substances (NIAS) such as degradation and/or reaction products, impurities and so on [6–8]. All these substances could migrate to the food and may suppose a risk for the consumer's health [5]. Owing to their diversity and complexity, many of the migrating substances have not been identified, and their toxicity has not been evaluated.

The identification of extractable compounds from the packaging materials, and therefore with the potential to migrate into the food, is the first and essential step that should be addressed in the risk assessment. To accomplish this task, non-targeted analytical methodologies are being applied. Depending on the nature of the migrant, which is volatile, semi-volatile or non-volatile, gas or liquid chromatography coupled to mass spectrometry are the techniques of choice. High-resolution mass spectrometry analyzers and in-source or collision-induced dissociation have shown to be a powerful tools and approaches, providing higher confidence in the identification.

Different approaches have been applied for preparing the sample, including Static Headspace, (HS) Purge & Trap, (P&T), thermal desorption (TD), solid-phase microextraction (SPME), re extraction and so on. A recent review article provides a comprehensive overview on the analytical techniques and extraction procedures for the identification and quantification of NIAS in food contact materials, analyzing their strengths and limitations [9].

In the present work, non-targeted methodologies were applied to investigate volatile and semi-volatile extractable compounds from bio-based and/or biodegradable food contact materials, specifically bio-polyethylene, bio-polypropylene and (bio)-polyester-based materials, as well as polylactic acid (PLA). Purge & Trap coupled to gas chromatography–low-resolution mass spectrometry (P&T-GC-LRMS) for the analysis of volatile compounds and gas chromatography coupled to high-resolution mass spectrometry (GC—HRMS) for the identification of semi-volatile compounds were used. Further, identification and structural elucidation were carried out based on in-house mass spectral libraries and scientific literature.

2. Experimental

2.1. Samples

Packaging materials for food contact labelled as bio-based and/or biodegradable, specifically bags for foodstuff, were either acquired in retailers in Spain (samples 1 to 15) or obtained from industrial suppliers, specifically films and raw materials (i.e. pellets) based on PLA (samples 16 and 17). The film sample was manufactured from the pellets. The polymer type of the samples was identified by FTIR spectroscopy and using KnowItAll IR Spectral Libraries of Polymers and Related Compounds. Samples were identified as made of bio-polyethylene (bio-PE) (sample 1), bio-polypropylene (bio-PP) (samples 6, 8, 9, 10, 11), bio-polyester (bio-PES; samples 2, 3, 4, 5, 7, 12, 13), bio-polyester-polyvinyl alcohol (bio-PES-PVOH; sample 15), and PLA (samples 14, 16, 17).

2.2. Chemicals and standard solutions

Acetonitrile (ACN) was purchased from Merck (LC-MS grade, Darmstadt, Germany). Toluene (> 99.85 %) was provided by Biosolve (LV-GV SuperTrave, Dieuze, France).

One deuterium-labelled cyclic (c) oligoester made of neopentyl glycol (NPG) and isophthalic acid (iPA) monomer units, specifically d_4-c (2NPG+2iPA) was synthesized in the frame of a previously published work [10]. It was used to check the instrumental performances across the GC—HRMS sequence as internal standards (IS). Five substances were confirmed by GC—HRMS with analytical standards purchased from Supelco (Merck, Darmstadt, Germany): 1,3-di-*tert*-butylbenzene (97 %), 2,4-di-*tert*-butylphenol (99 %), bis(2-ethylhexyl) phthalate (≥99.5 %) 13-docosenamide-(Z) (≥85 %), and tris(2,4-di-*tert*-butylphenyl) phosphate.

2.3. Analysis of volatile compounds by P&T-GC-LRMS

Volatile compounds were analysed using an ATOMx XYZ Purge and Trap (Ohio, USA) coupled to a GC–MS (Thermo Fischer Scientific, San José, CA, USA) with a Trace ISQ LT Single Quadrupole mass detector. Each sample (~0.8 g) was submitted to a stream of helium, which dragged the volatile substances present in the material into a trap. Within the ranges of 40–80 °C and 10–30 min, temperature and duration were considered optimums at 80 °C and 30 min. Trap was desorbed for 2 min at 250 °C. The inlet temperature was 200 °C. Volatile compounds were separated using a Rxi-624Sil MS column (30 *m* × 0.25 mm internal diameter, 1.40 μm film thickness, Restek, Bellefonte, PA, USA). The ramp temperature rose from 35 °C (held for 2 min) to 300 °C (rate of 9 °C/min, held for 10 min). Data were acquired in full-scan mode in the *m/z* range of 35–500. The ion source and transfer line temperatures were both set at 300 °C. Electron impact was 70 eV. The carrier gas was helium at 1 mL/min. Empty vials were analyzed between each sample in order to check for carry over. Compounds present in blanks were not considered further.

2.4. Analysis of semi-volatile compounds by GC-HRMS

Each sample (0.8 g) was extracted with acetonitrile (5 mL, 40 °C, 24 h) in a hermetically sealed vial. Extracts were concentrated to dryness under a gentle nitrogen stream and reconstituted in 25 μL of toluene containing IS at 1 ng/μL. Toluene extracts were injected in a GC Q Exactive (Thermo Fischer Scientific, San José, CA, USA) driven by Xcalibur software (v3.0.63.3). The inlet temperature was set at 300 °C. The injection volume was 2 μL and sample extracts were analysed in splitless mode for 1 min and the split flow was 50 mL/min. Semi-volatile compounds were separated using a DB-5MS column (30 *m* × 0.25 mm, 0.25 μm, Agilent Technologies, Palo Alto, CA, USA). The temperature ramped from 100 °C (held for 2 min) to 310 °C (10 °C/min, held 10 min). The carrier gas was helium at a flow of 1 mL/min.

Signals present in blanks were discarded to avoid considering compounds coming from external contamination. Mass spectrometric conditions were as follows: full scan ranged from 120 to 800 m/*z* and the nominal resolution was 120,000. Electron ionisation was performed at 70 eV. Ion source and MS transfer line were maintained at 300 °C and 325 °C, respectively. One-dimensional data were acquired from 6 to 32 min.

2.5. Data treatment and identification

Regarding volatile compounds analyzed by P&T-GC-LRMS, the mass spectrum of each peak was manually compared with spectra from commercial libraries NIST/EPA/NIH 11 (version 2.0) and Wiley Registry TM 8th edition.

Concerning the identification of semi-volatile compounds analyzed by GC—HRMS, data were processed with the online platform workflow4metabolomics.usegalaxy.fr. Peak picking relied on centWave algorithm using the following parameters: *m/z* tolerance, 3 ppm; peakwidth, c(3,30); prefilter step, 3 and 100,000; standard deviation, 6; percentage of FWHM width, 0.6 %. After retention time alignment was performed across files, the CAMERA R-package was used for componentization and annotation. Library search NIST/EPA/NIH (NIST14) was performed using a R script. The identification of semi-volatile compounds was made by comparison with the commercial library NIST/EPA/NIH (NIST14) consulting the available scientific literature and some of compounds were confirmed with analytical standards (when available) using the exact masses of their ions and retention time as criteria.

Only compounds tentatively identified with values of direct similarity index (SI) and reverse similarity index (RSI) above 700 were considered. Furthermore, five analytical standards were injected in the same conditions as sample extracts to confirm the identification at maximum confidence level.

The toxicity of substances for which there are no toxicological data was estimated using the Cramer decision tree (software Toxtree v3.1.0; Ideaconsult Ltd., Sofia, Bulgaria) [11].

It is an open-source application which classify the compounds based on their molecular structures into: class I (low toxicity) that are compounds with simple chemical structures, class II (intermediate toxicity) and class III (high toxicity). The latter class is assigned to compounds with reactive functional groups.

2.6. Confocal raman microscopy

To investigate the origin of the compound 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD), that is whether it was used as an additive or it was a component of the adhesive of a multilayer material, sample 7 was analyzed by confocal Raman microscopy. Raman spectra and images were recorded with a WITec confocal Raman microscopy alpha300R+ and using a 50x/0,8NA objective (Zeiss EC Epiplan Neofluar) (WITec GmbH, 89,081 Ulm, Germany). The wavelength and power of the laser were 532 nm and 15 mW, respectively and the integrated time was 0.3 s. The ST Japan database of polymers and polymer additives was used for identification purposes.

3. Results and discussion

3.1. Identification of volatile compounds by P&T-GC-LRMS

Optimal P&T conditions were determined in a preliminary assays. Sample 4 was selected to perform the analysis. First, durations of 10, 20 and 30 min at 80 °C were compared, showing that the longer the higher number of observed compounds. Thus, 37 chromatographic peaks were observed with 10 and 20 min of purge time and 41 chromatographic peaks when the purge time increased to 30 min. Second, temperatures of 40, 60 and 80 °C during 30 min were compared, showing that a more intense signals and higher number of compounds were observed at the highest temperature. Specifically, 29, 30 and 41 chromatographic peaks were detected at 40 °C, 60 °C and 80 °C, respectively. Optimized values of 80 °C during 30 min were then applied to the investigation of volatile substances in all samples.

A total of 125 volatile compounds were detected in bio-based and/or biodegradable materials for food contact using non-targeted strategy, among them, 100 were tentatively identified, including 15 substances authorized as additive, or monomer included according to Regulation (EU) No 10/2011 [12] on plastic food contact materials, linear and branched alkanes or alkenes, aldehydes, reaction and degradation products, etc. However, there are still, 12 compounds remained unknown, and 13 presented a structure of alkane and/or alkene, although its identification was not possible. All substances identified are listed in Table 1.

3.1.1. Bio-polyester based materials

Residues of PS monomer i.e. 2-propanediol/propylene glycol (PG), was identified in samples 7 and 5. So, this diol has probably been used as monomer in the synthesis of the polyester-based biopolymer.

In the rest of bio-PES based-samples, the identification of the oligomer 1,6-dioxacyclododecane-7,12-dione c(BD+AA), allowed us to presuppose that adipic acid (AA) and 1,4/1,3-butanediol (BD) were involved in the production of the polyester-based materials. This oligomer has been reported in a biodegradable blend composed of polyester and PLA [13].

The detection of 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) in sample 7 caught our attention. This compound has been reported to be used as non-ionic surfactant in the manufacture of coatings, adhesives, printing inks [14]. Raman analysis of sample 7 was conducted to investigate its possible origin. The characteristic band at 2350 cm^{-1} was not observed. However, the analysis revealed, that it is a multilayer material with a modified cellulose layer between polyester layers (Fig. 1). This finding allowed us to hypothesize that the diol comes from the adhesive used in the manufacture of the multilayer film.

Cyclohexanone was identified in some of the PS-based samples, what could denote that AA was also involved as starting monomer in their manufacture [15]. Another ketone, cyclopentanone, was identified in the samples and it has also been reported in a biopolymer based on polyester and PLA [13].

1,3,5-Trimethylbenzene was identified in sample 2. This substance has been described to produce trimellitic acid (TMA), and it is commonly used for branching the polymer chains [16,17].

Based on the identified compounds, we noticed that, within PS-based samples, fingerprints differed widely, due to varying starting monomers. Plasticizers such as 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) found in samples 2 and 3 or diisobutyl phthalate (DIPB) detected in sample 7 were previously reported in adhesives used in food packaging multilayer materials [18]. Both plasticizers have been reported in polyester-based coatings for food contact [19]. TXIB is included in the EU positive list of plastic food contact materials with a specific migration limit (SML) of 5 mg/kg [12].

2-Ethyl-1-hexanol, a substance used in the production of plasticizers [20], was found in all PS-based samples. It is authorized by Regulation (EU) No 10/2011 for plastic materials intended to be in contact with food with a SML of 30 mg/kg [12].

Antioxidants are often used in the manufacture of packaging materials, for example butylhydroxytoluene (BHT). This phenolic compound is authorized as food additive with a SML of 3 mg/kg [12]. Its degradation products, 3,5-di-tert-butyl-4-hydroxybenzaldehyde and 2, 6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one [21], were found in sample 7. The first compound was previously reported in water migrates from reusable biodegradable polyester bottles [22]. The second one was previously reported as leaching from baby bottles and it was classified by in silico tools as group 2B of toxicity, defined as substances with high priority for more genotoxicity data [23]. Another reported degradation product of BHT was 2,6-di-tert-butylbenzoquinone [24] found in PS-based and PP-based samples. It is also a well-known compound derived from antioxidants such as Irganox 1010 and Irgafos 168 [25].

Interestingly, other compounds were only identified in sample 7. Isothiocyanatocyclohexane is involved in the manufacture of foams, rubber, paints and varnishes [26]. 2,5-Diisobutylthiophene has been reported as aromatic compound [27]; and 2-phenoxyethoxybenzene has been described as sensitizer in thermal papers [28].

Branched alkanes, for example 2,2,4,6,6-pentamethylheptane, were identified in the polyester-PVOH based material.

3.1.2. PLA-based materials

Within the group of samples identified as PLA-based materials, caprolactone was identified as one of the main substances. It is usually employed as co-polymer in order to improve the properties of the material (e.g. degree of crystallinity) [29]. It was found in the film and respective raw material (pellet) (samples 16 and 17). In these samples, two other major substances were identified with highly intense signals: 1,4-dioxane-2,5-dione,3,6-dimethyl- and 1,4-dioxane-2,5-dione,3, 6-dimethyl-(3S-*cis*)-, which are the cyclic and linear lactide dimers, respectively. PLA can be produced often from lactic acid, and also often from cyclic dimer lactide through ring-opening polymerization [13,30]. Another compound, 2,3-pentanedione, was also identified. It is a known PLA degradation product for which some authors affirm that it is degraded during the period of storage at ambient conditions [31].

MS signals related to fragments of lactic acid oligomers, specifically

Table 1
Volatile compounds detected by P&T-GC-LRMS (n = 125).

t_R (min)	Compound	CAS	Formula	*m/z*	SI	RSI	Samples
5.48	Chloroform	67–66–3	$CHCl_3$	47, 83, 85	750	942	2, 3, 4, 7, 14
5.58	Tetrahydrofuran[1a]	109–99–9	C_4H_8O	42, 71	886	961	2, 3, 4, 5, 12, 13
6.22	Benzene	71–43–2	C_6H_6	78	877	956	2, 3
6.35	Acetic acid[1]	64–19–7	$C_2H_4O_2$	43, 45, 60	901	957	5, 6, 7, 8, 9, 10, 11, 12
6.68	Heptane	142–82–5	C_7H_{16}	43, 57, 71	896	967	2, 3, 4, 5, 6, 8, 9, 10, 11, 13, 14, 16, 17
7.13	2,3-Pentanedione	600–14–6	$C_5H_8O_2$	43, 57, 100	689	826	16, 17
7.14	Pentanal	110–62–3	$C_5H_{10}O$	44, 58	811	902	2, 5, 6, 8, 9
7.29	2,4-Dimethylfuran	3710–43–8	C_6H_8O	67, 96	910	923	11
7.41	2-Nitrobutane	600–24–8	$C_4H_9NO_2$	41, 57	760	887	6, 8, 9
8.59	Toluene	108–88–3	C_7H_8	91, 92	989	989	2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 17
8.78	1-Octene[1b]	111–66–0	C_8H_{16}	41, 55, 70	863	882	6, 8, 9
8.78	3-Methylideneheptane	1632–16–2	C_8H_{16}	55, 70	703	843	2, 4, 5
8.91	Octane	111–65–9	C_8H_{18}	43, 57, 85	841	919	2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14
9.40	Hexanal	66–25–1	$C_6H_{12}O$	41, 44, 56	811	940	2, 3, 4, 5, 6, 8, 9, 10, 11
9.43	2, 4-Dimethylheptane	2213–23–2	C_9H_{20}	43, 85	880	926	17
9.45	Cyclopentanone	120–92–3	C_5H_8O	55, 84	826	929	12, 13, 14
9.59	Acetic acid butyl ester[1]	123–86–4	$C_6H_{12}O_2$	43, 56	867	910	16, 17
9.73	Unknown compound			43, 109, 114			11
9.81	Propylene glycol[1]	57–55–6	$C_3H_8O_2$	43, 45	947	948	5, 7
10.28	Unknown compound			109, 124			4,5,12
10.31	4-Methyloctane	2216–34–4	C_9H_{20}	43, 85	915	932	16, 17
10.39	2,2-Dimethylpropanoic acid	75–98–9	$C_5H_{10}O_2$	41, 57	722	912	2, 6, 8, 9, 10, 11, 12
10.56	2,5-dimethylhexa-2,4-diene	764–13–6	C_8H_{14}	67, 95, 110	896	850	4, 5, 8
10.6	Furfural	98–01–1	$C_5H_4O_2$	39, 96	951	956	4, 5
10.68	Ethylbenzene	100–41–4	C_8H_{10}	91, 106	850	896	2, 3, 4, 6, 8, 9, 12, 13, 14, 16, 17
10.85	*p*-Xylene	106–42–3	C_8H_{10}	91, 106	887	972	2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 17
11.34	2-Propenoic acid, butyl ester[1c]	141–32–2	$C_7H_{12}O_2$	55, 73	918	930	16, 17
11.40	*o*-Xylene	95–47–6	C_8H_{10}	91, 106	940	952	2, 3, 4, 5, 6, 8, 9, 12, 13, 14, 16, 17
11.41	2,4,6-Trimethylheptane	2613–61–8	$C_{10}H_{22}$	43, 57, 85	829	923	10, 11
11.40–12.60	Alkanes			43, 57, 71			10, 11
11.60	Heptanal	111–71–7	$C_7H_{14}O$	43, 70	864	894	2, 4, 5, 6, 8, 9
11.76	Cyclohexanone	108–94–1	$C_6H_{10}O$	42, 55, 69, 98	953	959	2, 3, 4, 5, 14, 16, 17
12.10	α-Pinene[1]	80–56–8	$C_{10}H_{16}$	93	740	823	2, 3, 4, 5, 6, 8, 9
12.51	Bicyclo[2.2.1]heptane, 2,2-dimethyl-3-methylene-	79–92–5	$C_{10}H_{16}$	93, 121	792	908	12, 13, 14
12.89	2-Heptenal Z/E	57,266–86–1/ 18,829–55–5	$C_7H_{12}O$	83, 105			4
13.03	2,2,7,7-Tetramethyloctane	1071–31–4	$C_{12}H_{26}$	57	891	921	6, 8, 9, 10, 11
13.05	2,2,4,6,6-Pentamethylheptane	13,475–82–6	$C_{12}H_{26}$	57	940	940	12,13,14, 15
13.06	Decane	124–18–5	$C_{10}H_{22}$	43, 57	827	920	1, 2, 3, 4
13.20–13.60	Alkanes			43, 57, 71			10, 11
13.23	Benzaldehyde[1]	100–52–7	C_7H_6O	51, 77, 105, 106	961	973	2, 3, 5, 12
13.46	1,3,5-Trimethylbenzene	108–67–8	C_9H_{12}	105, 120	849	882	2
13.59	3-Methyl-2-pentanol	565–60–6	$C_6H_{14}O$	45	769	861	7
13.60	Octanal	124–13–0	$C_8H_{16}O$	41, 43, 57, 84	845	951	2, 3, 4, 5, 6, 8, 9, 12
13.8	2,2,4,4-Tetramethyloctane	62,183–79–3	$C_{12}H_{26}$	57, 99	867	916	6, 8, 9, 15
13.9–15.2	Alkane			43, 57, 71			10
13.96	*p*-Cymene	99–87–6	$C_{10}H_{14}$	119, 134	837	846	6, 8, 9, 12, 13, 14
13.99	Limonene	138–86–3	$C_{10}H_{16}$	68, 93	811	846	2, 3, 4, 5
14.17	Alkane			43, 57, 71			16, 17
14.20	2-Ethyl-1-hexanol[1d]	104–76–7	$C_8H_{18}O$	57	928	956	2, 3, 4, 5, 7, 12, 13, 14
14.27	Phenol[1]	108–95–2	$C_6H_{16}O$	66, 94	921	976	12
14.91	Undecane	1120–21–4	$C_{11}H_{24}$	43, 57, 71	916	943	1, 2, 3, 4, 5, 6, 8, 9, 16, 17
15.30	(E)-3-Methylundec- 4-ene	74,645–87–7	$C_{12}H_{24}$	41,43, 55, 57, 69	824	840	10, 11
15.45	Nonanal	124–19–6	$C_9H_{18}O$	41, 57	887	944	2, 3, 4, 5, 6, 7, 8, 9, 12, 13, 14
15.60–16.60	Alkanes						10, 11
15.63	Methyl benzoate[1]	93–58–3	$C_8H_8O_2$	77, 105, 136	793	928	6, 8, 9
16.14	1,2,4-Trichloorobenzene	120–82–1	$C_6H_3Cl_3$	180, 182	803	892	17
16.15	1,3,5-Trichlorobenzene	108–70–3	$C_6H_3Cl_3$	180, 182	781	804	2, 3, 4, 5
16.16	Alkane			43, 57, 71			12, 13, 14
16.52	2-(4-Methylcyclohexyl)propan-2-ol	498–81–7	$C_{10}H_{20}O$	59	778	875	2, 3, 4, 5
16.63	Dodecane	112–40–3	$C_{12}H_{26}$	43, 57, 71	943	943	1, 2, 3, 4, 5, 6, 8, 9, 12, 13, 14
16.71	1-Nonanol[1]	143–08–8	$C_9H_{20}O$	43, 56, 70	704	838	7
16.73	Butyl hexanoate	626–82–4	$C_{10}H_{20}O_2$	43, 56, 99, 117	718	848	14
16.73	Acetic acid benzyl ester	140–11–4	$C_9H_{10}O_2$	91, 108, 150	844	870	2, 3, 4
16.79	1,4-Dioxane-2,5-dione,3,6-dimethyl-	95–96–5	$C_6H_8O_4$	45, 56	915	940	16, 17

(*continued on next page*)

Table 1 (*continued*)

t_R (min)	Compound	CAS	Formula	*m/z*	SI	RSI	Samples
17.02	Menthol	1490–04–6	$C_{10}H_{20}O$	71, 81, 85	776	823	2, 3, 4
17.12	2-Oxepanone[1e]	502–44–3	$C_6H_{10}O_2$	42, 55, 84	914	915	16, 17
17.20	Decanal	112–31–2	$C_{10}H_{20}O$	43, 57	877	917	2, 3, 4, 5, 7, 12, 13, 14
17.33	α-Terpineol	98–55–5	$C_{10}H_{18}O$	59, 93, 121, 136	911	914	2, 3
17.56	Nonylcyclopentane	2882–98–6	$C_{14}H_{28}$	69, 83, 97	835	844	6, 8, 9
17.59	1,4-Dioxane-2,5-dione,3,6-dimethyl-(3S-*cis*)-	4511–42–6	$C_6H_8O_4$	45, 56	936	936	16, 17
17.67	2-Methyldodecane	1560–97–0	$C_{13}H_{28}$	43, 57, 71	902	908	6, 8, 9
17.78	Unknown compound			111, 125, 140			10, 11
17.82	1,2,4-Trichlorobenzene	120–82–1	$C_6H_3Cl_3$	180, 182	742	819	2
17.95	Alkane			43, 57, 71			16, 17
18.15	Isothiocyanatocyclohexane	1122–82–3	$C_7H_{11}NS$	55, 141	700	760	7
18.16	3-Tetradecene, (E)	41,446–68–8	$C_{14}H_{28}$	43, 55, 69, 83	906	924	6, 8, 9
18.16	Alkene			69, 83, 97, 111			2, 3, 4, 5
18.24	Tridecane	629–50–5	$C_{13}H_{28}$	43, 57, 71	951	954	1, 2, 3, 4, 5, 6, 8, 9
18.50	Alkane			43, 57, 71			10, 11
18.81	Undecanal	112–44–7	$C_{11}H_{22}O$	41, 85	740	874	7
18.83	Unknown compound			95, 121, 136			2, 3, 4, 5
19.30	Alkane			43, 57, 71			10, 11
19.58	Butoxyethoxyethyl acetate	124–17–4	$C_{10}H_{20}O_4$	43, 57, 87	906	933	5, 7
19.30	Unknown compound			56, 105			2, 3, 4, 5
19.75	Tetradecane	629–59–4	$C_{14}H_{30}$	43, 57, 71	948	969	1, 2, 3, 4, 5, 6, 8, 9
19.78	Unknown compound			138, 193			6, 8, 9, 10, 11
19.78	Hexyl hexanoate	6378–65–0	$C_{12}H_{24}O_4$	43, 99, 117	880	915	14
19.86	6,7-Dimethyl-3H-2-benzofuran-1-one	569–31–3	$C_{10}H_{10}O_4$	133, 162	763	835	17
19.86	1,2,3,4-Tetrahydro-1,1,6-trimethylnaphthalene	475–03–6	$C_{13}H_{18}$	159, 174	782	857	12
20.02	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate[1f]	6846–50–0	$C_6H_{30}O_4$	43, 71	861	861	2, 3
20.05	2-*tert*-butyl-5-methylphenol	88–60–8	$C_{11}H_{16}O$	121, 149, 164	822	876	7
20.23	(3-Hydroxy-2,2,4-trimethylpentyl) 2-methylpropanoate	77–68–9	$C_{12}H_{24}O_3$	43, 56,71	913	913	2, 3, 4, 5, 7, 12, 13, 14
20.32	Dodecanal	112–54–9	$C_{12}H_{24}O$	41, 43, 57	874	963	7
20.33	Cyclododecanol	1724–39–6	$C_{12}H_{24}O$	68, 82, 96	739	741	2, 3, 4, 5
20.45	2,6-Diisopropylphenyl isocyanate	28,178–42–9	$C_{13}H_{17}NO$	146, 160, 188, 203	866	910	17
20.57	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	126–86–3	$C_{14}H_{26}O_2$	109, 151	839	890	7
20.65	2-Methyltetradecane	1560–95–8	$C_{15}H_{32}$	57, 85	785	789	2, 3, 4, 5, 6, 8, 9
20.69	Unknown compound			69, 83			6, 8, 9
20.70	Phenoxybenzene	101–84–8	$C_{12}H_{10}O$	141, 170	754	946	2, 3, 4, 5, 7
20.88	Caryophyllene	87–44–5	$C_{15}H_{24}$	69, 133	850	890	13
20.97	Unknown compound			120, 162, 177	958	967	13
21.04	(5Z)-6,10-Dimethylundeca-5,9-dien-2-one	3879–26–3	$C_{13}H_{22}O$	43, 69	904	908	2, 3, 4, 12, 13, 14
21.13	Alkane			43, 57, 71			16, 17
21.50	1,3,6,10-Dodecatetraene,3,7,11-trimethyl-,(3E,6E)	502–61–4	$C_{15}H_{24}$	93, 107	953	970	14
21.51	*p*-Benzoquinone, 2,6-di-*tert*-butyl-	719–22–2	$C_{14}H_{20}O_2$	93, 177, 220	835	893	2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
21.53	Unknown compound			161, 175, 203, 218			7
21.59	2,6-Di-*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	10,396–80–2	$C_{15}H_{24}O_2$	137, 165, 180	715	737	7
21.72	Alkane			43, 57, 71			16, 17
21.85	Valencene	4630–07–3	$C_{15}H_{24}$	161, 204	902	921	6, 8, 9
21.86	Butylhydroxytoluene (BHT)[1 g]	128–37–0	$C_{15}H_{24}O$	177, 205, 220	729	877	2, 3, 4, 5, 7
22.12	Alkane			43, 57, 71			12, 13, 14
22.28	Unknown compound			123, 179, 194			7
22.36	Myristicin	607–91–0	$C_{11}H_{12}O_3$	192	897	972	2, 3
22.48	Hexadecane	544–76–3	$C_{16}H_{34}$	43, 57, 71	936	950	2, 3, 4, 5
22.66	2-Ethoxynaphthalene	93–18–5	$C_{12}H_{12}O$	115, 144, 172	828	928	2, 3, 4, 5
22.88	2,5-Diisobutylthiophene	54,845–33–9	$C_{12}H_{20}S$	153, 196	703	734	7
23.00	Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	74,381–40–1		43, 71	857	891	2, 3, 4, 5
23.00	Unknown compound, adipate structure			111, 129			6, 7, 8, 9
23.12	1, 6-Dioxacyclododecane-7, 12-dione	777–95–7	$C_{10}H_{16}O_4$	55, 84, 100, 129	789	817	2, 3, 4, 5, 12, 13, 14
23.35	Diethyl phthalate	84–66–2	$C_{12}H_{14}O_4$	149, 177	883	945	7
24.12	Unknown compound			67, 91			2,5
25.28	3,5-Di*tert*-butylbenzene-1,2-diol	1020–31–1	$C_{14}H_{22}O_2$	207, 222	853	868	7
25.66	3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde	1620–98–0	$C_{15}H_{22}O_2$	191, 219, 234	924	930	7
26.00	2-Phenoxyethoxybenzene	104–66–5	$C_{14}H_{14}O_2$	77, 121, 214	943	962	7
26.49	Phthalic acid, diisobutyl ester	84–69–5	$C_{16}H_{22}O_4$	149	758	864	7

*[1]authorized as additive or monomer (Reg 10/2011)

.[1a]SML = 0.6 mg/kg

[1b]SML = 15 mg/kg.

[1c]Group restriction SML = 6 mg/kg (expressed as acrylic acid).

[1d]SML = 30 mg/kg.

[1e]Group restriction SML: 0.05 mg/kg (expressed as the sum of 6-hydroxyhexanoic acid and caprolactone).

[1f]SML = 5 mg/kg (Only to be used in single-use gloves).
[1g]SML = 3 mg/kg.

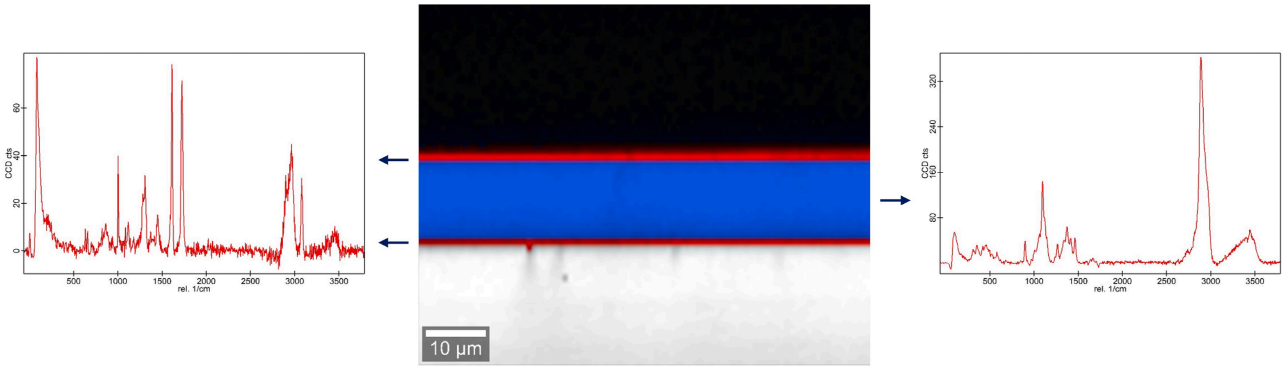

Fig. 1. Confocal Raman image of sample 7. Blue: modified cellulose layer, red: polyester layers.

m/z 128.0469 ($C_6H_8O_3$), *m/z* 200.0679 ($C_9H_{12}O_5$), *m/z* 272.0892 ($C_{12}H_{16}O_7$), *m/z* 344.1105 ($C_{15}H_{20}O_9$), and *m/z* 416.1316 ($C_{18}H_{24}O_{11}$) were also detected in samples 16 and 17.

Comparing PLA film (sample 16) and pellet (sample 17), no differences were observed in terms of identified compounds, except two compounds that were only present in the raw material (pellet). These were 2,6-diisopropylphenyl isocyanate and 6,7-dimethyl-3H-isobenzofuran-1-one. Some authors described 2,6-diisopropylphenyl isocyanate as a degradation product in polyurethane resins [32], while other authors consider it as compatibilizing agent to blend components in poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and PLA to generate enhanced polymers [33]. Concerning other compounds with a furanone structure, some authors reported the presence of these compounds produced from carboxylic acids and hydroxyl groups in specific positions of the polymer backbone [34].

3.1.3. Bio-polypropylene and bio-polyethylene based materials

In general, alkanes and alkenes were the most abundant compounds, identified mostly in PP and PE samples. Some linear alkanes found were heptane, octane, decane, undecane, dodecane, tridecane, tetradecane and hexadecane, and some branched alkanes like 2,4,6-trimethylheptane, 2,2,7,7-tetramethyloctane, 2,2,4,4-tetramethyloctane were also detected. It has been reported in the literature that aldehydes responsible of odors like octanal, hexanal or nonanal have been identified in PP samples. Nonanal was also described as oxidation products of these polyolefins [20]. Beside these compounds, other substances of the same family were identified in this work such as pentanal, heptanal, undecanal, dodecanal or terpenes like α-pinene, α-terpineol and caryophyllene.

A furan compound, 2,4-dimethylfuran, described as a degradation product in PP [35] was only found in one PP sample (sample 11).

Chloroform, toluene, tetrahydrofuran, ethylbenzene, o- and p-xylene, butoxyethoxyethyl acetate, 1,2,4-trichlorobenzene and 1,3,5-trichlorobenzene were present, likely as solvent residues.

In addition, Methyl benzoate was detected in PP samples (6, 8, 9). It is authorized as additive or starting substances in Regulation (EU) No 10/2011 [12] although its presence was also attributed to the photolytic decomposition of UV photoinitiators in food packaging [36].

3.2. Identification of semi-volatile compounds by GC-HRMS

Toluene extracts from bio-based and/or biodegradable materials were analyzed by GC—HRMS to identify semi-volatile substances. Table 2 summarizes the semi- volatile compounds detected in the biopolymers and their identification is discussed below.

A great variety of compounds were identified among them fatty acids, esters, oligoesters, amides, phthalates, phosphates. However, not all of them could be identified with commercial libraries and bibliography, since most of NIAS are not present in databases. Furthermore, there is scarce literature about biopolymers analyzed by GC—HRMS. Therefore, some compounds remained unidentified.

3.2.1. Bio-polyester based materials

The most intense components detected by GC—HRMS exhibited the characteristic fragment *m/z* 149.0235, which is specific from phthalic acid (PA) derivatives. This *m/z* was observed at several retention times. The mass spectra of these compounds are very similar; thus their unequivocal identification remains a challenge as suggested by Omer et al. 2019 [37]. In their work, 12 oligoesters were found. Some of these compounds with low molecular weight were tentatively identified based on precise mass of their ions, theoretical databases of oligomers (e.g. database NIAS-db 1.0) [10] and available literature. In addition, some of them have been reported and identified in starch-based biopolymers [7]. Their identification was very challenging due to extensive in-source fragmentation and absence of molecular ion. Different possible combinations identified are commented on. It must be considered that oligoesters are combinations of IAS monomers arising from incomplete polymerization or degradation or cyclization.

Cyclic combinations of adipic acid (AA) and/or phthalic acid (PA) with ethylene glycol (EG) and/or 1,3-butanediol or 1,4- (BD) were found in polyester samples. Different fragments observed that helped to interpret the results were the following: *m/z* 129.0546 (AA), 149.0234 (PA), 173.0809 (EG+AA), 193.0496 (EG+PA), 201.1116 (BD+AA), 221.0809 (BD+PA). It means that, oligoesters such as c(EG+AA), c (EG+PA), c(BD+PA) could be present in polyester samples. It should be stated that isomer identification for BD and PA was not possible. In fact, other combinations containing BD and PA were not elucidated, although some fragments could be present. Such is the case of 2BD+PA and BD+2PA; PA and BD+PA fragments constituting these molecules were observed beside *m/z* 293.1383, which corresponds to PA with 2 BD deprotonated with a water molecule and *m/z* 387.1078 (l(BD+2PA)), these fragments could come from the cyclic respective combination or other bigger oligoesters.

In sample 7, characteristic fragments that could come from these molecules were observed: *m/z* 149.0235 (PA), 193.0496 c(EG+PA), 208.0520 l(EG+PA), 341.0651/359.0760 l(EG+2PA), 427.1342 c (EG+NPG+2PA), 401.1233 l(NPG+2PA) and 468.1780 c(2NPG+2PA). They could come from the reported oligoesters. In what concerns to oligoesters toxicity, to the best of our knowledge, no toxicological data was available for the identified oligoesters. The Cramer class was determined as a first alert indication. Special attention should be paid to five (i.e. c(EG+PA), c(BD+PA) c(2BD+AA+PA) c(EG+NPG+2PA) and c

Table 2
Compounds detected by GC—HRMS ($n = 50$), along with SI and RSI for compounds identified by comparison with the NIST library.

t_R (min)	Compound	CAS	Formula	*m/z* with annotation	SI	RSI	TC	Samples
6.13	1,3-Di-*tert*-butylbenzene*	1014–60–4	$C_{14}H_{22}$	175.1481, 176.1516			I	8, 11
6.13	4-Pentylbenzoyl chloride	49,763–65–7	$C_{12}H_{15}ClO$	125.0598, 175.1482, 176.1516	769	700	III	2, 13, 14
6.97	Bicyclo[4.1.0]heptan-3-one, 7,7-dimethyl-4-methylene-, (1R)-	106,974–32–7	$C_{10}H_{14}O$	135.0442, 150.0676	940	984		13, 15
7.58	2-Acetonylcyclohexanone	6126–53–0	$C_9H_{14}O_2$	136.0520, 154.0626,	703	819	II	3, 5, 7, 8
8.21	2,6-Diisopropylphenyl isocyanate[2]	28,178–42–9	$C_{13}H_{17}NO$	146.0601, 188.1070, 203.1304			I	16, 17
9.40	Terephthalic acid, dimethyl ester (myristyl dodecanoate)[1]	120–61–6	$C_{10}H_{10}O_4$	163.0392, 179.0340			I	13
9.44	2,4-Di-*tert*-butylphenol*	96–76–4	$C_{14}H_{22}O$	191.1431, 192.1464, 205.1587,			I	1, 11, 13
9.47	1,3,3-Trimethylcyclohex-1-ene-4-carboxylic acid	13,746–43–5	$C_{10}H_{16}O_2$	125.0599, 153.0548, 168.0782	768	808	I	3, 8
9.83	2-Ethoxynaphthalene[2]	93–18–5	$C_{12}H_{12}O$	144.0571, 145.0605, 172.0884,			III	2, 3, 4, 5
10.46	Unknown compound, phthalic acid structure			149.0234, 176.0468				1, 2, 3, 5, 11, 13, 14, 15
10.47	Diethyl phthalate[2]	84–66–2	$C_{12}H_{14}O_4$	121.0286, 149.0235, 178.0625			I	2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 14, 15
10.85	Unknown compound, oligoester structure			201.1120 (AA+BD)				4, 5
10.99	2(3H)-Furanone, dihydro-5-pentyl-	104–61–0	$C_9H_{16}O_2$	121.0286, 128.0470, 138.0313, 200.0679	703	819	II	4, 5, 14
11.06	Benzophenone[1a]	119–61–9	$C_{13}H_{10}O$	181.0649, 182.0724			III	1, 13, 14, 15
11.09	c(EG+AA): 1,4-Dioxecane-5,10-dione	15,498–31–4	$C_8H_{12}O_4$	173.0809			I	2, 12, 13, 15
12.93	2-Ethylhexyl salicylate	118–60–5	$C_{15}H_{22}O_3$	121.0283, 138.0312			I	15
13.46	Dibutyl phthalate[1b]	84–74–2	$C_{16}H_{22}O_4$	121.0286, 149.0234, 223.0966			I	1, 2, 4, 5, 9, 13
13.81	2-Methylbutyl 2-hydroxybenzoate	51,115–63–0	$C_{12}H_{16}O_3$	120.0208, 121.0242, 138.0313	885	915	I	3, 4, 5, 7, 8, 10, 11, 12, 13
13.88	c(EG+PA): 3,4-dihydrobenzo[f][1,4]dioxocine-1,6-dione hydrate		$C_{10}H_8O_4$	149.0234 (PA), 193.04962 (EG+PA)			III	3, 4, 5
14.43	Unknown compound, phthalic acid structure			149.0234, 150.0265				1, 2, 3, 9, 11, 12, 14
14.46	n-Hexadecanoic acid (palmitic acid)[1]	57–10–3	$C_{16}H_{32}O_2$	129.0911, 213.1849	769	778	I	1, 2, 5, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17
15.14	PA isomer		$C_{16}H_{18}O_4$	149.0235, 203.0703, 204.0736	900	928		11, 13, 15
16.09	2,8,9-Trioxa-5-aza-1-silabicyclo(3.3.3)undecane, 1-methoxy-	4025–80–3	$C_7H_{15}NO_4Si$	130.0684, 174.0945	799	893	III	1, 9, 17
16.76	4-Aminobenzyl alcohol (Benzenemethanol, 4-amino-)	623–04–1	C_7H_9NO	123.0469	912	970	I	2, 4, 9, 11, 15
17.08	Tributyl acetylcitrate[1]	77–90–7	$C_{20}H_{34}O_8$	129.0183, 185.0808, 213.0759, 217.0344, 259.1541, 273.0971, 329.1592			I	1, 2, 3, 8, 11, 12
17.77	2-Propenoic acid, 3-(4-methoxyphenyl)-	830–09–1	$C_{10}H_{10}O_3$	161.0598, 178.0645	892	906	I	7, 8, 10, 12, 13, 14
17.99	Palmitic acid derivative							11, 13, 15
18.13	c(BD+PA): 3,4,5,6-tetrahydro-2,7-benzodioxecine-1,8-dione		$C_{12}H_{12}O_4$	149.0235 (PA), 221.0809 (BD+PA),			III	2, 3, 4, 5, 7, 12, 13, 14, 15
18.23	Unknown compound, lactic acid oligomer			145.0496 ($C_6H_9O_4$), 217.0709 ($C_9H_{13}O_6$)				2, 12, 13, 14
18.33	Propanedioic acid, dipropyl ester (dipropyl maleate)	1117–19–7	$C_9H_{16}O_4$	129.0547	884	986	I	5, 7, 9, 10, 11, 12
19.45	Unknown compound, phthalic acid structure			149.0234				1, 3, 5, 9, 11, 14, 15, 17
19.48	Bis(2-ethylhexyl)phthalate*[1c]	117–81–7	$C_{12}H_{14}O_4$	149.0234, 167.0340			I	1, 2, 11
20.89	N,N-diethyldodecanamide	222–118–3	$C_{16}H_{34}NO$	256.2636			III	2, 5, 12
21.06	Ethyl 4-amino-1H-imidazole, 4-amino-5-ethoxycarbonyl-carboxylate	21,190–16–9	$C_6H_9N_3O_2$	127.0755, 149.0234, 155.0703	817	952	III	2, 5, 12
21.40	13-Docosenamide, (Z)-*[1]	112–84–5	$C_{22}H_{43}NO$	126.0915, 128.1071, 121.1014, 294.2789, 135.1170			III	1, 2, 3, 4, 8, 9, 10, 12, 13, 14
22.36	LA oligomer cyclic			145.0496 ($C_6H_9O_4$), 217.0709 ($C_9H_{13}O_6$)				4, 5, 12
22.51	c(BD+AA): 1,6-dioxacyclododecane-7,12-dione[2]	777–95–7	$C_{10}H_{16}O_4$	129.0546 (AA), 201.1116			I	2, 3, 4, 5, 12, 13
24.07	α-Tocopherol acetate	58–95–7	$C_{31}H_{52}O_3$	165.0912, 430.3807, 472.3915	888	898	III	2, 3, 10
24.54	Unknown compound, oligoester structure		$C_{18}H_{14}O_8$	193.0496 c(EG+PA), 208.0520 l (EG+PA), 341.0651, 359.0759 l (EG+2PA)			I	7
25.05	c(EG+NPG+2PA): 18,18-dimethyl-7,8,18,19-tetrahydro-17H-dibenzo[f,o][1,4,9,13]tetraoxacycloheptadecine-5,10,15,21-tetraone		$C_{23}H_{22}O_8$	149.0234 (PA), 193.0496 c(EG+PA), 208.0520 l(EG+PA), 341.0651, 359.0759 l(EG+2PA), 427.1342 c (EG+NPG+2PA)			III	7
25.25	Unknown compound, oligoester strcuture		$C_{16}H_{22}O_6$	149.0235 (PA), 221.0809 (BD+PA), 293.1382 (2BD+PA)			I	2, 3, 4, 5, 12, 13, 14, 15
25.45	c(2BD+2AA) : 1,6,13,18-tetraoxacyclotetracosane-7,12,19,24-tetrone	78,837–87–3	$C_{20}H_{32}O_8$	400.2085			I	14

(*continued on next page*)

Table 2 (*continued*)

t_R (min)	Compound	CAS	Formula	*m/z* with annotation	SI	RSI	TC	Samples
25.91	PA oligomer			149.0234 (PA), 297.0388 (PA anhydride dimer)				7
26.01	Tris(2,4-ditert-butylphenyl) phosphite (Irgafos 168)[1]	31,570–04–4	$C_{42}H_{63}O_3P$	147.1169, 191.1431, 441.2918			III	1, 9
26.53	Unknown compound, oligoester structure		$C_{21}H_{20}O_8$	149.0234 (PA), 208.0520 l(EG+PA), 401.1233 l(NPG+2PA)			I	7
27.18	c(2NPG+2PA): 8,8,19,19-tetramethyl-8,9,19,20-tetrahydro-7H,18H-dibenzo[g,p][1,5,10,14] tetraoxacyclooctadecine-5,11,16,22-tetraone		$C_{26}H_{28}O_8$	149.0234 (PA), 208.0520 l(EG+PA), 401.1233 l(NPG+2PA), 468.1783 c (2NPG+2PA)			III	7
28.16	Tris(2,4-ditert-butylphenyl)phosphate*	95,906–11–9	$C_{42}H_{63}O_4P$	191.1430, 316.1987, 647.4253			III	1
28.56	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (Irganox 1076)[1]	2082–79–3	$C_{73}H_{108}O_{12}$	147.0806, 219.1744, 515.4467,				1
28.60	Unknown compound, oligoester structure		$C_{20}H_{18}O_8$	149.0235 (PA), 221.0809 (BD+PA), 387.1078 l(BD+2PA)			I	2, 3, 4, 5, 12, 14, 15
30.20	c(2BD+AA+PA): 3,4,5,6,9,10,11,12,15,16,17,18-dodecahydrobenzo[h][1,6,11,16]tetraoxacyclodocosine-1,8,13,20-tetraone hydrate		$C_{22}H_{28}O_8$	420.1783			III	14

*substances confirmed with analytical standard.
[1]authorized as additive or monomer (Reg. 10/2011).
[1a]SML = 0.6 mg/kg.
[1b]SML = 0.3 m/kg.
[1c]SML =: 1.5 m/kg.
[2]Substances identified by P&T. AA: Adipic acid; PA: Phthalic acid isomer; BD: 1,4 or 1,3-butanediol; EG: ethylenglycol; NPG: neopentylglycol; c: cyclic; l: linear.

(2NPG+2PA) out of the twelve found oligoesters, since they were classified as Cramer class III.

Concerning bio-PES-PVOH sample, oligoesters such as c(EG+AA) and c(BD+PA) as well as additives (e.g. benzophenone, diethyl phthalate and palmitic acid) were identified.

3.2.2. PLA-based materials

Two oligoesters namely, c(BD+PA) and c(2BD+AA+PA) were identified in the PLA-based materials. The latter was eluted at the end of the temperature gradient, so that larger and/or less volatile oligoesters could likely not be observed under these analytical conditions. Polyester oligomers have been reported as effective plasticizers to improve the properties of biopolymers [38]. Other plasticizers such as fatty acids (e.g., palmitic acid), often used in biopolymers, were also identified [39].

Furthermore, the detection of ions such as *m/z* 145.0497 ($C_6H_9O_4$) and 217.0709 ($C_9H_{13}O_6$) supports the presence of lactic acid oligomers.

2,6-Diisopropylphenyl isocyanate was identified in PLA pellets. It is commonly used in the synthesis of polymeric materials but, due to its toxicity, and to guarantee the safety of the biopolymers, it has been suggested to replace isocyanate groups by epoxy groups which have high reaction activity but lower toxicity [40]. Another compound identified in PLA pellets, namely 2,8,9-trioxa-5-aza-1-silabicyclo(3.3.3) undecane, 1-methoxy, belongs to Cramer class III.

Several compounds were identified in sample 14 (bag for foodstuff made of PLA-based material) including benzophenone, diethyl phthalate, 13-docosenamide-(Z) and furan derivatives (e.g., 2(3H)-furanone, dihydro-5-pentyl). Benzophenone is an authorized additive in plastic food contact materials with a SML of 0,6 mg/kg (Regulation 10/2011), and 13-docosenamide-(Z) is also listed as additive. Diethyl phthalate is commonly used as plasticizer and furanone derivatives have been reported as degradation products. Other compounds detected in sample 14 were 4-pentyl-benzoyl chloride and 2-propenoic acid, 3-(4-methoxyphenyl).

3.2.3. Bio-polypropylene and bio-polyethylene based materials

Two antioxidants, namely tris(2,4-ditert-butylphenyl) phosphite (Irgafos 168) and octadecyl 3-(3,5-di-tert-butyl-4- hydroxyphenyl)propionate (Irganox 1076), were identified in bio-PE and bio-PP. Degradation products of the antioxidants, i.e. 1,3-di-tert-butylbenzene and 2,4-di-tert-butylphenol, were also identified. Both were confirmed with analytical standards.

Moreover, it is interesting to remark the identification of substances associated to cleaning products such as 2-methylbutyl-2-hydroxybenzoate (isoamyl salicylate) in bio-PP samples. This compound has been reported to migrate into the food simulant 50 % ethanol (v/v) from recycled high-density polyethylene [41]. It was recently evaluated as fragrance ingredient used in cosmetics [42].

Plasticizers such as diethyl phthalate and dipropyl maleate reported as an alternative plasticizer in biopolymers, were identified in bio-PP samples [43].

2-Propenoic acid, 3-(4-methoxyphenyl)- was identified in bio-PP samples. An ester of this compound has been described in packaging materials [44]. 2,8,9-Trioxa-5-aza-1-silabicyclo(3.3.3)undecane, 1-methoxy, was identified in bio-PE and bio-PP, this compound was also identified in PLA pellets. Other compounds, which to the best of our knowledge have not been reported in food contact materials, were identified, such as 1,3,3-trimethylcyclohex-1-ene-4-carboxylic acid detected in bio-PP. This compound belongs to Cramer class I.

4. Conclusions

The use of the GC–MS techniques, namely P&T-GC-LRMS and GC—HRMS, enabled the identification of volatile and semi-volatile IAS and NIAS in bio-based and biodegradable FCMs, providing a picture of their chemical diversity. A total of 100 substances were tentatively identified by P&T-GC-LRMS, including monomers, other staring substances, additives, solvent residues and degradation products among others. GC—HRMS has demonstrated great potential in identifying NIAS such as oligoesters and degradation products. Both analytical techniques bring complementary information. Interestingly, in one of the PLA samples investigated, cyclic oligoesters such as c(BD+PA) and c(2BD+AA+PA) were identified, they have probably been used as plasticizing additives to improve the material properties. To the best of the authors' knowledge, they have not been previously reported in this type of polymer.

From the safety point of view, it is worth highlighting that only 9 out of the 50 substances detected by HRMS are included in the EU positive list of plastic food contact materials. It is also important to note that several of the identified compounds, especially some of the cyclic oligoesters, belong to Cramer class III (high toxicity). Once their presence is documented in the FCM, the next step is to document their migration in food or food simulants. It implies quantification; however not all standards are available and organic syntheses are required. Depending on the migration/exposure, hazard identification and characterization will be needed for risk assessment.

CRediT authorship contribution statement

P. Vázquez-Loureiro: Writing – original draft, Investigation, Formal analysis. **R. Cariou:** Writing – review & editing, Project administration, Methodology, Data curation. **G. Dervilly:** Supervision, Resources. **B. Le Bizec:** Funding acquisition. **A. Lestido-Cardama:** Writing – review & editing, Methodology, Data curation. **L. Barbosa-Pereira:** Supervision, Methodology, Conceptualization. **R. Sendón:** Project administration, Methodology, Conceptualization. **J. Bustos:** Writing – review & editing, Methodology, Conceptualization. **A. Gasco:** Writing – review & editing, Methodology. **P. Paseiro-Losada:** Writing – review & editing, Methodology, Data curation, Conceptualization. **A. Rodríguez Bernaldo de Quirós:** Writing – review & editing, Methodology, Funding acquisition, 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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Data availability

The data that has been used is confidential.

References

[1] E.L. Bradley, Biobased materials used in food contact applications: an assessment of the migration potential, York: The Food and Environment Research Agency (2010) 1–201.
[2] B. Geueke, Dossier – Bioplastics as food contact materials, Food Packaging Forum 10 (2014) 1–8, https://doi.org/10.5281/zenodo.33517.
[3] European Bioplastics, 2024. https://www.european-bioplastics.org/market/ (Accessed 16 February 2024).
[4] S. Ubeda, M. Aznar, P. Alfaro, C. Nerín, Migration of oligomers from a food contact biopolymer based on polylactic acid (PLA) and polyester, Anal. Bioanal. Chem. 411 (2019) 3521–3532, https://doi.org/10.1007/s00216-019-01831-0, a.
[5] L. Zimmermann, A. Dombrowski, C. Völker, M. Wagner, Are bioplastics and plant-based materials safer than conventional plastics? In vitro toxicity and chemical composition, Environ. Int. 145 (2020) 106066, https://doi.org/10.1016/j.envint.2020.106066.
[6] E. Canellas, P. Vera, C. Nerín, UPLC–ESI-Q-TOF-MSE and GC–MS identification and quantification of non-intentionally added substances coming from biodegradable food packaging, Anal. Bioanal. Chem. 407 (2015) 6781–6790, https://doi.org/10.1007/s00216-015-8848-2.
[7] J. Osorio, N. Dreolin, M. Aznar, C. Nerín, P. Hancock, Determination of volatile non intentionally added substances coming from a starch-based biopolymer intended for food contact by different gas chromatography-mass spectrometry approaches, J. Chromatogr. A 1599 (2019) 215–222, https://doi.org/10.1016/j.chroma.2019.04.007.
[8] E. Asensio, L. Montañés, C. Nerín, Migration of volatile compounds from natural biomaterials and their safety evaluation as food contact materials, Food Chem. Toxicol. 142 (2020) 111457, https://doi.org/10.1016/j.fct.2020.111457.
[9] C. Nerín, S. Bourdoux, B. Faust, T. Gude, C. Lesueur, T. Simat, A. Stoermer, E. Van Hoek, P. Oldring, Guidance in selecting analytical techniques for identification and quantification of non-intentionally added substances (NIAS) in food contact materials (FCMS), Food Addit. Contam.: Part A 39 (3) (2022) 620–643, https://doi.org/10.1080/19440049.2021.2012599.
[10] R. Cariou, M. Rivière, S. Hutinet, A. Tebbaa, D. Dubreuil, M. Mathé-Allainmat, J. Lebreton, B.Le Bizec, A. Tessier, G. Dervilly, Thorough investigation of non-volatile substances extractible from inner coatings of metallic cans and their occurrence in the canned vegetables, J. Hazard. Mater. 435 (2022) 129026, https://doi.org/10.1016/j.jhazmat.2022.129026.
[11] Toxtree v3.1.0 - toxic hazard estimation by decision tree approach. Available from: http://toxtree.sourceforge.net/download.html.
[12] European Commission, Commission Regulation (EU) No. 10/2011, on plastic materials and articles intended to come into contact with food, Off. J. Eur. Union 12 (2011) 1–89.
[13] S. Ubeda, M. Aznar, C. Nerín, Determination of volatile compounds and their sensory impact in a biopolymer based on polylactic acid (PLA) and polyester, Food Chem. 294 (2019) 171–178, https://doi.org/10.1016/j.foodchem.2019.05.069, b.
[14] N. Roegner, N. Pluym, O. Peschel, E. Leibold, A. Kachhadia, G. Scherer, M. Scherer, Determination of a specific metabolite for the non-ionic surfactant 2,4,7,9-tetra-methyl-5-decyne-4,7-diol (TMDD) by UPLC-MS/MS, J. Chromatogr. B. 1216 (2023) 123584, https://doi.org/10.1016/j.jchromb.2022.123584.
[15] D. Pan, G. Li, Y. Su, H. Wei, Z. Luo, Kinetic study for the oxidation of cyclohexanol and cyclohexanone with nitric acid to adipic acid, Chin. J. Chem. Eng. 29 (2021) 183–189, https://doi.org/10.1016/j.cjche.2020.05.011.
[16] N. Hirai, Y. Tatsukawa, M. Kameda, S. Sakaguchi, Y. Ishii, Aerobic oxidation of trimethylbenzenes catalyzed by N, N′, N″-trihydroxyisocyanuric acid (THICA) as a key catalyst, Tetrahedron. 62 (2006) 6695–6699, https://doi.org/10.1016/j.tet.2005.12.079.
[17] Y.G. Hsu, W.L. Yang, The effect of trimellitic acid on the thermal properties of polyester coating powder, J. Polym. Sci: Polymer Letters Edition. 20 (1982) 611–614.
[18] M. Aznar, P. Vera, E. Canellas, C. Nerín, P. Mercea, A. Störmer, Composition of the adhesives used in food packaging multilayer materials and migration studies from packaging to food, J. Mater. Chem. 21 (12) (2011) 4358–4370, https://doi.org/10.1039/C0JM04136J.
[19] A. Lestido-Cardama, P. Vázquez-Loureiro, R. Sendón, J. Bustos, M.I. Santillana, P. Paseiro Losada, A. Rodríguez Bernaldo de Quirós, Characterization of polyester coatings intended for food contact by different analytical techniques and migration testing by LC-MS^n, Polymers. (Basel) 14 (3) (2022) 487, https://doi.org/10.3390/polym14030487.
[20] P. Vera, E. Canellas, C. Nerín, Compounds responsible for off-odors in several samples composed by polypropylene, polyethylene, paper and cardboard used as food packaging materials, Food Chem. 309 (2020) 125792, https://doi.org/10.1016/j.foodchem.2019.125792.
[21] C. Carrero-Carralero, J. Escobar-Arnanz, M. Ros, S. Jiménez-Falcao, M.L. Sanz, L. Ramos, An untargeted evaluation of the volatile and semi-volatile compounds migrating into food simulants from polypropylene food containers by comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry, Talanta 195 (2019) 800–806, https://doi.org/10.1016/j.talanta.2018.12.011.
[22] S. Tisler, J.H. Christensen, Non-target screening for the identification of migrating compounds from reusable plastic bottles into drinking water, J. Hazard. Mater. 429 (2022) 128331, https://doi.org/10.1016/j.jhazmat.2022.128331.
[23] B. Mertens, C. Simon, M.V. Bossuyt, M. Onghena, T. Vandermarken, K. V. Langenhove, H. Demaegdt, E.V. Hoeck, J.V. Loco, K. Vandermeiren, A. Covaci, M.-L. Scippo, M. Elskens, L. Verschaeve, Investigation of the genotoxicity of substances migrating from polycarbonate replacement baby bottles to identify chemicals of high concern, Food Chem. Toxicol. 89 (2016) 126–137, https://doi.org/10.1016/j.fct.2016.01.009.
[24] B. Thiébaut, A. Lattuati-Derieux, M. Hocevar, L.B. Vilmont, Application of headspace SPME-GC–MS in characterisation of odorous volatile organic compounds emitted from magnetic tape coatings based on poly(urethane-ester) after natural and artificial ageing, Polym. Test. 26 (2) (2007) 243–256, https://doi.org/10.1016/j.polymertesting.2006.10.006.
[25] L.A. Espert de las Heras, S. Karlsson, Emission of possible odourous low molecular weight compounds in recycled biofibre/polypropylene composites monitored by head-space SPME-GC–MS, Polym. Degrad. Stabil. 90 (2005) 555–562, https://doi.org/10.1016/j.polymdegradstab.2005.03.009.
[26] E. Gallego, F.X. Roca, F. Perales, A. Ribes, G. Carrera, X. Guardino, M.J. Berenguer, Isocyanatocyclohexane and isothiocyanatocyclohexane levels in urban and industrial areas and possible emission-related activities, Atmos. Environ. 41 (37) (2007) 8228–8240, https://doi.org/10.1016/j.atmosenv.2007.06.036.
[27] F. Zha, S. Dong, J. Rao, B. Chen, The structural modification of pea protein concentrate with gum arabic by controlled Maillard reaction enhances its functional properties and flavor attributes, Food Hydrocoll. 92 (2019) 30–40, https://doi.org/10.1016/j.foodhyd.2019.01.046.
[28] M. Eckardt, T.J. Simat, Bisphenol A and alternatives in thermal paper receipts - a German market analysis from 2015 to 2017, Chemosphere 186 (2017) 1016–1025, https://doi.org/10.1016/j.chemosphere.2017.08.037.
[29] N. Khitas, K. Aouachria, M.T. Benaniba, Blending and plasticising effects on the behaviour of poly(lactic acid)/poly(ε -caprolactone), Polym. Polym. Compos. 26 (5–6) (2018) 337–345, https://doi.org/10.1177/0967391118795970.
[30] V.N. Glotova, M.K. Zamanova, A.V. Yarkova, D.S. Krutas, T.N. Izhenbina, V. T. Novikov, Influence of storage conditions on the stability of lactide, Procedia Chem. 10 (2014) 252–257, https://doi.org/10.1016/j.proche.2014.10.042.
[31] R. Salazar, S. Domenek, C. Plessis, V. Ducruet, Quantitative determination of volatile organic compounds formed during polylactide processing by MHS-SPME,

Polym. Degrad. Stab. 136 (2017) 80–88, https://doi.org/10.1016/j.polymdegradstab.2016.12.010.
[32] M. Watanabe, C. Nakata, W. Wu, K. Kawamoto, Y. Noma, Characterization of semi-volatile organic compounds emitted during heating of nitrogen-containing plastics at low temperature, Chemosphere 68 (11) (2007) 2063–2072, https://doi.org/10.1016/j.chemosphere.2007.02.022.
[33] J. González-Ausejo, E. Sánchez-Safont, J.M. Lagarón, R. Balart, L. Cabedo, J. Gámez-Pérez, Compatibilization of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)–poly(lactic acid) blends with diisocyanates, J. Appl. Polym. Sci. 134 (2017) 44806, https://doi.org/10.1002/app.44806.
[34] J. Lacoste, S. Carlsson, S. Falicki, D.M. Wiles, Polyethylene hydroperoxide decomposition products, Polym. Degrad. Stab. 34 (1–3) (1991) 309–323. https://www.sciencedirect.com/science/article/pii/S0142941806001930#bib38.
[35] R. Bernstein, S.M. Thornberg, A.N. Irwin, J.M. Hochrein, D.K. Derzon, S.B. Klamo, R.L. Clough, Radiation–oxidation mechanisms: volatile organic degradation products from polypropylene having selective C-13 labeling studied by GC/MS, Polym. Degrad. Stab. 93 (4) (2008) 854–870, https://doi.org/10.1016/j.polymdegradstab.2008.01.020.
[36] J.B. Scarsella, N. Zhang, T.G. Hartman, Identification and migration studies of photolytic decomposition products of UV-photoinitiators in food packaging, Molecules. 24 (2019) 3592, https://doi.org/10.3390/molecules24193592.
[37] E. Omer, E. Bichon, S. Hutinet, A.-L. Royer, F. Monteau, H. Germon, P. Hill, G. Remaud, G. Dervilly-Pinel, R. Cariou, B.Le Bizec, Toward the characterisation of non-intentionally added substances migrating from polyester-polyurethane lacquers by comprehensive gas chromatography-mass spectrometry technologies, J. Chromatogr., A. 1601 (2019) 327–334, https://doi.org/10.1016/j.chroma.2019.05.024.
[38] R. Ramos de Sousa Junior, C.A. Soares dos Santos, N. Minako Ito, A. Nizetti Suqueira, M. Lackner, D. Jackson dos Santos, PHB processability and property improvement with linear-chain polyester oligomers used as plasticizers, Polymers. (Basel) 14 (19) (2022) 4197, https://doi.org/10.3390/polym14194197.
[39] A. Moeini, N. Germann, M. Malinconico, G. Santagata, Formulation of secondary compounds as additives of biopolymer-based food packaging: a review, Trends. Food Sci. Technol. 114 (2021) 342–354, https://doi.org/10.1016/j.tifs.2021.05.040.
[40] W. Gao, Z. Lin, K. Cai, W. Pan, H. Li, Y. Liu, D. Peng, J. Fei, Effect of PBAT biodegradable mulch film extract on seed germination and seedlings metabolism of tobacco, Agriculture 12 (10) (2022) 1553, https://doi.org/10.3390/agriculture12101553.
[41] P. Vera, E. Canellas, Q.-Z. Su, D. Mercado, C. Nerín, Migration of volatile substances from recycled high density polyethylene to milk products, Food Packag. Shelf. Life 35 (2023) 101020, https://doi.org/10.1016/j.fpsl.2022.101020.
[42] A.M. Api, D. Belsito, D. Botelho, M. Bruze, G.A. Burton, M.A. Cancellieri, H. Chon, M.L. Dagli, W. Dekant, C. Deodhar, A.D. Fryer, L. Jones, K. Joshi, M. Kumar, A. Lapczynski, M. Lavelle, I. Lee, D.C. Liebler, H. Moustakas, J. Muldoon, T. M. Penning, G. Ritacco, J. Romine, N. Sadekar, T.W. Schultz, D. Selechnik, F. Siddiqi, I.G. Sipes, G. Sullivan, Y. Thakkar, Y. Tokura, RIFM fragrance ingredient safety assessment, benzoic acid, 2-hydroxy-, 2-methylbutyl ester, CAS Registry Number 51115-63-0, Food Chem. Toxicol. 182 (Supplement 1) (2023) 114135, https://doi.org/10.1016/j.fct.2023.114135.
[43] A. Enumo, I.P. Gross, R.H. Saatkamp, A.T.N. Pires, A.L. Parize, Evaluation of mechanical, thermal and morphological properties of PLA films plasticized with maleic acid and its propyl ester derivatives, Polym. Test. 88 (2020) 106552, https://doi.org/10.1016/j.polymertesting.2020.106552.
[44] Z.F. Chen, Q.B. Lin, Q.Z. Su, H.N. Zhong, C. Nerin, Identification of recycled polyethylene and virgin polyethylene based on untargeted migrants, Food Packag. Shelf. Life 30 (2021) 100762, https://doi.org/10.1016/j.fpsl.2021.100762.