DETERMINATION OF VOLATILE COMPOUNDS AND ITS SENSORY IMPACT IN A BIOPOLYMER BASED ON POLYLACTIC ACID (PLA) AND POLYESTER

S. Ubeda, M. Aznar, C. Nerín*

Department of Analytical Chemistry, EINA, University of Zaragoza, Campus Rio Ebro, María de Luna 3, 50018 Zaragoza

*Corresponding author:

E-mail address: cnerin@unizar.es (C. Nerín)

Tf: +34 976 761873; Fax: +34 976 762388

Postal address: Department of Analytical Chemistry, EINA, University of Zaragoza, Campus Rio Ebro, María de Luna 3, 50018 Zaragoza

Abstract

Polylactic acid (PLA) is one of the most commonly used biopolymers for manufacturing food packaging, its control is very important to ensure consumers' health. In this work, a blend of PLA and polyester was studied and its volatile composition in the polymer and in the migration to food simulants was determined by gas chromatography- mass spectrometry (GC-MS) and atmospheric pressure gas chromatography-quadrupole-time of flight mass spectrometry (APGC-QTOF). The results showed that both techniques provided complementary information, what was very relevant in order to have a complete information of biopolymer's composition. Some compounds such as lactide or cyclopentanone were detected only by GC-MS while others such as the cyclic dimer [AA-BD]$_2$ (AA:adipic acid, BD:butanediol) were detected only by APGC-MS. In migration, lactide, AA-BD and [AA-BD]$_2$ were identified in ethanol 95%. A GC-MS-Olfactometry study was also carried out. Some compounds showed sensory impact on the polymer odor but no in migration.

Keywords: non-intentionally added substances (NIAS); polylactic acid (PLA); food contact material; APGC-QTOF; off-odors; olfactometry

1. Introduction

The concern about the excessive use of plastics has increased linked to a rising trend towards the sustainable development that tends to decrease the use of fossil fuel and to enhance the concern for the environment. For this reason, biopolymers, that include biodegradable polymers and polymers coming from natural sources, have been promoted as key alternatives. Biopolymers obtained from renewable resources represent an interesting and cost-effective alternative route to commodity petrochemical-based materials. One of the most common biopolymers applications is the manufacturing of food packaging materials (Auras, Harte, & Selke, 2004; Rhim, Park, & Ha, 2013). One of the most promising bio-based polyesters aimed for food packaging is polylactic acid (PLA) (Panseri, Martino, Cagnardi, Celano, Tedesco, Castrica, et al., 2018), a biopolymer chemically synthesized using monomers obtained from agro-resources like wheat, corn, and cassava. PLA can be manufactured from lactic acid, or most commonly, from its cyclic dimmer, lactide through a ring opening polymerization. At the moment, due to its availability on the market, its low price and its mechanical and barrier properties, similar to PET, PLA is one of most used bio-polyesters, particularly for the manufacturing of packaging (Avérous, 2008; Bordes, Pollet, & Avérous, 2009).

Food packaging contributes to keep food safety and quality. However, packaging materials are not inert and mass transfer from them to foodstuff can take place, affecting consumers' health. Biopolymer packaging materials contain additives to stabilize the polymer during processing or to improve its properties, such as antioxidants, ultraviolet light absorbers, slip agents and plasticizers (Hahladakis, Velis, Weber, Iacovidou, & Purnell, 2018; Lau & Wong, 2000; Llana Ruiz-Cabello, Pichardo, Jiménez-Morillo, González-Vila, Guillamon, Bermudez, et al., 2017). They are considered IAS (intentionally added substances). Other molecules may also be present in the packaging as residual monomers or low molecular weight oligomers and even non-intentionally added substances (NIAS) (Arrieta, Parres, López, & Jiménez, 2013; Kameno, Yamada, Amimoto, Amimoto, Ikeda, & Koga, 2016; Mutsuga, Kawamura, & Tanamoto, 2008; Nerin, Alfaro, Aznar, & Domeño, 2013; Ubeda, Aznar, & Nerín, 2018; Úbeda, Aznar, Vera, Nerín, Henríquez, Taborda, et al., 2017). All these compounds can be volatile or non-volatile compounds and they could migrate to the food in contact and affect food safety or change its sensory properties.

To ensure food safety, all food contact materials (FCM) must comply with the Regulation (EU) no. 10/2011 (EC, 2011). This legislation includes a positive list of substances that can be present in migration at concentration values below its specific migration limit (SML). If the substances are not included in this list, their migration should not be found above 0.01 mg/kg. Due to this low value, it is important the use of analytical methodologies with high sensitivity for identification of compounds migrating from the FCM.

The identification of volatile compounds is possible when using highly sensitive analytical methods, such as gas chromatography-mass spectrometry (GC-MS) or Atmospheric Pressure Gas Chromatography coupled to quadrupole-time of flight mass spectrometry (APGC-QTOF)(Canellas, Vera, Domeño, Alfaro, & Nerín, 2012; Canellas, Vera, & Nerín, 2014). They are two powerful complementary techniques that allow the identification of volatile and semi-volatile compounds even though samples are at low level of concentration. GC–MS systems often use ionization under vacuum conditions, like electron impact ionization (EI). EI is considered as a hard ionization technique, meaning that the energy of the electrons is high enough to produce highly reproducible fragmentation patterns of small molecules. This fact allows the use of scientific libraries of mass spectra and an easy identification when the detected compound is recorded in the libraries. If it is not, the identification process becomes very complex. In contrast, chemical ionization (APCI) source and APGC are considered soft ionization techniques compared to EI, and fewer fragments are formed. When these techniques are coupled to high resolution mass spectrometry techniques, it is possible to have the exact mass of the parent ion and the structural elucidation process of the molecule is possible.Therefore, the APGC ionization process compared to EI will give us different structural information and for this reason, they are considered complementary techniques (Canellas et al. n, 2012; Canellas et al. , 2014; Cherta, Portolés, Pitarch, Beltran, López, Calatayud, et al., 2015; Domeño, Canellas, Alfaro, Rodriguez-Lafuente, & Nerin, 2012; Lv, Niu, Zhang, Shao, & Du, 2017; Sales, Cervera, Gil, Portolés, Pitarch, & Beltran, 2017; Stevens, Shi, & Hsu, 2013; ten Dam, Pussente, Scholl, Eppe, Schaechtele, & van Leeuwen, 2016).

Some volatile compounds present in FCM can modify the flavor composition, odor and properties of the packaged food, giving rise to different off-flavours. Aroma sorption and permeation through packaging materials can affect the sensory quality of food products

(Leelaphiwat, Harte, Auras, Ong, & Chonhenchob, 2017; Martínez-Bueno, Hernando, Uclés, Rajski, Cimmino, & Fernández-Alba, 2017; Osorio, Aznar, & Nerín, 2019; Salazar, Domenek, & Ducruet, 2014; Salazar, Domenek, Plessis, & Ducruet, 2017; Vera, Canellas, & Nerín, 2014; Vera, Uliaque, Canellas, Escudero, & Nerín, 2012). For this reason, it is important to study the aroma profile of the biodegradable polymers, in order to be sure that it will not modify the sensory properties of food in contact with it.

In this study, the main volatile and semi-volatile compounds of a biodegradable material intended to food packaging were identified. The key aroma compounds of the biopolymer blend, in both, the material and the migration simulants, were also determined by GC-Olfactometry-MS (GC-O-MS). The material under study was a blend of PLA and a polyester added to facilitate the processability. The blend was analyzed by total dissolution/precipitation and migration tests were applied with three food simulants at 60ºC for 10 days. The analysis were done by both techniques, GC-MS and APGC-QTOF.in order to have a more accurate composition of volatile potential migrants. The use of these three techniques provided a more complete profile of aroma and volatile compounds present in the blend samples containing PLA.

2. Materials and methods

2.1 Sample characteristics

A biodegradable blend composed by a polyester with 18% of PLA was used for this study. Information about the polyester blended to PLA was not provided by the supplier. Based on previous studies performed in our laboratory and the volatile and non-volatile substances found the attempt of *poly*(butylene adipate-co-terephthalate) can be considered. The samples were provided as pellets and films. The material was certified as biodegradable polymer.

Mass and bulk densities were 1.24-1.26 and 0.78 g/cm^3. Melt volume rate (MVR) was 7-11 mL/min. Melting points were 110-120 to 140-155 ºC. Permeation rates of water vapor at 38ºC and 90 % r.h. was 600 g·m^{-2}·d^{-1}. Good thermostability up to 230ºC. Film thickness was 0.17 mm.

2.2 Reagents and solvents

Lactide [4511-42-6] was from Sigma–Aldrich (Madrid, Spain). A cyclic ester oligomer composed by diethylene glycol (DEG), adipic acid (AA) was used as standard for oligomer quantification. It was synthetized and provided by an adhesives company and the purity and structure were confirmed by NMR at the University of Zaragoza. Octanal, 1-octen-3-one, E-2-nonenal, sotolon, citronellal and dodecanal were purchased from Sigma Aldrich and nonanal was by Fluka.

Dichloromethane, acetic acid and ethanol (HPLC quality) were supplied by Scharlau Chemie S.A. (Sentmenat, Spain). Ultra-pure water was obtained with a Water purification System Type I Ultrapure from Wasserlab (Navarra, Spain).

2.3 Sample treatment

2.3.1 Total dissolution/precipitation procedure

The protocol used for the dissolution of PLA samples, pellets as well as films, was based on the protocol developed by Aznar (Aznar, Ubeda, Dreolin, & Nerín, 2019), applying some modifications according to the final analysis methodology.

A quantity 0.25 g of PLA was weighted, 3 mL of dichloromethane were added and the mixture was shaken in an ultrasound machine for 1 hour until it was totally dissolved. Six mL of ethanol were added to the dissolved PLA under magnetic stirring (500 rpm, 15 min) for the precipitation of the polymer. After this time, the supernatant solvent was removed and stored in a vial. Afterward, 3 mL of ethanol were added to the precipitated polymer and the mixture was manually shaken. Then, the polymer was gently squeezed with a glass bar and the solvent was removed and mixed with the previous extract. The final extract was kept in the freezer for 1 hour and finally, it was filtered through a 0.25 μm PET filter. The final dissolution was concentrated 4 folds under a nitrogen current. 2 folds concentration was alternatively applied but the chromatogram showed a lower number of compounds. Total dissolution of PLA sample was performed in triplicate. These samples were analysed by GC-MS and APGC-QTOF with liquid injection.

2.3.2. Samples for direct analysis

The direct analysis was done on PLA blend films. They were cut in pieces of 1x1 cm^2, of approximately 0.4 g, and introduced in 20 mL vials. These samples were analysed by GC-O-MS with HS-SPME injection. They were analysed in triplicate.

2.4. Migration test

The migration analysis was performed by total immersion of the PLA blend films in three different food simulants. Food simulants were ethanol 95%, ethanol 10 % (A) and acetic acid 3% (B). Pieces of films were cut (5x1 cm^2) and introduced in 20 mL vials. Then, 18 g of food simulant were added fulfilling a ratio close to 6 dm^2/kg of simulant according to the Regulation 10/2011. After that, these vials were kept in the oven for 10 days at 60ºC. All the migration experiments were performed in triplicate.

Simulant ethanol 95% was analysed by liquid injection while ethanol 10% and acetic acid 3% were analysed by HS-SPME, transferring previously an aliquot of 4 mL to a 20 mL vial. Analyses were performed by GC-MS, GC-O-MS (both with electronic impact ionization) and APGC-QTOF in triplicate.

2.5 Instrumental analysis

2.5.1. Sample injection

The injection was performed in splitless mode and the detector temperature was fixed at 250 ºC. Liquid injection was performed with an injection volume of 1 µL. HS-SPME injection was carried out with a DVB/CAR/PDMS fibre with medium polarity and the vials were extracted at 80ºC during 15 minutes.

2.5.2 Gas Chromatography-mass spectrometry-olfactometry analysis (GC-O-MS)

The experiment was carried out using an Agilent Technologies a 7820 GC System coupled in parallel with a 5977B MSD single quadrupole mass spectrometer and a Phaser olfactory port from GL Sciences B.V. (Netherlands). The chromatographic column used was an HP-5MS (30 m length x 0.25 mm inner diameter x 0.25 µm film thickness). The carrier gas was He at 1 ml/min. The oven program began with an initial temperature of 40°C for 5 min and then temperature increased to 300°C at 10°C/min.

The MS acquisition was carried out in electron impact ionization mode and the temperature of source was 230 ºC. Scan mode was used between 50 and 450 amu. NIST 14 mass spectral library was used for the identification of the compounds, a minimum of 80% of matching was required to consider a compound as identified by NIST. Finally, the standards of the compounds were analysed for confirmatory purposes.

In order to determine the sensory impact of the volatile compounds present in the sample, an olfactometry analysis was also performed in parallel. The identification of the odorants was carried out by a comparison of odors and Kovats retention indices with bibliography from Flavornet Database (www.flavornet.org) and National Institute of Standards and Technology (https://webbook.nist.gov/chemistry/). For that, a standard mixture of alkanes C_8 to C_{21} was analysed under the same conditions as the samples and Kovats retention index were calculated. Some compounds were also confirmed by mass spectrometry, but this was not possible in some cases, since the sensitivity of the compound was higher by GC-O than by GC-MS. When the standards were commercially available they were injected to confirm compounds identification.

The olfactometry of each sample was performed by five trained GC/O sniffers. They were previously trained using the same methodology than Osorio (Osorio et al., 2019). For the analysis, they were asked to describe the aromas perceived and their intensity on a 3 point category scale (1 = weak odor; 2 = clear; and 3 = intense); half values were also allowed. The modified frequency percentage (MF%) was calculated for each odorant perceived to be able to determine the most important odorous compounds present in the sample. It was calculated with the following equation (Vera et al., 2012):

$$MF\ (\%) = \sqrt{F(\%)\ x\ I(\%)} \qquad \text{[equation 1]}$$

where F(%) is the detection frequency of an aromatic attribute expressed as percentage and I (%) is the average intensity expressed as percentage of the maximum intensity. Odors detected with a MF (%) higher than 50 represent the most important compounds present in each sample (Wrona, Vera, Pezo, & Nerín, 2017).

2.5.3 Atmospheric pressure gas chromatography-mass spectrometry quadrupole-time of flight (APGC-QTOF)

For the chromatographic analysis, an Agilent 6890N coupled to a CTC Analytics CombiPal autosampler was used. The capillary column used was an HP-5MS (30 m × 0.25 mm × 0.25 μm). The oven program was as follows: 60°C for 5 min, with a rate of 10°C/min up to 300°C, maintained for 5 min. The helium flow was 1.2 mL/min.

The detector was a quadrupole-time of flight analyser (QTOF) Xevo G2 from Waters (Milford, MA, USA) coupled to an atmospheric pressure gas chromatography (APGC) source. API positive polarity and sensitivity analyser mode were selected. The corona voltage was 2.2 kV and the corona current was 0.8 A. The probe temperature was 200ºC. The sampling cone and extraction cone voltage were 30 V and 3V respectively. The source temperature was 150 °C and the desolvation gas flow was 200 L/h. The mass range considered was m/z 50–550. MS^E mode was selected for the acquisition; for function 2, a collision ramp energy from 15 to 40 V was used. As lockmass, column bleed with the exact mass 281.0517 was used. The transfer line settings were as follows: make up gas used was nitrogen at 400 mL/min and the transfer line temperature was 350 °C. Data were collected and processed using MassLynx software from Waters.

3. Results and discussion

3.1 Volatile and semi-volatile compounds identified in PLA biopolymer by GC-MS

For the identification of compounds, the dissolved PLA samples were used. Extracts were analysed by liquid injection. Fig 1 shows a chromatogram of the extracts obtained by total dissolution of PLA blend film (1a) and pellets (1b) samples. This methodology was carried out to facility the identification process of unknown migrants. In the material, the concentration of the compounds is much higher than in migration. It is frequent to first analyze directly the polymer before migration assays in order to identify the potential migrants (Aznar et al., 2019; Nerin et al., 2013; Ubeda et al., 2018).Table 1 shows the main volatile compounds found in the sample. The intensity of the peaks is written in the third and fourth column for pellets and films respectively. The last column of table 1 shows the references where the compounds had been previously detected and the fragments of those compounds that were not identified. A total of 15 different volatile compounds were

identified in PLA blend pellets (13 compounds) and films (12 compounds) by GC-MS with a match value higher than 80% according to NIST library. Ten compounds were common in both samples. One of the most important identified compounds was lactide, the cyclic dimer of lactic acid. It is not listed in the positive list of Regulation EU/10/2011 (EC, 2011) and therefore it is important to control it. It could come from intramolecular transesterification, unzipping depolymerization or oxidative processes (Salazar et al., 2017). Adipic acid – Butanediol (AA-BD) was the most abundant substance in both kinds of samples, pellets and films. Its mass was previously detected by Bradley in bio-based materials used for food contact materials (Bradley, 2010) but it was not identified. Samples were a blend of PLA and polyester, so this compound probably came from the polyester component of the biopolymer. Based on previous studies on the non-volatile substances found in this material, where the *poly*(butylene adipate-co-terephthalate) (PBAT) monomer was identified (Aznar et al., 2019), the attempt of PBAT as the polyester blended to PLA can be considered. The compounds found with medium or high intensity in the film were oleamide, glycerol 1-palmitate, erucamide, N-[(9Z)-9-octadecen-1-yl]acetamide, glycerol 1-stearate, palmitic acid and a non identified compound. The compounds glycerol 1-palmitate, N-[(9Z)-9-octadecen-1-yl]acetamide and glycerol 1-stearate were previously detected by Martínez-Bueno (Martínez-Bueno et al., 2017). The intensity of the following compounds increased from pellets to films, probably because they were added during film manufacturing: glycerol palmitate, that is used as emulsifier; amides, that are slip agents and antiblocking additives used in films to reduce friction resistance; stearic acid esters, which are listed as approved monomers for food contact applications in the EU regulation (EC, 2011); oleamide and erucamide, that are commonly used as slip agents and are defined as indirect additives for food contact materials by US Food and Drug Administration(FDA, 2018; EC, 2011) and an unknown compound at 26.06 minutes, whose main fragments were 55. 73, 99.1, 141.1 and 168.1. Palmitic acid, that was only identified in films, is a slip agent and it is also an approved monomer for food contact material in the EU regulation (EC, 2011). It was identified with similar structures by Salazar (Salazar et al., 2017)..

Other compounds detected in films but at lower intensities were cyclopentanone, undecane and nonanal. Cyclopentanone could be explained by the radical reaction between aldehyde and ketones. Undecane could be either a compound used in the polymerization process or a

degradation product from additives or processing aids. Nonanal could be produced from trans-esterification reactions. These compounds were identified with the same intensity in PLA pellets and films. On the other hand, a few compounds such as 3-penten-2-ol, ethyl chloroacetate and chloroacetaldehyde were only detected in pellets, in all cases with low intensities. 3-penten-2-ol could be formed by hydrolysis of ester groups. Ethyl chloroacetate and cloroacetaldehyde could have been produced by the reaction with dichloromethane used during the dissolution/precipitation process and acetaldehyde.. Acetaldehyde was not identified, as it is difficult to detect it in GC-MS. Most of these compounds had been previously identified in PLA by Salazar (Salazar et al., 2017).

3.2 Volatile and semi-volatile compounds identified in the biopolymer by APGC-QTOF

As in GC-MS analysis, the dissolved pellets and film of the PLA blend samples were used for the identification of compounds. The compounds identified by APGC-QTOF are shown in Table 2 and Fig 2 shows the chromatograms of the analysis. The table is organized according to retention time. All the compounds were protonated [H+] during its ionization, except glycerol 1-palmitate and glycerol 1-stearate, detected without a water molecule due to a dehydration process during ionization. The intensity of these compounds is described in the table according to its abundance in the chromatogram. Fourteen compounds were identified by APGC-QTOF. Except the stereamide, that was only detected in the film, all of them were detected in pellets as well as in the film.The oligomer $[AA\text{-}BD]_2$, that had not been detected previously by GC-MS, was the most intense in the chromatogram together with poly(trimethylolpropane adipate) and 2 unknown compounds, 10.57_355.0686 and 31.90_466.0538 (retention time_exact mass). AA-BD ,coming from the polyester component was also detected with this instrument but with a lower intensity. They come from polyester component of the biopolymer. Poly(trimethylolpropane adipate) is a compound defined as indirect additive for food contact materials by Food and Drug Administration (FDA, 2018; EC, 2011). Other compounds found with medium intensity in the film were N,N-diethyldodecanamide, oleamide, glycerol 1-palmitate, erucamide. All of them increase their intensity in films. N,N-diethyldodecanamide was previously identified by Martínez-Bueno (Martínez-Bueno et al., 2017) and the rest were previously identified

and confirmed by GC-MS. Finally, compounds with lower intensities like palmitic acid, N-[(9Z)-9-octadecen-1-yl]acetamide and glycerol 1-stearate were identified. They had also been identified by GC-MS. Stearamide, a compound used as indirect additive for food contact materials by Food and Drug Administration (FDA, 2018; EC, 2011), and the unknown compound (25.30_387.2941) were also detected with low intensity.

3.3 Comparison of APGC-MS *vs.* GC-MS

Seven compounds were detected by both techniques, GC-MS (with EI ionization) and APGC-QTOF. They were [AA-BD] oligomer, palmitic acid, oleamide, glycerol 1-palmitate, N-[(9Z)-9-octadecen-1-yl]acetamide, glycerol 1-stearate and erucamide. Fig 3 shows the profile of these compounds in a biopolymer film sample analysed by both techniques. The areas of GC-MS divided by 100000 and the areas of APGC-MS divided by 1000 are represented in order to compare the results obtained. The profile in both techniques was similar; oleamide and palmitic acid showed the highest and the lowest intensities respectively in both analysis.. AA-BD was identified with higher intensity in GC-MS than in APGC-QTOF, however, its dimer was only identified by APGC-QTOF, where high resolution MS was available. Having the molecular ion in APGC spectra, makes possible the structural elucidation of the oligomers, whereas in EI the molecular ion barely appears and consequently the identification is much more difficult.

3.4 Identified compounds in migration tests

After the exposure of films to the simulants during 10 days at 60ºC, only 2 compounds were identified by GC-MS in ethanol 95% and none in ethanol 10% or acetic acid 3%. The results showed the presence of AA-BD and lactide. The concentration of AA-BD was between the LOD (310 µg/kg) and the LOQ (920 µg/kg). Due to the absence of commercial standards for AA-BD, the quantification was performed with a similar oligomer AA-DEG oligomer (adipic acid – diethylene glycol) available in the laboratory.

Similar results were obtained for lactide, whose concentration was also between the detection and quantification limits (LOD and LOQ), 540 µg/kg and 1700 ppb, respectively.

Only the dimer $[AA\text{-}BD]_2$ was identified in the migration test to ethanol 95% by APGC-MS and it was quantified with AA-DEG oligomer. In this case, LOD and LOQ were 2.8

mg/kg and 8.4 mg/kg, respectively and this compound was below LOQ. No compounds were identified in aqueous simulants, ethanol 10% and acetic acid 3%. The limit of detection of AA-DEG oligomer, used as standard, was 226 μg/kg.

3.5 Key aroma compounds in the PLA blend biopolymer and in the migration simulants after exposure

To identify the main key aroma compounds present in the PLA blend biopolymer, a direct analysis of the PLA sample by GC- O-MS was performed. Table 3 shows the odorants identified. For confirmation, retention index and aroma description were compared with data reported in the bibliography (Flavornet and NIST database). Some compounds were also confirmed by spectrum mass match in NIST library (✓) and standard injection (✓✓). A total of ten odorants with MF % values above 40 % were identified in PLA based biopolymer material. Most of them were ketones and aldehydes like 1-octen-3-one, octanal, 3,5 octadienone, 3-nonenal/3,6-nonadienal, nonanal, citronellal, E-2-nonenal and dodecanal. High concentration of aldehydes tend to be very pungent and overwhelming, but low concentration can show a wide range of aromas. Other compounds identified were sotolon and α-cubebene. The compound with the highest aromatic impact was sotolon with 91.3 % of MF. Sotolon could have been formed during the pellets manufacturing process due to temperature and pressure conditions, or present in the other raw materials used for its manufacture (Osorio et al., 2019). Nonanal, 1-octen-3-one and 3-nonenal/3,6-nonadienal had MF values over 70 (87.6, 79.6 and 74.8 % MF, respectively). Finally, E-2-nonenal, citronellal and α-cubebene were detected with values above 50 %. However, the results of olfactometry of migration samples did not show any compound with MF% values above 20% in any of the food simulants. This fact means that even though the material itself presents some aromas that could be described as off-flavours, they are not expected to modify the food aroma properties, as most of them disappear during the manufacture of the polymer from pellets to film.

4. Conclusions

The protocol for PLA blend sample treatment based on dissolution/precipitation allowed identifying volatile and semi-volatile compounds by GC-MS (with EI ionization) and

APGC-QTOF. The use of both techniques provided a more complete profile of the volatile compounds present in PLA blend biopolymer. Common compounds identified by both techniques showed more sensitivity by GC-MS than APGC-QTOF. However, the advantages provided by APGC, such as the presence of the molecular ion or the coupling to high resolution MS, facilitate the identification of oligomers and compounds which cannot be identified by the standard GC-MS using EI and quadrupole as detector. Then, the analysis by both techniques provides an accurate information of volatile compounds present in the material. The results of migration solutions showed that only AA-BD, $[AA\text{-}BD]_2$ and lactide were transferred to ethanol 95%, but in all cases below their limit of quantification. According to these results, at the studied conditions, these materials would be more recommended for aqueous food than for fatty food. In addition, even though some compounds present in the biopolymer showed a high sensory impact on the polymer odor, they were not detected in migration studies and therefore no changes in the sensory profile of packaged food are expected.

5. Acknowledgments

The authors would like to acknowledge MINECO (Spain) and FEDER funds for project AGL2015-67362-P and scholarship BES-2016-077159, and Project RYC-2012-11856 (Ramón y Cajal Research Program). The authors thank the Aragon Government and Fondo Social Europeo for the financial help given to GUIA group T-10.

Potential conflicts of interest do not exist

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Figure captions

Fig 1. Chromatograms of PLA films (1a) and pellets (1b) dissolution extracts by GC-MS. Numbers correspond to compounds in table 1 (s: siloxane of column, b:blanck).

Fig 2. Chromatograms of PLA films (2a) and pellets (2b) dissolution extracts by APGC-QTOF. Numbers correspond to compounds in table 2 (b: blanck).

Fig 3. Profile of seven compounds detected by both techniques, GC-MS and APGC-QTOF.

Table 1: Volatile and semi-volatile compounds identified in total dissolution of PLA films and pellets by GC-MS where rt is retention time and I is the intensity according to its relative abundance : I=1 (0-5%),I=2 (5-20%), I=3 (20-50%), I=4 (50-100%)

No	rt	I pellets	I films	Candidate	CAS Number	Molecular Formula	Remarks
1	6.18	2	nd	3-Penten-2-ol	1569-50-2	$C_{11}H_{14}O$	Detected similar by Salazar, R. 2017
2	7.80	1	1	Cyclopentanone[a]	120-92-3	C_5H_8O	Detected similar by Salazar, R. 2017
3	8.62	2	nd	Ethyl chloroacetate	105-39-5	$C_4H_7ClO_2$	Detected similar by Salazar, R. 2017
4	9.15	1	nd	Chloroacetaldehyde	107-20-0	C_2H_3ClO	Detected similar by Salazar, R. 2017
5	13.10	1	1	Undecane[a]	1120-21-4	$C_{11}H_{24}$	
6	13.14	1	1	Nonanal[a]	124-19-6	$C_9H_{18}O$	Detected by Salazar, R. 2017
7	14.20	2	2	Dimethyl-1,4-dioxane-2,5-dione [LACTIDE][a]	4511-42-6	$C_6H_8O_4$	Detected by Mutsuga, M. 2008 and Salazar, R. 2017
8	19.30	4	4	1,6-Dioxacyclododecane-7,12-dione [AA-BD] ✓	777-95-7	$C_{10}H_{16}O_4$	Detected by Bradley, 2010
9	23.52	nd	2	Palmitic acid[a]✓	57-10-3	$C_{16}H_{32}O_2$	Detected similar by Salazar, R. 2017
10	26.06	1	2	ni			Fragments: 55/73/99.1/141.1/168.1
11	27.18	nd	4	Oleamide✓	301-02-0	$C_{18}H_{35}NO$	Indirect additives in FDA 2018 and EC, 2011
12	28.32	2	3	Glycerol 1-palmitate✓	542-44-9	$C_{19}H_{38}O_4$	Detected by Martínez-Bueno, M.J 2017 and Bradley, 2010
13	28.76	1	2	N-[(9Z)-9-octadecen-1-yl]acetamide✓	40165-68-2	$C_{20}H_{39}NO$	Detected by Martínez-Bueno, M.J 2017
14	29.84	1	2	Glycerol 1-stearate[a]✓	123-94-4	$C_{21}H_{42}O_4$	Detected by Martínez-Bueno, M.J 2017 and Bradley, 2010
15	30.31	2	3	Erucamide[a]✓	112-84-5	$C_{22}H_{43}NO$	Indirect additives in FDA 2018 and EC, 2011

nd: non detected, ni: non identified, ✓compounds detected also in APGC-MS [a] Confirmed by standard

Table 2: Volatile and semi-volatile compounds identified in total dissolution of PLA films and pellets by APGC-MS where rt is retention time and I is the intensity according to its relative abundance: I=1 (0-5%),I=2 (5-20%), I=3 (20-50%), I=4 (50-100%)

No	rt	mass	Adduct	I pellets	I films	Molecular formula	Candidate CAS number	Remarks/Fragments
1	7.48	281.0519	[MH]+	3	4	C12H24O7	Poly(trimethylolpropane adipate) 28301-90-8	Detected by Aznar, M. 2019 Indirect additives in FDA 2018
2	10.57	355.0686	[MH]+	4	4	C15H14O10	ni	
3	16.25	201.1116	[MH]+	2	2	C10H16O4	1,6-Dioxacyclododecane-7,12-dione, [AA-BD] ✓ 777-95-7	Detected by Aznar, M. 2019 and Bradley, 2010
4	21.04	257.2462	[MH]+	2	2	C16H32O2	Palmitic acid ✓ 57-10-3	Detected similar by Salazar, R. 2017
5	22.89	256.2642	[MH]+	2	3	C16H33NO	N,N-Diethyldodecanamide 222-118-3	Detected by Martínez-Bueno, M.J 2017
6	24.44	282.2783	[MH]+	3	3	C18H35NO	Oleamide ✓ 301-02-0	Indirect additives in FDA 2018 and EC, 2011
7	24.62	284.2967	[MH]+	nd	2	C18H37NO	Stearamide 110-30-5	Indirect additives in FDA 2018 and EC, 2011
8	25.30	387.2941	[MH]+	2	2	C25H38O3/ C28H36N	ni	263.9876/131.0526
9	25.60	313.2749	$[MH]^+$-H_20	2	3	C19H38O4	Glycerol 1-palmitate✓ 542-44-9	Detected by Martínez-Bueno, M.J 2017 and Bradley, 2010
10	26.09	310.3124	[MH]+	2	2	C20H39NO	N-[(9Z)-9-octadecen-1-yl]acetamide✓ 40165-68-2	Detected by Martínez-Bueno, M.J 2017
11	27.16	341.3055	$[MH]^+$-H_20	2	2	C21H42O4	Glycerol 1-stearate ✓ 123-94-4	Detected by Martínez-Bueno, M.J 2017 and Bradley, 2010
12	27.61	338.3428	[MH]+	2	3	C22H43NO	Erucamide ✓ 112-84-5	Indirect additives in FDA 2018 and EC, 2011
13	28.89	401.2182	[MH]+	4	4	C20H32O8	1,6,13,18-Tetraoxacyclotetracosane-7,12,19,24-tetrone, $[AA\text{-}BD]_2$, 78837-87-3	Detected by Aznar, M. 2019 and Bradley, 2010
14	31.90	466.0538	[MH]+	4	4	---	ni	421.1882 /221.0834/149.0231

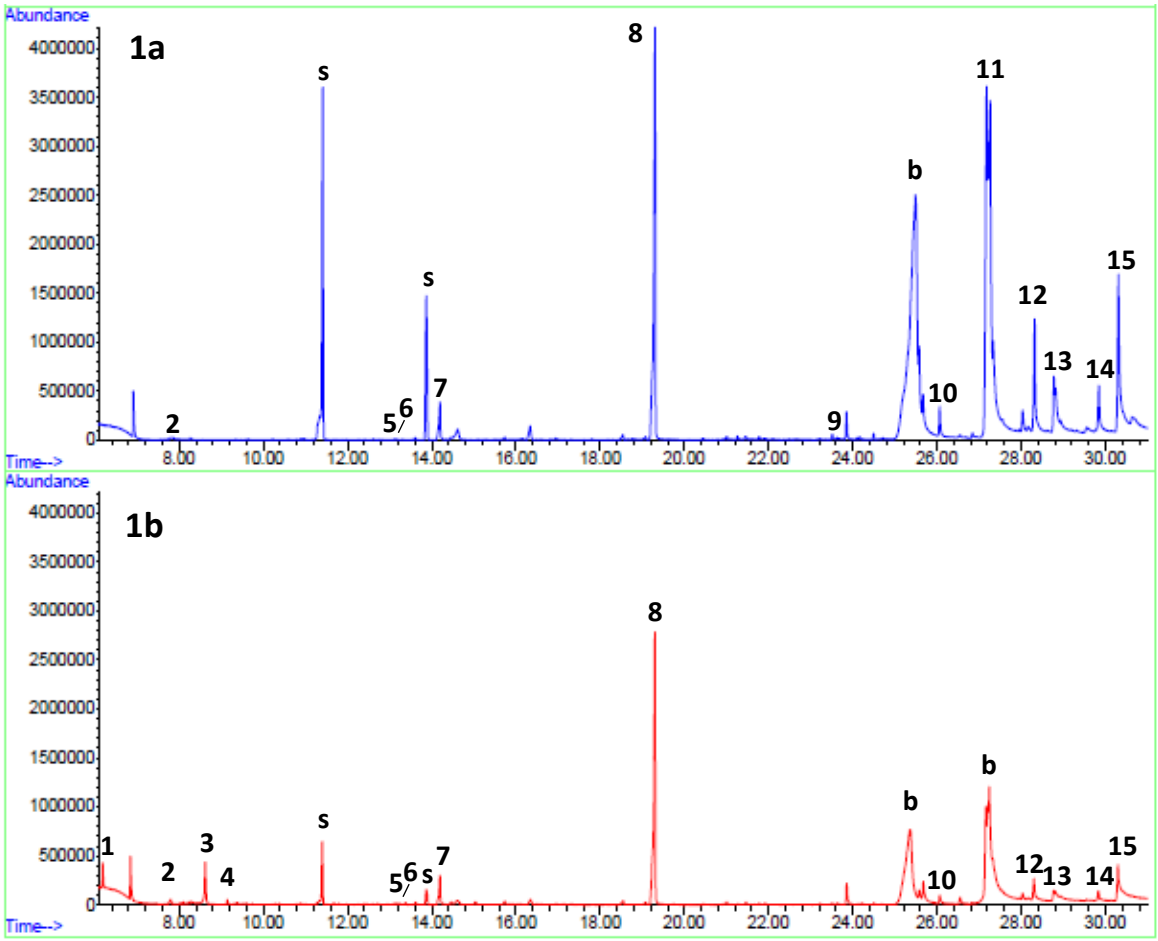
nd: non detected, ni: non identified, ✓compounds detected in GC-MS.

Table 3: Odorant compounds detected in PLA based biofilms. KI, experimental Kovats retention index; rt, retention time; MF, molecular formula.

KI	rt	MF (%)	Olfactory description	Candidates	CAS No	Molecular Formula	KI Bibliography[a]	Description Bibliography[a]
983	11.28	79.6	Mushroom, cucumber, sweet	1-octen-3-one✓✓	4312-99-6	$C_8H_{14}O$	975-983	Earth, mushrooms, moisture
1007	11.74	46.9	Aldehyde, fruity, sweet	octanal✓✓	124-13-0	$C_8H_{16}O$	1000-1011	Aldehyde, orange skin, citrus, floral
1084	13.05	42.4	Chemical, sweet	3,5 octadienone	38284-27-4	$C_8H_{12}O$	1066-1091	Fruit, fat, mushroom
1103	13.36	74.8	Aldehyde, mushroom, green	3-nonenal// 3,6-nonadienal	1120-21-4	$C_{11}H_{24}$	1100 // 1100	Cucumber, fat // fat, soap
1111	13.49	87.6	Aldehyde, chemical, green	nonanal✓✓	124-19-6	$C_9H_{18}O$	1098-1112	Fat, citrus, green
1117	13.58	91.3	Black licorice, toasted, burned	sotolon✓✓	28664-35-9	$C_6H_8O_3$	1079-1115	Black licorice, curry, maple syrup
1155	14.17	62.2	Sweet, flower	citronellal✓✓	106-23-0	$C_{10}H_{18}O$	1126-1167	Floral, sweet, citrus, green
1166	14.34	67.3	Lemon, cucumber, dried fruit	(E)-2-nonenal✓✓	18829-56-6	$C_9H_{16}O$	1156-1165	Fatty, cucumber, green, citrus
1350	16.91	51.6	Wet, green grass, floral	α-cubebene	17699-14-8	$C_{15}H_{24}$	1337-1360	Herb, wax
1389	17.42	40.0	Soap	dodecanal✓✓	112-54-9	$C_{12}H_{24}O$	1397-1417	Soap, orange skin, citrus, wax, floral

✓confirmed by spectrum mass-NIST; ✓✓confirmed by standard

[a]Data reported in Flavornet and NIST databases.



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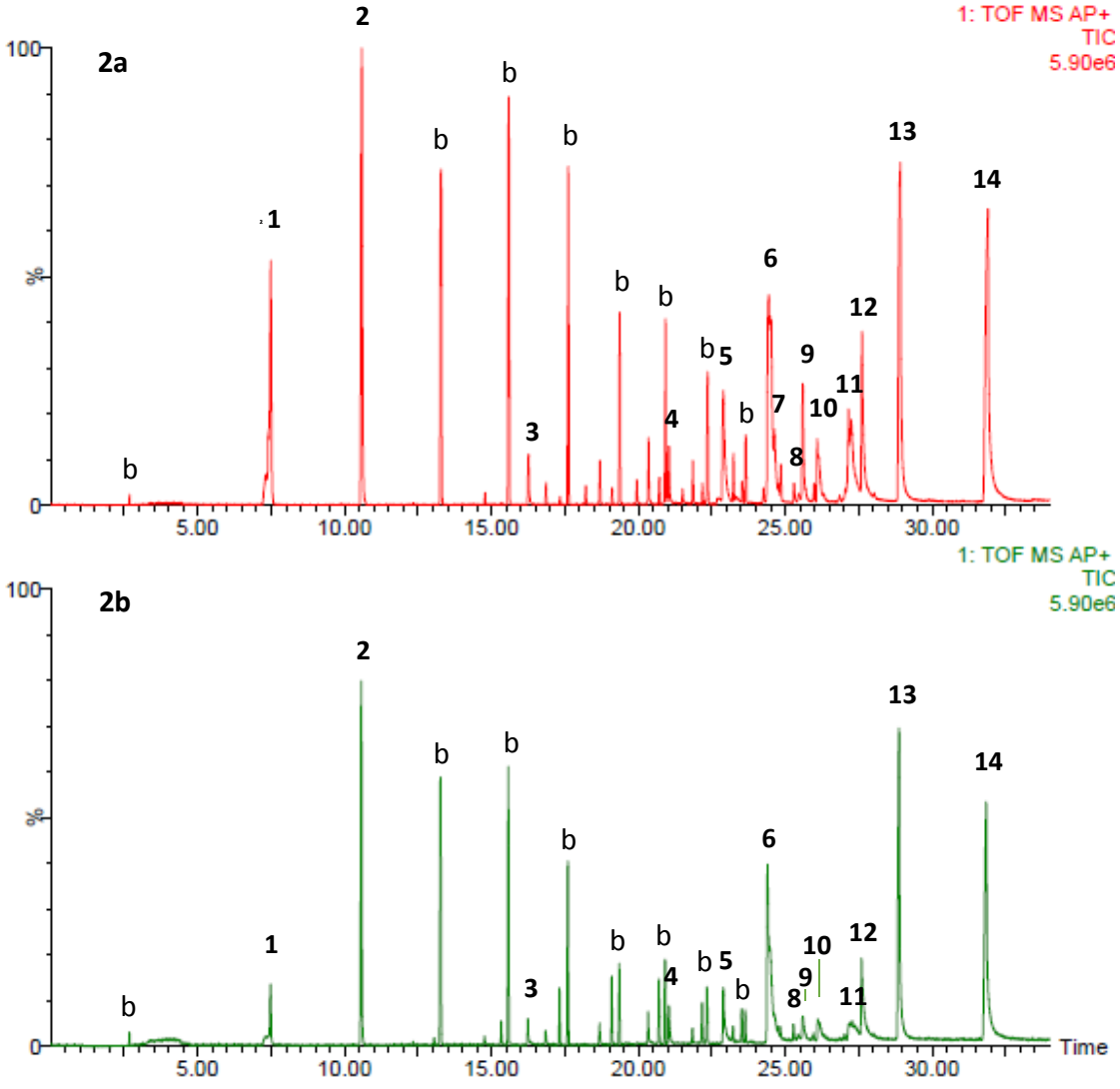
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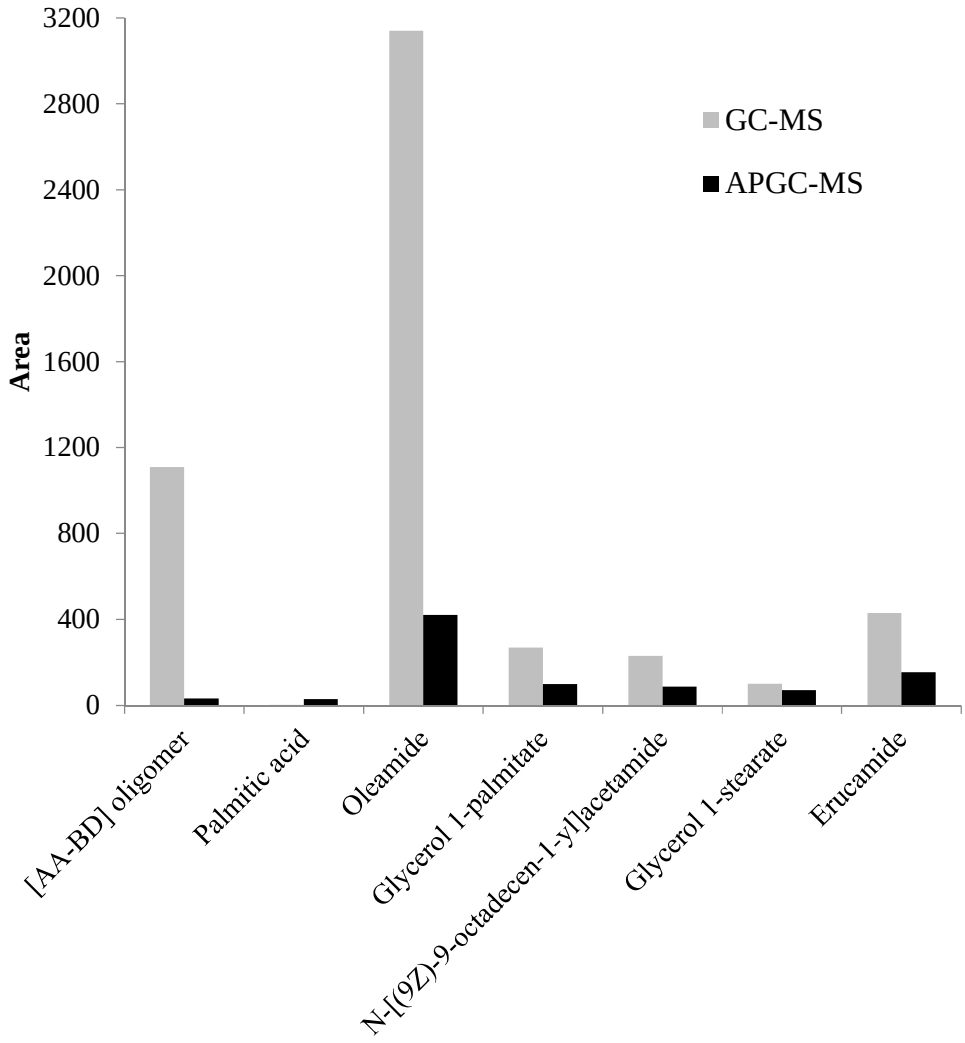
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