Compounds responsible for off-odors in several samples composed by polypropylene, polyethylene, paper and cardboard used as food packaging materials

Paula Vera[1], Elena Canellas[2] and Cristina Nerín[1]*

[1]Analytical Chemistry Department, GUIA Group, I3A, EINA, University of Zaragoza, Mª de Luna 3, 50018 Zaragoza, Spain

[2]Samtack Adhesivos Industriales, C/ Cerámica, nº3, Pol. Ind. Magarola Sud, 08292, Esparreguera, Barcelona (Spain)

*Corresponding author. Tel.: +34 976761873; Fax: +34 976762388. E-mail address: cnerin@unizar.es

pvera@unizar.es; elenac@unizar.es; cnerin@unizar.es

Keywords: GC-O-MS, migration, odor, food packaging

Abstract

Seven commercial samples, consisted of plastic bags, tetrabrik and box, were evaluated by gas chromatography-olfactometry-mass spectrometry (GC-O-MS) to find the compounds responsible for off-odors in different PP, PE, multilayer cardboard and paper materials used for food contact. Migration assays were carried out with Tenax as food simulant to analyze the food safety as well as to evaluate the odor intensity after migration assay. Forty six compounds with characteristic odors were directly found in the materials studied. The strongest odors identified were acetic, propanoic and butyric with vinegar and rancid odors and octanal, nonanal and decanal with fat/soup odors, all of them found in PP and PE samples. Trimethylbenzenes with solvent and oily odors as well as terpenes with weakly woody odors were found in cardboard and paper materials. After migration, all compounds were bellow the European Legislation limits and maximum migration values recommended by Cramer. However propanoic, acetic and butyric acid as well as aldehydes compounds, phenol and 1-octanol were detected by sniffers, after migration

assay, with high modified frequency (between 50 and 78 %), what could change the organoleptic properties of packaged food

1. Introduction

The main function of food packaging is a correct food preservation to guarantee food safety and quality. The safety is ensured avoiding the chemical contamination due to the transfer of compounds from the packaging to the food. This phenomenon called migration has been widely studied for different materials such as adhesives (Canellas, Vera, & Nerin, 2014, 2016; Nerin, Gaspar, Vera, Canellas, Aznar, & Mercea, 2013), plastic materials like polypropylene, polyethylene, polyester and cardboard for food contact (Chang, Kang, Park, Choi, Kim, & Han, 2019; Paseiro-Cerrato, DeJager, & Begley, 2019; Rubio, Valverde-Som, Sarabia, & Ortiz, 2019; Ubeda, Aznar, Vera, Nerin, Henriquez, Taborda, et al., 2017; Vera, Canellas, & Nerin, 2018). This chemical transfer is a major concern to the packaging industry which may produce rejection´s consumer and millenaries losses.

To guarantee this safety, the materials in contact with food must fulfill the European Regulation Nº 1935/2004 ("Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC,") about materials in contact with food. European Regulation 10/2011/EU ("COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food,") details the maximum amount of a single substance that can be transferred from plastic materials to the food, specific migration limits (SML) as well as the conditions of time, temperature and type of simulant to carry out the migration assay. Paper and Board are not harmonized as food packaging materials in Europe. However, there are recommendations in the proposal approved by the Council of Europe (CoE) (CoE 2002) that contains the list of substances, migration tests and specific migration limits of some contaminants.

The food quality is mainly obtained avoiding the changes in organoleptic properties and the loss of nutritive compounds. These organoleptic changes may be produced by the interaction between the packaging with the food, adding new off-odors that may come simply from composition of the material used (Czerny, 2017; Czerny & Buettner, 2009; Osorio, Aznar, & Nerin, 2019) or may be derived from the degradation products after manufacturing process, like irradiation (Salafranca, Clemente, Isella, Nerin, & Bosetti, 2015; Tyapkova, Czerny, & Buettner, 2009) or high temperatures exposure (Kontominas, Goulas, Badeka, & Nerantzaki, 2006), all of them producing a negative effect on the quality of packaged food.

In the food industry the quality control of odors is carried out by a sensory analysis usually performed by a trained panel, where an overall perception about the presence or absence of off–odors can be determined by the panelists. However, this methodology is no valid to determine individual odors coming from individual compounds.

The technique GC-O-MS is a methodology which allows us to detect individual odor compounds simultaneously by two detectors: one sniffing port with the human nose which acts as an odor detector and mass spectrometry detector. It means that a compound can be detected and defined by chemical and sensorial way at the same time. The human nose is a detector often much more sensitive than the MS detector, capable of detecting compounds with very low concentrations, even below the limit of detections obtained by mass spectrometry (Brattoli, de Gennaro, de Pinto, Loiotile, Lovascio, & Penza, 2011). Therefore, is capable of detecting odorous migrants which are usually at very low concentrations.

Thus, the main objective of this work was to determine the compounds responsible for the off-odor in different food contact materials, prioritizing those compounds which could affect with more intensity the packaged food. Most of solid foodstuffs have adsorbent properties and thus they can absorb odors from the packaging. Paper and board are well-known as responsible for off-odors and the packaged food could be negatively influenced by these off-odors. For this reason, in this work several packaging materials usually applied to dry foods or using paper and board were selected.

This work was divided in different tasks (1) to run a sensory analysis in order to describe the undesirable sensory attributes and their intensities in the different market materials (2) to get different profiles of odorous compounds of each material by GC-O-MS looking for the relation-ship with the sensory attributes found above (3) to carry out migration assays of each material, not only to quantify the likely mass transfer of odorous compounds in terms of possible human risk, but also, to evaluate the odor intensity of each migrant previously detected. This way, the suspect compounds that could change the organoleptic properties of the packed food would be identified.

2. Materials and methods

2.1. Reagents

Toluene (108-88-3), hexanal (66-25-1), b-pinene (127-91-3), ethyl benzene (100-41-4), p-xylene (106-42-3), o-xylene (95-47-6), limonene (138-86-3**),** 1,2,4-trimethyl benzene (95-63-6), octanal (124-13-0), 1,3,5-trimethyl benzene (108-67-8), cyclohexanone (108-94-1), 1,2,3-trimethyl benzene (526-73-8), 4,5-dimethyl thiazole (3581-91-7), 1-octanol (111-87-5), nonanal (124-19-6), acetic acid (64-19-7), furfural (98-01-1), durene (95-93-2), decanal (112-31-2), 2-ethyl-1-hexanol (104-76-7), propanoic acid (79-09-4), benzaldehyde (100-52-7), 2-undecanone (112-12-9), butyric acid (107-92-6), Benzoic acid (65-85-0), anisole (100-66-3), 4-methyl-benzaldehyde (104-87-0), estragole (140-67-0), acetophenone (98-86-2), 4-ethyl-benzaldehyde (4748-78-1), verbenone (1196-01-6), naphthalene (91-20-3), 4-isopropyl-benzaldehyde (122-03-2), 4-phenyl-1-cyclohexene (4994-16-5), 2-tridecanone (593-08-8), benzenemethanol, α-methyl (98-85-1), 3,4-dimethylacetophenone (3637-01-2), 4-ethylacetophenone (937-30-4), methylnaphthalene (90-12-0) tridecanol (112-70-9), phenol (128-95-2), 3-phenyl-2-propenal (104-55-2), m-cresol (108-39-4), tetradecanol (112-72-1), nonanoic acid (122-05-0), isophthalaldehyde (626-19-7) were purchased from Sigma-Aldrich Química S.A (Madrid, Spain). All of them were of analytical quality with purity > 98%. Ethanol, water and methanol of HPLC grade were supplied by Scharlau Chemie S.A (Sentmenat, Spain). Tenax TA 80/100 mesh was supplied by Supelco (Bellefonde, USA).

2.2. Market samples

Different types of samples consisting of five bags, one tetrabrik and one cardboard box used as food packaging materials were studied. They were made of different types of plastics (polypropylene and polyethylene), cardboard and paper without inks. All materials were from different European companies which manufacture different types of materials for food contact.

All of them were commercial samples used for different packaging purposes which had been returned from the market due to odor problems.Their final use were to package vegetables like tomatoes, dried whole fruits, others for pasta like macaroni, spaghetti, also for pastry products like cereals, biscuits, flour or bread or for sugar and eggs. Even though the selection of materials was limited, they could represent those materials more prone to be affected by off-odors. As was above mentioned, most of solid foodstuffs have adsorbent properties, what means that if off-odors are produced by the packaging materials, these foods would be affected. All materials under study corresponded to different claims for off-odor from customers

Table 1 shows the samples analyzed, the materials used and their final purposes

2.3. Sensory analysis

A sensory evaluation was carried out by six assessors (4 female and 2 male) previously trained for these type of samples. For this analysis, 1 dm^2 of each material (PP, PE, cardboard and paper) were placed in opaque glass vessels of 50 mL of capacity. Then, the panelists were asked to describe the characteristic odor of each material as well as the intensity of these attributes with a scale of 1 unit (level perception) to 3 unit (strong perception). This assay was carried out in a room at 20 ºC.

After that, the data of each material were averaged and performed in three spider diagrams where the values were grouped by type of material studied (PP, PE and cardboard-paper)

2.4. GC-O-MS

Chromatograph Agilent Technologies 7820A system (Madrid, Spain) coupled to 5977B MSN series mass selective detector and sniffing port supplied by GL Sciences B.V (Eindhoven, Netherlands) were used for the identification and migration of odor compounds.

Chromatographic separations were carried out on a BP-20 column (30mx0.25 mmx0.25µm) from SGE analytical science (Madrid, Spain). The oven temperature program was from 40 ºC (5 min), a ramp of temperature of 10ºC/min to a final temperature of 220ºC maintained for 10 min. Helium was used as carrier gas at 1 mL/min flow.

Acquisition was carried out in SCAN mode (50-450 m/z) for screening analysis and SIM mode for migration quantifications. The transfer line of the olfactometer was maintained at 200 °C and the sniffing port humidified with air.

HS-SPME injection was used for the identification of odor compounds, extracting 1 dm^2 of each material placed into a 20 mL vial. The fiber used for this purpose was DVD/CAR/PDMS of (50/30µm) thickness due to its high capacity of extraction of odor compounds demonstrated in previous works (Vera, Uliaque, Canellas, Escudero, & Nerin, 2012; Wrona, Vera, Pezo, & Nerin, 2017). The extraction conditions were as follows, 50ºC extraction temperature, 15 min extraction time and 2.5 min desorption time at 250 ºC.

One µL of migration extract was injected in splitless mode at 250ºC for the migration assays.

2.5. Identification of odorous compounds from these materials

To determine the odorous compounds, one dm^2 of each material was cut and placed in 20mL vials for HS-SPME extract with the conditions above described.

Six trained panelists sniffed the individual odorous compounds eluted from the GC column, described their odors and assigned intensities. These intensities were quantified using a scale from 1 to 3 units. The value of 1 corresponded to a weak odor (low intensity), 2 was a medium intensity and 3 corresponded to strong intensity of odor.

In order to highlight the most important odorous compounds of each sample, the modified frequency MF (%) was calculated following the equation, $MF(\%) = [F(\%)xI(\%)]^{0.5}$. Where F(%) corresponded to the percentage of sniffers that had detected each odor compound and I(%) was the average of the values of intensity written down by all the sniffers divided by three (Dravnieks, 1985, 354; Vera, Uliaque, Canellas, Escudero, & Nerin, 2012). All the odorous compounds with a MF value higher than 40 were considered as the most important representative compounds of each material and they were called "odorous market".

Afterwards, the identification of each "odorous market" was carried out using the NIST and WILEY mass spectra libraries as well as the use of a literature search. For this purpose, KI (kovat indexes), previously calculated, and organoleptic characteristics of “odorous market” were compared to the compounds with the same descriptions found in the literature, for example in the web page www.flavornet.org or in previous works (Vera, Uliaque, Canellas, Escudero, & Nerin, 2012; Wrona, Vera, Pezo, & Nerin, 2017)

Finally, to confirm the identification, these standards were injected under the same chromatographic conditions (GC-O-MS), matching their retention indexes, odor characteristics and mass spectra with “odorous market” under study.

2.6. Migration assays and risk assessment.

Migration assays of these materials were carry out using Tenax ® as food simulant, according to Commission Regulation 10/2011/EU on plastic materials intended to come into contact with food("COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food,"). In this legislation, Tenax simulant must be used as simulant for plastic materials that will be used to package dry food as is the case in this study.

On the other hand, the proposal approved by CoE for paper and board materials also recommends Tenax as simulant for migration tests due to their incompatibilities with liquid simulants.For this purpose, 1 x 4 cm cutouts of each material were placed in Petri dishes and covered with 0.16 grams of Tenax forming a uniform layer (4 g Tenax per dm^2 in accordance with UNE-EN-14338 ("UNE-EN 14338:2004. Papel y cartón para contacto alimentario. Condiciones para la determinación de la migración en papel y cartón utilizando óxido de polifenileno modificado (MPPO) como simulante.,"). Then, this system was kept in an oven at 60 ºC for 10 days. Afterwards, Tenax was extracted two consecutive times with 1 mL of ethanol and analyzed by GC-O-MS (Vera, Canellas, & Nerin, 2013; Vera, Uliaque, Canellas, Escudero, & Nerin, 2012).

Then, two different assays were carried out. In the first one, the same panelists sniffed back the migration samples eluted from the chromatographic column to check out if they were capable to detect the odor compounds identified previously and then, to calculate back their modified frequencies (MF%) and then, to highlight the compounds which could affect and change the organoleptic properties of the packaged food.

And the second one, the migrant odor concentrations were calculated in order to check the possible human risks. For this purpose, firstly the migration values were expressed in mg/Kg of simulant, considering the absolute mg migrated divided by the 0.08 dm^2 used in the migration test and also, the relation 6dm^2 / 1Kg of simulant (regulation 10/2011/EU) ("COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food,").

Then, these migrant values were compared with their SML belonging the positive list of the legislation 10/2011/EU of plastics ("COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food,"). When the compound was not legislated, it was applied the maximum values of human daily intake recommended by Cramer ("Threshold of toxicological concern (TTC). ILSI Europe concise monograph series (2005) "), that establishes these values depending on the theoretical toxicity of each compound based on their structures and according to software Toxtree®. It classifies the compounds into three categories, from Class I, low toxicity, to class III, high toxicity setting their daily intakes recommended into 1.8, 0.54 and 0.09 mg/Kg for class I, II and III respectively ("Risk Assessment of non-listed substances (NLS) and not-intentionally added substances (NIAS) under article19 of Plastic Europe ").

3. Results

3.1. Sensory evaluation

The sensory evaluations are shown in figure 1. Three spider diagrams, each one for each type of material (PP, PE and cardboard-paper) are plot with their characteristic odors and their intensities.

For PP samples (Figure 1a), the attributes as plastic, fat/soap and rancid were perceived at high intensity. In addition, moss/green and sweet/fruity presented a lower intensity and tar very weakly detectable. The sample PP1 was characterized besides of plastic odor (value 2.2 of intensity) by high rancid odor (1.7 of intensity). Moss aroma lower than1 was perceived. Similar tendency was found for PP3, with a highest intensity to rancid odor and a value of 2.3 and 2 for plastic odor. By contrast, the PP2 sample showed soft attributes mainly like plastic (1.5 of intensity) and moss (1.3 of intensity). Finally, the sample PP4 had the highest attributes, with values of 2.5 for plastic odor, 2.4 for fat and soap odor and around 1 for sweet/fruity and floral intensities. Some panelists found in this sample a weak tar odor.

The attributes perceived for the PE materials are shown in Figure 1b. These perceptions were fewer than for PP samples. In PE1 besides of plastic odor, a severe fat/soap odor was found. Also, a weak floral was detected in this material. The sample PE2 was characterized by a new moderate vinegar odor (1.3 of intensity) besides of mild sweet and floral odors.

Finally, the characteristic odors for cardboards and paper materials are illustrated in Figure 1c. The sensory tests showed that these samples can exhibit high odor potency while providing a large number of attributes with high intensity. Cardboard 1, besides of cardboard like odor, insensitive woody and oily odors were perceived (1.9 and 1.5 respectively). Other important attributes found with values around of 1 were fat/soap, solvent and green. It can be observed that both cardboards had similar smell profiles with some intensity values lower in cardboard 2 than in cardboard 1. For paper, the main characteristic odors found were fat/soap, green and cardboard like (1.7, 1.2 and 1.1 of intensity respectively).

3.2. Identification of odorous compounds.

Figure 2 shows the chromatogram of Cardboard 1 material analyzed by GC-O-MS, where the compounds with odor characteristics are highlighted with numbers and named in Table 2. As this figure shows, sixteen odorous compounds were found in this material, although the concentration of most of them were close to their detection limits and their peaks do not appear with clarity.

Forty six compounds with characteristic odors whose MF (%) >40 were found in the different materials studied. They are shown in Table 2 and ordered by their retention indices.

The most common compounds found in different materials were nonanal, 2-ethyl-1-hexanol, benzaldehyde, acetophenone and naphthalene. Nonanal was described as fat, citrus and green odors descriptors and it was defined with MF (%) higher than 70 in all materials. In bibliography, it is a very common compound, already detected in a lot of materials of polypropylene and cardboard (Czerny, 2017; Czerny & Buettner, 2009; Tyapkova, Czerny, & Buettner, 2009) and also like a thermal oxidation product in polyethylene (Wiedmer, Velasco-Schon, & Buettner, 2017).

2-ethyl-1-hexanol with a green odor is produced on a massive scale as solvent or also as precursor for production of plasticizers. Benzaldehyde (fruity, almond and cherry odor) can be obtained like an off-odor compound from recycled cardboard (*Handbook of odor*, 2017) as well as acetophenone with almond and flower odor. This last compound can be also used as component of coatings and inks. Finally naphthalene, with tar odor, may be detected in articles of daily use, foods and toys (Wiedmer, Velasco-Schon, & Buettner, 2017). All of them were detected in most of the samples, but their MF (%) was lower than 65 (%) in all materials. It means that most of the panelists were capable of detecting these compounds but not with high values of intensities.

The different compounds detected can be organized by different families. For example, aldehyde family constituted by compounds such as hexanal, octanal, nonanal and decanal all having a similar characteristic odors that corresponded to fat, soap, citrus. All of them had great values of MF (%) with values ranging between (72-92 %). They may be the responsible compounds for what the attributes fat/soup found in sensory evaluation for the samples PP4, PE1, Paper 1 and cardboard 1, as shown in Figure 1 (values 2.4, 1.6, 1.7 and 0.9 respectively).

Other aldehydes found were 4-methyl, 4-ethyl and p-propyl benzaldehyde with cherry, fruity and oily odors respectively. Besides furfural, isophthalaldehyde and 3-phenyl-2-propenal (cis-cinnamaldehyde) were perceived as bread, almond, sweet and cinnamon odors. All of them had MF (%) around 40 and they were only found in one material.

Several acids like acetic, propanoic, butyric with their typical vinegar and rancid odors were detected in PE2 and in two samples of PP (PP1 and PP3). They were important off-odors with MF values (%) higher than 85 %. Reviewing the Figure 1a and Figure 1b, this fact would coincide with rancid and vinegar attributes found for these samples in the sensory analysis. Other acids detected in two PE materials with a lower MF (%) were benzoic acid and nonanoic acid with urine and fat odor respectively.

Several terpenes were detected in the cardboards studies; they were l-limonene, b-pinene, longyfolene and verbenone. They are natural compounds found in several resins of plants like pine, that is used as raw material to manufacture the cardboard or paper. For this reason, they could be the responsible for the odor attributes like woody, found in Figure 1c for these types of materials.

Other family of compounds had a ketone group in their structures, like for example cyclohexanone, detected in the samples of paper and cardboard with a characteristic mint odor and a MF (%) around 60. Other compounds such as 2- undecanone and 2-tridecanone were found with MF (%) values of 84 and 58 respectively. They were detected in PP4 with floral, fruity and green odors. Or acetophenone, above named, detected in most of the samples as well as 3,4-dimethyl and 4-ethyl acetophenone, with a floral odors, both found in the PP4.

Some alcohols were found in the samples studied. Linear alcohols like 2-ethyl-1-hexanol (green odor) above mentioned and 1-octanol (moss and mushroom odors) were detected in PP1 and PP2 samples with higher values of % MF than 80. This compound may be the responsible for the moss odor found in the sensory assay for these samples (Figure 1a). Also, 1-tridecanol and 1-tetradecanol were detected. They are used as lubricants as well as for the manufacture of surfactants and plasticizers, and they were found in the sample PP3 with must and coconut odor respectively.

Other aromatic alcohols found in PP and PE samples were phenol, used to synthesize plastics and m-cresol as solvent. They had phenol and plastic odors respectively. Besides, Benzene-methanol α-methyl was detected in one sample of carboard 1 with a floral perception.

Other compound detected was 4,5-dimethyl thiazole in PP3 with a nutty and soap odor. Its functional use is as food additive for flavoring ingredient but nothing is found with the appearance of this in PP material.

The rest of the compounds can be grouped into aromatic family composed of at least a benzene ring into their structures. Toluene (paint odor), ethyl benzene (aromatic) and para and orto xylene (plastic and geranium odors) used as solvents and they were found in different PE and PP samples. Also, trimethyl benzenes were found in cardboard and paper materials which may be generated by methylation of toluene and xylenes and be used as sterilizing agents, gasoline additive or as solvent. They had plastic, oily and aromatic odors and they may be the perpetrators of these attributes perceived in the sensory assay for these materials.

Two compounds (anisole and estragole) had in their structures the benzene ring bond to methoxy group. They were detected in two PP (PP1 and PP2) and they had aromatic, phenolic and anise odors respectively. 4-phenyl-1-cyclohexene was detected in PE2 this compound was also found in other work as off-odors in a fancy dress accessory handbag for children (Wiedmer, Velasco-Schon, & Buettner, 2017).

Finally, two compounds were detected which had two benzene rings in their structures. They were naphthalene and methylnaphthalene, both with tar odor and a high MF (%) above 80%. It is worth noting that this odor attribute was previously perceived in the sensory assay (Figure 1a) in some PP materials as well as in the paper and both cardboards.

3.3. Migration from odor compounds.

The migration assay was carried out with Tenax ®, as above mentioned. After the migration test, the extracts of Tenax ® were analyzed by GC-O-MS for two purposes. Firstly, to sniff the samples and evaluate the migrants according to the MF (%) and secondly, to calculate the concentration of the migrants in order to check if they were below the specific migration limit (SML) and the values recommended by Cramer.

Analytical parameters of the GC–O–MS method are shown in Table 3. The limit of detection (LOD), limit of quantification (LOQ) and linear range for each compound are expressed as µg of compound per Kg of simulant. Good results were obtained in terms of linearity and limits of detection. LOD values were between 12 µg/Kg (ciclohexanone) and 135 µg/Kg (acetic acid).

The migrant concentrations and their MF (%) for each material are also shown in Table 3. Migration values are expressed as µg compound per Kg of simulant. MF(%) values are shown when they are higher than 20%, as was previously established.

Around fifty five percent of migration values were higher than their LOD or LOQ and a forty six percent approximately of MF (%) were higher than 20.

Only nine migrated compounds appeared in the positive list of substances in the European Regulation for plastics as contact materials. Two of which, 2-ethyl-1-hexanol and phenol have high SMLs corresponded to 30 and 3 mg/Kg (ppm) respectively and the rest of them were authorized without limit of migration.

The rest of the compounds (thirty seven) didn't appear in the positive list of European Regulation and then, due to lack of legislation, they were evaluated according to Cramer class. Six compounds (4,5-dimethyl thiazole, durene. estragole, verbenone, naphthalene and methyl naphthalene) were classified as Class III of toxicity and some ketones (cyclohexanone, 2-undecanone and 2-tridecanone) corresponded to Class II.

Comparing the migration values, all compounds were below European legislation or below the values recommended by Cramer according to their toxicities. Therefore, these materials were safe for food contact applications.

However, when analyzing these migrations with the method GC-O-MS and calculating their MF (%), important results were obtained.

In the sample PP1, the highest migration values, shown in the table 3, were obtained for 1-octanol and acetophenone 850±76 and 488±15 μg/Kg, respectively. The compounds with MF(%) >20 were 1-octanol (58%), butyric acid (60%) and, anisole (33%) with attributes like moss, rancid and aromatic odor. That it means, although all compounds were safe for food contact materials, these migrations were perceived by the analysts with high MF (%). Therefore, they could affect the organoleptic characteristics of packaged food changing their properties.

Similar tendency was found for PP2, where the compounds with the highest migration values were 1-octanol and anisole, obtaining also the highest MF (%) values, 56 and 32, respectively. These values were similar to those obtained for PP1 and above mentioned.

In PP3, the migration of most of compounds and their MF% were below their LOQ and their MF (%) < 20. In contrast, propanoic acid migrated 415±37 μg/Kg and its MF was 75%. This compound could be important because its rancid odor was perceived by a high number of sniffers and with a high intensity after migration. Besides, its attributes were already found in the previous sensory evaluation.

The aldehyde compounds such as octanal, nonanal and decanal had high MF (%) with values 50, 45 and 52 % respectively for PP4, all of them with soap and fat descriptors. This material had the highest number and concentration of compounds that migrated, with a MF (%)>20, for example, p-xylene, durene, 2-undecanone, 4-isopropyl-benzaldehyde, 2-tridecanone and 4-ethylacetophenone, methylnaphthalene and tetradecanol. The ketones group of compounds (2-undecanone and 2-tridecanone) had the highest values of migration 578±52 and 381±31 µg/Kg but below 540 µg/Kg recommended by Cramer for Class II of toxicity.

As above mentioned, in the migration of PE1, octanal, nonanal and decanal had the highest MF (%) of 55, 55 and 50 % respectively. For PE2, acetic acid obtained the highest value of MF (%) in all migration samples, as well as, phenol 60% of MF. The mean of these results was very important, because after migration, these migranting compounds were detected by sniffers with a high MF(%) and they had considerable relation-ship with the attributes found in the previous sensory evaluation.

For the paper and cardboard samples, two groups of compounds with MF% >20 can be underlined, one of them was aldehyde group with hexanal and nonanal with values between 31 and 55%. Besides, with MF (%) between 35 and 43% trimethyl benzenes were found. Also, the compounds longyfolene and verbenone were detected in the cardboard 1 and 2 with MF% of 45, 36 and 45 (%).

Finally, it is important to emphasize that the compounds toluene, nonanal, 2-ethyl hexanol, benzaldehyde and acetophenone, common in the plastic, paper and cardboard materials under study, had migration values higher for paper and cardboard materials than for PE and PP. This fact could be related with greater diffusion properties of the compounds in these materials.

4. Conclusion

The off-odor compounds from different materials commonly used for food packaging (PP, PE, paper and cardboard) have been evaluated. Firstly, a sensory evaluation has been directly carried out in the materials as well as an analysis by GC-O- MS, in order to relate previous sensorial attributes with the off-odor compounds identified by this technique. This tool has proved to be very useful to identify a great number of odorous compounds.

Forty six compounds with characteristic odor have been identified: the most common odorants found in most of the samples have been nonanal, 2-ethyl-1-hexanol, benzaldehyde, acetophenone and naphthtalene. Although the compounds with the strongest odors were aldehydes with fat/soup odor in PP, PE and paper samples. Acetic, propanoic and butyric with vinegar and rancid odors were found in PP samples. Terpenes and trymethylbenzenes with woody, solvent and oily odors have been identified in cardboard and paper samples.

Migration tests have been carried out and the same technique was applied to study the off-odors.. The purpose was not only to quantify the migrant concentrations, in order to evaluate possible human risk, but also, sniffing the migration samples to establish how the organoleptic properties of packaged food could be affected. All identified migrant compounds previously found were below both the limits of European Legislation and the migration values recommended by Cramer. However, propanoic, acetic and butyric acid as well as the aldehyde compounds (octanal, decanal, nonanal), phenol and 1-octanol were detected by sniffers with high MF (%), between 50-78 (%), after the migration tests.

These results emphasize the importance of using this methodology to be capable to highlight the off-odor migrant compound at very low concentration after the migration tests (most of them below LOD and LOQ in MS but well perceived by olfactometry). Even though the migration complies with the legislation and thus the materials do not pose a risk for human health, they may affect the properties of the packaged food, producing consumer complaints, higher production costs or even a possible loss of brand confidence.

5. Acknowledgements

The authors acknowledge the financial help given by Gobierno de Aragón and European Social Funds to GUIA group T53_17R.

Bibliography

Brattoli, M., de Gennaro, G., de Pinto, V., Loiotile, A. D., Lovascio, S., & Penza, M. (2011). Odour Detection Methods: Olfactometry and Chemical Sensors. *Sensors, 11*(5), 5290-5322.

Canellas, E., Vera, P., & Nerin, C. (2014). Atmospheric pressure gas chromatography coupled to quadrupole-time of flight mass spectrometry as a tool for identification of volatile migrants from autoadhesive labels used for direct food contact. *Journal of Mass Spectrometry, 49*(11), 1181-1190.

Canellas, E., Vera, P., & Nerin, C. (2016). Multiple headspace-solid phase microextraction for the determination of migrants coming from a self-stick label in fresh sausage. *Food Chemistry, 197*, 24-29.

COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food*.

Czerny, M. (2017). *Odors in Paper and Cardboard Packaging*. Cham: Springer International Publishing Ag.

Czerny, M., & Buettner, A. (2009). Odor-Active Compounds in Cardboard. *Journal of Agricultural and Food Chemistry, 57*(21), 9979-9984.

Chang, Y., Kang, K., Park, S. J., Choi, J. C., Kim, M., & Han, J. (2019). Experimental and theoretical study of polypropylene: Antioxidant migration with different food simulants and temperatures. *Journal of Food Engineering, 244*, 142-149.

Dravnieks. (1985, 354). *Atlas of odor character profiles*: ed.; ASTM: Philadelphia, PA.

Handbook of odor. (2017).

Kontominas, M. G., Goulas, A. E., Badeka, A. V., & Nerantzaki, A. (2006). Migration and sensory properties of plastics-based nets used as food-contacting materials under ambient and high temperature heating conditions. *Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment, 23*(6), 634-641.

Nerin, C., Gaspar, J., Vera, P., Canellas, E., Aznar, M., & Mercea, P. (2013). Determination of partition and diffusion coefficients of components of two rubber adhesives in different multilayer materials. *International Journal of Adhesion and Adhesives, 40*, 56-63.

Osorio, J., Aznar, M., & Nerin, C. (2019). Identification of key odorant compounds in starch-based polymers intended for food contact materials. *Food Chemistry, 285*, 39-45.

Paseiro-Cerrato, R., DeJager, L., & Begley, T. H. (2019). Determining the migration of nadic acid, terephthalic acid, isophthalic acid and two oligomers from polyester food cans into food in the US market. *Food Control, 101*, 69-76.

Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. *Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC*.

Risk Assessment of non-listed substances (NLS) and not-intentionally added substances (NIAS) under article19 of Plastic Europe *Risk Assessment of non-listed substances (NLS) and not-intentionally added substances (NIAS) under article19 of Plastic Europe*.

Rubio, L., Valverde-Som, L., Sarabia, L. A., & Ortiz, M. C. (2019). The behaviour of Tenax as food simulant in the migration of polymer additives from food contact materials by means of gas chromatography/mass spectrometry and PARAFAC. *Journal of Chromatography A, 1589*, 18-29.

Salafranca, J., Clemente, I., Isella, F., Nerin, C., & Bosetti, O. (2015). Influence of oxygen and long term storage on the profile of volatile compounds released from polymeric multilayer food contact materials sterilized by gamma irradiation. *Analytica Chimica Acta, 878*, 118-130.

Threshold of toxicological concern (TTC). ILSI Europe concise monograph series (2005) *Threshold of toxicological concern (TTC). ILSI Europe concise monograph series (2005)*.

Tyapkova, O., Czerny, M., & Buettner, A. (2009). Characterisation of flavour compounds formed by gamma-irradiation of polypropylene. *Polymer Degradation and Stability, 94*(5), 757-769.

Ubeda, S., Aznar, M., Vera, P., Nerin, C., Henriquez, L., Taborda, L., & Restrepo, C. (2017). Overall and specific migration from multilayer high barrier food contact materials - kinetic study of cyclic polyester oligomers migration. *Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment, 34*(10), 1784-1794.

UNE-EN 14338:2004. Papel y cartón para contacto alimentario. Condiciones para la determinación de la migración en papel y cartón utilizando óxido de polifenileno modificado (MPPO) como simulante. *UNE-EN 14338:2004. Papel y cartón para contacto alimentario. Condiciones para la determinación de la migración en papel y cartón utilizando óxido de polifenileno modificado (MPPO) como simulante*.

Vera, P., Canellas, E., & Nerin, C. (2013). Identification of non-volatile compounds and their migration from hot melt adhesives used in food packaging materials characterized by ultra-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry. *Analytical and Bioanalytical Chemistry, 405*(14), 4747-4754.

Vera, P., Canellas, E., & Nerin, C. (2018). Identification of non volatile migrant compounds and NIAS in polypropylene films used as food packaging characterized by UPLC-MS/QTOF. *Talanta, 188*, 750-762.

Vera, P., Uliaque, B., Canellas, E., Escudero, A., & Nerin, C. (2012). Identification and quantification of odorous compounds from adhesives used in food packaging materials by headspace solid phase extraction and headspace solid phase microextraction coupled to gas chromatography-olfactometry-mass spectrometry. *Analytica Chimica Acta, 745*, 53-63.

Wiedmer, C., Velasco-Schon, C., & Buettner, A. (2017). Characterization of off-odours and potentially harmful substances in a fancy dress accessory handbag for children. *Scientific Reports, 7*.

Wrona, M., Vera, P., Pezo, D., & Nerin, C. (2017). Identification and quantification of odours from oxobiodegradable polyethylene oxidised under a free radical flow by headspace solid-phase microextraction followed by gas chromatography-olfactometry-mass spectrometry. *Talanta, 172*, 37-44.

Table 1: Description of samples studied with their materials used and their purposes as food packaging materials

Samples studied	Description	Material	Code samples	Uses
Sample 1	Bag of plastic	Polypropylene	PP1	Cereals, flour and biscuits
Sample 2	Bag of plastic	Polypropylene	PP2	Dried fruit and vegetables.
Sample 2	Bag of paper with a transparent window	Paper Polypropylene	Paper1 PP2	Bread and pastry
Sample 3	Bag of plastic	Polypropylene	PP3	Dried pasta (macaroni, spaghetti..)
Sample 4	Bag of plastic	Polypropylene	PP4	Dried fruit and vegetables.
Sample 4	Bag of paper with a transparent window	Paper Polypropylene	Paper1 PP4	Bread and pastry
Sample 5	Bag of plastic with self-closing	Polyethylene of low density	PE1	Sandwich and biscuits to take away
Sample 6	Tetrabrick	Polypropylene of low density Cardboard	PE2 CB1	Sugar
Sample 7	Box	Cardboard	CB2	Eggs

Table 2: Odor compounds detected in the different materials ordered by their retention indexes. Their odors perceived as well as their modified frequency calculated for each material.

Nº	Odorous compounds	IK	Odor	Material detected	FM
1	Toluene	1046	Paint	Paper1 PP4 Cardboard 1	55 48 60
2	Hexanal	1087	Fat, grass	Paper 1 Cardboard 1	82 72
3	b-Pinene	1116	Resin	Cardboard 1	45
4	Ethyl benzene	1128	Aromatic	PE1	60
5	p-Xylene	1156	Plastic	PP4 PE1	82 66
6	o-Xylene	1183	Geranium	PE1	42
7	Limonene	1203	Pine	Paper 1 Cardboard 1 Cardboard 2	55 70 74
8	1,2,4-trimethyl benzene	1276	Plastic, sweet	Cardboard 1	48
9	Octanal	1280	Fat, soap	PP4 PE1	90 75
10	1,3,5-trimethyl benzene	1290	Oily, aromatic	Paper 1 Cardboard 1 Cardboard 2	45 60 52
11	Cyclohexanone	1308	Mint and acetone odor	Paper 1 Cardboard 1 Cardboard 2	55 65 63
12	1,2,3-trimethyl benzene	1337	Oily,aromatic	Cardboard 1	67
13	4,5-dimethyl thiazole	1380	Nutty, soap	PP3	43
14	1-octanol	1392	Moss, mushroom	PP1 PP2	82 85
15	Nonanal	1395	Fat, citrus, green	Paper 1 PP4 PE1 Cardboard 1 Cardboard 2	85 90 92 72 78
16	Acetic acid	1451	Vinegar	PE2	95
17	Furfural	1457	Bread, almond	PE2	48
18	Durene	1469	Sweet	PP4	54
19	Decanal	1484	Soap	PP4 PE1	78 69
20	2-ethyl-1-hexanol	1485	Green	PP1 PP2 PP3 Paper 1 Cardboard 1 Cardboard 2	65 50 55 62 43 47
21	Longyfolene	1510	Woody	Cardboard 1 Cardboard 2	72 69
22	Propanoic acid	1525	Rancid, pungent	PP3	96
23	Benzaldehyde	1542	Fruity, sweet, almond cherry	PP1 PP2 Paper 1 PP3 PE2 Cardboard 1 Cardboard 2	45 58 57 52 49 42 61
24	2-undecanone	1595	Floral, fruity	PP4	84

25	Butyric acid	1620	Cheese, Rancid	PP1 PP3	85 89
26	Benzoic acid	1640	Urine	PE1	45
27	Anisole	1654	Aromatic, phenolic	PP1 PP2	64 71
28	4-methyl-benzaldehyde	1654	cherry-like, sweet	PP3	43
29	Estragole	1658	Anise	PP1	40
30	Acetophenone	1671	Almond, flower	PP1 PP4 PE1 PE2 Paper 1 Cardboard 1 Cardboard 2	55 58 45 45 61 66 54
31	4-ethyl-benzaldehyde	1722	Fruity	PP4	43
32	Verbenone	1733	Spicy odor and camphoraceous	Cardboard 1	57
33	Naphthalene	1770	Tar	PP1 PP4 Paper1 Cardboard 1 Cardboard 2	66 49 52 61 55
34	P-isopropyl-benzaldehyde,	1799	Oily	PP4	46
35	2-Tridecanone	1807	Fruity, green	PP4	58
36	Benzenemethanol, α-methyl	1829	Floral	Cardboard 1	47
37	3,4-dimethylacetophenone	1863	Floral	PP4	44
38	4-ethylacetophenone	1868	Floral	PP4	58
39	Methylnaphthalene	1875	Tar	PP4	69
40	Tridecanol	1960	Moss	PP3	55
41	Phenol	1987	Phenol	PP3 PE2	42 61
42	3-phenyl-2-propenal (Cinnamaldehyde)	2033	Cinnamon	PP3	40
43	2-tert-butyl-5-methyl phenol(m-cresol)	2130	Plastic	PP4 PE1	73 45
44	Tetradecanol	2182	Coconut	PP3	42
45	Nonanoic acid	2204	Fat, green	PE2	62
46	Isophthalaldehyde	2341	Slight sweet	PP4	45

Table 3: Migration of odorous compounds previously identified, quantification ions (QI), analytical parameters as limit of detection (LOD), limit of quantification (LOQ) and linear range. Migration values for each material expressed as μg of compound per Kg of simulant. Modified frequently (MF%), SML according to European plastic legislation 10/2011 and toxicity class according to Cramer rules.

Nº	Odorous compounds	QI	LOD	LOQ	Linear range μg/Kg	Material detected	Migration ug/Kg	FM	SML μg/Kg	Cramer Class
1	Toluene	91	102	340	340-2300	Paper1 PP4 Cardboard 1	980±107 514±46 1340±190	31 <20 35		I
2	Hexanal	56	87	290	290-2500	Paper 1 Cardboard 1	353±28 375±35	55 55		I
3	b-Pinene	93	32	105	105-1030	Cardboard 1	657±63	<20		I
4	Ethyl benzene	91	16	53	53-650	PE1	175±16	24		I
5	p-Xylene	91	75	250	250-850	PP4 PE1	<LOD <LOD	33 30		I
6	o-Xylene	91	75	250	250-850	PE1	<LOD	<20		I
7	Limonene	68	100	333	333-1500	Paper 1 Cardboard 1 Cardboard 2	<LOD 335±12 <LOD	<20 <20 <20		I
8	1,2,4-trimethyl benzene	105	18	60	60-850	Cardboard 1	230±12	35		I
9	Octanal	56	63	210	210-3050	PP4 PE1	<LOD <LOD	50 55		I
10	1,3,5-trimethyl benzene	105	42	140	140-1080	Paper 1 Cardboard 1 Cardboard 2	<LOD <LOQ <LOQ	<20 43 43		I
11	Cyclohexanone	55	12	43	43-1030	Paper 1 Cardboard 1 Cardboard 2	<LOD <LOD <LOD	<20 <20 <20		II
12	1,2,3-trimethyl benzene	105	19	62	62-750	Cardboard 1	<LOQ	40		I
13	4,5-dimethyl thiazole	113	36	120	120-800	PP3	<LOD	<20		III
14	1-octanol	56	26	85	85-1090	PP1 PP2	850±76 892±133	58 56	Authorized without SML	
15	Nonanal	57	42	140	140-950	Paper 1 PP4 PE1	850±93 <LOQ 523±58 230±22	60 45 55 33		I

						Cardboard 1	303±29	31		
						Cardboard 2				
16	Acetic acid	60	135	450	450-2040	PE2	<LOQ	78	Authorized without SML	
17	Furfural	96	66	220	220-1700	PE2	<LOD	<20		III
18	Durene	119	54	180	180-1050	PP4	255±23	33		I
19	Decanal	55	33	110	110-1200	PP4	413±40	52		I
						PE1	405±53	50		
20	2-ethyl-1-hexanol	57	47	156	156-2400	PP1	<LOQ	<20	SML=30000	
						PP2	215±18	<20		
						PP3	<LOQ	<20		
						Paper 1	<LOD	<20		
						Cardboard 1	433±52	<20		
						Cardboard 2	515±72	<20		
21	Longyfolene	161	*	*	*	Cardboard 1	622±92	45		
						Cardboard 2	505±40	36		
22	Propanoic acid	74	110	370	370-870	PP3	415±37	75	Authorized without SML	
23	Benzaldehyde	77	22	73	73-950	PP1	181±16	<20	Authorized without SML	
						PP2	235±31	<20		
						Paper 1	358±31	<20		
						PP3	285±19	<20		
						PE2	279±30	<20		
						Cardboard 1	342±29	<20		
						Cardboard 2	410±37	<20		
24	2-undecanone	58	72	240	240-1800	PP4	578±52	45		II
25	Butyric acid	60	93	310	310-1070	PP1	<LOQ	60	Authorized without SML	
						PP3	<LOQ	58		
26	Benzoic acid	105	30	95	95-980	PE1	<LOD	<20	Authorized without SML	
27	Anisole	108	42	140	140-950	PP1	310±47	33		I
						PP2	325±52	32		
28	4-methyl-benzaldehyde	91	17	55	55-980	PP3	117±9	<20		I
29	Estragole	148	27	90	90-780	PP1	<LOQ	<20		III
30	Acetophenone	105	21	72	72-850	PP1	488±15	<20		I
						PP4	551±50	<20		

						PE1	255±26	<20		
						PE2	267±22	<20		
						Paper 1	732±59	<20		
						Cardboard 1	810±35	<20		
						Cardboard 2	623±60	<20		
31	4-ethyl-benzaldehyde	91	14	48	48-1010	PP4	<LOQ	<20		I
32	Verbenone	107	26	88	88-910	Cardboard 1	<LOQ	45		III
33	Naphthalene	128	32	105	105-1400	PP1	<LOQ	<20		III
						PP4	<LOD	<20		
						Paper1	<LOD	<20		
						Cardboard 1	<LOQ	<20		
						Cardboard 2	<LOQ	<20		
34	4-isopropyl-benzaldehyde	133	54	180	180-780	PP4	458±28	35		I
35	2-Tridecanone	58	75	250	250-1800	PP4	381±31	38		II
36	Benzenemethanol, α-methyl	79	28	95	95-780	Cardboard 1	455±41	<20		I
37	3,4-dimethylacetophenone	133	26	88	88-975	PP4	288±25	<20		I
38	4-ethylacetophenone	133	24	80	80-1050	PP4	584±53	39		I
39	Methylnaphthalene	128	39	130	130-1300	PP4	<LOQ	25		III
40	Tridecanol	55	22	75	75-540	PP3	<LOQ	25		I
41	Phenol	94	61	205	205-1900	PP3	<LOD	<20	SML=3000	
						PE2	415±39	41		
42	3-phenyl-2-propenal (Cinnamaldehyde)	131	54	180	180-1700	PP3	<LOD	<20		I
43	2-tert-butyl-5-methyl phenol(m-cresol)	108	30	98	98-580	PP4	358±31	35	Authorized without SML	
						PE1	<LOQ	<20		
44	Tetradecanol	55	57	190	190-650	PP3	<LOD	<20		I
45	Nonanoic acid	60	102	340	340-2800	PE2	<LOD	36		I
46	Isophthalaldehyde	134	33	110	110-850	PP4	<LOD	<20		I

*Quantified with the compound b-Pinene due to absence of commercial standard

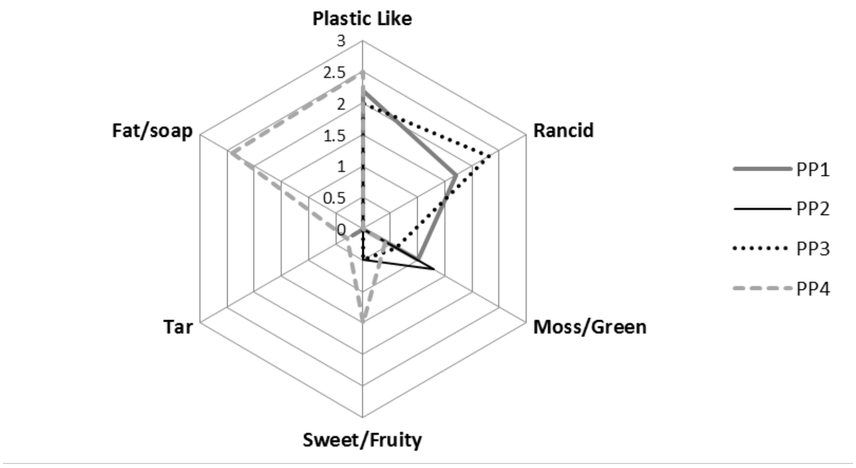

Figure 1a: Spider diagram for PP samples with their characteristic odors and their intensities.

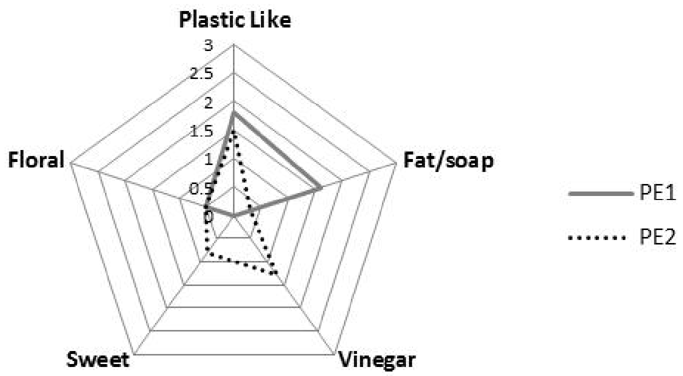

Figure 1b: Spider diagram for PE samples with their characteristic odors and their intensities.

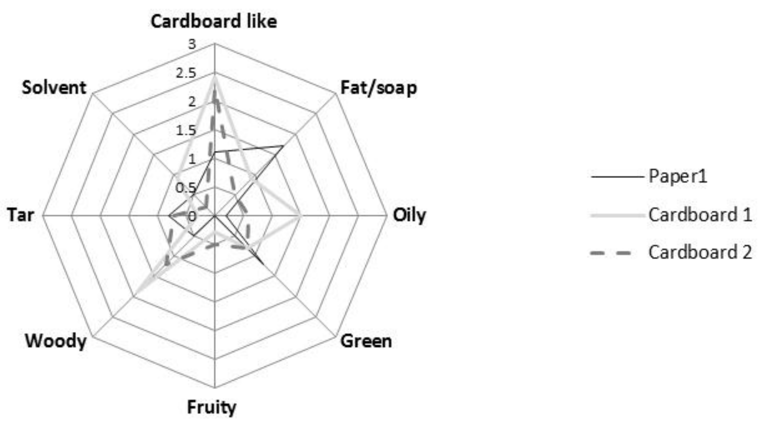

Figure 1c: Spider diagrams for cardboard and paper materials with their characteristic odors and their intensities.

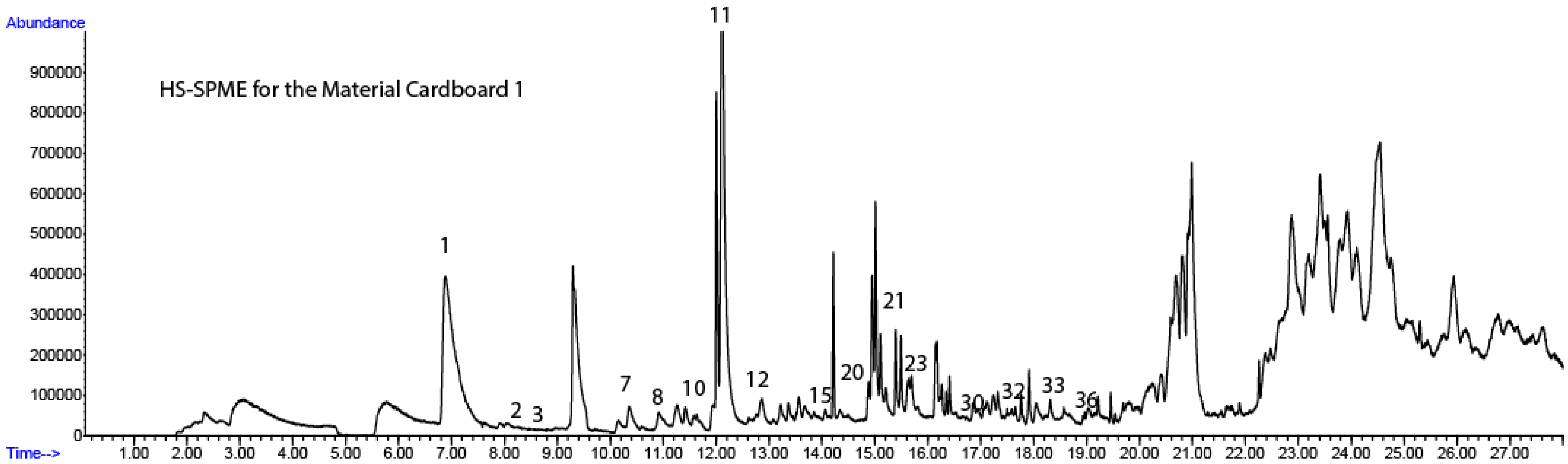

Figure 2: Cromatogram of GC-O-MS for the material Cardboard, analyzed by HS-SPME with the fiber DVB/CAR/PDMS (50/30 µm)