

1 Identification of key odorant compounds in starch-based polymers intended for food contact 2 materials

3 Jazmín OSORIO (jazminosorio@unizar.es), Margarita AZNAR (marga@unizar.es), Cristina
4 NERÍN* (cnerin@unizar.es)

5 *Analytical Chemistry Department, GULA Group, I3A, EINA, University of Zaragoza, M^a de Luna 3,*
6 *50018, Zaragoza, Spain.*

8 Abstract

9 Biopolymers used for food contact materials must be evaluated in order to ensure food safety and
10 quality. In this work, the aroma profile of starch-based packaging materials, presented as pellets and
11 films has been characterized. Headspace solid phase microextraction (HS-SPME) technique and gas
12 chromatography coupled to both mass spectrometry and a sniffing port (GC-MS-O) were used for
13 identification. In total, 35 odorant compounds were detected. The results showed that aldehydes
14 were the odorants with the highest aromatic impact in starch-based films. Eight odorant compounds,
15 such as trimethylamine, 1-octen-3-one, sotolon, (Z) and (E)-2-nonenal, p-vinylguaiaicol, eugenol
16 and 1-undecanol, defined as aroma-impact compounds, obtained modified frequency values (MF%)
17 above 60% in at least 3 out of 4 films. A sensory panel evaluated the toasted, sweet/fruity, green,
18 flower, distasteful, fat and spices notes in the films and it was observed that the quality of all
19 samples decreased when the toasted and spices notes increased.

20 **Keywords:** Biopolymers; Odorant compounds; Food contact materials; Sensory analysis;
21 Olfactometry

22 *Chemical compounds studied in this article*

23 Trimethylamine (PubChem CID: 1146); 1-Octen-3-one (PubChem CID: 61346); Sotolon
24 (PubChem CID: 62835); (Z)-2-Nonenal (PubChem CID: 5354833); (E) 2-Nonenal (PubChem CID:

5283335); p-Vinylguaiacol (PubChem CID: 332); Eugenol (PubChem CID: 3314); 1-Undecanol (PubChem CID: 8184).

1. Introduction

Biopolymers are increasingly used in food packaging, because they are abundant, renewable, environmentally friendly, biodegradable, and biocompatible. In addition, their mechanical properties such as durability, flexibility, high gloss, clarity, and tensile strength are often suitable for being used as packaging materials (Mittal, Chaudhry, & Luckachan, 2014; Othman, 2014; Rhim & Kim, 2013; Zhang, Rempel, & McLaren, 2014). Biopolymers include two different categories: synthetic and natural. Synthetic biopolymers can be produced by microorganisms such as the polyhydroxy-alkanoates (PHA) or by conventional chemical synthesis, such as polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVA) (Rhim & Kim, 2013). Natural polymers are developed using proteins such as gelatin, gluten or alginate, or carbohydrates such as cellulose, chitosan and starch as a raw material (Othman, 2014; Oun & Rhim, 2017). The starch-based polymers have been one of the most widely used for manufacturing bio-films, because starch is low cost, safe and abundant (Averous & Halley, 2014; Zhang et al., 2014). Their characteristics may be different depending on their origin, because they can come from different sources such as tubers (potato and cassava), cereal grains (corn, rice and wheat) or agro-food waste (Averous & Halley, 2014; González & Villanueva, 2011; Ribba, Garcia, D'Accorso, & Goyanes, 2017).

One important feature of starch-based biopolymers as food contact materials is the odor they can release, that affects the quality of packaged food. The manufacturing process is a critical source where the raw materials suffer extreme conditions, such as high temperatures, pressure and extrusion, among others, and different odorant compounds can be formed during this process (Wypych, 2013). The formation of these compounds can be enhanced because of the presence of amino acids and fatty acids in the polymer that easily degrade into different small compounds (Khlestkin, Peltek, & Kolchanov, 2018; Samavati, Emam-Djomeh, & Mehdinia, 2014; Wypych,

2013). Therefore, the analysis of odorant compounds is especially important since the organoleptic properties of food could be negatively modified.

The objective of the present study was to characterize the aroma profile of starch-based biopolymers intended for food packaging and to evaluate the presence of negative sensory attributes that could affect the organoleptic properties of food. For this purpose, the volatile compounds profile of 1 pellets sample and four different films coming from starch, were analyzed. The analysis was performed by headspace solid phase microextraction (HS-SPME) coupled simultaneously to a mass spectrometer and a sniffing port. (GC-MS-O). Retention index (RI), mass spectra and aromatic description were used to identify the compounds (Feng et al., 2015; Pino, Tolle, Gök, & Winterhalter, 2012). In addition, a sensory panel evaluated the olfactory attributes of packaging samples that were subsequently correlated to the odorant compounds previously identified.

2. Materials and methods

2.1. Reagents and solutions

Standards (E)-2-nonenal [18829-56-6]; 2-Phenoxyethanol [122-99-6]; p-vinylguaiacol [7786-61-0]; trimethylamine [75-50-3]; 1-undecanol [112-42-5]; sotolon [28664-35-9]; 1-octen-3-one [4312-99-6]; benzaldehyde [100-52-7]; (E)- cinnamaldehyde [14371-10-9]; decanal [112-31-2]; limonene [138-86-3]; dodecanal [112-54-9]; ethyl isovalerate [108-64-5]; ethyl octanoate [106-32-1]; toluene [108-88-3]; eugenol [97-53-0]; furfural [98-01-1]; linalool [78-70-6]; nonanal [124-19-6]; octanal [124-13-0]; and vanillin [121-33-5] were from Sigma–Aldrich (Madrid, Spain). Methanol (UHPLC-MS grade) was supplied by Scharlau (Setmenat, Spain). Standard of n-alkanes (C8 to C20) (40 mg L⁻¹ each, in hexane solution) and the SPME fibers were purchased to Supelco (Bellefonte, PA, USA). Ultra-pure water was obtained from Millipore Milli-Q system (Billerica, MA, USA).

2.2. Samples

73 In this work, different starch-based biopolymers for food packaging were supplied by a Packaging
74 Company. They were provided in different forms: 1 sample of starch powder, 1 sample of starch-
75 based pellets and 4 samples of starch-based films (BP1, BP2, BP3 and BP4). Film BP2 was
76 manufactured using the pellet samples from this study. BP1, BP2 and BP3 came from the starch
77 powder analyzed in this work. BP4 had a different origin. No additional information was provided
78 by the company. In order to have more data about the biopolymer composition, an ethanolic extract
79 was obtained and analyzed by UPLC-MS (QTOF). The analytical methodology and the compounds
80 identified are reported in supplementary material. Most of the compounds identified were PLA
81 (polylactic acid) oligomers and cyclic esters coming from polyesters. According to previous studies,
82 this biopolymer would be a blend of starch, PLA and a biodegradable polyester (Aznar, Ubeda,
83 Dreolin, & Nerín, 2018).

84 2.3. Analysis by GC-MS-O

85 The analyses of volatile compounds were carried out using a gas chromatograph 7890N coupled
86 through a split valve to a mass spectrometry detector 5977D (Agilent Technologies. Santa Clara,
87 CA) and a sniffing port (Phaser, GL Sciences, Germany). A HP-5MS column (30m x 25mm x
88 0.25µm film thickness) from Agilent technologies was used. The detector was set in SCAN
89 acquisition mode (45 - 350 m/z). The oven temperature ramp was as follows: initially 40°C for 5
90 min, 15°C min⁻¹ to 300 °C and held at 300 °C for 10 min. The SPME fiber was transferred manually
91 to the injection port and desorbed at 250°C for 2 min in splitless mode.

92 The transfer line of the olfactometer was heated at 200°C and the sniffing port was purged with
93 humidified air. Olfactometric analyses were carried out by six trained panelists.. Sniffing time was
94 approximately 20 min and each judge carried out a maximum of one session a day. During the
95 olfactometry, the panelists described the odors perceived and its intensity in a scale from 1 (low
96 intensity) to 3 (high intensity). Fractional values were also allowed.

97 2.4. Experimental design optimization of HS-SPME-GC-MS-O analysis

98 The pellets sample and the film BP2 were used for the optimization process because they showed
99 the highest intensity of global odor. A maximum total area of the integrated peaks was the selection
100 criteria for the optimal conditions.

101 2.4.1. Selection of the most appropriate SPME fiber.

102 Three different fibers were evaluated: polydimethylsiloxane (PDMS 100 μm),
103 polydimethylsiloxane/divinylbenzene (PDMS/DVB 65 μm) and
104 polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR 50/30 μm). Prior to the
105 analysis, the samples were conditioned during 2 min at 80°C. Afterwards, they were extracted at the
106 same temperature during 15 min and under agitation at 500 rpm. Injection and analysis were
107 carried out using the conditions described in section 2.3.

108 2.4.2. Selection of extraction conditions

109 Optimization was performed using an experimental design with the software package Modde 6.0
110 from Umetrics (Umea, Sweden). The experiments were carried out with the selected fiber. Two
111 variables selected were: extraction time (5, 15 and 25 min) and extraction temperature (60, 80 and
112 100°C). The cubic model was implemented. This model consisted of 17 different experiments,
113 where values of parameters (high, medium, low) were combined each other. The experiments were
114 carried out in randomized order.

115 2.5. Identification of odorous compounds and determination of its impact on aroma

116 For the identification of the main aroma active compounds different strategies were used. The
117 experimental mass spectra were compared to the mass spectra of NIST 2018 Standard Reference
118 Database and only matches above 800 were considered acceptable. In addition, the retention
119 indexes (RI) were calculated using a C8–C20 n-alkane standard solution (Jeleń, Majcher, Ginja, &
120 Kuligowski, 2013; Wrona, Vera, Pezo, & Nerin, 2017; Zellner et al., 2008).and compared with
121 those found either in the literature or in chemical databases such as NIST (NIST (National Institute

122 of Standards and Technology), 2017), Flavornet (Acree Terry; Arn Heinrich, 2004) or Chemspider
123 (Royal Society of Chemistry, 2015). Only those compounds with differences in RI below 1% were
124 considered. The odor described by the panelists was also compared with the compilation of aroma
125 compounds from databases, such as Flavornet or Pherobase (M El-Sayed Ashraf, 2003) and
126 previous bibliography (Barata et al., 2011; Feng et al., 2014; Vera, Uliaque, Canellas, Escudero, &
127 Nerín, 2012; Wrona et al., 2017). Additionally, those compounds whose standards were available,
128 were confirmed by the comparison of retention time and mass spectrum of the identified peak and
129 the standard.

130 For determining the aromatic impact of the compounds identified, their modified frequency MF (%)
131 was calculated according to the following equation (Vera et al., 2012)

132
$$\%MF = [F(\%) \times I(\%)]^{0.5}$$

133 where F (%) is the percentage of the sniffers that detected the smell (100 x number of sniffers that
134 detected the odorant/total number of sniffers) and I (%) is the average percentage of intensity (100 x
135 average I/3). The compounds with a %MF higher than 50% were considered as key compounds of
136 the sample base aroma (Wrona et al., 2017).

137 2.6. Sensory evaluation

138 A quantitative descriptive analysis (QDA) was carried out in all samples. The analysis was
139 performed following the methodology proposed by Yunzi Feng et al. (Feng et al., 2014, 2015). The
140 samples were evaluated according to the descriptors defined in section 2.5. The sensory evaluation
141 was carried out by twelve judges (20 to 45 years old, 8 female, 4 male), from the sensory panel.
142 They were previously trained using compounds with similar descriptions to the evaluated
143 descriptors: eugenol (spicy), ethyl isovalerate (fruit), ethyl octanoate (orange), limonene (citrus),
144 vanillin (vanilla), linalool (flower), and 1-octen-3-one (mushroom). The panel was trained
145 considering the most important attributes present in the sensory properties of starch-based polymer

146 samples based on the olfactometry results. Eight different descriptors were evaluated in a scale from
147 0 “very low intensity” to 5 “very high intensity”: toasted, sweet/fruity, green, flower, distasteful, fat,
148 earth and spices. Global intensity of the samples was also evaluated using the same scale. The
149 panelists also indicated the quality of the samples in a scale 0-5, where 5 was “like very much” and
150 0 was “dislike very much”. The sensory tests were carried out in a conditioned room.

151 **3. Results**

152 3.1. Optimization of HS-SPME analysis

153 The results from CAR/DVB/PDMS fiber showed the highest efficiency in the extraction of volatile
154 compounds compared to PDMS and PDMS/DVB phases. CAR/DVB/PDMS had been previously
155 regarded in the laboratory as a suitable fiber to extract compounds such as aldehydes, alcohols or
156 esters (Vera, Canellas, & Nerín, 2014; Vera et al., 2012).

157 For the optimization of the HS-SPME extraction conditions, the 2 parameters with the highest
158 relevance in extraction according to the literature were evaluated, extraction temperature and
159 extraction time (Vera et al., 2012; Wrona et al., 2017). Since pellets as well as BP2 film were solid
160 samples, the salting effect was not evaluated.

161 Figure 1 shows the 3-D response surface plot obtained from the experimental design performed in
162 order to determine the optimal conditions for the HS-SPME extraction. The maximum total area of
163 the peaks detected in the chromatogram was the response used for the selection of the best
164 conditions. The results showed that optimal extraction conditions were: PDMS/DVB/CAR 50/30
165 μm fiber, extraction time 15 min and extraction temperature 90°C.

166 3.2. Identification of odorous compounds.

167 Table 1 shows the odor active compounds detected by GC-MS-O in the samples with MF% values
168 above 20%. A total of 35 compounds were detected, and among them, 17 showed MF% values over
169 50% (marked in bold letters). They were classified according to its functional group (FG) into 8

170 categories: FG 1-amides and amines (5), FG 2- acids (2), FG 3- alcohols and phenols (5), FG 4-
171 aldehydes (10), FG 5- esters (2), FG 6- hydrocarbons (3), FG 7-ketones (3) and FG 8- others (5);
172 and according to their aroma group (AG) (Barata et al., 2011; Capone, Tufariello, & Siciliano,
173 2013) into 8 categories: AG 1 - toasted (5), AG 2 - fruity and sweet (1), AG 3 - flower (6), AG 4 -
174 chemical and distasteful (9), AG 5 - fat (1), AG 6 - spices (4), AG 7 - green (6) and AG 8 - earth
175 (3).

176 The compounds with the highest aroma role in starch-based films (MF% values above 60% in at
177 least 3 of the 4 films) were: trimethylamine, 1-octen-3-one, sotolon, (Z) and (E) 2-nonenal, p-
178 vinylguaiacol, eugenol and 1-undecanol. Except for trimethylamine, all of them had been
179 previously detected in pellets and/or starch. Its presence in the films could be due to degradation
180 processes during the film manufacturing. Trimethylamine, present in all the films, had a distasteful
181 fish aroma and could lead to off-flavours in the packaged food. 1-octen-3-one, sotolon and 1-
182 undecanol were only detected with MF% values above 20% in pellets. This fact suggests that they
183 could have been formed either during the pellets manufacturing process due to temperature and
184 pressure conditions, or present in the other raw materials used for its manufacture (Caillé, Salmon,
185 Bouvier, Roland, & Samson, 2017). Sotolon and p-vinylguaiacol were also detected in the starch
186 but their MF% was lower than in the films. However, other compounds such as eugenol, (Z) and (E)
187 2-nonenal were already present in starch at high MF%, what suggests that these compounds were
188 characteristic of the raw starch and not produced during the production of the biopolymer. Most of
189 the key odorous compounds in films belonged to spices or green aroma groups. Other compounds
190 with a clear aroma impact in at least 2 films were: nonanal, δ -valerolactam, 2-phenoxyethanol,
191 triacetin and a non-identified compound with RI 1094.

192 Figure 2a shows a bar chart of total MF% for each aroma group in the 4 films and figure 2b shows
193 the results for each functional group. Aroma groups “chemical and distasteful” (AG 4), “spices”
194 (AG 6) and “green” (AG 7) were the main aroma descriptors in the films. All the films showed a

195 similar pattern. Only film BP4, which came from a different starch, obtained lower MF% values for
196 almost all the descriptors. Sotolon, p-vinylguaiaicol and eugenol were the main compounds
197 responsible for the differences in MF% between BP4 and the other films. The type of starch used
198 and the temperature conditions used during the extrusion process can favor the formation of these
199 compounds (Espert, De Las Heras, & Karlsson, 2005; Wypych, 2013). Regarding the functional
200 groups, “alcohol and phenols” (FG 3) and “aldehydes” (FG 4) were the chemical families with the
201 highest impact on aroma profile of starch based films. The different films showed also a similar
202 pattern regarding the functional groups. In this case, BP4 showed lower MF% values especially for
203 “amides and amines” (FG 1) and “esters” (FG 5).

204 Fig. 3 showed a radial chart comparing MF% values in the raw starch and in the film BP2 for the
205 different functional groups (3b) and aroma groups (3a). As it can be seen, aldehydes, with green
206 aromas, are the compounds with the highest aroma impact in these materials. They can come from
207 the degradation of amino acids or formed by the beta oxidation and decarboxylation of fatty acids
208 (Feng et al., 2013, 2014; Gao et al., 2010; Steinhaus & Schieberle, 2007).. Fig. 3b also shows that
209 the aroma impact of the amides and amines and also of the unidentified compounds increased in the
210 film versus the raw material. The presence of amides and amines in the biomaterials is a significant
211 sign of deterioration, maybe caused by the exposure to the light and the environment (Wypych,
212 2013), which is more intense in films.

213 3.3. Sensory analysis

214 The overall quality as well as the intensity of the 8 aroma descriptors defined in the materials and
215 methods section were evaluated by a trained panel. Figure 4a showed the intensity of the descriptors
216 in the 4 films. Only 4 descriptors were detected by the panel: “fat”, “sweet”, “toasted” and “spices”,
217 being “spices” and “toasted” the most intense ones for most of the films. Only BP4 showed a low
218 intensity for these descriptors. This film was manufactured with a different starch and probably this
219 was the reason of the differences in the aroma perception. In addition, this film showed the highest

220 overall quality, probably because these 2 descriptors were not considered by the panel as
221 appropriate for a packaging material. According to the olfactometry, the highest differences in these
222 aroma groups between BP4 and the other films corresponded to sotolon, eugenol and caprolactam,
223 which obtained lower values in BP4.

224 In the sensory evaluation of starch (Figure 4b), the intensity of these descriptors was lower than in
225 the film. No more descriptors were detected in starch samples.

226

227 **4. Conclusion**

228 The main odorous compounds present in different starch-based biopolymers intended for food
229 packaging have been identified. Compounds such as trimethylamine, 1-octen-3-one, sotolon, (Z)
230 and (E) nonenal, eugenol or p-vinyguaiacol were the main ones responsible for the aroma of starch-
231 base films, and were mainly perceived with descriptors belonging to the aroma groups “chemical
232 and distasteful”, “spices” or “green”. The final perception of the films by the panelists was linked to
233 toasted and spicy notes. The three films coming from the same starch-based biopolymer showed a
234 similar aroma profile, which highlights the role of the initial starch in the final aroma of the
235 packaging material. These compounds could be transferred to packaged food and for this reason
236 migration studies would be necessary.

237 **Acknowledgements**

238 Project AGL2015-67362-P from MINECO (Spain) and FEDER funds and Project RYC-2012-
239 11856 from MINECO (Spain). Aragon Government and European Social Fund for the financial
240 help given to GUIA group T-10, Project FOODYPLAST (POCTEFA Program) from FEDER
241 funds.

242

243 Potential conflicts of interest do not exist.

244

245 **References**

246 Acree Terry; Arn Heinrich. (2004). Flavornet and human odor space. Retrieved July 13, 2018, from
247 <http://www.flavornet.org/flavornet.html>

248 Averous, L., & Halley, P. J. (2014). Starch Polymers: From the Field to Industrial Products. *Starch*
249 *Polymers: From Genetic Engineering to Green Applications*, 3–10.
250 <https://doi.org/10.1016/B978-0-444-53730-0.00018-X>

251 Aznar, M., Ubeda, S., Dreolin, N., & Nerín, C. (2018). Determination of non-volatile components
252 of a biodegradable food packaging material based on polyester and polylactic acid (PLA) and
253 its migration to food simulants. *Journal of Chromatography A*.
254 <https://doi.org/https://doi.org/10.1016/j.chroma.2018.10.055>

255 Barata, A., Campo, E., Malfeito-Ferreira, M., Loureiro, V., Cacho, J., & Ferreira, V. (2011).
256 Analytical and sensorial characterization of the aroma of wines produced with sour rotten
257 grapes using GC-O and GC-MS: Identification of key aroma compounds. *Journal of*
258 *Agricultural and Food Chemistry*, 59(6), 2543–2553. <https://doi.org/10.1021/jf104141f>

259 Caillé, S., Salmon, J. M., Bouvier, N., Roland, A., & Samson, A. (2017). Modification of the
260 olfactory sensory characteristics of Chardonnay wine through the increase in sotolon
261 concentration. *Food Quality and Preference*, 56, 225–230.
262 <https://doi.org/10.1016/j.foodqual.2016.08.001>

263 Capone, S., Tufariello, M., & Siciliano, P. (2013). Analytical characterisation of Negroamaro red
264 wines by “Aroma Wheels.” *Food Chemistry*, 141(3), 2906–2915.
265 <https://doi.org/10.1016/j.foodchem.2013.05.105>

- 266 Espert, A., De Las Heras, L. A., & Karlsson, S. (2005). Emission of possible odourous low
267 molecular weight compounds in recycled biofibre/polypropylene composites monitored by
268 head-space SPME-GC-MS. *Polymer Degradation and Stability*, 90(3), 555–562.
269 <https://doi.org/10.1016/j.polymdegradstab.2005.03.009>
- 270 Feng, Y., Cai, Y., Su, G., Zhao, H., Wang, C., & Zhao, M. (2014). Evaluation of aroma differences
271 between high-salt liquid-state fermentation and low-salt solid-state fermentation soy sauces
272 from China. *Food Chemistry*, 145, 126–134. <https://doi.org/10.1016/j.foodchem.2013.07.072>
- 273 Feng, Y., Cai, Y., Sun-Waterhouse, D., Cui, C., Su, G., Lin, L., & Zhao, M. (2015). Approaches of
274 aroma extraction dilution analysis (AEDA) for headspace solid phase microextraction and gas
275 chromatography-olfactometry (HS-SPME-GC-O): Altering sample amount, diluting the
276 sample or adjusting split ratio? *Food Chemistry*, 187, 44–52.
277 <https://doi.org/10.1016/j.foodchem.2015.03.138>
- 278 Feng, Y., Cui, C., Zhao, H., Gao, X., Zhao, M., & Sun, W. (2013). Effect of koji fermentation on
279 generation of volatile compounds in soy sauce production. *International Journal of Food*
280 *Science and Technology*, 48(3), 609–619. <https://doi.org/10.1111/ijfs.12006>
- 281 Gao, X. L., Cui, C., Zhao, H. F., Zhao, M. M., Yang, L., & Ren, J. Y. (2010). Changes in volatile
282 aroma compounds of traditional chinese-type soy sauce during moromi fermentation and heat
283 treatment. *Food Science and Biotechnology*, 19(4), 889–898. [https://doi.org/10.1007/s10068-](https://doi.org/10.1007/s10068-010-0126-7)
284 [010-0126-7](https://doi.org/10.1007/s10068-010-0126-7)
- 285 González, R. M., & Villanueva, M. P. (2011). Starch-based polymers for food packaging.
286 *Multifunctional and Nanoreinforced Polymers for Food Packaging*, 527–570.
287 <https://doi.org/10.1533/9780857092786.4.527>
- 288 Jeleń, H., Majcher, M., Ginja, A., & Kuligowski, M. (2013). Determination of compounds
289 responsible for tempeh aroma. *Food Chemistry*, 141(1), 459–465.

290 <https://doi.org/10.1016/j.foodchem.2013.03.047>

291 Khlestkin, V. K., Peltek, S. E., & Kolchanov, N. A. (2018). Review of direct chemical and
 292 biochemical transformations of starch. *Carbohydrate Polymers*, 181(September 2017), 460–
 293 476. <https://doi.org/10.1016/j.carbpol.2017.10.035>

294 M El-Sayed Ashraf. (2003). The Pherobase: Database of pheromones and semiochemicals.
 295 Retrieved July 13, 2018, from <http://www.pherobase.com/>

296 Mittal, V., Chaudhry, A. U., & Luckachan, G. E. (2014). Biopolymer - Thermally reduced graphene
 297 nanocomposites: Structural characterization and properties. *Materials Chemistry and Physics*,
 298 147(1–2), 319–332. <https://doi.org/10.1016/j.matchemphys.2014.05.007>

299 NIST (National Institute of Standards and Technology). (2017). Libro del Web de Química del
 300 NIST, SRD 69. Retrieved July 13, 2018, from <https://webbook.nist.gov/>

301 Othman, S. H. (2014). Bio-nanocomposite Materials for Food Packaging Applications: Types of
 302 Biopolymer and Nano-sized Filler. *Agriculture and Agricultural Science Procedia*, 2, 296–
 303 303. <https://doi.org/10.1016/j.aaspro.2014.11.042>

304 Oun, A. A., & Rhim, J. W. (2017). Effect of oxidized chitin nanocrystals isolated by ammonium
 305 persulfate method on the properties of carboxymethyl cellulose-based films. *Carbohydrate*
 306 *Polymers*, 175(August), 712–720. <https://doi.org/10.1016/j.carbpol.2017.08.052>

307 Pino, J. A., Tolle, S., Gök, R., & Winterhalter, P. (2012). Characterisation of odour-active
 308 compounds in aged rum. *Food Chemistry*, 132(3), 1436–1441.
 309 <https://doi.org/10.1016/j.foodchem.2011.11.133>

310 Rhim, J. W., & Kim, Y. T. (2013). *Biopolymer-Based Composite Packaging Materials with*
 311 *Nanoparticles. Innovations in Food Packaging: Second Edition*. Elsevier Ltd.
 312 <https://doi.org/10.1016/B978-0-12-394601-0.00017-5>

- 313 Ribba, L., Garcia, N. L., D'Accorso, N., & Goyanes, S. (2017). *Disadvantages of Starch-Based*
 314 *Materials, Feasible Alternatives in Order to Overcome These Limitations. Starch-Based*
 315 *Materials in Food Packaging: Processing, Characterization and Applications.*
 316 <https://doi.org/10.1016/B978-0-12-809439-6.00003-0>
- 317 Royal Society of Chemistry. (2015). ChemSpider | Search and share chemistry. Retrieved July 13,
 318 2018, from <http://www.chemspider.com/>
- 319 Samavati, V., Emam-Djomeh, Z., & Mehdinia, A. (2014). Thermodynamic and kinetic study of
 320 volatile compounds in biopolymer based dispersions. *Carbohydrate Polymers*, 99, 556–562.
 321 <https://doi.org/10.1016/j.carbpol.2013.08.059>
- 322 Steinhaus, P., & Schieberle, P. (2007). Characterization of the key aroma compounds in soy sauce
 323 using approaches of molecular sensory science. *Journal of Agricultural and Food Chemistry*,
 324 55(15), 6262–6269. <https://doi.org/10.1021/jf0709092>
- 325 Vera, P., Canellas, E., & Nerín, C. (2014). Migration of odorous compounds from adhesives used in
 326 market samples of food packaging materials by chromatography olfactometry and mass
 327 spectrometry (GC-O-MS). *Food Chemistry*, 145, 237–244.
 328 <https://doi.org/10.1016/j.foodchem.2013.06.087>
- 329 Vera, P., Uliaque, B., Canellas, E., Escudero, A., & Nerín, C. (2012). Identification and
 330 quantification of odorous compounds from adhesives used in food packaging materials by
 331 headspace solid phase extraction and headspace solid phase microextraction coupled to gas
 332 chromatography-olfactometry-mass spectrometry. *Analytica Chimica Acta*, 745, 53–63.
 333 <https://doi.org/10.1016/j.aca.2012.07.045>
- 334 Wrona, M., Vera, P., Pezo, D., & Nerín, C. (2017). Identification and quantification of odours from
 335 oxobiodegradable polyethylene oxidised under a free radical flow by headspace solid-phase
 336 microextraction followed by gas chromatography-olfactometry-mass spectrometry. *Talanta*,

337 172(July 2016), 37–44. <https://doi.org/10.1016/j.talanta.2017.05.022>

338 Wypych, G. (2013). *Handbook of Odors in Materials. Handbook of Odors in Materials* (Second
339 Edi, Vol. 1). ChemTec Publishing. <https://doi.org/10.1016/B978-1-895198-51-5.50013-9>

340 Zellner, B. d'Acampora, Bicchi, C., Dugo, P., Rubiolo, P., Dugo, G., & Mondello, L. (2008). Linear
341 retention indices in gas chromatographic analysis: a review. *Flavour and Fragrance Journal*.
342 <https://doi.org/10.1002/ffj.1887>

343 Zhang, Y., Rempel, C., & McLaren, D. (2014). *Thermoplastic Starch. Innovations in Food*
344 *Packaging*. Elsevier Ltd. <https://doi.org/10.1016/B978-0-12-394601-0.00016-3>

345

346 **Figure Captions**

347 **Fig. 1:** Response surface plot for the optimal conditions of HS-SPME analysis

348 **Fig. 2.** Bars chart of the addition of MF% values for the 4 starch-based films for a) aroma
349 descriptors and b) principal functional group

350 **Fig. 3.** Radial chart of the comparison between the starch, pellets and the film BP2 for a) aroma
351 descriptors and b) principal functional group. Axes represent the addition of MF% values.

352 **Fig 4.** Bars chart of the sensory test for comparison between a) the 4 starch-based films and b)
353 starch, and film BP2

Table 1: Identified odorous compounds with its retention index (RI) and its odor description perceived by the different assessors. Its modified frequency (MF%) by HS-SPME extraction in starch, pellet and four different types of films (BP1, BP2, BP3, BP4). AG. aroma group: 1 - toasted, 2 - fruity and sweet, 3 - flower, 4 - chemical and distasteful, 5 - fat, 6 - spices, 7 - green and 8 - earth. FG: functional group: 1 - amides and amines; 2 - acids, 3 - alcohols and phenols, 4 - aldehydes, 5 - esters, 6 - hydrocarbons, 7 - ketones.

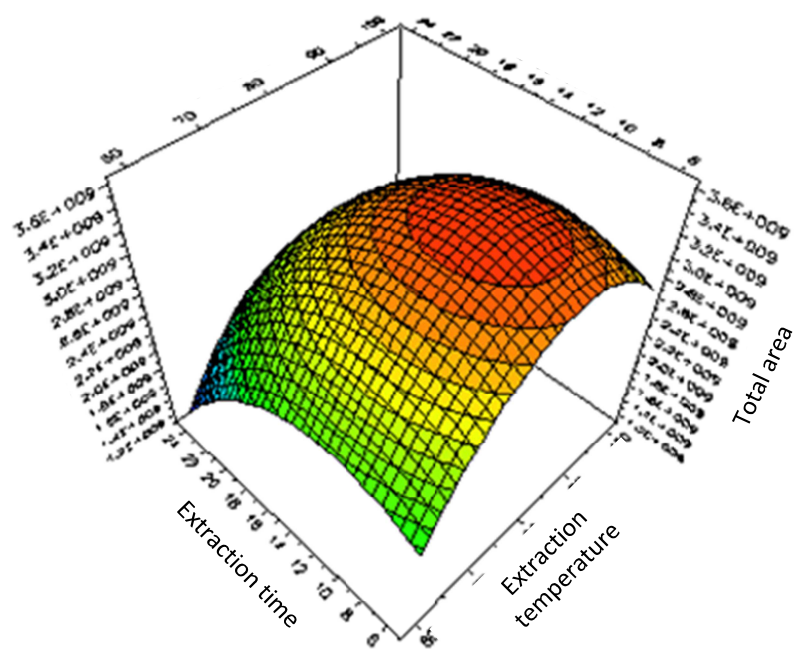
RT (min)	Reference RI	RI	Name	# CAS	Odor description	AG	FG	%MF Starch	%MF Pellet	%MF BP1	%MF BP2	%MF BP3	%MF BP4
2.30	369	491	Trimethylamine* ^a	75-50-3	Fish	4	1			85.6	81.6	85.6	70.7
8.44	829	823	Furfural*	98-01-1	Sweet, bread	1	4	25.8	11.5	8.2	8.2	23.1	11.5
9.10	865	862	m-Xylene*	108-38-3	Plastic	4	6	28.3	16.3	11.5	11.5	16.3	
9.95		904	Ni		Flower, sweet,	3			36.5	37.4	8.2	11.5	20.0
10.15		915	Ni		Fat, oily	5			25.8	28.3	42.4	42.4	14.1
11.40	960	958	Benzaldehyde*	100-52-7	Almond, burnt	1	4	28.3	23.1				
11.30	979	976	1-Octen-3-one* ^a	4312-99-6	Mushroom	8	7		73.0	74.8	52.9	85.6	73.0
11.80	1005	1001	Octanal*	124-13-0	Lemon, green	7	4	25.8	11.5		34.6	28.3	34.6
12.57	1012	1013	2-Acetylpyridine	1122-62-9	Popcorn	1	7	32.7	30.6		14.1		
13.06	1080	1079	2,5-dimethyl-3-ethylpyrazine	13360-65-1	Roast, mushroom	8	1	16.3	63.2	44.7	28.3	40.0	20.0
13.09		1083	Ni		Mushroom	8				25.8	25.8	28.3	14.1
13.25		1094	Ni		Burned	1			69.3	65.3	73.0	23.1	28.3
13.43	1100	1099	Undecane*	1120-21-4	Alkane	4	6	16.3	23.1	16.3		11.5	32.7
13.48	1104	1104	Nonanal*	124-19-6	Fat, citrus, green	7	4	28.3		46.9	52.9	51.0	
13.56	1110	1108	Sotolon* ^a	28664-35-9	Spices, licorice	6	5	16.3	100.0	87.6	93.1	73.0	
14.21	1149	1152	(Z)-2-Nonenal* ^a	60784-31-8	Cucumber, fruit	7	4	81.6		77.5	86.4	58.9	83.7
14.33	1160	1159	(E)-2-Nonenal* ^a	18829-56-6	Cucumber, green	7	4	85.6	36.5	65.3	74.8	69.3	76.6
14.52	1170	1171	Benzoic acid	65-85-0	Almond, sweet	1	2	38.3		44.7	36.5	71.2	73.0
14.60	1175	1177	δ-Valerolactam*	675-20-7	Piper, green	7	1	32.7	36.5	32.7	56.6	65.3	
14.98	1204	1205	Decanal*	112-31-2	Flower	3	4	28.3	28.3	44.7	44.7	11.5	16.3
15.23	1221	1220	2-Phenoxyethanol	122-99-6	Pleasant, green	7	3	79.6	44.7	49.0	61.1	56.6	73.0

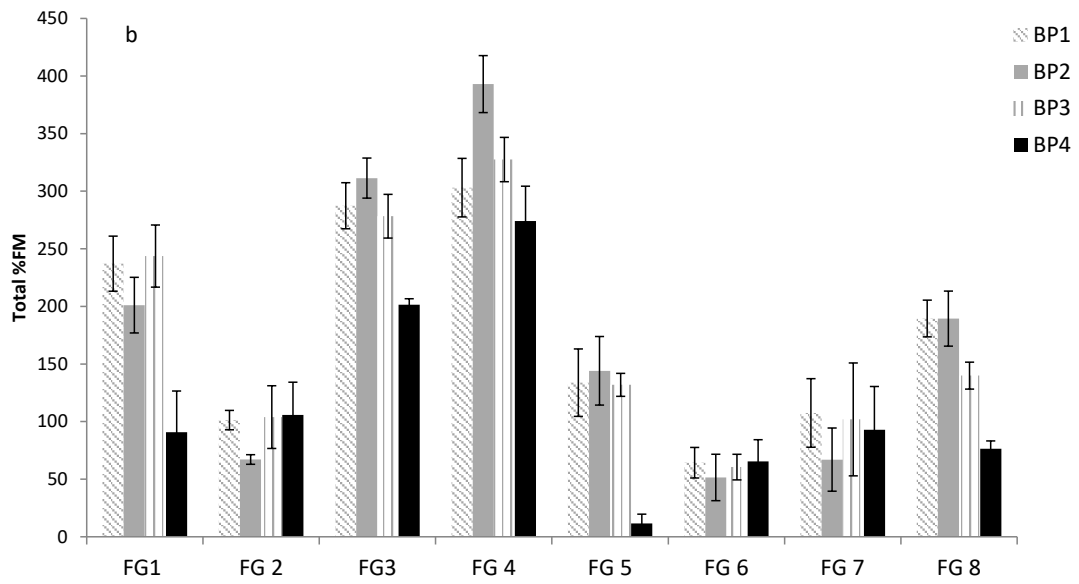
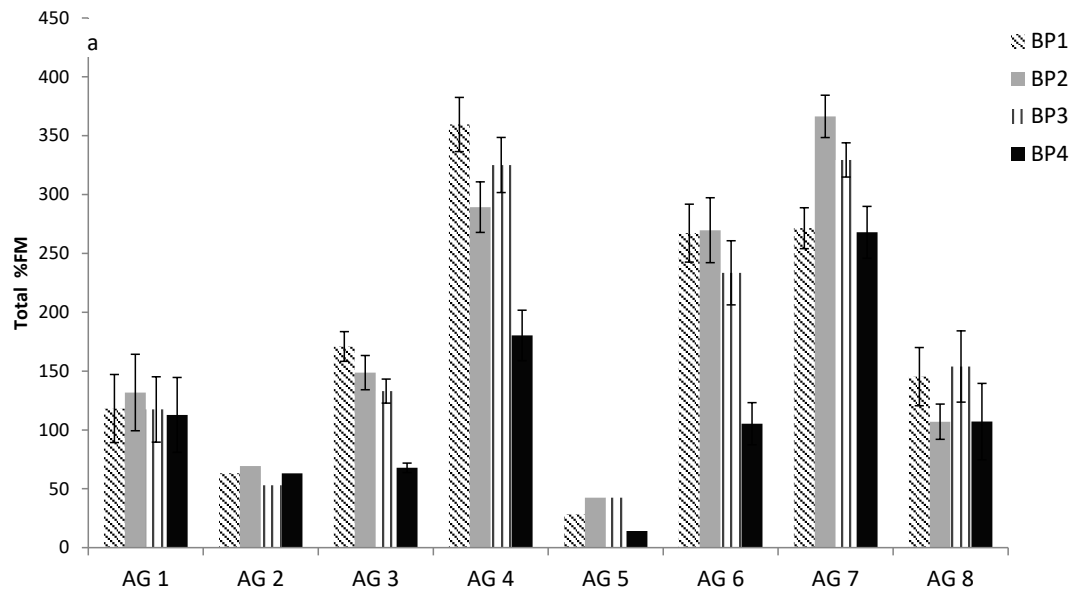
15.34	1223	1228	Benzothiazole	95-16-9	Gasoline, rubber	4	1		36.5	23.1		16.3	
15.70	1255	1254	Caprolactam*	105-60-2	Distasteful	4	1	11.5	11.5	51.0	34.6	36.5	
15.83	1272	1268	Nonanoic acid	112-05-0	Fat, distasteful	4	2	14.1	42.4	56.6	30.6	32.7	32.7
16.05	1283	1280	(E)-Cinnamaldehyde*	14371-10-9	Cinnamon, sweet	6	4	28.3	25.8	32.7	28.3	20.0	40.0
16.42	1304	1306	Undecanal	112-44-7	Sweet, flower	3	4	16.3	34.6	11.5	40.0	32.7	
16.67	1323	1322	p-vinylguaiaicol* ^a	7786-61-0	Clove, curry	6	3	32.7	65.3	65.3	73.0	58.9	65.3
16.90	1344	1340	Triacetin	102-76-1	Fat, chlorine	4	5	28.3		46.2	51.0	58.9	11.5
17.15	1364	1364	Eugenol*	97-53-0	Clove, honey	6	3	73.0		81.6	75.3	81.6	
17.30	1371	1374	1-Undecanol	112-42-5	Fruity, mandarin	2	3		32.7	63.2	69.3	52.9	63.2
17.63	1400	1399	Tetradecane*	629-59-4	Alkene	4	6	25.8	49.0	36.5	40.0	32.7	32.7
17.73		1409	Ni		Distasteful	4		16.3	80.0	32.7	40.0	34.6	
17.85	1419	1419	Dodecanal*	112-54-9	Flower	3	4	30.6		16.3	23.1	32.7	11.5
18.27	1448	1451	Geranyl acetone	3796-70-1	Flower	3	7			32.7		16.3	20.0
18.42	1463	1466	1-Dodecanol	112-53-8	Flower	3	3	25.8	16.3	28.3	32.7	28.3	

N.i: No identified. Marked in bold letters values over 50%

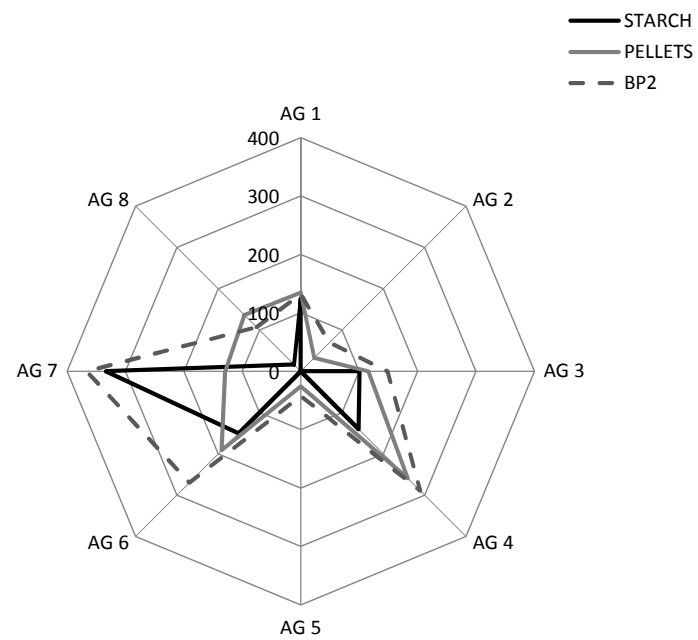
* Verified with standard

^a Odorant compounds selected as aroma-impact





a



b

