

1 **Safety assessment of natural materials for food contact in high temperature**  
2 **applications: migration studies with solid simulant (Tenax®)**

3 Sofia Nieves, Cristina Nerín and Esther Asensio\*

4

5 Department of Analytical Chemistry, Aragon Institute of Engineering Research I3A, CPS-  
6 University of Zaragoza, Torres Quevedo Building, María de Luna 3, 50018 Zaragoza, Spain

7 \*Corresponding author: Tel: +34 976765274. E-mail address: estherac@unizar.es

8 E-mail: 737160@unizar.es (Sofía Nieves); cnerin@unizar.es (Cristina Nerín)

9

10 **Abstract**

11 The concern of conventional plastics for food contact has opened the use of natural vegetal  
12 materials which can be used even at high temperature. However, their safety in use has to be  
13 carefully evaluated. This study shows the migration tests of volatile compounds to Tenax® at  
14 175 °C for 1 h. Hexadecanoic, octadecanoic and tetracosanoic acid were detected and  
15 quantified, presenting values well below the specific migration limits (SML) according to  
16 Regulation (EU) No 10/2011. Aldehydes were detected and semi-quantified and were generally  
17 below the migration limits established for compounds without SML. Compounds related to the  
18 manufacturing process of different types of food contact materials (FCM) were identified. The  
19 use of this type of dishes made from natural materials does not present a risk to the consumer  
20 due to the migration of volatile compounds when used at high temperature, in accordance with  
21 the conditions of use set by the manufacturer.

22

23 **Keywords:** migration, Tenax®, natural materials, SPME-GC/MS, high temperature

24

## 25 **1. Introduction**

26 Packaging is a fundamental and indispensable element in the production and consumption of  
27 food. However, most of the packaging materials can transfer their components to the food in  
28 contact with them, through the well-known process called migration. Migration of intentionally  
29 and non intentionally added substances (IAS and NIAS, respectively) poses a potential problem  
30 of food contamination from the packaging (Nerín et al., 2013; Leeman & Krul, 2015). Plastics  
31 occupy at the moment the greatest amount of food packaging, but their lack of degradability in  
32 the environment and the necessity of moving to circular economy, when single use plastics  
33 have been banned, has driven the appearance of alternative materials for food packaging.  
34 Among them, natural materials such as bamboo, wheat pulp or palm leaves are nowadays  
35 available in the market, promoted for being used even at high temperature. However, being  
36 natural materials does not imply that they are safe and for this reason, migration tests should be  
37 carefully done to guaranty their safety in use. Natural materials are also industrially processed  
38 and contain some additives, as IAS to facilitate the manufacture, handling and use in the  
39 market. However, they can also contain NIAS (Nerín et al., 2013, 2022; Asensio et al., 2020)  
40 among which pesticides, phytosterols and others can be present. In absence of specific  
41 regulation, that established for plastics can be used. The requirements of food contact plastics  
42 are included in Regulation (EU) No 10/2011 on plastic materials and objects intended to come  
43 into contact with food, and in its subsequent amendments (COMMISSION, 2011).

44 Another important problem related to the use of plastic containers is the environmental impact  
45 they generate, mainly due to the high amount of non degradable plastic waste. To reduce the  
46 impact of plastics in the environment, the European Commission decided to ban the single use  
47 plastics. This statement opens new alternatives such as the use of natural, biodegradable  
48 and/or compostable materials and also the use of recycled materials.

49 One of these alternatives is the use of food contact materials in tableware sector, mainly dishes  
50 or small plates for single use in catering, obtained from natural fibers of vegetable origin: wood,  
51 wheat pulp, bamboo or palm leaf, which are labelled '100% natural fabrication'. They have  
52 many advantages, highlighting both their availability around the world at an affordable price and  
53 their biodegradability. Other benefits that have been described include their low density, leading  
54 to lighter containers, their high rigidity and the lesser impact they have on the health of the  
55 operators involved in the manufacture (Berthet et al., 2015).

56 One of the most important natural vegetable materials in the current market is that made from  
57 bamboo fibers. This plant is progressively replacing wood since its cultivation time is much  
58 shorter than most of wood options. Its applications range from the manufacture of floors and  
59 ceilings to the production of fabrics and paper (Okokpujie et al., 2020). Bamboo containers  
60 stand out for their mechanical properties, including their high impact resistance, long durability  
61 and flexibility (Xie et al., 2019). However, special attention should be paid to the real bamboo  
62 objects for food contact and those theoretically made of bamboo, which in reality only involves  
63 bamboo powder as load in melamine, a synthetic plastic.

64 Another natural vegetable material available on the market is that made of wheat pulp. The  
65 residues of these crops can be used to obtain natural materials with great potential for  
66 construction, packaging or development of optoelectronic devices. These new fields of  
67 application are an excellent way to revalue the by-products of the wheat agricultural industry  
68 (Sánchez et al., 2016).

69 Like the wheat pulp, palm leaf has been considered as a residue from palm tree plantations,  
70 which disposal represents an environmental problem. It has been described that plant fibers  
71 from different parts of this tree can be used as natural materials thanks to their physical and  
72 mechanical properties, and also applied as a reinforcement material for polypropylene polymers  
73 or as a substitute material for wood (Xu et al., 2015).

74 In the same way as plastic containers and any other packaging material intended to be in  
75 contact with food, these new natural vegetable materials must be evaluated to guarantee food  
76 safety. These materials could contain resins, additives, natural ingredients which are not always  
77 safe and other NIAS that could migrate into food (Osorio et al., 2020) affecting the consumer  
78 health. As they are very new materials on the market, they are not specifically included in the  
79 legislation, unless any kind of plastic were involved in their production. However, Regulation  
80 (EU) No 1935/2004 (Parliament, E., & Union, 2004) on materials and objects intended to come  
81 into contact with food applies to any material intended for food contact and that includes also  
82 these natural vegetable materials.

83 To identify and quantify the compounds released by these new materials for food contact,  
84 migration tests must be carried out. For plastic materials for food contact, the migration  
85 conditions will depend on the intended use of the material, as established by Regulation (EU)  
86 No 10/2011 (COMMISSION, 2011). In the case of the natural materials studied in this work,  
87 there is no applicable legislation, so the most restrictive legislation for food contact has been  
88 considered to be applied. Asensio et al., (2020) carried out the identification and quantification  
89 of volatile compounds from the migration tests of two different types of dishes made of wheat  
90 and wood pulp for being used at room temperature with foods. However, it is important to note  
91 that some dishes made of vegetable materials can be used at high temperatures (oven or  
92 microwave up to 175 °C), so it is necessary to study the migration behaviour for high  
93 temperature applications. This is the main purpose of the present research.

94

## 95 **2. Material and methods**

### 96 **2.1. Reagents**

97 Absolut ethanol from Scharlab (Madrid, Spain) and poly (2,6-diphenyl-p-phenylene oxide)  
98 polymer (Tenax<sup>®</sup>) supplied by Supelco (Vidra Foc, Spain) were used. Nonanal (98%, CAS 124-  
99 19-6), hexadecanoic acid (99%, CAS 57-10-3), octadecanoic acid (98,5%, CAS 57-11-4) and  
100 methyl palmitate (>99% CAS 112-39-0) used as analytical standards for quantification were  
101 from Sigma-Aldrich (Spain). The stock solutions of the analytical standards used were prepared  
102 in absolute HPLC-grade ethanol with concentrations approximately 1,000 µg/g. All of them were  
103 subjected to gravimetric control. From the stock solutions, the corresponding dilutions of the

104 calibration curves were prepared at 20% ethanol with MilliQ water. These solutions were  
 105 injected into the SPME-GC/MS equipment within a maximum of 24 h after their preparation.




106

107 **2.2. Samples**

108 To carry out this study, samples of bamboo, wheat pulp and palm leaf dishes available in the  
 109 market (Table 1) were purchased from a Spanish supplier. All these materials are intended for  
 110 catering services. They are prepared to be in direct contact with hot food and, specifically, these  
 111 three types of dishes allow food to be heated in an oven/microwave, at high temperatures.

112

113 Table 1. Characteristics of the dishes selected for the study of migration at high temperature.

Composition	Size (cm)	Properties	Image
Bamboo	6 x 6	Recyclable, compostable, food contact material. Single use.	
Palm leaf 100% natural	11.5 x 11.5 x 1.5	Biodegradable, ecological and compostable. Well resistance to microwaves, ovens and freezers. Ideal for catering sector. Single use.	
Natural wheat pulp	Ø 23	Biodegradable, 100% compostable, Eco-friendly. It is recycled in the organic container. Microwave, oven and refrigerator safe. Ideal for catering sector. Single use.	

114

115 **2.3. Migration tests**

116 Although the temperature reached by the food in the microwave does not exceed 100 °C, these  
 117 dishes also they can be used in a conventional oven where the average temperature is around  
 118 180 °C. In accordance with Regulation (EU) No 10/2011 (COMMISSION, 2011), the time and  
 119 temperature conditions of 175 °C for 1 h were selected as the worst case scenario and  
 120 representative conditions of food heating when using this type of dishes in conventional oven or  
 121 microwave. Simulant E (Tenax® (poly (2,6-diphenyl-p-phenylene oxide))) was selected for the  
 122 migration tests. Before its use, Tenax® was previously cleaned according to the established  
 123 procedure by Vera et al. (2011). The amount of Tenax® (g) used in each test was calculated  
 124 based on the surface of contact (dm<sup>2</sup>), using a ratio of 4 g Tenax®/dm<sup>2</sup> according to the norm  
 125 UNE-EN 14338:2004.

126 To carry out the migration tests, 1 x 4 cm strips were cut from each of the three types of dishes  
 127 and placed on glass Petri dishes covered by an aluminum foil.

128 Following the ratio set in the above mentioned norm, 4 cm<sup>2</sup> of surface and 0.16 g of Tenax®  
 129 were used. Once the samples were prepared, they were covered with the glass lids of the Petri  
 130 dishes.

131 The extraction of volatile compounds trapped by Tenax<sup>®</sup> during the migration tests was carried  
132 out with ethanol. Once the migration test was over, the Petri dishes with the strips of material in  
133 contact with the simulant were removed from the oven, allowed to temperate for a few minutes,  
134 and then the Tenax<sup>®</sup> was transferred to 10 mL centrifuge vials. According to Vera et al. (2011)  
135 and Aznar et al. (2016), Tenax<sup>®</sup> samples were extracted consecutively twice with fractions of  
136 2.5 g and 2.0 g of absolute ethanol, gravimetrically controlled.  
137 For analysis by SPME-GC/MS, previous studies by Asensio et al. (2019), demonstrated that  
138 better results are obtained if the percentage of ethanol does not exceed 20%. Therefore, the  
139 extract collected in the 20 mL vial was diluted 5 times with MilliQ water until obtaining a 20%  
140 ethanol.

141

#### 142 **2.4. Migration study by SPME-GC/MS analysis**

143 Each diluted extract (20% EtOH) was analyzed by SPME-GC/MS with total immersion of the  
144 fiber into the simulant (Su et al., 2020). Two different fibers: DVB/CAR/PDMS fiber (50/30 µm)  
145 and PDMS fiber (100 µm) were tested. Asensio et al. (2019) showed that the best SPME  
146 conditions were extraction temperature 80 °C and extraction time 20 min. Stirring 2 min  
147 incubation time and 2 min desorption time were used. An amount of 2.0 g of sodium chloride  
148 (NaCl) was added to all samples.

149 GC/MS (Agilent 6890N with a MS 5975B mass spectrometer detector) coupled to the SPME  
150 system (CTC Analytics CombiPal autosampler) with a capillary column: HP-5MS (30 m × 0.25  
151 µm x 250 µm) was used. The oven program was 50 °C for 5 min, with rate of 10 °C/min up to  
152 300 °C, maintained 5 min. Data were acquired in SCAN mode ( $m/z = 50-600$ ). The identification  
153 of volatile compounds was carried out using the NIST Chemistry WebBook spectrum library  
154 present in the equipment software (> 85% automatically match).

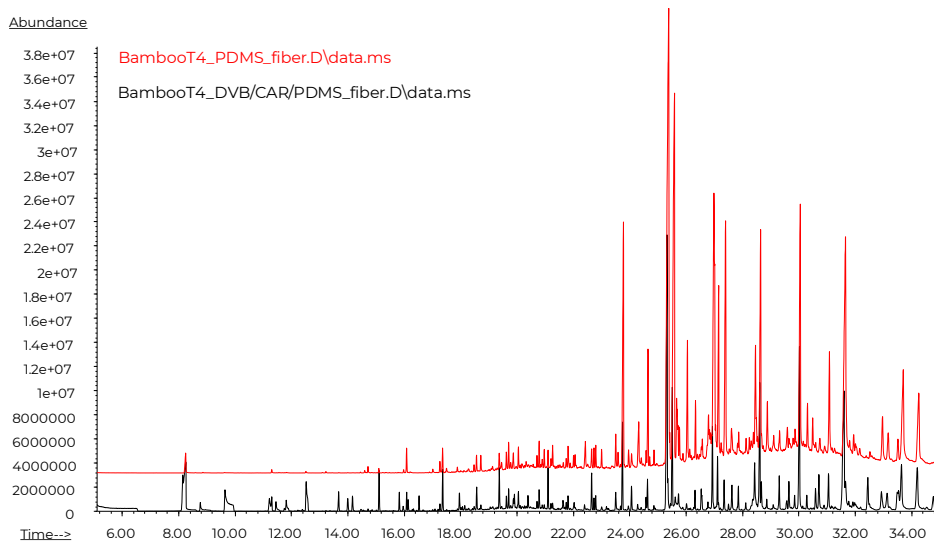
155 Kovats indices were determined to a correct tentative identification of the compounds, using a  
156 standard solution of n-alkanes (C10 to C30). For the quantification of the identified volatile  
157 compounds, calibration curves of the available standards were prepared, and the rest of the  
158 compounds of interest were semi-quantified according to standards with a similar structure or  
159 from the same family.

160

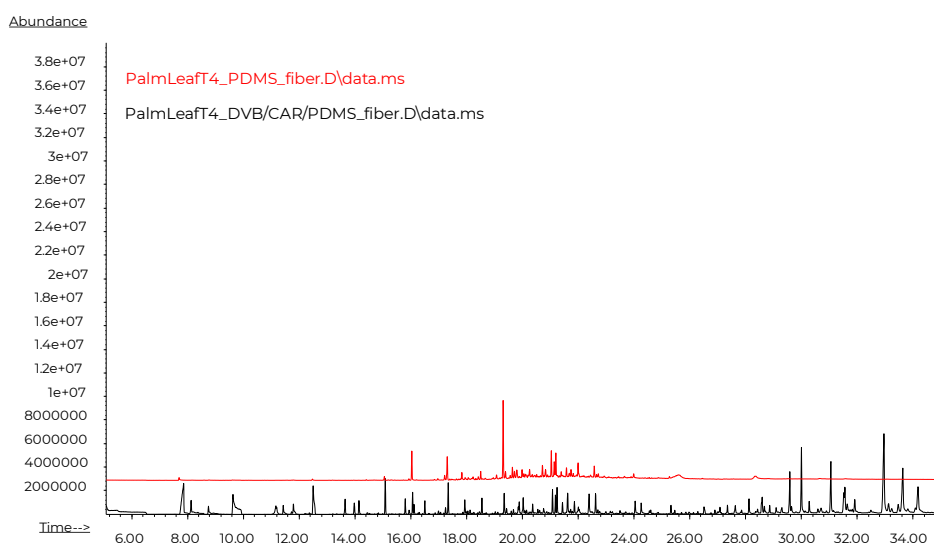
### 161 **3. Results and discussion**

#### 162 **3.1. SPME-GC/MS analysis**

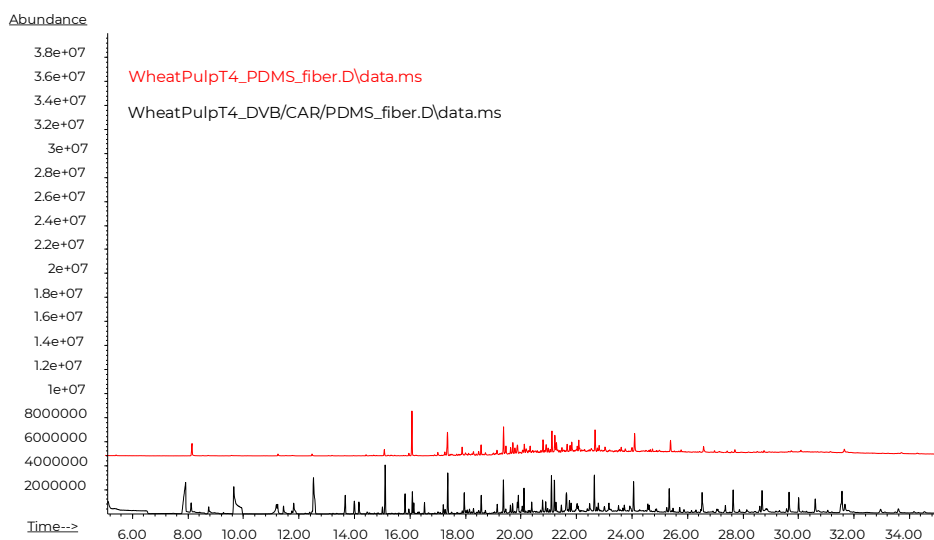
163 The chromatograms obtained from the migration tests, for the three types of dishes, are shown  
164 in Figure 1. The extracts were analysed by SPME-GC/MS using PDMS fiber and  
165 DVB/CAR/PDMS fiber.



166



167



168

169 Figure 1. Chromatograms obtained by SPME-GC/MS analysis with PDMS and DVB/CAR/PDMS  
 170 fibers of the migration test at 175 °C for the three dishes analyzed (bamboo, palm leaf and  
 171 wheat pulp).

172

173 As can be seen in Figure 1, the chromatographic profiles obtained with PDMS fiber for each of  
174 the three types of dishes are quite different, being the wheat pulp dish the one that shows  
175 compounds at very low concentration compared to the palm leaf and bamboo dishes. In  
176 contrast, using DVB/CAR/PDMS fiber, it can be seen that the chromatograms obtained are  
177 more similar, although, as in the case of the PDMS fiber, the wheat pulp dish is the one with the  
178 lowest migration of volatile compounds.

179 The presence of different volatile compounds was observed in all different dishes, using the two  
180 SPME fibers. Thus, in order to get the identification of as many volatile compounds as possible,  
181 the migration extracts of the three types of dishes were analyzed with both fibers.

182 The migration tests were used to determine specific levels of migration. The amount of a  
183 specific, identifiable substance that is transferred to food can be established from the data, and  
184 a risk assessment of the material can be performed. A risk assessment was conducted on the  
185 migrant compounds identified. Initially, the compounds were cross-checked versus the positive  
186 list provided in Regulation (EU) No 10/2011 (COMMISSION, 2011). The values recorded were  
187 then compared to their SML for plastic food contact material.

188 However, for analytes to which a toxicity value can be attributed, the threshold of toxicological  
189 concern (TTC) approach and Cramer classification, recommended by the European food safety  
190 authority (EFSA) (EFSA, 2012), is applied. Cramer is a theoretical approach and classifies the  
191 tentative toxicological potential of molecules into three toxicity classes (I–III) based on their  
192 chemical structure. Molecules identified in migration assays were assigned Cramer classes  
193 using Toxtree\_v3.1.0.1851® software, a flexible open-source software application predicting  
194 toxic effect of chemicals by applying decision tree approaches. Cramer classifies compounds  
195 based on their chemical structure into three categories: class I (low toxicity), class II (medium  
196 toxicity), and class III (high toxicity). Class I characterized by simple chemical structures, which  
197 are assigned a maximum estimated daily intake (EDI) of 1.80 mg/person/day. Class II having  
198 structures that are less innocuous than those from class I, and have a maximum EDI of 0.54  
199 mg/person/day. Finally, class III with a maximum EDI of 0.09 mg/person/day. Therefore, for  
200 European people eating 1 kg food per day, the SML based on the TTC approach will be as  
201 following:  $SML_{Class\ I} = 1.80\text{ mg/kg}$  of food/food simulant;  $SML_{Class\ II} = 0.54\text{ mg/kg}$  of food/food  
202 simulant;  $SML_{Class\ III} = 0.09\text{ mg/kg}$  of food/food simulant (PlasticsEurope, 2014; Boobis et al.,  
203 2017).

204 The confirmed and tentatively identified volatile compounds with the best matches found in the  
205 library search and their Kovats indices (KI) are listed in Table 2 for both fibers.

206 A total of 70 compounds were identified, respectively with both types of fibers in the three  
207 dishes under study (bamboo, palm leaf and wheat pulp). The bamboo dish was the one with the  
208 highest number of volatile migrants in both fibers, followed by the palm leaf dish. The one that  
209 released the least number of volatile compounds was the wheat pulp dish.

210

211

Table 2. Confirmed (\*) and tentatively identified (•) compounds by SPME-GC/MS with PDMS and DVB/CAR/PDMS fibers in migration tests.

R <sub>t</sub> (min)	Compounds	CAS	PDMS			DVB/CAR/PDMS			SML <sup>4</sup>	TTC	KI
			B <sup>1</sup>	PL <sup>2</sup>	WP <sup>3</sup>	B <sup>1</sup>	PL <sup>2</sup>	WP <sup>3</sup>			
13.21	dodecane*	112-40-3	•							I	1200
14.59	1-tridecene	2437-56-1	•			•				I	1293
14.70	tridecane*	629-50-5	•		•					I	1300
15.77	2,6,10-trimethyl-dodecane	3891-98-3	•							I	1378
15.59	2-methyltridecane	1560-96-9			•					I	1364
16.08	tetradecane*	629-59-4			•					I	1400
16.19	dodecanal	112-54-9	•							I	1408
17.26	1-pentadecene	13360-61-7	•	•		•	•	•		I	1491
17.49	tridecanal	10486-19-8	•							I	1509
18.71	tetradecanal	124-25-4		•	•	•	•	•		I	1610
19.60	1-heptadecene	6765-39-5	•		•	•	•	•		I	1689
19.85	pentadecanal	2765-11-9	•							I	1711
20.04	6,10,14-trimethyl-pentadecan-2-ol	69729-17-5				•	•	•		II	1728
20.69	(E)-3-octadecene	7206-19-1	•			•				I	1788
20.95	hexadecanal	629-80-1	•		•	•		•		I	1813
21.03	isopropyl myristate	110-27-0			•					I	1821
21.19	neophytadiene	504-96-1	•	•	•	•	•	•		I	1837
21.25	6,10,14-trimethyl-pentadecan-2-ona	502-69-2	•	•	•	•	•	•		II	1843
21.63	3,7,11,15-tetra methyl-2-hexadecen-1-ol	102608-53-7			•		•	•		I	1881
21.80	nonadecane*	629-92-5				•				I	1900
21.99	heptadecanal	629-90-3	•		•					I	1918
22.05	methyl palmitate*	112-39-0		•	•					I	1924
22.40	hexadecanoic acid*	57-10-3	•			•	•		< 60		1960
22.72	ethyl palmitate	628-97-7	•			•	•	•		I	1994
22.78	eicosane*	112-95-8	•			•					2000
22.99	octadecanal	638-66-4	•							I	2023

23.49	1-heneicosene	1599-68-4	•							2077
23.76	heneicosane*	629-94-7	•					•		2100
23.95	nonadecanal	17352-32-8	•							2127
24.31	octadecanoic acid*	57-11-4	•					•	< 60	2165
24.40	1-docosene	1599-67-3	•							2174
24.57	ethyl stearate	111-61-5	•					•		2193
24.64	docosane*	629-97-0	•					•		2200
25.34	(Z)-9-tricosene	27519-02-4	•					•		2278
25.54	tricosane*	638-67-5	•					•		2300
25.65	1,7-hexadecadiene	125110-62-5	•							2314
25.72	heneicosanal	51227-32-8						•		2325
25.98	4,8,12,16-tetramethyl-heptadecan -4-olide	96168-15-9						•		2358
26.30	tetracosane*	646-31-1						•		2400
26.94	(Z)-pentacos-12-ene	-	•							2476
26.97	1-pentacosene	16980-85-1	•					•		2480
26.99	glyceryl palmitate	542-44-9						•		2482
27.10	pentacosane*	629-62-9	•					•		2500
27.14	octyl palmitate	16958-85-3						•		2503
27.36	tricosanal	72934-02-2						•		2531
27.51	di-N-2-propyl-pentyl-phthalate	70910-37-1						•		2551
27.86	hexacosane*	630-01-3						•		2600
28.13	tetracosanal	57866-08-7	•					•		2634
28.46	1-heptacosene	15306-27-1	•					•		2684
28.65	heptacosane*	593-49-7	•					•		2700
29.12	tetracosanoic acid	557-59-5	•					•	< 60	2760
29.32	octacosane*	630-02-4	•					•		2800
29.57	squalene	111-02-4						•		2835
29.60	hexacosanal	26627-85-0	•					•		2839
29.87	1-nonacosene	18835-35-3	•							2876
30.04	nonacosane*	630-03-5	•					•		2900

30.31	heptacosanal	72934-03-3	•	•		•	•		I	2936
30.74	1-heptacosanol	2004-39-9				•			I	2993
31.08	octacosanal	22725-64-0	•	•	•	•		•	I	3040
31.52	hentriacontane*	630-04-6		•					I	3100
31.64	1-octacosanol	557-61-9	•	•		•	•	•	I	3116
32.47	dotriacontane*	544-85-4				•			I	3200
32.98	triacontanal	22725-63-9	•	•		•	•		I	3292
33.17	campesterol	474-62-4	•	•		•	•		III	3317
33.53	stigmasterol	83-48-7	•	•		•	•		II	3365
33.69	triacontyl acetate	41755-58-2	•	•	•		•	•	I	3387
34.26	clionasterol	83-47-6	•	•	•	•	•	•	III	3464

213 <sup>1</sup>B: bamboo, <sup>2</sup>PL: palm leaf, <sup>3</sup>WP: wheat pulp, <sup>4</sup>SML (Regulation (EU) No 10/2011)

214

215

216 As can be seen in Table 2, a large number of alkanes (from C<sub>12</sub> to C<sub>32</sub>), alkenes (from C<sub>13</sub> to  
217 C<sub>29</sub>) and aldehydes (from C<sub>12</sub> to C<sub>30</sub>) were extracted with both types of fibers. These groups are  
218 natural constituents of plants, and therefore of the matrix of biodishes (bamboo, palm leaf and  
219 wheat pulp). Although, the migration of these types of compounds in liquid food simulants and  
220 Tenax<sup>®</sup> from samples of plastic packaging materials (García-Ibarra et al., 2019) and expansive  
221 polystyrene containers (Song et al., 2019) has been studied. A series of non-aromatic  
222 hydrocarbons (1-tridecene, 2,6,10-trimethyldodecane, 1-pentadecen, 1-heptadecen, nonadecene,  
223 eicosane, heneicosane, docosane and pentacosane) and fatty oxygenated (dodecanal,  
224 tridecanal, tetradecanal, hexadecanal, isopropyl myristate and 6,10,14-trimethylpentadecan-2-  
225 one) have been identified present in food contact paperboards studied by Li et al., 2023.  
226 Their presence can also be due to the manufacturing process of the different types of FCM. In  
227 the case of bamboo, its presence can also be related to the degradation of the vegetable  
228 material, that is, oxidation reactions that can occur during the manufacturing process of the  
229 dishes, thus increasing the presence of these compounds and resulting in their later migration  
230 when the dish is heated (Osorio et al., 2020).

231 In this study, only three compounds: hexadecanoic acid (slip agent), octadecanoic acid  
232 (adhesive in food packaging) and tetracosanoic acid (additive) are listed in Regulation (EU) No  
233 10/2011 (COMMISSION, 2011). The selected food packaging materials haven't specific  
234 migration limits (SML) rather than these three compounds not having SML, what means that the  
235 applicable limit is < 60 mg/kg. These compounds are saturated fatty acids present in vegetable  
236 oils, and therefore their presence may be due to the vegetable composition of dishes as well as  
237 substances related to food packaging.

238 Isopropyl myristate (additive, plasticizer, lubricant), methyl palmitate (used as intermediate for  
239 detergents, emulsifiers, stabilizers, resins, lubricant, plasticizers and defoamer in food-contact  
240 coatings) and squalene (added to packaging materials during conventional mixing processes to  
241 thermoplastics) have been identified in migration extracts from plastic containers (García-Ibarra  
242 et al., 2019).

243 Eicosane was identified with both SPME fibers and only found in the migration extracts of the  
244 bamboo dishes. The presence of eicosane may be related to food contact materials as it is used  
245 as an indirect additive.

246 In the three types of dishes, and with the two SPME fibers used, the presence of 6,10,14-  
247 trimethyl-12-pentadecan-2-one has been identified in the migration extracts. This compound is  
248 classified as Cramer class II. It is a volatile compound that both wood and bark of plants can  
249 release when heated at high temperatures (Mastelic et al., 2006). In migration studies carried  
250 out by Asensio et al. (2020) with liquid simulants, this compound was already identified in the  
251 simulant D2 (95% ethanol) after the migration tests with wheat pulp dishes.

252 Three phytosterols, stigmasterol, campesterol and clionasterol were detected in migration  
253 extracts. Stigmasterol and campesterol were found in bamboo and palm leaf dishes with both  
254 types of fibers; and the clionasterol was present in the three types of dishes. Phytosterols are

255 among the bioactive compounds naturally present in palm vegetable oils and their by-products  
 256 or derivatives (Jalani et al., 2020) and foods (García-Llatas et al., 2021).

257 Although it is true that in SPME there is a competitive adsorption between the compounds, with  
 258 the risk of artifact formation during high-temperature desorption, leading to certain limitations in  
 259 quantitative. Due to the high number of simple aldehydes identified in the migration extracts, it  
 260 was decided to use a calibration with a nonanal standard for the tentative semi-quantification of  
 261 all the aldehydes present. In the case of saturated fatty acids and their corresponding ethyl and  
 262 methyl esters, they were tentative semi-quantified using hexadecanoic acid, octadecanoic acid  
 263 and methyl palmitate as calibration standards.

264 These standards were analyzed using the two selected SPME fibers. Correlation coefficients,  
 265 linear range, and limit of detection (LOD) and limit of quantification (LOQ) for the available  
 266 standards with both fibers are shown in Table 3.

267

268 Table 3. Correlation coefficients, linear range, and LOD and LOQ for the available standards.

PDMS fiber

Compounds	Correlation coefficient ( $r^2$ )	Linear range ( $\mu\text{g/kg}$ )	LOD ( $\mu\text{g/kg}$ )	LOQ ( $\mu\text{g/kg}$ )
nonanal	0.9977	28.1 – 491.3	14.68	28.1
hexadecanoic acid	0.9990	3.0 – 53.1	0.36	3.0
methyl palmitate	0.9964	2.7 – 48.4	0.68	2.7
octadecanoic acid	0.9980	3.2 – 56.3	0.54	3.2

DVB/CAR/PDMS fiber

Compounds	Correlation coefficient ( $r^2$ )	Linear range ( $\mu\text{g/kg}$ )	LOD ( $\mu\text{g/kg}$ )	LOQ ( $\mu\text{g/kg}$ )
nonanal	1.0000	114.1 – 475.8	13.98	114.1
methyl palmitate	0.9955	3.2 – 46.9	0.26	3.2
octadecanoic acid	0.9929	9.1 – 54.5	4.91	9.1

269

270 Table 4a and 4b show the real and tentative concentration values, expressed as mg/kg food  
 271 simulant (Tenax<sup>®</sup>) and mg/dm<sup>2</sup> with both types of fiber (PDMS and DVB/CAR/PDMS).

272

273 Table 4a. Compounds quantified and semi-quantified, expressed as mg/kg Tenax<sup>®</sup> and mg/dm<sup>2</sup>,  
 274 analyzed with PDMS fiber.

Compounds	Bamboo (mg/Tenax <sup>®</sup> )	Palm leaf (mg/Tenax <sup>®</sup> )	Wheat pulp (mg/Tenax <sup>®</sup> )
dodecanal <sup>a</sup>	1 ± 0.1	-	-
tridecanal <sup>a</sup>	4 ± 0.3	-	-
tetradecanal <sup>a</sup>	-	1.5 ± 0.11	3 ± 0.2
pentadecanal <sup>a</sup>	23 ± 3	-	-

hexadecanal <sup>a</sup>	16 ± 1.5	-	5 ± 0.7
heptadecanal <sup>a</sup>	10 ± 1	-	5 ± 0.9
methyl palmitate	-	0.19 ± 0.05	-
hexadecanoic acid	2 ± 0.2	-	-
ethyl palmitate <sup>b</sup>	0.19 ± 0.02	-	-
octadecanal <sup>a</sup>	16 ± 2	-	-
octadecanoic acid	5 ± 0.8	-	-
ethyl stearate <sup>b</sup>	0.18 ± 0.04	-	-
heneicosanal <sup>a</sup>	-	-	-
octyl palmitate <sup>b</sup>	-	-	-
tricosanal <sup>a</sup>	-	-	-
tetracosanal <sup>a</sup>	17 ± 2	-	-
tetracosanoic acid <sup>c</sup>	1 ± 0.34	-	-
hexacosanal <sup>a</sup>	36 ± 3	-	-
heptacosanal <sup>a</sup>	54 ± 2	-	-
octacosanal <sup>a</sup>	144 ± 29	-	-
triacontanal <sup>a</sup>	82 ± 2	-	-
Total	408.37	1.69	13.00

275 *Semi-quantified as (a)nonanal; (b)methyl palmitate and (c)hexadecanoic acid.*

276

277 Table 4b. Compounds quantified and semi-quantified, expressed as mg/kg Tenax<sup>®</sup>, analyzed  
278 with DVB/CAR/PDMS fiber.

Compounds	Bamboo (mg/Tenax <sup>®</sup> )	Palm leaf (mg/Tenax <sup>®</sup> )	Wheat pulp (mg/Tenax <sup>®</sup> )
dodecanal <sup>a</sup>	-	-	-
tridecanal <sup>a</sup>	-	-	-
tetradecanal <sup>a</sup>	6 ± 0.3	6 ± 0.9	6 ± 0.5
pentadecanal <sup>a</sup>	-	-	-
hexadecanal <sup>a</sup>	6 ± 0.5	-	6 ± 0.5
heptadecanal <sup>a</sup>	-	-	5 ± 0.98
methyl palmitate	-	-	-
hexadecanoic acid	-	13 ± 2	-
ethyl palmitate <sup>b</sup>	-	0.39 ± 0.05	0.28 ± 0.08
octadecanal <sup>a</sup>	-	-	-
octadecanoic acid	2 ± 0.2	3 ± 0.88	-
ethyl stearate <sup>b</sup>	0.57 ± 0.09	0.29 ± 0.05	-
heneicosanal <sup>a</sup>	-	-	6 ± 1.00
octyl palmitate <sup>b</sup>	-	-	0.3 ± 0.02
tricosanal <sup>a</sup>	13 ± 4	-	-
tetracosanal <sup>a</sup>	-	-	-

tetracosanoic acid <sup>c</sup>	6 ± 0.7	-	-
hexacosanal <sup>a</sup>	-	-	-
heptacosanal <sup>a</sup>	9 ± 1.8	-	-
octacosanal <sup>a</sup>	126 ± 14	-	-
triacontanal <sup>a</sup>	52 ± 2	-	-
<b>Total</b>	<b>220.57</b>	<b>22.68</b>	<b>23.58</b>

*Semi-quantified as <sup>(a)</sup>nonanal; <sup>(b)</sup>methyl palmitate and <sup>(c)</sup>hexadecanoic acid.*

279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312

The results obtained from show that, once again, the highest concentration of migrating volatile compounds comes from bamboo, followed by palm leaf and finally those made of wheat pulp dishes. The same behavior was observed in the chromatographic profiles already mentioned above. In the case of bamboo dishes, with both types of fiber, the migration is higher (408.37 and 220.57 mg/kg Tenax<sup>®</sup>, respectively) compared to palm leaf and wheat pulp dishes, where the opposite was found. In any case, the migration is low on the palm leaf dish (1.69 mg/kg Tenax<sup>®</sup>) and wheat pulp dish (13.00 mg/kg Tenax<sup>®</sup>), in both cases with the PDMS fiber. This behavior was also observed when the migration of non-volatile compounds was studied for these three types of natural vegetable materials (Wrona, 2023). Furthermore, previous studies carried out with this type of food contact materials (wheat pulp and wood dishes) in contact with liquid simulants showed that they are safe with respect to the volatile substances they release, under the intended conditions of use (Asensio, 2020). A review by Guan et al., 2023 refers to IAS analyses in bamboo and wooden FCM is generally not a problem, but has proven to be more challenging for NIAS. Due to a complex mixture of substances contained in plant-based materials, there is a need to improve databases for non-target screening of such chemicals. Three compounds, hexadecanoic acid, octadecanoic acid and tetracosanoic acid, are well below the SML according to Regulation (EU) No 10/2011 and its amendments (COMMISSION, 2011). The results obtained with the PDMS fiber showed that the three saturated fatty acids (hexadecanoic, octadecanoic and tetracosanoic) were found in the migration extracts of bamboo dishes, within a range between 1.06 and 5.02 mg/kg Tenax<sup>®</sup>. Furthermore, with DVB/CAR/PDMS fiber, three saturated fatty acids were found to migrate from bamboo and palm leaf dishes, from 2.08 mg/kg Tenax<sup>®</sup> for octadecanoic and tetracosanoic acid to 13.11 mg/kg Tenax<sup>®</sup> for hexadecanoic acid in palm leaf dishes. In all cases, the values were well below the maximum limit of 60 mg/kg for food contact plastic material. Methyl palmitate was identified in palm leaf and wheat pulp dishes with similar values in both (approx. 0.20 mg/kg Tenax<sup>®</sup>). Vapenká et al. (2016) and Vavrouš et al. (2016) also identified methyl palmitate as contaminant present in paper-based packaging materials (fiber matrix). The specific migration of non-listed compounds (not authorized) in the Regulation (EU) No 10/2011, for plastic materials, must be less than 10 µg/kg (COMMISSION, 2011). As can be seen in Tables 4a and 4b, the migration of all aldehydes exceed this value (for plastic food contact materials), in bamboo, palm leaf and wheat pulp dishes. This behavior was already

313 observed when the wheat pulp dishes were studied in contact with liquid simulants (Asensio et  
314 al., 2020), although in this study the concentrations found were much lower, of the order of  
315  $\mu\text{g}/\text{kg}$  compared to the  $\text{mg}/\text{kg}$  semi-quantified in these materials in contact with solid simulant  
316 (Tenax<sup>®</sup>) at high temperature (175 °C). Although this behavior may be influenced by the fact  
317 that Tenax<sup>®</sup> can show higher migrations than solid food (Otokesh et al., 2020).  
318 However, these compounds are tentative classified as Cramer class I and therefore a human  
319 exposure threshold in Europe is assigned to 1.8  $\text{mg}/\text{kg}$  of food. In this case, almost all the semi-  
320 quantified aldehydes exceeded this value. The explanation for the presence of these aldehydes  
321 in the migration extract can be attributed to the degradation of the vegetable material when  
322 heating the dishes at 175 °C for 1 h. As aldehydes have usually strong odours, their migration  
323 will likely affect as well the organoleptic characteristics of the food in contact with these dishes.  
324 This represents the real situation when such natural materials are used in conventional oven.  
325 As can be seen in Table 4a and 4b, none of the quantified and semi-quantified volatile  
326 compounds exceeds the 10  $\text{mg}/\text{dm}^2$  established for plastic food contact materials according in  
327 Regulation (EU) No 10/2011 (COMMISSION, 2011).

328

#### 329 **4. Conclusions**

330 After carrying out the migration tests with Tenax<sup>®</sup> as a food simulant under the established  
331 conditions (175 °C for 1 hour), the three food contact bio-materials analyzed (bamboo, palm leaf  
332 and wheat pulp) showed differences between them, both in the number and amount of volatile  
333 compounds identified and in the chromatographic analysis. The wheat pulp dish was the food  
334 contact natural material in which the least amount of volatile compounds migrated and the  
335 bamboo dish was the food contact bio-material in which the greatest number of volatile  
336 compounds migrated. It is important to note that some of the volatile compounds identified  
337 (mainly aldehydes) could affect the flavor and quality of foods; it would be interesting to  
338 continue studying the possible organoleptic effect.

339 In accordance with the only existing legislation (COMMISSION, 2011), which considers plastic  
340 materials as FCM, the use of this type of dishes made with natural vegetable materials in  
341 contact with food does not present a risk to the consumer due to the migration of volatile  
342 compounds when used at high temperatures, in accordance with the conditions of use set by  
343 the manufacturer. However, given the increase in the use of this type of dishes in contact with  
344 food, as an alternative to the use of plastic materials, it is necessary to continue the migration  
345 studies of more similar vegetable materials.

346

#### 347 **Acknowledgements**

348 The authors thank the funding provided by the project RTI2018-097805-B-I00 from the Spanish  
349 Ministry of Science and Innovations and by Gobierno de Aragón and Fondo Social Europeo to  
350 the GUIA T53\_23R.

351 **5. References**

- 352 Asensio, E., Peiró, T., & Nerín, C. (2019). Determination the set-off migration of ink in  
353 cardboard-cups used in coffee vending machines. *Food and Chemical Toxicology*, 130, 61–67.  
354 <https://doi.org/10.1016/j.fct.2019.05.022>
- 355 Asensio, E., Montañés, L., & Nerín, C (2020). Migration of volatile compounds from natural  
356 biomaterials and their safety evaluation as food contact materials. *Food and Chemical*  
357 *Toxicology*, 142, Article e111457. <https://doi.org/10.1016/j.fct.2020.111457>
- 358 Aznar, M., Alfaro, P., Nerín, C., Jones, E., & Riches, E. (2016). Progress in mass spectroscopy  
359 for the analysis of set-off phenomena in plastic food packaging. *Journal of chromatography A*,  
360 1543, 124–133. <https://doi.org/10.1016/j.chroma.2016.05.032>
- 361 Berthet, M.A., Angellier-Coussy, H., Chea, V., Guillard, V., Gastaldi, E., & Gontard, N. (2015).  
362 Sustainable food packaging: Valorising wheat straw fibers for tuning PHBV-based composites  
363 properties. *Composites Part A: Applied Science and Manufacturing*, 72, 139–147.  
364 <https://doi.org/10.1016/j.compositesa.2015.02.006>
- 365 Boobis, A.; Brown, P.; Cronin, M. T. D.; Edwards, J.; Galli, C. L.; Goodman, J.; Jacobs, A.;  
366 Kirkland, D., Luijten, M., Marsaux, C., Martin, M., Yang, C., & Hollnagel, H. M. (2017). Origin of  
367 the TTC values for compounds that are genotoxic and/or carcinogenic and an approach for their  
368 re-evaluation. *Critical Reviews in Toxicology*, 47(8), 710-732.  
369 <https://doi.org/10.1080/10408444.2017.1318822>
- 370 COMMISSION, T. E. (2011). Commission Regulation (EU) No 10/2011 of 14 January 2011 on  
371 plastic materials and articles intended to come into contact with food. *Official Journal of the*  
372 *European Union*.
- 373 EFSA Scientific Committee. (2012). Scientific Opinion on Exploring options for providing advice  
374 about possible human health risks based on the concept of Threshold of Toxicological Concern  
375 (TTC). *EFSA Journal*, 10(7), Article e2750. <https://doi.org/10.2903/j.efsa.2012.2750>
- 376 García-Ibarra, V., Rodríguez-Bernaldo de Quirós, A., Paseiro-Losada, P., & Sendón, R. (2019).  
377 Non-target analysis of intentionally and non intentionally added substances from plastic  
378 packaging materials and their migration into food simulants. *Food Packaging and Shelf Life*, 21,  
379 100325. <https://doi.org/10.1016/j.fpsl.2019.100325>
- 380 García-Llatas, G., Alegría, A., Barberá, R., & Cilla, A. (2021). Current methodologies for  
381 phytosterol analysis in foods. *Microchemical Journal*, 168, Article e106377.  
382 <https://doi.org/10.1016/j.microc.2021.106377>
- 383 Guan, M-Y., Zhong, H-N., Wang, Z-W., Yu, W-W. & Hu, C-Y. (2023). Chemical contaminants  
384 from food contact materials and articles made from or containing wood and bamboo – a review.  
385 *Food Additives & Contaminants: Part A*, 40 (3). <https://doi.org/10.1080/19440049.2023.2167003>
- 386 Jalani, N. F., Noorshamsiana, A. W., Hasamudin, W., Hassan, K., Hayawin, Z.N., & Ibrahim, M.  
387 F. (2020). Extraction and purification of phytosterols mixture from palm fatty acid distillate  
388 (PFAD) using multistage extraction processes. *Journal of Oil Palm Research*, 33(1), 93-102.  
389 <http://doi.org/10.21894/jopr.2020.0067>

390 Leeman, W., & Krul, L. (2015). Non-intentionally added substances in food contact materials:  
391 How to ensure consumer safety. *Current Opinion in Food Science*, 6, 33-37.  
392 <https://doi.org/10.1016/j.cofs.2015.11.003>

393 Li, H., Chen, L., Wu, X., Wu, S., Su, Q-Z., Dong, B., Li, D., Ma, T., Zhong, H., Wang, X., Zheng,  
394 J. & Nerín, C. (2023). Characterization of volatile organic compounds in food contact  
395 paperboards and elucidation of their potential origins from the perspective of the raw materials.  
396 *Food Packaging and Shelf Life*, 37, Article e101062. <https://doi.org/10.1016/j.fpsl.2023.101062>

397 Mastelic, J., Jerkovic, I., & Mesic, M. (2006). Volatile constituents from flowers, leaves, bark and  
398 wood of *Prunus mahaleb* L. *Flavour Fragrance Journal*, 21, 306–313.  
399 <https://doi.org/10.1002/ffj.1596>

400 Nerín, C., Alfaro, P., Aznar, M., & Domeño, C. (2013). The Challenge of identifying the non  
401 intentionally added substances (NIAS) from food packaging materials. A review. *Analytica*  
402 *Chimica Acta*, 775, 14–24. <https://doi.org/10.1016/j.aca.2013.02.028>

403 Nerín, C., Faust, B., Gude, T., Lesueur, C., Simat, T., Stoermer, A., Van Hoek, E., & Peter O.  
404 (2022). Guidance in selecting analytical techniques for identification and quantification of non-  
405 intentionally added substances (NIAS) in food contact materials (FCMs). *Food Additives &*  
406 *Contaminants: Part A*, 39, 620–643. <https://doi.org/10.1080/19440049.2021.2012599>

407 Norm UNE-EN 14338:2004. Paper and board intended to come into contact with foodstuffs -  
408 Conditions for determination of migration from paper and board using modified polyphenylene  
409 oxide (MPPO) as a simulant. <https://www.en-standard.eu/>

410 Okokpujie, I. P., Akinlabi, E. T., & Fayomi, O. O. (2020). Assessing the policy issues relating to  
411 the use of bamboo in the construction industry in Nigeria. *Heliyon*, 6(5), Article e04042.  
412 <https://doi.org/10.1016/j.heliyon.2020.e04042>

413 Osorio, J., Aznar, M., Nerín, C., Birse, N., Elliott, C., & Chevallier, O. (2020). Ambient mass  
414 spectrometry as a tool for a rapid and simultaneous determination of migrants coming from a  
415 bamboo-based biopolymer packaging. *Journal of Hazardous Materials*, 398, Article e122891.  
416 <https://doi.org/10.1016/j.jhazmat.2020.122891>

417 Otoukesh, M., Vera, P., Wrona, M., Nerín, C. & Es'haghi, Z. (2020). Migration of  
418 dihydroxyalkylamines from polypropylene coffee capsules to Tenax® and coffee by salt-  
419 assisted liquid–liquid extraction and liquid chromatography–mass spectrometry. *Food*  
420 *Chemistry*, 321, Article e126720. <https://doi.org/10.1016/j.foodchem.2020.126720>

421 Parliament, E., & Union, C.o.t. E. (2004). Regulation (EC) No 1935/2004 of the European  
422 Parliament and of the Council of 27 October 2004 on materials and articles intended to come  
423 into contact with food and repealing Directives 80/590/EEC and 89/109/ EEC. *Official Journal of*  
424 *the European Union*.

425 PlasticsEurope (2014). Risk Assessment of non-listed substances (NLS) and non-intentionally  
426 added substances (NIAS) under Article 19 of Commission Regulation (EU) No 10/2011 of 14  
427 January 2011 on plastic materials and articles intended to come into contact with food.

428 Retrieved from <https://plasticseurope.org/wp-content/uploads/2021/11/risk-assesment-of-non->  
429 [listed-substances-and-non-assesed-substances.pdf](https://plasticseurope.org/wp-content/uploads/2021/11/risk-assesment-of-non-listed-substances-and-non-assesed-substances.pdf). Accessed August 2, 2024.

430 Sánchez, R., Espinosa, E., Domínguez-Robles, J., Loaiza, J. M., & Rodríguez, A. (2016).  
431 Isolation and characterization of lignocellulose nanofibers from different wheat straw pulps.  
432 *International Journal of Biological Macromolecules*, 92, 1025–1033.  
433 <https://doi.org/10.1016/j.ijbiomac.2016.08.019>

434 Song, X-C., Wrona, M., Nerín, C., Lin, Q-B., & Zhong, H-N. (2019). Volatile non-intentionally  
435 added substances (NIAS) identified in recycled expanded polystyrene containers and their  
436 migration into food simulants. *Food Packaging and Shelf Life*, 20, Article e100318.  
437 <https://doi.org/10.1016/j.fpsl.2019.100318>

438 Su, Q., Vera, P., & Nerín, C. (2020). Direct immersion-solid-phase micro-extraction coupled to  
439 gas chromatography - mass spectrometry and response surface methodology for non-target  
440 screening of semi-volatile migrants from food contact materials. *Analytical Chemistry*, 92(7),  
441 5577-5584. <https://doi.org/10.1021/acs.analchem.0c00532>

442 Vapenká, L., Vavrouš, A., Votavová, L., Kejlová, K., Dobiáš, J., & Sosnovcová, J. (2016).  
443 Contaminants in the paper-based food packaging materials used in the Czech Republic. *Journal*  
444 *of Food and Nutrition Research*, 55(4), 361–373. Retrieved from <http://www.vup.sk>. Accessed  
445 August 2, 2024.

446 Vavrouš, A., Vapenká, L., Sosnovcová, J., Kejlová, K., Vrbík, K., & Jírová, D. (2016). Method for  
447 analysis of 68 organic contaminants in food contact paper using gas and liquid chromatography  
448 coupled with tandem mass spectrometry. *Food Control*, 60, Article e221e229.  
449 <https://doi.org/10.1016/j.foodcont.2015.07.043>

450 Vera, P., Aznar, M., Mercea, P. & Nerín, C. (2011). Study of hotmelt adhesives used in food  
451 packaging multilayer laminates. Evaluation of the main factors affecting migration to food.  
452 *Journal of Materials Chemistry*, 21, 420–431, 2011. <https://doi.org/10.1039/C0JM02183K>

453 Wrona, M., Román, A., Song, X-C., Nerín, C., Dreolin, N., Goshawk, J. & Asensio, E. (2023).  
454 Ultra-high performance liquid chromatography coupled to ion mobility quadrupole time-of-flight  
455 mass spectrometry for the identification of non-volatile compounds migrating from 'natural'  
456 dishes. *Journal of Chromatography A*, 1691, Article e463836.  
457 <https://doi.org/10.1016/j.chroma.2023.463836>

458 Xie, X., Zhou, Z., & Yan, Y. (2019). Flexural properties and impact behaviour analysis of  
459 bamboo cellulosic fibers filled cement based composites. *Construction and Building Materials*,  
460 220, 403–414. <https://doi.org/10.1016/j.conbuildmat.2019.06.029>

461 Xu, C., Zhu, S., Xing, C., Li, D., Zhu, N., & Zhou, H. (2015). Isolation and properties of cellulose  
462 nanofibrils from Coconut Palm Petioles by different mechanical process. *PLoS ONE*, 10(4),  
463 Article e0122123. <https://doi.org/10.1371/journal.pone.0122123>