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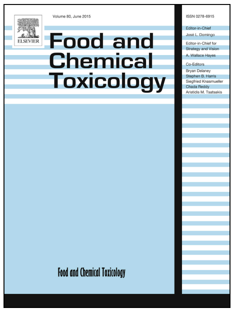

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Migration of volatile compounds from natural biomaterials and their safety evaluation as food contact materials

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Abstract

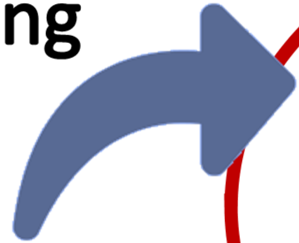
The concern for environmental conservation is increasing, and a very important factor to consider is the search for alternatives to the use of plastics in the food packaging industry. A good option is the manufacture of containers of biodegradable materials, such as the so-called biomaterials made of vegetable fibre such as wheat, wood, bamboo or palm leaf pulp. The migration of compounds from food packaging can cause alterations in food safety and acceptability. Therefore, their control through studies of specific migration is definitely important in the food industry. Specific migration has been studied in two types of dishes (wheat pulp and wood) in contact with three liquid simulants (ethanol 10%, acetic acid 3% and ethanol 95%). The analysis of migration extracts have been carried out by solid-phase microextraction coupled to gas chromatography (SPME-GC-MS) in the most suitable working conditions. In addition, those identified compounds considered of interest according to existing legislation have been quantified in order to assess whether exceed or not the migration limits established for some of them. The results obtained show that the quantified compounds are well below the specific migration limits (SML) set by the legislation, thereby showing the safety in use of this type of biodegradable dishes.

Keywords: biomaterial; specific migration; food safety; food packaging; biodegradable packaging.

Sustainable food packaging

Wood dishes

Wheat pulp dishes



	Compounds	RT (min)	CAS number	SML (mg/kg)	NOAEL (mg/kg bw/d)	TTC (class)	Origin or use categorization[a]
1	1,3,5-trimethylbenzene	8.99	108-67-8			I	adhesive
2	2-pentylfuran	9.50	3777-69-3		25.6		cereal
3	1-decyne	10.20	764-93-2			III	-
4	2-ethyl,1-hexanol[b]	10.28	104-76-7	30			adhesive/food contact/manufacturing paper
5	benzyl alcohol[b]	10.68	100-51-6	_[c]			adhesive/food contact/manufacturing paper
6	nonanal[b]	11.71	124-19-6			I	food contact
7	levoglucosenone	12.04	37112-31-5			III	wood/cereal
8	naphthalene	13.12	91-20-3			I	manufacturing plastics
9	4-allylanisole[b]	13.33	140-67-0		560		food contact/wood
10	decanal[b]	13.38	112-31-2			I	food contact
11	1,2,3,4-tetrahydro-1,1,6-trimethyl naphthalene	13.57	475-03-6			I	food industry
12	nonanoic acid	14.35	112-05-0		1500		adhesive/food contact
13	1-decanol	14.38	112-30-1			I	adhesive
14	2-undecanone	14.70	112-12-9			II	food contact
15	phthalic anhydride	15.04	85-44-9	_[c]			adhesive/food contact
16	2-undecenal	15.69	2463-77-6			I	-
17	trimethyllevoglucosan	16.03	2951-86-2			III	wood/cereal
18	ethyl decanoate	16.10	110-38-3			I	food contact
19	3-methyl-2-butenyl benzene	16.36	4489-84-3			I	-
20	6,10-dimethylundeca-5,9-dien-2-one	16.88	3796-70-1			I	food contact/adhesive
21	1-dodecanol	17.13	112-53-8		2000		manufacturing paper/food contact
22	tridecanal	17.59	10486-19-8			I	-
23	2,6-ditert-butyl-4-methylphenol[b]	17.63	128-37-0	3			adhesive/food contact/food service/paper/antioxidant
24	dodecanoic acid	18.17	143-07-7	_[c]			food contact/adhesive
25	ethyl dodecanoate	18.57	106-33-2			I	food contact
26	hexadecane	18.64	544-76-3			I	-
27	2,2,4-trimethyl-1,3-pentanedioldiisobutyrate[b]	18.67	6846-50-0	5			food contact
28	tetradecanal	18.82	124-25-4			I	food contact
29	decyl dodecanoate	19.16	1654-86-0			I	-

Regulation (EU) No. 10/2011

Simulant A (10% EtOH)

Simulant B (3% acetic acid)

Simulant D2 (95% EtOH)

SPME-GC-MS

Migration study

Migration of volatile compounds from natural biomaterials and their safety evaluation as food contact materials

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Abstract

The concern for environmental conservation is increasing, and a very important factor to consider is the search for alternatives to the use of plastics in the food packaging industry. A good option is the manufacture of containers of biodegradable materials, such as the so-called biomaterials made of vegetable fibre such as wheat, wood, bamboo or palm leaf pulp. The migration of compounds from food packaging can cause alterations in food safety and acceptability. Therefore, their control through studies of specific migration is definitely important in the food industry. Specific migration has been studied in two types of dishes (wheat pulp and wood) in contact with three liquid simulants (ethanol 10%, acetic acid 3% and ethanol 95%). The analysis of migration extracts have been carried out by solid-phase microextraction coupled to gas chromatography (SPME-GC-MS) in the most suitable working conditions. In addition, those identified compounds considered of interest according to existing legislation have been quantified in order to assess whether exceed or not the migration limits established for some of them. The results obtained show that the quantified compounds are well below the specific migration limits (SML) set by the legislation, thereby showing the safety in use of this type of biodegradable dishes.

Keywords: biomaterial; specific migration; food safety; food packaging; biodegradable packaging.

1. Introduction

During the last years, we have witnessed growing interest in the development of more environmentally friendly new materials as an alternative to conventional petroleum-derived materials. Among all the environmentally friendly alternative materials, products made from vegetal-fibre have received special attention. Nevertheless, few studies concerning the safety assessment of food packaging made of biodegradable materials by migration testing have been reported in the literature.

This environmental concern has increased interest in the development of sustainable food packaging, made either from recycled materials or from renewable or compostable sources. In these cases, the challenge is to ensure that they maintain their barrier properties and other functionalities that comply with the conservation, quality, safety and logistics needs required by industry and distribution, as well as the convenience and practicality in use and waste management demanded by the consumers (Calva-Estrada et al., 2019).

The current panorama shows a high consumption of plastics, so it seeks to replace these plastics used in a large number of containers, by new materials for food packaging. A very interesting option, which is available in the market, are the called ecological or biodegradable containers (biomaterials). These are biomaterials, such as wood, wheat pulp, bamboo or palm leaf, with which containers are prepared, mostly disposable, which are manufactured under 100% natural and "chemical-free" processes. The companies that supply them emphasize the chemical-free characteristics. Wood-based products have received great attention in a wide variety of fields. Hemicellulose-based barriers have been reported to display resistance against oil, grease, aroma and oxygen. Moreover, hydrophilic hemicelluloses offer promising barrier properties, and are easily modified (Helanto et al., 2019).

From the point of view of food safety, it is important to control these new materials available in the market for consumers use and to verify that no dangerous substance can migrate in quantities that are harmful to the health of consumers. These materials do not have a specific regulation, but the Regulation 1935/2004/CE applies to any FCM and therefore, it is important to study the substances that can be transferred from the container to the food in contact with them.

The increasing use of disposable dishes to dispense fast food or to serve food in events supplied by catering has created a market of new biomaterials. The demand for this type of dishes as an ecological and sustainable alternative, compared to the use of plastic materials, implies their study to ensure their safety.

In this work the specific migration from a series of dishes of new biomaterials (wood and wheat pulp) intended for food contact have been studied. The experiments were carried out with liquid simulants under suitable conditions of time and temperature depending on their intended use. All migrants found were identified and quantified.

2. Material and methods

2.1. Chemicals and analytical standards

Analytical standards used for quantification were bought in Sigma-Aldrich (Barcelona, Spain): 2-ethyl, 1-hexanol (CAS 104-76-7); benzyl alcohol (100-51-6), nonanal (CAS 124-19-6); 4-allylanisole (CAS 140-67-0); decanal (CAS 12-31-2); butylated hydroxytoluene (CAS 128-37-0); 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (CAS 6846-50-0); 2,6-diisopropyl naphthalene (CAS 24157-81-1); diisobutyl phthalate (CAS 84-69-5); hexadecanoic acid (CAS 57-10-3); dibutyl phthalate (CAS 84-74-2) erucamide (112-84-5) and butyl benzyl phthalate as internal standard(CAS 85-68-7). Ethanol was purchased from Scharlab (Madrid, Spain) and sodium chloride from Panreac (Barcelona, Spain).

All stocks solutions of the analytical standards were prepared at a concentration of 1000 •g/g in 20% ethanol and appropriate dilutions were made as required. 10 •L of an internal standard solution (1282.14 •g/g) were added to all working solutions and samples. All solutions and calibrants were under gravimetric control.

2.2. Samples

For the development of this study, two different types of dishes (wheat pulp and wood) available in the market for use in catering services were selected (Figure 1).In both cases these biomaterials were promoted for contact with any kind of foodstuff even at high temperature, up to 170 ºC (case of wheat pulp dishes).

2.3. Migration tests

As food contact materials, new biomaterials (wheat pulp, wood, bamboo...) are not harmonized in European legislation. The general requirements established by the frame Regulation (EC) No. 1935/2004 apply to any food contact material (FCM): they should not transfer their constituent to foodstuffs in quantities that could endanger human health or bring about an unacceptable change in the composition of the foodstuffs or a deterioration in the sensory characteristics. Thus, for the safety evaluation of of new biomaterials in contact with food, migration tests are required. In absence of specific recommendations for this purpose, the food simulants under the conditions established for plastics in contact with food (Regulation (EU) No. 10/2011) have been applied.

In accordance with Annex III of Regulation (EU) 10/2011, when studying a new material for use in contact with any kind of foodstuff, three simulants must be used: 10% ethanol (simulant A), 3% acetic acid (simulant B) and 95% ethanol (simulant D2). To carry out the migration tests, the ratio 6 dm^2/kg between the surface of the container and the amount of simulant must be met. Specific migration values will be expressed in mg/kg. According to Chapter

2.1.3 of Regulation (EU) No. 10/2011, 2 h at 70 °C were selected as contact conditions with simulants A and B.

During the study, the document Technical guidelines for compliance testing (JRC Science and Policy Reports, 2019) was used to set conventional test conditions and food simulants that can be used when testing in food simulant D2 is technically not feasible. The conditions recommended for non-polyolefin coatings (case of wood dishes with a cellulose coating), in the case of simulant D2 (ethanol 95%) is 30 min at 40 ºC as contact conditions. Isoctane is non polar solvent and mainly extracts the non polar substances. We expected to have a broader range of compounds with ethanol 95%, which is much more used as alternative fatty simulant to edible oil.

For both types of biomaterial, the tests were carried out in 20 mL glass vials. In order to maintain the ratio between the surface of material and the amount of simulant, in the case of simulants A and B, strips of material of 5 cm x 1 cm were cut; and for simulant D2 strips of 4 cm x 1 cm. In all cases, the strips were introduced into the vial and 18 mL of simulant were added under gravimetric control. Then, they were introduced in the oven at 70 °C for 2 h (simulants A and B) or 40 ºC for 30 min (simulant D2). A blank of each simulant was prepared and run under the same conditions. The migration tests were carried out by triplicate.

2.4. Migration study by SPME-GC-MS analysis

According to preliminary studies (Asensio et al., 2019) SPME conditions were extraction temperature 70 °C, extraction time 20 min, and DVB/CAR/PDMS fiber (50/30 •m). A stirring of 2800 g, 2 min incubation time and 2 min desorption time were used. GC-MS (Agilent 6890N with a MS 5975B mass spectrometer detector) coupled to the HS-SPME system (CTC Analytics CombiPal autosampler) with a capillary column: HP-5MS (30m x 0.25 •m x 250 •m) was used. The oven program was 50 °C for 5 min, with rate of 10 °C/min up to 300

°C, maintained 5 min. It was acquired in SCAN mode (m/z=50–600). The identification of volatile compounds was carried out using the NIST Chemistry WebBook spectrum library present in the equipment software.

Prior to SPME analysis, the simulants were allowed to reach room temperature. For the samples tested with simulants A and B, a 20 mL vial was completely filled and 2 g of sodium chloride (NaCl) were added. In the case of samples with simulant D2, it was diluted to 20% ethanol with distilled H_2O before the analysis. The SPME analysis was carried out using 20 mL vial completely filled with simulant and in the optimized conditions.

Qualitative analysis of the volatile compounds was carried out using the library mass spectra. Mass spectra were required to match the standard's top three ions and the percentage of NIST library match (>85% automatically match).

3. Results and discussion

3.1. Specific migration by SPME-GC-MS analysis

The SPME-GC-MS screening analysis of the biomaterial dishes (wheat pulp and wood) studied provided similar chromatograms for both types of samples with little differences (Figure 2). The identification of volatile compounds was carried out by using NIST Chemistry WebBook (05 version). Confirmation of some compounds was performed after injection of the respective pure standards. Correlation coefficients, working range, and LOD and LOQ for the available standards are shown in the Table 1.

Confirmed and tentatively identified volatile compounds with the best matches found during the library search are listed in Table 2. Those compounds without experimental data of toxicity (NOAEL) and no present in the positive list of EU Regulation 10/2011 were classified using the TTC (Threshold of Toxicological Concern) and Cramer rules (Toxtree v3.1.0.1851).

A total of 67 compounds have been identified. Most of them are used in manufacturing paper, adhesives and food packaging industry, its use being a priority in containers in contact with food, specifically in the manufacture of paper dishes. Vapenká et al., 2016 and Vavrouš et al., 2016 identified naphthalene, methyl hexadecanoate, diisobutyl phthalate and 2,6-diisopropylnaphtalene as contaminants presents in paper-based packaging materials. Further, Blanco-Zubiaguirre et al., 2019 identified pentadecanoic acid as migrant compound from paper/board packaging.

In this study, thirteen (13) compounds listed in the Regulation EU No. 10/2011 with a specific migration limit were found (2-ethyl, 1-hexanol; benzyl alcohol, phthalic anhydride, 2,6-ditert-butyl-4-methylphenol (BHT), dodecanoic acid, tetradecanoic acid, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, hexadecanoic acid, dibutyl phthalate, linoleic acid, oleic acid, octadecanoic acid and erucamide), all of them related to the food packaging industry, although the materials under study are not plastics.

Ten (10) compounds that have NOAEL values have been identified, three (3) of them (4-allylanisole, nonanoic acid and 1-dodecanol) are related to the food packaging industry (food contact). Four (4) compounds (2,6-diisopropylnaphtalene, diisobutyl phthalate, heptadecanoic acid and 1-docosanol) are related to manufacturing paper industry, and in particular in the case of 2,6-DiPN with the use of recycled paper/cardboard in the manufacturing of dishes (Weber et al, 2006; Nerín et al., 2004, 2007; Asensio et al., 2009, 2019; Vapenká et al., 2016). Regarding the other compounds having NOAEL values, the presence of 2-pentylfuran is related to the degradation of the cellulose present in the material of which these biodegradable dishes are made of (Risholm-Sundman et al., 1998; Lojewski et al., 2010). Similarly, the presence of octadecane and heneicosane is related to the degradation of cellulose fiber (Uwaremwe et al., 2017).

2-undecanone, 6,10,14-trimethyl-12-pentadecanone and 2-nonadecanone were classified as Cramer class II. They are volatile compounds that wood and bark can release when heated at high temperature (Mastelic et al., 2006). On the other hand, levoglucosenone, trimethyllevoglucosan, 1-decyne, 1-phenyl napthalene and (1-methyl-2,2-diphenyl cyclopropyl) sulfanyl benzene were classified as class III. They are likely coming from wood or cereal.

Table 3 shows the concentration values found in each of the analyzed samples. Significant differences were found between the type of dish (wheat pulp or wood) and the simulant (A, B and D2). It can be seen that there are a number of compounds that appear in both types of dishes: wheat pulp and wood. These compounds are nonanal, 4-allylanisole, decanal, phthalic anhydride, 1-dodecanol, ethyl dodecanoate, tetradecanal, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, and erucamide that are related to the food contact industry (dishes).

2,6-diisopropylnaphthalene and heptadecanoic acid, that are related to manufacturing paper industry and finally phthalic acid ethyl pentyl ester, henicosanal and docosanal that have vegetal origin, wood and wheat pulp, components. Even though the samples are natural biomaterials, they have been processed in the industry, what explains the presence of compounds common to other conventional plastics.

In the case of 4-allylanisole, that has a NOAEL of 560 mg/kg/d, values below 0.58 μg/kg were found in both types of dishes and in the three simulants. For nonanoic acid, with a NOAEL of 1500 mg/kg/d, a value of 0.73 μg/kg was quantified only in wheat pulp dishes with simulant B. In both types of dishes, 2,6-diisopropylnaphthalene (0.34 and 1.04 μg/kg) and heptadecanoic acid (0.34 and 1.04 μg/kg) were quantified, well below the NOAEL values of 150 mg/kg/d and 1000 mg/kg/d, respectively. For diisobutyl phthalate, with a NOAEL value of 100 mg/kg, the extracts showed values below the limit of quantification (μg/kg).

Migration of compounds no listed (no authorized) in EU Regulation No. 10/2011 should be lower than 10 μg/kg. As can be seen in Table 3, for the quantified compounds decanal, 2-undecenal, tridecanal, tetradecanal, pentadecanoic acid, henicosanal and tricosanal the migration does not exceed this value, while nonanal and docosanal, with 10.71 μg/kg in simulant B and 24.12 μg/kg in simulant D2 only in wood dishes, respectively, exceed this limit. However, both compounds are classified as class I according to the Cramer rules. For this class, a human exposure threshold of 30 μg/kg/d is assigned and these compounds were at lower concentration.

All the compounds with specific migration limit (SML) according to EU Regulation No. 10/2011 are below the limits set. Specifically, the estimated concentration is of the order of three times lower than the established limits (μg/kg versus mg/kg). Seven (7) compounds: 2-ethyl, 1-hexanol (2.40 μg/kg), dodecanoic acid (0.34-0.96 μg/kg), 2,6-ditert-butyl-4-methylphenol (0.54-0.66 μg/kg), 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (<LOQ), linoleic acid (0.67-3.27 μg/kg) and oleic acid (0.95-2.54 μg/kg) were quantified only in wood plates and its origin is related to manufacturing paper and food contact industry. Phthalic anhydride (0.30 and 0.32 μg/kg), tetradecanoic acid (1.20 and 0.37-1.67 μg/kg), hexadecanoic acid (2.69-25.52 and 7.70-37.47 μg/kg), dibutyl phthalate (3.05 and 3.44 μg/kg), octadecanoic acid (2.08-37.73 and 2.79-7.19 μg/kg) and erucamide (1.83 and 0.68 μg/kg) were quantified in both types of dishes, wheat pulp and wood. Only benzyl alcohol was quantified in wheat pulp dishes (0.39 μg/kg).

4. Conclusions

This study demonstrates that the wheat pulp and wood dishes used for single use in catering are safe with respect to volatile substances released from them, in intended use conditions. However, in both materials some compounds currently detected in conventional plastics were also found in specific migration analysis. This fact could be expected, as these materials have been processed as well in a packaging industry. In general, migration values are very low and comply with the legislation, even with the Regulation 10/2011/EU. Non-volatile substances will need further study, as the identification of migrants is much more difficult and requires a study in depth. In addition, some of these materials can be used at high temperatures (170 ºC) so it will be necessary to study the migration that takes place in these conditions.

Acknowledgements

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Table 1. Correlation coefficients, working range, and LOD and LOQ for the available standards

Compounds	Correlation coefficient	Working rang (μg/kg)	LOD (μg/kg)	LOQ (μg/kg)
2-ethyl,1-hexanol	0.9968	0.58 – 7.66	0.17	0.58
benzyl alcohol	0.9947	0.30 – 8.55	0.09	0.30
nonanal	0.9944	0.19 – 36.26	0.06	0.19
4-allylanisole	0.9937	0.21 – 7.51	0.09	0.21
decanal	0.9923	0.13 – 8.55	0.04	0.13
2,6-ditert-butyl-4-methylphenol	0.9941	0.50 – 5.22	0.19	0.50
2,2,4-trimethyl-1,3pentanediol diisobutyrate	0.9964	0.21 – 5.98	0.06	0.21
2,6-diisopropylnaphthalene	0.9899	0.34 – 6.67	0.11	0.34
diisobutyl phthalate	0.9912	0.80 – 18.08	0.12	0.80
hexadecanoic acid	0.9900	0.14 – 40.37	0.05	0.14
dibutyl phthalate	0.9920	0.56 – 87.65	0.17	0.56
erucamide	0.9923	0.60 – 4.45	0.15	0.60

Table 2. Confirmed and tentatively identified compounds by SPME-GC-MS in biomaterial dishes according to specific migration limits (SML) from the Regulation (EU) No. 10/2011, NOAEL values and Crammer classification.

	Compounds	RT (min)	CAS number	SML (mg/kg)	NOAEL (mg/kg bw/d)	TTC (class)	Origin or use categorization[a]
1	1,3,5-trimethylbenzene	8.99	108-67-8			I	*adhesive*
2	2-pentylfuran	9.50	3777-69-3		25.6		*cereal*
3	1-decyne	10.20	764-93-2			III	-
4	2-ethyl,1-hexanol[b]	10.28	104-76-7	30			*adhesive/food contact/manufacturing paper*
5	benzyl alcohol[b]	10.68	100-51-6	–[c]			*adhesive/food contact/manufacturing paper*
6	nonanal[b]	11.71	124-19-6			I	*food contact*
7	levoglucosenone	12.04	37112-31-5			III	*wood/cereal*
8	naphthalene	13.12	91-20-3			I	*manufacturing plastics*
9	4-allylanisole[b]	13.33	140-67-0		560		*food contact/wood*
10	decanal[b]	13.38	112-31-2			I	*food contact*
11	1,2,3,4-tetrahydro-1,1,6-trimethyl naphthalene	13.57	475-03-6			I	*food industry*
12	nonanoic acid	14.35	112-05-0		1500		*adhesive/food contact*
13	1-decanol	14.38	112-30-1			I	*adhesive*
14	2-undecanone	14.70	112-12-9			II	*food contact*
15	phthalic anhydride	15.04	85-44-9	–[c]			*adhesive/food contact*
16	2-undecenal	15.69	2463-77-6			I	-
17	trimethyllevoglucosan	16.03	2951-86-2			III	*wood/cereal*
18	ethyl decanoate	16.10	110-38-3			I	*food contact*
19	3-methyl-2-butenyl benzene	16.36	4489-84-3			I	-
20	6,10-dimethylundeca-5,9-dien-2-one	16.88	3796-70-1			I	*food contact/adhesive*
21	1-dodecanol	17.13	112-53-8		2000		*manufacturing paper/food contact*
22	tridecanal	17.59	10486-19-8			I	-
23	2,6-ditert-butyl-4-methylphenol[b]	17.63	128-37-0	3			*adhesive/food contact/food service/paper/antioxidant*
24	dodecanoic acid	18.17	143-07-7	–[c]			*food contact/adhesive*
25	ethyl dodecanoate	18.57	106-33-2			I	*food contact*
26	hexadecane	18.64	544-76-3			I	-
27	2,2,4-trimethyl-1,3-pentanedioldiisobutyrate[b]	18.67	6846-50-0	5			*food contact*
28	tetradecanal	18.82	124-25-4			I	*food contact*
29	decyl dodecanoate	19.16	1654-86-0			I	-
30	2-ethylhexyl 3,5,5-trimethyl hexanoate	19.36	70969-70-9			I	-
31	1,3-diisopropylnaphthalene	19.78	57122-16-4			I	-
32	heptadecane	19.78	629-78-7			I	-

33	2,6-diisopropylnaphthalene[b]	20.22	24157-81-1		150		*paper and board/ink*
34	tetradecanoic acid	20.44	544-63-8	_[c]			*food contact/adhesive/manufacturing paper*
35	octadecane	20.62	593-45-3		≥ 5000		-
36	phthalic acid, ethyl pentyl ester	20.73	NIST308936			I	-
37	7,11,15-trimethyl-3-methylidene1-hexadecene	21.29	504-96-1			I	-
38	6,10,14-trimethyl-l2-pentadecanone	21.35	502-69-2			II	-
39	pentadecanoic acid	21.48	1002-84-2			I	*adhesive/manufacturing paper*
40	diisobutyl phthalate[b]	21.62	84-69-5		100		*adhesive/manufacturing paper*
41	1-phenylnaphthalene	21.66	605-02-7			III	-
42	methyl hexadecanoate	22.17	112-39-0			I	*food contact*
43	11-hexadecanoic acid	22.30	2416-20-8			I	-
44	hexadecanoic acid[b]	22.51	57-10-3	_[c]			*food contact/adhesive/manufacturing paper*
45	dibutyl phthalate[b]	22.58	84-74-2	0.3			*manufacturing plastics, paper/food contact*
46	heptadecanoic acid	22.96	506-12-7		1000		*adhesive/manufacturing paper*
47	1-octadecanol	23.65	112-92-5			I	*manufacturing paper/adhesive/food contact*
48	heneicosane	23.71	629-94-7		500		-
49	1-nonadecene	23.80	18435-45-5			I	-
50	9-octadecenoic acid	24.12	112-79-8			I	-
51	linoleic acid	24.14	60-33-3	_[c]			*food contact*
52	oleic acid	24.18	112-80-1	_[c]			*manufacturing paper/adhesive/food contact*
53	octadecanoic acid	24.39	57-11-4	_[c]			*manufacturing paper/adhesive/food contact*
54	icosanal	24.47	2400-66-0			I	-
55	cyclopropyl phenyl ketone	24.59	3481-02-5			I	-
56	3,3,13,13-tetraethylpentadecane	25.26	NIST360423			I	-
57	1-docosanol	25.31	661-19-8		1000		*manufacturing paper*
58	9-hexadecenal	25.66	56219-04-6				-
59	henicosanal	25.82	51227-32-8			I	-
60	docosanal	26.64	57402-36-5			I	-
61	2-nonadecanone	27.12	629-66-3			II	-
62	henicosyl formate	27.27	77899-03-7			I	-
63	tricosanal	27.44	72934-02-2			I	-
64	(1-methyl-2,2-diphenylcyclopropyl) sulfanylbenzene	27.83	56728-02-0			III	-
65	erucamide[b]	29.29	112-84-5	_[c]			*adhesive/food contact*
66	octacosane	30.08	630-02-4			I	-
67	1-octacosanol	31.69	557-61-9			I	-

[a] *EPA CPDat Chemical and Product Categories;* [b] *Confirmed with standards;* [c] *Without Specific MigrationLlimit (60 mg/kg as limit of global migration limit applies).*

Table 3. Confirmed and tentatively identified compounds by SPME-GC-MS in simulants (A, B and D2).

	Compounds	RT (min)	CAS number	Wheat pulp dishes (µg/kg)			Wood dishes (µg/kg)		
				A	B	D2	A	B	D2
1	1,3,5-trimethylbenzene	8.99	108-67-8		•				
2	2-pentylfuran	9.50	3777-69-3	•					
3	1-decyne	10.20	764-93-2			•			
4	2-ethyl,1-hexanol	10.28	104-76-7					2.40±0.05	
5	benzyl alcohol	10.68	100-51-6	0.39±0.02					
6	nonanal	11.71	124-19-6	<LOQ	<LOQ	<LOQ	2.04±0.22	10.71±2.99	<LOQ
7	levoglucosenone	12.04	37112-31-5	•					
8	naphthalene	13.12	91-20-3				•	•	
90	4-allylanisole	13.33	140-67-0	<LOQ	<LOQ	<LOQ	<LOQ	0.58±0.02	0.21±0.05
10	decanal	13.38	112-31-2		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
11	1,2,3,4-tetrahydro-1,1,6-trimethyl naphthalene	13.57	475-03-6		•				
12	nonanoic acid[(1)]	14.35	112-05-0		0.73±0.20				
13	1-decanol	14.38	112-30-1					•	•
14	2-undecanone	14.70	112-12-9					•	
15	phthalic anhydride[(3)]	15.04	85-44-9		2.30±0.32			2.38±0.16	
16	2-undecenal[(2)]	15.69	2463-77-6					<LOQ	
17	trimethyllevoglucosan	16.03	2951-86-2		•				
18	ethyl decanoate	16.10	110-38-3			•			
19	3-methyl-2-butenyl benzene	16.36	4489-84-3		•				
20	6,10-dimethylundeca-5,9-dien-2-one	16.88	3796-70-1				•	•	
21	1-dodecanol	17.13	112-53-8	•		•	•		•
22	tridecanal[(2)]	17.59	10486-19-8			<LOQ			
23	2,6-ditert-butyl-4-methylphenol	17.63	128-37-0				0.54±0.02	0.66±0.10	
24	dodecanoic acid[(2)]	18.17	143-07-7				0.34±0.12	0.96±0.16	
25	ethyl dodecanoate	18.57	106-33-2			•			•
26	hexadecane	18.64	544-76-3						•
27	2,2,4-trimethyl-1,3-pentanedioldiisobutyrate	18.67	6846-50-0					<LOQ	
28	tetradecanal[(2)]	18.82	124-25-4	<LOQ		<LOQ			0.56±0.05
29	decyl dodecanoate	19.16	1654-86-0						•
30	2-ethylhexyl 3,5,5-trimethyl hexanoate	19.36	70969-70-9						•
31	1,3-diisopropylnaphthalate	19.78	57122-16-4				•		
32	heptadecane	19.78	629-78-7						•

33	2,6-diisopropylnaphthalene	20.22	24157-81-1		0.39±0.03	0.34±0.01		1.04±0.04
34	tetradecanoic acid[1]	20.44	544-63-8		1.20±0.45	0.37±0.19		1.67±0.27
35	octadecane	20.62	593-45-3					•
36	phthalic acid, ethyl pentyl ester	20.73	NIST308936	•		•		
37	7,11,15-trimethyl-3-methylidenehexadec-1-ene	21.29	504-96-1		•			
38	6,10,14-trimethy-l2-pentadecanone	21.35	502-69-2		•			
39	pentadecanoic acid[1]	21.48	1002-84-2		0.89±0.31			
40	diisobutyl phthalate	21.62	84-69-5		<LOQ	<LOQ		
41	1-phenylnaphthalene	21.66	605-02-7				•	
42	methyl hexadecanoate	22.17	112-39-0	•				
43	11-hexadecanoic acid	22.30	2416-20-8		•			
44	hexadecanoic acid	22.51	57-10-3	2.69±0.88	25.52±6.45	7.70±1.27		37.47±9.13
45	dibutyl phthalate	22.58	84-74-2	3.05±0.47		3.44±0.16		
46	heptadecanoic acid[1]	22.96	506-12-7		0.63±0.42			0.14±0.05
47	1-octadecanol	23.65	112-92-5		•			
48	heneicosane	23.71	629-94-7					•
49	1-nonadecene	23.80	18435-45-5					•
50	9-octadecenoic acid	24.12	112-79-8					•
51	linoleic acid[1]	24.14	60-33-3			0.67±0.15		3.27±1.70
52	oleic acid[1]	24.18	112-80-1			0.95±0.23		2.54±0.99
53	octadecanoic acid[1]	24.39	57-11-4	2.08±0.67	37.73±1.54	2.79±0.32		7.19±1.19
54	icosanal	24.47	2400-66-0					•
55	cyclopropyl phenyl ketone	24.59	3481-02-5				•	
56	3,3,13,13-tetraethylpentadecane	25.26	NIST360423					•
57	1-docosanol	25.31	661-19-8					•
58	9-hexadecenal	25.66	56219-04-6					•
59	henicosanal[2]	25.82	51227-32-8		<LOQ			7.09±0.56
60	docosanal[2]	26.64	57402-36-5		1.06±0.25			24.12±1.62
61	2-nonadecanone	27.12	629-66-3					•
62	henicosyl formate	27.27	77899-03-7					•
63	tricosanal[2]	27.44	72934-02-2		1.14±0.39			
64	(1-methyl-2,2-diphenylcyclopropyl) sulfanylbenzene	27.83	56728-02-0		•			
65	erucamide	29.29	112-84-5		1.83±0.22			0.68±0.17
66	octacosane	30.08	630-02-4		•			
67	1-octacosanol	31.69	557-61-9		•			

[1] *quantified as hexadecanoic acid,* [2] *quantified as nonanal* [3] *quantified as dibutyl phthalate*

Figure 1. Wheat pulp and wood dishes studied.

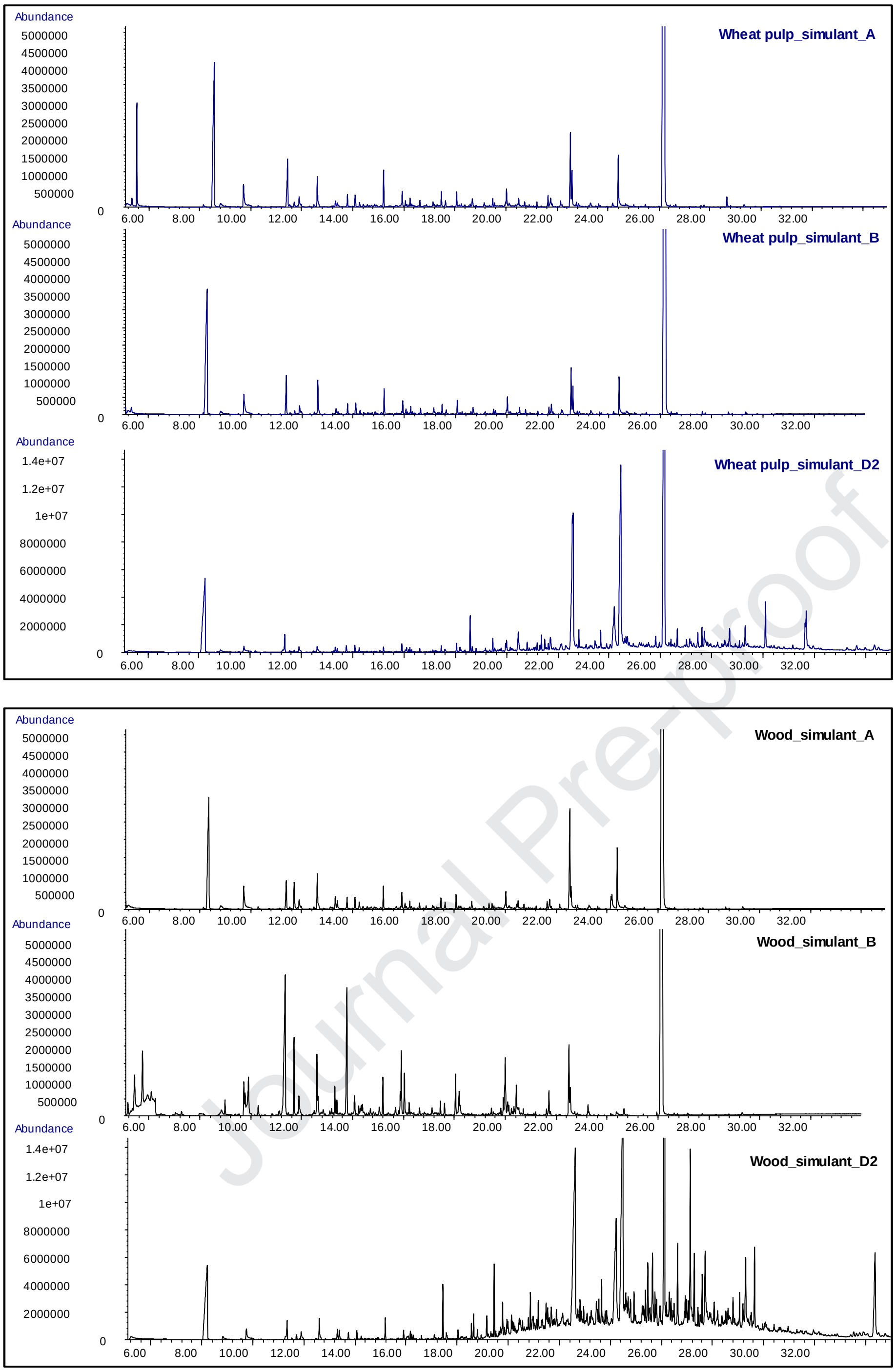

Figure 2. Chromatograms obtained from the SPME-GC-MS analysis of the wheat pulp and wood dishes with the three simulants studied (A, B and D2).

Highlights

- Migration tests with simulants 10% EtOH, 3% acetic acid and 90% EtOH were carried out
- SPME-GC-MS was applied for the analysis
- Migrant compounds from wheat pulp and wood were identified and quantified.
- The results obtained show that these dishes are safe.

CRediT authorship contribution statement

Esther Asensio: Conceptualization, Methodology, Investigation, Supervision, Writing - original draft.

Laura Montañés: Conceptualization, Methodology, Investigation.

Cristina Nerín: Supervision, Funding acquisition.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: