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Migration of mineral oil aromatic hydrocarbons (MOAH) from cardboard containers to dry food and prediction tool

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ABSTRACT

This research aimed to study the migration of mineral oil aromatic hydrocarbons (MOAH) from primary carton packages to dry foods, using 16 aromatic hydrocarbons as model substances, covering a wide range of molecular masses and chemical structures. Migration experiments were performed using modified polyphenylene oxide as a food simulant and couscous and polenta as dry foods. The migration tests were carried out to simulate storage at room temperature for long periods and in hot food containers as the worst scenario. Multivariate analysis algorithms were applied to correlate and group the migration of model substances, and a partial least squares regression (PLSR) model was built to predict the worst-case migration. The results showed strong correlations in the migration patterns of the model substances, based on their volatility, food matrix, migration time and temperature. Different behaviour between the migration of the most volatile and the heaviest model substances was observed.

1. Introduction

Paper and cardboard are frequently used as primary, secondary and tertiary food packaging materials; they are intended to contain, protect, transport and store food products. However, several scientific studies have shown that cardboard and paper packaging can be contaminated with mineral oil hydrocarbons (MOH), which could migrate from packaging to food in significant quantities (Biedermann & Grob, 2010; Buist et al., 2020; Dima, Verzera, & Grob, 2011; Lorenzini et al., 2010; Vollmer et al., 2011).

MOHs are complex mixtures of hydrocarbons that come mainly from petroleum; they are divided into mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH). MOSH has been associated with the formation of hepatic microgranulomas; however, due to the low incidence of lipogranulomas in the population, they are not considered toxicologically dangerous (Bevan, Harrison, Jeffery, & Mitchell, 2020). On the other hand, the MOAH fraction has been considered the most dangerous for human health since the presence of three or more aromatic rings in these compounds can present genotoxic and carcinogenic activity(Carrillo, van der Wiel, Danneels, Kral, & Boogaard, 2019; EFSA, 2012). This fraction is mainly composed of alkylated mono or polycyclic aromatic hydrocarbons and also contains, to a lesser extent, non-alkylated aromatic hydrocarbons and aromatic compounds with heteroatoms, mostly sulphur (EFSA, 2012).

There are several sources of MOAH: mineral oil-based offset inks used to decorate the surface of cardboard, recycled paper fibres, lubricants, waxes, adhesives, and processing aids used during the manufacture of packaging (Biedermann & Grob, 2010; Laine, Pitkänen, Ohra-aho, Gestranius, & Ketoja, 2016).

Migration from cardboard or paper depends on the structure of the material, the concentration of the migrant and its chemical-physical properties, the storage periods, environmental conditions, and the food type (Arvanitoyannis & Kotsanopoulos, 2014; Poças, Oliveira, Pereira, Brandsch, & Hogg, 2011). The movement of migrants through the porous structure of cardboard or paper occurs through adsorption/desorption processes, which are limited by the chemical nature of the cellulosic fibre and the migrant (Poças et al., 2011). The gaseous phase is the main route by which mineral oils are transferred to food, and therefore the volatile fraction is the most important one (Biedermann & Grob, 2012; Fiselier & Grob, 2011). Nevertheless, migration by direct contact is also relevant and has to be taken into account (Barp, Suman, Lambertini, & Moret, 2015; Eicher, Biedermann, Zurfluh, & Grob, 2015; Pack et al., 2020). There are no quantitative measures for the toxic potency of individual MOAH, but according to EFSA, they could be one or two orders of magnitude higher than that of MOSH. For this reason, EFSA considers that the intake values of MOAH that are

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supposed to come from migration from paper and cardboard (between 0.008 and 0.022 mg/kg bw/day for children and around 0.004 and 0.011 mg/kg bw/day for adults) could be a health concern (Buist et al., 2020; EFSA, 2012).

The migration study of MOAH from cardboard or paper to food is an arduous task. In addition to the complex chemical and physical processes that occur during migration, the MOAHs are made up of numerous isomers covering a wide range of volatility. Another challenging task is to find food packaging that contains different MOAHs at high enough concentration levels. To simplify this problem, some researchers have used surrogate substances to model the migration of MOHs from paper and study the barrier properties of different materials against MOHs (Ewender, Franz, & Welle, 2012; Guazzotti et al., 2015; Laine et al., 2016). Recently, Fengler and Gruber (2020) used surrogates to investigate MOSHs and MOAHs migration from paper packaging to two food simulants, Tenax (Van Den Houwe, Van Loco, Lynen, & Van Hoeck, 2018) and Sorb-Star (Fengler & Gruber, 2020).

There is no standardised method to test the migration of MOAH from cardboard materials. Although some authors maintain that Tenax (modified polyphenylene oxide) overestimates migration, it continues to be the simulant recommended to assess migration from cardboard (AENOR, 2004) and plastic materials (European Commission, 2011) intended to be in contact with dry food. Furthermore, the EU regulation 10/2011 suggests simulating the worst conditions of time and temperature during migration tests and increasing temperature to accelerate the migration in food stored for long periods (European Commission, 2011).

The main objective of this research was to study the migration behaviour of MOAHs from cardboard packaging materials to Tenax, as a food simulant, and to two different dry food samples, couscous and polenta. For this purpose, cardboard samples were previously fortified with 16 model substances that represent MOAH in a wide range of molecular masses and chemical structures. The use of model substances would provide more detailed information on the processes that occur during the migration of MOAH and facilitates the construction of a PLSR model to predict MOAH migration. The possibility of using mathematical models to predict the transfer of MOH from packaging to food would simplify the migration study of the materials and a quick risk assessment.

2. Materials and methods

2.1. Reagents and samples

Analytical standards: 1-methylnaphthalene (1- MN), 2-methylnaphthalene (2 –MN), biphenyl (BP), 2,6-dimethylnaphthalene (2,6-DMN), acenaphthene (ACE), 2,6-diisopropylnaphthalene (2,6-DIPN), 3,3′,5,5′-tetramethylbiphenyl (3,3′,5,5′-TMBP), 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), 1-methylpyrene (1-MPYR), benzo(b)naphtha(1,2-d)thiophene (BNT), chrysene (CHRY), benzo(b)fluoranthene (BbF), perylene (PER); and the standard mixture of saturated alkanes (C7–C40) of 1000 μg mL^{-1} for each component in n-hexane were purchased from Sigma-Aldrich (Madrid, Spain). While 9,9′-dimethylfluorene (9,9-DMF) was supplied by Tokyo Chemical Industry CO., LTD, and 3,6-dimethylphenanthrene (3,6-DMP) was obtained from Dr Ehrenstorfer (Augsburg, Germany). Acetone, n-hexane, and ethanol absolute for HPLC were from Panreac (Barcelona, Spain). Tenax TA 60/100 mesh was supplied by Supelco (Bellefonte, USA).

The cardboard used in the migration tests had a thickness of 1 mm and a grammage of 412 g m^{-2} and came from a container for dry food obtained in a Spanish supermarket. The dry foods evaluated, corn grits (polenta) and wheat semolina (couscous) of medium grain, were also bought in local commerce. Both the cardboard and the dry foods were previously analysed to verify that they were free of MOAH.

2.2. Model substances

Sixteen aromatic hydrocarbons were selected as model substances for the study. They were selected because they represent MOAH in a wide range of volatility, molecular weight, boiling points, and molecular structure. These compounds included alkylated and non-alkylated aromatic hydrocarbons, biphenyls and heterocyclic aromatic sulphur compounds, ranging from 142 to 252 Da (see Table 1), all were associated to the presence of MOAH in various types of minerals oils and proposed as MOAH markers (Jaén, Domeño, Alfaro, & Nerín, 2021).

Another selection criteria were based on the probability of studying the behaviour of the MOAH sub-fractions during migration. MOAH chromatograms are usually divided into sub-fractions, defined according to the retention time of a mixture of n-alkanes, analysed under the same chromatographic conditions as MOAH (Bratinova & Hoeskstra, 2019; Gruber et al., 2019, pp. 1–52). Selected substances elute in the range of MOAH sub-fractions noted for their potential to migrate C10 to C16 (1-MN, 2-MN, BP, 2,6-DMN, ACE, 9,9-DMF); C16 to C25 (2,6-DIPN, 3,3 ′, 5,5′-TMBP, 4-MDBT, 4, 6-DMDBT, 3,6-DMP, 1-MPYR, BNT) and C25–C35 (CHRY, BbF and PER). The location of the model substances in the different sub-fractions was carried out as indicated by (Bratinova & Hoeskstra, 2019).

2.3. Spiking procedure for the cardboard

Before the migration assays, cardboard sheets with an area of 0.08 dm^2 were prepared. These sheets were spiked with 50 μL of a standard solution of 350 mg L^{-1} of the model substances. The standard solution was evenly distributed with a syringe throughout the cardboard sheet. After that, the spiked cardboard sheet was left dry at room temperature for 1 h, and subsequently, migration tests were carried out with dry food samples and Tenax.

2.4. Migration test

The migration tests were carried out with two dry food (polenta and couscous) and a food simulant (Tenax). Before the migration tests, Tenax was purified by Soxhlet extraction with acetone for 6 h and subsequently dried in the oven at 160 °C for 6 h (AENOR, 2004). The dry food samples were subjected to extraction with hexane and analysis by GC-MS to verify that they were not contaminated with MOAH.

The time and temperature conditions for the migration tests were selected based on Regulation EU/10/2011 for plastics (European Commission, 2011) and considering the intended uses of cardboard materials in the worst conditions. These conditions were: 2 h at 70 °C in the case of hot food containers; and 10 days at 60 °C to simulate storage at room temperature for long periods. In addition, migration at 60 °C was also evaluated at 3 and 6 days in order to evaluate the migration kinetics.

The cardboard sheets spiked with the model substances were placed in direct contact with the dry food and the food simulant. For the tests with Tenax, 0.32 g of the food simulant were used according to the 4 g dm^{-2} ratio established by UNE-EN-14338 (AENOR, 2004). However, in the case of dry food, it was necessary to use 0.65 g to completely cover the surface of the cardboard and form a uniform layer. Finally, the whole was wrapped in aluminium foil, placed in a glass Petri dish of 6 cm in diameter and placed in the oven under the migration conditions. Three replicates and a blank were prepared for each assay.

2.5. Extraction of model substances from cardboard

To know the concentration of the model substances retained in the cardboard after the spiked and solvent evaporation stages, 7 spiked cardboard sheets were extracted following the conventional procedures for extracting mineral oils from cardboard and paper samples (Bundesinstitut für Risikobewertung (BfR) & Kantonales Labor Zurich (KLZH), 2011; Lorenzini et al., 2010; Vollmer et al., 2011) with slight

Table 1
Physical properties of the substances used to model MOAH migration, the concentration (mg dm^{-2})adsorbed by the donor cardboard and RSD (%).

Compound	Molecular formula	Molecular structure	MM (Da)	Log P	Boiling point (°C)	Donor cardboard (mg dm^{-2})	RSD (%)
2-methylnaphthalene	$C_{11}H_{10}$		142.197	3.91	240	0.05	4.38
1-methylnaphthalene	$C_{11}H_{10}$		142.197	3.91	243	0.05	4.94
Biphenyl	$C_{12}H_{10}$		154.208	3.98	258	0.07	5.38
2,6-dimethylnaphtalene	$C_{12}H_{12}$		156.224	4.37	264	0.07	5.91
Acenaphtene	$C_{12}H_{10}$		154.208	4.19	279	0.08	4.12
9,9′-dimethylfluorene	$C_{15}H_{14}$		194.272	5.20	301	0.09	8.54
2,6-diisopropylnaphtalene	$C_{16}H_{20}$		212.330	6.13	306	0.11	5.38
3,3′,5,5′-tetramethylbiphenyl	$C_{16}H_{18}$		210.314	5.82	301	0.11	5.98
4-methyldibenzotiophene	$C_{13}H_{10}S$		198.283	4.84	349	0.12	9.72
4,6-dimethyldibenzotiophene	$C_{14}H_{12}S$		212.310	5.30	365	0.13	5.99
3,6-dimethylphenanthrene	$C_{16}H_{14}$		206.282	5.60	363	0.14	2.19
1-methylpyrene	$C_{17}H_{12}$		216.277	5.63	387	0.15	8.54
Benzo(b)naphtho(2,1-d)tiophene	$C_{16}H_{10}S$		234.316	5.61	434	0.16	8.00
Chrysene	$C_{18}H_{12}$		228.288	5.91	448	0.18	6.84
Benzo(b)fluoranthene	$C_{20}H_{12}$		252.309	6.40	467	0.17	6.36
Perylene	$C_{20}H_{12}$		252.309	6.40	467	0.17	5.05

modifications. The procedure was as follows: the cartons enriched with the model substances were dried for 1 h at room temperature and afterwards cut into small pieces with a border of approximately 0.5 cm and placed in a 20 mL glass vial. Subsequently, 15 mL of hexane/ethanol mixture (1: 1) were added to each vial and placed in an ultrasonic bath for 2 h. Then, the extract was decanted into another vial, and 5 mL of water were added to separate the hexane from the ethanol. The supernatant was separated and concentrated under a gentle stream of nitrogen gas to 1 mL.

The same procedure was used to analyse the cardboard samples after migration and determine the concentration of the analytes remaining in the cardboard.

2.6. Extraction of migrated model substances from dry foods and food simulants

After migration, dry food, as well as Tenax samples, were transferred to 20 mL vials. Subsequently, 4 mL of hexane were added to each vial, and they were placed in an ultrasonic bath at room temperature for 1 h. After this time, the hexane extract was transferred to a clean vial, and the sample was subjected to two consecutive extractions following the same procedure. The extracts collected from each replica were pooled in a vial and concentrated under a gentle stream of nitrogen gas at 40 °C to 1 mL.

2.7. GC-MS

For the analysis, a gas chromatograph 7820 A GC coupled to a single quadrupole mass spectrometer 5977 B detector from Agilent Technologies (Santa Clara, CA, USA) was used. It was equipped with an electron ionisation (EI) ion source and a Combi PAL autosampler (CTC Analytics, Zwingen, Switzerland). A chromatographic column HP-5MS of 30 m length x 25 mm inner diameter x 0.25 μm film thickness from Agilent was used. Helium was used as carrier gas at a constant flow of 1 mL min^{-1}. The injection was performed at 270 °C in splitless mode, injection volume was 1 μL. The oven temperature program was as follows: initially 40 °C for 5 min, 10 °C min^{-1} to 300 °C and held at 300 °C for 10 min. MS analysis was carried out in SIM mode with 7 min solvent delay.

2.8. Statistical analysis

Unscrambler X10.3 software (Camo Analytics) was used for Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA), and Partial Least Squares Regression (PLSR).

For the PCA and HCA execution, the migration data were organised in a matrix with 16 variables (model substances) and 12 samples (migration tests). The PLSR model was built based on five predictor variables (boiling point, molecular mass, log P, solubility and migration time), and the response variable was the percentage of migration of the model substances in Tenax, polenta and couscous at 60 °C. Except for the migration time, the values of the predictor variables were taken from ChemSpider database.

3. Results and discussion

3.1. Model substances in the cardboard

Once the samples were analysed and it was confirmed that they were free of MOAHs, the cardboards were spiked with the model substances. The concentration of the model substances adsorbed by the donor cardboard and their physical properties are shown in Table 1. The aim of the study was to study the migration behavior of different MOAHs, in a wide range of polarities and chemical structures, from cardboard to Tenax and two different dry foods, under different migration conditions. Real samples would not contain so many MOAHs and, in addition, concentrations would be very low, making more difficult the analysis. For this reason, it was considered more interesting to spike the cardboards with a great variety of MOAHs that could reflect the migration behaviour of MOAHs with different structures, volatility or molecular

weights.

A high-concentration solution of the model substances (350 mg L^{-1}) was used to spike the donor cardboard. The reason was to ensure that, despite the possible loss of analytes due to volatilisation during the spiking analytes, drying or solvent evaporation, the amount adsorbed on the cardboard was high enough to provide reliable results.

In the event that the donor cardboard had adsorbed all the model substances, the expected concentration would be approximately 0.18 mg dm^{-2}. However, after evaporation of the solvent, the concentration detected ranged between 0.05 and 0.18 mg dm^{-2} with RSD values between 2 and 10% (see Table 1). The loss by evaporation of volatile substances during the cardboard spiking and drying process was evident. Substances with a low boiling point were the most affected. The heaviest substances had the highest concentrations in the donor cardboard. This concentration (Table 1) was considered the initial concentration of the model substances in the cardboard for future calculations.

3.2. Migration in the food simulant (Tenax)

For the purpose of this discussion, it should be remembered that the model substances represent three MOAH sub-fractions. Based on the elution range of the n-alkanes (Bratinova & Hoeskstra, 2019; Gruber et al., 2019, pp. 1–52), selected compounds were eluted in the ranges: C10–C16, C16–C25 and C25–C35 according to their volatility.

It is also important to note that the migration results of the model substances in Tenax and dry foods are expressed as a percentage related to the concentration detected in the spiked cardboard after the drying step and solvent volatilisation (see Table 1).

The migration results of the model substances in Tenax are presented in Fig. 1 A. As it can be seen, the migration percentage for the most volatile substances in the elution range C10–C16 was greater than 94%; besides, these substances reached their maximum migration on the third day. The substances with retention time between C16–C25 had a more heterogeneous behaviour with migrations ranging from 40 to 98%; the percentage of migration of this fraction decreases as a function of the model substances' molecular weight. Conversely, the heaviest compounds (eluted between C25–C35) with a slower migration rate reached equilibrium on the sixth day and migrated below 45%.

The migration of model substances decreased when increasing carbon number, and the heaviest compounds needed more time to reach the equilibrium. When dry food is in direct contact with cardboard, migration occurs through two mechanisms, gas phase and diffusion (Poças et al., 2011). In other words, model substances are transferred to dry foods both by gas and by diffusion depending on their volatility. The main mechanism of migration of volatile substances is through the gas phase; these compounds evaporate and then condense on the Tenax (Biedermann & Grob, 2012), and their migration is faster, while the heavier compounds migrate mainly by diffusion and reach equilibrium more slowly.

In addition, gradual losses in the percentage of migration the model substances of C16–C25 fraction were observed, which became more evident after 10 days of migration (Fig. 1A). It can be assumed that these losses are linked to desorption processes in Tenax favoured by temperature and migration time, already reported by (Nerín, Contín, & Asensio, 2007). In order to confirm this hypothesis, the model substances retained in the donor cardboard were extracted and analysed after migration; the results obtained were used to calculate the total percentage of substances released by the donor cardboard. Fig. S1 compares the percentage of model substances released by the donor cardboard at 60 °C for 10 days, with the percentage retained in the Tenax under the

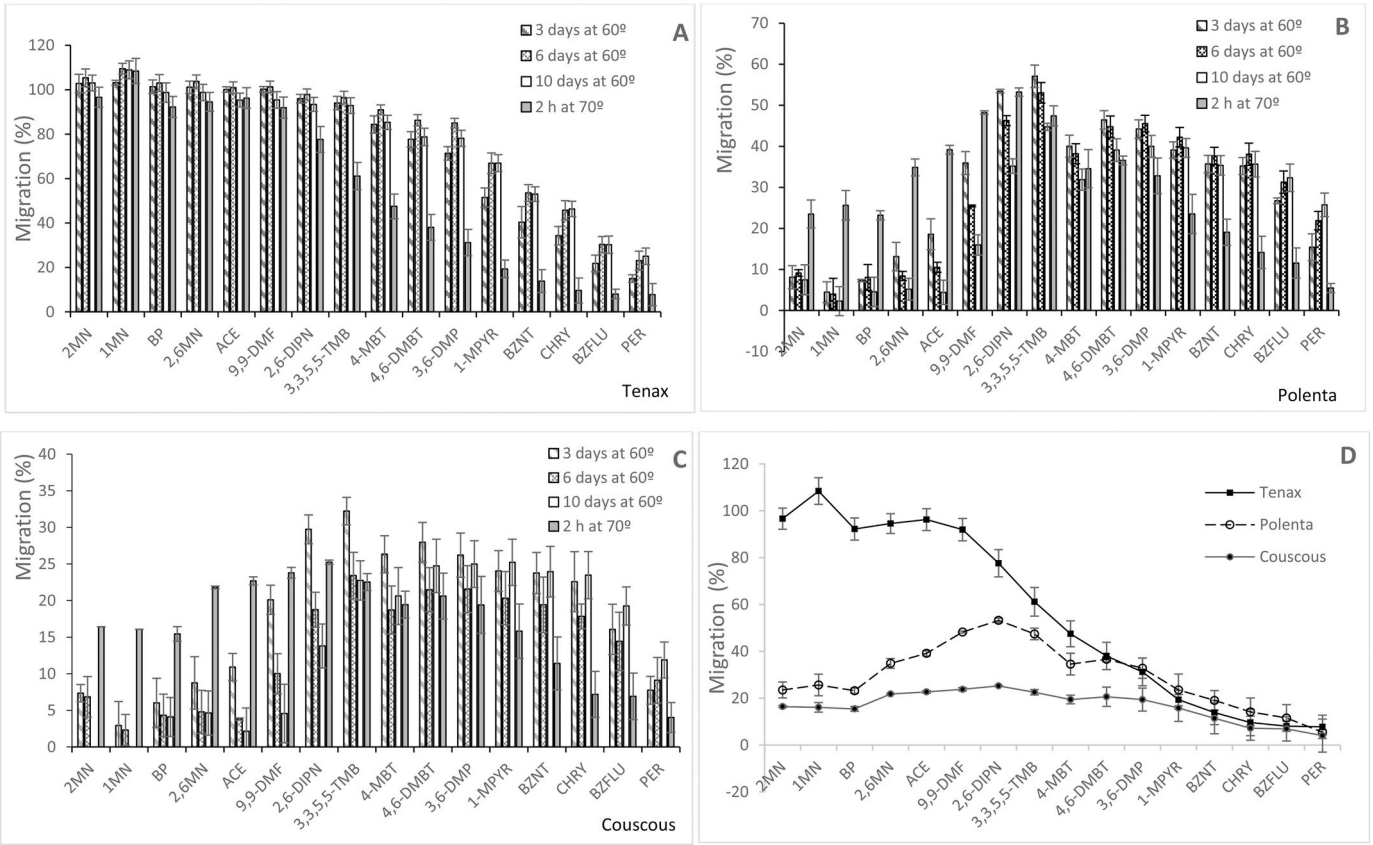

Fig. 1. Migration of model substances at 60 °C in different storage periods (3, 6 and 10 days) to Tenax (A), Polenta (B) and Cuscus (C). Migration of model substances at 70° for 2 h to Tenax, polenta and couscous (D). MOAH sub-fractions: C10 to C16 (1-MN, 2-MN, BP, 2,6-DMN, ACE, 9,9-DMF), C16 to C25 (2,6-DIPN, 3,3 ′,5,5′-TMBP, 4-MDBT, 4, 6-DMDBT, 3,6-DMP, 1-MPYR, BNT) and C25–C35 (CHRY, BbF and PER).

same conditions. The results showed that between 6 and 18% of the C16–C25 substances released by the cardboard were not found in the Tenax.

Fig. 1A also shows the behaviour of the model substances when the spiked cardboard was subjected to temperature close to 70 °C for short periods (2 h). Under these conditions, the percentages of migration of the most volatile substances (C10–C16) were very similar to those reached in longer periods of migration; however, the heaviest substances that migrate mainly by diffusion presented migration percentages lower than those obtained under longer storage conditions. Thus confirming that the more volatile hydrocarbons migrate faster and that their transfer rate from cardboard to food decreases with volatility (Biedermann & Grob, 2012; Hauder, Benz, Rüter, & Piringer, 2013).

3.3. Migration to dry foods

Fig. 1B and C shows the migration of model substances to polenta and couscous, respectively. As can be seen, the substances that model the C10–C16 fraction showed the lowest migration percentages and, in some cases, a tendency to decrease over time. In polenta, the migration of these substances was below 40%, while in couscous, it was below 25%. For some compounds such as 2-MN and 1-MN, no migration was observed in couscous after 10 days of migration. Probably the desorption phenomenon was more intense in the food matrix than in the Tenax.

On the other hand, the migration of C16–C25 fraction was below 60% in polenta and 35% in couscous. Most of these compounds reached their maximum migration after three days, observing that in some cases, these compounds also showed a gradual loss of their concentration over time, as it was previously observed in Tenax. The percentage of substances released by the cardboard was compared to the percentage of substances detected in polenta and couscous (see Figs. S2 and S3 respectively), clearly observing that a significant percentage of the model substances C10–C16 and C16–C25 released by the cardboard during migration, were not found in dry food. Therefore, 0% migration (in the case of undetected analytes) does not mean that migration did not occur, but that the dry food did not retain the analytes, and 100% migration would mean that the dry food adsorbed all the analytes released by the cardboard.

In contrast, the substances used to model the C25–C35 fraction of MOAH migrated slowly, at lower concentrations (see Fig. 1B and C) and did not show losses related to the desorption processes (see Figs. S2 and S3). These results agree with the results found by Eicher et al. (2015), concerning the migration of hydrocarbons with high boiling points, by direct contact, which is lower and slower than that of volatile hydrocarbons; however, it is not negligible (Eicher et al., 2015), and can represent a significant source of contamination for dry food.

In general, the content of the model substances in polenta was higher than in couscous. This can be attributed to the fact that the couscous particles were larger in diameter than polenta and therefore had a smaller exposed surface area, thus reducing the adsorption capacity of the food. On the other hand, Tenax is a fine, porous solid with a greater exposed surface and greater adsorption capacity than the tested dry foods. Consequently, the migration of MOAHs C10–C16 and C16–C25 was faster, and the migration values were greater than in dry food. However, the heavier substances (fraction MOAH C25–C35) showed a migratory behaviour to dry foods quite similar to Tenax, especially to polenta. The migratory behaviour of these substances confirms the good properties of Tenax as a food simulant for dry food, since migration values below the specific migration limit in this simulant will guarantee the safety of consumers as was also published by Triantafyllou et al. (Triantafyllou, Akrida-Demertzi, & Demertzis, 2007).

Fig. 1B and C also show the migration of the model substances in polenta and couscous at 70 °C for 2 h. The migration values of the fraction C10–C16 were higher than those obtained in prolonged storage conditions at 60 °C, thus indicating that the temperature plays a more important role than the exposure time. In the case of the C16–C25 fraction, it is evident that the increase in temperature also influences the migration mechanism, which could make substances with intermediate volatility more accessible for being transferred through the gas phase (Lorenzini et al., 2010). While in the heavier compounds of the C16–C25 fraction (3,6-DMP, 1-MPYR, BZNT) and the C25–C35 fraction, migration decreased as the number of carbons increases in the model substances. Furthermore, compared to migration in long storage periods, migration percentage was lower, suggesting that the exposure time was more important than the temperature.

Finally, Fig. 1D compares the migration of the model substances in Tenax, polenta and couscous at 70 °C for 2 h. The migration of the most volatile substances (C10–C16) was significantly higher in Tenax than in dry foods; however, for substances of intermediate volatility (fraction C16–C25), the migratory difference between Tenax and dry foods decreased with the increasing weight of the model substances. For the heavier substances (fraction C25–C35), the behaviour in Tenax is similar to that of dry foods. These facts also confirm that Tenax is a good solid food simulant, as it overestimates the migration of most types of solid food, as expected from a safety point of view.

As the paper and board samples were spiked with MOAHs, risk assessment of these samples cannot be evaluated. Initial analysis of MOAHs in the samples before being spiked confirmed that in this case, none of the samples contained MOAHs, what confirms that these samples are safe concerning the MOAHs.

3.4. Multivariate statistical analysis

In order to study the degree of association of model substances and identify possible migration patterns, known statistical tools of multivariate analysis were used, such as principal component analysis (PCA), hierarchical cluster analysis (HCA) and Partial least squares regression (PLSR).

Based on the similarity of the experimental results obtained at 60 °C and 70 °C, HCA classified the model substances into two large groups of compounds (see dendrogram of Fig. S4). The first group comprised the 6 most volatile substances (fraction MOAH C10–C16), and the second group included the 10 remaining substances. This classification was reinforced by the results observed in the model substances' correlation matrix (Table S1). The correlation matrix showed, with a significance below 0.05, that the most volatile compounds (C10–C16) had a positive and robust direct correlation among them, thus indicating that the migratory factors studied affect this type of substances in the same way and that its behaviour during migration was similar. The correlation for the rest of the substances showed considerable variability with positive correlation coefficients ranging from moderate to strong; these variations might result from the difference between the model substances' boiling points (Table 1). In contrast, the correlation between the most volatile compounds and the heaviest ones was low, showing different behaviours during migration.

Fig. 2 shows the PCA score graph for the migration values of the model substances for all the test conditions. For the construction of the graph, two principal components (PC1 and PC2) were chosen because these two components explained 98% of the total variance (Fig. S5), and PC1 retained 91% of the data variability. The tests with Tenax showed a markedly positive charge on PC1, associated with high migration values, especially for the most volatile compounds. Polenta and couscous migration samples were grouped on the left side of the chart, showing a more similar pattern. The chart also shows that migration test performed at 70 °C had, in general, higher values on PC2 than migration test performed at 60 °C, which is associated with higher migration values of the heaviest compounds at 60 °C, probably because migration time in these experiments was longer.

The possibility of predicting the migration of model substances in polenta, couscous and Tenax was explored by constructing PLSR models. The predictive capacity of the PLSR models was evaluated using the correlation coefficient (R2) and the root mean square error of estimation

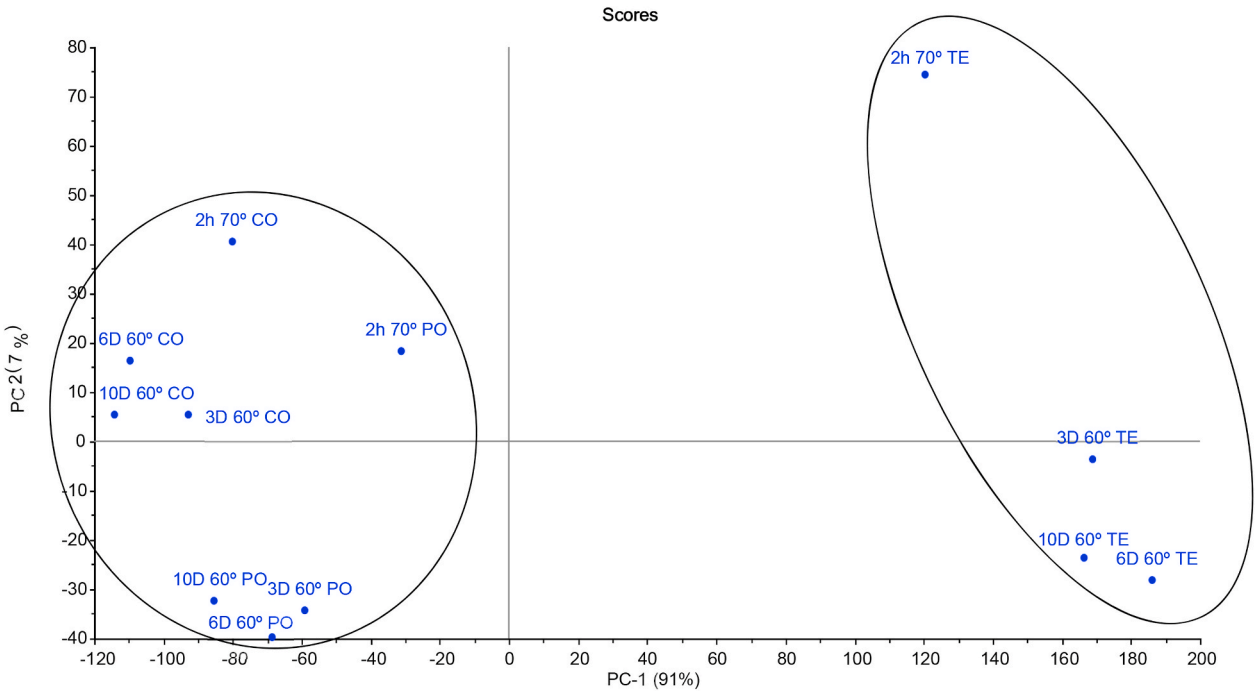

Fig. 2. PCA score plot of model substance migration.

(RMSE). The results showed a large dispersion of the data and little linearity for polenta and couscous. In contrast, the PLSR model for Tenax (see Fig. 3) shows good linearity with R2 values above 0.91 and RMSE less than 10%.

In other words, Tenax showed the best predictive capacity, and precise models could not be created to predict migration in polenta and couscous due to the variability of the data with respect to the storage period. Since the migration of the model substances in dry foods was lower than the migration in Tenax, the PLSR could be used to predict the migration of these compounds in the worst case.

4. Conclusion

The differences in the migratory behaviour of the MOAH model substances studied in this research were defined by their volatility, the chemical-physical nature of the food matrix and the migration conditions.

The most volatile substances migrated at a higher concentration and speed through the gas phase, being strongly adsorbed into Tenax, while in polenta and couscous, they were characterised by volatilisation and desorption phenomena. The heaviest substances migrated mainly by diffusion, and their behaviour was similar in both dry foods and Tenax.

The most volatile substances were characterised by presenting strong

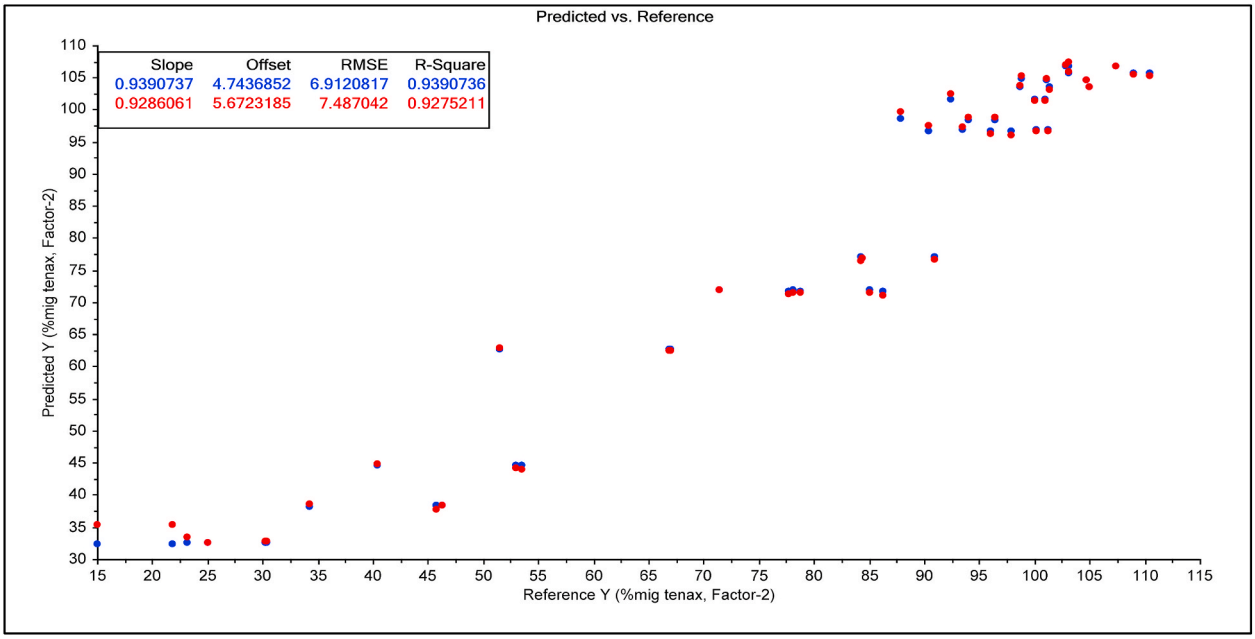

Fig. 3. Predicted migration versus actual migration at 60 °C in Tenax.

correlations between them and similar migratory behaviours. At the same time, the correlation of the substances with intermediate volatility was more variable; due to the influence of the migration temperature on the different migration mechanisms that these substances can suffer (diffusion and gas phase transference).

In general, the migration values of the model substances in Tenax were higher than in couscous and polenta, so it can be considered as the worst case in the simulation of migration to dry food. The PLSR model elaborated with the migration data in Tenax predicts migration values from the physicochemical properties of the model substances; this can be a very useful tool for future prediction experiments.

CRediT authorship contribution statement

Janira Jaén: Conceptualization, Methodology, Validation, Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Celia Domeño:** Conceptualization, Methodology, Validation, Investigation, Data curation, Writing – review & editing, Supervision. **Sara Úbeda:** Methodology, Investigation, Data curation. **Margarita Aznar:** Methodology, Investigation, Data curation, Formal analysis, Writing – review & editing. **Cristina Nerín:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodcont.2022.109016.

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