

# Identification of volatile and non-volatile migrants released during sous vide cooking by UPLC-IMS-QTOF and DI-SPME-GC-MS using a design of experiments approach

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## ABSTRACT

The rise of new culinary advances combined with science has made it possible to find new optimum methods of cooking, such as vacuum cooking (Sous Vide), that allow achieving pleasant textures, preserving the genuine nature of the food and also its original flavour. Sous Vide involves the direct contact of plastic materials with food during cooking, causing the possible release of chemical compounds that may alter the properties of the food and pose a risk to human health. In this work, the migration kinetics that takes place during this cooking process have been estimated thanks to a design of experiments (DoE). DoE has been applied to 4 samples of vacuum cooking bags containing 3 food simulants (ethanol 10%, acetic acid 3% and isooctane) under typical cooking conditions of the culinary technique. The study also allowed the identification of the main volatile and non-volatile migrants that can be transferred from this particular packaging. Twenty-nine non-volatile species were identified by ultra-high performance liquid chromatography coupled to a quadrupole-time-of-flight ion-mobility separation mass spectrometer (UPLC-IMS-QTOF) and sixty-four volatile species were identified by solid-phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS). Furthermore, a comprehensive literature analysis was conducted to explore the applications, origins, and potential toxicity of these compounds.

## 1. Introduction

In contemporary society, the fusion of scientific principles with culinary practices has catalyzed the emergence of "molecular gastronomy" or "molecular cuisine." This culinary paradigm constitutes a specialized scientific field dedicated to the exploration of chemical and physical processes inherent to culinary phenomena, thereby introducing a novel and progressive methodology to the culinary domain. Through the application of scientifically informed culinary techniques, molecular gastronomy endeavors to refine cooking methodologies to attain desirable textures while upholding the inherent essence and original flavors of ingredients to a heightened degree. A notable illustration of this scientific culinary approach is exemplified by the method of "sous vide" cooking (Baldwin, 2012). "Sous vide," a term originating from the French language, translates to "under vacuum." This culinary technique entails the placement of raw or precooked ingredients within a sealed, heat-resistant vessel known as a vacuum bag, followed by the removal of

air from the container. Subsequently, the ingredients undergo cooking at lower temperatures and for extended durations compared to conventional culinary methods.

Sous Vide cooking is typically executed within a flexible range of temperatures and durations, contingent upon the nature of the food being prepared, spanning from several minutes to hours and from low temperatures up to 80 °C. While discussions surrounding food safety primarily address the survival and proliferation of pathogens, the potential chemical hazards arising from packaging-to-food migration are often overlooked. European Parliament and Council Regulation (EC) No. 1935/2004 stipulates stringent guidelines regarding all food contact materials (FCM), mandating adherence to specific principles (European Parliament EU No, 1935/2004, (EU) No, 1935/2004, 2004). Among these criteria is the requirement for FCM to exhibit adequate inertness to prevent the transfer of hazardous substances through migration processes, thereby safeguarding consumer health and preserving the sensory attributes of food products. Furthermore, European Commission

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Regulation (EU) No. 10/2011, which pertains specifically to plastic FCM, permits the utilization of additives and other intentionally incorporated substances (IAS) in packaging production, subject to compliance with prescribed migration limits for these authorized constituents.

Nevertheless, there exists a category of substances Non Listed Substances (NLS) and non-intentionally added substances (NIAS), which may be present in plastic packaging materials (Nerín et al., 2022). These substances can arise in different ways, such as process contamination, residual impurities, parallel reactions during processing or degradation compounds by external factors (Commission Regulation EU No 10, 2011).

As technological progress accelerates and the call for advancements in food contact plastic materials intensifies, there is a heightened emphasis on ensuring food safety. Furthermore, the complexities surrounding the identification and measurement of non-authorized and non-intentionally added substances (NIAS) are amplified by the diverse array of polymeric matrices and the incorporation of novel additives employed in plastic packaging fabrication (Birgit, 2018).

Chromatographic techniques are extremely important tools for the determination of compounds present in FCM and many studies using gas chromatography coupled to mass spectrometry prove the efficiency of this technique in the determination of volatile NIAS.

Chromatographic methodologies serve as indispensable instruments for identify compounds within food contact materials (FCM), with numerous studies employing gas chromatography coupled to mass spectrometry showcasing the efficacy of this approach in identifying volatile NIAS (Paiva et al., 2021; Salazar et al., 2017; Souza Silva et al., 2017; Zitoun-Hamama et al., 2016). However, in the context of non-volatile compounds characterized by considerable structural complexity, the utilization of sophisticated tools and methodologies becomes imperative to uphold food safety standards and adhere to the regulatory framework delineated within food contact materials (FCM) regulations (Nerín et al., 2022).

An influential analytical method employed in the determination of non-volatile non-authorized and non-intentionally added substances (NIAS) is ultrahigh-performance liquid chromatography (UPLC) coupled with a quadrupole time-of-flight (QTOF) mass spectrometer (Vera et al., 2019, 2022).

Vacuum cooking broadens the aspect of the use of food packaging because it is no longer used only to store food; in this case the use is different because the food is going to be cooked inside it. In this work we have studied how cooking conditions will influence the migration of volatile and non-volatile compounds from the packaging used for this purpose to the food. Given the variability of times and temperatures used in this type of cooking, it is necessary to resort to the use of design of experiment (DoE) to explore the influence of the cooking conditions used on the transfer of volatile and non-volatile compounds from the plastic material to the cooked food. The cooking conditions under study will be time and temperature. Two types of multilayer materials, commonly used in this type of cooking and based on polypropylene, polyethylene and polyamide, were selected for this study.

The examination of various designated experiments was conducted through the application of solid-phase microextraction coupled with gas chromatography-mass spectrometry (SPME-GC-MS) and ultrahigh-performance liquid chromatography-ion mobility spectrometry-quadrupole time-of-flight mass spectrometry (UPLC-IMS-QTOF). Analysis of the identified non-authorized and non-intentionally added substances (NIAS) and intentionally added substances (IAS), in conjunction with the utilization of response surface methodology within the framework of design of experiments (DoE), facilitated the derivation of conclusions regarding the risk implications associated with vacuum cooking.

## 2. Material and methods

### 2.1. Chemicals

Ethanol absolute (HPLC quality) from Panreac (Barcelona, Spain), glacial acetic acid (technical grade) from Sigma-Aldrich Quimica S.A. (Madrid, Spain) and isooctane (UPLC-MS quality) from Honeywell (Madrid, Spain) were used to prepare the simulants. Ultrapure water was obtained from a Milli-Q Ultrametric Wasserlab GR 216071 (Madrid, Spain). Methanol (ultra-LC-MS quality) used in the mobile phase was from Honeywell (Madrid, Spain).

### 2.2. Samples

Four different samples of vacuum cooking bags were analyzed using the two types of materials commonly used in this type of cooking:

- Material 1: Polypropylene and bioriented polyamide (PP/PA)
- Material 2: High-density polyethylene and bioriented polyamide (HDPE/PA). This material was provided in two different formats: smooth and embossed surface (HDPE<sub>s</sub>/PA and HDPE<sub>e</sub>/PA).

The bags were manufactured by thermosealing of two multilayer films. The sealing process of the bags has been previously studied by comparing 3 replicates of each material with and without sealing for each simulant. Three of the bags were manufactured with HDPE/PA, using the different formats foreseen: (i) smooth surface (HDPE<sub>s</sub>/PA), (ii) embossed surface (HDPE<sub>e</sub>/PA), and (iii) mixed smooth and embossed surface (HDPE<sub>m</sub>/PA) in a 50% ratio. In all cases HDPE was the food contact side. The fourth sample (iv) was made of polypropylene and polyamide (PP/PA). In this case, PP was the food contact side. All the bags were purchased from official distributors and were labelled as FDA certified for being use in direct food contact.

### 2.3. Experiments

For the experiments, pouches of each sample (6 × 8 cm) were made by heat-sealing in triplicate for each experiment. In addition, three blanks were included in each experiment. The difference between replicates was found to be insignificant. The pouches were then filled with 20 mL of food simulant and vacuum sealed using Distform TekVac 410 vacuum filler (Lleida, Spain).

In this particular context, the packaging serves not as a means for food storage but as a vessel for direct cooking, thereby undergoing distinctive and stringent conditions of time and temperature. To explore the potential migration of packaging constituents to food under these novel culinary conditions, food simulants mandated by regulatory standards were employed, incorporating the actual parameters used in the cooking process. In adherence to European Regulation (Commission Regulation EU No 10, 2011), the selected food simulants included ethanol 10% (simulant A) and acetic acid 3% (simulant B) as aqueous simulants, along with ethanol 95% and isooctane as fat simulants.

Once the bags were ready, they were immersed in a water bath to reproduce the cooking conditions used in restaurants by the chefs.

According to the cooking conditions, Table 1 shows the conditions

**Table 1**  
Variables evaluated in the maximum area of volatile and semi-volatile.

Experiments	Assay time (v1)		Assay temperature (v2)	
	Real (min)	Normalized	Real (°C)	Normalized
E1	480	1	80	1
E2	480	1	50	-1
E3	15	-1	50	-1
E4	15	-1	80	1
Central Point (E5)	247,5	0	65	0

under which the experiments were carried out, using high and low time and temperature values. These conditions will be used to carry out the DoE as indicated in Section 2.4.

#### 2.4. Design of experiments and response surface methodology

To evaluate the transfer of the compounds migration in the different experiments, the response area of the volatile and non-volatile compounds was used. The combination of the variables; (v1) time and (v2) temperature was analyzed in their two levels, 1 (high) and -1 (low), described in Table 1 where the central point (CP) is shown. Therefore, a factorial design  $2^2$  was obtained for the four simulants and the four sous vide cooking bags. Moreover, for the analysis and organization of the data, Excel and Octave software were used. The results obtained were submitted to an ANOVA analysis. (Pereira & Pereira-Filho, 2018).

Finally, isoctane was chosen as D2 substitute simulant because bags filled with 95% ethanol collapsed under the vacuum and temperature conditions studied.

#### 2.5. Analysis of volatile and semi-volatile compounds by SPME-GC-MS

Analysis of volatile compounds was conducted utilizing a CTC Analytics Pal RSI 85, procured from CTC Analytics AG (Zwingen, Switzerland), interfaced with GC-MS instrumentation comprising a GC 8860 gas chromatograph coupled to a 5977B Mass Spectrometer, both sourced from Agilent (Palo Alto, CA, USA). Data acquisition was performed in full scan mode within the mass range of 45 to 450  $m/z$ .

Separation of analytes was achieved using an HP-5 MS column, also obtained from Agilent, with dimensions of 30 m x 0.25 mm and a film thickness of 0.25  $\mu\text{m}$ . The temperature program commenced at 40 °C for 3 min, followed by a ramp of 10 °C per minute until reaching a hold at 300 °C for 5 min. The injector was operated at a temperature of 250 °C in splitless mode, and helium served as the carrier gas at a flow rate of 1.2 mL per minute.

For the migration of volatile and semi-volatile compounds present into the ethanol 10% and acetic acid 3% simulants, a DVB/CAR/PDMS 50/30  $\mu\text{m}$  fiber was used in direct immersion mode in 18 mL of simulant. Paiva et al. (2021) have shown that this fiber is the most effective for the screening of unknown compounds. Incubation temperature and extraction time were 80 °C and 15 min, respectively.

However, isoctane simulant is not suitable for SPME, so liquid direct injection of 1  $\mu\text{L}$  was used. The same chromatographic conditions previously mentioned were used.

#### 2.6. Analysis of non-volatile compounds by UPLC IMS QTOF

For the analysis and characterization of non-volatile compounds, an ACQUITY UPLC I-Class system, coupled with a Vion IMS QTOF spectrometer featuring an electrospray ionization source (ESI), was utilized (Waters, Milford, MA). Ethanol 10% and acetic acid 3% simulants were subjected to direct injection, whereas isoctane samples underwent prior evaporation under a nitrogen current, followed by reconstitution with ethanol to the original volume to render them compatible for UPLC-reverse phase injection.

The chromatographic conditions used are those described by Vera et al. for the identification of NIAS in migration from polymeric films intended for food contact. A UPLC BEH C18 column (1.7  $\mu\text{m}$  particle size, 2.1 mm x 100 mm) was used with a flow rate of 0.3 mL/min at a temperature of 35 °C. Furthermore, the mobile phases were water and methanol with 0.1% formic acid (phase A and B respectively). The gradient used was 5% phase B to 100% phase B in 13 min. The injection volume was 5  $\mu\text{L}$ .

Data acquisition occurred in full scan sensitivity mode, encompassing both positive and negative ionization modes, with capillary voltage set to 1 kV and cone voltage to 30 V. Source and desolvation temperatures were maintained at 120 °C and 500 °C, respectively, with a

desolvation gas flow of 800 L/h. The instrument underwent calibration for a mass range spanning from 50 to 1200 Da. Additionally, data acquisition was conducted in high-definition mass spectrometry (HDMSE) mode. Subsequent data processing was executed using UNIFI v1.8 software (Waters, Milford, MA).

#### 2.7. Factorial design and calculations

Table 1 shows the complete summary of the design of experiments that resulted in the factorial design  $2^2$  with the 2 variables and its two levels, applied to the four sous vide cooking bags in 3 different simulants. This generated a total of 5 experiments for each sample (Table 1) and carried out in triplicate, resulting in 60 experiments in total. To these must be added the 3 blanks for each of the samples. The number of experiments was reduced to 15 (4 samples \* 3 food simulants + 3 blanks) thanks to the DoE. The area of maximum response was used to classify the best and worst sous vide cooking conditions depending on the type of surface and composition of the bag.

To obtain the results, the variables examined in sous vide cooking method were combined and the effect calculated using Eq. 1. Furthermore, the effects of the variables were evaluated according to the response surfaces methodology (RSM) (Pereira & Pereira-Filho, 2018).

$$\text{Effect} = \bar{X}_+ - \bar{X}_- \quad (1)$$

where  $\bar{X}_+$  and  $\bar{X}_-$  are the average of the responses of the variables at the high and low levels, respectively.

From the calculations analysed by excel and octave programs, and using Equation 2, the response surface was obtained Fig. 1 shows the RMS for the four different sous vide bags in the three food simulants.

$$\text{Response} = b_0 + b_1x_1 + b_2x_2 + b_{12}x_{12} \quad (2)$$

Where  $b_0$  is the coefficient related to the maximum migration area from the DoE experiments,  $b_1$ ,  $b_2$  and  $b_{12}$  are the coefficients related to the primary variables and the interaction of the two variables. In addition, the  $x_1$ ,  $x_2$  and  $x_{12}$  are the variables v1, v2 and interaction v1v2 normalized at their high (1) and low (-1) levels.

### 3. Results

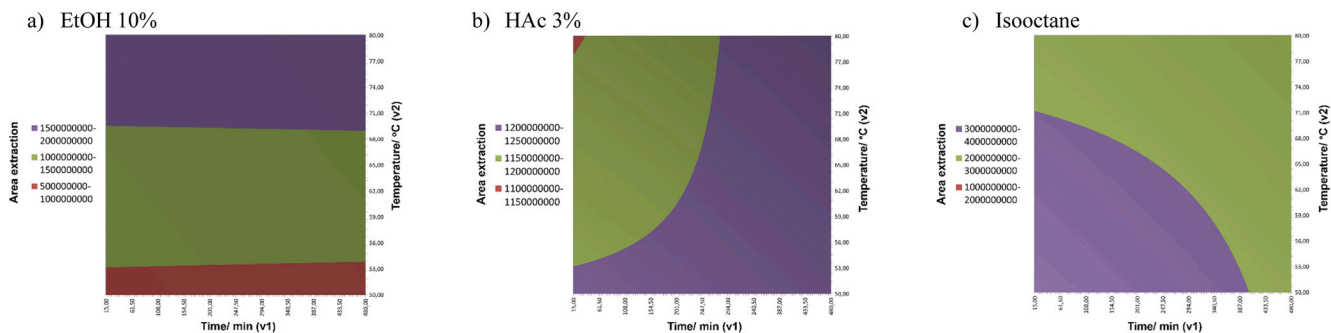
#### 3.1. Results of volatile compounds

##### 3.1.1. Effect of cooking conditions on total migration area volatile compounds

For every set of Design of Experiments (DoE), distinct response surfaces were derived, elucidating the diverse effects exerted by the coefficients computed through Equation 2. These coefficients represent both the primary variables and their corresponding second-order combinations, each imparting distinct influences upon the system under study. This variability is evident through the depiction of disparate Response Surfaces (RS) in Fig. 1, which portray the calculated and predicted maximum area of migrated compound simulants analyzed.

The variables v1 (representing time) and v2 (representing temperature) exhibit differential effects contingent upon the specific simulant and the material composition of the packaging. Fig. 1a (for EtOH 10%), 1b (for HAC 3%), and 1c (for Isooctane) illustrate the response of HDPEe/PA under varied conditions. Notably, for the EtOH 10% simulant, time demonstrates minimal influence, while temperature exerts a pronounced effect, suggesting heightened risk associated with cooking at elevated temperatures. Conversely, for the HAC 3% simulant, both v1 and v2 variables display notable influence, with compound transfer increasing substantially with prolonged time and elevated temperature. In the case of the Isooctane simulant, both variables are influential, with temperature demonstrating a particularly pronounced effect. However, such behavior is not consistently observed across all materials, highlighting variations in simulant responses based on material composition

Sample: (HDPEe/PA)



Sample: (HDPEs/PA)

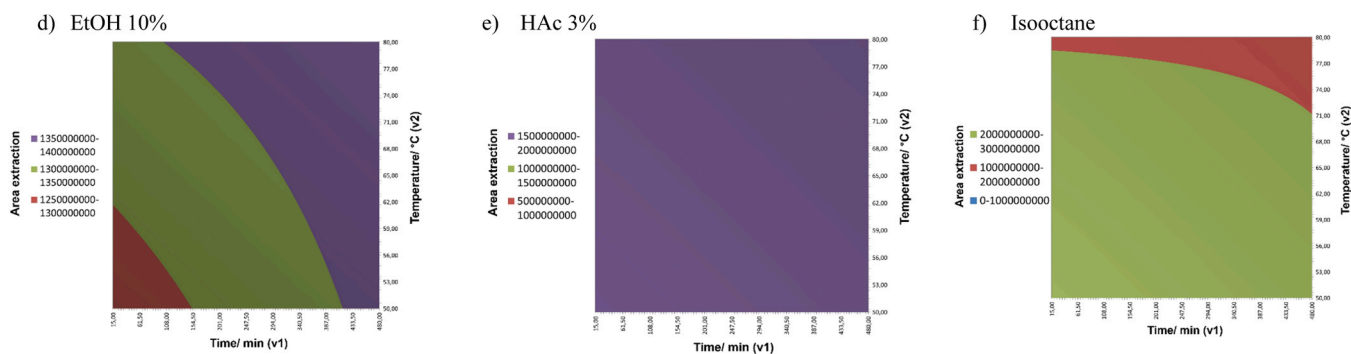


Fig. 1. Response Surface for the relationship between total migration area and the influence of variables time (v1) and temperature (v2) in volatile compounds for HDPEe/PA (a-c) and HDPEs/PA (d-f) bags in simulants A, B and D2.

(refer to Fig. 1d-f in Supplementary Material). Furthermore, the migration pattern diverges from that of other simulants, with the highest migration observed at lower temperatures, attributed to the rapid evaporation of volatile compounds from the liquid surface under high-temperature conditions.

In comparing the transference characteristics from HDPEe/PA and HDPEs/PA bag samples for the food simulant EtOH 10% (refer to Figs. 1a and 1d), notable disparities in response surfaces become evident. Specifically, for HDPEe/PA, temperature exerts a more significant influence on the maximum area than time. Conversely, for HDPEs/PA, the reverse holds true, with time exhibiting a notably more substantial impact on the area of transferred volatile compounds than temperature.

The literature reports that compounds with low molar mass have a higher diffusion process (Dole et al., 2006; Voultzatis et al., 2007). However, in the transfer of compounds from one surface to another, the molar mass is not the only determining factor, since other factors such as temperature, exposure time, type of simulant or the structure of the material also have a considerable influence on the diffusion process.

These considerable differences justify the importance of this study in order to predict the risk associated with sous vide cooking conditions for different kind of food.

### 3.1.2. Identification of volatile compounds

Sixty-four volatile and semi-volatile compounds were identified in tests on all four types of bags in all food simulants, using the NIST20 mass spectra library. Table 2 lists the compounds identified, as well as their retention time, CAS number and elemental composition for each of the materials (PP/PA, HDPEmix/PA, HDPEs/PA and HDPEe/PA) in each of the simulants used. Furthermore, the table shows (in parentheses) the number of trials in which the compound appears for each simulant. In addition, each compound was related to its use/origin, as described in EU 10/2011, Food Contact Chemicals database (Food Packaging Forum Foundation, 2020) and literature (Babity et al., 2021a; Benson, 2009;

Formanek et al., 1997; Gall et al., 2020; Gao et al., 2011; Gopala Krishnan et al., 1993; Kuki et al., 2017; Lai et al., 1997; Mustafa & Hamdi, 2016; Pluta et al., 2017; Sanches-Silva et al., 2014; Sapozhnikova et al., 2021; Silva et al., 2006; Vera et al., 2018; Wu et al., 2021) and/or FCCbd v5.

The identified compounds were categorized into two distinct groups, as depicted in Fig. 2: IAS and NIAS. Approximately 64% of the compounds fell under the classification of IAS, while the remaining 36% were classified as NIAS. Within the IAS category, compounds were further subdivided into distinct subgroups based on their properties and intended applications, as outlined in Table 2.

It has been decided to group the compounds found according to their use or origin. Consequently, the predominant representation of Intentionally Added Substances (IAS) is segmented into six distinct subgroups, comprising plasticizers, lubricants, antioxidants, printing inks, additives, and slip agents. Notably, plasticizers constitute 35% of the identified compounds in the analyzed samples, encompassing phthalates such as dimethyl phthalate, dibutyl phthalate, butyl benzyl phthalate, and bis(2-ethylhexyl) adipate. Phthalates have long been recognized as hazardous compounds, prompting ongoing evaluations by regulatory agencies regarding their usage in Food Contact Materials (FCM) production. Furthermore, the U.S. Food and Drug Administration ((FDA: Department of Health and Human Services, 2022)) permits the use of 23 types of phthalates in food packaging, while European Regulation (EU) No. 10/2011 stipulates migration limits ranging from 0.05 to 30 mg/kg for six specific phthalates. (Commission Regulation EU No 10, 2011).

On the other hand, additives (use not specified) represent 22% of the identified compounds list and range from dispersing agent to spacing agents and others. Furthermore, under the IAS group, 16% of the compounds were classified as slip agents and 14% as lubricants depending on their applications and properties. Antioxidant species (8%) such as butylated hydroxytoluene and 3,5-di-tert-butyl-4-hydroxybenzaldehyde have been identified.

As mentioned earlier, the NIAS group represented 36% of the

**Table 2**

Identified compounds by DI-SPME-GC-MS along with their retention time (RT in minutes), CAS number and molecular formula (MF) for PP/PA, HDPEmix/PA, HDPEs/PA and HDPE/PA in simulants A (ethanol 10%), B (acetic acid 3%) and D2 (isooctane).

RT (min)	Compound	CAS	MF	PP/PA	HDPEmix/PA	HDPEs/PA	HDPE/PA	USE
6,33	p-Xylene	106-42-3	C <sub>8</sub> H <sub>10</sub>	A (3) B (2) D2 (0)	A (3) B (2) D2 (1)	A (5) B (3) D2 (0)	A (4) B (3) D2 (2)	Contaminant (NIAS)
6,77	Styrene	100-42-5	C <sub>8</sub> H <sub>8</sub>	A (3) B (3) D2 (0)	A (3) B (3) D2 (1)	A (5) B (4) D2 (0)	A (4) B (3) D2 (0)	Contaminant (NIAS)
7,40	Oxime-, methoxy-phenyl-	1000222-86-6	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub>	A (4) B (0) D2 (0)	A (5) B (4) D2 (0)	A (5) B (5) D2 (1)	A (5) B (4) D2 (1)	Contaminant (NIAS)
9,39	p-Cymene	99-87-6	C <sub>10</sub> H <sub>14</sub>	A (0) B (0) D2 (2)	A (0) B (0) D2 (2)	-	A (0) B (0) D2 (1)	Printing inks (IAS)
9,96	gamma-Terpinene	99-85-4	C <sub>10</sub> H <sub>16</sub>	-	A (0) B (0) D2 (3)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	Flavoring agent, contaminant (NIAS)
10,04	Acetophenone	98-86-2	C <sub>8</sub> H <sub>8</sub> O	-	A (1) B (0) D2 (0)	A (0) B (1) D2 (1)	-	Catalyst for olefin polymerization, impurities (NIAS)
11,52	Benzoic acid	65-85-0	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Antimicrobial (IAS)
11,97	Naphthalene	91-20-3	C <sub>10</sub> H <sub>8</sub>	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	A (2) B (0) D2 (0)	Contaminant (NIAS)
12,41	Benzaldehyde, 3,4-dimethyl-	5973-71-7	C <sub>9</sub> H <sub>10</sub> O	A (0) B (2) D2 (0)	-	A (1) B (1) D2 (0)	A (1) B (2) D2 (0)	Lubricant (IAS)
12,57	Benzothiazole	95-16-9	C <sub>7</sub> H <sub>5</sub> NS	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	UV Absorber derivative (IAS)
12,86	Caprolactam	105-60-2	C <sub>6</sub> H <sub>11</sub> NO	A (0) B (1) D2 (4)	-	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	Manufacturing polyamide (NIAS)
13,06	Nonanoic acid	112-05-0	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	-	A (1) B (0) D2 (0)	A (1) B (1) D2 (0)	A (1) B (0) D2 (0)	Adhesive-food contact (IAS)
13,23	Cinnamaldehyde, (E)-	14371-10-9	C <sub>9</sub> H <sub>8</sub> O	A (0) B (0) D2 (1)	-	-	A (1) B (0) D2 (0)	Antibacterial, antifungus, antioxidant (IAS)
13,47	Phenol, p-tert-butyl-	98-54-4	C <sub>10</sub> H <sub>14</sub> O	-	-	A (2) B (0) D2 (0)	A (1) B (1) D2 (0)	Degradation from Irganox/Irgafos, contaminant (NIAS)
14,38	n-Decanoic acid	334-48-5	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Dispersing agent (IAS)
14,73	Copaene	3856-25-5	C <sub>15</sub> H <sub>24</sub>	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	Contaminant (NIAS)
15,29	Caryophyllene	87-44-5	C <sub>15</sub> H <sub>24</sub>	A (0) B (0) D2 (2)	A (0) B (0) D2 (2)	A (0) B (0) D2 (2)	A (0) B (0) D2 (3)	Antioxidant and antibacterial (IAS)
15,54	Acetic acid, cinnamyl ester	103-54-8	C <sub>11</sub> H <sub>12</sub> O <sub>2</sub>	A (0) B (0) D2 (3)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (3)	Flavoring agent, contaminant (IAS)
15,68	Dimethyl phthalate	131-11-3	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	-	A (1) B (1) D2 (0)	A (2) B (3) D2 (0)	A (3) B (2) D2 (0)	Plasticizer and additive (IAS)
15,87	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	719-22-2	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	A (0) B (3) D2 (0)	A (0) B (1) D2 (0)	A (0) B (2) D2 (0)	-	Degradation product of Irgafos 168 (NIAS)
16,34	2,4-Di-tert-butylphenol-	96-76-4	C <sub>14</sub> H <sub>22</sub> O	A (1) B (5) D2 (5)	A (5) B (5) D2 (3)	A (5) B (4) D2 (1)	A (5) B (5) D2 (2)	Degradation product of Irgafos 168 (NIAS)
16,41	Butylated Hydroxytoluene	128-37-0	C <sub>15</sub> H <sub>24</sub> O	A (0) B (1) D2 (0)	A (3) B (1) D2 (2)	A (4) B (4) D2 (2)	A (4) B (4) D2 (3)	Antioxidant (IAS)
17,37	Diethyl Phthalate	84-66-2	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	A (3) B (3) D2 (3)	A (3) B (4) D2 (1)	A (3) B (3) D2 (2)	A (3) B (3) D2 (2)	Plasticizer (IAS)
17,39	Caryophyllene oxide	1139-30-6	C <sub>15</sub> H <sub>24</sub> O	A (0) B (0) D2 (1)	-	A (0) B (0) D2 (1)	A (0) B (0) D2 (2)	Antioxidant (IAS)
17,86	Benzophenone	119-61-9	C <sub>13</sub> H <sub>10</sub> O	A (0) B (1) D2 (0)	A (2) B (0) D2 (0)	A (1) B (0) D2 (0)	-	Print ink (IAS)
18,42	Phthalic acid, ethyl pentyl ester	1000308-93-6	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub>	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	-	Plasticizer (IAS)
19,13	Tetradecanoic acid	544-63-8	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	-	A (1) B (0) D2 (0)	A (2) B (1) D2 (0)	A (1) B (2) D2 (0)	Additive (IAS)

(continued on next page)



Table 2 (continued)

RT (min)	Compound	CAS	MF	PP/PA	HDPEmix/PA	HDPEs/PA	HDPEe/PA	USE
19,30	Benzyl Benzoate	120-51-4	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	A (0) B (0) D2 (3)	A (0) B (0) D2 (2)	A (0) B (0) D2 (2)	A (0) B (0) D2 (1)	Plasticizer (IAS)
19,34	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	C <sub>15</sub> H <sub>22</sub> O <sub>2</sub>	A (2) B (2) D2 (0)	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	A (1) B (1) D2 (0)	Antioxidant (IAS)
20,18	Pentadecanoic acid	1002-84-2	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	-	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Adhesive (IAS)
20,37	Phthalic acid, isobutyl octyl ester	1010309-04-5	C <sub>20</sub> H <sub>30</sub> O <sub>4</sub>	A (1) B (0) D2 (0)	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Plasticizer (IAS)
20,90	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	C <sub>17</sub> H <sub>24</sub> O <sub>3</sub>	A (3) B (2) D2 (0)	A (4) B (1) D2 (0)	A (4) B (2) D2 (0)	A (3) B (2) D2 (0)	Degradation product of Irganox 1076 (NIAS)
21,03	Diphenyl sulfone	127-63-9	C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> S	A (1) B (1) D2 (0)	A (1) B (2) D2 (0)	A (2) B (2) D2 (0)	A (3) B (3) D2 (0)	Additive (IAS)
21,04	Palmitoleic acid	373-49-9	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	-	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Additive, surfactant, adhesive (IAS)
21,11	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)- 4-hydroxy-, methyl ester	6386-38-5	C <sub>18</sub> H <sub>28</sub> O <sub>3</sub>	A (3) B (3) D2 (0)	A (4) B (1) D2 (0)	A (5) B (0) D2 (0)	A (4) B (0) D2 (0)	Degradation product of Irganox 1076 (NIAS)
21,19	n-Hexadecanoic acid	57-10-3	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	A (3) B (2) D2 (1)	A (2) B (3) D2 (2)	A (2) B (2) D2 (1)	A (3) B (2) D2 (2)	Processing aid-emollient (IAS)
21,30	1,4-Dibutyl benzene-1,4-dicarboxylate	1962-75-0	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	-	-	-	A (1) B (0) D2 (0)	Plasticizer (IAS)
21,30	Dibutyl phthalate	84-74-2	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	A (1) B (1) D2 (0)	A (3) B (2) D2 (0)	-	A (1) B (0) D2 (0)	Plasticizer (IAS)
21,54	Hexadecanoic acid, ethyl ester	628-97-7	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	-	-	A (1) B (1) D2 (0)	A (0) B (0) D2 (1)	Flavoring agent-adyvant (NIAS)
21,60	3,5-di-tert-Butyl-4-hydroxyphenylpropionic acid	20170-32-5	C <sub>17</sub> H <sub>26</sub> O <sub>3</sub>	A (4) B (2) D2 (0)	A (3) B (2) D2 (0)	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Degradation product of Irganox 1010 and Irgafos 168 (NIAS)
21,88	9-Acetylphenanthrene	2039-77-2	C <sub>16</sub> H <sub>12</sub> O	A (2) B (2) D2 (0)	-	A (0) B (1) D2 (0)	-	Contamination (NIAS)
22,40	9-Octadecenitrile, (Z)-	112-91-4	C <sub>18</sub> H <sub>33</sub> N	A (0) B (0) D2 (2)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (2)	Lubricant (IAS)
22,86	6-Octadecenoic acid	1000336-66-8	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	-	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Lubricant degradation product (NIAS)
23,07	Octadecanoic acid	57-11-4	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	A (2) B (2) D2 (0)	A (0) B (3) D2 (0)	A (4) B (3) D2 (1)	A (3) B (3) D2 (2)	Plasticizer (IAS)
23,10	Palmitoleamide	106010-22-4	C <sub>16</sub> H <sub>31</sub> NO	-	-	-	A (0) B (0) D2 (2)	Lubricant (IAS)
23,12	Linoleic acid ethyl ester	544-35-4	C <sub>20</sub> H <sub>36</sub> O <sub>2</sub>	A (0) B (0) D2 (2)	A (0) B (0) D2 (1)	-	-	Antibacterial (IAS)
23,21	Phenanthrene, 3,9-bis(1,1-dimethylethyl)-	55125-03-6	C <sub>22</sub> H <sub>26</sub>	A (0) B (1) D2 (0)	A (1) B (1) D2 (0)	-	-	Contamination, (IAS)
23,26	Hexadecanamide	629-54-9	C <sub>16</sub> H <sub>33</sub> NO	A (0) B (1) D2 (0)	A (0) B (1) D2 (1)	A (0) B (0) D2 (2)	A (1) B (1) D2 (2)	Slip agent (IAS)
23,31	Hexadecanoic acid, butyl ester (butyl palmitate)	111-06-8	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	A (0) B (0) D2 (2)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	Spreading and softening agent (IAS)t
23,38	Octadecanoic acid, ethyl ester	111-61-5	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	-	A (2) B (0) D2 (0)	-	-	Lubricant (IAS)
23,95	N,N-Dimethylpalmitamide	3886-91-7	C <sub>18</sub> H <sub>37</sub> NO	-	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	-	Degradation process (NIAS)
24,00	Tributyl acetyl citrate	77-90-7	C <sub>20</sub> H <sub>34</sub> O <sub>8</sub>	A (0) B (1) D2 (0)	A (0) B (1) D2 (0)	A (2) B (2) D2 (0)	A (3) B (0) D2 (0)	Plasticizer (IAS)
24,17	1,8-Diazacyclotetradecane-2,9-dione	5776-79-4	C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	-	-	A (0) B (0) D2 (1)	-	Caprolactam dimer polymer (NIAS)
24,53	Octadecanamide	124-26-5	C <sub>18</sub> H <sub>37</sub> NO	A (0) B (1) D2 (0)	A (1) B (1) D2 (0)	-	A (1) B (1) D2 (0)	Resin Degradation Product (NIAS)
24,69	9-Octadecenamide, (Z)-	301-02-0	C <sub>18</sub> H <sub>35</sub> NO	A (1) B (1) D2 (5)	A (0) B (1) D2 (3)	A (0) B (0) D2 (4)	A (0) B (1) D2 (3)	Slip Agent (IAS)

(continued on next page)

Table 2 (continued)

RT (min)	Compound	CAS	MF	PP/PA	HDPEmix/PA	HDPEs/PA	HDPEe/PA	USE
24,73	Tetradecanamide	638-58-4	C <sub>14</sub> H <sub>29</sub> NO	A (0) B (1) D2 (0)	-	-	-	Lubricant Degradation Product (NIAS)
24,84	Benzyl butyl phthalate	85-68-7	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	A (0) B (1) D2 (0)	-	A (0) B (1) D2 (0)	A (1) B (1) D2 (0)	Plasticizer (IAS)
25,02	Octadecanoic acid, butyl ester (butyl stearate)	123-95-5	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	-	-	A (1) B (0) D2 (1)	A (1) B (0) D2 (1)	Lubricant (IAS)
25,13	Hexanedioic acid, bis(2-ethylhexyl) ester	103-23-1	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	A (1) B (0) D2 (0)	A (0) B (1) D2 (0)	A (3) B (0) D2 (0)	A (2) B (0) D2 (0)	Plasticizer (IAS)
25,27	Triphenyl phosphate	115-86-6	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	-	A (1) B (1) D2 (1)	A (3) B (0) D2 (0)	A (4) B (0) D2 (1)	Plasticizer (IAS)
26,02	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	23470-00-0	C <sub>19</sub> H <sub>38</sub> O <sub>4</sub>	A (1) B (0) D2 (0)	A (2) B (0) D2 (0)	A (1) B (0) D2 (0)	A (2) B (0) D2 (0)	Slip agent, antioxidant, plasticizer (IAS)
26,34	Bis(2-ethylhexyl) phthalate	117-81-7	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	-	A (0) B (1) D2 (0)	A (2) B (0) D2 (0)	A (1) B (0) D2 (0)	Plasticizer (IAS)
27,60	Octadecanoic acid, 2,3-dihydroxypropyl ester	123-94-4	C <sub>21</sub> H <sub>42</sub> O <sub>4</sub>	A (1) B (0) D2 (0)	A (0) B (1) D2 (0)	A (2) B (2) D2 (0)	A (2) B (0) D2 (0)	Slip agent (IAS)
28,03	13-Docosenamide, (Z)-	112-84-5	C <sub>22</sub> H <sub>43</sub> NO	A (1) B (0) D2 (0)	A (0) B (2) D2 (5)	A (1) B (2) D2 (4)	A (2) B (1) D2 (5)	Slip agent (IAS)

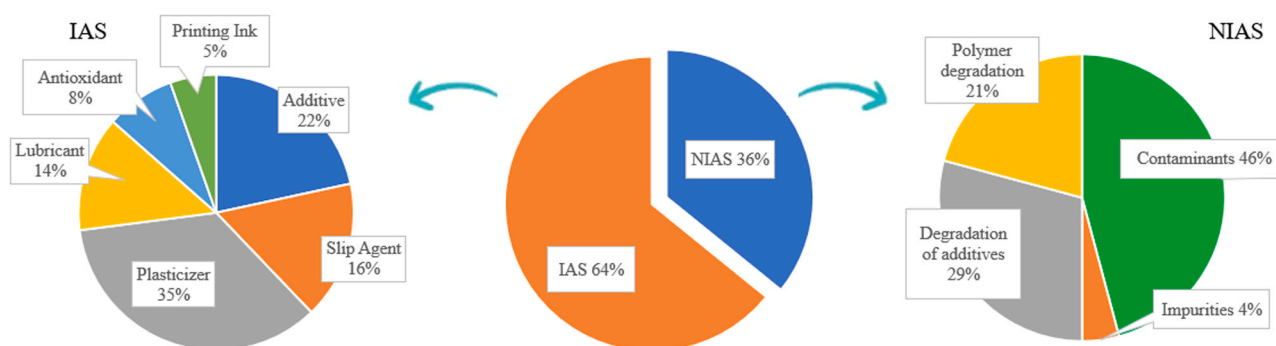


Fig. 2. Summary and classification of IAS and NIAS identified by DI-SPME-GC-MS.

identified compounds and they could have been generated by different processes described (Nerin et al., 2013). Thus, analytical resources and expertise are of extreme importance for the determination of these compounds (Nerin et al., 2013; Wrona & Nerin, 2019; Wrona & Nerin, 2020). The identified compounds were listed in four NIAS subgroups depending on its origin: degradation processes, degradation of additives, impurities, and contaminants.

The NIAS subgroup of contaminants consists of 46% of the identified compounds, some of them being styrene and PAHs derivatives. As described by Rochman et al., PAHs is polycyclic aromatic compounds commonly found in polystyrene and polyethylene plastics and are classified as environmental pollutants (Rochman et al., 2013). Therefore, the presence of styrene is a factor directly linked to the PAHs derivatives identified in the migration from vacuum cooking bags.

In the case of NIAS coming from additives degradation, which represent 29% of the identified compounds, a large part comes from the antioxidants Irgafos 168 and Irganox 1076, as in the case of compounds such as 2,4-di-tert-butylphenol, 2,5-cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl) and 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione. Furthermore, in the subgroup of NIAS coming from polymer degradation process (21%), copaene, 1,8-diazacyclotetradecane-2,9-dione (caprolactam dimer) and N,N-dimethylpalmitamide were identified. These compounds are polyamide alkanes and polyamide dimers from the degradation of the polymer chain, as the matrix (Bundesinstitut für Risikobewertung, 2018; Canellas et al., 2021).

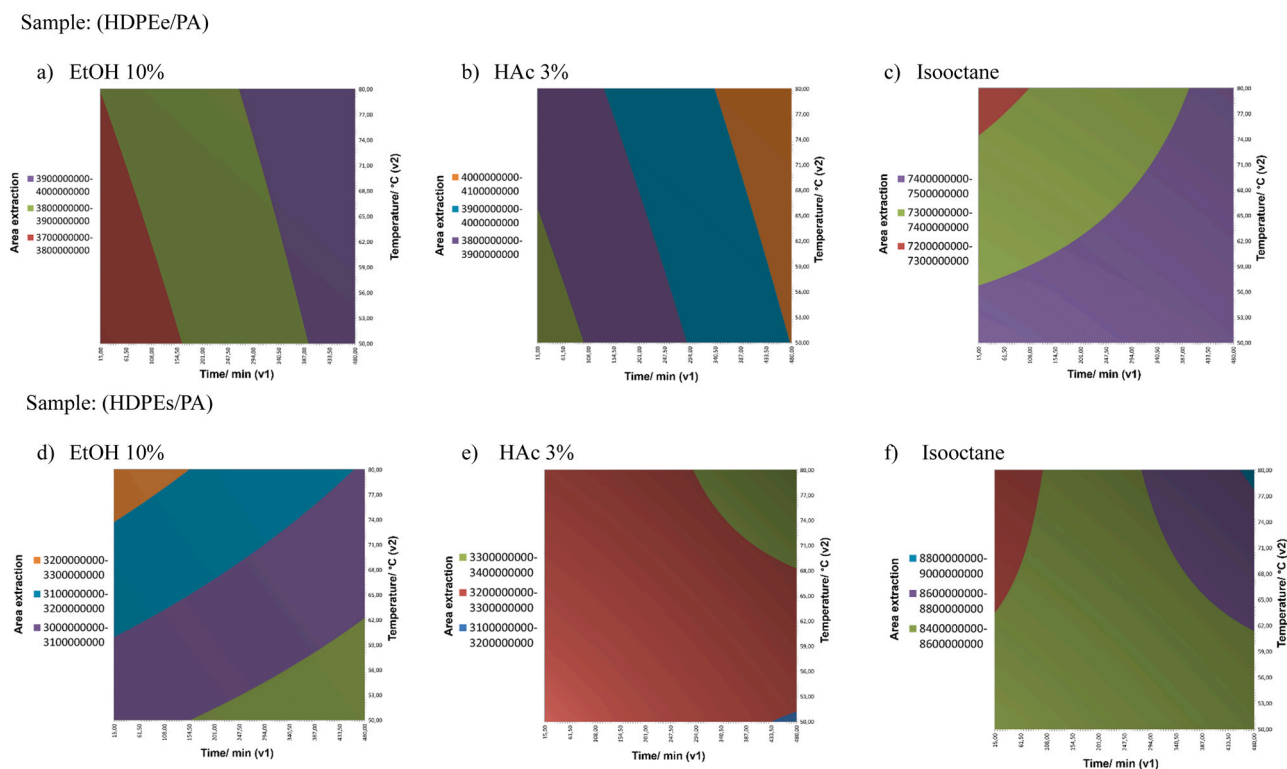
The EU directive 10/2011 lists some polyamide compounds, paying attention to the oligomers from these materials (Commission Regulation EU No 10, 2011). However, the German Federal Institute for Risk Assessment (BfR) has published a statement warning about the minimum contact with utensils containing polyamide 6 and 66, establishing a migration limit for oligomers and derivatives of 5 mg/kg (Bundesinstitut für Risikobewertung, 2018). This makes quantification studies necessary in order to guaranty the safety of materials intended to be in contact with food during the cooking process and not only as packaging.

### 3.2. Results of non-volatile compounds

#### 3.2.1. Effect of cooking conditions on total migration area non-volatile compounds

The results showed that, similar to volatile compounds, the impact of temperature and duration during sous vide cooking varies depending on both the material type and the simulant utilized. Fig. 3 presents the surface response for cooking bags fabricated from HDPEe/PA and HDPEs/PA. Notably, for the HDPEe/PA sample, the influence of these two variables is prominently observed across all three simulants (depicted in Fig. 3a-c). Furthermore, the extent of influence of these variables varies not only among different simulants but also between samples, as evidenced by the comparison of results between HDPEe/PA and HDPEs/PA (depicted in Fig. 3a-c and Fig. 3d-f).

While the trends in the influence of variables remain consistent for



**Fig. 3.** Response Surface for the relationship between total migration area and the influence of variables time (v1) and temperature (v2) in non-volatile compounds for HDPEe/PA (a-c) and HDPEs/PA (d-f) bags in simulants A, B and D2.

both volatile and nonvolatile substances, the complexity of their effects on migration processes has been previously discussed. This data allows for the observation that the diffusion of non-volatile compounds is closely associated with the ease of mobility within the polymeric chains. As mentioned earlier, temperature plays a crucial role in influencing the mobility of polymer chains and, consequently, the migration processes. For instance, in the case of HDPE, its glass transition temperature ( $T_g$ ) typically ranges between  $-30$  to  $-80$  °C. Consequently, higher temperatures applied to the material result in increased chain mobility, thereby enhancing the diffusion process (Voultzatis et al., 2007).

### 3.2.2. Identification of non-volatile compounds

From the analysis by UPLC-IMS-QTOF, 29 non-volatiles compounds were identified in the samples from the four different bag samples and the three simulants. The acceptance criteria for identification were defined with strict parameters, including a maximum allowable variation of 2% in collision cross-section (CCS), a mass error within 5 ppm, and a maximum retention time variation of 0.1 min. These criteria were applied consistently across all samples and were measured against an in-house library of injected standards for accurate identification (Canellas et al., 2021).

Table 3 lists the identified non-volatile compounds from their retention time, observed  $m/z$ , adduct, CCS value, CAS number and elemental composition. In addition, as in the case of volatiles, Table 3 also lists the compounds according to their use and origin, based on literature (Babity et al., 2021a; Benson, 2009; Formanek et al., 1997; Gall et al., 2020; Gao et al., 2011; Gopala Krishnan et al., 1993; Kuki et al., 2017; Lai et al., 1997; Mustafa & Hamdi, 2016; Pluta et al., 2017; Sanches-Silva et al., 2014; Sapozhnikova et al., 2021; Silva et al., 2006; Vera et al., 2018; Wu et al., 2021) and/or FCCbd v5. As it can be seen in Fig. 4, 86% of the compounds belonged to the IAS group and 14% to NIAS. Furthermore, the IAS group was divided into five subgroups classifying the compounds according to their origin and application as; stabilizers, antioxidants, additives, slip agents and plasticizers.

As observed, the predominant subgroup among non-volatile IAS was comprised of plasticizers, accounting for 46% of the identified compounds. Within this subgroup, some phthalates (dioctyl phthalate and diisononyl phthalate) are authorized in the 10/2011/EU (Beneventi et al., 2020). On the other hand, the subgroup of antioxidants represents 29% of the IAS listed in Table 3, including substances such as Irganox 1035, Irganox 1076 and Irgafos 168, listed and regulated for its use in the production of plastic packaging (Commission Regulation EU No 10, 2011). Furthermore, other subgroups with lower representatives were identified, such as stabilizers (17%), additives (4%) and slip agents (4%).

Non-volatiles NIAS, were subdivided into two major groups according to its origin: the subgroup of NIAS coming from degradation processes and contaminants, having the latter the highest percentage (75%) of the classified compounds. The compounds 1,9-nonanediol diacrylate, neopentyl glycol propoxylate and capric triglyceride, classified as contaminants, appear during the production of polyacrylate materials, which leads to the conclusion that these NIAS come from contamination processes during materials processing and manufacturing (Babity et al., 2021b; Sharman et al., 1995).

In contrast, the NIAS subgroup of additive of degradation represents 25% of the compounds identified, with the Bisphenol A diglycidyl ether (BADGE) as an example of this subgroup. As described in the literature, the BADGE is a monomer widely used in the production of food-contact materials adhesives (Sharman et al., 1995) and, as described by Petersen et al., the migration of this monomer into food has the potential to initiate various parallel reactions, consequently altering the organoleptic properties and integrity of both the food and the material (Petersen et al., 2008). This compound, comes from adhesives and is authorised in regulation 10/2011/EU Nerin et al. (2014).

### 3.2.3. Comparison of results for volatile and non-volatile compounds

As evidenced by the results obtained in the DoE experiment, the migration process is influenced not only on the type of compounds, but



**Table 3**

Identified compounds by UPLC-IMS-QTOF along with their retention time (RT in minutes), observed  $m/z$ , adduct, CCS value, CAS number and elemental composition for PP/PA, HDPEmix/PA, HDPEs/PA, and HDPE/PA in simulants A (ethanol 10%), B (acetic acid 3%) and D2 (isooctane).

RT (min)	Compound	$m/z$	Adduct	CCS	CAS	Composition	PP/PA	HDPEmix/PA	HDPEs/PA	HDPE/PA	USE
5,41	Triphenylphosphine oxide	279,0934	H+	162,74	791-28-6	C <sub>18</sub> H <sub>15</sub> PO	-	A (1) B (0) D2 (0)	-	-	Adhesive, polymerization initiation and stabilizer (IAS) Contaminant (NIAS)
6,26	Neopentyl glycol propoxylate	351,1772	Na+	178,76	84170-74-1	C <sub>17</sub> H <sub>28</sub> O <sub>6</sub>	A (0) B (1) D2 (0)	-	-	A (0) B (1) D2 (0)	Contaminant (NIAS)
6,56	BADGE	341,1751	H+	182,31	1675-54-3	C <sub>21</sub> H <sub>24</sub> O <sub>4</sub>	-	A (1) B (0) D2 (0)	-	-	Contaminant from adhesive (NIAS)
6,89	1,9-Nonanediol diacrylate	291,1569	Na+	166,49	107481-28-7	C <sub>15</sub> H <sub>24</sub> O <sub>4</sub>	-	-	-	A (0) B (2) D2 (0)	Adhesive degradation (NIAS)
7,30	2,2,4-trimethyl-1,3-pentadienol diisobutyrate (TXIB)	309,2037	Na+	171,41	6846-50-0	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	A (1) B (0) D2 (0)	-	-	-	Plasticizer (IAS)
7,6	Butyl 4-hydroxybenzoate	195,1013	H+	152,33	94-26-8	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	-	-	Antioxidant (IAS)
7,66	Bis(2-ethylbutyl) phthalate	335,2202	H+	185	7299-89-0	C <sub>20</sub> H <sub>30</sub> O <sub>4</sub>	A (2) B (3) D2 (0)	-	A (0) B (1) D2 (0)	-	Plasticizer (IAS)
7,78	Dibutyl sebacate	337,2342	Na+	184,38	109-43-3	C <sub>18</sub> H <sub>34</sub> O <sub>4</sub>	A (1) B (0) D2 (0)	-	A (1) B (0) D2 (0)	A (2) B (0) D2 (0)	Plasticizer (IAS)
7,87	Chimassorb 81	327,1951	H+	186,68	1843-05-6	C <sub>21</sub> H <sub>26</sub> O <sub>3</sub>	-	-	A (1) B (0) D2 (0)	A (1) B (0) D2 (0)	Ultraviolet absorber (IAS)
8,00	Glyceryl monostearate	381,2976	Na+	204,57	31566-31-1	C <sub>21</sub> H <sub>42</sub> O <sub>4</sub>	A (2) B (0) D2 (0)	-	A (2) B (0) D2 (0)	A (1) B (1) D2 (0)	Surfactant, UV absorber (IAS)
8,10	Bis(2-ethylhexyl) adipate	393,2995	Na+	218,84	103-23-1	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	-	A (2) B (0) D2 (0)	A (1) B (1) D2 (0)	-	Plasticizer (IAS)
8,16	Irganox 1035	665,3819	Na+	257,45	41484-35-9	C <sub>38</sub> H <sub>58</sub> O <sub>6</sub> S	A (1) B (0) D2 (0)	-	-	-	Antioxidant, UV absorber (IAS)
8,24	Erucamide	338,3415	H+	208,23	112-84-5	C <sub>22</sub> H <sub>43</sub> NO	-	A (0) B (0) D2 (2)	A (0) B (0) D2 (4)	A (0) B (0) D2 (3)	Stabilizer (IAS)
8,25	Diocetyl terephthalate	413,266	Na+	217,6	4654-26-6	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	-	-	-	A (1) B (0) D2 (0)	Plasticizer in PVC (IAS)
8,30	Diocetyl Phthalate	413,2644	Na+	219,29	117-81-7	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	A (0) B (0) D2 (2)	A (0) B (1) D2 (1)	-	A (0) B (1) D2 (0)	Plasticizer (IAS)
8,31	Diisononyl phthalate	441,2961	Na+	216,45	28553-12-0	C <sub>26</sub> H <sub>42</sub> O <sub>4</sub>	A (0) B (1) D2 (1)	A (2) B (1) D2 (0)	A (1) B (0) D2 (0)	A (2) B (0) D2 (0)	Plasticizer (IAS)
8,50	Didecyl phthalate	469,3271	Na+	231,34	84-77-5	C <sub>28</sub> H <sub>46</sub> O <sub>4</sub>	A (1) B (1) D2 (0)	A (1) B (1) D2 (0)	A (1) B (2) D2 (0)	A (1) B (1) D2 (0)	Plasticizer (IAS)
8,86	Docosanamide	340,3574	H+	211,98	3061-75-4	C <sub>22</sub> H <sub>45</sub> NO	-	A (0) B (0) D2 (1)	A (0) B (0) D2 (1)	A (0) B (0) D2 (3)	Slip agent (IAS)
9,24	alpha-Tocopherol	453,3711	Na+	223,56	59-02-9	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	A (0) B (1) D2 (0)	A (0) B (0) D2 (1)	-	A (0) B (0) D2 (2)	Antioxidant (IAS)
9,37	Tris(2,4-tert-butylphenyl) phosphate	685,4373	Na+	292,62	95906-11-9	C <sub>42</sub> H <sub>63</sub> O <sub>4</sub> P	A (2) B (1) D2 (4)	A (1) B (0) D2 (5)	A (0) B (2) D2 (5)	A (0) B (1) D2 (4)	Antioxidant (IAS)

(continued on next page)

Table 3 (continued)

RT (min)	Compound	m/z	Adduct	CCS	CAS	Composition	PP/PA	HDPEmix/PA	HDPEs/PA	HDPEe/PA	USE
9,40	Tris(2-ethylhexyl) trimellitate	547,3976	H+	234,06	3319-31-1	C <sub>33</sub> H <sub>54</sub> O <sub>6</sub>	-	A (0) B (1) D2 (0)	-	-	Plasticizer (IAS)
9,50	Irgafos 38	515,3653	H+	238,93	145650-60-8	C <sub>32</sub> H <sub>51</sub> O <sub>3</sub> P	A (2) B (2) D2 (0)	A (2) B (1) D2 (0)	A (2) B (1) D2 (0)	A (2) B (0) D2 (0)	Stabilizer (IAS)
9,64	N,N-Ethylenebis stearamide	615,5817	Na+	281,23	110-30-5	C <sub>38</sub> H <sub>76</sub> N <sub>2</sub> O <sub>2</sub>	A (0) B (1) D2 (3)	A (0) B (0) D2 (2)	A (0) B (0) D2 (2)	A (0) B (2) D2 (2)	Dispersing agent/ lubricant(IAS)
9,73	Capric triglyceride (Tricaprin)	577,4411	Na+	253,82	621-71-6	C <sub>33</sub> H <sub>62</sub> O <sub>6</sub>	A (2) B (1) D2 (0)	A (3) B (1) D2 (0)	A (2) B (0) D2 (0)	A (2) B (2) D2 (0)	Contaminant (NIAS)
9,73	Tocopheryl acetate	495,3805	Na+	227,44	7695-91-2	C <sub>31</sub> H <sub>52</sub> O <sub>3</sub>	A (1) B (0) D2 (0)	-	-	A (0) B (1) D2 (0)	Stabilizer (IAS)
9,83	Cyasorb 2908	497,3972	Na+	232,79	67845-93-6	C <sub>31</sub> H <sub>54</sub> O <sub>3</sub>	A (1) B (0) D2 (0)	A (0) B (1) D2 (0)	A (1) B (0) D2 (0)	-	Light stabilizer (IAS)
10,05	Irganox 1076	553,4594	Na+	250,33	2082-79-3	C <sub>35</sub> H <sub>62</sub> O <sub>3</sub>	A (0) B (0) D2 (3)	A (0) B (0) D2 (3)	A (0) B (1) D2 (4)	A (0) B (0) D2 (5)	Antioxidant (IAS)
10,48	Palmitic acid	591,4968	Na+	264,61	57-10-3	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	A (0) B (1) D2 (0)	-	A (0) B (1) D2 (0)	A (0) B (1) D2 (0)	Plasticizer (IAS)
11,37	Irgafos 168	647,4588	H+	284,86	31570-04-4	C <sub>42</sub> H <sub>63</sub> O <sub>3</sub> P	A (0) B (0) D2 (3)	A (0) B (0) D2 (2)	A (0) B (0) D2 (2)	A (0) B (0) D2 (1)	Antioxidant (IAS)

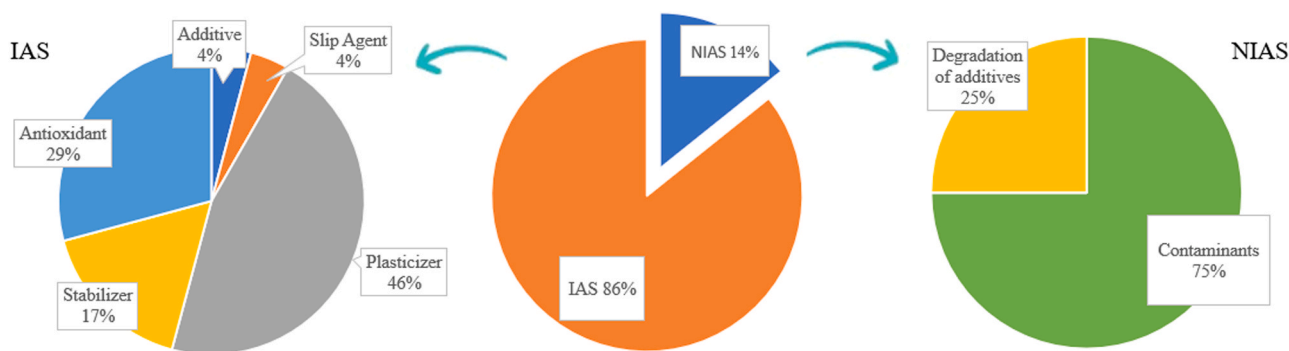


Fig. 4. Summary and classification of IAS and NIAS identified by UPLC-IMS-QTOF.

also on complex interactions between the simulant, the cooking conditions, and the type of material. To illustrate this point, Fig. 5 shows the maximum migration area of the samples in three different simulants as a function of the effect of the variables v1 (time) and v2 (temperature) and of the interaction v12 (interaction).

In the context of volatile compounds, the samples subjected to migration test in acid simulant (B) exhibited strong sensitivity to variable v1; the exposure time to the simulant is the determinant factor influencing the maximum transfer of the compounds contained in the material. In contrast, samples undergoing identical testing conditions with fatty simulant (D2) demonstrated a higher susceptibility to variable v2 (temperature) concerning the maximum migration. Regarding 10% ethanol simulant (A), no distinct trend in the influence of the variables was observed, suggesting that the dependency of the maximum migration also hinges mainly on the material type. It is observed that the interaction of the variables hardly influences as there is a clear trend towards time or temperature.

In the case of non-volatile compounds, the most clearly influencing variable is temperature for most materials and simulants. Secondly, the interaction of variables (V12) is the factor that most influences migration. However, when the material is HDPEe/PA, time is the most determining factor.

The isooctane (D2) shows a completely opposite behavior to the other two simulants as migration decreases with increasing time and temperature. This suggests that it is not a suitable simulant for this type of study.

#### 4. Conclusion

The increasing adoption of innovative culinary methodologies necessitates a reassessment of packaging materials to suit the new cooking conditions. One such instance is evident in sous vide cooking, characterized by the vacuum-sealing of food within bags and subsequent cooking at lower temperatures over extended durations compared to

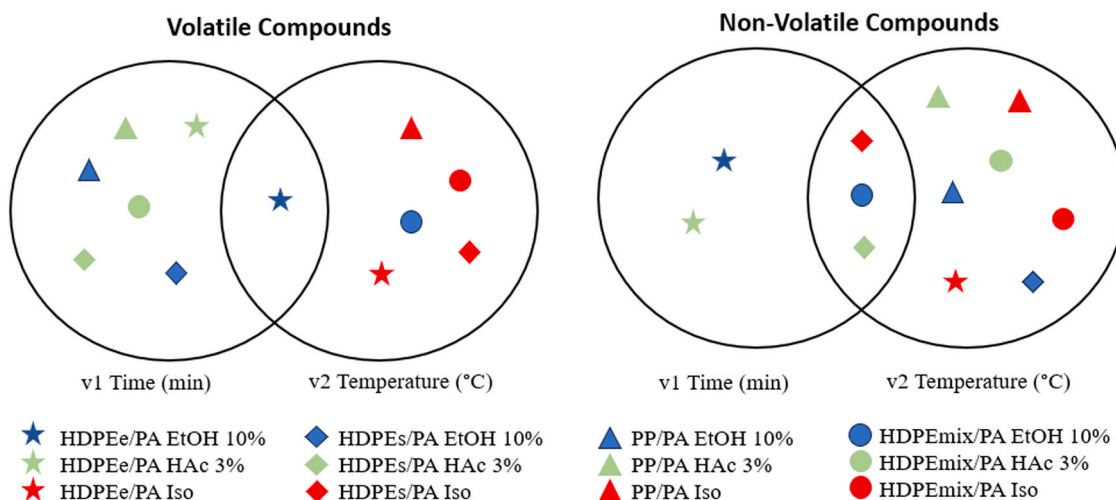


Fig. 5. Correlation of the variables time (v1) and temperature (v2) with the type of simulant and material for volatile and non-volatile compounds.

conventional methods. Employing a Design of Experiments approach revealed that the obtention of high migration values in this culinary technique was not uniquely linked to specific time/temperature conditions or to a specific food simulant but to cross factors that also included the polymers used for the bags manufacturing. While temperature seemed to be a determinant factor in the migration of non-volatile compounds in most of the bags, time played an equally important role in the migration of volatile compounds to aqueous simulants. Therefore, the control of both variables will be critical during sous vide cooking to guarantee the food safety of these materials. Regarding the nature of the migrants detected, the results displayed a high variety of migrated substances.

The analysis revealed the presence of numerous compounds including additives such as plasticisers or slip agents. A substantial proportion of the detected substances correspond to IAS of which 43 volatile compounds (64%) and 23 non-volatile compounds (86%) have been identified. A wide variety of NIAs has also been detected, many of them generated due to degradation processes that took place during the cooking process. Twenty-four volatile compounds (36%) and four non-volatile compounds (14%) were found.

These results highlight the need for further study of the use of the packaging when it is used for purposes other than storage, as in this work where it is used for direct cooking.

#### CRedit authorship contribution statement

**Carlos Estremera:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Celia Domeño:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Robert Paiva:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Data curation, Conceptualization. **Cristina Nerín:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Margarita Aznar:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

#### 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.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.fpsl.2024.101297](https://doi.org/10.1016/j.fpsl.2024.101297).

#### References

- Babity, S., Laszlo, E., & Brambilla, D. (2021a). Polymer-based microneedles for decentralized diagnostics and monitoring: Concepts, potentials, and challenges (American Chemical Society) *In Chemistry of Materials* (Vol. 33, Issue 18), 7148–7159. <https://doi.org/10.1021/acs.chemmater.1c01866>.
- Babity, S., Laszlo, E., & Brambilla, D. (2021b). Polymer-based microneedles for decentralized diagnostics and monitoring: Concepts, potentials, and challenges (American Chemical Society) *In Chemistry of Materials* (Vol. 33, Issue 18), 7148–7159. <https://doi.org/10.1021/acs.chemmater.1c01866>.
- Baldwin, D. E. (2012). Sous vide cooking: A review. *International Journal of Gastronomy and Food Science*, 1(1), 15–30. <https://doi.org/10.1016/j.ijgfs.2011.11.002>
- Beneventi, E., Tietz, T., & Merkel, S. (2020). Risk assessment of food contact materials. *EFSA Journal*, 18(S11), 1–11. <https://doi.org/10.2903/j.efsa.2020.e181109>
- Benson, R. (2009). Hazard to the developing male reproductive system from cumulative exposure to phthalate esters-dibutyl phthalate, diisobutyl phthalate, butylbenzyl phthalate, diethylhexyl phthalate, dipentyl phthalate, and diisononyl phthalate. *Regulatory Toxicology and Pharmacology*, 53(2), 90–101. <https://doi.org/10.1016/j.yrtph.2008.11.005>
- Birgit, G. (2018). Dossier - Non-intentionally added substances (NIAS). *Food Packaging Forum*. <https://doi.org/10.5281/zenodo.1265331>

- Bundesinstitut für Risikobewertung. (2018). Polyamide oligomers: plastic components from kitchen utensils. *Statement*, 014(30). <https://doi.org/10.17590/20180530-110731-0>
- Canellas, E., Vera, P., Song, X. C., Nerin, C., Goshawk, J., & Dreolin, N. (2021). The use of ion mobility time-of-flight mass spectrometry to assess the migration of polyamide 6 and polyamide 66 oligomers from kitchenware utensils to food. *Food Chemistry*, 350. <https://doi.org/10.1016/j.foodchem.2021.129260>
- Commission Regulation (EU) No 10. (2011). COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*, 21, 1–136.
- Dole, P., Feigenbaum, A. E., De La Cruz, C., Pastorelli, S., Paseiro, P., Hankemeier, T., Voulzatis, Y., Aucejo, S., Saillard, P., & Papaspyrides, C. (2006). Typical diffusion behaviour in packaging polymers - Application to functional barriers. *Food Additives and Contaminants*, 23(2), 202–211. <https://doi.org/10.1080/02652030500373661>
- European Parliament (EU) No 1935/2004. (2004). Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC.
- FDA: Department of Health and Human Services. (2022). *Indirect Food Additives: Adhesives and Components of Coatings; Paper and Paperboard Components; Polymers; Adjuvants, Production Aids, and Sanitizers*. (<https://www.regulations.gov>).
- Food Packaging Forum Foundation. (2020). *FCCmigex Database* (5).
- Formanek, Z., Kerry, J.P., Buckley, D.J., Morrissey, P.A., & Farkas, J. (1997). *Effects of Dietary Vitamin E Supplementation and Packaging on the Quality of Minced Beef*.
- Gall, M., Schweighuber, A., Buchberger, W., & Lang, R. W. (2020). Plastic bottle cap recycling—characterization of recycle composition and opportunities for design for circularity. *Sustainability (Switzerland)*, 12(24), 1–21. <https://doi.org/10.3390/su122410378>
- Gao, Y., Gu, Y., & Wei, Y. (2011). Determination of polymer additives-antioxidants and ultraviolet (UV) absorbers by high-performance liquid chromatography coupled with UV photodiode array detection in food simulants. *Journal of Agricultural and Food Chemistry*, 59(24), 12982–12989. <https://doi.org/10.1021/jf203257b>
- Gopala Krishnan, P. S., Choudhary, V., & Varma, I. K. (1993). Current Status of Urethane (Meth)acrylate Oligomers and Polymers. *Journal of Macromolecular Science, Part C*, 33(2), 147–180. <https://doi.org/10.1080/15321799308021561>
- Kuki, Á., Nagy, L., Nagy, T., Zsuga, M., & Kéki, S. (2017). Screening of additives and other chemicals in polyurethanes by direct analysis in real time mass spectrometry (DART-MS). *Analytical and Bioanalytical Chemistry*, 409(26), 6149–6162. <https://doi.org/10.1007/s00216-017-0553-x>
- Lai, H.-M., Padua, G. W., & Wei, L. S. (1997). Properties and Microstructure of Zein Sheets Plasticized with Palmitic and Stearic. *Acids (Vol. 74)*(Issue 1).
- Mustafa, Abdullah Yilmaz, & Hamdi, Temel (2016). Screening of Polymer Additives in Drinking Water Stored in PET Bottles by UHPLC-ESI-IT-TOF MS. *Journal of Environmental Science and Engineering A*, 5(2). <https://doi.org/10.17265/2162-5298/2016.02.001>
- Nerin, C., Alfaro, P., & Aznar, M. (2013). The challenge of identifying non-intentionally added substances from food packaging materials: A review. *Analytica Chimica Acta*, 775, 14–24. <https://doi.org/10.1016/j.aca.2013.02.028>
- Nerin, C., Bourdoux, S., Faust, B., Gude, T., Lesueur, C., Simat, T., Stoermer, A., Van Hoek, E., & Oldring, P. (2022). Guidance in selecting analytical techniques for identification and quantification of non-intentionally added substances (NIAS) in food contact materials (FCMS) (Taylor and Francis Ltd) *In Food Additives and Contaminants - Part A* (Vol. 39, Issue 3), 620–643. <https://doi.org/10.1080/19440049.2021.2012599>.
- Nerin, C., Ubeda, J. L., Alfaro, P., Dahmani, Y., Aznar, M., Canellas, E., & Aulsejo, R. (2014). Compounds from multilayer plastic bags cause reproductive failures in artificial insemination. *Scientific Reports*, 4. <https://doi.org/10.1038/srep04913>
- Paiva, R., Wrona, M., Nerin, C., Bertochi, I., Gavril, L., & Andrea, S. (2021). Importance of profile of volatile and off-odors compounds from different recycled polypropylene used for food applications. *Food Chemistry*, 350(January), Article 129250. <https://doi.org/10.1016/j.foodchem.2021.129250>
- Pereira, F. M. V., & Pereira-Filho, E. R. (2018). Application of free computational program in experimental design: A tutorial. *Quimica Nova*, 41(9), 1061–1071. <https://doi.org/10.21577/0100-4042.20170254>
- Petersen, H., Biereichel, A., Bursek, K., Simat, T. J., & Steinhart, H. (2008). Bisphenol A diglycidyl ether (BADGE) migrating from packaging material 'disappears' in food: reaction with food components. *Food Additives & Contaminants: Part A*, 25(7), 911–920. <https://doi.org/10.1080/02652030701837399>
- Pluta, M., Bojda, J., Piorkowska, E., Murariu, M., Bonnaud, L., & Dubois, P. (2017). The effect of halloysite nanotubes and N,N'-ethylenebis(stearamide) on the properties of polylactide nanocomposites with amorphous matrix. *Polymer Testing*, 61, 35–45. <https://doi.org/10.1016/j.polymertesting.2017.04.016>
- Rochman, C. M., Manzano, C., Hentschel, B. T., Simonich, S. L. M., & Hoh, E. (2013). Polystyrene plastic: A source and sink for polycyclic aromatic hydrocarbons in the marine environment. *Environmental Science and Technology*, 47(24), 13976–13984. <https://doi.org/10.1021/es403605f>
- Salazar, R., Domenech, S., Plessis, C., & Ducruet, V. (2017). Quantitative determination of volatile organic compounds formed during Polylactide processing by MHS-SPME. *Polymer Degradation and Stability*, 136, 80–88. <https://doi.org/10.1016/j.polymdegradstab.2016.12.010>
- Sanches-Silva, A., Costa, D., Albuquerque, T. G., Buonocore, G. G., Ramos, F., Castilho, M. C., Machado, A. V., & Costa, H. S. (2014). Trends in the use of natural antioxidants in active food packaging: a review. *Food Additives and Contaminants - Part A*, 31(3), 374–395. <https://doi.org/10.1080/19440049.2013.879215>
- Sapozhnikova, Y., Nuñez, A., & Johnston, J. (2021). Screening of chemicals migrating from plastic food contact materials for oven and microwave applications by liquid and gas chromatography - Orbitrap mass spectrometry. *Journal of Chromatography A*, 1651. <https://doi.org/10.1016/j.chroma.2021.462261>
- Sharman, M., Honeybone, C. A., Jickells, S. M., & Castle, L. (1995). Detection of residues of the epoxy adhesive component bisphenol A diglycidyl ether (BADGE) in microwave susceptors and its migration into food. *Food Additives and Contaminants*, 12(6), 779–787. <https://doi.org/10.1080/02652039509374370>
- Silva, A. S., García, R. S., Cooper, I., Franz, R., & Losada, P. P. (2006). Compilation of analytical methods and guidelines for the determination of selected model migrants from plastic packaging. *In Trends in Food Science and Technology* (Vol. 17, Issue 10), 535–546. <https://doi.org/10.1016/j.tifs.2006.04.009>
- Souza Silva, É. A., Saboia, G., Jorge, N. C., Hoffmann, C., dos Santos Isaias, R. M., Soares, G. L. G., & Zini, C. A. (2017). Development of a HS-SPME-GC/MS protocol assisted by chemometric tools to study herbivore-induced volatiles in *Myrcia splendens*. *Talanta*, 175, 9–20. <https://doi.org/10.1016/j.talanta.2017.06.063>
- Vera, P., Canellas, E., Barknowitz, G., Goshawk, J., & Nerin, C. (2019). Ion-mobility quadrupole time-of-flight mass spectrometry: A novel technique applied to migration of nonintentionally added substances from polyethylene films intended for use as food packaging. *Analytical Chemistry*, 91(20), 12741–12751. <https://doi.org/10.1021/acs.analchem.9b02238>
- Vera, P., Canellas, E., & Nerin, C. (2018). Identification of non volatile migrant compounds and NIAS in polypropylene films used as food packaging characterized by UPLC-MS/QTOF. *Talanta*, 188, 750–762. <https://doi.org/10.1016/j.talanta.2018.06.022>
- Vera, P., Canellas, E., Nerin, C., Dreolin, N., & Goshawk, J. (2022). The migration of NIAS from ethylene-vinyl acetate corks and their identification using gas chromatography mass spectrometry and liquid chromatography ion mobility quadrupole time-of-flight mass spectrometry. *Food Chemistry*, 366. <https://doi.org/10.1016/j.foodchem.2021.130592>
- Voulzatis, I. S., Papaspyrides, C. D., Tsenoglou, C. J., & Roussis, C. (2007). Diffusion of model contaminants in high-density polyethylene. *Macromolecular Materials and Engineering*, 292(3), 272–284. <https://doi.org/10.1002/mame.200600420>
- Wrona, M., & Nerin, C. (2019). CHAPTER 7: Risk assessment of plastic packaging for food applications. *In Food Chemistry, Function and Analysis (Vols 2019-Janua, Issue 10)*. <https://doi.org/10.1039/9781788012973-00163>
- Wrona, M., & Nerin, C. (2020). Analytical approaches for analysis of safety of modern food packaging: A review. *Molecules*, 25(3). <https://doi.org/10.3390/molecules25030752>
- Wu, X., Liu, P., Shi, H., Wang, H., Huang, H., Shi, Y., & Gao, S. (2021). Photo aging and fragmentation of polypropylene food packaging materials in artificial seawater. *Water Research*, 188. <https://doi.org/10.1016/j.watres.2020.116456>
- Zitoun-Hamama, O. A., Carpino, S., Rapisarda, T., Belvedere, G., Licitra, G., & Zidoune, M. N. E. (2016). Use of smart nose and GC/MS/O analysis to define volatile fingerprint of a goatskin bag cheese 'Bouhezza'. *Emirates Journal of Food and Agriculture*, 28(11), 746–754. <https://doi.org/10.9755/ejfa.2016-02-184>