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ORIGINAL PAPER

Identification and migration of degradation compounds from irradiation of multilayer polyamide 6 films for meat foodstuffs and cheese

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Abstract The aim of this work was to identify the degradation compounds produced during irradiation of multilayer polyamide 6 (PA-6) films and to study their migration into water and 95% ethanol food simulant. After irradiation of multilayer PA-6 films at 3, 7 and 12 kGy, degradation compounds were extracted using solid-phase microextraction, for which the time and temperature of extraction and stirring were optimized, and identified by gas chromatography–mass spectrometry. Caprolactam, 2-cyclopentylcyclopentanone and aldehydes, among other compounds, were identified in the headspace of the films. Polydimethylsiloxane was considered the best fiber for extraction. The optimum conditions of time, temperature and stirring to extract the compounds were 20 min, 80 °C and 225 rpm. For validation purposes, the compounds were quantified in water and 95% ethanol and the results showed high sensitivity, good precision and accuracy. Migration of compounds from irradiated and non-irradiated multilayer PA-6 films into water and 95% ethanol food simulants was carried out at 40 °C for 10 days. The method was efficient for the quantification of decaldehyde, 2-cyclopentylcyclopentanone and caprolactam that migrated from multilayer PA-6 films into food simulants.

Keywords Degradation compounds · γ radiation · Polyamide 6 · Migration · Solid-phase microextraction · Gas chromatography–mass spectrometry

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Introduction

Food irradiation as an alternative to thermal and chemical preservation methods has the advantages that it can be used for prepackaged foodstuffs and allows the use of different packaging materials, especially plastic packaging. Besides the benefits conferred to foods, irradiation of polymers can produce degradation compounds of low molecular mass (radiolysis products) and can affect mechanical, thermal and barrier properties as well as the migration behavior [1–5]. Among other low molecular mass compounds, degradation compounds, monomers, additives and oligomers have the potential to migrate from packaging into food in contact with it [6–8].

Only a few works have showed the effect of irradiation on migration of compounds from plastic packaging into food [3, 9–14]. Migration levels of some additives from plastic packaging were reduced after irradiation depending on the doses and the polymer [3, 9, 10]. Irradiated polyamide (PA) films used as food and pharmaceutical packaging showed no change in the volatile compound levels when compared with non-irradiated films [10]. Also,

caprolactam levels increased more than twofold in PA-6 films irradiated at 5 kGy and remained almost the same with doses from 5 to 200 kGy [14]. Aminocaproic acid was produced after irradiation of food packaging PA-6 films (25, 50 and 100 kGy), but no changes were observed in caprolactam levels. Moreover formamide, acetamide, propanamide, butanamide, pentanamide and hexanamide were also formed, among which pentanamide was the main radiolysis product [11–13]. Besides C_9 and C_{10} aliphatic hydrocarbons, other volatile compounds were formed during irradiation of PA-6 and PA-12 films [3].

Solid-phase microextraction (SPME) is a very efficient technique to extract volatile compounds from a wide range of matrixes, including polymers. Headspace (HS)-SPME combined with gas chromatography (GC)–flame ionization detection (FID) or GC–mass spectrometry (MS) was used to separate and identify volatile compounds from PA-66 [15–17] and polystyrene [18, 19] and to determine compounds migrating from poly(vinyl chloride) into aqueous solutions [20]. Butylated hydroxytoluene (BHT) in bottled water was analyzed using HS-SPME and direct SPME combined with GC-MS [21]. Impurities in industrial caprolactam produced from toluene were determined by SPME and GC-MS [22]. Identification and quantification of low molecular mass degradation products of antioxidants which migrated from polypropylene into 10% ethanol was carried out using SPME [23]. HS-SPME-GC-MS was also able to identify low molecular mass degradation products as hindered phenol antioxidants, cyclic imides, pyridines, chain fragments and cyclopentanones from virgin and recycled thermo-oxidized PA-66, besides migration of brominated benzenes from recycled PA-66 [24].

The aim of this work was to identify volatile compounds produced from irradiation of multilayer PA-6 films used as food packaging, especially for meat foodstuffs and cheese, and to study their migration from the packaging into food simulants.

Experimental

Chemicals and samples

Analytical standards of acetamide, propanamide, hexanamide, caprolactam, octaldehyde, decaldehyde, 1-phenylcyclohexene, diphenyl ether, tributyl phosphate (TBP), caprylic ether and BHT were from Sigma-Aldrich (Sreinheim, Germany), formamide, nonaldehyde and copaene were from Fluka (Buchs, Switzerland), pentanamide and 2-cyclopentylcyclopentanone were from Alfa Aesar (Karlsruhe, Germany) and butanamide was from Merck (Darmstadt, Germany), all of them higher than 95% purity. Stock solutions of the analytical standards were prepared in tetrahydrofuran (Merck, Darmstadt, Germany) and were stored at 4 °C. Working solutions were prepared by dilution in water food simulant or 95% ethanol food simulant as necessary.

Commercially available multilayer PA-6 films were supplied by the Brazilian producing companies, two brands used for meat foodstuffs and one brand used for cheese, named M1, M2 and M3, respectively.

Irradiation

Multilayer PA-6 films were irradiated in the Radiation Technology Center (CTR) of the Nuclear and Energetic Research Institute (IPEN), Brazil, using a Gamacell 60 cobalt irradiator of 12 kCi. Multilayer PA-6 films (2×3 and 10×10 cm^2) were placed in hermetically closed glass vials (20 mL) and subjected to 3 and 7 kGy (meat foodstuffs) and 12 kGy (cheese) [25].

Identification

Polydimethylsiloxane (PDMS), PDMS–divinylbenzene (PDMS/DVB) and Carbowax–DVB (CW/DVB) coated SPME fibers (Supelco, Bellefonte, PA, USA) with 100-, 65- and 65-μm thicknesses, respectively, were used in a qualitative previous screening. The fibers were exposed for 20 min at 25 °C to the HS of the vials containing irradiated and non-irradiated film samples. Desorption was carried out in the gas chromatograph injection port for 10 min. An HP 5890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled to a 5971-A MS detector was used. An HP-5MS (30 m×0.25 mm×0.25 μm) capillary column was utilized at 80 °C for 2 min, programmed at 20 °C/min up to 195 °C for 1 min, then heated to 320 °C at 10 °C/min and held for 2 min. Helium was the carrier gas (1.0 mL/min). Splitless mode (1 min) was used, and the injection and detection temperatures were 240 and 280 °C, respectively. The mass spectrometer was operated in electron impact mode (70 eV) and the masses were scanned over an m/z range of 45–400 amu. Compounds were identified by matching their mass spectra with the US National Institute of Standards and Technology (Gaithersburg, MD, USA) commercial library (purity criterion more than 85%). Retention time and fragmentation spectra of pure standards were obtained for confirmation.

SPME optimization

Among the parameters that can affect the extraction process, stirring, temperature and time of extraction were evaluated using PDMS fiber. The software MODDE 6.0 from Umetrics (Umeå, Sweden) was used to design the experiment and to perform the optimization. A factorial design (2^3) consisting of eight experiments plus four repetitions of center point was

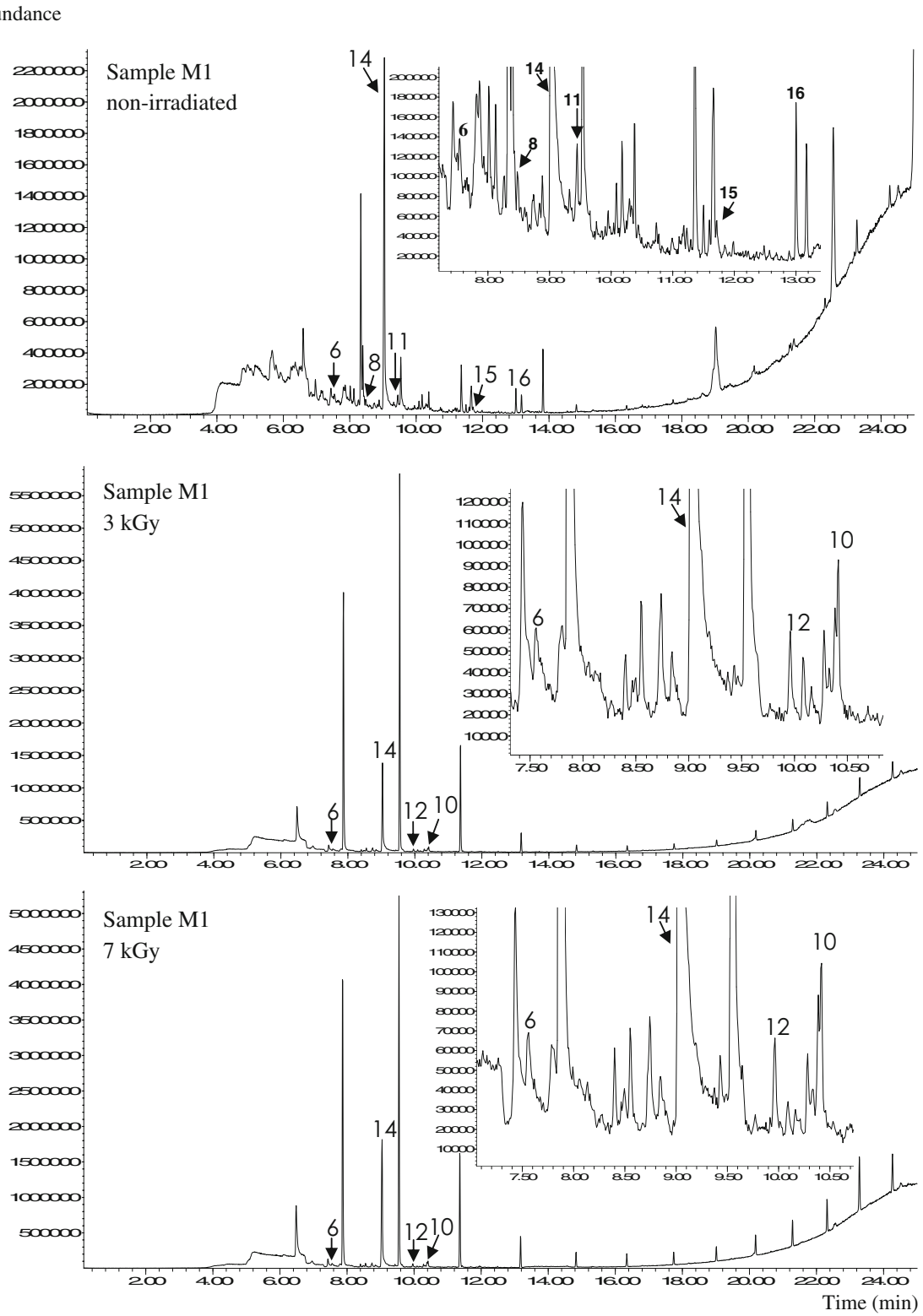


Fig. 1 Chromatograms obtained by headspace solid-phase microextraction (SPME)–gas chromatography–mass spectrometry, using polydimethylsiloxane fiber, from multilayer polyamide 6 films (sample M1) after irradiation with 0, 3 and 7 kGy. Numbered peaks are identified in Table 2

Table 1 Compounds identified in irradiated and non-irradiated multilayer polyamide 6 (PA-6) film samples, using headspace solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC-MS)

Samples	Irradiation doses (kGy)	Compounds										
		Octaldehyde	Nonaldehyde	Decaldehyde	Copaene	4-Phenylcyclohexene	2-Cyclopentylcyclopentanone	Diphenyl ether	BHT	TBP	Caprylic ether	Caprolactam
M1	0	–	1	1	–	–	1, 2, 3	–	1, 2, 3	1, 2, 3	–	1, 2, 3
	3	–	1, 3	3	1, 2, 3	1, 2, 3	–	–	–	–	–	1, 2, 3
	7	–	1, 3	3	1, 2, 3	1, 2, 3	–	–	–	–	–	1, 2, 3
	0	–	1, 2, 3	1, 2, 3	–	–	2, 3	1, 2, 3	–	–	2, 3	1, 2, 3
M2	3	–	1	1	1, 2, 3	1, 2, 3	–	–	–	–	–	1, 2, 3
	7	–	3	3	1, 2, 3	1, 2, 3	–	–	–	–	–	1, 2, 3
M3	0	–	1, 3	1, 2, 3	–	–	1, 2, 3	–	–	1, 2, 3	1, 2, 3	1, 2, 3
	12	3	1, 3	3	1, 2, 3	1, 2, 3	–	–	–	–	–	1, 2, 3

Fibers: PDMS (1); PDMS/DVB (2); CW/DVB (3)
BHT: Butylated hydroxytoluene; TBP: Tributyl phosphate

used, totalizing 12 experiments. Time (2–20 min) and temperature of extraction (25–80 °C) and stirring (100–350 rpm) were evaluated. The sum of the chromatographic peak areas of the 17 compounds studied and also the maximization of individual areas for each one were the optimization criteria adopted.

A standard solution containing 17 compounds was prepared in aqueous medium. They were extracted by immersion of PDMS fiber and then desorbed at the injection port of a Finnigan Focus gas chromatograph (Thermo Electron) equipped with an AS 3000 autosampler and a flame ionization detector. An SGV-1701 (60 m×0.25 mm×0.25 μm) capillary column was used. The column temperature was held at 40 °C for 1 min, then programmed at 10 °C/min to 195 °C for 1 min and finally heated at 10 °C/min up to 250 °C for 1 min. Helium was the carrier gas at a flow rate of 1.5 mL/min. The injection and detection temperatures were 240 and 280 °C, respectively. Splitless mode (1 min) was used.

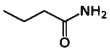
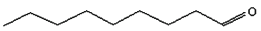
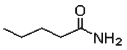
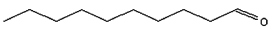
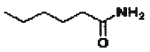
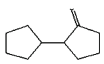
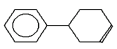
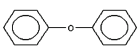
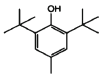
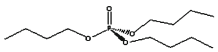
Validation

Linear range, precision, detection and quantification limits and accuracy were evaluated following the protocols reported in the literature [26–28]. Standard stock solutions containing 17 compounds were prepared in tetrahydrofuran and then diluted, as necessary, in water (ultrapure) and 95% ethanol, used as food simulants. These water standard solutions were subjected to SPME by immersion using a CTC-CombiPAL system coupled to an Agilent 6890N gas chromatograph equipped with an Agilent 5975B MS detector. An HP-5MS (30 m×0.25 mm×0.25 μm) capillary column was used, operated at 40 °C for 4 min, programmed at 10 °C/min up to 195 °C for 1 min, then heated to 250 °C at 10 °C/min and held for 1 min. The injection (splitless) and detection temperatures were 240 and 280 °C, respectively. Helium was the carrier gas at a flow rate of 1 mL/min. It was used for both scan (45–350 amu) and selected-ion monitoring (SIM) modes. Standard solutions of 95% ethanol were injected (1 μL) into the same GC system as described above. The same column was utilized at 50 °C for 4 min, programmed at 30 °C/min up to 80 °C for 1 min, and then heated to 250 °C for 1 min at 10 °C/min. The injection and detection temperatures were 250 and 280 °C, respectively. The same carrier gas was used at a flow rate of 1.5 mL/min, and the scan mode was the same as described in "Identification." The SIM mode was also applied.

Migration

For the migration assay, pieces of irradiated and non-irradiated films (2×3 cm^2) were, independently, placed in contact with water (15 mL) and 95% ethanol (15 mL) food simulants, inside glass vials which were hermetically

Table 2 Peak areas of water standard solution compounds extracted by different SPME fibers and analyzed by gas chromatography–flame ionization detection, and chemical structures of the substances

Compound	Chemical structure	Concentration (μg/g)	Peak area (mV)*		
			PDMS	CW/DVB	PDMS/DVB
Formamide (1)		34.8	ND	ND	ND
Acetamide (2)		66.7	ND	ND	ND
Octaldehyde (3)		24.4	60597540	12584860	48794340
Propanamide (4)		29.0	ND	ND	ND
Butanamide (5)		28.7	ND	ND	ND
Nonaldehyde (6)		25.6	111351100	42865650	93621740
Pentanamide (7)		26.8	ND	ND	ND
Decaldehyde (8)		25.8	108529800	50710090	80330860
Hexanamide (9)		24.4	ND	ND	ND
Copaene (10)		10.3	9130343	6247197	6311322
2-Cyclopentylcyclopentanone (11)		26.3	78138400	32167370	79202210
1-Phenylcyclohexene (12)		26.9	108549400	60057300	75222740
Diphenyl ether (13)		24.9	136650700	68711680	106518400
Caprolactam (14)		23.7	ND	ND	ND
Butylated hydroxytoluene (15)		38.2	72953500	37410030	46408510
Tributyl phosphate (16)		29.1	101691100	36616090	95223550
Caprylic ether (17)		31.3	3729200	3402816	3824276

ND. not detecded
*n=1

capped. These vials were stored in an oven thermostatically maintained at 40±1 °C for 10 days. Samples were analyzed in triplicate for each radiation dose. A blank prepared with non-irradiated PA-6 films in the simulant and another only with simulant were used as references, and were exposed and analyzed under the same conditions. After contact, film samples were removed and then the compounds that migrated into water were analyzed using SPME-GC-MS, while those that migrated into 95% ethanol were analyzed by GC-MS, using the same conditions described in "Validation." All migration tests were carried out by total immersion. Water simulant is generally used to simulate aqueous food and 95% ethanol is an alternative fatty-food simulant, used as a substitute for olive oil [29–31].

Results and discussion

Identification

After all the fibers had been exposed to the HS of the irradiated and non-irradiated multilayer PA-6 films for 20 min at 25 °C, the desorption was carried out in the injection port of the GC-MS system. The compounds identified are shown

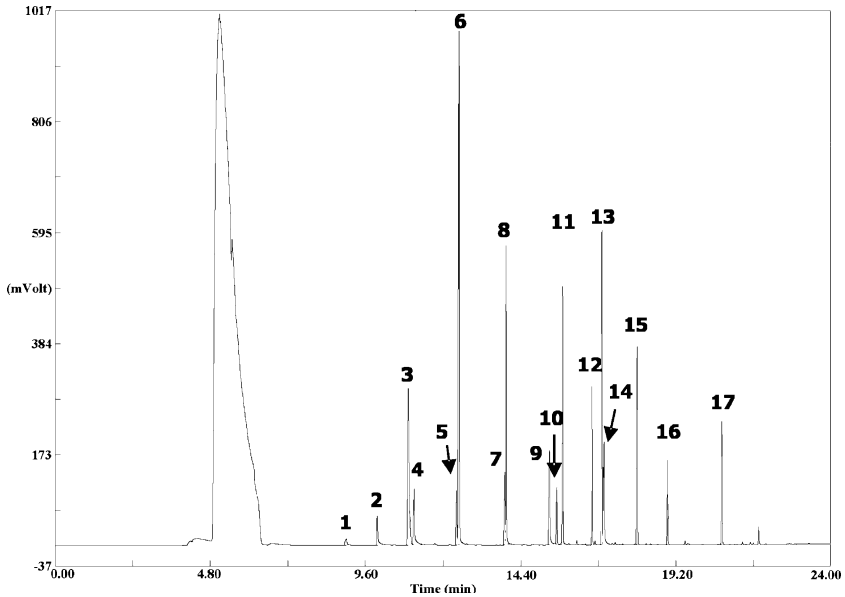


Fig. 2 Chromatogram obtained for the 17 compounds shown in Table 2, using polydimethylsiloxane fiber and gas chromatography–flame ionization detection

in Fig. 1 and Table 1. Figure 1 also shows the chromatograms of compounds extracted from multilayer PA-6 by PDMS and analyzed by GC-MS after irradiation with 0, 3 and 7 kGy. All the analyses were carried out in duplicate.

As can be seen from Table 1, nonaldehyde and decaldehyde were identified in all film samples, mainly when PDMS and CW/DVB fibers were used. Furthermore, decaldehyde showed a higher peak area than nonaldehyde for non-irradiated film samples. Octaldehyde was detected only in the irradiated M3 sample. Caprolactam showed the same behavior as decaldehyde and it was extracted by the three different fibers. Copaene and 4-phenylcyclohexene were extracted by all the fibers and was found only in irradiated films. On the other hand, 2-cyclopentylcyclopentanone, diphenyl ether, BHT, TBP and caprylic ether were identified only in non-irradiated film samples and were extracted by all fibers, with exception of caprylic ether, which was extracted only by PDMS/DVB and CW/DVB fibers.

The results indicated that caprolactam, 2-cyclopentylcyclopentanone, copaene, 4-phenylcyclohexene, diphenyl ether, BHT, TBP and caprylic ether could be used as irradiation markers. Copaene and 4-phenylcyclohexene could be considered as irradiation markers as they appeared only in irradiated film samples. In contrast, 2-cyclopentylcyclopentanone, diphenyl ether, BHT, TBP and caprylic ether appeared only in non-irradiated film samples. Caprolactam was found in both films, with a higher proportion in non-irradiated film samples.

In addition to the 11 compounds identified in the screening step, six amides were included as they were described as the main radiolysis products from irradiated PA-6 films [12, 13].

In the screening step it was not possible to choose which fiber showed the best extraction performance, making it necessary to carry out another experiment to select the fiber for the extraction process. To achieve this goal, all the SPME fibers were immersed in a water standard solution containing 17 compounds at 80 °C for 20 min and analyzed using GC-FID. The peak areas obtained for each fiber are shown in Table 2 as well as the chemical structures of the compounds studied.

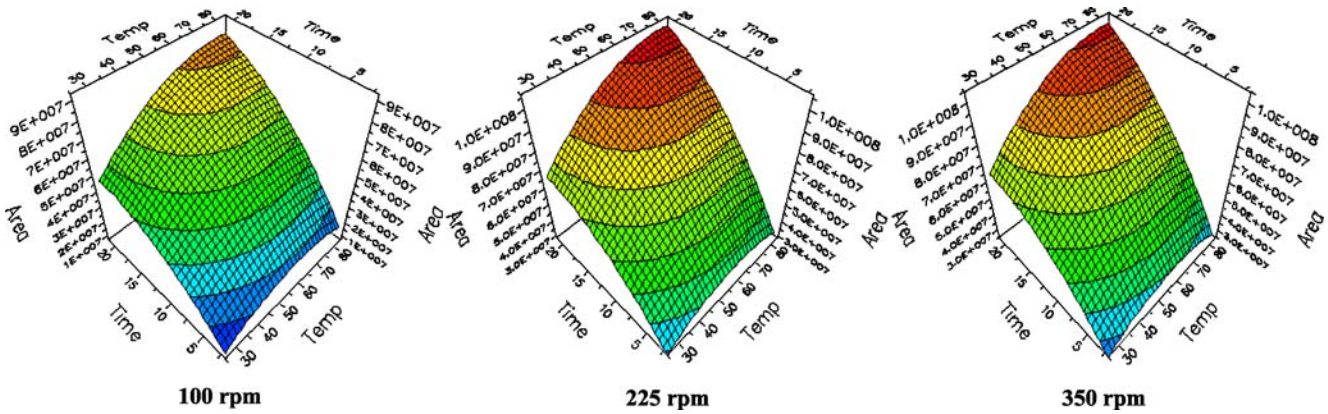


Fig. 3 Response surface methodology (RSM) total area graphics obtained from SPME optimization of 17 compounds shown in Fig. 2

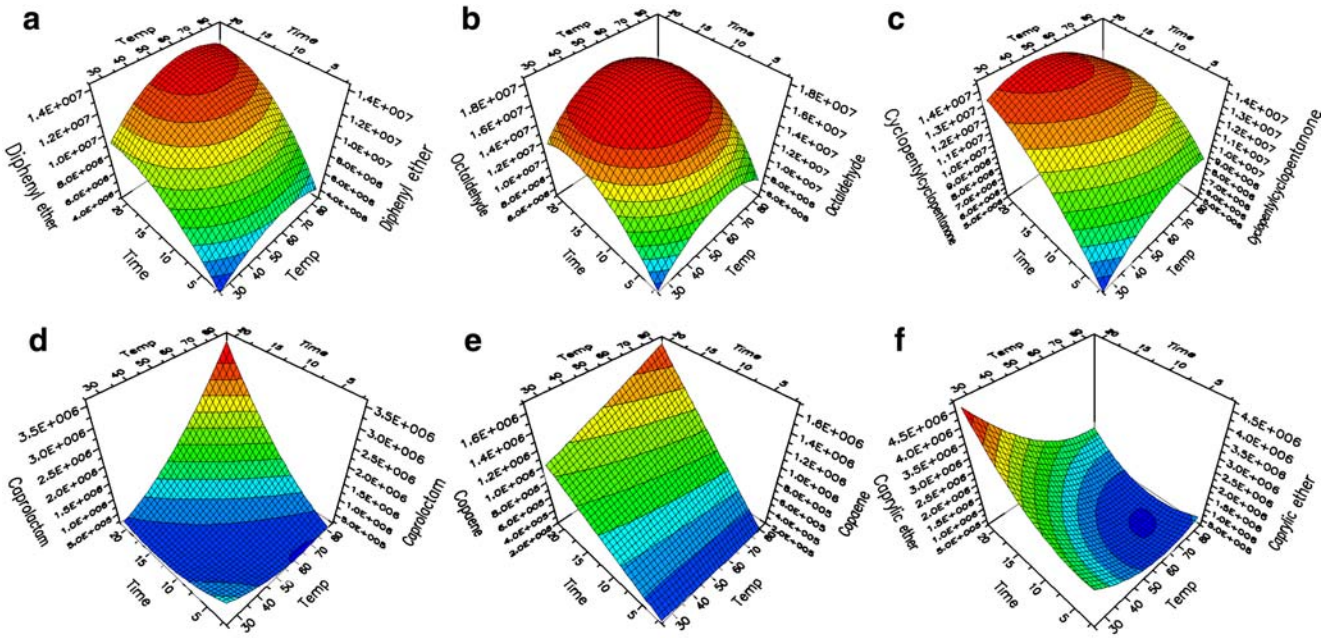


Fig. 4 RSM graphics obtained from SPME optimization for **a** diphenyl ether, **b** octanal, **c** 2-cyclopentylcyclopentanone, **d** caprolactam, **e** copaene and **f** caprylic ether at 225 rpm

As can be seen from Table 2, PDMS fiber showed higher peak area for most of the compounds when compared with PDMS/DVB and CW/DVB fibers, although the amides were not extracted under the conditions studied. On the basis of these results, PDMS was chosen to be used in the optimization step owing to its better fiber performance. Figure 2 shows the chromatogram obtained for the 17 compounds, shown in Table 2, which were extracted by PDMS and analyzed by GC-FID. It should be mentioned that all of them were extracted by PDMS, including the amides, because of the high concentrations used in this case.

Optimization

Response surface methodology (RSM) graphics obtained using MODDE indicated the extraction conditions to achieve the highest amount of compounds, expressed as total area. The highest peak areas were obtained when the extraction temperature was 80 °C, the extraction time was 20 min and stirring was at 225 rpm (Fig. 3).

Typical RSM graphics for individual compounds, caprolactam, octaldehyde, 2-cyclopentylcyclopentanone, diphenyl ether, caprylic ether and copaene, when 225 rpm was used, are shown in Fig. 4. Among 11 compounds identified in irradiated and non-irradiated multilayer PA-6 films, six (nonaldehyde, decaldehyde, 1-phenylcyclohexene, diphenyl ether, BHT and TBP) showed exactly the same behavior when 225 rpm was used. All of them showed the highest peak areas between 13.5 and 20 min and 45 and 80 °C (Fig. 4a), whereas octaldehyde showed the widest response range for time (7–20 min) and temperature (30–80 °C) when compared with the other compounds (Fig. 4b). 2-Cyclopentylcyclopentanone revealed the highest peak area between 14 and 20 min and 30 and 60 °C (Fig. 4c). All the amides showed the same behavior as caprolactam, with the highest peak area between 18.5 and 20 min and 79.5 and 80 °C (Fig. 4d). Similar results were observed for copaene (18–20 min, 66–80 °C) (Fig. 4e). Only caprylic ether showed clearly different behavior (19–20 min, 25–30 °C) (Fig. 4f).

Validation

A total time of 18 and 27 min was enough to separate all the 17 compounds in water and 95% ethanol food simulants, respectively. The characteristic ions 44 and 73 for propanamide, 44, 59 and 72 for butanamide, 57, 69 and 84 for octaldehyde, 44, 59 and 72 for pentanamide, 57, 70 and 98 for nonaldehyde, 59, 72 and 86 for hexanamide, 57, 70 and 82 for decaldehyde, 55, 84 and 113 for caprolactam, 55, 67 and 84 for 2-cyclopentylcyclopentanone, 105, 119 and 161 for copaene, 129 and 158 for 4-phenylcyclohexene, 141 and 170 for diphenyl ether, 57, 205 and 220 for BHT, 99, 155 and 211 for TBP and 57, 71 and 84 for caprylic ether were chosen for quantitative studies. Tables 3 and 4 present the base peak (m/z) of each compound.

Regarding linearity, a wide linear range was obtained for all the compounds. Calibration curves showed correlation coefficients (r), for a linear regression model, from 0.9762 to 0.9999 for water food simulant and from 0.9831 to 0.9996 for 95% ethanol, indicating a strong positive linear correlation

Table 3 Validation parameters to determine the compounds studied in water food simulant by SPME-GC-MS

Compounds	t_R (min)	Base Peak (m/z)	Water Food Simulant						
			Linear Range (μg.g-1)	Linear Coefficient (r)	Detection Limit (μg.g-1)	Quantification Limit (μg.g-1)	Spiked Level (μg.g-1)	Recovery[a] (%)	Precision[a] (%RSD)
Propanamide	7.6	44	25.30 - 862.00	0.9961	1.52	5.07	118.8	83.9±7.7	7.8
Butanamide	9.7	59	13.18 - 893.94	0.9970	1.36	4.55	123.20	103.9±9.8	7.7
Octaldehyde	10.8	57	2.95E-04 - 3.66	0.9886	9.58E-06	3.19E-05	0.22	91.7±0.0	0.7
Pentanamide	11.7	59	9.52 – 646.13	0.9986	0.43	1,42	89.10	114.4±6.0	5.9
Nonaldehyde	12.7	57	1.06E-04 - 1.94	0.9898	1.18E-05	3.93E-05	0.13	83.6±0.0	4.5
Hexanamide	13.4	59	6.51 - 441.61	0.9975	0.12	0.39	60.90	123.4±3.9	5.1
Decaldehyde	14.3	57	2.09E-05 - 2.95	0.9999	2.63E-06	8.78E-06	0.02	106.0±0.0	8.0
Caprolactam	15.0	55	11.12 - 754.17	0.9965	0.61	2.02	104.00	132.3±8.2	5.9
2-Cyclopentylcyclopentanone	15.6	84	2.34E-04 - 4.27	0.9995	5.59E-05	1.86E-04	0.08	119.5±0.0	3.1
Copaene	16.9	119	8.84E-05 - 0.80	0.9991	9.03E-07	3.01E-06	0.04	105.7±0.0	5.9
1-Phenylcyclohexene	17.1	129	7.25E-05 - 0.66	0.9872	1.24E-05	4.14E-05	0.20	104.1±0.0	7.3
Diphenyl ether	17.2	170	6.58E-05 - 2.59	0.9972	7.92E-06	2.64E-05	0.53	106.9±0.0	3.1
Butylated hydroxytoluene	18.6	205	3.93E-06 - 0.73	0.9970	1.76E-07	5.87E-07	0.04	120.9±0.0	8.1
Tributyl phosphate	20.1	99	1.02E-05 - 1.59	0.9987	2.40E-06	7.99E-06	0.37	106.9±0.1	14.7
Caprylic ether	20.3	57	1.88E-05 - 0.29	0.9898	4.32E-07	1.44E-06	0.02	90.7±0.0	7.8

[a] Mean of 6 replicates
Recovery (%) ± SD

Table 4 Validation parameters to determine the compounds studied in 95% ethanol by GC-MS

Compounds	t_R (min)	Base Peak (m/z)	95% Ethanol Food Simulant						
			Linear Range (μg.g-1)	Linear Coefficient (r)	Detection Limit (μg.g-1)	Quantification Limit (μg.g-1)	Spiked Level (μg.g-1)	Recovery[a] (%)	Precision[a] (%RSD)
Propanamide	5.2	44	3.30 - 259.84	0.9996	0.01	0.04	4.08	97.8±0.2	4.7
Butanamide	6.3	59	3.42 - 306.80	0.9939	0.01	0.02	4.23	97.3±0.3	6.3
Octaldehyde	7.0	57	0.48 - 456.72	0.9995	0.12	0.40	7.11	121.2±0.7	8.3
Pentanamide	7.7	59	2.47 - 221.75	0.9995	0.01	0.02	3.06	86.4±0.1	5.2
Nonaldehyde	8.5	57	0.25-242.34	0.9962	0.10	0.33	3.77	101.0±0.3	8.8
Hexanamide	9.1	59	1.69 - 151.56	0.9971	0.03	0.11	23.94	131.9±1.5	4.7
Decaldehyde	9.9	57	0.38 - 368.17	0.9886	0.11	0.38	7.44	91.9±0.5	7.1
Caprolactam	10.6	55	2.89 - 258.83	0.9961	0.05	0.15	5.38	83.7±0.2	4.6
2-Cyclopentylcyclopentanone	11.1	84	0.17 - 2418.76	0.9978	0.03	0.09	48.91	116.0±6.2	10.8
Copaene	12.3	119	0.10 - 99.42	0.9977	0.04	0.10	4.27	95.8±0.2	5.2
1-Phenylcyclohexene	12.6	129	0.43 - 91.66	0.9977	0.07	0.23	1.85	97.5±0.1	6.4
Diphenyl ether	12.6	170	0.50 - 478.47	0.9882	0.04	0.12	9.68	90.1±0.9	10.5
Butylated hydroxytoluene	13.9	205	0.10 - 91.66	0.9831	0.03	0.11	1.43	112.4±0.1	8.0
Tributyl phosphate	15.5	99	2.11 - 198.84	0.9973	0.13	0.43	8.54	108.7±0.5	5.0
Caprylic ether	15.6	57	0.07 - 35.73	0.9864	0.04	0.12	0.76	100.3±0.0	4.0

[a] Mean of 6 replicates
Recovery (%) ± SD

Table 5 Levels of migration of compounds from irradiated and non-irradiated multilayer PA-6 films into water and 95% ethanol food simulants

Compounds	Migration levels (μg/g)[a]							
	M1			M2			M3	
	0 kGy	3 kGy	7 kGy	0 kGy	3 kGy	7 kGy	0 kGy	12 kGy
Decaldehyde (water simulant)	0.004±0.000	ND	ND	0.004±0.000	ND	ND	ND	ND
Caprolactam (water simulant)	12.96±2.31	ND	ND	10.22±0.02	ND	ND	7.52±1.88	ND
2-Cyclopentylcyclopentanone (water simulant)	0.02±0.00	ND	ND	0.01±0.00	ND	ND	0.01±0.00	ND
Caprolactam (ethanol 95% simulant)	9.43±1.01	6.11±0.06	6.42±2.14	10.01±0.00	8.88±0.75	8.99±0.25	7.68±0.01	6.97±0.12

ND. not detected.
[a] Mean±SD value for two replicates, n=2.

between concentration and peak area. Sensitivity for amides in 95% ethanol food simulant was higher than in water food simulant. For all the other compounds, sensitivity showed the opposite behavior. Detection and quantification limits were 0.12–1.52 and 0.39–5.07 μg/g, respectively, for amides and were lower than 7.4×10^{-5} and 2.5×10^{-4} μg/g, respectively, for all the other compounds in water food simulants. For 95% ethanol detection limits were below 0.13 μg/g and quantification limits were below 0.43 μg/g. Accuracy was studied during the precision assay and was expressed as a percentage for the true value of the analyte in the sample and the value obtained by analysis. For recovery, one concentration level of standard solution was added to the matrix. Recovery values were from 83.6 to 123.4%, with a maximum relative standard deviation (RSD) of 14.7% for water simulant (Table 3), and from 83.7 to 121.2%, with a maximum RSD of 10.8% for 95% ethanol simulant (Table 4). Exceptions were hexanamide and caprolactam, which showed a recovery of 131.9 and 132.3%, respectively. It should be mentioned that even when very low spiking levels were used, a high recovery was obtained.

The validation of the method to determine caprolactam from non-irradiated multilayer PA-6 films in 3% acetic acid food simulant also showed good precision (RSD ≤ 4.3%) and accuracy (100–106% recovery) in a total time of 11 min [32], while olive oil food simulant showed a RSD of 3.8%, and a recovery of 88.6–112%, with the same time of analysis as 3% acetic acid [33].

Migration

The levels of compounds that migrated from irradiated and non-irradiated film samples into water and 95% ethanol food simulants are shown in Table 5.

Only three compounds migrated from irradiated and non-irradiated multilayer PA-6 film samples into water food simulant and one compound migrated into 95% ethanol food simulant. Migration of decaldehyde occurred only from non-irradiated M1 and M2 film samples, at a very low level, into water food simulant. 2-Cyclopentylcyclopentanone also migrated only from non-irradiated film samples (M1, M2 and M3) into water food simulant. High levels of caprolactam migrated from non-irradiated film samples into water food simulant. Also, there were high migration levels of caprolactam into 95% ethanol from irradiated and non-irradiated multilayer PA-6 film samples (M1, M2 and M3). Besides, caprolactam levels reduced with the increase of radiation dose from 0 to 3 kGy, and stayed the same up to 7 kGy, for M1 and M2, while the caprolactam levels also reduced for M3 with increasing irradiation (Table 5). The migration level of caprolactam was in accordance with the limits established by European and Brazilian legislation (15 mg/kg) [29, 30]. The amount of caprolactam that migrated from non-irradiated multilayer PA-6 films into 3% acetic acid food simulant was 6.9–10.5 mg/kg [32], very similar to the levels obtained in this work.

Conclusions

PDMS was the best fiber for extraction of volatile compounds from irradiated and non-irradiated multilayer PA-6 films, with the highest peak area for most of the compounds. The best conditions of time, temperature and stirring to extract the compounds studied using SPME were 20 min, 80 °C and 225 rpm. The method was validated, showing high sensitivity, good precision and accuracy. It was considered very efficient for quantification of the compounds that migrated from multilayer PA-6 films into water and 95% ethanol food simulants. Decaldehyde and 2-cyclopentylcyclopentanone migrated from multilayer PA-6 film samples into water and caprolactam migrated into both food simulants.

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References

1. Chmielewski AG (2006) Packaging for food irradiation. Institute of Nuclear Chemistry and Technology, Warsaw
2. Zygoura PD, Goulas AE, Riganakos KA, Kontominas MG (2007) J Food Eng 78(3):870–877
3. Stoffers NH, Linssen JPH, Franz R, Welle F (2004) Radiat Phys Chem 71:203–206
4. Welle F, Mauer A, Franz R (2002) Radiat Phys Chem 63:841–844
5. Bureau G (1996) In: Bureau G, Multon JL (eds) Food packaging technology 2. VCH, New York
6. Nerín C (2002) In: Catalá R, Gavara R (eds) Migración de componentes y residuos de envase en contacto con alimentos. Instituto de Agroquímica y Tecnología de Alimentos, Valencia
7. Monteiro M, Nerín C, Reyes FGR (1999) Packag Technol Sci 12:241–248
8. Demertzis PG, Franz R, Welle F (1999) Packag Technol Sci 12:119–130
9. Ito R, Seshimo F, Haishima Y, Hasegawa C et al (2005) Int J Pharm 3003:104–112
10. Jeon DH, Park GY, Kwak IS, Lee KH, Park HJ (2006) Lebensm Wiss Technol 40(1):151–156
11. Yagoubi N, Baillet A, Pellerin F, Ferrier D (1995) Nucl Instrum Methods Phys Res B 105:340–344
12. Buchalla R, Boess C, Bögl KW (1999) Radiat Phys Chem 56 (3):353–367
13. Buchalla R, Begley TH, Morehouse KM (2002) Radiat Phys Chem 63(3–6):837–840
14. Park GY, Cho SY, Jeon DH, Kwak IS, Lee KH, Park HJ (2006) Radiat Phys Chem 75:1055–1059
15. Gröning M, Hakkarainen M (2001) J Chromatogr A 932(1–2):1–11
16. Gröning M, Hakkarainen M (2004) J Chromatogr A 1052:61–68
17. Gröning M, Hakkarainen M (2004) J Chromatogr A 1052:151–159
18. Kusch P, Knupp G (2002) J Sep Sci 25:539–542
19. Kusch P, Knupp G (2004) J Polym Environ 12(2):83–87
20. Hakkarainen M (2003) J Chromatogr A 1010:9–16
21. Tombesi NB, Freije RH, Augusto F (2004) J Braz Chem Soc 15 (5):658–663
22. Li N, Zou J (2006) J Appl Polym Sci 100:3141–3144
23. Burman L, Albertsson A-C, Höglund A (2005) J Chromatogr A 1080:107–116
24. Hakkarainen M, Gröning M, Albertsson A-C (2003) J Appl Polym Sci 89:867–873
25. International Atomic Energy Agency (2002) TRS-409. Dosimetry for food irradiation. International Atomic Energy Agency, Vienna
26. Lanças FM (2004) Validação de métodos cromatográficos de análise, Rima, São Carlos
27. Ribani M, Bottoli CBG, Collins CH, Jardim ICSF, Melo LFC (2004) Quim Nova 27(5):771–780
28. International Union of Pure and Applied Chemistry (2006) Harmonised guidelines for the in-house validation of methods of analysis. http://www.iupac.org/divisions/V/501/draftoct19.pdf
29. European Commission (2002) Off J Eur Community L220/18
30. Agência Nacional de Vigilância Sanitária (ANVISA) (1999) Regulamentos técnicos: disposições gerais para embalagens e equipamentos plásticos em contato com alimentos e seus anexos. Resolução n.° 105, de 19 de maio de 1999. http://e-legis.anvisa.gov.br/leisref/public/showAct.php?id=19772&word
31. European Council (1997) Off J Eur Community L222:10–15
32. Félix JS, Padula M, Manzoli JE, Monteiro M (2007) Cienc Tecnol Alim 27(Supl):27–32
33. Félix JS, Padula M, Manzoli JE, Monteiro M (2006) Alim Nutr 17 (3):329–335