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Effects of γ-irradiation on caprolactam level from multilayer PA-6 films for food packaging: Development and validation of a gas chromatographic method

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ABSTRACT

A gas chromatographic method to determine caprolactam in multilayer PA-6 films used for meat foodstuffs and cheese was developed and validated. A wide linear range (0.8–400 μg/ml), RSD ⩽ 4.1% and recovery higher than 90.0% were obtained for the chromatographic system, while precision and accuracy of the method showed RSD ⩽ 3.8%, recovery from 95.5–100.0% and LOQ of 32 μg/g. Irradiated (3, 7 and 12 kGy) and non-irradiated commercial films were analyzed. Most of them increased caprolactam levels with the increase of irradiation doses.

1. Introduction

Polyamide 6 (PA-6) is a very versatile polymer used mainly as mono- and multilayer films. Polyolefins, ethylene-vinyl acetate (EVA) copolymer or ionomers in laminated or coextruded structures provide sealing and water vapor barrier to PA (Sarantópoulos et al., 2002). PA-6 is widely used as food packaging, particularly due to the mechanical, thermal, chemical and fatty resistance, besides gas and aroma barriers (Begley et al., 1995). PA-6 films have been used in Brazil as vacuum and modified atmosphere packaging for cheese and meat foodstuffs, and also as cook-in packaging for processed meat and foodstuffs, which may be cooked inside the package. PA-6 microwave and roasting bags and boil-in-the-bag are also used over the world to warm, cook or bake foods inside the packaging using microwave or conventional oven (Soto-Valdez et al., 1997).

Caprolactam is the monomer used for manufacturing PA-6 synthetic fibers as well as films used for food contact. This monomer remains inside the resin once polymerization reaction is not complete (Barkby and Lawson, 1993; Begley et al., 1995). Low molecular mass oligomers, reaction by-products and degradation compounds can also be formed during polymerization and all of them have the potential to migrate into the food in contact (Soto-Valdez et al., 1997; Nerín, 2002).

Irradiation is used as a food preservation method to destroy micro-organisms and increase shelf-life. Irradiation doses usually range from 10 to 1 kGy for sprouting inhibition of potatoes, onions, garlic, etc., 1–10 kGy for fresh meat and seafood, as well as vegetables and fruits, and 10–100 kGy, mainly for food sterilization (IAEA, 2002). Irradiation of foodstuffs has an additional advantage. It can be used in pre-packaged foodstuffs to avoid microbial recontamination, besides allowing the use of different packaging materials (EC, 1999; ANVISA, 2001; USFDA, 2005).

Sterilization of pre-packaged foodstuffs with ionizing radiation is considered an alternative to other sterilization methods (USFDA, 2007). But when polymers are irradiated, low molecular mass compounds (radiolysis products) are formed (Stoffers et al., 2004) as a result of molecular excitation, ionization and chemical reactions that can affect the polymer physicochemical structure. Changes in the mechanical, thermal and barrier polymer properties may also occur, as well as in the migration behavior (Buchalla et al., 1999).

The aim of this work was to determine caprolactam in multilayer PA-6 films used for cheese and meat foodstuffs, and to develop an analytical HRGC method to determine caprolactam in these films.

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2. Experimental

2.1. Chemicals, standards and PA-6 films

Caprolactam monomer, 98% pure quality, was used as analytical standard as well as caprylolactam, 99% pure quality, used as internal standard, both purchased from Sigma Aldrich (Buchs, Switizerland).

Commercially available multilayer PA-6 films were supplied by the Brazilian producing companies, eight brands used for meat foodstuffs, named 1–8, and five brands used for cheese, named 9–13. Multilayer PA-6 films for meat foodstuffs were constituted by PA-6 and PA-6/PA-66 (67% of homopolymer, 20% of copolymer) layers, and a masterbatch of additives. All of them were from different companies. Multilayer PA-6 films for cheese showed structures basically formed by PA/adhesive/PA/Sealant layer (PE or EVA structure). They were also from different companies.

Methanol, ethanol, dichloromethane and acetone, HPLC grade, were purchased from Tedia Company (Fairfield, USA).

2.2. Solutions

A standard stock solution of caprolactam (1250 μg/ml) and an internal standard solution of caprylolactam (70 μg/ml), both prepared in methanol, were kept at 0 °C for not more than 3 months. Working methanol solutions were then prepared as needed. Calibration was performed with diluted working solutions in methanol.

2.3. Irradiation of PA-6 films

Multilayer PA-6 films were irradiated in the Radiation Technology Center (CTR) of the Nuclear and Energetic Research Institute (IPEN), SP, Brazil, using a Gamacell 60 cobalt irradiator of 12 KCi. Multilayer PA-6 films ($10 \times 10\,cm^2$) were disposed in hermetically closed glass vials (50 ml) and submitted to 3, 7 and 12 kGy (IAEA, 2002).

2.4. Chromatographic conditions

Chromatographic analyses were performed in a 17-A Shimadzu gas chromatograph (GC) (Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionization detector (FID). A DB-1701 (J&W Scientific, Folsom, USA) capillary column (30 m × 0.25 mm and 0.25 μm film thickness) was used. The column temperature started at 110 °C, programmed at 10 °C/min up to 180 °C for 1 min, then heated to 200 °C at 10 °C/min and held for 2 min. Hydrogen was the carrier gas and nitrogen was the make-up gas. Injections (1 μl) were made at 240 °C in split mode (1:20). Detector temperature was 250 °C.

A Varian Saturn 2000 GC/MS/MS workstation equipped with a CP-3800 gas chromatograph coupled to a Model 2000 Ion-Trap Tandem Mass Spectrometer, Model 1079, a programmable injector and a CP-8200 Autosampler (Varian, Walnut Creek, CA, USA) was used in scan mode (30–350m/z). A Factor Four VF5-MS capillary column (30 m × 0.25 mm × 0.25 μm film thickness) (Varian, Walnut Creek, CA, USA) was also used under the same conditions of the GC/FID. Helium was the carrier gas. Injections (1 μl) were made at 240 °C in splitless mode. Detector temperature was 250 °C.

2.5. Extraction of caprolactam from PA-6 films

Samples (0.5000 g) of multilayer PA-6 films were manually cut into pieces (1 cm^2), extracted with methanol (30.0 ml) under an ultrasonic bath for 60 min and filtered (PTFE). An aliquot (4 ml) of this filtered methanol extract was put in a volumetric flask, the internal standard solution was added and the volume was adjusted with methanol. Then this solution was injected in the GC–FID.

2.6. Recovery

Standard solutions containing caprolactam in methanol (64, 200, 1005 μg/ml) were placed in contact with multilayer PA-6 film samples (0.5000 g) for 2 h and then the extraction procedure described was undertaken.

2.7. Quantitation

For quantitation, peak area was measured and internal standard procedure was used for both calibration and real sample analysis.

Caprolactam levels from commercial films were submitted to ANOVA. Tukey test was used to compare differences among means at $p \leqslant 0.05$.

3. Results and discussion

The chromatographic conditions used to separate caprolactam and caprylolactam provided good resolution. The identity of caprolactam in the multilayer PA-6 film extracts was confirmed by GC/MS/MS. The presence of interferent compounds or those that overlap the caprolactam and capriylolactam signals was not observed.

In order to establish a suitable step for the extraction of caprolactam from the multilayer films, ethanol, methanol, acetone, dichloromethane and water were investigated as solvent extractors. According to literature (Barkby and Lawson, 1993; Stoffers et al., 2004), water and ethanol/water (95%V/V) were efficient to extract caprolactam. On the other hand, ethanol 10–15% (V/V), water, acetic acid 3% (V/V) and olive oil are used as simulants in migration studies as recommended by legislations (EC, 1990; ANVISA, 1999; USFDA, 2005). Methanol was included due to its polarity that is close to ethanol and also because it was used as solvent to prepare the standard solutions (EC, 2004). Acetone was used because of its intermediate polarity, and dichloromethane because it was described as a good extractor of intermediate polarity compounds from plastic packaging (Monteiro et al., 1996, 1998; Costley et al., 1997). Samples of multilayer PA-6 film (brand 5) were submitted to the extraction procedure, as described before, using all these solvents. An aliquot taken from each solvent extract after 0, 15, 30, 45 and 60 min of extraction was filtered PTFE, added to internal standard and then the extract was analyzed in the GC/FID, in triplicate. Peak areas obtained for each solvent extraction at each extraction period were submitted to ANOVA and Tukey test. A significant difference ($p \leqslant 0.05$) appeared depending on the solvent. The higher the extraction time, the higher the peak area and the amount of caprolactam extracted. Among the studied extraction periods, methanol was considered the best solvent showing the highest caprolactam amount ($p \leqslant 0.05$) at 60 min of extraction.

3.1. Validation

Validation was carried out following the protocols reported in literature (Currie, 1999; Lanças, 2004; Ribani et al., 2004; IUPAC, 2006). The calibration curve for caprolactam was linear over a wide concentration range (0.8–400 μg/mL), with a correlation

coefficient (r) of 0.99999. Ten replicates of each calibration curve concentration (0.8, 3.2, 40, 80, 400 μg/ml) were performed and relative standard deviations (RSD) were less than 5.9% for all of them.

Linearity was also studied using the concentration/area ratio of caprolactam/caprylolactam versus the concentration of the caprolactam/caprylolactam used in the calibration curve, expressed in logarithmic scale. It was verified that the solution concentrations used in the calibration curve were within the confidence interval of 95% (Fig. 1).

Precision is an important criterion to evaluate an analytical method or equipment system performance (Currie, 1999; Ribani et al., 2004; IUPAC, 2006). The precision of the chromatographic system was evaluated using repeatability and intermediate precision. Repeatability was carried out using an intra-day precision essay, which was analyzed at three concentration levels, in triplicate. Intermediate precision was carried out using an inter-day precision essay, which was analyzed at three concentrations, in septuplicate. The RSD values obtained from the intra- and inter-day precision essays were less than 2.7% and 4.1%, respectively (Table 1). The results were fairly good for the concentration levels investigated.

The accuracy of the chromatographic response was studied during the intermediate precision evaluation and was expressed as the percentage between the true value of the analyte in the sample and the value obtained by analysis. Table 1 shows that the values obtained were higher than 90.0%, indicating good accuracy from the chromatographic system.

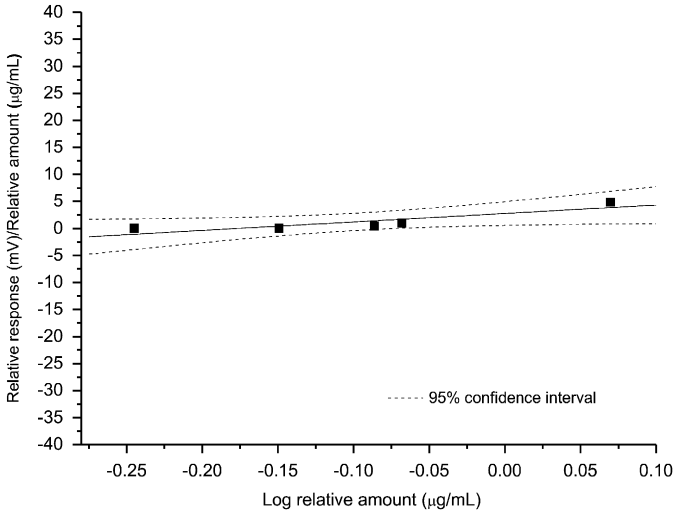

Fig. 1. Concentration/area ratio of caprolactam/caprylolactam versus concentration of caprolactam/caprylolactam used in the calibration curve, expressed in logarithmic scale. Values inside dash lines are between confidence interval of 95%.

The precision of the method and the accuracy were evaluated via recovery using different spiked levels. Recovery was measured as the response of a processed spiked matrix standard, expressed as the percentage of the response of a pure standard, which had not been subjected to sample pretreatment. It indicates whether the method provides a response for the entire amount of analyte that is present in the sample (Currie, 1999; Lanças, 2004; Ribani et al., 2004). Recovery was calculated as the ratio between the response after extraction and response of pure standard and was expressed as a percentage (%). For recovery, three concentration levels of standard solution were added to the matrix. One brand of multilayer PA-6 film for meat foodstuffs (brand 5) was used in the recovery essay. For each concentration level added, two extractions were carried out, where two injections were made in reference to each extraction. Recovery values for the three spiked levels studied were from 95.5% to 100.0%, having a maximum RSD of 3.8% (Table 2), indicating good accuracy and precision of the method.

The limit of detection (LOD) of the chromatographic system was determined experimentally using successive dilutions of a caprolactam stock solution of 0.2 μg/mL, which were injected into the chromatographic system ($n = 6$). The LOD ($S/N = 3{:}1$) value obtained was 0.2 ng.

The LOQ of the method was determined using the recovery study. The LOQ corresponded to the lowest quantity of caprolactam, determined with accuracy and precision, in the linear response interval of the detector and within the confidence interval of 95%. The LOQ of the method was 32 μg/g (RSD = 1.6%).

3.2. Quantitation

The method was used to quantify caprolactam in multilayer PA-6 films from eight commercial brands used for meat foodstuffs and other five used for cheese, both irradiated and non-irradiated. The extraction from the PA-6 films was carried out in triplicate and two injections of each extraction were made into the chromatographic system. The chromatogram of the blank did not show any interference in the t_R band of the analyte of interest nor the internal standard, indicating the quality of the solvent and the efficiency of the procedure used to clean the glassware. The blank test was constituted by submitting the solvent used to the same procedure used for the sample, for all analytical steps.

Table 2
Recovery (%) of caprolactam from multilayer PA-6 film

	Spiked level (μg/g)		
	64	200	1005
Recovery[a]	100.0 ± 1.6	97.6 ± 3.7	95.6 ± 2.3
RSD[b]	1.6	3.8	2.4

[a] Mean of recovery (%), $n = 4$.
[b] RSD, relative standard deviation (%).

Table 1
Precision and accuracy of the chromatographic system

	Repeatability (intra-day precision) $n = 3$			Intermediate precision (inter-day precision) $n = 7$		
Spiked level (μg/ml)	1.6	10.0	160.0	1.6	10.0	160.0
Found[a] (μg/ml)	1.5 ± 0.0	9.3 ± 0.3	149.2 ± 0.7	1.5 ± 0.1	9.0 ± 0.4	146.4 ± 2.6
RSD[b]	0.6	2.7	0.5	2.5	4.1	1.8
Accuracy[c]				94.3	90.1	91.5

[a] Mean of six replicates of the found value ± standard deviation (SD).
[b] RSD, relative standard deviation (%).
[c] Accuracy (%).

Typical chromatograms for quantitation of caprolactam in multilayer PA-6 films, non-irradiated ones (0 kGy) and irradiated at 3 and 7 kGy for meat foodstuffs are in Fig. 2.

The ANOVA and Tukey test results (Tables 3 and 4) showed significant differences ($p \leqslant 0.05$) between the levels of caprolactam in multilayer PA-6 films. For non-irradiated multilayer PA-6 films for meat foodstuffs brand 6 was higher ($p \leqslant 0.05$) than brands 1, 3 and 5, which showed no difference among themselves ($p > 0.05$), but were higher than brands 2, 4, 7 and 8 ($p \leqslant 0.05$). For non-irradiated multilayer PA-6 films for cheese, brand 10 was higher ($p \leqslant 0.05$) than brand 11, which showed significant difference ($p \leqslant 0.05$) from brand 9. Non-irradiated multilayer PA-6 films of brand 6 for meat foodstuffs and brand 10 for cheese showed the highest level of caprolactam ($p \leqslant 0.05$), 2773.3 and 3015.5 mg/kg PA-6 film, respectively.

When 3 kGy irradiation dose was used in multilayer PA-6 films for meat foodstuffs brand 5 showed higher caprolactam level ($p \leqslant 0.05$) than brands 1 and 6, which were different ($p \leqslant 0.05$) from brands 2, 3, 7 and 8. Brand 4 showed the lowest caprolactam level ($p \leqslant 0.05$). Multilayer PA-6 films for meat foodstuffs submitted to 7 kGy showed a caprolactam level difference ($p \leqslant 0.05$) between brand 1 and brands 2, 3 and 5 ($p > 0.05$), which were higher ($p \leqslant 0.05$) than brands 4, 6 and 8. Brand 7 showed the lowest caprolactam level ($p \leqslant 0.05$). Multilayer PA-6 films for cheese irradiated with 12 kGy showed a difference ($p \leqslant 0.05$) between caprolactam levels of brand 10 and brands 9 and 11, which did not differ between each other ($p > 0.05$). Brands 12 and 13 showed values of caprolactam levels below the LOQ of the method, avoiding quantification. Despite the differences between the brands, all of them showed the same magnitude of caprolactam levels.

Considering the effect of irradiation in multilayer PA-6 films for meat foodstuffs, brands 1, 2, 3 and 8 showed the same behavior, an increase in caprolactam levels with the increase of irradiation doses. Caprolactam levels of these brands improved from zero to 7 kGy ($p \leqslant 0.05$). On the other hand, brand 6 showed the opposite behavior, a decrease in caprolactam levels ($p \leqslant 0.05$) with irradiation doses, while there was no effect on brand 4, that is, the increase of irradiation doses did not promote differences ($p > 0.05$) in caprolactam levels. Brands 5 and 7 improved caprolactam levels from zero to 3 kGy and then showed a reduction up to 7 kGy.

Table 3
Quantities of caprolactam (mg/kg) found in multilayer PA-6 films used for meat foodstuffs

	Irradiation doses		
	0 kGy	3 kGy	7 kGy
Brand 1*	$2440.2^{bC} \pm 102.8$	$2682.9^{bB} \pm 68.2$	$3362.5^{aA} \pm 44.9$
Brand 2*	$2076.0^{cC} \pm 46.6$	$2370.1^{cB} \pm 12.4$	$2724.7^{bA} \pm 87.8$
Brand 3*	$2413.9^{bB} \pm 64.1$	$2394.1^{cB} \pm 41.8$	$2656.6^{bA} \pm 115.9$
Brand 4*	$2136.1^{cA} \pm 13.2$	$2162.9^{dA} \pm 16.6$	$2221.4^{cA} \pm 37.1$
Brand 5*	$2455.7^{bC} \pm 29.3$	$3012.1^{aA} \pm 20.3$	$2611.9^{bB} \pm 20.4$
Brand 6*	$2773.3^{aA} \pm 38.9$	$2530.2^{bB} \pm 84.1$	$2229.7^{cC} \pm 57.9$
Brand 7*	$2144.4^{cB} \pm 42.5$	$2216.6^{cA} \pm 50.9$	$1819.7^{dC} \pm 27.5$
Brand 8*	$2054.5^{cB} \pm 0.9$	$2263.4^{cA} \pm 102.6$	$2342.9^{cA} \pm 63.4$

Mean of four replicates of the found value ± standard deviation (SD).
Means within the same columns followed by the same small letters are not significantly different ($p \leqslant 0.05$).
Means within the same lines followed by the same capital letters are not significantly different ($p \leqslant 0.05$).
* Multilayer PA-6 films containing PA-6 and PA-6/PA-66 (67% of homopolymer, 20% of copolymer) layers and masterbatch of additives, all from different companies.

Table 4
Quantities of caprolactam (mg/kg) found in multilayer PA-6 films used for cheese

	Irradiation doses	
	0 kGy	12 kGy
Brand 9**	$1816.3^{cA} \pm 6.7$	$1840.9^{bA} \pm 38.1$
Brand 10**	$3015.6^{aA} \pm 59.3$	$2507.6^{aB} \pm 167.4$
Brand 11**	$2450.7^{bA} \pm 35.7$	$1886.9^{bB} \pm 75.8$
Brand 12**	–*	–*
Brand 13**	–*	–*

Mean of four replicates of the found value ± standard deviation (SD).
Means within the same columns followed by the same small letters are not significantly different ($p \leqslant 0.05$).
Means within the same lines followed by the same capital letters are not significantly different ($p \leqslant 0.05$).
* Lower than LOQ.
** Multilayer PA-6 films like PA/Adhesive/PA/Adhesive/Sealant layer (PE or EVA structure) from different companies.

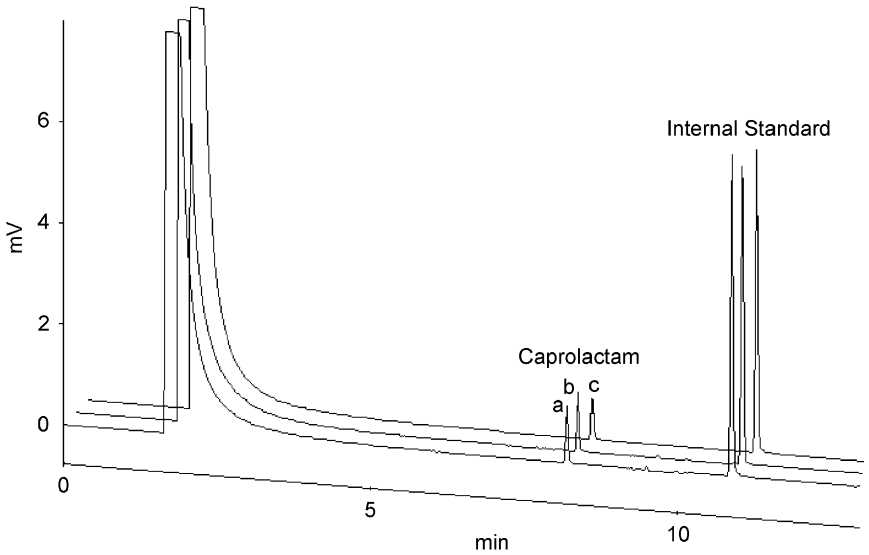

Fig. 2. Typical chromatograms for quantitation of caprolactam in multilayer PA-6 films for meat foodstuffs: (a) non-irradiated (0 kGy); (b) irradiated at 3 kGy; and (c) irradiated at 7 kGy. Conditions: column temperature started at 110 °C, programmed at 10 °C/min up to 180 °C for 1 min, then heated to 200 °C at 10 °C/min and held for 2 min. Hydrogen was the carrier gas and nitrogen was the make-up gas. Injections (1 μl) were made at 240 °C in split mode (1:20). Detector temperature was 250 °C.

Irradiation of multilayer PA-6 films for cheese showed reduction in caprolactam levels ($p \leqslant 0.05$) of brands 10 and 11, while there was no effect in caprolactam levels ($p > 0.05$) of brand 9.

The results showed that the effect of irradiation in the multilayer PA-6 films might promote increase, reduction or no modification of the residual level of caprolactam when compared to non-irradiated multilayer PA-6 films used for meat foodstuffs and cheese. The increase of caprolactam level could be explained by degradation of polymer, while reduction could be due to the crosslinking of residual caprolactam with other compounds. The different behavior of multilayer PA-6 films may occur due to the different constitutions of the packaging and, especially, due to the doses and dose rates. Thus, to elucidate such questions, studies with this approach should be carried out. It should be mentioned that the results obtained in this work were the first reported for Brazilian PA-6 films used for meat foodstuffs and cheese.

4. Conclusion

The method developed can be successfully used to determine caprolactam in multilayer PA-6 films used for meat foodstuffs and cheese.

Irradiation affected caprolactam levels of the multilayer PA-6 films used for meat foodstuffs and cheese, pointing out the necessity of more detailed studies on the influence of rate and dose irradiations over food plastic packaging.

The levels of caprolactam were the first reported for Brazilian multilayer PA-6 films used for meat foodstuffs and cheese.

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