

## Detecting ultraviolet C radiation under polyethylene terephthalate (PET) packaging by thermoluminescence analysis using commercial dosimeters

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### ABSTRACT

Food irradiation is a proven technology that enhances food quality and safety by removing microorganisms and extending shelf life. Ultraviolet C radiation (UVC) has recently attracted interest due to its potential to inactivate foodborne pathogens. It relies on several advantages; however, there is limited research on its efficacy and safety particularly concerning food packaging materials such as polyethylene terephthalate (PET).

This study reports on the effect of UVC radiation on commercial thermoluminescence dosimeters (namely, TLD-100, TLD-200, TLD-400 and GR-200) placed under PET films with different thicknesses (0.10, 0.42, and 0.60 mm). The results indicate the potential use of these materials for the detection of UVC radiation passing through the randomly selected PET samples. Fourier transform infrared spectroscopy assesses potential structural and chemical alterations in the PET induced by UVC exposure.

### 1. Introduction

Food irradiation is a technology that has been employed for many years to enhance the quality and safety of food products. The Food and Drug Administration (FDA) has approved several food irradiation methods, including gamma rays (with <sup>60</sup>Co or <sup>137</sup>Cs radioisotopes), electron beams (with high energy reaching up to 10 MeV), X-rays (with high energy reaching up to 5 MeV) and, most recently, ultraviolet (UV) radiation (at a wavelength of 253.7 nm) (Ghazala, 2020). These methods are effective in eliminating and/or reducing harmful bacteria and parasites in food products, as well as in extending their shelf life (Ben-Fadhel et al., 2021; Prajapati, Asrey, Varghese, Singh, & Pal Singh, 2021; Soro et al., 2021; Tao et al., 2019). Specifically, UVC exposure (in the range of 200–280 nm) can be a useful tool to inactivate pathogenic bacteria in food and food contact surfaces (Belović, Kevrešan, Pestorić, & Mastilović, 2015; Prajapati et al., 2021). This technology offers several advantages to ensure food safety, such as: (i) germinal ability to damage the DNA of pathogenic microorganisms, (ii) does not produce chemical residues, (iii) color, texture, flavor and even enzyme activity are preserved, (iv) it is a simple, cold and dry process, (v) requires low maintenance and (vi) is an inexpensive method (Guerrero-Beltrán & Barbosa-Cánovas, 2004). However, the use of UVC irradiation in food

processing is still an emerging technology, and there is limited research on its efficacy and safety compared to those material which are designed to pharmaceutical products or medical devices (Foschi, Giorgi, Ambretti, Lazzarotto, & Violante, 2023).

Prior to irradiation, food is typically packaged (Ghazala, 2020), and implementing this methodology requires addressing at least two essential aspects: (i) determine the potential damage that the radiation exposure could induce in the polymer (polyethylene terephthalate -PET- in this case) usually employed as commercial packaging material, and (ii) detect the UVC irradiation. For such purposes, there are two optimal techniques that allow determining both items, namely, Fourier transform infrared spectroscopy (FTIR) and thermoluminescence (TL). Despite the significance of these techniques, there has been a scarcity of studies involving them in the analysis of food packaging materials exposed to UVC radiation, particularly polymeric materials like PET (Chun, Kim, Lee, Yu, & Song, 2010; Jamalzadeh & Sobkowicz, 2022). PET, which is widely used in food packaging applications, stands out as a highly favorable material due to its stability, cost effectiveness, light weight nature, flexibility, transparency, acceptable recyclability and its excellent barrier, among others (Fernández-Menéndez, García-López, Argielles, Fernández, & Viña, 2020; Zhang et al., 2022).

UVC radiation could induce alterations in the chemical and physical

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properties of the polymers (Andrady et al., 2023) including: (i) *photo-oxidation*, breaking chemical bonds in the polymer, leading to chain fragmentation and a subsequent reduction in mechanical strength; (ii) *radical formation*, initiating additional polymerization or degradation reactions; (iii) *bleaching effect*, disrupting pigments or colorants present in PET; (iv) *reduced fatigue resistance*, making it more susceptible to cracking or failure under cyclic loads; (v) *introduction of functional groups*, into the polymer structure, altering its chemical and physical properties; and/or, (vi) *changes in optical properties*, affecting characteristics such as transmittance and reflectance (Andrady et al., 2023). In this sense, FTIR provides a method for analyzing such potential conformational changes and microscopic deformations in food packaging plastic films. FTIR, which is a vibrational spectroscopy technique based on the fundamental vibrational motions of functional groups within the polymeric lattice, provides structural insights at the molecular level without the need for chemical or physical pre-treatment of samples (Hu, Huyan, Ding, Dong, & Yu, 2020; Junqueira-Gonçalves, Alarcón, & Niranjana, 2013; Paiva, Wrona, Nerín, & Cruz, 2022).

On the other hand, while food irradiation is approved in almost 60 countries (Ghazala, 2020), there is currently no established method to discriminate UV-irradiated food, which would allow regulatory authorities to rely on a tool to certify correct labeling or validate a standard procedure to determine the total absorbed dose, among others similar to the EN 1788 standard procedure (EN, 1788, 2001). This tool would be based on identifying irradiated food through changes in biological, chemical, and physical properties (Correcher & Garcia-Guinea, 2011, 2013). In this context, TL technique appears as one of the most suitable, effective, cost efficient and accurate method for such purpose. TL relies on the emission of light from a dielectric solid sample (insulator or semiconductor) when it is heated after being irradiated (artificially or naturally) by ionizing or partially ionizing radiation. During the analytical heating, a photomultiplier tube detects the TL signal, which is recorded as a function of wavelength or temperature. The resulting curve, known as a glow curve or TL curve, exhibits luminescent intensity and shape patterns that correspond to radiation dose and heating rate (McKeever, 1986).

There are several detectors and dosimeters that have the capability of detecting and recording UVC radiation, including electronic devices and synthetic dosimeters with different compositions, i.e., TLD-100 (LiF: Ti, Mg), TLD-200 (CaF<sub>2</sub>: Mn), TLD-400 (CaF<sub>2</sub>: Dy) and GR-200 (LiF: Mg, Cu, P), among others (Boronat et al., 2023). As a result, TL analysis, among other techniques, is essential for determining the structures, compositions, polymorphic properties and genetic characteristics of materials. In this context, intrinsic, structural, surface and extrinsic defects contribute to distinct luminescence emissions.

This study reports on the preliminary findings regarding the effect of UVC radiation on commercial dosimeters (namely, TLD-100, TLD-200, TLD-400 and GR-200) placed under PET films with different thicknesses (0.10, 0.42 and 0.60 mm) to determine their UVC-TL responses exposed to radiation through the plastic. Additionally, PET samples have been characterized by FTIR spectroscopy to analyze potential changes in the plastic structure due to UVC exposure.

## 2. Materials and methods

This study was performed on PET samples with different thickness of 0.10 mm (PET 1), 0.42 mm (PET 2) and 0.60 mm (PET 3), randomly selected from grocery stores at Madrid (Spain).

The structural characterization of the plastic materials was carried out by means of ATR-FTIR spectroscopy. Infrared absorption spectra of the samples were measured at room temperature (RT) within the wavenumber range from 4000 to 400 cm<sup>-1</sup>, employing a Spectrum FT-IR-4100 spectrometer equipped with the ATR PRO ONE Accessory (ATR-FTIR) and using Spectra Manager® software, provided by JASCO (Tokyo, Japan). The spectral resolution employed for the measurements was 4 cm<sup>-1</sup>.

UVC exposure consisted of 1 h at RT was performed on an automated irradiator developed at CIEMAT (Delgado, Unamuno, Muñiz, Correcher, & Gómez Ros, 1996). It allows UV illumination with a TUV-6 W Hg lamp (254.7 nm, 0.03 W·m<sup>-2</sup> of UV irradiance value at 10 cm). Commercial dosimeters, namely LiF: Ti, Mg (TLD-100), CaF<sub>2</sub>: Dy (TLD-200), CaF<sub>2</sub>: Mn (TLD-400), provided by Harshaw Chemical Company (Ohio, USA) with sizes of 0.32 × 0.32 × 0.09 cm<sup>3</sup> each one, and LiF: Mg, Cu, P (GR-200) disks of 4.5 Ø 0.8 mm<sup>3</sup> dimensions supplied by Beijing Shiying Radiation Detector Works (China), were used as UVC detectors. These dosimeters were placed under the PET samples to investigate the extent of radiation that can penetrate through the plastic and potentially reach the food during post-packaging irradiation.

Before the subsequent irradiation, dosimeters were formerly annealed at 400 ± 1 °C for 1 h employing the electrical oven to eliminate any residual data and 1 h of cooling rate. The effect of UVC radiation was assessed by examining the TL properties of the mentioned detectors. TL measurements were performed employing an automated Risø TL reader model TL DA-12 provided with an EMI 9635 QA photomultiplier (Bøtter-Jensen & Duller, 1992). The emission was studied through a FIB002-blue filter (provided by Melles-Griot Company) peaked at 320 - 480 nm, 80 ± 16 nm of FWHM and 60% of transmittance. The TL reader is also supplied with a <sup>90</sup>Sr / <sup>90</sup>Y source with a dose rate of 0.011 Gy·s<sup>-1</sup> calibrated with a <sup>137</sup>Cs photon source in a secondary standard laboratory (Correcher & Delgado, 1998). All the TL measurements were obtained using a linear heating rate of 5 °C·s<sup>-1</sup> from room temperature up to 400 °C in a N<sub>2</sub> atmosphere. A second TL readout of the TLDs to obtain the background due to the incandescence and detector noise; it was directly subtracted from the TL data.

## 3. Results and discussion

### 3.1. Sample characterization: FTIR spectroscopy

FTIR spectroscopy has been employed to investigate potential variations in the structural and chemical properties of PET samples, which is a material commonly used in food packaging applications (Fernández-Menéndez et al., 2020; Zhang et al., 2022). The aim of this characterization is to comprehensively assess the influence of UVC radiation on PET samples with different thicknesses, a factor that could significantly affect the ability of UVC to irradiate the packaged food. PET is a well-known thermoplastic polymer synthesized through the polymerization of repetitive ethylene terephthalate units, as illustrated by the following chemical formula in Fig. 1A.

According to Day & Wiles (1972), UV exposure could induce an increase in the concentration of carboxylic acid end groups (-COOH) and the generation of volatile products (CO and CO<sub>2</sub>) and free radicals. This phenomenon is commonly referred to as the *photo-oxidation* process, shown in Fig. 1B.

These authors explained the distinction between the *photolysis process*, which occurs under vacuum conditions, and *photo-oxidation process*, which takes place in the presence of oxygen (an aspect directly relevant to our current investigation). Consequently, no disparities in the composition of the volatile products were observed when the experiments were performed in ambient air instead of vacuum conditions. However, there was a notable increase in the production of CO<sub>2</sub>. This discrepancy suggests the participation of oxygen in the reactions responsible for CO<sub>2</sub> formation in the presence of air. Furthermore, the quantum yields for the initial rates of CO and -COOH end groups formation was nearly identical to those achieved under vacuum conditions. This consistency can be explained with the same primary reactions, specifically reaction [2] (Fig. 1B) following a primary photolytic chain scission sequence to yield CO, and reaction [3] (Fig. 1B) via a Norrish type II photoelimination mechanism to generate -COOH. Additionally, the enhanced production of CO<sub>2</sub> under UV irradiation in the presence of air can likely be attributed to the formation of hydroperoxides (reactions [4-8], Fig. 1B).



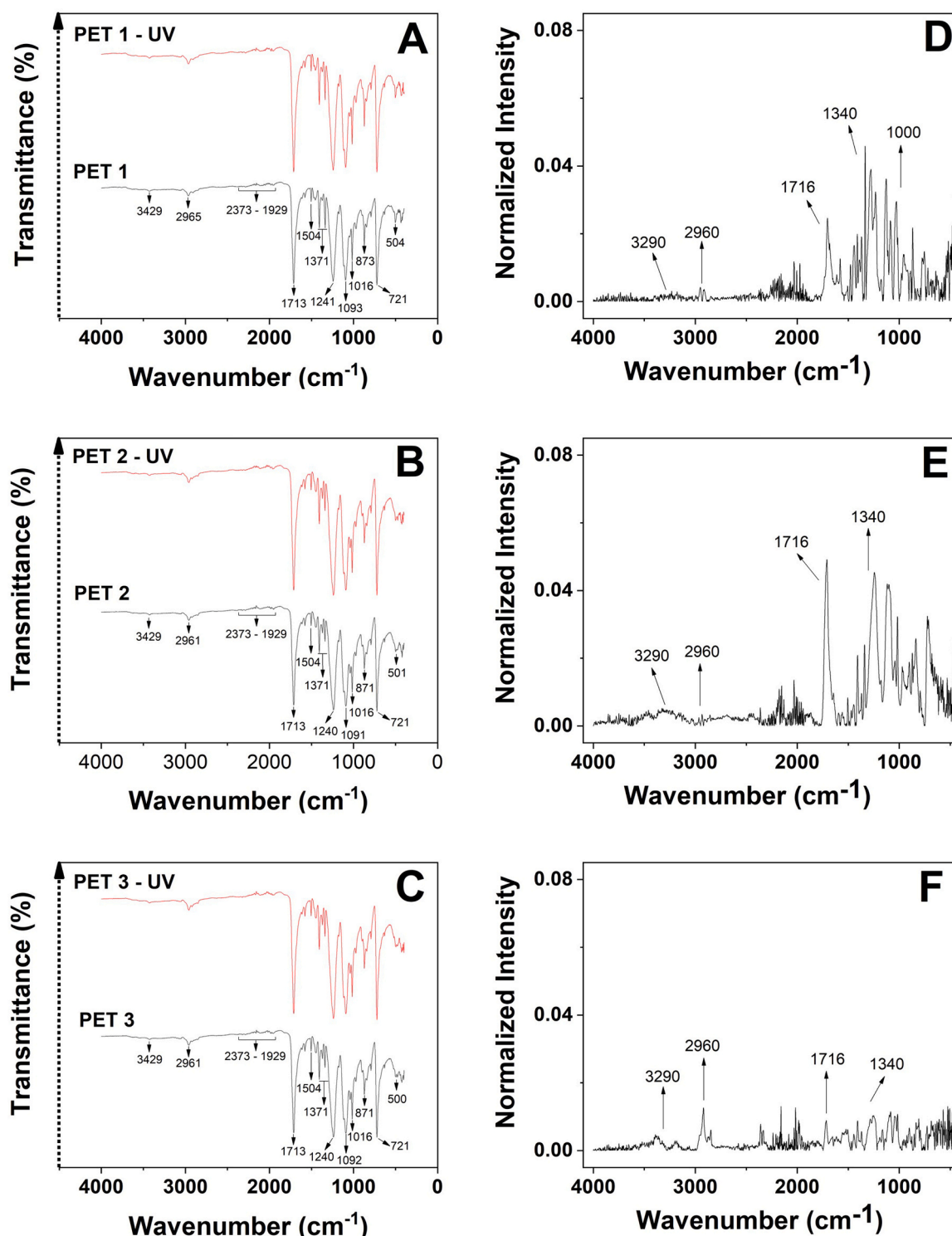


Fig. 2. FTIR and Normalized FTIR spectra of non-irradiated and UVC irradiated PET food packaging samples with different thicknesses: (A and D) PET 1 (0.10 mm), (B and E) PET 2 (0.42 mm) and (C and F) PET 3 (0.60 mm). Note that the signal of the UVC-irradiated PET samples has been intentionally shifted to avoid spectral overlap.

is observed. Factors such as temperature or other forms of energy (i.e., UVC radiation), can induce a transition from the *gauche* to the *trans* form, resulting in an increase in *crystalline* content. Such crystallization can also be influenced by stretching, depending on the temperature, which has led to debates regarding the precise assignments of absorption bands in the IR spectrum concerning crystallinity and changes in chain conformation (Table 1). Specifically, the bands at 1471, 1341, 1123, 972, and 849  $\text{cm}^{-1}$  serve as markers for the *crystalline* structure of PET in

its *trans* configuration, whereas bands at 1371, 1044, and 898  $\text{cm}^{-1}$  characterize the *amorphous* form with a *cis* configuration (Donelli et al., 2010). Conformational changes in the material are associated with variations in optical density and alterations in polymer density and electrical properties, particularly within the structured (*trans*) regions. These alterations lead to a decrease in polarization and dielectric constant, and the extent of variations in the loss tangent and dielectric strength depends on the reduction in molecular mass (Chen et al., 2012).

**Table 1**  
Assignment of vibrational modes for observed FTIR bands in PET food packaging samples.

Wavenumber (cm <sup>-1</sup> )						Assignment	Conformation
PET1	PET1 - UVC	PET2	PET2 - UVC	PET3	PET3 - UVC		
3424	3424	3424	3427	3428	3429	O-H stretching (Hydroxyl groups)	Crystalline
3290	3290	3290	3290	3293	3293	O-H stretching (Carboxylic acid end groups)	-
2964	2964	2960	2960	2960	2958	C-H stretching (Aromatic and aliphatic)	Amorphous, cis
-	2164	-	2164	-	2166	CO stretching vibration	-
2107	2106	2111	2114	2108	2107	C-H stretching (Aromatic skeleton)	-
1710	1710	1712	1712	1711	1712	C=O stretching (Carboxylic acid end groups)	Crystalline
1575	1579	1578	1578	1578	1578	C=C stretching (Aromatic skeleton)	Amorphous
1505	1503	1504	1505	1505	1505	Para-substituted benzene ring, C=C stretching (Aromatic skeleton) and CH in-plane bending ring	Crystalline
1453	1453	1447	1447	1446	1449	CH <sub>2</sub> bending and O-CH bending	Amorphous, cis/ gauche
1406	1406	1408	1408	1407	1408	Para-substituted benzene ring, CH in-plane bending (Aromatic skeleton) and CC stretching	-
1339	1339	1341	1341	1341	1341	OCH bending, C-C Alkane, =CH <sub>2</sub> wagging, bending and wagging vibrational modes of the ethylene glycol	Crystalline, trans
1242	1242	1238	1238	1239	1240	C=C stretching (phenyl ring), C(=O)-O stretching and C=O in-plane bending	Amorphous, cis
1172	1172	1175	1175	1176	1175	Aromatic - 1, 4 substituted ring and ring CH in-plane bending	-
1093	1095	1091	1092	1091	1090	Methylene group and C-O stretching (ester group)	-
1016	1016	1016	1016	1016	1016	C-H in-plane stretching, ring CCC bending and ring CH in-plane bending	Amorphous, gauche
872	872	870	871	871	871	Para-substituted benzene ring, ring CH out-of-plane bending, ring-ester C-C out-of-plane bending, C=O out-of-plane bending and ring torsion	-
790	790	792	792	792	792	ring CH out-of-plane bending, C=O rocking and CCO bending	-
722	722	722	722	722	722	C=O out-of-plane bending, ring torsion and ring C-H out-of-plane bending	Crystalline
502	501	497	499	495	496	Several bending/torsion vibrations	-
433	431	422	426	426	428	Several bending/torsion vibrations	-

Previous studies have elucidated the effects of different radiation sources on the FTIR spectra of PET, including UV radiation, gamma rays and ions irradiation, among others (Dworecki, Hasegawa, Sudlitz, & Wasik, 2000; Fechine et al., 2007; Nair, Sharma, Sharma, & Diwan, 2020; Prasad et al., 2011). These investigations have revealed discernible alterations in the molecular structure of the polymer, including changes in the intensities and positions of characteristic absorption peaks. For example, Fechine et al. (2007), reported that carboxyl acid end groups (-COOH) are formed during UV radiation due to a *photo-oxidation* process. This is evidenced by the increase of absorption at 3290 cm<sup>-1</sup>, attributed to O-H stretching vibrations at carboxylic acid functional groups. Such groups are generated during the *photo-oxidation* of PET as a consequence of the reaction with the ester groups, leading to a significant reduction in mechanical properties. In a study by Nair et al. (2020), the effects of UVC irradiation were investigated at different exposure times. Their FTIR spectra indicated that the extent of damage to various bonds in the polymer is insignificant and increases with longer irradiation times. Damage induced by UVC irradiation is evident from the shifting of peaks (at 1235, 1093, 631 and 435 cm<sup>-1</sup>) in the FTIR spectra to slightly higher wavenumbers. However, other bands in the PET FTIR spectra show resistance to UV irradiation and do not degrade further. Additionally, Prasad et al. (2011) investigated the effects of gamma irradiation at different doses on PET (up to 135 kGy), and it was found that no significant changes in the existing C-H and O-H stretching vibration of different types of H-bonds in the PET and also no alkyne group (at 3294 cm<sup>-1</sup>) was detected in the region of 3600–2500 cm<sup>-1</sup>. Moreover, their XRD and FTIR results support each other in finding no

loss of crystallinity.

Thus, Dworecki et al. (2000) employed ion irradiation with N<sup>4+</sup>, O<sup>5+</sup> and Kr<sup>9+</sup> ions, causing structural damage, attributed to several processes, including crosslinking of adjacent unsaturated radicals, amorphization of the crystalline fraction of the polymer, chain scission and oxidative reactions. These authors observed significant alterations in the infrared absorption bands within the spectral ranges of 3914–2970 cm<sup>-1</sup>, 1683–1578 cm<sup>-1</sup> and 631–506 cm<sup>-1</sup>, which were primarily associated with the methylene group. Moreover, changes in the absorption spectra within the regions of 1740–1660 cm<sup>-1</sup> and 1660–1600 cm<sup>-1</sup> were ascribed to carbonyl group vibrations.

As appreciated in Fig. 2 (D-F), the normalized FTIR spectra of both non-irradiated PET samples and those irradiated with UVC for 1 h displayed minimal changes, with differences of less than 5% of transmittance respect to the mean value after UVC treatment. This observation confirms the resilience of bands within the PET FTIR spectra against UVC irradiation, demonstrating their resistance to further degradation. However, it is worth noting that a few subtle alterations were observed, as detailed below:

- (i) A slight increase in the signal can be observed at 3290 cm<sup>-1</sup>, attributed to O-H stretching vibrations in carboxylic acid end functional groups formed during PET *photo-oxidation* process.
- (ii) UVC irradiation can induce the disruption of C-H stretching vibrations of both aromatic and aliphatic groups in the polymeric chain, leading to an increase in the FTIR signal at 2960 cm<sup>-1</sup>.

- (iii) The FTIR absorption peak at  $1716\text{ cm}^{-1}$ , corresponding to C=O stretching vibrations in carboxylic acid end groups, is among the most intense peak in FTIR spectra. Significant alterations in peak intensity or position were assumed following UVC radiation treatment, based on existing literature. However, contrary to expectations, this peak does not exhibit any significant change in intensity or position.
- (iv) UVC irradiation can induce a shift of peaks in the FTIR spectra to slightly higher wavenumbers, specifically from  $1340\text{ cm}^{-1}$  to  $420\text{ cm}^{-1}$ . This phenomenon becoming more pronounced as the thickness increases.
- (v) Additionally, the peak centered at  $1000\text{ cm}^{-1}$ , associated with the O-CH<sub>2</sub> bond aromatic moiety, exclusively arises in recycled materials. According to the literature, this observation could indicate the prevalence of degradation in recycled streams or the potential influence of isopropyl alcohol (IPA), which is commonly detected in bottles, as evidenced by the PET 1 sample (Fig. 2D) (Silva, 2016).

### 3.2. UVC-TL emissions of commercial dosimeters (TLD-100, TLD-200, TLD-400 and GR-200)

The investigation of PET shielding against UVC radiation holds significant importance in accurately detecting the potential radiation that reaches packaged food items. For such purpose, several commercial UVC detectors (Boronat et al., 2023), namely TLD-100 (LiF: Ti, Mg), TLD-200 (CaF<sub>2</sub>: Dy), TLD-400 (CaF<sub>2</sub>: Mn) and GR-200 (LiF: Mg, Cu, P), have been employed to check the yield of the UVC radiation concerning the

thickness of the PET samples. This approach enables a qualitative discrimination between irradiated and non-irradiated PET packaging, thereby ensuring the quality and safety of food products.

Such commercial materials were employed as UVC radiation detectors for PET samples, and their corresponding UVC-induced TL emissions are presented in Fig. 3. Each of these emissions provides insights into fundamental characteristics associated with the interaction between UVC exposure and the distinct dosimeters, depending on the thickness of the PET material.

#### 3.2.1. UVC effect on the TL response of TLD-100 (LiF: Ti, Mg)

As appreciated in Fig. 3 (A-C), the results reveal the presence of two groups of components in UVC-induced TL glow emissions:

- (i) The TL glow emission in the lower temperature range (up to  $\sim 270\text{ }^\circ\text{C}$ ) consists of three maxima at  $\sim 165\text{ }^\circ\text{C}$ ,  $\sim 200\text{ }^\circ\text{C}$  and  $\sim 250\text{ }^\circ\text{C}$ , which are entirely linked to the ionizing component of the UVC radiation. The appearance of these maxima could be due to the formation of  $\text{Ti}^{4+} - \text{OH}^-$  defect complexes in conjunction with  $\text{Mg}^{2+}$  vacancies (referred to as Mg-dipoles),  $\text{Mg}^{2+}$  dipoles and/or  $\text{Ti}^{4+} - \text{OH}^-/\text{Mg}^{2+}$ -trimer defect complexes (Dryden & Shuter, 1973). Furthermore, several studies have demonstrated the significant presence of  $\text{OH}^-$  ions, with an ionic radius of  $1.37\text{ \AA}$ , replacing  $\text{F}^-$  ions ( $1.33\text{ \AA}$ ) within the LiF crystal lattice of the TLD-100 material. These hydroxyl groups are favorable to react with the metals found in the TLD-100 material, namely  $\text{Ti}^{4+}$  and  $\text{Mg}^{2+}$ . Consequently, it can be assumed that an increase in the concentration of  $\text{OH}^-$  ions within the matrix could enhance TL sensitivity (Weiss, Horowitz, & Oster, 2008).

Thus, PET 1 (Fig. 3A) and PET 2 (Fig. 3B) exhibit nearly identical

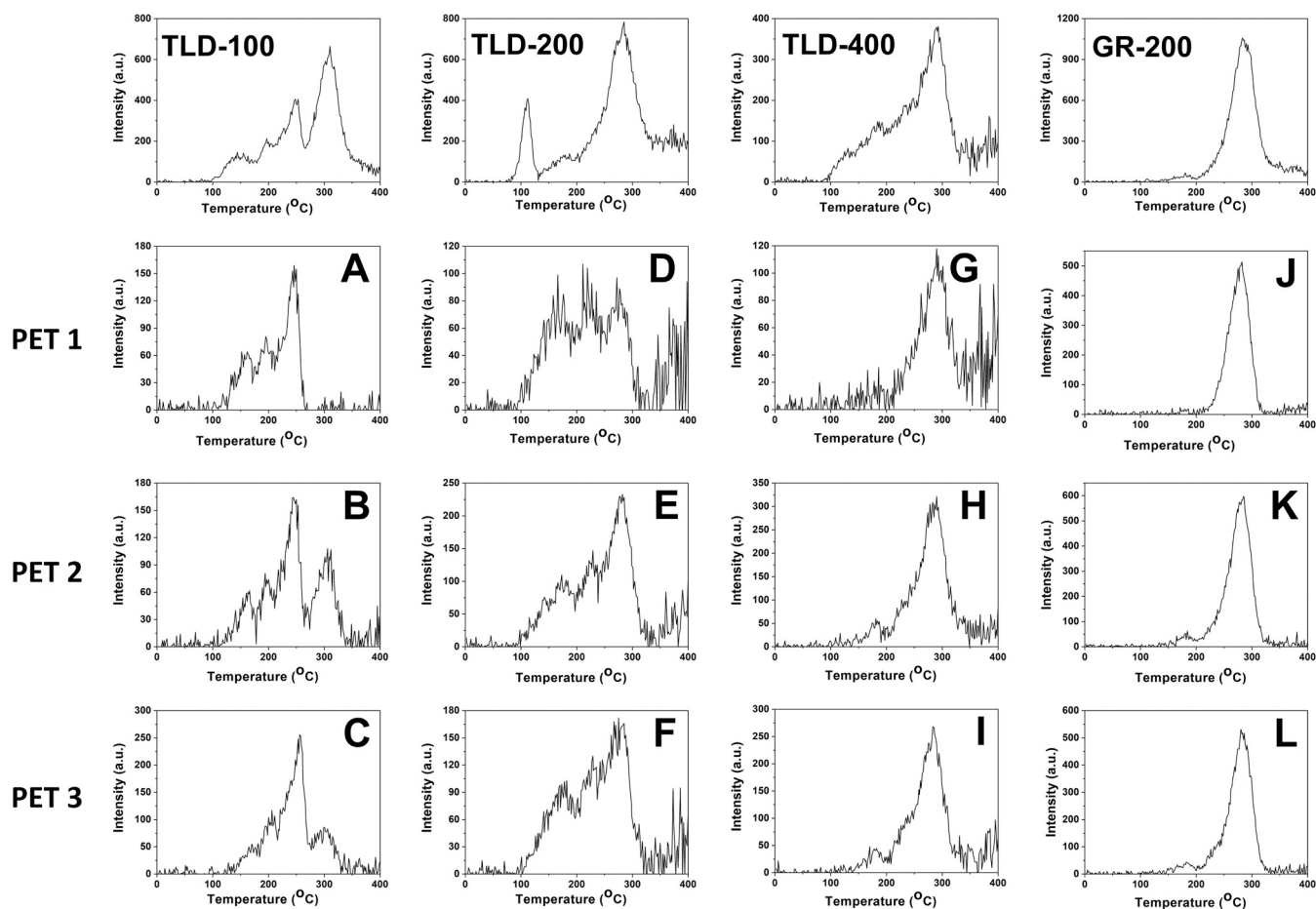


Fig. 3. UVC-induced TL spectra of PET food packaging samples with different thicknesses (PET 1, PET 2 and PET 3, corresponding respectively to the 2nd, 3rd and 4th line plots) and commercial dosimeters (TLD-100, TLD-200, TLD-400 and GR-200, corresponding respectively to the 1st, 2nd, 3rd and 4th columns). Note that the 1st line plot illustrates the UVC-induced TL spectra of the dosimeters without PET food packaging samples (Boronat et al., 2023).

peak intensity ratios of 2:2:5 and 2:3:6, respectively. In contrast, PET 3 (Fig. 3C) shows a comparable pattern with an intensity ratio of 1:2:5. These maxima consistently display apparently similar intensity ratios across different PET thicknesses. However, it is important to emphasize that even minor deviations should be taken into consideration. Specifically, while the peak centered at  $\sim 230$  °C is less pronounced in PET 1 (Fig. 3A) and PET 2 (Fig. 3B), a change in slope is observed for PET 3 (Fig. 3C). This could suggest that as the thickness of the sample increases, it tends to absorb the non-ionizing component of UVC radiation while allowing the ionizing component to pass through. Therefore, variations in PET thicknesses used in this study (0.10, 0.42, and 0.60 mm), could result in significant differences in terms of the ionizing component of the UVC-induced TL glow emissions (up to  $\sim 270$  °C).

And (ii), the TL emission at higher temperatures (over  $\sim 270$  °C) is mainly associated with the non-ionizing component of the UVC radiation. In this case, a single TL emission peak is observed at  $\sim 305$  °C and it serves as an indicator of the interaction between the non-ionizing component of UVC radiation and the dosimeters. PET 1 (Fig. 3A) exhibits a relatively low intensity value of  $\sim 15$  a.u. within the emission peak centered at  $\sim 300$  °C, while PET 2 (Fig. 3B) and PET 3 (Fig. 3C) display similar responses with intensity values of  $\sim 90$  and  $\sim 70$  a.u., respectively. This consistent response to the non-ionizing component suggests a similar sensitivity to UVC radiation in the TLD-100 under these increased PET thicknesses (0.42, and 0.60 mm), which could be related to the permeability of the PET samples to the non-ionizing component of UVC radiation.

In summary, the TLD-100 dosimeter exhibits a high temperature signal peaked at  $\sim 305$  °C, which is associated with the non-ionizing component of UVC radiation and is predominantly in PET samples of greater thickness (PET 2 and PET 3), displaying similar pattern observed in the TLD-100 dosimeter without plastic sample (1:1:3:4) in terms of both curve shape and intensity relationships. However, this signal is not consistently observable across all PET samples, in this case, limitations become pronounced when thinner plastic samples are considered (PET 1). This significant dispersion of the results indicates that TLD-100 does not appear to be a potential UVC detector under these measurement conditions. Furthermore, FTIR analysis does not reveal any discernible degradation of the PET materials following UVC exposure, confirming their robustness under these experimental conditions.

### 3.2.2. UVC effect on the TL response of TLD-200 (CaF<sub>2</sub>: Dy)

The UVC-induced TL emissions from the TLD-200 dosimeter employed under the PET samples (Fig. 3 (D-F)) show the existence of three distinct groups of components:

(i) And (ii), the TL glow emission occurring within the temperature range from  $\sim 165$  °C to  $\sim 230$  °C, would be associated with non-ionizing component of the UVC irradiation.

Conversely, (iii) the TL emission at higher temperatures, centered at  $\sim 280$  °C and extending up to  $\sim 350$  °C, would be mostly linked to the ionizing component of the UVC radiation. According to Boronat et al. (2023), these maxima could be attributed to structural defects and impurities induced by Dy<sup>3+</sup> ions, with an atomic radii of 1.59 Å, residing within Ca<sup>2+</sup> sites (1.74 Å) in the CaF<sub>2</sub> crystal lattice.

Considering the relative intensity values of these three groups of components, PET 1 (Fig. 3D) displays a ratio of 1:1:1, PET 2 (Fig. 3E) exhibits a ratio of 3:4:7 and PET 3 (Fig. 3F) shows a ratio of 3:4:5. It is important to note that the thickness of the samples (0.10, 0.42, and 0.60 mm) used in this study result in significant variations within the temperature range of  $\sim 165$  °C to 230 °C, attributed to the non-ionizing component of the UVC irradiation. Moreover, one can also appreciate differences concerning the ionizing component of the UVC-induced TL glow emissions (peaked at  $\sim 280$  °C). This phenomenon could be linked to the ability of the PET samples to allow the transmission of the non-ionizing component of the UVC radiation. Significantly, for the thicker PET samples (PET 2 with 0.42 mm and PET 3 with 0.60 mm), the increase in both TL signals is more prominent, especially for PET 2.

Therefore, the TLD-200 dosimeter demonstrates effective UVC detection capabilities by consistently displaying UVC response levels within the temperature range from  $\sim 165$  °C to 230 °C (linked to the non-ionizing component of the UVC radiation) for the three PET samples studied. Samples exhibit distinct behavior compared to the TLD-200 dosimeter without a plastic sample (4:1:8) in both curve shape and intensity relationships. As previously discussed, these observations primarily concern PET samples with greater thickness. When thinner plastic samples are examined, limitations become more evident, requiring careful interpretation. Moreover, FTIR analysis indicates that there is no observable degradation of the PET materials after exposure to UVC, providing additional evidence of the durability of these materials in the experimental settings.

### 3.2.3. UVC effect on the TL response of TLD-400 (CaF<sub>2</sub>: Mn)

As depicted in Fig. 3 (G-H), UVC-induced TL emissions on TLD-400 under PET samples exhibit behavior consistent with previous characterizations of this specific material under UVC radiation (Boronat et al., 2023). These emissions can be classified into two distinct groups of components:

(i) Several TL glow emissions displaying up to  $\sim 200$  °C, attributed to the influence of the non-ionizing component of the UVC radiation. These emissions could be related to structural defects and the presence of Mn<sup>2+</sup> impurities (with atomic radii of 1.17 Å) that are placed in Ca<sup>2+</sup> sites (1.74 Å) in the CaF<sub>2</sub> crystal lattice (Topaksu, Correcher, & Garcia-Guinea, 2016; Yazici, Bedir, & Sökücü, 2007).

And (ii), a broad maximum centered at  $\sim 280$  °C, mainly associated with the ionizing component of UVC radiation.

Thus, the TL signal exhibited by TLD-400 under PET 1 sample (Fig. 3G) is almost negligible at lower temperatures, suggesting minimal response to UVC radiation up to  $\sim 200$  °C, and this could be due to the minimum thickness of the sample (0.10 mm). Conversely, it displays a broad peak centered at  $\sim 280$  °C, with an intensity of  $\sim 90$  a.u., which can be attributed to the ionizing component of the UVC radiation. However, TLD-400 under PET 1 displays the lowest intensity value up to  $\sim 200$  °C (linked to UVC radiation), when compared to signals obtained from TLD-400 materials placed under PET 2 and PET 3 samples. Due to such limited radiation transmission by the PET 1 sample, it is expected that UVC radiation will have a reduced impact on the packaged food during the irradiation process.

On the contrary, TL signal from TLD-400 under both PET 2 (Fig. 3H) and PET 3 (Fig. 3I) exhibits a 1:7 ratio of relative intensity values for the prominent components centered at  $\sim 175$  °C and 280 °C, due to the ionizing component of UVC radiation. This suggests that the thicker PET samples have a negligible impact on their response to UVC radiation (at  $\sim 175$  °C), and both samples have a similar ability to allow the passage of the UVC light. Moreover, the TLD-400 dosimeter without plastic sample displays 1:4 ratio of relative intensity values for these groups of components.

Therefore, the TLD-400 dosimeter displays a TL signal observed up to  $\sim 200$  °C, linked to the UVC radiation and is mainly relevant for thicker PET samples (PET 2 and PET 3). However, the signal is not uniformly detectable in all PET samples, and its limitations become more apparent, especially when evaluating thinner plastic samples (PET 1). The substantial variability in results suggests that TLD-400 could not be a suitable dosimeter for UVC detection under these measurement conditions. Additionally, FTIR analysis confirms the absence of any detectable degradation in PET materials following UVC exposure, further supporting the durability of these materials in the experimental conditions.

### 3.2.4. UVC effect on the TL response of GR-200 (LiF: Mg, Cu, P)

UVC-induced TL emissions of PET samples on a GR-200 material (Fig. 3 (J-L)) display a peak centered at  $\sim 280$  °C, attributed to the ionizing component of the UVC radiation. This emission could be associated with the recombination of crystalline defects such as, H-F defects (color centers in the LiF crystal lattice) and V<sub>k</sub> –e centers (related to

vacancies and electron traps) (Yang, Wang, Townsend, & Gao, 2008). This sensitivity to the ionizing component of the UVC radiation is observed at higher temperatures (at  $\sim 280^\circ\text{C}$ ), with a negligible TL signal at lower temperatures (at  $\sim 180^\circ\text{C}$ ). Consequently, GR-200 could serve as a suitable dosimeter for detecting ionizing radiation, whereas it is unable to discriminate between UVC and ionizing radiation (Boronat et al., 2023).

Hence, PET 1 (Fig. 3J) displays an intensity of  $\sim 460$  a.u. in the peak centered at  $\sim 280^\circ\text{C}$ , with an insignificant TL signal at lower temperatures. In contrast, both PET 2 (Fig. 3K) and PET 3 (Fig. 3L) exhibit a similar pattern, showing an intensity ratio of 1:14 between the two main signals centered at  $\sim 180^\circ\text{C}$  and  $\sim 280^\circ\text{C}$  (associated with the ionizing component of UVC radiation). As previously outlined, these findings are primarily applicable to thicker PET samples. Analyzing thinner plastic samples presents challenges, requiring careful and thorough interpretation. Additionally, FTIR analysis further corroborates the durability of PET materials under the experimental conditions, as it reveals no discernible degradation following exposure to UVC radiation.

#### 4. Conclusions

The present study enhances our understanding of the intricate relationship between UVC radiation and PET materials, particularly in post-packaging irradiation treatment for food safety and quality control. UVC radiation can penetrate PET samples regardless of their thickness; however, its efficiency is significantly influenced by the thickness of the material. This phenomenon underscores the crucial importance for food packaging companies to comprehensively evaluate the chemical composition and thickness of their materials for optimal UVC post-packaging treatment.

These preliminary results demonstrate the capacity of UVC radiation to cause intricate chemical alterations in the molecular structure of PET, as evidenced by the subtle alterations observed in FTIR spectra. Specifically, UVC could induce: (i) the formation of carboxylic acid end groups due to increased O–H stretching vibrations (at  $3290\text{ cm}^{-1}$ ), (ii) disruptions in both aromatic and aliphatic C–H stretching vibrations (at  $2960\text{ cm}^{-1}$ ) and (iii) a shift in FTIR peaks to slightly higher wavenumbers, which becomes more pronounced with increasing thickness. Furthermore, the stability of the C=O stretching peak (at  $1716\text{ cm}^{-1}$ ) indicates resistance of PET samples to degradation under UVC radiation.

On the other hand, an in-depth analysis of TL emissions provides detailed insights into the capabilities and limitations of several dosimeter materials in UVC radiation detection. The TLD-200 dosimeter demonstrates potential as a UVC detector due to its UVC-TL response ranging from  $\sim 165^\circ\text{C}$  to  $\sim 230^\circ\text{C}$ , linked to the non-ionizing component of the UVC radiation. In contrast, TLD-100, TLD-400 and GR-200 dosimeters do not exhibit promise as UVC detectors due to the significant dispersion in results, which are not consistently observed across all PET samples. These discrepancies are particularly noticeable in thicker PET samples, underscoring the importance of sample thickness in accurate detection and interpretation of results.

Thus, this methodology confirms the capability to reliably detect food product irradiation after just one hour of exposure, enhancing confidence in detection even during prolonged UVC exposure. Consequently, this comprehensive analysis has expanded our scientific understanding and offers practical insights for industries using UVC-PET irradiated products.

#### CRedit authorship contribution statement

**C. Boronat:** Investigation, Writing - Original Draft and Writing - Review & Editing. **V. Correcher:** Investigation, Writing - Review & Editing and Supervision. **J. C. Bravo-Yagüe:** Investigation, Writing - Review & Editing and Supervision.

#### 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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