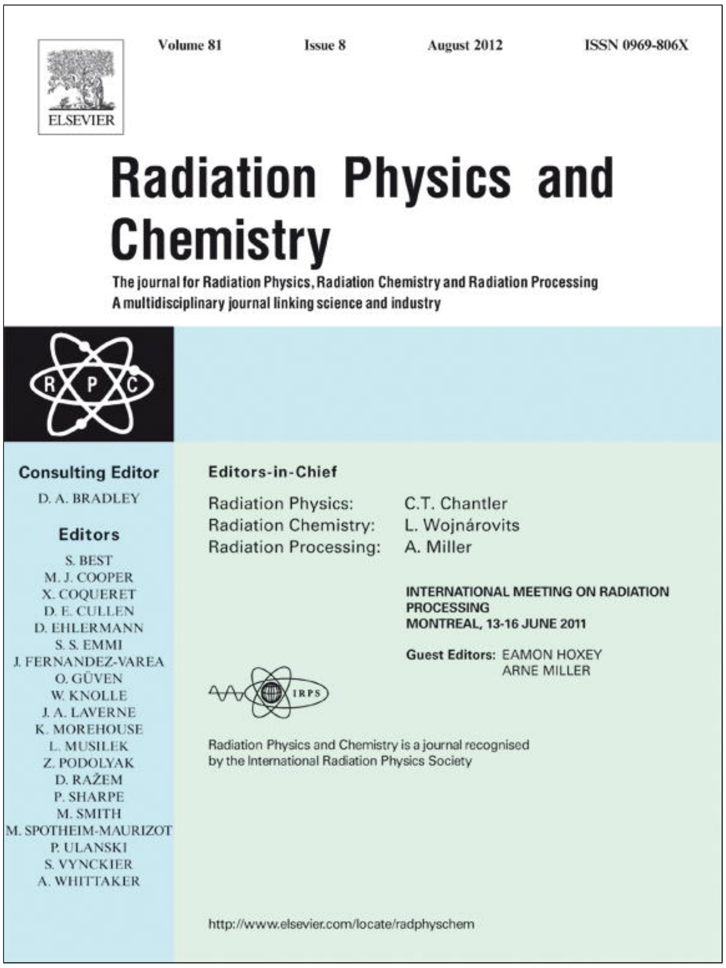

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Photo- and thermally stimulated luminescence of polyminerals extracted from herbs and spices

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ABSTRACT

Ionizing radiation processing is a widely employed method for preservative treatment of foodstuffs. Usually it is possible to detect irradiated herbs and spices by resorting to luminescence techniques, in particular photo- and thermostimulated luminescence. For these techniques to be useful, it is necessary to characterize the response to radiation of each particular herb or spice. In this work, the thermoluminescence (TL) and photostimulated luminescence (PSL) properties of inorganic polymineral fractions extracted from commercial herbs and spices previously irradiated for disinfestation purposes have been analyzed. Samples of mint, cinnamon, chamomile, paprika, black pepper, coriander and Jamaica flower were irradiated from 50 to 400 Gy by using a beta source. The X-ray diffraction (XRD) analysis has shown that the mineral fractions consist mainly of quartz and feldspars. The PSL and TL response as a function of the absorbed dose, and their fading at room temperature have been determined. The TL glow curves have been deconvolved in order to obtain characteristic kinetics parameters in each case. The results of this work show that PSL and TL are reliable techniques for detection and analysis of irradiated foodstuffs.

1. Introduction

Food irradiation is a well-accepted method to reduce foodborne diseases and to extend food shelf-life by inhibiting the growth of microorganisms [IAEA, 1991; WHO, 1999]. Irradiation processing for food preservation has been recognized by the Codex Alimentarius Commission as a safe technology [IAEA, 1991; WHO, 1999; FAO/WHO, 2002]. This technology has become a better alternative over other techniques like those using toxic chemical gases such as ethylene oxide, which are dangerous for humans and environment [UNEP, 1997]. Furthermore, it is well known that foodstuffs are quite often infested by insects or larvae that require less than 0.4 kGy dose treatment for phytosanitary control, and it seems in North American market (Canada, United States and Mexico) that foodborne illnesses are caused more frequently by domestic food products than those imported [Holley, 2011].

Several methods based on the detection of radiation-induced changes of the physical, chemical or microbiological food properties are widely used in order to classify foods as irradiated or not-irradiated [WHO, 1999; FAO/WHO, 2002]. The most reliable physical methods for detection purposes are photostimulated luminescence (PSL) and thermally stimulated luminescence, also dubbed thermoluminescence (TL) [EN 13751, 2002; EN 1788, 2001]. Luminescence emission occurs when crystalline components present in the inorganic fraction extracted from samples previously irradiated, i.e. quartz or feldspar, are either photo- or thermally stimulated. During irradiation free charge carriers are produced in the crystals, which may be trapped by localized states within the band gap. These charge can be remain trapped for certain period of time depending to the trap depth and the corresponding activation energy associated to the trapping levels. During optical or thermal stimulation, the trapped charges are released from the traps and radiatively recombine themselves emitting light as PSL or TL detectable signals. Currently, the PSL and TL methods are standardized for detection of irradiated herbs, spices, seafood, fruits and vegetables in the European Community [EN 13751, 2002; EN 1788, 2001]. However, more luminescent data information about the PSL and TL properties of mineral fractions extracted from spices and herbs are needed to improve the accuracy of the detection methods to control of irradiated food.

This work contributes to the study of the PSL and TL properties of inorganic polyminerals extracted from seven commercial herbs and spices previously irradiated for disinfestation purposes. Polymineral fraction of mint, cinnamon, chamomile, paprika,

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black pepper, coriander and Jamaica flower, were studied and the feasibility of using the PSL technique for irradiated food identification is discussed. In each case, the characteristic structure of the TL glow curve acts as a fingerprint of the minerals involved. For this reason the complex structure of the TL glow curves of the samples was deconvolved in single peaks by using a deconvolution method based on the general order kinetic model [May and Partridge, 1964]. In particular, the kinetics parameters such as the activation energy, the frequency factor and the kinetic order, were evaluated.

2. Experimental

A batch of seven dried herb and spices samples, namely, mint, cinnamon, chamomile, paprika, black pepper, coriander, and Jamaica flower, were purchased from commercial companies in Mexico. 30 g samples of each spice were selected and the inorganic polymineral powder was separated from the organic part by using a centrifugation procedure. In particular, each sample was mixed with ethanol-water (60-40 parts) solution in constant agitation and centrifugation, during 24 h and 2 h, respectively. To remove organic residual parts, the polymineral fraction was washed with H_2O_2 solution and bidistilled water. The polymineral powder was washed with 4 ml of 1 M chloride acid in order to dissolve salts like carbonates. Following the polyminerals samples were washed with bidistilled water again and dried with acetone. All samples were stored in darkness and at room temperature (RT) before and after irradiation. Sieves having 10, 53 and 149 μm nominal mesh were employed to separate each polymineral sample according to different grain sizes.

X-Ray Diffraction (XRD) of the polymineral fractions was carried out by using a Siemens D5000 diffractometer, equipped with a Cu-Ni filter. The XRD patterns of the samples were compared to the American Standard of Test Materials (ASTM) X-Ray Powder Diffraction data files. The mineral powder (4 mg) was mounted onto aluminum disks for beta irradiation. All samples were exposed to the ^{90}Sr/^{90}Y source of a Risø TL/OSL-DA-15 reader (5 Gy/min). TL and PSL readouts were carried out immediately after irradiation in a Risø TL/OSL-DA-15 reader. TL glow curves were recorded from RT to 470 °C with a linear heating rate of 2 °C/s. PSL readouts were performed by infrared (IR) stimulation at RT by using an IR laser (830 nm, 0.4 W/cm^2). Stimulated luminescence was measured in the 300–600 nm range by using a Schott BG-39 detection filter.

3. Results and discussion

Table 1 shows the mineral composition of the samples characterized by XRD. The analysis reveals the presence of quartz and feldspars at different concentration in the polymineral samples. It is worth mentioning that other authors have been reported different concentration of the mineral parts in similar foodstuffs samples, which seems to depend on their geographical origin [Sanderson et al., 1995; Alvarez et al., 1999; Cruz-Zaragoza et al., 2006; Gómez-Ros et al., 2006]. In Table 1 the grain size samples featuring the highest TL intensity have been only included. In what follows, only the samples listed in Table 1 have been employed in the TL and PSL experiments.

Table 1
Mineral composition of the analyzed samples.

Sample (*Scientific name*)	Grain size	Assigned mineral phase	Relative amount
Paprika (*Capsicum annuum L*)	53 μm	Quartz Albite Ortose	60% 30% 10%
Mint (*Mentha spicata*)	10 μm	Quartz Plagioclase Anphibole	50% 30% 20%
Chamomile (*Matricaria recutita*)	149 μm	Quartz Plagioclase Anphibole	40% 30% 30%
Jamaica Flowers (*Hibiscus sabdariffa L*)	10 μm	Quartz Plagioclase Illite	45% 35% 20%
Black Pepper (*Piper nigrum*)	149 μm	Quartz	Mainly
Cinnamon (*Cinnamomum L.*)	10 μm	Quartz	Mainly
Coriander (*Coriandrum sativum*)	149 μm	Quartz	Mainly

3.1. Thermoluminescence (TL)

Fig. 1 shows the TL glow curves of the polyminerals extracted from the different samples. All the samples were irradiated with the same doses, namely 50, 100, 200, and 400 Gy. In all cases, the luminescence of non irradiated samples, namely the background luminescence, is shown in dash. The glow curve of black pepper shows a single well-resolved TL glow peak with temperature maximum at 100 °C, followed by other peaks at about 150, 220 and 370 °C. These peaks could be related to quartz present in the mineral fraction [Guzmán et al., 2011; Stoneham and Stokes, 1991]. The quartz-related peak at 100–110 °C is also observable in the glow curves of mint and paprika, but having a lower relative intensity, which could be related to the presence of feldspar in the mineral composition of mint and paprika [Kitis, et al., 2005; Duller, 1997] (see Table 1). In these samples, the TL peaks at 220 and 150 °C present higher intensity than in the sample corresponding to black pepper. On the other hand, the glow curves of cinnamon, chamomile, coriander, and Jamaica flower show a broad TL band stretching from 50 to 350 °C with maxima at 100, 186, 190 and 146 °C, respectively. These bands seems to be composed of several overlapping peaks as expected from a complex trap distribution, which in turn depends on the kind of impurities the mineral fraction is made up of [Duller, 1997; Gómez-Ros et al., 2006]. As to the un-irradiated samples, their glows curves are quite different from those irradiates, which demonstrates the feasibility of using TL for detecting irradiated food from extracted polymineral samples.

It was observed, that the polymineral fraction from mint, paprika and black pepper samples exhibit a minimum of their first glow peaks at around 130 °C. Because the glow curves of irradiated foodstuffs normally exhibit a maximum between 150–250 °C, the European standard [EN1788, 2001] recommended this interval for analysis. In our case, a complex glow curves structure was observed for all polymineral samples, and then the analysis depends on the shapes of the glow curves and their relative TL sensitivities of the mineral components in the samples.

The TL response of the different samples has been characterized as the area under the glow curve between 130 °C to 450 °C. Lower temperature peaks of the glow curve has been excluded, since they show thermal fading (see Section 3.3). In Fig. 2(a) the calculated areas are shown as function of dose. A good linearity in the dose range analyzed (50–400 Gy) for all samples (adjusted $R^2 = 0.999$) is observed. The only exception is the black pepper polymineral that shows a sublinear response although no saturation effect is observed at the used doses. The integrated TL signals between 130 and 450 °C for these foodstuffs can be relevant in routine food control and may be useful for dose assessment of

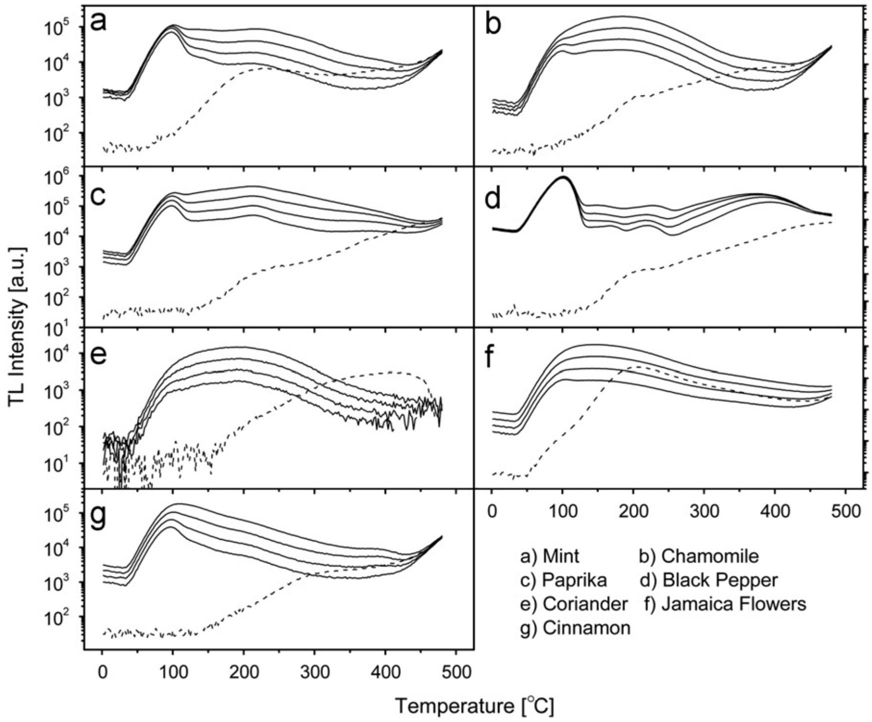

Fig. 1. TL glow curves of the polymineral samples irradiated with doses of 400, 200, 100 and 50 Gy, from top to bottom one after another. In all case, the luminescence of non irradiated samples is shown in dash line.

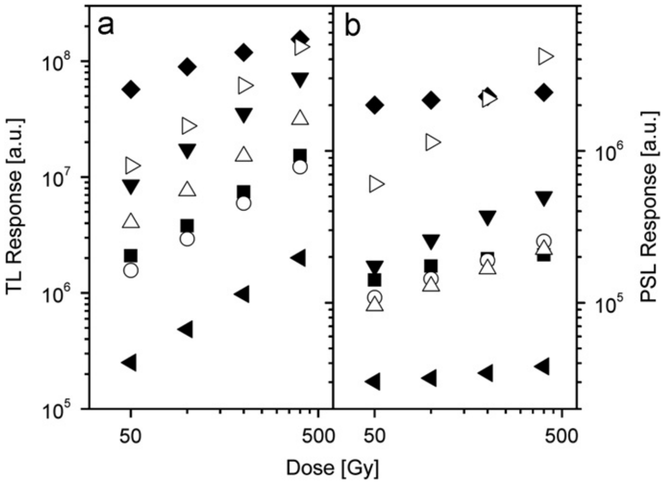

Fig. 2. TL (a) and PSL (b) response as a function of dose of black pepper (solid diamond), mint (solid square), cinnamon (open circle), chamomile (open up triangle), paprika (solid down triangle), coriander (solid left triangle) and Jamaica flowers (open right triangle).

commercial samples. The linear behavior of the dose-response is a good TL characteristic for dosimetric application in foodstuff disinfestation.

3.2. Photostimulated luminescence (PSL)

The PSL decay curves of the polymineral samples irradiated with a dose of 400 Gy are shown in Fig. 3. All the measurements were performed immediately after irradiation. The PSL response for Jamaica flowers and coriander exhibit a fast decay and the signal disappears after 20 s. On the other hand, the PSL curves of mint, cinnamon, chamomile and paprika can be fitted by two decaying exponential functions featuring a short decay component (10 s meanlife) and a very slow decay component characterized by meanlifes longer than 50 s. The PSL of black pepper exhibits a rather unusual behavior. In fact, a fast PSL decay is observed during the first seconds followed by a rise of the PSL signal, which reaches a maximum intensity at 50 s, when begins to decrease very slowly. No PSL of black pepper is observed if the first TL peak is bleached by annealing the sample at 100 °C before PSL readout. This result implies that the trap responsible for this TL peak is mainly involved in the described anomalous process.

Although quartz is the main component present in all the polymineral samples, large differences in the PSL response from the different samples has been observed. Similar behavior of the PSL response was reported by Kuhns et al. (2000) in a variety of quartz samples from different sources. Indeed, a universal behavior for quartz has not been obtained because its luminescence response depends of the impurities on the samples also [Duller, 1997; Alvarez, et al., 1999; Guzmán et al., 2011]. However, the shape of the PSL response, in particular of black pepper, is difficult to interpret, since it results from a complex pattern of defects interactions. Fig. 2 (b) shows the area under the PSL curve as a function of irradiation dose. In this case, only the Jamaica flowers have good linearity in the dose range analyzed. All of the other samples present a sublinear behavior but none reaches the saturation region.

3.3. TL and PSL fading

The TL and PSL fading recorded after storing irradiated samples during different time periods in darkness and at RT has been investigated. It has been found that the TL intensity of the polyminerals extracted from the different samples decreases after the first three days of storing between 30 and 60% with respect to the intensity measured immediately after irradiation. In general, it has been observed that these decreases appear in the low temperature peaks, as expected. In the case of black pepper, cinnamon and paprika, the first peak fully disappears but the peaks at higher temperatures remain unchanged. For the other samples, a decrease of the low temperature part of the broad glow band is observed. Then a superposition of several TL glow peaks present in these polyminerals is possible.

On the other hand, the PSL response, i.e., the area under the PSL curve of the mint, cinnamon, chamomile, paprika and Jamaica flower samples, present a decrease between 25 up to 50% of the original value, after three days of storing. In the case of black

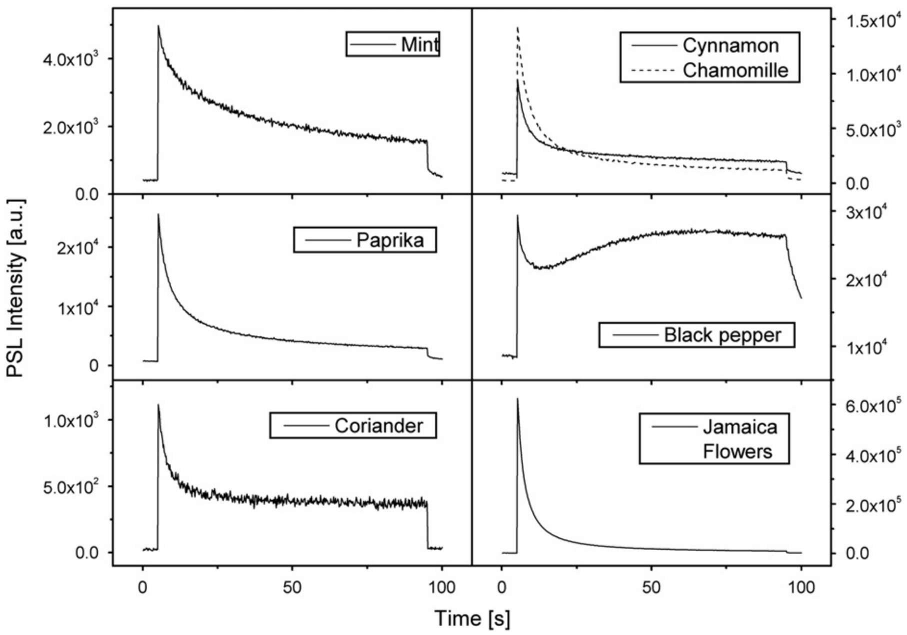

Fig. 3. PSL response of the samples irradiated to 400 Gy.

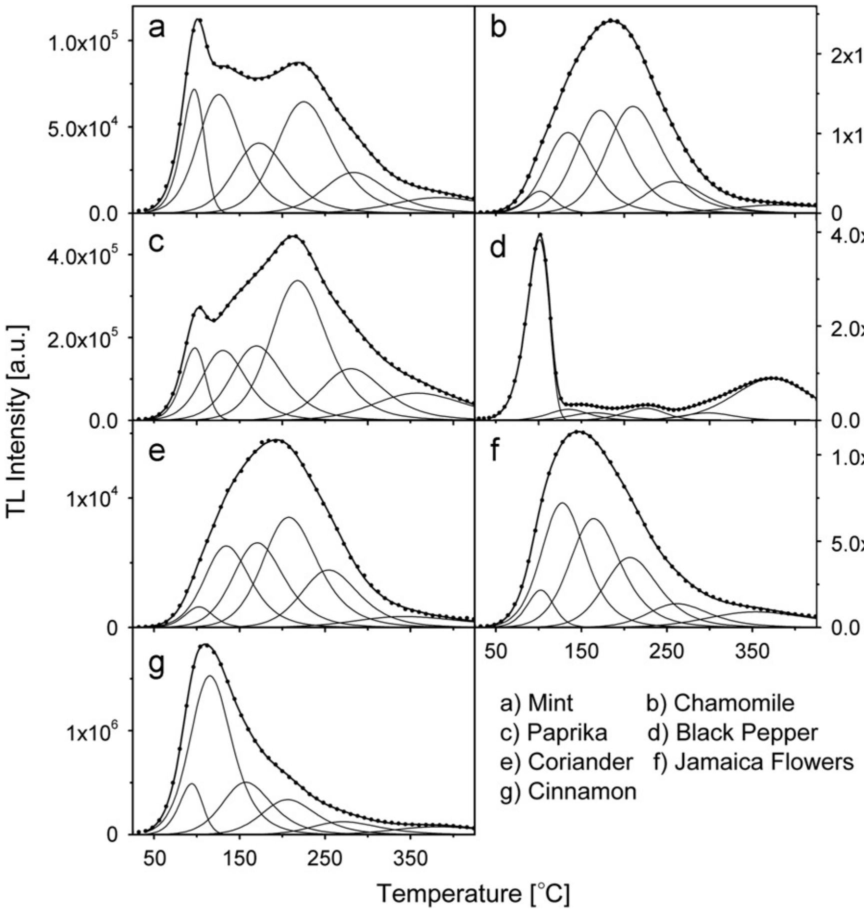

Fig. 4. Experimental (black points) and deconvolved (black line) glow curves for the inorganic fraction extracted from studied spices.

pepper, the PSL intensity goes to zero at the same time the first TL glow peak fully disappears. As, previously noted, it is seems that the traps responsible for the low temperature TL glow peak in the black pepper are the same involved in the PSL signal. It is well known that the 110 °C glow peak is related to quartz and it is sensible to thermal fading. There is also evidence that some correlation between optically stimulated luminescence sensitivity change and TL peak sensitivity change also exist, i.e., in both luminescence processes the same recombination center is involved [Stoneham and Stokes, 1991]. Finally, the PSL intensity from coriander decreases up to 20% when measured three days after storing with respect to the original signal. Then it shows a constant PSL response, no matter storing time.

3.4. Deconvolution analysis

The complex structure of the TL glow curves from all polymineral samples has been deconvolved by assuming the general order kinetics (GOK) model [May and Partridge, 1964]. Goodness of fit was evaluated by means of the figure of merit (*FOM*) [Horowitz and Yossian, 1995]. The kinetics parameters have been obtained for all samples irradiated with 400 Gy. After fitting activation energies (E) values ranging from 0.73 up to 1.02 eV have been obtained with *FOM* values lower than 1.1%, indicating a good fit of the experimental glow curves. Order kinetics (b) values between 1.1 and 2.2 have been obtained and frequency factors from 2.5×10^{8} to $2\times10^{13}\,\mathrm{s}^{-1}$, which are acceptable values according to the usually assumed frequency factors expected in solid matter [Chen and Kirsh (1981)]. Fig. 4 shows the experimental and deconvolved glow curves for the different samples. According to the fitting procedure the glow curves have kinetics parameter values, which fairly similar among the different curves. A good agreement is observed respect to results previously obtained [Gómez-Ros et al., 2006; Cruz-Zaragoza et al., 2006; Guzmán et al., 2011] for similar samples.

4. Conclusions

In this work the PSL and TL response of polymineral fractions extracted from several herbs and spices have been studied from the point of view of its application to irradiation detection of irradiated food. The PSL and TL–dose response show a good linearity within the dose range analyzed (50–400 Gy). In general, the TL glow curves of the studied foodstuffs show a single broad band composed of several overlapping peaks, which extends from 50 to 400 °C. The different glow curves have been successfully deconvolved by six glow peaks in all polyminerals samples and the activation energy were calculated assuming the general order kinetics model (0.73–1.02 eV). The first TL peak (96–102 °C) is clearly involved in PSL and TL fading decay in all the samples. However, the glow peaks at higher temperatures (130–450 °C) are stable at room temperature and permit in principle to use TL and PSL techniques for irradiated foodstuff detection that can be relevant in routine food control and useful for dose assessment of commercial samples. In black pepper, the PSL intensity goes to zero at the same time that the first TL glow peak fully disappears. It is seems that the traps responsible for the low temperature TL glow peak are the same involved in the PSL of black pepper, but not in the case of the other samples. Summarizing, this work demonstrates the feasibility of using TL and PSL as a tool for dose assessment of this kind of irradiated herbs a spices, which are of interest for the Mexican food market.

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