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Luminescence detection and dose assessment of irradiated Yerba Mate (*Ilex paraguariensis*) tea leaves

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HIGHLIGHTS

- Samples of Yerba Mate tea leaves from Argentina were studied by TL and PSL methods.
- The polyminerals showed a good sensitivity to gamma radiation and UV light (530 nm).
- The Yerba Mate was detected as irradiated at a dose of 400 Gy using PSL.
- The TL and PSL responses can be used for dose control in commercial Yerba Mate.

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ABSTRACT

Imported commercial samples of Yerba Mate (*Ilex paraguariensis*) tea leaves were characterized by thermoluminescence (TL) and photoluminescence (PSL) physical methods. Samples of Yerba Mate were irradiated between 0.5–50 Gy and 20 Gy–5 kGy gamma doses by using two different dose rates from ^{60}Co irradiators. The Electron Dispersive Analysis (EDS) shows that the inorganic fraction is mainly composed by quartz and Ca-feldspars minerals. These polyminerals show a good sensitivity to gamma radiation and to UV light (530 nm). Linear dose–response curves were obtained between 0.5 and 12 Gy at low dose-rate, and with 20 to 500 Gy at high dose-rate of gamma radiation. At higher doses (600 Gy) an apparent slow saturation effect was observed. Low fading of the TL signal was found. The detection limits of TL and PSL are 6 Gy and 300 Gy, respectively. Results show that luminescence emission (TL and PSL) is a reliable method for detection of irradiation Yerba Mate.

1. Introduction

The preservation and sterilization of commercial foods using ionizing radiation are used in many countries as an alternative over the other known methods such as refrigeration, freezing and heat or chemical treatments (Farkas, 1998). Different foods like fruit, vegetables, spices and herbs are commonly exposed to varying doses of ionizing radiation (Cruz-Zaragoza et al., 2012; Marcazzó et al., 2012). With health protection purposes of the consumer the Codex Alimentarius Commission (FAO/WHO food standards; FAO/WHO, 2002) was implemented. There are diverse standardized techniques for the detection of the irradiated foods which include biological, physical and chemical means (Chauhan et al., 2009; Delincée, 1998; EN 13708, 2002; EN 13751, 2009; EN 1788, 2001). The physical techniques such as thermoluminescence (TL) and photoluminescence (PSL) present favorable characteristics to be used in the detection of irradiated foods. The TL phenomenon is the thermally stimulated light emission from a mineral (insulator or semiconductor) previously irradiated (Furetta, 2003). When a mineral is irradiated the ionizing radiation produce free electron–hole pairs that then can be trapped in metastable energy levels in the forbidden band. After irradiation, the electron–hole pairs trapped in the metastable energy levels are released by the heating of the mineral and the light emission is observed from the recombination of the released the electron–hole pairs. On the other hand, the photoluminescence (PSL) phenomenon is the emission of light by a mineral under photoluminescence stimulation by using infrared radiation. The PSL technique provides a fast discrimination of the irradiated and non-irradiated foods. Furthermore it allows readouts of organic and inorganic samples that contain minerals. Recently investigations were mainly focused in the identification and detection of

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the irradiated and non-irradiated foodstuffs in the market. About 10% of the commercial examined products, by using TL and PSL methods, have been identified as irradiated products and they were not correctly labeled (Ahn et al., 2013; Bortolin et al., 2009; Kim et al., 2014; Pal et al., 2010; Boniglia et al., 2009). Then it is important to identify the irradiated foodstuffs. In this paper, we report the luminescence response (TL and PSL) and dose assessment of gamma irradiated Yerba Mate (*Ilex paraguariensis*) tea leaves.

2. Materials and methods

Commercial imported samples of Yerba Mate (*Ilex paraguariensis*) tea leaves from Argentina were acquired in the market of Mexico City. To separate the polymineral fraction of the Yerba Mate the following steps were performed. A quantity of 30 g of Yerba Mate into a pure water–ethanol (500 mL) solution was kept in constant agitation during 24 h to separate the inorganic fraction. The polyminerals were separated from the organic matter by means several washing with hydrogen peroxide. Next the polyminerals were washed with hydrochloric acid to eliminate the residual organic matter. The polyminerals were dried with acetone at room temperature. The dried samples were sieved to obtain ≤ 74 μm grains sizes for TL measurements.

The morphology and chemical composition of the polymineral samples were observed in a JEOL scanning electron microscope (SEM) model JSM-5410LV with an EDS (Si–Li:Na) detector. The polyminerals were irradiated using ^{60}Co gamma rays with high (90 Gy/min) and low (0.22 Gy/min) dose rates. The low dose rate was obtained from Gammacell-200 irradiator. A Gammabeam 651PT semi-industrial irradiator was used to irradiate the samples in order to obtain high gamma doses. The samples were irradiated from 0.5 up to 50 Gy using low dose rate, and between 20 Gy to 5 kGy with high dose rate. The polymineral samples were stored in darkness at RT. The TL measurements were performed by using a Harshaw TLD reader model 3500. The TL glow curves were obtained from RT to 400 °C with 2 °C/s heating rate. To eliminate the spurious TL signals of the glow curves the measurements were taken under nitrogen atmosphere. Pulsed Photostimulated Luminescence (PSL) response of the non-irradiated and irradiated Yerba Mate (1–500 Gy) samples was carried out using a SURRC PSL Irradiated Food Screening System. The PSL system is comprised of control unit, sample chamber, detector assembly and an array of infrared diodes to excite the whole (inorganic and organic parts) sample. Whole samples of 5.65 g of Yerba Mate were used for each PSL measurement. The PSL response was recorded in the measuring mode (photon counts per second, pcs) at the rate of counts/60 s. The samples of Yerba Mate were classified in irradiated, intermediate and non-irradiated depending of the total PSL response. Samples with total PSL response below to 700 pcs were classified as non-irradiated, and samples with total PSL response over to 5000 pcs were classified as irradiated according to the calibration of the PSL system. Finally, samples with PSL response between 700 and 5000 pcs were separated as intermediate, requiring other type of analysis to classify that response. All the TL and PSL measurements were carry out under the same experimental conditions using two aliquots of polyminerals and whole Yerba Mate, respectively. The results were reported as the average of the data response of the two aliquots.

3. Results and discussion

3.1. TL response

The polymineral fraction of Yerba Mate tea leaves was characterized using Scanning Electron Microscopy (SEM). The SEM micrography shows a non-uniform agglomeration of quartz and Ca-feldspars parts. The chemical composition was identified by using an EDS probe and also Cl, K and Fe ions where found.

Samples of Yerba Mate (*Ilex paraguariensis*) were analyzed by TL and PSL methods to obtain its luminescent properties. The TL glow curve of the polyminerals irradiated with gamma rays of ^{60}Co (20 Gy) showed the formation of two glow peaks located at approximately 91 °C and 200 °C (Fig. 1). The change in the TL intensity and an apparent shift of the maximum glow peak (91 °C) were observed at different dose rates. This behavior could be related to the traps filling and detrapping mechanisms competing along with the recombination processes, and these may depend on the electron–hole rate produced by the different gamma dose rates. The physical nature of the different height of the TL peaks is not yet well understood. However, the TL intensity of this polyminerals samples is dependent of the dose rate used. The structure of the TL glow curves were caused by the presence of quartz and feldspar in the polyminerals. The TL peak at 91 °C is related to the presence of quartz (Kitis et al., 2005) and the broad peak at 200 °C could be assigned to feldspar or quartz (Correcher et al., 1998). When the polyminerals were irradiated with UV light (60 min at 530 nm) the TL glow curve displays a slight shift of the higher peak towards higher temperatures (127 °C). This TL response could be caused by the activation of different traps in the quartz as a consequent of the irradiation with UV light at 530 nm (Fig. 1).

Fig. 2 shows the dose–response of the polyminerals obtained between 0.5 and 50 Gy (Fig. 2a) at a low dose rate (0.22 Gy/min), and with 20 Gy to 5 kGy (Fig. 2b) at high dose-rate (90 Gy/min). The dose–response at low dose rate presented a linear range between 0.5 and 12 Gy, with a linear fit of $r^2=0.98$ (inset in Fig. 2a). The effect of saturation of the dose–response, at low dose rate, was observed after 12 Gy. In the range from 0.5 up to 500 Gy a linear response behavior was measured for the samples irradiated at high dose range (Fig. 2b). The linear behavior shows a good linear fit with $r^2=0.99$ (inset in Fig. 2b). The polyminerals irradiated with high dose rate presented an apparent slow saturation effect at 600 Gy (Fig. 2b). The reproducibility of the polymineral samples was observed after nine successive cycles of irradiation-readout. The TL glow curves were recorded immediately after the

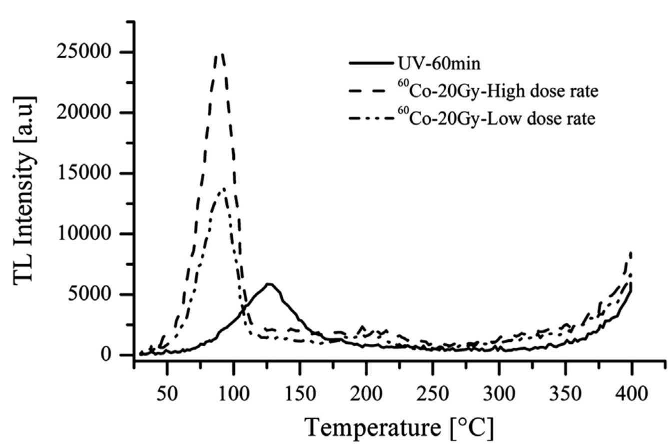

Fig. 1. TL glow curves of polyminerals irradiated with ^{60}Co gamma rays and green UV radiation. All curves were obtained at a heating rate of 2 °C/s. Different TL intensity of the glow curves were observed with low (0.22 Gy/min) and high (90 Gy/min) dose rates. A broad glow curve was obtained with UV radiation.

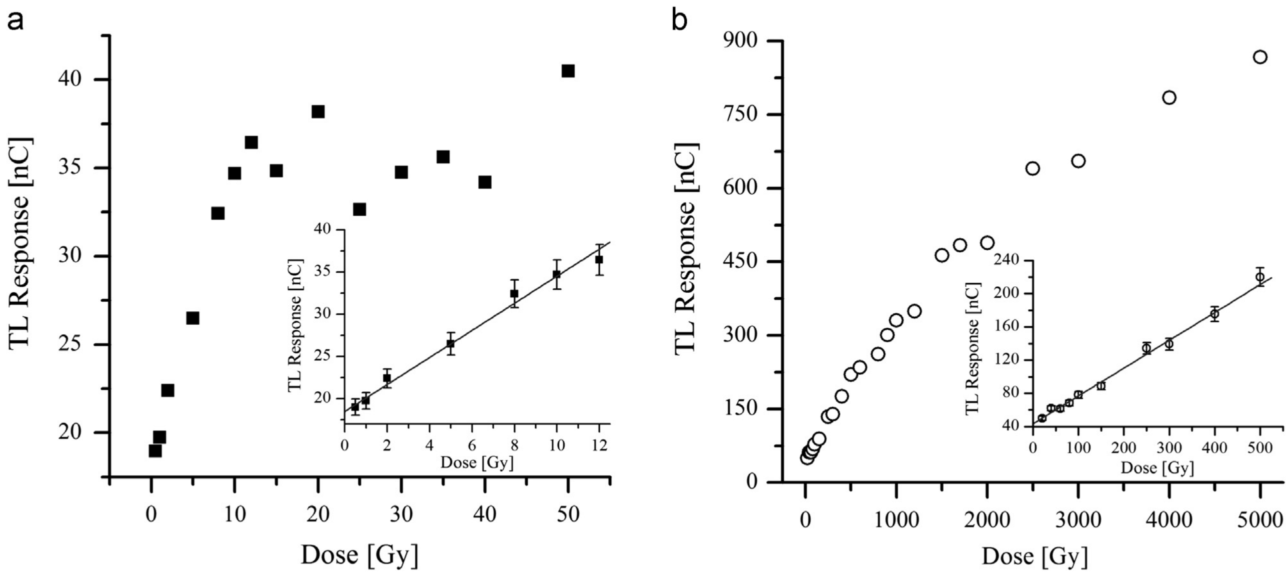

Fig. 2. TL response as a function of the dose of the polyminerals irradiated at (a) low dose rate (0.22 Gy/min), and (b) high dose rate (90 Gy/min). The inset shows the linear dose range, and each data point shown is the mean of two integrated-TL aliquots and the error bars of 5% of each point of the TL response.

irradiation with 50 Gy gamma dose. The polyminerals show a good reproducibility of TL signals at about 4% of the standard deviation.

The fading effect of the TL response was observed from 0 up to 60 days after the irradiation of the samples. The polyminerals samples were irradiated at 20 and 50 Gy doses by using low and high dose rates, respectively. The irradiated polyminerals were stored in darkness at room temperature. Fig. 3 shows the fading effect of the TL response of the polyminerals as function of stored time. The TL response presented a strong fading during the first storage hours. The TL intensity decreased about 37% and 32% for a low and high dose rates, respectively (inset in Fig. 3). These drops in the TL intensity were caused by the decrease of the most intense peak located at 91 °C, which could be related with the characteristic peak of quartz at a temperature of 110 °C and is well known that this peak displays a strong thermal fading at room temperature (Monaca et al., 2013). Also, the peak presented a slight shift towards higher values of the temperature when the stored time increases. This behavior could be associated with the electron transfer from their shallowest traps to the conduction band and followed the charge pair recombination in the gap at room temperature during the storage time of the polimineral sample. There is an important reduction of TL intensity (about 60% for both dose rates) two days after irradiation of the polyminerals. The total TL intensity of the first peak (91 °C) in the polyminerals disappears after 1 day of storage time. The TL response shows a slow fading about a factor of two during the storage time of up to 60 days (inset in Fig. 3).

3.2. PSL characteristics

Fig. 4 shows the PSL measurements of the Yerba Mate irradiated in laboratory between 1 and 500 Gy gamma dose range. The samples were discriminated from two thresholds (horizontals lines in Fig. 4) as irradiated, intermediate and non-irradiated samples. The PSL response of five non-irradiated samples was used as the PSL background. All samples were selected from the same brand of Yerba Mate. Samples irradiated at 1, 10 and 50 Gy were classified as non-irradiated due to the fact that the PSL values were less than the lower threshold (700 pcs) value. Intermediate samples with PSL values of 2062, 2789 and 2852 pcs were irradiated at

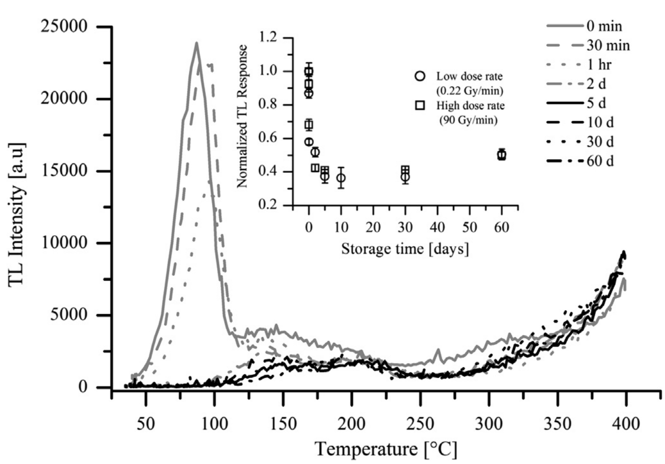

Fig. 3. Effect of the fading on the TL glow curves of the polyminerals. The first glow peak disappears after 1 day of storage time. The inset displays the integrated TL response as a function of the storage period and the error bars represent the mean of the standard deviation ($n=2$).

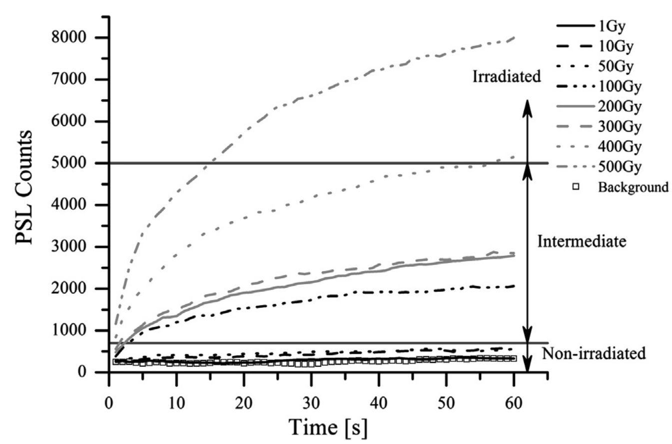

Fig. 4. PSL measurements of the Yerba Mate irradiated from 1 up to 500 Gy gamma doses. The horizontals lines represent the thresholds values. Only samples previously irradiated between 400 and 500 Gy were discriminated as irradiated samples. Five samples from the same brand of Yerba Mate as they were acquired in the market were measured, and their PSL response considered as background was similar to the samples irradiated with 1 Gy. Each PSL curve is the average of two whole samples measured.

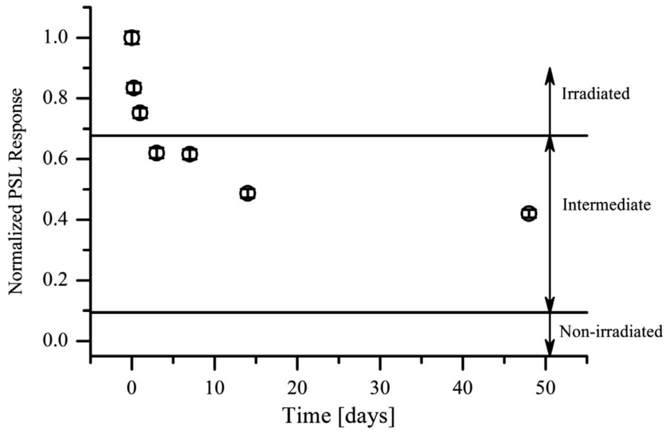

Fig. 5. Normalized PSL responses of the Yerba Mate as a function of the storage time, re-normalized to unity at the first point. After one day of storage at RT is possible to identify between irradiated and non-irradiated samples. The error bars represent the normalized error provided by the PSL equipment.

100, 200 and 300 Gy, respectively. In this case, the PSL values were not enough to identify the irradiated samples. On the other hand, the samples of the Yerba Mate irradiated with a doses of 400 and 500 Gy were discriminated as irradiated samples, which presented PSL values (5149 and 7998 pcs) above the upper threshold (5000 pcs). These doses (400–500 Gy) are useful to detect insect disinfestation of foodstuffs.

The PSL measurements up to 48 days after irradiation of the Yerba Mate are displayed in Fig. 5. The PSL response and thresholds values are normalized to the value of the sample measurement immediately after irradiation. The irradiated samples (400 Gy) were stored at room temperature in the darkness. After a day the irradiated samples were classified as irradiated with a decrease in the pcs intensity of 25%. Therefore, after 1 day of storage it is possible to identify between irradiated and non-irradiated samples by PSL measurements. The PSL responses of the Yerba Mate were discriminated as intermediate in the range of 3 to 48 days. Anomalous fading tests should be performed on feldspars extracted from Yerba Mate, in order to ensure the applicability of the PSL method, since this effect frequently appears with feldspar samples.

4. Conclusions

The polyminerals separated from commercial dry Yerba Mate tea leaves show a well solved TL glow curve at different dose rates of gamma radiation. The TL glow curve presented two peaks at 91 °C and 200 °C that are related with the presence of quartz and Ca-feldspar. The polyminerals showed a linear dose–response from 0.5 up to 12 Gy and 20 up to 500 Gy at low and high dose rates of gamma radiation, respectively. The poly-mineral fraction shows a good TL response to 530 nm UV light. Since feldspars are more sensitive to radiation, it is possible that the major part of the TL response in Yerba Mate comes from feldspars. The fading effect showed a strong decrease of TL intensity after the first storage hours and a quite slow decrease in the range of 2 to 60 days. The Yerba Mate was classified as irradiated sample at a dose of 400 and 500 Gy by using PSL method. After one day of storage at RT it was possible to distinguish between irradiated and non-irradiated samples by PSL technique. The PSL is an effective method to classify the irradiated Yerba Mate samples due to enough polymineral concentration in the samples and also provides a prompt answer. The poly-mineral fraction exhibits enough sensitivity to radiation inducing high TL and PSL signals that can be used for identification purposes for dose control in the commercial irradiation of Yerba Mate tea leaves for preservation purposes.

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