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Thermoluminescence study of polyminerals extracted from clove and marjoram for detection purposes

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ABSTRACT

Food irradiation is a widely employed technology for food treatment. Since in several countries no regulations prevail, it is difficult to detect whether food has been irradiated or not. Among different analytical methods the study of the thermoluminescent (TL) emission of polymineral extracted from food is one of the most useful physical identification method. The aim of this work is to analyze the TL properties of inorganic polyminerals extracted from commercial clove (*Syzygium aromaticum L.*) and marjoram (*Origanum majorana L.*) spices exposed to ^{60}Co gamma radiation for detection purposes. The feasibility of using the TL method for irradiated food detection and absorbed dose determination is assessed.

1. Introduction

Food irradiation is being increasingly used worldwide as an effective treatment for eliminating pathogen microorganisms and pests. It is also useful in order to extend the shelf-life of foodstuffs. The exposition of food to ionizing irradiation has been recognized by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) as a safe and effective technology (IAEA, 1991, 2000a, 2000b; WHO, 1999; FAO/WHO, 2002). Besides, it is a good alternative to chemical gases containing ethylene oxide and methyl bromide, which are dangerous for health and environment (UNEP, 1997).

Spices, dry vegetables, fruits and grains are normally exposed to different gamma doses for sterilization and preservation (FAO/WHO, 2002; Sanderson et al., 1995; Farkas, 1998; Raffi et al., 2000; IFST, 2006; Hirneisen et al., 2010). In order to discriminate between irradiated and non-irradiated food, several physical, chemical and biological methods are frequently used (Calderón et al., 1995; Farkas, 1998; Chung et al., 2002; Cruz-Zaragoza et al., 2010). Among of them, the thermoluminescence (TL) method is an acceptable method due to its high precision (EN 1788, 2001, Calderón et al., 1995; Chung et al., 2002). However, the TL response and the glow curve shape of the samples depend strongly on the mineral composition of each foodstuff (Pinnioja and Pajo, 1995; Engin, 2007; Gómez-Ros et al., 2006; Favalli et al., 2006; Furetta and Cruz-Zaragoza, 2007; Cruz-Zaragoza et al., 2010). For this reason, it is important to analyze the TL characteristics of the glow curves for identification purposes in each case.

This work focuses on the TL properties of the polyminerals extracted from irradiated clove and marjoram in order to discriminate in each case between irradiated and non-irradiated samples, to determine both the minimal detectable dose and the irradiation dose. Finally, the kinetics parameters such as the activation energies and the frequency factors from glow curves were obtained by assuming the general order kinetics (GOK) model (May and Partridge, 1964; Rasheedy, 1993) in order to characterize each glow curve for identification purposes.

2. Experimental

Samples of clove (*Syzygium aromaticum L.*) and marjoram (*Origanum majorana L.*) were obtained from an imported commercial batch purchased in the market of Mexico City. The polymineral fraction was extracted from the whole samples by agitation in a stirring plate at room temperature (RT). 25 g of the sample was put into a 1 L of double-distilled water and kept in constant agitation during 48 h in order to separate the inorganic fraction. Following agitation the organic part was decanted and the sediment was washed with hydrogen peroxide in order to eliminate the organic residual matter attached to the minerals.

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Again the sediment sample was washed by using hydrochloric acid to eliminate carbonate fraction. Finally, the polymineral fraction was dried with acetone at RT. The polymineral powder was sieved to obtain samples of grain size of 53 μm and 149 μm. About 4 mg of powder sample of each grain size were deposited onto a batch of aluminum disks. Then, an acetone drop was poured into each disk for obtaining a homogeneous grain deposition. Several samples for both clove and marjoram were prepared with this procedure for the irradiation and TL measurements.

The irradiations were performed by using a ^{60}Co Gammacell-200 irradiator rendering a dose rate of 0.5 Gy/min at the sample position. All samples were kept in darkness and at RT before and after irradiation. The samples were exposed from 5 to 400 Gy of ionizing gamma radiation. The TL glow curves were recorded by using a Harshaw TL reader model 3500 with a linear heating rate of 2 °C/sec. The measurements were performed under a continuous nitrogen flux to reduce spurious TL signals. The TL signal was integrated from RT to 400 °C. The ultraviolet (UV) bleaching of the TL signals was performed by using an Hg lamp source model OS-9286 from Pasco Scientific Company which provides a light beam irradiance of 0.1 μW/cm^2.

The mineral composition of the samples was determined by X-Ray Diffraction (XRD) with a Rigaku Geigerflex D-MAX/A Diffractometer. The micrographs were obtained with a Jeol model JSM-5410LV scanning electron microscope (SEM) featuring an EDS (Si–Li:Na) detector. The energy-dispersive spectra (EDS) were readout for different regions of each sample and particle size in order to determine the elements present in the polymineral sample.

3. Results and discussion

Two different particle sizes were selected from the inorganic fraction extracted from clove and marjoram spices, namely 53 μm and 149 μm. Fig. 1 shows the XRD patterns of the investigated samples. The inorganic fraction extracted from clove is mainly composed of quartz (SiO_2). On the other hand, the XRD pattern of the polyminerals extracted from marjoram confirms that quartz and feldspars are present in the polymineral fraction of this spice. More than 40 different regions on the surface of each sample and particle size were taken into account for EDS analysis. Table 1 shows the mineral fraction analysis by EDS. A good agreement with the XRD data was obtained. EDS shows that only O, Si and C elements are present in the polyminerals extracted from clove. This result agrees with the corresponding XRD pattern, where it was observed that clove is made of SiO_2 mainly. On the other hand, EDS analysis reveals that Na, Mg, Al, K, Ca, Fe and Ti elements are present in the inorganic fraction extracted from marjoram. These elements are generally present in feldspars. Figs. 2(a) and (b) shows the EDS of polyminerals extracted from clove and marjoram, respectively. The SEM micrographs of the mineral fraction extracted from clove and marjoram are shown in Figs. 2(c) and (d), respectively.

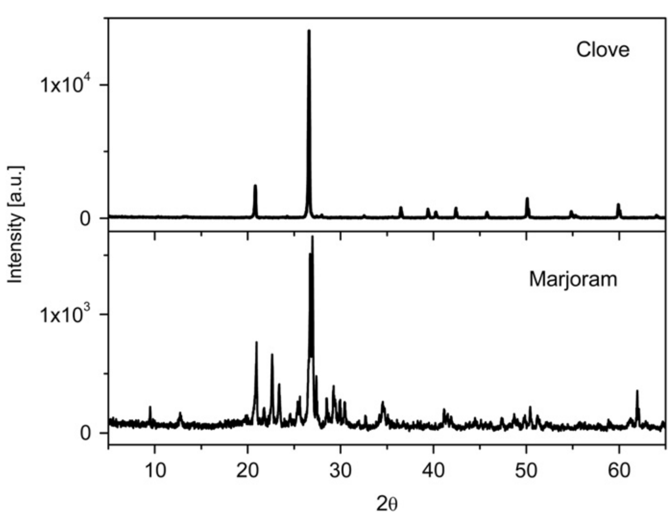

Fig. 1. XRD spectra of polyminerals extracted from clove and marjoram.

Fig. 3 shows the TL glow curves of the polyminerals irradiated at different gamma doses. The TL intensity is slightly higher for the 149 μm grain size marjoram and slightly lower for the same grain size for the polyminerals extracted from clove. All the glow curves present a TL glow peak at 82 °C, which is a typical TL peak of quartz (Ogundare et al., 2006; Toktamis et al., 2007), along with others peaks at about 110, 130, 180, 250 and 350 °C. These peaks may also be related to quartz present in the mineral fraction. However, the relative TL intensity of the peaks could be affected by the feldspar fraction present in the samples. Although it could be difficult to explain how quartz and feldspars containing different elements affect the TL glow curve of the inorganic fractions, it seems that the complexity of the glow curves may be ascribed to the kind of elements present in the foodstuffs (Correcher et al., 2004; Favalli et al., 2006; Furetta and Cruz-Zaragoza, 2007; Guzmán et al., 2011).

The TL response as a function of dose is shown in Fig. 4. A good linearity (R^2=0.99 for marjoram and R^2=0.98 for clove) has been obtained for each grain size, i.e., no saturation effect is observed from 5 to 400 Gy. It is common that for sterilization process the irradiation doses range from 1 kGy up to 40 kGy depending to the desired effect in the food. On the other hand, commercial herbs and spices are irradiated below 0.5 kGy for disinfestations and preservation purposes in order to eliminate parasites and insects mainly. In this work the samples were irradiated with doses from 5 to 400 Gy in order to assess the feasibility of using the TL technique for identification of irradiated food and develop a method for dose reconstruction for low doses. More investigations would be necessary to fully validate the method at higher doses.

The reproducibility of the signal after successive irradiation-readout cycles was also analyzed in order to choice the correct procedure to be followed for the dose reconstruction. In this study, a percentage standard deviation (PSD) of only 0.7% and 1.4% has been observed for the marjoram of 53 μm and 149 μm particle sizes, respectively. On the other hand, a PSD of 7% and 4% has been observed for the clove of 53 μm and 149 μm particle

Table 1
Mineral fraction analysis by EDS for polyminerals samples and particle sizes of 53 and 149 μm.

Sample	O	Si	C	Na	Mg	Al	K	Ca	Fe	Ti	Total (%)
Clove 53 μm	47.4	29.1	23.5								100
149 μm	49.2	32.3	18.5								100
Marjoram 53 μm	46.8	17.9	20.9	1.4	1.2	5.3	0.9	2.4	2.8	0.4	100
149 μm	47.6	21.4	13.5	2.4	1.2	7.4	1.1	2.9	2.5		100

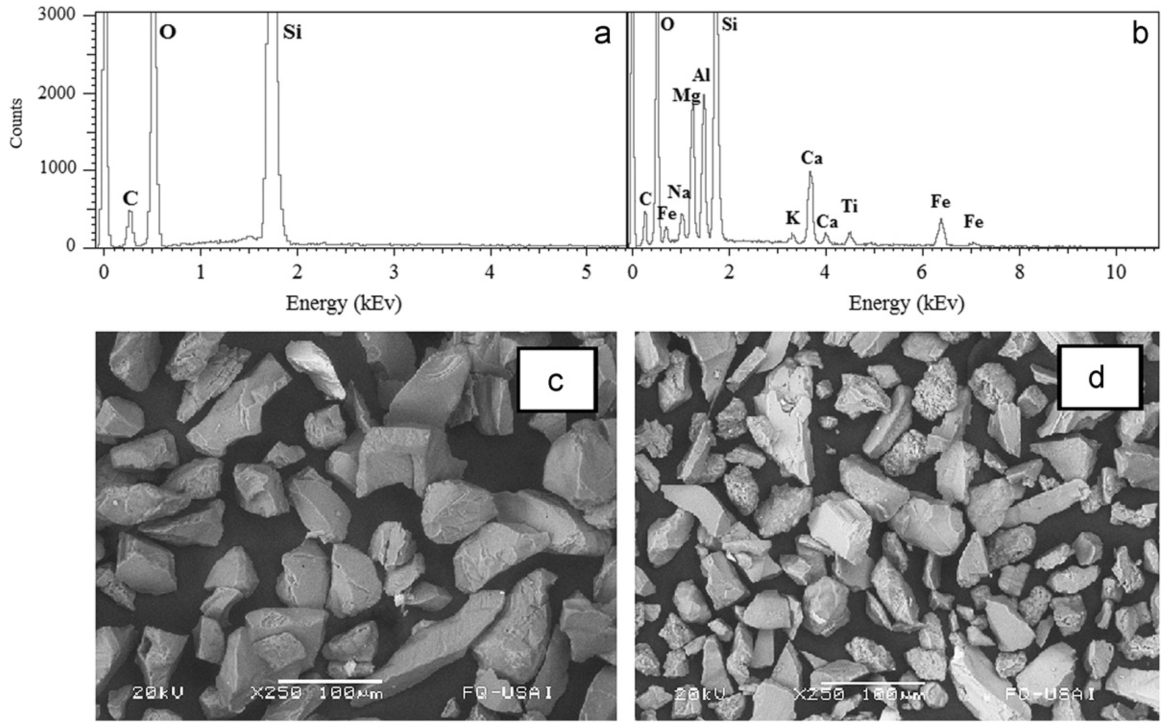

Fig. 2. On the top, EDS analysis of the minerals extracted from (a) clove and (b) marjoram, respectively. On the bottom, SEM micrographs of the mineral fraction extracted from (c) clove and (d) marjoram, respectively. The EDS and SEM micrographs are shown for 53 µm particle sizes.

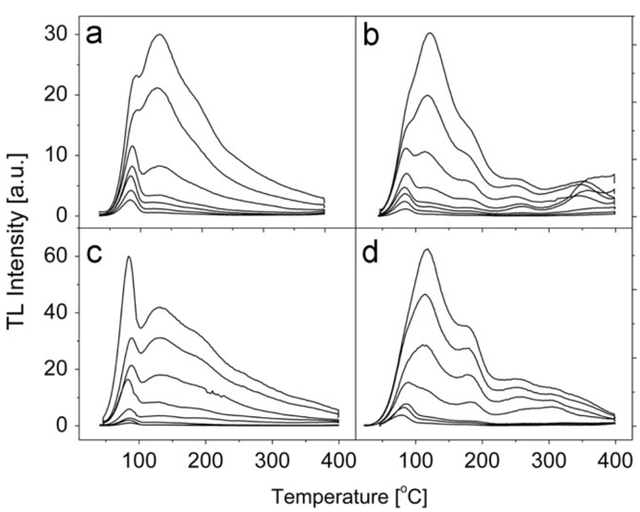

Fig. 3. TL glow curves of the polyminerals expose to 400, 300, 200, 100, 50, 30, 20 and 10 Gy, from top to bottom one after another for (a) marjoram 53 µm, (b) clove 53 µm, (c) marjoram 149 µm and (d) clove 149 µm.

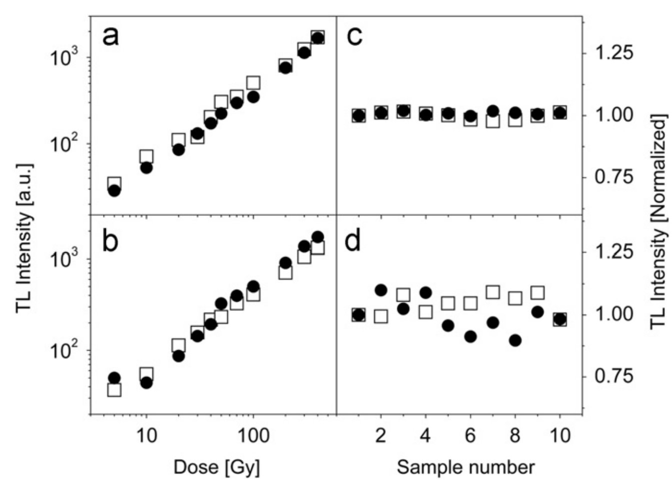

Fig. 4. Left: TL response as a function of dose of (a) marjoram and (b) clove. Right: Reproducibility of the TL response of (c) marjoram and (d) clove, respectively. In (c) and (d), samples irradiated at 20 Gy were normalized to the first value. The open square is for 149 µm and the solid circles for 53 µm particle sizes. Error bars are smaller than the symbol size.

sizes, respectively (Fig. 4(d)). This is a good result for dose estimation because the very good reproducibility of the signal after successive irradiation-readout cycles does not affect the obtained dose values. In other works, PSD of about 40% and 60% are reported (D'Oca et al., 2010). Furthermore, it seems that the presence of small concentration of the ions elements in the feldspars can improves the linearity and reproducibility of the TL signal, although more investigations are necessary to confirm the last assertion.

Fig. 5 shows the TL fading of the polyminerals extracted from marjoram (a) and clove (b), respectively. Samples were irradiated with a dose of 20 Gy and stored at RT in darkness. The TL response, defined as the total area under the glow curve, decreases up to approximately 20% and 25% of the original value in the case of marjoram and clove, respectively, after the first two months of storage. The low temperature peaks are the most affected by fading, since they likely correspond to shallow traps present in the material. On the other hand, the intensity of the high temperature peaks decreases very slowly as a function of storage time. If only the area under the high temperature peaks is considered, i.e., if the glow curve is integrated from 230 °C up to 400 °C, the TL response of marjoram and clove reduces up to 50% and 70% of the original values after two months of storage (Fig. 6). In all cases and regardless of the storage time it is possible to distinguish between irradiated and not irradiated samples (EN 1788, 2001). Besides a very acceptable estimation of the irradiated dose with a PSD < 30% can be obtained (D'Oca et al., 2010).

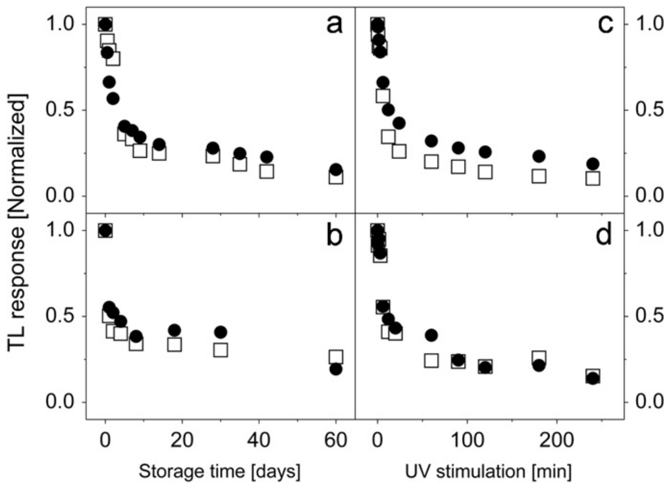

Fig. 5. Left: Behavior of the total area under the TL glow curve as a function of storage time at RT and in darkness of (a) marjoram and (b) clove. Right: Behavior of the TL glow curve as function of the exposure time to UV light of (c) marjoram and (d) clove, respectively. Samples were irradiated with 20 Gy. The open square is for 149 μm and the solid circles for 53 μm particle sizes. Error bars are smaller than the symbol size.

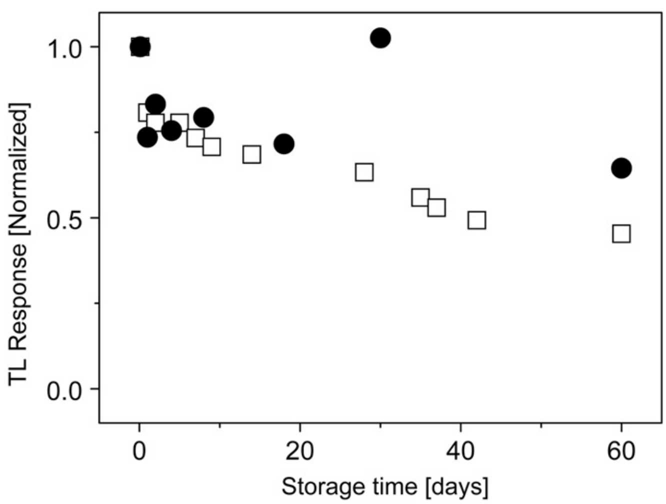

Fig. 6. Behavior of the area under the TL glow curve integrated from 230 to 400 °C for samples of clove (solid circles) and marjoram (open squares) irradiated with 20 Gy.

Figs. 5(c) and (d) show the influence of ultraviolet (UV) light on TL glow curves of polymineral extracted from marjoram and clove, respectively. Polyminerals were irradiated with a dose of 20 Gy and exposed to UV light for different periods of time. The integrated TL response decreases during UV irradiation as a double exponential function given by $I(t)=I_1\ \exp\ (-t/\tau_1)+I_2\exp(-t/\tau_2)$. The best-fitting values obtained for the lifetime τ_1 and τ_2 were 7 ± 3 and 125 ± 15 min respectively, regardless of the spice or grain size analyzed. The fast component characterized by the short lifetime corresponds to the TL emission of low temperature glow peak, which disappears completely after the first 12 min. The slow component having a lifetime $\tau_2>120$ min corresponds to the peaks located at higher temperatures.

Because of the complex shape of the glow curves from polyminerals fractions of marjoram and clove, the kinetic parameters values were determined through a glow curve deconvolution (GCD) procedure, by assuming a General Order Kinetic (GOK) model (May and Partridge, 1964; Rasheedy, 1993). The goodness of fit was evaluated by using the figure of merit (*FOM*). The TL glow curves were successfully deconvoluted by six overlapping glow peaks (Fig. 7). The activation energy (*E*), frequency factor (*s*) and kinetic order (*b*) values (Table 2) are similar for the two different particle sizes, which describe accurately the thermoluminescent process. *FOM* values ranging from 0.7 to 1.1% indicate that a very good fit was obtained (Horowitz and Yossian, 1995).

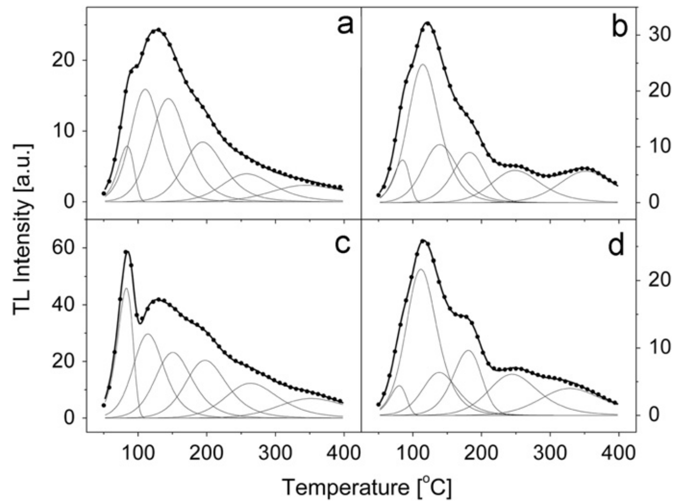

Fig. 7. Experimental (black points) and deconvolved (black line) glow curves for the inorganic fraction extracted from (a) marjoram 53 μm, (b) clove 53 μm, (c) marjoram 149 μm and (d) clove 149 μm. Samples were irradiated with 400 Gy.

Table 2
Kinetic parameters obtained for the glow curves by assuming the GOK model.

	T_{max} (°C)	*E* (eV)	*s* (s^{-1})	*b*	*FOM*
Clove 53 μm					0.7%
Peak 1	84	0.92	4.5×10^{12}	1.0	
Peak 2	114	0.76	2.0×10^{13}	2.0	
Peak 3	144	0.76	7.9×10^{12}	2.0	
Peak 4	182	0.87	1.2×10^{11}	1.5	
Peak 5	248	0.87	1.1×10^{12}	2.0	
Peak 6	352	1.07	1.7×10^{11}	1.8	
Clove 149 μm					0.9%
Peak 1	80	0.89	5.0×10^{12}	1.0	
Peak 2	112	0.76	2.6×10^{13}	2.0	
Peak 3	138	0.76	1.2×10^{13}	2.0	
Peak 4	180	0.93	1.1×10^{11}	1.3	
Peak 5	244	0.85	1.0×10^{12}	2.0	
Peak 6	328	0.92	9.2×10^{11}	2.1	
Marjoram 53 μm					1.1%
Peak 1	84	0.92	4.5×10^{12}	1.0	
Peak 2	110	0.76	2.0×10^{13}	2.0	
Peak 3	144	0.76	2.7×10^{12}	2.0	
Peak 4	194	0.85	3.4×10^{12}	2.0	
Peak 5	258	0.86	4.3×10^{11}	2.0	
Peak 6	344	0.80	1.3×10^{11}	2.1	
Marjoram 149 μm					1.1%
Peak 1	82	0.93	7.0×10^{12}	1.0	
Peak 2	114	0.76	1.9×10^{13}	2.0	
Peak 3	150	0.77	2.8×10^{12}	2.0	
Peak 4	198	0.85	3.1×10^{12}	2.0	
Peak 5	264	0.86	3.2×10^{11}	2.0	
Peak 6	352	0.87	9.2×10^{10}	2.1	

4. Conclusion

The XRD analysis shows that the inorganic fraction extracted from clove is only composed of quartz. In the polymineral fraction of marjoram not only quartz was found but also feldspars. Accordingly, EDS studies show that only O, Si ions and a low concentration of C are present in the polyminerals of clove spice. Besides the mentioned elements, small amounts of Na, Mg, Al, K, Ca, Fe and Ti ions are also present in marjoram. A good linearity of the TL response for both studied spices was obtained showing that the TL method permits to discriminate between irradiated and non-irradiated spices. The richness of the ions content of marjoram seems to increase the complexity of their glow curve and, at the same time, improve the reproducibility and linearity of the TL response. Furthermore, it is possible give an acceptable estimation of the irradiated dose with a percentage standard deviation less than 30% in the first two months of storage. However, more investigation to validate this assertion for doses above 0.5 kGy would be necessary.

Fading of the TL signal of both spices is observed after storing the corresponding polymineral samples at room temperature. The maximum reduction is no higher than 75% and occurs after two months. Similar bleaching occurs if the samples are illuminated with UV light. In both cases, traps related to the low temperature glow peak are emptied.

The glow curves of the polyminerals extracted from clove and marjoram are broad and rather complex. These curves were deconvolved by assuming six general order glow peaks having activation energies between 0.76 and 0.92 eV.

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