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Thermoluminescence (TL) of Minerals Separated from Irradiated Mussel

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Abstract

This study was carried out to determine whether detection of minerals separated from irradiated mussel could be could be done by thermoluminescence (TL) method. After the minerals were separated by sodium polytungstate solution (2.0 g/mL) from irradiated mussel, organic compounds remaining in the minerals were removed by acid-base treatment and dried at 50°C overnight, and then the minerals were measured through TL. The TL intensities of separated minerals at different irradiation doses during storage conditions of room and darkroom were obtained. TL intensity of first glow curves for minerals separated from irradiated mussel showed linear increase from the control to 5 kGy and slight increase from 5 kGy to 10 kGy. Since glow curve ratios of G2, G3 and G4, calculated from re-irradiated minerals measured immediately after irradiation and after storage of three months were over 0.5, detection of irradiation was possible. G1, which showed the glow curve ratios above 0.1, was classified as non-irradiated samples because the unique first glow curve was not found within the recommended temperature interval (150~230°C). Hence, on the basis of TL intensity, and glow curve ratio and shape, it is possible to correctly identify irradaited mussels after mineral separation during storage.

Key words: mineral, mussel, irradiation, thermoluminescence (TL)

INTRODUCTION

Irradiation has been widely accepted in many countries as a reliable and safe method for both preserving and improving hygienic quality of foods. Suitable detection techniques, for confirming the identity of irradiated products, are needed in order to facilitate international trade, regulate irradiated food, and to assure that consumers have free choice for use of non-irradiated and irradiated foods (1). Currently, detection techniques have been developed for many foods to ensure detection reliability, demonstrating the enormous interest in irradiated food, which may reflect an increased awareness of the benefits of food irradiation. Shellfish are especially susceptible to improper handling, poor quality control, and microbial contamination caused by pathogens such as species of *Salmonella* and *Vibrio* (2). Therefore, in the future, irradiation of shellfish such as mussel should be considered by governments to prevent microbial contamination. With increased demand for the irradiation of shellfish, a detection technique has been developed for correct and comprehensive identification of irradiation (3).

TL is a radiation-specific phenomena caused by the energy stored by trapping charge carriers following irradiation (4). When exposed to ionizing radiation, most materials store energy by trapping charge carriers at structural, interstitial or impure sites. Subsequent heat stimulation in the range of 50~350°C at a constant rate of 5~10°C/s releases the trapped charge carriers, resulting in the TL emissions. The energy release by such stored energy by thermal stimulation can result in detectable luminescence emission (5,6). The TL technique is relatively simple and more reliable than other methods. The TL technique has potential for the identification of various irradiated foods. TL has been studied for various foods such as spices, herbs (7-10), fruits (11), onions, potato (12), and seafoods such as prawn, squid, shrimp, lobster, crayfish, scampi and fish (13-16). TL is considered to be a reliable method for the detection of all irradiated spices (17-22). Previous TL detection studies for shellfish were not carried out on mineral residues shellfish, but from shellfish shell powder (23).

Therefore, the aim of this study was to observe the changes in TL intensity to storage conditions (room and darkroom) after separation of minerals from irradiated mussel using a sodium polytungstate solution (2.0 g/mL).

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MATERIALS AND METHODS

Materials and irradiation

Mussels were purchased from a local market in Daejeon, Korea. The mussel samples (500 g) were packed with air in polyethylene bags and irradiated using a Co-60 source (AECL, IR-79, Ontario, Canada) with 1, 5, and 10 kGy at a dose rate of 10 kGy/h at the Korea Atomic Energy Research Institute, Daejeon, Korea. Total absorbed dose was determined using a ceric-cerous dosimeter (24,25).

Separation of minerals

After irradiation, 500 g samples (irradiated mussel itself) were washed in 5 L distilled water for 5 min. The wash solutions containing minerals were filtered through a nylon cloth (250-μm), and the constituents retained were discarded. The solution was allowed to settle for about 5 min to separate the sediment minerals from the supernatant. The sediment minerals were suspended in 5 mL sodium polytungstate [$Na_6O_{39}W_{12}.H_2O$] (Fluka 71913) solution which was adjusted to a concentration of 2.0 g/mL by the addition of water for the separation of minerals and adhering organic materials. The solution containing minerals was centrifuged for 2 min at 1,000 rpm after ultrasonic treatment for 5 min. The low-density layer was decanted off. This procedure was repeated until all the organic materials were removed. After the sodium polytungstate solution was removed, the minerals were washed twice in water and pelleted through centrifugation at 1,000 rpm, followed by a treatment with 1 M HCl for 10 min to remove carbonates. After neutralizing with 1 M NH_4OH for 10 min, the solution was discarded. The solution containing minerals was washed twice with deionized water and centrifuged at 1,000 rpm for 2 min to separate the mineral fraction. After the supernatant was decanted, the remaining water was then rinsed off with 3 mL of acetone twice and dried in a laboratory oven at 50°C for 3 h. The dried minerals (1 mg) were deposited onto a clean stainless steel disc (10 mm diameter, 0.5 mm thickness), fixed with silicon solution [silicon rubber (LDC 210, Dow Corning Korea Ltd., Seoul, Korea) and hexane at a 1:5 ratio], dried and measured with a TL reader (24). After mineral separation, the samples used to evaluate storage at ambient room conditions were stored in the laboratory in a glass bottle and the samples for dark room conditions were stored in a drying oven (K.M.C-1203P3, Vision Scientific Co., Ltd., Seoul, Korea) at room temperature.

Thermoluminescence (TL) measurement and evaluation

TL measurement was carried out using a TL reader (Harshaw 3500, Wermelskirchen, Germany) with temperatures ranging from 50 to 320°C at a heating rate of 6°C/s and held at 320°C for 10 s. The light emission was recorded in a temperature-dependent mode as a glow curve and was measured in the units of nano coulombs (nC). After the first glow curve was measured, the discs with the minerals were subsequently re-irradiated using Co-60 gamma rays with a dose of 1, 5 and 10 kGy. The TL intensity was measured again after the re-irradiation step (second glow curve). The glow curve ratios I (G1) (the first glow curve of non-irradiated samples/the second glow curve of irradiated samples at 1 and 5 kGy) and II (G2, G3, G4) (the first glow curve per irradiation dose (G2=1 kGy, G3=5 kGy, G4=10 kGy)/the second glow curve of irradiated samples at 1, 5 and 10 kGy) were then determined.

Glow curve ratios of irradiated samples are typically greater than 0.5, whereas those of non-irradiated samples are generally below 0.1 (26). If glow curve ratios between 0.1 and 0.5 are obtained, interpretation of the glow curve shapes is needed to determine whether or not the sample had been irradiated, since the shapes of first glow curve appeared in a higher temperature region than those of the second glow curve (26). Therefore, the above definition above was applied in this research.

Statistical analysis

Significant differences among treatments were determined by using ANOVA and Duncan's multiple range test using SPSS (Statistical Package for Social Science) version 7.5. All measurements were repeated 3 times. Significance of the results was established at $p<0.05$.

RESULTS AND DISCUSSION

TL intensity of the mineral separated from irradiated mussel

Table 1 shows that the TL intensities of the minerals separated from non-irradiated and irradiated mussel, measured immediately after irradiation, have an increase up to 5 kGy and slight increases from 5 kGy to 10 kGy. These results were similar to those reported for shell powder by Ziegelmann et al. (23). The TL intensities measured after three months were decreased in proportion to storage periods, but there were no significant differences between samples stored under different conditions (room and darkroom). However, since the irradiated samples showed higher TL intensities than those of the non-irradiated samples regardless of storage conditions, the detection of irradiation for irradiated mussel was possible even after three months. Therefore, we concluded that measuring the TL intensity of minerals isolated from mussels is a suitable method for

Table 1. The TL intensities of the first glow curves of minerals separated from irradiated mussel after different storage conditions (Unit: nano coulomb of nC/mg)

Storage periods and conditions		Irradiation dose (kGy)			
		Control[2)]	1	5	10
Control[1)]		214.9±11.6^{cA}	1,504.9±94.8^{bA}	5,138.1±860.1^{aA}	5,662.2±553.1^{aA}
After three months	Room	293.7±51.5^{dA}	733.4±79.2^{cB}	1,736.9±167.6^{bC}	2,397.5±324.1^{aB}
	Darkroom	235.3±24.3^{dA}	705.7±114.9^{cB}	2,166.6±154.7^{bB}	2,938.0±438.2^{aB}

[1)]Control=sample measured immediately after irradiation.
[2)]Control=non-irradiated sample of mean±standard deviation for 3 measurements.
[a-d]Means with the same superscripts in each row are not significantly different among group by Duncan's multiple range test in one way ANOVA ($p<0.05$).
[A-C]Means with the same superscripts in each column are not significantly different among group by Duncan's multiple range test in one way ANOVA ($p<0.05$).

the detection of irradiation. Several studies have reported that generally, the TL intensities of minerals separated from irradiated samples are higher than those of non-irradiated samples (9,11,16). Schreiber et al. (27) reported that TL emission occurs when the excited electrons return to the original level at a certain temperature, and this principle is well observed in present study also.

TL intensities of second glow curve and glow curve ratios

Several studies have demonstrated that comparing the glow curve ratios as well as an analysis of glow curve shapes is preferable for discriminating between irradiated and non-irradiated samples (7,11,16). In addition, Hammerton and Banos (17) reported the clear identification of irradiated spice samples after the re-irradiation step; the TL ratios (glow curve ratio) varied between 0.0039 and 0.19 for non-irradiated samples and between 0.79 and 2.4 for samples irradiated at 5 kGy. The TL intensities of second glow curves needed for calculations of glow curve ratios are shown in Table 2. The TL intensities of the second glow curves increased with increasing re-irradiation dose and at 10 kGy increased slightly compared to that of 5 kGy. However, there is no observed difference in the TL intensities by the storage conditions and times periods. Second TL intensity was greater than the first TL intensity. It might be caused by a structural change, which can store more energy through the electron of mineral by irradiation.

The glow curve ratios calculated from the first glow curve irradiation dose (0, 1, 5 and 10 kGy) divided by the second glow curve of each re-irradiation dose (1, 5 and 10 kGy) are shown in Table 3. Generally, TL glow curve ratios from irradiated samples are typically greater than 0.5, whereas those from non-irradiated samples are below 0.1 (24). Since glow curve ratios of G2 in control, G3 and G4 calculated from re-irradiated (1, 5 and 10 kGy) mussel (separated mineral) in control measured immediately after irradiation were over 0.5, detection was possible by glow curve ratios. On the other hand, glow curve ratios calculated after storage for three months were possible only in G3 and G4. If glow curve ratios between 0.1 and 0.5 are obtained, interpretation of the shape of the glow curves is needed to decide whether the sample has been irradiated or not (26). Hence, G1 exhibited a glow curve ratio above 0.1, and the shapes of the glow curves were used to interpret results. Since the shapes of unique first glow curve was only seen in irradiated samples and not in non-irradiated sample, it can be classified as non-irradiated.

Shape of glow curve

If the glow curve ratios between 0.1 and 0.5 or below 0.1 are obtained, interpretation of the shape of the glow

Table 2. TL intensities of the second glow curves of minerals separated from irradiated mussel after different storage conditions (Unit: nano coulomb of nC/mg)

Storage periods and conditions		Irradiation dose (kGy)		
		1	5	10
Control[1)]		898.4±123.9^{bB}	1,407.9±88.1^{bB}	2,149.6±410.9^{aB}
After three months	Room	1,339.9±323.5^{bA}	2,415.2±424.9^{aA}	3,228.7±254.3^{cA}
	Darkroom	991.2±35.1^{bB}	1,516.2±20.7^{bB}	2,187.7±133.1^{aB}

[1)]Control=sample measured immediately after irradiation.
[a-c]Means with the same superscripts in each row are not significantly different among group by Duncan's multiple range test in one way ANOVA ($p<0.05$).
[A-B]Means with the same superscripts in each column are not significantly different among group by Duncan's multiple range test in one way ANOVA ($p<0.05$).

Table 3. The changes of glow curve ratios of minerals separated from irradiated mussel after different storage conditions

Storage periods and conditions		Irradiation dose (kGy)	Glow curve ratios			
			G I	G II		
			G1[2)]	G2[3)]	G3[4)]	G4[5)]
Control[1)]		1 kGy	0.2392	1.7753	5.7192	6.0325
		5 kGy	0.1526	1.0689	3.6495	4.0217
		10 kGy	0.0999	0.7001	2.3903	2.6341
After three months	Room	1 kGy	0.2192	0.5473	1.2963	1.7893
		5 kGy	0.1216	0.3037	0.7192	0.9927
		10 kGy	0.0910	0.2272	0.5380	0.7426
	Darkroom	1 kGy	0.2374	0.7120	2.1858	2.9647
		5 kGy	0.1552	0.4654	1.4290	1.9377
		10 kGy	0.1076	0.3226	0.9903	1.3430

[1)]Control=sample measured immediately after irradiation.
[2)]G1=first glow curve of non-irradiated sample/second glow curve of re-irradiated sample at 1, 5 or 10 kGy.
[3)]G2=first glow curve of irradiated sample at 1 kGy/second glow curve of re-irradiated sample at 1, 5 or 10 kGy.
[4)]G3=first glow curve of irradiated sample at 5 kGy/second glow curve of re-irradiated sample at 1, 5 or 10 kGy.
[5)]G4=first glow curve of irradiated sample at 10 kGy/second glow curve of re-irradiated sample at 1, 5 or 10 kGy.

curves is needed to decide whether the sample has been irradiated or not (26). Usually, the first glow curves of irradiated foodstuffs exhibit a maximum peak between 150°C up to 250°C, whereas the low level natural radioactivity causes TL signals in the deep traps above 300°C (26). The general pattern in the first and the second glow curve of the irradiated mussel are shown in Fig. 1~3. The unique first glow curve was between 150°C and 250°C in irradiated samples. In addition, since the shape of the second glow curve was shown at the lower domain than that of the first glow curve, the detection of irradiated mussel is possible by the shape of glow curves. As compared with the TL intensity of first glow curves measured after storage under room and darkroom conditions for 3 months was lower than that of measured immediately after irradiation (Fig. 2 and 3). These results

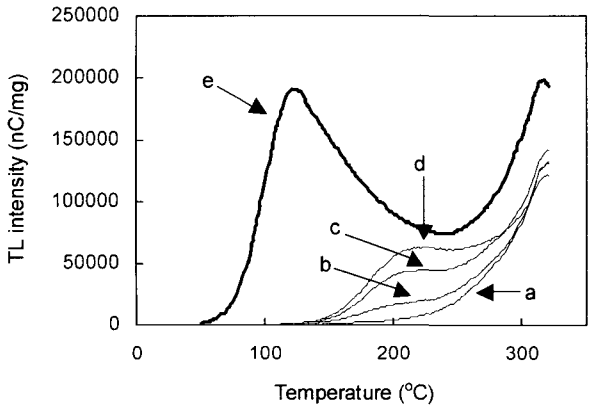

Fig. 2. The TL intensity of the first and the second glow curves of minerals separated from the irradiated mussel after stored during 3 months in room condition.
a) non-irradiated sample, b) 1 kGy, c) 5 kGy, d) 10 kGy, e) second glow curve re-irradiated at 1 kGy.

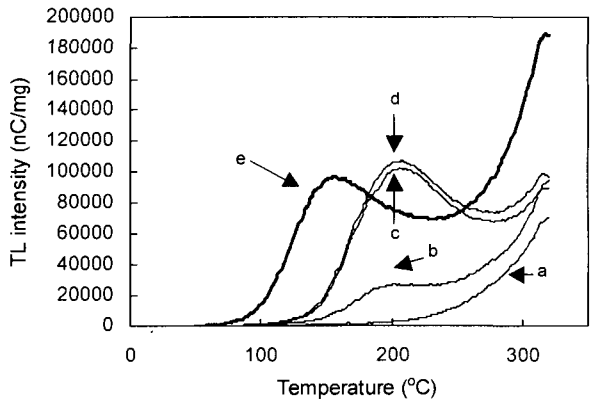

Fig. 1. The TL intensity of the first and the second glow curves of minerals separated from the irradiated mussel on the immediate measurements after irradiation at various doses.
a) non-irradiated sample, b) 1 kGy, c) 5 kGy, d) 10 kGy, e) second glow curve re-irradiated at 1 kGy.

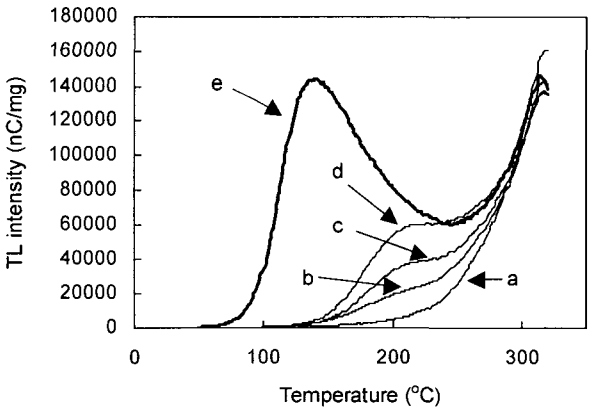

Fig. 3. The TL intensity of the first and the second glow curves of minerals separated from the irradiated mussel after stored during 3 months in darkroom condition.
a) non-irradiated sample, b) 1 kGy, c) 5 kGy, d) 10 kGy, e) second glow curve re-irradiated at 1 kGy.

suggest that identification of irradiated mussel is possible by TL intensity, glow curve ratio, and shape of glow curve of TL, measured after separation of minerals from samples.

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