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Identification of Irradiated Granule-Type *Ramen* Soup Powder by Pulsed Photostimulated Luminescence and Thermoluminescence during Storage

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Abstract

This study was carried out to establish a method for determining if granule-type *Ramen* soup powder has been irradiated. Thermoluminescence (TL) and pulsed photostimulated luminescence (PPSL) were used as the detection methods through observed changes of TL and PPSL intensities after storage under differing conditions. PPSL intensities increased with increases in irradiation doses. The threshold level of PPSL was below 412 ± 58 photon counts regardless of storage conditions (room and darkroom) after 10 months. TL intensities also increased with increasing irradiation doses. The coefficients (R^2) of PPSL (0.74~0.94) and TL intensities (0.92~0.58) were very highly correlated with irradiation dose. The PPSL and TL intensities were decreased after 10 months of storage. These results indicate that discrimination of irradiated from non-irradiated granule - type *Ramen* soup powder is possible using TL and PPSL methods despite the decrease in intensities of TL and PPSL with increasing storage times.

Key words: granule type *Ramen* soup powders, gamma irradiation, thermoluminescence, pulsed photostimulated luminescence

INTRODUCTION

Since irradiation for preserving *Ramen* soup powder has received government approval, it has been a useful technology for protecting against pathogenic microorganisms (1-4). However, detection techniques, which can determine if a product has been treated with irradiation, are needed in order to monitor and control irradiated food and to assure that irradiated foods are properly labeled, enabling consumers to make informed choices for or against irradiated foods (5-7).

Thermoluminescence (TL) and pulsed photostimulated luminescence (PPSL); which use heat and light, respectively, to stimulate the release of trapped charge carriers; are radiation specific phenomena that can be exploited as physical detection methods (8-18). Previous studies have used potential detection methods, which measure the release of trapped energy from inorganic compounds after thermal or light stimulation, for measuring *Ramen* soup seasoning powders (3,4). However, no TL or PPSL methods have been developed for granule type *Ramen* soup powder because of difficulties in working with the small samples required for the techniques (about 1~10 mg) (3,4, 19-21).

Granule-type *Ramen* soup powder (caramel-base *Ramen* soup powder called *Zajangmen* soup powder) is a commonly used condiment in Korea that imparts a unique taste in instant *Zajangmen*, but has been highly susceptible to microbial contamination because of ingredients that also act as a good growth media for bacteria (3,4,21,22).

Therefore, this study was conducted to develop and verify procedures, considering storage time and conditions, for the detection of irradiation in granule type *Ramen* soup powders using TL and PPSL detection methods.

MATERIALS AND METHODS

Materials

Granule-type *Ramens* soup powder (instant *Zajangmen* soup powder) was obtained from a local company. The soup powder was prepared for testing by grinding in a food processor (FM 680T, Hanil Co., Seoul, Korea) for 1 min and passing through a 50-mesh sieve (Chung Gye Industry Mfg. Co., Seoul, Korea). Non-irradiated powder was used as a control sample, and additional samples were irradiated for testing.

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Irradiation

The ground samples (20 g) were individually packed for irradiation in polyethylene film (thickness: 0.03 mm) (W3.5×L3.5×T0.5) and irradiated using a Co-60 irradiator (AECL, IR-79, Ontario, Canada) at doses of 0.1, 0.5, 1, 5, and 10 kGy at the Korea Atomic Energy Research Institute. The total absorbed dose was determined using a ceric-cerous dosimeter. The irradiated samples were used directly for TL and PPSL measurements without further preparation other than storage.

Storage conditions

After irradiation, the samples to be tested after storage under room conditions were stored for 10 months in the laboratory with exposure to existing sunlight and fluorescent light. The samples to be tested after storage in darkroom conditions were stored in a chamber oven (K.M.C-1203P3, Vision Scientific Co., LTD, Seoul, Korea), to block exposure to light, and maintained at room temperature for 10 months.

Proximate analysis

Moisture, crude protein, crude fat and ash contents were determined in triplicates using air-oven drying, a protein auto analyzer (Auto Kjeldahl System B-339, Büchi Labortechnik AG, Flawil, Switzerland) using 6.25 as a converting factor from nitrogen to protein, Soxhlet method, and muffle furnace method, respectively (23). Total carbohydrate content was estimated by subtracting moisture, crude protein, crude fat, and ash weights from 100% of the total sample weights. Salt content was analyzed by the 0.1 N $AgNO_3$ titration method (24,25). The moisture, crude protein, crude fat, ash, salt and carbohydrate contents of the standard sample were 5.6%, 14.7%, 5.0%, 18.3%, 14.3% and 56.3%, respectively.

Thermoluminescence (TL)

Samples (5 mg) were deposited onto a clean stainless steel disc (10 mm diameter, 0.5 mm thickness), and fixed with a silicon solution [silicon rubber (LDC 210, Dow Corning Korea Ltd, Seoul, Korea) and hexane in the ratio of 1 : 5], and oven dried at 50°C. Prepared samples were measured using a thermoluminescence (TL) reader (Harshaw 3500, Wermelskirchen, Germany) with heat ranging from 50 to 320°C at a rate of 6°C/s and held at 320°C for 10 sec. The light emission was recorded ina temperature-dependent mode as a glow curve and was measured in units of nano coulombs (nC). Maximum TL temperature was defined as the temperature resulting in the maximum photon count in the first and second glow curves (26-28).

PPSL system and measurement

Measurement of PPSL intensity was carried out using a PPSL system (Scottish Universities Research and Reactor Centre, Glasgow, UK). The PPSL system is composed of a control unit, sample chamber, and detector head assembly. The control unit contains a stimulation source, which is comprised of an array of infrared light (880~940 nm) emitting diodes pulsed symmetrically on and off for equal periods of time. The PPSL signal is detected by a bi-alkali cathode photomultiplier tube operating in the photon counting mode and automatically recorded on a personal computer connected to the PPSL system. Optical filtration is used to define both the stimulation and detection wavebands. The samples (1 mg) were placed in 50 mm diameter disposable petri dishes (Bibby Sterilin types 122, Glasgow, UK) and were measured in the sample chamber for 60 sec. Radiation-induced photon counts (PPSL intensity) emitting per second from the samples were automatically accumulated in a personal computer and presented as the photon counts accumulated after 30 and 60 sec (29-31).

RESULTS AND DISCUSSION

TL intensity

TL intensities of the samples immediately after irradiation at 0, 0.1, 0.5, 1, 5 and 10 kGy were 356±55, 713±62, 868±61, 815±80, 1,527±110 and 1,792±152, respectively, showing dose-dependent increases with increasing irradiation doses (Table 1).

These results are similar to the results of Yi et al. on TL intensities with increasing irradiation dose in minerals separated from Korean perilla and sesame seeds (28), shrimp flavored seasoning powder (2), *Ramen* soup powder (1), and minerals separated from shellfish (27). TL intensities measured after three months of storage decreased linearly with increasing storage time, but there were no significant effects of storage conditions (normal room

Table 1. TL intensities of glow curves of granule-type *Ramen* soup powders measured immediately after irradiation

(unit: nano coulombs (nC))

Storage conditions	Storage periods (month)	Irradiation dose (kGy)					
		0	0.1	0.5	1	5	10
	0	356±55	713±62	868±61	815±80	1,527±110	1,792±152
Room	10	288±33	342±11	303±38	357±77	556±32	592±76
Darkroom	10	337±35	351±29	401±23	375±30	603±49	512±25

and darkroom). However, because irradiated samples exhibited higher TL intensities than those of the non-irradiated samples, except for irradiation doses below 1 kGy, under all conditions; detection of irradiation was still possible after 10 months for samples irradiated at 5 or 10 kGy.

PPSL intensity

PPSL intensities for samples irradiated at 0, 0.1, 0.5, 1, 5 and 10 kGy are shown in Table 2. PPSL intensities increased with increased irradiation doses. Generally, the PPSL intensities of irradiated samples are higher than those of non-irradiated samples and increased with irradiation dose (1,2,8,2-14,29), which is consistent with our results. Detection of irradiation by the PPSL system is based on higher radiation-induced PPSL signals in irradiated samples than in non-irradiated samples (15-18,30). Therefore, since the irradiated samples showed higher PPSL intensities than the non-irradiated samples, detection of irradiation was possible. There were no significant differences in PPSL intensities among non-irradiated granule-type *Ramen* soup powders. Threshold levels, defined as accumulated PPSL signals of non-irradiated samples were below 412±58 photon counts regardless of storage conditions or time up to the 10 months.

Correlation equation and coefficients

Correlation equation and coefficients showed high linear correlations between irradiation doses and PPSL and TL intensities for granule - type *Ramen* soup powder (Fig. 1 and 2), with correlation coefficients for PPSL intensity of 0.74~0.94 and TL intensity of 0.92~0.58.

Shape of glow curve and maximum TL temperature

Maximum TL temperature, the temperature of the highest peak point on the glow curve, is a convenient factor for distinguishing luminescence properties between TL glow curves of irradiated samples. The shape and appearance

Table 2. The changes in PPSL intensities of irradiated granule-type *Ramen* soup powder during storage of 10 months under room or darkroom conditions (unit: photon counts)

Measurement time (sec)	Storage conditions	Storage periods (Month)	Irradiation dose (kGy) 0	0.1	0.5	1	5	10
30		0	344±7	158,060±27,271	819,347±55,263	1,096,145±274,890	5,129,502±1,509,961	6,656,205±2,021,572
	Room	10	358±77	79,300±29,177	597,039±163,700	695,120±376,326	1,868,379±926,836	3,006,025±449,741
	Darkroom	10	286±45	175,642±25,629	766,207±36,791	822,243±84,998	2,754,369±489,455	2,851,005±228,582
60		0	412±58	204,627±37,855	1,087,126±72,783	1,470,433±363,620	7,107,486±2,070,081	9,270,157±2,803,509
	Room	10	361±61	104,002±36,944	809,302±228,636	941,280±499,744	2,617,035±1,319,455	4,259,762±123,181
	Darkroom	10	281±38	231,175±36,635	1,072,006±123,271	1,089,884±126,056	4,030,083±569,572	4,051,265±329,305

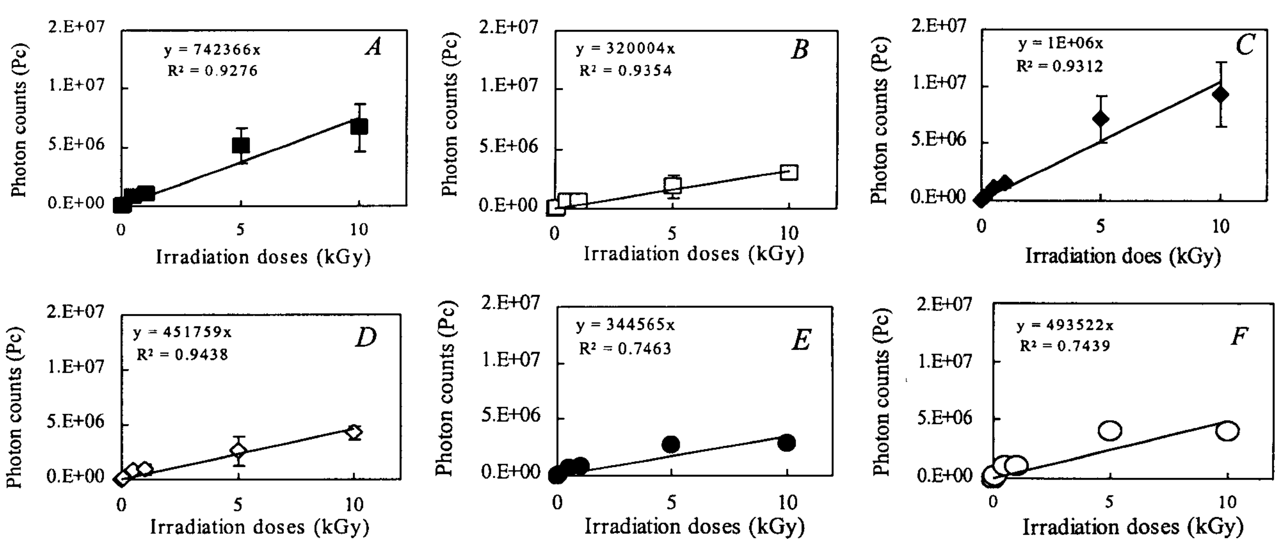

Fig. 1. Correlation equations and coefficients between PPSL intensities and irradiation doses in granule-type *Ramen* soup powders.
A: sample measured immediately after irradiation for 30 s.
B: sample measured after storage for 10 months under room condition for 30 s.
C: sample measured immediately after irradiation for 60 s.
D: sample measured after storage for 10 months under room condition for 60 s.
E: sample measured after storage for 10 months under darkroom condition for 30 s.
F: sample measured after storage for 10 months under darkroom condition for 60 s.

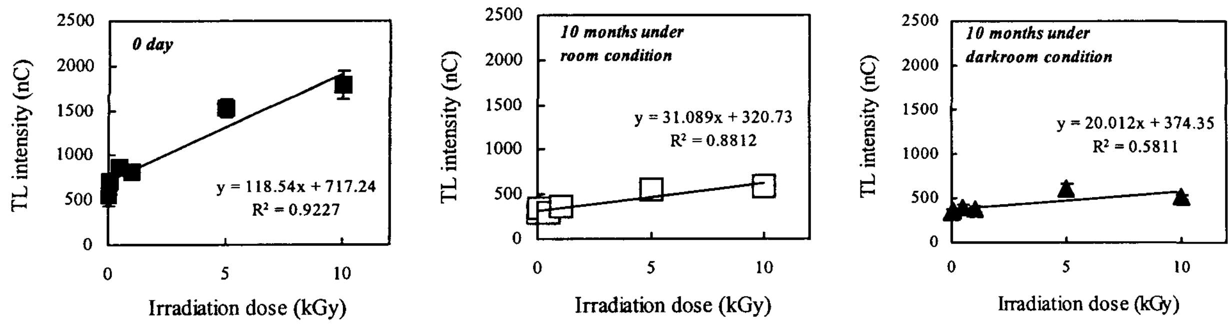

Fig. 2. Correlation equations and coefficients between TL intensities and irradiation doses in irradiated granule-type *Ramen* soup powders.

of the glow curves can also be used, but shapes are subject to greater change between samples and are difficult to interpret, whereas maximum TL temperature is easily read and provides consistent results.

Table 3 shows that maximum TL temperatures of the first glow curves measured immediately after irradiation were between 188.5±7.3~191.3±6.2. Maximum TL temperatures of the first glow curves measured after 10 months of storage in normal room and darkroom conditions were between 220.7±4.5~225.7±9.3 and 221.4±5.5~221.8 ±6.3, respectively. Shapes of TL glow curves measured immediately after irradiation at the various doses, and the same samples after 10 months of storage, are shown in Fig. 3, 4 and 5. Since irradiated samples (above 1 kGy) had unique TL glow curves when activated at temperatures in the range of 170~200, but non-irradiated samples did not, identification of irradiated samples was possible by observing the unique TL glow curves in samples irradiated at doses of 5 and 10 kGy. Although TL glow curve intensities declined after 10 months of storage, the decline was not sufficient to impair identification of the unique first glow curves in samples stored under either of the conditions if irradiated at 5 and or kGy. Hence, it was possible to distinguish between non-irradiated and irradiated samples by comparing shapes of unique TL glow curves.

Decay rates of PPSL and TL intensities

Decay rates of PPSL and TL intensities of non-irradiated and irradiated granule type *Ramen* soup powders were monitored during 10 months of storage under normal room and darkroom conditions (Table 4). Ten months of storage

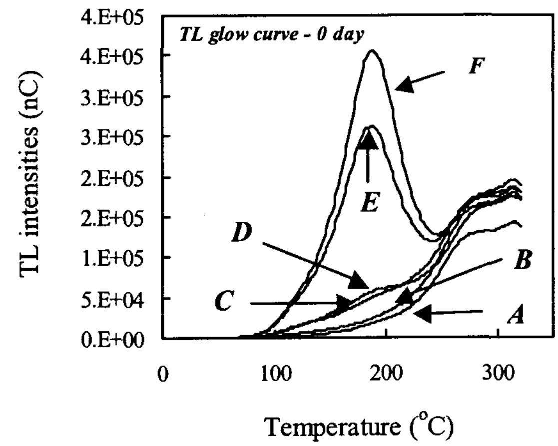

Fig. 3. Properties of TL glow curves of granule type *Ramen* soup powder measured immediately after irradiation.
A: Unirradiated sample, B: 0.1 kGy, C: 0.5 kGy, D: 1 kGy, E: 5 kGy, F: 10 kGy.

resulted in the PPSL and TL signals falling to approximately 25.61~63.17% and 52.03~66.96% for those stored in normal room conditions and 25.88~56.30% and 50.77~71.43% for those in darkroom condition, respectively. Similar decay rates of PPSL and TL intensities after storage under normal room and darkroom conditions were reported by Yi et al. (1,16,27,28,30). They reported that PPSL and TL intensities of minerals separated from shellfish after 3 months and of *Ramen* soup powders after 10 months decreased regardless of storage conditions and this result agreed with our results as shown above. However, the PPSL intensities decreased a little more rapidly in samples stored in normal room conditions than those in dark-

Table 3. Maximum TL temperatures of first TL glow curves measured in granule-type *Ramen* soup powders irradiated at various irradiation doses (unit: °C)

Storage conditions	Storage periods (month)	Irradiation dose (kGy)					
		Control[1)]	0.1	0.5	1	5	10
	0	ND[2)]	ND	ND	ND	188.5±7.3	191.3±6.2
Room	10	ND	ND	NC[3)]	ND	220.7±4.5	225.7±9.3
Darkroom	10	ND	ND	ND	ND	221.4±5.5	221.8±6.3

[1)]Unirradiated sample. [2)]Not detected. [3)]Not clear.

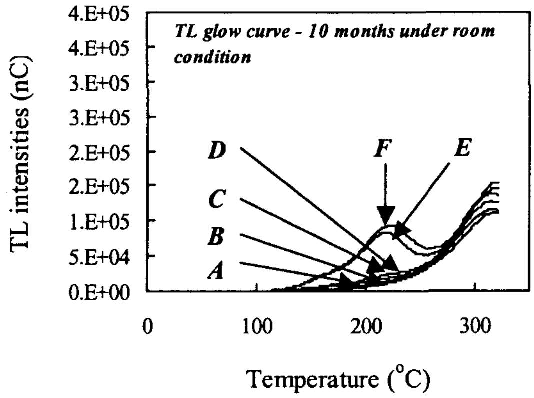

Fig. 4. Properties of TL glow curves of granule type *Ramen* soup powder measured after storage for 10 months under room condition.
A: Unirradiated sample, B: 0.1 kGy, C: 0.5 kGy, D: 1 kGy, E: 5 kGy, F: 10 kGy.

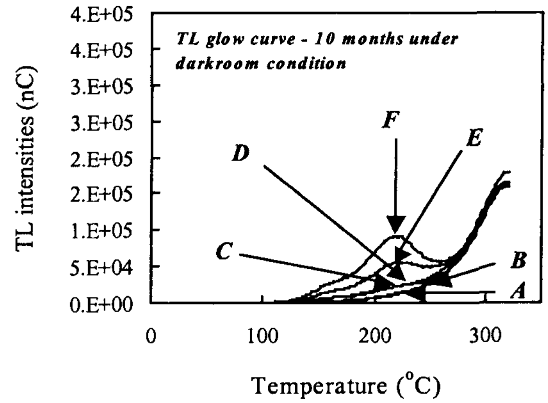

Fig. 5. Properties of TL glow curves of granule type *Ramen* soup powder measured after storage for 10 months under darkroom condition.
A: Unirradiated sample, B: 0.1 kGy, C: 0.5 kGy, D: 1 kGy, E: 5 kGy, F: 10 kGy.

Table 4. The decay rate calculated from PPSL intensities in 60 sec measurement time and TL intensities of irradiated granule-type *Ramen* soup powder measured during storage of 10 months under room and darkroom conditions (unit: %)

Intensities	Storage conditions	Storage periods (month)	Irradiation dose (kGy) 0	0.1	0.5	1	5	10
		0	NC[1)]	0	0	0	0	0
PPSL	Room	10	NC	49.17	25.61	35.99	63.17	54.05
	Darkroom	10	NC	ND[2)]	0.01	25.88	43.29	56.30
		0	NC	0	0	0	0	0
TL	Room	10	NC	52.03	65.09	56.19	63.59	66.96
	Darkroom	10	NC	50.77	53.80	53.98	60.51	71.43

[1)]Not calculated. [2)]Not decreased.

room conditions.

Yi et al. (30) suggested that the greater decline in PPSL intensities in samples stored where they are exposed to light was due to stimulation by sunlight and other ambient light, rather than an infrared light source, which caused an emission of radiation-induced PPSL photons trapped in the sample. That explanation seems plausible and we concur that ambient light excitation leads to the decreased accumulated PPSL signals.

These TL results demonstrate that it is possible to discriminate irradiated samples from non-irradiated samples by TL, except at lower irradiation doses (0.1, 0.5 and 1 kGy). The PPSL results also indicate that, although the PPSL intensity decreased with increasing storage times, detection of irradiated samples by PPSL is still possible after up to 10 months since irradiated samples still have higher photon counts than those of non-irradiated samples regardless of storage conditions.

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