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Detection of γ-Irradiated Sesame Seeds before and after Roasting by Analyzing Photostimulated Luminescence, Thermoluminescence, and Electron Spin Resonance

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Sesame seeds were irradiated using a ^{60}Co irradiator (0−4 kGy) and then roasted (220 °C for 10 min). To identify the irradiation treatment, physical detection methods like photostimulated luminescence (PSL), thermoluminescence (TL), and electron spin resonance (ESR) have been investigated before and after roasting. The photon counts of the irradiated samples (nonroasted and roasted) were higher than those of nonirradiated ones, making it possible to distinguish the two samples. The threshold values of nonroasted and roasted samples increased linearly with the irradiation dose, respectively. The TL for the nonirradiated nonroasted and roasted samples presented a lower peak at about 300 °C, but irradiated samples showed a higher peak at around 150 °C. The areas of TL glow curves were 15 times higher in nonroasted as compared with roasted samples. TL ratio [integrated area of TL_1 (the first glow)/TL_2 (the second glow)] obtained by the reirradiation step was 0 in nonirradiated samples and more than 0.15 in irradiated samples. The radiation-induced ESR signals originating from cellulose were determined in irradiated samples before and after roasting.

KEYWORDS: Sesame seeds; roasting; irradiation; PSL; TL; ESR; detection

INTRODUCTION

The roasted sesame seed (*Sesamum indicum* L.) has a typical sweet and pleasant aroma and is traditionally used as a condiment in many oriental foods in Korea (*1*). These seeds are particularly vulnerable to insect infestation, which leads to a reduction in quality and shelf life and causes public health hazard. The use of ionizing radiation is accepted as an effective treatment for the disinfestation of sesame in Brazil and Cuba (*2*). With the increase in the commercialization of irradiation technology, the demand for a convenient and reliable method for the detection of irradiated foods has grown. Photostimulated luminescence (PSL), thermoluminescence (TL), and electron spin resonance (ESR) are physical methods that have been demonstrated to be useful for the identification of irradiated cereal grains (*3*).

PSL and TL are radiation-specific phenomena from energy stored by trapped charge carriers following irradiation (*4*). The PSL detection method has been studied as a screening method using whole samples for many irradiated foods including brown shrimps, herbs, spices, seasonings, and shellfish (*5*). TL has been tested for detecting various foods, such as spices and herbs (*6*), shellfish (*7*), foods containing salt (*8*), potatoes (*9*), dried fruits (*10*), and dried anchovy and shrimp (*11*). Results of the studies revealed that it is an appropriate method for detecting irradiated foods, from which silicate minerals could be isolated (*12*). ESR spectroscopy can measure free ions or radicals produced by dissociation molecules resulting form irradiation energy (*13*). It has been successfully employed for the detection of some irradiated aromatic herbs, spices, fruits (*14*), and dried teas (*15*). Hence, the aim of this research was to investigate PSL, TL, and ESR characteristics for the detection of irradiated sesame before and after roasting.

MATERIALS AND METHODS

Materials, Irradiation, and Roasting Treatment. Sesame seeds were purchased from local markets in Daegu, South Korea. Sesame seeds were packed (2 kg in each pack) in low-density polyethylene film and irradiated at doses ranging from 0 to 4 kGy using a Cobalt-60 γ irradiator (100 kCi point source AECL, IR-79, MDS Nordion International Co. Ltd., Ottawa, ON, Canada) at the Korean Atomic Energy Research Institute (Daejon, South Korea). A ceric/cerous dosimeter (Harwell, United Kingdom) was used to confirm the total absorbed doses, and the error range was within ±5.6%. Two kilograms of the samples was roasted at 220 °C with agitation (50 rpm) for 10 min (*16, 17*) using an electric roaster (JIS-E04, JEIL Ind. Co. Ltd.,

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Table 1. PSL Analysis of Irradiated Sesame at Different Doses

	irradiation dose (kGy)				
sample	0	0.5	1	2	4
nonroasted	303 ± 48[a](−)[b]	68794 ± 20477(+)	102943 ± 51384(+)	162287 ± 108891(+)	327661 ± 153163(+)
roasted[c]	294 ± 118(−)	49662 ± 6193(+)	71259 ± 21196(+)	97362 ± 14458(+)	180219 ± 84533(+)

[a] Mean ± SD ($n = 3$) (unit, PC). [b] Threshold value: $T_1 = 700$ (nonirradiated), $T_2 = 5000$ (irradiated), (−) < T_1, T_1 < (M) < T_2, and (+) > T_2. [c] Sesame seeds were roasted at 220 °C for 10 min.

Seoul, South Korea), which are the commercial conditions for roasting the sesame seeds. Nonirradiated control and irradiated sesame seeds before and after roasting treatment were stored under dark conditions at room temperature (20 ± 1 °C).

PSL Measurements. PSL measurements were performed as described by EN 13751 (*18*) using a SURRC PPSL Irradiated Food Screening System (SURRC, Glasgow, United Kingdom). The PPSL system (serial; 0021, SURRC; Scottish Universities Research and Reactor Centre, United Kingdom) was used for PSL measurement of the whole samples (≤5 g) placed in a disposable Petri dish with a 50 mm diameter (Bibby sterlin type 122, Glasgow, United Kingdom). The PSL signal was recorded at a rate of counts/60 s for both the control and the irradiated samples. The PSL signals (photon counts, PCs) emitted from the sample per second were automatically accumulated in the PC and presented as counts/60 s. PSL signals were compared with two thresholds, the lower threshold (T_1, 700 counts/60 s) and upper threshold (T_2, 5000 counts/60 s). Signals between the two thresholds were classified as intermediate, which requires further investigations for the confirmation of the test samples whether or not they have been irradiated. Distribution and handling of the samples were carried out under subdued lighting.

X-ray Diffraction (XRD) Measurements. A multipurpose X-ray diffractometer (MP XRD, X′ Pert Pro, PANalytical, The Netherlands) was used to characterize the inorganic dust minerals (0.5 g) present in sesame seeds. The X-ray diffractometer was calibrated using silicon powder (corundum) as a standard reference material, and all of the measurements were conducted under the following conditions: X′ celerator (Ultra fast) detector; 0−60 degrees of scan angle; 11.9 deg/s of scan rate, Gonio of scan axis; continuous scan mode; and radiations of Cu Kα having a wavelength of 1.540598 Ao. The XRD spectra for the inorganic dust mineral samples were obtained between 0 and 60° θ at a 2° θ scan. Each peak of the XRD spectra was identified by comparing it with the reference data of 400 mineral candidates.

TL Measurements. The methods for TL analysis were conducted based upon the EN 1788 (*12*) in which the inorganic minerals (≥0.5 mg) were separated from the samples by rinsing the surface of the sesame seeds from each batch ($n = 3$). TL measurements were performed using the TLD system (Harshaw TLD-4500, Dreieich, Germany) with pure N_2 gas (99.99%). The temperature increased from 50 to 400 °C at a scan rate of 5 °C/s. After the TL glow curve (the first glow, TL_1) measurement, the TL characteristics in minerals were completely removed by annealing (400 °C, 5 s). To normalize the result of TL_1, the tested minerals were reirradiated at 1 kGy, and the TL glow curve (the second glow, TL_2) was measured. Finally, the TL ratio (integrated area of TL_1/TL_2 between 150 and 250 °C) was calculated as the threshold value: less than 0.1 for nonirradiated samples and more than 0.1 for irradiated ones.

ESR Measurements. ESR spectroscopy was performed according to European Standards to detect cellulose radicals using EN 1787 (*19*). Measurements were carried out in ESR spectrometer (JES-TE300, Tokyo, Japan). Samples were dried in an oven (40 °C) for 48 h to remove moisture and short-life ESR signals. The dried samples were ground, and about 0.5 g was placed in a ESR quartz tube ($n = 3$). The ESR spectrum was measured at a microwave frequency of 9.187 GHz, a magnetic field of 327.22 ± 0.5 mT, a microwave power of 0.4 mW, modulation of 100 kHz, a time constant of 0.03 s, a sweep width of 10 mT, and a sweep time of 30 s using an ESR spectrometer (JES-TE300, Jeol Co., Tokyo, Japan). At this time, the spectra of samples were scanned to record the signal intensity (peak-to-peak height).

Statistical Analysis. All measurements were done for three different packs ($n = 3$). The data were analyzed using Origin 6.0 (Microcal Software Inc., Northampton, MA) (*20*).

RESULTS AND DISCUSSION

PSL Characteristics. Table 1 shows the results of the PSL PCs for the control and γ-irradiated sesame seeds before and after roasting. The PCs of both nonirradiated samples before and after roasting treatment were 303 and 294, which were less than the lower threshold value (700 counts/60 s), indicating a clear negative (T_1, nonirradiated). On the other hand, the PCs of the irradiated sesame seeds (nonroasted and roasted) were higher than those of nonirradiated ones (5000 counts/60s), making it possible to screen the two samples (*18*). The threshold values of nonroasted and roasted samples increased linearly with the irradiation dose, respectively. In a surveillance check conducted in the United Kingdom in 1996, the PSL was also used as a first screening method for several products, followed later by TL measurement to confirm those samples that had been identified as “intermediate” (lower threshold T_1 of 700 counts/60 s) or “positive” (upper threshold T_2 of 5000 counts/60 s).

Mineral Composition. After the mineral phase was separated from the whole sample, its composition was determined using XRD. The results of the XRD analysis on the composition of inorganic dust minerals contaminating sesame seeds are shown in **Figure 1** and **Table 2**. The mineral composition in relative abundance indicated the presence of quartz, feldspar, and clay mineral (muscovite and kaolinite) in all of the dust samples. The main mineral ingredients are feldspar (55%) and quartz (38%). Quartz and feldspar can be the sources of signals in PSL and TL analyses (*21, 22*).

TL Characteristics. The TL analysis of the contaminated minerals isolated from foodstuffs is a promising method for irradiation identification (*4, 12, 22, 23*). **Table 3** shows TL signal intensity of separated minerals from the irradiated sesame seeds at 0−4 kGy absorbed doses before and after roasting at commercial conditions of 220 °C for 10 min (*16, 17*). The intensity of the glow curves for both irradiated and nonirradiated samples showed a significant difference. TL measurement revealed the first TL glow curves (TL_1) with very low intensity at 200−300 °C in nonirradiated samples but with higher intensity between 150 and 250 °C in irradiated samples at 0.5−4 kGy, which implies that large differences can be found not only in TL glow curve shapes but also in TL signal intensity between irradiated and nonirradiated samples (**Figure 2**). The integrated TL areas from 150 to 250 °C linearly increased with irradiation doses. TL ratios (TL_1/TL_2 measured after 1 kGy irradiation for the TL_1-tested mineral) calculated through the normalization step were adopted to enhance the reliability of TL_1 results (*12, 24*). The European Committee for Standardization (CEN) has proposed thresholds not employing the whole integrated area of the glow curve but just the interval (150−250 °C). When using this recommended temperature interval, TL ratios of irradiated samples are typically greater than 0.5, whereas those of nonirradiated samples are below 0.1. If the ratio is between

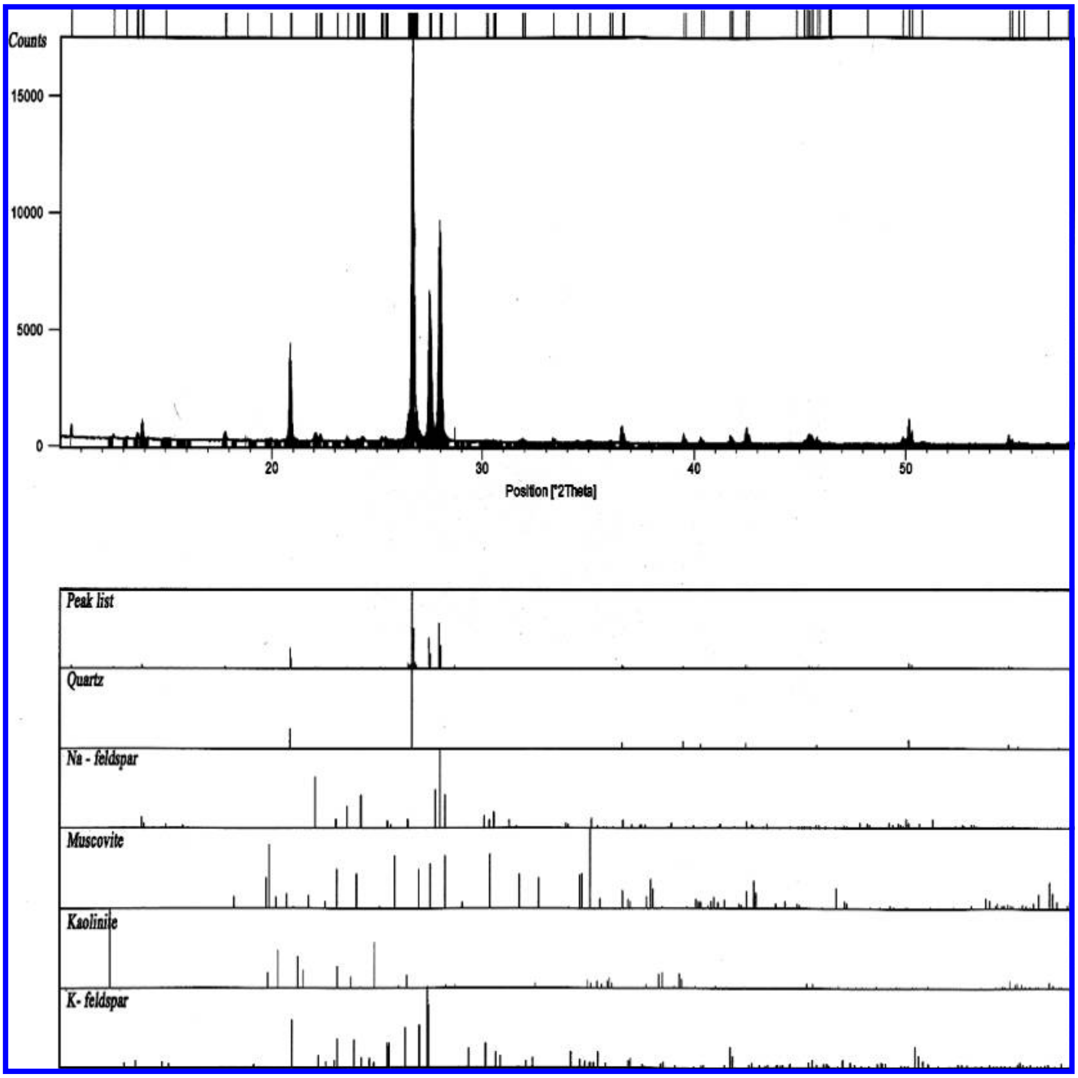

Figure 1. XRD spectrum of inorganic dust particles separated from sesame.

Table 2. Chemical Analysis by XRD of Inorganic Dust Particles Separated from Sesame (Unit, wt %)

		feldspar		clay mineral		
sample	quartz	Na-feldspar	K-feldspar	muscovite	kaolinite	total
sesame seeds	38.2 ± 0.3[a]	35.7 ± 0.4	18.6 ± 0.2	6.5 ± 0.2	1.0 ± 0.1	100.0

[a] Mean ± SD ($n = 2$).

Table 3. TL Ratio of Minerals Separated from Irradiated Sesame at Different Doses

		irradiation dose (kGy)					
TL glows	sample	0	0.5	1	2	4	*F* value[a]
TL_1	nonroasted	0.06 ± 0.00[b]	9.00 ± 0.35 d	23.76 ± 2.77 c	30.87 ± 0.26 b	38.51 ± 2.15 s	267.05***
	roasted[c]	0.04 ± 0.01 g	2.02 ± 0.32 fg	3.35 ± 0.76 ef	4.08 ± 1.21 ef	5.61 ± 0.30 e	
TL_2	nonroasted	33.17 ± 9.19 a	27.20 ± 1.05 ab	26.91 ± 2.41 ab	21.60 ± 0.54 bc	16.55 ± 0.74cd	9.84***
	roasted	13.90 ± 0.66 cd	13.57 ± 1.48 d	16.23 ± 1.95 cd	13.49 ± 2.25 d	12.06 ± 2.33 d	
TL ratio[d]	nonroasted	0.00 ± 0.00 f	0.33 ± 0.01 de	0.89 ± 0.18 c	1.44 ± 0.02 b	2.33 ± 0.23 a	116.89***
	roasted	0.00 ± 0.00 f	0.15 ± 0.01 ef	0.20 ± 0.02 ef	0.30 ± 0.04 de	0.47 ± 0.07 d	

[a] $*p < 0.1$, $**p < 0.05$, and $***p < 0.01$. [b] Mean ± SD ($n = 3$). [c] Sesame seeds were roasted at 220 °C for 10 min. [d] Integrated TL_1/TL_2. 10 × MDL = 1.73×10^2 nC; integration temperature interval, 150−250 °C.

0.1 and 0.5, then the shape of the glow curve should be taken into account (*12*). The TL ratios, as a threshold value for the irradiated nonroasted samples, were 0.33 or higher. For all irradiated (0.5−4 kGy) samples after roasting, the ratio was 0.15−0.47. The shape of the glow curve, according to the CEN, is enough to be used to correctly identify all irradiated samples after roasting. Hence, it was apparent that both the intensity of the first glow curves (TL_1) and the temperature ranges where the peaks appeared can also be used as parameters for identifying irradiation treatment of sesame seeds (*25*).

ESR Characteristics. A single signal is observed in the ESR spectra of all irradiated and nonirradiated sesame seeds by

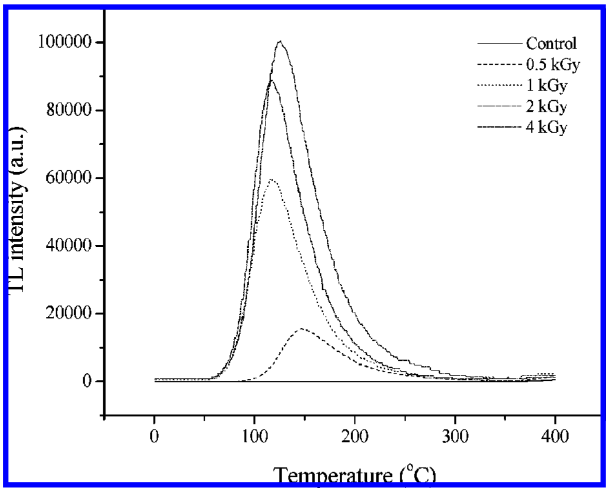

Figure 2. TL glow curve of minerals separated from irradiated sesame at different doses.

Table 4. ESR Signal Intensity of Irradiated Sesame at Different Doses[a]

	irradiation dose (kGy)				
sample	0	0.5	1	2	4
nonroasted		598 ± 30[a]	1023 ± 38	1867 ± 56	2341 ± 70
roasted[b])		355 ± 41	537 ± 40	1094 ± 71	1578 ± 94

[a] Mean ± SD (n = 3). [b] Sesame seeds were roasted at 220 °C for 10 min.

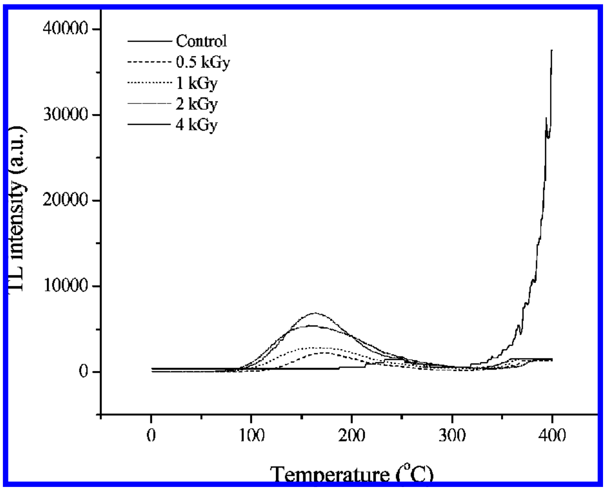

Figure 3. TL glow curve of minerals separated from roasted irradiated sesame at 220 °C for 10 min.

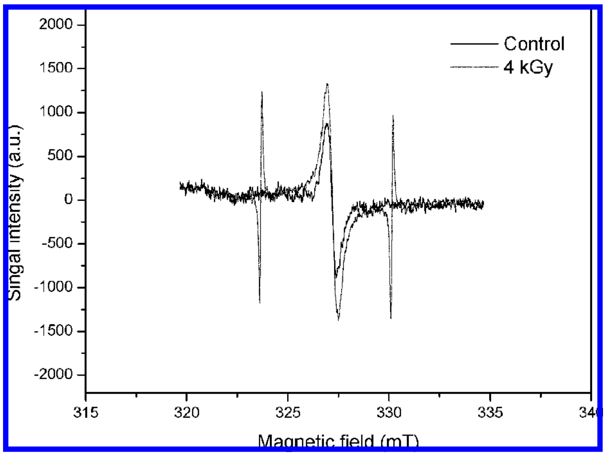

Figure 4. Characteristic ESR spectra of irradiated sesame at different doses.

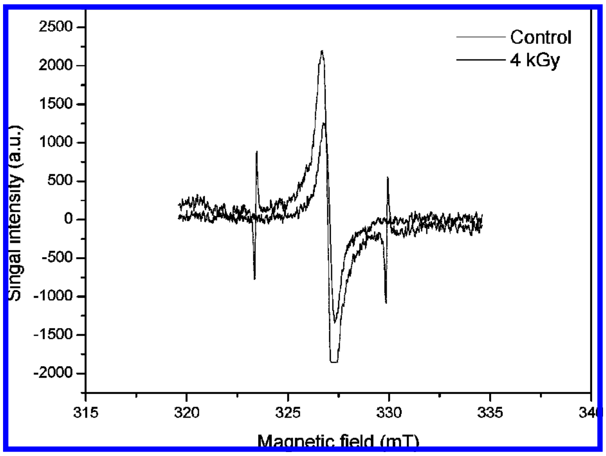

Figure 5. Characteristic ESR spectra of roasted irradiated sesame at 220 °C for 10 min.

roasting (**Table 4**). A pair of lines occurs to the left and right of the central signal in ESR spectra due to the cellulose radicals formed by ionizing radiation (*4, 8, 12*). The spacing of this radiation-induced signal pair is about 6.0 mT and is symptomatic of the radiation treatment it underwent. The g values (center of spectrum) were at 2.001 ± 0.0005 for irradiated sesame seeds before and after roasting. In the case of the irradiated samples, the intensity of signals was increased significantly with the irradiation dose. Furthermore, the ESR spectra of irradiated samples before and after roasting (**Figures 4** and **5**) showed a sharp increase in their signal intensities as compared to the control without creating any apparent pattern changes in their spectra. On the other hand, the sextet, which is due to the presence of Mn^{2+} ions, was measured in both control and irradiated samples. The ESR signal from Mn^{2+} is influenced by fluctuation of Mn^{2+} bonding in the plant protein complexes (*26*). However, the sextet had no effect on the radiation-induced signal of sesame seeds (**Figure 3**).

In conclusion, the PCs of the irradiated samples (non-roasted or roasted) were higher than those of the nonirradiated ones, making it possible to distinguish irradiated from nonirradiated ones. The inorganic dust particles from the sesame seeds were mainly composed of feldspar and quartz minerals, in which the former could be the predominant source of signals in luminescence analyses. The intensity of the first glow curves (TL_1) and the temperature ranges where the peaks appeared were confirmed as the identification parameters for irradiated sesame seeds even after roasting treatment. The TL ratios calculated through the normalization step could enhance the reliability of TL_1 results. The radiation-induced ESR signals originating from cellulose were determined in irradiated samples before and after roasting. Finally, applications of different analytical methods, such as PSL, TL, and ESR, could detect irradiated sesame seeds even after roasting treatment.

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