Food Sci. Biotechnol. Vol. 18, No. 2, pp. 374 ~ 378 (2009)

Food Science and Biotechnology

Properties of PSL, TL, and ESR to Identify the Irradiated Sesame Seeds after Steaming

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Abstract Three physical methods, photostimulated luminescence (PSL), thermoluminescence (TL), and electron spin resonance (ESR), have been applied to detect the irradiation treatment for the non- and steamed sesame seed samples. PSL successfully screened the irradiated samples from the non-irradiated control by comparing their photon counts (PCs) with the lower (less than 700 count/60 sec) and upper threshold values (higher than 5,000 count/60 sec). TL signals were still detected in all irradiated samples even after steaming, which was reconfirmed with TL ratios [integrated area of TL_1 (the first glow)/ TL_2 (the second glow)] through re-irradiation step. ESR spectrometry showed that radiation-induced cellulose radicals were detected in all the irradiated samples irrespective of steaming treatment. Identification of the irradiated sesame seeds was possible even after steaming by analyzing PSL, TL, and ESR.

Keywords: sesame seed, irradiation, steaming, photostimulated luminescence, thermoluminescence, electron spin resonance

Introduction

Sesame seed (*Sesamum indicum* L.), the oldest oilseed crop for about 6,000 years (1), is mainly produced in China, India, Myanmar, and Sudan contributing to approximately 70% of its total world production (2). There are various forms and methods of using sesame seed and oil worldwide. East Asian countries, including Korea, Japan, and China, have a wide variety of sesame seed products. For instance, sesame seed is generally used as roasted seed and oils, paste-like product, and topping for baked foods (1). The processing treatments of sesame seed conducted in previous studies, included roasting (3), toasting (4), steaming (5,6), puffing, and pressure and microwave cooking (5,7).

Consumption of sesame seeds, oils, and seed products is steadily increasing worldwide. These seeds are particularly vulnerable to insect infestation which leads to a reduction in quality and shelf-life, and causes public health hazard. Irradiation technology has positive effects in preventing the decay of food products by decontaminating the micro-organisms as well as improving the safety and shelf-stability without compromising the nutritional or sensorial quality (8). The use of ionizing radiation is accepted as an effective treatment for the disinfestations of sesame in Cuba (max. 2 kGy) (9).

During the last decades, studies on the detection methods for irradiated foods have been extensively carried out not only to increase consumer confidence but also to promote international trade, that were based on the biological and physicochemical changes that occur in foods exposed to irradiation (10-12). Detection techniques have now been adopted by the European Committee for Standardization (CEN) (12) and on which the General Codex Methods for the Detection of Irradiated Foods were established (13). Physical detection methods, such as photostimulated luminescence (PSL), electron spin resonance (ESR), and thermoluminescence (TL), were selected in this study. PSL and TL methods are based on the emission of light when energy trapped in crystalline lattices during irradiation is released by optical or thermal stimulation (11). ESR could be used for the detecting of radiation-induced radicals of irradiated food (10).

However, further researches are required for the detection of irradiated foods after processing even though there have been studies on roasting (14-17), cooking (14,18,19), and milling (17,20). The objective of this study was to investigate PSL, TL, and ESR characteristics for the detection of irradiated sesame seeds before and after steaming.

Materials and Methods

Materials, irradiation, and steam treatment The samples of sesame seeds were purchased in local markets in Daegu, Korea. Sesame seeds were packed (2 kg/pack) in low density polyethylene (LDPE) film and irradiated at doses 0.5, 1, 2, 4 kGy using cobalt-60 gamma irradiator (100 kCi point source AECL, IR-79; MDS Nordion International Co., Ltd., Ottawa, ON, Canada) at the Korean Atomic Energy Research Institute (KAERI), Daejeon, Korea. A ceric/cerous dosimeter (Harwell, Didcot, UK) was used to confirm the total absorbed doses and the error range was within ±5.6%. Half of the samples were steamed for 20 min on a boiling waterbath. All samples were stored

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Received August 19, 2008; revised September 30, 2008;
Accepted October 11, 2008

at refrigerated temperature (4±1°C) until used.

Photostimulated luminescence (PSL) measurements The PSL measurements of irradiated sesame seeds at doses ranging from 0 to 4 kGy were performed as described by EN 13751 (21) using a Scottish Universities Research and Reactor Center (SURRC) PPSL Irradiated Food Screening System (serial 0021; Glasgow, UK). The PPSL system 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, UK) without any further treatment. The PSL signal was conducted for both the control and irradiated samples under the following conditions: a rate of count/60 sec, dark counts of 32.90±00 and light counts of 44.00±20 of the PMT noise conditions. PSL signals were compared with 2 thresholds, the lower threshold (T_1, 700 count/60 sec) and upper threshold (T_2, 5,000 count/60 sec). Signals between the 2 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.

Thermoluminescence (TL) measurements The methods for TL analysis were conducted based upon the EN 1788 (22) in which the inorganic dust minerals (≥0.5 mg) were separated from the samples by rinsing the surface of sesame seeds from each batch (n=3). For separation of adhering inorganic dust minerals form sesame seeds samples, about 300 g samples was rinsed with water after ultrasonic agitation (10 min) using a nylon sieve (125-μm). To separate the remaining organic matrix from the minerals, the minerals were treated with polytungstate solution (density 2.0 g/cm^3, $Na_6W_{12}O_{39}\cdot H_2O$), followed by HCl and NH_4OH. Subsequently, they were washed with water and acetone, fixed onto an aluminium disc using silicon, and placed in an oven at 50°C overnight before analysis using the Thermolunescence Dosimetry (TLD) system. TL measurement was performed using the TLD system (Harshaw TLD-4500; Dreieich, Germany) with pure N_2 gas (99.99%). The temperature increased from the initial temperature (50°C) to the final temperature (400°C) at a rate of 5°C/sec. After the TL glow curve (the first glow, TL_1) measurement, the TL characteristics in minerals were completely removed by annealing (400°C, 5 sec. To normalize TL_1, the tested minerals were re-irradiated at 1 kGy, and the TL glow curve (2nd glow, TL_2) was measured. Finally, the TL ratio (integrated area of TL_1/TL_2 between 150-250°C) was calculated as the threshold values; less than 0.1 for non-irradiated samples and more than 0.5 for irradiated ones. For the samples between 0.1 and 0.5, the shape of the maxima of TL_1 might confirm whether the sample is irradiated or not (24).

Electron spin resonance (ESR) measurements ESR measurements were performed according to the EN 1787 European standard (23) using ESR spectrometer (JES-TE300; Jeol Co., Tokyo, Japan). Samples were dried in an oven (40°C) for 48 hr to remove moisture and short-life ESR signals. The dried samples were ground and about 0.5 g were placed in an 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 sec, a sweep width of 10 mT, and a sweep time of 30 sec. The ESR signal strengths of samples were measured as the differences of signal heights between the major 2 peaks present in the ESR spectrum (peak to peak height).

Statistical analysis All measurements were done for 3 different packs (n=3). The data were analyzed using Origin 6.0 (Microcal Software Inc, Northampton, MA, USA).

Results and Discussion

PSL characteristics The data obtained from the analysis of PSL for non-irradiated and irradiated (0.5, 1, 2, and 4 kGy) samples before and after steaming are shown in Table 1. The moisture contents of non- and steamed sesame seeds were 8.07±0.54 and 6.15±0.43%, respectively. PSL signals revealed that the photon counts (PCs) of the non-irradiated samples before and after steaming were 303±48 and 365±7, respectively, which were much lower than the threshold value (700 count/60 sec), indicating that samples were not irradiated. However, even 0.5 kGy-irradiated samples showed 68,794 PCs, which were higher than the upper threshold value (5,000 count/60 sec), thereby identifying as irradiated. The regression analysis indicates that the PCs increased significantly with the irradiation dose. On the other hand, while PSL PCs of 0.5 kGy-irradiated sesame seeds decreased after steam treatment by approximately 90% as compared with the non-steamed

Table 1. Photostimulated luminescence (PSL) analysis of irradiated sesame seeds before and after steaming

Sample	Irradiation dose (kGy)					Correlation equation and coefficient[1)]	F-value[2)]
	0	0.5	1	2	4		
Non-steamed	303±48[3)d] (-)[4)]	68,794±20477[c] (+)	102,943±51384[c] (+)	162,287±108891[b] (+)	327,661±153163[a] (+)	y=77958x+15461 R^2=0.9901	10.87***
Steamed[5)]	365±7[d] (-)	6,243±262[d] (+)	6,246±117[d] (+)	40,690±9403[c] (+)	54,463±12908[c] (+)	y=14659x-386 R^2=0.9079	

1)x: irradiation dose (kGy), y: photon count.
2)***p<0.01.
3)Mean±SD (n=3), (unit: photon count); a-dMeans with the different superscripts are significantly different among groups by Duncans's multiple-range test in one-way ANOVA.
4)Threshold value: T_1=700 (non-irradiated), T_2=5,000 (irradiated), (-)<T_1, T_1<(M)<T_2, (+)>T_2.
5)Sesame seeds were steaming for 20 min on a boiling waterbath.

Table 2. Thermoluminescence (TL) ratio of minerals separated from irradiated sesame seeds before and after steaming

TL glow	Sample	Irradiation dose (kGy)					Correlation equation and coefficient[1)]	F-value[2)]
		0	0.5	1	2	4		
TL_1	Non-steamed	0.06±0.00[e3)]	9.00±0.35[d]	23.76±2.77[c]	30.87±0.26[b]	38.51±2.15[a]	y=9.074x+6.829 R^2=0.8296	71.90***
	Steamed[4)]	0.05±0.01[e]	5.02±0.21[ed]	8.93±1.01[d]	31.99±6.85[b]	35.09±1.96[ab]	y=9.416x+2.092 R^2=0.8486	
TL_2	Non-steamed	33.17±9.19[bcde]	27.20±1.05[def]	26.91±2.41[def]	21.60±0.54[ef]	16.55±0.74[f]	y=-3.824x+30.82 R^2=0.9243	8.09***
	Steamed	48.05±7.38[a]	42.49±2.35[ab]	29.96±3.05[cde]	39.57±7.94[abc]	34.20±1.95[bcd]	y=-2.426x+42.493 R^2=0.2957	
TL ratio[5)]	Non-steamed	0.00±0.00[d]	0.33±0.01[d]	0.89±0.18[c]	1.44±0.70[b]	2.33±0.23[a]	y=0.5770x+0.1325 R^2=0.9725	36.96***
	Steamed	0.00±0.00[d]	0.12±0.00[d]	0.30±0.00[d]	0.81±0.01[c]	1.03±0.12[c]	y=0.2710x+0.0455 R^2=0.9182	

1)x, irradiation dose (kGy); y, TL glow.
2)****p*<0.01.
3)Mean±SD (*n*=3); a-eMeans with the different superscripts are significantly different among groups by Duncans's multiple-range test in one-way ANOVA.
4)Sesame seeds were steamed for 20 min on a boiling waterbath.
5)Integrated TL_1/TL_2; 10×MDL=1.73×10^2 nC integration temperature interval 150-250°C.

sample irradiated at 0.5 kGy even though it could still be identified as irradiated, which might be resulted from the light emission from minerals exposed to steaming (11). Based upon the results that the non-irradiated sesame seeds (non- and steamed) gave clear negative values while irradiated ones had positive results, PSL was found to be useful as a screening tool for identifying the irradiated sesame seeds even after steaming treatment.

TL characteristics TL method was employed to analyze whether irradiation treatment has been applied to sesame seeds (non- and steamed). The data shown in Table 2 comprises the first glow curve (TL_1), second glow curve (TL_2) which was recorded after re-irradiation step of the same mineral particles used for recording TL_1, and TL ratios [integrated area of TL_1 (1st glow)/TL_2 (2nd glow)] of non-irradiated and irradiated samples. Based upon the glow curves of non-steamed sesame seeds previously reported by Lee *et al.* (24), the glow curves of steamed sesame seeds were shown at temperature ranging from 50 to 400°C as shown in Fig. 1. The data in Table 2 showed that the response of TL_1 for both non- and steamed sesame seeds increased linearly with the irradiation dose (p<0.01). Similar phenomena with lower intensities of both PSL signals and TL ratios were found in steamed samples than the non-steamed samples following irradiation, but irradiated sesame seeds could be identified after steam treatment. The CEN proposed threshold values of glow curve ratios for non-irradiated (≤0.1) and irradiated (≥0.5) samples. For the samples with glow curve ratios between 0.1 and 0.5, the shape of the maxima of the first glow curve (TL_1) might confirm whether the sample is irradiated or not (21). In this study, the non-irradiated samples showed TL ratio less than 0.1, while the samples irradiated at more than 0.5 kGy irrespective of steaming had ratios higher than 0.1 (24). The irradiation treatment of these 3 samples was confirmed by studying the shape of the peak of the maxima of TL_1 which appeared between the temperature ranges of 150-250°C, mandatory for irradiated samples. The non-irradiated samples showed their maxima above this temperature. All the other irradiated samples had TL ratios higher than 0.5 and the shapes of the maxima of the first glow curves occur within the temperature range prescribed for irradiated samples (Fig. 1). Hence, TL study has a potential to identify the irradiation of samples provided that there is a probability of isolating even a very small amount of contaminating mineral particles from the samples. Apart from the quartz or feldspar, biogenic minerals present in the eggshells and shellfish may also be used in order to identify the irradiation treatment (25).

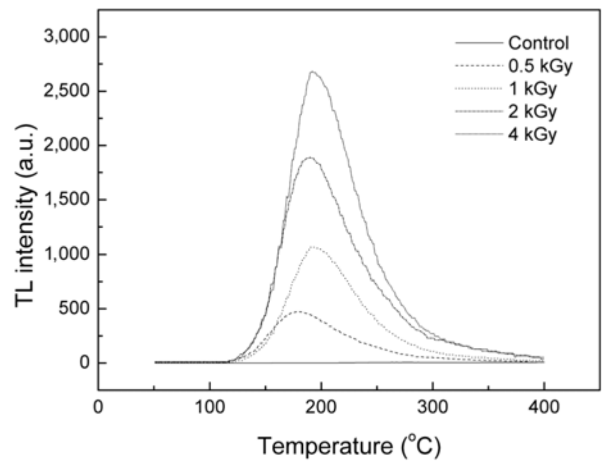

Fig. 1. Thermoluminescence (TL) glow curve of minerals separated from irradiated sesame seeds at different doses after steaming for 20 min on boiling waterbath.

ESR characteristics TL technique becomes ineffective when there was no available mineral particles on the surface

Table 3. ESR signal intensity of irradiated sesame seeds before and after steaming

Sample	Irradiation dose (kGy)					Correlation equation and coefficient[1)]	F-value[2)]
	0	0.5	1	2	4		
Non-steamed	-	598±30[e3)]	1023±38[d]	1867±56[b]	2341±70[a]	y=485.65x+546.65 R^2=0.9037	677.87***
Steamed[4)]	-	309±15[f]	629±8[e]	1014±30[d]	1385±23[c]	y=334.35x+165.68 R^2=0.9247	

[1)]x, irradiation dose (kGy); y, ESR signal intensity.
[2)]***p<0.01.
[3)]Mean±SD (n=3); [a-f]With the different superscripts are significantly different among groups by Duncans's multiple-range test in one-way ANOVA.
[4)]Sesame seeds were steaming for 20 min on a boiling waterbath.

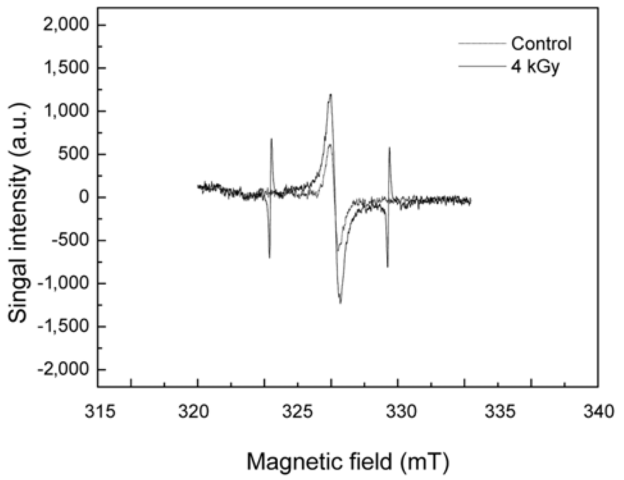

Fig. 2. Characteristic ESR spectra of 4 kGy-irradiated sesame seeds after steaming for 20 min on boiling waterbath.

of the food under investigation. Then, ESR spectrometry and DNA comet assay can be used for irradiation identification in different foods (14). In this study, ESR method was employed based upon the generation of radicals in irradiated matrices. The radiation-induced cellulose radicals were observed for the irradiated sesame samples after steaming as shown in Fig. 2, which are similar to the corresponding ESR spectra as reported previously (24). Table 3 showed the intensities of ESR signals determined for the non-irradiated and irradiated sesame seeds before and after steaming. The spacing of specific ESR spectra with a signal (g=2.02385-2.02403, 1.98701-1.98718) is about 6 mT which was derived from radiation induced cellulose radicals (25). In both non- and steamed samples, the ESR signal intensities increased with irradiation dose. But the ESR signal intensities were lower in steamed samples than in non-steamed samples. The irradiated sesame seeds could be identified by analyzing the ESR characteristics even after steaming.

In conclusion, PSL method was useful as a screening tool for differentiating the irradiated from non-irradiated sesame seed samples before and after steaming. Result of TL analysis revealed that steaming has no effect on the TL signals. With the help of TL_1 and TL ratios [integrated area of TL_1 (1^{st} glow)/TL_2 (2^{nd} glow)], all the samples were successfully identified. In both non- and steamed sesame seeds, the radiation-induced cellulose radicals were detected, showing the increased ESR signal intensities with irradiation dose. As a result, 3 different techniques, such as PSL, TL, and ESR could be applied to the identification of irradiated sesame seeds at 0.5-4 kGy even after steaming.

References

1. Namiki M. Nutraceutical functions of sesame: A review. Crit. Rev. Food Sci. 47: 651-673 (2007)
2. FAO. Major food and agricultural commodities production. Available from: http://www.fao.org/es/ess/top/commodity.html. Accessed Jun. 7, 2008.
3. Shimoda M, Nakada Y, Nakashima M, Osajima Y. Quantitative comparison of volatile flavor compounds in deep-roasted and light-roasted sesame seed oil. J. Agr. Food Chem. 45: 3193-3196 (1997)
4. Park D, Maga JA. Sensory evaluation of crude toasted canola and sesame seed oil. J. Food Lipids 4: 137-143 (1997)
5. Abou-Gharbia HA, Shehata AAY, Shahidi F. Effect of processing on oxidative stability and lipid classes of sesame oil. Food Res. Int. 33: 331-340 (2000)
6. El-Adawy TA, Mansour EH. Nutritional and physicochemical evaluations of *tahina* (sesame butter) prepared from heat-treated sesame seeds. J. Sci. Food Agr. 80: 2005-2011 (2000)
7. Mahajan A, Bhardwaj S, Dua S. Traditional processing treatments as a promising approach to enhance the functional properties of rapeseed (*Brassica campestris* var. toria) and sesame seed (*Sesamum indicum*) meals. J. Agr. Food Chem. 47: 3093-3098 (1999)
8. Kwon JH. Effects of gamma irradiation and methyl bromide fumigation on the quality of fresh chestnuts during storage. Food Sci. Biotechnol. 14: 181-184 (2005)
9. IAEA. International consultative group on food irradiation. Available from: http://www.iaea.org/icgfi/data. Accessed Jun. 7, 2008.
10. IAEA. Analytical Detection Methods for Irradiated Foods-A Review of Current Literature. IAEA-TECDOC-587. International Atomic Energy Agency, Vienna, Austria. p. 172 (1991)
11. Delincée H. Detection of food treated with ionizing radiation. Trends Food Sci. Tech. 9: 73-82 (1998)
12. Delincée H. Analytical methods to identify irradiated food. Radiat. Phys. Chem. 63: 455-458 (2002)
13. FAO/WHO CODEX STAN. General codex methods for the detection of irradiated foods. CODEX STAN 231-2001. Rev.1. (2003)
14. Bhat R, Sridhar KR. Detection of free radicals in electron beam-irradiated *Mucuna pruriens* (L. DC.) seeds by electron spin resonance. Food Sci. Technol. Int. 13: 249-257 (2007)
15. Bhushan B, Bhat R, Sharma A. Status of free radicals in Indian monsooned coffee beans-irradiated for disinfestations. J. Agr. Food Chem. 51: 4960-4964 (2003)
16. Hwang KT, Hong JS, Yang JS, Sohn HS, Weller CL. Detection of alkanes and alkenes for identifying irradiated cereals. J. Am. Oil Chem. Soc. 78: 1145-1149 (2001)
17. Hwang KT, Kim JE, Park JM, Yang JS. Effects of roasting,

powdering, and storing irradiated soybeans on hydrocarbon detection for identifying post-irradiation of soybeans. Food Chem. 102: 263-269 (2007)
18. Marchioni E, Horvatovich P, Ndiaye B, Miesch M, Hasselmann C. Detection of low amount of irradiated ingredients in non-irradiated precooked meals. Radiat. Phys. Chem. 63: 447-450 (2002)
19. Obana H, Furuta M, Tanaka Y. Detection of 2-alkylcyclobutanones in irradiated meat, poultry, and egg after cooking. Radiat. Phys. Chem. 63: 447-450 (2002)
20. Kispeter J, Horvath LJ, Szabo I. The occurrence of free radicals in milled and irradiated paprika as detected by ESR. Radiat. Phys. Chem. 55: 757-760 (1999)
21. EN 13751. Foodstuffs-Detection of irradiated food using photostimulated luminescence. European Committee for Standardization, Brussels, Belgium (2002)
22. EN 1788. Foodstuffs-Detection of irradiated food from which silicate minerals can be isolated, method by thermoluminescence. European Committee for Standardization, Brussels, Belgium (2001)
23. EN 1787. Foodstuffs-Detection of irradiated food containing cellulose by ESR spectroscopy. European Committee of Standardization, Brussels, Belgium (2001)
24. Lee J, Kausar T, Kim BK, Kwon JH. Detection of γ-irradiated sesame seeds before and after roasting by analyzing photostimulated luminescence, thermoluminescence, and electron spin resonance. J. Agr. Food Chem. 56: 7184-7188 (2008)
25. Bhatti IA, Lee J, Jang YD, Kim KS, Kwon JH. Analysis of shellfish by thermoluminescence and X-ray diffraction method: Knowledge of gamma-ray treatment and mineral characterization. Radiat. Phys. Chem. 77: 663-668 (2008)