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Properties of Pulsed Photostimulated Luminescence and Thermoluminescence for Detection of Gamma-Irradiated Teas during Storage

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Abstract

Green, black and oolong teas were irradiated by ^{60}Co-gamma rays (0～10 kGy) and were investigated for detection of irradiation treatment using pulsed photostimulated luminescence (PPSL) and thermoluminescence (TL) during storage. Teas irradiated at 2.5 kGy or more showed a photon count of greater than 5000 counts/60 sec while the non-irradiated yielded only 650～1000 count/60 sec. Correlation coefficients between irradiation dose and photon counts/60 sec were 0.8951, 0.7934 and 0.9007 for green, black and oolong teas, respectively. The TL glow curves for minerals isolated from the non-irradiated teas were situated at about 300°C with a low intensity, but for irradiated samples were approximately 150°C with a high intensity. The TL ratios (TL_1/TL_2), calculated from values after initial radiation and then after re-irradiation of the teas, were below 0.1 for the non-irradiated samples and higher than 1.44 for all irradiated samples, enhanced the reliability of the identification results for TL. The signal intensity of PPSL and TL for irradiated teas decreased with the lapse of post-irradiation storage time at room temperature but was still distinguishable from that of the non-irradiated samples even after one year.

Key words: teas, irradiation, PSL, TL, storage

INTRODUCTION

Tea is an important trade commodity that is prone to microbial contamination and pest damage at all stages, from the production period throughout storage and marketing. The conventional fumigation methods with chemicals (ethylene oxide, methyl bromide, phophine, etc.) have been prohibited or are being increasingly restricted due to food safety or environmental concerns, necessitating the development of alternative methods of decontamination (1). Food irradiation has been widely accepted and is now legally recognized in many countries as a reliable and safe method for both preserving and improving the hygienic quality of foods. A number of factors have highlighted the need for development of analytical methods for detecting irradiated foods. Reliable detection methods would increase consumer confidence in their ability to make informed decisions about irradiated foods and promote greater distribution and international trade in irradiated food by facilitating the evaluation of compliance with regulations related to use of irradiation in different countries and increasing public understanding of irradiated foods (2,3). Detection methods for irradiated foods may be classified into three basic categories as; chemical, physical and biological analysis. Photostimulated luminescence (PSL) and thermoluminescence (TL) are physical methods that have been demonstrated to be useful for the identification of irradiated spices and herbs (3).

PSL and TL are radiation-specific phenomena from energy stored by trapped charge carriers following irradiation (4). Releasing such stored energy by optical or thermal stimulation can result in a detectable luminescence emission (2). The PSL detection method has been studied as a screening method using whole samples for many irradiated foods including brown shrimp, herbs, spices, seasonings, shellfish (5,6) and white ginseng powder (7). TL has been tested as a detection method for various foods, such as spices and herbs (8), shellfish (9), and Korean traditional foods containing salt (10). Results of the studied revealed that they are appropriate methods for detecting irradiated foods, from which silicate minerals could be isolated (11).

The aim of this study is to determine the applicability of PSL or TL for identification of irradiated green, black, and oolong teas and to investigate the stability of PSL and TL signals during the post-irradiation period.

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MATERIALS AND METHODS

Materials, irradiation and storage

Three kinds of teas, green (Korean), black (Sri Lankan) and oolong (Chinese) were purchased from H. Tea Co. in Korea and packaged in a commercial PE film prior to irradiation. Gamma irradiation was carried out in a ^{60}Co irradiator at the Korean Atomic Energy Research Institute (KAERI) in Daejon, Korea. The doses ranged from 0 to 10 kGy for the prepackaged samples; and the target doses were confirmed by a ceric / cerous dosimeter (±5.6%).

Photostimulated luminescence analysis (PSL)

A PSL measurement was performed on a SURRC Pulsed PSL Irradiated Food Screening System (SURRC, Glasgow, UK). The signal levels were compared for the two thresholds, a lower threshold (T_1, 700 counts/60 sec) and an upper threshold (T_2, 5000 counts/60 sec) (12).

Thermoluminescence analysis (TL)

Minerals were separated from the test samples by a density separation procedure for TL analysis using a TL reader (Harshaw TLD-4200, Germany) at temperatures ranging between 50~400°C (13). The first glow curve (TL_1) was compared with the second glow curve (TL_2) obtained after re-irradiation at 1 kGy. The ratios of TL_1/TL_2 were calculated for both irradiated and non-irradiated samples to verify the reliability of detection results. Samples were stored in a dark room for one year.

Statistical analysis

Data was subjected to analysis of variance (ANOVA) by using SAS software. Differences between groups were separated by Duncan's multiple range test (14).

RESULTS AND DISCUSSION

Photostimulated luminescence characteristics

The photon counts from non-irradiated samples were 1001 counts/60 sec for green tea, 786 counts/60 sec for black tea and 650 counts/60 sec for oolong tea (Table 1). In previous reports on PSL measurements for different foods such as dried spices, condiments and shrimp, photon counts ranging between 700 counts/60 sec and 1000 counts/60 sec were detected in non-irradiated foods, while irradiated foods showed a higher photon count (4000~5000) (6,13). Chung et al. (15) also found photon counts for non-irradiated shrimp of more than 700 counts /60 sec. Radiation-induced PPSL signals increased significantly with irradiation doses up to 10 kGy. Based on these threshold values, PSL measurements were suitable for green, black and oolong teas in order to detect whether or not they had been irradiated. These results were consistent with reports indicating that the accumulated PSL signals of irradiated Chinese sesame and perilla seeds, Sudanese seeds (16), Korean sesame and perilla seeds (17), corn powder (18), starches, cereals and beans (19) were higher than those of the same food that had not been irradiated, and the increase was highly correlated with the irradiation dose. As mentioned above, non-irradiated green and black teas yielded intermediate signals, requiring other detection method like TL or ESR (electron spin resonance) for the verification of results (6). The PSL method, however, is regarded as a simple, yet effective, screening tool. Yi and Yang (20) suggested that, if the PPSL response of irradiated materials is significantly greater than that of non-irradiated materials, or if the fading of the PPSL response is low during long-term storage, the PPSL measurement may be suitable for the detection of food irradiation. Therefore, the decay rates were observed for the accumulated PPSL signals in the non-irradiated and irradiated green, black and oolong teas during storage. The PPSL signals of all irradiated samples were apparently influenced by the storage period. These results were consistant with the reports

Table 1. Pulsed photostimulated luminescence characteristics of irradiated teas at different doses

Sample	Storage period (month)	Irradiation dose (kGy)					Correlation equation and coefficient[2)]	
		0	2.5	5	7.5	10		
Green tea	0	$1001 \pm 213^{1)ex}$	20773 ± 150^{dx}	21293 ± 153^{cx}	31257 ± 182^{bx}	36125 ± 195^{ax}	$Y=8073.2x-2129.8$	$R^2=0.8950$
	12	1067 ± 213^{cx}	5172 ± 4223^{by}	20097 ± 2945^{ax}	23230 ± 9395^{ax}	28676 ± 13012^{ax}	$Y=7327.6x-6334.4$	$R^2=0.9431$
Black tea	0	786 ± 494^{ex}	5202 ± 443^{dx}	6038 ± 988^{cx}	7076 ± 194^{bx}	7327 ± 196^{ax}	$Y=1495.6x+799$	$R^2=0.7934$
	12	384 ± 91^{cy}	2280 ± 839^{by}	2884 ± 470^{by}	4064 ± 1349^{ay}	4839 ± 927^{ay}	$Y=1069.4x-318$	$R^2=0.9668$
Oolong tea	0	650 ± 91^{ex}	8353 ± 101^{dx}	10894 ± 113^{cx}	13714 ± 125^{bx}	15117 ± 130^{ax}	$Y=3429.5x-542.9$	$R^2=0.9007$
	12	688 ± 494^{dx}	3782 ± 560^{cy}	5520 ± 951^{by}	7157 ± 147^{ay}	7212 ± 1389^{ay}	$Y=1642.3x-55.1$	$R^2=0.9048$

[1)] Means of triplicate ± standard deviation. Unit: Counts/60 sec.

[2)] x: Irradiation dose (kGy), Y: Photon count.

[a-e] Mean values within a row followed by the same superscript are not significantly different ($p<0.05$).

[x-y] Mean values within a column for each sample followed by the same superscript are not significantly different ($p<0.05$).

on Ramen soup powder that PPSL was influenced by light as well as the storage time (21). The accumulated PPSL signals of the green, black and oolong teas irradiated at 10 kGy after 12 months decreased to approximately 20.62, 33.95 and 52.29% of the initial values, respectively. Although the accumulated PPSL signals of all tea samples decreased during the storage period, there was still a marked difference in the photon counts between the irradiated and non-irradiated samples (the irradiated sample had a higher photon count). These results suggest that still possible to distinguish irradiated from non-irradiated teas, even after a 12 month-storage period.

Thermoluminescence characteristics

The TL glow curves of minerals isolated from the irradiated and non-irradiated green, black and oolong teas were recorded within 2 weeks after irradiation. The glow curves from the irradiated samples peaked at approximately 150°C with high intensity, whereas the non-irradiated samples peaked at temperature above 300°C (Fig. 1). The intensities of the glow curves were significantly higher in the irradiated than non-irradiated samples ($p < 0.05$). The European Committee for Standardization (CEN) has proposed threshold values by employing only the areas within the recommended temperature interval (150 ~250°C) and not the entire integration area of the glow curve. It has been found that reliability of detection can be improved by extracting the minerals from samples, plating them on a stainless steel disc, re-irradiating the sample, and comparing the TL with a previous TL (TL_1 to TL_2) (22-24). Therefore, the irradiated and non-irradiated samples were gamma-irradiation at 1 kGy and the TL_1 to TL_2 ratio was calculated. The TL ratio (integrated TL_1/TL_2) from the irradiated samples are typically greater than 0.5, whereas those from non-irradiated samples are generally less than 0.1 (Table 2). It is known that the TL signals are stable and can be analyzed after a long-term post-irradiation period (25). Therefore, the storage effects on the TL signals were determined for each sample. Fig. 2 illustrates the changes in TL intensity of irradiated green, black and oolong teas at 5 kGy after 12 months of storage at room temperature. Compared to the TL measurement taken soon after irradiation, the TL intensity after 12 months decreased in all irradiated green, black and oolong teas. Nevertheless, the difference in the TL ratio between the irradiated and non-ir-

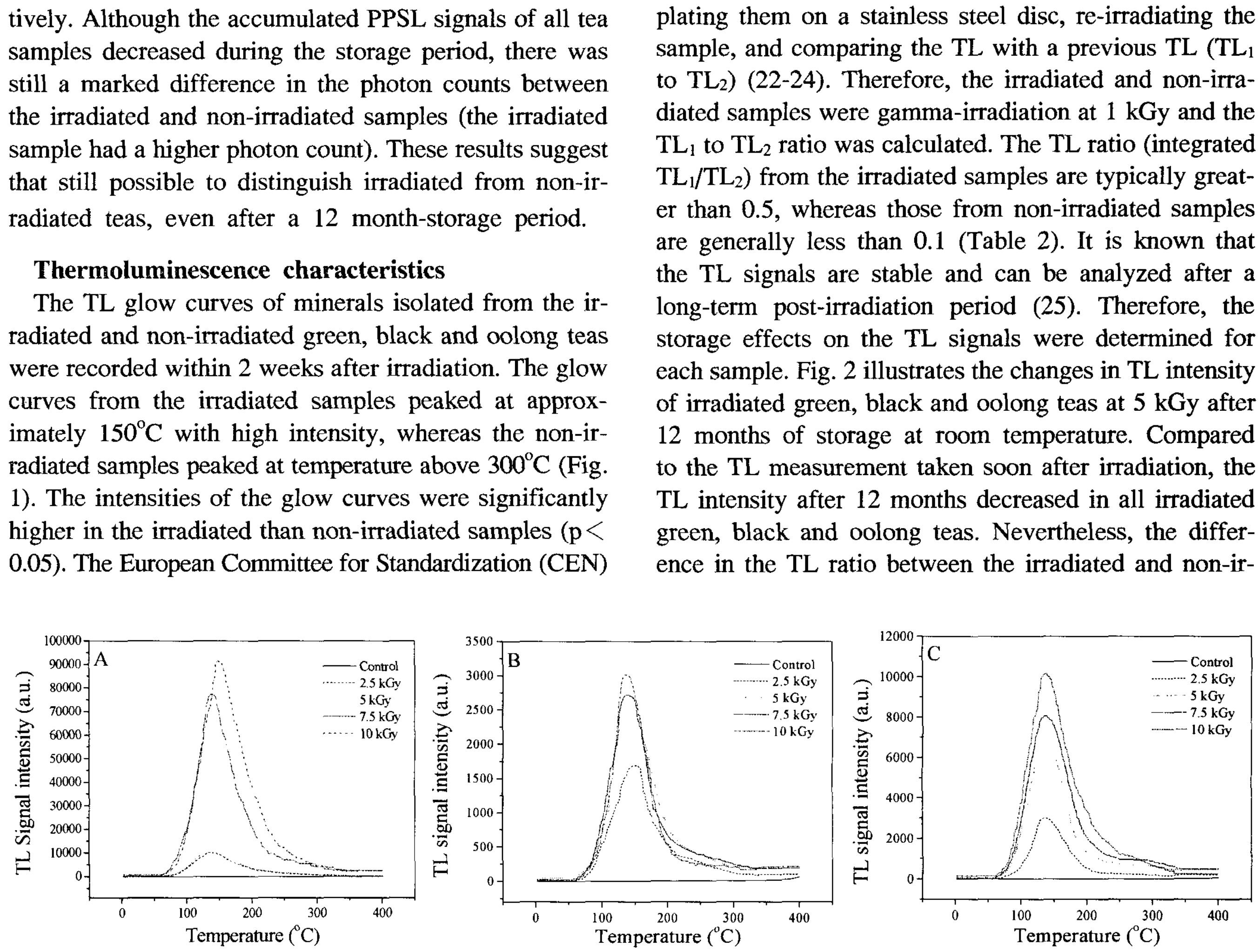

Fig. 1. Glow curves of minerals separated from teas irradiated at different doses (A: Green tea, B: Black tea, C: Oolong tea).

Table 2. TL ratio of minerals separated from irradiated teas at different doses

Sample	Storage period (month)	TL ratio[1)]					Correlation equation and coefficient[2)]	
		0 kGy	2.5 kGy	5 kGy	7.5 kGy	10 kGy		
Green tea	0	$0.01 \pm 0.00^{3)ex}$	2.66 ± 0.11^{dx}	3.14 ± 0.09^{cx}	3.52 ± 0.14^{bx}	3.96 ± 0.19^{ax}	$Y=0.8746x+0.03465$	$R^2=0.792$
	12	0.01 ± 0.00^{ex}	1.33 ± 0.10^{dy}	1.43 ± 0.03^{cy}	1.76 ± 0.14^{by}	2.30 ± 0.05^{ay}	$Y=0.5030x-0.14340$	$R^2=0.872$
Black tea	0	0.01 ± 0.01^{ex}	1.44 ± 0.14^{dx}	2.04 ± 0.09^{cx}	4.10 ± 0.16^{bx}	4.78 ± 0.14^{ax}	$Y=1.2179x-1.17900$	$R^2=0.973$
	12	0.01 ± 0.00^{ex}	1.08 ± 0.12^{dy}	1.27 ± 0.08^{cy}	2.04 ± 0.04^{by}	2.34 ± 0.13^{ay}	$Y=0.5537x-0.30360$	$R^2=0.952$
Oolong tea	0	0.06 ± 0.04^{ex}	1.81 ± 0.06^{dx}	1.99 ± 0.13^{cx}	3.02 ± 0.06^{bx}	3.17 ± 0.03^{ax}	$Y=0.7425x-0.21890$	$R^2=0.889$
	12	0.01 ± 0.00^{ex}	1.25 ± 0.16^{dy}	1.63 ± 0.04^{cy}	2.01 ± 0.08^{by}	2.91 ± 0.14^{ay}	$Y=0.6575x-0.14410$	$R^2=0.948$

[1)] Integrated TL_1/TL_2.
[2)] x: Irradiation dose (kGy), Y: TL ratio.
[3)] Mean of triplicates.
[a-e] Mean values within a row followed by the same superscript are not significantly different ($p < 0.05$).
[x-y] Mean values within a column for each sample followed by the same superscript are not significantly different ($p < 0.05$).

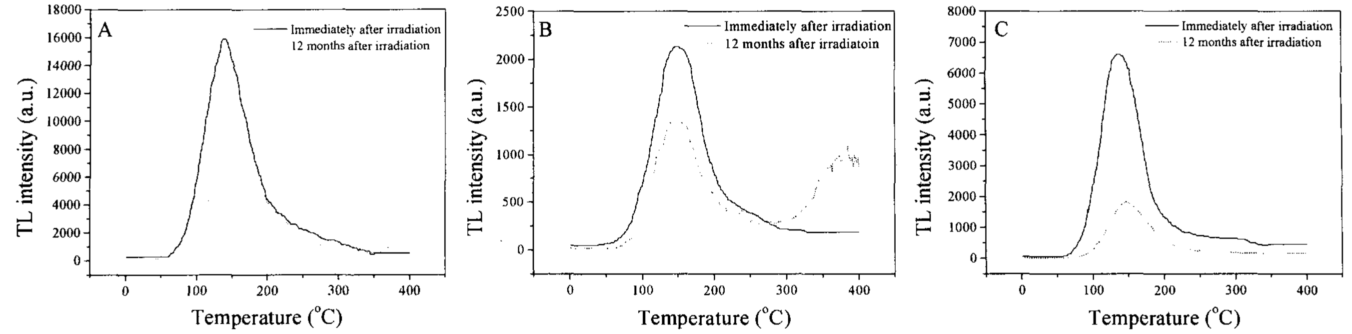

Fig. 2. Stability of TL glow curves for 5 kGy gamma-irradiated teas after a 12 month storage period at room temperature (A: Green tea, B: Black tea, C: Oolong tea).

radiated teas was sufficient to discriminate between them, even after 12 months of storage at room temperature (26-28).

It can be concluded that the irradiation treatment of dried teas, such as green, black and oolong teas can be identified with PSL or TL methods. PSL has been proven to be useful as a screening method, when a large number of samples need to be identified. To receive verifiable proof of irradiation, however, TL is recommended as a means of verification. Despite the fading of PSL and TL signals over time it is still possible to distinguish between irradiated and non-irradiated teas, even after one year of storage.

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REFERENCES

1. UNEP. 1995. Montreal protocol on substances that deplete the ozone layer. In *Report of the methyl bromide technical option committee*. ISBN 92-807-1448-1, Nairobi, Kenya. p 139-168.
2. Delincée H. 1998. Detection of food treated with ionizing radiation. *Trends Food Sci Technol* 9: 73-82.
3. Delincée H. 2002. Analytical methods to identify irradiated food-a review. *Radiat Phys Chem* 63: 455-458.
4. McMurray CH, Stewart EM, Gray R, Pearce J. 1996. *Detection methods for irradiated foods-current status*. Royal Society of Chemistry, Cambridge, UK.
5. Sanderson DCW, Carmichael LA, Naylor JD. 1996a. Recent advances in thermoluminescence and photostimulated luminescence detection methods for irradiated foods. In *Detection methods for irradiated foods*. McMurray CH, Stewart EM, Gray R, Pearce J, eds. The Royal Society of Chemisty, Cambridge, UK. p 124-138.
6. Sanderson DCW, Carmichael LA, Spencer JQ, Naylor JD. 1996b. Luminescence detection of shellfish. In *Detection methods for irradiated foods*. McMurray CH, Stewart EM, Gray R, Pearce J, eds. The Royal Society of Chemisty, Cambridge, UK. p 139-148.
7. Chung HW, Delincée H, Kwon JH. 2000. Photostimulated luminescence-thermoluminescence application to detection of irradiated white ginseng powder. *Korean J Food Sci Technol* 32: 265-270.
8. Autio T, Pinnoja S. 1990. Identification of irradiated foods by the thermoluminescence of mineral contamination. *Z Leberns Unters Forsch* 191: 177-180.
9. Schreiber GA, Hoffmann A, Helle N, Bgl KW. 1994a. Methods for routine control of irradiated food. Determination of irradiation status of shellfish by thermoluminescence analysis. *Radiat Phys Chem* 43: 533-544.
10. Kwon JH, Chung HW, Byun MW, Kang IJ. 1998. Thermoluminescence detection of Korean traditional foods exposed to gamma and electron beam irradiation. *Radiat Phys Chem* 52: 151-156.
11. European Committee Standard. 1997. Detection of irradiated food from which silicate minerals can be isolated, Method by thermoluminscence. English version of DIN EN 1788 Brussek, Bekgium.
12. Bayram G, Delincée H. 2004. Identification of irradiated Turkish foodstuffs combining various physical detection methods. *Food Control* 15: 81-91.
13. Khan HM, Bhatti IA, Delince H. 2002. Thermoluminescence of contaminating minerals for the detection of radiation treatment of dried fruits. *Radiat Phys Chem* 63: 403-406.
14. SAS. 2001. *SAS User's Guide*. Statistical Analysis System Institute. Version 8.0. Cary, NC, USA.
15. Chung HW, Delincée H, Kwon JH. 2002. The application of different detection methods for irradiated dried anchovy and shrimp. *Radiat Phys Chem* 63: 411-414.
16. Sanderson DCW, Carmichael LA, Fisk S. 1997. An international collaborative blind trial of photostimulated luminescence detection of irradiated herbs, spices and seasonings. Final Report, MAFFIB073.
17. Yi SD, Woo SH, Yang JS. 2001. Pulsed photostimulated luminescence (PPSL) of irradiated imported sesame and perilla seeds. *Korean J Food Sci Technol* 33: 173-177.
18. Yi SD, Woo SH, Yang JS. 2000. The use of pulsed photostimulated luminescence (PPSL) and thermoluminescence (TL) for detection of irradiated perilla and sesame seeds. *J Food Sc Nutr* 5: 142-147.
19. Yi SD, Chang KS, Yang JS. 2001. Trial to identify irradiated corn powder by viscometric and pulsed photostimulated luminescence (PPSL) methods. *J Food Hyg Safety* 16: 82-87.

20. Yi SD, Yang JS. 2000. The application of a pulsed photostimulated luminescence (PPSL) method for the detection of irradiated foodstuffs. *J Food Sci Nutr* 5: 136-141.
21. Yi SD, Yang JS, Oh MJ, Chang KS. 2002. Effect of storage conditions and the role of ash content in thermoluminescence (TL) characteristics and pulsed photostimulated luminescence (PPSL) at Ramen (instant noodle) soup powders irradiated at different particle size. *Food Sci Biotechnol* 11: 147-160.
22. Yi SD, Yang JS. 2001. Properties of pulsed photostimulated luminescence and thermoluminescence of gamma-irradiated shrimp-taste seasoning powder. *Food Sci Biotechnol* 10: 408-413.
23. Sanderson DCW, Slater C, Cairns KJ. 1989. Thermoluminescence of foods: origin and implications for deleting irradiations. *Radiat Phys Chem* 34: 915-924.
24. Delincée H. 1992. Detection methods for irradiated foods. In *Irradiation for the food sector*. Proceeding Symp. Agriculture Canada, Saint Hyacinthe (Que-bec) Canada. p 24-60.
25. Wagner U, Jokob M, Leffke A, Helle N, Bgl KW, Schreiber GA. 1993. Methods for routine control; viscosity analysis on pepper-thermoluminescence analysis on minerals of spices, herbs, fruit and vegetables. In *Recent advances on detection of irradiated foods*. Leanardi M, Belliardo JJ, Raffi JJ, eds. EUR 14315, Commission of European Communities, Luxerbourg. p 155-172.
26. Schreiber GA, Wagner U, Leffke A, Helle N, Ammon J, Buchholtz HV, Delincée H, Estendorfer S, Fuchs K, Grabowski von HU, Kruspe W, Mainczyk K, Mung H, Nootenboom H, Schleich C, Vreden N, Wiesorek C, Bgl KW. 1993. *Thermoluminscence analysis to detect irradiated spices, herbs and spices-and herb mixture-an intercomparison study.* Beiricht des instituts fur sozialmedizin und epidemiologie des bundesgesund-heitsamtes, SozEp-Heft 2/1993, Bundesgesundheitsamt, Berlin.
27. Kwon JH, Jeong J, Chung HW. 2002. Thermoluminescence characteristics of minerals from irradiated potatoes of different origins of production. *Radiat Phys Chem* 63: 415-418.
28. Mamoon A, Abdul-Fattah AA, Abdulfaraj WH. 1994. Thermoluminescence of irradiated herbs and spices. *Radiat Phys Chem* 44: 203-206.

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