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Identification of Gamma Irradiation of Imported Spices

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Abstract

Photostimulated Luminescence (PSL), Electron Spin Resonance (ESR) and Thermoluminescence (TL) analysis were conducted to detect irradiation treatment of imported whole and ground spices. The screening by PSL detected no irradiation treatment, except in the ground thyme and bay leaves which exhibited photon counts in the intermediate level. Irradiation of the two spices was detected after irradiating them at 1.0, 3.0, 5.0 and 10.0 kGy, and then subjecting them to PSL analysis, which resulted in the significantly low photons of non-irradiated spices compared to that at 1.0 kGy, indicating that the photon counts varied depending on the amount of inorganic mineral debris in the spices. To confirm a successful detection by using PSL, ESR and TL methods, some spices were selected, irradiated at 5.0 and 10.0 kGy, and subjected to the detection methods. PSL identified the irradiated spices except the cassia, which showed very weak PSL sensitivity, but was identified by ESR analysis. Also, the ESR and TL exhibited the typical signals induced by irradiation treatment and were able to successfully detect all of the irradiated spices. In addition, we found a positive correlation between the intensity of ESR and TL signals and irradiation doses.

Key words: imported spices, gamma irradiation, PSL, ESR, TL

INTRODUCTION

Spices and seasonings are one of the groups of products that are commonly irradiated and have widespread international approval for irradiation processing. The quantities of spices and dried seasonings, which were irradiated to improve their hygienic status, have increased from about 8,000 ton in 1987 to over 80,000 ton in 1998 (1). In addition to spices and seasonings, some other food items are also approved for irradiation and it is expected that more foodstuffs will be approved for irradiation. In the future, it is expected that gamma irradiation processing of food will grow, but the growing pace may be very different in the various parts of the world. Diehl (1) reported that in the United States, the rapid growth of irradiation processing is likely to continue, but the progress in the European Union has become slower. Some countries may take positions close to the United States, whereas some others are as reluctant as the European Union.

Approval of a food item for irradiation treatment in Korea requires changes to the laws regulating irradiated foods. Regulation of irradiated foods will provide beneficial information to consumers who still have a vague concern about the use irradiation for food processing, although irradiation technology has been successfully applied in sterilization of medical supplies and packaging materials (2). One major part of authorizing a regulation is to build a database for irradiated foods, which should be detected by using the detection methods developed by European Committee for Standardization (CEN).

Photostimulated Luminescence (PSL), Electron Spin Resonance (ESR) and Thermoluminescence (TL) have been used to reliably detect irradiation treatment of foods. PSL and TL are radiation specific phenomenon resulted from releasing the energy stored by the trapped charge carriers in inorganic minerals generated during irradiation of foods. Release of this stored energy by optical stimulation (PSL) and heating (TL) can be detected by determining photon counts and generating glow curves, respectively (3). On the other hand, ESR analysis is applied to foods containing cellulose, crystalline sugar, and hard and dry components. ESR spectrometry detects an un-paired electron, which results from breaks in the

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paired electrons in foods by the energy imparted by irradiation treatment (4). The aims of this study were to validate methods for assessing the irradiation status of spices imported from foreign countries by using PSL, ESR and TL analysis and to help build a database of food irradiation detection methods.

MATERIALS AND METHODS

Sample preparation

The imported spices were obtained from a local company in Daejeon. They were imported from the United State, India, Turkey, Egypt, Canada, Singapore, Tanzania, Indonesia and Israel. Whole spices were thyme, oregano, majoram and basil; ground spices were tarragon, majoram, thyme, cadamon, rosemary, dill, turmeric, coriander, fenugreek, celery, black pepper, fennel, nutmeg, oregano, anise, bay leaves, sage, basil, mustard, white pepper, gloves, cassia and parsley flakes. Eight non-irradiated spices, whole thyme, oregano and parsley, and the ground rosemary, sage, turmeric and black pepper, were used as the controls.

For the identification of gamma irradiation, the ground dill, turmeric, fenugreek, nutmeg and cassia were randomly selected for Photostimulated Luminescence (PSL) and Electron Spin Resonance (ESR) analysis. Because of the limitations of detection methods and the lack of availability of other suitable samples, whole majoram, basil and oregano were selected for Thermoluminescence (TL) analysis.

Irradiation

The selected spices were prepared for examining the efficiency of detection methods by packing them in polyethylene bags followed by irradiation at 5.0 and 10.0 kGy with the ^{60}Co irradiator (point source, AECL, IR-79, MDS Nordion International Co., Ltd., Ottawa, Ontario, Canada) in the Korea Atomic Energy Research Institute (KAERI). The strength was approximately 100 kCi at a dose rate of 70 Gy/min at 15 ± 0.5°C; the actual doses were within $\pm2\%$ of the target dose. Dosimetry was performed using 5 mm-diameter alanine dosimeters (Bruker Instruments, Rheinstetten, Germany), and the free radical signal was measured using a Bruker EMS 104 EPR Analyzer.

Photostimulated Luminescence (PSL) measurement

The spices were analyzed by PSL analysis in accordance with the CEN 13751 developed by European Committee for Standardization (5). Samples were dispensed onto a disposable petri-dish (50 mm in diameter) and spread into a thin layer, and subjected to a SURRC PSL Irradiated Food Screening System (PPSL 0021, Scottish Universities Research and Reactor Center, Glasgow, UK). The petri-dish with the sample was loaded into the sample chamber and measured for 60 s while the photons, which were detected every second, were accumulated. The accumulated photon count (APC) for the lower threshold T1 of 700 counts/60 s and the upper threshold T2 of 5000 counts/60 s were used to classify the irradiated and non-irradiated samples, respectively. PSL intensities below the lower threshold were classified as non-irradiated samples, whereas PSL signals above the upper threshold were regarded as irradiated samples. Signal levels between the two thresholds were classified as intermediate samples, for which further investigation was needed. All measurements were conducted in triplicate.

Electron Spin Resonance (ESR) measurement

ESR analysis was performed according to the CEN 1787, which is the standard detection method for an irradiated food containing cellulose using ESR spectroscopy (6). The ground spices ($0.1\sim0.2$ g) were placed in an ESR tube (4.0 mm in diameter). The same amount of samples could produce the same density of the sample and fill the cavity of the ESR spectroscopy. The ESR measurements were performed with an ESR X-band spectrometer (JES-TE 300 ESR spectrometer, Jeol Co., Tokyo, Japan). All spectra were recorded at an ambient temperature and in the same fixed position in the ESR cavity to ensure a uniform and reproducible measurement of the sample. The spectrometer was set with a magnetic center field of 328.098 mT, microwave frequency of 9.215 GHz, microwave power of 0.636 mW, modulation amplitude of 50 mT, modulation frequency of 100 kHz, and a sweep width of 15 mT. Three TL measurements were performed for all samples.

Thermoluminescence (TL) measurement

TL analysis was conducted in accordance with the CEN 1788 developed by European Committee of Standardization (7). Silicate minerals adhering on the surface of the samples were extracted by density separation using a sodium meta-tungstate solution (density of 2.8 g/mL). Upon TL measurement, the dry silicate minerals ($1.5\sim2.0$ mg) were deposited onto stainless steel disc, which was fixed with a droplet of silicon solution (Silicon ICP/DCP standard solution, Aldrich Chemical Co., Inc., Milwaukee, WI, USA). The disc with minerals was subjected to a Thermoluminescence Dosimetry (TLD) reader (Harshaw/TLD-4200, Dreieich, Germany). A TLD reader was set at an initial temperature of 50°C, and the disc was heated within the temperature range of 50 to 320°C at a heating rate of 6°C/s, and annealed at 320°C for 10 s. While the disc was being heated, the signals were recorded and used for the detection of irradiated samples. All measurements were conducted in triplicate.

Statistical analysis

The ESR data was analyzed using Bruker Win-EPR (version 2.11) software, and plotted using OriginPro 7.0 (OriginLab Corporation, Northampton, MA, USA) software program. TL data was also plotted using OriginPro 7.0.

RESULTS AND DISCUSSION

Detection of imported spices

All 29 imported spices were subjected to a Photostimulated Luminescence (PSL) analysis to determine whether or not they had been treated by gamma irradiation. PSL analysis is usually used for rapid screening for irradiated food, in about one minute without sample preparation. Table 1 shows the PSL measurements of the imported spice samples. Most samples except, the ground thyme and bay leaves, gave photon counts of less than 700 counts/60 s, which was the threshold value for non-irradiated food. The photon counts of thyme and bay leaves were 887.0±119.52 and 2844.17±180.32, respectively. Besides those 2 samples, the other 27 spice samples were determined not to have been irradiated. Furthermore, the PSL measurement of 8 imported spices was compared with their non-irradiated control spices in Table 2 showing the control and imported spices yielded the similar level of photon counts. Due to the lack of control samples, although we could compare the 8 spices with their controls, it will be desirable to compare the rest of spices with matching control samples.

To confirm the irradiation treatment of the ground thyme and bay leaves, they were irradiated at 1.0, 3.0, 5.0 and 10.0 kGy and subjected to PSL analysis. Table 3 shows the PSL measurement of those 2 spices. The thyme at 0 kGy gave the photon counts of 760 counts/60 s, which was close to the threshold value for non-irradiated food. Whereas the photon counts at 1.0 kGy was 447750.2±53387.3, which was significantly higher than the photons at 0 kGy. On the other hand, the ground bay leaves at 0 kGy yielded the photon counts of 2628.2 ±690.9, which was in the intermediate level. However, the bay leaves at 1.0 kGy gave the photon counts of 197831.9±183210.9, which was also significantly higher than the photons at 0 kGy. The higher photon counts of bay leaves at 0 kGy suggests that there might be a large amount of inorganic mineral debris, which was the major source of the higher photons. According to the CEN 13751 (5), irradiated food with insufficient PSL sensitivity, negative results might occur. In contrast, for non-irradiated sample with high PSL sensitivity, positive results might also occur occasionally.

Table 2. Comparison of the Photostimulated Luminescence measurement of 8 spice samples[1] with their control values (Unit: photon counts)

	Control	Imported
W thyme	328.24±125.17	373.45±50.92
W oregano	397.91±130.95	442.45±291.36
W parsley	301.23±46.61	331.44±49.80
GR rosemary	230.56±122.17	285.10±15.83
GR sage	232.23±83.21	390.95±101.12
GR turmeric	423.24±70.01	491.96±3.54
GR black pepper	149.05±0.71	284.43±56.48

[1]Average and standard deviation of three measurements.

Table 1. Photostimulated Luminescence measurement of imported spices from several countries (Unit: photon counts)

Countries	Spices		Countries	Spices	
USA	Whole thyme	373.45±50.92 (-)[1]	India	GR turmeric	491.96±3.54 (-)
	GR tarragon	341.94±33.23 (-)		GR coriander	425.79±59.68 (-)
	GR majoram	389.45±76.37 (-)		GR fenugreek	476.46±88.84 (-)
	GR thyme	887.00±119.52 (±)[2]		GR celery	413.45±31.11 (-)
	GR cadamon	502.46±28.28 (-)		GR black pepper	284.43±56.48 (-)
	GR rosemary	285.10±15.83 (-)		GR fennel	516.46±26.87 (-)
	GR dill	415.45±12.73 (-)		GR nutmeg	372.44±56.03 (-)
Turkey	GR oregano	466.12±96.53 (-)		GR cumin	430.45±16.97 (-)
	GR anise	253.43±168.31 (-)	Egypt	GR basil	219.43±82.43 (-)
	GR bay leaves	2844.17±180.32 (±)		Whole majoram	433.78±61.51 (-)
	GR sage	390.95±101.12 (-)		Whole basil	339.44±82.04 (-)
	Whole oregano	442.45±291.36 (-)	Singapore	GR white pepper	244.76±71.44 (-)
Canada	GR mustard	230.43±134.36 (-)	Indonesia	GR cassia	327.11±86.52 (-)
	Whole mustard	390.95±201.55 (-)			
Tanzania	GR gloves	252.09±39.71 (-)			
Israel	Parsley flake	331.44±49.80 (-)			

[1]Less than 700 counts/60 s (negative).
[2]Between 700 and 5,000 counts/60 s (intermediate).

Table 3. PSL measurements of ground bay leaves and thyme at the various irradiation doses (kGy) (Units: photon counts)

	Doses (kGy)				
	0	1.0	3.0	5.0	10.0
GR thyme	760.1±13.4[1)]	447750.2±53387.3	679229.3±29000.6	785180.9±83923.7	734245.4±78261.9
GR bay leaves	2628.2±690.9	197831.9±183210.9	274977.1±81750.8	310349.6±102411.8	480568.2±305215.0

[1)]Average and standard deviation of three measurements.

Identification of irradiated spices by physical detection methods

The experiment was extended to identify gamma irradiation treatments by using PSL, ESR and TL analyses. Due to the lack of spice samples and also the measurement limitation of each detection method, only the ground dill, turmeric, fenugreek, nutmeg and cassia were selected for PSL and ESR analyses, and the whole majoram, basil and oregano were selected for TL analysis.

PSL detection

The PSL measurements for the selected spice samples are shown in Table 4. The irradiated dill, turmeric, fenugreek and nutmeg at 5.0 and 10.0 kGy gave photon counts above 5000 counts/60 s, clearly distinguishing them from the non-irradiated samples. However, it was found that, as shown in Table 4, the ground fenugreek irradiated at the higher dose (10.0 kGy) did not always yield higher photon counts than at lower doses (5.0 kGy). Upon considering the variation of PSL measurement, Bayram and Delincée (8) reported that the PSL sensitivity tended not to depend on the irradiation doses, and it was likely due to variations in the presence of minerals accidentally accumulationg on the surface of the dispensed sample layer. Also as indicated in the CEN 13751 (5), the PSL sensitivity of a sample depends on the quantities and types of minerals within the individual sample. In principle, a PSL analysis system can be used as a screening method to detect gamma irradiation treatment of a food containing inorganic mineral debris.

It was also found that the cassia yielded very low photon counts; 835.87±153.95 and 1179.57±80.62 at 5.0 and 10.0 kGy, respectively. In general, in this case, the determination should be pending until other clearer information can support the results. From these results, we can conclude that successful detection will require using more than one detection method. Therefore the application of other detection techniques was investigated. The 5 selected samples were subjected to ESR analysis to confirm the PSL measurements.

ESR detection

Fig. 1 shows the ESR spectra of the ground dill (a), turmeric (b), fenugreek (c), nutmeg (d) and cassia (e). According to the CEN 1787 (6), a single signal occurs as a pair of lines formed by an ionizing radiation to the left (at lower field) and right (at higher field) of the central signal. The determination of irradiation treatment is made based on the signal intensity. The signal intensity of an irradiated food is usually far greater than that of a non-irradiated food, so that a food with a high signal intensity is differentiated from one with a low signal intensity.

The ESR spectra of those 5 selected spices illustrate that they show the typical single signal spectra at the g-value (center of spectrum) of 2.007±0.0006, which was the paramagnetic centers by cellulose. The intensities of ESR signals of the spices irradiated at 5.0 and 10.0 kGy were higher than those of non-irradiated samples, differentiating them from the irradiated spices. In particular, the intensities of the ESR spectra of cassia irradiated at 5.0 and 10.0 kGy were significantly higher than at 0 kGy, demonstrating that irradiated cassia can be clearly distinguished from the control.

To confirm the signal intensity, the peak heights of the irradiated spices were compared to those of the non-irradiated spices in Table 5. The peak heights of spices irradiated at 5.0 and 10.0 kGy were much higher than

Table 4. Photostimulated Luminescence measurement of imported spices irradiated at 5.0 and 10.0 kGy
(Unit: photon counts)

Spices	Doses		
	0	5	10
GR dill	368.44±81.91[1)]	76394.78±22537.66	82752.96±6343.57
GR turmeric	605.80±197.20	444598.0±65099.90	551463.7±142639.90
GR fenugreek	476.46±88.84	159279.4±70116.85	108151.3±6393.66
GR nutmeg	372.44±56.03	11055.12±1606.55	22508.16±1001.27
GR cassia	327.11±86.52	835.87±153.95	1179.57±80.62

[1)]Average and standard deviation of photon counts of three measurements.

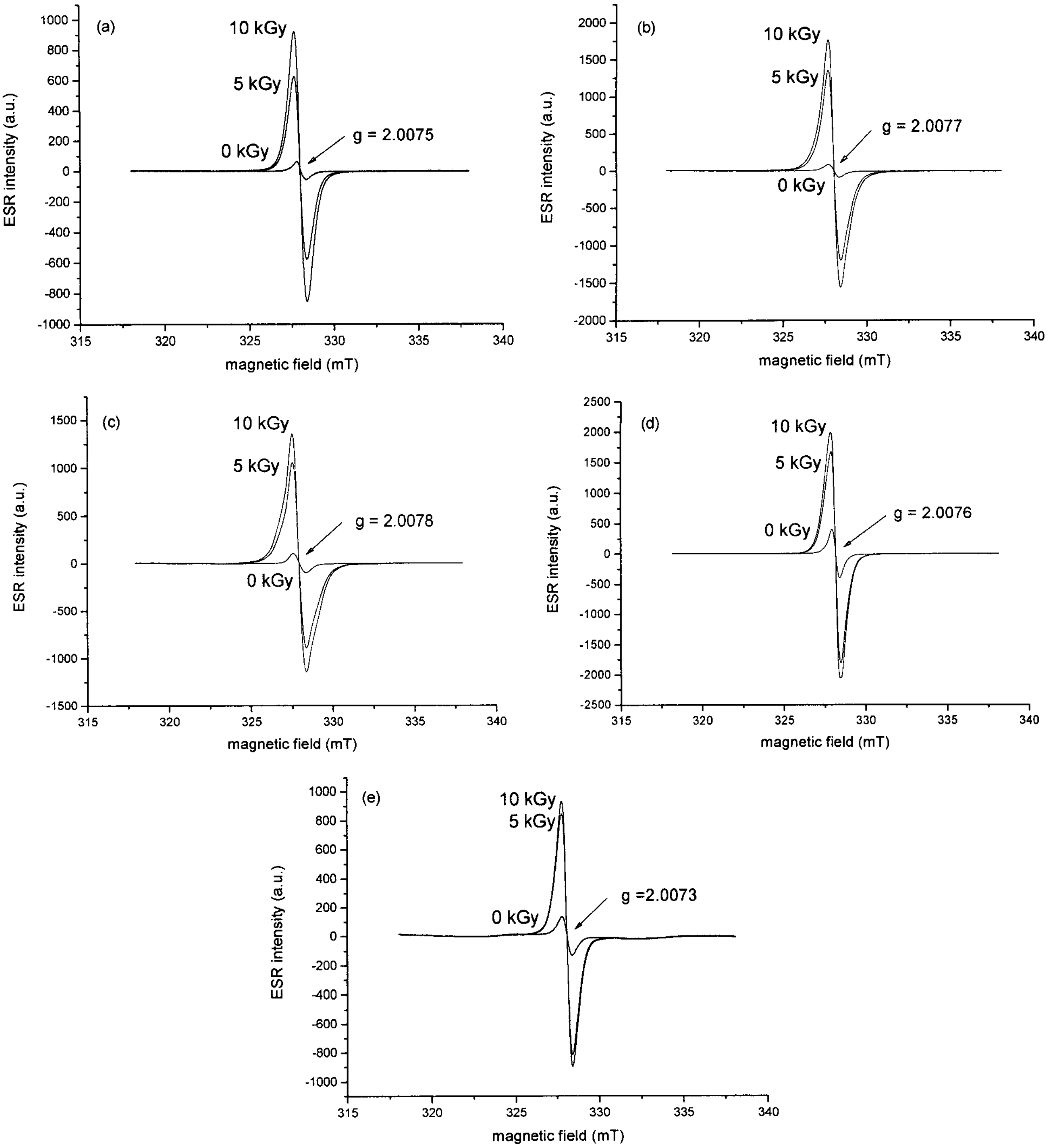

Fig. 1. ESR spectra of the ground dill (a), turmeric (b), fenugreek (c), nutmeg (d) and cassia (e) irradiated at 5.0 and 10.0 kGy.

Table 5. Peak height of ESR spectra for the spices irradiated at 5.0 and 10.0 kGy

		Irradiation doses (kGy)	
		5.0	10.0
GR dill	123.7±6.4	1207.0±43.9[1)]	1780.7±77.2
GR turmeric	175.0±7.0	2557.3±230.7	3327.7±111.7
GR fenugreek	208.0±13.2	1952.0±89.5	2504.7±136.9
GR nutmeg	808.0±63.0	3495.3±234.9	4061.3±21.2
GR cassia	272.0±23.5	1733.7±77.6	1828.3±81.9

[1)]Average and standard deviation of three measurements.

those of the non-irradiated controls. Therefore, it was determined that the peak height of signals along with the ESR spectra can clearly distinguish irradiated spices from non-irradiated controls. In addition, although the peak height increment was not as great as the difference between 0 kGy and 5.0 kGy, and the peak height for the 5.0 to 10.0 kGy increment was still increased. Furthermore, it was found from the ESR spectra and the peak height that there was a positive correlation between the ESR intensity and the irradiation doses. Therefore, the ESR analysis system could be used to estimate the applied doses to food by a positive correlation between the applied doses and the generated signal intensities (9,10).

TL detection

The TL glow curves for majoram (a), basil (b) and oregano (c) are shown in Fig. 2. According to the CEN 1788 (7), the glow curve of an irradiated food usually exhibits its peak in the temperature between 150 and 250 °C, whereas no typical glow curve is exhibited at temperatures above 300°C for non-irradiated foods. Light emission resulting from heating the silicate minerals was recorded as the TL intensity, which was the amount of light detected per unit temperature interval at a given heating rate. The glow curves of the spices in Fig. 2 show the typical shape of glow curves, which clearly differentiate irradiated from non-irradiated samples. The glow peaks occurred at around 150°C which was at slightly lower temperatures compared to other studies (11,12). Nevertheless, those samples can be classified as being irradiated due to the shape of their glow curves. In addition, the glow curves indicate that the TL intensities are increased at radiation dose increments from 5.0 to 10.0 kGy.

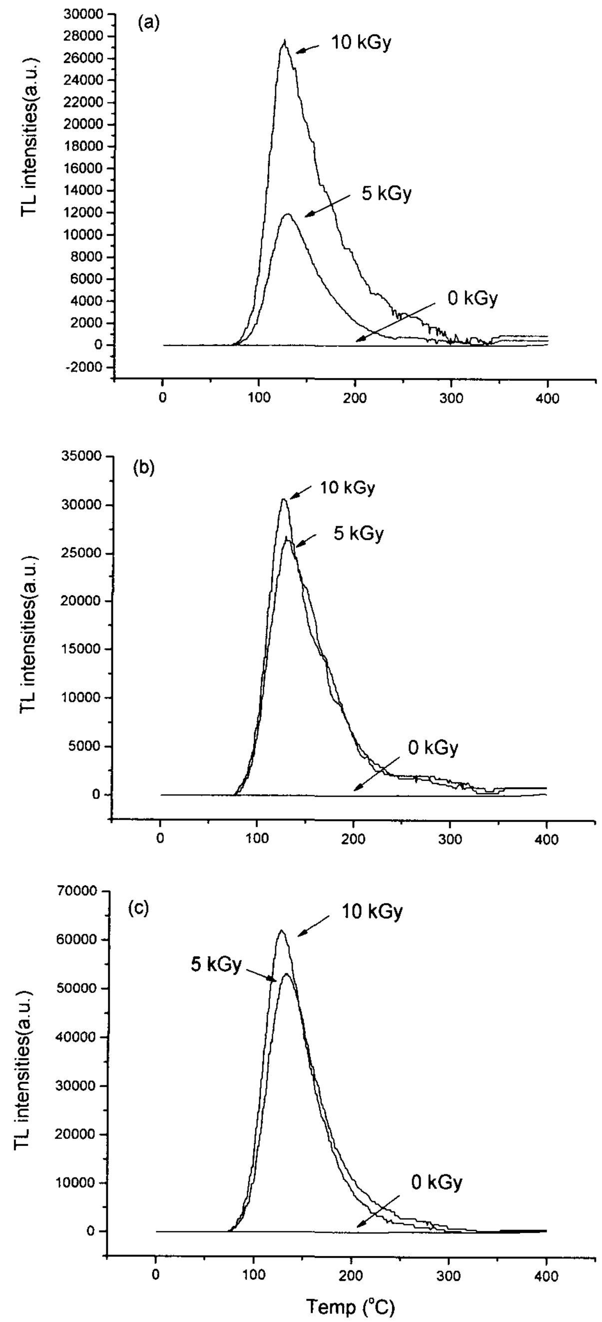

Fig. 2. TL glow curves of the whole majoram (a), basil (b) and oregano (c) irradiated at 5.0 and 10.0 kGy.

CONCLUSIONS

The imported whole and ground spices were screened for irradiation treatment by PSL, ESR and TL methods. The overall screening by PSL analysis detected no irradiation treatment of the spices except for the ground thyme and bay leaves, which had photon counts in the intermediate range. To clearly identify them, the photons of the two spices were measured by PSL after irradiating them at 1.0, 3.0, 5.0 and 10.0 kGy resulting in differentiation of the non-irradiated from the irradiated spices. The comparison of some spices with their controls could also improve the confidence in the identification of the irradiated spices. To confirm a successful detection, the selected spices were irradiated at 5.0 and 10.0 kGy, and subjected to PSL, ESR and TL analyses. The PSL detected the irradiated samples, except the cassia which showed very weak PSL sensitivity. However, by adding ESR, all selected irradiated spices could be differentiated from the non-irradiated ones. Furthermore, the TL results exhibited the typical signals induced by irradiation treatment, detecting the irradiated spices successfully. In addition the signal intensity of ESR and TL analysis increased with irradiation doses, which showed a positive correlation between doses and the signal intensity. From these results, it could be concluded that PSL analysis will be useful as a screening method to detect irradiated foods quickly in about one minute. And ESR and TL analyses will be reliable detection methods to ensure the detection of irradiation treatment, and for confirming the results of PSL analysis for identification of irradiated foods.

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