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Detection of Low Dose-Gamma Irradiated Spices by Photostimulated Luminescence (PSL) Technique

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Abstract: Photostimulated Luminescence (PSL) has been widely used as a rapid screening technique for the detection of various irradiated foods. This study aims to investigate the efficacy of the PSL technique in the detection of low dose-gamma irradiated spices available in the Malaysia market. Samples of clove, coriander, fenugreek, turmeric powder and curry powder were irradiated at very low doses; 0 (control), 0.2, 0.5 and 1 kGy using Cobalt-60 as a source. PSL measurements and analysis were undertaken under subdued lighting following EN 13751 methods. The PSL value in the form of photon counts (PCs/60s) of all samples as a function of the irradiation dose after 7 days of storage were determined which revealed that the PSL value increases proportionally to the radiation dose applied. The PSL also was able to discriminate between the non-irradiated (<700 PCs/60s, negative) and irradiated (>5000 PCs/60s, positive) samples after 7 days of storage. Coriander generates the highest PCs at the lowest dose (0.2 kGy) and highest dose (1 kGy) after that storage period. The PSL value of all spice samples is considered accurate and consistent at all irradiation doses. This technique is highly reliable for the detection of irradiated spices available in the Malaysia market.

Keywords: Photostimulated Luminescence (PSL), food irradiation, spices, low dose, irradiation detection

1. Introduction

Seasoning, preservatives and many types of spices are widely known in different cultures around the world. Among them, clove, coriander, fenugreek, turmeric powder and curry powder are widely used in Malaysian cooking as flavoring materials. Processing and storage of the spices and spice products might expose them to insect pests like beetle and moth pests. Eventually, their activity in a conducive environment (high moisture) results in the contamination of insect fragments, excreta (uric acid), mycotoxins and pathogenic microbes in spices [1]. Even though washing them before use could eliminate the contaminations and cooking it could kill the microorganisms, some spore-forming microbes like *Genera Bacillus* and *Clostridium* are resistant to heat (high temperature) and still survive during cooking. This situation requires a safe, effective and reliable preservation method that could reduce or eliminate such microorganisms in spices, while retaining their quality [2].

Ionizing radiation is a promising method in enhancing the hygienic quality of spices for consumer safety by effectively inhibiting insects and microorganisms activities responsible for spoilage, corresponding to the dose applied. This treatment involves the direct exposure of spices and their packaging to gamma rays, X-rays or electron beam at a dose below 1 kGy to control insect pests and at a medium dose of less than 10 kGy to reduce certain pathogenic microorganisms without causing adverse effects on their quality especially sensory and physicochemical properties [3]. Sensory property is the sensual qualities generated by the predominating chemical components present in the individual spices such as bitter, spicy, sweet and floral [4], while physicochemical property is defined as the intrinsic

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physical and chemical characteristics of spices such as color, solubility, rheology, enzyme susceptibility and thermal properties [5].

According to U.S. Food & Drug Administration (FDA), irradiation process does not make spices radioactive as the radiant energy only passes through them and they are never in contact with the radioactive sources [6]. Moreover, the maximum irradiation dose (absorbed dose) allowed is only 100 kGy and the Cobalt-60 as a source specific for food irradiation only emits radiation at low energies which is between 0.1 to 10 MeV [3], making it incapable to modify nucleus in the targeted spices, thus making them impossible to become radioactive and emit radiation [7]. In Malaysia, the sale of irradiated foods including teas, spices, herbs, grains and frozen food has been enforced in 2013 by the Ministry of Health and in accordance with the national and international regulations [8]. Prior to retail, they must undergo a strict monitoring process including irradiation detection and dose identification by the responsible authorities for proper labelling purposes.

The labelling of the 'Radura' symbol on the packaging of irradiated foods indicating that it has been 'irradiated' or 'treated with radiation' which automatically declaring that the irradiated food is not radioactive is very important in gaining and enhancing consumer confidence, choice and safety. This is because most of the consumers are still reluctant to accept irradiated foods and they would only buy them if they are assured that every irradiated food is not radioactive and there is labelling of the 'Radura' symbol on their packaging [9]. Extensive research on the development of various detection methods for irradiated foods has led to the validation of nine standard methods by the European Committee with regard to the physical, chemical, biological and microbiological changes in food products during irradiation, although these changes are minimal [10].

Among those methods, thermoluminescence (TL) and photostimulated luminescence (PSL) are the leading methods or techniques for the detection of irradiated spices as they contain silicate minerals. Both techniques apply luminescence properties, which is the emission of light in the form of glow and photon counts (intensity) from irradiated foods containing silicate minerals that store radiation energy [11]. TL analysis requires a complicated mineral separation process from irradiated foods prior to detection [12] and this is a very time-consuming method. In contrast, PSL analysis enables direct measurement and rapid screening techniques of irradiated foods for detection purposes [13]. Hence, considering the increasing use of PSL as a rapid screening technique for the detection of irradiated spices worldwide [14-17], and there are no published data available on the chosen spice samples irradiated at dose below 1 kGy, this present study aims to investigate the efficacy of this technique in the detection of irradiated chosen spices available in the Malaysia market at a very low dose, which is below than 1 kGy.

2. Materials and Methods

2.1 Preparation and Irradiation of Samples

Five spice samples, namely clove (*Syzygium aromaticum*), coriander (*Coriandrum sativum*), fenugreek (*Trigonella foenum-graecum*), turmeric powder and curry powder were purchased from the local market in Bangi, Selangor, Malaysia. The samples were packed in black polyethylene bags (to ensure no light could enter the spice samples) and irradiated in a gamma cell (located at National University of Malaysia) at a very low dose; 0 (control), 0.2, 0.5 and 1.0 kGy using cobalt-60 as a source. The exposure was at the dose rate of 1.962 kGy/hr. All samples (control and irradiated) were stored in a dark room at room temperature (27 ± 2°C) for 7 days to simulate rapid retail and trade within Malaysia.

2.2 Detection and Analysis of Samples

Control (non-irradiated) and irradiated samples were identified using Photostimulated Luminescence (PSL) measurement following EN 13751 method [13]. The instrument was composed of a control unit, sample chamber and detector head assembly, and supported with SUERC (Scottish Universities Environmental Research Centre) software program for analysis purposes. Prior to detection of samples, the PSL value in the form of photon counts per minute (PCs/60s) of each 50 mm diameter disposable petri dish (Bibby sterilin type 122, Glasgow, UK) that was intended to use were firstly measured for detection and validation from any irradiation contamination. The petri dish was specially designed for PSL measurement. Further, each spice sample was placed in the 'screened' petri dish as shown in Fig. 1 and measured in the PSL sample chamber for the 60s (1 minute) with measuring mode of photon counts per minute (PCs/60s). All measurements of samples were done in triplicates (n = 3) and under subdued lighting.

The status of the samples was determined using PSL screening analysis which consists of two specific thresholds, T_1 (negative) and T_2 (positive) as these thresholds were used routinely at Scottish Universities Research and Reactor Centre (SURRC) for commercial analysis [15]. T_1 refers to PCs less than 700 PCs/60s and any samples that generate PCs less than T_1 will be classified as 'non-irradiated'. T_2 referring to PCs more than 5000 PCs/60s and 'irradiated' status will be designated to any sample that generate PCs more than this threshold. For samples that generate PCs between these two thresholds (700 to 5000 PCs/60s), they will be classified as 'intermediate' and require further investigation using calibrated PSL to determine the sensitivity of the samples.

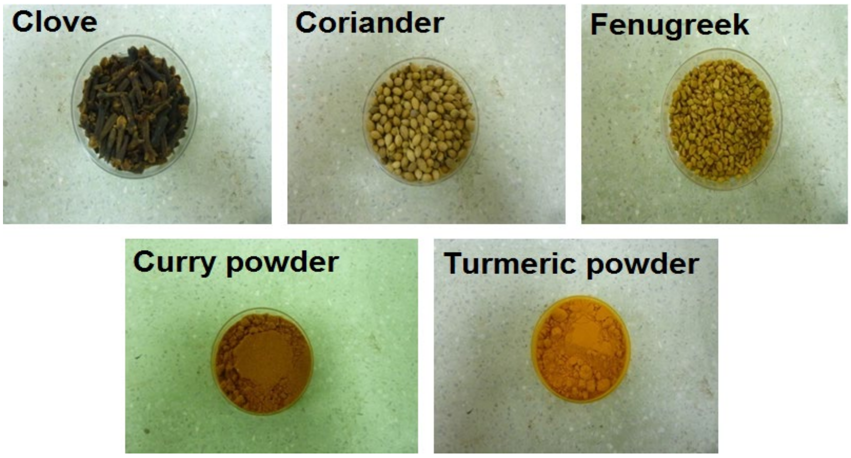

Fig. 1 - Spice samples prior to PSL screening analysis

3. Results and Discussion

The PSL value in the form of photon counts per minute (PCs/60s) of each sample before and after irradiation (0.2, 0.5 and 1 kGy) after 7 days of storage are tabulated in Table 1. The tabulated data are the mean value and its uncertainty of the three measurements (n = 3) taken for each sample. Fig. 2 and 3 shows the PSL photon counts (PCs/60s) as the function of irradiation dose (kGy) of each sample after 7 days of storage. From the graph, it can be seen that the PCs of all samples increase as the irradiation dose increase which indicates that all spice samples has successfully absorb and stored radiation energy according to the dose applied and the PSL analysis are able to detect all irradiated spices. It is clear that higher irradiation dose lead to the greater amount of radiation energy absorbed and stored within the spice samples, and thus contributing to more elevated photon counts. Before irradiation, all samples have negative PCs, which is less than 700 PCs/60s (T_1 threshold), thus validating the 'non-irradiated' status of the samples as clearly seen in Fig. 3 (a). At 0.2, 0.5 and 1 kGy, all samples have PCs more than 5000 PCs/60s which is in the category of T_2 threshold (positive), validating that the samples have been 'irradiated'. No sample has generated PCs within the 'intermediate' category, which is between 700 to 5000 PCs/60s as clearly shown in fig. 2, thus obviously indicating that PSL technique can correctly differentiate between non-irradiated and irradiated spice samples at very low doses.

Table 1 - PSL value (PCs/60s) of each sample (n = 3) before and after irradiation (0.2, 0.5 and 1 kGy) after 7 days of storage

Sample	Irradiation Dose (kGy)	PSL Value (PCs/60s)	Classification
Clove	0	300 ± 46	Non-irradiated
	0.2	5140 ± 81	Irradiated
	0.5	13 489 ± 118	Irradiated
	1.0	36 633 ± 187	Irradiated
Coriander	0	296 ± 45	Non-irradiated
	0.2	27 588 ± 189	Irradiated
	0.5	35 028 ± 179	Irradiated
	1.0	124 685 ± 354	Irradiated
Fenugreek	0	308 ± 47	Non-irradiated
	0.2	16 139 ± 141	Irradiated
	0.5	25 841 ± 177	Irradiated
	1.0	45 103 ± 230	Irradiated
Turmeric powder	0	327 ± 50	Non-irradiated
	0.2	5742 ± 90	Irradiated
	0.5	14 467 ± 127	Irradiated
	1.0	25 139 ± 172	Irradiated
Curry powder	0	552 ± 84	Non-irradiated
	0.2	25 251 ± 173	Irradiated
	0.5	55 187 ± 282	Irradiated

	1.0	115 105 ± 346	Irradiated

Among all of the samples, coriander generate the highest PCs at 0.2 kGy, which is 27 588 ± 189 PCs/60s followed by curry powder (25 251 ± 173 PCs/60s), whereas the lowest PCs have been generated by clove with 5140 ± 81 PCs/60s as shown in Fig. 3 (b). At 0.5 kGy, the highest PCs have been generated by curry powder with 55 187 ± 282 PCs/60s and followed by coriander that has generate 35 028 ± 179 PCs/60s. The lowest PCs have been generated by clove with the value of 13 489 ± 118 PCs/60s. Coriander is ahead of other samples when it generated the highest PCs at 1 kGy, which is 124 685 ± 354 PCs/60s and followed by curry powder as the second highest (115 105 ± 346 PCs/60s), while turmeric powder had the lowest PCs with the value of 25 139 ± 172 PCs/60s at this maximum dose which is compatible to control insect pests.

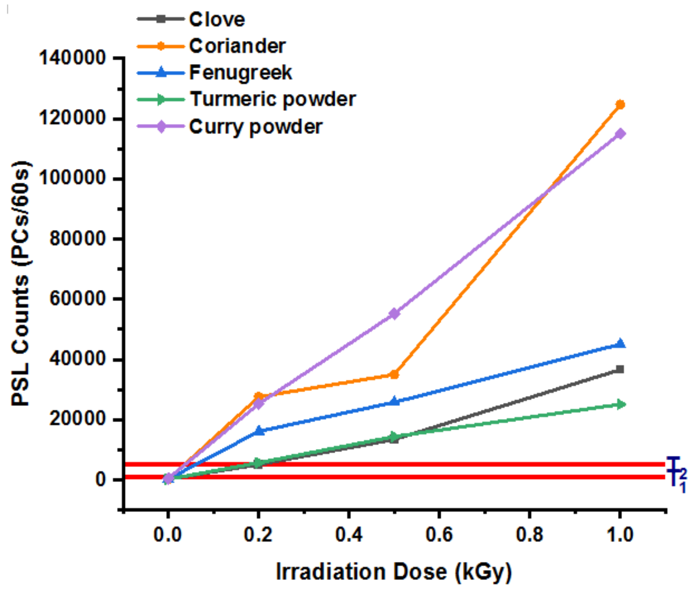

Fig. 2 - PSL value curves for the irradiated spice samples at 0.2, 0.5 and 1 kGy after 7 days of storage

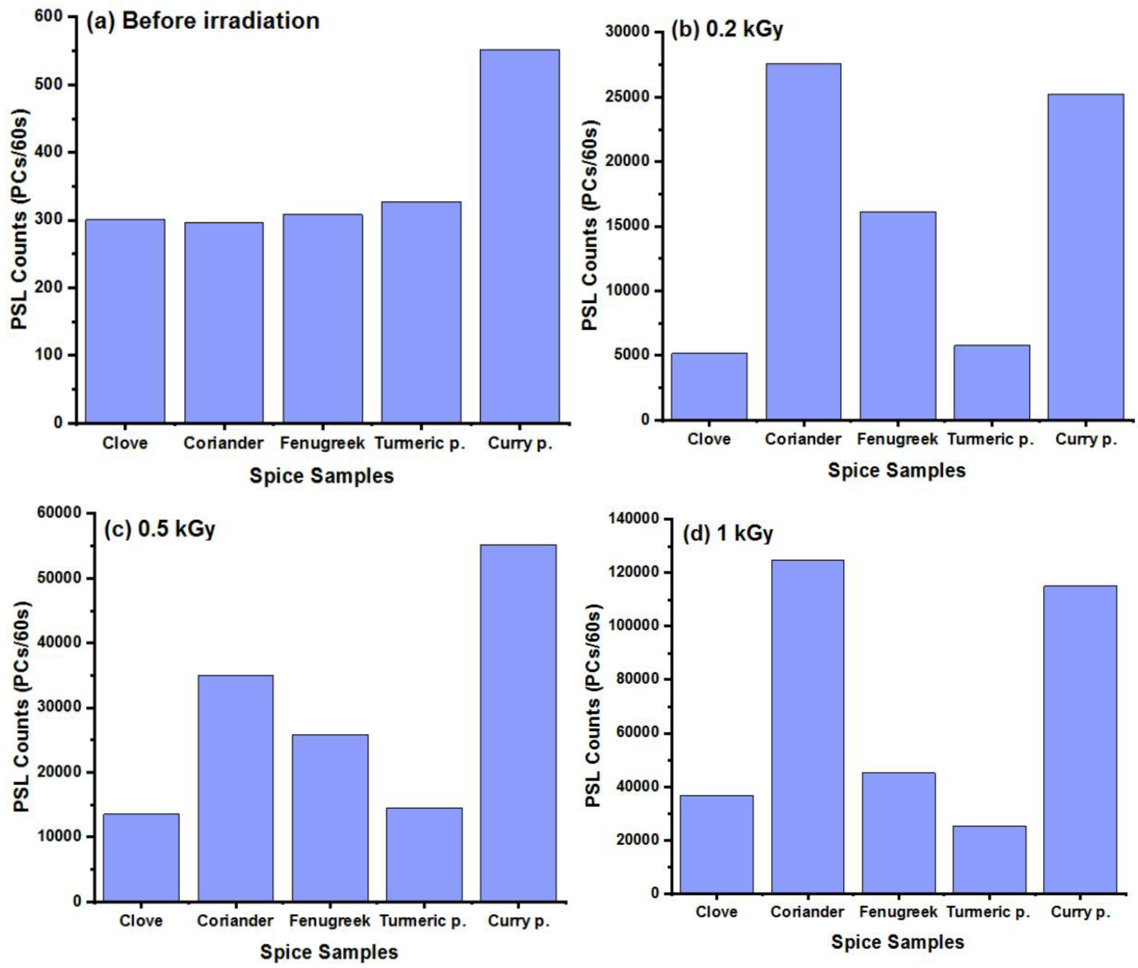

Fig. 3 - PSL value of spice samples at (a) before irradiation (b) 0.2 kGy (c) 0.5 kGy and (d) 1 kGy after 7 days of storage

The variation of PSL photon counts (PSL sensitivity) of the irradiated spices obtained in this present study is highly correlated with the types and quantities of silicate minerals such as feldspar and quarts present in the individual sample [13]. High quantity and radiation energy-dominant silicate minerals will absorb and store more radiation energy during irradiation and then contributing to elevated PSL photon counts. Thus, it can be said that coriander and curry powder might contain higher quantities and more radiation energy-dominant silicate minerals than other samples as they generates highest PCs at all irradiation doses. Same goes to clove and turmeric powder that might contain low quantities and less radiation energy-dominant silicate minerals as they possess lowest PCs at all irradiation doses.

In addition, unblended samples like clove, coriander and fenugreek grant optimum photon counts while blended products such as turmeric powder and curry powder may contain debris which will affect PSL sensitivities [13]. This declaration is in very good agreement with the results obtained in this present study for both blended and unblended samples, as clearly demonstrated in Fig. 3 and Fig. 4.

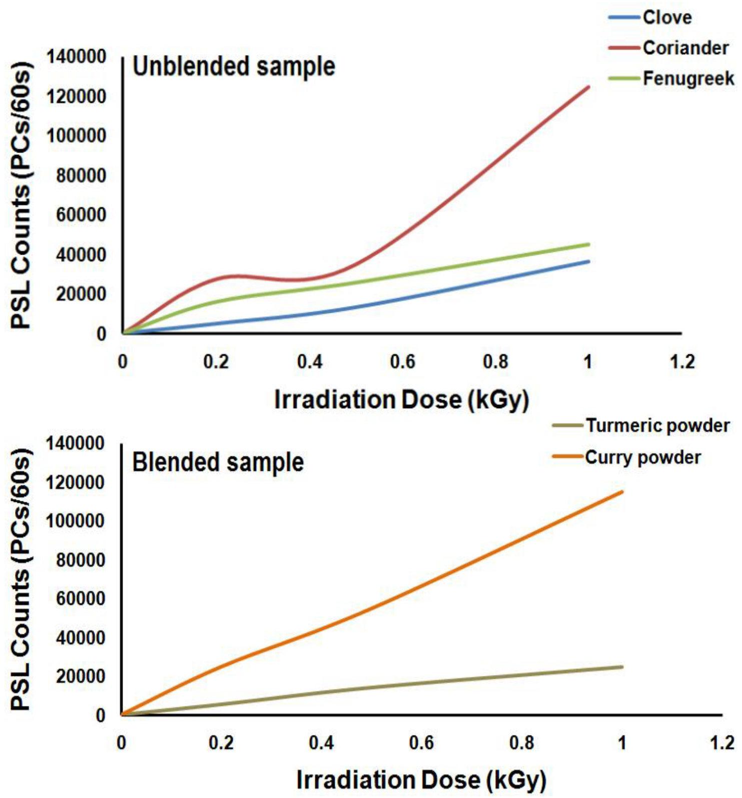

Fig. 4 - PSL value trend of unblended and blended samples at all irradiation doses after 7 days of storage

Before irradiation, curry powder and turmeric powder (blended samples) dominates the PSL value (fig. 3 (a)) which indicates high PSL sensitivity towards these samples that may contain some amount of debris although they do not store any radiation energy yet. While after irradiation at all doses, the PSL value has been dominated by coriander and curry powder which proves the high optimum photon counts by the irradiated unblended sample (coriander) and the high sensitivity of PSL technique in detecting irradiated curry powder (blended sample) that may contain high amount of debris, respectively. Same goes to clove as the unblended sample that demonstrated consistent low optimum photon counts at all irradiation doses and turmeric powder as blended sample that might contain lower amount of debris than curry powder that led to low PSL sensitivity towards it at all irradiation doses as clearly shown in Fig. 3 and 4, respectively.

Although the light-induced fading in PSL sensitivity should not be neglected [18], it is not a major contributing factor in the variation of PSL photon counts obtained in this present study as all samples have been stored in a dark room and the PSL analysis was undertaken under subdued lighting. Thus, the PSL value of all spice samples obtained in this present study is considered accurate and consistent at all irradiation doses, hence validating the high efficacy and high sensitivity of PSL analysis in the detection of different types of irradiated spices available in the Malaysia market.

Direct comparison of PSL value of all samples obtained in this present study with the published literature in terms of the same radiation dose and storage time cannot be made since no similar data is available at the moment. However, it is clear that the results obtained in this present study are in very good agreement with the findings reported elsewhere [15,16] which conclude that PSL technique can successfully discriminate between the 'non-irradiated' and 'irradiated' spices at any irradiation dose and storage time, the PSL value increases proportionally to the irradiation dose applied and the PSL value obtained are highly correlated with the quantities and types of silicate minerals present in the individual sample . Thus, from all of the evidences found in this present study, it is clear that the PSL is a highly reliable technique for rapid screening analysis for the detection of different irradiated spices available in the Malaysia market.

4. Conclusion

In this study, the efficacy of the photostimulated luminescence (PSL) technique in detecting and distinguishing the non-irradiated and irradiated spices available in the Malaysian market at a very low dose after 7 days of storage was investigated. The dose applied was very low; 0 (control), 0.2, 0.5 and 1 kGy. The results obtained revealed that this technique can correctly discriminate between the non-irradiated and irradiated spice samples at a very low dose. The

PCs of all samples increase as the irradiation dose increase after 7 days of storage. This study also revealed that coriander is the most sensitive sample to PSL measurement as it generate highest PCs at the lowest dose (0.2 kGy) and the highest dose (1 kGy), followed by curry powder that generate highest PCs at 0.5 kGy. The less sensitive sample to PSL measurement at all irradiation doses was demonstrated by clove and turmeric powder. The PSL value of all spice samples obtained in this present study is accurate and consistent at all irradiation doses, hence validating the high efficacy and high sensitivity of PSL technique in the detection of different types of irradiated spices. Overall, the PSL technique is proven highly reliable to be utilized as an initial approach for the detection of different irradiated spices available in the Malaysia market.

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