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Effectiveness of thermoluminescence analysis to detect low quantity of gamma-irradiated component in non-irradiated mushroom powders

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ABSTRACT

Gamma-irradiated (0–10 kGy) dried mushrooms (*Lentinus edodes*) powders were mixed at different ratios (1–10%) in the non-irradiated samples and investigated using photostimulated-luminescence (PSL), electron spin resonance (ESR) and thermoluminescence (TL) techniques. The PSL results were negative for all samples at 1% mixing ratio, whereas intermediate results were observed for the samples containing 5% or 10% irradiated component with the exception (positive) of 10% mixing of 10 kGy-irradiated sample. The ESR analysis showed the presence of crystalline sugar radicals in the irradiated samples but the radiation-specific spectral features were absent in the mixed samples. TL analysis showed the radiation-specific TL glow curves; however, the complicated results were observed at 1% mixing of 2 and 5 kGy-irradiated samples, which required careful evaluations to draw the final conclusion about the irradiation status of the samples. TL ratios could only confirm the results of samples with 5% and 10% mixing of 10 kGy, and 10% mixing of 5 kGy-irradiated components. SEM-EDX analysis showed that feldspar and quartz were major contaminating minerals, responsible for the radiation-specific luminescence characteristics.

1. Introduction

Oak or shiitake mushrooms (*Lentinus edodes*) have 25.4% of the world's total mushroom production [1], which are well-known for their functional properties and being consumed in both fresh and dried forms [2]. Their safe use and effective marketing are related to the improved shelf life with best hygienic quality, where insect pest infestation and spoilage and pathogenic microorganisms are major concerns [3]. Modern technologies are required to serve the increased demand of both fresh and dried mushrooms and their products [4,5]. The practical effectiveness of irradiation technology has attained great attention, where the major concerns related to the nutritional safety were properly addressed by extensive research [6]. The dried mushrooms (grouped as food additives) may be irradiated up to 50 kGy for different technical objectives [7], but the irradiation dose of 1–10 kGy is officially permitted for dried mushrooms in different countries [5].

Irradiation technology has proved its scientific and practical worth; however, different national and international regulations require proper monitoring and traceability of process and product. Proper labeling of irradiated food to protect consumer's right of choice is also mandatory. The reliable identification techniques are important to check the conformance with the applied regulations [5]. Thermoluminescence (TL) analysis depending upon the radiation-specific luminescence properties of contaminating silicate minerals is regarded as most effective technique to confirm the irradiation status of food materials [8,9]. TL properties, especially intensities of TL glow curves of irradiated samples greatly depend on the quality and quantity of silicate minerals (quartz, feldspar, etc.). Therefore, after the first measurement (TL_1), same minerals are again irradiated and used as reference to confirm the quality and reliability of the results [10].

Photostimulated luminescence (PSL) analysis could be used in a very short time without any complicated sample pretreatment [11]. The PSL signals could be greatly variable depending upon the amount and type of contaminating minerals on the samples surfaces. Therefore, this technique is recommended as a screening approach, where confirmations of the results are always needed [12].

Electron spin resonance (ESR) analysis is one of the most practical and non-destructive method as it depends upon radiation-induced free radicals in the food matrix [13,14]. Excellent results, targeting radiation-induced cellulose and crystalline sugar radicals, were reported to identify the irradiation history of different dried mushroom samples [3,15]. Recently, Akram et al. [16] reported the ESR-based improved detection of dried *L. edodes* mushrooms.

In practical environment of food processing, inclusion of irradiated material in non-irradiated food matrix is possible. This might be a challenge for the all available detection methods that

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already have limitations regarding their practical application and reliability [17]. In this study, the applicability of TL, PSL and ESR techniques for the identification of irradiated component (small quantity) in non-irradiated mushroom powders is investigated. The contaminating minerals were the source of radiation-specific luminescence properties, which were also characterized to develop better understanding of this study.

2. Materials and methods

2.1. Materials and irradiation

Dried (moisture content 9.6%) shiitake mushrooms (*L. edodes*) were purchased from a market in Daegu, South Korea and irradiated (0, 2, 5, 10 kGy at dose rate of 2.1 kGy/h) using a Co-60 gamma-ray source (AECL, IR-79, MDS Nordion International Co. Ltd., Ottawa, Ontario, Canada) at the Korean Atomic Energy Research Institute in Jeongeup, Korea. Absorbed doses were calibrated using alanine dosimeters with a diameter of 5 mm (Bruker Instruments, Rheinstetten, Germany), and the free-radical signals were analyzed using a Bruker EMS 104 EPR analyzer (Bruker Instruments).

2.2. Preparation of sample blends

In order to confirm the potential of different analytical techniques to identify the irradiated component of low quantity in non-irradiated matrix, the samples were ground (40 mesh pass) and the blends ($n=3$) with irradiated components at concentrations of 1%, 5%, and 10% were prepared by mixing 5, 25 and 50 g of irradiated sample per 500 g of sample, respectively [18]. All the samples were stored at room temperature in polyethylene bags until analysis.

2.3. Pulsed photostimulated luminescence (PPSL) measurements

A SURRC PPSL Irradiated Food Screening System (SURRC; Scottish Universities Research and Reactor Centre, Glasgow, UK) was used, where the analyses were conducted in accordance to the protocol EN 13751 [11]. The photon counts (PCs) of the samples ($n=3$) were recorded in the measuring mode and were presented as PCs/60 s. The results were interpreted using the lower threshold ($T_1=700$ counts/60 s) and upper threshold ($T_2=5000$ counts/60 s). The samples with PCs $< T_1$ were interpreted as non-irradiated, whereas those $> T_2$ were categorized as irradiated samples. The PCs value between T_1 and T_2 (intermediate) required further examinations to confirm the irradiation history of samples [11].

2.4. Electron spin resonance (ESR) analysis

ESR measurements were performed, at the second day of irradiation, in accordance to the protocols EN 1787 [13] and EN 13708 [14] using an X-band ESR spectrometer (JES-TE 300, Jeol Co., Tokyo, Japan) targeting the radiation-induced cellulose and crystalline sugar radicals, respectively. A quartz ESR tube (5 mm diameter) containing about 0.1 g of ground sample was used to measure ESR signals at room temperature under the following conditions: microwave power, 5 mW; microwave frequency, 9.10–9.11 GHz; center field, 324 ± 2 mT; sweep width, 10–25 mT; modulation frequency, 100 kHz; modulation width, 1–2 mT; amplitude, 50–400; sweep time, 30 s; and time constant, 0.03 s.

2.5. Thermoluminescence (TL) measurements

Mushroom powder (100 g) sample was washed with distilled water over a nylon sieve (pore size 150 μm). The separation of contaminating minerals was performed thorough density separation using sodium polytungstate (density 2.0 g/cm^3) and about 0.2 mg of separated minerals were shifted to the TL discs (diameter 10 mm and thickness 0.25 mm) for the analysis as described in the EN 1788 [10]. A TLD instrument (Harshaw TLD-3500, Dreieich, Germany) was used, where the sample discs were heated from room temperature to 400 °C at the rate of 5 °C/s under continuous nitrogen (99.99%) flush. After obtaining the first TL glow curve (TL_1), the measured minerals on the discs were 1 kGy re-irradiated and the second TL glow curve (TL_2) was also obtained. To calculate TL ratio (TL_1/TL_2), the TL temperature range (155 and 225 °C) was determined using LiF-100® as described in EN 1788: 2001 annex B. The protocol EN 1788 [10] was used to interpret the results using radiation-induced TL glow curve features and TL ratio.

2.6. Energy dispersive X-ray spectrometer spectroscopy (SEM/EDX)

SEM/EDX measurements were conducted to characterize the elemental composition of the isolated minerals from the samples. The samples were coated with gold and the analysis was performed using S4300 Hitachi Co., Tokyo, Japan at acceleration voltage of 15 kV.

3. Results and discussion

3.1. PSL characteristics

The PSL method does not need any complicated sample pretreatment, resulting in quick screening of food materials in accordance to their irradiation status [11,17]. The PSL count of non-irradiated (control) dried mushroom powder was 252 ± 40.3 ($n=3$) showing the absence of irradiation history of the samples (Table 1). However, very high PSL count was observed for the 2 kGy-irradiated sample, and there was a dose-dependent increase in PSL counts on 5 and 10 kGy irradiation. Different contaminating minerals especially silicate minerals present in the samples were responsible for these results showing the high sensitivity of samples against irradiation treatment [11]. In the blended samples

Table 1
The accumulated photon count (PCs/60 s) from dried *L. edodes* mushroom powders containing irradiated component at different blending ratios.

Blending ratio (%)	Irradiation dose (kGy)			
	0	2	5	10
100	252 ± 40.3[a] (−)[b]	35472 ± 5515.4 (+)	90773.5 ± 30472.8 (+)	123079 ± 33207.9 (+)
1	NA	313 ± 83.4 (−)	424 ± 26.9 (−)	687.5 ± 228.4 (−)
5	NA	1107 ± 96.9 (M)	1447 ± 271.6 (M)	3979 ± 1374.6 (M)
10	NA	2082 ± 221.3 (M)	2847 ± 202.2 (M)	18575 ± 1593.1 (+)

NA = not applicable.

[a] Mean ± standard deviation ($n=3$).

[b] Threshold value: $T_1=700$ (non-irradiated), $T_2=5000$ (irradiated), (−) $< T_1$, $T_1 <$ (M) $< T_2$, (+) $> T_2$.