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Study of Photostimulated- and Thermo-luminescence Characteristics for Detecting Irradiated Kiwifruit

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Photostimulated luminescence (PSL) and thermo-luminescence (TL) analyses were conducted to detect irradiated kiwifruits. Samples were irradiated with Co-60 γ-rays at 0–2 kGy. The freeze-dried kiwifruit peel showed 309 photon counts (PCs) for nonirradiated samples that accounted for less than the lower threshold value (700 counts/60 s, negative) and above 9306 PCs for 1 and 2 kGy-irradiated samples, which was higher than the upper threshold value (5000 counts/60 s, positive). However, PSL signals of irradiated samples remarkably decreased after 6 weeks of storage. The TL measurement using minerals isolated from the whole kiwifruit surface revealed a glow curve (TL_1) with a low intensity at 200–300 °C in nonirradiated samples but with a higher intensity at around 180 °C in irradiated samples at 1 kGy or more. The TL ratios, integrated areas of TL_1/TL_2 that was measured after 1 kGy re-irradiation for the TL_1-tested minerals, were less than 0.1 in nonirradiated samples and higher than 0.1 in irradiated ones and could verify TL_1 results. The inorganic dust minerals used were mainly composed of feldspar and quartz.

KEYWORDS: Kiwifruit; irradiation; detection; PSL; TL

INTRODUCTION

Food irradiation is commercialized in about 40 countries (*1*). Thus, informative labeling is needed to enhance the consumers' understanding of irradiated food and facilitate its distribution and international trade (*2*). Identification of irradiated over nonirradiated foods is highly recommendable to confirm both compliance with existing regulations and beneficial effects of irradiation treatment (*2–4*).

There are concerns about the importation of foreign agricultural commodities in terms of securing their quality and safety as well as quarantine. The quarantine treatment for pest or other microbial control is required to protect domestic plants and animals (*4–6*). Although heat treatment (*7*), fumigation (*8*), cold-storage treatment (*9*), and controlled atmospheric treatment (*10*) have been applied selectively as quarantine methods, they have some defects, such as a lack of efficiency, quality deterioration, cost, and treatment time (*5, 6*). Moreover, fumigation with methyl bromide will be prohibited because it was reported to be an environmentally disruptive substance (*6*). Irradiation has been recognized as one of the alternative quarantine treatments to chemical fumigants and temperature controls for agricultural and fishery commodities (*4, 6, 11*).

Studies on the identification and/or detection methods for irradiated foods have been carried out on the basis of the biological and physicochemical changes in foods exposed to irradiation during the last few decades (*2, 3, 12*). Photostimulated luminescence (PSL), thermoluminescence (TL), electron spin resonance (ESR), hydrocarbons, and 2-alkylcyclobutanones determination by gas chromatography/mass spectrometry (GC/MS), DNA comet assay, and direct epifluorescent filter technique/aerobic plate count (DEFT/APC) procedures have now been adopted by the European Committee for Standardization (CEN) (*3*) and on which the General Codex Methods for the Detection of Irradiated Foods were established (*13*).

For fresh fruits and vegetables, irradiation is approved at doses ranging from 1 to 3 kGy in different countries for quarantine treatment, microbial control, delay of ripening, and shelf-life extension (*1*). Kiwifruit is one of various agricultural commodities for international trade, and recently, the importation of kiwifruits into Korea from different countries has been increasing (*14*). Fortunately, it was found that the DNA comet assay for the kiwifruit seeds and electron spin resonance (ESR) analysis for the fruit core or flesh were suitable for the detection of radiation-induced markers in irradiated kiwifruits (*15*).

In this work, luminescence analytical methods were applied for different parts of kiwifruits to determine radiation-induced changes in inorganic dust minerals separated from the irradiated samples, thereby detecting irradiated kiwifruits during storage.

MATERIALS AND METHODS

Materials and Irradiation. Kiwifruits imported from New Zealand were purchased from four wholesale markets in Daegu, South Korea, within 1 week period. All of the kiwifruits were mixed well before

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Table 1. PSL Characteristics of Irradiated Kiwifruits during Storage (Unit: PCs/60 s)

part	storage period (week)	irradiation dose (kGy) 0	1	2
flesh	0	254 ± 223[a] (−)[b]	558 ± 15 (−)	2271 ± 788 (M)
	6	399 ± 16 (−)	326 ± 208 (−)	564 ± 41 (−)
peel	0	309 ± 41 (−)	9306 ± 552 (+)	10982 ± 386 (+)
	6	328 ± 102 (−)	1815 ± 128 (M)	4841 ± 854 (M)

[a] Mean ± standard deviation (n = 3). [b] Threshold value: T_1 = 700 (nonirradiated), T_2 = 5000 (irradiated), (−) < T_1, T_1 < (M) < T_2, and (+) > T_2.

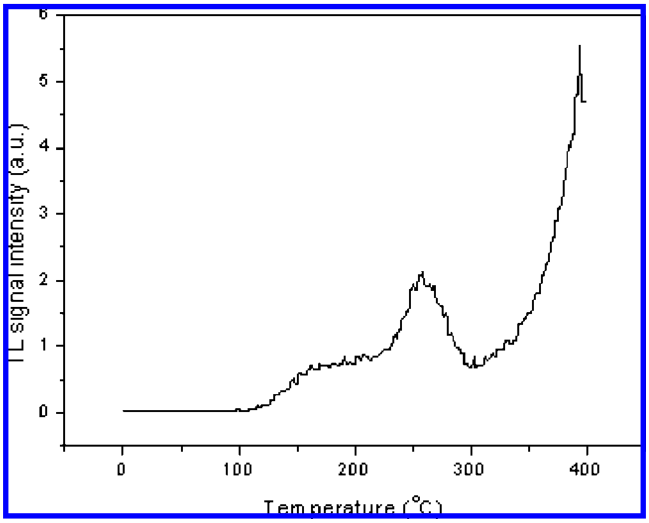

Figure 1. Typical TL glow curve of minerals separated from nonirradiated kiwifruits.

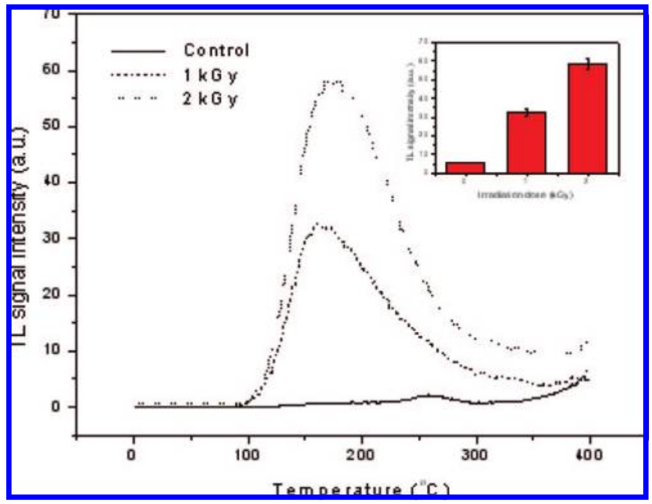

Figure 2. TL glow curve intensities of minerals separated from irradiated kiwifruits at different doses.

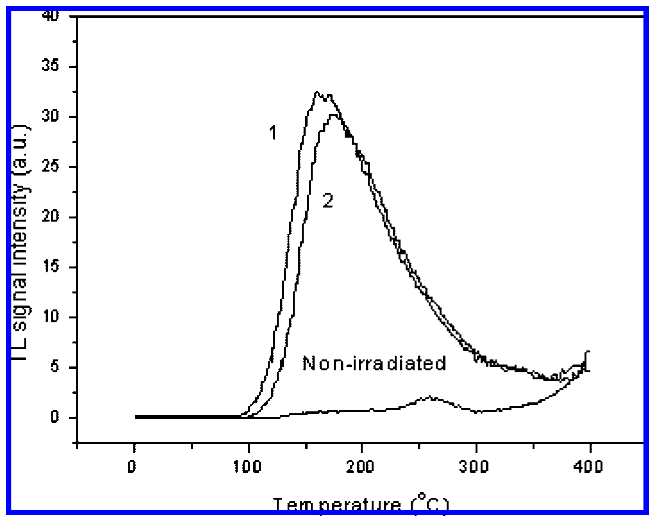

Figure 3. TL glow curves of minerals separated from 1 kGy irradiated kiwifruits after 6 weeks of storage (1, 0 week; 2, 6th week after irradiation).

packaging 20 fruits in each pack with low-density polyethylene (LDPE) film and irradiated at doses ranging from 0 to 2 kGy using a Co-60 γ irradiator (100 kCi point source AECL, IR-79, MDS Nordion International Co. Ltd., Ottawa, Canada) at the Korean Atomic Energy Research Institute (KAERI). A ceric−cerous dosimeter (Harwell, U.K.) was used to confirm the total absorbed doses, and the error range was within ±5.6%. The irradiated and nonirradiated control samples were stored under dark conditions at refrigeration temperature (4 ± 1 °C) for 6 weeks to confirm the stability of detection parameters.

PSL Measurements. The PSL measurement was performed as described by EN 13751 (*16*) using a SURRC PPSL Irradiated Food Screening System (SURRC, Glasgow, U.K.). A total of 20 kiwifruits from each pack (n = 3) were used to obtain the flesh and peel before freeze-drying (Model SFDSF12, Sewon Freezing Engineering Co., Seoul, Korea) for PSL measurements. The PPSL system (serial; 0021, SURRC; Scottish Universities Research and Reactor Centre, U.K) was used for PSL measurement of the ground samples (≤5 g) placed in a disposable Petri dish with a 50 mm diameter (Bibby sterlin type 122, Glasgow, U.K.). The PSL signal was recorded at a rate of counts/60 s for both the control and irradiated samples. The PSL signals [photon counts (PCs)] emitted from the sample per second were automatically accumulated in the PC and presented as counts/60 s. PSL signals were compared to two thresholds, the lower threshold (T_1, 700 counts/60 s) and upper threshold (T_2, 5000 counts/60 s), even though they are specific for herbs and spices. Signals between two thresholds were classified intermediate, which requires further investigations for the confirmation of the test samples whether or not they have been irradiated (*16*). Distribution and handling of the samples were carried out under subdued lighting.

TL Measurements. The methods for TL analysis were conducted on the basis of the EN 1788 (*17*), in which the inorganic dust minerals (≥0.2 mg) were separated from the samples by rinsing the surface of 20 kiwifruits from each batch (n = 3). The 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/s. After the TL glow curve (the first glow, TL_1) measurement, the TL characteristics in minerals were completely removed by annealing (400 °C, 5 s). To normalize TL_1, the tested minerals were re-irradiated at 1 kGy and the TL glow curve (second glow, TL_2) was measured. Finally, the TL ratio (integrated area of TL_1/TL_2 between 150 and 250 °C) was calculated as the threshold values: less than 0.1 for nonirradiated samples and more than 0.1 for irradiated ones (*17*).

X-ray Diffraction Measurements. A multipurpose X-ray diffractometer (MP XRD, X′ Pert Pro, PANalytical, Netherland) was used to characterize the inorganic dust minerals (≤5 mg) present in kiwifruit peels. The X-ray diffractometer was calibrated using silicon powder (corundum) as a standard reference material, and all of the measurements were conducted under the following conditions: X'celerator (Ultra fast) detector, 10−70° of scan angle, 11.9 deg/s of scan rate, Gonio of scan axis, continuous scan mode, and radiations of Cu Kα having a wavelength of 1.540598 A°. The XRD spectra for the inorganic dust mineral samples (≤5 mg) were obtained between 10 and 70°θ at a 2°θ scan. Each peak of the XRD spectra was identified by comparing it to the reference data of 400 mineral candidates.

Statistical Analysis. All measurements were performed for three different packs (n = 3). The data were analyzed using Origin 6.0 (Microcal Software, Inc., Northampton, MA) (*18*).

Table 2. TL Glow Curve Values (150–250 °C) and TL Ratios (TL_1/TL_2) of Inorganic Dust Minerals Separated from Irradiated Kiwifruits

TL glows	storage period (week)	irradiation dose (kGy)			*F* value
		0	1	2	
TL_1	0	0.027 ± 0.004 d[a]	1.624 ± 0.146 b	2.276 ± 0.152 a	207.49[b]
	6	0.032 ± 0.004 d	1.228 ± 0.026 c	2.185 ± 0.115 a	
TL_2	0	1.421 ± 0.013 b	2.557 ± 0.045 a	2.479 ± 0.415 a	16.54[b]
	6	1.524 ± 0.016 b	1.562 ± 0.025 b	2.288 ± 0.153 a	
TL ratio	0	0.019 ± 0.002 d	0.635 ± 0.038 c	0.918 ± 0.139 ab	90.12[b]
	6	0.021 ± 0.003 d	0.786 ± 0.027 bc	0.955 ± 0.117 a	

[a] Mean ± standard deviation ($n = 3$). [b] 150 to 250 °C $p < 0.01$.

Table 3. Relative Abundance of Minerals Separated from Kiwifruits Using an X-ray Diffractometer

sample	relative abundance (%)		
	Na-feldspar	quartz	total
kiwifruit peel	51.8 ± 0.4[a]	48.2 ± 0.5	100.0

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

RESULTS AND DISCUSSION

Mineral contamination can occur not only as a result of the wind but also through the direct contact of soil to kiwifruits. Minerals store energy in the form of trapped charge carriers when exposed to ionizing radiations. Luminescence is light emitted from materials when stimulated by light in the case of PSL and heat in the case of TL, as a result of charge-trapping and detrapping processes at defect sites within the material of the lattice (*2, 3, 19*).

PSL Characteristics. For the screening of irradiated kiwifruits, the PCs of its flesh and peel were measured depending upon the irradiation dose and storage period (**Table 1**). In the case of flesh, the PCs for both nonirradiated control and 1 kGy irradiated samples were 558 or less, which was less than the lower threshold value (700 counts/60 s), indicating them as negative (T_1, nonirradiated). Also, the 2 kGy irradiated samples showed intermediate PCs (threshold value T_1-T_2, M) with 2271 counts. Thus, it was concluded that the use of kiwifruit flesh was not suitable for PSL measurement (*16*). The freeze-dried kiwifruit peel, however, showed 309 PCs (negative, T_1) for the nonirradiated samples and above 9306 PCs (positive, T_2) for 1 or 2 kGy irradiated samples, which were higher than the upper threshold value (5000 counts/60 s), thereby easily screening them out as irradiated. On the other hand, the PCs of stored samples for 6 weeks under dark conditions at refrigeration temperature (4 ± 1 °C) decreased to 1815 and 4841 PCs in 1 and 2 kGy irradiated samples, respectively, which were between the lower and upper threshold values, requiring other analytical methods for discriminating irradiated kiwifruits from nonirradiated ones (*16, 20, 21*). Yi and Yang (*22*) suggested that if the PSL responses of materials isolated from irradiated foods are significantly greater than those of nonirradiated ones or if the fading of the PSL response is low during the long-term storage, the PSL measurement may be suitable for the detection of food irradiation.

TL Characteristics. The TL analysis of the contaminated minerals isolated from foodstuffs is a promising method for irradiation identification (*2, 3, 17, 20*). The TL measurement using inorganic dust minerals separated from the whole kiwifruit surface revealed glow curves (TL_1) with very low intensity at 200–300 °C in nonirradiated samples (**Figure 1**) but with a much higher intensity between 150 °C and 250 °C in irradiated samples at 1 or 2 kGy (**Figure 2**), which implies the very large differences not only in TL glow curve shapes but also in TL signal intensity between irradiated and nonirradiated samples (**Figures 1** and **2**). The integrated TL areas from 150 to 250 °C linearly increased with irradiation doses ($R^2 = 0.9998$); hence, it was apparent that both the intensity of the first glow curves (TL_1) and the temperature ranges where the peaks appeared can be also used as parameters for identifying irradiation treatment (*16, 20*). Thus, the first TL measurement possibly allowed us to identify the irradiation treatment of kiwifruits by comparing the shape as well as the intensity of the TL_1 glow curve (**Figures 1** and **2**).

Meanwhile, the changes in TL_1 glow curves and their stability were observed after 6 weeks of storage at refrigeration temperature, which was deemed as the marketable period of the fruits based on the preliminary sensory evaluation (*23*). The TL_1 characteristics, both the temperature range where the peak appeared and the intensity of the peak, for the 6-month-stored samples, were still reproducible for differentiating the irradiated samples from the nonirradiated control (**Figure 3**), even though the subsequent storage caused insignificant changes in glow curves' intensity and temperature ranges where the peak appears. These negligible changes could be due to the short-term storage at low temperature under dark conditions for the fresh kiwifruits. With the lapse of storage time at room temperature under light exposure, a decrease in the TL signal intensity and its shifting phenomenon of temperature from lower to higher ranges were reported (*24*). This result was supported by TL characteristics measured for irradiated spices including ginger, cumin, chili, and potatoes under different storage conditions (*25, 26*).

It can be understood by the fact that the TL response also depends upon the nature and the quantity of minerals on the aluminum disk used for TL analysis, besides the amount of absorbed radiation. Thus, the normalization of the TL_1 results is necessary for avoiding the effects of the amount and nature of minerals used, which can lead to false results. TL ratios (TL_1/TL_2 measured after 1 kGy irradiation for the TL_1-tested mineral) calculated through the normalization step are adopted to enhance the reliability of TL_1 results (*17, 21*). The TL ratios, as a threshold value for the irradiated kiwifruits, were higher than 0.635 in irradiated samples, while they were 0.019 in nonirradiated samples. After 6 weeks of storage, the difference in TL ratios between the nonirradiated and irradiated samples was still apparent for identifying each other, showing 0.021 and more than 0.786, respectively (**Table 2**). All of the TL_2 values were much higher than 0.015 nC that was 10 × MDL (minimum detectable integrated TL intensity level) for the integration temperature interval from 150 to 250°C. It was found that the measurement of TL ratios would be a reliable tool for the identification of irradiated kiwifruits even after post-irradiation storage. Our results on TL ratios were in agreement with the reported TL threshold values for the nonirradiated (<0.1) and irradiated (>0.1) ones (*17*).

Mineral Composition. The results of the XRD analysis on the composition of inorganic dust minerals contaminating kiwifruit samples are shown in **Table 3**. The mineral composition in relative abundance was very simple, being composed of both feldspar (51.8%, $NaAlSi_3O_8^-$) and quartz (48.2%, SiO_2). Those two minerals can be the source of signals in PSL and TL analyses (*19, 27*). This result was consistent with the reports of Engin (*19*) and Chung (*27*) that only quartz and feldspar minerals were found in inorganic dust samples separated from both black peppers and wild sesame. It supports our results that feldspar shows a very high TL sensitivity, while a possible influence of quartz on the glow curves is practically not observed (*26, 28*).

In conclusion, the PSL measurements were only applicable to the peel of the fruit for irradiation detection soon after irradiation. On the other hand, for the TL analysis on the minerals separated from the peel, both the intensity of the first glow curves (TL_1) and the temperature ranges where the peaks appeared were confirmed as the identification parameters for irradiated kiwifruits during the post-irradiation marketable period. The TL ratios (TL_1/TL_2) calculated through the normalization step could enhance the reliability of TL_1 results (*17, 20, 21*). The inorganic dust minerals from the kiwifruit peel were mainly composed of feldspar and quartz, in which the former could be the predominant source of signals in PSL and TL analyses (*19, 26, 29*).

LITERATURE CITED

(1) International Atomic Energy Agency (IAEA). Database on approvals for irradiated foods (supplement). Food and Environmental Protection Newsletters, 2006; Vol. 9, pp 21–59.
(2) International Atomic Energy Agency (IAEA). Analytical detection methods for irradiated foods, a review of current literature. IAEA-TECDOC-587, 1991; p 172.
(3) Delincée, H. Analytical methods to identify irradiated food—A review. *Radiat. Phys. Chem.* **2002**, *63*, 455–458.
(4) Farkas, J. Irradiation as a method for decontaminating food. *Int. J. Food Microbiol.* **1998**, *44*, 189–204.
(5) Kwon, Y. J.; Huh, E. Y.; Kwon, J. H.; Byun, M. W. Quarantine status of agricultural products for export and application prospects of irradiation technology. *Food Sci. Ind.* **1999**, *32*, 80–90.
(6) United Nations Environment Programme (UNEP). Montreal protocol on substances that deplete the ozone layer, report of the methyl bromide technical options committee. 1995; p 294.
(7) Couey, M. Heat treatment for control of postharvest diseases and insect pests of fruits. *HortScience* **1989**, *24*, 198–202.
(8) Becker, J. O.; Ohr, H. D.; Grech, N. M.; McGiffen, M. E., Jr.; Sims, J. J. Evaluation of methyl iodide as a soil fumigation in container and small field plot studies. *Pestic. Sci.* **1998**, *52*, 58–62.
(9) Gould, W. P.; Sharp, J. L. Cold-storage quarantine treatment for carambolas infested with the Caribbean fruit fly (Diphtheria: Tephritidae). *J. Econ. Entomol.* **1990**, *83*, 458–460.
(10) Delate, K. M.; Brecht, J. K.; Coffelt, J. A. Controlled atmosphere treatments for control of sweet potato weevil (Coleoptera: Curculionidae) in stored tropical sweet potatoes. *J. Econ. Entomol.* **1990**, *83*, 461–465.
(11) Farkas, J. Irradiation for better foods. *Trends Food Sci. Technol.* **2006**, *17*, 148–152.
(12) Delincée, H. Detection of food treated with ionizing radiation. *Trends Food Sci. Technol.* **1998**, *9*, 73–82.
(13) FAO/WHO CODEX STAN. General Codex Methods for the Detection of Irradiated Foods, CODEX STAN 231-2001, Rev. 1, 2003.
(14) Korea Agricultural Trade Information (KATI). Korea agricultural trade information homepage. 2006, www.kati.co.kr.
(15) Jo, D.; Kwon, J. H. Detection of radiation-induced markers from parts of irradiated kiwifruits. *Food Control* **2006**, *17*, 617–621.
(16) EN 13751. Foodstuffs—Detection of irradiated food using photostimulated luminescence. European Committee for Standardization, Brussels, Belgium, 2002.
(17) EN 1788. Foodstuffs—Detection of irradiated food from which silicate minerals can be isolated, method by thermoluminescence. European Committee for Standardization, Brussels, Belgium, 2001.
(18) Origin. Origin tutorial manual, version 6.0. Microcal Software, Inc., Northampton, MA, 1999; pp 20–45.
(19) Engin, B. Thermoluminescence parameters and kinetics of irradiated inorganic dust collected from black peppers. *Food Control* **2007**, *18*, 243–250.
(20) Sanderson, D. C. W.; Carmichael, L. A.; Fisk, S. Establishing luminescence methods to detect irradiated foods. *Food Sci. Technol. Today* **1998**, *12*, 97–102.
(21) Kwon, J. H.; Jeong, J. Y.; Lee, E. Y.; Jo, D.; Noh, J. E.; Lee, J. E. Multiple detection to identify irradiated brown rice of different origins. *Food Sci. Biotechnol.* **2002**, *11*, 215–219.
(22) Yi, S. D.; Yang, J. S. The application of pulsed photostimulated luminescence (PPSL) method for the detection of irradiated foodstuffs. *J. Food Sci. Nutr.* **2000**, *5*, 136–141.
(23) Larmond, E. Methods for sensory evaluation of foods. Canada Department of Agriculture, Ottawa, Canada, 1973; Publication 1284, pp 27–30.
(24) Hammerton, K. M.; Banos, C. Detection of irradiated spices by thermoluminescence analysis, In *Detection Methods for Irradiated Foods*, McMurray, The Royal Society of Chemistry: Cambridge, U.K., 1996; pp 168–171.
(25) Mamoon, A.; Abdul-Fattah, A. A.; Abulfaraj, W. H. Thermoluminescence of irradiated herbs and spices. *Radiat. Phys. Chem.* **1994**, *44*, 203–206.
(26) Kwon, J. H.; Jeong, J. Y.; Chung, H. W. Thermoluminescence characteristics of minerals from irradiated potatoes of different origins of production. *Radiat. Phys. Chem.* **2002**, *63*, 415–418.
(27) Chung, H. W. Characterization of irradiated foods by thermoluminescence and electron spin resonance measurements for their identification. Ph.D. Thesis, Kyungpook National University, Daegu, Korea, 2000.
(28) Pinnioja, S.; Lindberg, A. Effect of mineral composition on thermoluminescence detection of irradiated seafood. *Radiat. Meas.* **1998**, *29*, 651–661.
(29) Soika, C.; Delincée, H. Thermoluminescence analysis for detection of irradiated food—Luminescence characteristics of minerals for different types of radiation and radiation dose. *Lebensm.-Wiss. Technol.* **2000**, *33*, 431–439.

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