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The application of different detection methods for irradiated dried anchovy and shrimp

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Abstract

Three different techniques, photostimulated luminescence (PSL), electron spin resonance (ESR) and thermoluminescence (TL) were applied for the detection of dried anchovy and shrimp exposed to electron beam at 0–10 kGy. PSL values for irradiated samples were more than 5000 photon counts/60 s, upper threshold (T_2), whereas those of non-irradiated samples were <700 counts (lower threshold, T_1) in anchovy and intermediate values of T_1–T_2 in shrimp. ESR measurements using both the whole samples did not show any signals specific to irradiation. However, in the case of anchovy it was possible to use bone for ESR detection, showing typical signals ($g = 2.002$, 1.998). Minerals separated from both the samples for TL measurement showed that non-irradiated samples were characterised by glow curves situated at about 300°C with low intensity, while all irradiated samples showed glow peaked at about 200°C and its intensity was high enough to be discriminated from the non-irradiated ones. Furthermore, normalization by a re-irradiation enhanced the reliability of detection results of TL. In conclusion, a multi-step detection using different methods enhances confidence in the detection of irradiated food. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Irradiated food; Muli-step detection; PSL/ESR/TL; Dried anchovy and shrimp

1. Introduction

In view of the growing interest in food irradiation technology, a reliable method for detecting irradiated foods requires to enforce legal controls and improve international trade in compliance with labeling regulations. Many detection techniques have been tested on various food products, and some emerging analytical methods are being examined for their suitability. Three different detection methods, such as photostimulated luminescence (PSL), electron spin resonance (ESR) spectroscopy and thermoluminescence (TL), were selected in this study because they have been demonstrated to be practical for certain food products (Delincée, 1998). PSL and TL are radiation-specific phenomena from energy stored by trapped charge carriers following irradiation (Sanderson et al., 1996a). Releasing such stored energy by optical or thermal stimulation can result in a detectable luminescence emission. PSL detection method has been studied as a screening method using whole samples for many irradiated foods including brown shrimp, herbs, spices, seasonings, and shellfish (Sanderson et al., 1996a, b), and white ginseng powder (Chung et al., 2000). TL has been tested for detecting various foods, such as spices and herbs (Autio and Pinnioja, 1990), shellfish (Schreiber et al., 1994), foods containing salt (Kwon et al., 1998), and was adopted as a standard method for detecting irradiated foods, from which silicate minerals can be isolated (EN 1788, 1996). ESR has been also used to detect irradiated food that contains bone (EN 1786, 1996). The shapes of ESR signals vary with the types of free radicals induced by irradiation in different foods (IAEA, 1991; Desrosiers and Simic, 1988; Dodd et al., 1988). The purpose of this work is to investigate how three different detection methods can be applied to verify whether dried anchovy and shrimp have been irradiated or not.

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2. Experimental

Dried anchovy and shrimp (MC: 20 ± %) were purchased at a wholesale market in Taegu, Korea. Samples were packed in polyethylene bags (thickness: < 2.0 cm) and exposed to accelerated electrons of 10 MeV with a dose rate of 3.6×10^{11} Gy/h at the Federal Research Centre for Nutrition, Karlsruhe. The applied doses, 2.5–10 kGy, were ensured by means of GAF chromic film dosimeters (International Speciality Products, Wayne, USA). Firstly, PSL measurement was performed by a SURRC Pulsed PSL irradiated food screening system (lower threshold/T_1: 700 photon counts/60 s; upper threshold/T_2: 5000 counts). All dispensing and handling of the samples were carried out under subdued lighting. Secondly, ESR spectroscopy was carried out for the samples, previously dried in a vacuum oven at 40°C for 4 h, to detect hydroxyapatite radicals induced by irradiation. A Bruker EMS 104 spectrometer (Bruker, Rheinstetten, Germany) was operated with modulation amplitude of 2.85 G, microwave power of 10 mW, microwave frequency of 9.76 GHz and receiver gain 60 dB. ESR signal intensities were measured as the peak-to-peak height of the major component and reported in arbitrary units (EN 1786, 1996). Finally, minerals were separated from the samples by a density separation procedure for TL analyses (EN 1788, 1996) by TL/OSL System TL-DA-15 (Risø, Roskilde, Denmark). The first glow curve (TL1) was compared with the second curve (TL2) obtained through a re-irradiation step at 1 kGy. The ratios of TL1–TL2 (TL1/TL2) were calculated for both irradiated and non-irradiated samples to verify the reliability of detection results with TL1 (EN 1788, 1996). All determinations were made more than in duplicate.

3. Results and discussion

3.1. Photostimulated luminescence detection

Table 1 shows the values of PSL measurement for dried anchovy and shrimp. The photon counts of non-irradiated samples were less than 334 for anchovy and ranged from 1,539 to 1,885 for shrimp. However, the photon counts of the irradiated anchovy and shrimp were > 7,000. In previous reports on PSL measurements for different foods, such as dried spices, condiments and shrimp, photon counts of 700–1000 were normally detected in the non-irradiated foods, while irradiated foods showed higher than 4000–5000 photon counts (Sanderson et al., 1996a, b, 1997). Based on these threshold values, dried anchovy was suitable for PSL measurement to detect whether it has been irradiated or not. For dried shrimps, the lower threshold needs to be adjusted, but the differences between the values for irradiated and non-irradiated samples are enormous. More work with several varieties of dried shrimps from different origins will be necessary. In the interlaboratory test using 40 kinds of herbs, spices, seasonings, and 4 blends with a maximum dose of 10 kGy, 98.6% of all samples were correctly identified by PSL (Sanderson et al., 1997). Similarly, a satisfactory result was found for irradiated white ginseng powder (Chung et al., 2000).

3.2. Electron spin resonance detection

ESR spectroscopy did not show any signals specific to irradiation when measured using whole samples of dried anchovy and shrimp. Unlike a lobster or a prawn, dried shrimp's cuticle is too soft to be applied to ESR detection. But the specific ESR spectra with a signal ($g = 2.002$, 1.998), that was derived from radiation-induced hydroxyapatite radicals (EN 1786, 1996), could be observed in the case of the bone separated from dried anchovy (Fig. 1). As shown in Fig. 1, peak-to-peak signal intensities increased with radiation doses. Recent studies of ESR spectroscopy on fish bone demonstrated the promising potential of this method (Empis et al., 1995). In the in-house blind trials on Norway lobster (*Nephrops norvegicus*), all 72 coded samples examined were identified with a 100% success rate (Stewart and Stevenson, 1997). Collaborative trials showed good results for brown shrimp and Norway lobster, thereby leading to the official adoption of the ESR method in Germany. Moreover, the potential of ESR spectroscopy

Table 1
Photostimulated luminescence determinations of irradiated dried anchovy and shrimp with different doses

Sample	Irradiation dose (kGy)				
	0	2.5	5	7.5	10
Anchovy	168 ± 165[a](−)[b]	7783 ± 774 (+)[d]	29,742 ± 2570(+)	9236 ± 1622(+)	9220 ± 712(+)
Shrimp	1712 ± 173(M)[c]	523,472 ± 81,590(+)	357,274 ± 79,288(+)	1,204,810 ± 617,179(+)	442,082 ± 306,824(+)

[a] Means of duplicates ± standard deviation.
[b] Less than 700 counts/60 s.
[c] 700–5000 counts/60 s.
[d] More than 5000 counts/60 s.

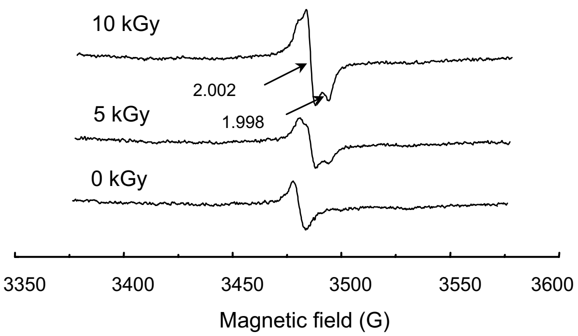

Fig. 1. Typical ESR spectra derived from bone separated from irradiated dried anchovy.

has been confirmed in detection of irradiated oysters and mussels (Raffi et al., 1996). However, the variability of ESR signals depending on the origins of the shell and the species requires investigation along with a blind trial for their validation.

3.3. Thermoluminescence detection

The intensity of glow curves for separated minerals from irradiated and non-irradiated samples showed a remarkable difference. The position of glow curve was not clear through all temperature ranges in non-irradiated anchovy, but that for the irradiated anchovy peaked at about 207°C (Fig. 2). In the case of dried shrimp, the glow curves peaked at 203°C for irradiated samples and at about 300°C for non-irradiated ones. The areas of the first TL glow curve (TL1) for the irradiated samples at 2.5 kGy, ranging from 150°C to 250°C, were at least 17 times higher in anchovy and 330 times higher in shrimp, respectively, than those of the non-irradiated samples. The integrated areas of glow curves increased with applied doses. Although the intensity of the TL1 for irradiated samples was high enough for discrimination from that of non-irradiated ones, normalization by a re-irradiation at 1 kGy (TL2) made it possible to clarify the detection results, as shown in Figs. 2 and 3. The ratios of areas for TL1–TL2 determined for irradiated and non-irradiated anchovy were <0.009 for non-irradiated sample and more than 1.465 for irradiated ones at 2.5–10 kGy, respectively. Similar results were observed in dried shrimp, with <0.013 for non-irradiated sample and higher than 1.559 for irradiated samples. Therefore, it was possible to discriminate clearly between irradiated and non-irradiated dried anchovy and shrimp by comparing their TL ratios. Our findings confirmed the numerous promising results reported by many scientists (Sanderson et al., 1996a, b; Schreiber et al., 1994; Carmichael et al., 1994).

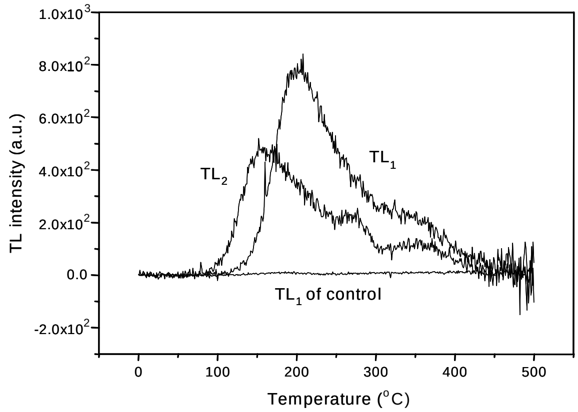

Fig. 2. The normalization of TL glow curves by re-irradiation for 2.5 kGy-irradiated dried anchovy (TL1: glow curve before re-irradiation, TL2: glow curve after re-irradiation at 1 kGy).

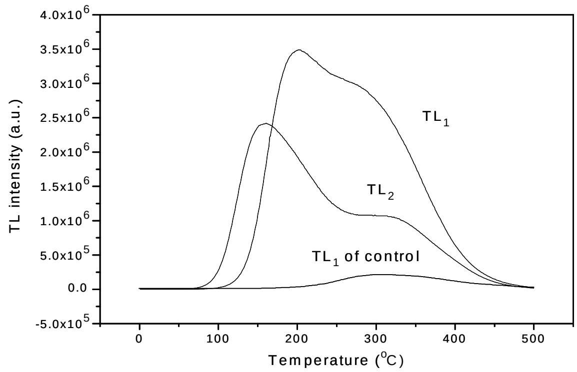

Fig. 3. The normalization of TL glow curves by re-irradiation for 2.5 kGy-irradiated dried shrimp (TL1: glow curve before re-irradiation, TL2: glow curve after re-irradiation at 1 kGy).

4. Conclusion

Three different techniques were applied for the detection of dried anchovy and shrimp when exposed to electron beam. PSL proved to be a screening means for the irradiated samples. The bone separated from dried anchovy was suitable for ESR spectroscopy by determining radiation-induced hydroxyapatite radicals. The minerals separated from irradiated dried anchovy and shrimp showed typical TL glow curves as compared with those of non-irradiated samples, making it possible to discriminate between the two. Furthermore, normalization by a re-irradiation step greatly enhanced the reliability of detection results of TL. As a result, it shows that a multi-step detection using different methods enhances confidence in the detection of irradiated food.

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