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Analysis of shellfish by thermoluminescence and X-ray diffraction methods: Knowledge of gamma-ray treatment and mineral characterization

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Abstract

To investigate the detection of irradiated shellfish, seven kinds of shellfish samples were gamma irradiated at 3 and 6 kGy. The first-glow curves for all the control and irradiated shellfish samples were recorded between temperatures of 50 and 400 °C at a heating rate of 5 °C/s. All the samples, the first glow curves (TL_1) of which have been recorded, were re-irradiated at 1 kGy for the normalization of results. Their second glow curves (TL_2) were obtained at the same conditions in order to achieve the thermoluminescence (TL) ratios (TL_1/TL_2). The TL method proactively identified the whole shellfish samples by using the calcite, aragonite and quartz minerals that are present in the shells. The X-ray diffraction spectroscopy has been used as an analytical tool for the characterization of minerals that are present in the shells as inorganic materials along with biomaterial.

Keywords: Shellfish; Irradiation; Thermoluminescence; Minerals; X-ray diffraction

1. Introduction

The popularity of eating shellfish can be traced over several centuries and it is among the staple food items in the world. A widespread disease occurred in Europe and America in 1924 due to pathogens in the shellfish. As a result, the National Shellfish Sanitation Program was developed in the US in 1925 (David, 1994). Seafood is comparatively vulnerable to pathogenic microorganisms such as *Salmonella*, *Escherichia coli*, *Shigella* and *Vibro* that grow rapidly and cause spoilage, which can cause disease in human. In Europe, the fumigation of seafood for the reduction of microbial load is being replaced by irradiation processing due to the production of toxic residues (Thayer et al. (1996) on http://www.cast-science.org/cast/pub/rad_ip; Fields et al. (1996) on http://mbao.org/1996airc/0720fields). Irradiation treatment is an alternative and it can efficiently reduce the bio-burden without any harmful effects. Irradiation of seafood is permitted in tropical regions where a warm and humid climate favors the growth of pathogenic microbes (Pinnioja and Lindberg, 1998). In the US, irradiation can be applied to a variety of foods, including wheat flour, white potatoes, pork, poultry, meat, fruits and vegetables, herbs and spices. The US Food and Drug Administration (FDA) announced a few amendments regarding food additive regulations. One such rule is that ionizing radiation will be used for the control of *Vibrio* species and other foodborne pathogens in fresh or frozen mollusk shellfish, including oysters, mussels, clams, etc. (Anon (2005) on www.nukewatch.com/index.html, Anon (2006), on http://www.mnbeef.org/images/food). With a rapid increase of irradiated food commodities and their movement in trade between nations, the need for detection will be of prime importance in order to implement the system of legislative control of false labeling.

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Several physical, chemical and biological methods have been standardized for the detection of different kinds of foods. Thermoluminescence (TL) technique is seen as being effective for food items that contain grit as a contaminant (Sanderson, 1990; Sanderson et al., 1989, 2003a–c; Khan et al., 1998; Khan and Bhatti, 1999; Kwon et al., 2000; Pinnioja et al., 1999a, b; Choi et al., 2004). Silicate minerals have been recommended for study since they yield intense TL signals on irradiation. Carbonate and clay are commonly found in seafood, but the use of carbonate minerals for irradiation identification by the TL technique has not been studied extensively (Pinnioja and Lindberg, 1998).

In this study, we have tried to identify irradiated shellfish by the direct measurement of TL using the biogenic material from shells. The characterization of minerals present in the shells of shellfish was also performed by using X-ray diffraction (XRD) spectroscopy on seven types of shellfish to support the TL results.

2. Materials and methods

2.1. Samples and irradiation

Seven types of shellfish, melanian snail, corbicula, ark shell, solen, Gomphina melanaegis, scallop and short-necked calm, were purchased from a fish market in Daegu, South Korea. All fishes were packed in polyethylene bags and irradiated at 3 and 6 kGy using a Co-60 source at the Korea Atomic Energy Research Institute (KAERI) in Daejeon, Korea. The absorbed dose and dose rate were measured by using an aniline dosimeter.

2.2. TL measurements

The shells of the control and irradiated shellfish were isolated, washed with re-distilled water (RDW), and treated with 1% HCl for 2 min. Finally, the samples were washed several times with RDW thoroughly and put in a dry oven at 50 °C for 18 h (Engine and Guven, 2000). The dried shells were ground into small particles and loaded onto an aluminum disc, with an internal diameter of 0.6 mm for TL measurements, which were performed on the shell samples by a 4500 TL Reader (HARSHAW, Germany) at the Instrumentation Center, Kyungpook National University in Daegu. The TLD reader, based on the method of EN 1788 (1996), was operated between 50 and 400 °C, at a heating rate of 5 °C/s. The first glow curves (signal intensity versus temperature) were measured for the control and irradiated samples containing minerals in the structural part of the shells of shellfish. In order to get unequivocal results, the samples, the TL_1 of which have been already recorded, were administered in the re-irradiation step 1 kGy for the second glow curves (TL_2) under the same conditions as for TL_1 measurements, which was done in order to obtain the TL ratios (TL_1/TL_2).

2.3. XRD analysis

All the shellfish samples were ground into fine powder using pestle and mortar and transferred to a silicon holder for XRD analysis. A multipurpose X-ray diffractometer (MP XRD, X' Pert Pro, PANalytical, Netherlands) at the Korea Basic Science Institute (KBSI) in Daegu, South Korea, was used to characterize the minerals present in the shells of shellfish. The X-ray diffractometer was calibrated using silicon powder (corundum) as a standard reference material (SRM) and all measurements were conducted under the following conditions:

Detector: X'celerator (ultra-fast) detector
Scan angle: 10–70°
Scan rate: 11.9°/s
Scan axis: gonio
Scan mode: continuous
Used radiation: Cu Kα with a wavelength of 1.540598 Å

XRD spectra for each sample were obtained between 10° and 70° θ at a scan of 2° θ. Each peak of the XRD spectra was identified by comparing with the reference data of 400 mineral candidates.

2.4. Statistical analysis

Significant differences among the treatments were determined using ANOVA and Duncan's multiple range tests from the statistical analysis system (SAS) software, version 9.1. All measurements were performed in duplicate and the significance of the results was established at $p<0.05$.

3. Results and discussion

3.1. Shapes of TL glow curves

The TL results of the seven types of the control and irradiated shellfish at 3 and 6 kGy are summarized in Table 1. The integrated areas of the first glow curves (TL_1) for the irradiated samples are higher than those of the controls in each type of shellfish.

The TL_1 glow curves for all the control and irradiated samples have been integrated between temperatures of 50 and 400 °C and are shown in Figs. 1–7. Fig. 1 shows the TL_1 for the control and irradiated melanian snail samples at 3 and 6 kGy. The TL signals are weak but detectable from 225 to 275 °C for 3 kGy and from 100 to 200 °C for 6 kGy irradiated samples. The shapes of the maxima of TL glow curves are related to the existence of different traps, which are created by ionizing radiation. The holes and electron traps in the carbonate minerals by different kinds of radiation have already been reported (Urbina et al., 1998). In the case of corbicula, the TL glow curves for the control and irradiated samples are shown in Fig. 2. All the TL spectra appeared in the temperature range of