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Thermoluminescence of contaminating minerals for the detection of radiation treatment of dried fruits

H.M. Khan[a,]*, Ijaz A. Bhatti[a], Henry Delincée[b]

[a] *Radiation Chemistry Laboratory, National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar 25120, Pakistan*

[b] *Institute of Nutritional Physiology, Federal Research Centre for Nutrition, Haid-und-Neu Str. 9, D-76131 Karlsruhe, Germany*

Abstract

Several types of dry fruits (pistachio nut, dried apricot, almond and raisins) have been investigated for detection of their radiation treatment by gamma rays or electron beam using thermoluminescence (TL) measurements. These samples were irradiated to 1.0–3.0 kGy (gamma rays) or 0.75–3.9 kGy (10 MeV electron beam). Thermoluminescence glow curves for the contaminating minerals separated from the dry fruits were recorded between the temperature range of 50°C and 500°C. In all the cases, the intensity of TL signal for the irradiated dry fruits was 1–3 orders of magnitudes higher than the TL intensity of the corresponding unirradiated control samples allowing clear distinction between the irradiated and unirradiated samples. These results were normalized by re-irradiating the mineral grains with a gamma-ray dose of 1.0 kGy, and a second glow curve was recorded. The ratio of intensity of the first glow curve (TL_1) to that after the normalization dose (TL_2), i.e. (TL_1/TL_2) was determined and compared with the recommended threshold values. These parameters, together with comparison of the shape of the first glow curve, gave unequivocal results about the radiation treatment of the dry fruit samples. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Food irradiation; Detection methods; Thermoluminescence; Glow curves; Dry fruits

1. Introduction

Food irradiation has been recognized as a reliable and safe method for the preservation of food and to improve hygienic quality of foods. A number of factors have highlighted the need for the development of analytical methods to detect irradiated treatment of foods. These factors include commercialization of food irradiation throughout the world, greater international trade in irradiated food and different regulations relating to use of this technology in different countries (Delincée, 1998; McMurray et al., 1996). In the last several years, several detection methods have been developed as a result of international efforts and co-operation; The thermoluminescence (TL) method has emerged as one of the important, reliable and validated detection methods for those food items which are contaminated with inorganic material, such as quartz or dust particles even when the amount of mineral debris is very low (Delincée, 1998; CEN, 1996; MAFF, 1993). Thermoluminescence is a radiation specific phenomenon where energy stored by trapped charge carriers as a result of irradiation can be released by thermal stimulation and detected in form of a glow curve. In our previous studies, we have investigated TL for detection of radiation treatment of some types of spices, dates and legumes (Khan and Delincée, 1995a, b; Khan et al., 1998). For the present study, we have selected dry fruits, which is a cash crop of northern area of Pakistan. They can be stored for a long time; however, during storage a significant quantity is normally lost due to insect infestation and microbial contamination. Irradiation is a promising technique to

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*Corresponding author. Tel.: +92-91-921-6766; fax: +92-91-921-6671.

E-mail address: hmkhan@upesh.edu (H.M. Khan).

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control insect infestation and microbial contamination in dry fruits. Therefore, in the present work, four types of dry fruits have been selected to study the detection of the radiation treatment by TL.

2. Experimental

Four types of dry fruits, i.e. dried apricot (*Arminiaca*), almond (*Prunus amygdalus*), pistachio nut (*Pistacia vera*) and raisins (*Vitis vinifera*) were purchased from the local market of Peshawar. A second sample of pistachio nut (pistachio 2) was purchased from Karlsruhe. These samples were packed in polyethylene bags and irradiated by gamma rays (radiation dose of 1.0 and 3.0 kGy) using a ^{60}Co gamma-ray source at the Nuclear Institute for Food and Agriculture, Tarnab, Peshawar (dose rate 0.60 Gy/s). The second sample of pistachio nut was irradiated by electron beam from a 10 MeV linear accelerator (dose rate 10^8 Gy/s) to doses of 0.75, 2.2 and 3.9 kGy. Re-irradiation of samples for normalization of TL results was carried out using a ^{60}Co gamma source in Karlsruhe (Gammacell 220, dose rate 0.13 Gy/s). These radiation sources were calibrated using Fricke dosimeter or radiochromic films (Sehested, 1970; McLaughlin et al., 1991).

The method used for the isolation of mineral particles from dry fruits was similar to that described by us earlier (Khan and Delincée, 1995a, b; Khan et al., 1998; CEN, 1996). Thermoluminescence measurements were performed using a PC based ELSEC model-7185 TL reader equipped with pure nitrogen cooling system. The instrument was calibrated with a ^{14}C light source and the heating plate and optical system were thoroughly cleaned before measurements. The TL reader operates from 50°C to 500°C at a heating rate of 10°C/s. Thermoluminescence glow curves for minerals separated from irradiated and unirradiated samples of the dry fruits were recorded and integrated areas from 70°C to 500°C determined (TL_1). For the normalization of results, re-irradiation of the minerals was carefully carried out using ^{60}Co gamma-ray source with a predetermined normalization dose. The second TL measurement for the re-irradiated disc was performed under the same conditions as that for the first TL measurement and area for the resulting second glow curve (TL_2) was recorded. This glow curve was compared with the first glow curve for the identification of irradiation treatment using the ratio of the area of first glow curve to that of the second glow curve (TL_1/TL_2).

3. Results and discussion

Thermoluminescence glow curves for the mineral contaminants isolated from the irradiated and unirradiated dry fruit samples were recorded within 1 month of irradiation. However, it is known that TL signals are stable and can be analysed after long post-irradiation storage time (Schreiber et al., 1993). Fig. 1 shows typical glow curves for unirradiated (bottom) and irradiated (top) samples of pistachio nut. In these figures, glow curves 1 represent the first glow curve without re-irradiation, whereas the second glow curve in each figure (marked as glow curve 2) shows the TL response after re-irradiation, which will be discussed later. Integrated area for each glow curve in the temperature range of 70–500°C was determined. It was found that the integrated areas of first glow curves (TL_1) for the samples irradiated to gamma-ray dose of 1.0 and 3.0 kGy or to electron beam dose of 0.75–3.9 kGy in all the cases were much higher (15–1000 times) than the corresponding unirradiated control samples. A comparison showing this large difference in TL response of the irradiated and unirradiated dry fruit samples is presented in terms of bar diagram in Fig. 2. Generally, the area of the glow curve for samples irradiated to higher doses is larger than the corresponding samples irradiated to lower doses. However, in the case of apricot samples, TL

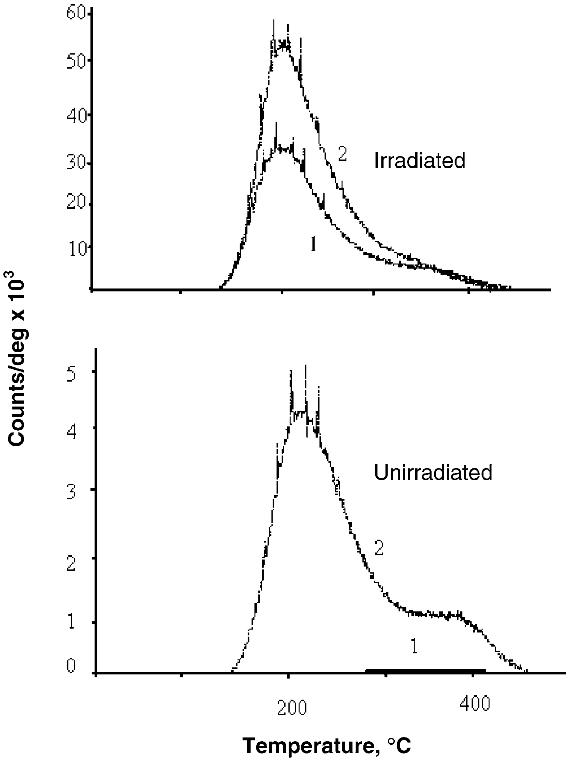

Fig. 1. Glow curves for unirradiated (bottom) and irradiated (top, 0.75 kGy) pistachio nut; (1) represents the glow curve before re-irradiation whereas (2) shows the glow curve after re-irradiation.

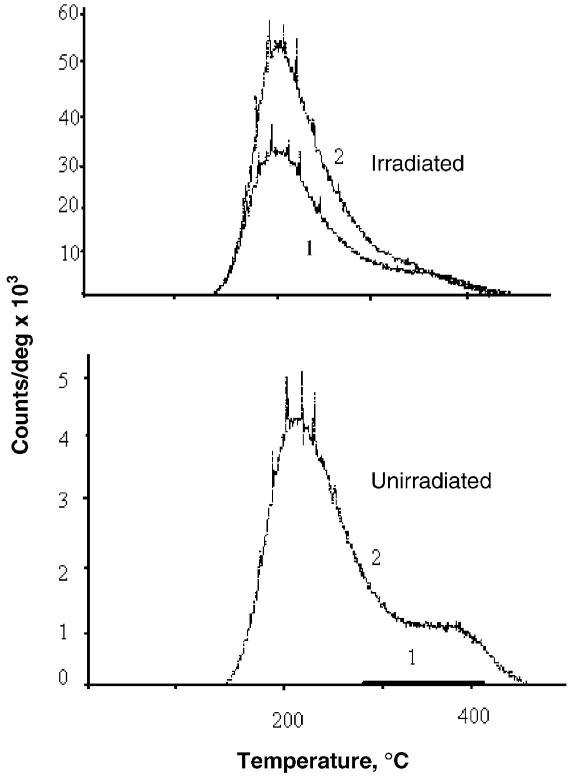

Fig. 2. Comparison of ratio of areas of first glow curve to second glow curve (TL_1/TL_2) on log scale for unirradiated samples (0 kGy, ratio of 0.1 or less) and gamma or electron irradiated dry fruit samples (ratio of 0.6 or more).

response of sample irradiated to an absorbed dose of 3.0 kGy is less than the sample irradiated to 1.0 kGy (Fig. 2). It can be explained by the fact that the TL response also depends upon the nature and the quantity of mineral particles deposited on the steel disc used for TL measurement, besides on the amount of radiation.

Normalization of first glow curve results is necessary in order to avoid the effects of amount and nature of mineral particles, which can result in false results. The TL results were normalized by carefully re-irradiating the stainless steel disc with the deposited minerals (for which first glow curve has already been recorded) to a specific dose and recording the second glow curve. For the dry fruit samples, a re-irradiation dose of 1.0 kGy was applied to all samples, except for the second pistachio nut samples (control sample and the one irradiated to 0.75 kGy) for which a re-irradiation dose of 0.75 kGy was used. Typical second glow curves for the pistachio nut samples (labelled as 2) are also shown in Fig. 1. The ratios of integrated areas of the first glow curve to that of the second glow curve (TL_1/TL_2) was calculated for irradiated and unirradiated samples of dry fruits. The ratio (TL_1/TL_2) for all unirradiated samples was <0.11 and for all irradiated samples the ratio was 0.61 or higher. These results are summarized in Fig. 2 where the (TL_1/TL_2) ratios for all the 16 samples have been plotted (on log scale) for unirradiated and irradiated samples to show the difference in (TL_1/TL_2) ratios. On the basis of (TL_1/TL_2) ratio, it is possible to correctly identify all the irradiated samples without the availability of a similar control sample.

Different threshold values for ratio TL_1/TL_2 have been suggested by different laboratories as a result of comprehensive studies. In an intercomparison study on spices, herbs and their mixtures, performed by Federal Health Office, Germany (Schreiber et al., 1993), a threshold value of 0.6 was recommended. Below this value, a sample would be considered as unirradiated and vice versa. European Committee for Standardization (CEN) has proposed other thresholds not employing the whole integrated area (50–500°C) of the glow curve, but just the areas evaluated over a recommended temperature interval (± 10°C up to ± 40°C in the range of 150–250°C). Using this recommended temperature interval, TL glow ratio from irradiated samples are typically >0.5, whereas those from unirradiated samples are generally below 0.1. If this ratio is between 0.1 and 0.5, then the shape of the glow curve should be taken into account (CEN, 1996). In the present study, there were only three samples with the TL_1/TL_2 ratio in the range of 0.1–0.6 (i.e. unirradiated apricot (0.11); irradiated raisin, 1 kGy (0.61) and irradiated pistachio, 1 kGy (0.62)), therefore, shapes of the glow curves for these samples were also considered. It is generally found that the maximum of glow curve for irradiated samples is exhibited within the temperature range of 150–250°C whereas for unirradiated materials it appears at temperature above 300°C due to low-level natural radioactivity that causes signals in deep traps. In the present work, the TL_1/TL_2 ratio in case of unirradiated apricot sample was close to the threshold value (0.11) but the maximum of glow curve was observed above 300°C, suggesting that it was not previously irradiated. Similarly, for raisin and pistachio samples with TL ratio of 0.61 and 0.62, respectively, the maxima of first glow curves were below 250°C, suggesting that the two samples had previously been irradiated. Glow curve areas in the temperature range of 170–246°C were also calculated, as suggested by the German Health Office study on spices (Schreiber et al., 1993) and in accordance with CEN (1996); however, very similar TL ratios were obtained leading to the same conclusions.

It can be concluded that dry fruit samples can be analysed successfully for previous radiation treatment by measuring TL response of the adhering dust particles. Unequivocal detection of dry fruits is possible if the TL response is normalized by re-irradiation and if the shape of the glow curve is also considered.

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Erratum

Erratum to “Thermoluminescence of contaminating minerals for the detection of radiation treatment of dried fruits” [Radiation Physics and Chemistry 63 (2002) 403–406][☆]

H.M. Khan[a,*], Ijaz A. Batti[a], Henry Delincée[b]

[a] *Radiation Chemistry Laboratory, National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar 25120, Pakistan*

[b] *Institute of Nutritional Physiology, Federal Research Centre for Nutrition, Haid-und-Neu Str. 9, D-76131 Karlsruhe, Germany*

The Publisher regrets that in the above paper Figs. 2 and 3 were missing and Fig. 1 was duplicated. The correct and definitive figures are reproduced below.

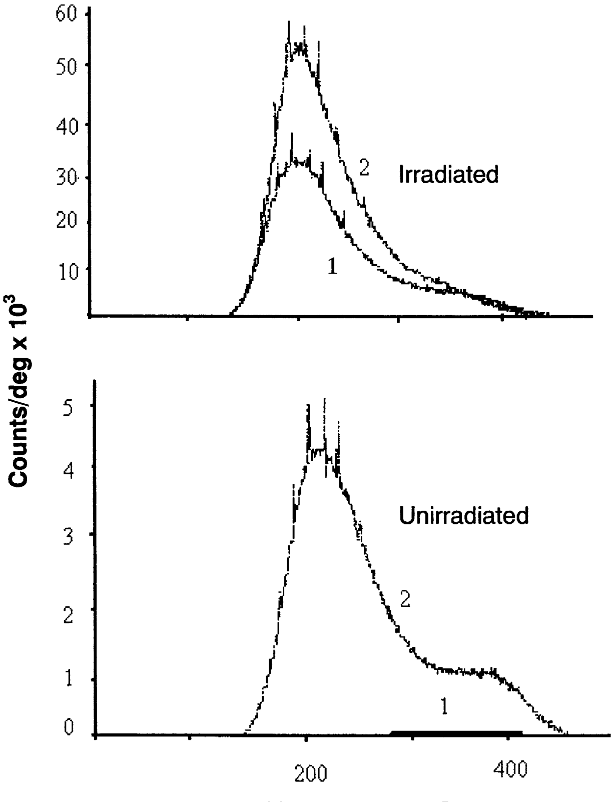

Fig. 1. Glow curves for unirradiated (bottom) and irradiated (top, 0.75 kGy) pistachio nut. (1) Represents the glow curve before re-irradiation whereas (2) shows the glow curve after re-irradiation.

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*Corresponding author. Tel.: +92-9-2921-6766; fax: +92-9-1921-6671.

E-mail address: hmkhan@upesh.edu (H.M. Khan).

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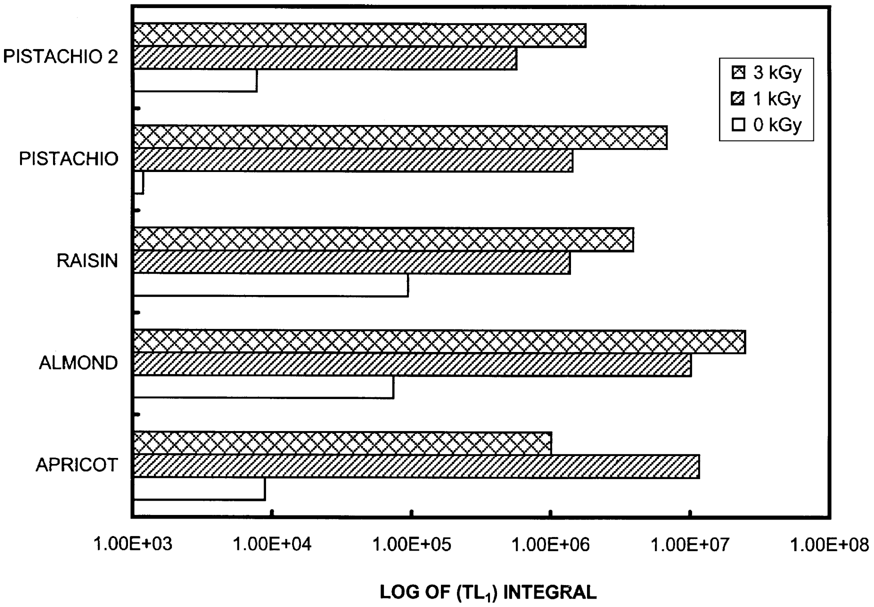

Fig. 2. Comparison of integrated area of first glow curve (TL_1) for unirradiated and irradiated dry fruits. For Pistachio 2 samples, doses are 0, 0.75 and 2.2 kGy instead of 0, 1, 3 kGy.

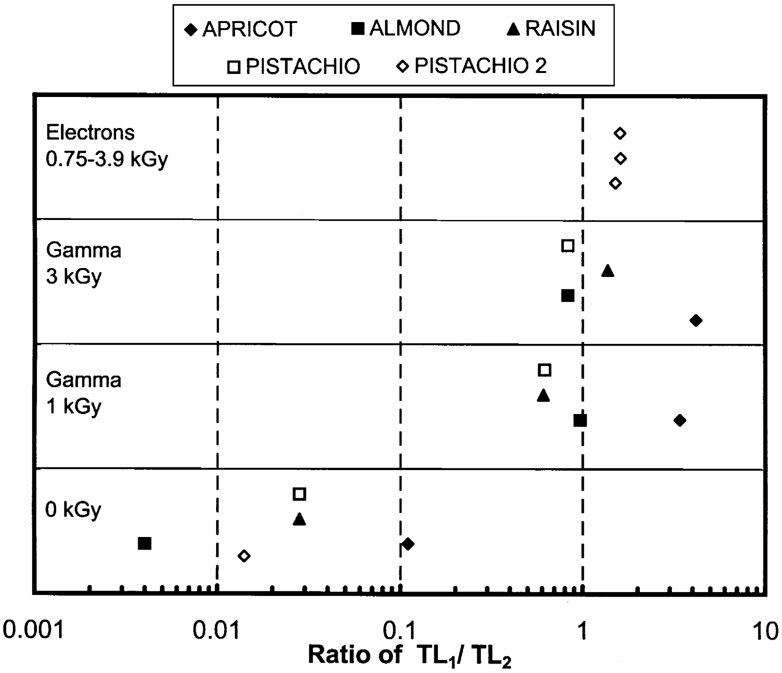

Fig. 3. Comparison of ratio of areas of first glow curve to second glow curve (TL_1/TL_2) on log scale for unirradiated samples (0 kGy, ratio of 0.1 or less) and gamma or electron irradiated dry fruit samples (ratio of 0.6 or more).