Pergamon

0969-806X(95)00248-0

Radiat. Phys. Chem. Vol. 46, No. 4–6, pp. 717–720, 1995

0969-806X/95 $9.50 + 0.00

DETECTION OF IRRADIATION TREATMENT OF DATES USING THERMOLUMINESCENCE OF MINERAL CONTAMINANTS

Hasan M. Khan* and Henry Delincée
Institute of Nutritional Physiology, Federal Research Centre for Nutrition,
Engesserstrasse 20, 76131 Karlsruhe. GERMANY

ABSTRACT

Four types of dates have been studied for the detection of irradiation treatment using thermoluminescence (TL) from the mineral contaminants adhering to the dates. The results were normalized using a re-irradiation step to improve identification method. These date samples were either irradiated using Co-60 gamma rays to 1.0 kGy or electron accelerator to 0.75, 2.2 and 3.9 kGy. The difference in the intensity of TL glow curve for minerals separated from the irradiated samples as compared to unirradiated samples makes it possible to distinguish irradiated dates from unirradiated dates. After normalization step, the ratio of first glow curve to the second glow curve is more than 1.0 for all irradiated samples and much less than 0.1 for un-irradiated samples making detection of irradiated dates more reliable.

KEY WORDS

Irradiated food, thermoluminescence, detection method, mineral contaminants, dates.

INTRODUCTION

Thermoluminescence (TL) is an important routine method for detection of irradiation treatment of species and other food items(Delincée, 1993). It has been found that origin of this TL signal in food samples mainly lies in the insoluble mineral and dust particles concomitant to food items and not in the organic matrix (Sanderson, 1990). By separating these mineral from the food samples, such as spices, and performing TL analysis on these minerals alone produce much better results. This clear discrimination between irradiated and unirradiated food samples, such as date samples, was not achievable when whole date or date powder were analyzed by TL without previous separation of minerals(Sarifzadeh and Sohrabpur, 1993). The reliability of results can further be improved if the TL response is normalized by a re-irradiation step which eliminates the problems associated with the different amounts and composition of insoluble minerals from different lots of spices and other food items. As a part of our work on detection of irradiation treatment of dry and fresh foods, in this paper we are presenting our results on TL detection of different types of date samples.

* Alexander von Humboldt fellow from National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar 25120. Pakistan

EXPERIMENTAL

Two types of packed Tunisian dates and one type of packed Iranian date (Zadhi) were purchased from the local market whereas one type of fresh Tunisian dates were collected direct from tree. About 100 g of each date sample was packed in polyethylene bag and irradiated either by cobalt-60 gamma ray source (Gammacell 220, dose rate about 0.13 Gy/s) or using a 10 Mev linear accelerator (dose rate 10^8 Gy/s). Dose rate at Gammacell was determined using Fricke solution whereas exact doses given to samples during electron beam irradiation were determined with the help of Gafchromic film dosimeter. Thermoluminescence measurements were carried out using ELSEC 7185 TL reader with heating rate of 10 °C/s and final temperature of 500 °C. The heating chamber of TL reader was flushed with pure nitrogen (99.996%) and the system was calibrated with a carbon-14 light source. The amount of sample was about 0.5-2 mg mineral deposited onto a clean stainless steel disc (10 mm diameter, 0.5 mm thickness). The TL reader automatically first heats the sample to record TL glow and then heats it a second time to record black body background which is subtracted from the first TL glow and the resulting glow curve is stored on a floppy diskette.

For separation of minerals from date samples, about 100 g of sample was suspended in water, agitated with ultra sound for 15 minutes, filtered and washed thoroughly with distilled water. The minerals in the filtrate were allowed to settle and transferred to a centrifuge tube. Polytungestate solution (density 2 g/ml) was added to separate organic residue from the minerals, stirred thoroughly and centrifuged. The separated minerals were washed with water and HCl, neutralized with ammonia and rinsed with acetone to remove water. The isolated minerals were deposited carefully on a very clean stainless steel disc which was pre-irradiated and did not show any TL signal.

RESULTS AND DISCUSSION

Four types of dates were checked in the present study. The first type of date (Tunisian packed dates) was irradiated using electron beam from Linac and the radiation doses given were 0.75, 2.2 and 3.9 kGy. The intensity of glow curve for separated minerals from the above samples and that from the unirradiated sample showed marked difference. Figure 1 shows two representative glow curves; one for unirradiated sample (curve 1 on left hand side) and second for irradiated sample (curve 1 on right hand side). The area of glow curve for any of the electron irradiated dates was at least 150 times higher than the area of glow curve for unirradiated sample. Therefore discrimination between irradiated and unirradiated dates just on the basis of first glow curve from separated mineral is possible, as shown in Figure 2. In this frequency histogram, bars with number 1 shows that areas of full glow curves (70 - 500 °C) for three electron irradiated samples are from 150 to 600 times more then the area from the unirradiated sample for the first type of dates.

Other three types of dates (Tunisian fresh date(3), Tunisian packed date(2) and Iranian packed date(4)) were irradiated by gamma rays and each sample was administered a radiation dose of 1.0 kGy. The shape of glow curve for gamma irradiated samples was very similar to the shape of glow curve resulting from electron irradiated dates. It also indicated that different type of date samples from different origins have similar type of dust or sand contaminants resulting in similar glow curves. For these samples also, the intensity of TL response for irradiated dates is much higher than the response from corresponding unirradiated dates (bars numbered 2, 3 and 4 in Figure 2). Therefore, detection of irradiation treatment just on the basis of first glow is possible.

For the results shown in Figure 2, area of whole glow curve (70 - 500 °C) were used. However an attempt was made to compare other temperature regions also, such as temperature area II and III, recommended by the TL intercomparison study conducted by Federal Health Office of Germany

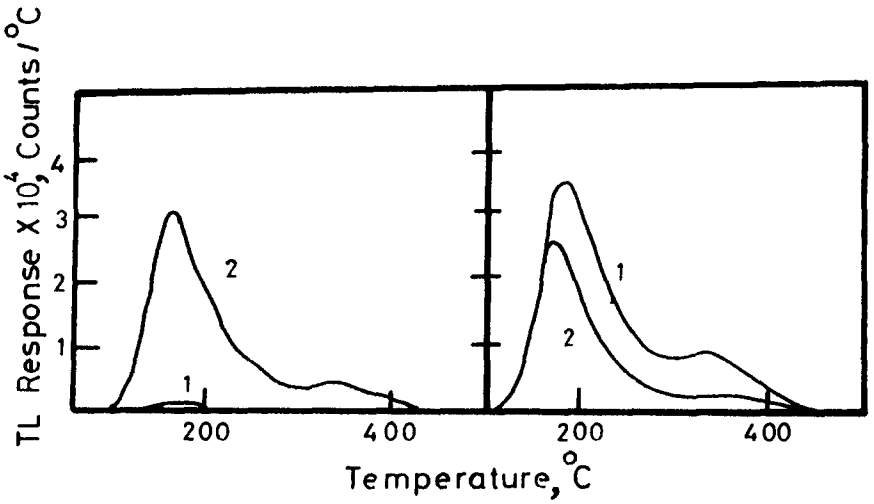

Fig. 1. Representative glow curves for unirradiated (left) and electron beam irradiated (right, 0.75 kGy) date samples.
1: glow curve before re-irradiation step
2: glow curve after re-irradiation dose of 0.75 kGy.

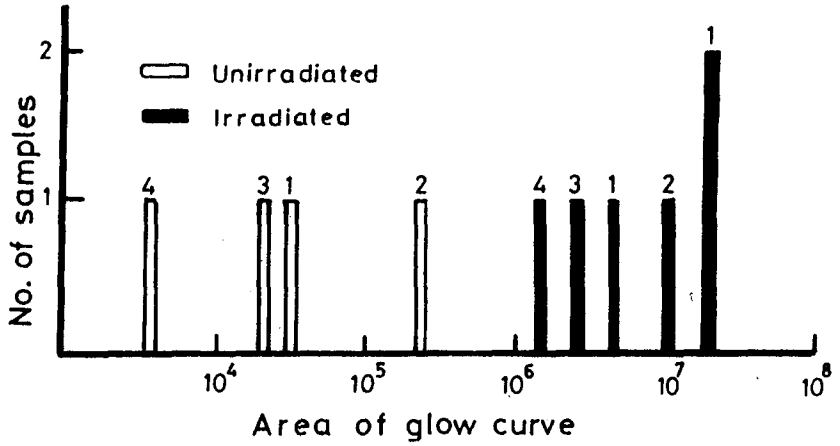

Fig. 2. Frequency histogram for TL response from minerals separated from 10 date samples. Bar numbers show the type of dates.

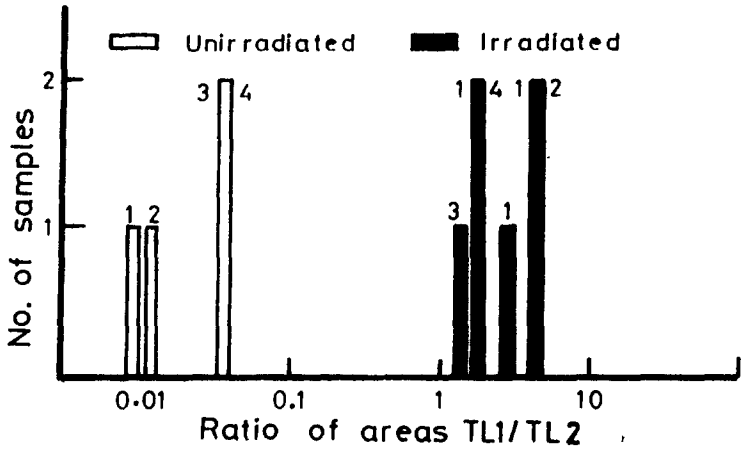

Fig. 3. Frequency histogram for ratio of glow curves for 10 date samples. Bar numbers show the type of dates.

(Schreiber *et al.*, 1993), which corresponds to (170 - 246 °C) on our instrument. Never-the-less, no improvement in results could be found using these selected temperature regions in the present study. It has been shown that TL detection of irradiation treatment in spices, fruit and vegetables, normalization of results by a re-irradiation step greatly improves the reliability of the results (Delincée 1993, Pinnioja 1993). Therefore, normalization of these results by re-irradiating the steel discs with deposited minerals was carried out.

For the first type of date samples, the minerals separated were normalized by giving them a re-irradiation gamma ray dose of 0.75 kGy (for unirradiated sample and for sample irradiated to 0.75 kGy) or 1.0 kGy. The second glow curve for these re-irradiated minerals (TL2) was determined, as shown in Figure 1 (curve 2), and compared with the first glow curve (TL1). The ratio of areas for first glow to second glow (TL1/TL2) was determined for irradiated and unirradiated samples as shown in Figure 3. The figure shows that for unirradiated sample, the ratio is small (<0.01) whereas for all irradiated samples, the ratio is more than 1.8. Several threshold values for the ratio (TL1/TL2) have been suggested to determine if the sample is pre-irradiated. TL intercomparison study for irradiated spices, herbs and spices-and-herbs mixtures carried out by Federal Health Office of Germany (Schreiber *et al.*, 1993), has recommended a value of 0.6. If the ratio is less than 0.6, the sample is expected to be unirradiated whereas for irradiated samples, the ratio is expected to be higher than 0.6. On the basis of this threshold value also, all electron irradiated and unirradiated samples can be correctly identified.

For other three samples of date irradiated by gamma rays, a re-irradiation dose of 1.0 kGy was given to the minerals separated on steel discs and ratio of (TL1/TL2) determined for each of the irradiated and unirradiated samples. For these samples also, the ratio of TL1/TL2 for unirradiated dates is less than 0.04, whereas for all irradiated samples, this ratio is more than 1.6, as shown in Figure 3. Determination of (TL1/TL2) ratio for other temperature regions, such as (170 -246 °C), gives similar results. Therefore on the basis of these results also an unequivocal discrimination between irradiated and unirradiated date samples can be achieved.

It can be concluded that irradiated treatment of dates by gamma rays or electron beam can be detected using TL of mineral contaminants and normalization by a re-irradiation step provides more definite discrimination between irradiated and unirradiated samples.

REFERENCES

Delincée, H. (1993). Control of irradiated foods: Recent developments in analytical methods, *Radiat. Phys. Chem.* 42, 351-357.

Pinnioja, S. (1993). Suitability of thermoluminescence method for detection of irradiated food, *Radiat. Phys. Chem.* 42, 397-400.

Sanderson, D.C.W. (1990). Luminescence detection of irradiated foods, Food irradiation and the chemist, (D.E. Johnston and M.H. Stevenson, eds.), The Royal Society of Chemistry, Cambridge. pp. 25-56.

Schreiber G.A. *et al.* (1993). Thermoluminescence analysis to detect irradiated spices, herbs and herbs-and-herbs mixtures- An intercomparison study, Federal Health Office, SozEp-Hefte 3, Berlin.

Sharifzadeh, M. and M. Sohrabpour (1993). Investigation of the irradiation history of the dates and pistachio nuts using thermoluminescence technique, *Radiat. Phys. Chem.* 42, 407-411.