Pergamon

Radiat. Phys. Chem. Vol. 52, Nos 1–6, pp. 145–149, 1998

Printed in Great Britain
PII: S0969-806X(98)00064-4
0969-806X/98 $19.00 + 0.00

IDENTIFICATION OF IRRADIATED PULSES BY THERMOLUMINESCENCE OF THE CONTAMINATING MINERALS

Hasan M. KHAN[1], Ijaz A. BHATTI[1] and Henry DELINCÉE[2]

[1]National Centre of Excellence in Physical Chemistry,
University of Peshawar, Peshawar 25120. PAKISTAN.

[2]Institute of Nutritional Physiology, Federal Research Centre for Nutrition,
Engesserstrasse 20, D-76131 Karlsruhe. GERMANY

ABSTRACT

Thermoluminescence (TL) response of contaminating minerals from six samples of pulses commonly consumed in Pakistan has been studied for identification of irradiation treatment. The samples were irradiated by Co-60 gamma rays at 0.3, 0.5 and 1.0 kGy, or by 10 MeV electrons using an accelerator at 0.75 and 2.2 kGy. Generally, the TL intensity for minerals separated from irradiated samples was higher than for unirradiated samples. To normalize the results, separated minerals deposited on stainless steel discs were re-irradiated by a normalizing dose and TL response was redetermined. The ratio of the area of the first glow curve to the second glow curve was more than 0.8 for all irradiated samples and less than 0.03 for most of the unirradiated samples. For those unirradiated samples where the ratio of the glow curves was more then 0.03, the shapes of the glow curves were compared. Taking this criterion into consideration, all 21 unirradiated and irradiated samples of pulses were identified correctly. Therefore, a normalization procedure by re-irradiation of minerals and analysis of TL glow curve shapes lead to unequivocal identification of radiation treatment of pulses.

KEYWORDS

Food irradiation; detection method; thermoluminescence; pulses; mineral contaminants

INTRODUCTION

With an increase in commercialization of food irradiation, there is a need to find a convenient and reliable method for detection of irradiated foods. A number of methods have been investigated over the last several years and methods based on detection of radicals in the irradiated foods, such as by electron spin resonance (ESR) or thermoluminescence (TL) detection have shown significant potential (Stevenson and Stewart, 1995). Several interlaboratory blind trials have been carried out and up till now 5 standard methods have been formulated on a European level (Delincée 1996). In our previous studies we have shown that separating contaminating mineral debris from the foods and finding TL glow curves for these minerals followed by normalization of the results with a fixed re-irradiation dose can give reliable results for spices, herbs and date samples (Khan and Delincée, 1995a,b).

Legumes or pulses constitute an important part of total dietary intake in several developing countries, including Pakistan. These pulses with a high content of protein provide the most practical mean of eradicating protein malnutrition. These pulses are normally subjected to irradiation for insect disinfestation and radurization. In the present study, some of the pulses most commonly used by the general public in Pakistan have been investigated for detection of radiation treatment of gamma rays or 10 Mev electrons by using TL methodology.

EXPERIMENTAL

Six samples of pulses of Asian origin were purchased from the local markets in Peshawar and Karlsruhe. For separation of mineral contaminants, about 100 g of each sample was mixed with water and after ultrasonic and centrifugal treatments, a density gradient of polytungstate solution was used to separate remaining organic matrix from the minerals. Details about the procedure have been given elsewhere (Khan and Delincée 1995a,b; Schreiber *et al.*, 1993, see also the European Standard EN-1788:1996). The samples, packed in plastic bags, were either irradiated by gamma rays from a cobalt-60 source in Karlsruhe (Gammacell 220, dose rate 0.13 Gy/s), a cobalt-60 source at Peshawar (Issledovatel, dose rate 0.65 Gy/s) or by a beam of electrons from a 10-MeV linear accelerator (dose rate 10^8 Gy/s). The dose rates for cobalt-60 sources were determined using Fricke dosimeter solution whereas the doses given to the samples during electron beam irradiation were determined with the help of GafChromic film dosimeters (McLaughlin *et al.*, 1991).

An ELSEC model 7185 TL reader with a heating rate of 10 °C/s and a final temperature of 500 °C was used for thermoluminescence measurements. The heating chamber of TL reader was flushed with pure nitrogen and the system was checked with a carbon-14 light source. The minerals separated from each sample (about 0.2-1 mg) were deposited onto a clean stainless steel disc. The TL reader automatically first heats the sample to record TL glow and then, after cooling, heats it a second time to record black-body background emission, which is subtracted from the first TL glow and the resulting glow curve is displayed and stored. The discs with minerals were subsequently irradiated using cobalt-60 gamma rays with a normalizing dose of 0.3, 0.5, 0.75 or to a maximum of 1 kGy, according to the original dose given to the pulses. The TL response after the re-irradiation step was measured again (second glow curve, TL2) and compared with the first glow curve (TL1) determined above.

RESULTS AND DISCUSSION

Six samples of pulses, commonly consumed in Pakistan were analyzed for detection of a radiation treatment. A list of these samples and radiation doses administered to them is given in Table 1.

These samples were irradiated by gamma rays up to a maximum dose of 1 kGy or by an electron beam to 0.75 and 2.2 kGy. The minerals separated from each irradiated or unirradiated sample were deposited on steel discs and TL glow curves were measured. For most of the samples, the glow curves of minerals from the pulses were recorded about one to two weeks after irradiation, but for samples number 5 and 6, which were irradiated in Peshawar, the glow curves were recorded after about one month of irradiation. However, it is known that TL signals are quite stable even if measured after several months of post-irradiation storage (Schreiber *et al.*, 1993).

Table 1. List of pulses and radiation doses used in the present study.

Sample No:	Common name	Botanical name	Radiation dose, kGy
1	Black lentils	*Lens esculenta*	0.75, 2.2 (electron), 0.3
2	Black gram	*Phaseolus radiatus*	0.3, 0.5, 1.0
3	Gram	*Cicer arietinum*	0.3, 0.5, 1.0
4	Red lentils	*Lens esculenta*	0.5, 1.0
5	Red beans	*Phaseolus lunatus*	0.5, 1.0
6	Red lentils (broken)	*Lens esculenta*	0.5, 1.0

While the shapes of the glow curves, whether the samples had been irradiated by gamma rays or by electron beam were similar, all showing a maximum around 170-200°C, the thermoluminescence responses for irradiated samples were much higher than the responses of unirradiated samples. A comparison of the integrated glow-curve amplitudes (in term of area of whole glow curve from 50 to 450 °C) for unirradiated pulses and for the samples irradiated to either 0.3 or 0.5 kGy by gamma rays is shown in Figure 1. The figure shows that the TL integral for most irradiated samples is at least one order of magnitude higher than for the corresponding unirradiated samples.

The first glow curve is generally normalized by a re-irradiation step, to eliminate the effects of nature and amount of minerals deposited on the disc. It has been found that this re-irradiation followed by comparison of the integral of first glow curve (before re-irradiation) to the second glow curve (after re-irradiation) increases the reliability of the identification procedure and exclude the possibility of false-positive identifications (Sanderson *et al.*, 1989; Khan and Delincée, 1995a,b). Using their measuring conditions, unirradiated samples are expected to have TL1/TL2 ratios less than 0.1, whereas irradiated samples have this ratio

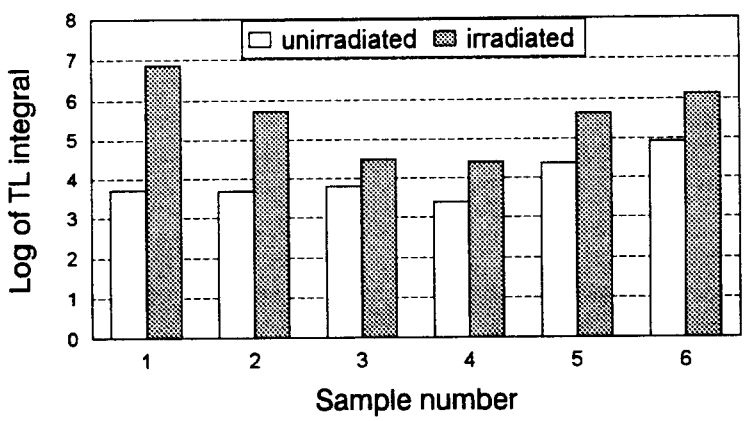

Figure 1. Values of logarithm of TL integral of the first glow curve for unirradiated and irradiated pulses.

close to 1. It shall be noted, however, that these classification criteria depend on the radiation dose originally administered to the food and on the radiation dose used for normalization. The latter criteria were obtained for food items irradiated at or above a dose of 1 kGy and a normalization dose of about 1 kGy. In this work, the minerals deposited on disc for each of the above samples were administered a re-irradiation gamma-ray dose corresponding to the original dose given to the samples up to a maximum of 1 kGy. Unirradiated samples were administered a dose of 0.3 or 0.5 kGy. The ratio of area of first glow curve to that for the second glow curve (TL1/TL2) was evaluated. The results are summarized in Figure 2 which shows the ratios of TL1/TL2 for all the irradiated and unirradiated samples. Out of six unirradiated samples, the TL1/TL2 ratio for four samples is less than 0.03 and can be classified as unirradiated on the basis of TL ratios. For the remaining two unirradiated samples (samples number 3 and 5), the values are 0.35 and 1.19, respectively. It should be recognized, however, that the normalization dose was markedly lower than 1 kGy. On the other hand, for all the irradiated samples, the values of ratio TL1/TL2 are more than 0.8 (Fig.2). In addition, the typical glow shape for irradiated samples was observed. Therefore, all irradiated samples can be classified correctly.

In several studies, comparison of TL1/TL2 values as well as analysis of glow curve shape have been preferred for identifying irradiated and unirradiated samples (MAFF, 1993; Pinnioja *et al.*, 1993; Khan and Delincée, 1995b). In the recent European Standard EN-1788:1996 prepared by the European Committee for Standardization (CEN), it is proposed that if the TL glow ratio evaluated over a recommended temperature interval, is between 0.1 and 0.5, the shape of the glow curves should be studied to decide whether the sample has been irradiated or not. Again, it should be emphasized that this Standard at present pertains only to food items irradiated with at least 1 kGy, and a normalization dose of 1 kGy. Other radiation doses will affect the classification numbers. Generally valid, however, is that irradiated samples, in principle, will show TL maxima below 250 °C whereas unirradiated samples exhibit maxima in higher temperature regions. Two of our unirradiated samples showed unexpected high TL ratios: 0.35 for no. 3 and even 1.19 for no. 5. However, as already pointed out, the normalization dose was markedly lower than 1 kGy. If 1 kGy had been used, lower TL ratios had been obtained. In addition, in this work whole glow curves were compared instead of recommended temperature intervals. But possibly, still values above 0.1 for the TL glow ratio may have resulted. Therefore, interpretation of the shape of the glow

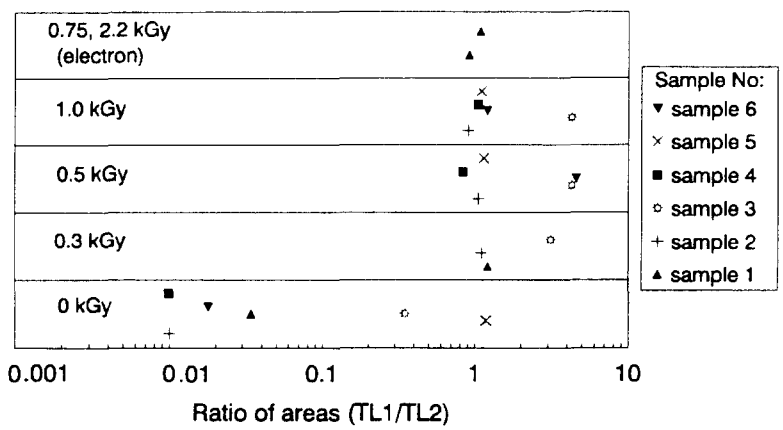

Figure 2. Ratio of areas of first glow curve to second glow curve (TL1/TL2) for unirradiated and irradiated pulses.

curve is needed to decide whether the samples have been irradiated or not. When the shape of the glow curves for these two samples were considered, both samples clearly showed first glow curves with maxima around 340-350°C, whereas the second glow curves after irradiation with a normalization dose exhibited maxima about 170-180°C. Therefore, these samples can be classified as unirradiated, although TL glow ratios were high. Thus, all 21 unirradiated and irradiated samples of pulses could be correctly identified.

Our results show the importance of interpretation of glow curve shape before unequivocal detection of samples can be made. While most of the samples of pulses in the present study can be immediately identified by re-irradiating the separated minerals and comparing the ratio of TL1/TL2, there are still some samples which may give doubtful or false results. When the shape of glow curve is also considered in addition to the TL glow ratio, all the pulse samples in the present study could be detected unequivocally. Therefore, samples of pulses irradiated to 0.3 kGy or more can be identified for irradiation treatment by thermoluminescence analysis of contaminating minerals.

REFERENCES

Delincée H. (1996) Detection methods for irradiated foods - An overview. *Radiat. Phys. Chem.* **48**, 378-379.

Khan H.M. and H. Delincée (1995a) Detection of irradiation treatment of dates using thermoluminescence of mineral contaminants. *Radiat. Phys. Chem.* **46**, 717-720.

Khan, H.M. and H. Delincée (1995b) Detection of radiation treatment of spices and herbs of Asian origin using thermoluminescence of mineral contaminants. *Appl. Radiat. Isot.* **46**, 1071-1075.

MAFF (1993) MAFF validated methods for the analysis of foodstuffs. No: V 27. Detection of irradiated herbs and spices. *J. Assoc. Publ. Analysts* **29**, 187-200.

McLaughlin, W.L., Y. Chen, C.G. Soares, A. Miller, G. Van Dyke, and D.F. Lewis (1991) Sensitometry of the response of a new radiochromic film dosimeter to gamma radiation and electron beams. *Nucl. Instr. Methods Phys. Res.* **A302**, 165-176.

Pinnioja S., T. Autio, E. Niemi and O. Pensala (1993) Import control of irradiated foods by thermoluminescence method. *Z. Lebensm. Unters. Forsch.* **196**, 111-115.

Sanderson D.C.W., C. Slater and K.J. Cairns (1989) Thermoluminescence of foods: origins and implications for detecting irradiations. *Radiat. Phys. Chem.* **34**, 915-924.

Schreiber G.A., U. Wagner, A. Leffke, N. Helle, J. Ammon, H.-V. Buchholtz, H. Delincée, S. Estendorfer, K. Fuchs, H.-U. von Grabowski, W. Kruspe, K. Mainczyk, H. Munz, H. Nootenboom, C. Schleich, N. Vreden, C. Wiezorek, and K.W. Bögl (1993) Thermoluminescence analysis to detect irradiated spices, herbs and spice- and herb mixtures - an intercomparison study. Bericht des Instituts fur Sozialmedizin und Epidemiologie des Bundesgesundheitsamtes. SozEp-Heft 2/1993, Bundesgesundheitsamt, Berlin.

Stevenson, M.H. and E.M. Stewart (1995) Identification of irradiated food: The current status. *Radiat. Phys. Chem.* **46**, 653-658.