Thermoluminescence Method for Detection of Irradiated Black Pepper

[1]HASAN MAHMOOD KHAN* AND [2]IJAZ AHMAD BHATTI
[1]*Radiation Chemistry Laboratory, National Centre of Excellence in Physical Chemistry, University Post Office, Peshawar 25120, Pakistan.*
[2]*Department of Chemistry, Agriculture University, Faisalabad, Pakistan.*

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Summary: Thermoluminescence (TL) method was investigated for detection of radiation treatment of black pepper (*Piper nigrum*), irradiated to gamma ray doses of 1.0 kGy and 5.0 kGy. The TL response of the minerals isolated from irradiated samples was much higher as compared to that of un-irradiated control samples. For the normalisation of results the separated minerals were re-irradiated to a normalisation dose of 1.0 kGy and TL glow curve recorded a second time. By comparing the glow curves of irradiated and unirradiated samples, it was possible to separate the irradiated samples from unirradiated ones. For laboratories having re-irradiation facilities, more accurate detection was possible by finding the ratio of the areas of first and second (re-irradiated) glow curves (TL_1/TL_2), which was confirmed by comparing the shapes of the glow curves of irradiated and un-irradiated samples.

Introduction

Food irradiation is gaining popularity because of better public awareness and increasing number of countries are permitting irradiation of foods. The number of different food commodities that have been cleared for irradiation by regulatory authorities is growing. Since the changes produced in the irradiated food are very minor and are similar to those produced by other food processing methods (such as heating, drying, etc.), it is difficult to distinguish unirradiated food in a market from the food that has been irradiated previously. However, development of some suitable, reliable and rapid methods for the identification of irradiated foods will enhance consumer confidence and will further protect their right of free choice among unirradiated or irradiated foods. Techniques ranging from physico-chemical methods to contemporary analytical tools like TL and electron spin resonance (ESR) have been tried so far in order to know the irradiation history of foods [1, 2].

Thermoluminescence technique was introduced long time ago for detection of irradiated food without recognizing the origin of TL [3]. However, this technique became promising when it was recognised that the TL signals actually originate from the minerals or dust particles that contaminate the food items, such as spices [4, 5]. With the development of procedures for the isolation of mineral particles, such as quartz or sand particles, and further normalisation of TL glow curve results to a common dose, this technique has gained a lot of potential as screening test for irradiation and identification [6-10]. This method can be applied to all those foods that contain even small amount of wind blown dust or mineral particles. Several blind trials have been performed to check the potential and validity of the method [11].

Black pepper and other spices have long storage life and they are stored as such or in ground form for several years. During storage, insects can deteriorate the condition and quality of stored material. However, irradiation technology can be used for control of insect infestations and microbial load and for reduction of pathogenic microorganisms, instead of conventional indigenous methods, such as fumigation with ethylene oxide, drying, heating, etc. This radiation treatment of black pepper is preferred since it is safer, economical and rapid with no associated toxicity. In the present work black pepper, which is commonly used in Pakistan and other South East Asian countries, has been investigated for irradiation identification using TL technique.

Results and Discussion

The TL glow curve of mineral contaminants separated from the irradiated and un-irradiated samples of black pepper was carried out and

*To whom all correspondence should be addressed.

examined by measuring the areas of glow curves between the temperature range of 50-500 °C. Typical glow curves for unirradiated black pepper sample and that irradiated to 5 kGy are shown in Figs. 1 and 2, respectively. The glow curves marked 1 in the Figs. represent the first glow curve for the unirradiated and irradiated samples. The glow curves marked 2 in the Figs. represent the TL measurements after re-irradiation of the separated minerals to 1.0 kGy, as discussed later. It is apparent that the intensity of the glow curve for the irradiated sample (Fig. 2, curve 1) is much higher as compared to the intensity of the unirradiated sample (Fig. 1, curve 1). In several cases, this difference in the intensity of the first glow curves of the unirradiated and irradiated samples (without re-irradiation) can be used to detect radiation treatment of the foods. Therefore, laboratories having no access to re-irradiation facilities (such as Cobalt-60 radiation source), can use this simplified method as a screening test for irradiation treatment. The irradiated samples have normally much higher glow curve intensity as compared to un-irradiated samples.

In Table-1, TL results for unirradiated samples of black pepper and those irradiated to 1 and 5 kGy have been summarised. This Table gives the area of first glow curve TL_1 integrated from 50-500 ^{0}C as well as glow curve areas after normalisation dose of 1 kGy administered to the mineral contaminants TL_2, as well as the ratio of TL_1/TL_2 for these samples.

It is known that the shape and intensity of the first glow curve TL_1 depend upon the nature and amount of the minerals deposited on the disk while recording the glow curve [4]. Therefore, comparing only the first glow curves, which often gives correct results, is not a reliable method. As a further improvement in the method, the TL results can be normalised by a re-irradiation step with a specific radiation dose when there is some doubt in identification using only TL_1 comparison. After re-irradiation, the second glow curve is recorded TL_2 and then the ratio of TL_1/TL_2 is considered to find out the irradiation treatment [4, 6].

In the normalisation step, the re-irradiation treatment of separated minerals of black pepper was carried out with a specific dose of 1 kGy, and second glow curve TL_2 was recorded as shown by glow curves marked 2 in Figs. 1 and 2. The ratio of areas

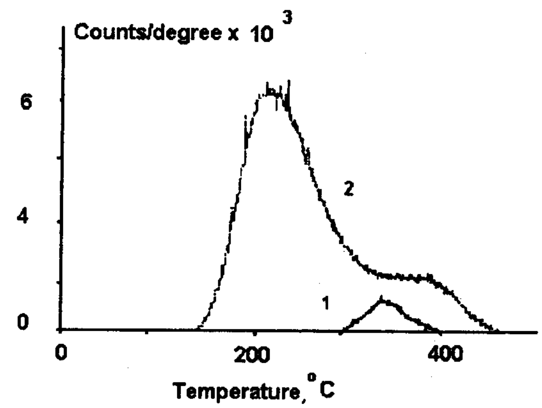

Fig. 1: Glow curve for *unirradiated* black pepper sample. (1): Glow curve before re-irradiation step; (2): Glow curve after re-irradiation step.

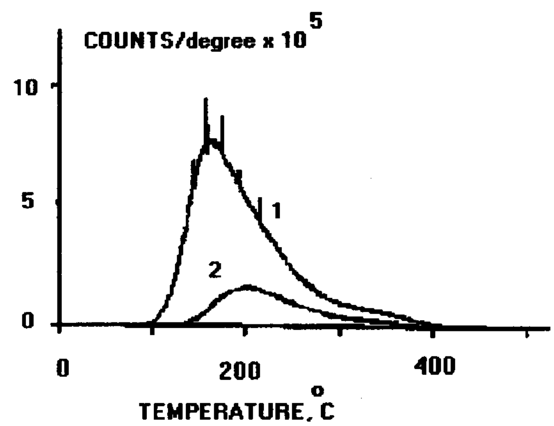

Fig. 2: Glow curve for black pepper sample *irradiated* to 5.0 kGy. (1): Glow curve before re-irradiation step; (2): Glow curve after re-irradiation step.

under the first and second glow curves TL_1/TL_2 for all the irradiated and unirradiated spices samples was calculated as given in the Table-1. The ratio of areas of glow curves TL_1/TL_2 for un-irradiated samples of black pepper was 0.12 (Table-1) while for all the irradiated samples, the ratio was more than 0.4 (*i.e.* 0.45 for sample irradiated to 1 kGy and 51.3 for sample irradiated to 5 kGy).

As a result of comprehensive studies, different threshold values for TL_1/TL_2 ratio have been suggested by different laboratories. TL inter-

Table-1: Areas of first glow curves (TL_1), areas of second glow curves (TL_2) and ratios of the TL_1/TL_2 for black pepper samples.

NO	SAMPLES	DOSE	TL_1 50-500°C	TL_2* 50-500°C	TL_1/TL_2
1	Un-irradiated	0 kGy	1.84×10^5	1.59×10^6	0.12
2	Irradiated	1 kGy	4.91×10^5	1.13×10^6	0.45
3	Irradiated	5 kGy	36.83×10^6	7.18×10^5	51.3

*Re-irradiation dose for normalisation (TL_2) = 1 kGy.

comparison study on irradiated spices, herbs and spice-and-herb mixtures, carried out by Federal Health Office, Germany [11], a threshold TL_1/TL_2 value of 0.6 has been recommended *i.e.* below this value, the sample would be considered as unirradiated and those samples having TL_1/TL_2 ratio more than 0.6 will be considered as irradiated. In a recent European Standard, prepared by European Committee for Standardisation (CEN), it is proposed that if the TL ratio evaluated over a recommended temperature interval is between 0.1 and 0.5, the shape of the glow curve should be studied [12]. Therefore, according to this proposal, the TL_1/TL_2 ratio for unirradiated samples should be less then 0.1 and for irradiated samples, the ratio should be more then 0.5.

Therefore, the shapes of the glow curves were studied for two samples that give results between 0.1 and 0.5. Usually the maximum of glow curve is exhibited within the temperature range of 150 - 250 °C for irradiated materials. On the other hand, for un-irradiated samples, the glow curve maximum appears above 300 °C due to low-level natural radioactivity, which causes signal in deep traps [13- 15].

The glow curves shown in Figs. 1 and 2 were compared and locations of maxima of glow curves were determined. In Fig. 1, the glow curve 1 is for unirradiated black pepper sample and has its maximum around 350 °C, whereas glow curve 2 was obtained after re-irradiation which showed glow curve maximum around 210 °C. Similarly other glow curves shown in Fig. 2 for irradiated black pepper sample (curve 1), or after re-irradiation (curve 2), showed glow curve maxima below 250 °C. This result confirms that curve 1 in Fig. 1 is for unirradiated sample while the other curves represent irradiated samples.

Therefore, the present work shows that all the samples of black pepper (irradiated to 1 or 5 kGy and unirradiated) can be identified correctly considering first glow curve TL_1, ratio of areas TL_1/TL_2 as well as the shape and position of glow curve maxima.

Experimental

The samples of black pepper were purchased from the local market (Utility Store Corporation of Pakistan, Peshawar), packed in the polyethylene bags and irradiated to gamma ray doses of 1.0 and 5.0 kGy using Co-60 source at the Nuclear Institute for Food and Agriculture (NIFA), Tarnab, Peshawar. The dose rate of the gamma irradiator was measured using Fricke dosimeter or GAF-radiochromic films [16, 17]. After radiation treatment, the samples were treated for mineral separation. The method used for the isolation of mineral particles from spices is given below and was similar to that described in our previous work [14, 15, 18, 19].

Irradiated or un-irradiated control sample (about 10 g) was suspended in distilled water, homogenised well and placed for ultrasonic treatment for about 15 minutes using ultrasonic bath. The sample was filtered through nylon sieve into a large beaker and the sample retained on the nylon sieve was thoroughly washed with jet of distilled water. The mineral contaminants along with the organic part of spices were left in the beaker. The organic matter was decanted off by washing several times with water and the mineral portion was transferred to the tubes for centrifugation. The supernatant liquid and other materials were sucked off with the help of Pasteur pipettes, and saturated K_2CO_3 solution (density 1.922g/cm^3) was added as density gradient to separate the remaining organic residue from the minerals. K_2CO_3 was completely sucked off and the isolated minerals were washed with H_2O and 2-4 ml of 1 M HCl was added to dissolve salts like carbonates. For neutralisation, 2-4 ml of 1 M NH_4OH solution was added and minerals were washed with H_2O followed by addition of 3 ml acetone to remove remaining water. The minerals along with acetone were transferred to a highly clean stainless steel disc of about 10mm diameter. The discs with minerals were put into an oven at 50 °C for about half an hour before TL measurements [11, 15, 18].

Thermoluminescence measurements were performed using a PC coupled ELSEC model-7185 TL reader equipped with pure nitrogen cooling system. The instrument was calibrated with C-14 light source and the heating plate and optical system were thoroughly cleaned before measurements. The TL reader operates from 50 ^{0}C to 500 ^{0}C at heating rate of 10 ^{0}C/s. The TL glow curves (signal intensity versus temperature) for minerals separated from irradiated and unirradiated samples of the spices were recorded and the data was stored on the floppy diskette. This is known as first TL flow curve TL_1. For the normalisation of results, re-irradiation of the minerals with discs (for which TL_1 has been measured) was carefully carried out using Co-60 gamma ray source with a common normalisation dose of 1.0 kGy. The second TL measurement for the re-irradiated disc was performed under the same conditions as that for the first TL measurement. The resulting glow curve is called second glow curve TL_2. This glow curve is 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).

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