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Applications of TL and EPR Spectroscopy in Detection and Dosimetry of Food Irradiation

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Abstract:
The need for reliable and routine tests to determine whether or not food has been irradiated has arisen as a result of the progress made in commercialization of the food irradiation technology, increased international trade in irradiated foods, and consumer demand for clear labeling of the treated food. On the other hand, the effectiveness of processing of food by ionizing radiation depends on proper delivery of absorbed dose and its reliable measurement. Thermoluminescence (TL) and Electron Paramagnetic Resonance (EPR) spectroscopy are most promising techniques based on physical principles. Primarily the TL glow (TL 1) from the isolated minerals from various foods was measured. After first TL measurement the isolated minerals were re-irradiated with normalized radiation dose, and TL glow (TL 2) was determined. The shape of the TL glows and the ratio were employed to give a verdict on detection of irradiation. In case of EPR spectroscopy the EPR spectra of the food samples and thermal and relaxation behavior of the paramagnetic centres were studied to identify radiation treatment. In case of radiation dosimetry for food irradiation at sub-ambient temperatures, $CaSO_4$ based TL phosphors were studied. An attempt was made to understand the change in TL characteristics of the phosphors by TL-EPR correlation studies.

Keywords: Food irradiation, Thermoluminescence, EPR spectroscopy, Detection, Dosimetry

1. INTRODUCTION

Food irradiation is the treatment of food by ionizing radiation. The process involves exposing food, either packaged or in bulk, to carefully controlled doses of ionizing radiation for a specific time to achieve certain desirable objectives. In 1980, A Joint Expert Committee of Food and Agriculture Organization / International Atomic Energy Agency / World Health Organization on Food Irradiation (JECFI) [1] concluded "The irradiation treatment of any food commodity up to an overall average dose of 10 kGy present no toxicological hazard; toxicological testing of foods so treated is no longer required." As a consequence, food irradiation is now legally accepted in many countries.

The need for reliable and routine tests to determine whether or not food has been irradiated has arisen as a result of the progress made in commercialization of the food irradiation technology, increased international trade in irradiated foods, differing regulations relating to the use of the technology in many countries, and consumer demand for clear labeling of the treated food. It is presumed that the availability of such tests would help strengthen national regulations on irradiation of specific foods, and enhance consumer confidence in such regulations.
The effectiveness of processing of food by ionizing radiation depends on proper delivery of absorbed dose and its reliable measurement. For food destined for international trade, it is of utmost importance that the dosimetry techniques used for dose determination are carried out accurately and that the process is monitored in accordance with the internationally accepted procedures. Correct application of dosimetry to radiation processing of food is an important issue [2]. External influences such as the temperatures of dose measurement, accuracy in a rather narrow dose range are the other problems that confront dosimetry.

An attempt has been made to study the identification methodology of irradiated foods with commercially relevant doses based on physical methods namely, Thermoluminescence (TL) measurements and Electron Paramagnetic Resonance (EPR) spectroscopy. In case of measurements of absorbed dose, investigations were carried out to understand the mechanism of modified $CaSO_4$ based thermoluminescence phosphors by TL-EPR correlation studies and to find out the efficacy of the phosphor as a food irradiation dosimeter.

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2. EXPERIMENTAL

2.1. Sample irradiation. Irradiation of food commodities and dosimeters were carried out using a cobalt-60 irradiator (GC-5000, BRIT, Mumbai) at FTD, BARC, Mumbai. The calibration of the gamma chamber was carried out using Fricke reference standard dosimeters [3].

2.2. EPR spectroscopy. EPR measurements were performed using a Bruker EMX spectrometer (Bruker, Gemany). The electron relaxation behavior of radicals in food samples was studied by varying the microwave field strength. The thermal behavior of the signal was studied using BVT 3000 of BRUKER. The position of the radiation – induced EPR signal was compared with that of the standard 2, 2, diphenyl-1-picrylhydrazyl (DPPH) with g = 2.0032.

2.3. TL analysis. A chemical route of density separation [4] was standardized in order to separate minerals and organic materials from the food. Thermoluminescence analysis was carried out using TL 1009I Reader (Nucleonix Systems, India). Nitrogen was flushed in the heating chamber to reduce spurious TL arising due to the presence of oxygen. The initial temperature was 40ºC, which was increased to 320ºC by linear heating at a rate of 5ºC/s. In case of dosimetry, TL phosphors $CaSO_4$: Dy and $CaSO_4$: (Dy, Bi) were used. Polycrystalline $CaSO_4$:Dy (0.2 mol %) was procured from Renentech Laboratory Private Ltd, Mumbai, $CaSO_4$:(Dy^{3+},Bi^{3+}) phosphor was prepared by re-crystallization method following the recipe of Yamahashita [5]. The concentration of Dy was 0.05 mol%, while the concentration of Bi was 0.05, 0.2 and 0.5 mol%. Pre-irradiation thermal treatment of commercial CaSO4: Dy phosphor was carried out using a furnace at 700-900°C. Phosphor were exposed to gamma radiation from Cobalt 60 source at room temperature, chilling temperature (0±4ºC), freezing temperature (-10±2ºC) and liquid nitrogen temperature (-196ºC).

3. RESULTS AND DISCUSSION

3.1. Identification of irradiated foods using TL techniques

The TL measurements were employed on a wide spectrum of food commodities namely rice, potato, ginger and shrimp. Primarily the TL glow (TL 1) from the isolated minerals from various foods was measured. After first TL measurement the isolated minerals were re-irradiated with normalized radiation dose (normally 1 kGy), and TL glow (TL 2) was determined. The shape of TL 1 and TL 2 and their ratio were employed to give a verdict on detection of irradiation.

3.1.1. Identification of irradiated Basmati rice. Fig. 1a shows the EDX spectrum of polyminerals isolated from rice, which mainly composed of quartz (SiO_2) and K-feldspars ($KAlSi_3O_8^-$) with a higher abundance of quartz (about 59.6 %) than K-feldspars (20.7 %). Apart from quartz and feldspar, traces of FeO (4.0 %), Na_2O (4.1 %), CaO (11.1%) were also identified [6]. Fig. 1b shows the TL intensities of glow curves for separated polyminerals from the nonirradiated and irradiated rice samples 10 d after radiation treatment. In case of irradiated sample the glow curve was characterized by a low temperature peak at about 184±4ºC and a high temperature peak at about 282±5ºC. The position of glow peak for nonirradiated sample through all temperature ranges was not clear. The ratio of areas for first glow curve to second glow curve (TL 1/TL 2) determined for nonirradiated samples was 0.002±0.023, while for irradiated sample 0.69±0.085. Higher values of ratio in irradiated rice samples are in good agreement with the European Standard EN 1788, 1997.

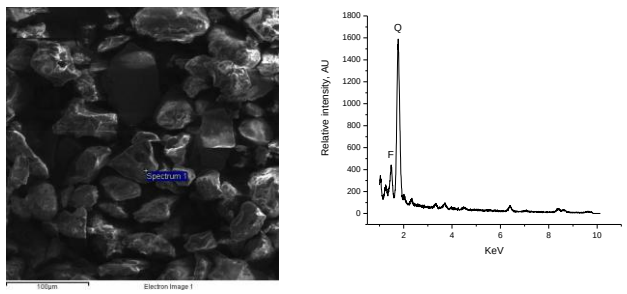


Fig.1a. SEM image, and EDX spectrum of the polyminerals extracted from rice**.**

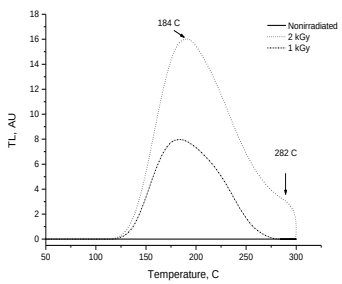


Fig.1.b. TL glows of isolated minerals from nonirradiated and irradiated rice

3.1.2. Identification of irradiated potato and ginger. The TL intensities of the glow curves for both the nonirradiated and irradiated potato showed significant difference even after a storage period of one month.

Around 86 fold increases in TL glow (TL 1) of irradiated samples in comparison with nonirradiated ones was observed. Fig. 2a exhibited the TL glow of the irradiated and nonirradiated samples. The ratio of TL1 / TL 2 for nonirradiated samples was 0.003±0.0005 and for irradiated samples it was 0.25±0.052. In case of ginger around 50 fold increase in integral TL glow (TL 1) in irradiated samples was observed (Fig. 2b). The ratio of TL 1 / TL 2 for nonirradiated ginger was negligibly small. Whereas, in case of irradiated (80 Gy) ginger the same was measured as 0.02±0.0011.

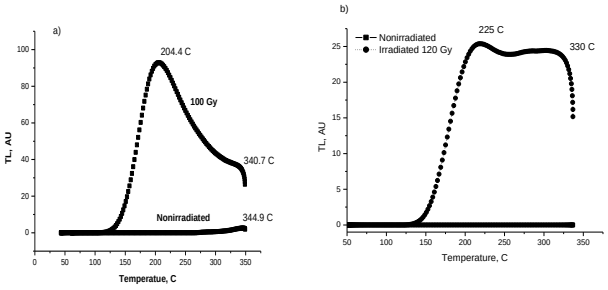
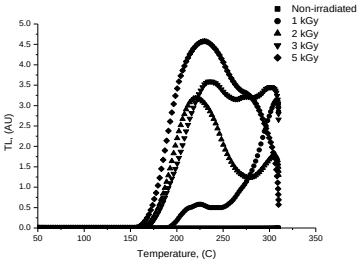


Fig.2. TL glows of minerals isolated from a) potato and b) ginger**.**

3.1.3. Identification of irradiated shrimp. Fig. 3 shows the TL glows of nonirradiated and irradiated minerals isolated from shrimp recorded after a storage period of 45 days. For all irradiated samples, the areas under glow 1 were 30 to 35 times higher compared to that of nonirradiated samples. All irradiated samples were characterized by glow peak at 225°C±6.5° C. Possibility of identification of irradiated shrimp after cooking was also investigated. Detection of irradiated shrimp even after cooking was possible from the first glow curve (TL1) of the isolated minerals after prolonged storage.



3.2. Identification using EPR technique

EPR spectroscopy was employed to identify irradiated rice and cashew nut. In order to determine the electron relaxation behavior of radicals, the microwave field strength was varied between 0.06 – 50 mW to obtain progressive saturation behavior (PSB). The thermal behavior of the EPR signal was studied from room temperature (25°C) to 300°C.

3.2.1. Identification of irradiated Basmati rice. Fig. 4a, shows the EPR signal of nonirradiated rice samples exhibiting a weak singlet characterized by g = 2.0049 ± 0.0004 and ΔB_{pp} = 1.3 mT, centered around 346.1 mT. Fig. 4b shows a complex spectrum immediately after irradiation (1 kGy) with an increase in signal intensity. The exposure to gamma radiation leads to change in rice matrix, producing two new types of paramagnetic species. One pair of intense satellite lines at a distance of 6 mT and the other less intense pair of lines situated at a distance of 2.6 mT. These radiation specific signals observed in the rice matrix were not particularly stable and disappeared after 3 - 4 days. The electron relaxation behavior of radicals (Fig.5) showed early saturation of central singlet in nonirradiated sample even after 90 days and gave a signature of irradiation [6].

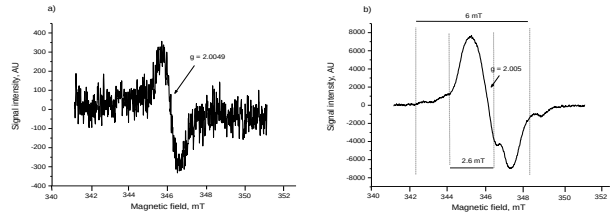


Fig4. EPR spectra of a) nonirradiated, b) irradiated rice samples

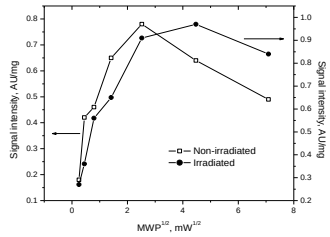


Fig.5. Relaxation behavior of nonirradiated and irradiated (1 kGy) rice sample 90 d after irradiation**.**

3.2.2. Identification of irradiated Cashew nut. Fig. 6a shows a complex spectrum immediately after irradiation (1 kGy) of cashew sample with an increase in signal intensity by a factor of 11. Other short lived paramagnetic species with axially symmetric spectrum was characterized by an anisotropic g tensor ($g_\perp$ = 2.0069 and $g_\parallel$ = 2.0000). This signal could possibly be of CO_2^- radical ion formed during the breakdown of fatty acid. In order to identify the irradiated cashew sample thermal behavior of the EPR signal is depicted in Fig. 6b. With the increase of temperature from 27 to 97°C, signal intensities of nonirradiated and roasted samples were observed to be almost unchanged, but, that of irradiated samples showed a fast fall of about 50 % [7].

3.3 Studies on TL phosphors for food irradiation dosimetry

Dosimetry is of paramount importance in any commercial irradiation facility. The evaluation of absorbed dose at low temperatures irradiation of food using a cost effective and simple system is a challenging task.

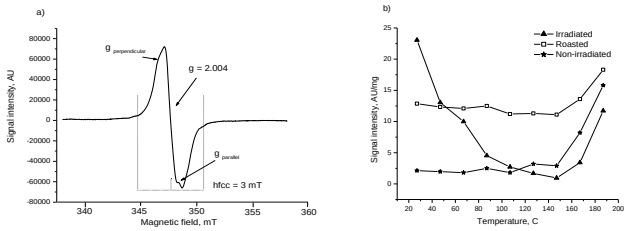


Fig.6. a) EPR signal of cashew nut, b) thermal behavior

3.3.1. Studies on $CaSO_4$: Dy phosphor. To evaluate the crystal capacities of irradiated commercial $CaSO_4$: Dy (0.2 mol %), the integral TL was measured at three different temperatures, chilled (0±4ºC), frozen (-10 ±2ºC) and liquid nitrogen temperature (-196ºC) with two different doses 0.4 and 1 kGy (Fig. 7a) and no difference in TL output was observed. Determination of TL intensity of the low temperature peak was difficult due to its broad nature. In order to address this problem commercially available $CaSO_4$: Dy phosphor was subjected to pre-irradiation thermal treatments at 700, 800 and 900ºC for a period of 2 h. The change in glow curve structures with the annealing temperatures is shown in Fig. 7b.

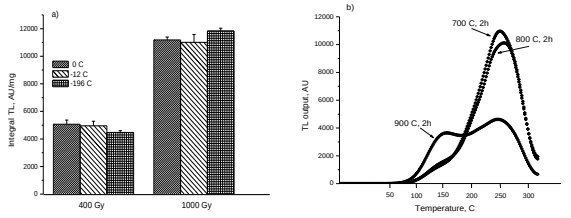


Fig.7. a) TL output at low temperatures, b) TL glows after thermal treatments

In order to understand the change in TL glows, EPR spectra were recorded at -196ºC (77°K) as shown in Fig. 8a. EPR spectrum exhibited three radiation induced radicals. These radicals were characterized as g = 2.0031±0.001, 2.0038±0.0005 and 2.0113±0.0006, and were attributed to SO_3^-, SO_4^- and O_3^-, respectively [8]. In order to investigate the role of radiation induced paramagnetic centers in TL glow, the thermal behavior of the EPR lines were studied from room temperature to 300°C. The thermal characteristics revealed that SO_4^- could be responsible for the enhancement of the low temperature peak intensity (Fig. 8b). An increased sensitivity and linearity of low temperature peak with dose up to 4 kGy were observed.

3.3.1. Studies on $CaSO_4$: (Dy, Bi) phosphor. Fig. 9a shows the glow curve of $CaSO_4$: (Dy, Bi) with varying concentration of Bi (0.05, 0.2 and 0.5 mol %). It was seen that with increasing concentration of Bi, the peak intensity was reduced.

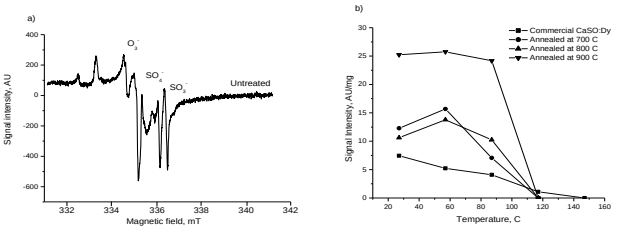


Fig. 8 a) EPR spectra of annealed sample
b) thermal behavior of the radicals

Fig. 9b shows the EPR spectra of $CaSO_4$: (Dy, Bi) with different concentrations of Bi and irradiated to a gamma dose of 1 kGy. Three prominent lines were observed with g values 2.023, 2.0089 and 2.004, respectively [9]. From the study it was evident that EPR line intensities of SO_4^- radical ions reduced drastically in 250°C annealed phosphor as compared to that in non-annealed samples. These results confirmed the role of sulphoxy radical ions in the dosimetric peak.

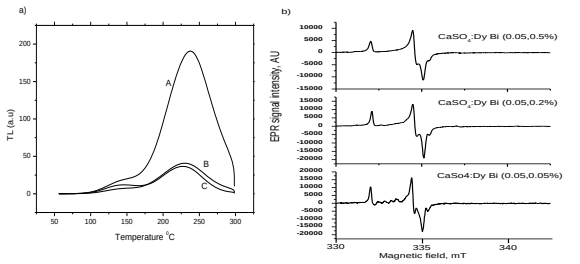


Fig. 9a) TL glows, b) EPR spectra of $CaSO_4$: (Dy, Bi)

The dose response of the phosphor with Bi (0.2 mol %) did not reveal well defined relation with increasing radiation dose. However, the dose response of the $CaSO_4$: (Dy, Bi) (0.5 mol %) was well fitted using a second order polynomial (R^2 = 0.99129) and useful for food irradiation.

4. CONCLUSION

Improved approach based on EPR spectroscopy, thermal behavior and relaxation characteristics of the paramagnetic centres were found to be useful tools in identification of irradiated food commodities even after a prolonged storage. TL glow curve shapes and the ratio of the TL glows (TL1/ TL 2) were also successful to detect irradiated foods.

Post-preparation thermal treatments of $CaSO_4$: Dy phosphor revealed structural change in TL glow curve exhibiting increased sensitivity of the low temperature peak that could be usefully exploited for low temperature dosimetry and reduction in TL sensitivity of $CaSO_4$: (Dy, Bi) with Bi concentration 0.5 mol % could be explored as a suitable dosimeter in food irradiation dosimetry.

References:

1. FAO/IAEA/WHO. Technical Report Series No 659, 1981.
2. Bogl et al. Foods. Institut fur Strahlenhygiene des Bundesgesondheitsamtes, 1988.
3. ASTM Standard, E 1026. 2002.
4. European Standards EN 1788, 1996
5. Yamahashita et al, In: Proc. 2nd Int. Conf. on Luminescence Dosimetry, 1968.
6. Sanyal et al, Food Chem, 2009.
7. Sanyal et al, J. Agric Food Chem, 2008.
8. Sanyal et al, Radiat. Meas, 2010.
9. Bakshi et al, Appl. Radiat. Isotope, 2011.