Application of Thermoluminescence Measurements To Detect Irradiated Strawberries

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The thermoluminescence intensity of unirradiated and irradiated strawberries was studied with regard to dose response, storage time, and different varieties. An identification method could finally be developed. Further investigations were carried out to determine the origin of the thermoluminescence effect, which was found to be attributable to mineral grains adhering to the sample surface.

INTRODUCTION

The increasing number of approved food irradiations in the 1980s requires control procedures to ensure safety, health standards, and proper trade regulations in regard to irradiated products. Postirradiation identification methods are of general interest to ascertain that legally imposed food laws are not violated, control international trade, prevent irradiation from becoming a compensation treatment for low level hygienic products, supervise correct labeling, and control the absorbed dose.

Among other methods, luminescence measuring techniques promise fast and reliable identification of irradiated foods (Bögl and Heide, 1984, 1985; Bögl et al., 1988; Delincée, 1987; Heide and Bögl, 1985, 1987, 1988a; Moriarty et al., 1988; Kolbak, 1988). Since identifications of spices and dried vegetables by thermoluminescence (TL) and chemiluminescence (CL) have become official methods of food control in the Federal Republic of Germany (Amtliche Sammlung, 1989), more emphasis has been put on the development of detection methods in fresh food. In fact, it has been known for several years that detection of irradiated fresh or frozen food is possible—also when the foods contain high quantities of water—by measuring the thermally stimulated luminescence (referred to as TL). Different techniques were used: (1) TL was measured (Heide and Bögl, 1988b) when released by heating fresh food from room temperature to 150 (Figure 1, apple peel) or 300 °C (Figure 1, mushroom). (2) Luminescence is observed when the temperature, e.g., of mushrooms, is elevated to 50 °C (Rippen and Kaltenhäuser, 1988). (3) Luminescence is thermally stimulated by heating frozen shrimps (Figure 2) from −20 to 85 °C in a microwave oven.

As another fresh food of interest, strawberries were similarly examined. To prevent spoilage and prolong shelf life, the irradiation of strawberries is allowed in several countries (e.g., Argentina, Brazil, Chile, Israel, South Africa, Thailand; in France and other countries, irradiated strawberries have been sold on a test market basis labeled as radiation treated). On the basis of the studies of Sanderson et al. (1989), who explained the TL signals of irradiated spices and herbs as being caused by mineral grains adhering to sample surfaces, it was assumed that strawberries, usually contaminated with small amounts of soil and minerals, may also exhibit TL signals after irradiation. This has been confirmed by experimental work and optimization experiments. The identification of irradiated strawberries by TL measurements is now ready for application.

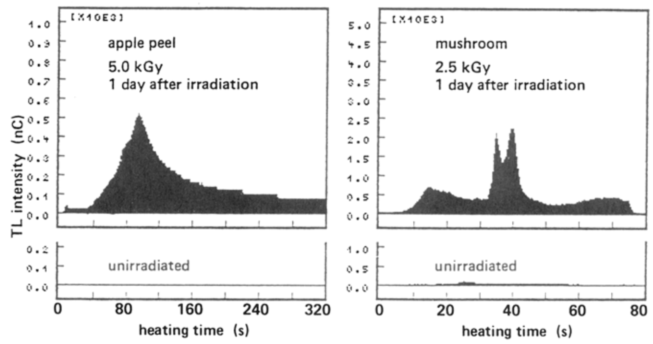

Figure 1. TL glow curves of unirradiated and irradiated apple peel and mushroom (champignon).

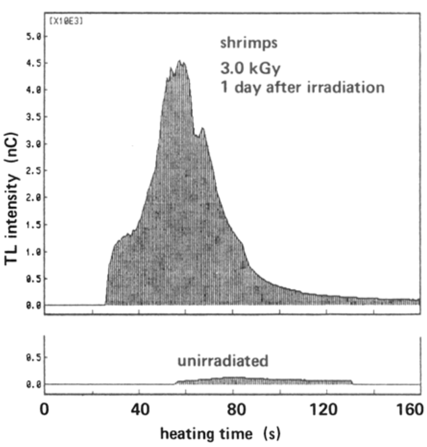

Figure 2. TL glow curves of unirradiated and irradiated shrimps.

A further method to detect irradiated strawberries is based on electron spin resonance (ESR) measurements (Raffi et al., 1988). ESR spectroscopy is only appropriate for systems with net electron spin momentum, e.g., free radicals as they are created during interaction of materials with ionizing radiation. Since radicals are very reactive, particularly with water in liquids or in materials with high water content, they are relatively stable only in solid phases. As the strawberry pulp has a water content of about 90%, free radicals tend to be unstable, but due to the lower water content in achenes (less than 8–10%), the radicals are here considerably stable even after a storage time of more than 1 week. The physical process of TL is based on electrons being transferred to an excited state by ionizing radiation and returning to a ground state emitting light when

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thermally stimulated. Compared to ESR, this effect is less influenced by the water content of the material.

MATERIALS AND METHODS

Samples and Sample Preparations. During May and June 1989, strawberries of different regions of Europe were obtained from the market. To reduce spoilage of unirradiated samples, they were kept at 8–10 °C in the dark until measurement. For luminescence measurements, the achenes producing an increased TL background were removed from the fruit with tweezers and a thin slice (ca. 1 cm^2, equal to 50–70 mg) was cut off. With the cutting area faced downward, this fruit piece was put on an aluminum disk (i.d. = 1 cm × 0.05 mm) and placed in the TL measuring chamber. To avoid evaporation during heating, a glass cover slip was put on the sample.

Parallel to fruit measurements, the adhering soil particles, such as sand, were removed from the strawberries by agitation in an ultrasonic bath (Sonorex TK52, Bandelin Electronic) at room temperature: 50 mL of water was put into a 100-mL centrifuge tube and 20 strawberries were successively treated by ultrasound for 1 min each. Following centrifugation (5 min at 6000 rpm), the supernatant was decanted and the sediment was dried at room temperature in a vacuum desiccator after evaporation with nitrogen. Aliquots of about 0.3–0.5 mg were taken for TL measurements.

Irradiated samples and blanks were processed in a parallel manner through all stages.

Thermoluminescence Measurements. The strawberries were heated from ambient temperature to 300 °C, and TL glow curves were recorded at a heating rate of 8 °C s^{-1} by using a Harshaw 2000A TL reader. The total heating time was 80 s, and the high voltage of the photomultiplier tube was set at 800 V. Measurements were carried out by flowing nitrogen (4 L min^{-1}) over the sample to reduce spurious luminescence.

The measuring conditions for soil were the same, except total heating time could be reduced to 40 s and high voltage to 700 V because of the much smaller amount but higher sensitivity of the material.

Irradiation. About 250 g of strawberries was put in a glass beaker and irradiated in a ^{60}Co γ radiation cell at room temperature. The dose rate was about 3 kGy/h and the radiation dose 3 kGy. The absorbed doses quoted have maximum errors of ±10%. To obtain dose response curves, two different strawberry batches were each separated into four aliquots of which three were irradiated with 1, 2, and 3 kGy, respectively.

Evaluation. Fivefold analyses were carried out for each sample, and the measurements showing the highest and lowest values were canceled, meaning that mean value and standard deviation were calculated from three measuring values.

RESULTS AND DISCUSSION

The TL responses of 10 different lots of strawberries and the corresponding separated soil have been examined prior to and at different times after irradiation. Characteristic TL glow curves from strawberries and separated soil are shown in Figures 3 and 4.

As one step in optimizing the ratio (TL intensity of irradiated sample/TL intensity of unirradiated sample) the achenes must be removed from the fruit. Without the achenes, the ratio rose from about 7 to 51 (Figure 5). Likewise, an optimum ratio can be gained by setting the high-voltage scale of the photomultiplier tube to 800 V (Figure 6). Because the TL intensities of the unirradiated and irradiated samples increase with the voltage, although not the ratio, the experimental conditions need to be balanced. Experiments at different heating rates did not improve the results, and the amount of strawberry being measured is of little influence. Weights between 50 and 70 mg are sufficient, because the size (surface area) of the strawberry piece is of primary importance where TL intensity is concerned. Interferences of sunlight (UV) or storage temperature were not observed if the samples were kept in the dark 24 h before measurement.

Dose response curves obtained from two varieties (Figure 7) show that the TL intensity is on a nearly linear increase in the commercially applied dose range of 1–3 kGy. Since the TL intensity is dependent on the amount of adhering minerals and the radiation dose, dose responses curves of whole sample measurements cannot be completely reproducible.

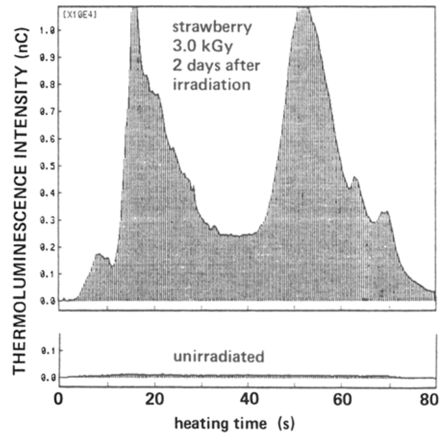

Figure 3. TL glow curves of unirradiated and irradiated strawberries.

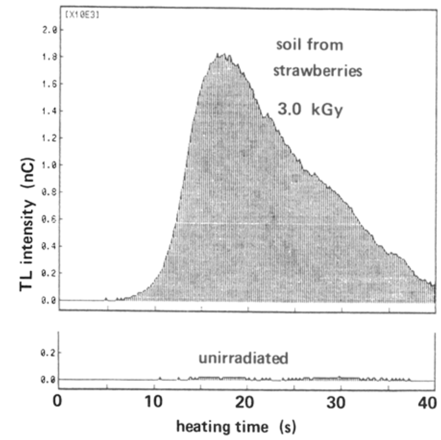

Figure 4. TL glow curves of unirradiated and irradiated soil separated from strawberries 3 days after irradiation and measured 1 week later.

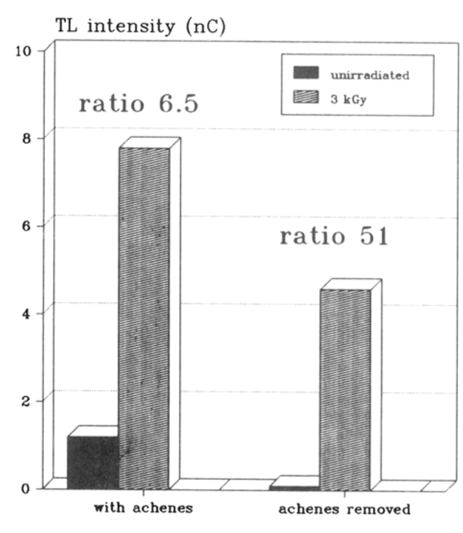

Figure 5. TL intensity of strawberries with and without the achenes.

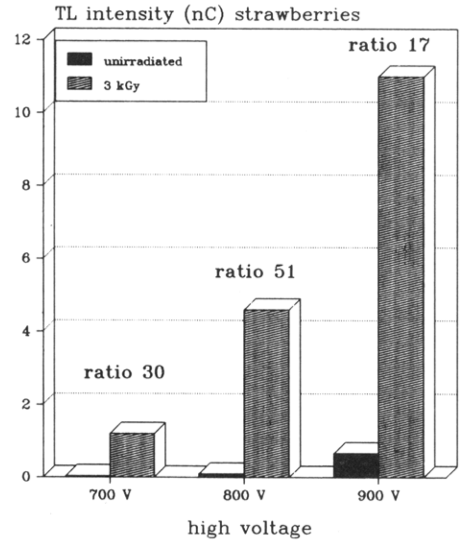

Figure 6. TL intensity of strawberries measured at different voltages.

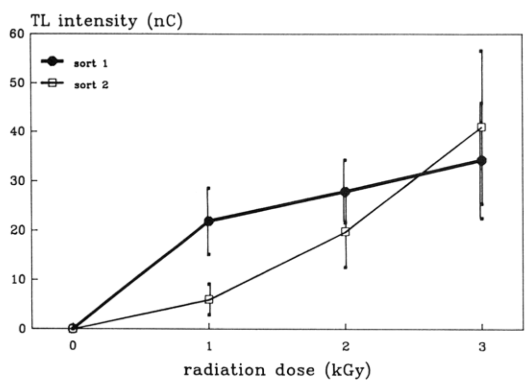

Figure 7. TL intensity of strawberries of different provinces (sorts 1 and 2) as a function of radiation dose.

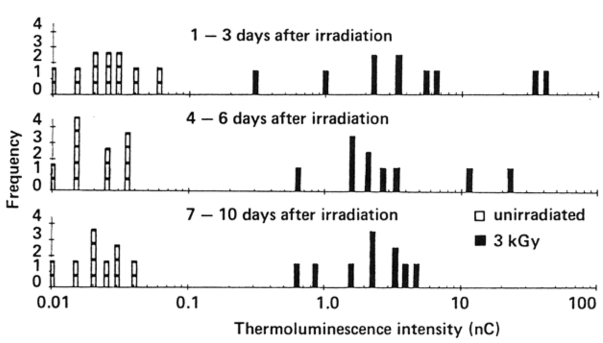

Figure 8. TL intensity ranges of unirradiated and irradiated strawberries (10 varieties) measured during storage time.

For TL measurements to be used in routine control analysis, a threshold value is needed above which strawberries can be declared as irradiated. Therefore, the scheme developed for spices was followed, and 10 different varieties from various regions were measured at different times after irradiation (Figure 8). In all cases, the results show that the irradiated strawberries can be very clearly distinguished from the unirradiated fruits. A threshold value can be ascertained by taking the highest intensity of an unirradiated sample into account, which is 0.06 nC. From an assumed factor of 3, which was proven as reliable by a collaborative study (Heide et al., 1989), a threshold of 0.2 nC can be calculated. Consequently, all irradiated samples can be identified. Further varieties were investigated later. The TL intensities of these samples

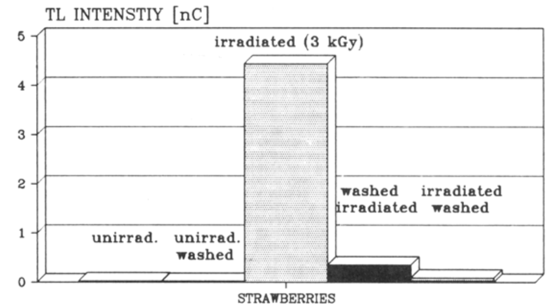

Figure 9. TL intensity of unwashed and washed strawberries.

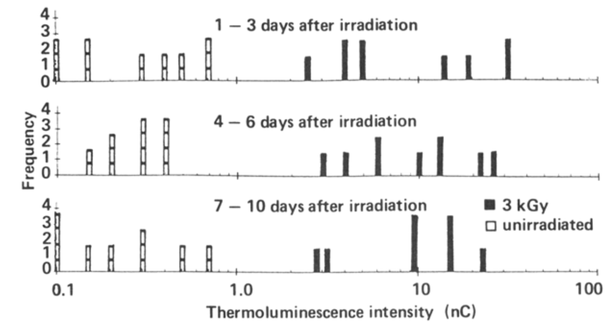

Figure 10. TL intensity ranges of soil separated from unirradiated and irradiated strawberries.

were in identical intensity ranges as determined for unirradiated and irradiated strawberries. It has been proved that the TL signal is stable for longer than the expected marketing time for strawberries. This was confirmed by storage experiments of the fruits, which showed nearly no fading of the TL intensity during the investigation time of 10 days.

Investigations on the origin of the TL effect were carried out with washed and unwashed fruits. The results are shown in Figure 9. After washing, the TL intensities of the irradiated strawberries are much decreased but still above the threshold value of 0.2 nC. Furthermore, the practical relevance to suppress radiation treatment by washing the fruit may be limited by high processing costs and the additional detection by ESR measurements. When the sediment from the washing water is examined (Figure 4), typical TL glow curves appear. Accordingly, identification can in general be made also by measuring the TL intensity of the soil separated from the fruits. Figure 10 summarizes the results from investigations on soil separated from different varieties of strawberries. Comparison with Figure 8 shows that measuring the separated impurities is here of no advantage for differentiating between irradiated and unirradiated samples, so that the time-saving method of measuring whole strawberry pieces is preferable. However, the method for separating impurities needs to be further improved since the separated material should consist of only minerals, whereas, in this case, it still contained organic substances from fruit and soil. Purification of the sediment by, for example, the method of Sanderson et al. (1989), suggests an improved ratio to be calculated from the intensity ranges.

It is intended to include TL measurements as a routine technique for the identification of radiation-treated strawberries in the German official collection of food control methods. In addition, the likelihood of detecting radiation treatment in other fruits or vegetables usually contaminated with mineral grains will also be examined.

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