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LUMINESCENCE TECHNIQUES TO IDENTIFY THE TREATMENT OF FOODS BY IONIZING RADIATION

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Abstract

About a decade ago two luminescence techniques, thermoluminescence (TL) and chemiluminescence (CL), were first described as methods for the detection of irradiated spices. It has now been established that the CL method can be used to screen only certain foodstuffs for irradiation. The TL method, instead, has been developed for clear identification of foods irradiated with at least 1 kGy and contaminated by minerals. The method is therefore suitable for a wide range of foodstuffs and it has been applied by laboratories for routine control. The latest findings prove that even irradiation with very low doses used to inhibit the sprouting of potatoes and onions can be clearly detected. In addition to CL and TL, other luminescence techniques which were described as suitable to detect irradiated food, i.e. the photo-stimulated luminescence and the H_2O_2-stimulated CL, are briefly reviewed.

Key words: Irradiation, food, food irradiation, luminescence, thermoluminescence, chemiluminescence, photostimulated luminescence, spices, fruit, shellfish.

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Introduction

The treatment of foods by ionizing radiation can prolong shelf life and reduce potential health hazards caused by pathogenic microorganisms. The consumer's acceptance of irradiated food differs from country to country. However, there is general agreement that irradiated food must be labelled. For the control of adherence to labelling regulations and irradiation bans, international research activities sponsored by the Bureau of Reference of the European Community and the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture have resulted in the development of a broad range of detection methods in recent years (Bögl *et al.*, 1988; Raffi and Belliardo, 1991; Delincée, 1991, 1993; Leonardi *et al.*, 1993; Schreiber *et al.*, 1993a). Beside gas chromatographic detection of certain radiation-induced hydrocarbons and 2-alkylcyclobutanones in the fat fraction of foods (Nawar *et al.*, 1990; Morehouse and Ku, 1990; Meier and Biedermann, 1990; Stevenson *et al.*, 1992; Sjöberg *et al.*, 1992; Schreiber *et al.*, 1993b; Spiegelberg *et al.*, 1994) and the detection of radiation-specific radicals in dry components of foods by electron spin resonance spectroscopy (Raffi, 1992; Desrosiers *et al.*, 1990; Helle *et al.*, 1992; Schreiber *et al.*, 1993c), luminescence techniques are used to screen for and to identify irradiated foodstuffs.

It was shown that chemiluminescence (CL) and thermoluminescence (TL) of irradiated spices and herbs were increased after irradiation (Bögl and Heide, 1983; Heide and Bögl, 1984). For determination of luminescence intensities, aliquots of the products were either suspended in an aqueous solution of a photosensitizer (for CL) or heated in a TL reader. Therefore, these techniques are called whole sample techniques. Examination of a broad range of spices and herbs using both techniques revealed large inter-sample variation of luminescence intensities before, but above all, after irradiation (Heide and Bögl, 1990; Heide *et al.*, 1992). Thus, the irradiation treatment of some samples could be detected clearly, while in others no such detection was possible (Heide *et al.*, 1989; Schreiber *et al.*, 1993d).

Table 1. Factual differences in log decades (D) of **a)** first-glow TL intensities as well as **b)** TL signals (first/second glow) between minerals isolated from non-irradiated and irradiated shellfish samples calculated from differences (A) between mean values of non-irradiated and irradiated samples and their respective standard deviations (B and C).

	Integration areas					
II	III	IV	V	VI	total	I
X-3IB to X-2IB	X-2IB to X-IB	X-IB to X	X to X+IB	X+IB to X+2IB		X-2IB to X
a) TL intensities						
A. Differences of mean TL intensities:						
2.80	3.11	2.97	2.51	2.07	2.13	3.01
B. Standard deviations of mean TL intensities of non-irradiated samples:						
0.22	0.36	0.48	0.59	0.62	0.52	0.44
C. Standard deviations of mean TL intensities of irradiated samples:						
0.92	0.85	0.81	0.82	0.82	0.80	0.82
D. Differences (A) minus standard deviation for non-irradiated (B) and irradiated (C) samples:						
1.66	**1.90**	**1.69**	**1.11**	**0.63**	**0.80**	**1.76**
b) TL signals						
A. Differences of mean TL signals:						
2.44	2.81	2.71	2.28	1.85	1.84	2.73
B. Standard deviations of mean TL signals of non-irradiated samples:						
0.67	0.61	0.60	0.53	0.47	0.37	0.58
C. Standard deviations of mean TL signals of irradiated samples:						
0.38	0.26	0.17	0.18	0.20	0.13	0.18
D. Differences (A) minus standard deviation for non-irradiated (B) and irradiated (C) samples:						
1.39	**1.94**	**1.94**	**1.56**	**1.18**	**1.34**	**1.96**

X = temperature of peak V

IB = [temperature$_{(Peak\ VI)}$ - temperature$_{(Peak\ V)}$] / 2

Apart from a brief reference to other luminescence techniques, such as CL and photo-stimulated luminescence, this review describes the development of the TL method for a clear detection of irradiation treatment of foods with doses equal or higher than 1 kGy. New results are presented which show it is possible to detect irradiation treatment doses in the range of 0.02-0.20 kGy used for the inhibition of sprouting.

Materials and Methods

In this section, only methods used to obtain unpublished results are described.

Thermoluminescence

Heating conditions. Samples were heated in a TL reader, a single photon counter (Bøtter-Jensen, 1988), from 70°C to 500°C at a heating rate of 6°C/min. Light emission was recorded in a temperature-dependant mode as glow curves.

Mineral analysis. All glassware and other materials used for the preparation of mineral samples were scrupulously cleaned to remove dust and adhering particles. From each product, two mineral samples were prepared for independent analyses (approx. 0.1-5 mg). Minerals from spices, herbs, fruit, vegetables and mussels were preconcentrated by rinsing the product with water. In the case of shrimps, guts of several animals were dissected and cut into small pieces with a scalpel to isolate minerals.

For the separation of minerals and organic material, the sample was suspended in a 15 ml centrifuge tube in 5 ml polytungstate solution [$Na_6W_{12}O_{39} * H_2O$] which had been adjusted to a density of 2 g/ml by addition of water. After a 5 minute ultrasonic treatment, the minerals were pelleted by 2 minute centrifugation at 1000 g. After adding small amounts of water, the organic material at the top of the polytungstate solution was sucked off by vacuum. This procedure was repeated until all

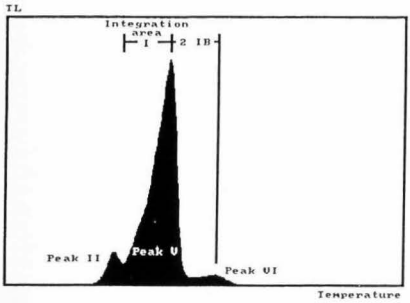

Figure 1. Glow curve of an LiF chip irradiated with 0.1 Gy. Integration area I and the temperature difference 2IB between peak V and peak VI are marked (see Table 1).

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the organic material had been removed. Then, the polytungstate solution was removed and the minerals were washed once in water (minerals sedimented within 5 minutes or pelleted by a short centrifugation at 1000 g). The minerals were treated by 1 ml of 1 M HCl for 10 minutes. After neutralizing by means of NH_4OH, the solution was sucked off. Minerals were again washed twice with water. After total removal of water, 2 ml acetone were added. Minerals were taken up in acetone with a Pasteur pipette to transfer them to a stainless steel disk (diameter 0.9 cm; thickness 0.5 mm). The minerals on the disk were stored overnight at 50°C and glowed in the TL reader mentioned above.

For normalization of first-glow TL intensities, the already measured mineral sample was irradiated with a ^{60}Co γ-ray dose of 1 kGy. The sample was heated again to record the second-glow TL intensities, using the same heating conditions as above. Integration of first-glow curves resulted in the TL intensities of a sample. The normalized TL intensity of a sample, which for the purposes of this study had been defined as the TL signal, was obtained by dividing the first-glow TL value by the second-glow one.

Glow curves were integrated for the whole record (total integral) or within certain temperature ranges. Temperatures for integration were defined by the TL release temperature of peak V and the difference of TL release temperatures of peaks V and VI of irradiated LiF chips (Fig. 1 and Table 1).

Light exposure

Potatoes were stored for a period of 16 days in the dark (control), under conditions of normal and non-artificial indoor lighting (day/night rhythm), under conditions of permanent neon lighting (24 hours/ day; 36 W; distance between sample and neon light source 75 cm), and in the open. For the last-mentioned sample, the duration of direct sunlight exposure is indicated in Fig. 2. At given times, minerals were isolated and analyzed as described above.

Normalization of TL intensities by ^{90}Sr ß-rays and ultraviolet (UV) irradiation

Normalization of first-glow TL intensities was obtained using ^{90}Sr ß-rays and UV-irradiation in addition to the ^{60}Co γ-rays. The ^{90}Sr source (Amersham-Buchler) was installed in the Risφ TL reader (Bøtter-Jensen, 1988) for automatic irradiation after first glowings. The dose rate at the position of the stainless steel discs was cross-calibrated with the ^{60}Co γ-ray source using quartz and was determined to be 1.7 ± 0.2 Gy/min. After ^{90}Sr irradiation, the fading rate per hour was found to be about 30%, 5%, 2% and 0.5% within 30 minutes, between 30 minutes and 2 hours, between 2 and 5 hours, and between 15 and 35 hours, after irradiation, respectively. Second-glow readings were taken 20 ± 3 hours after ^{90}Sr irradiation.

Unless otherwise indicated, UV-irradiation (using 254 nm) was performed at a distance of 23 cm and a power of 15 W for 16 hours. TL intensities were recorded 1 hour after the end of exposure.

Chemiluminescence

Aliquots of frozen chicken meat (about 50 mg) were placed in a cell of an LKB 1251 luminometer. The reaction was initiated by automatic injection of 0.2 ml of a reagent solution (0.1 mM luminol, 3.8 mM hemin, 11.8 mM sodium carbonate, pH 10.5). Light emissions were recorded for 5 seconds as glow curves.

Results and Discussion

Thermoluminescence

The reason for large inter-sample variation in the case of TL has been revealed by Sanderson *et al.* (1989a, b). By the separation of organic components and mineral contaminants of spices and herbs, it was shown that minerals emitted radiation-induced TL, whereas the organics produced non-specific signals. Therefore, TL intensity of whole samples mainly depends on the degree of mineral contamination. However, even isolated minerals of irradiated products exhibit different TL intensities since various kinds of minerals (quartz, feldspar, etc.) emit intensities after irradiation which may differ by several orders of magnitude (Autio and Pinnioja, 1990). For a clear identification of irradiation, therefore, TL intensities have to be normalized which is achieved by re-irradiation of the already measured samples with a dose of at least 1 kGy (Sanderson *et al.*, 1989b). The ratio of first-glow intensity and

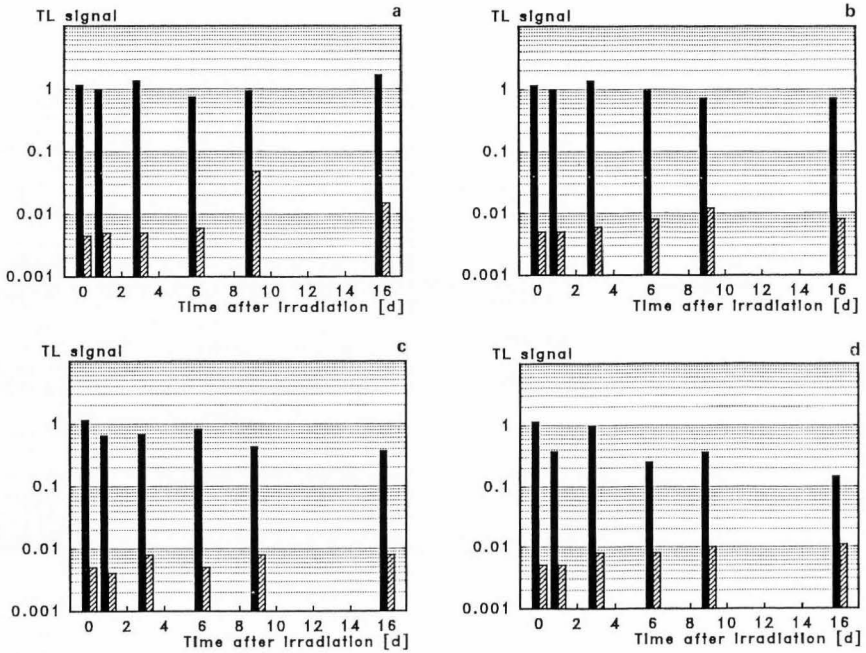

Figure 2. TL signals of minerals isolated from (**hatched bars**) non-irradiated and (**solid bars**) irradiated (1 kGy) potatoes which were stored for 16 days under different lighting conditions. **a)** Controls stored in the dark. **b)** Storage in a room under conditions of normal, not artificial lighting (day/night rhythm). **c)** Storage under conditions of permanent artificial lighting (neon 36 W; distance 75 cm). **d)** Storage in the open air. The duration of sun light exposure was 4, 21, 39, 59 and 90 hours after the 1st, 3rd, 6th, 9th, and 16th day, respectively.

second glow intensity is about 1 if the sample has been irradiated prior to examination with doses larger than 1 kGy. This ratio is referred to as the TL signal.

In an inter-laboratory study, all 7 laboratories achieved clearly separate TL signals for labelled non-irradiated and irradiated spice and herb samples (Sanderson *et al.*, 1993). In another inter-comparison study involving 14 laboratories (most of them food control laboratories), 18 coded spice, herb as well as spice-and-herb mixtures had to be identified 3 and 9 months after irradiation (Schreiber *et al.*, 1993d). Out of a total number of 317 samples, 99.1% were correctly identified as either non-irradiated or irradiated on the basis of a threshold value of 0.7 for TL signals. Only 3 irradiated samples could not be identified which meant that no false-positive result was reported. This clearly showed that the TL mineral method is ready for routine application. Consequently, the United Kingdom and Germany have included the method in their collaboratively-tested non-statutory methods list and in the collections of official methods according to the German Food Act, respectively.

By whole sample analysis, increased TL intensities were not only shown for irradiated spices and herbs but also for irradiated apples (Heide and Bögl, 1988). Measurements were done by heating a piece of the surface in a TL reader. After the source of light had been identified (Sanderson *et al.*, 1989a, b), it could be concluded that irradiation treatment of food contaminated by minerals may be identified by TL analysis. By whole sample analysis, increased TL intensities were measured for strawberries and mushrooms irradiated with doses of

2 kGy and 3 kGy (Heide *et al.*, 1990; Guggenberger *et al.*, 1991). However, the inter-sample variation was again too large for a clear identification in every case. Wagner *et al.* (1993a,b) achieved clearly separate TL signals for minerals isolated from non-irradiated and irradiated strawberries and mushrooms. In an inter-comparison study involving 12 laboratories (again most of them food control laboratories) performed to identify non-irradiated and irradiated (1.4-1.6 kGy) mango, papaya, strawberry, and mushroom samples, only 66 % of irradiated samples could be clearly identified, using a threshold value of 0.6 (Schreiber *et al.*, 1993e). However, in this inter-comparison study minerals became lost from the surface of fruit during transport between the irradiation facility and the participating laboratories since fruit became soft and juicy and arrived at the laboratories in a bad condition. It is very important to note that again none of the non-irradiated samples was classified as irradiated.

Another application of the TL mineral technique was introduced by Autio and Pinnioja (1993a, b) and Pinnioja (1993). In Finland, illegally imported irradiated products could be identified by the isolation of minerals from the guts of shrimps and prawns. In a survey conducted in Germany, 25 different products of shrimps, prawns and mussels were examined, using the same technique (Schreiber *et al.*, 1994). None of the samples was identified as irradiated although it could be shown that commercially used doses of 2 kGy can be clearly identified in such products.

Integration of glow curves

Depending on the 'depth of the trap', the excited electron will return to the original level at a certain temperature accompanied by light emission. The stability of the excited electron increases with the 'depth of the trap' or with the temperature at which light is released; fading increases with decreasing release temperature and vice versa. Therefore, TL which is induced by natural radiation can only be measured at very high temperatures (above ca. 300°C) since at lower temperatures the induction rate is smaller than the fading rate. TL induced by high doses of artificial radiation, on the other hand, is also released at intermediate (ca. 200-300°C) and low temperatures (< ca. 200°C). Therefore, the differences of TL intensities between non-irradiated and irradiated samples is most pronounced in the low and intermediate temperature ranges. In the low temperature range, however, fading is so strong that the measurable TL intensities depend largely on the time period elapsing between irradiation and analysis. Since in routine control, the time of irradiation is normally not known, the most suitable integration area of glow curves lies within the intermediate temperature range. During the TL inter-comparison studies conducted at the Federal Health Office, the glow curves of all mineral samples were integrated in 6 different temperature ranges by the participating laboratories (Schreiber *et al.*, 1993d, e). Although minerals were extracted from different products (spices, herbs, spice-and-herb mixtures, fruit, and mushrooms) and at different times after irradiation (about 2 weeks, 3 and 9 months) performed with quite different doses (about 1 kGy to 11 kGy), data of both inter-comparison studies revealed maximum differences between non-irradiated and irradiated samples within the same temperature range. This area which had been defined as integration area I was described by the characteristic TL spectrum of irradiated LiF (Fig. 1) for all the different TL readers used in the inter-comparison studies because differences in temperature control and measurement of different TL readers might be too large for a temperature definition using absolute values (Sanderson *et al.*, 1993; Schreiber *et al.*, 1993d). In a further study to identify irradiation treatment of shellfish by TL analysis of minerals, maximum TL differences were again determined in integration area I (Table 1) (Schreiber *et al.*, 1994). Therefore, it can be concluded that integration area I is well suited to establish large differences in TL intensities and TL signals between minerals isolated from non-irradiated and irradiated foods.

Effect of light exposure on TL intensities

Radiation-induced TL intensities decrease if minerals are exposed to light. Therefore, it was proposed to perform the examination of minerals under safe light conditions (red light) (Sanderson *et al.*, 1989b). It was necessary to determine whether light exposure might interfere with the detection of irradiated food via TL since fruit and vegetables, in particular, might have been exposed to light for prolonged periods in retail stores.

Potatoes, which were either non-treated or irradiated with 1 kGy, were stored over a period of 16 days under conditions of normal indoor lighting (non-artificial; day/night rhythm), under conditions of permanent neon lighting, and in the open for exposure to sunlight (Fig. 2). In comparison to the controls which had been stored in the dark, TL signals of samples stored under conditions of normal indoor lighting did not change significantly ($p < 0.05$). The same was true of samples stored under conditions of permanent neon lighting although the mean TL signals decreased. Only TL signals of irradiated samples stored in the open decreased significantly.

It can be concluded that although TL intensities decrease due to light exposure, irradiated food samples will in most cases be identified. Nevertheless, light exposure should be avoided and non-exposed samples should be taken for routine food control, if possible.

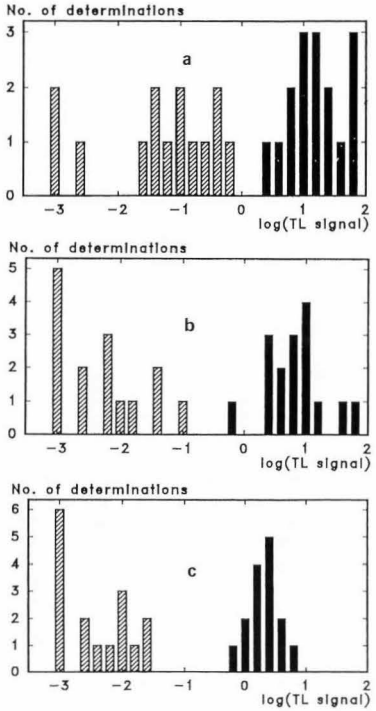

Figure 3. TL signals of minerals isolated from (**hatched bars**) non-irradiated and (**solid bars**) irradiated (6 kGy) pepper and paprika samples after normalization with ^{60}Co γ-ray doses of **a**) 100 Gy, **b**) 500 Gy and **c**) 1 kGy. After TL intensities of all samples were determined in first glowings, the same mineral samples were irradiated with the indicated doses. Each irradiation was followed by a second glowing. TL intensities of the first glowings were divided by the respective TL intensities of the second glowings to obtain TL signals.

Normalization of TL intensities by different types and qualities of radiation

Normalization doses of 1 kGy can only be applied over acceptable time periods using γ-ray sources. However, most food control laboratories in Germany do not have γ radiation facilities so that samples have to be dispatched to irradiation plants which is very inconvenient. Therefore, it was determined if other radiation

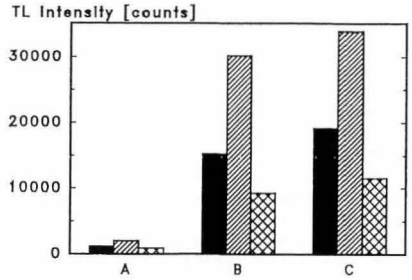

Figure 4. TL intensities of 3 different mineral samples (**solid or hatched bars**) after UV irradiation (**15 W**) in a distance of 23 cm using **A**) 365 nm for 1 hour; **B**) 254 nm for 1 hour; and **C**) 254 nm for 16 hours.

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qualities could be used for normalization although they would not be suitable for applying saturating doses (over acceptable periods).

At first, γ-ray doses below the saturation dose were applied. Clearly separated TL signals were obtained for minerals from non-irradiated and irradiated spice samples (Fig. 3). If a ^{90}Sr ß-ray source was used for irradiation with approximately 120 Gy, clearly separate ratios were also obtained for non-irradiated and irradiated samples. Even UV rays induced TL (Fig. 4). A comparison of TL intensities induced by γ, ß and UV_{254nm} rays on the same samples showed that the relative intensities remained very similar whereas absolute intensities changed considerably decreasing in the order, γ, ß and UV rays. Consequently, the ratios of first-glow and second-glow intensities will increase, whereas the values for non-irradiated and irradiated samples remain separate (Fig. 5).

Identification of food treated with doses below 1 kGy by thermoluminescence

In the inter-laboratory study conducted to identify irradiated fruit and vegetables, potatoes irradiated with 200 Gy were examined since doses between 50 Gy and 200 Gy are commonly used to inhibit sprouting. Considerably increased TL intensities were obtained for irradiated samples. However, TL signals were smaller than the threshold value of 0.6 after normalization using a re-irradiation dose of 1 kGy. Nevertheless, TL signals of non-irradiated and irradiated samples were clearly separated and after additional normalization of the TL intensities of the same samples by a γ-ray dose of 200 Gy, TL signals of about 1 were obtained for irradiated samples (Schreiber *et al.*, 1993e).

To show whether such low doses can be identified

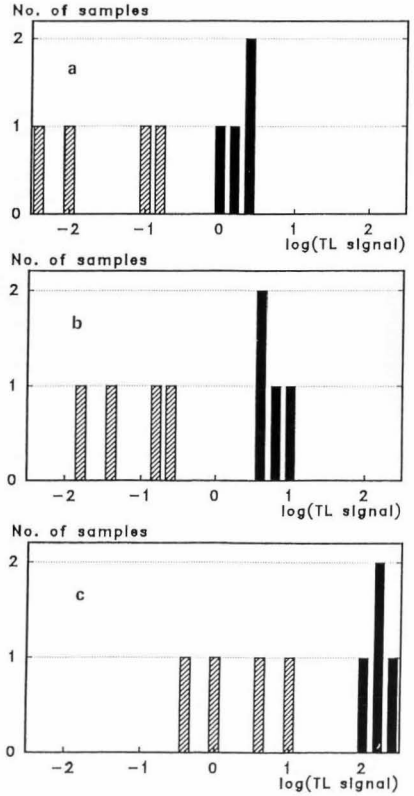

Figure 5. TL signals of the same (**hatched bars**) non-irradiated and (**solid bars**) irradiated mineral samples normalized with **a**) 1 kGy of ^{60}Co γ-rays, **b**) ca. 120 Gy of ^{90}Sr ß-rays and **c**) UV irradiation for 16 hours (254 nm).

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in routine control, TL intensities of minerals isolated from potatoes which had either been irradiated with 80 Gy or not treated were determined. After first-glow reading, the same samples were re-irradiated over varying periods (15 to 120 minutes) with a ^{90}Sr ß-ray source. Each irradiation was followed by a second glow reading. TL signals calculated from the first glow and the respective second glow were dependent on the irradiation dose (or period), however, the differences between TL signals of non-irradiated and irradiated samples did

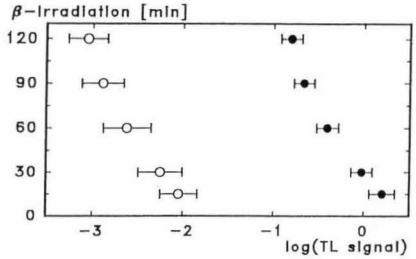

Figure 6. TL signals of minerals isolated from a potato sample either (**hollow circles**) non-irradiated or (**solid circles**) γ-irradiated with 80 Gy in dependence of ß re-irradiation time. After first glowing, the same samples were irradiated using a ^{90}Sr ß source for various time periods (dose rate 1.7 ± 0.2 Gy/min). Each irradiation was followed by a second glowing. Glow curves were integrated in area I (see Fig. 1). Geometrical means and standard deviations of first-glow to second-glow ratios (TL signals) of 5 samples analyzed in parallel are shown.

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not change significantly (Fig. 6). Although the data indicate that an irradiation period of 15 minutes is sufficient, it was decided to use a ß-irradiation period of 30 minutes (ca. 50 Gy) in order to obtain TL intensities well over background. Measurements were performed as follows:

Three different potato samples (P I, P II, P III) were either not irradiated or irradiated with a γ dose of 80 Gy or 95 Gy. TL signals were determined 2 days later. The difference between the TL signals of non-irradiated and irradiated samples was about 2 logs (Fig. 7). For two onion samples (O I, O II), a difference of about half a log between non-irradiated and γ-irradiated (20 Gy or 40 Gy) samples was found. Two strawberry samples (S I, S II) and 1 mushroom sample (M I) were examined which had not been irradiated or γ-irradiated with 55 Gy, 145 Gy or 580 Gy. Again, TL signal differences between non-irradiated and irradiated samples were determined to be about 2 logs. In the latter case, TL signals were either very similar or decreased only slightly during a second analysis 8 to 10 days after irradiation. This period was considered to be about the normal storage period for strawberries and mushrooms. Six weeks after irradiation, TL signals of irradiated onion sample I were very similar to those determined within 2 days after irradiation. The same was true of potato sample I which was analyzed a second time 13 weeks after irradiation. Twelve to thirteen weeks after

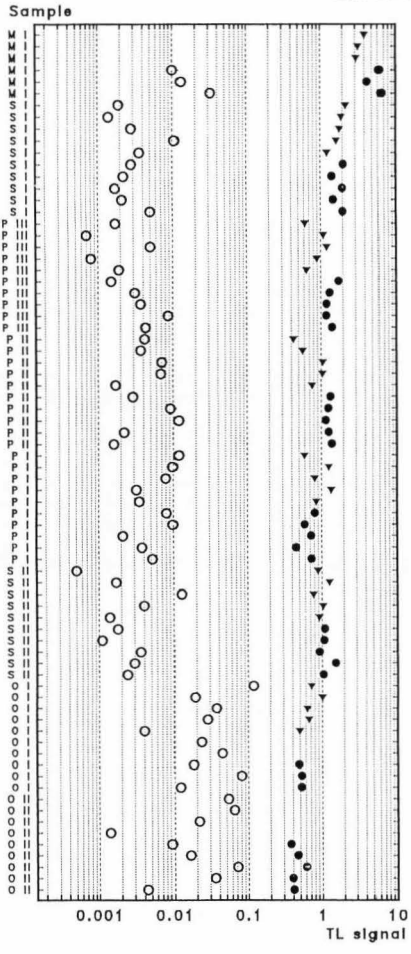

Figure 7 (at left). TL signals of minerals isolated from 2 onion (O I, O II), 2 strawberry (S I, S II), 3 potato (P I, P II, P III) and 1 mushroom sample (M I) either (**hollow circles**) non-irradiated or irradiated with ^{60}Co γ-rays (determined in 3 to 10 parallel analyses). Irradiated samples were analyzed (**solid circles**) within 2 days after irradiation and (**solid triangles**) after 8 to 10 days (S I, S II, M I), after 6 weeks (O I) or after 12 to 13 weeks (P I, P II, P III). Samples are arranged on the y axis in the order of the dose: O II, O I, S II, P I, P II, P III, S I and M I were irradiated with ^{60}Co γ-ray doses of 20, 40, 55, 80, 95, 95, 145 and 580 Gy ± ca. 10%, respectively. After first glowing, the same samples were irradiated using a ^{90}Sr ß-ray source for 30 minutes (dose rate 1.7 ± 0.2 Gy/min). Second-glow readings were performed 20 ± 3 hours after first-glow readings. Glow curves were integrated in area I (see Fig. 1) to calculate TL signals.

irradiation, intensities of TL signals of potato samples II and III were significantly lower, although only by a factor of about 3 to 4. A summary of all the measurements performed on samples irradiated with low doses revealed that all irradiated samples could be clearly discriminated from non-irradiated ones (Fig. 7). On the basis of these results, it can be concluded that even doses used to inhibit sprouting of potatoes, onions or garlic can be clearly detected by TL analysis in routine control, which means that the respective non-irradiated control samples need not be available. Except for the very time consuming chromosome analysis, so far, no other technique has been reported to detect clearly such low doses on food. Further measurements will be performed over a wider range of samples and over longer periods of storage to determine the TL signal variations of non-irradiated and irradiated samples.

Chemiluminescence

Light is emitted when irradiated substances are dissolved or suspended in a solvent. This effect is called lyoluminescence or CL. If a sample is suspended in pure water, generally little or no effect is observed. Therefore, photo-sensitizers like luminol are added to enhance the light yield. Involved in the process of CL are free radicals, oxides, peroxides and other radiation-induced products which are, however, often not irradiation-specific.

Extensive studies on spice products revealed large inter-sample variations (Heide and Bögl, 1990; Heide *et al.*, 1992). Similar to the TL whole sample analysis, some irradiated products could be clearly identified by their CL while others could not. Since this method is very fast and easy to perform, it can be used to screen foods for irradiated products.

Recently, studies were initiated in our laboratory on frozen products since it has been reported that CL intensities might give an indication about radiation treatment (Bögl and Heide, 1985; Heide and Bögl, 1990). Meat samples were taken from 11 different non-irradiated chicken carcasses. After irradiation with doses of 2.5 kGy and 4.5 kGy, increased CL could be measured over a period of 30 days. However, the populations of

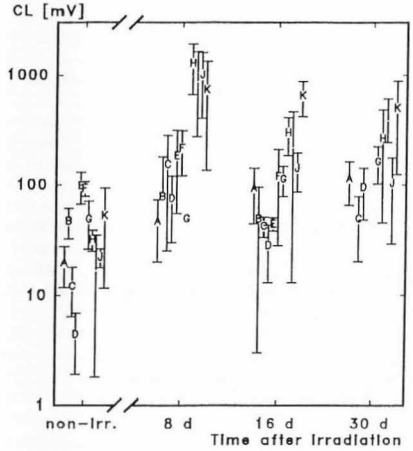

Figure 8. CL of 11 different frozen chicken carcasses (A - K) before and after irradiation with (A - F) 2.5 - kGy and (G - K) 4.5 kGy. Irradiated samples were examined over a period of 30 days. From each chicken carcass sample, CL mean values (integrals determined for 5 seconds) and standard deviations of 6 aliquots measured in parallel are shown.

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mean values as well as standard deviations of non-irradiated and irradiated samples overlapped considerably (Fig. 8). Currently, other frozen products are being examined.

Hydrogen peroxide-stimulated chemiluminescence

Hydrogen peroxide-stimulated CL was used to measure relative changes in the ability to oxidize a sample. First examinations were performed on different varieties of apples (Lewin *et al.*, 1993). Half ml of homogenized apples were injected into a cell containing an aqueous solution of 3% H_2O_2. It could be shown that CL, which were measured over a time period of 5 minutes after injection, increased with the dose. Further studies will have to be conducted to determine inter-sample variation and to find whether the method might be used for screening.

Photo-stimulated luminescence

Release of trapped energy as luminescence can be achieved not only thermally and chemically, but also by using light as a stimulus. This process is known as optically stimulated or photo-stimulated luminescence (OSL or PSL). Sanderson (1991) examined irradiated food using this technique. Emissions from irradiated foods showed anti-Stokes behaviour since their wavelengths were shorter than the wavelengths used for excitation. Examinations were conducted on entire condiments and herbs, on minerals isolated from these products, as well as on bones and shells. It was reported that non-irradiated samples produce background signals only, whereas distinct luminescence was measured after excitation with infrared light even if products had been irradiated at 100 Gy only. Since further data have not yet been published, the potential of this method to detect irradiated foods remains to be assessed.

Conclusions

Different luminescence techniques were applied to identify irradiated foods. Whereas, CL techniques can only be used for screening, since changes are not irradiation-specific, and the potential of PSL is not yet clear, extensive studies have shown the value of using TL. After the source of light had been discovered, it became evident that the technique was able to prove irradiation treatment in food contaminated by minerals. Meanwhile, the normalization procedure has been modified to identify doses used for the inhibition of sprouting. The technique can be, therefore, regarded as the most sensitive physical method to identify irradiated food available today.

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Discussion with Reviewers

H. Delincée: Since the value of the TL signal (ratio of first glow to second glow) is strongly dependent on the dose given to the minerals before the second glow, how can dose calibration be ascertained so that various laboratories can achieve comparable results and set up numerical threshold levels?

Authors: For identification of samples irradiated with at least 1 kGy, a dose of 1 kGy is sufficient for normalization although higher doses (until about 5 - 10 kGy)

can be used. For irradiated samples one will always achieve TL signals of about 1 (varying from about 0.5 to 10). For non-irradiated samples TL signals smaller than 0.1 will be achieved. Therefore, the gap between irradiated and non-irradiated samples should be large enough to set thresholds (see Schreiber *et al.* 1993d,e). For products which are normally only irradiated with 0.02 — 0.2 Gy it is quite reasonable to use a normalization dose in this same dose range. Since the TL intensity is linear dependent on dose until about 1 kGy one can even determine the dose range which was used to irradiated the food (however, one has to consider also the fading of TL intensities). This can be done by repeated irradiation of the sample with different normalization doses. Thus, only a proper dose measurement is needed to compare results of different laboratories.

H. Delincée: Is it ascertained that TL glow curves for minerals usually present in food products are identical, regardless of the quality of radiation (in this case ^{60}Co γ-, ^{90}Sr ß-rays and UV at 254 nm)?
Authors: The TL intensity depends from the dose of ionizing radiation. There are no differences in glow curve shapes either for γ or ß irradiation. Also, the shape of the glow curves after UV exposure are very similar to glow curves measured after treatment of samples by ionizing radiation. The TL intensities after UV irradiation are, however, much smaller than after irradiation of minerals by a ß dose of 100 Gy, for example. TL intensities could not be largely increased by extension of UV exposure time. For example, the TL intensities were increased largely after 1 hour of UV exposure (in comparison to non-exposed samples), however, between 1 hour and 16 hours of exposure, the further increase was only slight. Also, it is important to note that exposures with 365 nm hardly induce TL, whereas 254 nm do.

H. Delincée: How is the fading of the TL intensity in irradiated onions and potatoes after commercial long-term storage and how can it be taken into consideration for a proper identification of radiation treatment?
Authors: Our laboratory is currently doing a long term study (one year) on potatoes irradiated with doses of 60 — 90 Gy. Until now determinations of TL intensities were done 1 day as well as 1, 2, 3, 5, 10, 15, 20 and 25 weeks after irradiation. In comparison to the first measurement, two weeks after irradiation intensities were decreased to about 50%, and 5 weeks after irradiation to about 40%. During the time after, TL intensities were decreasing very slowly. Until now, the TL signals were in each case clearly higher than TL signals determined on non-irradiated samples. These data will be published after completion of the study.