# Thermoluminescence Analysis for Detection of Irradiated Food—Luminescence Characteristics of Minerals for Different Types of Radiation and Radiation Doses

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*Thermoluminescence analysis is used to detect radiation processing of foods which are contaminated with sand or dust. Silicate minerals are isolated, their radiation-induced luminescence is measured and compared to the thermoluminescence from a second measurement after exposure to a defined radiation dose (normalization). In the present study, the mineral mixture 'sand' and its main components feldspar and quartz were investigated for their thermoluminescence behaviour using different types of radiation, in order to determine adequate radiation sources for the purpose of normalization. The material was irradiated with types of ionizing radiation commonly used for commercial food irradiation, i.e. accelerated electrons with beam energies of 5 MeV as well as 10 MeV, and $^{60}$Co-γ-rays. After thermoluminescence measurements, samples were re-irradiated using either accelerated electrons with beam energies of 2 MeV, 5 MeV or 10 MeV, or $^{60}$Co-γ-rays, $^{90}$Sr-β-rays or ultraviolet rays (200–280 nm). Evaluation of the first and corresponding second glow curve revealed that their shapes depend on the type of minerals in the mixture. The second radiation treatment (normalization) is satisfactory when accelerated electrons (2, 5 and 10 MeV) as well as $^{60}$Co-γ-rays and $^{90}$Sr-β-rays are employed. Normalization with ultraviolet rays, however, has only a limited range of use.*



**Keywords:** food irradiation; irradiation identification; thermoluminescence; silicate minerals; type of radiation

## Introduction

Treatment of food with ionizing energy—food irradiation—is a preservation process which contributes to prolong shelf-life and to reduce health hazards caused by pathogenic micro-organisms (1, 2). In 1980, a Joint FAO/IAEA/WHO Expert Committee concluded that food irradiation is safe up to an overall average radiation dose of 10 kGy (3). A Joint FAO/IAEA/WHO Study Group confirmed this finding again in 1997 and concluded that foods treated with doses even greater than 10 kGy can be considered safe and nutritionally adequate when produced under established Good Manufacturing Practice (4). At present, this preservation technique is permitted for various food products in more than 40 countries (5). However, in several other countries, bans or no regulations prevail, i.e. there is no uniform legislation (6). A harmonized regulation for the irradiation of herbs and spices in the European Union shall come into force in the Member States only in September 2000 (7). Labelling is deemed necessary in order to ensure the freedom of choice for consumers (8). In 1988, at the international conference 'The Acceptance, Control of and Trade in Irradiated Food', it was recommended that the compliance with labelling regulations should be checked directly in the food. That meant that existing analytical detection methods of radiation treatment had to be improved and new methods developed (9).

Thermoluminescence (TL) analysis is one of such identification methods. It is based on the physical changes in minerals (from sand and dust) which are concomitant to many food products. Silicate minerals are able to store the energy imparted by radiation. Heat stimulation releases some of this stored energy in the form of light. A thermoluminescence reader measures the amount of light which is emitted during controlled heating (10).

Luminescence was discovered by Sir Robert Boyle in 1663, who noted a kind of 'glimmering light' from a diamond by 'taking it to bed with me, and holding it a good while upon a warm part of my naked body' (11). This phenomenon was naturally induced luminescence

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caused by exposure of the diamond to natural radiation. In 1895, Wiedemann and Schmidt observed artificially induced luminescence produced by cathode rays in a large number of substances, e.g. alkali halides, by heating; they called it 'thermoluminescence' (12). Over the last fifty years, thermoluminescence (TL) has developed into a powerful methodology with many different application fields such as: a) radiation dosimetry, including clinical applications, e.g. therapeutical treatment of cancer patients; b) age determination in archaeology and geology; c) mineral prospecting, e.g. for uranium sources; d) study of meteorites and lunar material; e) solid-state defect structure analysis and f) other applications (11, 13–17). An early application of thermoluminescence related to food was described by Chadwick and Oosterheert in 1967, who measured the thermoluminescence of tomato seeds irradiated at liquid nitrogen temperature with X-rays at 0.05–1.0 kGy (18). To use thermoluminescence as a detection means for irradiated food was first proposed by Heide and Bögl in 1984. They suggested detecting the radiation treatment of spices and herbs by investigating whole samples: a few mg of spices were heated in a commercial TL reader—usually employed for dosimetry—and the light emission recorded as a function of increasing temperature of the spice sample (19). This led to the idea that spices and herbs themselves may exhibit thermoluminescence. In some interlaboratory studies (20–22), large inter-sample variations were observed, however. In 1989, Sanderson *et al.* reported that the origins of luminescence are contaminating minerals (sand and dust) in the spice samples. Thereupon, the mineral grains were isolated for TL analysis. The detection of radiation treatment was improved by normalization, i.e. re-irradiation of the minerals (23, 24). This second irradiation of the isolated mineral grains fixed on a stainless steel disc for TL measurement allows for differences in mineral composition—e.g. feldspar and quartz—and the different mineral weights. The first and second glow curves are compared and the ratio of integrated TL intensities of Glow 1 to Glow 2, evaluated over a defined temperature interval is calculated. This TL glow ratio, thus obtained, is used to indicate radiation treatment of the food, since the population of irradiated samples in principle yields higher TL glow ratios than that of non-irradiated samples. Glow shape parameters offer additional evidence for identifying irradiated foods. After these modifications, the method was extended to other food items carrying concomitant minerals, e.g. potatoes (25), strawberries and mushrooms (26, 27), onions, mangoes and papayas (27) as well as shellfish (25–29). Successful interlaboratory tests with herbs and spices as well as their mixtures (30–32) and shrimps (33, 34) led to the adoption of the method for these food items as a European Standard in 1996 (10), and nowadays it is used routinely in food control laboratories. However, to some of these laboratories the normalization step presents problems, because they do not have suitable facilities for the second, normalizing irradiation. They have to send their discs with isolated silicate minerals to other facilities in the region. This shipment may lead to loss of minerals from the discs and may cost much time.

The aim of the present study was to find adequate re-irradiation sources which could be used in food control laboratories, preferably without complicated licensing problems. For this purpose, both a mineral mixture and its main components, feldspar and quartz, were investigated to estimate the different luminescence characteristics appearing after different types of radiation.

## Materials and Methods

*Preparation of samples*

Mineral mixtures with a high proportion of feldspar often stick to the surface of vegetable foods, whereas mineral mixtures with a high proportion of quartz frequently appear in seafood (35). 'Pure' feldspar and quartz, as well as a mineral mixture, were therefore studied. [It should be kept in mind, however, that thermoluminescence is an extremely sensitive method, and that even the purest materials—as tested by chemical analysis—are 'impure' from the point of view of thermoluminescence (11).]

The pure minerals 'potassium feldspar' from Amberger Kaolinwerk GmbH & Co KG Hirschberg, and 'quartz' (fine granular, washed and calcined GR for analysis) from Merck Darmstadt, as well as a mineral mixture 'sand' from soil at Eggenstein-Leopoldshafen (from the Research Centre Karlsruhe) were analysed. For the preparation of mineral samples, all glassware and other materials were cleaned, in order to remove dust and adhering particles.

'Potassium feldspar' and 'sand', suspended in distilled water, were filtered through nylon sieve cloth of 125 µm, 'quartz' through one of 250 µm in pore size. Further preparation (e.g. removal of possible organic components by density separation) and fixation of the minerals on the discs for TL measurements was carried out according to EN 1788: 1996 (10). The amount of minerals taken for TL measurements varied between 0.4 and 4.0 mg depending upon the sensitivity of materials and the radiation dose. Since a rather large range of doses was investigated, this variation was necessary in order to achieve enough TL response, and on the other hand in order to avoid saturation of the photomultiplier. At least three parallel discs were prepared for each type of radiation and each dose.

*First irradiation and first TL measurement*

The pure minerals 'potassium feldspar' and 'quartz', as well as the mineral mixture 'sand', were exposed to several types of radiation used in food irradiation, e.g. accelerated electrons of 5 MeV or 10 MeV, both generated by a linear accelerator, model CIRCE III (Thomson-CSF Linac, St. Aubin, France), at the Federal Research Centre for Nutrition Karlsruhe (dose rate for both beam energies in the pulse $10^7$ Gy/s, average dose rate $2 \times 10^4$ Gy/s), as well as $^{60}$Co-$\gamma$-rays (two photon quants 1.17 and 1.33 MeV) from a Gammacell 220 (Nordion, Canada) at the Research Centre Karlsruhe (dose rate $6.78 \times 10^{-2}$ Gy/s). The applied radiation doses were 0.2 kGy ( $\pm$ 5%) corresponding to the lower dose range in

food irradiation, and 5.0 kGy ( ± 10%) corresponding to the medium range. Doses were always checked by means of GAFchromic film dosimeters, International Speciality Products, Wayne, USA (36). After radiation treatment, the samples were stored overnight in a laboratory oven at 50 °C which simulates normal fading of the TL signal. TL measurements were carried out by using an ELSEC model 7185 TL reader (Littlemore, Oxford, UK) at a heating rate of 6 °C/s and a final temperature of 500 °C. The heating chamber of the TL reader was flushed with pure nitrogen (99.996%) for cooling and to avoid non-specific signals caused by organic contaminants burning. The system was calibrated using a $^{14}C$ light source. The sample was first heated automatically by the TL reader to record the TL glow and then, after cooling, was heated again to record the black-body radiation background. This background emission was subtracted from the first glow, and the resulting net-glow curve was recorded and stored. Non-irradiated identical controls were also measured. The depicted TL curves are typical examples of the various treatments which were shown to be reproducible. Peak positions varied usually only about 5% or less.

*Normalization*

The first glow curve was compared to a second curve obtained after a re-irradiation step to eliminate the effects of different composition and/or weight of minerals deposited on the disc. For this purpose, six different types of radiation were used, four conventional sources: 1) 2 MeV accelerated electrons (average dose rate 260 Gy/s), generated by a Van de Graaff accelerator (Vivirad-High Voltage Co., Handschuhheim, France) of the research centre 'AERIAL' in Strasbourg; 2) and 3) 5 MeV or 10 MeV accelerated electrons both generated by the linear accelerator at the Federal Research Centre for Nutrition Karlsruhe; 4) $^{60}Co$-$\gamma$-rays from the Gammacell 220 at the Research Centre Karlsruhe; and two alternative radiation sources: 5) $\beta$-rays from a $^{90}Sr/^{90}Y$-source (0.546 MeV for $^{90}Sr$, 2.274 MeV for $^{90}Y$, dose rate $3.53 \times 10^{-4}$ Gy/s, about 1.15 GBq, Amersham Buchler GmbH & Co KG, Braunschweig, Germany) at the Research Centre Karlsruhe; 6) ultraviolet rays from a lamp (1000 W, 200–280 nm, Dr. Gröbel UV-Elektronik GmbH, Ettlingen, Germany) whose illumination was adjusted to 0.5 J/cm$^2$. A sensor registered the dose.

Samples irradiated at 0.2 kGy were re-irradiated at 0.25 kGy ( ± 5%), whereas samples irradiated at 5.0 kGy were re-irradiated at 1.0 kGy ( ± 10%). Some samples were treated by ultraviolet rays at a dose of 0.5 J/cm$^2$, regardless of the first radiation dose. This re-irradiation dose was chosen after investigations by the official food control laboratory in Karlsruhe had shown that it produced a maximum TL signal (37). The non-irradiated controls were also treated by the different types of radiation and established radiation doses.

After re-irradiation, samples were stored overnight at 50 °C in a laboratory oven before the second glow curve was recorded by the TL reader under the same measurement conditions used for the first glow curve.

## Results

There are two important criteria for the identification of irradiated food items:

1. The first one is the shape and the position of the resulting glow curve. Minerals of non-irradiated samples produce low intensity glow curves in the high temperature region. These minerals have been exposed to low level natural radioactivity; fading at ambient temperatures over prolonged periods has led to empty low energy traps whereas the deep traps of about 300 °C and above remain preserved (10, 25, 38). Typical glow curves of minerals from irradiated food products show maxima between 150 °C and 300 °C and a much higher intensity.
2. The second criterion is the TL glow ratio which is evaluated over a certain recommended temperature interval. The integrals of Glow 1 and Glow 2 TL intensities are calculated over this temperature interval, and the ratio Glow 1/Glow 2 yields the TL glow ratio. According to EN 1788 (10), the TL ratio from irradiated samples is typically greater than 0.5, whereas that from non-irradiated samples is generally below 0.1. If TL glow ratios between 0.1 and 0.5 are obtained, the shape of the glow curve needs to be taken into consideration.

*'Potassium feldspar'*

Non-irradiated samples, i.e. samples naturally irradiated from the environment only showing the archaeological background dose, exhibited a TL signal of maximum intensity at a glow temperature of about 270 °C (**Fig. 1**, Glow $1_{non\text{-}irr.}$). It should be recognized that the given temperatures are not calibrated values but reflect the conditions in the TL reader used. These conditions are characterized by measurement of lithium fluoride (LiF, TLD-100) which in our TL reader results in a temperature of 259 °C for peak V and 311 °C for peak VI (see also ref. 10). This non-irradiated 'feldspar' glow curve is characterized by a regular ascent and descent. These samples already produced rather high levels of signal

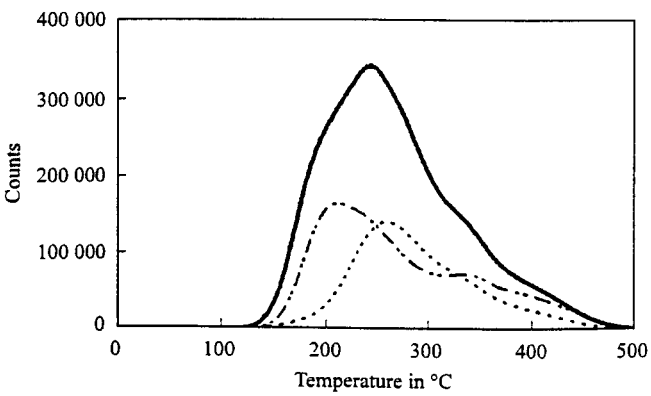


**Fig. 1** TL glow curves of potassium feldspar, low dose irradiation. — Glow $1_{irr.}$: 10 MeV electrons, 0.2 kGy; ····· Glow $1_{non\text{-}irr.}$: archaeological background dose; -·-· Glow 2: $^{90}Sr$-$\beta$-rays for normalization, 0.25 kGy. Sample weight: 2.2 mg

intensity. Irradiation of these samples for normalization led to glow curves with an intensity maximum at about 200 °C (**Fig. 1**, Glow 2) independent of radiation dose. The shape of these second glow curves were independent of the type of radiation and radiation dose. The different position of the maxima in the first and second glow curves allowed a definite judgement of these samples as having been originally non-irradiated.

Samples irradiated with the lower radiation dose (0.2 kGy) first (**Fig. 1**, Glow $1_{irr.}$) produced glow curves more influenced by the original natural radiation than by the artificially generated one. Identical glow curves were obtained for 10 MeV and 5 MeV electrons, and $^{60}$Co-$\gamma$-rays. The glow curve maximum had shifted slightly to the lower temperature region by approximately 10 °C. The ascent of this curve was steep but convex, whereas the descent was less steep. The shape of the curve is imaginable by super-positioning of Glow $1_{non\text{-}irr.}$ and Glow 2. After re-irradiation of the low-dose irradiated sample by a second radiation dose of 0.25 kGy, the glow curve is identical to the second glow curve of the non-irradiated sample (**Fig. 1**, Glow 2). The clear difference between the first and the second glow curve rendered a decision about a previous radiation treatment rather difficult. In this case, a very careful interpretation of the glow curves is needed.

When 'potassium feldspar' was irradiated at a medium dose of 5.0 kGy, the superposition with the 'archaeological' glow curve is no longer predominant (**Fig. 2**, Glow $1_{irr.}$). Independent of the type of first irradiation treatment, either accelerated electrons or $^{60}$Co-$\gamma$-rays, the curve showed a peak at a temperature of $\sim$ 200 °C, and two smaller peaks on the trailing shoulder of the curve. Please note that the quantity of irradiated feldspar was much less than in **Fig. 1**, otherwise saturation of the photomultiplier would have occurred. Since no linearity in TL intensity was observed, neither in dose response nor in mass dependency, comparison of TL intensities for different radiation doses with different amounts of minerals is difficult. The glow curves after the re-irradiation treatment with 1.0 kGy (**Fig. 2**, Glow 2) had a shape identical to that of the glow curves generated by the lower normalization dose of 0.25 kGy (cf. **Fig. 1**, Glow 2) and similar to that of the curves obtained after the first irradiation. The main peak of these curves was also found at about 200 °C, thus allowing easy identification.

Although glow curves after UV treatment for normalization were similar in position and shape to the glow curves generated by other types of radiation, they had a much lower intensity (**Fig. 2**, Glow $2_{UV}$). To take these lower intensities into account, conversion factors ( $\sim$ 100 and $\sim$ 250, depending on the first radiation dose) were necessary for a comparison. In principle, UV irradiation proved suitable for a normalization treatment.

*Mineral mixture 'sand'*

Examination of all glow curves indicated that their shapes did not depend on the type of radiation used in this experiment. The curves of non-irradiated 'sand' samples, i.e. naturally irradiated samples, had their highest intensity in the temperature region of 290–350 °C (**Fig. 3**, Glow $1_{non\text{-}irr.}$). Irradiation of these non-irradiated samples produced glow curves with an intensity maximum at about 200 °C (**Fig. 3**, Glow 2). These curves had a steep ascent and a less steep descent. The differences between the first and the second curve showed clearly that the samples had not been irradiated.

Irradiation of the 'sand' samples with the lower radiation dose of 0.2 kGy produced glow curves little influenced by original natural radiation exposure (**Fig. 3**, Glow $1_{irr.}$). The form of the descending part of the curve indicated this slight influence of natural radiation. The curve maximum was again at about 200 °C, thus the peak had shifted significantly to a lower temperature region in comparison with non-irradiated samples. Re-irradiation of these low-dose irradiated samples resulted in second glow curves (**Fig. 3**, Glow 2) comparable to the first ones. However, the descending part in the temperature range of 200–300 °C was steeper. A comparison of the first and the second glow curve made it clear that the samples had been irradiated.

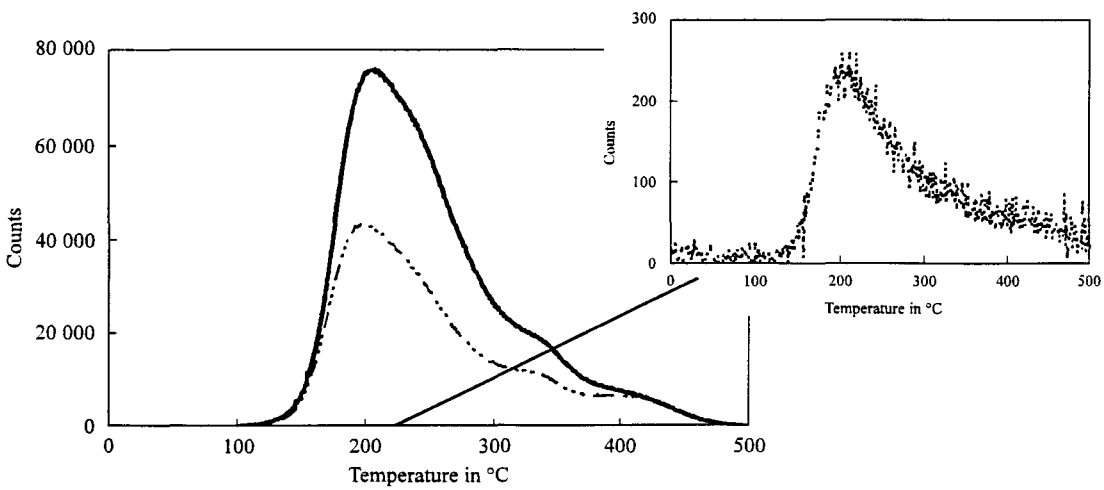


**Fig. 2** TL glow curves of potassium feldspar, medium dose irradiation. —Glow $1_{irr.}$: 5 MeV electrons, 5.0 kGy; - · · · - Glow 2: $^{60}$Co-$\gamma$-rays for normalization, 1.0 kGy; · · · · Glow $2_{UV}$: UV rays for normalization, 0.5 J/cm$^2$. Sample weight: 0.4 mg

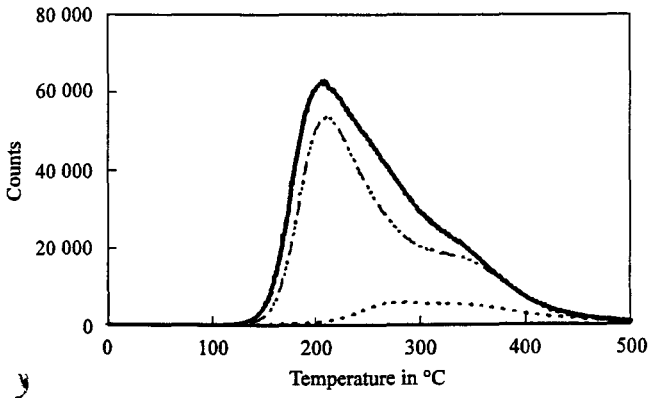


**Fig. 3** TL glow curves of the mineral mixture 'sand', low dose irradiation. — Glow $1_{irr.}$: 10 MeV electrons, 0.2 kGy; ····· Glow $1_{non\text{-}irr.}$: archaeological background dose; – ··· – Glow 2: $^{60}$Co-$\gamma$-rays for normalization, 0.25 kGy. Sample weight: 2.4 mg

When 'sand' samples were irradiated at a medium dose of 5.0 kGy, natural radiation exposure did no longer influence the shape of the glow curve (**Fig. 4**, Glow $1_{irr.}$). The maximum TL intensity was at about 200 °C, i.e. the peak had again shifted to the lower temperature region as compared to the naturally irradiated sample. The glow curves produced by a 1.0 kGy normalization dose (**Fig. 4**, Glow 2) were in the same temperature region and had the same shape as the curves obtained after the first radiation treatment; its shape was essentially identical to Glow 2 obtained at lower dose (cf. **Fig. 3**, Glow 2). The peak maximum was again at about 200 °C and, therefore, due to the same peak position in the first and second glow curve, a definite identification of the samples as having been irradiated was possible.

Re-irradiation of the 'sand' samples by ultraviolet rays resulted in glow curves which—similar to those induced by other types of re-irradiation—started to ascend up to a maximum at about 200 °C (**Fig. 4**, Glow $2_{UV}$). However, having reached a maximum, they formed a marked plateau and the TL intensity was several orders of magnitude lower than that of the glow curves of 'sand' obtained from other radiation sources. A quantitative comparison with other glow curves of 'sand' required therefore conversion factors ( ~ 100 and ~ 250).

*'Quartz'*

Glow curves of non-irradiated 'quartz' exhibited only background signals, because the Merck quartz natural signals had already been annihilated by a rigorous heat treatment (1080 °C for 20–30 min). The glow curves obtained after the first radiation treatment had different shapes, depending on the different types of radiation (**Figs. 5–8**, Glow 1). These differences in shape were affected by the radiation dose. At the lower dose (0.2 kGy) glow curves with three to four peaks were obtained (**Fig. 5**, Glow $1_{gamma}$, Glow $1_{electrons}$) which seemed to not differ in shape for various radiation sources. But TL intensity differed for the various types of radiation at equal doses. The glow curves induced by $^{60}$Co-$\gamma$-rays (**Fig. 5**, Glow $1_{gamma}$) exhibited a higher TL intensity than those obtained from accelerated electrons (**Fig. 5**, Glow $1_{electrons}$). It should be noted, however, that the TL sensitivity of 'quartz' was much lower than that of 'feldspar'. This observation is in agreement with other authors (16, 25, 39). Re-irradiation of samples first irradiated at the lower radiation dose produced glow curves whose shape was practically independent of the type of radiation used. These glow curves showed again three to four overlapping peaks (**Fig. 6**, Glow 2), of which the first was the most dominant, and in addition Glow 2 exhibited much higher intensity than the corresponding Glow 1. This effect may be attributed to a sensitisation of the quartz by irradiation and/or subsequent heating for reading the TL signal (11, 39–41).

The situation was different when a medium dose of 5.0 kGy was applied. With accelerated electrons, glow curves with three peaks of different intensity were obtained, the third of which was the highest (**Fig. 7**, Glow $1_{electrons}$). Glow curves induced by $^{60}$Co-$\gamma$-rays were characterized by a relatively small peak at about 200 °C and a dominating peak at about 390 °C (**Fig. 8**, Glow $1_{gamma}$). The last peak always had the highest TL intensity, independent of

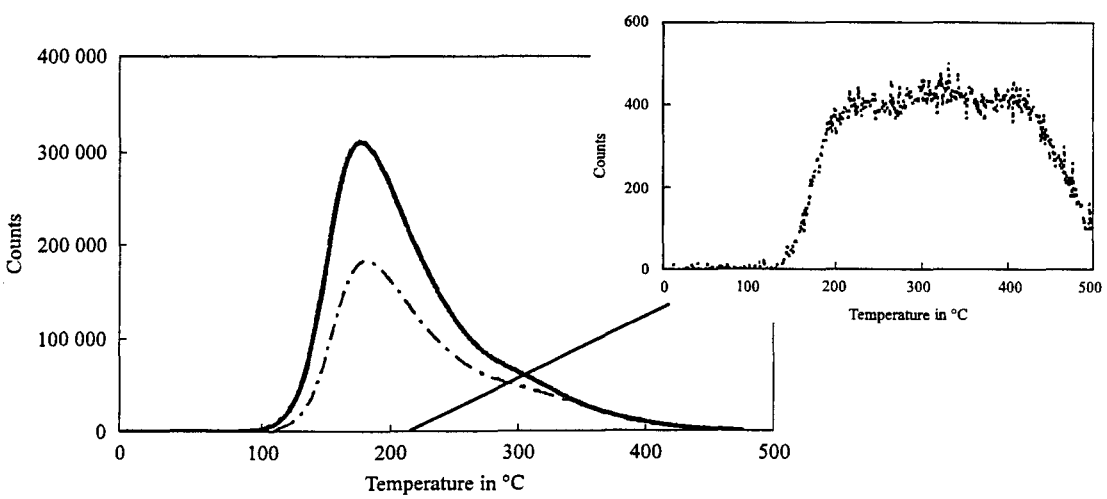


**Fig. 4** TL glow curves of the mineral mixture 'sand', medium dose irradiation. — Glow $1_{irr.}$: 10 MeV electrons, 5.0 kGy; – · – Glow 2.: 2 MeV electrons for normalization, 1.0 kGy; ·· ·· ·· Glow $2_{UV}$: UV rays for normalization, 0.5 J/cm$^2$. Sample weight: 1.2 mg

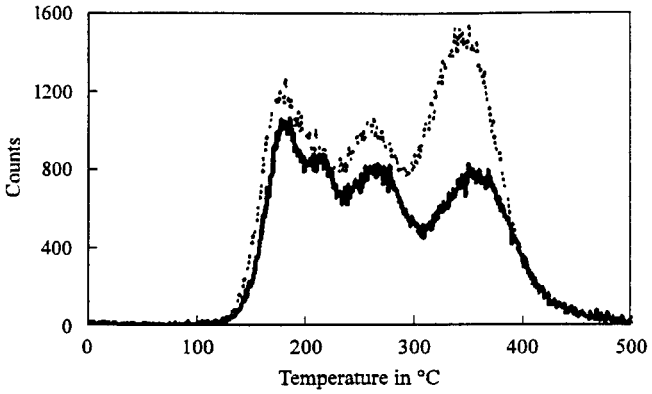


**Fig. 5** TL glow curves of quartz, low dose irradiation. — Glow $1_{electrons}$: 5 MeV electrons, 0.2 kGy; ... ... Glow $1_{gamma}$: $^{60}$Co-$\gamma$-rays, 0.2 kGy. Sample weight: 2.8 mg

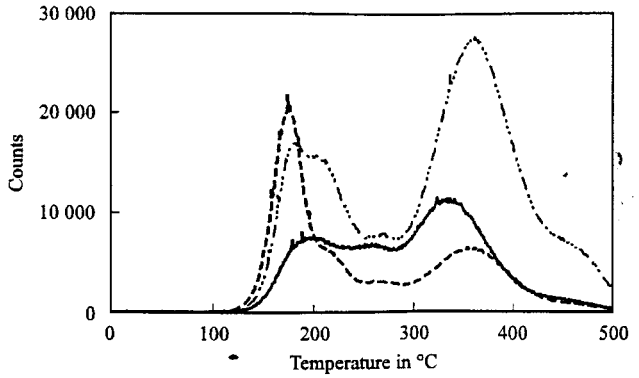


**Fig. 7** TL glow curves of quartz, medium dose irradiation. — Glow $1_{electrons}$: 10 MeV electrons, 5.0 kGy; ---- Glow $2_{electrons}$: 10 MeV electrons for normalization, 1.0 kGy; – ··· – Glow $2_{gamma}$: $^{60}$Co-$\gamma$-rays for normalization, 1.0 kGy. Sample weight: 3.7 mg

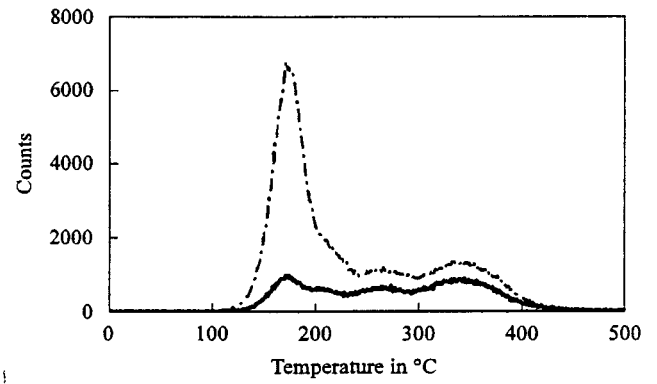


**Fig. 6** TL glow curves of quartz, low dose irradiation. —Glow $1_{irr.}$: 10 MeV electrons, 0.2 kGy; – · – Glow 2: 2 MeV electrons for normalization, 0.25 kGy. Sample weight: 2.8 mg

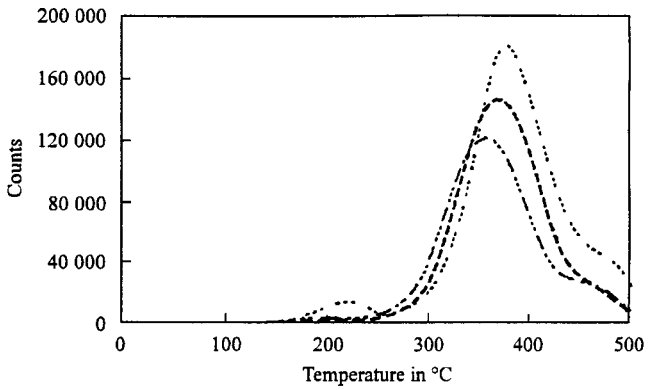


**Fig. 8** TL glow curves of quartz, medium dose irradiation. ··· ··· Glow $1_{gamma}$: $^{60}$Co-$\gamma$-rays, 5.0 kGy; – ··· – Glow $2_{gamma}$: $^{60}$Co-$\gamma$-rays for normalization, 1.0 kGy; ---- Glow $2_{electrons}$: 10 MeV electrons for normalization, 1.0 kGy. Sample weight: 1.4 mg

the type of radiation used, if the radiation dose was high enough. However, great differences existed in the TL intensity of the glow curves. The intensity of glow curves induced by $^{60}$Co-$\gamma$-rays was several orders of magnitude higher than that of curves generated by accelerated electrons.

When 'quartz' samples, first irradiated at 5.0 kGy, were re-irradiated at a dose of 1.0 kGy, glow curves different in shape, position and intensity were obtained, depending upon the type of radiation used, and surprisingly enough, also upon the type of the first radiation treatment. After a first irradiation with electrons, re-irradiation with electrons for all used beam energies produced glow curves (**Fig. 7**, Glow $2_{electrons}$) which were characterized by four overlapping peaks, of which the first was the main peak. In the case of the first irradiation with $^{60}$Co-$\gamma$-rays and subsequent re-irradiation with electrons (**Fig. 8**, Glow $2_{electrons}$), the shape and position of the second glow curve were similar to the first one, characteristic of $^{60}$Co-$\gamma$-rays, but the 200 °C peak failed to appear. Thus, a memory effect from the first type of irradiation influenced the second glow curve. Re-irradiation with $^{60}$Co-$\gamma$-rays yielded glow curves with either two or four peaks, depending upon the type of the first radiation treatment. If the first irradiation used electrons (**Fig. 7**, Glow $1_{electrons}$), the second glow curve by $\gamma$-rays (**Fig. 7**, Glow $2_{gamma}$) showed four peaks with the dominant one at about 370 °C. If the first and second treatments had used $^{60}$Co-$\gamma$-rays, the second glow curve was similar to the first with a slight shift of the main peak to lower temperatures ( ~ 350 °C), but the peak at 200 °C had largely disappeared (**Fig. 8**, Glow $2_{gamma}$).

By re-irradiation of 'quartz' samples with $^{90}$Sr-$\beta$-rays (figure not shown), the main peak was observed at 390 °C when electrons had been applied in the first treatment. This second glow curve had three lower peaks in the temperature range of 150–300 °C. When $^{60}$Co-$\gamma$-rays had been used first, the second glow curve showed virtually no peak in this temperature range and the main peak appeared at about 350 °C.

Re-irradiation by ultraviolet rays failed in 'quartz' samples, as no TL intensities were observed up to a final temperature of 500 °C.

*TL intensity integrals of the materials used*

A further aid in deciding whether a sample has been irradiated or not is the TL glow ratio. Nine integration regions were selected to determine the temperature region with the best discrimination between non-irradiated

and irradiated samples. The entire temperature region of 70–500 °C, as well as the so-called integration region I which is defined by means of irradiated LiF (TLD-100) chips (10), were used for evaluation; in our case I corresponded to a temperature interval 197–259 °C. The remaining seven temperature regions (73–197 °C, 197–228 °C, 228–259 °C, 259–290 °C, 259–321 °C, 290–321 °C, 321–445 °C) were defined considering the positions of the LiF peaks, which also serve to compare TL readings from various laboratories using different systems for TL analysis.

After integration of the glow curves by temperature regions, the ratio Glow 1/Glow 2 was calculated. The ratios of non-irradiated and irradiated 'potassium feldspar' samples and of the mineral mixture 'sand' samples have shown that the discrimination was satisfactory in the entire temperature region (70–500 °C) and even better in the recommended temperature interval I. The suitability of the temperature interval I is in agreement with the European Standard EN 1788: 1996 (10). The situation was different for 'quartz'. On the basis of the glow curve ratios, a generalized judgement about the most suitable integration region could not be made because of the different glow curves which were obtained by different types of radiation. In these special cases with pure 'quartz', a qualitative interpretation of the glow curve shapes had resulted in a better judgement than the use of TL ratios.

## Discussion

In this work, the influence of various radiation sources on the TL glow curves of 'pure' silicate minerals, such as 'potassium feldspar' and 'quartz', and of a common mineral mixture present on food products, 'sand', was investigated. It should be recognized that depending on the origin of the mineral samples, their formation and environmental exposure, their impurities and varying crystal defects, their pre-treatment, e.g. pre-heating or signal bleaching by light, a large variety of glow curves are produced. The measuring conditions, e.g. heating rate, optical filters, play another role (11, 16). Both for 'pure' feldspar and quartz samples many different types of glow curves have been described (11, 16, 40, 42). The obtained results are valid for the minerals employed in this study. The first glow curves of 'feldspar' were identical for each radiation dose independent of the type of radiation. Normalization with all types of radiation, except UV-rays, produced similar second glow curves for each radiation dose, higher intensities being observed with increasing dose. The UV-induced glow curves had a much lower intensity and, therefore, needed to be scaled up by conversion factors, in order to compare them with glow curves generated by the other types of radiation. Further experiments are necessary to determine the TL reaction immediately after re-irradiation with UV rays and to estimate the fading characteristics (influence of time and temperature on signal intensity). In comparison with 'quartz', the 'feldspar' samples showed a very high TL sensitivity, when comparable quantities of material were analysed (16, 25, 39). However, also for feldspars a wide variation has been observed in TL intensity influenced by changes in the mineral lattice structure (16, 43, 44).

Shape and position of glow curves of the mineral mixture 'sand' had similar characteristics as for 'feldspar'. This may be explained by feldspar which has a very high TL sensitivity dominating in the mixture. A possible influence of quartz on the glow curves was practically not observed.

In contrast to those of 'feldspar' and 'sand', shape, position and intensity of 'quartz' glow curves were strongly dependent on the type of radiation applied. Differences in TL intensity were already recognizable after a first low dose (0.2 kGy). Treatment with $^{60}$Co-$\gamma$-rays resulted in glow curves of higher intensity than those obtained from accelerated electrons. The intensity differences grew with increasing radiation dose. This effect has been observed previously (45). Differences in shape and position of the glow curves also increased with higher doses. Whereas irradiation with accelerated electrons produced glow curves with three to four peaks, those induced by $^{60}$Co-$\gamma$-rays exhibited only two peaks. In any case, after a dose of 5.0 kGy, the last peak was the highest; it was most distinct in the curves induced by $^{60}$Co-$\gamma$-rays. The shapes of the glow curves induced by re-irradiation were influenced by the type of radiation used for the first treatment. Irradiation with photons from radioactive sources revealed a stronger influence on the shape of the glow curves than irradiation with electrons. This phenomenon may be caused either by a dose-rate effect or by dependence on the radiant energy. Further experiments with 'quartz' are necessary to find out the reasons behind the different signal intensities and shapes of the glow curves obtained. When UV-light was used for normalization, no TL signals could be observed in the 'quartz' samples. Thus, this procedure could not be used if mineral samples consist of quartz only. Such mineral samples may be imaginable for some food products, e.g. shrimps from particular areas where the sand consists of quartz only. Although UV-radiation has been indicated for the purpose of normalization (27, 37, 46), it clearly has some limitations. On the other hand, the other types of radiation employed in this study seem suitable for normalization. The use of $^{90}$Sr-$\beta$-rays has already been described (27, 46) and seems to have general advantages. In contrast to the present results, in another study glow curve shapes were noted to be very similar for $\gamma$-, $\beta$- or UV-irradiation (46). This may be explained by the mixture of minerals isolated from the food samples under investigation. If, for example, feldspar dominates the TL behaviour, an independence of the type of radiation may be expected. In addition to the above mentioned types of radiation, X-rays have also been employed for normalization, yielding good results (31, 47).

## Conclusion

This study on thermoluminescence analysis to identify irradiated food has shown that the share and the sensitivity of various silicate minerals, which may contaminate

food products, may be responsible for different glow curve shapes obtained after treatment with different types of radiation. Re-irradiation for the purpose of normalization was successfully carried out with accelerated electrons of 2, 5 and 10 MeV, with $^{60}$Co-$\gamma$-rays and with $^{90}$Sr-$\beta$-rays. The suitability of ultraviolet rays for normalization seems to be limited because of the much weaker TL signal. However, normalization of glow curves of isolated minerals containing quartz as a single component is not possible by UV rays.

It can be concluded that food control laboratories may apply $^{90}$Sr-$\beta$-rays as a substitute source of radiation as well as accelerated electrons and $^{60}$Co-$\gamma$-rays as conventional types of radiation for the purpose of normalization in TL measurements. $^{90}$Sr-$\beta$-sources have the advantage that their license for use can be obtained much more easily. In addition, the system can be built 'self-shielded' and no specially shielded rooms are required.

Thermoluminescence analysis is a means of discriminating between non-irradiated and irradiated pure minerals and mineral mixtures. Although in this study pure 'quartz' samples presented some problems, it should be recognized that in most cases food carries concomitant mineral mixtures instead of pure minerals. Due to the high TL sensitivity of feldspar which, consequently, dominates the glow curves, these mixtures show luminescence characteristics which will in most cases be independent of the radiation sources used and, therefore, serve for reliable discrimination between irradiated and non-irradiated samples.

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## References

1 WORLD HEALTH ORGANIZATION (WHO). *Safety and nutritional adequacy of irradiated food.* Geneva (1994)
2 DIEHL, J. F. *Safety of irradiated food.* 2nd edition. New York: Marcel Dekker (1995)
3 WORLD HEALTH ORGANIZATION (WHO). Wholesomeness of irradiated food. Report of a Joint FAO/IAEA/WHO Expert Committee, Geneva. *Technical Report Series*, **659** (1981)
4 WORLD HEALTH ORGANIZATION (WHO). High-dose irradiation: wholesomeness of food irradiated with doses above 10 kGy. Report of a Joint FAO/IAEA/WHO Study Group, Geneva. *Technical Report Series*, **890** (1999)
5 ANON. Clearance of item by country. *Food and Environmental Protection Newsletter (IAEA, Vienna)*, **1** (2 Supplement), 1–17 (1998)
6 EHLERMANN, D. A. E. AND AMMON, J. Legal bestrahlt. Bestrahlte Lebensmittel in Deutschland zugelassen. *Zeitschrift für die Lebensmittelwirtschaft*, **48**, 18–20 (1997)
7 ANON. Directive 1999/2/EC of the European Parliament and of the Council of 22 February 1999 on the approximation of the laws of the Member States concerning foods and food ingredients treated with ionising radiation. *Official Journal of the European Communities*, **L66**, 16–25 (1999)
8 ANON. Guidelines for consumer protection. United Nations, New York, ST/ESA/170 (1986)
9 ANON. International document on food irradiation. Proc Int Conf: Acceptance, Control of and Trade in Irradiated Food, Geneva. IAEA (Ed). Vienna, 135–143 (1989)
10 EN 1788. Foodstuffs — Detection of irradiated food from which silicate minerals can be isolated — Method by thermoluminescence. European Committee for Standardization. Brussels (1996)
11 MCKEEVER, S. W. S. *Thermoluminescence of solids.* Cambridge: University Press (1985)
12 WIEDEMANN, E. AND SCHMIDT, G. C.: Über Lumineszenz. In: *Annalen der Physik und Chemie, Neue Folge*, **54**, 604–625 (1895)
13 MCDOUGALL, D. J. *Thermoluminescence of geological materials.* London: Academic Press (1968)
14 HOROWITZ, Y. S. *Thermoluminescence and thermoluminescent dosimetry.* Vol. I–III. Boca Raton, Florida: CRC Press (1984)
15 AITKEN, M. J. *Thermoluminescence dating.* London: Academic Press (1985)
16 KRBETSCHEK, M. R., GÖTZE, J., DIETRICH, A. AND TRAUTMANN, T. Spectral information from minerals relevant for luminescence dating. *Radiation Measurements*, **27**, 695–748 (1997)
17 BØTTER-JENSEN, L. Luminescence techniques: instrumentation and methods. *Radiation Measurements*, **27**, 749–768 (1997)
18 CHADWICK, K. H. AND OOSTERHEERT, W. F. Radiation induced thermoluminescence of tomato seeds at low temperature. In: EGBERT, H. G. (Ed), Proc. Symp. Microdosimetry, 13–15. November 1967, Ispra. *Brussels: European Communities*, **EUR-3747**, pp. 633–641 (1968)
19 HEIDE, L. AND BÖGL, K. W. Die Messung der Thermolumineszenz—Ein neues Verfahren zur Identifizierung strahlenbehandelter Gewürze. Neuherberg: Institut für Strahlenhygiene des Bundesgesundheitsamtes, *ISH-Heft* **58** (1984)
20 HEIDE, L. AND BÖGL, K. W. Routine application of luminescence techniques to identify irradiated spices — a first counter check trial with 7 different research and food control laboratories. In: *Health impact, identification and dosimetry of irradiated foods.* Neuherberg: Institut für Strahlenhygiene des Bundesgesundheitsamtes, *ISH-Heft* **125**, 233–244 (1988)
21 HEIDE, L., DELINCÉE, H., DEMMER, D., EICHENAUER, D., VON GRABOWSKI, H.-U., PFEILSTICKER, K., REDL, H., SCHILLING, M. AND BÖGL, K. W. Ein erster Ringversuch zur Identifizierung strahlenbehandelter Gewürze mit Hilfe von Lumineszenzmessungen. Neuherberg: Institut für Strahlenhygiene des Bundesgesundheitsamtes, *ISH-Heft* **101** (1986)
22 HEIDE, L., AMMON, J., BEZCNER, J., DELINCÉE, H., DEMMER, D., EICHENAUER, D., VON GRABOWSKI, H.-U., GUGGENBERGER, R., GULDBORG, M., MEIER, W., PFEILSTICKER, K., REDL, H., SANDERSON, D. C. W., SCHILLING, M., SPIEGELBERG, A. AND BÖGL, K. W. Thermolumineszenz- und Chemilumineszenzmessungen zur Identifizierung strahlenbehandelter Gewürze: Ein europäischer Ringversuch. Neuherberg: Institut für Strahlenhygiene des Bundesgesundheitsamtes, *ISH-Heft* **130** (1989)

23 SANDERSON, D. C. W., SLATER, C. AND CAIRNS, K. J. Thermoluminescence of foods: origins and implications for detecting irradiation. *Radiation Physics and Chemistry*, **34**, 915–924 (1989)

24 SANDERSON, D. C. W., SLATER, C. AND CAIRNS, K. J. Detection of irradiated food. *Nature*, **340**, 23–24 (1989)

25 AUTIO, T. AND PINNIOJA, S. Identification of irradiated foods by the thermoluminescence of mineral contamination. *Zeitschrift für Lebensmittel-Untersuchung und -Forschung*, **191**, 177–180 (1990)

26 DELINCÉE, H. Detection methods for irradiated food. Proceedings Symp. 'Irradiation for the food sector', Saint-Hyacinthe (Québec), 13 May, 1992, Agriculture Canada, 24–60 (1992)

27 WAGNER, U., HELLE, N., BÖGL, K. W. AND SCHREIBER, G. A. Thermolumineszenz bestrahlter Lebensmittel. Berlin: Bundesgesundheitsamt, *SozEp-Heft* **10/1993** (1993)

28 SCHREIBER, G. A., HOFFMANN, A., HELLE, N. AND BÖGL, K. W. Methods for routine control of irradiated food: Determination of the irradiation status of shellfish by thermoluminescence analysis. *Radiation Physics and Chemistry*, **43**, 533–544 (1994)

29 PINNIOJA, S. AND PAJO, L. Thermoluminescence of minerals useful for identification of irradiated seafood. *Radiation Physics and Chemistry*, **46**, 753–756 (1995)

30 SANDERSON, D. C. W., SCHREIBER, G. A. AND CARMICHAEL, L. A. A European Interlaboratory Trial of TL Detection of Irradiated Herbs and Spices. Glasgow: SURRC Report (1991)

31 SCHREIBER, G. A., WAGNER, U., LEFFKE, A., HELLE, N., AMMON, J., BUCHHOLTZ, H.-V., DELINCÉE, H., ESTENDORFER, S., FUCHS, K., VON GRABOWSKI, H.-U., KRUSPE, W., MAINCZYK, K., MÜNZ, H., NOOTENBOOM, H., SCHLEICH, C., VREDEN, N., WIEZOREK, C., AND BÖGL, K. W. Thermoluminescence analysis to detect irradiated spices, herbs and spice-and-herb mixtures — an intercomparison study. Berlin: Bundesgesundheitsamt, *SozEp-Heft* **2/1993** (1993)

32 SCHREIBER, G. A., HELLE, N., AND BÖGL, K. W. An interlaboratory trial on the identification of irradiated spices, herbs, and spice-herb mixtures by thermoluminescence analysis. *J. AOAC Int.*, **78**, 88–93 (1995)

33 SCHREIBER, G. A., MAGER, M., AMMON, J., BRUNNER, J., BUCHHOLTZ, H.-V., BUTZ, B., DELINCÉE, H., FIENITZ, B., FROHMUTH, G., HAMMERTON, K., JAHR, D., KISPÉTER, J., KLEIN, H., KRUSPE, W., KÜHN, T., MAINCZYK, K., MEYER, H., MÜNZ, H., NOOTENBOOM, H., PFORDT, J., PINNIOJA, S., ROBERTS, P. B., SANDERSON, D. C. W., SCHLEICH, C., VREDEN, N., ZACHÄUS, U., ZEHNDER, H. J. AND BÖGL, K. W. An interlaboratory study on the detection of irradiated shrimps by thermoluminescence analysis. Berlin: Bundesamt für gesundheitlichen Verbraucherschutz und Veterinärmedizin, *BGVV-Heft* **03/1995** (1995)

34 SCHREIBER, G. A., HELLE, N., SCHULZKI, G., LINKE, B., SPIEGELBERG, A., MAGER, M., AND BÖGL, K. W. Interlaboratory tests to identify irradiation treatment of various foods via Gas Chromatographic detection of hydrocarbons, ESR spectroscopy and TL analysis. In: MCMURRAY, C. H., STEWART, E. M., GRAY, R. AND J. PEARCE (Eds.), *Detection Methods for Irradiated Foods. Current Status*, Cambridge: Royal Society of Chemistry, pp. 98–107 (1996)

35 ZIEGELMANN, B. Lumineszenz- und Elektronenspinresonanzuntersuchungen mineralischer Verunreinigungen und calcifizierter Bestandteile von Lebensmitteln zum Nachweis einer Strahlenbehandlung. Berlin: Bundesamt für gesundheitlichen Verbraucherschutz und Veterinärmedizin, *BgVV-Heft* **01/1998** (1998)

36 MCLAUGHLIN, W. L., CHEN, Y., SOARES, C. G., MILLER, A., VAN DYKE, G. AND LEWIS, D. F. Sensitometry of the response of a new radiochromic film dosimeter to gamma radiation and electron beams. *Nuclear Instruments and Methods in Physics Research*, **A302**, 165–176 (1991)

37 ANON. Jahresbericht der Chemischen Landesuntersuchungsanstalt Karlsruhe 1997, pp. 126–132 (1997)

38 SCHREIBER G. A. Thermoluminescence and photostimulated luminescence techniques to identifiy irradiated foods. In: MCMURRAY, C. H., STEWART, E. M., GRAY, R. AND J. PEARCE (Eds.), *Detection Methods for Irradiated Foods. Current Status*, Cambridge: Royal Society of Chemistry, pp. 121–123 (1996)

39 ZIEGELMANN, B., BÖGL, K. W. AND SCHREIBER, G. A. Thermoluminescence and Electron Spin Resonance Investigations of Minerals for the Detection of Irradiated Foods. *Journal of Agricultural and Food Chemistry*, **46**, 4604–4609 (1998)

40 MCKEEVER, S. W. S. Thermoluminescence in quartz and silica. *Radiation Protection Dosimetry*, **8**, 81–98 (1984)

41 RENDELL, H. M., TOWNSEND, R. A., WOOD, R. A. AND LUFF, B. J. Thermal treatments and emission spectra of TL from quartz. *Radiation Measurements*, **23**, 441–449 (1994)

42 RINK, W. J., RHODES, E. J. AND GRÜN, R. Thermoluminescence from igneous and natural hydrothermal vein quartz: dose response after optical bleaching. *Radiation Measurements*, **23**, 159–173 (1994)

43 PINNIOJA, S., SIITARI-KAUPPI, M. AND LINDBERG, A. Effect of feldspar composition on thermoluminescence in minerals separated from food. *Radiation Physics and Chemistry*, **54**, 505–516 (1999)

44 PINNIOJA, S., SIITARI-KAUPPI, M., JERNSTRÖM, J. AND LINDBERG, A. Detection of irradiated foods by luminescence of contaminating minerals-effect of mineral composition on luminescence intensity. *Radiation Physics and Chemistry*, **55**, 743–747 (1999)

45 EHLERMANN, D. A. E. Comparison of ESR/TLD Analyses for Quartz as Routine Dosimeter. *Applied Radiation and Isotopes*, **47**, 1547–1550 (1996)

46 SCHREIBER, G. A., ZIEGELMANN, B., QUITZSCH, G., HELLE, N., AND BÖGL, K. W. Luminescence Techniques to Identify the Treatment of Foods by Ionizing Radiation. *Food Structure*, **12**, 385–396 (1993)

47 SCHREIBER, G. A., WAGNER, U., HELLE, N., AMMON, J., BUCHHOLTZ, H.-V., DELINCÉE, H., ESTENDORFER, S., VON GRABOWSKI, H.-U., KRUSPE, W., MAINCZYK, K., MÜNZ, H., SCHLEICH, C., VREDEN, N., WIEZOREK, C. AND BÖGL, K. W. Thermoluminescence analysis to detect irradiated fruit and vegetables–an intercomparison study. Berlin: Bundesgesundheitsamt, *SozEp-Hefte* **3/1993** (1993)