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Detection of irradiated components in flavour blends composed of non-irradiated spices, herbs and vegetable seasonings by thermoluminescence method

Kazimiera Malec-Czechowska, Wacław Stachowicz

Abstract The results of experiments on the detection of irradiated component in commercial flavour blends composed of a mixture of non-irradiated spices, herbs and seasonings are presented. A method based on the thermoluminescence measurements on silicate minerals isolated from blends has been adapted. It has been proved that by applying this technique it is possible to detect 0.05% by weight of paprika, irradiated earlier with a dose of 7 kGy, which was a minor component of non-irradiated flavour blends.

Key words detection • irradiated foods • blends • thermoluminescence

K. Malec-Czechowska✉, W. Stachowicz
Laboratory for the Detection of Irradiated Foods,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22/ 814 02 10, Fax: +48 22/ 811 15 32,
e-mail: slinz@orange.ichtj.waw.pl

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Introduction

The regulation referring to the treatment and trade with irradiated foods are expressed in two directives issued by the European Parliament and the Council numbered 1999/2/EC and 1999/3/EC [2, 3]. According to Directive 1999/2/EC, the irradiated foodstuffs, but also foods produced with an admixture of irradiated component(s) should be labelled.

In order to be able to verify the labelling of irradiated foods, it is necessary to apply reliable detection methods capable to identify various groups of irradiated foods and irradiated components in foods not irradiated as a whole. A list of irradiated food products accepted currently for free distribution on the EU market, according to the Directive 1999/3/EC, comprises dried aromatic herbs, spices and vegetable seasoning.

The detection of irradiated spices, dried aromatic herbs and vegetable seasonings is achieved with the use of several methods. Some of these methods have the status of European Standards, for example, EPR spectroscopy for the detection of irradiated foods containing cellulose (EN 1786) or thermoluminescence for the detection of irradiated food from which silicate minerals can be isolated (EN 1788) [4, 5].

The products listed in Directive 1999/3/EC appear more and more frequently on food market in the form of multi-component blends used in the food industry to enrich the flavour of foodstuffs and dishes. Commercial flavour blends may contain some of the irradiated components, which, after the control done before radiation treatment, did not meet the microbiological requirements.

Thermoluminescence (TL) of silicate minerals is a method generally used for the detection of irradiation in spices, herbs and seasonings as well as in their commercial compositions. The method has been validated with different stuffs, but irradiated as a whole only. The vast literature on this subject can be found elsewhere (see [4] – Appendix no. 4). The evaluation of TL analysis on blends, as given in the standard, admits to specify the sample as irradiated even if the glow ratio is lower than 0.1. However, the shape of the glow curve of a sample before re-irradiation (Glow 1) must indicate clearly a TL maximum within the range 150–250°C, specific for irradiated silicate minerals.

The aim of the present study is to show what is the lowest detectable level of the content of irradiated constituent in multicomponent flavour blends composed of spices, herbs and seasonings with the use of thermoluminescence method.

The paper compiles the results of the work on thermoluminescence detection of different amounts of irradiated paprika in non-irradiated blends composed of spices, herbs and vegetable seasonings which are used in the food industry for the preparation of cold sauces and flavour paste.

Materials and methods

Preparation of samples for TL analysis

Four kinds of commercially available products, i.e. flavour mixtures, were used in experiments. The samples of products were purchased in several grocery shops in Warsaw. These products are composites of spices, herbs, vegetable seasonings and other additives, e.g. E 330, as given in Table 1. All tested products contain paprika as one of the components. The samples were examined by the TL method based on EN-1788:2001 whether are or are not irradiated. It has been proven by the TL method that the products taken for experiments were not irradiated and hence it was assumed that they do not contain irradiated paprika at all (0%).

From each kind of the product model samples were prepared with a known content of powdered paprika irradiated with 7 kGy of gamma rays. The content of irradiated paprika in the model samples was as follows: 0.05%, 0.10%, 0.30%, 1.0% and 5.0% by weight. The separation of silicate minerals from the samples was proceeded by procedure recommended in the standard. 10 g of the sample was suspended in 100 ml of the re-distilled water, treated with ultrasound for about 5 min to loosen the adhering minerals and then sieved through a 125 μm nylon mesh into a large beaker. Most of the water with organic material was decanted. The mineral sediment, after removing of water, was transferred into a centrifuge tube to which ca. 2 ml of sodium polytungstate water solution (density ca. 2 g/ml) was added. The content of the centrifuge tube was treated with ultrasound for 5 min and centrifuged. Upon removal by suction of water layer, the mineral fraction was washed twice with water to remove the polytungstate residues and treated with HCl (1 mol/l) solution to dissolve carbonates adhering to the silicate minerals. The acid was neutralised using ammonium hydroxide solution, 1 mol/l. The solvent was removed by short centrifugation and the minerals were washed three times with water and three times with acetone and transferred with a Pasteur pipette into the stainless steel cups as used in the TL reader. Upon evaporation of acetone, the minerals were fixed in the cup using a silicone spray and stored overnight at 50°C in a laboratory oven.

The minerals isolated from individual sample were placed into three parallel cups for TL measurement.

Table 1. Composition of flavour blends investigated.

Commertial name of blends	Composition
Herbal composite for salad	Dried parsley, onion leaves (chive), paprika, leek, onion, celery, dill, carrot, lovage
Mixed spices for filling the cottage cheese	Paprika, salt, onion, parsley, garlic, chive, black pepper, cayenne, nutmeg, basil
Seasoning for butter	Onion, salt, white pepper, E 620, garlic, powered mustard, parsley, E 330, dill, chive, lovage, parsnip, paprika
Seasoning for salad	Chive, white mustard, parsley, tarragon, garlic, onion, nutmeg, pepper, paprika

TL measurements

The thermoluminescence was measured with the use of a computer operated TL reader, type TL/OSL, model TL-DA-15, Risø National Laboratory, Denmark, under the following conditions: initial temperature 50°C, final temperature 500°C, heating rate 6°C/s.

The glow curves (Glow 1) of the minerals were recorded and then, for the purpose of normalisation, the minerals were irradiated with 1 kGy of gamma rays in a ^{60}Co source "Issledovatel". Thereafter, the glow curves (Glow 2) were recorded under the same measuring conditions.

Results and discussion

TL intensities of silicate minerals integrated over the temperature range 214–284°C (Glow 1 and Glow 2) as well as the TL glow ratio (k_{TL}) for the tested products without irradiated paprika and containing different percentage of irradiated paprika are given in Table 2. The adopted temperature range meets the requirement of EN 1788:2001. This interval is defined by evaluating the glow curve of irradiated (0.5 Gy) LiF chips (TLD-100) and was estimated for the TL reader as equal to 214–284°C.

The TL glow ratio (k_{TL}) is defined as the ratio of integrated TL intensities of Glow 1 to Glow 2 evaluated over the adopted temperature range. The glow curves (Glow 1) of silicate minerals isolated from the samples are shown in Figs. 1–4. The curves marked with arrows correspond to the content (percentage) of irradiated paprika. The results shown in Figs. 1–4 were obtained from the TL measurements for one of the three parallel samples of minerals. The results of two remaining samples of each set were similar.

The silicate minerals are natural contaminants of spices, herbs and seasonings. They are mainly composed of quartz and feldspar. Thermoluminescence characteristics of these minerals for different types of radiation and radiation doses was proved in earlier works [1, 6–9]. The glow curves

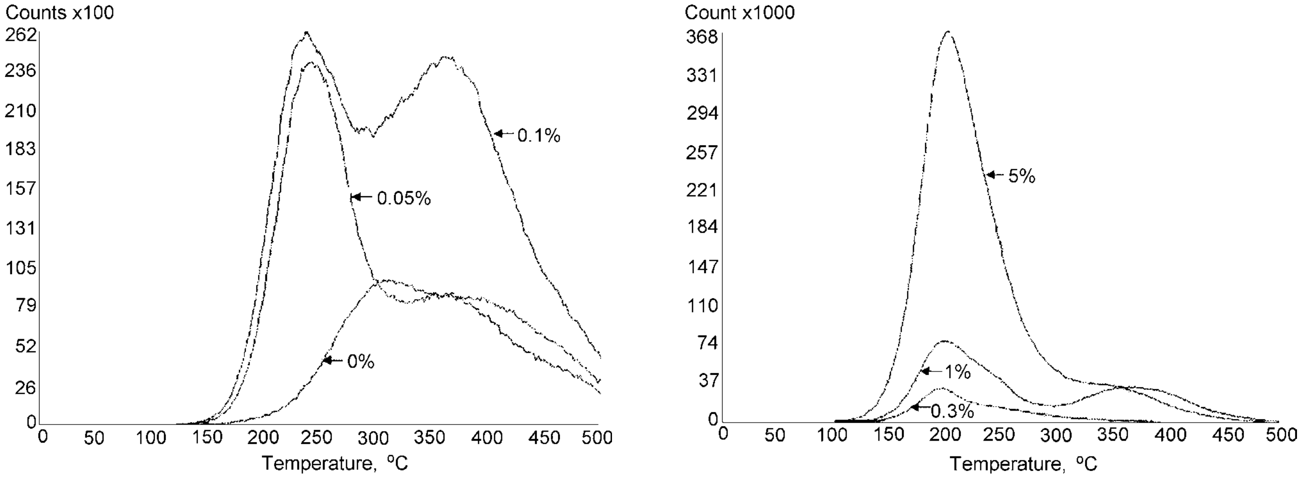

Fig. 1. TL Glow 1 curves of silicate minerals isolated from herbal composite for salad containing different amounts of irradiated paprika.

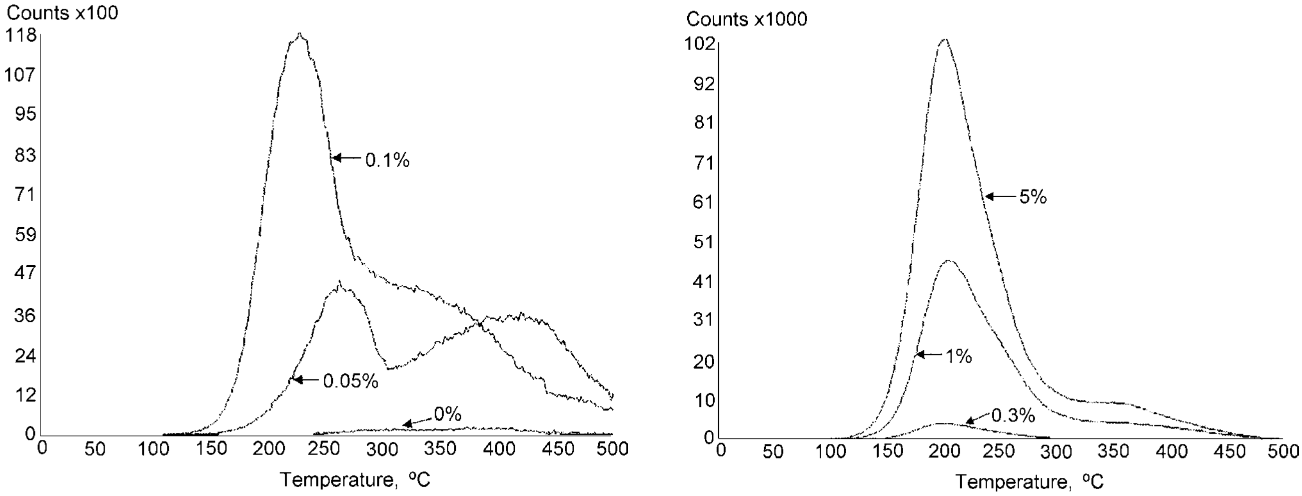

Fig. 2. TL Glow 1 curves of silicate minerals isolated from mixed spices for the filling cottage cheese containing different amounts of irradiated paprika.

(Glow 1) recorded for minerals isolated from the samples which did not contain irradiated paprika resemble those recorded for non-irradiated silicate minerals and were characterised by thermoluminescence with a maximum laying over 300°C (Figs. 1–4, glow curves marked "0%" on the left side graphs). On the other side, the Glow 1 of minerals isolated from samples which contain the admixture of radiation treated paprika of increasing concentration exhibit relatively strong thermoluminescence peaks with a maximum located within the range of 235 ± 23°C accom-

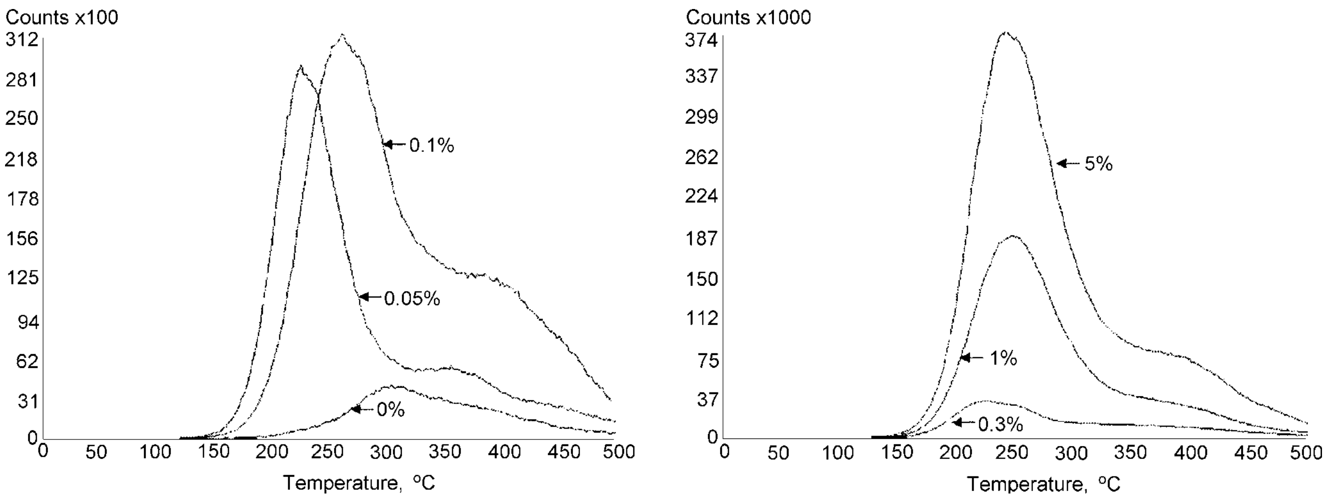

Fig. 3. TL Glow 1 curves of silicate minerals isolated from seasoning for butter containing different amounts of irradiated paprika.

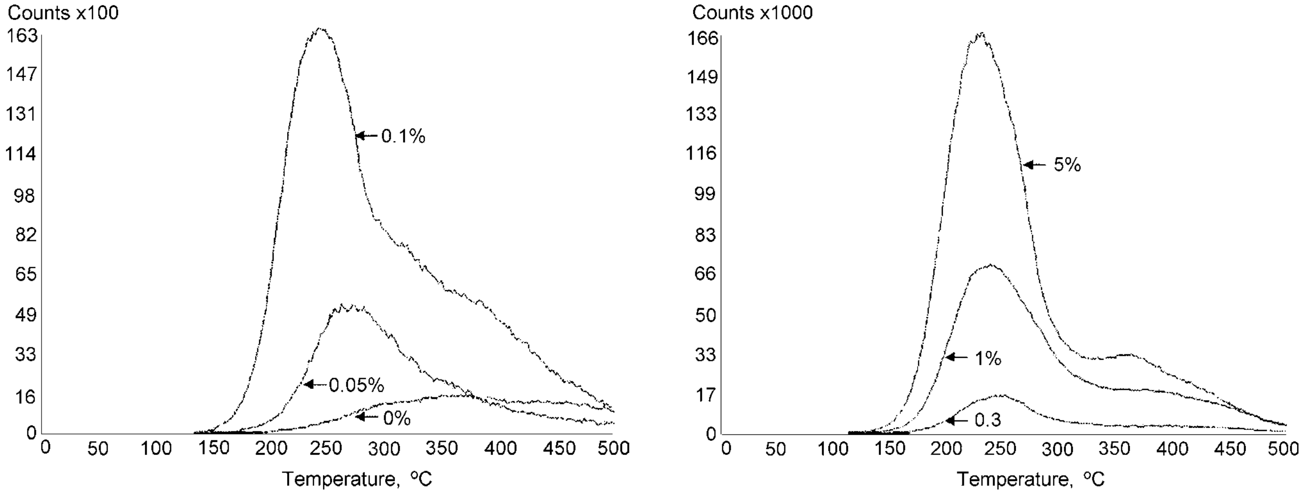

Fig. 4. TL Glow 1 curves of silicate minerals isolated from seasoning for salad containing different amounts of irradiated paprika.

Table 2. Thermoluminescence intensities integrated over the temperature range 214–284°C and TL glow ratio (k_{TL}) of silicate minerals isolated from flavour blends enriched with irradiated paprika of different concentrations.

Name of the product	The percentage of irradiated paprika (% by weight)	TL intensity Glow 1	TL intensity Glow 2	TL glow ratio k_{TL}	k_{TL} ± SD
Herbal composite for salad	0	152,053	53,377,264	0.003	0.002 ± 0.001
		39,457	37,106,329	0.001	
		16,115	9,817,211	0.002	
	0.05	180,816	65,667,430	0.003	0.011 ± 0.007
		721,449	66,474,249	0.011	
		660,058	36,179,951	0.018	
	0.1	246,658	67,119,553	0.004	0.009 ± 0.009
		828,599	40,700,188	0.020	
		238,977	50,683,086	0.004	
	0.3	333,066	19,458,284	0.017	0.033 ± 0.031
		42,025	3,090,589	0.013	
		499,785	7,300,188	0.068	
	1.0	242,069	2,176,588	0.111	0.128 ± 0.077
		1,412,755	23,523,210	0.060	
		207,287	977,769	0.212	
	5.0	6,269,088	9,888,509	0.634	0.357 ± 0.265
		219,904	2,085,533	0.105	
		7,608,947	22,939,498	0.332	
Mixed spices for filling the cottage cheese	0	3459	988,470	0.003	0.005 ± 0.002
		9141	1,191,349	0.007	
		2342	428,291	0.005	
	0.05	141,465	14,670,874	0.010	0.010 ± 0.003
		17,493	2,531,100	0.007	
		120,859	8,574,786	0.014	
	0.1	60,818	18,396,767	0.003	0.018 ± 0.017
		299,909	18,265,455	0.016	
		787,742	22,081,453	0.036	
	0.3	752,262	1,717,930	0.439	0.235 ± 0.176
		26,478	191,880	0.138	
		377,567	2,949,059	0.128	
	0.1	8,946,062	24,985,566	0.358	0.653 ± 0.287
		4,995,771	5,358,096	0.932	
		6,399,180	9,558,935	0.669	
	5.0	16,117,694	12,127,504	1.329	1.474 ± 0.129
		5,662,439	3,593,316	1.576	
		21,944,401	14,475,864	1.516	

Table 2. Continued.

Name of the product	The percentage of irradiated paprika (% by weight)	TL intensity Glow 1	TL intensity Glow 2	TL glow ratio k_{TL}	k_{TL} ± SD
Seasoning for butter	0	54,055 18,735 23,593	8,663,349 6,058,057 7,817,880	0.006 0.003 0.003	0.004 ± 0.002
	0.05	174,791 91,393 720,451	43,206,830 1,654,237 22,035,465	0.054 0.055 0.033	0.047 ± 0.012
	0.1	924,639 104,946 512,597	11,236,828 2,483,768 4,434,268	0.082 0.042 0.118	0.081 ± 0.038
	0.3	977,213 245,583 202,970	53,634,466 5,300,052 16,928,825	0.018 0.043 0.012	0.024 ± 0.016
	1.0	5,663,481 6,437,827 4,187,461	9,547,648 13,084,191 4,596,232	0.593 0.492 0.911	0.665 ± 0.289
	5.0	11,526,011 45,806,991 14,580,130	6,598,972 13,155,902 18,959,249	1.746 3.481 0.769	1.999 ± 1.373
Seasoning for salad	0	4334 3234 17,372	1,670,485 932,050 3,051,155	0.002 0.003 0.006	0.004 ± 0.002
	0.05	37,047 16,062 136,829	5,357,096 12,042,125 1,256,374	0.007 0.001 0.109	0.039 ± 0.061
	0.1	504,450 2,047,666 64,360	5,600,320 23,284,606 4,111,089	0.090 0.088 0.016	0.065 ± 0.042
	0.3	31,054 241,019 447,250	1,674,752 8,090,177 3,939,626	0.018 0.030 0.113	0.054 ± 0.052
	1.0	2,148,384 1,363,540 2,478,278	10,792,409 2,982,825 5,715,670	0.199 0.457 0.434	0.363 ± 0.143
	5.0	4,659,230 28,266,396 20,861,141	5,315,304 30,599,989 28,586,363	0.876 0.923 0.729	0.843 ± 0.101

panied by less intense thermoluminescence peaks at higher temperature (Figs. 1–4). The thermoluminescence in lower temperature is very specific for radiation treated silicate minerals. The mineral fraction isolated from model samples containing irradiated paprika is, of course, a mixture of minerals isolated from non irradiated components and irradiated paprika. The composition and the amounts of minerals isolated from different samples may vary significantly and, consequently, the relative ratio of irradiated to non-irradiated minerals depends strongly on the specificity of minerals in individual constituents of blends. Thus, the varying intensities of thermoluminescence peaks in glow curves may appear. This is why the thermoluminescence method as adapted to detection of irradiation in foods has a qualitative character only. It has to be strongly stressed, however, that not the relative intensities of TL peaks in glow curve, but rather the presence or absence of the maximum in the low temperature range (150–250°C) is a proof of irradiation. The low temperature maxima typical for radiation treated minerals were identified in the records of glow curves taken with all samples containing irradiated paprika, even containing 0.05%. A comparison of the records of samples with lower and higher content of irradiated stuff shows conclusively that the irradiation induced TL maximum in the glow curves recorded with a low content sample shifts to lower or higher temperatures. The shift of the TL maximum to higher temperatures was registered with minerals extracted from mixed spices for filling the cottage cheese (Fig. 2) and from seasoning for salad (Fig. 4). On the other side, the shift to lower temperatures occurs with minerals isolated from the herbal composition for salad (Fig. 1) and from seasoning for butter (Fig. 3). This effect results from a very different proportion between the intensities of radiation induced and "native" TL peaks in glow curves of samples containing different admixtures of irradiated stuff.

The TL glow ratio k_{TL} (Glow 1/Glow 2), which is obtained after re-irradiation of minerals with a dose of 1 kGy of ionising radiation, is generally used to evaluate whether sample was or was not irradiated. If k_{TL} exceeds 0.1 it may be said that the sample was irradiated. The numbers lower than 0.1 are typical for not irradiated samples. This is certainly true for samples irradiated as a whole. However, with blends containing a small admixture of irradiated component this criterion of radiation treatment does not necessarily apply. It is the consequence of a significant influence of the composition and quality of non-irradiated minerals on the shape of the Glow 1 curve, as discussed earlier. The lack of the consequent increase of k_{TL} with increasing content of irradiated paprika is observed on the sample of seasoning for butter, content 0.3% (see Table 2). It is probably effected by a very different composition of minerals isolated from blends. In the case, when the concentration of paprika exceeded 1.0% by weight, the criterion for the evaluation of samples as irradiated or non-irradiated on the basis of the k_{TL} certainly obeys.

Conclusions

The thermoluminescence measurement on silicate minerals isolated from the blends composed of spices, herbs, and seasonings can be successfully used for the detection of irradiation derived from one of their components. It is possible to detect in a blend the irradiated component which appears at a concentration of 0.05% by weight or higher.

As follows from the present investigation, the basic criterion for the confirmation of appearance of irradiated component in multicomponent blends of spices, herbs and seasonings is a careful analysis of the shape of the Glow 1 curve recorded with minerals isolated from the product. The proof of irradiation is the appearance of thermoluminescence maximum within the temperature range 150–250°C. The important finding of the present investigation is that it is possible to prove radiation treatment of a certain component in a blend if its content is as low as 0.05% by weight. The detection is possible since the shape of thermoluminescence curve (Glow 1) is markedly different from that observed with non-irradiated sample of the same stuff. On the other hand, under the consecutive increase of the content of irradiated component in a blend the TL coefficient remains still lower than 0.1 and reaches the threshold level (0.1) when the concentration of irradiated component is higher than 1%. This has been proved for all the four blends investigated through this study.

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