Reliability of light-stimulated photoluminescence (PSL) in detection of irradiated food comparison with thermoluminescence method (TL)

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Abstract. The detection of irradiation of several classes of food products with the use of thermoluminescence (TL) and photostimulated luminescence (PPSL) has been proceeded. The comparison of the results obtained by both methods has been done and reliability of the PPSL method as compared with the TL method evaluated. Conclusion concerning the usefulness of such evaluation to the practice has been drawn.

Key words: irradiation • detection • food products • spices • herbs • blends • photostimulated luminescence (PPSL) • thermoluminescence (TL)

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Introduction

A number of more or less sophisticated methods of analysis based on physical, chemical and biological detection methods have been adapted and subsequently used for the detection of irradiated foodstuffs. Among numerous methods tested, only nine were chosen as reliable enough to be applied for the control of radiation treatment in foods and subsequently received the status of European Standards. One of physical methods approved by the European Committee for Standardization (CEN) as European Standard EN 13751 on 5th August 2002 is photostimulated luminescence.

The principle of the method lies with the release of luminescence from the sample stimulated by the pulses of IR light (PPSL) in contrast to the typical PSL method that employs continuous illumination only. The method has been developed and satisfactorily tested by Sanderson and his group at the Scottish Universities Research and Reactor Centre (SURRC) [6–8]. The unique PPSL measuring device designed by SURRC is widely used for the detection of irradiation in foods and now possesses the recommendation of CEN.

The thermoluminescence (TL) method for the detection of irradiated food has been developed much earlier on the basis of the instrumentation typically used for the dating of archaeological remains and/or personal dosimetry. The method received the status of European Standard in 1996 (revised on 18 August 2001) [1].

The principle of both methods is similar and lies with the release of radiation energy which is stored by trapped charge carriers in minerals (i.e. silicates) the inherent components of spices, herbs, seasonings and

many others foodstuffs. The difference lies with the use of different ways stimulating the release of this energy (visible light) from the traps. In the TL method it is achieved by heating the sample (thermoluminescence), while in PPSL by illuminating it with the pulses of IR light (PPSL) [9]. In both methods the released light, i.e. the cascade of photons is captured and measured with the use of photomultiplier tubes. The result is obtained in the form of a record with the number of counts measured, while in TL the relationship between the number of counts and heating temperature in the form of a grafts is also available.

The examination of food samples by the thermoluminescence method needs the isolation of mineral components from food. The goal of this procedure is to eliminate the temperature damage of the dominating organic components of food sample by heating and to avoid the negative effect of the natural dispersion of minerals in the bulk of food decreasing markedly the effectiveness of the detection. The TL method based on the examination of minerals isolated from food is a very sensitive method enabling the detection of radiation treatment in all kinds of food from which silicate minerals can be isolated. The analytical procedure to achieve a good mineral separation from food samples is not an easy task and needs special care, good experience and skilfulness indeed. In addition, it is time-consuming and for that reason the result of analysis is available typically after a few days only. In contrast to the latter, the PPSL method does not need mineral isolation and/or further sample preparation except of cutting to pieces, if necessary. Consequently, the measuring procedure is simple and fast. However, as compared with the TL method, the PPSL method has several limitations. The PPSL response is not equal if various groups of foods are measured. For that reason, the PPSL method may not deliver reliable results of the measurement obtained with some foods despite they contain minerals which are detectable by the TL method. On the other hand, if a complex sample, i.e. the blend of spices, for example, contains table salt, glutamate or sorbiniane, it cannot be measured by the PPSL at all. It is because these highly crystalline products when irradiated give usually rise to a very strong luminescence that can damage the photomultiplier. By the TL analysis such problem does not exist since in the course of the isolation of minerals the soluble inorganic components are dissolved and then eliminated by washing. Fine powdering of spices, the procedure that becomes more and more a common practice in the food industry decreases very often the PPSL response below the acceptable level, too [3].

The intention of the present study is to establish the area of the applicability of the PPSL method in respect to the variety of foodstuffs which are usually the subject of examination whether irradiated or not. At present, the contribution of multicomponent and powdered samples to the overall number of food samples examined is increasing and exceeds the number of samples composed of crushed spices and herbs only. However, the latter products were dominating in food market even not very long ago. As a reference for the evaluation of the PPSL method, the results obtained by the TL examination of the same samples as measured by PPSL were used.

Instrumentation and methods

Thermoluminescence measurements have been conducted with the use of PC operated TL reader, type TL/OSL, model TL-DA-15, Risø National Laboratory, Denmark as shown in Fig. 1. The measuring conditions were as follows: initial heating temperature 50°C, final temperature 500°C, heating rate 6°C/s.

All samples (isolated minerals) after the first TL measurement (glow 1) were, for the sake of normalization, irradiated with a dose of 1 kGy of gamma rays from a ^{60}Co gamma source "Issledovatel" (dose rate 1.129 kGy/h) [3]. Thereafter, TL measurements (glow 2) were repeated again.

The analytical methodology of sample preparation and measuring conditions were adapted in accordance with the procedures given in PN-EN 1788:2001.

Preparation of samples, according to our research procedure compiles grinding, density measurement, separation of minerals with sodium polytungstate

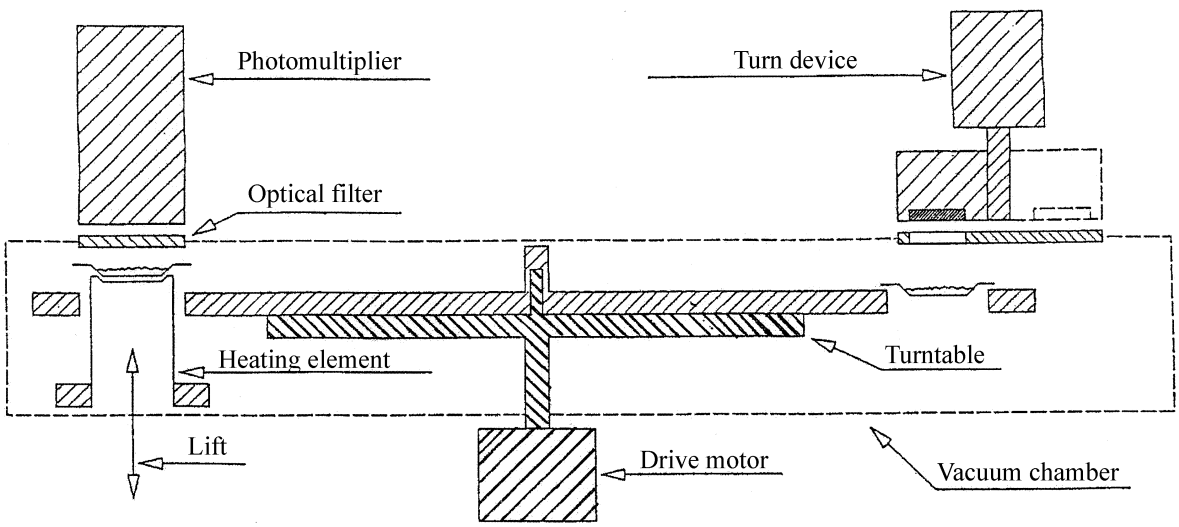

Fig. 1. Schematic presentation of TL apparatus. Block schema of TL/OSL System (from *Users manual*, Risø National Laboratory. Risø 1996, 21 pages).

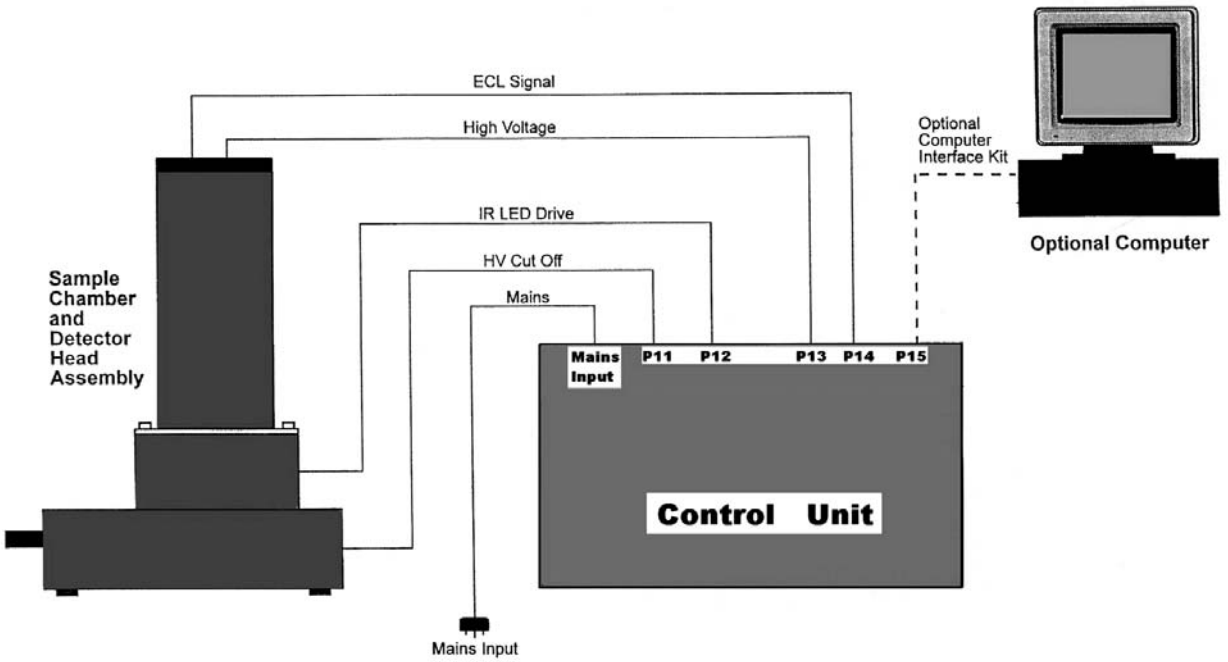

Fig. 2. Block schematic and interconnection diagram of the PPSL apparatus (from *Users manual*, Scottish Universities Research and Reactor Centre. Cambridge 2004, 17 pages).

solution (d = 2 g/cc), washing and drying of a debris of minerals. This procedure takes normally a full working day.

According to PN-EN 1788:2001, two criteria obey for the qualification of food sample as irradiated or not irradiated:

1. Glow ratio (glow 1/glow 2) lower than 0.1 indicates that the sample is not irradiated and, if glow ratio is higher then 0.1 the sample is classified as irradiated.
2. Localization of radiation induced thermoluminescence glow peak integrated within the temperature range 150–250°C near to 220°C on the temperature scale. The details can be found in PN-EN 1788:2001 standard [1, 3].

Preparation of samples for the PPSL examination follows the PN-EN 13751:2002 and laboratory research procedure: leaves, roots, fruits or powdered spices or herbs, etc., are placed in opened Petri dishes, 50 mm in diameter, which are routinely used with SURRC PPSL instrument, which is shown in Fig. 2. Calibrated PPSL measurements with normalizing irradiation were adapted only in the present study. All samples, after PPSL measurement were irradiated with a dose of 4 kGy and measured again [2, 4]. Such treatment delivers more reliable and adequate results. The criterion for classification food samples as irradiated, not irradiated or not measurable by PPSL depends on the number of counts recorded before and after normalizing irradiation.

Typically, with irradiated samples only a small increase of PPSL signal is observed after normalizing irradiation, whereas with not irradiated the increase is markedly high.

A lower threshold (T_1 = 700 counts/60 s) and an upper threshold (T_2 = 5000 counts/60 s) are used to classify sample as not irradiated (below 700 counts per 60 s) or irradiated (above 5000 counts per 60 s) [2, 5].

In the case the count number lies between two threshold values the result is classified as intermediate one. In most cases samples giving rise to intermediate result are classified as not measurable by PPSL and should undergo further examination by means of the thermoluminescence method (TL) [4, 6].

Having both methods adapted in the Laboratory, a series of parallel experiments was conducted to prove the applicability of the PPSL method to detect irradiation in the variety of spices, herbs, multicomponent products containing spices, herbs and other flavour ingredients, commonly available in food market.

Current research programme covered also the PPSL analysis of archival samples that have been examined earlier by the thermoluminescence method.

Materials

All food products that were the subject of present investigation are listed below in Table 1. The products are collected in eight groups enabling their formal identification.

Results

The results of the examination of the samples by means of both the PPSL and TL detection methods are comprehended below in Table 2 and Fig. 3. From the comparison of the numbers of results obtained by both methods that were found consistent from the one hand or not consistent from the other hand, it was possible to indicate ranges of the reliability of the PPSL method as related to a given groups of food product. This kind of study should be systematically extended by newly processed food products enabling to construct a sort of pre-selection list containing the names of the products which could be analysed by PPSL only. The sample that will be qualified as not giving a reliable result in

Table 1. Commercial food products examined by the PPSL and TL methods

Groups of products	Kinds of samples
Seasonings and spices	Paprika chips red, paprika granulate, sweet paprika Israel, paprika chips green, white pepper, red Bell pepper, black pepper, multicolour pepper, China chilli crushed, chilli granules, jalapeno red granules, oregano ground
Row seasoning herbs	Garden thyme, hoary basil, sweet marjoram, garden lovage, Grecian laurel, common fennel pimento (Jamaica tree pepper)
Plant extracts	Asiatic ginseng extract dried, *Silibina Tec*. (milk thistle extract phospholipids), common valerian extract dried vegetal extract
Pharmaceuticals	Maidenhair tree, chamomile, fragon rhizome, linden blossom, bio dandelion-mix, *Luteina*
Fresh fruits and vegetables	Strawberry fresh, onion, shallot, garlic
Dried vegetables and mushrooms	Zucchini flakes, Chinese hibiscus blossom dried, caraway, garlic granules, onion sliced, chives chopped, edible boletus dried, Polish mushroom dried
Processed food products	*Angkak*-red food colour-origin, *Acido Acetilglicir. Tec*. (poison sumac), seasoning mixed for salad
Food colouring dyes	Colouring dye maidenhair tree based, whortleberry

Table 2. Qualification of samples measured by PPSL compared with TL results

	PPSL results consistent with TL	Divergences			
		Samples not measurable by PPSL TL only	Samples not irradiated TL approval needed	Too low sensitivity of PPSL method; TL approval recommended	PPSL results non consistent with TL
Number of samples	64	19	3	14	36

the PPSL method should be directed for the TL analysis, despite the suggestion of a customer, for example. The pre-selection of samples for PPSL examination on the basis of the earlier model experiments seems very useful from the practical point of view. Having such pre-selection list of food products it will be possible to eliminate the duplicate analyses by the PPSL and TL methods of any sample, the situation that occurring quite often now.

The total number of samples examined was 100. The consistent results were obtained with 64 samples (about 2/3), while not consistent with 36 samples (about 1/3) of the total number of samples (Fig. 3).

There are three types of divergences of the PPSL results as compared with the TL results. Nineteen samples (52.7% of the total number, i.e. above 1/2) could not be classified by means of PPSL. Three samples (8.3% of 36 samples in question) were qualified as not irradiated (the resultant screening measure was intermediate, while calibration measurement was positive) or better not be investigated by means of the PPSL method. With fourteen samples (38.8% of 36 samples in question, i.e. above 1/3) the source of divergences was too low considering the sensitivity of PPSL method. However, for a vast majority of the samples (almost 2/3) the results obtained by both the PPSL and TL methods were found fully consistent.

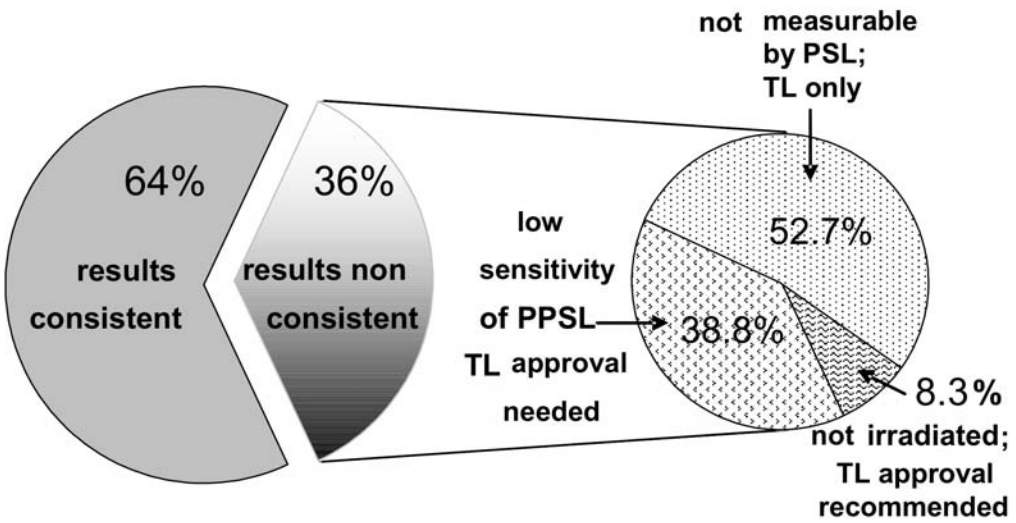

Fig. 3. Comparison of the results obtained by means of PPSL and TL methods.

Table 3. Characteristics of investigated groups of spices and seasonings related to the discrepancy in PPSL results. Classification according to PN-EN 13751:2002

Classes of food products	Samples not measurable by means of PPSL; TL only	Samples non-irradiated and/or needing to be approved by TL	Too low sensitivity of PPSL method; TL approval recommended
Seasonings and spices	x		x
Row seasoning herbs			x
Plant extracts	x		x
Pharmaceuticals	x	x	x
Fresh fruits and vegetables			x
Dried vegetables and mushrooms			x
Processed food products	x	x	
Food colouring dyes	x		

Discussion of results

Each of the three divergences discussed above compiles various products that are classified in Table 3.

For example, the type "samples not measurable by means of PPSL-TL only" is represented by several products as seasonings and spices, plant extracts, pharmaceuticals, processed food products and food colouring dyes, respectively.

The type "samples non-irradiated and/or needing to be approved by TL" gathers such products as pharmaceuticals and processed food products only.

And finally, the type "too low sensitivity of the PPSL method; TL approval recommended" is represented by seasonings and spices, row seasoning herbs, plant extracts, pharmaceuticals, fresh fruits and vegetables, dried vegetables and mushrooms.

The conclusion from the above analysis is that despite the fact that some differences between the types do appear, it is really not possible to predict in advance that new products will deliver a reliable response in PPSL. In other words, each product needs individual treatment and should be included in a preselection list.

The above consideration supports the view that the PPSL method as a typical screening method is very simple and fast but has several limitations. It is less sensitive than the TL method, but the main problem lies with a very different response in comparison with the TL method. In the case of TL method the response, i.e. the number of counts depends roughly on the content of silicate minerals in food. In the case of PPSL there are several factors not fully defined but capable of limiting strongly or even eliminating the release of luminescence from the bulk of sample despite the fact that the latter contains minerals. This means that it is possible to meet food samples which will be quite easily measured by the TL method, but are not measurable in PPSL. The best solution, is in our opinion, to conduct model experiments with the use of very different food samples exposed to irradiation in order to construct the extensive list of food products with the designation whether they can or cannot undergo further PPSL analysis. An example of the preselection list is given and discussed throughly in this study.

References

1. EN 1788 (1996) Foodstuffs – thermoluminescence detection of irradiated food from which silicate minerals can be isolated. CEN/TC 275/WG. Technical European Committee for Standardization, Brussels
2. Guzik GP, Stachowicz W (2005) Photostimulated luminescence, fast method of detection of irradiated foodstuffs. Raporty IChTJ. Seria B no. 3/2005. INCT, Warszawa 2005 (in Polish)
3. PN-EN 1788 (2001) Foodstuffs – thermoluminescence detection of irradiated food from which silicate minerals can be isolated. European Committee for Standardization, Brussels
4. PN-EN 13751 (2002) (U) Foodstuffs – detection of irradiated food using photostimulated luminescence. European Committee for Standardization, Brussels
5. Sanderson DCW, Carmichael LA, Fisk S (1998) Establishing luminescence methods to detect irradiated foods. Food Sci Technol Today 12;2:97–102
6. Sanderson DCW, Carmichael LA, Naylor JD (1995) Photostimulated luminescence and thermoluminescence techniques for the detection of irradiated food. Food Sci Technol Today 9;3:150–154
7. Sanderson DCW, Carmichael LA, Naylor JD (1996) Recent advances in thermoluminescence and photostimulated luminescence detection methods for irradiated foods. In: Detection methods for irradiated foods – current status. Royal Society of Chemistry, Cambridge, pp 124–138
8. Sanderson DCW, Slater C, Cairns KJ (1989) Thermoluminescence of foods: origins and implications for detecting irradiation. Radiat Phys Chem 34:915–924
9. Soika Ch, Delincée H (2000) Luminescence measurements for identifying irradiated spices and herbs. Lebensmittels – Wissenschaft und Technologie (Food Science and Technology) 33:440–443