

## **EFFECTS OF RADIATION DOSES ON THE PHOTOSTIMULATED LUMINESCENCE RESPONSE OF CERTAIN HERBS AND SPICES**

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### **Abstract**

Ionizing radiation applied on food eliminates harmful microorganisms, prevents sprouting and delays ripening. All methods for detection of irradiated food are based on physical, chemical, biological or microbiological changes caused by the treatment with ionizing radiation. When minerals are exposed to ionizing radiation, they accumulate radiation energy and store it in the crystal lattice, by which some electrons remain trapped in the lattice. When these minerals are exposed to optical stimulation, trapped electrons are released. The phenomenon, called optically stimulated luminescence or photostimulated luminescence, occurs when released electrons recombine with holes from luminescence centers in the lattice, resulting in emission of light with certain wavelengths.

In this paper, the results of measurements performed on seven different samples of herbs and spices are presented. In order to make a comparison between luminescence signals from samples treated with different doses, unirradiated samples are treated with Co-60 with doses of 1 kGy, 5 kGy and 10 kGy. In all cases it was shown that the higher the applied dose, the higher the luminescence signal.

Keywords: food, ionizing radiation, photostimulated luminescence.

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### **1. Introduction**

Different technologies and methods have been developed and applied to enhance food quality. One of them is the method in which food is exposed to carefully controlled doses of ionizing radiation. This technology destroys harmful microorganisms, prevents sprouting and delays ripening in some fruits and vegetables [1]. Irradiation reduces the use of pesticides and preservatives. This process involves almost no heat, so irradiated foodstuffs remain raw after the treatment. Ionizing radiation is the reason for formation of radicals in food. These radicals can have a direct effect on microorganisms in food with destabilization of DNA, or an indirect effect by forming ions of water which destroy cell components [2]. Different kinds of food are treated with different doses of radiation, which depends on the desired results and type of food. Studies have shown that doses below 10 kGy are not susceptible to toxicological hazard [3]. In some cases plastic packaging may lead to migration of harmful components into foodstuffs [4], so the kind of material used for packaging has to be taken into account.

Development of this method for food preservation, commercial use of ionizing radiation for enhancing food quality and trade with treated food arise the need of reliable and routine tests for detection of irradiated food.

All methods for detection of irradiated food may be classified in three groups: biological, chemical and physical methods. The ideal method for detection should measure a specific effect of the ionizing radiation, which is proportional to the dose and should not depend on the processing and storage of food and the length of time between the treatment and the testing [5].

Physical methods, including measuring impedance, viscosity, thermal analysis, nuclear magnetic resonance, electron spin resonance, luminescence, are based on detection of changes in physical properties [6]. One simple physical method for detection of irradiated food is optically stimulated luminescence or *photostimulated luminescence* (PSL). Samples are stimulated with a pulsed infra-red radiation, and the signal is detected at the end of each pulse. This method gives reliable results only if the food contains sufficient amount of minerals [7–9]. Minerals are substances that are responsible for storage of energy in the defects of their crystal lattice as a result of exposure to ionizing radiation. Optical stimulation releases electrons that have been trapped in the lattice. These electrons return from the excited state to the ground state by losing part of their excess energy as photons, thus a signal could be observed and measured as a luminescence response.

All standardized methods for detection of irradiated food are qualitative, which means that the absorbed doses cannot be precisely determined after treatment. The shape and quantity of the foodstuffs during the treatment, as well as the type and quantity of minerals in food, can affect the result. Efforts are being made to estimate the doses of ionising radiation by which certain foodstuffs have been treated [10–11]. In order to establish fast and qualitative estimation of the applied dose during the treatment we studied the influence of dose on the luminescence signal. Studied samples were treated with doses of 1 kGy, 5 kGy and 10 kGy.

Analytical detection of irradiation processing of food is very important to implement Quality Control of treated food at all levels. Currently, national legislation is based on respecting European Directives, their harmonization with national legislation and other laws and rules. Detection of irradiated food in Europe is regulated under European Legislation L66/16-25 (1999), covering Directives 1999/2/EC and 1999/3/EC [12–13]. Regulation for specific safety requirements of the food treated with ionizing radiation (Official Gazette of Republic of Macedonia, No. 63/2014) has been adopted on the basis of Article 8 paragraph 1 of the Law of food safety and products and materials that come in contact with food, of the Statute of Republic of Macedonia (Official Gazette of Republic of Macedonia, No. 54/2002 and 84/2007) [14–15].

## 2. Experimental

### 2.1. Description of equipment

Detection of irradiated food is performed by the SUERC *pulsed photostimulated luminescence* (PPSL) system designed and developed at the Scottish Universities Research and Reactor Centre. The procedure has been set according to EU standard for detection of irradiated food – EN 13751:2002, Foodstuffs – Detection of irradiated food using Photostimulated Luminescence. Equipment consists of two main parts: a control unit and a detector head. The detection technique of the system is shown in Fig. 1 and Fig. 2.

Figure 2 illustrates the relative timing of the stimulation light source and photon counter during a preset 15 second test period when the system is operating in the screening mode.

When the IR LEDs are on, the photon counter accumulates PSL signal counts from the test sample, plus the system background counts which are principally due to dark counts from the PMT. While the IR LEDs are off, the system background counts are subtracted from the accumulated counts. This ‘Up-Down’ count system minimizes the effect of the system background signal, thereby increasing the dynamic range and system detectivity for weak PSL emitters [16].

The PMT dark count is temperature-sensitive and approximately doubles for every 5°C rise. Fluctuation in the dark count is described by a Poisson distribution; hence the statistical

variation in the dark count rate is proportional to the square root of its mean. Optimum system performance is obtained when the equipment is kept at ambient temperatures.

When testing with an empty sample chamber, the accumulated count may fall below zero. The reason for this are the variations in Up and Down counts due to either the statistical nature of the background count or to small changes in the relative durations of the Up and Down periods. To ensure that this does not happen, the photon counter is pre-loaded with 256 counts at the start of each measurement.

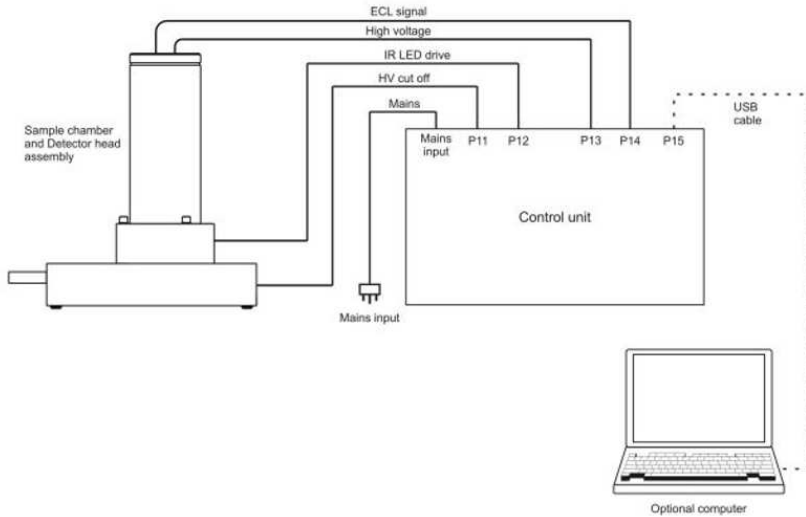


Fig. 1. The Interconnection Diagram of the SUERC PPSL System [16].

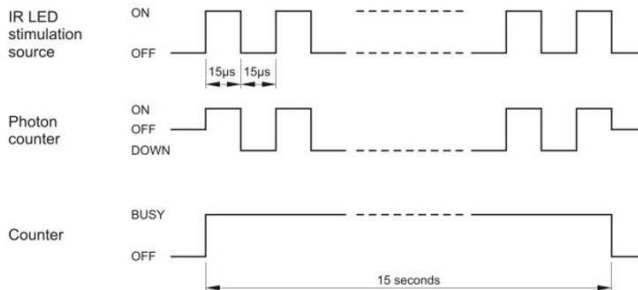


Fig. 2. The time distribution and shape of the signal of the SUERC PPSL System [16].

The main application of this system is rapid screening/detection of irradiated herbs, spices and seasonings, and may be used either in the stand-alone mode or in conjunction with a computer for data storage [16]. The wavelength of stimulating light is in the interval of 450–950 nm, and the obtained signal has wavelengths in the interval of 300–350 nm. The whole system is portable and intended for indoor use. The method is cheap, rapid and applicable for a wide range of foodstuffs. Samples can be tested with almost no preparation and without any damage to them. During measurements samples are stimulated by an array of infra-red light emitting diodes which are pulsed symmetrically on and off for equal periods. Luminescence is measured using a patented digital lock-in photon counting method by using a cathode photomultiplier tube (type: 9814B02 from the manufacturer ET Enterprises Limited). This is

a bi-alkali, high-gain, low-background photomultiplier tube. Optical filtering is used to define both the stimulation and detection wavebands. Irradiated samples produce a specific signal which is detected and quantified. The registered signal level is compared with two reference threshold values [17]. Most irradiated samples produce signals above the high threshold, and most unirradiated samples produce signals below the low threshold. Intermediate signal levels between the two thresholds suggest that further tests should be made. These thresholds are different for different kind of samples, and their values are obtained according to the reference data, but an experienced person may change the default values [18]. The signal produced by tested samples may vary according to their mineral content [8]. It depends on the quantity and type of inorganic material in food. Also, it may weaken after exposure of samples to natural or artificial light [18–19]. This phenomenon, usually called optical fading, is observed especially during first six months of exposure, during which the luminescence signal drops down continuously [9]. Studies have shown that natural light has a greater effect on optical fading than artificial light [20]. A high signal may be detected even with samples of food that have not been irradiated. The reason for this is their natural exposure to ionizing radiation from winds, soil, *etc.* [21] When using an instrument in a conjunction with a computer, the SUERC PPSL Console is necessary. It presents graphically the dependence of the PSL signal counts on time, by measuring the counts once in a second for 60 seconds. It also calculates the standard deviations from these results. When using it in the stand-alone mode, the intensity of measured signal is indicated by three LED indicators. The green indicator is turned on when the produced signal is below the low threshold (“negative” result). The yellow indicator shows that the signal is between the two thresholds (“intermediate” result). The red indicator is turned on when the signal is above the high threshold (“positive” result).

## **2.2. Samples**

The tested samples of herbs and spices including: paprika, alfalfa, dong qui, green tea, mint, turmeric and thyme tea, have been received from the Scottish Universities Research and Reactor Centre. For the measurements, the samples were placed in disposable plastic Petri dishes suitable for the instrument, in the form of a thin layer. The tests were performed on two portions of each sample. As the measurement lasted for 60 seconds, and the results were obtained once in a second, 60 points were presented graphically for each sample, giving the dependence of the total counts on the dose. Irradiation of the samples was done using Co-60 as an irradiation source at the Institute of Nuclear Sciences in Vinca, Serbia. In order to obtain doses of 1 kGy, 5 kGy and 10 kGy, the irradiation time was 204 seconds, 17 minutes and 34 minutes, respectively.

## **2.3. Description of measurements**

The measurements were performed according to the procedure described in [22]. The detection of irradiated food using PSL were performed by two methods: the screening method and the calibrated method. The screening method does not need any special preparation of samples. The calibrated method is used for validation of the results obtained with the screening method. For performing the calibrated method, the samples are exposed to ionizing radiation after the initial screening measurement. After that, the measurement of an irradiated sample is repeated. If the sample has been originally irradiated, only a small rise in the PSL signal counts after this exposure to ionizing radiation will be observed, while unirradiated samples usually show a significant increase in the PSL signal counts. The samples were exposed to a dose of 1 kGy for performing the calibrated method [18]. The obtained results are presented graphically and eventually a certificate is prepared. The procedure is confirmed by applying

it to a number of samples. The calibrated method is also used when the samples have been exposed to light, so that the screening method does not give reliable results. The calibrated method is used for precise distinguishing the unirradiated samples and samples that are not sensitive to PSL. It is recommended that the measurements are undertaken for two portions of each sample. In the case the results obtained for these portions are not conclusive, the measurements should be performed for four more portions of the sample, and the two highest results should be taken into consideration. In this paper we performed measurements on seven different samples of herbs and spices. All samples were primary tested by the screening method. The samples were also tested by using the calibrated method, after exposing each sample to a dose of 1 kGy using Co-60. The calibrated method of PSL was performed in order to validate and confirm the results. The tests were also performed after exposition of samples to doses of 5 kGy and 10 kGy. The absorbed dose was controlled using the ethanol chlorine benzene standard, with an uncertainty of 2%. The irradiation system is calibrated at RISO Laboratory in Denmark.

### 3. Results and discussion

The obtained results for PSL measurements on all tested samples are shown in Table 1. The following figures present graphically the dependence of the PSL signal counts on time. The detection system measures the counts once in a second for 60 seconds, so 60 points are presented on each chart. The software calculates the standard deviations from these results. The samples give different results after the same treatment because of their different mineral content.

Table 1. The registered total counts  $N$ , from the PSL measurements on the samples.

No.	Sample	$N$			
		0 kGy	1 kGy	5 kGy	10 kGy
1	Paprika standard	1261 ± 48	946501±973	2243722 ± 1498	2773709 ± 1666
2	Alfalfa	1988 ± 60	873252 ± 935	2718305 ± 1649	3131849 ± 1770
3	Dong qui	2051 ± 56	1186266 ± 1090	2330155 ± 1527	2838005 ± 1685
4	Green tea	739 ± 43	26733 ± 167	76220 ± 278	106669 ± 328
5	Mint	485 ± 40	78981 ± 283	154225 ± 394	206810 ± 456
6	Turmeric	513 ± 40	104990 ± 326	353964 ± 596	355481 ± 597
7	Thyme tea	897 ± 44	55419 ± 238	112956 ± 338	163970 ± 406

The total counts  $\ln N$ , as a function of time  $t$ , for some of the tested samples, are presented in Fig. 3 and Fig. 4.

A paprika standard sample gave an intermediate screening result, which does not give an exact identification of the irradiation history of the sample. Because of that, measurements using the calibrated method were performed after treating the samples by ionizing radiation with a dose of 1 kGy using Co-60 as a source of ionizing radiation. After the treatment, measurements were done for the second time and a positive result was obtained. This confirms that the sample was not previously irradiated. After treatment with higher doses, an increase of the number of total counts has been observed. The above observation is presented in Fig. 3. The alfalfa, paprika and dong qui samples showed similar results.

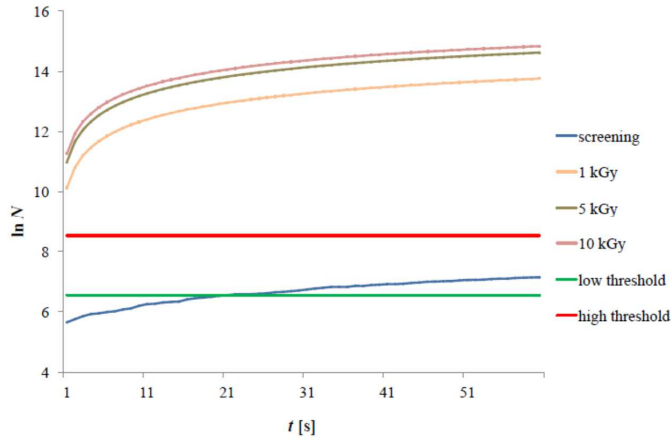


Fig. 3. The PSL measurements of paprika standard for an unirradiated sample (screening method) and samples treated with doses of 1 kGy, 5 kGy and 10 kGy (Co-60 as an irradiation source).

A mint sample gave a negative screening result. After treatment with a dose of 1 kGy, a positive result was obtained, which confirms that the sample has not been irradiated before testing. After treatment with higher doses, an increase of the number of total counts has been noticed. The thyme tea sample gave similar results. The results for a mint sample are shown in Fig. 4. Similar results were obtained for the samples of green tea, mint, turmeric and thyme tea.

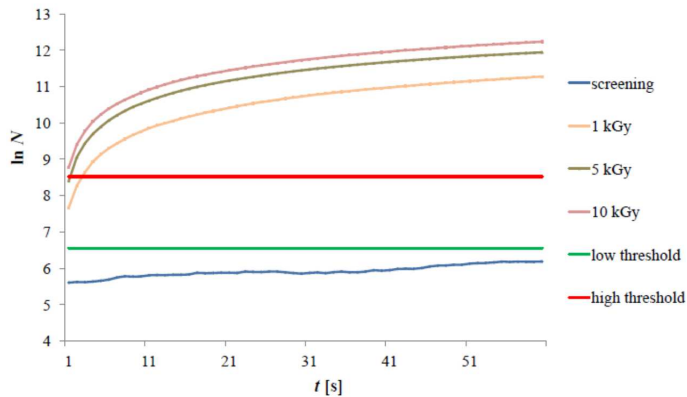


Fig. 4. The PSL measurements of mint for an unirradiated sample (screening method) and samples treated with doses of 1 kGy, 5 kGy and 10 kGy (Co-60 as an irradiation source).

The obtained results confirm validity of the procedure for all tested samples. All of them are correctly identified as unirradiated. Besides that, the study of the influence of dose on the luminescence signal in all cases showed that the higher the dose applied on samples, the greater the luminescence signal. This can serve as a base for further studies of dose estimation [9–10].

The results of PSL measurements for all tested samples irradiated with different doses are shown in Table 2. Standard deviation –  $\sigma$  and measurement uncertainty –  $u$  for the total counts from all 60 values have been calculated according to the following formulas:

$$\sigma = \sqrt{\frac{\sum_i (\ln N_i - \overline{\ln N})^2}{59}}, \quad (1)$$

and

$$u = \frac{\sigma}{\sqrt{60}}. \tag{2}$$

Table 2. Standard deviation –  $\sigma$  and measurement uncertainty –  $u$  of total counts from the PSL measurements on samples.

	Sample	ln N					
		1 kGy		5 kGy		10 kGy	
		$\sigma$	$u$	$\sigma$	$u$	$\sigma$	$u$
1	Paprika standard	0,21239038	0,02741948	0,238821415	0,030831712	0,231563694	0,029894744
2	Alfalfa	0,24378165	0,03147208	0,29664052	0,03829613	0,29372451	0,03791967
3	Dong qui	0,24109032	0,03112463	0,27621648	0,03565939	0,29031491	0,03747949
4	Green tea	0,21229289	0,02740689	0,25483323	0,03289883	0,31458119	0,04061226
5	Mint	0,1962257	0,02533263	0,2613148	0,0337356	0,24707366	0,03189707
6	Turmeric	0,22113866	0,02854888	0,32828703	0,04238167	0,32247145	0,04163089
7	Thyme	0,275362	0,03554908	0,21316774	0,02751984	0,20445422	0,02639493

The values presented in Table 2 show that there are no significant differences between the deviations for different doses. The deviations are very small, which means that the measurements have been performed with a very low measurement uncertainty.

The dependence of total counts ln N on dose D for all tested samples is shown in Fig. 5 and Fig. 6.

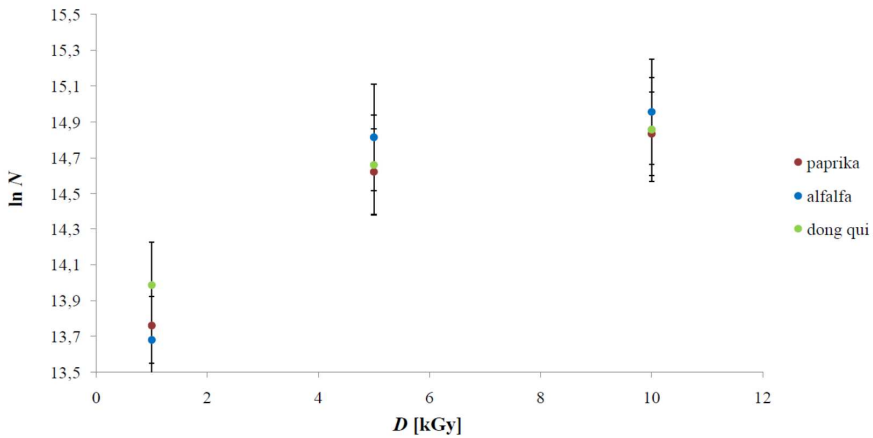


Fig. 5. A plot of total counts against dose for the paprika, alfalfa and dong qui samples.

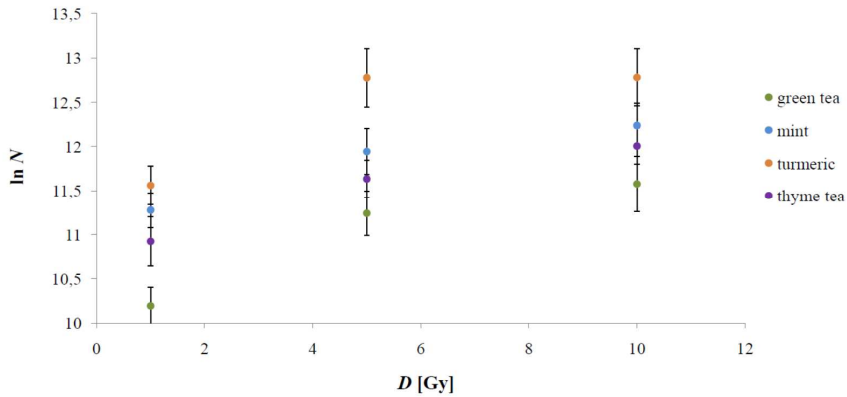


Fig. 6. A plot of total counts against dose for the green tea, mint, turmeric and thyme tea samples.

#### 4. Conclusion

Irradiation enhances food quality by destroying harmful microorganisms.

The aim of the presented research was to study the dependence of the luminescence signal on the applied radiation dose. Thus, a number of measurements and analysis of different samples have been undertaken, indicating that the results are comparable with the EU standard, and validity of the procedure for analysis of irradiated food is completely confirmed. Also, a study of the influence of radiation doses on the luminescence signal has been undertaken, which showed that there is a dependence of the signal on the radiation dose.

Even though dosimeters are used for the dose determination during treatment of foodstuffs, the exact absorbed dose may vary depending on the geometry of the package and quantity of packed food. According to the results of the work presented in this paper, which confirm that there is a clear dependence of the luminescence signal on a dose, we suggest that the PSL measurements can serve as an initial step to establishing a procedure of the dose estimation for different types of irradiated food. An exact determination, or even estimation, of the absorbed dose cannot be done regardless the storage conditions, mineral content, irradiation conditions, *etc.* The results also show that the deviations of the results are not significant and that the measurements were performed with a low measurement uncertainty, confirming the reliability of the measurement procedure.

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