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Detection of gamma irradiated spices with OSL method and its reliability

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Abstract

Objective: Irradiation has been accepted as an effective food safety method for various foods over 50 years. Gamma rays from radioactive isotopes of Cobalt 60 or Cesium 137 are used for food irradiation applications. Main concern about food irradiation is the detection of these irradiated foods and also loss of detection of irradiation through storage period. Photo Stimulated Luminescence (PSL) is one of the physical techniques that can be used for irradiation detection. The aim of this study is to analyse the behaviour of PSL signals of irradiated spices with respect to storage period, storage temperature, origin and type of samples.

Material and Methods: Red pepper, thyme and cumin were used as samples and 4°C and 25°C were selected as storage temperature. Storage period was set as six months after irradiation application. During six months storage period, PSL signal was not detectable for most of the origin and sample type. At the end of sixth month, an spin resonance spectroscopy (ESR) analysis was performed to detect the accuracy of the PSL technique.

Results: With respect to the results of these experiments, it was seen that, most of the samples was observed as false un-irradiated by PSL technique, however ESR analyse the samples as irradiated at the end of sixth month.

Conclusion: According to the statistical analysis, origin and type of sample were determined as the dependent parameters of PSL detection.

Keywords: Spices; Gamma Irradiation; Photo Stimulated Luminescence (PSL)

Introduction

Food irradiation is applied as controlled amount of ionizing radiation (with sufficient energy to create positive and negative charges) which includes gamma rays from radioactive isotopes Cobalt-60 and Cesium-137 (1).

Gamma rays are the specific energies that normally come from the spontaneous decay of radionuclide which is not naturally occured and unstable. The radionuclide that is used for the irradiation of food materials is mainly Cobalt-60. The aim of food irradiation applications are the preventing germination of some foods, killing of insects in grains or dried foods, retardation of ripening period, increasing shelf life and killing microorganisms in herbs and spices (2).

Mainly; gamma irradiation in food industry is used for the prevention of microbial growth and health problems as well as decreasing the economic losses because of microbial deteriorations of food products, unexpected recalls because of outbreaks, loss of consumers' confidence and loyalty. Due to such reasons, microbial inactivation mechanism of the technique becomes important for its application process (3).

The parameters that effect the microbial reduction due to irradiation process can be listed as: size of the microorganisms, age of the microorganisms, radiation absorbed dose, type of microorganisms, absence or presence of oxygen and time of exposure.

1.1 Irradiation Detection and Regulations

The level of irradiation in different food systems is regulated by different authorities in every country; in general this value is in the range of 1-10 kGy for pasteurization processes and above 10 kGy for sterilization purposes (4). Foods such as wheat, wheat flour, white potatoes, pork, fruits, vegetables, herbs, spices, poultry, meat and animal feeds and also enzymes are approved for irradiation application process by most of the irradiation authorities (5). The main concern of irradiation process for the market is the consumer acceptance and loss of detection of irradiation through storage time. At this step, detection of irradiation after processing becomes an important point for both consumer acceptance and reliability of irradiation.

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1.1.1 Detection Methods

There are several valid and accurate methods used all over the world for food irradiation detection. The irradiation process, when applied at usual doses; namely equal to or less than 10 kGy, involves few chemical changes on food rather than other treatments such as heating or freezing (6).

The most important irradiation detection methods are electron spin resonance spectroscopy (ESR), thermoluminescence (TL), Photo Stimulated Luminescence (PSL) and DNA Comet Assay. Among them; the luminescence techniques are some of the common used techniques for irradiation detection. Luminescence can arise from the thermal or optical stimulation of minerals that have been previously exposed to ionizing radiation. Irradiation creates free charges in the solid which may be captured by lattice defects acting as traps. If the matter has a crystalline structure, the excited charge carriers can remain trapped in the crystalline lattice defects. When heat or light is applied to the sample, the stored charges are released and recombined resulting in a light emission (7). If the system is stimulated by heat, mechanism is called as thermoluminescence (TL), and if the system is stimulated by light, it is called as photo stimulated luminescence (PSL). The recorded luminescence intensity is proportional to the absorbed radiation dose.

Photo stimulated luminescence (PSL) is one of the accurate methods used all over the world for determination of irradiated foods. Luminescence can arise from the thermal or optical stimulation of minerals that have been previously exposed to ionizing radiation. Irradiation creates free charges in the solid which may be captured by lattice defects acting as traps. If the sample has materials in crystalline structure, the excited charge carriers can remain trapped in the crystalline lattice defects (8).

Food is contaminated by very small quantities of silicate minerals such as quartz and feldspar for most of the time and presence of these minerals on the food materials can be important for a reliable signal measurement. For both TL and PSL techniques, signal sources are the minerals in the sample. In TL measurements, due to the high temperature, organic materials in samples are burned and can cause failure of detection and also the system. Therefore, it is reasonable to separate inorganic minerals and organic compounds and analyze only inorganic compounds. However in PSL, there is no need for separation of inorganic minerals and organic compounds during measurement since no heating is required, therefore samples are not denatured (9).

PSL is specified as a method for the detection of irradiated foods by European Standards and it is based on optical stimulation of mineral debris, typically silicates, bioinorganic materials such as calcite, feldspar. Irradiation of food causes such minerals to store energy in their charge carriers. When stimulated with optical energy, the trapped energy is released in the charge carriers as luminescence (10). In this technique, trapped electrons are stimulated with appropriate wavelength and intensity of light, and luminescence is monitored as a function of stimulation time. Observed luminescence is due to recombination of electrons at whole traps which act as recombination centers (Figure1).

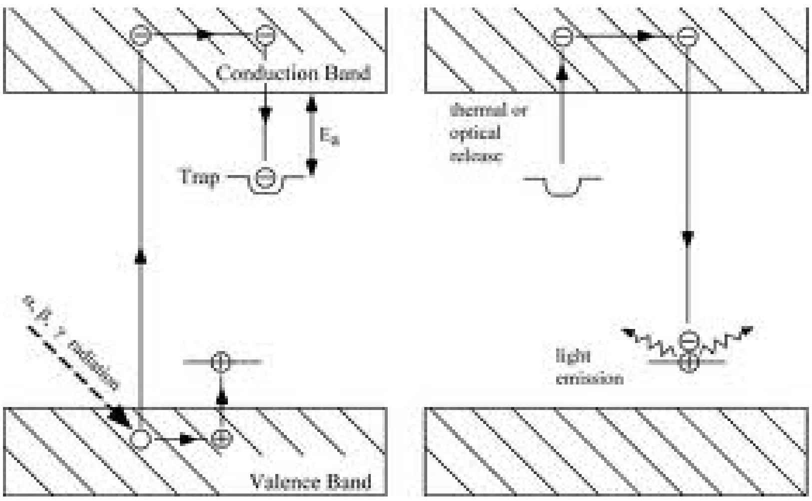


Figure 1: Simplified band model for describing luminescence mechanism (http://rses.anu.edu.tr)

If the food is irradiated, the signal is strong; obviously a weak signal would indicate a non- irradiated food. In occurrence of an intermediate signal, the sample can be estimated as a mixture of irradiated and non- irradiated foods or the sample may have a low sensitivity (7). Due to this analysis, PSL sensitivity of the product becomes important. Sensitivity depends on quantity and type of minerals in the sample.

In PSL detection, if irradiated samples are treated once more, just a small increase is observed in PSL signals since only left electrons are transferred to the upper level; however unirradiated samples cause a substantial increase in PSL after the first irradiation (11).

Materials and Method

Radiation Source

Cobalt-60 is not naturally occurred and is produced by neutron bombardment in a nuclear reactor of the metal Nickel-59. It is then doubly encapsulated in stainless steel “pencils” to prevent any leakage during its usage in a radiation plant. When not used, the gamma “source” is stored in a pool of water (4). In the case of foods or some another products irradiation process, the source is pulled out of the water into a chamber with massive concrete walls. Foods or medical products to be irradiated are brought into the chamber, and are exposed to the rays for a defined period of time. After the process is finished, the source is returned to the water tank. The irradiation treatment is done within an irradiation room in a typical plant. The radiation source is fixed on the elevator system and when it is not used the source is localized in a water tank.

Irradiation Treatment

In TAEA (Turkish Atomic Energy Authority; the boxes were placed in 45x45x90 cm size irradiation boxes and loaded on horizontal conveyor and transported to the irradiation room. The irradiation treatment takes place in this room and samples are passing across the gamma source (Cobalt-60) and absorbed the radiation.

The process is continued till reaching the wanted absorbed dose (10 kGy) for samples. After process ends, gamma source is placed back in the water.

Samples

Spice samples (red pepper, thyme and cumin) were obtained from local spice markets located in Adana, İzmir, Maraş and Ankara without subjected to gamma irradiation. Gamma irradiated and unirradiated samples were stored both at refrigeration temperature (4°C) and room temperature (25°C). The spice samples were kept in small bags and covered with aluminum foil and placed in opaque boxes which are not transparent to light.

Irradiation Detection

For irradiation detection, the samples were loaded on 10 mm aluminum disks in a red lightened room. Disks were initially covered with silicon oil in order to paste spices. A thin layer of spice was put on aluminum disk. After samples were prepared, they were loaded into PSL equipment. Each sample was monitored for 200 seconds in order to obtain reliable signals from the samples. During the analysis, spice samples were placed in a light sealed system which did not expose any interfering light except the light coming from the system source.

2.1 PSL Detection System

PSL detection system is composed of a stimulation light source, a sensitive photo detector and sample holder (Figure 2). Depending on the type of mineral in the sample, Infra-red (IR) (~ 880 nm) and blue light (~470 nm) can be used as light sources.

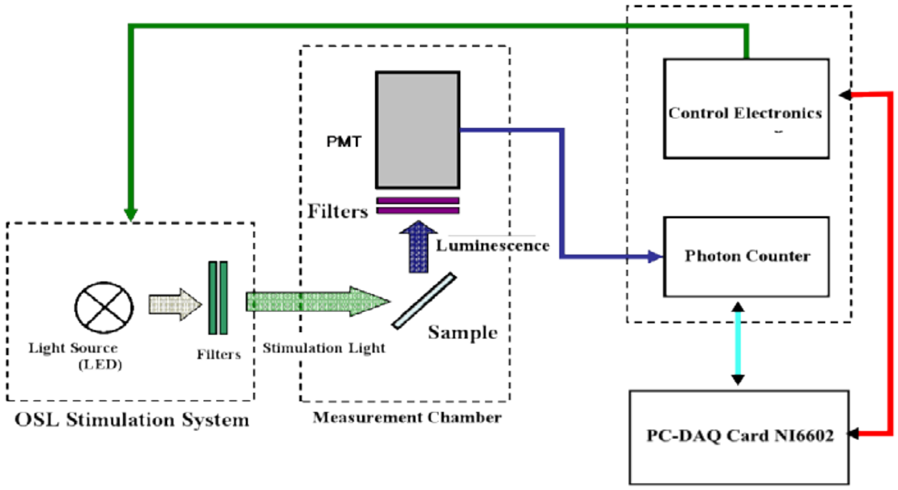


Figure 2: System of PSL detector (15)

Luminescence was detected in photon counting mode using a photomultiplier tube with a bi alkali photocathode (Electron Tubes, 9532 Q) with a UV band pass filter (Hoya U-340) transmitting wavelengths between 280-380 nm. Stimulation was done with a blue light source employing a cluster of 24 blue light emitting diodes. Power density on the sample was 30mW/cm^2. Intense blue light was used in order to measure lower doses in spice samples.

For the stimulation, light emitting diodes (LED) were used due to their long life and easier availability. In this technique, photo multiplier tubes (PMT) were used as photo detectors. The signals obtained from PMT were in the form of pulses and pulses were counted by a computer connected to the equipment with USB cable.

2.1.1 Irradiation Detection

For PSL measurement, data was taken (200 seconds with one second intervals) until a stabilized signal value was reached. PSL measurements were made in triplicates for each samples studied. In order to confirm the irradiation process, background PSL signal values were monitored for all unirradiated samples. Background value is defined as the lowest value of PSL signal monitored before irradiation. The experiment parameters were defined as time of storage, storage temperature, sample type and origin. Measurements were carried for 6 months based on the counter stay of samples on markets.

2.2 Statistical Analysis

The analysis of regression was carried out to investigate the effect of experiment parameters on the final treated product irradiation detection by using MiniTAB (Version 16). Multi way ANOVA (analysis of variance) were used for comparison of means. Significance was accepted at 0.05 level of probability ($p<0.05$). Mean separation was performed by LSD (least significant difference) for multiple comparisons of means. All measurements were performed in triplicate.

Results and Discussion

During experiments, three different samples (red pepper, thyme, cumin) from four different origins (Adana, Izmir, Maras, Ankara) were used to obtain reliable data and minimize the error coming from the origin of the samples such as amount of inorganic materials or dust and also type of inorganic materials. According to the results of PSL measurements; background PSL signal value is mostly affected by origin and type of samples. Samples from different origins were observed to have different background PSL signal intensity values (between 450 and 1230 cps) (Table 1).

Table 1: Background PSL signal values of Red Pepper, Cumin and Thyme Samples for all origins

Origins	Red Pepper	Thyme	Cumin
Adana	462±5.4%	991±5.8%	1214±4.6%
İzmir	1013±10.2%	969±4.2%	787±2.7%
Maras	402±5.4%	864±12.4%	1256±4.2%
Ankara	755±8.5%	783±21%	1014±4.6%

3.1 PSL Signal Values After Irradiation

After irradiation (10 kGy), the samples were analyzed for their PSL signal values (Table 2). In order to prevent the optical fading for long term storage, meaning losing PSL signals due to light, samples were stored in dark (12).

Table 2: Average PSL Signal Values for Irradiated Samples from All Origins

Origins	Red pepper	Thyme	Cumin
Adana	20778±6.2%	1425±7.1%	3515±2.9%
İzmir	1223±3.1%	1054±10.3%	756±2.8%
Maras	1024±2.9%	1631±10.5%	994±4.9%
Ankara	663±9.2%	1421±17.4%	969±7.4%

The reason of measuring high PSL signal value of Adana samples after irradiation can be due to the amount of dust in the sample and also the amount of traps in the mineral debris. This situation might have caused high amount of electron transfer resulted high luminescence formation. However, PSL signal of other three red pepper samples were lower than the expected. The reason for such observation may be due to the presence of shallow traps (lack of deep traps) and the lower amount of dust when compared to Adana red pepper. The captured electrons in such traps can be lost at room temperature with little optical effect (8).

The increase of PSL signal value levels for all samples of irradiated thymes were approximately in the same range. However, difference in PSL signal values in Maras and Ankara originated thyme samples seem more detectable than Adana and İzmir originated thyme samples.

Table 3: Percent Change of PSL Signal Intense Values After Irradiation Treatment

Origins	Red pepper	Thyme	Cumin
Adana	97.8%	30.5%	65.5%
İzmir	17.2%	-	-
Maras	60.7%	46.9%	-
Ankara	-	44.9%	-

Cumin from Adana is the only sample that resulted in observable increase of PSL signal value after irradiation. PSL signal value levels of other cumin samples were only background PSL signals.

3.2 PSL Signal Value Change with respect to Time and Temperature

Spice type and origin show different responses to the irradiation process, so similar increase or decrease behaviors in PSL signal values were not observed after irradiation of the samples. This shows that spice type and origin are the key parameters for irradiation detection using PSL method. In order to determine whether time was a parameter for PSL detection, monthly analyses were done for each origin and sample type. In addition to time dependency, the samples were stored at 4°C as refrigeration temperature and 25°C as room temperature to analyze the effect of storage temperature on PSL measurement. With this approach, the presence of shallow traps were also studied (if there are shallow traps in samples, electrons in these traps are lost at room temperature with time) (13).

First group consist of red pepper, thyme, cumin from Adana, red pepper and thyme from Maras and thyme from Ankara. Those samples had detectable PSL signals during the storage time, at two different temperatures (Table 4-6-7).

Table 4: PSL Value Analyses of Adana Red Pepper/Thyme/Cumin Between Background and Six Month Storage (-1 refers to unirradiated samples, 0 as just irradiated samples and 1, 2, 3, 4 and 6 refer to the analysed months)

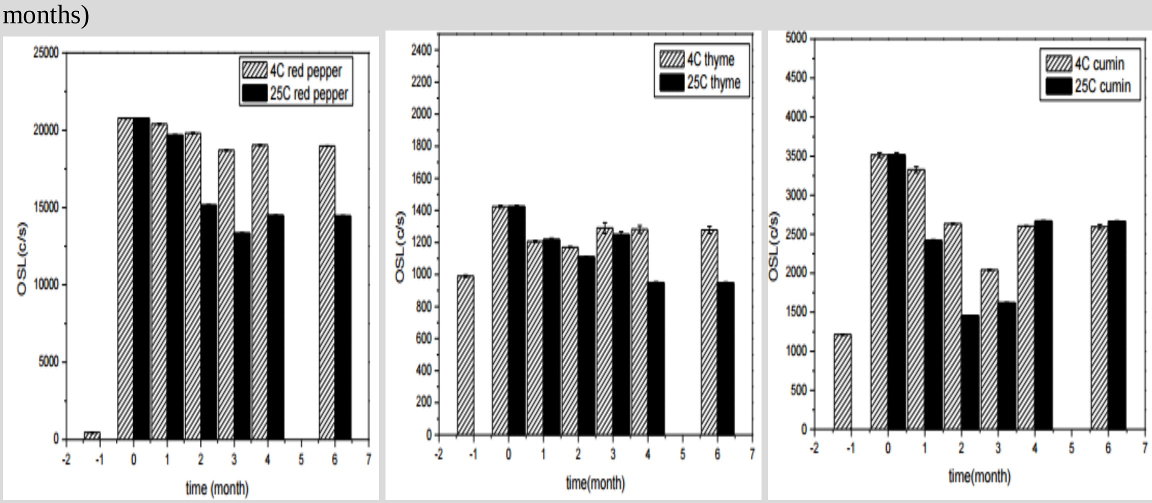
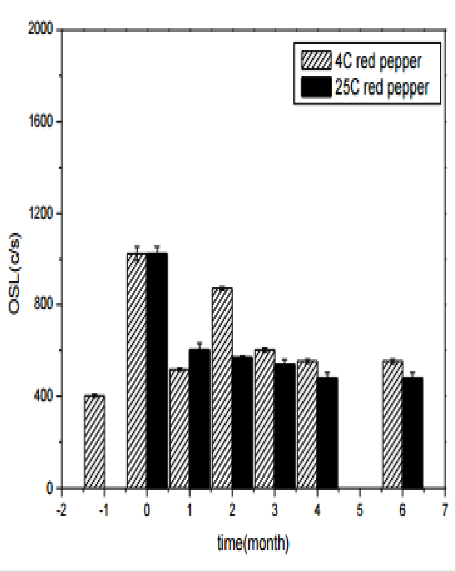


Table 6: PSL Value Analyses of Maraş Red Pepper/Thyme Between Background and Six Month Storage (-1 refers to unirradiated samples, 0 as just irradiated samples and 1, 2, 3, 4 and 6 refer to the analysed months)



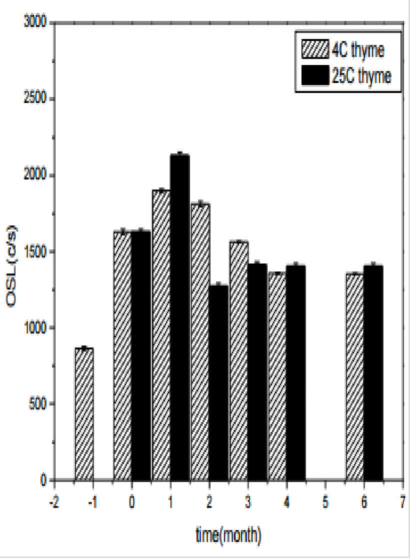
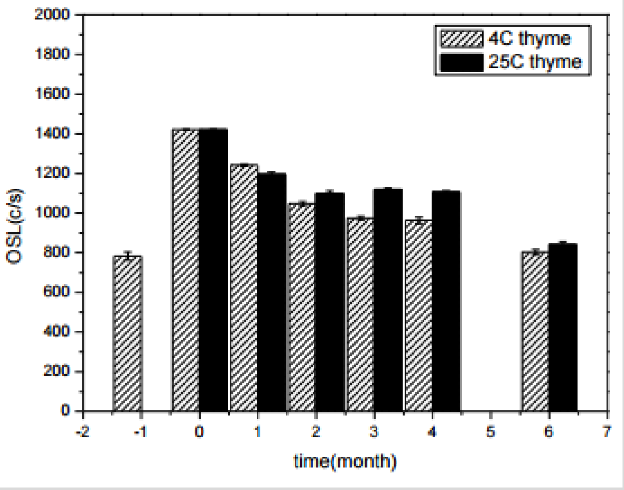


Table 7: PSL Value Analyses of Ankara Thyme Between Background and Six Month Storage (-1 refers to unirradiated samples, 0 as just irradiated samples and 1, 2, 3, 4 and 6 refer to the analysed months)



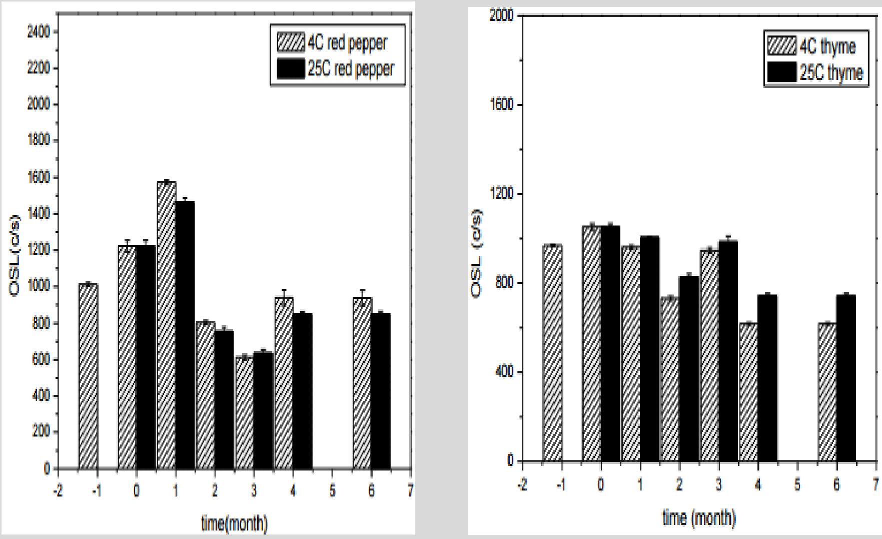
Second group consisted of red pepper and thyme of İzmir and had detectable signals, though in low levels, in the early mounths of storage , however, the observed levels dropped down to the ground level after then. The most probable reason of this is the presence of shallow traps in the studied samples (Table 5).

Cumin samples from İzmir, Ankara, Maras and red pepper from Ankara were in the third group and nearly no increase of PSL signal value was observed after their irradiation.

3.3 ESR Results of Samples

ESR detection was done for only red pepper samples of Adana, İzmir, Maras and Ankara at the sixth month in order to compare the obtained OSL results with ESR results at the end of the experimental duration. Also the reason of making ESR for only sixth month is that, no detection observation for İzmir, Maras and Ankara at the end of sixth month. By this way, significant difference between Adana samples and the others can be explained clearly.

Table 5: PSL Value Analyses of İzmir Red Pepper/Thyme Between Background and Six Month Storage (-1 refers to unirradiated samples, 0 as just irradiated samples and 1, 2, 3, 4 and 6 refer to the analysed months)



In ESR analyses, all the samples show a similar cellulose peak (Figure 3). This means that, they were irradiated homogeneously with the same amount of gamma ray. The cellulose peak is clearly observed and this means that, detection with ESR is more appropriate after six month. At this step, it can be easily understood that, there is enormous effect of light, so optical fading, on irradiation detection by using PSL system.

In addition to these, the significant difference on PSL signals of Adana samples from others can be explained as the difference of amount of dust and also the structural difference of dust.

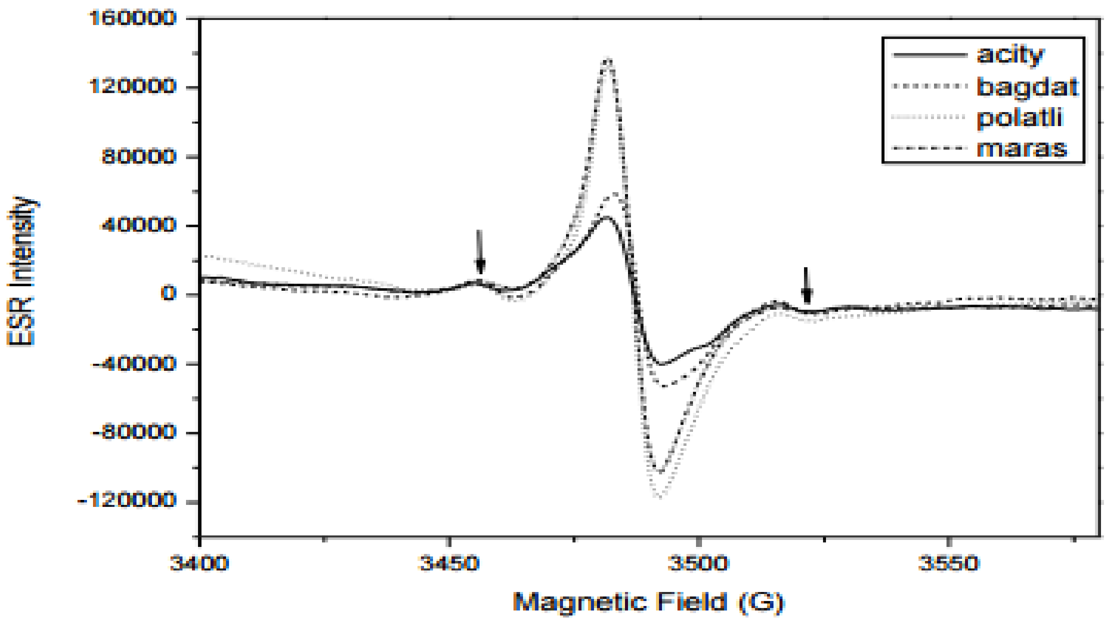


Figure 3: Results of ESR measurements at the end of six month for red peppers from all origins (Arrows represent radiation induced cellulose peaks and magnetic field difference between peeaks is nearly 60 Gauss)

3.4 Statistical Analysis

PSL signal was used as the response parameter in order to analyze the detection loss. The parameters having effect on PSL were chosen as time, temperature, origin of spices and type of spices.

In order to determine the effect of time, monthly PSL signal value measurements were performed for 6 month (average time of the spices to be on the market shelf was given as 4 months).

For the effect of temperature on PSL signals, storage temperatures were set as 4°C and 25°C.

4 way ANOVA (General Linear Model) was used in order to analyze the parameters' effects on PSL signal value detection. Data were obtained as PSL versus spice types, origin, time and temperature.

Spice types and origin were considered as suitable to be taken as parameters of PSL detection. However, the selected time interval and selected temperatures could not be seen as parameters of PSL detection according to the resulted p- values. The confidence interval was selected as 95%, so p values lower than 0.05 were considered as significantly different and were selected as significant determiners of the system (Table 8).

According to the results of the Tukeys Test (95%), red pepper was significantly different than cumin and thyme with respect to PSL response. This can be due to the structure or dust content/amount of red pepper. It may have more free electrons than other samples which might cause higher PSL signals after irradiation applications.

With respect to origin Adana samples were significantly different from İzmir Spices, Maras and Ankara samples. This may be most probably due to the amount and type of dust on the samples.

Conclusion

The results of the studies show that PSL can be used as an efficient technique in the laboratories or customs for determination of the irradiation application of spices because it is rapid, cost effective and samples are not affected by the system. Main drawback experienced in these studies is the inconvenience of the system to be applicable to all type of food.

PSL signal value deviations in red pepper samples were more than the ones in other spice samples. This shows that type of sample and origin have a significant effect on background PSL values of the samples.

The reasons for such kind of a deviation may be explained as, non-homogenous nature of spices, different humidity values of different samples and type and amount of dust in the nature of spices.

In statistical analysis, origin and spice types were determined as significant parameters of PSL detection of irradiated samples. However storage time and storage temperature were not significant on PSL signal detection during storage.

The advantages of PSL system can be summarized such; it is rapid, cost effective. However, the disadvantages may be explained as follows; there may be risk of inaccuracy and there are decays of signals with storage time (if they are not stored at dark) and on repeated measurements (14).

Conflict of interest: The authors declare they have no potential conflicts of interest with respect to the research, authorship, and/or publication of this article, and declare study has ethical permissions if required..

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