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ESTIMATION OF THE ACTIVATION ENERGY VALUES FROM THE THERMOLUMINESCENCE GLOW CURVES TO DETECT IRRADIATED CHILLI POWDER

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ABSTRACT

This report presents the estimation of the activation energy (E) values from the thermoluminescence (TL) glow curves showed by the whole glow peak (WGP) method that allows us to distinguish between irradiated and non-irradiated chilli powder samples. The E values of non-irradiated samples maintain 0.65 eV whereas irradiated ones reach 0.84 eV or upper. Furthermore, the E values are obtained from the result of comparison between the chilli powder irradiated with different doses (2, 4, 6 and 8 kGy) stored for 30 days and other unknown chilli powder samples in Vietnam.

Keywords: thermoluminescence, chilli, activation energy, WGP, dose**.**

TÓM TẮT

Đánh giá các giá trị năng lượng bẫy từ đường cong nhiệt huỳnh quang để phát hiện bột ớt chiếu xạ

Báo cáo này trình bày việc đánh giá các giá trị năng lượng bẫy (E) từ những đường cong nhiệt huỳnh quang bằng phương pháp WGP nhằm phân biệt giữa bột ớt chiếu xạ và không chiếu xạ. Giá trị E của mẫu không chiếu xạ là 0.65 eV trong khi những mẫu được chiếu xạ không nhỏ hơn 0.84 eV. Ngoài ra, những giá trị của E thu được từ kết quả so sánh giữa những mẫu ớt chiếu xạ với liều chiếu khác nhau (2, 4, 6 và 8 kGy) bảo quản mẫu khoảng 30 ngày và những bột ớt khác chưa biết ở Việt Nam.

Từ khóa: nhiệt huỳnh quang, ớt, năng lượng bẫy, đỉnh phát quang toàn phần, liều.

1. Introduction

According to the European Standard protocol [1], thermoluminescence (TL) is an acceptable method to distinguish irradiated and non-irradiated spices, herbs, seasonings and vegetables among others. TL technique is based on the luminescence emission from polymineral phases (mainly quartz, carbonates, feldspars and clays) isolated from

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foodstuffs [2]. This mẹthod is empirically observed by heating a previously irradiated dosimeter. The TL intensity emitted as a function of temperature is called a glow curve. The emission glow peaks characteristic of a glow curve are due to trapping centres at different trap depths. Initial irradiation stores TL energy in the crystal [3]. The ratio of integrated TL intensities of the glow 1 to the glow 2 over a stated temperature interval (glow ratio) is evaluated. The irradiated samples exhibit a different glow ratio from the samples that are not irradiated, and the shape and position of the peaks provide further information about the irradiation status of the samples. The TL glow ratios from irradiated samples are typically greater than 0.1, whereas those from non-irradiated samples are usually below 0.1 [4-6]. This paper studies on the TL glow curve of material isolated from chilli powder with different irradiation doses. But to distinguish irradiated and non-irradiated samples, the method of estimation for activation energy (E) to detect irradiated food was used in stead of basing on the TL glow ratios [7].

It is well-known that TL material usually exhibits a very complex TL glow curve structure with non-well peaks and as such, it cannot be analyzed by using the commonly accepted- physical models to explain the trap structure [3]. The E values calculated by modeled first-, second- and general-orders of kinetics based on the computer program. There are various methods to explain about TL process and evaluating the kinetic parameters from TL glow curves. These analysis methods include: glow curve deconvolution (GCD), computerized glow curve deconvolution (CGCD), peak shape (PS), initial rise (IR), whole glow peak (WGP), isothermal decay (ID), three-points (TP), additive dose (AD) [8- 3- 9- 10] and etc. In range of this paper, the experimental data was used to calculate E values by using the WGP method. This paper reports on the estimation of the energy values calculated by the TL glow curves of polymineral phases isolated from both the irradiated chilli powder and unknown chilli powder samples in Vietnam, by using the WGP method in order to determine the E value for detecting irradiated food.

2. Materials and methods

2.1. Material

The chilli powder was collected from local markets in Vietnam, where the irradiation processing for food preservation has not yet implemented. These samples were subdivided into polyethylene holders with mass of 20 g for each. Before irradiation and analysis, the samples were stored in the dark in condition of room temperature. The chilli powder samples as a whole, as well as minerals transferred on discs, were irradiated under electronic equilibrium conditions with a Cobalt-60 gamma irradiator (Gamma chamber GC-5000, BRIT, India) at the Nuclear Research Institute (NRI) in Dalat. The procedure recommended by the European Standard protocol [1] was followed to separate minerals from the chilli powder; it consisted of the following main steps: (i) filtering the chilli powder with water three times before being treated by ultrasounds and centrifuge, (ii) isolating the minerals from the organic materials by means of a density gradient of sodium polytungstate solution (with density of 2.0 g/cm^3), (iii) dissolveing the carbonates adhering to the silicate minerals by adding hydrochloric acid; the acid in excess was afterwards neutralized by using ammonium hydroxide, (iv) removing the water from the separated minerals being resuspended in acetone and deposited on a stainless steel disc (3 mm thick, 15 mm diameter), with thick borders to avoid leakage of the material. The resuspension in acetone was repeated to collect as much mineral as possible. The steel discs were previously cleaned with acetone and ultrasound treatment. An Rexon-reader machine UL-320 (equipped with PC and Windows applications software) was used to record and analyze the thermoluminescence (TL) curves; the following instrumental setting was chosen: initial temperature of 70°C, speed heating of $5^oC/s$, final temperature of from 150^oC to 250^oC. After mineral isolation and after irradiation, the samples were stored at 50^oC overnight before using TL measurements.

2.2. Methods

The WGP method that is based on the whole area under a glow peak instead of one section of the TL glow-curve. WGP method is known as "area method" of analysis, and is based on the measurement of the integral under a glow peak; it can be applied when a well-isolated and clean peak is available. The value of the integral n(T) of the TL intensity over a certain temperature region can be estimated by the area under the glow curve from a given temperature T_0 in the initial rise region, up to the final temperature T_f at the end of the glow peak (Figure 1). A plot of $\ln(I/n^b)$ versus 1/kT yields a straight line of a slope −E. If the kinetic order *b* is known, a broad range of temperatures in which the curve is a straight line. When the kinetic order is unknown, several lines are drawn with various values of *b* and the best straight line is chosen [11].

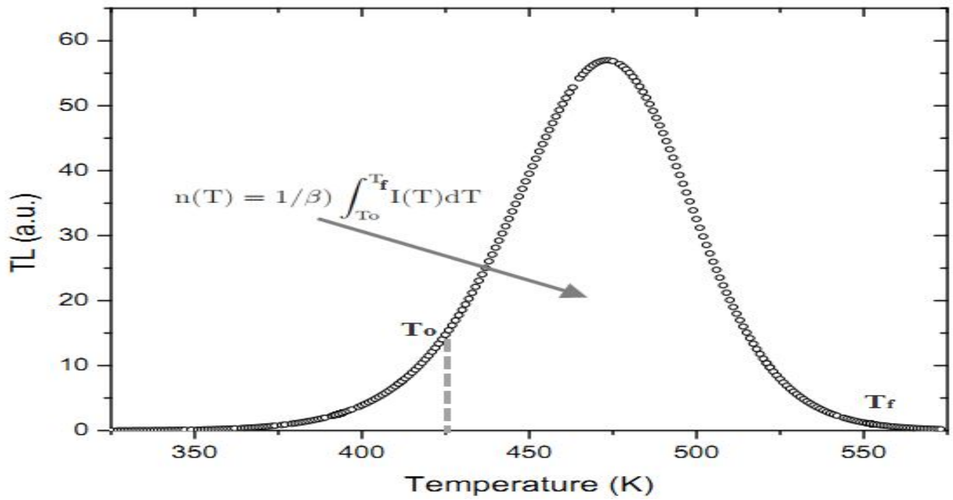

Figure 1. *Whole glow peak method*

3. Results and discussion

The effect of the absorbed doses on the TL values toward chilli powder obtained at different temperatures is presented in Figure 2. It is observed that the TL values at each temperature degree increased at the same time with increasing absorbed dose in the product. Maximum TL values for each dose are seen at 200°C. As observed, the main differences between irradiated and non-irradiated samples are based on (i) the intensity and (ii) the shape of the glow emission [7]. The obtained ratio between the TL intensities of the samples allows us to discriminate irradiated and non-irradiated samples. The intensity of the irradiated samples is, at least, three times higher than the value of the TL from the non-irradiated samples.

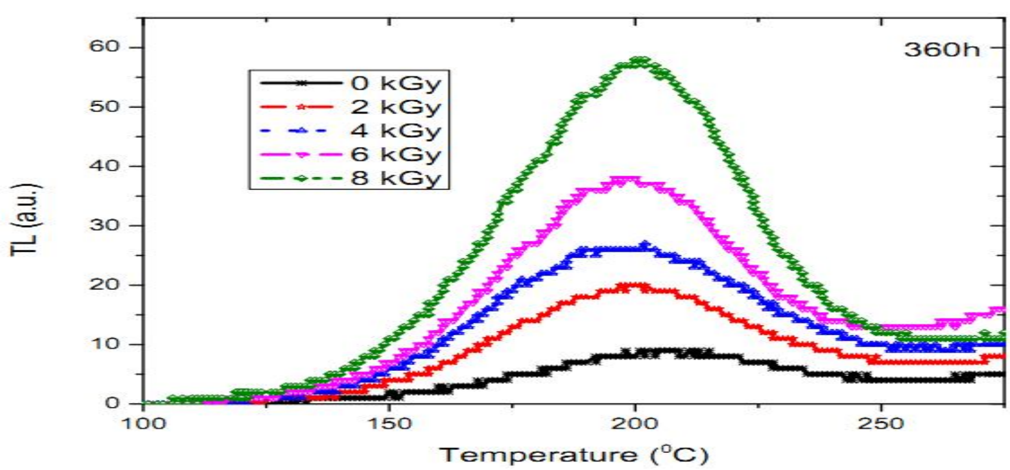

Figure 2. *Thermoluminescence intensities of irradiated chilli powder*

The E values obtained by the WGP methods for chilli powder are illustrated in Table 1. The E values for different doses (0 and 8 kGy) at the same times of storage (360 h) is significantly different from Figure 3. The effect of the storage is demonstrated in Figure 4, where as expected, the intensity of the 8 kGy-irradiated samples decreases with the elapsed time due to the fading effect that also contributes to modify the shape of the curve. The 8 kGy TL curves stored for 360 h starts to grow up to the temperatures at 147°C whereas the starting point of the glow emission from samples stored at 720 h raises at 135°C. Such behaviour is well correlated with the estimated E values for 8 kGy-irradiated samples stored from 360 h to 720 h, as observed in Figure 2. This kinetic parameter is gradually increasing with the elapsed time from 0.84 to 0.88 eV. Therefore, it can be seen that the estimation of the E values using the WGP method could be used to determine the length of time between irradiation processing and the TL analysis. The polymineral phase isolated from chilli powder samples (that studied under laboratory driven conditions) is compared to the dust obtained of unknown chilli powder sample in Vietnam. As appreciated in Figure 5 (sample No. 12 in Table 1), the TL emission of unknown sample contrasts mainly in the shape of the TL curve structure obtained to the non-irradiated chilli powder sample. The estimated E value for this unknown sample is 0.88 eV that is fairly well-correlated with the parameters corresponding to the irradiated dust from the chilli powder samples stored for longer times. On this basis, we can confirm that this sample has been probably irradiated and stored for 720 h with its doses of lower than 6 kGy or irradiated and stored for 360 h and its doses of higher than 8 kGy. Regarding the sample No. 13 in Table 1, the E value is counted at 0.69. Comparing with other sample in this table (the samples No. 1 and No. 6 with E is 0.65 and 0.69 respectively), we can go to conclusion that this sample is not irradiated with the stored time about 720 h (Figure 6).

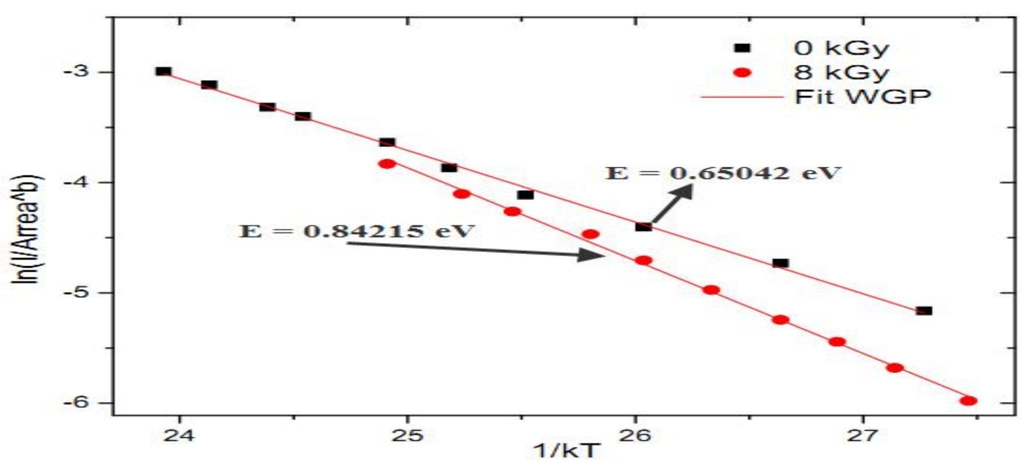

Figure 3. *The E values for different doses (0 and 8 kGy) at the same times of storage*

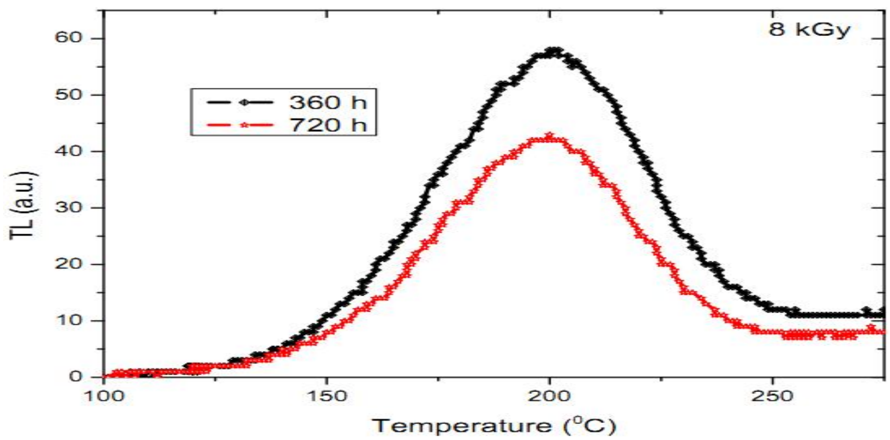

Figure 4. *TL emission from a 8 kGy gamma iradiated polymineral phases isolated from chilli powder after 360 and 720 h of storage*

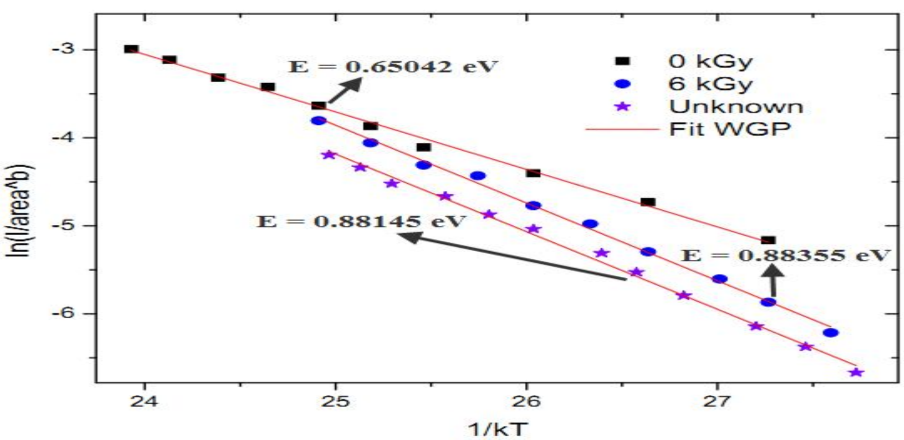

Figure 5. *The polymineral phase isolated from chilli powder samples studied under laboratory driven conditions are compared to the dust obtained from an unknown chilli powder sample in Vietnam*

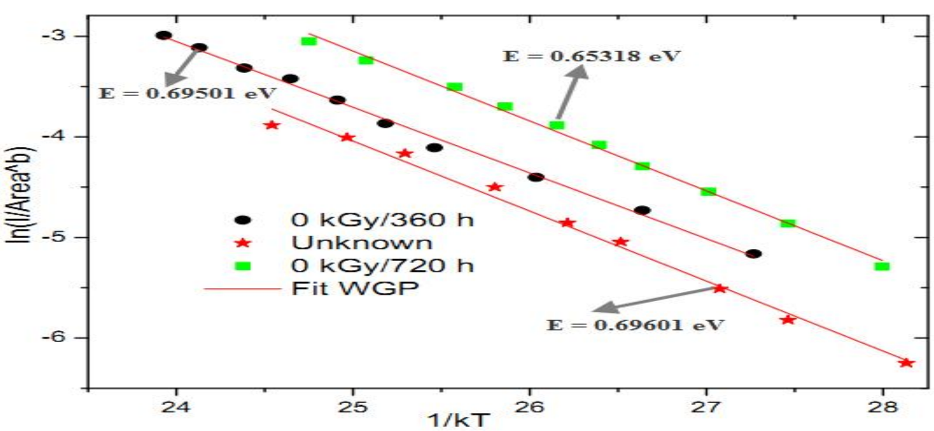

Figure 6. *Non-irradiated chilli powder samples are compared to an unknown chilli powder sample in Vietnam*

Table 1. E values (in eV), range used for the WGP analysis and the linear fitting parameters (where r is the regression coefficient of fitting) obtained from the TL glow emission of polymineral phase isolated from Vietnam chilli powder at different doses and times of storage

No	Dose/Storage	Range (^{0}C)	E (eV)	r
1	0 kGy/360 h	150 - 199	0.65042	0.99750
2	2 kGy/360 h	148 - 176	0.92123	0.99628
3	4 kGy/360 h	144 -174	0.91498	0.99818
4	6 kGy/360 h	145 -190	0.88355	0.99612
5	8 kGy/360 h	147 -190	0.84215	0.99715
6	0 kGy/720 h	139 - 193	0.69501	0.9949
7	2 kGy/720 h	133 - 176	0.99359	0.9966
8	4 kGy/720 h	141 - 175	0.93147	0.99748
9	6 kGy/720 h	135 - 198	0.90841	0.997
10	8 kGy/720 h	135 -185	0.88308	0.99676
11	2 kGy/1440 h	141 -187	0.93847	0.99676

The calculation of the activation energies using WGP method can be considered as a reasonably good estimation, although this calculation can vary according to the preheating temperature. Compared to the detection of irradiation food based on the normal the glow ratios [4- 1- 12], WGP method is calculated to ensure the fewest errors, correlation coefficient (r) must be at least 0.99 to identify irradiated foods [7]. Therefore, estimating E to identify irradiated food or non-irradiated one needs to use many different methods to analyze and compare.

4. Conclusions

The results showed that WGP method can be used to determine for food irradiation. The determination is not based on TL intensity of materials but basing on E values. The samples are still defined to be irradiated without re-irradiating. The E value of irradiated samples and non-irradiated ones are greatly different. E values of non-irradiated samples line at 0.65 eV whereas gamma irradiation reaches at least 0.84 eV. Compared with other methods, the WGP requires more sufficiently experimental data consequently, bringing to the positive results. Therefore, this method can not only be applied in practice for determining the dose of the chilli powder but also for other foodstuffs in Vietnam.

Furthermore when applying the method to the unknown chili powder samples in the market, the results showed that almost these chilli powder samples were irradiated and the absorbed dose was within the allowed limit.

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