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Determination of activation energy and order of kinetics at different temperatures of thermoluminescent Meretrix Castra Marine biogenic shells

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Abstract : The TSL glow curve characteristics of ten biogenic shell samples of southern Tamilnadu are put to analysis. The glow curves of unannealed sample shows only one peak at 330°C. The sample irradiated with a gamma does of 500 Gy shows an additional peak at 130°C, when recorded with linear heating rate of 10°C/sec. The annealed sample also shows the same trend. The kinetic parameters such as activation energy (*E*). frequency factor (*S*) and order of kinetics (*b*) are evaluated using partial heating, peak shape, isothermal and initial rise methods. The activation energies are determined in two different thermal treatments (below 500°C and above 500°C). Below 500oC annealing shows second order kinetics and above 500oC shows first order kinetics. This result is confirmed through the behaviour of dose response.

Keywords : Aragonite, biogenic shells, kinetic parameters, TSL

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1. Introduction

Calcite, dolomite, aragonite, magnesite, feldspar and quartz are some important minerals which are thermoluminescent in nature. $CaCO_3$ is a mineral, found in many geological formations in two different structures. One is calcite ($CaCO_3$) in rhombohedral structure and the other is aragonite ($CaCO_3$) in orthorhombic structure. It has been of particular interest in studies of thermoluminescence because it is abundant in natural form. The thermostimulated luminescence (TSL) characteristics of any material is customarily labelled by a few parameters such as (i) the order of kinetics obeying the process of TSL (ii) the activation energy (or) trap depth and (iii) the frequency factor. A method for

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calculating activation energies (E) by TSL glow curve was given Urbach [1] for the first time. The TSL properties of synthetic phosphor depend largely on the dopant concentration. But in natural samples. The TSL properties rely on the several factors such as their geneses, chemical composition, incorporation of impurity and geological history [2,3]. The first theoretical treatment of an isolated TSL peak was given by Randall and Wilkins [4]. Further development and convenient method for investigating the TSL kinetic parameters was proposed by Chen and Kirsh [5].

Many authors have studied on the TSL glow curves and TSL spectral characteristics of calcites [6-10]. Very few studies on kinetics have been attempted.

In the present investigation, an attempt was made to study the TSL kinetic parameters of ten biogenic shells, belonging to Meretrix Castra variety, collected from prominent locations of Tuticorin coastal area of southern Tamilnadu region, India. It has promising applications in geological and archaeological dating and dosimetry. In fact, the order of kinetics of TSL peak is an important parameter, as the accuracy of TSL dating largely depends on order of kinetics or not [11,12].

The TSL glow curves of unannealed and annealed samples are analysed and their kinetic parameters such as activation energy (E), frequency factor (S) and order of kinetics (b) are evaluated using various methods.

2. Materials and methods

The ten natural marine biogenic shells belonging to Meretrix Castra variety were collected from geologically important locations of Tuticorin, coastal area of southern Tamilnadu region, India. They were ground using agate mortar and sieved to the grain size of 125 – 250 μ. The samples were washed for 2 min with 1 % HCl solution and distilled water to remove organic materials present if any. These dried samples were used to carryout the natural thermoluminescence (NTL) and artificially induced themoluminescence (ATL) measurements. All the samples were annealed in air atmosphere at the temperature ranging from 200°C to 700°C with an interval of 50°C for 1hr duration in a muffle furnace and the TSL measurements (ATL) were carried out. The TSL sensitivity was found to be maximum at 450°C. The annealed samples (450°C) were irradiated by using ^{60}Co - gamma source with a dose rate of 680Gy/hr and the TSL measurements were taken using Nucleonix TLD-96 readout with a heating rate of 10°C/sec. The TSL glow curves were recorded immediately after irradiation to avoid fading. The data were collected from computer after subtraction of black body radiation.

2.1 Methods of kinetic analysis :

An attempt was made to analyse the TSL glow peaks assuming the monoenergetic trap model. Several methods for the analysis of the glow curves have been proposed to determine activation energy (E), and they are reviewed by Shalgaonkar and Narlikar [13]. The order of kinetics and activation energies are determined by partial heating method [4], peak

shape method [5], isothermal decay method [14] and initial rise method [14]. The experimental values of E and b were used to find out the frequency factor (S).The general mathematical expression relating the parameters E, b and S is

$$\frac{\beta E}{KT_m^2} = S\exp\left(\frac{-E}{KT_m}\right)1+(b-1)\left(\frac{2KT_m}{E}\right)$$

where β is the linear heating rate, T_m the glow peak temperature, K the Boltzman constant, E the activation energy, S the frequency factor and b the order of kinetics.

3. Results and discussion

3.1 Glow curve characteristics

The TSL glow curve measurements were carried out with various treatments for all the ten samples which shows similar structure in respect of shape, intensity and peak position. Typical glow curves of natural and natural plus irradiated are shown in Figure 1

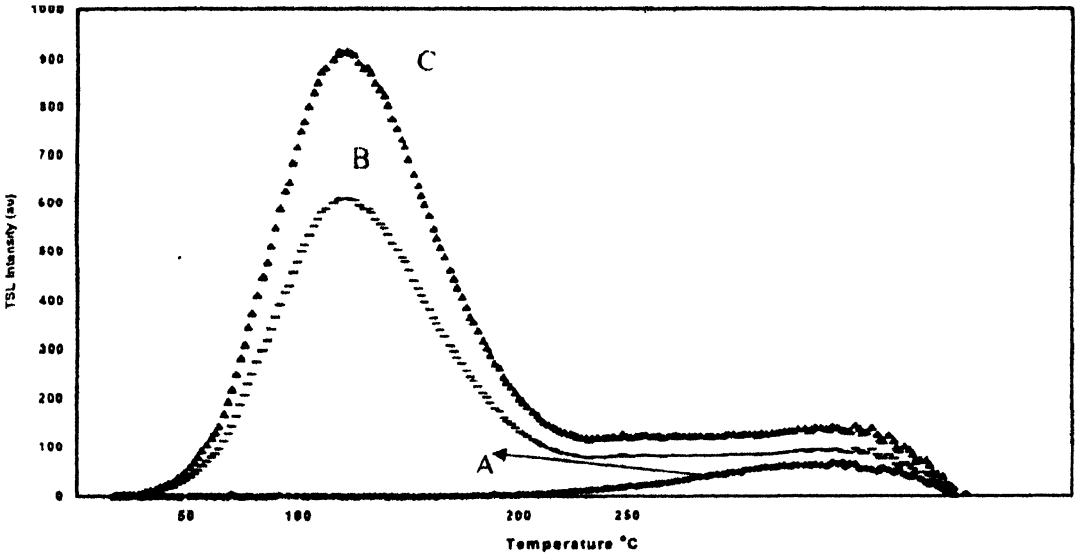

Figure 1. TL glow curve characteristics of aragonite (A) NTL, (B) NTL+Dose and (C) after preheating at 350°C for 1 hr.

together with preheated biogenic shell sample. Natural glow curve of biogenic shell samples consist of a low intensity peak at a high temperature of 330°C (Figure 1A). The gamma irradiated samples yielded one additional high intensity peak at around 130°C (Figure 1B). It was found that the 330°C NTL peak got saturated quickly at a dose of 100 Gy. Debenham [15] have also obtained similar results for the TL peaks above 300°C for natural calcites. However, there is no reported value for saturation in the case of aragonite material. After preheating at 350°C the glow curves were observed to be similar to that of gamma irradiated sample in respect of peak shape and position, but, there has been an increase in

The general formula proposed by Chen [5] for the peak shape method is given by

$$E_\alpha = C_\alpha\left(KT_m^2/\alpha\right) - b_\alpha(2KT_m),$$

where α represents any of τ, δ and ω, the C_α and b_α values depend on the symmetry factor μ_g and this is equal to δ/ω. If μ_g is 0.42 the TSL glow peak is due to first order kinetics and if it is 0.52, then the peak is due to second order kinetics [5].

Using this method, the symmetry factor (μ_g) for the samples are calculated from the TSL glow peaks of unannealed (*u*) and annealed (*a*) samples (Below 500°C). They are found to be nearly μ_g=0.52 within the experimental error. These values agree very well with the second order kinetics. The determination of average activation energy values of ten samples studied by this method using either total width (E_ω) or half width (E_δ and E_τ) obtained for these two glow peaks (130°C and 330°C) are 0.782 ± 0.003, 1.761 ± 0.004 for unannealed samples and 0.743 ± 0.003, 1.733 ± 0.004 for annealed samples. On comparison with earlier work on natural samples [11,12], the trend observed in the present study seems different regarding the order of kinetics, which may be due to variation in impurities present in these samples. It is difficult to compare the behaviour of the observed glow curve as the literature for the same is not available.

The symmetry factor (μ_g) for annealed sample above 500°C is calculated from the TSL glow peak of 160ºC, which is found to be nearly μ_g=0.42 within the experimental error. This value agrees very well with the first order kinetics. The activation energy of this glow peak (160°C) shows 0.727 ± 0.004. This indicates that the order of kinetics is changed but the activation energy value remains almost the same.

3.4 Isothermal decay method

In isothermal decay method, the TSL material is kept at a constant temperature and the light emission, which decays as a function of time (t), is monitored. In first order kinetics, a plot of ln(I/Io) against t will result in a straight line of slope $m = S \exp(-E/KT)$. If the decay is monitored at different temperatures the slope is obtained. A plot of ln(m) against $1/T$ will give a straight line of slope E/K from which E can be calculated.

In the case of general order kinetics, a plot of $(I/Io)^{(1-b)/b}$ *versus* t should be a straight line and the activation energy (E) can be directly obtained from Boltzman plot of the slopes. This method gives estimation of the order of kinetics also and is perhaps the only method unaffected by temperature dependent factors such as frequency factor and quantum efficiency.

The isothermal decay curve of 130°C TSL glow peak of annealed sample with the exposure of 500 Gy at 60° and 80°C is shown in Figure 3. The values of $(I/Io)^{(1-b)/b}$ are plotted against decay time with the different values of b in the interval of 0.1 (Figure 4). However, for the sake of clarity, only three plots with b=1.1, 1.6 and 2.0 are shown in Figure 4. The straight line indicates the order of kinetics *i.e.*, b=2. The averaged out activation energies (E_{iso}) determined by the slope of the straight lines for the decay recorded at 60°C and 80°C shows 0.778 ± 0.003 and 0.758 ± 0.003 for annealed samples

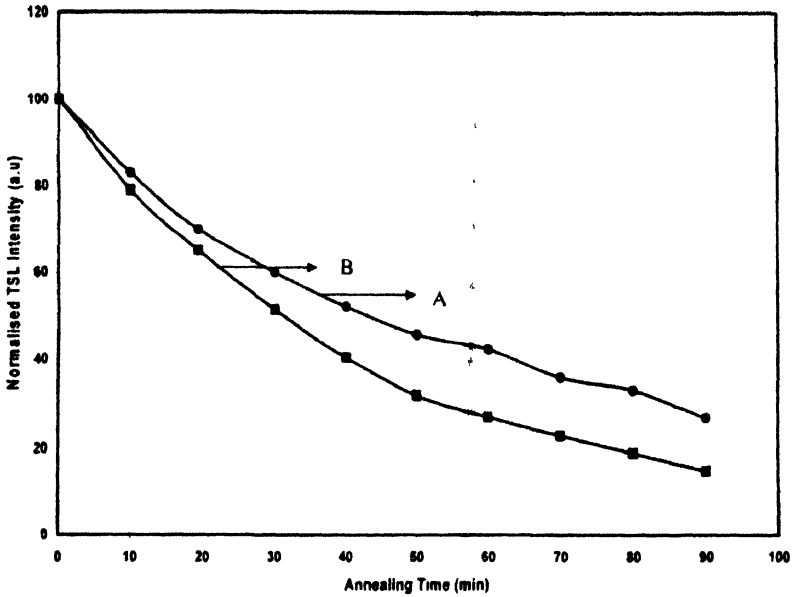

Figure 3. Isothermal decay of 130°C glow peak of calcite after an exposure of 500 Gy at temperatures (A) 80°C and (B) 60°C.

(400°C). The same type of measurement were carried out for another TSL peak 330°C which shows the activation energies 1.772 ± 0.004 for unannealed samples and 0.758 ± 0.003, 1.748 ± 0.004 for annealed samples (400°C). These results are in good agreement with the values calculated by previous method (peak shape method).

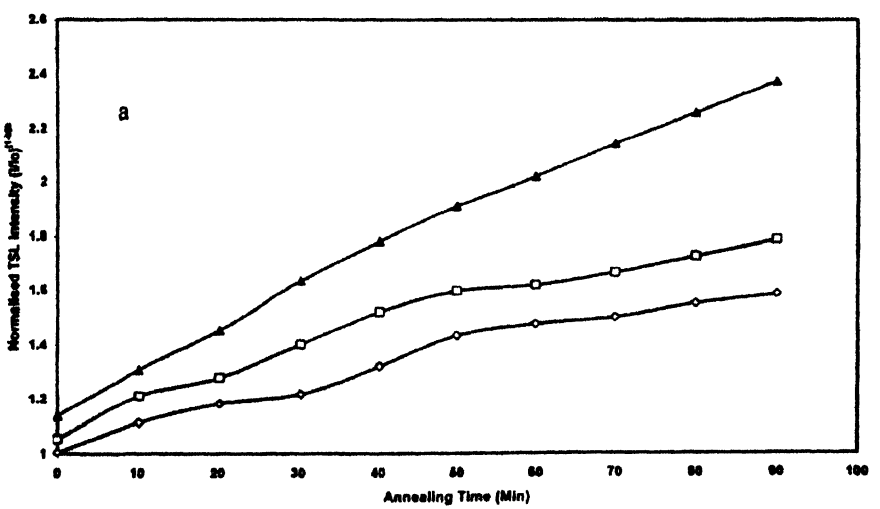

Figure 4a. Plot of $(I/I_0)^{(1-b)/b}$ *verses* annealing time for 130°C glow peak of biogenic shell for (A) b=1.1(◇); (B) b=1.6 (□) and (C) b=2.0 (▲). Decay recorded at (a) 60°C.

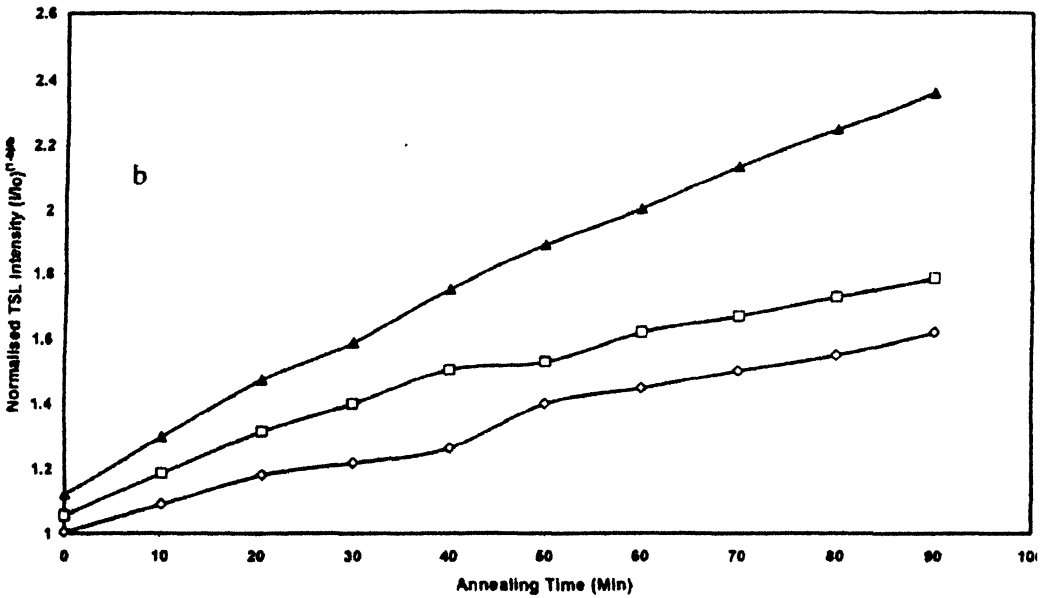

Figure 4b. Plot of $(I/Io)^{(1-b)/b}$ *verses* annealing time for 130°C glow peak of biogenic shell for (A) b=1.1(◇); (B) b=1.6 (□) and (C) b=2.0 (▲). Decay recorded at (a) 80°C.

Similarly, the measurements were carried out for 160°C TSL peak of annealed sample (above 500°C) which shows the first order kinetics. The activation energy of this glow peak (160°C) shows a value of 0.709 ± 0.004. Thus, it is clear that the order of kinetics only changes and the energy values remains the same.

3.5 Initial rise method

For the investigation by Initial rise method, the quantity of material is divided into two parts after the irradiation; one part can be used to record the full TSL glow peak under evaluation, the remaining part can be heated repeatedly many number of times in such a way that each heating is terminated at a temperature where the TSL intensity reached is hardly 10% of the peak intensity recorded in the first experiment. Series of partial readings are made for each treated sample, with a rapid cooling after each reading. A study of high temperature peaks was performed after a thermal treatment of the sample which empties the traps corresponding to the first peak. Thereby a plot of ln*I* versus 1/*T* produces a straight line whose slope gives E/K and E is evaluated.

Figure 5 shows a plot of *lnI verses* 1/*T* for the glow peaks (130°C & 330°C) of a representative sample, which gives a straight line. The similar results are obtained for all the other samples. The average activation energies (E_{if}) obtained by this method shows 0.782 ± 0.003, 1.761 ± 0.004 for unannealed samples and 0.743 ± 0.003, 1.733 ± 0.004 for annealed samples. Similarly, the measurement were carried out for 160°C TSL peak of annealed sample (above 500°C) which shows the activation energy 0.712 ± 0.004. These results are very much similar to those calculated by the previous methods.

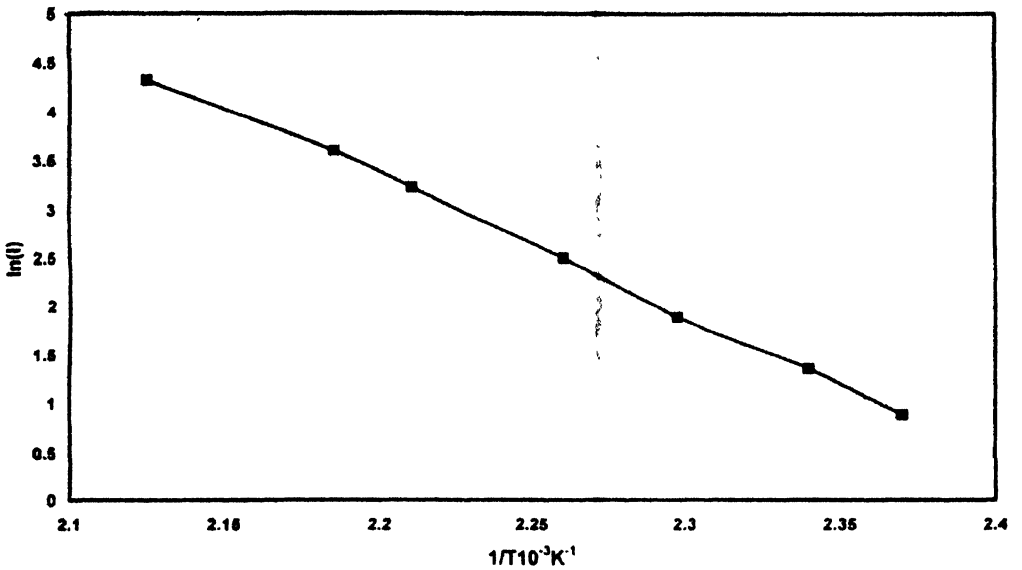

Figure 5. Initial raise plot of 130°C glow peak of natural biogenic shells.

By using the calculated values of activation energies from peak shape and isothermal methods, the averaged out frequency factors of the five samples obtained from the peaks (130°C, 330°C) show 2.712×10^{10}, 1.789×10^{19}, 2.017×10^{10}, 1.183×10^{19} for unannealed samples and 2.420×10^{10}, 1.347×10^{19}, 2.320×10^{10}, 1.431×10^{19} for annealed samples respectively.

Thus, the result shows clearly that there is no difference between the values of activation energy of annealed (Below 500°C) and unannealed samples. From this, it is observed that the annealing procedure of the sample does not affect the nature of the trapping centers. By comparing the results obtained by Ponnusamy *et al* [22], for other type of calcite samples, the present results agree very well with their findings. But the order of kinetics is differed with annealing temperature in two categories. The first one follow the second order kinetics below the annealing temperature 500°C and the second one follow the first order kinetics above the annealing temperature 500°C. This may due to the structural disorderness induced by heating above a temperature of 500°C.

3.6 Dose response :

The samples were exposed with different gamma doses. Figures 6 and 7 show the glow curve of biogenic shell sample irradiated with different gamma doses. A systematic shifting of T_m towards the lower temperature side with increase of gamma dose is observed in the case of 130°C. All the samples follow the same trend. The peak maxima shifted towards the lower temperature side with an increase in dose is a clear evidence of the second order kinetics [23,24]. On the other hand, a systematic shifting of T_m towards the higher temperature side with an increase of gamma dose is observed in the case of 160°C peak. The

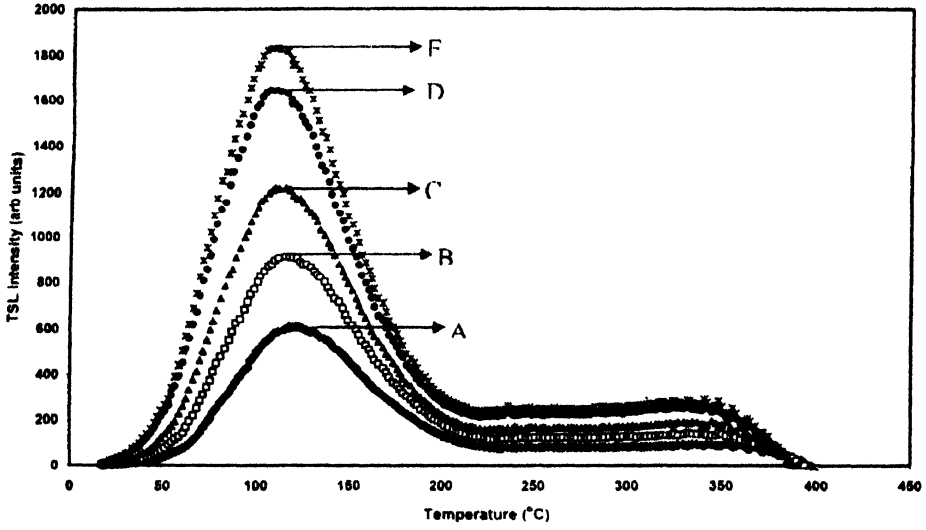

Figure 6. The 130°C glow curve of biogenic shell treated with different gamma doses (A) 880 Gy, (B) 850 Gy, (C) 900 Gy, (D) 950 Gy and (E) 1000 Gy

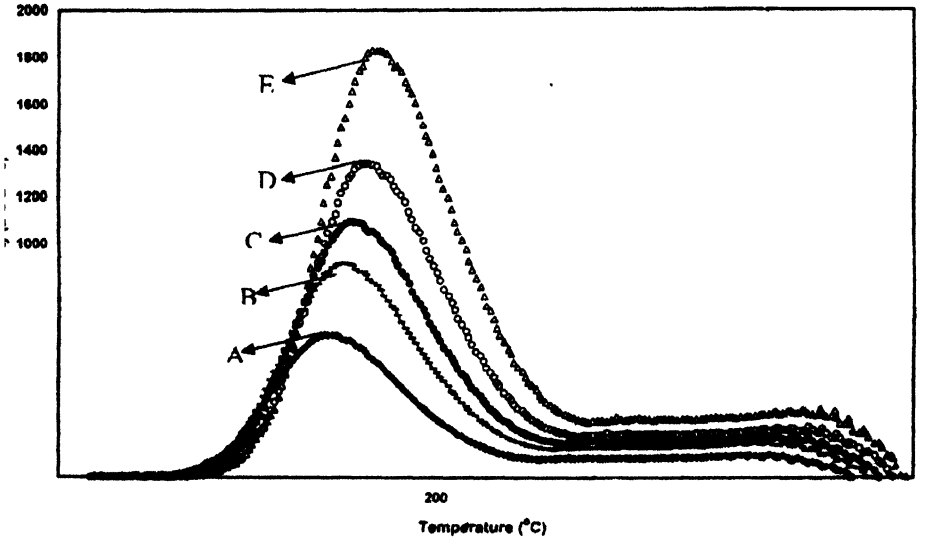

Figure 7. The 160°C glow curve of biogenic shell treated with different gamma doses (A) 880 Gy, (B) 850 Gy, (C) 900 Gy, (D) 950 Gy and (E) 1050 Gy

peak maxima get shifted towards the higher temperature side with an increase of dose is a clear evidence of the first order kinetics [24]. This result exactly matches with the previous methods as discussed elsewhere.

4. Conclusion

The natural biogenic shells belonging to Meretrix Castra variety samples, studied in the present work, irradiated with gamma dose after a convenient thermal treatment, show two TSL peaks at 130°C and 330°C, using a linear heating rate of 10°C/sec. The obtained results evidenced that the annealing procedure does not affect the nature of trapping centre. But, the order of kinetics changes with annealing temperature in two different ways.

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