

Thermoluminescent dose reconstruction using quartz extracted from unfired buildings

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Abstract. The use of thermoluminescence (TL) is very useful for application in retrospective dosimetry, that is, for inference of the dose of radiation undergone for some material. The calculation of the lifetime of TL peaks can help to clarify which TL intensity is due to the dose of environmental radiation and which is proceeding from the accident with radiation. In this work, the kinetic order (b), activation energy (Et) and the frequency factor (s) were obtained for quartz samples that had been extracted from unfired buildings. It was observed the occurrence of peaks in the 150 °C – 250 °C range, that corresponds to a range commonly used in retrospective dosimetry, due to its shorter lifetime when compared with TL geological signal. The analysis of the peaks was done through several well known methods, namely the peak shape (PS), curve fitting (CF) and heating rate (HR) methods. To confirm the structure of the sample, additional X-ray diffraction was made.

Keywords: Thermoluminescence, quartz, kinetic parameters, retrospective dosimetry

1. Introduction

The retrospective dosimetry for luminescence using ceramics, or materials that had undergone burning during manufacture, as is the case of the brick, roofing tile, amongst others, is one of the kinds to find the cumulative dose due to an accident involving ionizing radiation. Those materials contain quartz (SiO₂), a thermoluminescent sensitive one that belongs to the family of silicates [1].

Thermoluminescence has been applied for dosimetry of ionizing radiation since 1940's, when the number of workers exposed to this type of radiation was increasing and efforts had been made in developing new types of dosimeters [2]. However, materials not annealed, as mortar and concrete, are commonly found in industrial places and, particularly, in nuclear installations. These materials also contain quartz, that is normally less thermoluminescent sensitive than the quartz found in annealed materials. Therefore, now the interest is come back toward the use of construction materials, to extend the application scope, being one of the new challenges of retrospective dosimetry. Thus, the main goal of retrospective dosimetry is the development of a trustworthy methodology for the reconstruction of the dose received by construction materials in a radioactive accident [3].

The kinetic parameters of the thermoluminescent peaks are important to characterize the material, as they allow getting the lifetime of those peaks. These parameters are: the kinetic order (b), the activation energy (E_a) and the frequency factor (s). There are three primary requirements for the usage of these natural dosimeters:

- Absence of an accumulated saturated natural dose from the geological period;
- The ability to hold back a register of the exposition to the accident, with worthless fade-out, in the interval between exposition and measurement;
- The ability to determine the cumulative dose of natural sources of radiation.

Quartz is one of materials that match all those requirements.

This work has for purpose to present a methodology for attainment of the extracted quartz grains from mortar and techniques to evaluate the sample, as well as kinetic parameters, in the temperature range of 150 – 250 °C, commonly used in retrospective dosimetry. Through X-ray diffraction (XRD), it was possible to determine the constituents of the sample, and the kinetic parameters had been evaluated using the peak shape (PS), curve fitting (CF) and heating rate (HR) methods, that allow calculating the lifetime of the peaks.

2. Materials and methods

2.1. Sample preparation and TL measurement

The first stage in retrospective dosimetry requires the separation of the present quartz in the sample. In this work, common mortar of construction was chosen. So, the mortar was pulverized to allow a better penetration of chemical agents used in removal of undesirable residues. The powder was then treated in a concentrated HCl + HNO₃ solution during 2 hours, to dissolve the present organic material. To this followed a wash with distilled water and an acid treatment to dissolve calcite, often found in this kind of sample. A new wash in distilled water was made. Finally, the sample was dry in a greenhouse at room temperature for 24 hours.

Grains with sizes between 75 – 200 µm were chosen and then shared in two parts, one for measurement of natural TL emission, increased of an artificial dose of 300 Gy of beta radiation, and another for measurement of TL emission after an annealing of 400 °C for 1 hour, plus additional dose of 300 Gy of beta radiation. The samples had been irradiated with a ⁹⁰Sr/⁹⁰Y, with dose rate of 0,376 Gy/min during 13,3 hours.

Thermoluminescent signal of samples was taken immediately after irradiation in a homemade TL reader. The reader is composed by a platinum plate, whose function is store the sample for the heating. This plate is enclosed in a drawer to prevent noise from external light. The plate is connected to the exit of a transformer, connected in the potency module. That potency module is linked to a signal converter. With the aid of software developed at the Physics Department, the current is controlled with a constant heating rate during the TL measurement. The current is controlled and monitored through a Chromel-Alumel thermocouple, that sends the tension sign to the computer through signal converter, the material emits light, which is captured by a EMI 9789-B photomultiplier. This photomultiplier is fed by a source of high variable tension (0 - 3000 KV).

2.1.1. *Kinetic order.* By the PS method it was found that the peaks obey first order kinetics. This is in concordance with descriptions found in literature [2].

2.1.2. *Peak shape methods.* The method based on the shape of the peak utilizes just two or three points from the glow-curve. Usually, these are the maximum of the peak T_m and either, the low and high temperature half-heights at T_1 and T_2 (see figure1).

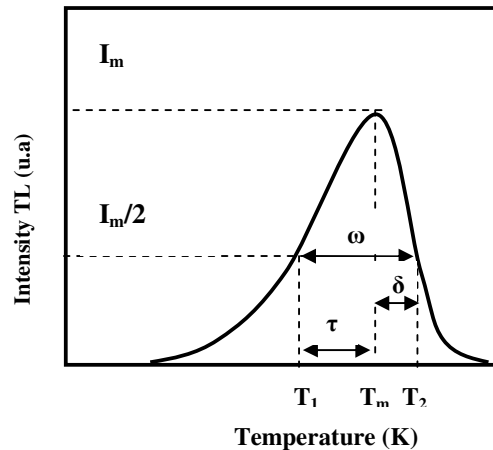


Figure 1 A schematic thermoluminescence peak showing the maximum temperature T_m , the low and high temperatures of half intensity T_1 and T_2 and the half widths $\omega = T_2 - T_1$, $\delta = T_2 - T_m$ and $\tau = T_m - T_1$.

However, because the shape of the peak is strongly affected by kinetics order then the method is dependent on the order of kinetics. Starting from a great number of formulas for the cases of first and of second order several of these methods were appearing.

It was Chen (1969) who analyzed those methods and obtained a complete expression [5]. Chen's equation will be quoted here. Chen (1997) gives three equations each for first- and second-order peaks, relating the trap depth to either the full width of the peak at its half-height ($\omega = T_2 - T_1$), its low-temperature half-width ($\tau = T_m - T_1$), or its high-temperature half-width ($\delta = T_2 - T_m$).

A general formula for E was given namely:

$$E = c_y (kT_m^2 / y) - b_y (2kT_m) \quad (1)$$

where y is ω , τ or δ . The constant c_y and b_y for the three methods, for general order kinetics, are given in table 1. The geometrical factor $\mu_g = \delta/\omega$ will give a value of 0.42 for 1st order kinetics and 0.52 for 2nd order kinetics[3].

Table 1 – c_y and b_y values for first order kinetics

	ω	τ	δ
c_y	2,52	1,51	0,976
b_y	1,0	1,58	0

2.1.3. Curve fitting method. The most popular model of thermoluminescence is based on the two levels model, on trap-one recombination centre, which allows writing equations describing a single TL peak, i.e., the first- and the second-order kinetics equations [5]. In the first order it is assumed that only recombination is present, while which in the second it is assumed that recombination and retrapping are both present. Since in this work only 1st order kinetics will be analyzed, only the first-order kinetics equation will be given:

$$I(T) = n_0 s \exp(-E/kT) \times \exp \left[-(s/\beta) \int_{T_0}^T \exp(-E/kT) dT \right] \quad (2)$$

where $I(T)$ is the glow-peak intensity, E (eV) the activation energy, s (s^{-1}) the frequency factor, n_0 (cm^{-3}) the initial concentration of the trapped charges, k ($eV K^{-1}$) the Boltzmann constant, T (K) the absolute temperature, T_0 (K) the initial temperature and β ($K s^{-1}$) is the constant heating rate. For numerical calculations of TL intensity it is necessary to evaluate the integral

$$F(T, E) = \int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT, \quad (3)$$

This integral can be solved by successive integrations by parts, giving then

$$F(T, E) = T \exp\left(-\frac{E}{kT}\right) \sum_{n=1}^{\infty} \left(\frac{kT}{E}\right)^n (-1)^n n! \quad (4)$$

However, in the most practical cases only the following simple expression is considered:

$$F(T, E) = \frac{kT}{E} \exp\left(-\frac{E}{kT}\right) \left(1 - \frac{2kT}{E}\right) \quad (5)$$

The computed curve is then compared with the actual experimental curve and a root-mean-square (RMS) deviation between the two is calculated. The procedure continues by sequentially changing the E , s and b values until a minimum value of the RMS deviation is reached [5].

2.1.4. Heating rate method. This method considers the temperature of maximum of one peak. Varying the heating rate, the peak position shifts to higher values. Applying several heating rates, one can obtain the values of E and s by plotting

$$\ln\left(\frac{T_m^2}{\beta}\right) \times \left(\frac{1}{T_m}\right) \quad (6)$$

and calculating the values of the angular and linear coefficients of the straight line given by (6).

In the other cases, the frequency factor can be calculated through

$$s = \frac{\beta E_\gamma}{kT_m^2} \exp\left(\frac{E_\gamma}{kT_m}\right) \quad (7)$$

and the lifetime is given by

$$\tau = s^{-1} \exp(E/kT) \quad (8)$$

3. Results and discussion

Figure 2 shows the TL glow curve of quartz extracted from cement, with thermal annealing of 400 °C/1h, and without annealing, both irradiated with a dose of 300 Gy and held in a constant heating rate of 5 K/s.

3.1. Peak Shape

Figure 3 shows the TL glow curves of the peaks with temperature of maximum between 150-250 °C. For attainment of these curves, it was necessary to make a thermal cleaning [5], with intention of isolate the TL peaks for analysis, since quartz present several overlapping peaks. After the thermal cleaning, the geometrical factor was calculated, resulting in a value of 0.42 for both curves, indicating 1st order kinetics. The values of activation energy, frequency factor and lifetime of those peaks are shown in table 2.

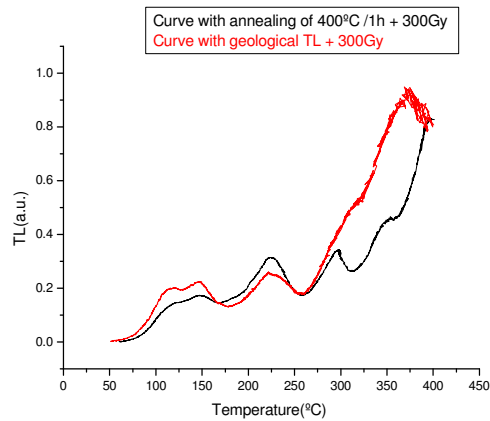


Figure 2 – TL glow curve of quartz, irradiated with a dose of 300 Gy.

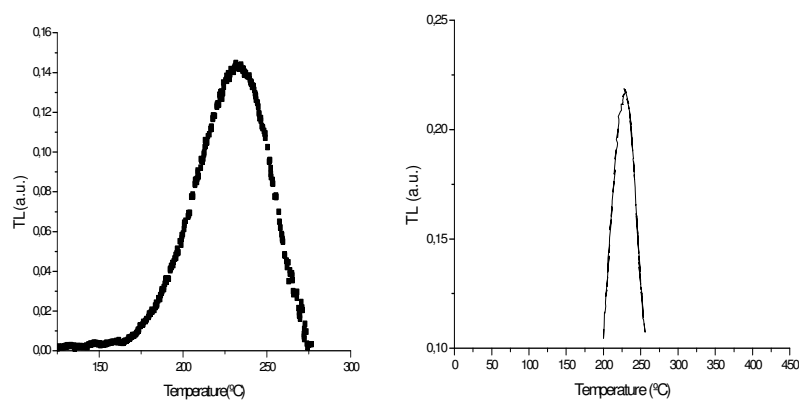


Figure 3 – Quartz TL glow curve with and without thermal annealing, respectively.

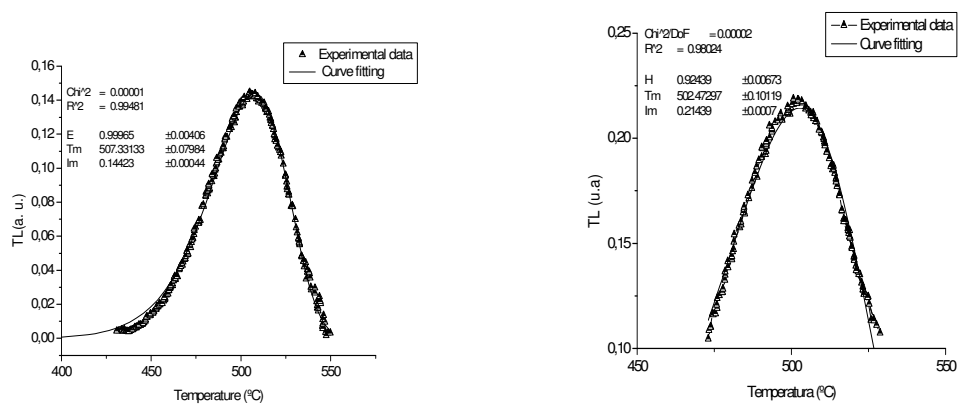


Figure 4 – Adjusted TL glow curve for the peaks between 150 and 250 °C

3.2. Curve fitting

Figure 4 shows the experimental curve and the adjusted curve for 1st order kinetics. The correct application of this method demands that the peak is completely isolated of the adjacent peaks, as well as in the peak shape method. The frequency factor was gotten indirectly through the equation (7). The values are also shown in table 2.

3.3. Heating rate method

The biggest advantage of this method is that it's needed only the data of maximum intensity (I_m , T_m), with no necessity of a thermal cleaning process as in the previous methods. To the application of this method, heating rates of $2^\circ\text{C}/\text{s}^{-1}$, $4^\circ\text{C}/\text{s}^{-1}$, $5^\circ\text{C}/\text{s}^{-1}$, $8^\circ\text{C}/\text{s}^{-1}$, $10^\circ\text{C}/\text{s}^{-1}$ were utilized.

Figure 5 shows the resulting straight lines for the peaks with and without annealing, respectively

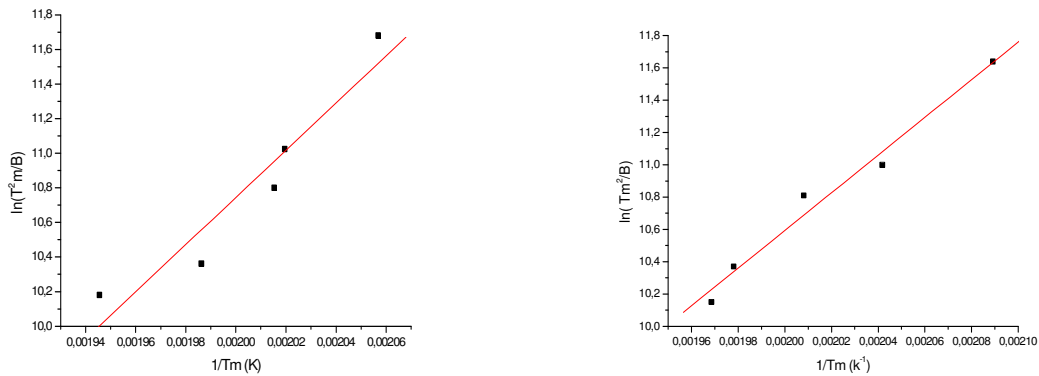


Figure 5 – Heating rate method for the quartz samples with and without annealing, respectively.

4. X-ray diffraction

The verification of the crystalline phases of the sample was made through x-ray diffraction measurements. The Rietveld method [8] was used to make the refinement with the powder diffraction pattern, and software (DBWS9807) was utilized as described by Young et al. [9]. The full width at half maximum of all peaks, as well as asymmetric coefficients, scale factor, lattice parameters and polynomial parameters of the background line were refined.

The refinements of data obtained through analysis of the XRD pattern are shown in figure 6. One of the samples utilizes the mechanism described in [3] and [12], as well as [10]. In another sample, we have utilized the method described here.

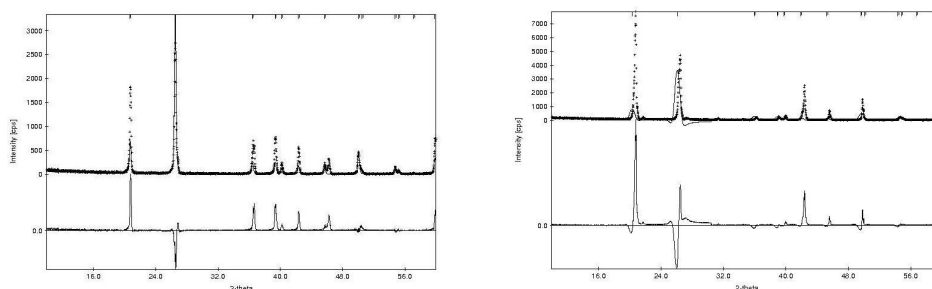


Figure 6 – XRD experimental curve with theoretical refinement for the samples

Quartz belongs to a trigonal crystalline system, P3₂21 spatial group. The data from refinement indicates the following crystallographic parameters: $a = b = 4.9130(5) \text{ \AA}$, $c = 5.4050(2) \text{ \AA}$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The values of expected error (R) and obtained error (R-WP) had been for the sample with regal-water, 4.05% e 13.45%, respectively, and for the conventional method, 38.05% e 46.45%, respectively. The R-WP/R ratio was 3.31, a very good value due to the crystalline degree of quartz. The obtained error indicates that the calculated diffractogram for the sample with regal-water presents 88.55% of similarity with the experimental diffractogram.

The tables 2, 3-a and 3-b summarizes the results obtained in this work. As can be seen, there exist a good agreement between the results through the applied methods. Comparing our results with those found in literature, a good agreement is also found.

Table 2- Kinetic parameters of peaks between 150°C e 250°C of quartz extracted from mortar without annealing.

Peak temperature (°C)	Activation energy (eV)	Frequency factor (s ⁻¹)	Method	Lifetime at 15°C (years)
234±1	0,96±0,02	(4,03±1,73)x 10 ⁸	PS	(2,8±0,6)
234±1	0,99	(1,52)x10 ⁹	CF	4,3
-	1,17	(2,1)x10 ¹¹	HR	47,1

Table 3-a - Kinetic parameters of peaks between 150°C e 250°C of quartz extracted from mortar with annealing (400 °C/1h)

Peak temperature (°C)	Activation energy (eV)	Frequency factor (s ⁻¹)	Method	Lifetime at 15°C (years)
232±1	0,910±0,002	(2,53±0,15)x10 ⁸	PS	(1,08±0,04)
229±1	0,92	(3,64)x10 ⁸	CF	1,09
-	1,00	(3,88)x10 ⁹	HR	3,10

Table 3-b - Kinetic parameters of 225°C peak of not annealed quartz.

Peak temperature (°C)	Activation energy (eV)	Frequency factor (s ⁻¹)	Method	Lifetime at 15°C (years)
225±1	1,16±0,06	(1,2±1,6)x10 ¹¹	PS	(50±40)
225±1	1,16±0,06	(1,17±0,20)x10 ¹¹	CF	(50±10)

5. Conclusions

The methodology developed in the sample preparation of the extracted mortar of construction materials was efficient due to the oxidation power of the regal-water. The methods applied in the attainment of kinetic parameters have shown good results. The geological TL present in quartz in the range of temperature commonly used for retrospective dosimetry was very small, due to its very short lifetime. Through refinement of the data of XRD by Rietveld method, we could verify just one crystallographic phase and to calculate the grain size of this material. The peak found between 150 and 250 °C has demonstrated sufficient stability for its use in dosimetry of radioactive accidents. The usage of construction material not burnt, as mortar and concrete, can be used in a trustworthy way in retrospective dosimetry.

6. Acknowledgements

The authors acknowledge to the Fundação de Apoio a Pesquisa e a Inovação Tecnológica de Sergipe (FAPITEC-SE), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support and to the Instituto de Pesquisas Energéticas e Nucleares (IPEN-SP) for the sample irradiation.

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