Applied Radiation and Isotopes 153 (2019) 108843

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Thermoluminescence glow curve deconvolution for discrete and continuous trap distributions

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HIGHLIGHTS

- New software for thermoluminescence glow curve deconvolution has been developped.
- Accurate algebraic equations for first order and general order kinetics have been obtained.
- New equation for a continuous trap distribution has been obtained.
- Both discrete and continuous trap equations, the considered parameters can be estimated from the glow curve analysis.
- Results with simulated glow curve is presented and discussed.

ARTICLE INFO

Keywords:
Thermoluminescence
Glow curve
Deconvolution
Thermoluminescent dosimetry

ABSTRACT

Deconvolution analysis of the thermoluminiscent (TL) glow curves proved to be a good complementary method to characterize the individual glow peaks by fitting their kinetic parameters. In this work, new software has been developed for the automatic deconvolution of TL glow curves, assuming either discrete or continuous distribution of trapping centres. The guess estimation of the kinetic parameters is done automatically and can be manually modified, thus allowing the use of the software for routine, processing a large number of measurements, as well as for research purposes. The equations, the methods and the results of the first test are described in detail. The software has been developed by integrating Fortran code and Visual Studio tools to create a graphic easy-to-use environment and permits to obtain the fitted values for the parameters according to the considered model.

1. Introduction

The analysis of thermoluminescence (TL) glow curves (GC) has been extensively used to characterize the glow peak structure over some thirty years (Horowitz and Yossian, 1995), starting from early works using first order kinetics and simplifications like Podgorsak approximation (McKeever, 1980; Horowitz and Moscovitch, 1986; Delgado and Gómez-Ros, 1988, 1990) to recent advances dealing with theoretical and practical considerations about peaks overlapping (Sadek and Kitis, 2018; Kitis and Pagonis, 2019). The fitting methods depend on the assumed models for TL emission, their mathematical equations and the corresponding parameters that permit to describe quantitatively the GC. Because of the complexity of the models dealing with multiple trapping and recombination centres that cannot permit to obtain explicit equations for TL emission, first order kinetics (FOK) (Muñiz et al., 1995; Gómez-Ros et al., 1999; Puchalska and Bilski, 2006) and general order kinetics (GOK) (Gómez-Ros et al., 2002a; Gómez-Ros and Kitis, 2002) are commonly used in the glow curve deconvolution software.

In all the cases, fitting procedures require a first estimation for the parameters, accurate enough to get convergence and such estimation needs to be automatically obtained when a large number of GCs is going to be analysed. Moreover, either discrete or continuous distribution of traps can be found in TL materials (McKeever, 1988), making more difficult to obtain a guess estimation for the kinetic parameters directly from the GC shape in case of a continuous distribution.

This communication describes the TL equations, methods and results of newly developed automatic glow curve deconvolution software, suitable to analyse TL glow curves assuming FOK, GOK and continuous distributions of trapping centres. The analysis of discrete trap distribution is mainly based on previous works for FOK (Muñiz et al., 1995; Gómez-Ros et al., 1999) and GOK (Gómez-Ros and Kitis, 2002) but adding an improved capability for the automatic detection of individual glow peaks and the automatic initial guess estimation of fitting parameters. For the continuous distribution of traps, an entirely new

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https://doi.org/10.1016/j.apradiso.2019.108843
Received 26 March 2019; Received in revised form 19 July 2019; Accepted 5 August 2019
Available online 05 August 2019
0969-8043/

method has been developed.

2. Materials and methods

2.1. Fitting equations

The TL intensity for a glow peak following first order kinetics (FOK), i.e. when retrapping probability is negligible, is given in case of linear heating by the equation (McKeever, 1988):

$$I(T) = s\, n_0 \exp\left(-\frac{E}{kT}\right)\exp\left\{-\frac{s}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right\} \quad (1)$$

where n_o is the initial density of trapped charge carriers, s is the frequency factor, k is the Boltzmann constant, E is the activation energy and $T(t) = T_0 + \beta t$ is the linear heating profile. The kinetics parameters (E, s, n_0) can be replaced by the set of parameters (E, T_M, I_M), where the temperature and intensity of the maximum, T_M and I_M, are obtained from the maximum condition (dI/dT) = 0 thus giving:

$$\frac{E}{K\,T_M^2} = \frac{s}{\beta}\exp\left(-\frac{E}{K\,T_M}\right) \quad (2)$$

so equation (1) becomes:

$$I(T) = I_M \exp\left(\frac{E}{kT_M} - \frac{E}{kT}\right)\exp\left\{-\frac{E}{kT_M^2}\int_{T_M}^{T}\exp\left(\frac{E}{kT_M} - \frac{E}{kT'}\right)dT'\right\} \quad (3)$$

The use of (E, T_M, I_M) to characterize individual glow peaks instead of (E, s, n_0) is more convenient as they all three have a geometrical meaning (width, position and intensity, respectively) so it is easier to get a first estimation from the analysis of the glow curve shape, in particular using the calculated 1st and 2nd derivatives and their local minima, as it will be explained in next section.

The integral appearing in equations (1) and (3) can be expressed in terms of the exponential integral function of second order $E_2(x)$ (Abramowitz and Stegun, 1980):

$$\int_{T_M}^{T}\exp\left(\frac{E}{kT_M} - \frac{E}{kT'}\right)dT' =$$

$$= T\exp\left(\frac{E}{kT_M}\right)E_2\left(\frac{E}{kT}\right) - T_M\exp\left(\frac{E}{kT_M}\right)E_2\left(\frac{E}{kT_M}\right) =$$

$$= \exp\left(\frac{E}{kT_M} - \frac{E}{kT}\right)T\exp\left(\frac{E}{kT}\right)E_2\left(\frac{E}{kT}\right) - T_M\exp\left(\frac{E}{kT_M}\right)E_2\left(\frac{E}{kT_M}\right) \quad (4)$$

Because of the integral cannot be solved in an analytical form, asymptotic approximations have been used in previous works (Chen and McKeever, 1997; Kitis et al., 1998). Alternatively, $E_2(x)$ can be evaluated using rational approximations as the following (Abramowitz and Stegun, 1980):

$$\exp(x)E_2(x) \approx R(x) = 1 - \frac{0.250621 + 2.334733x + x^2}{1.681534 + 3.330657x + x^2} \quad (5)$$

As it is discussed in the annex, the rational approximation (5) is more accurate than the asymptotic one for values of E/kT < 50. Moreover, the comparison between the values obtained using equation (5) and the built-in implementation of $E_2(x)$ in Matlab and Maple shows a relative discrepancy lower than 0.4% within a wide range (0.5 < E/kT < 600), that covers the combination of E and T usually found and it is low enough to be used for fitting purposes.

Then, equation (4) is can be written as:

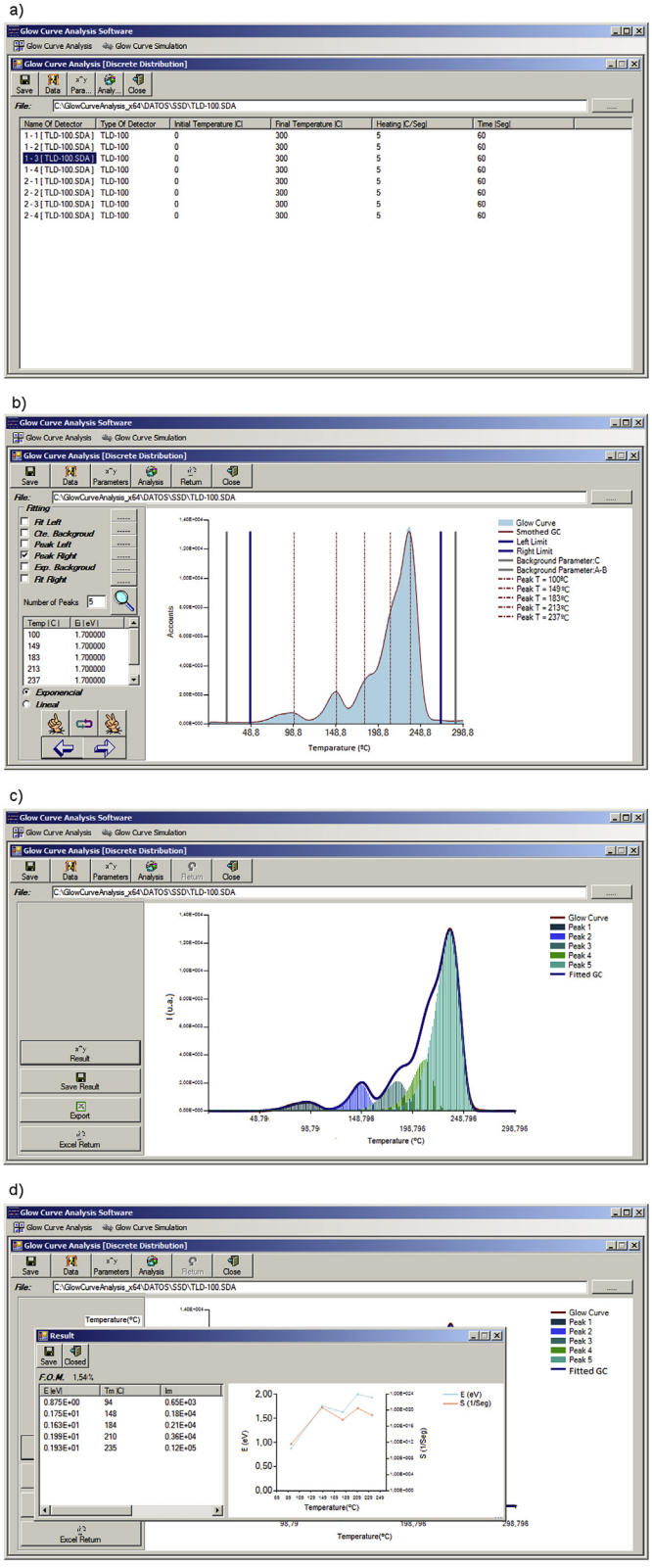

Fig. 1. Example of the deconvolution software work flow: a) file(s) selection; b) graphical parameter estimation; c) fitted glow curve; d) fitted parameters.

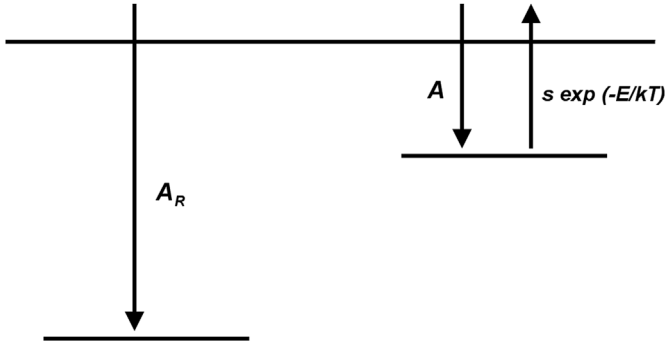

Fig. 2. Schematic energy levels and transitions scheme corresponding to one electron trap and one recombination centre (OTOR). The parameters are described in the text.

Table 1
Kinetic parameters values used to simulate the glow peak due to a continuous trap distribution. For every value of E_0, two values of s and five values of σ have been considered ($6 \times 2 \times 5 = 60$ combinations of values, either for an exponential and a Gaussian distribution).

distribution type	n_0 (cm^{-3})	E_0 (eV)	s (s^{-1})	σ
exponential	10^6	0.60	10^6, 10^7	0.05, 0.075, 0.1, 0.125,
		0.80	10^8, 10^9	0.15
		1.00	10^{10}, 10^{11}	
		1.20	10^{12}, 10^{13}	
		1.40	10^{14}, 10^{15}	
		1.60	10^{16}, 10^{17}	
Gaussian	10^6	0.80	10^6, 10^7	0.05, 0.063, 0.076,
		1.00	10^8, 10^9	0.089, 0.102
		1.20	10^{10}, 10^{11}	
		1.40	10^{12}, 10^{13}	
		1.60	10^{14}, 10^{15}	
		1.80	10^{16}, 10^{17}	

Table 2
Comparison between the fitted and reference T_M, E and area values for the glow curve REFGLOW.001 (β = 1 K/s). FOM is compared with the values obtained by the participants in the GLOCANIN project.

parameter		peak
T_M (K)	reference	490.5
	fitted	490.6
	deviation	0.02%
E (eV)	reference	1.1824
	fitted	1.1798
	deviation	−0.22%
area (a.u.)	reference	490003
	fitted	489299
	deviation	−0.14%
FOM	GLOCANIN	0.010%–3.98%
	fitted	0.017%

$$\int_{T_M}^{T} \exp\left(\frac{E}{kT_M} - \frac{E}{kT'}\right)dT' = \\ = \exp\left(\frac{E}{kT_M} - \frac{E}{kT}\right) T\, R\left(\frac{E}{kT}\right) - T_M\, R\left(\frac{E}{kT_M}\right) \quad (6)$$

and equation (3) can be rewritten as

Table 3
Comparison between the fitted and reference T_M, E and area values for the glow curve REFGLOW.002 (β = 8.4 K/s). FOM is compared with the values obtained by the participants in the GLOCANIN project.

parameter		peak 2	peak 3	peak 4	peak 5
T_M (K)	reference	417.2	456.6	484.1	511.7
	fitted	417.3	456.6	484	511.7
	deviation	0.05%	0.00%	−0.02%	0.00%
E (eV)	reference	1.3834	1.4833	1.5832	2.0038
	fitted	1.382	1.4819	1.5808	1.9911
	deviation	−0.10%	−0.09%	−0.15%	−0.63%
area (a.u.)	reference	11100	16898	27401	47302
	fitted	11094	16859	27229	47535
	deviation	−0.05%	−0.23%	−0.63%	0.49%
FOM	GLOCANIN	0.01%–4.46%			
	fitted	0.06%			

Table 4
Fitted T_M, E and area values for the glow curve REFGLOW.010 (β = 6 K/s). Because of this is an experimentally measured curve, only the FOM is compared with the values obtained by the participants in the GLOCANIN project.

parameter		peak 2	peak 3	peak 4	peak 5
T_M (K)	fitted	415.0	454.2	482.3	509.5
E (eV)	fitted	1.281	1.462	1.441	2.118
area (a.u.)	fitted	4278	4220	6606	9636
FOM	GLOCANIN	4.12% – 8.22%			
	fitted	3.15%			

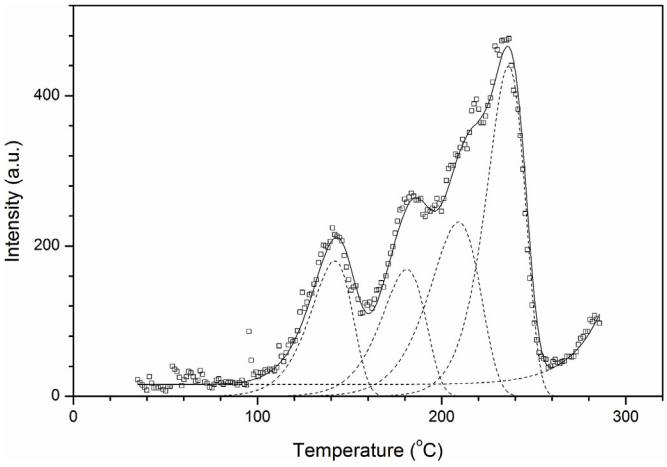

Fig. 3. Glow curve fitting of the reference GC REFGLOW.010.

$$I(T) = I_M \exp\left(\frac{E}{kT_M} - \frac{E}{kT}\right)\cdot \\ \cdot\exp\left\{-\frac{E}{kT_M}\left[R\left(\frac{E}{kT_M}\right) - \frac{T}{T_M}\exp\left(\frac{E}{kT_M} - \frac{E}{kT}\right)R\left(\frac{E}{kT}\right)\right]\right\} \quad (7)$$

that includes only algebraic operations so it is adequate to be used in fitting algorithms where many iterative evaluations are required.

For general order kinetic (GOK) and a linear heating rate, β, the TL intensity is given by (McKeever, 1988):

$$I(T) = s\, n_0 \exp\left(-\frac{E}{K\,T}\right)\left\{1 + (b-1)\frac{s}{\beta}\int_{T_0}^{T_M}\exp\left(-\frac{E}{K\,T'}\right)dT'\right\}^{-\frac{b}{b-1}} \quad (8)$$

where b is the kinetic order. The kinetic parameters s and n_0 can be

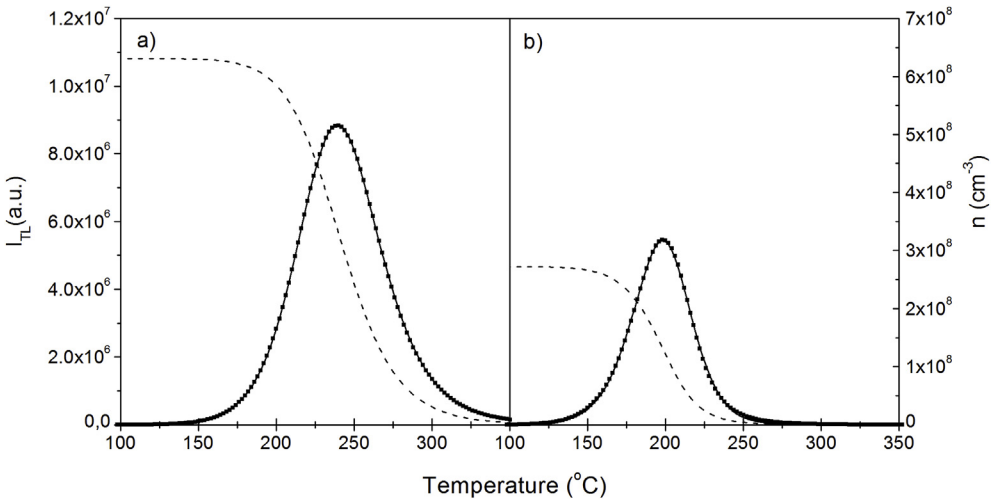

Fig. 4. Fitting results for GOK glow curves assuming a) recombination/retrapping ratio = 1, $A = A_R$; and b) dominant recombination, $A < A_R$. approximations conditions. In both cases, squares are the simulated glow curve (left y-axis), solid line is the fitted GC (left y-axis) and dashed line is the concentration of trapped carriers (right y-axis).

Table 5
Comparison between the fitted and reference E values for two glow curve simulated assuming the OTOR model and fitted by the GOK equation. The fitted kinetic order, b, is also compared with the trapping and recombination probabity values, respectively A and A_R.

parameter		$(A = A_R)$	$(A < A_R)$
A (cm^3s^{-1})	reference	10^{-7}	10^{-9}
A_R (cm^3s^{-1})	reference	10^{-7}	10^{-7}
b	fitted	2.00	1.58
E (eV)	reference	1.20	1.20
	fitted	1.19	1.28
	deviation	−0.5%	6.8%
FOM	fitted	0.26%	2.3%

again replaced by the temperature and intensity of the maximum, T_M and I_M, applying the condition $(dI/dT) = 0$:

$$\frac{E}{K \cdot T_M^2}\left\{1 + (b-1)\frac{s}{\beta}\int_{T_0}^{T_M} exp\left(-\frac{E}{K\,T'}\right)dT'\right\} = \frac{s}{\beta}\exp\left(-\frac{E}{K\,T_M}\right) \quad (9)$$

and now equation (7) can be rewritten as:

$$I(T) = I_M \exp\left(\frac{E}{K\,T_M} - \frac{E}{K\,T}\right)\cdot \left\{1 + \left(\frac{b-1}{b}\right)\frac{E}{K\,T_M}\int_{T_M}^{T}\exp\left(\frac{E}{kT_M} - \frac{E}{kT'}\right)dT'\right\}^{\frac{-b}{b-1}} \quad (10)$$

where the four parameters (T_M, I_M, E, b) have a geometrical meaning in the peak (position, intensity, width and symmetry respectively). equation (9) can be also rewritten using the rational approximation (4,5) resulting:

$$I(T) = I_M \exp\left(\frac{E}{KT_M} - \frac{E}{KT}\right)\cdot \left\{1 + \left(\frac{b-1}{b}\right)\frac{E}{KT_M}\left[\left(\frac{T}{T_M}\right)exp\left(\frac{E}{K\,T_M} - \frac{E}{K\,T}\right)R\left(\frac{E}{kT}\right) - R\left(\frac{E}{kT_M}\right)\right]\right\}^{\frac{-b}{b-1}} \quad (11)$$

All the equations considered above, either for first order or general order kinetics, describe the TL emission due to discrete trapping centres, characterized by single values of activation energy E and frequency factor, s. The TL can also arise from an energy distribution of traps, $n(E)$. Assuming first order kinetics and a linear heating rate, β, the TL is given by (Kitis and Gómez-Ros, 2000; Chen and McKeever, 1997; Gómez-Ros et al., 2006c):

$$I(T) = \int_{E_1}^{E_2} s\,n(E)\exp\left(-\frac{E}{K\,T}\right)\exp\left\{-\frac{s}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{K\,T'}\right)dT'\right\}\cdot dE \quad (12)$$

Following previous works (Gómez-Ros et al., 2006a), two mathematical forms of the trap distributions have been considered: an exponential and a Gaussian distribution. For the Gaussian distribution, the trap density is:

$$n_{Gauss}(E) = \frac{n_0}{\sqrt{2\pi}\,\sigma}\,e^{-\frac{(E-E_0)^2}{2\sigma^2}} \quad (13)$$

and for the exponential distribution, it is:

$$n_{exp}(E) = \frac{n_0}{\sigma}\,e^{-\frac{E-E_0}{\sigma}} \quad (14)$$

where n_0 is the total concentration of trapped charges, and E_0 and σ are constant describing the position and width of the distribution.

In the case of a continuous traps distribution, the conditions for the temperature and intensity of the maximum, $(dI/dT)_{T=T_M} = 0$, $I(T_M) = I_M$ applied to equation (11) does not permit to rewrite it explicitly in terms of T_M and I_M. Nevertheless, it is possible to define two new parameters, T_N and I_N, fulfilling the conditions:

$$\frac{E}{K\,T_N^2} = \frac{s}{\beta}\exp\left(-\frac{E}{K\,T_N}\right) \quad (15)$$

$$I(T_N) = I_N \quad (16)$$

It should be noted that neither T_N is the temperature of the maximum nor I_N is the corresponding maximum intensity but, as it will be detailed in section 3, it has been found they are close enough to T_M and I_M values respectively to be use as a guess estimation for the fitting of a glow curve due to a continuous traps distribution.

Using definitions (14) and (15), it is possible to rewrite equation (11), both in case of Gaussian and exponential distribution, replacing s and n_0 by T_N and I_N, thus giving after some algebraic manipulation:

$$I(T) = I_N \cdot \frac{\int_{E_1}^{E_2} f(E)\,exp\left(-\frac{E}{kT}\right)exp\left\{-\frac{E_0}{kT_N}exp\left(\frac{E_0}{kT_N}\right)\int_{T_0}^{T}exp\left(-\frac{E}{kT'}\right)dT'\right\}dE}{\int_{E_1}^{E_2} f(E)\,exp\left(-\frac{E}{kT}\right)exp\left\{-\frac{E_0}{kT_N}exp\left(\frac{E_0}{kT_N}\right)\int_{T_0}^{T_N}exp\left(-\frac{E}{kT'}\right)dT'\right\}dE} \quad (17)$$

where $n(E) = n_0\,f(E)$.

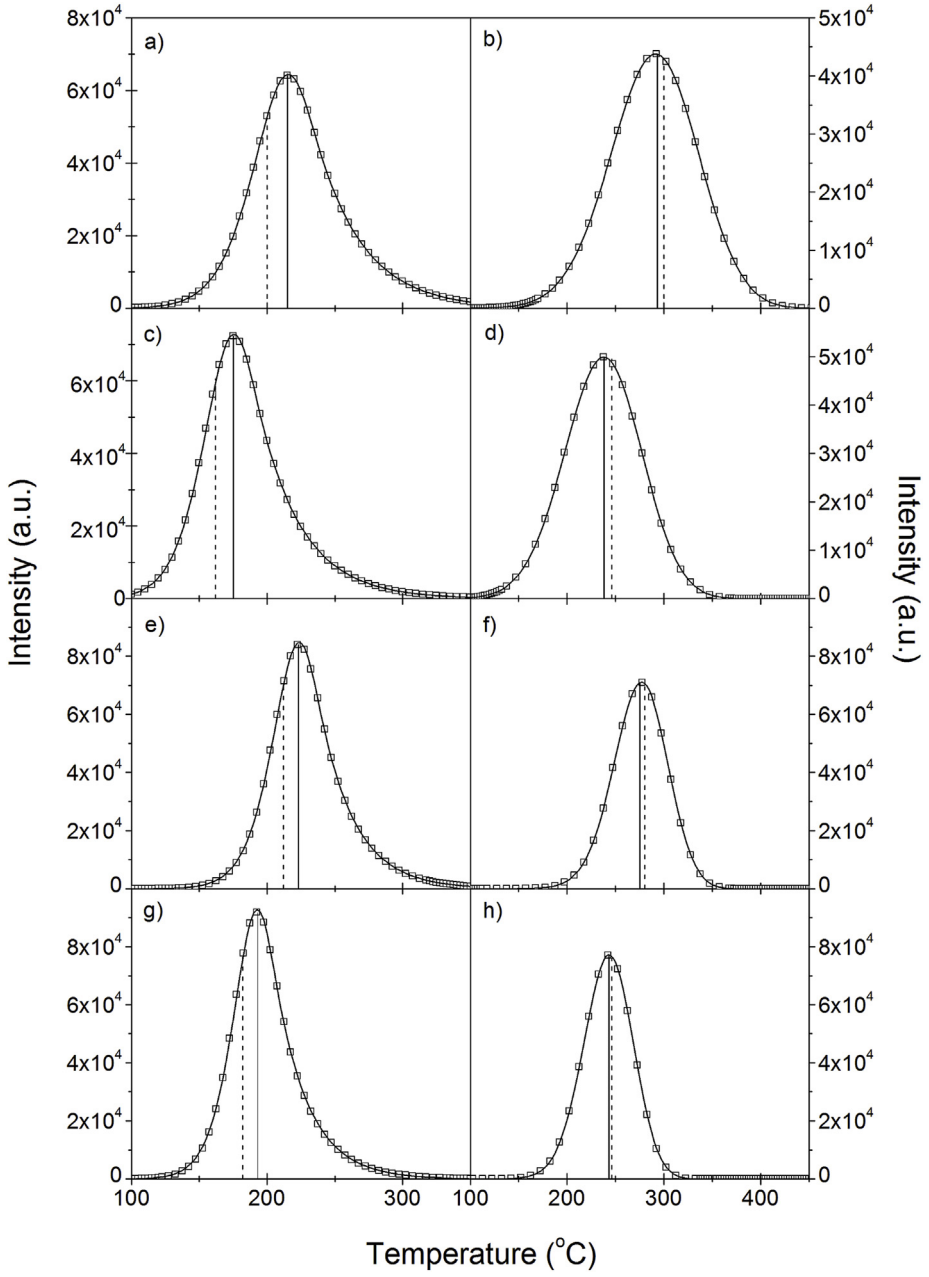

Fig. 5. Fitting of glow curves produced by continuous exponential trap distributions. (σ = 0.075): a) E_0 = 1eV, s = $10^{10}s^{-1}$; c) E_0 = 1eV, s = $10^{11}s^{-1}$; e) E_0 = 1.4eV, s = $10^{10}s^{-1}$; g) E_0 = 1.4eV, s = $10^{10}s^{-1}$; and Gaussian trap distributions (σ = 0.065): b) E_0 = 1eV, s = $10^{8}s^{-1}$; d) E_0 = 1eV, s = $10^{9}s^{-1}$; f) E_0 = 1.6eV, s = $10^{14}\,s^{-1}$ h) E_0 = 1.6eV, s = $10^{15}\,s^{-1}$. In all the cases, squares are the simulated glow curve, solid line is the fitted curve, vertical solid line is the maximum temperature, T_M, and vertical dashed line is the T_N parameter.

Table 6
Comparison between the fitted and reference E_0, σ and *s* values for ten glow curves simulated assuming a continuous exponential distribution of traps (β = 5 K/s).

E_0 (eV)			σ			s (s^{-1})			FOM
ref.	fitted	dev.	ref.	fitted	dev.	ref.	fitted	dev.	
1.00	0.975	−2.5%	0.05	0.049	−1.6%	10^{10}	6.0×10^{9}	−39%	0.57%
1.00	0.967	−3.3%	0.05	0.049	−2.1%	10^{11}	4.7×10^{10}	−52%	0.85%
1.00	0.975	−2.5%	0.075	0.074	−1.6%	10^{10}	6.1×10^{9}	−39%	0.46%
1.00	0.967	−3.3%	0.075	0.073	−2.2%	10^{11}	4.8×10^{10}	−52%	0.66%
1.00	0.975	−2.5%	0.1	0.098	−1.6%	10^{10}	6.1×10^{9}	−39%	0.38%
1.00	0.968	−3.2%	0.1	0.098	−2.3%	10^{11}	4.8×10^{10}	−52%	0.55%
1.00	0.976	−2.4%	0.125	0.123	−1.6%	10^{10}	6.2×10^{9}	−38%	0.33%
1.00	0.968	−3.2%	0.125	0.122	−2.3%	10^{11}	4.9×10^{10}	−51%	0.45%
1.00	0.976	−2.4%	0.15	0.147	−1.7%	10^{10}	6.3×10^{9}	−37%	0.30%
1.00	0.968	−3.2%	0.15	0.146	−2.5%	10^{11}	4.9×10^{10}	−51%	0.47%

Table 7
Comparison between the fitted and reference E_0, σ and s values for ten glow curves simulated assuming a continuous Gaussian distribution of traps (β = 5 K/s).

E_0 (eV)			σ			s (s^{-1})			FOM
ref.	fitted	dev.	ref.	fitted	dev.	ref.	fitted	dev.	
1.00	0.990	−1.0%	0.05	0.050	−0.2%	10^8	8.9×10^7	11%	0.13%
1.00	0.989	−1.1%	0.05	0.050	0.04%	10^9	8.8×10^8	12%	0.17%
1.00	0.990	−1.0%	0.075	0.063	−0.3%	10^8	8.9×10^7	11%	0.10%
1.00	0.989	−1.1%	0.075	0.063	−0.2%	10^9	8.8×10^8	12%	0.13%
1.00	0.987	−1.3%	0.1	0.076	−0.5%	10^8	7.9×10^7	20%	0.08%
1.00	0.988	−1.2%	0.1	0.076	−0.5%	10^9	8.6×10^8	14%	0.10%
1.00	0.986	−1.4%	0.125	0.088	−0.9%	10^8	8.2×10^7	18%	0.07%
1.00	0.976	−2.4%	0.125	0.087	−2.1%	10^9	6.4×10^8	36%	0.09%
1.00	0.974	−2.6%	0.15	0.099	−2.5%	10^8	6.3×10^7	37%	0.07%
1.00	0.960	−4.0%	0.15	0.098	−3.9%	10^9	4.4×10^8	56%	0.09%

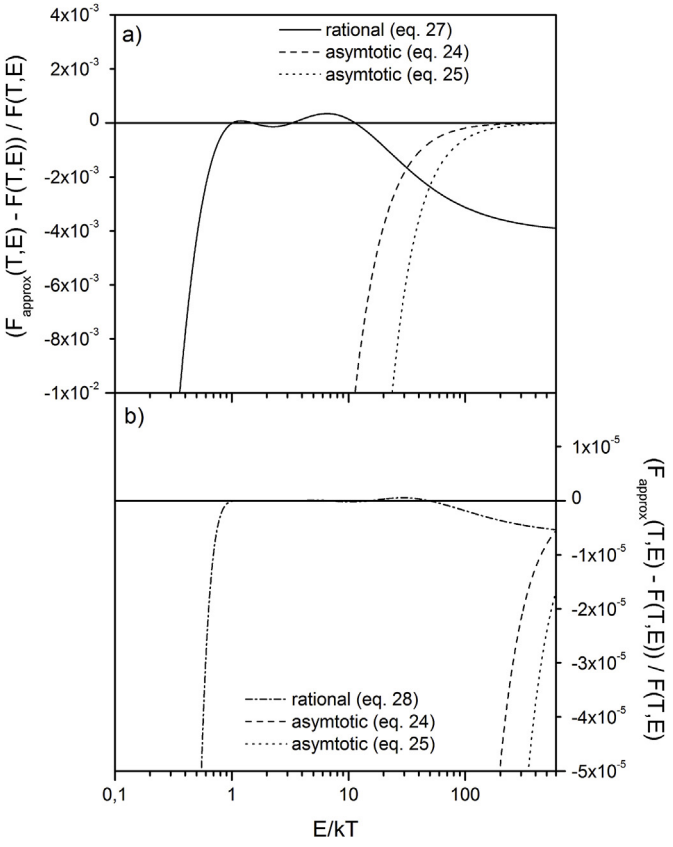

Fig. 6. Comparison of asymptotic and rational approximations to TL integral evaluated using a built-in function of the second order exponential integral, E_2(E/kT). See the text for the discussion.

As it has been done for discrete traps, equation (16) can be rewritten using the rational approximation (4,5), obtaining the equation:

$$I(T) = I_N \cdot \frac{\int_{E_1}^{E_2} f(E)\, exp\left(-\frac{E}{kT}\right) exp\left\{-\frac{E_0}{kT_N}\left(\frac{T}{T_N}\right) exp\left(\frac{E_0}{kT_N} - \frac{E}{kT}\right) R\left(\frac{E}{kT}\right)\right\} dE}{\int_{E_1}^{E_2} f(E)\, exp\left(-\frac{E}{kT}\right) exp\left\{-\frac{E_0}{kT_N} exp\left(\frac{E_0}{kT_N} - \frac{E}{kT_N}\right) R\left(\frac{E}{kT_N}\right)\right\} dE} \quad (18)$$

In both equations (16) and (17), the two energy integrals cannot be solved so they need to be evaluated numerically, for instance using the extended Simpson's Rule (Abramowitz and Stegun, 1980).

2.2. Deconvolution program

A new GC deconvolution software has been developed to deal with FOK, GOK and continuous distribution of traps, based on equations (6), (10) and (17) discussed above (an example of the work flow is illustrated in Fig. 1). The software uses Intel® Parallel Studio XE 2015 Composer Edition for Fortran Windows Integration, Microsoft Visual Studio 2010, and Visual Basic for Applications and Microsoft Office Package to create two-tier architecture that integrates FORTRAN code with the latest version of Visual Studio (2010) through the creation of new DLLs to provide a visual environment to operate the code. The application permits to open the output files from different TLD readers (Harshaw, Risø, Panasonic) and performs the following tasks: i) individual background subtraction; ii) first estimation of the glow peaks fitting parameters: (T_M, I_M, E) in case of FOK, (T_M, I_M, E, b) for GOK, (T_N, I_N, E_0, σ) for a continuous trap distribution; iii) global glow curve fitting; and iv) calculation of glow peak areas and the kinetic parameters not directly obtained from the fitting (frequency factor).

Assuming a linear heating profile, background signal is fitted by the sum of a constant and an exponential part:

$$I_{background} = Aexp(T/B) + C \quad (19)$$

where either A or C can be zero. In case of discrete traps, the guess estimation of the glow peaks parameters T_M, I_M is obtained from the analysis of the calculated first and second derivatives (Gómez-Ros et al., 1999). The initial value for activation energy, E, is not so critical for most of the values usually found (between 0.5 and 2.5 eV), once an accurate estimation of the position and intensity of the maximum is provided. Therefore, a default value of 1.8 eV is assumed to guarantee the initial shape of the peaks is narrow enough to avoid strong overlapping. Analogously, a default guess value of 1.5 is assumed for the kinetic order, b although it is possible to change it whenever needed.

In case of a continuous trap distribution, although the values for T_M and I_M do not exactly correspond to T_N and I_N, they are respectively close enough to provide a good initial guess for these parameters, as it is discussed in section 3.

The glow curve fitting is performed using an iterative Levenberg–Marquard algorithm to minimise the χ^2 defined as:

$$\chi^2 = \sum_i [I_i - F(T_i,\ x_1 \ldots x_n,\ y_1 \ldots y_n,\ \ldots)]^2 \quad (20)$$

where $F(T, x_1 \ldots x_n, y_1 \ldots y_n, \ldots)$ is the function used to describe the glow curve by a sum of n individual peaks, each one characterized by a set of parameters depending on the considered kinetic model and the corresponding equation (6) and (10)or (16). Then, the figure of merit (FOM) is used as a measure of the goodness-of-fit for the whole glow curve (Horowitz and Yossian, 1995):

$$FOM = \sum_i \frac{|I_i - I^{fitted}(x_i)|}{Area} \times 100 \quad (21)$$

2.3. TL glow curves

Three sets of TL glow curves have been used to analyse the performance of the developed software, based on the methods and the corresponding equations described in section 2.1.

For first order kinetics, the reference glow curves from the GLOCANIN project (Bos et al., 1993, 1994) have been used: REFGLOW.001, (a single synthetic glow peak), REFGLOW.002 (four synthetic glow peaks) and REFGLOW.010 (LiF:Ti,Mg TLD-100 glow curve, read at a linear heating rate of 6 °C/s after irradiation at 200 μGy absorbed dose).

For general order kinetic, the one-trap- one-recombination-centre (OTOR) model (McKeever, 1988; Gómez-Ros et al., 2006b) was used to produce a set of 80 synthetic glow curves for the same number of combinations of trapping parameters (Gómez-Ros et al., 2006b). The corresponding energy level diagram with the allowed transition is

shown in Fig. 2: electron trapping (with probability A), thermal release of trapped electron (with probabilitys $exp(-E/kT)$, where s is the frequency factor, E is the activation energy, k is the Boltzmann constant and T is the temperature) and electron radiative recombination (with probability A_R).

For the continuous distribution of traps, a new set of synthetic glow curves have been obtained by direct evaluation of equation (11). To consider a representative group of possible situations, 120 different combination of values for E_0, s and σ, has been employed, summarize in Table 1.

3. Results and discussion

As a first test to analyse FOK glow curves, the software has been used with the reference GLOCANIN curves. For the synthetic glow curves (Tables 2 and 3), the obtained FOM is in the order of the best value obtained by the participants in the GLOCANIN project. Moreover, the relative deviation between the fitted and the reference parameters is negligible for T_M and very low for E and the individual glow peak area ($< 0.7\%$). For the experimentally measured glow curve REFGLOW.010 (Table 4 and Fig. 3), there are not reference values to compare the fitted parameters but the obtained FOM (3.15%) is better than those obtained by all the participants in GLOCANIN (4.12%–8.22%).

To evaluate the case of GOK glow peaks, the set of synthetic glow curves based on the OTOR model described in section 2.3 has been used. Fig. 4 and Table 5 show the result for two selected representative cases. When $A = A_R$ (retrapping-recombination ratio = 1), a very good fitting by a second order kinetic glow peak ($b = 2$) is obtained (low FOM and fitted activation energy E very close to the reference value). When $A < A_R$ (recombination is the dominant process), the glow peak is fitted by a kinetic order value between 1 and 2. In this case, the GOK model is actually an empirical approximation that permits to fit the shape of the glow peak (FOM in the order of 3%, fitted E deviated from the reference value around 10%) (McKeever, 1988; Gómez-Ros et al., 2006b).

The situation in case of a continuous traps distribution is more complicated because an initial estimation for the parameters in equation (11) cannot be easily obtained from the glow curve itself. Therefore, equation (17), depending on E_0, σ and alternative parameters T_N and I_N defined in equations (14) and (15) of equation (17), has been used to fit the set of 120 simulated glow curves described in section 2.3.

Fig. 5 illustrates the results for eight selected glow curves, four of them corresponding to exponential distributions (a, c, e and g) and the other four to Gaussian distributions (b, d, f, h). Similar results have been obtained in all the cases, where the use of T_M and I_M values, directly calculated from the glow curve, as guess values for T_N and I_N proved to be good enough to permit the convergence of the fitting algorithm with a resulting FOM lower than 1%.

Detailed numerical results for the ten glow curves corresponding to $E_0 = 1$eV are listed in Table 6 (exponential distribution) and Table 7 (Gaussian distributions). The relative difference between fitted and reference values for E and σ ranges in 1%–3%. Nevertheless, the fitted s values are very different from the reference ones, up to 50% for exponential distributions. This is a consequence of the dependence of TL intensity on s and E parameters, following a relationship of the type:

$$\mathrm{s}\exp\left(-\frac{\mathrm{E}}{\mathrm{K\,T}}\right) \tag{22}$$

where relatively big changes in frequency factor, s, can be compensated by small changes in activation energy, E (E_0 and σ in case of a continuous distribution), as it can be observed in Table 6. Therefore, the glow curve deconvolution in case of a continuous trap distribution provides a good way to characterize the activation energy distribution although the frequency factor may result inaccurately determined. Dealing with experimentally measured glow curves, the combined use of complementary techniques, glow curve deconvolution, initial rise (IR), various heating rates (VHR), T_M-T_{STOP}, can be required (Chen and McKeever, 1997).

4. Conclusions

New software for automatic glow curve deconvolution has been developed. The program works in a fully visual environment and provides the values of kinetic parameters, glow peak area and FOM assuming discrete (FOK, GOK) or continuous distribution of traps. In all the cases, the guess estimation for the fitting parameters is automatically obtained from the glow curve shape although it can be manually modified, if desired.

The analysis of GLOCANIN reference curves shows improved results in case of FOK. For GOK, the FOM also indicates a very good fitting, in particular when second order kinetics is found due to similar retrapping-recombination probabilities. In the other cases, a good fitting is also obtained, considering that GOK is an empirical approximation to the OTOR model used to simulate the synthetic glow curves.

The modified equation (17) for a continuous distribution of traps demonstrated that the new parameters T_N, I_N, are close enough respectively to the temperature and the intensity of the maximum, T_M and I_M, to obtain a good convergence using them as initial guess estimations for T_N, I_N.

4.1. Annex: evaluation of the TL integral and their approximations

The equations appearing in the description of TL emission, requires evaluating the integral (Chen and McKeever, 1997):

$$F(T,E) = \int_0^{\mathrm{T}} \exp\left(-\frac{\mathrm{E}}{\mathrm{kT'}}\right)\mathrm{dT'} \tag{23}$$

Although this integral cannot be solved in terms of elementary functions, it can be evaluated using the second order exponential integral, $E_2(x)$ (Abramowitz and Stegun, 1980):

$$\frac{1}{T}F(T,E) = E_2\left(\frac{\mathrm{E}}{\mathrm{kT}}\right) \tag{24}$$

Several asymptotic approximations have been developed to be applied for large enough values of E/kT. One of them is (Chen and McKeever, 1997; Kitis et al., 1998):

$$\frac{1}{T}F_1^{(asym)}(T,E) = \frac{kT}{E}\exp\left(-\frac{\mathrm{E}}{\mathrm{kT}}\right)\left(1-\frac{2kT}{E}\right) \tag{25}$$

And another more accurate one (Chen and McKeever, 1997):

$$\frac{1}{T}F_2^{(asym)}(T,E) = \frac{kT}{E+2kT}\exp\left(-\frac{\mathrm{E}}{\mathrm{kT}}\right) \tag{26}$$

As an alternative to equations (24) and (25), rational approximations can be also used (Abramowitz and Stegun, 1980). The general form is:

$$\frac{1}{T}F^{(rat)}(T,E) = \mathrm{T}\exp\left(-\frac{\mathrm{E}}{\mathrm{kT}}\right)R\left(\frac{E}{kT}\right) \tag{27}$$

where:

$$R(x) = 1 - \frac{0.250621 + 2.334733x + x^2}{1.681534 + 3.330657x + x^2} \tag{28}$$

Or:

$$R'(x) = 1 - \frac{0.2677737343 + 8.6347608925\,x + 18.0590169730\,x^2 + 8.5733287401\,x^3 + x^4}{3.9584969228 + 21.0996530827\,x + 25.6329561486\,x^2 + 9.5733223454\,x^3 + x^4} \tag{29}$$

Fig. 6a compares accuracy of the asymptotic approximations (24)

and (25) and the rational approximation (27) as a function of E/kT. As it can be seen, rational approximation is better for $E/kT < 49.5$ in case of equation (24) and for $E/kT < 31.7$ in case of equation (25). Moreover, this rational approximation shows a relative difference with respect to the built-in E_2 function lower than 0.004 for $0.5 < E/kT < 600$, enough for fitting purposes taking into account the usually expected uncertainties.

For completeness, Fig. 6b also compares the asymptotic approximations (24) and (25) and the rational approximation (28) as a function of E/kT. In this case, rational approximation is better for all the values of E/kT. Relative difference with respect to the built-in E2 function is lower than 5.5×10^{-6} for $1 < E/kT < 600$.

Acknowledgements

This work is being partially supported by the Spanish Ministry of Economy and Competivity (MINECO) under Grant FIS2015-64793-C02.

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