Non linear approach of TL response to dose: polynomial approximation.

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Abstract: *In the field of luminescence or electron spin resonance dating, exploitation of data techniques are under investigation in order to make the dating results more accurate. A non linear approach of natural dose determination is presented, using a polynomial fitting of thermoluminescence growth-curves (intensity of signals versus irradiation dose). This is based on the usual implicit assumption that the zeroing procedures performed to remove the signals due to natural irradiation do not affect the shape of the growth-curves. The basis and way of use of this polynomial approximation are detailed.*

A review of the additive dose technique and growth curve fitting

a) Experimental process for natural dose determination

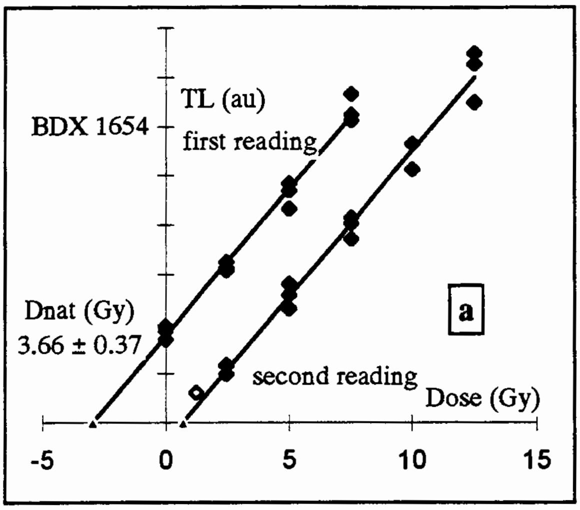
The usual procedure for natural dose measurement consists in reading a first series of additive dosed identical aliquots of the material to be dated. This first series of experiments is followed, after zeroing the natural signals of new aliquots, by a second series of laboratory irradiations and readings. These second reading experiments, second glow-curves of thermoluminescence, are used to regenerate the signal and to build the growth curve of the intensity with the laboratory dose administered to the sample. This curve is then fitted through the experimental points of the first series of experiments (natural plus artificial dosed material) assuming that the zeroing procedure does not affect the growth characteristics. The intercept of the curve with the dose-axis at null intensity allows the natural dose evaluation (Zimmerman, 1971; Fleming, 1979; Aitken, 1985).

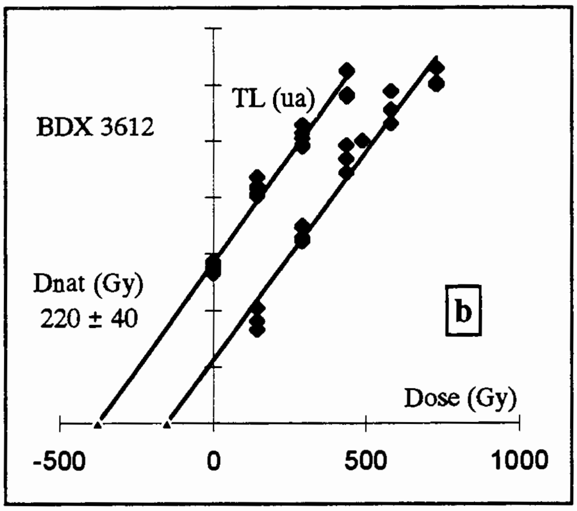
b) Linear fitting of growth curves

The simplest and well known exploitation of data consists of a linear fit of the first reading points with a regression line whose intercept with the x-axis (dose-axis) gives a first "uncorrected" value of the natural dose, D. To take into account the non linearity behaviour of the TL-response to dose, the same treatment is carried out with the second reading experiments . The extrapolation of the best fit line with the x-axis gives a corrective term, d, which is algebrically added to D in order to obtain the natural dose [1]:

$$D_{nat} = D + d \qquad [1]$$

This kind of treatment is convenient when the experimental behaviour is "not so far" from linearity. Practically, when the absolute value of the corrective term d does not exceed 10 to 15 % of the total natural dose, one may consider that the linear approximation is a satisfying tool for dose determination. However, if the growth curve of the material exhibits a significant non linearity _ a supralinearity which corresponds to an enhancement of sensitivity with the increasing irradiation dose, or a saturation of signal, which demonstrates a limited ability for charge trapping _ the utilization of a linear fit can produce large errors or uncertainties in dose determination. Several examples are given at figure 1: fig. 1a shows a typical supralinear feature of fine grains (mainly quartz) extracted from a medieval brick sampled at the Saragosse cathedral (Spain), fig. 1b a saturating growth curve of heated fine grains, quartz and feldspars, extracted from a mousterian fire area of Grotte XVI, Dordogne (France) and fig. 1c an intermediate, nearly linear, growth curve of fine grains, (quartz and a small amount of potash feldspar), from a piece of early neolithic pottery sampled at Matera-Trasano, Basilicate (Italy). In most cases, the question is the reliability of dose determination using linear regressions of growth curves.





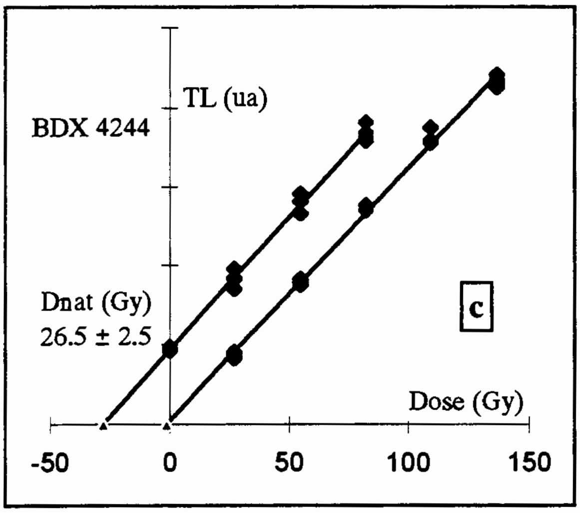


Figure 1
Linear fit of growth curves; D_{nat} values are given by the distance in unit of dose between the intercepts of the best fit regression line with dose axis for both first and second reading experimental points, marked by triangles. Fig. 1a shows a supralinear behaviour of fine grains, mainly quartz, extracted from a medieval brick, BDX 1654, at the Saragosse cathedral (Spain); the white diamond shaped point was not taken into account for the regression calculations. Fig. 1b: a saturating growth of heated fine quartz grains collected in a mousterian fire area at Grotte XVI, Cénac et St Julien, Dordogne (France), BDX 3612. Fig. 1c: an intermediate growth of TL with dose exhibited by fine grains of quartz extracted from a piece of early neolithic pottery collected at Matera Trasano, Basilicate (Italy), BDX 4244. The second reading intensities of TL have been corrected from sensitivity changes.

function	remarks and references
[2] $I = A.(1 - e^{-ax})$	single exponential, deduced from one trap kinetics model. (Mejdahl, 1985; Poljakov and Hütt, 1990; Grün and Brumby, 1994; Lamothe *et al.*, 1994).
[3] $I = A.(1 - e^{-ax}) + B.x$	same as [2] including a linear term, B.x, related to the creation of new traps during irradiation. (Schwarcz, 1994; Grün and Mc Donald,1989).
[4] $I = A.(1 - e^{-ax^{\gamma}})$	the γ exponent to the dose x allows to reproduce non-linearity effects at low doses. (Grün and Mc Donald, 1989; Barabas *et al.*, 1992;...).
[5] $I = A.(1 - e^{-ax})^{\alpha}$	The α exponent, if greater than unity, simulates the supralinearity behaviour. (Valladas and Gillot, 1978).
[6] $I = A.(1 - e^{-ax}) - B.(1 - e^{-bx})$	This linear combination of 2 exponential functions is deduced from a kinetics model involving two linked traps. (Ninagawa *et al.*, 1992).

Table 1: exponential based functions used in natural dose determination: short comments and some references.

Note that a strictly correct measurement of the natural dose by linear fitting requires irradiation doses used for second reading experiments to be equal to those which were used during the first series of experiments, i.e. the sum of the natural dose and the artificial doses, which implies the previous knowledge of the natural dose... i.e. that which is being determined. This problem gives rise to the most common limitations in linear fit. To solve it, more convenient functions are used.

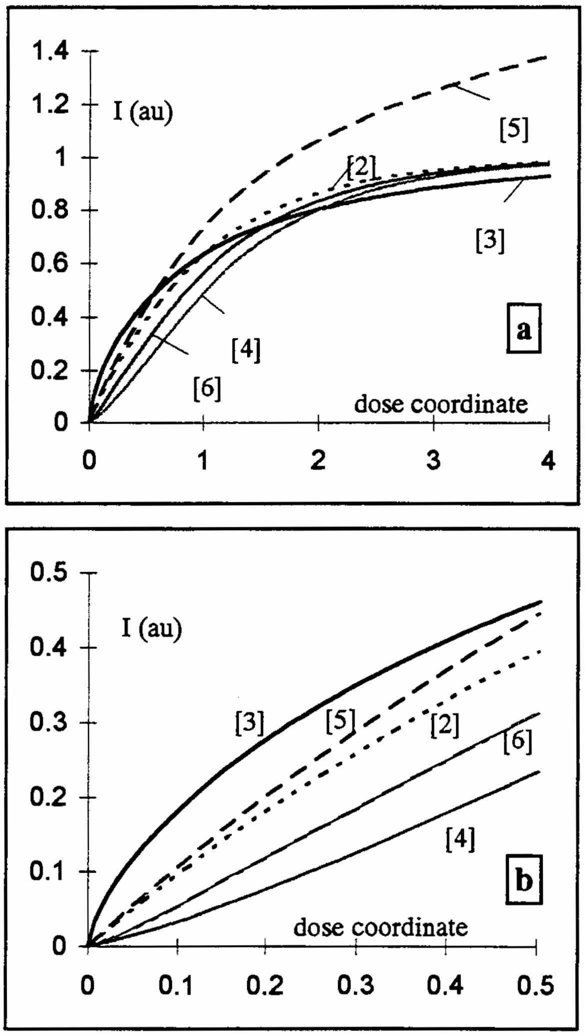


Figure 2
Graphic display of functions reported in table 1: the curve numbers recall those of functions in table 1. Figure 2a shows the general shape of the curves until 'high' dose saturation; figure 2b details the low dose region. Curves [5] and [6] reproduce the supralinearity behaviour of TL that many samples exhibit after β irradiation. (* list of parameters used for this representation: function [2]: A=1, a=1; [3]: A=1, a=1, B=0,1; [4]: A=1, a=1, γ=0.7; [5]: A=1, a=1, α=1.25; [6]: A=1.5, a=1, B=0.5, b=2.5).*

c) Non linear fitting of growth curves
One of the most common approaches of the variation of the signal intensity, I, with the dose x, is a saturating exponential [2] as reported in table 1. This model is deduced from kinetics studies involving one single trap. Since it cannot be of general use, other functions including saturating exponentials have already been suggested in the field of luminescence or electron dating and are displayed in table 1. All of these representations are based on both theoretical models and empirical observations. An additive exponent to the dose or to the saturating function itself, relations [4] and [5], reproduces the supralinearity or sublinearity curvature of growth curves in the low dose region. Figure 2 provides a comparison of these exponential based functions. Note that this kind of representation of the growth curves has been successfully carried out with highly irradiated materials in the field of geological dating (see table 1 for references).

Since the main application of TL at the Bordeaux dating laboratory concerns archaeological materials (Schvoerer *et al.*, 1974; Bechtel, 1983; Guibert *et al.*, 1994), mostly ceramics, which are usually younger and less irradiated than geological ones, other types of functions were preferred in order to describe a supralinear behaviour as well as a saturating growth. On the other hand, exponential functions based on trap filling models involving one or two traps of a particular type of mineral did not seem appropriate to describe the complex properties of the TL signals originating from polymineral fine grains, according to the technique usually performed in Bordeaux. Investigations had been carried out to check the reliability of polynomial approximation in natural dose determination during the early 1990's in Bordeaux. Polynomial fitting technique is now of general use by our group (Guibert *et al*, 1994). Other authors have also reported recent dating results using a polynomial approach for growth curve fitting and natural dose determination (Mercier *et al.*, 1991; Chawla *et al.*, 1992; Loyer *et al.*, 1995).
We will present in the following sections the basic principle and the use of polynomials for natural dose determination .

Natural dose determination principle by a least square method
As presented above, the natural dose is determined by the intercept of the "natural plus dose" growth curve with the dose-axis. The first step of the measurement procedure is to choose the more appropriate function. This operation is generally done with the second

reading experiments: let this function be $f_2(x)$ where x is the laboratory dose and the index 2 recalls this is related to the experimental data of the second reading series of records. If the material behaves ideally, the signal to dose response, either natural or artificial, does not change with the annealing process by either heating, or bleaching or a combination of both. Changes in sensitivity are usually observed; however, in most cases, the zeroing procedure does not affect the relative variations of intensity of signals with dose. Hence, supported by experimental evidence, we can write that, if f_1 describes the growth curve for the first reading experiments, f_1 and f_2 are assumed to be linked by the following relationship [7]:

$$f_1(x) = A.f_2(x+D_{nat}) \qquad [7]$$

where x is the laboratory dose, A a multiplicative factor which characterizes the differences in sensitivity observed between first and second reading and D_{nat} the natural dose which is being determined. First and second growth curves have the same characteristics; a translation of dose D_{nat} - changing $f_2(x)$ into $f_2(x+D_{nat})$ - and an application of a scale factor equal to the ratio of sensitivities, A, are the only differences between the first and second growth curves.

To determine D_{nat}, the best fit of $f_1(x)$ through the experimental points (Intensity / dose) corresponding to the first reading will minimize the quadratic sum E of the differences between the experimental points and the $f_1(x)$ function:

$$E = \sum_{i=1}^{n}(y_i - f_1(x_i))^2 \qquad [8]$$

with y_i and x_i respectively being the signal intensity and the dose absorbed by the i^{th} aliquot. According to the relation [7], [8] becomes:

$$E = \sum_{i=1}^{n}(y_i - A.f_2(x_i+D_{nat}))^2 \qquad [9]$$

where n is the number of experimental data obtained during the first reading experiments. This least square procedure means that the best adjusted values of A and D_{nat} verify the following expressions [10] and [11], at the same time:

$$\frac{\delta E}{\delta A} = 0 \Rightarrow$$

$$\sum_{i=1}^{n} f_2(x_i+D_{nat}).(y_i - A.f_2(x_i+D_{nat})) = 0 \qquad [10]$$

$$\frac{\delta E}{\delta D_{nat}} = 0 \Rightarrow$$

$$\sum_{i=1}^{n} f_2'(x_i+D_{nat}).(y_i - A.f_2(x_i+D_{nat})) = 0 \qquad [11]$$

where f_2' is the first derivative function of f_2 respect to D_{nat}.

Finally, the determination of the natural dose is equivalent to solve the general equation system just mentionned. Since the function f_2 has no particular form, these relations are of very general interest and can be applied to any type of derivable function, exponential as well as polynomial.

Polynomial approximation.

a) Polynomial fitting of second reading growth curve. The starting point of the polynomial approach is that the intensity equals zero when no irradiation was delivered to the sample to be dated: $f2(0) = 0$. Consequently, particular kinds of function are looked for whose general formulae are given by relation [12]:

$$f_2(x) = x.S_2(x) \qquad [12]$$

where $S_2(x)$ is the mean sensitivity of the material being studied, varying with the dose x in the case of non linear growth. With such a formula, the growth curve which characterizes the second reading experiments is forced to start at zero, for no irradiation. Practically, $S_2(x)$ is approximated by polynomial functions, deduced from a vectorial basis of orthogonal polynomials (Draper and Smith, 1966). A set of N polynomials is defined whose degree ranges from 0 to N-1, where N is the number of strictly different doses administered to the sample during the second reading experiments.

Figures 3a to 3c illustrate a polynomial fit of the experimental mean sensitivity, evaluated by the ratio of signal intensity to dose, in different examples of growth from fine grains of archaeological materials previously presented.

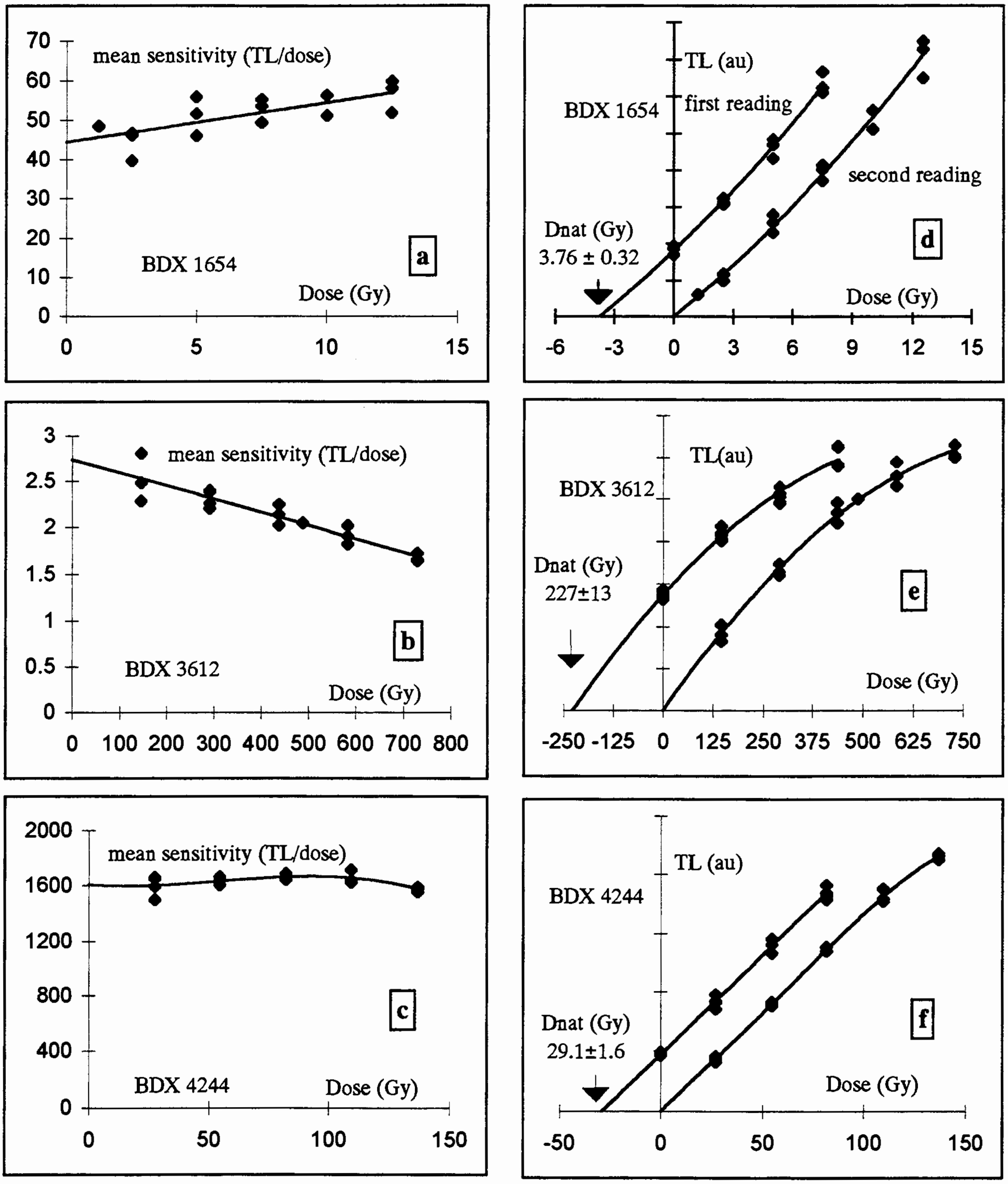


Figure 3: *Mean TL sensitivity (ratio of intensity to dose) and TL intensity as a function of laboratory dose: experimental points and polynomial fitting (same examples as in fig.1). Fig 3a and 3d, medieval sample BDX 1654 dated 1259±49 AD: a first order polynomial fit of the mean TL sensitivity has been choosen, TL growth curves are thus approached by a parabola. Fig 3b and 3e, heated fine grains of quartz from a mousterian fire area, BDX 3612, dated 65.6±4.6 ky: first order polynomial for mean sensitivity and second order for growth curves. Fig 3c and 3f: fine grain from the early neolithic potery, BDX 4244, dated 5910±440 BC: 3rd order polynomial for sensitivity, 4th order for TL growth curves. Corrections for differences in sensitivity between first growth and regenerated growth have been taken into account in order to make the curves parallel and easy to compare.*

b) Natural dose evaluation.
The second reading growth curve is at this stage approached by N different polynomial functions $f_{2,k}(x) = x.P_{2,k}(x)$ with x being the dose and $P_{2,k}(x)$ the k^{th} degree polynomial.

The least square fit of polynomials $f_{2,k}(x)$ through the experimental points of the first series of measurements (natural plus laboratory irradiated aliquots) is done using the method previously described. N different values of D_{nat} are then obtained according to the existence of the N different polynomial functions $f_{2,k}(x)$ which satisfy the equations [10] and [11].

At this stage of data exploitation, the chronologist has to choose the best representation among the N possibilities. For that purpose, the N sums of squares E_k which characterize the quality of the polynomial fitting, deduced from the expression [9] are evaluated and displayed (see appendix 1 for a desciption of a computerised procedure):

$$E_k = \sum_{i=1}^{n} (y_i - A_k.f_{2,k}(x_i+D_{nat,k}))^2 \qquad [13]$$

with k being the degree of the polynomial function $f_{2,k}$, n the number of the first series experiments, y_i the signal intensity of the i^{th} experiment, x_i the corresponding laboratory dose; A_k and $D_{nat,k}$ are the best adjusted values of A and D_{nat} obtained with the k^{th} degree polynomial. An estimate of the quality of the calculation is also given by a graphic representation of mean sensitivity and growth curves as displayed in figures 3a to 3f and commented in corresponding caption.

The polynomial function which gives the least sum of squares, E_k, is selected and if several polynomials seem to be available, the one of lower degree is usually preferred in order to avoid some meaningless pseudo oscillations of the growth curves which may occur when the statistical dispersion of the experimental data is high. By this way, the natural dose is determined.
In order to avoid some possible divergences caused by the extrapolation of the polynomial function out of the range of dose within which it had been defined, a simple rule of thumb is to be respected: the range of laboratory irradiation doses related to the second reading experiments must include the total range of doses, natural dose plus laboratory doses, related to the first series of experiments.

c) Uncertainty evaluation.
Here, we will consider the uncertainty brought on natural dose by the dispersion of signal intensities although other sources of error may exist as, for example, the error on dose rate of calibrated radioactive sources.
The signal intensity originating from different aliquots is assumed to randomly fluctuate. For each experimental point indexed i, an estimate of the uncertainty, the standard-deviation σ_i, is associated to the signal intensity, y_i (appendix 2: evaluation of σ_i).
The evaluation of the standard deviation of D_{nat} results from the usual formula [14] giving the standard-deviation of a function of several parameters affected by independent random fluctuations (CEA, 1978):

$$\sigma D_{nat} = \left(\sum_{i=1}^{m} \left(\frac{\delta D_{nat}}{\delta y_i}.\sigma_i\right)^2 \right)^{1/2} \qquad [14]$$

with m being the total number of measurements including the first series of records, "natural plus dosed" aliquots, and the second series, "regenerated" aliquots. However, since the analytical expression of D_{nat} as a function of signal intensities y_i, is *a priori* unknown, a computerised calculation of σD_{nat} is operated following the expression [15] which derives from the previous one:

$$\sigma D_{nat} = \left(\sum_{i=1}^{m} (\Delta D_{nat,i})^2 \right)^{1/2} \qquad [15]$$

where $\Delta D_{nat,i}$ represents the deviation between D_{nat} and a new and transient value of the natural dose calculated by changing the i^{th} intensity y_i into $y_i+\sigma_i$, keeping all other parameters constant.

Conclusion
Many samples to be dated exhibit a non-linear growth of TL with irradiation dose. In order to make the natural dose measurement more accurate and reliable, some researchers have attempted to model the experimental behaviour, signal response to dose, with more appropriate functions than simple lines. Exponential functions or a linear combination of exponential functions had already been presented; they are deduced from kinetics models involving one or two trap-centers, assuming, as usual, a linear

relationship between signal intensity and trapped charge population.

Without questionning the previous work, we suggest a more empirical approach for natural dose evaluation, because we think that trap-filling and emptying mechanisms are generally more complicated than those described by only one or two traps. Obviously, this is true with polymineral fine grains (poly-kinetics...) from archaeological samples. A polynomial approximation of growth curves, based on the experimental behaviour of the material being dated, provides a satisfying versatility and can be successfully used in many situations in order to determine the archaeological or geological natural dose.

Acknowledgements

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Appendix 1

The natural dose is evaluated using a 'home-made' software package, called "polytl" which is a part of an application, written in C language and devoted to the control of an automatised TL apparatus built at the CRPAA laboratory and to the exploitation of data (determination of plateaux region, activation energies, natural doses,...).

The calculation of D_{nat} using polynomials is carried out as follows: in the expression [11], the parameter A can be written:

$$A = \frac{<fy>}{<ff>} \qquad [16]$$

according to a concise representation with:

$$<fy> = \frac{1}{n}\sum_{i=1}^{n} y_i.f_2'(x_i+D_{nat})$$

and $$<ff> = \frac{1}{n}\sum_{i=1}^{n} f_2'(x_i+D_{nat}).f_2(x_i+D_{nat})\ .$$

The new expression of A, [16], replaces the old one in [10] which becomes:

$$R = <fy> - \frac{<fy>}{<ff>} <f^2> = 0 \qquad [17]$$

with $$<fy> = \frac{1}{n}\sum_{i=1}^{n} y_i.f_2(x_i+D_{nat})$$

and $$<f^2> = \frac{1}{n}\sum_{i=1}^{n}(f_2(x_i+D_{nat}))^2$$

The equation [17], R=0, is true for the final value of the natural dose D_{nat}. In practice, solutions of the equation [17] are numerically found using an iterative process. From the user's point of view, the parameters sent to "polytl" are the addresses of TL intensities, laboratory doses and TL curve identificator tables. The natural dose calculation is then carried out by the computer. A set of N polynomial functions is displayed. To facilitate the choice of a particular function, the quadratic sums, E_k, expression [13], are shown with the D_{nat} values and the required number of iterations. Mean sensitivity and growth curves (figure 3) are also displayed and can be used for estimating the validity of the fit. The results can be output to a printer or into an ASCII file readable by many commercial software packages for data treatment.

Appendix 2

The standard deviation of TL intensities are evaluated by two different ways:

i. the first one is deduced from the assumption that the standard deviation is constant whatever the intensities;

ii. the second one is based upon the assumption that dispersion of signal intensity leads to dispersion in weight of the aliquots; the standard deviation is thus proportionnal to signal intensity and, in other words, the relative standard deviation is assumed to be constant.

According to the user's choice, the absolute and relative standard deviations are the quadratic mean value of respectively absolute difference and relative difference between the observed signal intensity and the one expected with the best fit polynomial. As the natural dose measurement needs two series of experiments, two independent values of the absolute or relative standard deviations are then determined and utilized for the uncertainty evaluation.

Reviewer

Ann Wintle

Comments

This paper provides a useful summary of the general types of curves used for fitting growth curves. The reader can find a similar criticism of the use of inappropriate fitting procedures in a recent paper by Grün (1996) where he suggests that the use of linear fitting to the "apparently linear" part of an exponential growth curve can produce large systematic errors. In his paper, Grün draws attention to the use of combined regeneration and additive dose data sets, as used in the "Australian slide method" (Prescott et al., 1993) and by Sanzelle et al. (1993). This approach is generalized in equation (7) of Guibert et al (above), where allowance for a sensitivity change between the data sets is made.

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