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Spectral Deconvolution of Fossil Tooth Enamel Electron Paramagnetic Resonance Spectrum

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Abstract

In this work the ESR method has been applied to determine the age of fossil tooth enamel found in Mingachevir archeological site (Azerbaijan, Mingachevir). The EPR spectrum of tooth enamel has been deconvoluted into four individual Gaussian lines. Equivalent dose (Absorbed dose in tooth enamel that was historically accumulated due to natural irradiation) calculated using dose-response curves of individual Gaussian lines shows significantly different values. Peak 1 (with g= 2.006848) gives a significantly lower, Peak 4 (with g=2.002942) a significantly higher value of absorbed dose. The use of integrated spectra gives lower absorption dose values than the use of differential spectra.

Keywords: EPR dating, Deconvolution, Tooth enamel, Fossil tooth, Age determination, Mingachevir.

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Ethical: This study follows all ethical practices during writing.

Contents

1. Introduction

Electron Paramagnetic Resonance (EPR) spectroscopy widely used in EPR dating and retrospective dosimetry [1] and teeth enamel is one of the important biological dosimeters for retrospective assessment of absorbed dose. Irradiation of tooth enamel generates stable radicals, which can be measured by EPR spectroscopy. The absorbed dose is assumed to be in linear dependence with the intensity of the EPR spectrum of those radicals. The lifetime of the radiation induced signals (RIS) has been estimated at around 10^9 years at 25 degree C [2] which enables estimation the age of fossil tooth at least up to $1x10^6$ years and more.Estimates of the lower limits of absorbed dose detection resulted in the range 67-561 mGy [3]. But the results of dose measurements obtained by different techniques may differ significantly, especially at low doses [4]. The evaluation of absorbed dose may be influenced by several factors including sample preparation procedures [5] and determination of the intensity of the RIS signal [4]. It has been established that EPR signal of tooth enamel consist of both native signal and radiation induced signal with a complex nature [6]. Conventionally, peak to peak measurements or the height of the peak maximum of absorption spectrum are used for the evaluation of absorbed dose. For the vast majority of EPR age determination the conventional peak to peak dose evaluation method has been used. However, there is a debate that spectrum deconvolution of EPR spectra may yield considerably different dose values than peak to peak dose evaluation [7] which was not supported by later investigations [8]. Nevertheless, deconvolution of EPR spectrum is one of the powerful tools in identification the underlining components of complex spectrum. In this work we investigated the complex EPR spectrum in fossil teeth enamel and described it as a superposition of several more elementary signals.

2. Experimental

The investigated object was fossil tooth of elephant (*Palaeoloxodonantiquus*[1]) found in Mingachevir district of Azerbaijan in 2010 with well-preserved teeth. Sample preparation and ESR measurement procedures were as follows. The enamel was initially removed from teeth using a dental drill and water cooling. The 1.5 mm mean thickness enamel was then placed in a 30% NaOH solution for one day in order to disinfect it and separate any remaining dentine.

50±5 μm from the inside and the outside of the enamel surface was stripped using a dental drill to ensure that natural alpha radiation had no effect for the fossil tooth enamel samples. In total 2 g. of enamel was collected from both fossil and modern tooth and it was air-dried at room temperature for three days. Half of the samples were powdered using agate mortar 100-160 μm of powder was separated for further measurements. Enamel powder (0.1 g.) and single fragment (bulk) samples were placed separately inside glass tubes (Suprasil) for the measurements of EPR signals.

The samples were then irradiated at ambient temperature using ^{60}Co source with additional doses and ESR signals were measured at the same conditions. Dose rate of the ^{60}Co source has been determined by Magnettech Miniscope MS400 EPR Spectrometer using individually wrapped, bar code labeled BioMax Alanine Dosimeter Films (developed by Eastman Kodak Company). Irradiation of samples has been conducted at fixed location around ^{60}Co source and does rate was 0.149Gy/s.

ESR signal for the samples was measured with a Bruker EMXplus (X-band) spectrometer. The spectrometer parameters used were: 3522 G central field, 100 G scan range, 3.2 G amplitude modulation, 100kHz modulation frequency, 163.840ms time constant and 2.12mW power.

In order to deconvolute the overall signal into its components it is important to choose the appropriate model function. In this study we used a number of combinations of model functions. Lorentzian lines, and combinations of Gaussianand Lorentzian lines were omitted since they did not fulfill the conditions where there was a possibility to identify the same signal in each of the samples. Gaussian line shape model was chosen as the experimental spectra were measured at room temperature where all signals should be broadened to pure Gaussian lines:

$$f_i(H) = e^{-\frac{(H-H_i^o)}{2\sigma_i^2}} \quad i = 1,2,3,4 \qquad (1)$$

where H_i^o is the center and σ_i the half-width of the line i.

Experimental absorption signal was deconvoluted into N individual components by fitting a model function (2) to the integrated spectrum:

$$I(H) = \sum_{i=1}^{N} A_i f_i(H) + c \qquad (2)$$

where the $f_i(H)$ are line shape function, Gaussian or Lorentzian line shapes, A_i are the respective amplitudes of these lines in the individual spectrum and c is a constant.$I(H)$ is a height of(or intensity) absorption spectra at the magnetic field H. The fit is a non-linear fit using the Marquardt-Levenberg method [5] i.e. minimizing$\chi^2 = \sum(I(H_i) - y_i)^2$for a set of experimental data points (H_ι, y_i) [5]. Fitting Gaussian lines added one by one until a further signal added to the model function had a negligible contribution in the fit or turned up at random positions.

3. Results and Discussions

Figure 1 illustrates a typical fit of four Gaussian line shape functions (1) into fossil teeth EPR spectrum. Numerations of the peaks are arbitrary and they have been assigned for identification purposes. The characteristic parameters of the peaks are illustrated in Table 1. Though the heights of the peaks differ from each other, the areas under each of the four spectrums are roughly equal and account for the same number of spins. Five equal aliquots of fossil teeth powder irradiated at different dose from 44.7 to 223 Gy. Integrated EPR spectrum of unirradiated

[1]The **straight-tusked elephant** (*Palaeoloxodonantiquus*) is an extinct species of elephant that inhabited Europe during the Middle and Late Pleistocene (781,000–50,000 years before present). It was formerly thought to be closely related to the living Asian elephant; however, in 2016, DNA sequence analysis showed that its closest extant relative is actually the African forest elephant, *Loxodontacyclotis*. It is closer to *L. cyclotis* than *L. cyclotis* is to the African bush elephant, *L. africana*, thus invalidating the genus *Loxodonta* as currently recognized. (*Callaway, E. (2016-09-16). "Elephant history rewritten by ancient genomes". Nature.*doi:10.1038/nature.2016.20622.)

(labeled as natural) and five irradiated samples are illustrated in Figure 2. Fixed deconvoluted parameters (line center and g-factor) found for the unirradiated sample were applied for the deconvolution of the irradiated samples. The four Gaussian line shape model consistently produces the lowest χ^2 values of all other tested models.

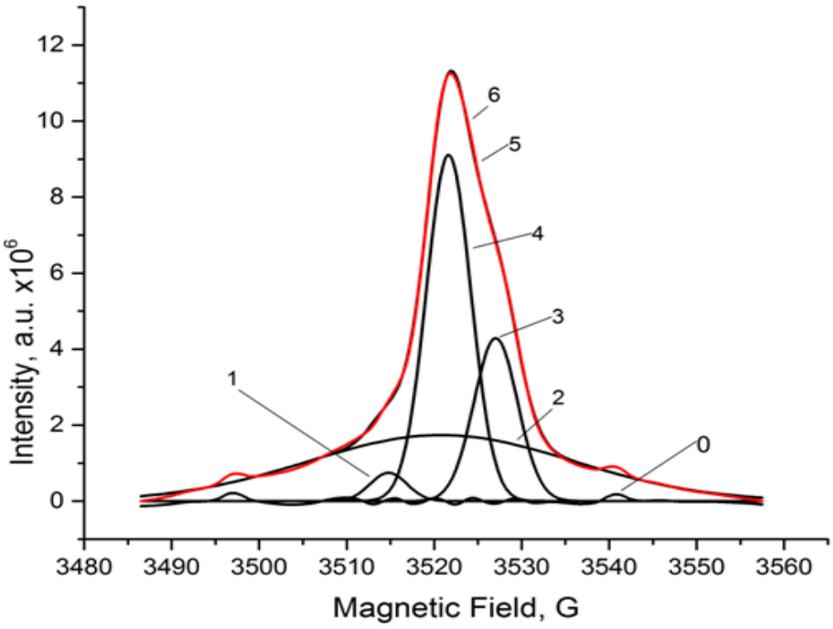

Figure-1. Integrated EPR spectrum of fossil elephant teeth (6). The plot shows the experimental data as the best fit (5) obtained from the four Gaussian lines model and the four individual Gaussian components (1-4) and residuals (0) calculated by this model. The total fitted curve (5) and experimental data (6) are too close together to be visually resolved over most of the spectrum.

Table 1 summarizes the characteristic parameters of the deconvoluted peaks which are in line with the reported earlier dates [7]. It has been calculated the characteristic peaks for the irradiated samples presented in Figure 2 using the four Gaussian line model presented above.

Table-1. The characteristic parameters of the deconvoluted peak obtained for the unirradiated natural teeth enamel.

Peak Index	Peak Type	Area Fit	Max Height	Full width, 2σ, G	Center Max, G	g-factor
1	Gaussian	3.92E+06	744257.772	4.94378	3514.79476	2.006848
2	Gaussian	6.57E+07	1.74E+06	35.52748	3520.8021	2.003424
3	Gaussian	2.70E+07	4.29E+06	5.91187	3527.04196	1.99988
4	Gaussian	5.82E+07	9.11E+06	6.00842	3521.65005	2.002942

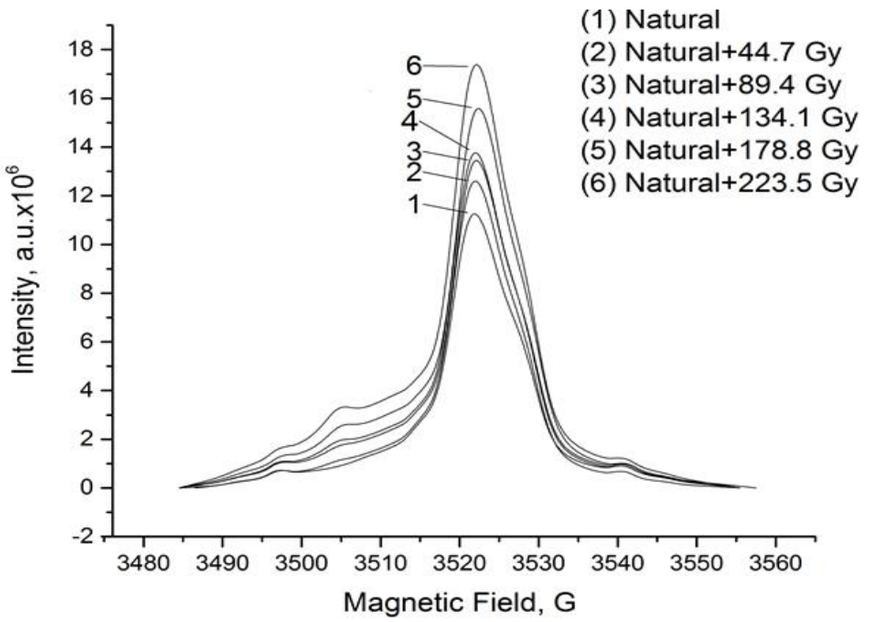

Figure-2. Integrated EPR spectrum of fossil teeth enamel irradiated at different dose. The spectrum of sample labeled as natural (1) did not receive additional laboratory dose. The other samples (2-6) were irradiated at dose rate 0.149 Gy/s.

Figure 3 shows the dose-response curves determined for the individual peaks corresponding to peak 1 with the g-factor of 2.006848 (Figure 3 b); peak 3 with the g-factor of 1.99988(Figure 3 a); and peak 4 with the g-factor of 2.002942 (Figure 3 c). Integrated EPR spectrum (without deconvolution) dose-response curve is presented in Figure 3d. Deconvoluted peak 2 intensity corresponding to g factor of 2.003424 did not show any dependency from the irradiated dose. Back interpolation of lines enables calculation of initial dose absorbed by fossil teeth enamel at point of X intercept, i.e. the point where the plotted line cross the Dose line in the Figure 3. Calculated dose for the different methods are presented in Table 2.

Table-2. Calculated dose for the different methods

Peak Index	Peak Type	g-factor	Calculated dose, Gy
1	Gaussian	2.006848	140
2	Gaussian	2.003424	N/A
3	Gaussian	1.99988	405
4	Gaussian	2.002942	586
Integrated spectrum	Figure 3 d		438
Differential spectrum	conventional method		512

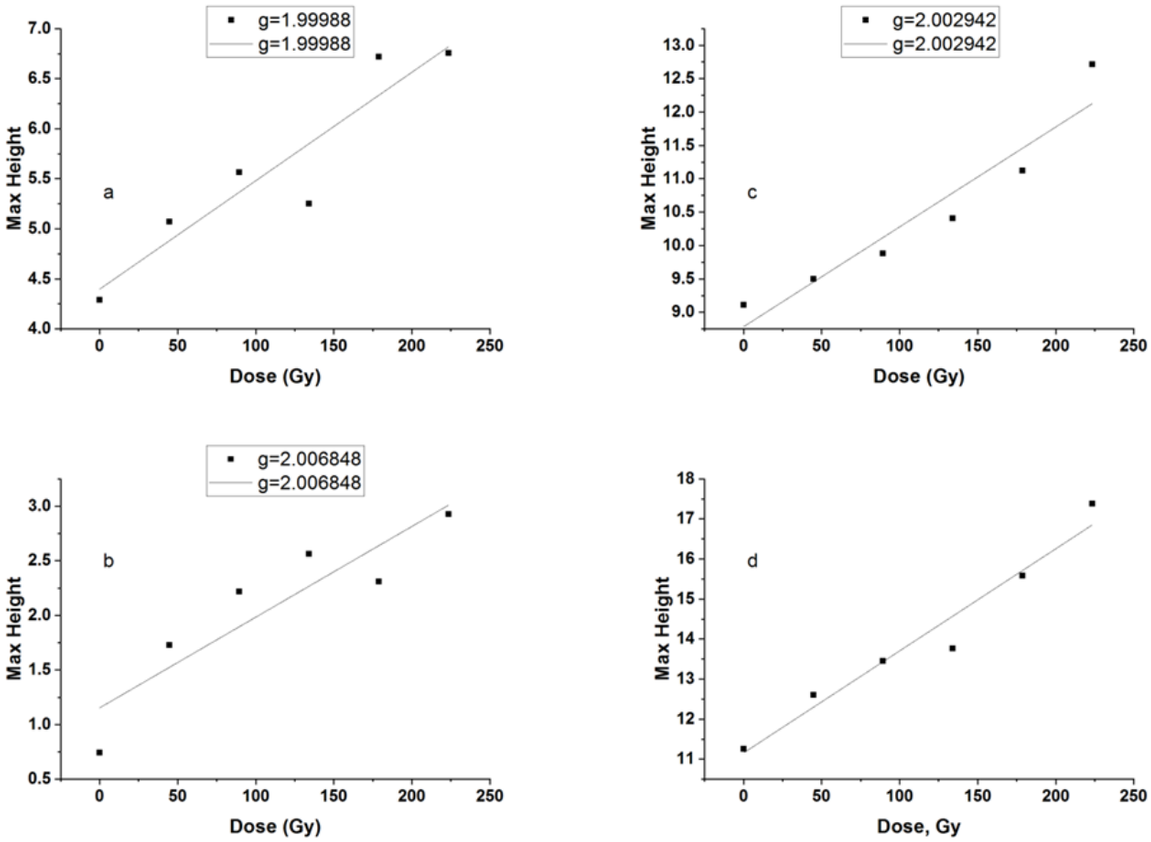

Figure-3. Dose-response curves with the use of four Gaussian line shapes. The curves were fitted with OriginPro 2018b. Dose-response curves are shown for the signals g=1.99988 (a), g=2.006848 (b), g=2.002942 (c) and linear plotting of maximum heights of integrated EPR spectrum (see: figure 2) against the dose (d). Dose-response curve for the signal at g=2.003424 is not presented here due to high errors.

4. Conclusions

Deconvolution of integral EPR spectrum by four Gaussian lines method produces well correlated peaks but in this study they do not agree with each other. Peak 1 (with g= 2.006848) gives a significantly lower value of absorbed dose, while Peak 4 (with g=2.002942) gives a significantly higher value of absorbed dose.

The use of integrated spectra gives lower absorption dose values than the use of differential spectra.

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