Dose determination on fossil tooth enamel using ESR spectrum deconvolution with Gaussian and Lorentzian peak shapes

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Abstract. *ESR spectrum decomposition was carried out with the commercial PeakFit program using Gaussian and Lorentzian peak shapes. The results show that there is at least one component in the ESR spectrum that yields significantly lower dose values than the central peak region which is used for conventional peak-to-peak dose determinations. Both deconvolution methods yield closely similar results to simple plateaux dose assessments, which are presently much faster to perform.*

Introduction

Recent publications have shown that the central region around g=2 of ESR spectra of tooth enamel consists of a number of separate peaks (e.g. Jonas et al. 1994, Jonas & Grün 1997). Jonas (1997) concluded that probably all published dose values on enamel may be erroneous. He used a fitting program developed for mainframes which required extremely long calculation times. Fortunately, commercial programs do pretty much the same, although some restrictions such as constant peak ratios or line widening cannot be implemented. In this study, the program PeakFit v4.0 (AISN Software 1995, distributed by Jandel Scientific) was used, which applies the same fitting optimisation strategies as the Jonas program.

Jonas (1997) used Gaussian line shapes for spectrum deconvolution and observed four main peaks with the following parameters (g-value; line width): #1 (2.0023; 3.8 G); #2 (1.9995; 5.1 G); #3 (2.0068; 23.4 G) and #4 (2.0034; 12.1 G - note that all line widths here and in the tables are in 2-σ). Peaks #1 and #2 may constitute an axial peak which has been attributed to the CO_2^- radical. In principle, this radical ought to have three principle g-values (see Table 1) and deconvolution of ESR spectra of powdered fossil tooth enamel using Lorentzian functions results in three distinctive peaks (Callens, pers. comm.).

Radical	g_x	g_y	g_z	line width (G)
CO_2^-	2.0033	1.9972	2.0021	4.8
CO_3^{3-}	2.0044	2.0033	2.0018	1.3
CO^-	2.0061	2.0033	2.0018	1.6

Table 1: *Line parameters for various radicals in hydroxyapatite (Callens et al. 1995)*

The rationale of this paper was to check whether spectrum deconvolution using Gaussian and Lorentzian peak shapes gives different results in dose estimation and whether these are different from peak-to-peak or plateau dose assessments. Fitting was applied on sample 1047 (a bovid tooth from Florisbad) for which extensive reproducibility tests have been carried out (Grün & Clapp 1996; Grün 1998). Forty powdered aliquots of a sample 1047 were irradiated in ten irradiation steps and each aliquot was measured ten times, resulting in 400 D_e estimations. The peak-to-peak dose value of this sample is 75.8±2.1 Gy, the rising dose plateau of the absorption spectrum ranges between 76.1±3.9 and 81.9±4.1 Gy and the dose value derived from the maximum of the absorption spectrum is 77.9±3.4 Gy. All of these results are statistically indistinguishable, but the somewhat higher dose values obtained from the absorption spectra (i.e. resulting form integration of a conventional derivative spectrum) was interpreted that some non-radiation sensitive peaks may interfere with the radiation sensitive. The reason for using a fossil rather than an artificially

irradiated, recent sample lies in the fact that due to the long mean life of the signals involved, nearly all components of the irradiated sample will give the same, artificial dose. This may be useful for source calibration and inter-laboratory tests but cannot be used for identifying problems in the dose estimation of fossil samples (see also Grün 1998). Unfortunately, it is not possible to assess which dose value is correct on the basis of its independent assessment, because it is neither possible to date teeth precisely by independent means (radiocarbon dating is strongly influenced by rapid exchange of secondary carbonate; see Grün et al. 1997 and U-series dating is dependent on U-uptake; see Grün & McDermott 1994) nor to estimate the dose rate accurately (due to variations in water content in the sediment and dentine as well as uranium uptake in enamel and dentine).

Experimental

For details of experimental setup, measurement parameters and spectrum manipulation see Grün (1998). PeakFit runs on IBM compatible computers and a typical deconvolution calculation (once the peak parameters are defined) takes between 20 and 60 seconds on a PC with a 150 MHz Pentium processor. In this study, I used the averaged spectra from the ten repeated measurements of each dose step of the first aliquot. Firstly, the ten averaged ESR spectra of the ten dose steps were integrated (without baseline corrections), aligned on the maximum intensity and normalised on maximum peak intensity. This ensured that the influence of each spectrum on the averaged spectrum was more or less the same. Then the spectra were added and averaged. This averaged spectrum was used for deconvolution and estimation of the peak parameters. Peak width and position were then locked for the fitting of the individual spectra representing the different dose steps. Gaussian curves are described by:

$$\text{ESR Intensity} = \text{Amplitude} \exp(-0.5 \, (\text{Magnetic Field} - \text{Line Centre})/1\text{-}\sigma \text{ Line Width})^2)$$

and Lorentzian by:

$$\text{ESR Intensity} = \text{Amplitude} / (1 + (\text{Magnetic Field} - \text{Line Centre})/1\text{-} \sigma \text{ Line Width})^2)$$

The differences between Gaussian and Lorentzian line shapes are relatively small, Lorentzian peaks have longer tail ends (see Figure 1). Figure 1A shows the derivative averaged ESR spectrum of sample 1047. It is dominated by an apparently axial peak which has been attributed to CO_2^- (e.g. Callens et al. 1995). The quintet which is centred on the top of the large central signal at g = 2.0032 (*) has been attributed to alanine (Ikeya 1982) or a dimethyl radical (Bouchez et al. 1988), the line at g=2.0056 (+) may be due to CO^- (see Fig. 3b of Callens et al. 1995) or a free radical (Bouchez et al. 1988) which could be SO_2^- (Barabas 1992, Ikeya 1993). The isotropic line at g = 2.0114 (#) is a rotating CO_3^--radical (Moens et al. 1993).

Results and discussion

Following the experiments of Jonas (1997), the ESR spectra were firstly deconvoluted using 4 Gaussian and 4 Lorentzian peaks. For a reasonable fit of the Lorentzian peaks it was necessary to introduce a further line at high magnetic fields (L5). The resulting parameters are shown in Table 1 and Figures 1B and 1C.

The g-values were calculated by using a DPPH standard. There seems to be an offset of 0.0005 between these values and those of Jonas (1997) who used a Mn^{2+} standard. The Gaussian lines attributed to CO_2^- (#1 and #2 of Jonas and lines G3 and G4 in this study) agree fairly well whilst the other two lines have considerably different line widths and central positions. However, this is not surprising, because Jonas (1997) used scans over about 80 G whereas this study uses 120 G wide scans.

As can be seen in Figure 1B-D, the integrated spectrum shows already significant ESR-intensity at ± 40 G around the main peak. Thus, the deconvolution results in the much wider line G2. Both studies have in common that the central peak is represented by two Gaussian peaks (which may combine into an axial line shape) which are overlapped by two wider lines. The three Lorentzian lines representing the central peak are only interfered by one other line.
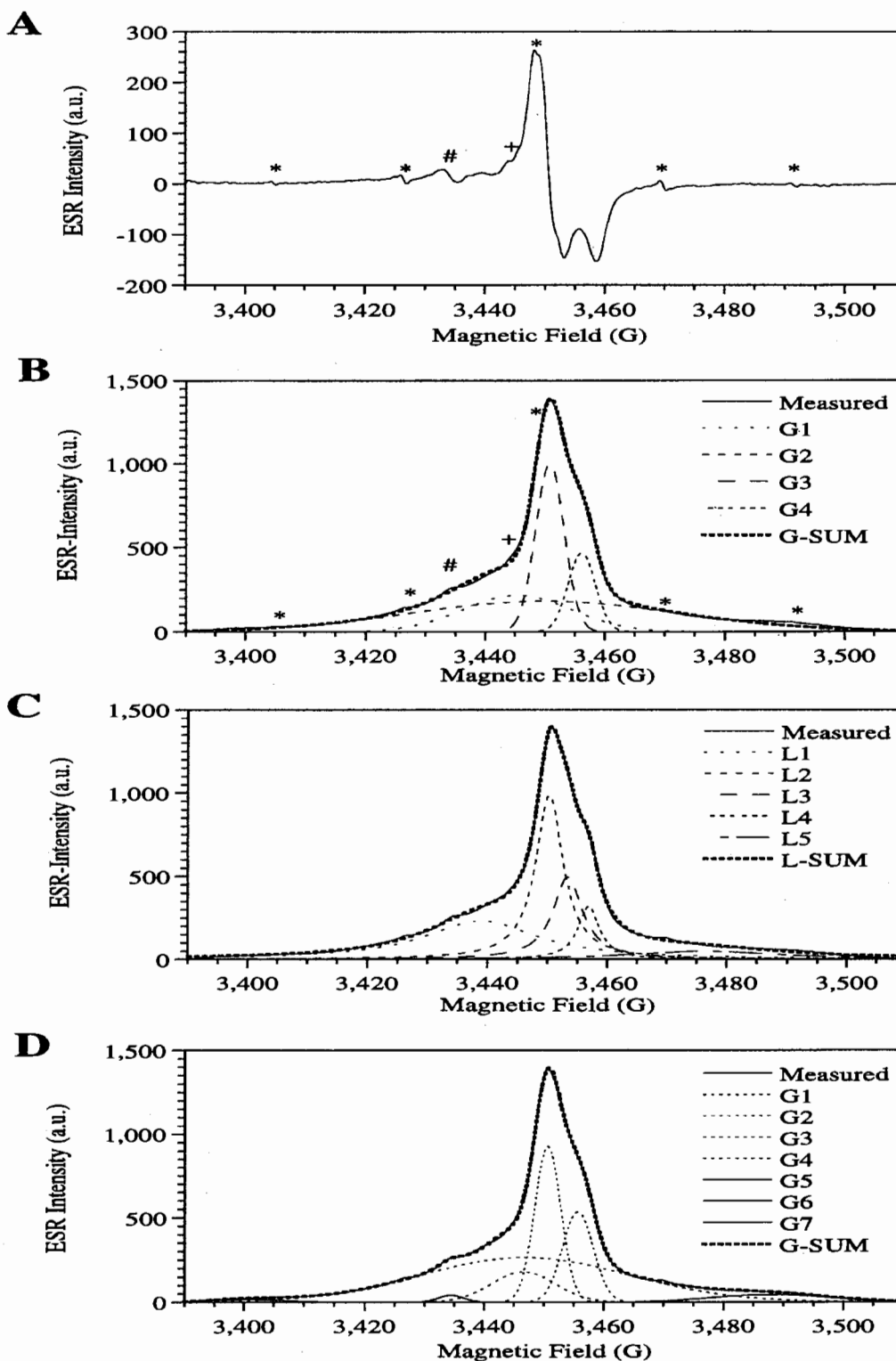
Figure 1

A: Averaged derivative spectrum of sample 1047. It is dominated by an apparently axial peak which has been

attributed to CO_2^- . The quintet which is centred on the top of the large central signal at g = 2.0032 (*)
has been attributed to alanine or a dimethyl radical; the line at g=2.0056 (+) may be due to CO^- or a

free radical which could be SO_2^-. The isotropic line at g = 2.0114 (#) is a rotating CO_3^--radical.

B: Fitting of the integrated spectrum with 4 Gaussian peaks, for peak parameters see Table 2.
C: Fitting of the integrated spectrum with five Lorentzian peaks.
D: Fitting of the integrated spectrum with seven Gaussian peaks.

It can be seen that the ESR spectrum is not 100% fitted by the four Gaussian lines, particularly around 3333 G, the location of the isotropic CO_3^- radical (#) and at 3490 G. Therefore, a second Gaussian deconvolution experiment was carried out, using seven peaks (r^2 = .9998). As can be seen in Figure 1D, the two central peaks (G3: g=2.0019; width: 4.4 G and G4: g=1.9990; width: 5.1G) change little, but the position, width and relative intensity of G1 (g=2.0043; width: 10.6 G) and G2 (g=2.0041; width 35 G) change substantially

Using the integrated areas of the four and seven Gaussian and five Lorentzian lines, the dose values given in Table 3 were obtained.

The fitting of the ESR spectra with Gaussian line shapes with either 4 or 7 peaks yielded more robust results than the Lorentzian line shapes and were accompanied with better correlation coefficients. This may be an indication that Lorentzian peak shapes are not as appropriate for this sample as the Gaussian. The dose response of the total integral yields 88±10 Gy and its fitting is considerably worse than the fitting of any of the above components.

All three experiments have in common that the first line (G1 and L1), which strongly interferes with G3, yields significantly lower dose values than the central peaks. The wide line G2 yields the same dose value as the central peak region. Furthermore, those lines which are less influenced by the first line (G4, L4) give somewhat higher dose values than G3 or L2, L3. This may be taken as indication that the different components are not completely separated by the deconvolution process. On the other hand, the

derivative spectrum shows various interferences of the central peak region (see Figure 1A) which are not resolved in the integrated spectrum. These peaks may well influence the dose value of G3 and L2, L3.

The dose values derived from the central peak region (G3&4, L2-4) are all slightly higher than the peak-to-peak dose value of the derivative spectra of 75.8±2.1 G. The dose results of G3 and G4 agree very well with the two ends of the "rising plateau" observed by Grün (1998) which yielded dose values of 76.1±3.9 in the region of G3 and 81.9±4.1 Gy in the region of G4. Considering the effect of G1 on G3, the most realistic dose value ought to derive from G4 (around 82 Gy) which is about 8% higher than the conventional peak-to-peak dose value. The dose response curve of L5 shows by far the largest scatter of the data points (it is also the smallest peak) and the L5 dose value is probably not too significant.

Similarly to the experiments of Jonas (1997), it not possible to relate the Gaussian and Lorentzian peaks directly to components of the CO_2^- or CO_3^--radicals. The line widths of G3 and G4 indicate a relationship with the CO_2^- radical whereas G1 may represent the whole CO_3^--radical. Clearly, the best solution for realistic dose assessment lies in the fitting of physically meaningful line shapes to the ESR spectra. However, so far the dose response curves of such deconvolution methods have yielded dose response curves which contain significantly more scatter than any of the methods discussed in this paper (Callens, pers. comm.).

No	Gaussian peaks				Lorentzian peaks			
	Position (G)	g-value	Width (G)	Amplitude	Position (G)	g-value	Width (G)	Amplitude
1	3445.4	2.0050	18.0	216	3439.0	2.0087	22.6	231
2	3449.9	2.0024	44.4	181	3450.4	2.0021	5.6	977
3	3450.9	2.0018	4.8	998	3453.4	2.0004	6.0	494
4	3456.2	1.9987	4.6	466	3457.0	1.9983	4.4	318
5					3476.2	1.9872	29.0	48
r^2		0.9988				0.9983		

Table 2: *Results of spectrum deconvolution of the averaged spectrum of sample 1047 (see Figure 1). The labelling is simply sequential and should not be used to infer any relationship between the Gaussian and Lorentzian peaks.*

It is clear that extensive calculation times on main-frames are not required for adequate spectrum deconvolution using Gaussian or Lorentzian line shapes. The time for routine spectrum preparation, deconvolution and fitting may be in the range of one hour per sample. This compares to one to two minutes for plateau fitting. Considering that the plateau dose values are closely similar to those of deconvolution (at least in this case), it seems most economical to calculate plateaux first and invoke deconvolution as check and on selected sets which indicate stronger interferences of the central peak region (see e.g. Grün & Jonas 1996)

No	4 Gaussian peaks Dose (Gy)		Lorentzian peaks Dose (Gy)		7 Gaussian peaks Dose (Gy)
1	40.2±1.6		37.4±5.9		41.5±4.1
2	78±45		78.7±2.2		75±15
3	78.7±2.1		73.1±3.4		75.3±2.6
4	82.7±1.9		114±11		82.2±2.5
G3&4	80.3±2.0	L2-4	82.5±5.0	G3&4	77.6±2.5

Table 3. *Dose results*

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Reviewer
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