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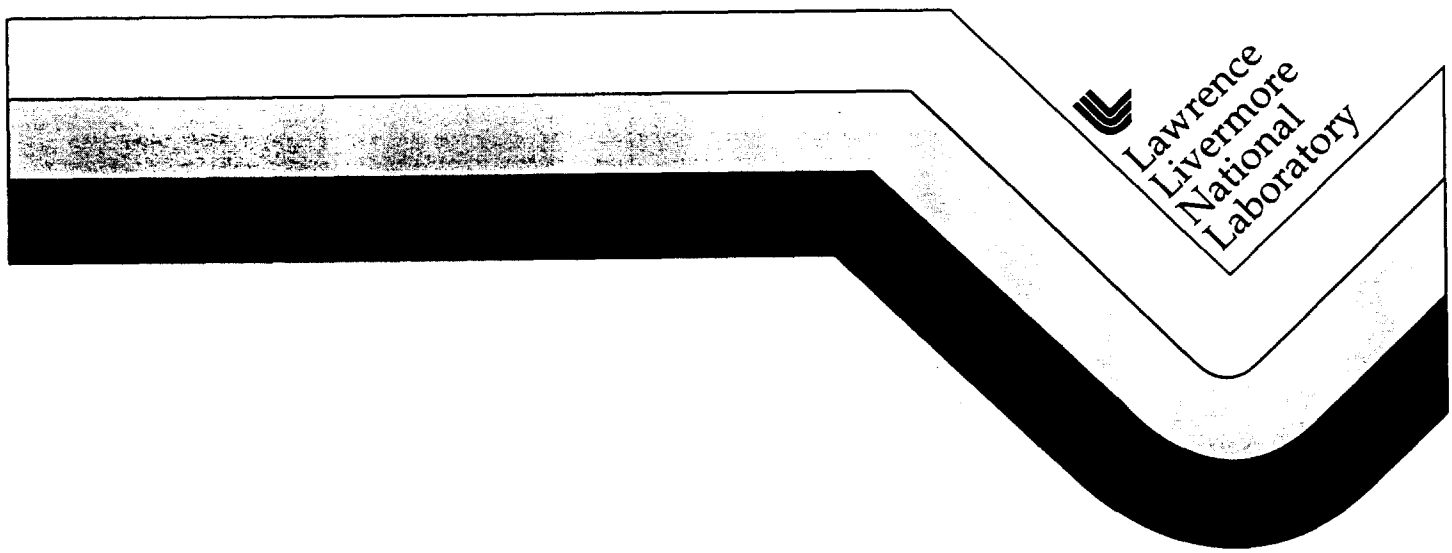

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PROPERTIES OF LIGHT INDUCED EPR SIGNALS IN ENAMEL AND THEIR POSSIBLE INTERFERENCE WITH GAMMA-INDUCED SIGNALS

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Abstract - Exposure of enamel to U.V. light (sunlight and artificial) results in EPR signals with g-factors of of 2.0018 (perpendicular), 1.9975 (parallel), 2.0045, 2.0052 and 2.0083. The first two signals correspond to the components of the radiation induced signal and the third signal corresponds to the native signal reported in dosimetry and dating studies. The remaining two signals were found to be stable and sensitive to both gamma and sunlight exposure. Their sensitivity response to light and radiation was considerably different which gives rise to the possibility that the g = 2.0052 and g = 2.0083 signals might be used as indicators of the dose resulting from light exposure.

1. INTRODUCTION

The problem of accounting for the influence of sunlight exposure on the radiation induced EPR signal in enamel has not been resolved. It is known, that sunlight affects both the signal at g = 2.0045 (Oduwole and Sales, 1991) and the anisotropic signal with $g_{\perp}$ = 2.0018, $g_{\parallel}$ = 1.9975 (Ivannikov *et al.*, in press), of which the latter is usually used for retrospective dose determination (Aldrich and Pass, 1988; Ikeya, 1994; Serezhenkov *et al.*, 1992) and archeological dating (Grun et al., 1987; Grun, 1991). This phenomena may be a real threat to EPR dosimetry, since at the present time it is not possible to distinquish

between radiation and sunlight induced fractions of the signal at $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$. One possible solution is to exclude incisors from dosimetry studies as these are the teeth most affected by sunlight. However, such an approach seems to be oversimplified. In certain cases not only incisors, but canines and even molars may be subjected to sunlight exposure. In addition, it should be taken into account that in some cases in the states of the former Soviet Union, exposure to ultraviolet light is used as a medical procedure. In these cases dose reconstruction is even more difficult. Therefore, it would be desirable to have some indicators of possible exposure of enamel to sunlight or ultraviolet light. The present work is dedicated to establishing such criteria.

2. MATERIALS AND METHODS

Enamel grains in the size range 250-600 μm were obtained by mechanical removal of dentine from tooth caps by means of a dental drill with subsequent crushing in an agate mortar. Four samples designated S2, S5, S6 and T2 were prepared. In addition, an enamel plate with a thickness of 1.10 ± 0.01 mm was prepared by polishing bulk enamel on a diamond disk. This plate was called F2 and was used for determining the light dose profile.

The enamel samples were exposed in the following manner. The sample S5 was exposed in a plastic cuvette covered with a UV light transparent quartz plate. This plate was used to protect the sample from weathering. Exposure of this sample was only done on sunny days. The sample was exposed for a total of 10 days. The EPR spectra were collected at the end of each exposure day. Measurements were also made during the time between sunny days. The sample S6 was exposed under a wide spectrum UV lamp (Oriel, model 66187) at a distance of ca. 15 cm from lens. The EPR spectra of this sample was registered for different intervals of exposure time in the range from 1 second up to several hours. The samples S2 and F2 were exposed under a monochromatic UV lamp with a

wavelength of 254 nm (Eprom Eraser, model DE-4) at a distance 4 cm from lamp axis. The total exposure time was 8 hours, the plate F2 was exposed from two sides during 4 hours each. Sample T2 was irradiated using a Co-60 gamma-source (Isotope Product Laboratory, Burbank, CA 91504) with a dose of 80 Gy.

The spectra registration was done with a x-band EPR spectrometer, model ESP 300E, Bruker Insruments. Microwave power and modulation amplitude were varied over a wide range. Other parameters of spectra registration were as follows: modulation frequency 100 kHz, sweep width 10 mT, time constant 20 ms, conversion time 20 ms, number of accumulations 60-120. The 3rd and 4th lines of Mn2+ : MgO were used as an "in situ" standard, placed within the resonator cavity. Intensity of the EPR signals were measured as peak-to-peak values following manipulation of the original spectra. All manipulation were done after g-factor normalization of the original spectra.

The spectra of samples recorded at a microwave powers of more than 2 mW were corrected by subtracting the spectra of an empty tube which were registered under same conditions and during the same day as the spectra of the studied sample. This resulted in considerable reductions of influence of spectrometer drifts on the accuracy of low intensity signal measurements.

The spectrum of a standard native signal was subtracted when the intensity of the signal with $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$ was measured (only the g-perpendicular component was used). This standard signal was obtained from a mixture of enamel from 30-40 non-irradiated teeth of people under 25-year age. The intensity of the standard native signal was adjusted to equal the intensity of the native signal of the analyzed spectrum.

Finally the spectrum of a standard radiation induced signal was subtracted when parameters of EPR signals with $g = 2.0052$ and $g = 2.0083$ were determined. This spectra corresponded to sample T2 and was registered more than one month after irradiation so that all transient signals had decayed. Parameters of registration were the same as for spectra of investigated sample.

Sample F2 was etched in a low concentration (0.1 %) solution of HCl to determine EPR signal intensity profiles. The spectrum of the sample was recorded after every 1.5 min. of stepwise etching.

3. RESULTS

Fig. 1 shows the results of evaluating sample S5. The parameters were chosen to comply with values actually used in EPR dosimetry. The microwave power was 10 mW and the modulation amplitude 0.5 mT. Spectrum a corresponds to the original non-irradiated sample, spectrum b to the sample after exposure on the roof for 10 sunny days. Spectra c and d were obtained as a result of subtraction according to following relationship

$$c,d = a - k \times b, \qquad (1)$$

where the coefficient k was equal to 1.0 and 2.0 for spectra c and d respectively.

The positions of the four different signals are indicated with numbers 1-4 and are defined in the caption for Fig. 1. In the next figure (Fig. 2.) the spectra of sample S6 are shown. They were recorded with the same parameters of registration as the previous ones. The spectra in Fig. 2 are as follows: spectrum a corresponds to spectrum of the sample before irradiation, spectrum b, after exposure for 15 hours under a wide-spectrum UV lamp, spectra c and d were obtained in the same way as spectra c and d in Fig. 1. For clarity, spectrum d is shown at 2X magnification.

It can be seen in Figs. 1 and 2 that ultraviolet light produces the same set of EPR signals as sunlight exposure, but with a slightly different intensity.

The spectra of samples T2 and S2 which were taken with a microwave power of 0.4 mW and modulation amplitude of 0.2 mT are shown in the Fig. 3. Spectrum a shows the T2 sample which received a gamma dose of 80 Gy, spectrum b is sample S2 after

exposure to 8 hours of monochromatic UV with a wavelength of 254 nm, spectrum c is the result of subtracting b and a according to formula (1) with some coefficient k and spectrum d is the result of subtraction of spectrum c and the scaled spectrum of sample S2 before exposure. After these manipulations we can clearly see the peak corresponding to g = 2.0052.

Fig. 4. shows the increase in signal size as a function of exposure time. Curve a corresponds to the signal at $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$ in sample S5. This increase was expressed in terms of dose using Co-60 calibration. Curve b shows the change for the g = 2.0045 signal in sample S6. This curve was normalized to the initial value seen before exposure.

The time axis for the curve a is time of exposure to sunlight, while for curve b this is exposure time under the broad spectrum UV lamp. Curve a shows a linear growth of signal intensity with a slightly changing day-to-day increment, while the curve b saturates as a factor of 6 is approached.

Fig. 5 shows the intensity profile of signals generated by UV exposure as a function of depth from the surface of exposed sample. Curve 1 is the intensity profile of the signal at $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$, curve 2 is the signal at g = 2.0052. Extrapolation of the experimental points was done assuming exponential decrease, the coefficients used were -0.016 mm^{-1} and -0.0092 mm^{-1} for curves 1 and 2 respectively.

4. DISCUSSION

As can be seen in Figs. 1 and 2, sunlight and UV light exposure generate the same parametric centers in enamel. This made it practical in some cases to use U.V. light generated signals as a substitute for those generated by sunlight which is relatively ineffective. In particular, g-factors and widths determined in this study were done using samples exposed under ultraviolet lamps.

An example of such a determination is shown in the Fig. 3 for the signal at g = 2.0052. It was previously found that this signal was seen better at low microwave power levels. Consequently, a microwave power 0.4 mW and modulation amplitude 0.2 mT were chosen for registration of the spectra shown in Fig. 3. The spectra of sample S2, which was exposed during 8 hours under ultraviolet lamp with wavelength 254 nm, and T2, which was irradiated with dose 80 Gy with the Co-60 source, were recorded with these parameters. A comparison of initial spectra of samples S2 and T2 (a and b in the Fig. 3) showed that gamma and UV exposure generate the same set of lines in EPR spectra, but the intensity ratio of different EPR lines was significantly different for these two types of exposure. This difference is clearly seen in the Fig. 3 for the line with g = 2.0052, where the ratio of its intensity to intensity of line at g = 2.0018 is several times higher in the case of UV exposure than for gamma-ray exposure. Properties of the signal at g = 2.0088 are quite similar, although this signal is more pronounced at the higher microwave power. In addition, this signal is normally overlapped with strong neighboring signals (as may be seen in Fig. 3, a and b).

Different intensity ratios of EPR signals in enamel after gamma and UV exposure, together with different behavior of intensity of these signals as a function of microwave power, gives rise to the possibility of separating EPR signals at g = 2.0052 and g = 2.0088 in enamel by subtraction. The final result of such subtraction is shown in the Fig. 3d, for the signal at g = 2.0052. As a criteria of correctness of the applied procedure we have used the fact that EPR spectra of enamel after sunlight and ultraviolet light exposure could be rather well described using only three different EPR signals at low microwave power and four signals at moderate levels of microwave power; two of three (four) signals are well-known EPR signals in enamel at g = 2.0045 and $g_{\perp}$ = 2.0018, $g_{\parallel}$ = 1.9975. Comparative analysis of spectra after gamma and UV exposure revealed, that gamma radiation may also produce stable EPR centers at g = 2.0052 and g = 2.0088. In particular, the enamel peak close to g = 2.0056 which is usually observed after irradiation of samples with a gamma-

dose of less than 50 Gy at low and moderate levels of microwave power, is actually a result of overlapping of two signals: one with g = 2.0052, the oother at $g_{\perp}$ = 2.0018, $g_{\parallel}$ = 1.9975, Therefore, this peak is not related to the native signal at g = 2.0045.

The signals at g = 2.0052 and g = 2.0088 are quite stable. There were no changes when the samples were heated to 95 C for 72 hours. The difference in yield of the described signals for various types of exposure suggests using it as a criterion to determine how much sunlight an investigated sample received. The intensity ratio of g = 2.0088 and g = 2.0018 signals after removal of the g = 2.0045 signal by subtraction, is one possible example. As may be seen in Fig. 1d, this ratio is equal to ca. 0.33 for the sample which was exposed to sunlight only. At the other extreme is exposure to gamma radiation only. In this case the ratio is close to zero. It is natural to expect that the ratio will be between 0 and 0.33 for samples exposed to both radiation and sunlight. This information could be used to correct the value of the g = 2.0018 signal.

Presently, there are many questions which need to be answered before this technique can be used. In particular, as may be seen from Fig. 5, the intensity of light-induced signals attenuate considerably with depth of enamel, and it is not yet clear whether the ratio remains unchanged or if it depends on the thickness of the enamel layer in the tooth. Solving this and other problems is necessary if we want to determine precisely contributions of sunlight exposure to intensity of EPR signal with g = 2.0018 in enamel.

The increase of intensity of the signal with $g_{\perp}$ = 2.0018, $g_{\parallel}$ = 1.9975 is illustrated in Fig. 4a. The signal induced by one sunny day corresponds to a dose of 209 mGy of gamma irradiation. Fig. 4 shows that this intensity increase varied for different days. This is probably related to varying cloud conditions, solar activity, etc., which were not taken into account.

The complex behavior of the g = 2.0045 signal also causes problems with estimating the magnitude of the g = 2.0018 signal. Concerning this problem, the intensity of the g = 2.0045 signal of sample S5 increased ca. 2.36 times on the first day and then

dropped to 1.42 times for the second exposure day. After the second exposure day the intensity change increased up to 3.09, then dropped down again to 1.68, 42 hours later. These fluctuations continued for the duration of the experiment. As can be seen in Fig. 4b, the intensity of the native signal may increase ca. 6 times due to UV exposure and then decreases to a higher than initial level after UV exposure ceases. Precise estimation of the native signal is also hampered because intensity of other EPR signals in enamel increase significantly with exposure time and these signals hinder the measurement of the signal with $g = 2.0045$. Anyway, it is clear that such complex behavior of the $g = 2.0045$ signal leads to difficulties in determination of intensity of the $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$ signal if a subtraction technique is used. The following criteria of subtraction was used for getting curve a in Fig. 4. The coefficient of subtraction was selected in such a way that the resulting spectrum looked similar to curve d in the Fig. 1. Clearly, the accuracy of such a method is better when the intensity of the signal at $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$ is higher, i.e. the total exposure time of the sample to sunlight was high.

Finally, a short comment the data in Fig. 5. The depth at which the signals attenuated by a factor of $g = 2.718$ was determined. This value was equal to 63 μm for the EPR signal with $g_{\perp} = 2.0018$, $g_{\parallel} = 1.9975$ and 109 μm for the signal with $g = 2.0052$. Taking into account that the sample used in the dose profile study was exposed to monochromatic light (with wavelength of 254 nm), the difference in intensity profiles of different EPR signals may be explained by an indirect mechanism of generating EPR centers with ultraviolet light. First, the energy is probably transferred from photons to some intermediate carriers (e.g. electrons, scattered photons, etc.) which, in their turn, interact with corresponding centers in enamel and bring them to the paramagnetic state. If this is so, then the energy of the intermediate carriers may range from minimum values up to a maximum which depends on the different free path distances. If different paramagnetic centers in enamel are generated by carriers with different energies (and mean free path distances), then we will have intensity profiles of the type seen in Fig. 5.

Using data of Fig. 5, it is possible to estimate how much enamel needs to be removed from a tooth to reduce the contribution of UV component to the total dose.

We can use the following empirical relationship to determine how much enamel to remove from incisors. The total surface area of enamel is ca. 50 mm^2. The weight of pure enamel in an incisor is ca. 150 mg. Assuming that we need to remove the surface layer to a depth of 63 μm and taking into account that the density of enamel is 2.75 g/cm^3, then ca. 86 mg of enamel should be removed. Thus, ca. 64 mg of enamel remains, which may be enough if the gamma dose is on the order of 200 mGy or more. The real loss of enamel due to etching may be significantly reduced if etching could be applied to external (front) part of incisor only. This may be achieved by cutting the tooth in two (inner and outer) parts and etching the front half only which has a dentine layer on the back. Combining the method of etching with the method of estimating the ratio of the signals at g = 2.0088 and g = 2.0018 will allow an increase the accuracy of dose determination in enamel exposed to sunlight and gamma irradiation.

5. CONCLUSION

It has been shown that exposure to sunlight will produce at least four different paramagnetic centers in enamel. Two of these centers are well-known with g = 2.0045 and $g_\perp$ = 2.0018, $g_\parallel$ = 1.9975, the other two with g-factors of 2.0052 and 2.0088 were identified in the present work by means of varying microwave power and selective subtraction of spectra. It was found that the spectra of samples exposed to sunlight and gamma irradiation have the same sets of EPR signals, but with different relative line intensities. This property combined with using intensity profiles of some the light induced EPR signals may be used to correct the g = 2.0018, g =1.9975 signal for light exposure.

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FIGURE CAPTIONS

Fig. 1. EPR Spectra of sample S5 recorded at 10 mW microwave power and 0.5 mT modulation amplitude. Spectrum a was collected before exposure, spectrum b - after 10 days exposure to sunlight, c - result of subtracting spectra a from spectra b using k = 1.0 (see text), d - subtraction of the same spectra, but with k = 2.0. The positions of four EPR signals, which are usually generated by sunlight or ultraviolet light, are numbered 1 through 4. The g-factors of these lines are: line 1, 2.0045, line 2, 2.0052, line 3, 2.0018 and line 4, 2.0088. The first three values correspond to the center points of the signals while the value given for line 4 is the low field maximum.

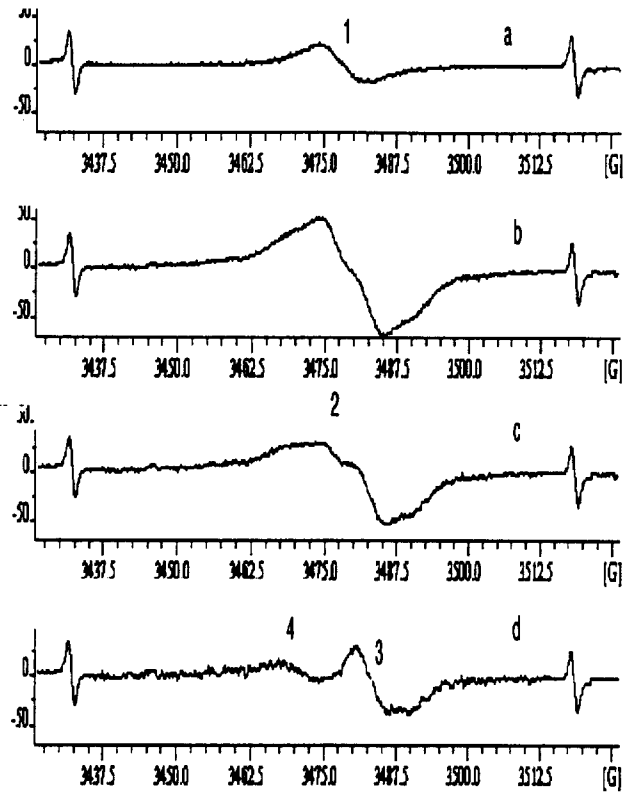
Fig. 2. EPR Spectra of the sample S2 recorded at 10 mW microwave power and 0.4 mT modulation. Spectrum a was collected before exposure, spectrum b - after 15 hours exposure to UV light, c - result of subtracting spectrum a from spectrum b using k = 1.0, d - the result of subtracting spectrum a from spectrum b with k = 2.0. See Fig. 1 for other details.

Fig. 3. Effects of gamma irradiation and UV exposure. Spectrum a - sample T2 after 80 Gy gamma ray irradiation, spectrum b - sample S2 after 8 hours of exposure with 254 nm UV lamp, spectrum c - obtained by subtracting spectrum a from spectrum b

using an arbitrary k, spectra d - result of subtracting the spectrum of sample S2 taken before irradiation (not shown in this figure) from spectrum c. The signal shown in figure is primarily line 2 (g = 2.0052).

Fig. 4. Intensity of signals with $g_{\perp}$ = 2.0018, $g_{\parallel}$ = 1.9975 (curve a) and with g = 2.0045 (curve b) as function of exposure time for the sunlight and ultraviolet light respectively. The fit to curve b is a pair of saturating exponentials fit which is indicative of multiple signals being present, a single saturating exponential gave a visually bad.

Fig. 5. Attenuation of intensity of the light induced signals in tooth enamel as function of depth from the surface of tooth. Line 1 is the signal with $g_{\perp}$ = 2.0018, $g_{\parallel}$ = 1.9975, line 2 - the signal with g = 2.0052.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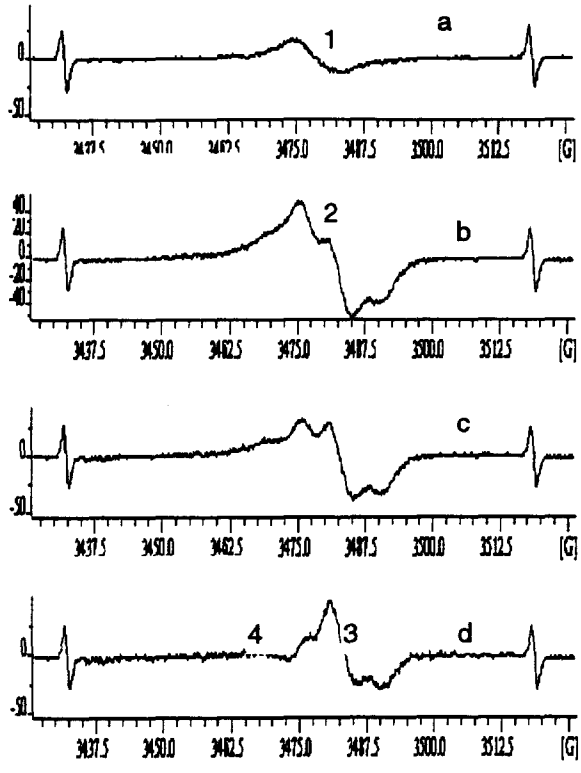
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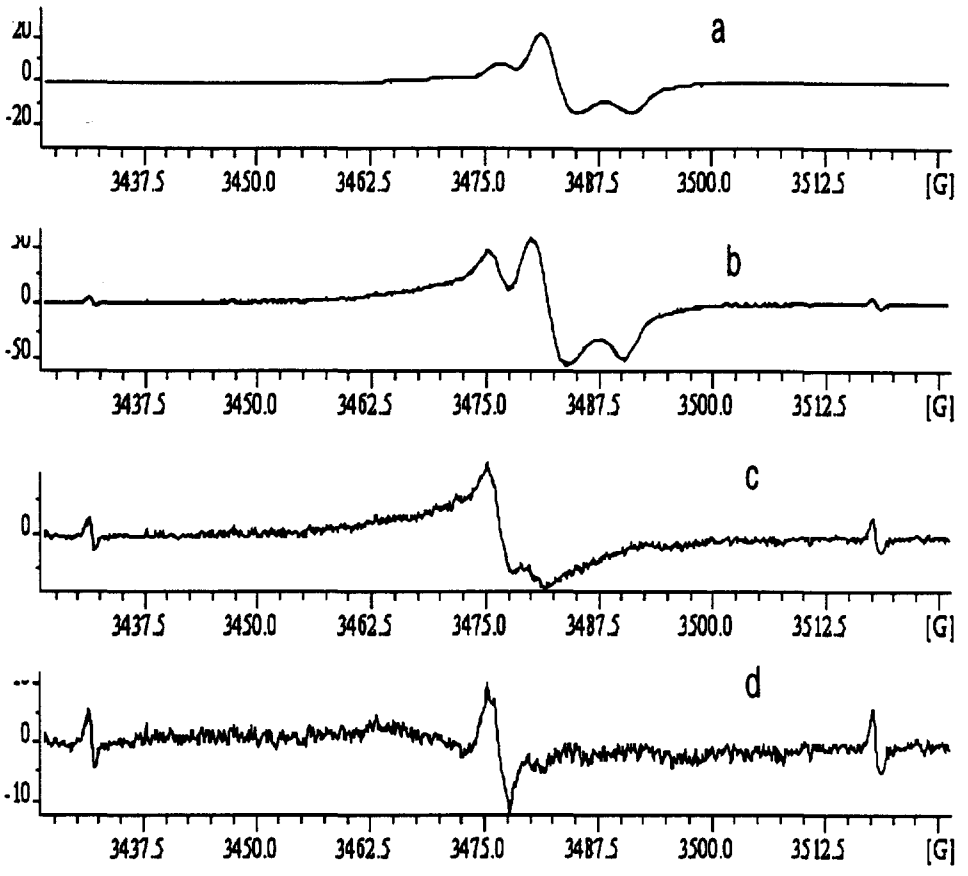
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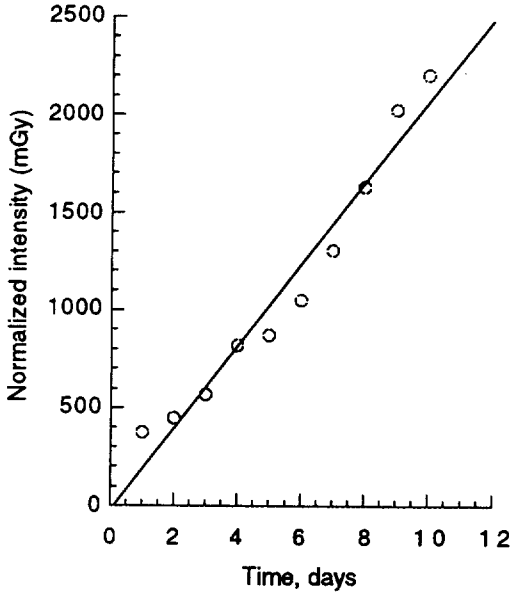
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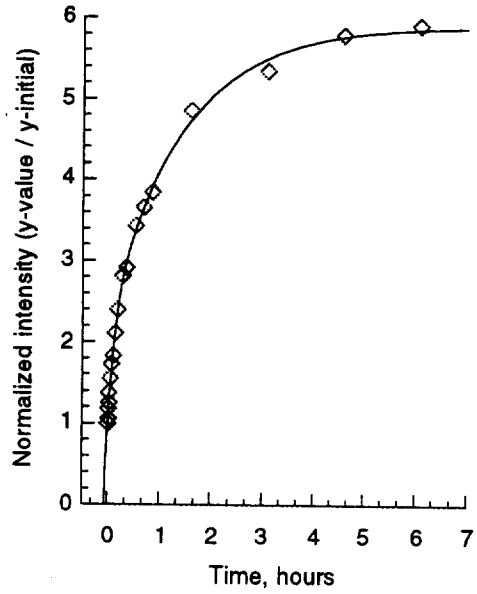
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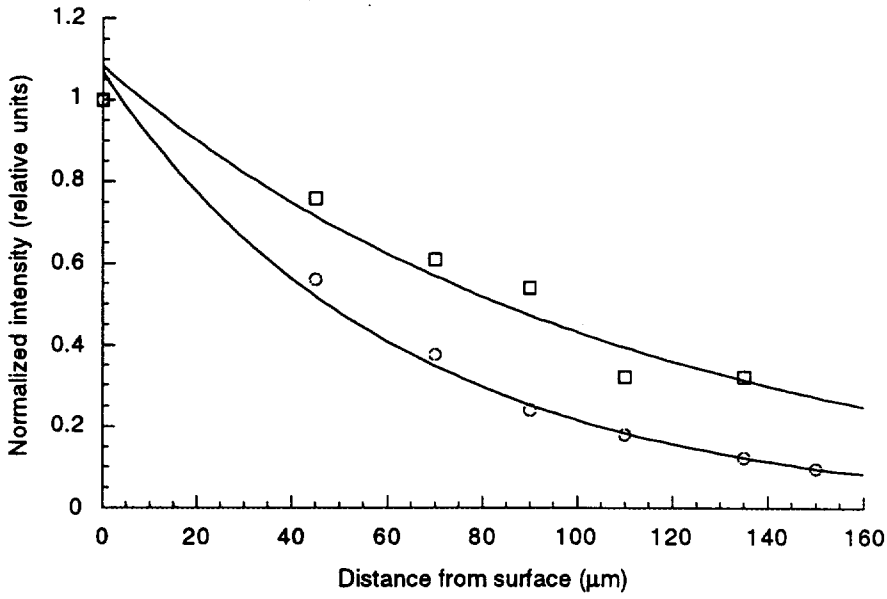
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Distance from surface (μm)

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