



Determination of Optimal Modulation Amplitude for Electron Spin Resonance (ESR) Dating and Dosimetry Studies of Tooth Enamel

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Abstract

Fossil remains, which provide important information about past life and ecology, are especially important in natural history and life evolution. Recently, many interdisciplinary dating studies have been conducted and many different techniques have been used to investigate the data obtained in this field. Electron Spin Resonance (ESR) (or alternatively, Electron Paramagnetic Resonance, EPR) is one of the methods used in absolute dating and dosimetry studies. It is based on determination of the radiation-centered radicals obtained from the radiation dose absorbed by irradiated materials.

One of the important problems in dosimetry and dating studies performed with ESR method is the dependence of experimental parameters on the accumulated dose. The accumulated dose value is effective in determining the actual result of the dating and dosimetric samples. This value is influenced from the stability of the ESR centers, experimental stages, sample preparation or measurement processes.

In this study, how the modulation amplitude parameter affects ESR signal intensity in ESR dating and dosimetry studies of tooth enamel investigated. The selective archaeological animal tooth enamel sample was used from the archaeological site of Köşk Höyük, in Turkey for experimental studies. This sample was prepared with combined processes of mechanical and chemical treatment of tooth in laboratory. Tooth enamel sample was irradiated by ⁶⁰Co gamma-ray source in dose of 1kGy. After irradiation, ESR spectra were recorded at different modulation amplitude values at room temperature using X-band ESR Spectrometer. According to the results obtained, the most suitable modulation amplitude values for ESR measurements of tooth enamel sample examined in the study.

Keywords: ESR, Tooth Enamel, Dating, Dosimetry, Modulation Amplitude.

Diş Minesinin Elektron Spin Rezonans (ESR) Tarihlendirme ve Dozimetri Çalışmalarında En Uygun Modülasyon Genliğinin Belirlenmesi

Öz

Geçmiş yaşam ve ekoloji hakkında önemli bilgiler veren fosil kalıntıları, özellikle doğa tarihi ve canlı evriminde önemli bir yere sahiptir. Son zamanlarda, bu alanda elde edilen verileri değerlendirmek için disiplinler arası tarihlendirme çalışmaları yapılmakta ve birçok farklı teknik kullanılmaktadır.

Elektron Spin Rezonans (ESR) (veya diğer adıyla Elektron Paramanyetik Rezonans, (EPR)) mutlak tarihlendirme ve dozimetri çalışmalarında kullanılan yöntemlerden biridir. Işınlanmış materyaller tarafından soğrulan radyasyon dozu sonucu elde edilen radyasyon merkezli radikallerin belirlenmesi ile ilgilidir. ESR yöntemi ile yapılan dozimetri ve tarihlendirme çalışmalarında önemli sorunlardan birisi, deneysel parametrelerin biriken doz üzerinde bağımlılığının olmasıdır. Materyallerin gerçek yaşlarının belirlenmesinde etkili olan doz değeri ESR merkezlerinin kararlılığından, numune hazırlama ya da ölçüm işlemleri gibi çeşitli aşamalardan etkilenmektedir.

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Bu çalışmada, diş minesi ile yapılan ESR tarihlendirme ve dozimetri çalışmalarında modülasyon genliği parametresinin ESR sinyal şiddetini nasıl etkilediği incelendi. Deneysel çalışma için, Köşkhöyük arkeoloji kazı alanından çıkarılan arkeolojik hayvan diş minesi örneği kullanıldı. Ölçüm işleminden önce diş minesi örneği, laboratuvar ortamında diş üzerine mekanik ve kimyasal işlemler uygulanarak hazırlandı. Daha sonra örnek, ⁶⁰Co gama-kaynağı ile yaklaşık 1kGy ışınladı. Işınlama işleminden sonra örneğin ESR spektrumları X-Band ESR Spektrometresi yardımıyla oda sıcaklığında farklı modülasyon genliği değerlerinde kaydedildi. Elde edilen sonuçlara göre, çalışmada incelenen diş minesi örneğinin ESR ölçümleri için en uygun modülasyon genliği değeri belirlendi.

Anahtar Kelimeler: ESR, Diş minesi, Tarihlendirme, Dozimetri, Modülasyon Genliği.

1. Introduction

Electron Spin Resonance (ESR) (or alternatively, Electron Paramagnetic Resonance, EPR) is a powerful and sensitive method for identification of paramagnetic centers and free radicals in solids and liquids (Karatas, 2012; Jonas, 1997). It provides a detailed description for different materials and widely used for a lot of area such as medicine (Sarcan et al., 2020); archaeology (Duval et al., 2018); geology (Lopes et al., 2020); industrial irradiations (Karatas, et al., 2016); dosimetry (Toyoda et al., 2020); dose reconstruction for several radiation events and accidents (Skvortsov et al., 2000) etc.

One of the most reliable materials in dosimetry and dating studies using Electron Spin Resonance (ESR) method is tooth enamel (Duval et al., 2018; Grün, 1989; Han et al., 2016; Harsman et al, 2018; Jonas, 1997; Scholom & Desrosiers, 2014; Todaka et al, 2020). ESR dosimetry and dating using tooth enamel sample is based on detection of the long-lived radiation-induced centers in material (Grün, 1991; Fattibene & Callens, 1002010; Ikeya, 1993). The concentration of these centers can be used to determine the burial time and the radiation dose absorbed by sample (Ivannikov et al., 2002; Rink & Thomson, 2015; Vatnitsky, 2002).

There are many important parameters that affect the intensity of the ESR dosimetric signal, which is a function of the magnetic field, such as microwave power and modulation amplitude (Fattibene & Callens, 2010; Lyons et al., 1988; Murphy, 2009). In many studies with the ESR spectrometer, modulation amplitude is a less determining parameter compared to microwave power (Fattibene & Callens, 2010; Ikeya, 1993; Ivannikov et al., 2002; Galtsev et al., 1996). Considering the previous studies, it has been observed that the variation of this value is quite small (Fattibene & Callens, 2010; Ikeya, 1993). However, the ESR signal often increases linearly at low values of modulation amplitude. When the modulation amplitude becomes comparable to the line width, the signal growth gradually decreases and the lines begin to distort gradually (Ikeya, 1993; Ivannikov et al., 2002). Therefore, to minimize distortions in the ESR signal, it is necessary to take the modulation amplitude smaller than the line width of the ESR signal (Poole, 1982).

In this study, Electron Spin Resonance (ESR) spectra of fossil animal tooth enamel recorded at different modulation amplitude is investigated. The effects of modulation amplitude parameter on ESR signal intensity of tooth enamel studies were obtained experimentally.

2. Material and Method

2.1. Sample Description

In this study, an animal tooth with 3 cm long, obtained from archaeological site of Köşk Höyük, Niğde, Turkey was used. When selecting the tooth sample, a considerable care was taken, that the sample had not any broken and disease, to ensure that the results obtained from the experimental studies are reliable. The sample was brought to the laboratory without cleaning the sediments on it.

2.2. Sample Preparation

In this study, sample preparation was carried out at laboratory in Niğde Ömer Halisdemir University. Firstly, sample was washed in pure water and dried at room temperature. The dried tooth sample was cut transversely using a diamond dentist drill. The crown part and the root part were separated from each other. All parts were kept for one day in the ultrasonic bath at room temperature. After they thoroughly washed with pure water and dried at 30°C in the oven. The dentine parts remaining in the enamel layer on the dried tooth fragments were carefully scraped with a dental drill. The enamel pieces obtained were kept in chemical solvent for cleaning the other calcite components. Then washed with distilled water, and kept in another chemical solvent for removing the organic components contained therein. After samples were washed with pure water again and left to dry.

The dried enamel pieces were grinded and then eliminated in size of 45 µm - 125 µm with using sieves. The powder tooth enamel sample obtained was weighed and placed in sample container for measurements.

2.3. Sample Irradiation

In this study, irradiation of powder tooth enamel sample was performed with ⁶⁰Co gamma-source with a speed of 1.993 kGy/h per hour in irradiation laboratory of Çekmece Nuclear Research and Training Center (ÇNAEM), Turkey. The amount of radiation dose absorbed by sample was calculated with speed of the source and irradiation dose was determined as 1kGy.

2.4. ESR Measurements

After irradiating the powder sample, it was used for obtaining the modulation amplitude of the ESR. ESR spectra of tooth enamel sample have been recorded by using Bruker EMX model X- band ESR Spectrometer in IFW, Dresden, Germany at room temperature. Powder tooth enamel sample has been placed in ESR quartz tube and centered vertically in cavity. The field derivative of microwave power absorption (dP/dH) has been recorded as a function of static magnetic field. The ESR

measurements have been set to obtain analyzable ESR signals as following: The microwave power was 10mW, the modulation frequency was 100 kHz and different modulation amplitude values were between 0.25G and 10G.

3. Results and Discussion

In this study, ESR spectra of gamma irradiated powder tooth enamel sample were recorded at different modulation amplitude values (0.25G, 0.50G, 0.75G, 1G, 2G, 3G, 4G, 5G, 6G, 7G, 8G, 9G, 10G) at room temperature. These ESR spectra are shown in Figure 1.

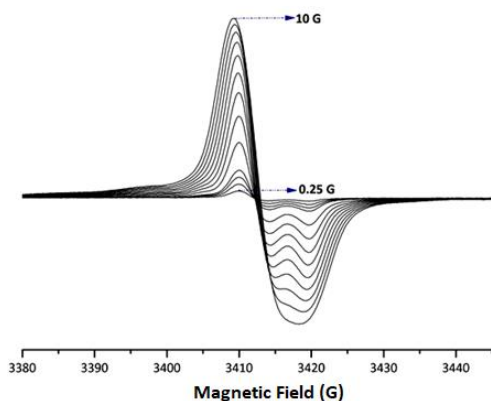


Figure 1. ESR spectra of 1kGy irradiated powder tooth enamel sample recorded in different modulation amplitudes according to magnetic field

As seen in Figure 1., when the modulation amplitude started to increase, deformations of the ESR signal were observed. The expected dating or dosimetric signal was clearly visible at low modulation amplitude values. However, as the modulation amplitude increases, the two splitting peaks at the bottom of the spectrum are increasingly being observed as a single peak. Because, when the line widths of the two split peaks were compared with modulation amplitude values, the line widths of the peaks were smaller than modulation amplitude at high modulation amplitude values. Therefore, at high modulation amplitude values, the distance between two peaks were closed and started to be a single peak.

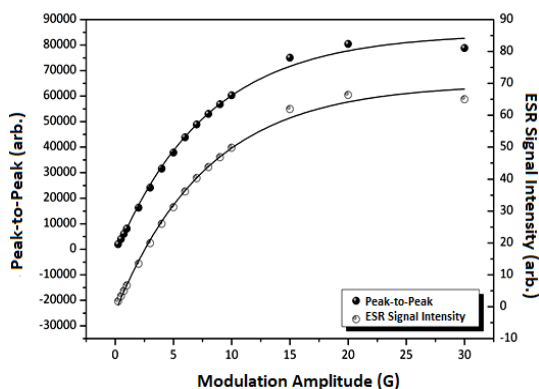


Figure 2. Variation of ESR signal intensity and peak to peak values of 1kGy irradiated tooth enamel sample with different modulation amplitudes

In Figure 2., variation of ESR signal intensity and peak to peak values of 1kGy irradiated powder tooth enamel sample with different modulation amplitudes are shown. It is seen in Figure.2 that the modulation amplitude increased in direct proportion with the signal intensity. As the modulation amplitude increased, the signal intensity increased until the distance between the two splitting peaks at the bottom of the spectrum was closed. Then signal intensity remained constant when two splitting peaks were combined into a single peak.

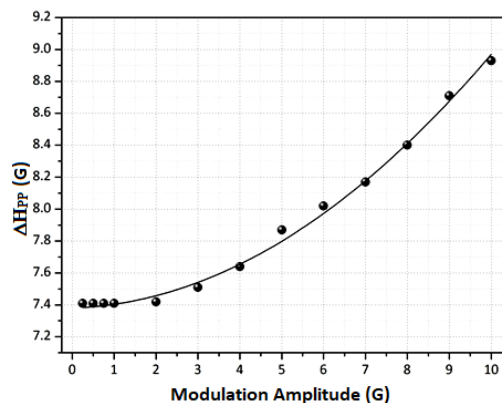


Figure 3. Variation between ΔH_{pp} values of 1kGy irradiated powder tooth enamel sample and different modulation amplitudes

In Figure.3, the magnetic field variations observed in the ESR signal intensity, ΔH_{pp} , were investigated at different modulation amplitude values. According to the spectra at different modulation amplitude values ranging from 0.25 G to 10 G; ΔH_{pp} values were stable until ~ 2 G modulation amplitude and then increased sharply after this value. So, this figure clearly showed that the optimal modulation amplitude values for the dating and dosimetry signal of the tooth enamel sample from Köşkhöyük were between 0.25G and 2G.

It has been experimentally proven that the line width of the dating and dosimetric signal of the tooth enamel sample is around 3G, with the curve fit using the Gaussian function (Ikeya, 1993; Bulur, 1998). The results will be misleading when a higher value than 3G is set for dating and dosimetric studies. So, it is necessary to determine the best value for the modulation amplitude. The smaller modulation amplitude value helps dissolve overlapping signals and prevents deviations in the signal-to-noise ratio results. The behaviors of the ESR peaks obtained at low modulation amplitude clearly indicate that there are multiple overlapping signals with different relaxation behaviors in the respective region of the spectra. The high modulation amplitude value in the dating and dosimetric signals causes the other signals to be hidden. So, the results obtained in this study are agreement with literature and show that the modulation amplitude value should be less than 3G.

4. Conclusions and Recommendations

According to the ESR results of fossil tooth enamel samples, the modulation amplitude was found to be one of the most important parameters affecting the signal intensity in the ESR dating and dosimetric measurements of the tooth enamel

sample. Dosimetric and dating signal for tooth enamel sample is hidden at high values of modulation amplitude. So, when the modulation amplitude is set higher than 3G in ESR dosimetry and dating studies of tooth enamel, the results will be misleading. In this study, the most suitable modulation amplitude values for ESR dating and dosimetry measurements of tooth enamel sample from Köşkhöyük was found to be between 0.25G and 2G. This result is agreement with literature.

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References

- Duval, M., Grün, R., Pares, J. M., Martin-Frances, L., Campana, I., Rosell, J., Shao, Q., Arsuaga, J. L., Carbonell, E. & Bermudez de Castro, J. M. (2018). The first direct ESR dating of a hominin tooth from Atapuerca Gran Dolina TD-6 (Spain) supports the antiquity of Homo antecessor. *Quaternary Geochronology*, 47, 120-137. <https://doi.org/10.1016/j.quageo.2018.05.001>.
- Fattibene, P., & Callens, F. (2010). EPR dosimetry with tooth enamel: A review. *Applied Radiation and Isotopes*, 68, 2033-2116. <http://dx.doi.org/10.1016/j.apradiso.2010.05.016>.
- Galtsev, V. E., Galtseva E. V. & Lebedev (1996). Optimal registration conditions for tooth EPR dosimetry at low accumulated dose. *Applied Radiation Isotopes*, 47(11/12), 1311-1315. [http://dx.doi.org/10.1016/S0969-8043\(96\)00147-9](http://dx.doi.org/10.1016/S0969-8043(96)00147-9).
- Grün, R. (1989). Electron spin resonance (ESR) dating. *Quaternary International* 1, 65-109. [http://dx.doi.org/10.1016/1040-6182\(89\)90010-4](http://dx.doi.org/10.1016/1040-6182(89)90010-4).
- Grün, R. (1991). Potential and problems of ESR dating. *Nuclear Tracks and Radiation Measurements*, 18(1/2), 143-153. [https://doi.org/10.1016/1359-0189\(91\)90106-R](https://doi.org/10.1016/1359-0189(91)90106-R).
- Han, F., Sun, C., Bahain, J. J., Zhao, J., Lin, M., Xing, S., & Yin, G. (2016). Coupled ESR and U-series dating of fossil teeth from Yiyuan Hominin Site, Northern China. *Quaternary International*, 400, 195-201. <http://dx.doi.org/10.1016/J.QUAINT.2015.05.052>.
- Harsman, A., Toyoda, S. & Johnson, T. (2018). Suitability of Japanese wild boar tooth enamel for use as an electron spin resonance dosimeter. *Radiation Measurements*, 116, 46-50. <https://doi.org/10.1016/j.radmeas.2018.07.001>.
- Ikeya, M. (1993). *New applications of ESR-dating, dosimetry, and microscopy*. 2nd Edition, World Scientific Publication, Singapore.
- Ivannikov, A.I., Trompier, F., Gaillard-Lecanu, E., Skvortsov, V.G. & Stepanenko, V.F. (2002). Optimisation of recording conditions for the electron paramagnetic resonance signal used in dental enamel dosimetry. *Radiation Protection Dosimetry*, 101(1-4), 531-538. <http://dx.doi.org/10.1093/oxfordjournals.rpd.a006043>.
- Jonas, M. (1997). Concept and Methods of ESR dating. *Radiation Measurements*, 27(5/6), 943-973. [http://dx.doi.org/10.1016/S1350-4487\(97\)00202-3](http://dx.doi.org/10.1016/S1350-4487(97)00202-3).
- Karatas, O. & Aras, E. (2012). Electron Paramagnetic Resonance (EPR) of Gamma-Irradiated Single Crystals of Ethan-1, 2 Disulfonic Acid Disodium. *Journal of Molecular Structure*, 1027, 49-52.
- Karatas, O., Aras, E., Karadag, A. H., İşlek, Y. (2016). Electron Paramagnetic Resonance (EPR) study of gamma-irradiated methyl 4-methyl benzoate (C₉H₁₀O₂). *Radiation Effects & Defect in Solid*, 171(7-8), 651-657. <https://doi.org/10.1080/10420150.2016.1240175>.
- Lopes, R. P., Pereira, J. C., Kinoshita, A., Mollemberg, M., Barbosa Jr., F. & Baffa, O. (2020). Geological and taphonomic significance of electron spin resonance (ESR) ages of Middle-Late Pleistocene marine shells from barrier-lagoon systems of Southern Brazil. *Journal of South American Earth Sciences*, 101, 102605. <https://doi.org/10.1016/j.jsames.2020.102605>.
- Lyons, R. G., Bowmaker, G. A. & O'Connor, C. J. (1988). Dependence of accumulated dose in ESR dating on microwave power: A contra-indication to the routine use of low power levels. *Nuclear Tracks and Radiation Measurements*, 14(1/2), 243-251.
- Murphy, D. M. (2009). *EPR (Electron Paramagnetic Resonance) spectroscopy of polycrystalline oxide systems*, Wiley Publication, Weinheim.
- Bulur, E. (1998). Investigation of paramagnetic properties of tooth enamels by Electron Spin Resonance (ESR) Technique. PhD thesis, The Middle East Technical University, p.56.
- Poole, C.P. (1982). *ESR: A comprehensive treatise on experimental techniques*. 2nd Edition, John Wiley&Sons, Inc., Newyork.
- Rink, W.J. & Thompson, J.W. (2015). *Encyclopedia of Scientific Dating Methods*, Springer Publication, Netherlands, 239-254.
- Sarcan, E. T., Tas, A., Silindir-Günay, M., Ozer, A. Y., Colak, S. & Hekimoglu, B. (2020). ESR investigations of x-ray exposed drugs. *Journal of Pharmaceutical and Biomedical Analysis*, 188, 113311. <https://doi.org/10.1016/j.jpba.2020.113311>.
- Sholom, S., & Desrosiers, M. F. (2014). EPR and OSL emergency dosimetry with teeth: a direct comparison of two techniques. *Radiation Measurements*, 71, 494-497. <http://dx.doi.org/10.1016/j.radmeas.2014.03.015>.
- Skvortsov, V. G., Ivannikov, A. I., Stepanenko, V. F., Tsyb, A. F., Khamidova, L. G., Kondrashov, A. E., & Tikunov, D. D. (2000). Application of EPR retrospective dosimetry for large-scale accidental situation. *Applied Radiation and Isotopes*, 52, 1275-1282.
- Todaka, A., Toyoda S., Natsuhori, M., Okada, K., Sato, I., Sato, H. & Sasaki, J. (2020). ESR assessment of tooth enamel dose from cattle bred in areas contaminated due to the Fukushima Dai-ichi nuclear power plant accident. *Radiation Measurements*, 136, 106357. <https://doi.org/10.1016/j.radmeas.2020.106357>.
- Toyoda, S., Murahashi, M. & Ivannikov, A. (2020). ESR tooth enamel retrospective dosimetry quoted as spin numbers. *Radiation Measurements*, 135, 106333. <https://doi.org/10.1016/j.radmeas.2020.106333>.
- Vatnitsky, S. (2002). Use of electron paramagnetic resonance dosimetry with tooth enamel for retrospective dose assessment. *International Atomic Energy Agency (IAEA), (IAEA-TECDOC-1331), Austria*.