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Investigation of Radiation Effects on Coffee Beans Using ESR Technique

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Abstract. In this study, radiation effects on coffee beans have been investigated by Electron Spin Resonance (ESR) technique. ESR spectra of natural and irradiated samples at different doses between 0.5 Gy and 11 kGy by ^{60}Co gamma source were recorded with X-band ESR spectrometer and, radiation dose, ESR microwave power and cavity temperature dependency of paramagnetic centers were investigated. At the results of dose-response and kinetic studies it was determined that the paramagnetic centers in coffee beans are stable, and sensitive to radiation. Thus, it is shown that the irradiated beans can be used for detection as radiation dosimeter in the investigated dose range.

***Keywords*:** Electron Spin Resonance (ESR), coffee beans, irradiation.

Radyasyonun Kahve Çekirdeklerine Etkisinin ESR Tekniği ile İncelenmesi

Özet. Bu çalışmada kahve çekirdeği üzerine radyasyonun etkisi Elektron Spin Rezonans (ESR) tekniğiyle incelenmiştir. Doğal ve ^{60}Co gama kaynağı ile 0.5 Gy ile 11 kGy doz aralığında farklı dozlarda ışınlanmış örneklerin spektrumları X-band ESR spektrometresiyle kaydedilmiş ve oluşan paramanyetik merkezlerin radyasyona, ESR mikrodalga gücüne ve kavite sıcaklığına bağlı değişimleri araştırılmıştır. Doz-cevap ve kinetik çalışmalar sonucunda kahve çekirdeğindeki paramanyetik merkezin radyasyona duyarlı ve kararlı olduğu belirlenmiş, incelenen doz aralığında dozimetrik amaçlı ve ışınlanmış gıda dedeksiyonu için kullanılabilirliği gösterilmiştir.

***Anahtar Kelimeler*:** Elektron Spin Rezonans (ESR), kahve çekirdeği, ışınlama.

1. INTRODUCTION

Electron Spin Resonance (ESR) has been successfully applied to copper salts by Russian physicist Y.K. Zavoisky in 1945 for the first time [1] and, it is the unique spectroscopic method that can be used to examine both organic and inorganic specimens by making it possible to direct determination of the paramagnetic centers in the host material [2].

High-energy radiation can create paramagnetic centers in many substances and the intensity of the paramagnetic centers is proportional to the amount of radiation exposed by the material, i.e., dose of absorption.

Therefore, if radiation (UV, X-ray, α, β, γ) sensitive paramagnetic centers are formed in any material and these centers are stable, ESR signals

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of these centers can be used in the measurement of the radiation dose that absorbed.

The ESR dosimetry method is based on the principle of determining the intensity of radicals generated by irradiation in order to determine the amount of absorbed dose by the material, and the materials used for this purpose are called ESR dosimeters.

Because of food products are especially easily accessible, it is very important that they can be used as an ESR dosimeter in the case of radiation accidents [3, 4]

Irradiation has also been recognized around the world as one of the most effective methods of reducing food production losses, extending shelf life, and ensuring food safety [5-8].

As a result of its social and economic benefits, radiation sterilization has a widespread usage in the world, so in recent years, the volume of irradiated food products on market shelves have been growing steadily.

Although food irradiation is a proven sterilization technique today through scientific works and legal regulations in this area, in order to gain consumer confidence and to facilitate the international trade, it is very important to determine whether the food is irradiated or not, and to determine the absorbed dose in the case of irradiation.

ESR is a powerful spectroscopic technique used in irradiated food detection and in the search of paramagnetic centers created by radiation since it allows direct examination of the paramagnetic centers formed by irradiation and can be applied without harming the organic samples [4, 9-15].

In this study, the effect of irradiation on coffee samples which has an important place in our life was investigated using ESR technique. Radiation sensitivity and stability of the paramagnetic centers induced by irradiation were determined.

2. MATERIALS AND METHODS

The coffee beans which were purchased from a local market, cleaned with distilled water and dried at room temperature without exposure to sunlight. Then they were gently grinded with an agate mortar and sieved to have 125-250 μm grain sized samples. Finally, the powdered samples were packed in equal mass and irradiated at a radiation dose range of 0.5 kGy to 11 kGy at room temperature using the ^{60}Co irradiation facilities of the Turkish Atomic Energy Authority Sarayköy Nuclear Research and Application Center (SANAEM).

ESR spectra of the both natural and the irradiated samples were recorded at several spectrometer conditions with JEOL JesFa-300X-band ESR spectrometer located in Selcuk University Advanced Technology Research and Application Center ESR Laboratory. Kinetic measurements were done using JEOL liquid nitrogen temperature control unit. The g value of the paramagnetic center was calculated by using Mn^{2+} signals of the MgO (Mn^{2+}) sample which are used as a standard in JEOL ESR spectrometers.

3. RESULTS AND DISCUSSION

In order to determine the magnetic properties of natural coffee beans, firstly, ESR spectra of the non-irradiated powdered samples were recorded at room temperature. As shown in Figure 1, an ESR signal with the g value 2.0047 were observed at the ESR spectrum taken at 1 mW microwave power and 500 mT magnetic field sweep width. According to this spectrum, naturel coffee beans have paramagnetic structure, also it is seen that there are no signal due to iron oxide or manganese impurities.

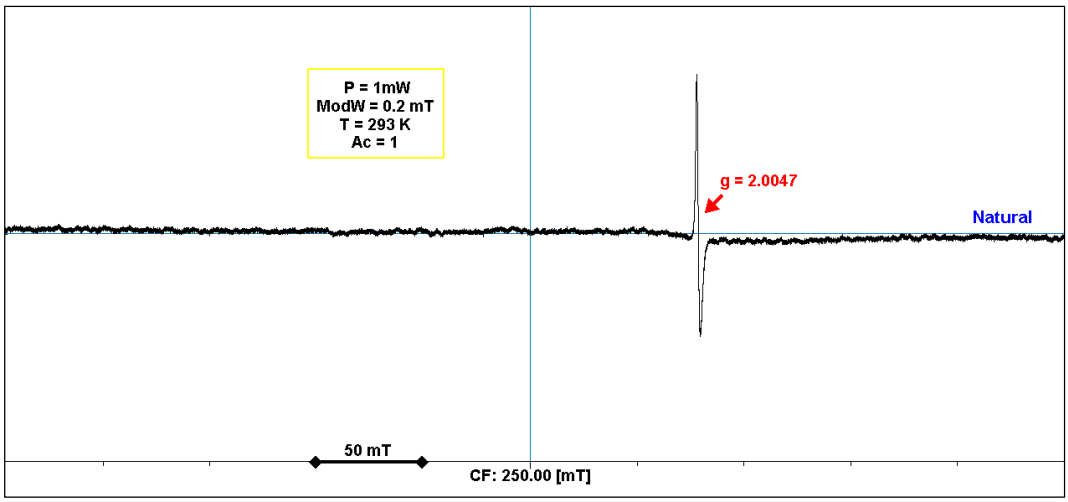

Figure 1. ESR spectra of natural coffee beans recorded at 500 mT sweep width.

In order to investigate the effect of radiation, the powdered samples packed in equal mass were irradiated at a radiation dose range of 0.5 kGy to 11 kGy. The ESR spectra of natural and 5 kGy irradiated samples were given in Figure 2. As can be seen from the spectra, the intensity of g=2.0047 signal increased due to the radiation dose and there is not any other radiation induced signal except this.

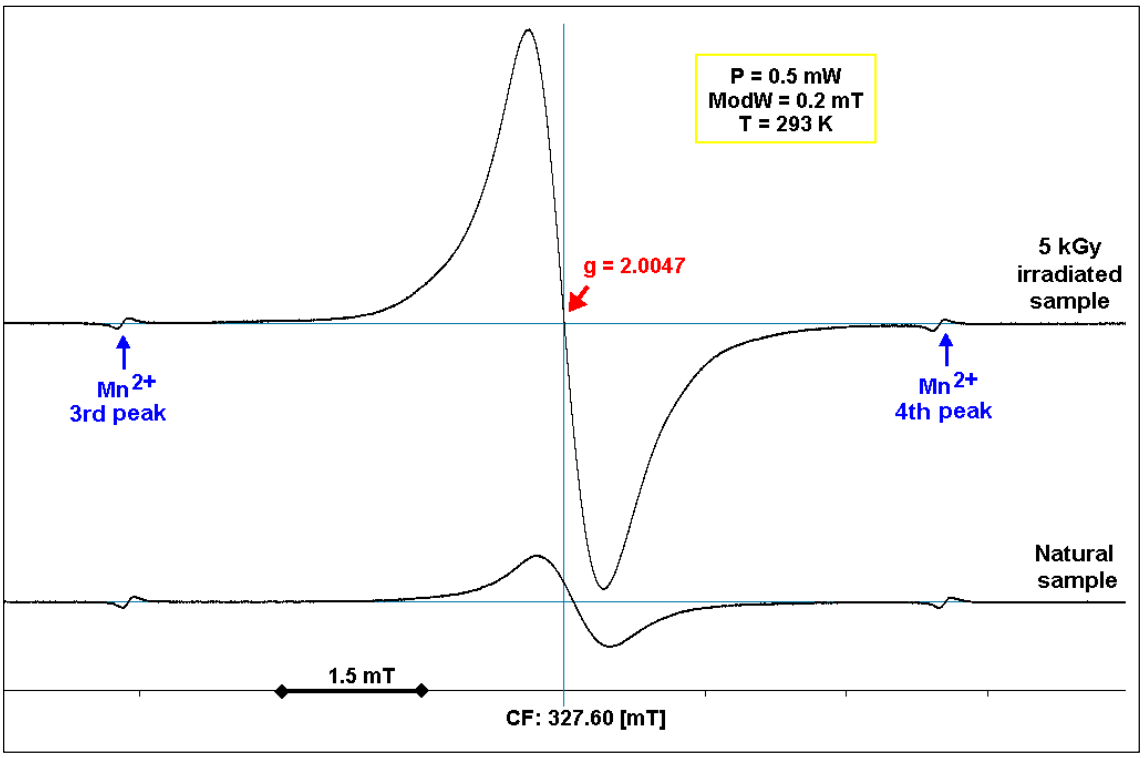

Figure 2. ESR spectra of natural and 5 kGy irradiated coffee bean samples.

In order to observe the changings of these signals due to microwave power and to determine whether they are belongs to same paramagnetic center or not, the ESR spectra of the natural and 11 kGy irradiated samples were recorded at the range of 0.1mW and 4 mW microwave power and, the graphs of ESR signal intensities were plotted versus square root of microwave power. According to graphs in given Figure 3 the dependence on the microwave power of signal intensities are the same

for both natural and irradiated samples and the signal intensities increase exponentially between approximately 0.1 mW and 0.7 mW powers and saturate at approximately 1 mW of microwave power.

It has determined that the the g=2.0047 signal which is observed in the natural sample and, of which intensity increased depending on the dose of applied radiation is belong to semiquinone radical observed in cellulose containing foods and known to be sensitive to radiation [4].

In order to determine dependency of signals at ESR spectra of samples to the radiation, they were irradiated between 0.5 kGy and 11 kGy doses and, the spectra were recorded at 0.5 mW microwave power far from the saturation point and at room temperature. The dose response curve of g=2.0047 signal is shown in Figure 4, and the data of this curve is best fitted to $y(x)=y_0+a(1-\exp(-bx))$ function where the fit parameters are found as $y_0=453\pm70$, $a=3824\pm240$, $b=0.1743\pm0.0249$ with the $R^2=0.99$ correlation coefficient.

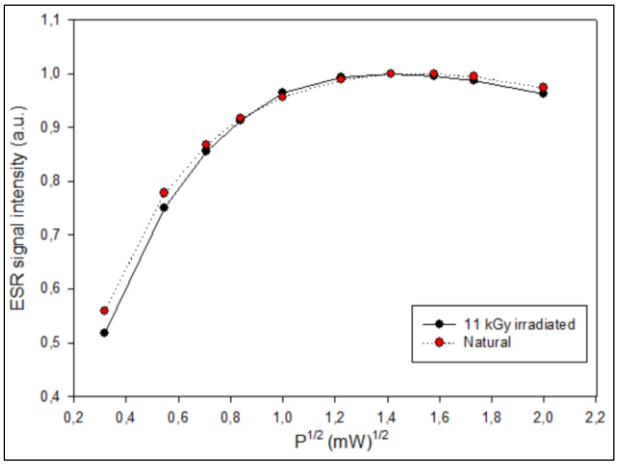

Figure 3. Microwave dependence of g=2.0047 signal.

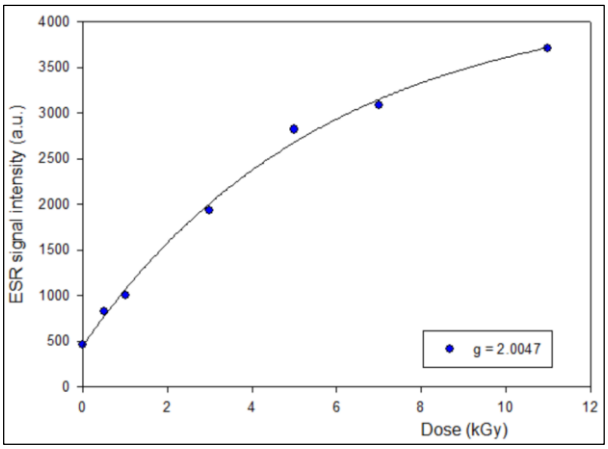

Figure 4. Dose response curve of g=2.0047 signal.

For determining the thermal stability of the radiation sensitive g=2.0047 signal, the ESR spectra of 7 kGy irradiated sample were recorded at 50 ° C spectrometer temperature at intervals of 3-5 minutes up to 65 minutes and, the isotherm curves of these signals for both irradiated and natural samples are given in Figure 5.

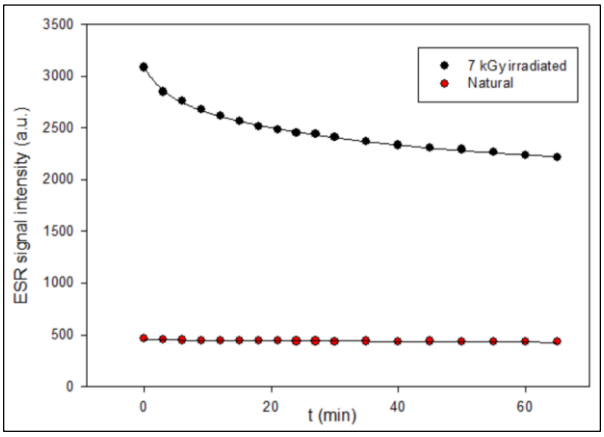

Figure 5. Isothermal annealing curve of g=2.0047 signal for natural and irradiated samples at T=50 °C constant temperature.

As clearly seen from the graph given in Figure 5, while the isotherm curve of the natural sample has not changed over time and remained constant, that of the 7 kGy irradiated sample was best fitted to the function shaped $I(t)=I_{01}\exp(-k_1t)+I_{02}\exp(-k_2t)$.

For irradiated specimen fit parameters of isotherm curve function were calculated as; $I_{01}=447.05\pm24.37$, $k_1=0.1607\pm0.0171$, $I_{02}=2626.07\pm23.71$, $k_2=0.0029\pm0.0002$ with the

correlation coefficient R^2=0.99. Here, I_{01} and I_{02} are the initial ESR signal intensities of two different paramagnetic centers, and k_1 and k_2 are the frequency factors of these paramagnetic centers at 50 °C constant temperature. According to these parameters; it was determined that the investigated signal had two different components with a thermal-life of τ_1 = 6.22 minutes and τ_2=344.8 minutes at this temperature.

It becomes definite from the kinetic measurements at 50 °C that there are an unstable short-lived radical and a stable long-lived radical in the sample. Also, interestingly the isotherm curve behaviors at this temperature for natural and irradiated specimens are different and this is very important both to distinguish the two radicals induced by radiation and to determine if the sample is irradiated or not.

After the annealing process for 65 minutes at 50 °C, the natural and irradiated samples were annealed between 50 °C - 150 °C temperatures at 10 °C intervals for 3 minutes constant time and, ESR spectra of the samples were recorded at each temperature.

The change of g=2.0047 signal depending on the temperature is given in Figure 6. According to this graph it has been determined that in the case of 7 kGy irradiated coffee, the increasing part of the paramagnetic center due to the irradiation effect is completely quenched at 120 °C temperature, and the intensity of signal is now equal that of natural sample. It was also determined that the signal intensity of the natural sample weakened slightly to +150 °C, but still does not quench.

Additionally, in order to determine the room temperature stability of the radiation sensitive paramagnetic center with g=2.0047, assigned to semiquinone radical, the natural and 5 kGy irradiated specimens were stored at room temperature for 1.5 months and ESR spectra of them were recorded for 2-5 days intervals during this time. The decay curves for room temperature of the signal in natural and irradiated specimens are shown in Figure 7. According to the room temperature kinetics study, it was determined that at the end of 1.5 months, the signal intensity of the 5 kGy irradiated coffee sample decreased by only 36% of the initial value. As expected, the natural signal has not changed.

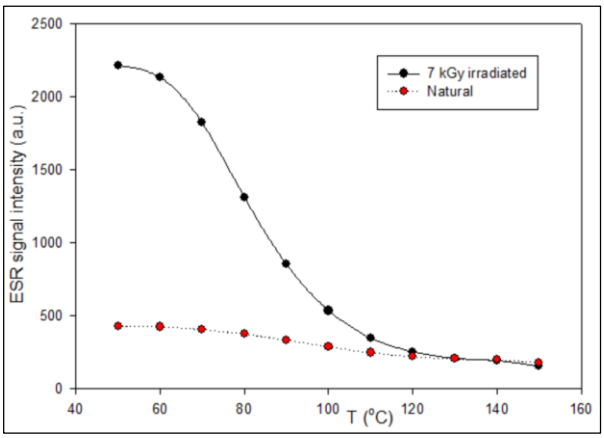

Figure 6. Isochronal annealing curve of g=2.0047 signal for natural and irradiated samples between T=50 °C and T=150 °C temperatures.

The room temperature isotherm curve of the irradiated example was fitted to the $I(t)=I_{01}\exp(-k_1t)+I_{02}\exp(-k_2t)$ shaped function and the fit parameters were found as; I_{01}=386.50±61.17, k_1=1.3720±0.6085, I_{02}=2435.24±37.78, k_2=0.0010±0.0006 with correlation coefficient R^2=0.95. As observed in the annealing process at 50 °C, there are a short-lived unstable radical and a long-lived stable radical in sample. Room temperature lifetime of these radicals were determined as respectively, τ_1=0.729±0.324 day and τ_2=1000±600 day. As clearly seen, the life of the stable radical is quite long.

In all kinetic studies performed, g=2.0047 signal in natural and irradiated coffee samples exhibited different behaviors and irradiated specimens could be distinguished by kinetic measurements.

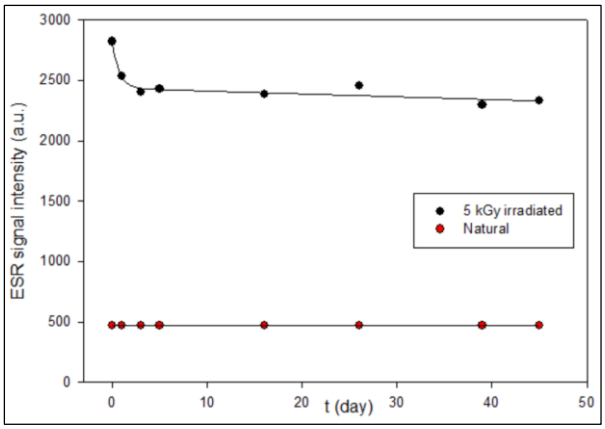

Figure 7. Room temperature kinetic behavior of g=2.0047 signal for natural and 5 kGy irradiated samples.

In this study, the results obtained by ESR analysis of natural and irradiated coffee beans can be summarized as follows:

- It has been determined that radiation sensitive short-lived and long-lived paramagnetic centers are formed in the magnetic field region which are same that of radical formed in natural specimen, so the signals belonging these paramagnetic centers overlap and, form an envelope.
- It was observed by the kinetic measurements that the radiation sensitive paramagnetic center with the g value 2.0047 in coffee beans, was stable and did not completely disappear at 50 ^{o}C annealing temperature and, fairy stable at room temperature. The reason for the stability is that the coffee bean has a hard structure, which gives an advantage in terms of signal detectability or stability with respect to other foods containing cellulose.
- While the presence of this signal in the natural sample can be thought that it may limit its use as radiation dosimetry, it is shown that the signal has quite different kinetic property for natural and irradiated specimens. Thus, the discriminability of natural and irradiated specimens by kinetic studies indicates that the signal can be used in irradiated food detection and as a radiation dosimeter for the investigated dose range.

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