Irradiation detection of oilseed crops by electron spin resonance Postprint

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Abstract

The ESR signal of black sesame, soybean, peanut irradiated with 0 9 kGy absorbed dose was determined and the characteristics and intensity were different. The relationship between signal intensity and absorbed doses was also investigated .The results showed that the ESR spectra of irradiated samples inhibited obvious variation compared to those un-irradiated. The dose-response curves of the samples exposed to gamma rays could be described well by binomial function. Besides, the ESR signal intensity was related to the species of samples. This study may be a method for detection of irradiated oilseed by ESR.

Full Text

Preamble

Irradiation Detection of Oilseed Crops by Electron Spin Resonance

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Abstract
The ESR signals of black sesame, soybean, and peanut irradiated with 0–9 kGy absorbed dose were determined, showing different characteristics and intensities. The relationship between signal intensity and absorbed dose was also investigated. The results showed that the ESR spectra of irradiated samples exhibited obvious variation compared to unirradiated controls. The dose-response curves of samples exposed to gamma rays could be described well by binomial function. Additionally, the ESR signal intensity was related to the species of

samples. This study demonstrates a potential method for detection of irradiated oilseeds by ESR.

Key words: Irradiation, Detection, Electron spin resonance (ESR)

Introduction

Oilseed crops are important agricultural products in international trade. Most oilseeds are consumed as roasted, oil-extracted, or steamed products. However, approximately 25% of these agricultural products suffer from mildew or insect infestation before consumption. Food irradiation, also known as cold pasteurization, is used to ensure food safety and sterility by eliminating or minimizing pathogenic organisms. This processing involves the controlled application of energy from ionizing radiations such as gamma rays, X-rays, and electron beams for food preservation, which can not only enhance the shelf life of food but also optimize storage conditions [1 3]. Ionizing radiation is strong enough to produce free radicals from atoms [4]. Structural damage caused by these free radicals inhibits microbial multiplication, leading to physiological changes that result in the microorganism's inability to replicate [5]. Almost 40 countries, including India, have approved the use of irradiation for over 100 food items, though it remains prohibited in some countries. To facilitate international trade, control of irradiated food can be supported by analytical methods suitable for directly detecting whether a product has been treated with radiation, using the food itself as a radiation marker [6,7].

Based on physical, chemical, biological, and microbiological changes in food products during irradiation, various methods are used for detecting irradiated foods, including physical methods, chemical methods, biological methods, and DNA methods. Physical methods include Electron Spin Resonance (ESR), luminescence techniques, thermoluminescence (TL), photoluminescence (PL), and chemoluminescence (CL) [8 10]. The ESR principle is based on quantum theory and irradiation-produced long-lived paramagnetic active sites of free radicals in organic and inorganic complexes, which has been accepted as a standard method (Committee Europe de Normalization) in the EU community. ESR spectroscopy is characterized by rapidity, specificity, ease of performance, and quantitative estimation [10,11], and is widely used in irradiation detection for various foods and packaging materials.

This paper aims to detect the minimum physical and chemical changes in the irradiation process of oilseed samples (black sesame, peanut, and soybean) using ESR. While detection of irradiated peanut and black sesame has been studied individually by many scientists using ESR technique [12], no papers have reported comparative ESR studies with multiple oilseed crops to discuss similarities and distinctions among them. The ESR investigation on irradiated oilseeds will be described in our work.

2. Materials and Methods

Oilseed samples (black sesame, soybean, and peanut) were purchased from local farmers in Hangzhou, China. Samples were dried in an electric vacuum drying oven until reaching (8$±$2)% moisture content, then crushed with a high-speed crusher. Samples were packed (10 g per pack) in low-density polyethylene ziplock bags and divided into two parts: one for irradiation and another for control. Samples were irradiated at room temperature by a ^{60}Co gamma source at the Institute of Nuclear Agricultural Science of Zhejiang University, Hangzhou (China) with a dose rate of 0.5 kGy/h and absorbed doses of 0.5, 1, 2, 3, 5, 7, and 9 kGy, respectively, with five parallel samples (10 g per pack) for each irradiation dose. The absorbed dose was calibrated with standard silver dichromate (Fricke dosimeter). The uncertainty in radiation doses was approximately $±3±$2)°C) in the dark for further measurement.

ESR measurements of unirradiated (control) and irradiated samples were performed under normal laboratory conditions (approximately 20$±2°$Cand$30±$2% relative humidity) as soon as possible after irradiation. The ESR spectra were obtained using a Bruker A-300 (9–10 GHz) spectrometer equipped with a cylindrical cavity. Quartz tubes with an inner diameter of 5 mm were filled with approximately 30 mg of whole seed samples for each measurement. The tube was centered in the microwave cavity in exactly the same position for each measurement. The spectrometer parameters were: central field 336 mT, microwave power 0.5 mW, modulation frequency 100 kHz, modulation amplitude 0.4 mT, scan range 10 mT, and sweep time 49.925 s. Strong pitch (g=2.0028) was used as a standard sample for measuring the g-factor. Each data point represents the average of at least four independent measurements. The experimental error was estimated to be $±$5%. In this work, the intensity of the ESR signal was measured as the peak-to-peak height of the signal.

3. Results and Discussion

3.1 ESR Spectra of Unirradiated (Control) and Irradiated Oilseed Samples

An ESR singlet was observed in the ESR spectra of all irradiated and unirradiated (control) oilseed samples. In irradiated samples, the intensity of the singlet increased significantly with irradiation dose. The ESR spectra of unirradiated and irradiated oilseed crops are shown in [Figure 1: see original paper].

It has been found that unirradiated samples also exhibit an ESR signal, which can be assigned to cellulose in the plant as reported by Seiichi Saiki et al. (2011). Meanwhile, crushing and storing samples may produce an ESR singlet. Within the irradiation dose range studied, the ESR intensity showed a positive correlation with absorbed dose. Similar correlations have also been obtained for other foodstuffs [13]. Irradiated oilseeds (black sesame, peanut, and soybean) can be easily distinguished if the absorbed dose exceeds 0.5 kGy.

3.2 Dose-Response Curve

As shown in [Figure 2: see original paper], the ESR singlet in the central field of 336 mT increased with absorbed dose. The relationship between ESR intensity and absorbed dose can be described by fitting functions as listed in . Here, Y represents ESR intensity derived from the peak-to-peak amplitude of the ESR singlet, X represents absorbed dose, and R^2 represents the correlation coefficient.

Previous studies have reported that hydrocarbons and 2-alkylcyclobutanones could form during irradiation of sesame seeds, and that hydrocarbons such as 1,7-hexadecadiene and 8-heptadecene could be used as markers to identify irradiated sesame seeds. 2-Alkylcyclobutanones were detected only in irradiated samples at doses >0.5 kGy (2008). Younan Zhu et al. have discussed the initial radicals formed from linoleic acid and linolenic acid irradiated at 77 K and the secondary radicals annealed to room temperature [14]. Therefore, it can be supposed that the signal detected by ESR may be contributed by both linoleic acid and linolenic acid. However, further qualitative and quantitative analysis is still needed. The mathematical function can be used to research the dose-response curve, which can help estimate the dose received by unknown samples using re-irradiation in commercial facilities [15,16].

3.3 Effect of Storage Time on the ESR Singlet

Oilseed crop samples irradiated at 0, 0.5, 2, and 9 kGy were stored under normal laboratory conditions, and their ESR spectra were recorded over 6 months at 30-day intervals. As shown in [Figure 3: see original paper], for black sesame irradiated at 2 kGy, the signal intensity decreased very rapidly in the first 30 days and then decreased more slowly. After 180 days of storage, the signal intensity reduced to approximately 53% of the initial value. Therefore, distinguishing between irradiated and unirradiated samples can still be made even at the end of the 180-day storage period. On the other hand, the rapid decrease of signal intensity in the first 30 days may come from linoleic acid carbon-centered radicals, which have a higher decay constant [17], and a similar phenomenon has been observed in studies of chicken meat and pork [18,19]. However, no significant variation in g-factor or line-width was observed during the storage period.

Conclusion

The intensity of ESR signals from irradiated oilseed samples increases with absorbed dose. The relationship between signal intensity and absorbed dose can be described by fitting functions, with correlation coefficients of soybean (R^2=0.9835) $\geq$ peanut (R^2=0.9764) $\geq$ black sesame (R^2=0.9617). Since the ESR singlet of irradiated oilseed samples can be detected over a storage time of 6 months, ESR determination may be used to distinguish whether oilseeds have been irradiated. The formation mechanism of radicals in oilseeds subjected to irradiation has been discussed.