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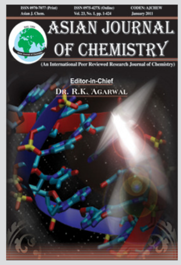

ESR: A Sensitive Technique to Irradiation Treatment of Dry Fruits

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Food irradiation is a preservation technique reported as "cold sterilization", since it has antimicrobial effects without heat increase. Standardization of detection methods for irradiated foods is important for consumer's satisfaction and for the regulatory control purpose. In the present study, electron spin resonance is used to detect irradiated linseeds, chickpea, black eye beans and red beans. This technique successfully identified all the irradiated samples even treated at low doses. It was found that a sharp symmetrical ESR signal at g = 2.00 typical for free radicals appeared in case of irradiated commodities. In linseeds, chickpea, black eye beans and red beans, cellulosic radicals are produced which act as paramagnetic centers. The intensity of this ESR signal increased with the absorbed radiation dose in all the food commodities. The results of this study showed that radiation identification by ESR is authentic and reliable.

Key Words: Electron spin resonance, Radicals, Irradiation, Paramagnetic centers.

INTRODUCTION

Irradiating food is a physical process of exposing food to ionizing radiation without risks of induction of radioactivity and unwanted changes, if irradiation is done within permissible radiation dose recommended by international agencies. Radiation processing has emerged as a clean, safe and effective method to sterilize, disinfect and preserve food and agricultural commodities[1].

For more than 100 years, researchers have been involved in experimenting on the irradiation of foodstuffs. During the early 1950's only isotopes radiation sources existed. Soon after the discovery of X-rays in 1896, they were used for medical sterilization, dental diagnostics and for treatment of disease. By 1905, patents had been filed in the Great Britain and in the US to use irradiation to improve the condition of food. US Army Laboraties in Chicago, Illinois and Natick carried out the innovative research in to irradiation of food at high doses. Irradiation of fresh and frozen poultry was permitted in 1992 and red meat irradiation was approved in 1997[2,3]. International agencies such as International Atomic Energy Agency, Food and Drug Association, World Health Organization (IAEA/FDA/WHO) have recommended that any food item irradiated up to γ-rays dose of 10 kGy is wholesome and beyond any risk. The European Union has recently published the new List of Member States, authorizations of those food and food ingredients which are permitted to be treated with ionizing radiation[4]. In order to distinguish between irradiated and un-irradiated food products as well as to determine their absorbed doses, different physical, chemical and biological methods have been suggested depending upon the nature and type of food material. Control of irradiated food in the market is a requisite of European Union regulations. When the food-stuff is irradiated physical, chemical and biological changes are produced which are so small that cannot be detected by ordinary methods. Therefore sensitive and reliable analytical techniques are required to detect these very minute changes. These radiolytic specific changes can serve as a diagnostic marker for the identification of irradiated foods[5].

Electron spin resonance (ESR) detects radicals, which are radiation specific and are stable in dry and solid components of the food *e.g.*, seeds, bones and shells *etc*. other than these, ESR can also detect typical 'cellulosic radicals'[6]. Viscosity measurements, shear rate variation, pH for gelatinization are some other easy approaches in order to handle physical methods used in many laboratories for irradiation identification[7]. Electron paramagnetic resonance spectroscopy detects paramagnetic centres (*e.g.*, radicals), produced due to irradiation or to other compounds present. Radiation-induced free radicals can be detected in dry and solid parts of the food such as bones (hydroxyapatite radicals), pips seeds, peels, stones, (cellulose radicals) or in dried fruits (sugar radicals) and also in some herbs and spices (containing cellulose). ESR signals, however, may diminish with time. Results are affected by water contents and the nature of foodstuffs[8]. Since electron paramagnetic resonance spectroscopic technique is specific, simple and rapid and its instrumentation is still quite expensive, the method seems to be competent for a large number of food products. One of its applications is on the foods of plant origin containing cellulose[9] and stones, shells, dried spice or strawberry seeds (achenes). ESR spectroscopy can reconstruct accidental exposures. Electron spin resonance is a non-destructive technique that is based on the number of unpaired spins created on irradiation in the irradiated materials[10].

ESR biodosimetry has recently completed a period of successful development and progress. It represents the most reliable and sensitive biodosimetry for retrospective and emergency dosimetry. At present, EPR/ESR method probably represents the only technique in biodosimetry that is future-oriented and has almost science fiction-like application using selected human tissues directly for radiation detection and quantification. This may be of important for occupational, civil and military purposes where the evaluation of individual doses at elevated levels is concerned, originating from radiological incidents including nuclear emergencies or terrorism in the absence of appropriate physical devices for dose measurement.

EXPERIMENTAL

Irradiation of samples: Samples of linseeds, chickpea, black eye beans and red beans were purchased from the local market of Faisalabad and were irradiated at Nuclear Institute for Food and Agriculture (NIFA), Peshawar, Pakistan, using Co-60 γ radiation source. Samples were irradiated to the absorbed doses ranging from 0-10 kGy as recommended by the international organizations such as FAO, IAEA and WHO1.

ESR measurements: Electron spin resonance (ESR) or electron paramagnetic resonance (EPR) measurements were carried out according to the EN[9]. European standard using ESR spectrometer (JESTE 300; Jeol Co., Tokyo, Japan) at Center for instrumentation, Kyungpook National University, Daegn, South Korea. Samples of linseeds, chickpea, black eye beans and red beans were dried at 40 ºC for 48 h to remove short life ESR signals and moisture. About 0.5 g of dried and finally ground samples were placed in an ESR quartz tube. The ESR spectra for the un-irradiated and irradiated samples were recorded at conditions, which are as follows: magnetic field: 327.22 ± 0.5 mT, microwave frequency: 9.187 GHZ, microwave power: 0.4 mW, modulation frequency: 100 KHZ, time constant: 0.03 s, sweep width: 10 mT, sweep time: 30 s.

RESULTS AND DISCUSSION

Electron spin resonance is a simple, fast and sensitive technique for irradiation detection in various foods. Free radicals generated by γ irradiation are trapped in bones, shells or other hard or cellulosic parts of the foods. These free radicals give typical signal, in the ESR spectrum that can be potentially applied for irradiation identification. The intensity of ESR signal or its peak height is proportional to free radicals, which is linearly co-related with the absorbed radiation dose[11].

In this study ESR spectrum was recorded for linseed, chickpea, black eye bean and red bean at a scan range of 400 mT. A characteristic and symmetrical ESR signal in upper and lower magnetic field was produced in case of irradiated samples of all the seeds where as un-irradiated samples did not show the specific signal as shown in the Figs. 1-4. In all the irradiated samples, ESR signal is sharp and specific with g = 2.00, typical for free radical where unpaired electron is present. The g-value was obtained form the amplitude of the central peak using software. In linseed, chickpea, black eye bean and red bean cellulosic radicals are produced after irradiation at all the applied doses which act as the paramagnetic centers giving typical ESR signal with g ~ 2.00. It may be calculated as reported by Ukai *et al.*[12]. Many authors cited that signals in the vicinity of g = 2.000 or 1.998 are related to organic free radicals or cellulosic radicals generated by biochemical or radiation induced reactions.

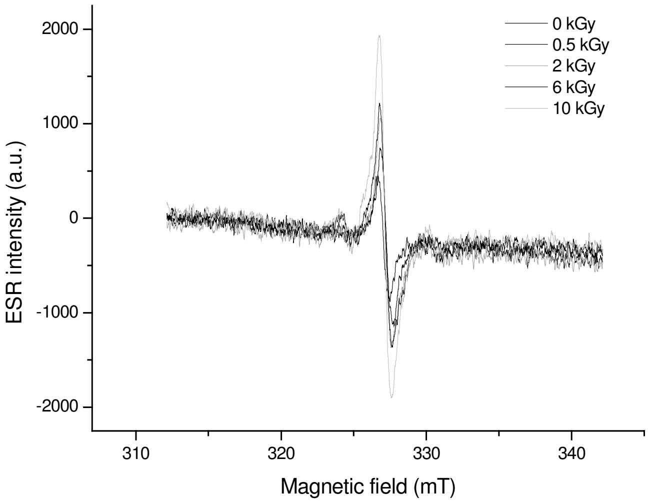

Fig. 1. ESR spectra of un-irradiated and irradiated chickpea shells

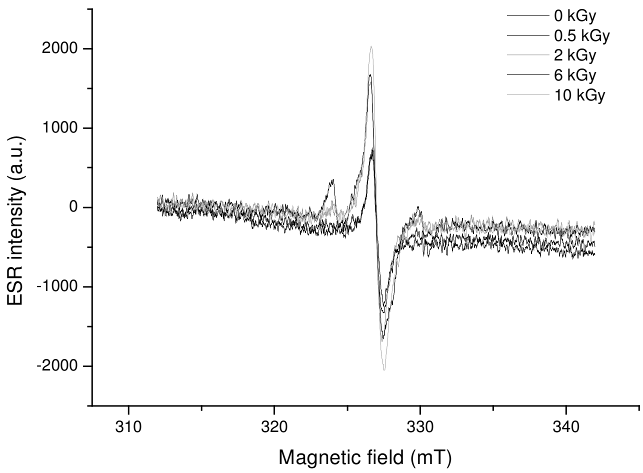

Fig. 2. ESR spectra of un-irradiated and irradiated red beans shells

When unpaired electrons are present at defects in solids the ESR signals can be obtained. In the ESR spectroscopy, it is possible to find the number of paramagnetic centers present in a substance from the intensity of the ESR signals. The area under the double-integrated ESR signal is related to the number of paramagnetic centers or radiation induced free radicals, which, in turn, is correlated to the amount of radiation given to the substances. Hence, it is possible to determine the absorbed dose of a substance from the intensity of ESR signal[11].

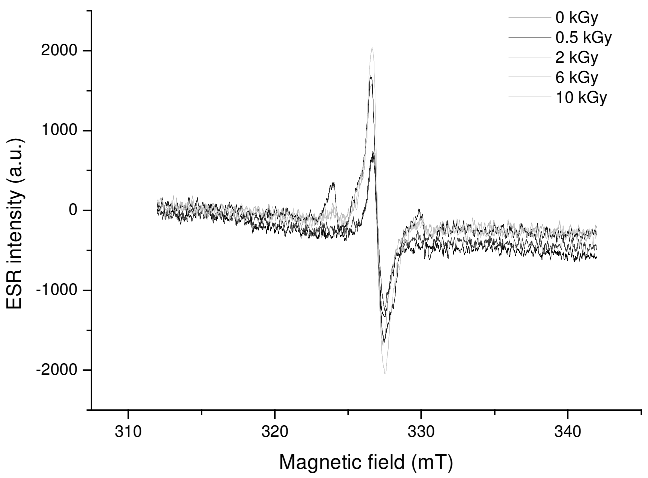

Fig. 3. ESR spectra of un-irradiated and irradiated black eye beans shells

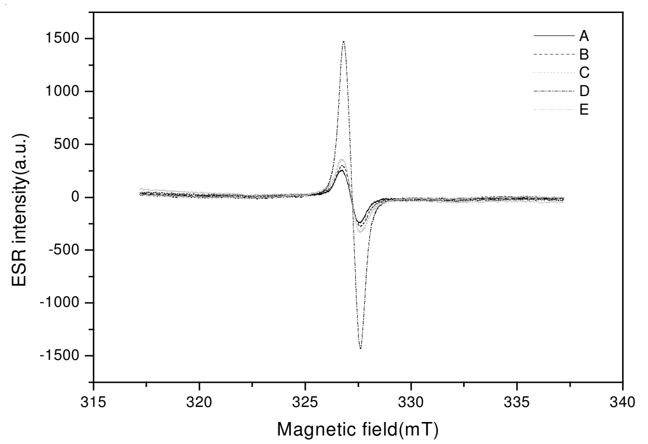

Fig. 4. ESR spectra of un-irradiated and irradiated linseeds shells (A = 0, B = 1, C = 2, D = 6 and E = 10 kGy)

In all the samples of linseed, chickpeas, black bean and red bean, the area under the ESR signal or peak height increased with increased radiation doses (Figs. 1-4). These results are in consistent with the previous studies conducted on dried vegetables and in shellfish also showed that ESR signal intensity was dose dependent *i.e.*, it increased linearly with γ-irradiation dose[13,14]. Electron spin resonance technique clearly discriminated all the radiated samples from the control and gave 100 % correct results. Hence it is a non-destructive technique and is being widely used in many food control laboratories. The potential of this technique had explored using different food items in order to classify the radiation treatment. Wheat flour, drugs and excipients, egg shells, shellfish were correctly identified as irradiated[11,15,16]. One report was also available in which it has been mentioned that ESR was unable to identify the radiation treatment in chestnut shells and pulp[17]. Polat and Korkmaz[18] detected radiation using ESR in different types of blended tea in Turkey. Detailed ESR investigation on irradiated black and rooibos tea to an absorbed dose of 0.5-10 kGy was carried out. Un-irradiated black and rooibos tea samples exhibited a weak, symmetric ESR singlet signal centered at g = 2.0043 with peak-to-peak line widths of 1.00 and 0.64 mT, respectively the electron spin resonance spectroscopy is recommended as a simple and non-destructive technique for foods rich in dry contents, since ionizing radiation induces free radicals in them that persists for a longer time as compared to the free radicals in the water rich food stuff.

Conclusion

Results of this study demonstrate the suitability and reliability of employing ESR technique for recognition of free radicals present naturally or produced after and radiation in linseeds, chickpea, black eye beans and red beans. Cellulosic radicals that are the paramagnetic centers in these seeds increased with the increase of absorbed radiation doses. This method needs small amount of material for sampling and it is specific, simple, non-destructive and rapid (0.5 h) but needs expensive equipment.

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