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Analytical Methods

Detection of gamma irradiated fig seeds by analysing electron spin resonance

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ABSTRACT

Seeds of fig produced in Turkey were studied by electron spin resonance (ESR) technique for detection purposes. Unirradiated fig seeds (control) exhibited a weak ESR singlet at $g = 2.0052 \pm 0.0003$ (native signal). Irradiation induced at least one additional intense singlet overlapping to the control signal and caused a significant increase in signal intensity without any changes in spectral patterns. Variation of ESR signal intensity of irradiated samples at room temperature with time in a long-term showed that free radicals responsible from the ESR spectrum of fig seeds were not stable but detectable after 80 days. Annealing studies at five different temperatures were used to determine the kinetic behaviour and activation energy of the radiation-induced radicals in fig seeds. A study on microwave saturation characteristics and thermal behaviour of the ESR singlet ($g = 2.0052$) in irradiated and unirradiated fig seed samples was also carried out by using ESR technique. These preliminary results indicate that microwave saturation characteristics of the ESR signal at room and low temperatures may be useful method to distinguish irradiated fig seeds from unirradiated ones.

1. Introduction

Food irradiation has been recognised as a reliable and safe method to prolong shelf-life of food and to improve its hygienic quality (WHO, 1999). The permitted limit of irradiation dose in foods was stated as 10 kGy (FAO/WHO, 1984; WHO, 1981). Three dose ranges have been defined in food processing according to the effects achieved: between 0.1 and 1 kGy (sterilisation of insects, destruction of parasites, and inhibition of the germination of bulbs and tubers); between 1 and 10 kGy (elimination of pathogenic bacteria and increase in the shelf life of food by reduction of the spoilage flora); and more than 10 kGy (sterilisation of spices and aromatic herbs) (Marchioni, 2008). Developing reliable methods to control irradiated foods is very important from the aspect of view of legal controls, labelling regulations and of course, customer confidence.

One of the frequently used physical detection techniques is electron spin resonance (ESR) (Bayram & Delincée, 2004; Desrosiers, 1996; Korkmaz & Polat, 2004; Polovka, Brezová, & Šimko, 2007; Raffi & Agnel, 1989; Raffi & Stocker, 1996). It has been successfully employed for the detection of some irradiated aromatic herbs, spices, fruits (Korkmaz & Polat, 2001; Raffi et al., 2000), and dried teas (Çam & Engin, 2010; Polat & Korkmaz, 2008). The ESR spectroscopy is a powerful and practical technique, so European standards have been released concerning food containing bone (EN 1786, 1997), crystalline sugar (EN 13708, 2001) and cellulose (EN 1787, 2000). ESR is a nondestructive standard method that enables a quick measurement of free ions or radicals produced by dissociation molecules resulting from irradiation energy (Raffi & Benzaria, 1993). In some cases, radiation-induced free radicals in food samples cannot be used to identify irradiated foodstuffs due to their short life times at storage conditions. ESR can be used as a detection method only if the radiation-induced radicals are stable over the maximum commercial storage time of food and if the corresponding resonance signals are clearly distinguishable from those of unirradiated material, which are never available for commercial samples (Douifı, Raffi, Stocker, & Dole, 1998). This may only happen in the solid and dry components of food, where the rigid structure of the matrix inhibits radicals reacting with each other or with the food components present in wet portion (Douifı et al., 1998). Thus, in the present study, the seeds of fig were selected for the detection of irradiated fig samples.

Insect infestation and spoilage flora during storage are major problems of fig, resulting in economic losses. Irradiation is increasingly being recognised as an effective technology to reduce postharvest losses and improve quality (Sanyal & Sharma, 2009). In this work, the radiation doses were applied in the range of 0.3–6 kGy in order to cover the recommended doses for insect disinfestations (0.1–1 kGy) and increase in the shelf-life of some fruits by reduction of the spoilage flora (1–5 kGy) (ACSH, 1988; Marchioni, 2008). Fig is one of the major fruits consumed all over the world. However, there were little works related to ESR spectroscopic features of radiation-induced radical specie in seeds of fig

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(Stachowicz, Burlinska, Michalik, Goclawska, & Ostrowski, 1995; Yordanov & Pachova, 2006). Therefore, more detailed information, especially related to the kinetic features and activation energies of the contributing radical species at room and higher temperatures, are needed. In this work, we aimed (i) to construct dose–response curve and determine microwave saturation features of the control (unirradiated) and radiation-induced resonance signals (ii) to investigate decay characteristics of control and radiation-induced ESR signals at room and high temperatures and lastly (iii) to investigate the feasibility of ESR technique to distinguish irradiated and unirradiated figs by using their seeds.

2. Materials and methods

Fresh figs used in this work were purchased from local markets in Ankara, Turkey and they had not been irradiated. They were crushed in a water bath and their seeds were extracted. Extracted seeds were washed several times with water and then, were left to dry at room temperature for one week. Dried seeds were irradiated, at room temperature, by a ^{60}Co gamma source at the Sarayköy Establishment of the Turkish Atomic Energy Authority in Ankara (Turkey) with a dose rate of 2.34 kGy/h. Seed samples were irradiated at 0.3, 0.6, 1, 1.5, 2, 2.5, 3, 4, 5 and 6 kGy dose values in order to get dose–response curve. The dose values mentioned in this paper have been calibrated with standard ferrous sulphate solution (Fricke dosimeter). The uncertainty in radiation doses was nearly ±3%. The samples were protected from light during irradiation and transportation to the measurement laboratory and then, stored in closed plastic bags at room temperature (21 ± 2 °C) in the dark. In the actual practise of food irradiation the whole figs are irradiated. Based on ESR signal intensities, extracted seeds and seeds with their pulp receive almost the same dose in the experimental error limits (±4%). Therefore, in this work, extracted seed samples were used as experimental material. As the mechanical crushing was not found to affect the ESR spectra significantly, the whole seed samples were used for ESR measurements in the present work.

Variable temperature studies on control (unirradiated) sample and the sample irradiated at a dose of 3 kGy were performed in a temperature range of 130–370 K by recording the ESR spectra 5 min after each temperature setting. A long-term decay feature of the radiation-induced resonance signal at room temperature was performed over a period of 80 days using a sample irradiated at a dose of 3 kGy. The kinetic feature of the radiation-induced resonance signal at high temperatures (313, 333, 353, 373, 393 K) was also investigated. The seeds of figs were transferred, after irradiation process, to the ovens at temperatures mentioned above, then their ESR spectra were recorded regularly over a time interval of 0–60 min after cooling them to room temperature following predetermined heating times (3, 6, 10, 20, 40, 60 min). The activation energy value of the radiation-induced radical specie was calculated from Arrhenius plot.

ESR measurements of unirradiated (control) and irradiated seed samples were performed at normal laboratory conditions (about 21 ± 2 °C and 25 ± 3% relative humidity) about 2 h after the irradiation. The ESR spectra were recorded by the use of a computer-interfaced Bruker EMX 131 X-band ($\nu \approx 9$ GHz) spectrometer equipped with a cylindrical cavity. The quartz tubes with inner diameter of 4 mm were filled with nearly 100 mg of whole seed samples for each measurement. Each tube was centred in the microwave cavity exactly in the same position. The spectrometer was retuned between the measurements of each aliquot, but care needs to be taken that other spectrometer operating conditions remain constant. The spectrometer parameters used were central field 348 mT, modulation amplitude 0.1 mT, modulation frequency 100 kHz, microwave power 0.5 mW, scan range 10 mT, time constant 327.7 ms and sweep time 83.9 s. Sample temperature inside the microwave cavity was monitored with a digital temperature control unit (Bruker ER 4111-VT). The latter gave us the opportunity of measuring the temperature with an accuracy of ±0.5 K at the sample site. The strong pitch ($g = 2.0028$) was used as a standard sample for measuring g-factor. Each data point was the average of at least four independent measurements. Thus, the experimental error was estimated to be ±4%. During this work, the intensity of the ESR signal was measured as the peak-to-peak height of the signal, and is reported in arbitrary units (*a.u.*).

3. Results and discussion

3.1. ESR spectra of unirradiated (control) and irradiated fig seeds

An ESR singlet is observed in ESR spectra of all irradiated and unirradiated (control) fig seeds. In the case of the irradiated samples, the intensity of singlet was increased significantly with the irradiation dose. The ESR spectra of the unirradiated and irradiated whole seeds of fig are shown in Fig. 1. The g value and peak-to-peak line width (ΔH_{PP}) of the singlet were found to be 2.0052 ± 0.0003 and 0.80 ± 0.02 mT, respectively, for both control and irradiated samples. Similar ESR spectra were also obtained for another seeds (Desrosiers & McLaughlin, 1989; Mangaonkar, Natarajan, Sastry, Padwal Desai, & Kulkarni, 1997;Yordanov & Pachova, 2006). The origin of the weak ESR singlet observed in unirradiated seed samples is not clear. However, this signal can be attributed to semiquinone-like free radicals produced by the oxidation of polyphenolic compounds present in plants (Polovka, Brezová, & Staško, 2003; Polovka et al., 2006; Raffi & Agnel, 1989). These stable free radicals were always detectable in the unirradiated (control) seed samples. A second intense singlet must be present in irradiated seeds in order to explain the relatively high signal intensity increases of the ESR singlet with irradiation, as also pointed out by Raffi et al. (2000). The origin of this second singlet is also unknown. This contributing radical to the ESR spectra of irradiated fig seeds may be attributed to radiation-induced free radicals of quinones, phenols, etc., present in the plant. It is important to emphasise that in the studied dose range even after irradiation at 10 kGy, the cellulose (EN 1787, 2000) or sugar-like

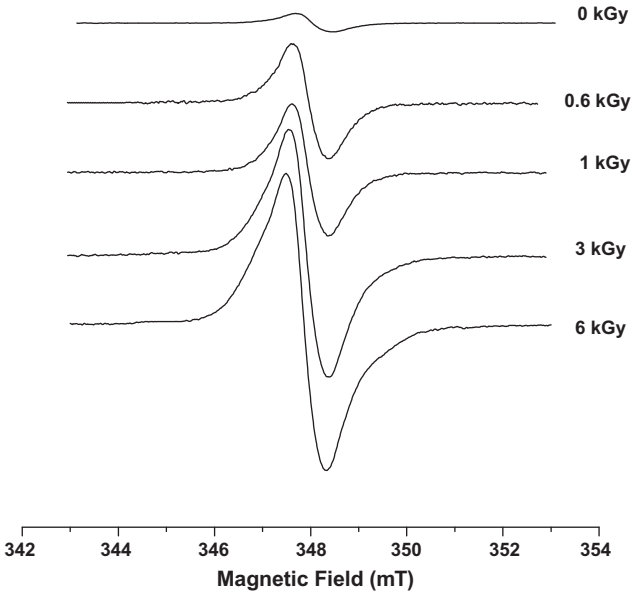

Fig. 1. Typical ESR signals of unirradiated (control) and irradiated fig seeds.