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Application of the ESR spectroscopy to estimate the original dose in irradiated chicken bone

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Abstract

The paper discusses the results of an investigation aimed to use the ESR spectroscopy as a quantitative procedure to estimate the original dose in irradiated chicken. The time stability of the ESR signal was at first carried out, to obtain a correction factor to be applied to the dose estimated with the added dose method. Our results show that this procedure gives an estimation of the original dose within $\pm 25\%$.

Keywords: Irradiated food; Electron spin resonance; Radiation treatment; Hydroxyapatite

1. Introduction

Among the physical methods that have been validated by the European Community for the identification of irradiated food, the electron spin resonance electron spin resonance (ESR) spectroscopy is recommended as a simple and non-destructive technique for foods containing bone, since ionizing radiation induces free radicals in hydroxyapatite, a constituent of bone. The aim of this work was to use the ESR spectroscopy also as a quantitative procedure to estimate the original dose in irradiated chicken bone.

2. Materials and methods

2.1. Sample preparation

Each sample of the bone was prepared for ESR measurements according to the European protocol 1786 (EN, 1996), to eliminate spurious signals due to bone marrow residue: from each drumstick, a bone sample was taken only from central part of the femur (containing great amount of hydroxyapatite), and meat, marrow and connective tissue were removed by scraping and washing in water. The bones were freeze-dried and reduced into specimens of about 100 mg in mass and 10 mm long each; such dimensions were chosen to fit the sample in an ESR suprasyl tube; each specimen was numbered, for identification purposes and to insert into the ESR tube always in the same vertical position.

2.2. Irradiation

The samples were irradiated inside a polymethyl methacrylate holder, to obtain the electronic-equilibrium conditions, with a ^{60}Co panoramic irradiator IGS-3. The dose values were calculated using irradiation time and the dose rate (2.00 kGy/h) was measured with the Fricke dosimetry.

2.3. ESR measurements

The ESR spectra were recorded at room temperature with a Bruker ECS 106 X band spectrometer, equipped with a TE_{102} rectangular cavity, operating at: microwave

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power 5 mW, modulation amplitude 2 mT, time constant 82 ms. For quantitative determinations (fading studies and dose evaluation), the dose-dependent amplitude of the central line in the ESR signal was used.

3. Results and discussion

3.1. Qualitative analysis

Fig. 1 shows the ESR spectra of a chicken bone sample before (a) and after irradiation at 5 kGy (b). In the ESR spectrum of the unirradiated sample, only the symmetric shape assigned to an organic radical derived from collagen (Wieser et al., 1994; Polat et al., 1997) is present, whereas the irradiated sample shows the typical ESR signal shape, due to the CO_2^- radical in the hydroxyapatite of bone, as well as the collagen signal (Schramm and Rossi, 2000).

According to the European Standard, the presence in the ESR spectrum of the hydroxyapatite signal is sufficient to distinguish the sample as irradiated.

3.2. Stability of the ESR signal

The stability of induced free radicals in the sample matrices, and therefore of the ESR signal intensity, is one of the crucial elements for the identification of irradiated food within the shelf life of the product itself (Onori et al., 1996; Polat et al., 1997).

Therefore, the time behavior of samples irradiated at 2, 4 and 8 kGy and stored for 120 days at two different temperature conditions (for each dose one at room temperature and one at −4 °C) was studied. The ESR spectra were recorded at various time intervals after irradiation; the measured intensity (the peak-to-peak amplitude of the central line, H, shown in Fig. 1b) was normalized to the value measured soon after irradiation.

The time profile plots of a specimen irradiated at 2 kGy and stored at room temperature (Fig. 2) shows a gradual decrease of the ESR signal intensity with time; in fact, during the first 10 days after irradiation, it decreases to about 75% of the initial value; afterwards, the signal intensity decreases more slowly and is about 70% after 120 days.

The experimental measured values of H were best fitted as a function of time t using the function ($r^2 = 0.984$)

$$H = \frac{1}{1 + at^b} \tag{1}$$

that describes a 'non-homogeneous' kinetics (a and b are constants, optimized by the least-squares fitting process). Using function (1), the value of H extrapolated at 1 year after irradiation still results in being more than 100 times higher than in the control unirradiated sample. This time interval is comparable to, or even longer than, the shelf life of the product.

In samples irradiated at 4 and 8 kGy and stored at room conditions, the same percentage decrease is observed; in particular, the residual signal intensity is about 73% and 74%, respectively, in the first 10 days, and 60% and 70% after 120 days.

Fig. 3 shows the decay of the ESR signal intensity for a bone sample irradiated at 2 kGy and stored at −4 °C. It can be seen that the decline in signal intensity is less pronounced than in the samples stored at room temperature; after a reduction in the first 10 days after irradiation,

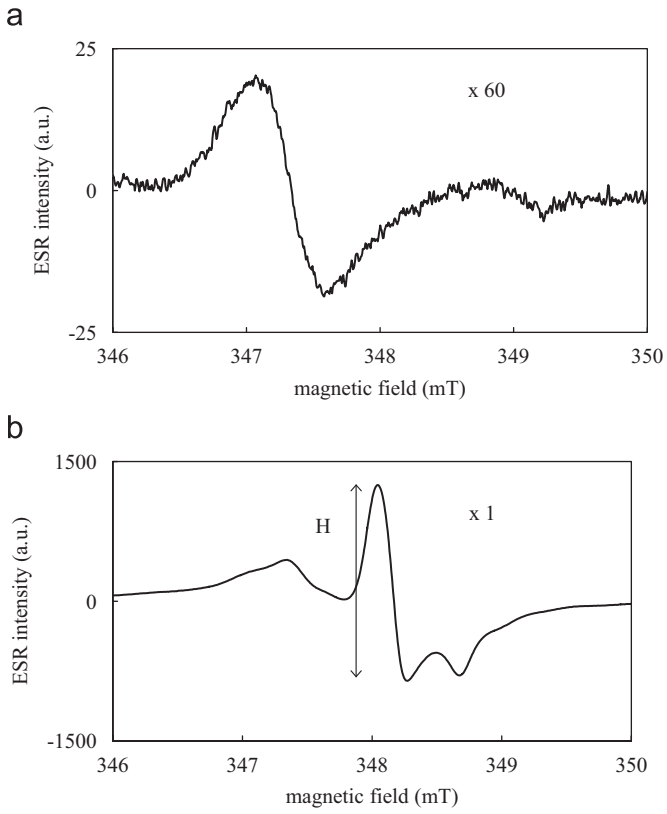

Fig. 1. ESR spectra of (a) unirradiated and of (b) irradiated (5 kGy) drumstick bones. Spectrum (a) was recorded with a receiver gain 60 times higher than spectrum (b), where the signal intensity H used for quantitative purposes is indicated.

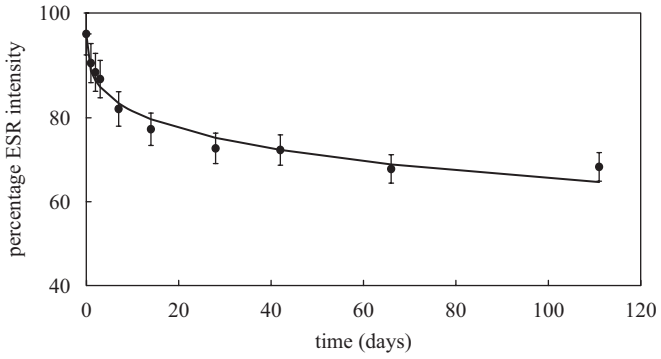

Fig. 2. Percentage ESR signal intensity as a function of storage time for a bone sample irradiated at 2 kGy and stored at room temperature; error bars correspond to ± 1 standard deviation; the continuous line is the fitting function (1) in the text.

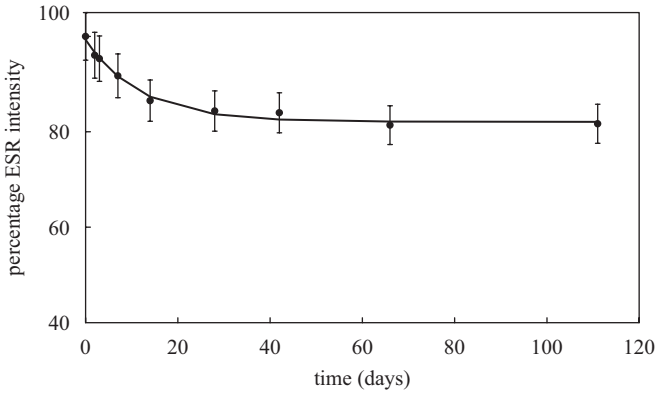

Fig. 3. Percentage ESR signal intensity as a function of storage time for a bone sample irradiated at 2 kGy and stored at −4 °C; error bars correspond to ± 1 standard deviation; the continuous line is the fitting function (2) in the text.

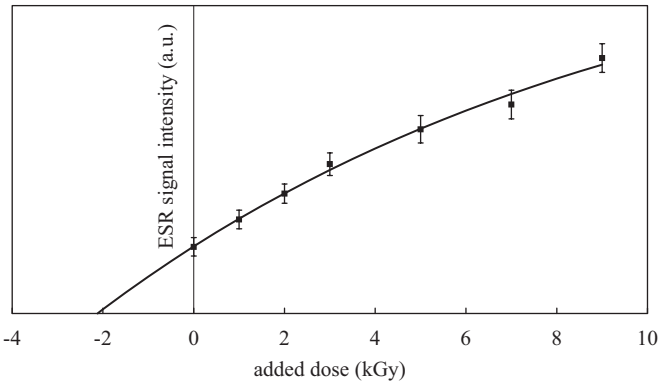

Fig. 4. ESR signal intensity vs. added dose for a bone sample originally irradiated at 2 kGy; error bars correspond to ± 1 standard deviation; the continuous line is the fitting function (3) in the text.

the intensity remains indeed constant at about 80% of the initial value.

In this case, the best fit of the experimental results was found with the following function ($r^2 = 0.993$) that takes better into account than function (1) the higher stability of the signal

$$H = a + be^{-ct} \tag{2}$$

the value of H extrapolated at 1 year after irradiation still results in being more than 100 times higher than in the control unirradiated sample.

Similar results were obtained with sample irradiated at 4 and 8 kGy and stored at −4 °C.

These results are the final confirmation that ESR is a powerful technique for the identification of irradiated food studied in this research, for long time intervals, even after the duration of its shelf life.

3.3. Estimation of original irradiation dose

Estimation of original irradiation dose is very important to decide whether or not the food was irradiated within the upper permitted dose limit of 10 kGy.

For this study, the additive dose method (Bordi et al., 1994; Chawla and Thomas, 2004) was applied; this method requires a series of additional irradiation doses; the original ESR signal amplitude, H_0 (due to the original dose D_0) was measured; after each added dose (D_i) the measured signal H_i corresponds to the original ESR signal intensity (H_0) plus the contribution due to the additional dose D_i. Once the relationship between the ESR signal intensity and the added dose in the sample is found, the original dose value (D_0) is determined from the intersection of the fitting function with the abscissa.

As an example of the method, Fig. 4 shows the relationship between ESR signal intensity of one drumstick bone irradiated at original dose of 2 kGy (D_0) and the added dose.

For these experimental values, the best fit was obtained with the function (Desrosiers, 1991):

$$H = a\left(1 - e^{-\frac{(D+b)}{c}}\right), \tag{3}$$

where a, b and c are constants, optimized by the least-squares fitting process. The value of b allows to estimate D_0 ($H = 0$ when $D = -b$).

The same procedure was applied to other two different chicken drumsticks. The estimated dose was 2.10, 2.12 and 1.89 kGy for the three samples, respectively, in each case within ±5% of the original dose. This result shows that the added dose method can be usefully applied on chicken soon after the radiation treatment.

The same method has been applied to three drumsticks of chickens irradiated at original dose 4 kGy, but 6 months after original irradiation, to check if the method can be successfully applied even on stored irradiated meat. In this case, the estimated dose was 2.00, 2.00 and 3.50 kGy for the three samples, respectively.

The differences between estimated and original dose are due to the long-term decay; in fact if the results are corrected for the known fading (function (1) or function (2)), an estimated dose between 3 and 5 kGy is obtained. This correction should be applied on a sample under investigation if the packing age is more than 1 week. Anyway, the added dose method permits to decide whether or not the sample was irradiated within the permitted dose limits.

4. Conclusion

An investigation on the time stability of the ESR signal in irradiated chicken bones was carried out: the signal intensity decreases during the first 10 days after irradiation, and remains almost constant afterwards (at about the 70–80% of the value soon after irradiation, depending on the storage conditions). This means that when dose reconstruction is performed in a bone sample for which neither the dose nor the elapsed time after irradiation is

known, the estimated dose should be corrected, in the hypothesis that the sample is in the market at least 1 week after the radiation treatment. Our results show that the additive dose method gives an estimation of the original dose within $\pm 25\%$.

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