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# Evaluation of the original dose in irradiated dried fruit by EPR spectroscopy

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ABSTRACT

The electron paramagnetic resonance spectroscopy (EPR) is one of the physical methods, recommended by the European Committee for Standardization, for the identification of irradiated food containing cellulose, such as dried fruit. In this work the applicability of EPR as identification method of irradiated pistachios, hazelnuts, peanuts, chestnuts, pumpkin seeds is evaluated; the time stability of the radiation induced signal is studied and the single aliquot additive dose method is used to evaluate the dose in the product.



## 1. Introduction

Hazelnuts and similar foodstuffs, such as pistachios, peanuts, chestnuts and pumpkin seeds, play a significant role in human nutrition, especially as sources of vitamins (B complex vitamins, C and E). These foodstuffs, together with fruits and vegetables, have been strongly associated with reduced risk for some forms of cancer, heart disease, stroke, and other chronic diseases.

The treatment of this kind of food by ionizing radiation can be used to reduce food spoilage due to microorganism and to significantly decrease insect infestation, enhancing, this way, the hygienic quality and extending the shelf life of food itself. Moreover, vitamin losses in foods irradiated at doses up to 1 kGy are considered to be insignificant. At higher doses the change in nutritional value caused by irradiation depends on a number of factors. They include the specific vitamin, the radiation dose to which the food has been exposed, the type of food, the packaging, and the processing conditions, such as temperature during irradiation and storage time. Irradiation did not cause any significant change in the composition of nuts and doses sufficient to kill all infesting insects had no adverse effects on either nutritional value or the sensory quality of nuts (Khan, 1993).

Distinguishing irradiated from unirradiated food is very important to increase the general consumer acceptance and consequently to facilitate the commercialization and trade of irradiated food; for this purpose, reliable analytical techniques should be available to identify irradiated foodstuffs for legal control purposes. The electron paramagnetic resonance (EPR) spectroscopy is a physical method that has been validated by the European Committee for Standardization for detecting radiation-processed foodstuff containing cellulose, such as shells of pistachios, nuts, spices and strawberries (EN 1787, 2000).

In the present study, the detection with the EPR technique of radiation induced free radicals in cellulose of irradiated shells of pistachios, hazelnuts, peanuts, chestnuts, pumpkin seeds has been investigated, as well as the time stability of these radicals; an estimation of the absorbed dose in irradiated dried fruits has been obtained using the single aliquot additive dose method.

## 2. Materials and methods

### 2.1. Sample preparation

Pistachios, hazelnuts, peanuts, chestnuts and pumpkin seeds were purchased in local Sicilian markets. Small pieces (between 50 mg and 100 mg) were removed from the shells of irradiated dried fruits, with size and shape suitable to be placed as a whole, without any grinding or powdering, inside the suprasyl quartz tube used for the EPR measurements.

### 2.2. Irradiation

Dried fruits were irradiated with a $^{60}Co$ panoramic irradiator in the range 1.5–5.0 kGy; samples were located inside a Perspex holder, to obtain the electronic-equilibrium conditions required to achieve a good dose distribution; the dose values were evaluated with an overall uncertainty of about ±10%.

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### 2.3. EPR measurements

The EPR spectra were recorded at room temperature with a Bruker ECS 106 X band spectrometer, equipped with a $TE_{102}$ rectangular cavity, operating at: microwave power 0.4 mW, modulation amplitude 2 mT, time constant 82 ms. For the quantitative analysis (fading study and dose evaluation) the dose-dependent amplitude of the satellite lines in the EPR spectrum was used.

## 3. Results and discussion

### 3.1. Qualitative analysis

The EPR spectra of shells pieces of pistachio, hazelnuts, peanuts, chestnuts and pumpkin seeds were recorded before and after irradiation at 5 kGy. In the EPR spectra of the unirradiated samples only the endogenous central signal is present, whereas the samples irradiated at 5 kGy show the irradiation specific line pair of the cellulose radical, spaced about 6.05 mT, and an increased intensity of the central line; the relative intensity of the satellite lines depends on the content of cellulose in the shells of each sample. As an example, Fig. 1 shows the spectra of a pistachio sample.

According to the European Standard (EN 1787, 2000), the presence in the EPR spectrum of the line pair of cellulose is sufficient to distinguish the sample as irradiated; anyway, the absence of this signal does not represent evidence that the sample was not irradiated, since the signal intensity may be too low to be measurable, due either to a too low dose, or to small cellulose content, or to instability of the free radicals induced in the sample. Moreover, the presence of the satellite lines depends in large amount on a subjective visual inspection of the spectrum. Consequently, to define an analytical procedure providing an unequivocal identification of the satellite lines, we evaluated, for each investigated fruit, the Lowest Detectable Signal (LDS) as the mean background signal plus three standard deviations. As a practical rule, the sample is to be treated as irradiated if, in both region of the spectrum were the satellite lines are expected to appear, the ratio h between the peak-to-peak (H) signal intensity and the LDS is higher than one.

Table 1 shows the obtained averaged results for all analyzed samples soon after irradiation at 1.5–3.0 and 5.0 kGy. The identification of the irradiation treatment was unambiguous for pistachios, hazelnuts and chestnuts even at the lowest applied dose; as for peanuts, the identification was not possible only for the 1.5 kGy irradiated samples, whereas only the 5 kGy irradiated pumpkin seeds could be correctly identified.

### 3.2. Stability of the EPR signal

The stability of the free radicals radio-induced in cellulose is one of the critical factors for the identification of irradiated food within the shelf life of the product itself (Onori et al., 1996). Therefore, a study was carried out on the time behaviour of the satellite lines intensity of pistachio, hazelnut, peanut, chestnut and pumpkin seeds samples, irradiated and subsequently stored at room conditions, as they are usually stored and commercialized.

As an example, Fig. 2 shows the time profile of $H_R$ (the percentage signal intensity of the satellite line at the right of the central signal) for a pistachio sample irradiated at 5 kGy; the value of $H_R$ fairly rapidly drops to approximately 30% of the original value after roughly one month, and decreases more slowly afterwards. The measured values of $H_R$ were best fitted ($r^2 = 0.995$) as a function of time $t$ using the following function (shown as a continuous line in Fig. 2):

$$H = \frac{1}{1 + at^b} \quad (1)$$

that describes a 'non-homogeneous' kinetics ($a$ and $b$ are constants, optimized by the least squares fitting process).

Using the function (1), the value of $H_R$ extrapolated at one year (this time interval is comparable with the shelf life of the product) results to be about 10% of the value measured soon after irradiation, but is still twice the LDS, allowing a clear identification of the irradiation treatment. The same analysis was carried out for all doses and all kind of dried fruits under investigation, with analogous results. Table 2 reports the time range after irradiation, within which the identification of the irradiation treatment is still possible, since the residual H is still higher than the LDS.

### 3.3. Estimation of the original dose

The estimation of the original dose is very important as a quality control to evaluate whether or not the food was irradiated within the upper permitted dose limit of 10 kGy.

To this aim, the Single Aliquot Additive Dose method (SAAD) (Bordi et al., 1994; Murray et al., 1997) was applied; this method requires a series of additional doses, applied to the same sample

**Table 1**
Ratio $h$ between the EPR signal intensity and the Lowest Detectable Signal for the satellite lines at the left ($h_L$) and the right ($h_R$) of the endogenous central signal, after irradiation at three different dose values.

| | 1.5 kGy | | 3 kGy | | 5 kGy | |
|---|---|---|---|---|---|---|
| | $h_L$ | $h_R$ | $h_L$ | $h_R$ | $h_L$ | $h_R$ |
| Pistachio | 4.8 | 4.2 | 6.9 | 5.9 | 19.6 | 14.5 |
| Hazelnut | 5.0 | 3.8 | 7.6 | 6.2 | 17.4 | 15.3 |
| Chestnut | 1.4 | 1.5 | 1.5 | 1.2 | 3.2 | 3.4 |
| Peanut | <1 | <1 | 1.1 | 1.0 | 4.5 | 3.9 |
| Pumpkin | <1 | <1 | <1 | <1 | 1.4 | 1.3 |

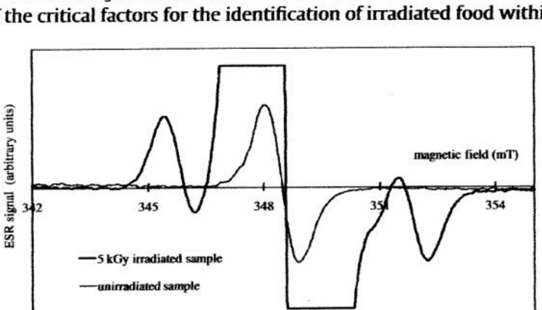


**Fig. 1.** EPR spectra of a sample of pistachio before and after irradiation at 5 kGy.

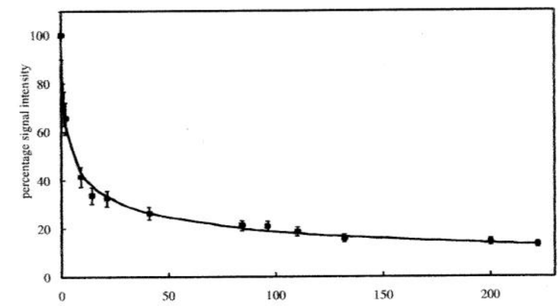


**Fig. 2.** Time behaviour of the signal intensity of the satellite line at the right of the central signal for a pistachio sample irradiated at 5 kGy and stored at room conditions.

**Table 2**
Time interval after irradiation, within which the identification is still possible.

| | 1.5 kGy | 3 kGy | 5 kGy |
|---|---|---|---|
| Pistachio | >1 year | >1 year | >1 year |
| Hazelnut | >1 year | >1 year | >1 year |
| Chestnut | One week | One week | One month |
| Peanut | One day | One week | Three months |
| Pumpkin | – | – | One day |

aliquot; the original EPR signal intensity, $H_0$ (due to the original dose $D_0$), is measured; after each added dose ($D_i$) the measured signal $H_i$ corresponds to $H_0$ plus the contribution due to the additional dose $D_i$. Once the relationship between the EPR 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.

The SAAD method was applied to pistachio and hazelnut samples irradiated at the original dose of 4.0 or 5.0 kGy; both satellite lines were used for dose reconstruction and three added doses of 1 kGy each were used for dose reconstruction. For these experimental values the best fit was obtained with the function (Desrosiers, 1991):

$$H = a\left(1 - e^{-\frac{D+b}{c}}\right) \tag{2}$$

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 $D = -b$). Fig. 3 shows the results regarding an hazelnut sample, and all the obtained results are reported in Table 3. For the 5 kGy samples, the method was carried out after four months storage and the estimated dose was therefore corrected for fading, according to the results described in Section 3.2. In a real case, when the time elapsed after irradiation is not known, only the residual dose is assessable; considering the time behaviour of the ESR signal (Fig. 2) and that dried fruit is presumably commercialized between a few weeks and one year after irradiation, it can be assumed that the signal decreased to about 20% of the original value; the corresponding correction factor can be applied to roughly estimate the original dose.

The observed discrepancies (between 12% and 40%) between the delivered and the reconstructed doses (Table 3) are not in

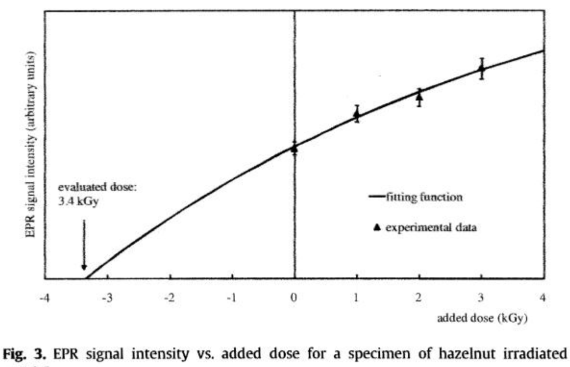


**Fig. 3.** EPR signal intensity vs. added dose for a specimen of hazelnut irradiated at 4 kGy.

**Table 3**
Reconstructed dose values using the SAAD method on the satellite lines; for the 5 kGy sample the method was applied four months after irradiation, and correction for fading was applied. The estimated uncertainty in the reconstructed dose is about ±20%.

| Nominal dose | 4.0 kGy | | 5.0 kGy | |
|---|---|---|---|---|
| | $h_L$ | $h_R$ | $h_L$ | $h_R$ |
| Pistachio | 2.4 | 2.5 | 3.1 | 3.3 |
| Hazelnut | 3.5 | 3.5 | 3.3 | 3.8 |

disagreement with other published data (Alberti et al., 2011; Sin et al., 2005). To achieve higher precision and to make the methodology definitive, much more than three added doses per sample are required and more detailed information on fading are needed (De Jesus et al., 2000), as well as higher accuracy in the added dose values.

## 4. Conclusions

The preliminary results presented in this paper show that the identification of irradiated dried fruits can be carried out with the ESR spectroscopy, but in some cases the radiation induced signal is not sufficiently stable to ensure identification a few months after irradiation. The additive dose methodology could be effectively used to retrospectively estimate the original dose in irradiated pistachios and hazelnuts within the shelf life of these foodstuffs, although the whole procedure must be improved, as previously discussed.

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