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An inter-laboratory comparison to evaluate the suitability of EN 1787 standard to detect irradiation in plant-origin foods with health benefits

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ABSTRACT

This paper reports the results of a study carried out to verify the applicability of the EN 1787 method, which uses the Electron Spin Resonance (ESR) technique for the identification of irradiated plant-origin foods with health benefits. The method was tested on samples of herbal ingredients of Plant Food Supplements (PFSs), nuts and fresh blueberries. Untreated and irradiated samples of *Camellia sinensis* (leaves) *Ginkgo biloba* (leaves), *Glycine* max (seeds), *Silybum marianum* (fruits), *Vaccinium myrtillus* (fruits), almonds, hazelnuts, peanuts, pistachios, walnuts and fresh blueberries were analysed. The work includes an inter-laboratory blind test involving five Italian laboratories that perform routine analyses for the official control of irradiated food. A total of 180 untreated and irradiated samples of PFS ingredients, nuts and fresh blueberries were analysed. The analyses on the irradiated samples were replicated even a long time after irradiation (up to two years depending on the matrix) to test the reliability of the method throughout the shelf life of the products.

The results were matrix-dependent: all the 5 kGy irradiated nuts and the 1 kGy-irradiated blueberries were correctly classified, whereas herbal ingredients showed complex ESR spectra with spurious signals which often prevented the correct classification of the sample.

1. Introduction

Plants growing in an open environment are exposed to chemical and microbiological hazards. Since there is not a cleansing step that can remove all contaminants, the prevention of contamination during the production stages is of outmost importance (Piniero & Diaz, 2007). To preserve the hygienic quality and ensure shelf life, the treatment of foodstuffs with ionising radiation has been largely used against microbial deterioration during transport and storage. (FAO/WHO, 2002; FAO/WHO, 2004; Kume, Furuta, Todoriki, Uenoyama, & Kobayashi, 2009; Kume & Todoriki, 2013; Ihsanullah & Rashid, 2017; Roberts, 2014; WHO, 1999). In the European Union food irradiation is regulated by Directive, 1999 and Directive, 1999, which state that the treatment foods are subject to must be indicated. Every year, all Member States are to notify the European Commission of the results of the tests performed to detect irradiated foods, and check the related labelling. EN 1787, 2000 is one of the analytical methods set out by the European Committee for Standardisation for the official control of irradiated foods. It uses the Electron Spin Resonance (ESR) technique to identify the radical induced in cellulose by ionising radiation; this radical yields an ESR spectrum characterised by two weak satellite lines at a specific distance (about 6.0 mT) from each other and symmetrically located on the sides of an intense peak detectable in untreated samples as well. The central peak, whose intensity strongly increases after irradiation, is indeed the results of the superposition of different signals including the central component of the two satellite lines (Bortolin, Bustos Griffin, Cruz-Zaragoza, De Coste, & Onori, 2006; Chiappinelli et al., 2019; Franco et al., 2004; Tomaiuolo et al., 2018). The application of the

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method is simple and time-saving: no laborious sample preparation is required and the measurement usually takes a few minutes. In addition, once validated the method does not require confirmation of the non-negative results. The method has been internationally validated through trials for pistachio nut shells, strawberries and paprika (Linke et al., 1995; Linke et al., 1996; Raffi, 1992; Raffi, Stevenson, Kent, Thiery, & Belliardo, 1992; Schreiber et al., 1993; Schreiber et al., 1996) but, in principle, it could be applicable to all vegetables containing cellulose (Chiappinelli et al., 2019; Jeong, Akram, Ahn, & Kwon, 2014; Jo, Kyung, Park, & Kwon, 2016; Maghraby, Salama, Sami, Mansour, & El Sayed, 2014; Raffi et al., 1989; Sezer, Ece, Uslu, Osmen, & Savin, 2019; Shahbaz, Akram, Ahn, & Kwon, 2013; Tomaiuolo et al., 2018). In practice, however, its reliability in detecting irradiation is limited when the sample has a low content of crystalline cellulose and/or a high moisture content, which favours radical recombination leading to false negative results (Bortolin, Bustos Griffin, Cruz-Zaragoza, De Coste, & Onori, 2006; Kwon, Ahn, Akram, Son, & Lee, 2013; Yordanov, Lagunov, & Dimov, 2009). Moisture is a limitation especially in water-containing matrices, e.g., fresh fruit, for the fast fading of the signal yields false negatives. Recently, however, false positive classifications have been made for nuts (hazelnuts and walnuts): owing to shell bleaching by chemical reagents, ESR signals look similar to those induced by ionising radiation (Butz & Hildebrand, 2006; Werner, Straub, Zumsteeg, & Kuntz, 2020). Problems were also met when applying the method to herbs and spices because the presence of intrinsic radicals responsible for “spurious” signals makes the ESR spectra complex and difficult to interpret (Ahn, Akram, Jo, & Kwon, 2012; Kim, Ahn, Shahbaz, Kim, & Kwon, 2014; Sanyal et al., 2014; Yordanov et al., 2009).

Given such limitations, for a correct application of the method in official controls it is critical to investigate the characteristics of the ESR spectra of each single matrix or group of matrices, as well as monitor their signal stability during the shelf life of the product. The present work aimed to test the applicability of EN 1787 Standard for the identification of plant-origin food with health benefits, such as fruit and herbal ingredients for PFSs which are largely consumed all around the word. To this purpose, samples were analysed of nuts (almonds, hazelnuts, peanuts, pistachios and walnuts), fresh blueberries and herbs, namely *Camellia sinensis*, *Ginkgo biloba, Glycine max, Silybum marianum, Vaccinium myrtillus*, in the forms of dried raw material (leaves, fruits, seeds) and dried extract. Reliable analytical methods are urgently needed since official checks in Europe on products at the marketing stage have found that non-negligible percentages of plant food supplements (PFSs) and their ingredients were irradiated and incorrectly labeled. (http://ec.europa.eu/food/safety/biosafety/irradiation/reports; Boniglia, Aureli, Bortolin, & Onori, 2009).

The present work involved five Italian laboratories engaged in the official control of irradiated foods. After a preliminary intra-laboratory validation of the analytical procedure applied to the matrices chosen for the study, an inter-laboratory blind test was organised, where 180 untreated and irradiated samples of PFS ingredients, nuts and fresh blueberries were analysed. The irradiated samples were analysed even a long time (up to two years depending on the matrix) after irradiation to test the applicability of the method throughout the shelf life of the products. The irradiation dose values for the different samples were chosen among those commonly used all over the world. The applied doses depend on the food items and on the purpose of irradiation; in particular, herbal ingredients and nuts are irradiated at doses ranging from 3 to 10 kGy to eliminate microbial pathogens, insect pests, mold, and other spoilage organisms, whereas fresh blueberries at doses ranging from 0.15 to 1 kGy for phytosanitary purposes against fruit flies and other critical plant pests. For this study dried herbal ingredients and nuts were irradiated at 5 kGy, and blueberries at 0.15 and 1 kGy. In the preliminary intra-laboratory step of the work herbal ingredients were irradiated also at 1 kGy to test the sensitivity of the method in detecting lower doses than those normally applied to these matrices.

2. Materials and methods

2.1. Samples

The matrices were PFS ingredients, nuts and fresh fruits. All the products were not labeled as treated by ionizing radiation, nevertheless analyses were performed by EN 1788 method on all the samples as received to check if they had been irradiated and not correctly labeled. Before analysis all the products were stored at room conditions inside their original packaging.

2.1.1. PFS ingredients

Five dried herbal ingredients were chosen from among the most commonly used for PFSs, in the form of both raw materials (leaves, fruits, seeds) and herbal extracts: *Camellia sinensis* (leaves), *Ginkgo biloba* (leaves), *Glycine* max (seeds), *Silybum marianum* (fruits), *Vaccinium myrtillus* (fruits) were purchased from herbalists whereas the corresponding herbal extracts were produced by Indena S.p.A (Italy). For each product, the analyses were performed on untreated and irradiated samples.

2.1.2. Fruit

Samples of almonds, hazelnuts, peanuts, pistachios, walnuts and fresh blueberries were purchased at the local markets in different Italian regions.

2.2. Irradiation

Sample irradiation was performed at room temperature with a low-energy X-ray irradiator (RS 2400 Rad source Inc.) operating at 150 kV and 45 mA with a dose rate of 40 Gy min^{-1} as measured with a calibrated ion chamber (Rad-cal Inc.). The technical characteristics of this facility (radiation quality and energy), compatible with those required by the European legislation, allowed to simulate a real radiation treatment in an industrial plant. The uniformity of the dose was obtained by irradiating the food matrices in sample holders inside a carousel rotating around the X-ray tube. Dosimetric properties were tested by the Electron Spin Resonance alanine pellet system. The absorbed doses hereby reported are doses to water measured by alanine dosimeters with a diameter of 5 mm (Bruker, Rheinstetten, Germany) and an uncertainty of about 5%. The products were irradiated and stored, at room conditions of temperature and humidity, in light-protected containers. Dried herbal ingredients were irradiated at 1 and 5 kGy, nuts at 5 kGy and blueberries at 0.1 and 1 kGy (Table 1).

Table 1
Scheme of the intra-laboratory validation test.

Category	Matrix	Dose (kGy)	Monitoring period	No. of laboratories
PFSs	*Camellia sinensis* *Ginkgo biloba* *Glycine max* *Silybum marianum* *Vaccinium myrtillus*	1; 5	2 years	3
Nuts	Almonds Hazelnuts Peanuts Pistachios Walnuts	5	2 years	4
Fresh fruit	Blueberries	0.15; 1	3 weeks	4

2.3. ESR analysis

2.3.1. Intra-laboratory validation tests

For the analyses, four laboratories followed the procedure described in the EN 1787 standard, according to the scheme reported in Table 1. All four laboratories carried out tests on nuts and fresh blueberries on untreated samples and on samples irradiated with doses of 0.15 kGy and 1 kGy (blueberries), and 5 kGy (nuts). Three of them also analysed PSF ingredients (raw materials and extracts) in untreated samples and samples irradiated at 1 kGy and 5 kGy.

The validation tests included checks of signal stability under normal storage conditions in order to verify the reliability of the method during the shelf life of the products. The measurements were thus periodically repeated on the same aliquot since the ESR measurement does not cause the disappearance of the signal. After irradiation, signal stability was checked once or two/three times a week, depending on the rate of decrease. ESR signals of PFS ingredients and nuts were monitored up to two years after irradiation, while on blueberries the measurements were repeated more often but always within three weeks (more or less their shelf life). The results obtained by the participants were compared, and an analytical procedure was agreed upon.

2.3.2. Inter-laboratory validation test

To validate the ESR procedure elaborated during the intra-laboratory validation step, a blind test was carried out, involving five laboratories (Table 2). A total number of 180 samples (75 PFS ingredients, 75 nuts and 30 fresh blueberry samples) were prepared and identified with a specific code. Specifically, 25 untreated and 50 irradiated (5 kGy) samples of PFS ingredients, 25 untreated and 50 irradiated (5 kGy) nut samples, and 10 untreated, 10 irradiated at 0.15 kGy and 10 irradiated at 1 kGy blueberry samples were prepared and sent to the laboratories. Irradiation and shipping were completed within a week. The majority of the samples were irradiated just before shipping. To confirm the stability of the signal and the reliability of the method throughout shelf life, 25 out of the 50 irradiated PFS ingredients and 25 out of the 50 irradiated nuts samples were taken from among those treated with ionizing radiation about two years before for the intra-laboratory tests. Regarding PFS ingredients, as the ESR method turned out to be unsuitable for detecting herbal extracts during the preliminary tests, the trial was limited to raw materials.

2.3.3. Sample preparation

For ESR measurement, about 100 mg of PFS ingredients and nut shells were cut, where necessary, into pieces small enough for the ESR tube. Measurements for *Glycine* max were performed on both whole seeds and outer peel. Fresh blueberries were prepared following the procedure described for strawberries in EN 1787. Before measurement, the samples were kept at about 45 °C for about 1 h to reduce the moisture content of the matrices.

Table 2
Scheme of the inter-laboratory blind test.

Category	Matrix	Dose (kGy)	No. of samples	No. of laboratories
PFSs	*Camellia sinensis* *Ginkgo biloba* *Glycine max* *Silybum marianum* *Vaccinium myrtillus*	5	75[a]	5
Nuts	Almonds Hazelnuts Peanuts Pistachios Walnuts	5	75[a]	5
Fresh fruit	Blueberries	0.15; 1	30	5

[a] 25 out of 50 irradiated PFS ingredients and 25 out of 50 irradiated nut samples had been treated with ionizing radiation about two years before the analysis.

2.3.4. ESR measurements

ESR measurements were performed at room temperature and humidity with different models of Bruker spectrometers operating in the X band: Elexsys with a Bruker Super High Q cavity (one laboratory), E-Scan Food Analyzer (three laboratories) and EMX with a Bruker Very High Quality cavity (one laboratory). Parameters were set as indicated in the EN 1787 standard. Frequency: 9.78–9.93 GHz, depending on the equipment; center field: about 350 mT; sweep width: about 20 mT; microwave power: 0.4–0.8 mW; modulation amplitude: 0.4–0.9 mT; sweep speed: 5 mT/min-10 mT/min; number of scans: 3–64, depending on the equipment. The samples were inserted in Suprasil tubes with a diameter of 4-5 mm.

3. Results and discussion

3.1. Intra-laboratory validation tests

These tests showed that ESR spectra of plant-origin foods are generally complex and difficult to interpret, owing to the presence of different radical species in the chemical composition of these matrices. The classification of the samples was unambiguous for nuts and 1 kGy-irradiated blueberries, whereas PFS ingredient spectra showed overlapping signals which made it difficult to classify the samples. On the whole, the results obtained by the participating laboratories were in agreement, and a common analytical procedure was set up to be used for the inter-laboratory blind test.

3.1.1. PFS ingredients

Fig. 1 shows the ESR spectra of the untreated products. As expected, in agreement with the EN 1787 standard, in all the untreated samples of raw materials a symmetric signal was always well visible, with intensity depending on the specific matrix. Besides that, in most of the samples other unidentifiable peaks, but certainly not attributable to irradiated cellulose, were visible on each side of the central signal.

Difficult to interpret, complex spectra were recorded with samples irradiated at 1 kGy. Better results were obtained with samples re-irradiated at 5 kGy whose spectra were easier to interpret. Irradiated *Glycine* max gave the best results (Fig. 2), especially when only the outer peel of the seeds was used. The satellite lines, specific of irradiation, were visible also in the irradiated samples of *Silybum marianum* but often the left line appeared not completely resolved, as shown in Fig. 3. Conversely, *Camellis sinensis* (Fig. 4) *Ginkgo biloba* (Fig. 5) and *Vaccinium myrtillus* (Fig. 6) showed spectra where such lines were not always detectable.

The spectra showed no significant shape variations with time, and the satellite lines, if any, were well visible more or less throughout the entire observation period, depending on the matrix and the characteristics (sensitivity and calibration) of the measurement equipment. Herbal extracts yielded unsatisfactory results: the spectra were extremely complex, with multiple peaks, and the radiation-induced signal could not be identified in any of the samples, regardless of the dose.

3.1.2. Fruit

The samples of almonds, hazelnuts, pistachios, walnuts, irradiated (5 kGy) and untreated, were all properly identified; their spectra appeared very similar to those reported in the EN standard 1787, with the satellite lines well visible in the case of irradiated samples. No false positive results were obtained with hazelnuts and walnuts, which indicated that the nuts had not been bleached. As expected and recently reported for hazelnuts and walnuts by Chiappinelli et al. (2019) and Tomaiuolo et al. (2018), the intensity of the satellite lines decreased with time (Fig. 7), but they were still visible for a long time (two years

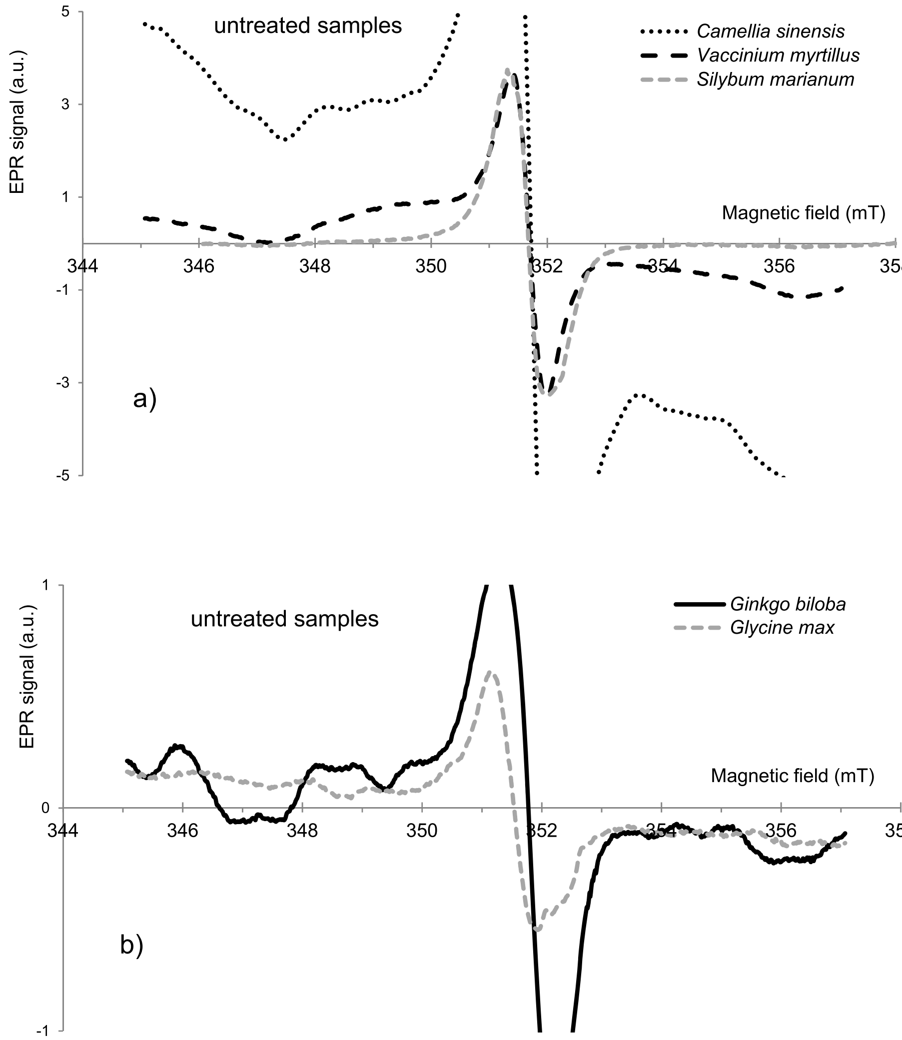

Fig. 1. ESR spectra of untreated samples.

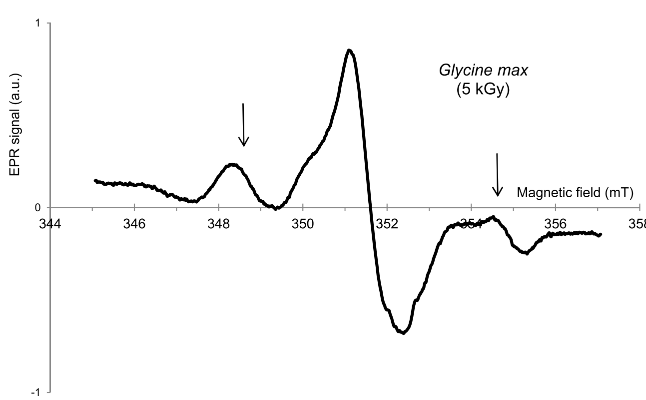

Fig. 2. ESR spectra of a sample of *Glycine* max (seeds) after irradiation at 5 kGy. The satellite lines are well evident.

after irradiation and more). As an example, Fig. 8 reports the ESR-spectra of irradiated almonds recorded at different times after irradiation. Fig. 8. b shows an evident decrease also of the central peak which supports the presence in that structure of not stable radiation-induced signals already reported in literature and, in particular, of a central line belonging to the same structure of the satellite lines, as confirmed by Chiappinelli et al. (2019) and Tomaiuolo et al. (2018).

Peanuts provided slightly different results; 2 out of 15 samples were

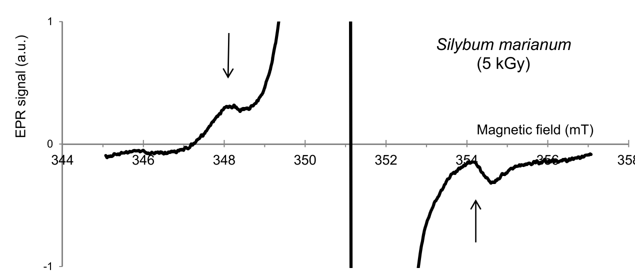

Fig. 3. ESR spectra of a sample of *Silybum marianum* (fruits) after irradiation at 5 kGy. The satellite lines are visible but the left one is not completely resolved.

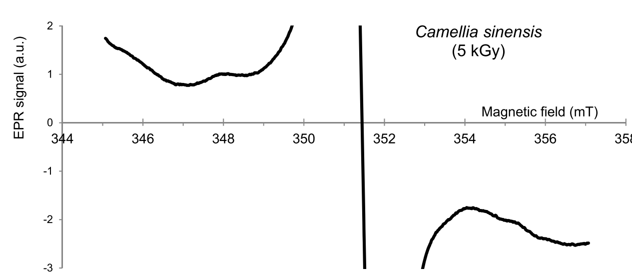

Fig. 4. ESR spectra of a sample of *Camellia sinensis* (leaves) after irradiation at 5 kGy. The satellite lines are not cleraly visible.

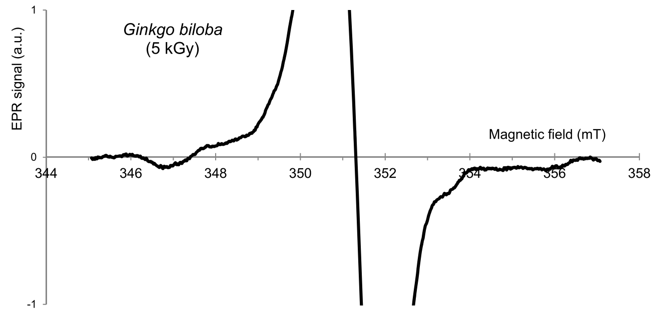

Fig. 5. ESR spectra of a sample of *Ginkgo biloba* (leaves) after irradiation at 5 kGy. The satellite lines cannot be detected.

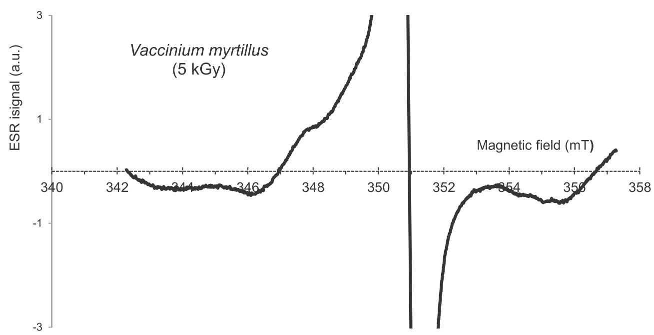

Fig. 6. ESR spectra of a sample of *Vaccinium myrtillus* (fruits) after irradiation at 5 kGy. The satellite lines cannot be detected.

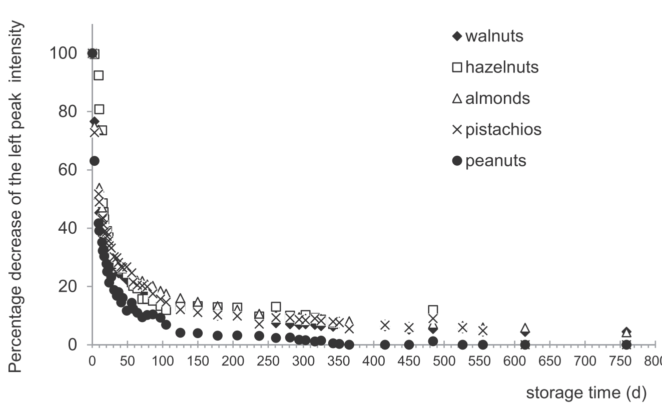

Fig. 7. Percentage decrease of the left satellite line of 5 kGy irradiated nuts. Each value is the mean of three measurements repeated on the same aliquot; the error bar is smaller than the symbol used in graph.

not correctly identified and the fading was faster (Fig. 7). Moreover, the characteristics of the spectrum were also slightly different as shown in Fig. 9, where the distance between satellite lines is reported for the various nuts. The values in the graph were obtained from measurements repeated on the same aliquot at different times after irradiation. The value for such distance is clearly higher for peanuts than for the other nuts. This is likely attributable to the specific composition of peanut shells. As a point of fact, peanuts are classified as legumes, not nuts.

Fresh blueberries were analysed at different times within 3 weeks, which corresponds more or less to their shelf life. The samples irradiated at 1 kGy were correctly identified, whereas the ones irradiated at a low dose (0.15 kGy) all showed similar spectra in which only the satellite line on the right could be seen (Fig. 10).

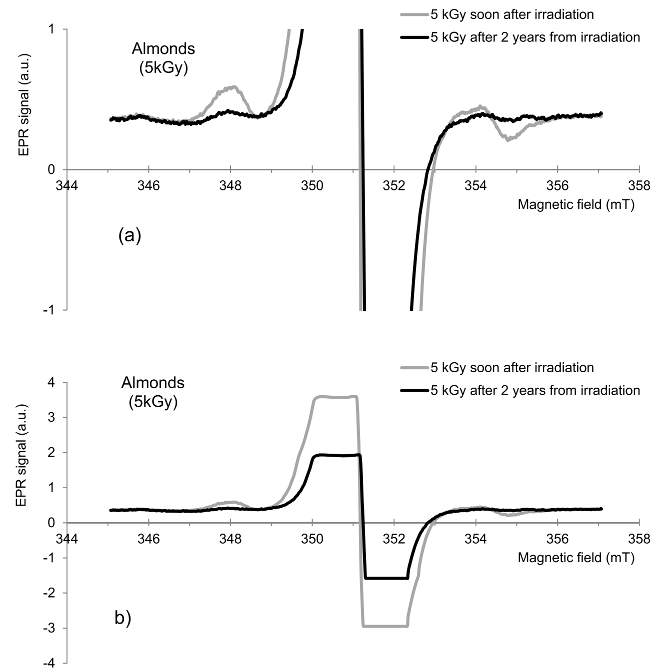

Fig. 8. ESR spectra of a sample of almonds irradiated at 5 kGy. a) The radiation-induced satellite lines are still well visible about 2 years after irradiation. b) The central peak appears strongly reduced after two years from irradiation.

3.2. Inter-laboratory validation test

All the matrices and the results of the ESR inter-laboratory validation test are reported in Tables 3–5.

PFS ingredients. Since the ESR method turned out to be unsuitable to detect herbal extracts during the preliminary intra-laboratory tests, the trial was limited to raw materials.

Glycine max. On the basis of the results of the preliminary tests, only the outer peel of the fruit was used.

Herbal ingredients. 80% of samples (60 out of 75) were correctly identified; the remaining 20% (15 samples) gave false negative (11 samples) or false positive (4 samples) classifications.

Nuts. Only 2 peanut samples (one untreated and one 5 kGy irradiated) out of a total of 75 samples (less than 3%) could not be correctly identified.

Fresh fruit. Blueberries were correctly identified only at 1 kGy.

These results confirmed that the ESR method can be used for the routine official checks on samples of almonds, hazelnuts, pistachios and walnuts, but not for peanuts or PFS ingredients such as *Camellia sinensis*, *Ginkgo biloba, Glycine max, Sylibum fructus* and *Vaccinium myrtillus*, which gave incorrect classifications. Irradiated fresh blueberries detection seemed to depend on the dose of treatment, which limits the applicability of the method to this matrix.

4. Conclusions

This study confirmed that the ESR spectra of plant-origin foods are generally complex and difficult to interpret as the result of a large variety of natural components, e.g., radicals. In particular, PFS ingredients showed overlapping signals due to the presence of different intrinsic radical species, which made it difficult to recognize the satellite lines typical of irradiated cellulose. The identification of the radiation-induced signal was unambiguous for nuts (with the exception of peanuts), for both untreated and irradiated samples. Fresh blueberries were correctly identified, even after 3 weeks, their shelf life approximately, but only those samples that had been irradiated at 1 kGy.

In conclusions, below some recommendation reflecting the final

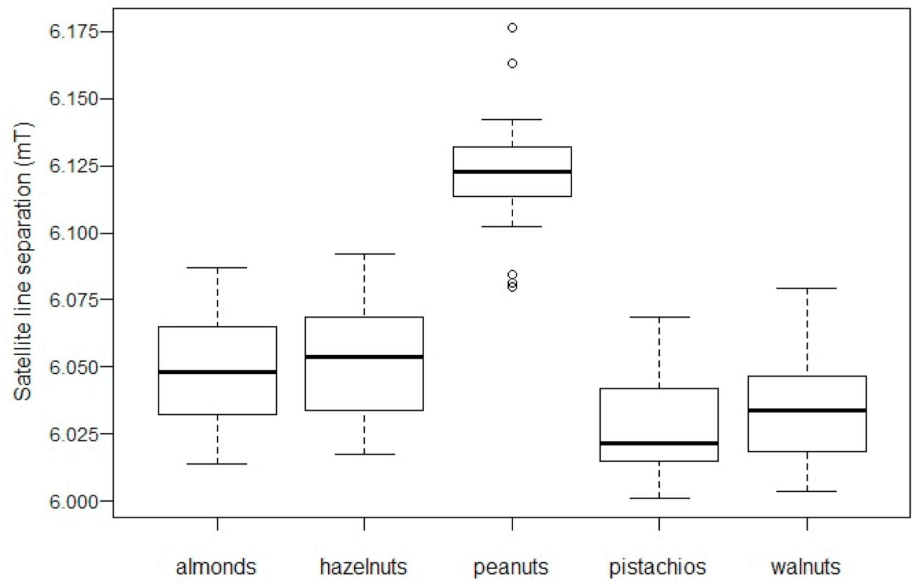

Fig. 9. Distance between satellite lines for the various nuts. The line in the box represents the median of measurements repeated on the same aliquot at different times after irradiation.

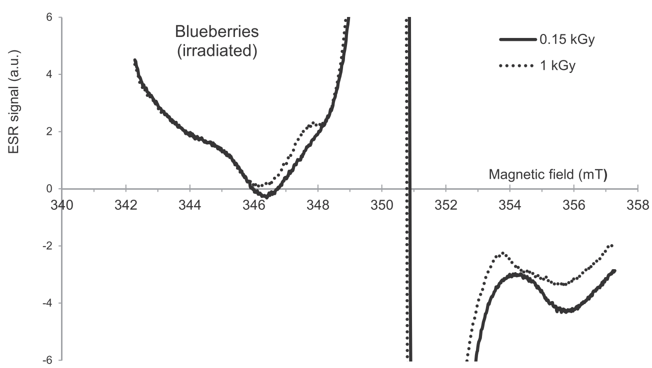

Fig. 10. ESR spectra of irradiated blueberries. The left satellite line cannot be clearly detected in the ESR spectrum of the 0.15 kGy irradiated sample.

stage of the inter-comparison.

PFS ingredients. The results were matrix dependent. Therefore, to avoid unambiguous interpretation of the spectra, it is worth verifying the reliability of the method on each single matrix before applying it for official controls.

Nuts. The results of the inter-comparison confirmed that the ESR method can be used for routine official checks on samples of almonds, hazelnuts, pistachios and walnuts. However, further investigations should be periodically conducted to verify whether bleached samples giving false positives are present on the Italian market.

Table 4
Inter-laboratory results: nuts.

Matrix	untreated samples	Irradiated samples	Correctly identified	False negative[a]	False positive[b]
Almonds	5	10	15	0	0
Hazelnuts	5	10	15	0	0
Peanuts	5	10	13	1	1
Pistachios	5	10	15	0	0
Walnuts	5	10	15	0	0
Total	**25**	**50**	**73**	**1**	**1**

[a] false negative: irradiated samples identified as untreated
[b] false positive: untreated samples identified as irradiated

Fresh blueberries. ESR response of these matrices resulted dose dependent. Therefore, as the treatment dose can be unknown, the method is to be considered not reliable for official control analyses on these products.

Declaration of competing interest

The corresponding author certify that all authors have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non –financial interest (such as personal or

Table 3
Inter-laboratory results: PFS ingredients (raw materials).

Matrix	Untreated samples	Irradiated samples	Correctly identified	False negative[a]	False positive[b]
Camellia sinensis	5	10	13	2	0
Ginkgo biloba	5	10	9	5	1
Glycine max	5	10	14	1	0
Silybum marianum	5	10	13	0	2
Vaccinium myrtillus	5	10	11	3	1
Total	**25**	**50**	**60**	**11**	**4**

[a] false negative: irradiated samples identified as untreated
[b] false positive: untreated samples identified as irradiated

Table 5
Inter-laboratory results: fresh blueberries.

Matrix	Untreated samples	Irradiated samples	Correctly identified samples	False negative[a]	False positive[b]
Blueberries	10	20	22	8	0
Total	**10**	**20**	**22**	**8**	**0**

[a] False negative: irradiated samples identified as untreated.
[b] false positive: untreated samples identified as irradiated.

professional relationships, affiliations, knowledge or beliefs) in the subject matter or material discussed in this manuscript.

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