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Review

Various approaches in EPR identification of gamma-irradiated plant foodstuffs: A review

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A R T I C L E I N F O

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A B S T R A C T

Irradiation of food in the world is becoming a preferred method for their sterilization and extending their shelf life. For the purpose of trade with regard to the rights of consumers is necessary marking of irradiated foodstuffs, and the use of appropriate methods for unambiguous identification of radiation treatment. One-third of the current standards of the European Union to identify irradiated foods use the method of the Electron Paramagnetic Resonance (EPR) spectroscopy. On the other hand the current standards for irradiated foods of plant origin have some weaknesses that led to the development of new methodologies for the identification of irradiated food. New approaches for EPR identification of radiation treatment of herbs and spices when the specific signal is absent or disappeared after irradiation are discussed. Direct EPR measurements of dried fruits and vegetables and different pretreatments for fresh samples are reviewed.

1. Introduction

One of the significant health problems in the world are infectious diseases that spread mainly through food and water. At the same time the need for food continues to increase, due to increased population on Earth. Therefore, the problems associated with processing and storage of food are especially essential and require the use of effective methods to prevent them from spoiling. Traditional methods for sterilization of food products are salting, pasteurization, canning and adding chemicals (preservatives). Although widely used in practice, these methods are expensive, associated with energy consumption and are difficult to apply to all kinds of foods. Therefore interest is the emerging new opportunity to prevent food from spoiling quickly and prolong its shelf life, i.e. high energy irradiation. Food irradiation has the potential to replace various food additives such as sodium nitrite, as well as fumigants ethylene dibromide, ethylene oxide and methyl bromide. This is significant because these fumigants may exhibit human toxicities and/or adverse effects on the atmosphere-ozone layer (Haire, Chen, Janzen, Fraser, & Lynch, 1997). In the past three decades, food irradiation is established as a fast, inexpensive and reliable technological process to improve their quality and prolong their shelf life.

The cornerstone of food irradiation was set with the adoption of the Codex World-wide General Standard for irradiated foods in 1983 and a significant revision in 2003. The General Standard states that the minimum absorbed dose should be sufficient to achieve the technological purpose and the maximum absorbed dose should be less than that which would compromise consumer safety, wholesomeness or would adversely affect structural integrity, functional properties, or sensory attributes. The maximum dose absorbed by a food should not exceed 10 kGy except when necessary to achieve a legitimate technological purpose. The General Standard also requires irradiated food to be labelled in accordance with the Codex General Standard for the Labelling of Prepackaged Food. This Standard requires the label of a food which has been treated with ionizing radiation to carry a written statement indicating that treatment in close proximity to the name of the food. The use of the international food irradiation symbol, Radura, is optional, but when it is used, it shall be in close proximity to the name of the food. When an irradiated product is used as an ingredient in another food, this shall be so declared in the list of ingredients. Approximately 60 countries have approved the use of food irradiation. However, the Standard does not name specific foods that may or may not be irradiated. All food maybe irradiated to the maximum approved absorbed dose (Roberts, 2016). The global volumes of irradiated food in the marketplace are difficult to estimate. The 2005 survey indicated a total of 405,000 tons of food was commercially irradiated world-wide (Kume, Furata, Todoriki, Uenoyama, & Kobayashi, 2009). The 2010 survey had more limited regional coverage and indicated a total of approximately 400,000 tons in the USA, parts of Asia and the EU alone. Irradiated food volumes continue to decrease in Europe (nevertheless the number of countries conducting irradiation is higher) but there has been considerable growth in applications of irradiation in China, particularly, and also in other Asian countries since 2010. In Belgium,

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France and the Netherlands many food items were irradiated commercially. In the Czech Republic, Estonia, Germany, Poland, Romania and Spain only dried aromatic herbs, spices, and vegetable seasoning were irradiated. Countries including Spain, Estonia and Romania started food irradiation recently, new irradiation facilities were approved in Bulgaria and Estonia in 2010 (Kume & Todoriki, 2013). More recent consumer studies are not available for the EU. As it concerns space food, NASA is still using several items irradiated at 44 kGy, however, NASA is also evaluating improved retort techniques as an alternative (Ehlermann, 2016a).

From the beginning several consumer organizations voiced concerns whether it would be 'safe' to consume irradiated food, at all. However, in now more than 100 years of research the questions raised are resolved and the consumers accept irradiated food where it has become available together with an understandable explanation of the new technology (Ehlermann, 2016b). Therefore, and in order consumers to be informed about how food processing by a World Health Organization (WHO) recommended the development of methods by which to determine whether a food has been irradiated and to make inspections consistent with existing regulations. From the latter requirement arises the need for finding and developing analytical methods to be applied directly on foodstuff and analyzed to prove its radiation treatment. EPR spectroscopy is a leading method for identifying radiation treated food as it has a number of advantages such as specificity, sensitivity, accuracy, independence, requires little and simple sample preparation, has nondestructive nature and speed of measurement and also with construction of portable spectrometers have already been resolved the problem of expensive and heavy equipment. Main disadvantage of EPR spectroscopy is that it is uncalibrated method for the quantitative measurements (Yordanov, 1994).

2. Early investigations on irradiated foodstuffs

2.1. Spices

Spices are the first food product in which it applies to the industrial use treatment with high-energy radiation such as a novel method for sterilization and their research with EPR spectroscopy dates from 1970. After more than four decades spices remain the most - often irradiated food product. One of the first spices subjected to analysis is the red pepper, as it is widely spread in the diet of consumers around the world. Non-irradiated paprika has singlet signal which is slightly asymmetric with g-factor 2.0044. Following irradiation with various doses was observed only increase the intensity. The difficulties in establishing the radiation coming from the fact that there is only a singlet line before and after radiation treatment. After three months storage of samples of red pepper irradiated with doses of 5 to 50 kGy measured difference in the concentration of spins in both samples is negligible (Beczner, Farkas, Watterich, Mailath, & Kiss, 1986). Similar results were obtained by other authors who have extended the samples, including cinnamon, black pepper and dry mustard. The resulting EPR spectra before irradiation, which are analogous are regarded as spectra of free radicals trapped in a solid matrix. It is assumed that the signal of non-irradiated samples is inherent in the vegetables and spices and originated from phenolic components. After irradiation a strong increase in the intensity of the natural signal with a dose was observed, which varies widely depending on the water content. The authors believe that free radicals which are formed as a result of the irradiation, are few. Proof of this are the different kinetic observations about the disappearance of free radicals at low and high doses. The intensity of the radiation induced signals decrease slowly with time, is not affected by the presence of air and disappears completely after treatment with water. Such signals can hardly be used for the identification of radiation, and even more - less on the quantitative determination of a dose (Yang, Mossoba, Merin, & Rosenthal, 1987). Therefore interest is the article for irradiated red pepper, where except intense central line, two additional signals at a distance of 6 mT (60 G) from each other were detected. These signals have not been registered under heating the sample and appear only after irradiation (Wieser & Regulla, 1986).

2.2. Fruits

Initial studies of fresh fruit with EPR spectroscopy were focused on registering the spectra of these parts of the fruit, which have low water content such as seeds, stones, skins and stalks.

The first EPR experiment is on non- and irradiated seeds of fresh strawberries being proposed procedure for proving radiation treatment (Raffi, Agnel, Buscarlet, & Martin, 1988). In another article the same authors expand research on seeds from raspberries, currants, figs, blueberries, apples, pears, kiwi, cantaloupe and watermelon, stems of apples and pears, as well as stones from plums and cherries (Raffi & Agnel, 1989). EPR spectrum of interest is irradiated seeds of strawberries, which consists of three overlapping signals. One, contains 6 lines and g = 2.0014 is attributed to the ions of Mn^{2+}. This signal is present in both the irradiated and non-irradiated samples. It is believed that ions of manganese within the fruit from the soil on which they are grown. Ions of Mn^{2+} are EPR active, but radiation insensitive, i.e. the intensity of the signal is not influenced by the absorbed dose, and cannot serve as proof for radiation treatment of the product (Pilbrow, Troup, Hutton, & Hunter, 1996). Another signal is singlet, which is also observed in the non- and irradiated sample, is a natural signal due to free radicals by metabolic processes within fruit. The presence of this signal can be explained by the existence of a radical linked to the photosystem II, partially permitted hyperfine structure, g-factor ranging from 2.0043 to 2.0047 and the Δ H from 1.5 to 2.0 mT. Usually associated with the presence of Mn, and probably originates from the membrane-bound semi-quinone. Its intensity increases with radiation dose, but is strongly dependent on water content and therefore cannot be used as a proof of radiation. In-extensive studies of irradiated strawberry seeds have demonstrated the presence of another signal present only in irradiated samples. It is assumed that it is complicated - doublet or triplet. The measured g-factor is 2.0043, and the hyperfine coupling constant in case it is doublet, A_H 6 = mT. It is assumed that for the EPR spectrum is responsible radical derived from a molecule of a substance present in a significant amount in the test environment. It is made the assumption that this molecule may be cellulose, pectin, hemicellulose or lignin. Despite all the research done is not established with certainty whether these satellite lines are part of the doublet or triplet, but has been proven to belong to the free radicals induced by gamma rays in cellulose and can serve as an indication of irradiated solid parts of the fruits (Raffi & Agnel, 1989). Other authors did not observe the satellite lines characteristic of irradiation (Desrosiers & McLaughlin, 1989; Dodd & Swallow, 1985). The first study of freeze-dried fruit is made for blackberries and raspberries. In irradiated samples only the spectrum of Mn^{2+} with singlet signal was detected. The absence of satellite lines can be explained by the fact that the signal/noise ratio is insufficient for their registration (Desrosiers & McLaughlin, 1989).

3. European standards

As a result of research done up to 1990 European Committee for Standardization (EN) initially adopted six standards for the identification of radiation-treated food products. Later are accepted the remaining four. Currently, within the European Union operate a total of ten standards, of which six primary and four for "screening" purpose. Three of the main standards for the identification of irradiated food using the method of EPR spectroscopy. The first standard refers to meat products containing bones in which gamma rays generate paramagnetic centers in hydroxyapatite (EN 1786, 1996). This protocol provides unambiguous evidence that the sample was irradiated. In the other two protocols, standardized for food of plant origin EPR spectroscopy detect