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ScienceDirect
Food Control 19 (2008) 1076–1085
FOOD CONTROL
www.elsevier.com/locate/foodcont

Effect of various parameters on detection of irradiated fish and oregano using the ESR and PSL methods ☆

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Received 22 August 2007; received in revised form 12 November 2007; accepted 17 November 2007

Abstract

Control of irradiated food on the market is a requirement of EU regulations. In order to improve checks of irradiated food in Greece, electron spin resonance (ESR) and photostimulated luminescence (PSL) were tested to detect electron beam radiation treatment of representative samples, namely fish (herring) and aromatic plant (oregano). The absorbed irradiation doses for both food samples were 1, 4 and 10 kGy. The effect of thermal treatment and storage time of fish samples on the sensitivity of ESR method as well as the effect of light exposure (after irradiation treatment) and storage time of oregano samples on the sensitivity of PSL method was studied. In addition, the suitability of both methods for two food samples was studied. For fish samples, the detection of irradiation treatment was based on ESR or PSL signal of fish bones. The results showed that PSL is a sensitive detection method for irradiated oregano samples allowing verification of irradiation treatment for all absorbed doses but this is not a sensitive detection method for irradiated herring containing bones. In contrast, ESR allowed verification of the irradiation treatment of fish bone samples but this is not a sensitive method for irradiated oregano samples. Daylight exposure of oregano samples (10 klux, 9 h) produced a strong effect on the PSL signal of all irradiated samples decreasing or disappearing the irradiation signal, while the thermal treatment (100 ± 1 °C, 1 h) of fish bones was produced a clear decreasing effect on the ESR signal of irradiated samples mainly for the higher dose of 10 kGy. The storage time strongly affected the PSL signal intensity of oregano samples as well as the ESR signal intensity of herring bone samples but the samples could be correctly identified as irradiated after a storage time of seven months.

Keywords: Food irradiation detection; Absorbed dose; PSL; ESR; Oregano; Herring; Light exposure; Temperature effect; Storage effect

1. Introduction

Food irradiation is a food preservation method reported as "cold sterilization" as a result of the antimicrobial effect of this method without heat treatment of foods.

Despite of international reports in respect to wholesomeness of irradiated foods (WHO, 1981, 1994); today this method is approved by the EU and USA only for a limited number of foods or food products and for a limited range of doses (EC, 1999a, 1999b; Morehouse, 2002). Particularly, in Europe, consumers have remained sceptical about food irradiation and EU took the lead in developing detection methods (Delincée, 2002; Ehlermann, 2005; EU, 2006b). The irradiation of dried aromatic herbs, spices and vegetable seasonings is authorised in the EU Directive 1999/3/EC (EC, 1999b). In addition, six Member States have national authorisations for certain foods in accordance with Directive 1999/2/EC (EC, 1999a; EU, 2006a). According to the same directive, any irradiated food or any irradiated food ingredient of a compound food must be labelled with the words "irradiated" or "treated with ionizing radiation".

☆ The experimental work was done at the Federal Research Centre for Nutrition and Food, Karlsruhe, Germany.

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doi:10.1016/j.foodcont.2007.11.007

According to Directive 1999/2/EC of EU (EC, 1999a) on the approximation of the laws of the Member States concerning food and food ingredients treated with ionizing radiation, the Member States shall forward to the Commission every year the result of checks carried out at the product marketing stage and the methods used to detect irradiated foods. However, as reported by the EU (EU, 2006b) some foods checked in the Member States had been irradiated and were not labelled.

For the enforcement of the correct labelling or to detect non-authorized products, several analytical methods have been standardized by the European Committee for Standardization (CEN). Thus, there is a great interest for methods suitable to identify irradiated foods as well as for the applicability of these methods to foods with different composition.

The methods used for the identification of irradiated foods may be classified under three broad categories: physical, chemical and biological (Delincée, 1993; EU, 2006c; Haire, Chen, Janzen, Fraser, & Lynch, 1997). Two of the more widely used physical detection methods are electron spin resonance (ESR) and photostimulated luminescence (PSL). These methods are standardized by the European Committee for Standardization (CEN) for the detection of irradiated foods (CEN, 1996, 2000, 2002) and are rapid and simple for immediately indicating a possible irradiation treatment of food.

ESR is a technique which detects free radicals produced as a result of the irradiation process. Free radicals possess at least one unpaired electron, and this feature permits their detection by ESR (Haire et al., 1997). An intense external magnetic field produces a difference between the energy levels of the electron spins leading to resonance absorption of the applied microwave beam in the spectrometer. The radiation induced ESR signal is attributed to trapped radicals in hydroxyapatite which is the principal component of bones or to cellulose radicals for foods containing cellulose (CEN, 1996, 2000).

PSL is based on the emission of trapped energy as light which may be induced photochemically (Haire et al., 1997). Mineral debris, typically silicates or bioinorganic materials such as calcite can be found in most foods. These materials store energy when exposed to ionizing radiation (CEN, 2002).

Each of the above reported methods has various limitations. The applicability of these methods differs among various foods as a result of different food composition. In addition, other parameters such as the temperature and light conditions as well as the time after irradiation treatment influence their applicability (Bortolin et al., 2007; Cutrubinis, Delincée, Stahl, Roder, & Schaller, 2005; Empis, Silva, Nunes, & Andrade, 1995; Eschrig, Stahl, Delincée, Schaller, & Roder, 2007; Haire et al., 1997; Lea, Dodd, & Swallow, 1988; Malec-Czechowska, Strzelczak, Dancewicz, Stachowicz, & Delincée, 2003; Tabner & Tabner, 1996). The detection limits and sensitivity of ESR method are influenced by the degrees of mineralization and crystallinity of hydroxyapatite in the sample. In general, the bones of larger animals are high mineralized with low minimum detectable doses (CEN, 1996). Similarly, PSL sensitivity of a sample depends on the quantities and types of minerals within the individual samples. Optimum results are obtained from unblended products (CEN, 2002). However, PSL is a not time-consuming technique which may be only used for screening purposes (CEN, 2002).

Herring (*Clupea harengus*) is a popular fish species in Germany and North Europe while oregano is a characteristic spice of the Mediterranean cuisine widely used in raw or cooked foods. Thus, the objective of this study was to further investigate the applicability of these two physical detection methods (ESR and PSL) on irradiated herring and oregano samples. Parameters influencing the stability of the ESR and PSL signals of these food samples such as temperature (simulation of cooking conditions), light (daylight, office light) as well as the storage time were studied. The reasons for the choice of these parameters are that the light stimulate the release of most of the charge carriers trapped at structural cites during irradiation treatment of a food reducing the PSL intensity (CEN, 2002) while the thermal treatment liberate a number of radicals trapped previously as a result of irradiation treatment of a food reducing the ESR signal (CEN, 1996, 2000). These investigations will help to improve the testing of irradiated food on the market in Greece as required by the present EU legislation.

2. Materials and methods

2.1. Fish and oregano samples

Fresh herring (*Clupea harengus*) was purchased from a local market (Karlsruhe, Germany). Fishing ground was the North Sea, Germany. Dried oregano (*Origanum vulgare*) packaged in plastic bags was purchased also from a local market (Karlsruhe, Germany).

2.2. Irradiation process and dosimetry

Whole herring samples and oregano samples were irradiated with high energy electrons by a 10 MeV electron beam (Circe III linear accelerator, Linac Technologies SA, Orsay, France) at the Federal Research Centre for Nutrition and Food, Karlsruhe, Germany. The radiation absorbed doses were 1, 4 and 10 kGy and measured using alanine dosimeters type EMS 914-1005 (Bruker Biospin, Karlsruhe, Germany).

2.3. Photostimulated luminescence (PSL) method

PSL measurements of herring bone samples and oregano samples were carried out according to European Standard EN 13751 (EC, 2002) using a SURRC PPSL Irradiated Food Screening system (SURRC, Glasgow,