Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 110 (2008) 531–537
FOOD CHEMISTRY
www.elsevier.com/locate/foodchem

Analytical Methods

Solid phase microextraction as a methodology in the detection of irradiation markers in ground beef

M.M. Caja, M.L. Ruiz del Castillo *, G.P. Blanch

Instituto de Fermentaciones Industriales. Consejo Superior de Investigaciones Científicas (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

Received 14 September 2007; received in revised form 31 January 2008; accepted 10 February 2008

Abstract

The usefulness of solid phase microextraction (SPME) to detect the occurrence of the irradiation markers 2-dodecylcyclobutanone (2-DCB) and 1,3-bis(1,1-dimethylethyl)benzene in irradiated ground beef was evaluated. To that aim, beef samples were irradiated with different irradiation doses and subsequently examined together with non-irradiated beef samples used as control samples. The SPME conditions applied were selected as a result of performing an optimization process including different fibers (PDMS, DVB/CAR/PDMS, polyacrylate and PDMS/DVB), as well as extraction times (10, 25 and 40 min) and temperatures (40 and 60 °C). For comparison, 2-DCB and 1,3-bis(1,1-dimethylethyl)benzene were additionally identified in some of the samples by steam distillation–solvent extraction (SDE). Although this study is a preliminary work, from the results obtained SPME seemed to be a rapid and valuable technique to determine 2-DCB and 1,3-bis(1,1-dimethylethyl)benzene in ground beef subjected to irradiation, offering advantages over other methods reported in the literature. In addition, SPME allowed to confirm the validity of 2-DCB as an useful marker to distinguish non-irradiated from irradiated ground beef. On the contrary, the occurrence of 1,3-bis(1,1-dimethylethyl)benzene was however established in both types of samples by SPME and SDE.

Keywords: SPME; Irradiation; 2-Dodecylcyclobutanone; 1,3-Bis(1,1-dimethylethyl)benzene; Ground beef

1. Introduction

Over the last few years there has been an increasing demand for new techniques for food preservation replacing the use of hazardous chemicals (Bhattacharjee, Singhal, Gholap, Variyar, & Bongirwar, 2003). Among them, food irradiation has been demonstrated to be particularly effective in inactivating pathogens, decreasing microbial load and extending shelf life without appreciable alteration in food quality (Giroux & Lacroix, 1998; Thomas, 1986; Urbain, 1986). However, despite repeated assurances that irradiation is one of the safest methods to preserve foodstuffs, nowadays consumers still demand labeled foods by legislation to avoid unknown risks. For that reason, new methods capable of differentiating between irradiated and non-irradiated foods are currently sought.

A number of biological, physical and chemical methods have been developed for detecting irradiated foods. In this regard, although the biological (Nation, Smittle, & Milne, 1995; Scotter, Beardwood, & Wood, 1995; Wirtanen, Salo, Karwoski, & Sjöberg, 1995) and physical (Desrosiers, 1996; Dodd, 1995; Rahman, Haque, & Sumar, 1995) methods have widely demonstrated their usefulness in the detection of irradiated foods, the chemical methods are the most commonly used. As chemical methods, it can be emphasized those based on the detection of marker compounds of irradiation, such as 2-alkylcyclobutanones (Boyd et al., 1991; Crone, Hamilton, & Stevenson, 1992) and radiation-induced lipid-derived long-chain volatile hydrocarbons (Bergaentzle, Sanquer, Hasselman, & Marchioni, 1994; Morehouse, Kiesel, & Ku, 1993). The usefulness of the former markers is known long ago and the relation

* Corresponding author. Tel.: +34 91 5622900; fax: +34 91 5644853.
E-mail address: ifir312@ifi.csic.es (M.L. Ruiz del Castillo).

0308-8146/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2008.02.024

between its occurrence and the employment of an ionizing radiation is at present doubtless (Stevenson, 1994; Stewart, Moore, Graham, McRoberts, & Hamilton, 2000). Regarding long-chain volatile hydrocarbons, some authors have recently proposed 1,3-bis(1,1-dimethylethyl)benzene as an indicator in the identification of irradiated beef extract powders (Kim, Cho, Ahn, Cho, & Cha, 2005). However, in contrast to 2-alkylcyclobutanones, the validity of this compound as an irradiation marker has only been determined usable in this specific study and more studies would be needed to extend the application field of this indicator to irradiated samples other than beef extract powders.

The European standard (EN1785) method for the identification of irradiated lipid-containing foods is based on the detection of 2-alkylcyclobutanones by means of solvent extraction followed by Florisil chromatography. This method was validated in 1996 by Ministry of Agriculture, Fisheries and Food validated method (MAFF V37) (MAFF, 1996) and implies extremely long overall analysis time (72–84 h), large organic solvent volumes, high economic cost and relatively high explosion risk (McMurray, Brannigen, Hamilton, Boyd, & Stevenson, 1999; Rahman, Haque, & Sumar, 1996). These limitations have been overcome by using a supercritical fluid extraction (SFE) method to also detect 2-alkylcyclobutanones, which has more recently been proposed as an alternative to the official method (Gadgil, Hachmeister, & Smith, 2002; Rahman, Matabudall, Haque, & Sumar, 1995; Tewfik, Ismail, & Sumar, 1998). Advantages of the SFE approach are the remarkable reduction in the extraction time (from 6–18 h to 30 min), the larger amount of sample that can be used and the higher efficiency in extracting low levels of 2-alkylcyclobutanones. Nonetheless, SFE is not a technology easily accessible to all laboratories owing mainly to the high initial economic cost. Accordingly, the search for additional methods to identify irradiated foods would be valuable in routine analysis of irradiated foods.

In this regard, solid phase microextraction (SPME) has demonstrated to be an interesting methodology to isolate minor compounds from complex matrices (Arthur & Pawliszyn, 1998; Pawliszyn, 1995; Zhang & Pawliszyn, 1993; Zhang, Yang, & Pawliszyn, 1994). It is rapid, accessible, inexpensive and simple handling. The usefulness of SPME in studying volatile compounds obtained as a consequence of the application of irradiation to foodstuffs has occasionally been reported. However, most of these works are not aimed to identify irradiation indicators but volatile sulfur compounds, which have been described to give off a pungent odor at low concentrations (Fan & Sokorai, 2002; Fan, Sommers, Thayer, & Lehotay, 2002). In fact, reports on the application of SPME to the determination of irradiation markers are extremely scarce. Specifically, Kim et al. (2005) identified irradiation volatile markers in beef extract powder by SPME while Thomazini, Contreras, and Miyagusku (2006) applied this sample preparation technique to the detection of markers in irradiated chicken thigh.

The goal of this investigation was to study the usefulness of SPME to distinguish irradiated from non-irradiated ground beef through the occurrence of 2-DCB and 1,3-bis(1,1-dimethylethyl)benzene.

2. Materials and methods

2.1. Samples and materials

2-DCB and 1,3-bis(1,1-dimethylethyl)benzene standards used in the identification of the target compounds were obtained from Sigma–Aldrich (Madrid, Spain). Dichloromethane and Milli-Q water employed in the preparation of the standard solution as well as in the SPME and SDE extractions were obtained from SDS (Peypin, France) and from a Milli-Q water purification system (Millipore, Milford, MA), respectively. A standard solution containing 10 mg of each compound in 10 ml of dichloromethane was used to optimize the chromatographic separation and the extraction conditions used in SPME.

Six beef samples (fat content around 30%) used for human consumption, which had not been submitted to any treatment, were purchased from the local market. Five of them were not irradiated to be used as control samples (Samples 1–5). On the contrary, Sample 6 was vacuum-packed in nylon/polyethylene bags (100 g each) to be subjected to irradiation. The bags were irradiated using electron beam at targeted absorbed doses of 2.0 (Sample 7), 4.0 (Sample 8) and 8.0 kGy (Sample 9) (IONMED Esterilización, S.A., Cuenca, Spain). The irradiation dose applied in each case was monitored by using a radiochromic film dosimeter. The rest of Sample 6 was also used as a control sample. Both non-irradiated (Samples 1–6) and irradiated samples (Samples 7–9) were finally frozen at −18 °C until their analysis.

2.2. Solid phase microextraction (SPME)

The isolation of 2-DCB and 1,3-bis(1,1-dimethylethyl)benzene was carried out for all samples by solid phase microextraction (SPME). A fused silica fiber coated with a 100 μm layer of polydimethylsiloxane installed in a holder for manual use (Supelco, Madrid, Spain) was utilized. Before using the SPME fiber, it was conditioned in the injector of the gas chromatograph at 250 °C for 30 min. A 2.0 g weight of the frozen ground beef plus 2.0 ml of Milli-Q water were placed into a 10.0 ml vial, which was sealed with plastic film suitable for the SPME extraction (i.e., low water permeability, insensitivity to moisture vapor and the commonest reagents). The simple addition of water enabled the sample to be thawed. Experimentation was performed by exposing the fiber to the headspace of the sample for 10 min at 40 °C. Prior to the extraction, an incubation time of 10 min was applied to enrich the headspace in the target compounds. As later explained in results and discussion, the extraction conditions (fiber type, extraction temperature and exposure time) were selected as