



Irradiated ground beef patties: Dose and dose-age estimation by volatile compounds measurement



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ABSTRACT

Volatile compounds produced by irradiation in ground beef patties, packaged under vacuum, were extracted by head-space solid-phase micro-extraction and quantified by gas-chromatography coupled to mass-spectrometry. The study was carried out at levels of irradiation, ranging from 0.5 to 8 kGy. Among the 101 detected volatiles compounds, 25 resulted correlated with dose. On the basis of further measurements at 30 and 120 days after irradiation, the most stable compounds with time were identified. To estimate the dose just after irradiation, linear combinations of selections of possible dose markers were obtained via partial least squares regression. A further data analysis showed that it is possible to reconstruct both the irradiation dose and the time elapsed after irradiation from the ratio between the peak areas of some dose markers. The adopted experimental procedure combined with a proper data analysis may lead to dose or dose/age reconstruction in a rapid, simple and efficient way.

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1. Introduction

Since irradiation (beta, gamma and X-rays, UV-C) has been introduced as a successful technique to improve food safety, a reliable control of used doses has been required (O'Bryan, Crandall, Ricke, & Olson, 2008) and different procedures have been studied in this view (Chauhan, Kumar, Nadanasabapathy, & Bawa, 2009).

Chemical methods applied to meat products are based on changes in lipid fraction, mainly in fatty acid moieties. Among the compounds produced after irradiation of meat, markers of choice according to reference procedures proposed by the European Committee of Standardization (EN 1784 and EN 1785 methods, 2003) are 2-alkyl(C_{n-4})-cyclobutanones (2-ACB) and hydrocarbons (HC) (C_{n-1}:0 and C_{n-2}:1), both coming from C_n fatty acids. Such reference procedures imply long overall analysis time (almost two days) and large organic solvent use. As for 2-ACB also for HC alternative techniques, like solid-phase extraction (SPE), have been proposed to overcome these criticisms (Kim, Lee, & Hong, 2004). In our laboratory head-space solid-phase micro-extraction (HS-SPME), a well-known quick and solvent-free technique, has been recently applied to the extraction of 2-dodecylcyclobutanone from

ground beef patties before its determination by gas-chromatography coupled to mass-spectrometry (GC–MS) (Soncin et al., 2012). Also for HC determination in irradiated meat products HS-SPME has been proposed (Barba, Santa-Maria, Herraiz, & Calvo, 2012; Li, Ha, Wang, & Li, 2010). On the other hand, as regards analysis of volatile compounds, Rivas-Canedo, Juez-Ojeda, Nunez, and Fernandez-Garcia (2011) concluded that SPME proved to be more sensitive and provided wider information than dynamic head-space (DHE) often used for meat products (Nam, Lee, Ahn, & Kwon, 2011). In the cited references about HC in irradiated meat, according to the used operative conditions, only those with chain longer than 14 carbon atoms were considered as useful dose-dependent compounds. Furthermore different linear relationships were obtained between each single HC marker content and used doses. In particular Kim et al. (2004) identified eight dose-dependent HC after a unique time delay after irradiation of beef; Nam et al. (2011) studied six HC immediately after irradiation and after 60 days of storage at 4 °C of irradiated sausages, while Li et al. (2010) considered the dose dependence of only 1,7-hexadecadiene and 8-heptadecene in irradiated beef.

The present study is focused on the search of dose and age dependent markers in ground beef patties irradiated under vacuum at 4 °C in the range 0.5–8 kGy.

A dose range wider than the typical ranges adopted in meat irradiation procedures has been chosen with the aim of

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highlighting the effect of intense irradiation. Besides, one cannot exclude that doses greater than the ones at present approved by law may be allowed in the future or fraudulently given. The first aim of this work is to take account of a larger number of volatile compounds, including low boiling ones, by improving extraction and chromatographic conditions of the HS-SPME–GC–MS method, in order to take advantage of a larger set of dose-dependent volatiles compounds.

The second goal is to propose a data processing approach able to reconstruct the dose and the time delay on the basis of the identified dose-dependent volatile compounds measured by a rapid and simple analytical procedure.

2. Material and methods

2.1. Chemicals and samples

All the standard compounds were purchased from Sigma–Aldrich (Buchs, Switzerland). A loin beef sample was purchased from a local butcher, where it was ground and pressed into patties (about 150 g each). Twenty-six equivalent specimens were vacuum-packed in nylon/polyethylene bags and stored at $-20\text{ }^{\circ}\text{C}$. The day after the preparation two specimens were brought to $4\text{ }^{\circ}\text{C}$ and used as control samples the remaining 24 specimens were irradiated at 0.5, 2, 4, 8 kGy (6 for each dose), at a temperature of $4 \pm 2\text{ }^{\circ}\text{C}$, using a ^{60}Co gamma-ray industrial source available at Gammaton S.r.l. (Guanzate, Como, Italy). Plants, processes and dose measurements carried out at this irradiation facility are UNI EN ISO 9002, UNI EN 46002, EN 552 and ISO 11137 certified. The irradiation was carried out at the dose rate of 1.0 kGy h^{-1} . The adsorbed doses were checked at Gammaton S.r.l. by means of spectrophotometric measurements on standard dosimeters. The error on the measured doses was $\pm 1\%$. All samples were frozen and stored at $-20\text{ }^{\circ}\text{C}$ until the analysis was performed. Control samples and 2 samples irradiated at each dose were analyzed within 24 h after irradiation (time 0); 2 samples for each dose were analyzed after 1 and 4 months after irradiation.

2.2. Sample preparation and extraction by HS-SPME

All samples were prepared by just thawing ground beef patties and weighing finely cut portions (8 g) in HS 20 ml glass vials, fitted with cap equipped with silicon/PTFE septa (Supelco, Bellefonte, PA, USA). A temperature of $37\text{ }^{\circ}\text{C}$ was selected for both the equilibration and extraction steps. To keep the temperature constant during analysis, the vials were maintained in a hot plate (CTC Analytics, Zwingen, Switzerland). At the end of the sample equilibration time (10 min), a conditioned (90 min at $250\text{ }^{\circ}\text{C}$) $65\text{ }\mu\text{m}$ polydimethylsiloxane/divinylbenzene (PDMS/DVB) StableFlex fiber (Supelco, Bellefonte, PA, USA) was exposed to the headspace of the sample for analyte extraction (60 min) by CombiPAL system injector autosampler (CTC Analytics, Zwingen, Switzerland).

2.3. Gas chromatography–mass spectrometry apparatus and conditions

Analyses were performed with a Trace GC Ultra coupled to a quadrupole mass spectrometer (MS) Trace DSQII (Thermo-Fisher Scientific, Waltham, MA, USA) and equipped with an Rtx-Wax column ($30\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ film thickness) (Restek, Bellefonte, PA, USA).

Oven temperature programme was: from $35\text{ }^{\circ}\text{C}$, hold 8 min, to $60\text{ }^{\circ}\text{C}$ at $4\text{ }^{\circ}\text{C min}^{-1}$, then from $60\text{ }^{\circ}\text{C}$ to $160\text{ }^{\circ}\text{C}$ at $6\text{ }^{\circ}\text{C min}^{-1}$ and finally from 160 to 200 at $20\text{ }^{\circ}\text{C min}^{-1}$. Helium was the carrier gas, at flow rate of 1 ml min^{-1} . Carry over and peaks originating from

the fibre were regularly assessed by running blank samples. After each analysis fibres were immediately thermally desorbed in the GC injector for 5 min at $250\text{ }^{\circ}\text{C}$ to prevent contaminations.

MS operated in electron impact (EI) ionization mode at 70 eV. Ion source temperature was $250\text{ }^{\circ}\text{C}$. Compounds were identified by comparing the retention times of the chromatographic peak and the corresponding MS fragmentation patterns with those of authentic compounds analyzed under the same conditions when available, or by comparing the MS spectra with those from the National Institute of Standards and Technology (NIST) MS spectral database.

The quantitative results were expressed as peak areas (arbitrary units). All analyses were done in duplicate and data are expressed as mean value.

3. Results and discussion

3.1. Experimental results

3.1.1. Operative conditions

In the experimental conditions proposed so far in literature for the analysis of volatile irradiation markers by SPME technique, long chain hydrocarbons were easily detected while low-molecular compounds were not deeply investigated. In preliminary experiments both CAR/PDMS and DVB/PDMS fibers were tested in irradiated samples: according to the prevision, CAR/PDMS resulted more specific for polar compounds and less suitable to absorb apolar high molecular weight compounds. Thus DVB/PDMS was finally chosen, being hydrocarbons, among volatiles, the most significant irradiation markers. The DVB/PDMS fiber was also recently proposed by Li et al. (2010) to extract at high temperature long chain hydrocarbon, 1,7-hexadecadiene and 8-heptadecene, in irradiated chilled beef. In our case temperature and extraction time were changed in order to absorb short chain hydrocarbon too, and to prevent degradation of substances present in original samples.

Under the described conditions over one hundred volatiles compounds were detected in samples irradiated at 8 kGy. Among these compounds, 30 ones (those listed with “a” superscript in Table 1) show a content increase with dose immediately after irradiation. Therefore the adopted procedure allows obtaining a high number of possible volatile markers of irradiation to be considered. In order to verify the stability of these compounds during storage at $-20\text{ }^{\circ}\text{C}$, volatile analysis was again performed after one and four months.

3.1.2. Irradiation dose markers

The possible irradiation dose markers here considered derive from C_n fatty acids moieties: as expected they are linear $\text{C}_{n-1}:0$ alkanes and $\text{C}_{n-2}:1$ alkenes with the exception of 1-decyne (hydrocarbon with a triple bond), which for the first time appears as an irradiation product. A probable mechanism for its formation can be the hydrogen atom loss of the 1-decene vinyl radical derived from the chain breaking of an $\omega-9$ unsaturated fatty acid like oleic one.

About the specificity of the linear hydrocarbon as irradiation markers, it must be taken into account that in several studies saturated and monounsaturated hydrocarbons are present also in control samples, probably derived from processing contamination or from packaging materials. For example: pentadecane, heptadecane and 1-hexadecene have been found in raw beef meat (Kwon et al., 2012), pentadecane has been found also in not irradiated dry-cured ham (Martinez, Barba, Santa-Maria, & Herraiz, 2011) and 1-hexadecene has been found in sausage (Nam et al., 2011). Furthermore, among the compounds suitable as markers, 1-octene and decane have been found in raw beef (Insausti, Beriain, Gorraiz, & Purroy, 2002).

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