Food Control 59 (2016) 581–590

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Profiling, distribution and levels of carcinogenic polycyclic aromatic hydrocarbons in traditional smoked plant and animal foods

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ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form
16 June 2015
Accepted 18 June 2015
Available online 23 June 2015

Keywords:
PAHs
Traditional smoke foods
Smoked bread
Smoked paprika
Smoked cheese
Smoked garlic pork sausage

ABSTRACT

The purpose of this study was to evaluate the concentration of polycyclic aromatic hydrocarbons (PAH8 plus fluoranthene and pyrene) in "Pan de Cea" bread, "Pimentón de La Vera" paprika, "San Simón da Costa", "Idiazábal" and "Humus" cheeses, and "Chorizo" garlic pork sausage. Results obtained showed that harmless low molecular weight compounds (Fluoranthene and Pyrene) represented the major contribution to the total PAHs. The most important PAHs according to the levels found were those in the 4 PAHs group (the rest of PAHs to add a total of 8 were contributing at very low levels). PAH4 and PAH8 levels showed percentages ranging from 6.0 to 7.0 % in bread, 16–17 % in paprika, 23–28 % in cheese and 20–24 % in meat sausages, respectively. B(a)P did not exceed the imposed limits in the EU. Bread showed the lower PAH concentration (3.4 μg/kg) followed by cheese (88 μg/kg), smoked sausage (1779 μg/kg) and paprika (9937 μg/kg). "Pimentón de la Vera" paprika is a condiment consumed in small quantities. The PAH profile had in common the decrease in PAH content as their molecular weight increased. These results showed that the contamination detected in "Pan de Cea" bread samples was very low, so that the consumption of this product does not pose a health risk. In cheese samples, the PAH contamination was detected meanly in rind, that accounted around the 100% of the total contamination. In meat sausages samples, the 90% of the total PAHs determined were accumulated in the casing. Considering the edible part, the PAH4 and B(a)P mean contents were below the limit established. Although, the highest PAH levels were detected in "Pimentón de la Vera" paprika, it should be pointed out that this product is a condiment consumed in small quantities and not in an everyday basis, it does not represent a risk for consumers. In cheese and meat sausage, according our estimates, the removal of the external part can be considered a good consumer practices to reduce the ingestion of PAHs.

1. Introduction

Originally the purpose of smoking was to preserve the food. Nowadays smoking is primarily used to achieve the characteristic taste and appearance of smoked food and to a minor degree to obtain preservation. The traditional smoking process can be conducted in several ways, both from an organoleptic point of view and in the light of health aspects (COE, 1992). Some of the constituents in the smoke and in the smoke condensates may give rise to health problems e.g. the polycyclic aromatic hydrocarbons (PAHs). As it is well known, they are a group of chemical compounds that are formed during the incomplete combustion or pyrolysis of organic matter by a series of complex chemical reactions (Yebra-Pimentel, Fernández-González, Martínez Carballo, & Simal-Gándara, 2012). They accumulate on the surface to migrate after into the smoked products.

The European Food Safety Agency (EFSA) in an opinion article released in 2008, pointed that the carcinogenicity of PAHs through oral administration is the most relevant (EFSA, 2008). In particular, benzo(a)pyrene (B(a)P) has been reported to produce tumours of the gastrointestinal tract, liver, lungs and mammary glands of mice and rats. According to the Commission Regulation No 1881/2006 (EC, 2006a) B(a)P could be used as marker for the occurrence of

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http://dx.doi.org/10.1016/j.foodcont.2015.06.036
0956-7135/

PAHs in different types of food. Since September 2012 a new Regulation that modified the previous legislation (EC, 2006a) is applicable for these compounds in foodstuffs (EC, 2011) and establishes the four PAHs (PAH4): B(a)P, Chr, benzo(b)fluoranthene (B(b)FA) and benzo(a)anthracene (B(a)A) as the most suitable indicators of PAH in food. EFSA Panel suggested using the PAH4 marker as better indicator of the occurrence of PAHs in food than a benzo(a)pyrene (EFSA, 2008).

In the traditional smoking process, a fire is make using dried wood. The kind of wood used depends on tradition and normally it will differ from country to country. This variable, as well as, moisture content, oxygen availability and combustion temperature will contribute to PAH contamination. Although, It is probable that PAHs will be accumulated mainly on the products surface, some diffusion could take place to inner layers (Simko, 2005), where water activity and fat content have a determinant role in the diffusion process (Martorell et al., 2010). On the other hand, the presence of barriers such as the casing (in meat sausage) or rind (in cheese) are especially effective as barrier for soot (with plenty of PAHs) and can interfere with PAHs migration into products internal layers (García-Falcón & Simal-Gándara, 2005; Guillén & Sopelana, 2004).

To our knowledge, the evaluation of PAH levels in the typical Spanish bread ("Pan de Cea") and paprika ("Pimentón de la Vera") is presented for the first time in the present study. Moreover, the PAH levels in other smoked traditional foods were also considered as the most typical from Northwest Spain such as: garlic pork sausage ("Chorizo"), and cheese ("San Simón da Costa", "Idiazábal" and "Humus") in order to compare their PAH content. Three of the four selected products have quality labels (Protected Designation of Origin – PDO and Protected Geographical Indication – PGI) that differentiate them and provide added value. So, "Pan de Cea" is bread with PGI, "Pimentón de la Vera" is a paprika with PDO and "San Simón da Costa" and "Idiazábal" are two types of cheeses with PDO. All these products are approved by the Council Regulation (EC) No. 510/2006 of 20 March 2006 on the protection of geographical indications and designations of origin for agricultural products and foodstuffs (EC, 2006b).

Due to the great impact of these products on the Spanish economy because of their characteristic taste, high nutritional value and high level and variety of production, the principal aim of this study was the evaluation of 10 PAHs (PAH8 indicated by EFSA plus the widely distributed fluoranthene (F) and pyrene (P)) in these selected traditional smoked foods, taking into account that the smoking step is a critical point in the increase in PAHs levels.

2. Materials and methods

2.1. Sampling

For this study, all the selected samples (bread, paprika, cheese and meat sausages) were purchased in different market places from Northwest Spain. In Fig. 1 the smoked processes for each of these products are shown, and the results were expressed in concentrations of each PAH in mass by product mass, mass by fat mass and mass by surface area. Fat was determined by exhausting Soxhlet extraction. Surface was estimated by surface area formulas as the sum of all the areas of all the shapes that cover the surface of the food (in the case of bread, cheese and chorizo), and by Brunauer–Emmett–Teller (BET) method based on the physical adsorption of gas molecules on a solid surface for the measurement of the specific surface area of paprika.

2.1.1. Bread

"Pan de Cea" is a bread that is baked in a standard wooden oven only in Cea area (Galicia-Spain) and must meet certain requirements of elaboration conditions defined in a Galician Regulation called "Regulation of the protected geographical indication Pan de Cea and its Regulatory Council" (DOGA, 2010). Samples of bread ("Pan de Cea") were collected in five different bakeries from San Cristovo de Cea, a village near the city of Ourense (Galicia). The five samples used in this study were collected from pieces of 500 g. The bread's crust and inside each bakery were separated, homogenized in a food mixer, codified, and stored at room temperature until analysis.

2.1.2. Paprika

"Pimentón de La Vera" is a product elaborated in La Vera area (Extremadura-Spain) based on traditional farming. . In the first step the fruits are dried with smoke produced by oak wood (10–15 days) and then the dry peppers are subjected to grinding by stone mill. "Pimentón de La Vera" is a product with PDO from Extremadura entered in the Community registered under Commission Regulation (EC) No 982/2007 of the Commission (EC, 2007). The seven samples of smoked paprika ("Pimentón de la Vera") in the sweet sour version with a mix of Jaranda, Jariza and Jeromin varieties were purchased in different delicatessen markets from Ourense and were codified and stored at room temperature until analysis in the following month.

2.1.3. Cheese

"San Simón da Costa" is a kind of smoked cheese produced only in Terra Chá area (Galicia-Spain), under traditional processing techniques and shown a typical triangular or pear shape. The wood used for smoking is from a typical tree that grows up in the production area, the birch, providing to the product smoky aromas of birch. "San Simón da Costa" is a PDO registered under Commission Regulation (EC) No 1229/2008 of the Commission (EC, 2008). "Idiazábal" is another smoked cheese with "Protected Designation of Origin (PDO)" and it is currently protected by the Ministry of Agriculture, Fisheries and Food of Spain (BOE 03/12/1993). This cheese is produced only in País Vasco and Navarra (Spain). "Humus" is another smoked cheese from La Quesera de Rueda (Rueda, Valladolid, Spain). The five selected samples of smoked cheese (2 "San Simón da Costa", 2 "Idiazábal" and 1 "Humus") were purchased in different market places from Ourense and Valladolid. These samples were peeled and the rind (corresponding to thickness of approximately 0.50 cm) and the core (more interior part) were codified, homogenized in a food mixer and stored at −18 °C until analysis. The rind and core of each sample were analyzed separately.

2.1.4. Smoked meat sausages

"Chorizo" is a sausage only made of minced pork meat with salt, garlic and paprika, which gives its typical flavor and color. This product after the casing-filling is dried under wood smoke. For the smoked meat sausages ("chorizo"), eight samples manufactured by 8 different industrial pork manufacturers following the traditional methods, were obtained in local markets from Ourense. In order to prepare the samples for analysis, they were peeled off and both casing and meat were codified, cut in pieces and homogenized in a food mixer. Casings were frozen and stored at −18 °C until analysis, whereas the meat was frozen at −80 °C and subsequently freeze-dried (48 h) previously to the analysis.

2.2. Chemicals, solutions and materials

The ten PAHs studied (Fluoranthene (F, 99%), Pyrene (P, 98%), Benzo(a)anthracene (B(a)A, 98%), Chrysene (Chr, 99%), Benzo(b) fluoranthene (B(b)F, 98%), Benzo(k)fluoranthene (B(k)F, 98%),Benzo(a)pyrene (B(a)P, 97%), Dibenzo(a,h)pyrene (DB(a,h)P, 99%),