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Elimination of polycyclic aromatic hydrocarbons from smoked sausages by migration into polyethylene packaging

Jana Semanová [a], Božena Skláršová [b], Peter Šimon [c], Peter Šimko [b,*]

[a] HighChem Ltd., Lešková 11, 811 04 Bratislava, Slovak Republic
[b] Institute of Food Science and Nutrition, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic
[c] Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

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ABSTRACT

The objective of this work was a study of interactions between a smoked meat product and plastic packaging to find a possibility of elimination of polycyclic aromatic hydrocarbons (PAH) from smoked sausages by migration into the packaging. Smoked meat sausages were packed into o-polyamide/low density polyethylene laminated film and content of four PAH was determined at 0, 15, 30, 45, 60, 75, 90, 120, 150 and 180 min by HPLC. During this time, total PAH4 content decreased from 30.1 to 5.7 μg/kg, benzo[*a*]anthracene decreased from 11.5 to 2.1 μg/kg, chrysene from 9.4 to 1.9 μg/kg, benzo[*b*]fluoranthene from 5.3 to 0.6 μg/kg and benzo[*a*]pyrene from 3.9 to 1.1 μg/kg while PAH4 content in non-packed sausages remained at a constant level. So, while sausages did not meet European safety limits set for PAH4 content of 12 μg/kg and 2 μg/kg for benzo[*a*]pyrene before packaging, these limits were met at the end of the experiment. This decrease was brought about by migration of PAH4 from sausages into low density polyethylene packaging bulk and the measure of decrease can be predicted by a kinetic equation, making it possible to calculate PAH content equal to any time of experiment as well as the time of interaction necessary to fulfil EU legislative limits.

1. Introduction

Smoking of meat and meat products is one of the oldest processing methods applied in food technology. Smoke gives not only special taste, colour and aroma to food, but also enhances preservation due to the dehydrating, bactericidal and antioxidant properties of smoke (Škaljac et al., 2014). In general, smoke is generated during incomplete combustion of wood with limited access of oxygen and elevated temperature and, if applied for smoking, is directly in contact with exposed foods (Šimko, 2005). Apart from sensory attractive compounds (mainly phenol derivatives, carbonyls, organic acids, lactones, etc.), smoke also contains hazardous compounds such as polycyclic aromatic hydrocarbons (PAH) which are recognised as dangerous food contaminants, due to their known (or suspected) carcinogenicity and/or mutagenicity (European Food Safety Authority, 2008). Intensity of formation and final content of PAH in smoked foods depends on various factors, e.g., conditions of smoke generation, exposure of smoked products to daylight (the light initialises oxidation processes of PAH deposited on the surface of smoked products with their subsequent photolytic decomposition). Also, specific surface of products, type and properties of package (size pores and polarity are limiting for PAH migration inside of products, where they are protected from light decomposition), fat content and mode of smoking can affect considerably final content of these dangerous compounds (Ledesma, Rendueles, & Díaz, 2016; Šimko, 2005).

Due to the harmful effects of PAH toward living organisms, some countries have limited PAH content in smoked foods. Since benzo[*a*]pyrene (B[a]P) has one of the most carcinogenic potentials of all PAH compounds, it has been set as the reference compound for overall risk assessment of food contamination by PAH in some European countries (Šimko, 2002). Also, the Scientific Committee on Food (European Commission, 2002) confirmed it as suitable marker for the occurrence of PAH in foods on the European market. Later, the content of B[a]P in smoked meat products was limited to

* Corresponding author.
E-mail address: qsimko@stuba.sk (P. Šimko).

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5 μg/kg according to the European Commission's Regulation No. 1881/2006 (2006). On the basis of a comprehensive survey of PAH presence in foods, the European Food Safety Authority (2008) proposed – apart from B[a]P – including also other reference compounds, such as benzo[*a*]anthracene (B[a]A), chrysene (CHR) and benzo[*b*]fluoranthene (B[b]F). Consequently, both maximum content of B[a]P and sum of all four compounds (PAH4) in various foods were established by the European Commission's Regulation No. 835/2011 (2011a). For smoked foods, the maximum B[a]P content remained at 5 μg/kg and PAH4 content was set to 30 μg/kg until 31st August 2014. Since 1st September 2014, the maximum limit of B[a]P content has been lowered to 2 μg/kg and the allowable content of PAH4 to 12 μg/kg (European Commission, 2011a).

A large number of studies have been published on isolation of PAH from smoked meat products by extraction, which is a crucial step in the quantitative analysis of PAH (Purcaro, Moret, & Conte, 2013). Papers discussed various extraction techniques, such as saponification (Santos, Gomes, & Roseiro, 2011), Soxhlet extraction (Plaza-Bolaños, Frenich, & Vidal, 2010), ultrasonic extraction (Lorenzo, Purriños, Fontán, & Franco, 2010), microwave-assisted extraction (Kamankesh, Mohammadi, Hosseini & Modarres Tehrani, 2015) and their combinations (Ghasemzadeh-Mohammadi, Mohammadi, Hashemi, Khaksar, & Haratian, 2012; Purcaro, Moret, & Conte, 2009). Accelerated solvent extraction (ASE) makes it possible to carry out simultaneous extraction and in-cell clean-up of PAH fractions, which simplifies considerably determination and shortens the time of analysis (Vazquez-Roig & Picó, 2015). Such an approach was applied for smoked fish (Lund, Duedahl-Olesen, & Christensen, 2009) and smoked sausages (Suranová, Semanová, Skláršová, & Šimko, 2015).

Content of PAH in foods was believed to remain at a constant value for years. However, during experiments with liquid smoke flavours (LSF) it was found that the PAH concentration could be variable. When LSF was packed into low density polyethylene (LDPE) receptacles, PAH concentration decreased by two orders during 14 days (Šimko & Bruncková, 1993). As found later, this decrease was due to migration of PAH into LDPE and the measure of decrease depends on time of interactions and values of diffusion coefficients of PAH (Šimko, Šimon, Khunová, Karovičová, & Drdák, 1994). Chen and Chen (2005) lowered B[a]P content in roasted duck skin from 3.5 μg/kg to 0.9 μg/kg during 24 h after packaging into LDPE film.

While there is no information regarding behaviour of PAH in smoked meat products after packaging in LDPE, the aim of this study was to observe this phenomenon and apply, if possible, a suitable kinetic equation for prediction of changes in PAH content during storage.

2. Materials and methods

2.1. Film

Laminated film (RE-PACK s.r.o., Žilina, Slovak Republic) was composed of two polymers, outer o-polyamide has thickness 15 μm, contact (inner) LDPE was 50 μm. Film pouches, size 170 × 200 mm were used for vacuum packaging.

2.2. Sausages

Fresh, non-smoked "Domáce" sausages were bought in a local market in Bratislava, Slovak Republic. In general, "Domáce" sausages belong to a group of typical meat products consumed in considerable quantities in the Slovak Republic. They are commonly made from boneless pork hams, shoulders and slab bacon. The proper amounts of each are cut and ground through a 7-mm plate of a meat grinder. The mixture is then combined with seasoning ingredients (NaC1, black and red pepper, and garlic), and stuffed into natural casings. After chopping, they were analysed for fat (51%), moisture (30%), crude protein (19%) and PAH4 content. Then sausages were smoked by hot smoke directly over a fire (ca. 1.8 m distance) in a home smokehouse for 12 h, and the smoke was generated from a mixture of beech chips and filings. Thermal combustion of the wood and intensity of smoke generation was affected by wetting the wood twice per hour. After smoking, sausages were divided into two groups: the first group was packed immediately in film using a vacuum packaging machine, while the second one was unpacked and served as a reference sample. All samples were protected against daylight to prevent light decomposition of PAH and stored at 15 °C. Both groups were sampled at 0, 15, 30, 45, 60, 90, 120, 150 and 180 min. All samples were analysed in triplicate.

2.3. Chemicals

B[a]A, B[b]F, B[a]P and CHR applied as standards were of analytical grade, purchased from Supelco (Bellefonte, PA) in solid state. Standards were dissolved in acetonitrile to prepare standard solutions for spiking purposes. Poly(acrylic acid), partial sodium salt-graft-poly(ethylene oxide) was of analytical grade, purchased from Sigma–Aldrich (Munich, Germany) in solid state. Silica gel 40 was of analytical grade, purchased from Merck (Darmstadt, Germany).

2.4. Solvents

n-Hexane and acetone of analytical grade, acetonitrile and methanol of HPLC grade were purchased from Merck. The solvents were redistilled just before use.

2.5. Extraction and pre-separation of PAH4 fraction

For extraction, about 1 g of homogenised (in a Grindomix knife mill; Retsch, Haan, Germany) smoked sausage, mixed with the same amount of the drying material poly(acrylic acid), partial sodium salt-graft-poly(ethylene oxide) was taken. A 33-mL extraction cell was plugged with cellulose microfibre filter at the outlet to prevent washing out of the sorbent. Then, 10 g of activated silica gel (activated at 140 °C for 18 h) was put into the extraction cell and the sample was then covered by another microfibre filter. The extraction was performed in ASE equipment (ASE 350; Dionex, Sunnyvale, CA) using *n*-hexane at 100 °C and 10 MPa at a static time of 10 min. The flush volume was 60%, the purge time was 120 s. Static cycle was accomplished three times. Then, the extract was evaporated in a water bath to dryness (40 °C) using a nitrogen stream. Finally, the residue was dissolved in acetonitrile and analysed by HPLC (Suranová et al., 2015).

2.6. HPLC conditions

HPLC analyses were carried out with Shimadzu equipment (Kyoto, Japan) consisting of solvent delivery module LC-20AD, autosampler SIL-20A, degasser DGU-20A5, column oven CTO-20A, communications bus module CBM-20A, diode array detector SPD-M20A and fluorescence detector RF-10AXL. The analytical separation was performed on a Zorbax Eclipse XDB-C_{18} (100 mm × 4.6 mm × 1.8 μm) column (maintained at 35 °C) connected to a Zorbax Eclipse PAH guard column (12.5 mm × 4.6 mm × 5 μm) (Agilent, Santa Clara, CA) using isocratic elution with mobile phase acetonitrile/water 70:30 (v/v) at a flow rate of 1.2 mL/min. Fluorescence detector operated at excitation/emission wavelength 260/410 nm for B[a]P, 275/385 nm for