
Polycyclic aromatic hydrocarbons in smoked ham

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Abstract

The aim of this work was to determine the content of four polycyclic aromatic hydrocarbons (PAHs) in household-produced smoked meat. Ham was manufactured in traditional drying facilities and smoking cabinets in Serbia. PAHs can significantly influence smoked meat quality and safety. The total content of the PAHs was 11.51 µg/kg in ham manufactured in drying cabinets and 0.16 µg/kg in ham produced in smoking facilities. The most abundant of all PAHs was chrysene. Benzo[a]pyrene was detected in hams manufactured in traditional dryers in southwestern Serbia in concentrations lower than maximum residue level set in current Regulation in Republic of Serbia.

1. Introduction

Despite the increasing awareness of food safety and the significance of the safe food production, there are still some meat products that can contain traces of carcinogenic substances. Smoking is one of the oldest technologies for

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the conservation of meat and fishery products. Smoking is defined as the process of penetration of volatiles resulting from thermal destruction of wood into the surface of meat or fish products.

Polycyclic aromatic hydrocarbons (PAHs) are generally classified as relatively persistent organic environmental contaminants. The most significant PAH compound is benzo[a]pyrene, and food is a significant source of benzo[a]pyrene in Europe due to PAHs in oils, fats and cereals which represent a high percentage of European diets. Chemically, PAHs belong to a large class of organic compounds whose structure consists of two or more aromatic rings. They are characterised by low water solubility. These lipophilic compounds are the product of organic matter combustion, the most significant sources being thermo-energetic facilities (power plants, central heating facilities) and traffic. PAHs are present in atmosphere, geosphere, hydrosphere, etc. Smoking is one of the oldest methods of food preservation and is based on exposure of meat products to smoke originating from wood combustion. Smoke not only gives special taste, colour and aroma to food, but also enhances preservation due to the dehydrating, bactericidal and antioxidant properties of smoke. Jira et al. determined that 99% of all PAHs are located at the surface of the food product, which has a mass fraction of 22% of the total product weight. Significance of PAHs lies in carcinogenicity or suspect carcinogenicity of some of these compounds.

Commission Regulation EU 1881/2006 sets maximum residue levels of benzo[a]pyrene in various food commodities. Four EU priority PAHs were measured within this study: benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene and chrysene. Benzo[a]pyrene is used as the indicator of carcinogenicity. Toxic equivalency factor (TEF) is used in order to estimate carcinogenic potential of measured PAHs in respect to carcinogenicity of benzo[a]pyrene.

The aim of this paper is to compare the distribution of measured PAHs in ham smoked in drying and smoking cabinets.

2. Materials and methods

We analysed dried meat, ham manufactured in households from southwestern Serbia and Vojvodina by drying and smoking in traditional drying and smoking cabinets.

Smoking in southwestern Serbia is performed in drying facilities without windows and with modest ventilation systems. Salted meat is hung on hooks at the height of 1.5-2m. Meat smoking takes place during daylight when constant fire is maintained in the facility, while overnight meat is rested as fires are extinguished.

In Vojvodina, dry meat is manufactured in smoking cabinets that have side openings and constant air (smoke) circulation, while smoking takes place using low intensity burning without flame. Meat is positioned higher than 3m from the fireplace.

After processing, meat samples were packed and transported according to the Council Directive 2005/10/EC.

2.1. Solutions and standards

The PAH stock standard solution (502 μg/ml of 16 polyaromatic hydrocarbons) was diluted in acetone to yield spiking solutions 0.5, 1, 5, 10, 50 μg/ml. The spiking solutions were used to prepare the calibration curves in the matrix blank extract by appropriate dilutions.

2.2. Sample preparation

Dried ham was chopped into small cubes and then comminuted thoroughly to achieve sample homogeneity. The sample extraction method used the QuECHERS method followed by dSPE.

Samples containing 3.0 g of meat were weighed into centrifuge tubes. To each sample, 12 ml aliquot of deionized water and 15 ml aliquot of ACN were added. The samples were vortexed for 1 minute. Then 6 g of MgSO₄ and 1.5 g of sodium acetate was added to each centrifuge tube and centrifuged at 3000 rpm for 5 min.

The upper layer (1 ml) was transferred was transferred into a dSPE tube containing 150 mg MgSO₄, 50 mg PSA, 50 mg C18 and vortexed for 1 minute. The dSPE tube was then centrifuged on 4000 rpm for 5 min. The liquid from the tube was transferred to a GC vial and analyzed by SIM GC/MS.
2.3. GCMS analysis

The identification of PAHs was based on the comparison of the retention times of the peaks and target ions with those obtained from standard mixture of PAHs (standards supplied by instrument manufacturer).

The quantification was based on external calibrations curves prepared from the standard solution of each of the PAHs. The coefficients of determination ($r^2$) for the PAH standard calibration plots were benzo[b]fluoranthene (0.99945) benzo[a]anthracene (0.99926), chrysene (0.99963) and benzo[a]pyrene (0.99972).

2.4. Instrumentation

The GC/MS instrument was Agilent 7890B/5977A MSD. The GC operating conditions were as follows: fused silica column (30m*0.25μm film of HP-5M). Injector temperature was set at 280°C using splitless mode and volume injected was 4 μl. The column temperature was programmed as follows: hold at 50°C for 0.4 min; 50-195°C at 25°C/min, hold 1.5 min; 195-265 at 8°C/min ; 20°C/min to 315°C for 1.25 minutes. MSD temperature was 280°C. Verification of peaks was carried out based on retention times and target ions compared to those of external PAHs. Procedural blank and solvent blanks were analysed and quantified, but no PAHs were found in these blanks.

3. Results and discussion

Fig. 1 shows the average concentrations of PAHs in ham samples manufactured in drying facilities and smoking cabinets.

![Fig. 1. Distribution of PAHs in ham from drying facilities and smoking cabinets.](image)

The dominant PAH compound in analysed hams manufactured in drying facilities and smoking cabinets was chrysene. Its concentration was 3.64 μg/kg in hams manufactured in drying facilities and 0.13 μg/kg in hams produced in smoking cabinets. The sum of the four PAH compounds was 11.51 μg/kg and 0.16 μg/kg in hams produced in drying facilities and smoking cabinets respectively. Concentrations of benzo[a]pyrene and sum of PAH4 compounds did not exceed maximum residue levels set in EU Regulation No 1881/2006.

Muculis et al indicate that the production of smoked meat products with PAH4 levels less than 10 μg/kg is possible in non-intensely smoked products. Wretling et al reported nine samples of traditionally smoked meat in Sweden that showed high Benzo[a]pyrene levels ranging from 6.6 to 36.9μg/kg, exceeding the 5.0μg/kg maximum
level for smoked meat and fish established by the European Commission (Regulation (EC) No 208/2005)\textsuperscript{13}. These samples were produced by traditional “sauna” smoking, where the food is directly exposed to hot smoke from a burning log fire. Six samples of smoked fish had Benzo[a]pyrene levels exceeding 5.0μg/kg, the concentrations ranging from 8.4 to 14.4μg/kg.

Ciecierska et al\textsuperscript{14} published research into traditionally smoked ham, in which 12 PAHs were determined in external parts and 8 PAHs in interiors. PAHs contamination of these products’ exterior was about 23.59 μg/kg. For internal parts 3.26 μg/kg of a total of 15 PAHs was found. Benzo[a]pyrene levels were 0.43 μg/kg and 0.27 μg/kg in external and interior parts, respectively.

4. Conclusion

This study has shown that the samples of smoked ham were contaminated with various concentrations of individual PAHs according to the smoking process. The type of smoking influence the total PAH content in smoked pork hams, intensive smoking in drying facilities giving higher concentration of PAHs compound. The distributions of the four PAHs which are considered most important by EU standards were similar in the pork ham regardless of its production (in meat dryers or smokers).

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References

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