ACTA SCIENTIARUM POLONORUM *Acta Sci. Pol., Technol. Aliment. 6(4) 2007, 17-28*

INFLUENCE OF SMOKING PROCESS ON POLYCYCLIC AROMATIC HYDROCARBONS' CONTENT IN MEAT PRODUCTS*

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Abstract. The PAHs content in four groups of meat products industrially and traditionally smoked was determined. Methodology applied for the study included fat's extraction, PAHs isolation using GPC and consequently qualitative-quantitative compound's determination by HPLC-FLD/DAD. Mostly traditional method of smoking affected the higher total PAHs contamination. For all products smoked using both methods it was proved that internal parts had a significantly lower total PAHs contamination as well as each individual PAH content than exteriors of the same products. Irrespectively of smoking method applied, benso[a]pyrene's content was much lower than maximum tolerable limit of 5 $\mu g \cdot kg^{-1}$, which was set for smoked meat products in Commision Regulation (EC) No. 208/2005.

Key words: polycyclic aromatic hydrocarbons, smoking process, meat products

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) comprise the largest class of chemical compounds, containing two or more fused aromatic rings made up of carbon and hydrogen atoms, known to be genotoxic agents [SCF... 2002]. PAHs are formed in incomplete combustion processes which occur whenever wood, coal or oil are burnt. Owing to their mode of formation, PAHs are almost ubiquitous in the environment and therefore enter to our food chain, especially via the air and soil [Falco et al. 2003, Lage Yusty and Cortizo Daviña 2005, Šimko 2002, Tfouni et al. 2007, Vazquez Troche et al. 2000]. However, these contaminants are widespread in foodstuffs not only as a result of the environmental pollution but also as a consequence of some thermal treatments, which are used in the preparation and manufacturing of foods [Guillen et al. 1997, Philips 1999]. Processing procedures, such as smoking, drying, roasting, baking or frying are

*The research was founded by the grant KBN no 501 0928 00 29.

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recognized as a major source of food contamination by PAHs [Codex... 2005, Moret et al. 2005, SCF... 2002, Yurchenko and Mölder 2005].

The preservation of food (such as meat and fish products) by curing it with wood smoke has been used since antiquity. As the generation of wood smoke is an example of incomplete combustion, undoubtedly PAHs are generated [Codex... 2005, Philips 1999, SCF 2002]. Originally the purpose was to preserve the food, partly by drying and partly by adding anti-microbiological constituents such as phenols from the smoke to the food. At the present time smoking is mainly used to achieve the characteristic taste and appearance of smoked food with preservation playing a minor role. However, smoking has an influence on the shelf life of food because smoke may inhibit growth of some microorganisms depending on the contents of some components like phenols in the smoked food.

According to the Commission Recommendation 2005/108/EC [Official... 2005 a] further analyses of 15 genotoxic PAHs in food, listed by The Scientific Committee on Food, are necessary, especially in these kinds of foodstuffs, for which the maximum tolerable limit of benzo[a]pyrene has been set in Commission Regulation (EC) No. 208/2005 [Official... 2005 b]. One of the groups of food, for which contamination of benzo[a]pyrene and others genotoxic PAHs should be monitored, are smoked meat products.

It is thought that PAHs contamination of smoked foods can be significantly reduced by replacing conventional (traditional) direct smoking (with smoke developed in the smoking chamber, traditionally in smokehouses) with indirect smoking. The latter is obtained by an external smoke generator, which, in modern industrialized kilns, is operated automatically under carefully controlled conditions, and smoke can be washed from particles before coming into contact with the food.

Therefore, according to the Commission Recommendation, the objective of this research was to conduct studies on 15 PAHs contamination of meat products smoked both in industrial and traditional way and to determine the effect of smoking process on PAHs content in these products.

MATERIAL AND METHODS

Material

The material investigated compromise of four groups of meat products: hams, cooked cured loins, raw cured loins and medium-ground sausages. Production of these goods was conducted in one of the Warsaw surrounding meat processing plant under GMP (good manufacturing practice). The material taken for the research came from the same three productive charges.

For the purpose of examining the influence of smoking process on PAHs content, three batches of meat products were smoked applying modern and traditional smoking technology. However, the traditional (conventional) smoking was also conducted at the same meat processing plant.

Method of smoking process

Industrial method of smoking included drying of meats' surface and smoking in industrial smoking chamber with an external smoke generator (Lutetia). This process of thermal treatment was conducted in the following order: light drying of meats' surface (150 min, 50-60°C), hot smoking (30 min, 65-70°C) and steaming until the temperature of 68-72°C in centre of these products was reached (with the exception of raw cured loins). Finally they were cooled by using cold air to temperature below 10°C.

Traditional method of smoking was conducted in designed smoking kilns following pattern of old smoking chambers with internal smoke generator and furnace. A trolley with meat products was introduced on tracks and using the heat of intensive burning of wooden balks, and simultaneously by the small emission of smoke these products were dried. After this stage the fire was extinguished and the wood sawdust were glowing generating dense smoke under conditions of small access of oxygen. Total time of drying and smoking process in the traditional chamber was 3 hours and 45 minutes for hams, cooked cured loins, raw cured loins and about 3 hours for medium-ground sausages. After that time smoked products were steamed until the temperature of 68-72°C in centre of these goods was reached (with the exception of raw cured loins). Subsequently they were chilled to temperature below 10°C.

Finally, smoked meat products from traditional as well as industrial smoking chamber were chilled in temperature of 4°C for 24 hours.

Determination of PAHs

The determinations of PAHs in smoked meat products were performed. In order to examine PAHs diffusion from products' exteriors to their interiors, from every investigated assortment two representative samples were collected for the study. The first ones were external parts of smoked meat products (a surface and about 0.5 cm layer below the surface), whereas the other ones were internal parts of the same goods. In case of all assortments three samples were taken to the determination of PAHs content.

10-15 g of meat products previously ground in meat grinder (with meshes' diameter 0.3 mm) were homogenized with anhydrous sodium sulfate (10-20 g). Next, after adding 100 cm^3 hexane/acetone mixture (60/40, v/v), the sample was sonicated for 30 minutes and organic phase was filtered off solid residues. The glassware and filter were washed two times with 20 cm^3 hexane/acetone mixture (60/40, v/v) and combined with filtrate, which was subsequently evaporated almost to dryness (few drops) and redissolved in cyclohexane.

Further clean-up of cyclohexane extract was conducted using column for gel permeation chromatography – Bio-Beads S-X3 330 × 10 mm. 1 cm^3 of the cyclohexane extract was injected on the column. Chromatographic separation was performed by isocratic method using mixture cyclohexane/ethyl acetate (50/50, v/v) as mobile phase with flow 0.8 ml/min. The first fraction (0-15 cm^3) containing coloring materials and lipids was discarded, while the second containing PAHs (successive 7 cm^3) was collected and concentrated under gentle stream of nitrogen for further analysis.

Collected fraction of PAHs, after evaporation and dissolving in acetonitrile (1 cm^3), was analyzed by HPLC, Shimadzu, consisted of liquid chromatograph LC-10ATVP, diode array detector SPD-M10AVP, fluorescence detector RF-10A XL, degasser DGU-

-14A, auto injector SIL-10ADVP and system controller SCL-10AVP, working under dedicated software LabSolution 2.1. Chromatographic analysis was conducted using Baker's reversed phase chromatographic column BAKERBOND PAH-16 Plus 250 × 3 mm, 5 µm. Column temperature was 30°C and gradient method of acetonitrile/water, 70/30 (A) and acetonitrile (B) with constant flow of mobile phase 0.5 ml/min was applied. For the PAHs determination following detection parameters was used: diode array detector DAD – 254 nm; fluorescence detector FLD (Ex/Em) – 270/420 nm, 270/500 nm, 270/470 nm. Qualitative-quantitative determination was carried out using external standard method.

In this paper for 15 investigated compounds following abbreviations were assigned: Cyclopenta[c,d]pyrene – C[c,d]p, Benzo[a]anthracene – B[a]a, Chrysene – Chr, 5--Metylchrysene – 5-MChr, Benzo[j]fluoranthene – B[j]f, Benzo[b]fluoranthene – B[b]f, Benzo[k]fluoranthene – B[k]f, Benzo[a]pyrene – B[a]p, Dibenzo[a,h]anthracene – D[a,h]a, Dibenzo[a,l]pyrene – D[a,l]p, Benzo[g,h,i]perylene – B[g,h,i]p, Indeno[c,d] pyrene – I[c,d]p, Dibenzo[a,e]pyrene – D[a,e]p, Dibenzo[a,i]pyrene – D[a,i]p, Dibenzo [a,h]pyrene – D[a,h]p.

Statistical analysis

The experimental design was intended to determine the influence of smoking process on PAHs content in meat products. The obtained results were statistically analyzed using Statgraphics Plus 4.1 sofware. To estimate the significance of the differences between the means of total and individual PAHs content in traditionally and industrially smoked meat products as well as internal and external parts of the same one good, t-test was used, at significance level $\alpha = 0.05$. The experiment was carried out in three replications.

RESULTS AND DISCUSSION

Mean values of PAHs content in the investigated meat products smoked in modern smoke chamber and traditionally are presented in Tables 1 and 2. For every group of meat products, PAHs contamination levels for external and internal parts are presented. In Table 3 statistical analysis of smoking method's effect on the content of particular individual PAH in every meat products (test LSD) is shown. Moreover, analogically statistical analysis of smoking method's influence on the total content of PAHs in these goods (test LSD) is presented in Table 4.

In case of hams, which were smoked using industrial method, out of 15 investigated PAHs, 14 compounds were detected in external parts and 7 in internal ones. The sum of PAHs (Σ 15 PAHs) in exterior of these goods was equal to 24.43 $\mu g \cdot kg^{-1}$, whereas in interior 2.78 $\mu g \cdot kg^{-1}$ was determined. Benzo[a]pyrene's content was at the level of 0.37 $\mu g \cdot kg^{-1}$ in external parts and 0.28 $\mu g \cdot kg^{-1}$ in the deeper ones. In hams, for which traditional method of smoking was applied, 12 PAHs were determined in external parts and 8 ones in interior. PAHs contamination of these product's exterior was about 23.59 $\mu g \cdot kg^{-1}$. For internal parts 3.26 $\mu g \cdot kg^{-1}$of Σ 15 PAHs was found. Content of benzo[a]pyrene was equal to 0.43 $\mu g \cdot kg^{-1}$ in external parts, but for interior 0.27 $\mu g \cdot kg^{-1}$ was determined (Table 1, 2).

Table 1. Mean content of 15 PAHs in meat products industrially smoked, $\mu g \cdot kg^{-1}$
Tabela 1. Średnia zawartość 15 WWA w produktach mięsnych wędzonych metodą przemysłową, $\mu g \cdot kg^{-1}$

PAHs – WWA	Hams – Szynki		Cooked cured loins Polędwice parzone		Raw cured loins Polędwice nieparzone		Medium-ground sausages Kiełbasy średnio rozdrobnione	
	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa
Cyclopenta[c,d]pyrene Cyklopenta[c,d]piren	1.62^{A1} ± 0.25	0.53^{a1} ± 0,15	0.07 ± 0.04	n.d. n.w.	n.d. n.w.	n.d. n.w.	11.39^{D1} ± 0.47	7.07^{d1} ± 0.42
Benzo[a]anthracene Benzo[a]antracen	8.88^{A2} ± 0.78	0.41^{a2} ± 0.01	6.48^{B1} ± 0.45	0.38^{b1} ± 0.00	2.56^{C1} ± 0.36	0.27^{c1} ± 0.09	8.78^{D2} ± 0.20	1.29^{d2} ± 0.02
Chrysene Chryzen	6.29^{A3} ± 0.46	0.56^{a3} ± 0.02	4.46^{B2} ± 0.40	0.48^{b2} ± 0.06	2.08^{C2} ± 0.06	0.35^{c2} ± 0.14	6.63^{D3} ± 0.52	0.55^{d3} ± 0.05
5-Metylchrysene 5-metylchryzen	1.72^{A4} ± 0.14	0.28^{a4} ± 0.00	2.73^{B3} ± 0.28	0.30^{b3} ± 0.00	1.15^{C3} ± 0.21	0.26^{c3} ± 0.02	2.06^{D4} ± 0.05	0.36^{d4} ± 0.03
Benzo[j]fluoranthene Benzo[j]fluoranten	0.31 ± 0.09	n.d. n.w.	0.31 ± 0.05	n.d. n.w.	n.d. n.w.	n.d. n.w.	1.20 ± 0.17	n.d. n.w.
Benzo[b]fluoranthene Benzo[b]fluoranten	0.91^{A5} ± 0.05	0.46^{a5} ± 0.03	0.71^{B4} ± 0.02	0.33^{b4} ± 0.01	1.13^{C4} ± 0.20	0.27^{c4} ± 0.01	1.19^{D5} ± 0.13	0.68^{d5} ± 0.12
Benzo[k]fluoranthene Benzo[k]fluoranten	0.90^{A6} ± 0.11	0.26^{a6} ± 0.01	0.65^{B5} ± 0.02	0.28^{b5} ± 0.00	0.28^{C5} ± 0.01	0.25^{c5} ± 0.01	1.15^{D6} ± 0.03	0.27^{d6} ± 0.01
Benzo[a]pyrene Benzo[a]piren	0.37^{A7} ± 0.01	0.28^{a7} ± 0.00	0.30^{B6} ± 0.01	0.28^{b6} ± 0.00	0.32^{C6} ± 0.01	0.28^{c6} ± 0.01	0.89^{D7} ± 0.05	0.32^{d7} ± 0.01
Dibenzo[a,h]anthracene Dibenzo[a,h]antracen	0.49 ± 0.02	n.d. n.w.	0.45^{B7} ± 0.00	0.42^{b7} ± 0.01	0.46 ± 0.00	n.d. n.w.	0.61 ± 0.02	n.d. n.w.
Dibenzo[a,l]pyrene Dibenzo[a,l]piren	0.52 ± 0.02	n.d. n.w.	0.43 ± 0.00	n.d. n.w.	0.47 ± 0.01	n.d. n.w.	0.68 ± 0.06	n.d. n.w.
Benzo[g,h,i]perylene Benzo[g,h,i]perylen	0.63 ± 0.00	n.d. n.w.	0.47^{B8} ± 0.01	0.44^{b8} ± 0.00	0.51^{C7} ± 0.01	0.48^{c7} ± 0.01	0.70 ± 0.01	n.d. n.w.
Indeno[c,d]pyrene Indeno[c,d]piren	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	0.97 ± 0.07	n.d. n.w.
Dibenzo[a,e]pyrene Dibenzo[a,e]piren	0.55 ± 0.02	n.d. n.w.	0.48^{B9} ± 0.03	0.43^{b9} ± 0.00	0.47^{C8} ± 0.00	0.44^{c8} ± 0.00	0.72^{D8} ± 0.14	0.50^{d8} ± 0.01
Dibenzo[a,i]pyrene Dibenzo[a,i]piren	0.58 ± 0.02	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	0.61 ± 0.03	n.d. n.w.
Dibenzo[a,h]pyrene Dibenzo[a,h]piren	0.65 ± 0.03	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	0.69 ± 0.03	n.d. n.w.
∑ 15 PAHs ∑ 15 WWA	24.43^{A0} ± 1.65	2.78^{a0} ± 0.18	17.54^{B0} ± 1.11	3.34^{b0} ± 0.06	9.42^{C0} ± 0.16	2.59^{c0} ± 0.27	38.27^{D0} ± 0.65	11.05^{d0} ± 0.56

n.d. – not detected.

A1, a1; B2, b2; C3, c3; D4, d4 – the same small and capital letters by the same number (within one from four comparisons) in indices of two mean values denote statistically significant difference between means at $\alpha = 0.05$ level.

n.w. – nie wykryto.

A1, a1; B2, b2; C3, c3; D4, d4 – ta sama mała oraz wielka litera przy tej samej cyfrze (w ramach jednego z czterech porównań) w indeksach dwóch wartości średnich oznaczają statystycznie istotną różnicę między średnimi na poziomie $\alpha = 0,05$.

Table 2. Mean content of 15 PAHs in meat products traditionally smoked, μg·kg^{-1}
Tabela 2. Średnia zawartość 15 WWA w produktach mięsnych wędzonych metodą tradycyjną, μg·kg^{-1}

PAHs – WWA	Hams – Szynki		Cooked cured loins Polędwice parzone		Raw cured loins Polędwice nieparzone		Medium-ground sausages Kiełbasy średnio rozdrobnione	
	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa
Cyclopenta[c,d]pyrene Cyklopenta[c,d]piren	3.26^{E1} ± 0.25	0.49^{e1} ± 0.06	1.27 ± 0.21	n.d. n.w.	n.d.. n.w.	n.d. n.w.	12.17^{H1} ± 2.57	7.78^{h1} ± 0.34
Benzo[a]anthracene Benzo[a]antracen	6.74^{E2} ± 0.39	0.40^{e2} ± 0.05	9.25^{F1} ± 0.22	0.22^{f1} ± 0.00	2.65^{G1} ± 0.10	0.32^{g1} ± 0.04	5.86^{H2} ± 0.13	1.51^{h2} ± 0.02
Chrysene Chryzen	6.20^{E3} ± 0.69	0.68^{e3} ± 0.08	9.12^{F2} ± 0.81	0.42^{f2} ± 0.01	3.35^{G2} ± 0.16	0.42^{g2} ± 0.06	5.07^{H3} ± 0.34	0.57^{h3} ± 0.03
5-Metylchrysene 5-metylchryzen	1.28^{E4} ± 0.19	0.28^{e4} ± 0.01	2.98^{F3} ± 0.13	0.31^{f3} ± 0.00	0.81^{G3} ± 0.04	0.29^{g3} ± 0.02	1.39^{H4} ± 0.02	0.38^{h4} ± 0.01
Benzo[j]fluoranthene Benzo[j]fluoranten	0.59 ± 0.24	n.d. n.w.	0.43 ± 0.04	n.d. n.w.	0.31 ± 0.02	n.d. n.w.	0.83 ± 0.07	n.d. n.w.
Benzo[b]fluoranthene Benzo[b]fluoranten	1.50^{E5} ± 0.10	0.46^{e5} ± 0.03	0.87^{F4} ± 0.02	0.28^{f4} ± 0.00	0.55 ± 0.05	n.d. n.w.	0.72^{H5} ± 0.03	0.61^{h5} ± 0.02
Benzo[k]fluoranthene Benzo[k]fluoranten	1.15^{E6} ± 0.04	0.24^{e6} ± 0.00	1.12^{F5} ± 0.05	0.24^{f5} ± 0.00	0.53 ± 0.04	n.d. n.w.	0.89^{H6} ± 0.02	0.28^{h6} ± 0.00
Benzo[a]pyrene Benzo[a]piren	0.43^{E7} ± 0.02	0.27^{e7} ± 0.00	0.37^{F6} ± 0.01	0.29^{f6} ± 0.00	0.34 ± 0.00	n.d. n.w.	0.40^{H7} ± 0.02	0.31^{h7} ± 0.01
Dibenzo[a,h]anthracene Dibenzo[a,h]antracen	0.53 ± 0.01	n.d. n.w.	0.49^{F7} ± 0.00	0.46^{f7} ± 0.01	0.52 ± 0.00	n.d. n.w.	0.47 ± 0.01	n.d. n.w.
Dibenzo[a,l]pyrene Dibenzo[a,l]piren	0.58 ± 0.00	n.d. n.w.	0.50^{F8} ± 0.01	0.46^{f8} ± 0.00	0.51 ± 0.00	n.d. n.w.	0.45 ± 0.01	n.d. n.w.
Benzo[g,h,i]perylene Benzo[g,h,i]perylen	0.72 ± 0.04	n.d. n.w.	0.79^{F9} ± 0.03	0.48^{f9} ± 0.01	0.63^{G4} ± 0.00	0.49^{g4} ± 0.01	0.61^{H8} ± 0.02	0.48^{h8} ± 0.00
Indeno[c,d]pyrene Indeno[c,d]piren	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.
Dibenzo[a,e]pyrene Dibenzo[a,e]piren	0.62^{E8} ± 0.01	0.44^{e8} ± 0.00	0.49^{F10} ± 0.01	0.45^{f10} ± 0.00	0.51 ± 0.00	n.d. n.w.	0.63^{H9} ± 0.03	0.53^{h9} ± 0.01
Dibenzo[a,i]pyrene Dibenzo[a,i]piren	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.
Dibenzo[a,h]pyrene Dibenzo[a,h]piren	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	n.d. n.w.	0.64 ± 0.00	n.d. n.w.
∑ 15 PAHs ∑ 15 WWA	23.59^{E0} ± 0.75	3.26^{e0} ± 0.11	27.69^{F0} ± 0.50	3.61^{f0} ± 0.01	10.70^{G0} ± 0.26	1.52^{g0} ± 0.12	30.11^{H0} ± 2.40	12.45^{h0} ± 0.36

n.d. – not detected.

E1, e1; F2, f2; G3, g3; H4, h4 – the same small and capital letters by the same number (within one from four comparisons) in indices of two mean values denote statistically significant difference between means at α = 0.05 level.

n.w. – nie wykryto.

E1, e1; F2, f2; G3, g3; H4, h4 – ta sama mała oraz wielka litera przy tej samej cyfrze (w ramach jednego z czterech porównań) w indeksach dwóch wartości średnich oznaczają statystycznie istotną różnicę między średnimi na poziomie α = 0,05.

Table 3. Statistical analysis of influence of smoking method on particular PAH content in investigated meat products (test LSD)
Tabela 3. Analiza statystyczna wpływu metody wędzenia na zawartość poszczególnych WWA w badanych produktach mięsnych (test NIR)

Product Produkt	part of product część produktu	Method of smoking (1 – industrial, 2 – traditional) Metoda wędzenia (1 – przemysłowa, 2 – tradycyjna)															
		C[c,d]p	B[a]a	Chr	5-MChr	B[j]f	B[b]f	B[k]f	B[a]p	D[a,h]a	D[a,l]p	B[g,h,i]p	I[c,d]p	D[a,e]p	D[a,i]p	D[a,h]p
Hams Szynki	external zewnętrzna	1	2	1	2	1	1	1	1	1	1	1	–	1	2	2
		2	1	2	1	2	2	2	2	2	2	2		2	1	1
	internal środkowa	1	1	1	1	–	1	2	1	–	–	–	–	1	–	–
		2	2	2	2		2	1	2					2		
Cooked cured loins Polędwice parzone	external zewnętrzna	1	1	1	1	1	1	1	1	1	1	1	–	1	–	–
		2	2	2	2	2	2	2	2	2	2	2		2		
	internal środkowa		2	1	1	–	2	2	1	1	1	1	–	1	–	–
			1	2	2		1	1	2	2	2	2		2		
Raw cured loins Polędwice nieparzone	external zewnętrzna	–	1	1	2	1	1	1	1	1	1	1	–	1	–	–
			2	2	1	2	2	2	2	2	2	2		2		
	internal środkowa	–	1	1	1	–	2	2	2	–	–	1	–	2	–	–
			2	2	2		1	1	1			2		1		
Medium- -ground sausages Kiełbasy średnio rozdrobnione	external zewnętrzna	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2
		2	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	internal środkowa	1	1	1	1	–	1	1	1	–	–	1	–	1	–	–
		2	2	2	2		2	2	2			2		2		

C[c,d]p – Cyclopenta[c,d]pyrene, B[a]a – Benzo[a]anthracene, Chr – Chrysene, 5-MChr – 5-Metylchrysene, B[j]f – Benzo[j]fluoranthene, B[b]f – Benzo[b]fluoranthene, B[k]f – Benzo[k]fluoranthene, B[a]p – Benzo[a]pyrene, D[a,h]a – Dibenzo[a,h]anthracene, D[a,l]p – Dibenzo[a,l]pyrene, B[g,h,i]p – Benzo[g,h,i] perylene, I[c,d]p – Indeno[c,d]pyrene, D[a,e]p – Dibenzo[a,e]pyrene, D[a,i]p – Dibenzo[a,i]pyrene, D[a,h]p – Dibenzo[a,h]pyrene.

C[c,d]p – cyklopenta[c,d]piren, B[a]a – benzo[a]antracen, Chr – chryzen, 5-MChr – 5-metylchryzen, B[j]f – benzo[j]fluoranten, B[b]f – benzo[b]fluoranten, B[k]f – benzo[k]fluoranten, B[a]p – benzo[a]piren, D[a,h]a – dibenzo[a,h]antracen, D[a,l]p – dibenzo[a,l]piren, B[g,h,i]p – benzo[g,h,i]perylen, I[c,d]p – indeno [c,d]piren, D[a,e]p – dibenzo[a,e]piren, D[a,i]p – dibenzo[a,i]piren, D[a,h]p – dibenzo[a,h]piren.

In a research conducted by Jira [2004] dealing with PAHs contamination of smoked hams, following mean concentrations of particular PAHs was found: 0.13 $\mu g \cdot kg^{-1}$ for B[a]p, 0.61 $\mu g \cdot kg^{-1}$ for B[a]a, 0.02 $\mu g \cdot kg^{-1}$ for D[a,h]a and 0.21 $\mu g \cdot kg^{-1}$ of B[b]f's content. In this paper similar amounts of mentioned PAHs were observed in internal parts of the investigated hams. Moreover, for smoked hams the level of 16 PAHs (EPA list)

Table 4. Statistical analysis of influence of smoking method on total PAHs content in investigated meat products (test LSD)
Tabela 4. Analiza statystyczna wpływu metody wędzenia na sumaryczną zawartość WWA w badanych produktach mięsnych (test NIR)

Method of smoking Metoda wędzenia	Hams Szynki		Cooked cured loins Polędwice parzone		Raw cured loins Polędwice nieparzone		Medium-ground sausages Kiełbasy średnio rozdrobnione	
	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa	external part część zewnętrzna	internal part część środkowa
1 – industrial 1 – przemysłowa	1	1	1	1	1	2	2	1
2 – traditional 2 – tradycyjna	2	2	2	2	2	1	1	2

was determined by Jankowski [2004]. The mean content of these compounds, which was also assessed by Jira, was as follows: 0.62 $\mu g \cdot kg^{-1}$ of B[a]p, 1.44 $\mu g \cdot kg^{-1}$ of B[a]a, 0.12 $\mu g \cdot kg^{-1}$ of D[a,h]a and 0.32 $\mu g \cdot kg^{-1}$ of B[b]f's concentration. Benzo[a]pyrene content's analysis in smoked hams was also investigated by Kazerouni et al. [2001], who stated the mean value of this compound at the level of 0.13 $\mu g \cdot kg^{-1}$.

For hams smoked in industrial as well as in traditional way, it was shown, that exteriors of products mentioned above had statistically significant higher total PAHs content and also contents of each individual PAH than internal parts of these goods (Tables 1, 2).

In case of 12 analysed compounds, statistical significance of differences in mean content of particular PAHs in exterior of hams depending on smoking method was proved. For 8 PAHs, significant higher amounts of these compounds were found in hams traditionally smoked. Though industrial method of smoking affected the higher content of 4 PAHs – B[a]a, 5-MChr, D[a,i]p, D[a,h]p. When it comes to internal parts, the type of smoking process diversifies content of only 3 compounds – Chr, B[k]f, D[a,e]p (Table 3).

However, statistical analysis, dealing with influence of smoking process on the sum of 15 PAHs in hams, did not reveal a significant difference between industrial and traditional smoking when it comes to external parts. On the contrary, interiors of hams smoked in traditional way showed statistically significant higher 15 PAHs content than industrially treated ones (Table 4).

In exteriors of cooked cured loins, among all investigated PAHs, 12 compounds were determined both in traditionally and industrially smoked ones. Σ 15 PAHs contamination of external parts of these products industrially smoked was 17.54 $\mu g \cdot kg^{-1}$, while for the same parts smoked in traditional way 27.69 $\mu g \cdot kg^{-1}$ was found. Benzo[a]pyrene's content was estimated as equal 0.30 $\mu g \cdot kg^{-1}$ in these loins, for which industrial smoking method was applied, and 0.37 $\mu g \cdot kg^{-1}$ for traditional treatment (Table 1, 2). In internal parts of these goods smoked in modern (industrial) way 9 PAHs were assessed, whereas for interiors smoked conventionally, apart from the same compounds, additional D[a,l]p were found. The sum of 15 PAHs in deeper part's of cooked loins industrially smoked was equal to 3.34 $\mu g \cdot kg^{-1}$, however by using traditional process was at the level of 3.61 $\mu g \cdot kg^{-1}$. Content of benzo[a]pyrene in interiors of these meat

products was equal to 0.28 $\mu g \cdot kg^{-1}$ in industrially smoked parts and 0.29 $\mu g \cdot kg^{-1}$ in conventional ones (Table 1, 2).

Statistical comparison between external and internal parts' contamination showed that cooked cured loin's interiors both industrially and traditionally treated had significantly lower 15 PAHs content as well as the content of every PAH than these meat products' exteriors, which had undergone respectively the first and the second type of processing (Table 1, 2).

For 10 of 12 detected compounds, which were found in external parts of cooked cured loins, it was confirmed that traditional smoking significantly increased particular PAHs content. In case of interiors, 6 compounds were assessed at the higher level by using conventional method of smoking, while concentrations of 3 PAHs – B[a]a, B[b]f, B[k]f – were significantly higher for industrially treated ones (Table 3).

Moreover, for both parts of cooked cured loins, it was statistically confirmed that conventional smoking process influenced significantly higher summary of PAHs content (Table 4).

Among all products under investigation raw cured loins, either traditionally or industrially smoked presented the lowest 15 PAHs content. External parts of these assortment smoked industrially and traditionally showed Σ 15 PAHs contamination as equal respectively 9.42 $\mu g \cdot kg^{-1}$ and 10.70 $\mu g \cdot kg^{-1}$ (Table 1, 2). When it comes to industrial treatment 10 PAHs were determined, however conventional process caused formation of 11 PAHs. In exteriors of raw cured loins industrially smoked 0.32 $\mu g \cdot kg^{-1}$ of benzo[a]pyrene's content was determined, and 0.34 $\mu g \cdot kg^{-1}$ for the same parts but traditionally treated. For internal parts of these goods smoked in modern way 2.59 $\mu g \cdot kg^{-1}$ of Σ 15 PAHs was shown. On the other hand, total contamination by PAHs was equal 1.52 $\mu g \cdot kg^{-1}$ for conventional method of smoking. In interiors of these products industrially processed 8 PAHs were assessed, and 0.28 $\mu g \cdot kg^{-1}$ of benzo[a]pyrene's content was determined. However, in conventionally treated ones only 4 compounds were detected, without that one, which played a role of PAHs' indicator – B[a]p.

The same group of meat products (smoked raw cured loins) was also investigated by Jankowski [2004]. The mean B[a]p's contamination was stated at the level of 0.59 $\mu g \cdot kg^{-1}$. However, taking into consideration the standard deviation of the result mentioned above (0.33 $\mu g \cdot kg^{-1}$), it can be noticed that results of B[a]p's content revealed in this paper were very similar.

For raw cured loins smoked using both methods, it was statistically proved that external parts were characterized by a significant higher Σ 15 PAHs contamination and also particular compounds' content than internal parts of these goods (Table 1, 2).

Similarly to cooked cured loins, in case of 9 PAHs found in exteriors of raw cured loins significantly higher content was assessed for traditional smoking process (Table 3). Conversely, for internal parts of these assortment four compounds were determined at the significantly higher level when industrial method of processing was used (B[b]f, B[k]f, B[a]p, D[a, e]p).

These results were also proved by statistical analysis concerning the relation between smoking method and Σ 15 PAHs contamination of both external and internal parts of raw cured loins. Therefore external parts smoked in traditional way revealed significantly higher PAHs content than industrial ones. On the contrary, for interiors of these goods industrial method caused significantly higher contamination by the analysed compounds (Table 4).

For medium-ground sausages, the research showed that Σ 15 PAHs of exteriors industrially smoked was equal to 38.27 $\mu g \cdot kg^{-1}$, whereas for traditional method it was about 30.11 $\mu g \cdot kg^{-1}$. In these parts of sausages industrially processed 15 PAHs were assessed, but in case of traditional process 13 of them. Mean content of B[a]p was determined at the level of 0.89 $\mu g \cdot kg^{-1}$ for sausages industrially smoked and 0.40 $\mu g \cdot kg^{-1}$ for conventional method. Meanwhile for interiors of sausages smoked in industrial way, 8 PAHs were detected, and benzo[a]pyrene's content at the level of 0.32 $\mu g \cdot kg^{-1}$. In case of the same parts but traditionally processed 9 compounds were detected and 0.31 $\mu g \cdot kg^{-1}$ of benzo[a]pyrene's content was determined. The sum of the analysed compounds in internal parts of sausages was equal to 11.05 $\mu g \cdot kg^{-1}$ with industrial method applied, while using traditional smoking reached 12.45 $\mu g \cdot kg^{-1}$ (Table 1, 2).

Garcia Falcon et al. [1996] in a research concerning benzo[a]pyrene's content in sausages traditionally smoked determined its mean content as equal 0.02 $\mu g \cdot kg^{-1}$. In case of cocktail sausages B[a]p was even not detected, however, for frankfurter style sausages the maximum content of B[a]p was equal 0.051 $\mu g \cdot kg^{-1}$. Analysis of smoked raw sausages was also conducted by Jira [2004]. Following mean content of a few PAHs were determined: 0.12 $\mu g \cdot kg^{-1}$ of B[a]p, 0.27 $\mu g \cdot kg^{-1}$ of B[a]a, 0.023 $\mu g \cdot kg^{-1}$ of D[a,h]a and 0.23 of B[b]f's content. Furthermore, studies dealing with sausages' PAHs contamination were also performed by Jankowski [2004]. The research revealed that for medium-ground sausages industrially smoked (Podwawelska type) the mean content of PAHs detected also by Jira, was as follows: 0.30 $\mu g \cdot kg^{-1}$ of B[a]p, 2.20 $\mu g \cdot kg^{-1}$ of B[a]a, 0.15 $\mu g \cdot kg^{-1}$ of D[a,h]a and 0.98 $\mu g \cdot kg^{-1}$ of B[b]f's content. Therefore, the results reported by Jankowski [2004] were very similar to the results of this paper for interiors of medium-ground sausages industrially smoked.

In comparison to the other investigated products, for sausages the least significant difference was observed between external and internal parts' total contamination in both smoking methods. With regard to a small diameter of such meat products, these results confirmed that diffusion of PAHs to the internal parts of such goods is considerable. Moreover, for each of smoking methods it was proved that exteriors of these assortment had statistically significant higher content of each individual PAH than internal parts (Tables 1, 2).

On the basis of statistical analysis, it was stated that industrial method of smoking significantly increased PAHs content in external parts of sausages. It was observed in case of 14 analysed compounds (Table 3) and also for the sum of 15 PAHs (Table 4). Conversely in internal parts, for none of PAHs industrial smoking significantly affected higher content of these compounds. Otherwise, for sausage's interiors it was shown that traditional smoking led to a significantly higher content of investigated contaminants (Table 4).

For two methods of smoking, in all meat products under investigation, B[a]p's content did not exceed the maximum tolerable limit of 5 $\mu g \cdot kg^{-1}$ according to the Commission Regulation (EC) No. 208/2005 [Official... 2005 b]. However, the data reported in the literature on PAHs in smoked foods are highly variable. The main reason for such discrepancies is the differences in the procedures used for smoking. The type and composition of wood and herbs used to smoke foods, use of direct or indirect smoking, the type of generator used, the accessibility of oxygen, temperature and smoking time all contribute to its inconsistencies [SCF... 2002]. Karl and Leinemann [1996] in their research compared PAHs content in smoked fishery products from modern smoking kilns with external smoke generation with products from traditional smoking kilns where the smoke was generated in direct contact with the product. The average benzo[a]pyrene concentration determined for the traditional kilns was 1.2 $\mu g \cdot kg^{-1}$ and 0.1 $\mu g \cdot kg^{-1}$ for the

modern kilns. These results are confirmed also by Šimko [2002], who stated that technologically correct smoking process contaminates products only with small concentrations of PAHs.

CONCLUSIONS

1. Traditional method of smoking affected the higher contamination PAHs than industrial proceess. It was statistically confirmed for cooked cured loins (both internal and external parts), for internal parts of hams and medium-ground sausages and also for exteriors of raw cured loins.

2. Industrial smoking process influenced higher PAHs content only in case of interiors of raw cured loins and exteriors of medium-ground sausages.

3. For all products smoked using both methods it was proved that interiors had a significantly lower PAHs contamination as well as each individual PAH content than exteriors of the same products.

4. Irrespectively of the smoking method applied, benzo[a]pyrene's content was much lower than maximum tolerable limit of 5 $\mu g \cdot kg^{-1}$, which was set for smoked meat products in Commission Regulation (EC) No. 208/2005. Therefore industrial and even traditional smoking of meat is a safe process.

REFERENCES

Codex Committee on Food Additives and Contaminants (CCFAC). 2005. Discussion paper on polycyclic aromatic hydrocarbons contamination. 37th Session, The Hague, the Netherlands.

Falco G., Domingo J.L., Llobet J.M., Teixido A., Casas C., Muller L., 2003. Polycyclic aromatic hydrocarbons in foods: human exposure through the diet in Catalonia, Spain. J. Food Prot. 66 (12), 2325-2331.

Garcia Falcon M.S., Gonzales Amigo S., Lage Yusty M.A., Lopez de Alda Villaizan M.J., Simal Lozano J., 1996. Enrichment of benzo[a]pyrene in smoked food products and determination by high-performance liquid chromatography-fluorescence detection. J. Chromatogr. A, 753, 207-215.

Guillen M.D., Sopelana P., Partearroyo M.A., 1997. Food as a source of polycyclic aromatic carcinogens. Rev. Environ. Health 12, 133-146.

Jankowski P.S., 2004. Analiza wielopierścieniowych węglowodorów aromatycznych w wybranych grupach produktów spożywczych. Rozprawa doktorska [Analysis of polycyclic aromatic hydrocarbons contamination in choosen group of foodstuff. PhD's dissertation]. Akad. Morska Gdynia [typescript, in Polish].

Jira W., 2004. A GC/MS method for the determination of carcinogenic polycyclic aromatic hydrocarbons in smoked meat products and liquid smokes. Eur. Food Res. Technol. 218, 208-212.

Karl H., Leinemann M., 1996. Determination of polycyclic aromatic hydrocarbons in smoked fishery products from different smoking kilns. Z. Lebensm.-Untersuch. Forsch. A, 202, 458-464.

Kazerouni N., Sinha R., Che-Han H., Greenberg A., Rothman N., 2001. Analysis of 200 food items for benzo[a]pyrene and estimation of its intake in an epidemiologic study. Food Chem. Toxicol. 39, 423-436.

Lage Yusty M.A., Cortizo Daviña J.L., 2005. Supercritical fluid extraction and high-performance liquid chromatography – fluorescence detection method for polycyclic aromatic hydrocarbons investigation in vegetable oil. Food Cont. 16, 59-64.

Moret S., Purcaro G., Conte L.S., 2005. Polycyclic aromatic hydrocarbons in vegetable oils from canned foods. Eur. J. Lipid Sci. Technol. 107, 488-496.
Official Journal of the European Union. 2005 a. L 34/3. Commission Recommendation 2005/ 108/EC of 4 February 2005.
Official Journal of the European Union. 2005 b. L 34/3. Commission Regulation (EC) 208/2005.
Philips D.H., 1999. Polycyclic aromatic hydrocarbons in the diet. Mut. Res. 443, 139-147.
SCF, European Commission. 2002. Opinion of the Scientific Committee on food on the risk to human health of polycyclic aromatic hydrocarbons in food (expressed on 4 December 2002). Brussels, Belgium.
Šimko P., 2002. Determination of polycyclic aromatic hydrocarbons in smoked meat products and smoke flavouring food additives. J. Chromatogr. B, 770, 3-18.
Tfouni S.A.V., Machado R.M.D., Camargo M.C.R., Vitorino S.H.P., Vicente E., Toledo M.C.F., 2007. Determination of polycyclic aromatic hydrocarbons in cachaça by HPLC with fluorescence detection. Food Chem. 101, 334-338.
Vazquez Troche S., Garcia Falcon M.S., Gonzales Amigo S., Lage Yusty M.A, Simal Lozano J., 2000. Enrichment of benzo[a]pyrene in vegetable oils and determination by HPLC-FL. Talanta 51, 1069-1076.
Yurchenko S., Mölder U., 2005. The determination of polycyclic aromatic hydrocarbons in smoked fish by gas chromatography mass spectrometry with positive-ion chemical ionization. J. Food Comp. Anal. 18, 857-869.

WPŁYW METODY WĘDZENIA NA ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W PRODUKTACH MIĘSNYCH

Streszczenie. W pracy badano zawartość WWA w czterech grupach produktów mięsnych wędzonych metodą przemysłową oraz tradycyjną. Metodyka badań obejmowała ekstrakcję tłuszczu, izolację WWA z zastosowaniem techniki chromatografii żelowej oraz jakościowe i ilościowe oznaczenie związków z użyciem chromatografii cieczowej z selektywnymi detektorami (HPLC–FLD/DAD). Tradycyjna metoda wędzenia wpłynęła na wyższy poziom skażenia przez WWA większości analizowanych próbek. W wypadku wszystkich produktów wędzonych w sposób zarówno tradycyjny, jak i przemysłowy zaobserwowano, iż całkowita zawartość sumy WWA oraz zawartość poszczególnych WWA w części środkowej produktów była istotnie statystycznie niższa w porównaniu z częścią zewnętrzną tego samego asortymentu. Niezależnie od zastosowanej metody wędzenia, zawartość benzo[a]pirenu była istotnie niższa od dopuszczalnego maksymalnego limitu 5 $\mu g \cdot kg^{-1}$, ustanowionego w Rozporządzeniu Komisji UE nr 208/2005 dla grupy produktów mięsnych wędzonych.

Słowa kluczowe: wielopierścieniowe węglowodory aromatyczne (WWA), proces wędzenia, produkty mięsne

Accepted for print – Zaakceptowano do druku: 10.10.2007

For citation – Do cytowania: Ciecierska M., Obiedziński M., 2007. Influence of smoking process on polycyclic aromatic hydrocarbons' content in meat products. Acta Sci. Pol., Technol. Aliment. 6 (4), 17-28.