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CANNED FISH PRODUCTS CONTAMINATION BY POLYCYCLIC AROMATIC HYDROCARBONS*

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Abstract. According to the Commission Recommendation 20005/108/EC further analyses of 15 genotoxic PAHs (listed by The Scientific Committee on Food) in food are necessary. The objective of this research was to study contamination of canned smoked fish products in oil by these 15 PAHs. The material investigated were canned smoked sprats in oil available in Warsaw agglomeration. Both oils from canned food and sprats itself were analysed. Among all products under investigation it was shown that oils derived from canned smoked sprats had statistically significant higher total content of PAHs than sprats from this canned fish product.

Key words: polycyclic aromatic hydrocarbons (PAHs), canned fish products, HPLC--FLD/DAD

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous chemical compounds, known to be carcinogenic, originating from incomplete combustion of organic matter [Vazquez Troche et al. 2000, Kishikawa et al. 2003, Lage Yusty and Cortizo Daviña 2005, Okuda et al. 2006, Tfouni et al. 2007]. They are formed by four to seven fused benzene rings (called heavy PAHs), among which the most important one as indicator is benzo[a]pyrene. They have been the subject of much concern in recent years due to their toxic potential. The earliest examples of occupational cancer among chimney sweeps, workers exposed to coal-tar products and workers in iron foundries, coke ovens and aluminium production plants, are generally agreed to be the result of exposure to PAHs [Philips 1999].

PAHs are being found throughout the environment in water, air, soil, and therefore also in food [Falco et al. 2003]. For the sake of permanent formation and presence of

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these compounds in the environment, food contamination is realistic at every stage of food life. However, their presence in food originates mainly from thermal treatment in the preparation and manufacturing of foods [Guillen et al. 1997, Philips 1999, Opinion... 2002, Discussion... 2005]. Processing procedures, such as smoking or drying and cooking of foods at high temperatures like grilling, roasting or frying are recognized as a major source of contamination by PAHs [Moret and Conte 2000, Vazquez Troche et al. 2000, Šimko 2002, Discussion... 2005, Moret et al. 2005, Yurchenko and Mölder 2005].

It has been estimated that human intake of PAHs from food is considerably higher than from ambient air or drinking water, edible oils and fats being the most contributing sources because of their lipofilic nature [Cejpek et al. 1998, Moret and Conte 2000, Barranco et al. 2003].

Traditional smoking of food such as meat and fish products has been used for centuries in many countries. 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. However, now primarily it is used to achieve the characteristic taste and appearance of smoked food with preservation playing the minor role. Nowadays smoking is still widely used in fish processing and is largely a highly industrialized process involving modern controlled kilns. Nevertheless, traditional smokehouses are still used fairly widely. Since the generation of wood smoke is an example of incomplete combustion, undoubtedly PAHs are generated [Philips 1999, Discussion... 2005, Stołyhwo and Sikorski 2005]. When it comes to canned fish products, it is known that the oil has mainly a preservative function and consumers usually discharge most of it before fish consumption. On the other hand, some people consumed oil entirely with the product not being aware of possible relatively high level of carcinogenic PAHs contamination.

The Scientific Committee for Food concluded in its opinion of 4 December 2002 [Opinion... 2002] that a number of heavy PAHs are carcinogens (genotoxic) and that benzo[a]pyrene can be used as a marker for the occurrence and effect of these carcinogenic PAH in food. The list of genotoxic PAH comprise cyclopenta[c,d]pyrene, benzo[a]anthracene, chrysene, 5-metylchrysene, benzo[j]fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, dibenzo[a,l]pyrene, benzo[g,h,i]perylene, indeno[c,d]pyrene, dibenzo[a,e]pyrene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene. According to the Commission Recommendation 2005/108/EC, further analyses of these genotoxic PAHs in food are necessary.

With the background provided, according to the Commission Recommendation, the aim of this research was to conduct studies on 15 PAHs contamination of canned smoked fish products in oil, in order to assess the level of contamination both in oils from canned food and fish itself.

MATERIAL AND METHODS

The material investigated were five can smoked sprats in oil available in Warsaw agglomeration. Both oils from canned food and sprats themselves were analysed. The investigated products were manufactured by five various manufacturers and named canned fish product A, B, C, D and E. From every assortment three samples (three canned fish products) were taken to the study. All three samples of the same product were analysed in three repetitions.

Methodology applied for the study consisted of fat extraction (only in case of sprats samples), PAHs isolation using GPC – gel permeation chromatography and conse-

quently qualitative-quantitative compound's determination by high pressure liquid chromatography with selective detectors (HPLC-FLD/DAD).

2 g of filtered sprats (from the oil), were homogenized with anhydrous sodium sulfate (2 g). Next, after adding 20 cm^3 hexane/acetone mixture (60/40, v/v), the sample of sprats was placed in ultrasonic bath for 30 minutes. Subsequently solid parts were filtered off from the extract. The obtained filtrate after evaporation almost to dryness was dissolved in cyclohexane (5 cm^3).

Isolation of PAHs from sprat's fat extract (done before), as well as from the oil fraction of canned product was obtained using column for gel permeation chromatography – Bio-Beads S-X3 330 × 10 mm. For that purpose 1 cm^3 of the cyclohexane extract obtained before or 1 cm^3 of the oil solution in cyclohexane (100 $mg \cdot cm^{-3}$) was injected on the column. Chromatographic separation was performed by isocratic method. Total flow was 0.8 ml/min, and mixture cyclohexane/ethyl acetate (50/50, v/v) was used as mobile phase.

Collected fraction of PAHs, after evaporation to 1 cm^3, was analysed 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, co-operated with computer programme LabSolution 2.1. Chromatographic analyses were conducted using Baker's chromatographic column named BAKERBOND PAH-16 Plus 250 × 3 mm, 5 µm. Column temperature was isothermal at 30°C. Gradient method with total flow 0.5 ml/min and solvent mixture, as mobile phase, acetonitrile/water, 70/30 (A) and acetonitrile (B) was applied. The following gradient elution programme was used: 0-20 min, 0% B; 20-43 min, 0-100% B; 43-60 min, 100% B; 60-63 min, 100-0% B. 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 method of external standard, consisted of 15 PAHs.

The obtained results were statistically worked out using Statgraphics Plus 4.1 programme. To appraise the significance of the differences between the means of PAHs content in sprats and oil from the same one canned fish product, Tuckey's test was used, at significance level $\alpha = 0.05$, where $n = 9$.

RESULTS AND DISCUSSION

In Table 1, for every canned food, level of sprats contamination as well as oil's PAHs content from these product was shown, whereas Table 2 presents mean content of PAHs in investigated canned smoked fish products.

Among all products under investigation it was shown that oils derived from canned smoked sprats had statistically significant higher total content of PAHs than sprats from this canned food. The least though significant difference was observed for canned fish product C. Total PAHs contamination of oil derived from these product was about 7--times higher than contamination of sprat. The greatest difference between oil and sprat was shown for canned food B. The content of 15 PAHs in oil was about 11-times higher than sprat from this assortment. Total PAHs content in all oils under investigation ranged from 94.79 $\mu g \cdot kg^{-1}$ to 562.03 $\mu g \cdot kg^{-1}$, whereas for sprats were within 12.68--85.55 $\mu g \cdot kg^{-1}$ (Table 1).

Table 1. Mean content of 15 PAHs in canned fish products (oil and sprat) under investigation, μg·kg^{-1}
Tabela 1. Średnia zawartość 15 WWA w badanych konserwach rybnych (zalewa olejowa i szprot), μg·kg^{-1}

PAHs – WWA	Canned fish product – Konserwa rybna									
	A		B		C		D		E	
	oil olej	sprat szprot	oil olej	sprat szprot	oil olej	sprat szprot	oil olej	sprat szprot	oil olej	sprat szprot
1	2	3	4	5	6	7	8	9	10	11
Cyclopenta[c,d]pyrene Cyklopenta[c,d]piren	33.23^{A1} ± 3.39	6.09^{a1} ± 0.82	45.24^{B1} ± 2.31	6.39^{b1} ± 1.18	88.36^{C1} ± 8.31	16.16^{c1} ± 1.82	20.05^{D1} ± 1.78	4.76^{d1} ± 0.35	28.62^{E1} ± 2.31	3.21^{e1} ± 0.42
Benzo[a]anthracene Benzo[a]antracen	31.01^{A2} ± 1.62	2.27^{a2} ± 0.62	22.27^{B2} ± 0.84	1.39^{b2} ± 0.08	145.11^{C2} ± 1.61	22.64^{c2} ± 2.24	15.52^{D2} ± 1.32	1.97^{d2} ± 0.23	22.34^{E2} ± 1.95	2.52^{e2} ± 0.31
Chrysene Chryzen	22.39^{A3} ± 1.44	1.62^{a3} ± 0.56	11.58^{B3} ± 1.78	0.94^{b3} ± 0.11	61.92^{C3} ± 3.51	10.60^{c3} ± 1.41	10.68^{D3} ± 0.98	1.34^{d3} ± 0.20	6.42^{E3} ± 0.42	1.24^{e3} ± 0.20
5-metylchrysene 5-metylchryzen	3.56^{A4} ± 0.29	0.14^{a4} ± 0.05	0.18^{B4} ± 0.08	0.14^{b4} ± 0.04	21.83^{C4} ± 1.89	2.25^{e4} ± 0.21	2.56^{D4} ± 0.21	0.50^{d4} ± 0.13	2.35^{E4} ± 0.18	0.52^{e4} ± 0.15
Benzo[j]fluoranthene Benzo[j]fluoranten	8.42^{A5} ± 0.41	0.76^{a5} ± 0.14	2.20^{B5} ± 0.31	0.91^{b5} ± 0.22	20.75^{C5} ± 0.31	3.63^{c5} ± 0.35	5.78^{D5} ± 0.32	0.53^{d5} ± 0.18	2.98^{E5} ± 0.23	0.98^{e5} ± 0.18
Benzo[b]fluoranthene Benzo[b]fluoranten	8.55^{A6} ± 0.42	0.72^{a6} ± 0.16	2.74^{B6} ± 0.43	0.98^{b6} ± 0.15	19.63^{C6} ± 0.74	3.60^{c6} ± 0.34	6.68^{D6} ± 0.47	0.49^{d6} ± 0.2	3.75^{E6} ± 0.31	1.11^{e6} ± 0.16
Benzo[k]fluoranthene Benzo[k]fluoranten	3.72^{A7} ± 0.27	0.13^{a7} ± 0.05	0.15^{B7} ± 0.03	0.12^{b7} ± 0.02	11.35^{C7} ± 0.04	1.71^{c7} ± 0.24	2.59^{D7} ± 0.32	0.11^{d7} ± 0.07	0.52^{E7} ± 0.11	0.20^{e7} ± 0.08
Benzo[a]pyrene Benzo[a]piren	7.87^{A8} ± 0.95	0.73^{a8} ± 0.08	0.99^{B8} ± 0.22	0.52^{b8} ± 0.11	15.28^{C8} ± 0.93	3.09^{c8} ± 0.41	5.49^{D8} ± 0.49	0.47^{d8} ± 0.18	1.23^{E8} ± 0.21	0.45^{e8} ± 0.10

Table 1 – cont.

1	2	3	4	5	6	7	8	9	10	11
Dibenzo[a,h]anthracene Dibenzo[a,h]antracen	0.11^{A9} ± 0.01	0.08^{a9} ± 0.01	0.41^{B9} ± 0.02	0.06^{b9} ± 0.02	0.10^{C9} ± 0.03	0.05^{c9} ± 0.01	0.13^{D9} ± 0.02	0.07^{d9} ± 0.01	0.35^{E9} ± 0.10	0.13^{e9} ± 0.06
Dibenzo[a,l]pyrene Dibenzo[a,l]piren	0.43^{A10} ± 0.12	0.01^{a10} ± 0.00	0.16^{B10} ± 0.06	0.13^{b10} ± 0.04	2.18^{C10} ± 0.25	0.46^{c10} ± 0.02	0.30^{D10} ± 0.1	0.09^{d10} ± 0.05	0.30^{E10} ± 0.09	0.11^{e10} ± 0.03
Benzo[g,h,i]perylene Benzo[g,h,i]perylen	16.33^{A11} ± 0.51	1.04^{a11} ± 0.15	68.13^{B11} ± 5.61	3.91^{b11} ± 0.12	85.67^{C11} ± 2.59	10.48^{c11} ± 1.40	12.20^{D11} ± 1.11	1.01^{d11} ± 0.15	15.78^{E11} ± 1.23	1.75^{e11} ± 0.15
Indeno[c,d]pyrene Indeno[c,d]piren	16.46^{A12} ± 0.98	1.17^{a12} ± 0.46	77.06^{B12} ± 6.08	4.99^{b12} ± 0.68	89.24^{C12} ± 3.77	10.85^{c12} ± 1.12	12.58^{D12} ± 1.54	1.23^{d12} ± 0.18	17.47^{E12} ± 1.37	1.46^{e12} ± 0.13
Dibenzo[a,e]pyrene Dibenzo[a,e]piren	0.37^{A13} ± 0.09	0.25^{a13} ± 0.05	1.21^{B13} ± 0.06	0.32^{b13} ± 0.02	0.60^{C13} ± 0.19	0.03^{c13} ± 0.02	0.23^{D13} ± 0.04	0.11^{d13} ± 0.02	1.11^{E13} ± 0.12	0.42^{e13} ± 0.05
Dibenzo[a,i]pyrene Dibenzo[a,i]piren	n.d. – n.w.	n.d. – n.w.	n.d. – n.w.	n.w. – n.d.	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.w. – n.d.	n.d. – n.w.	n.d. – n.w.	n.d. – n.w.	n.d. – n.w.	n.d. – n.w.	n.d. – n.w.
∑ 15 PAHs ∑ 15 WWA	152.47^{A0} ± 6.16	15.00^{a0} ± 2.39	232.32^{B0} ± 15.34	20.81^{b0} ± 1.49	562.03^{C0} ± 10.84	85.55^{c0} ± 7.83	94.79^{D0} ± 6.65	12.68^{d0} ± 2.30	103.22^{E0} ± 7.28	14.10^{e0} ± 2.50

n.d. – not detected.

A1, a1; B2, b2; C3, c3 – the same small and capital letters by the same number (within one from five 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 – ta sama mała oraz wielka litera przy tej samej cyfrze (w ramach jednego z pięciu 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 canned fish products under investigation, μg·kg^{-1}
Tabela 2. Średnia zawartość 15 WWA w badanych konserwach rybnych, μg·kg^{-1}

PAHs – WWA	Canned fish product – Konserwa rybna				
	A	B	C	D	E
Cyclopenta[c,d]pyrene Cyklopenta[c,d]piren	16.95 ± 1.85	21.93 ± 1.63	37.82 ± 3.77	9.35 ± 0.78	13.37 ± 1.18
Benzo[a]anthracene Benzo[a]antracen	13.77 ± 1.02	9.74 ± 0.39	59.38 ± 2.05	6.04 ± 0.56	10.45 ± 0.97
Chrysene Chryzen	9.93 ± 0.91	5.19 ± 0.78	26.00 ± 2.04	4.14 ± 0.43	3.31 ± 0.29
5-metylchrysene 5-metylchryzen	1.51 ± 0.15	0.16 ± 0.06	8.13 ± 0.71	1.12 ± 0.15	1.25 ± 0.16
Benzo[j]fluoranthene Benzo[j]fluoranten	3.82 ± 0.25	1.43 ± 0.26	8.76 ± 0.34	2.11 ± 0.22	1.78 ± 0.2
Benzo[b]fluoranthene Benzo[b]fluoranten	3.85 ± 0.27	1.68 ± 0.26	8.41 ± 0.46	2.35 ± 0.28	2.17 ± 0.22
Benzo[k]fluoranthene Benzo[k]fluoranten	1.57 ± 0.14	0.13 ± 0.02	4.60 ± 0.18	0.85 ± 0.15	0.33 ± 0.09
Benzo[a]pyrene Benzo[a]piren	3.59 ± 0.43	0.71 ± 0.15	6.75 ± 0.57	1.98 ± 0.27	0.76 ± 0.14
Dibenzo[a,h]anthracene Dibenzo[a,h]antracen	0.09 ± 0.01	0.20 ± 0.02	0.06 ± 0.02	0.09 ± 0.01	0.22 ± 0.08
Dibenzo[a,l]pyrene Dibenzo[a,l]piren	0.18 ± 0.05	0.14 ± 0.05	0.97 ± 0.09	0.15 ± 0.07	0.19 ± 0.05
Benzo[g,h,i]perylene Benzo[g,h,i]perylen	7.15 ± 0.29	29.60 ± 2.32	33.04 ± 1.75	4.37 ± 0.44	7.36 ± 0.58
Indeno[c,d]pyrene Indeno[c,d]piren	7.29 ± 0.67	33.82 ± 2.84	34.37 ± 1.91	4.64 ± 0.59	7.86 ± 0.63
Dibenzo[a,e]pyrene Dibenzo[a,e]piren	0.30 ± 0.07	0.68 ± 0.04	0.20 ± 0.07	0.15 ± 0.03	0.70 ± 0.08
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.
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.
∑ 15 PAHs ∑ 15 WWA	69.99 ± 6.09	105.41 ± 8.81	228.50 ± 13.96	37.31 ± 3.98	49.75 ± 4.66

n.d. – not detected.
n.w. – nie wykryto.

Statistical analysis indicated, that also in the event of all investigated canned food, the content of each individual PAH in oil was significant higher than in sprat from the same product. Taking into consideration the lipophilic nature of PAHs, results obtained from this study proved that oil can act as a solvent able to extract these compounds from contaminated food. Studies conducted by Yurchenko and Mölder [2005] also showed that the formation of PAHs in samples of smoked sprats influence on their concentration in oil and hence that PAHs can migrate into oil from contaminated sprats. The extent of migration is dependent on the lipophilic character of the product and its storage time [Yurchenko and Mölder 2005]. Stołyhwo and Sikorski [2005] also thought, that in smoked canned fish in oil the contamination may be carried by the vegetable oil. In the case of fish products, we cannot exclude the possibility that to what degree PAHs remain in fish lipid without passing to the vegetable oils [Moret et al. 2005].

Contamination of oils from canned sprats A, C and D by benzo[a]pyrene was respectively about 4, 8, and 3-times higher than maximum tolerable limit stated in Commission Regulation for edible oils (EC) no. 208/2005 (2 $\mu g \cdot kg^{-1}$). In case of two oils – from canned sprat B and E benzo[a]pyrene's content didn't exceed this limit and was equal respectively 0.99 and 1.23 $\mu g \cdot kg^{-1}$.

Benzo[a]pyrene's content in examined oil samples ranged from 0.99 $\mu g \cdot kg^{-1}$ to 15.28 $\mu g \cdot kg^{-1}$ (Table 1). Moret et al. [2005] in research dealing with PAHs contamination in vegetable oils from canned food, found benzo[a]pyrene's content in range 0.1--1.9 $\mu g \cdot kg^{-1}$, so maximum tolerable limit of this compound was not exceed. However, it must be pointed out that quite frequently olive Pomace oil, which is usually employed in the frying or cooking of foods especially in catering industry, is used in canned food. Guillen et al. [2004] in research concerning contamination of olive Pomace oil (commercially available on Spanish market) showed the presence of a very high number of PAHs in very high concentrations in most of the olive Pomace oil samples studied. When it comes to benzo[a]pyrene it's content in range 0.35-92.71 $\mu g \cdot kg^{-1}$ was found [Guillen et al. 2004]. Studies dealing with contamination of smoked sprats in oil (concerning also both fraction – smoked sprat and oil) carried through by Yurchenko and Mölder indicated that mean benzo[a]pyrene's concentration in oil from analysed canned sprats was equal 7.70 $\mu g \cdot kg^{-1}$.

Contamination of all investigated sprats by benzo[a]pyrene was lower than maximum tolerable limit stated in Commission Regulation for smoked fish (EC) no. 208/2005 (5 $\mu g \cdot kg^{-1}$). The content of this carcinogenic compound in the analysed sprats were within 0.45-3.09 $\mu g \cdot kg^{-1}$. Taking into consideration PAHs level in the whole canned fish products (sprat and oil together) only for canned food C benzo[a]pyrene's level exceed the limit of 5 $\mu g \cdot kg^{-1}$ (Table 2). Similar results were revealed in research conducted by Karl and Leinemann [1996], in which benzo[a]pyrene's content in smoked sprat from traditional smoking kilns ranged from 0.8 $\mu g \cdot kg^{-1}$ to 4.1 $\mu g \cdot kg^{-1}$. On the other hand studies performed by Yurchenko and Mölder [2005] showed mean benzo[a]pyrene's concentration in smoked sprats (derived from canned sprats in oil) being equal 0.65 $\mu g \cdot kg^{-1}$.

Hot smoked sprats from traditional smoking kilns are rated as the most contaminated smoked fish products due to the fact that they are eaten with the skin. It is well known that the concentrations of PAHs in the skin of smoked fish are much higher than those in the flesh. However some experts assert that only smoked sprats from traditional kilns are of superior quality [Karl and Leinemann 1996].

Considering contamination of smoked fishes it ought to be pointed out that PAHs content can vary in considerable range, especially depending on several variables like the properties of the fish, method and parameters of smoking, degree of smoking, composition of the smoke and exposure of the edible parts to the smoke [Lawrence and Weber 1984, Changrasekhar and Kaveriappa 1985, Moret et. al. 1997, Stołyhwo and Sikorski 2005, Yurchenko and Mölder 2005]. In oil sardines, smoked for 6 hours at 45--70°C in a traditional kiln using smoke generated at 400-600°C, the concentration of benzo[a]pyrene was about 12 $\mu g \cdot kg^{-1}$. When smoking at 45°C in filtered smoke generator at 300-400°C lasted 3.5 hours and was followed by sun-drying for 4-5 hours, the content of this compound was only about 1.6 $\mu g \cdot kg^{-1}$ [Changrasekhar and Kaveriappa 1985].

From the group of the most carcinogenic PAHs, dibenzo[a,i]pyrene and dibenzo-[a,h]pyrene was not detected. However, in case of one oil – from canned sprat C, content of dibenzo[a,l]pyrene (the most carcinogenic compound among all PAHs known so far) slightly exceeded 2 $\mu g \cdot kg^{-1}$.

SUMMARY

1. Contamination of oils derived from canned smoked sprats was statistically significantly higher than contamination of sprats from these canned fish products.

2. Benzo[a]pyrene's content in 3 from 5 investigated oils exceeded respectively about 4, 8 and 3-times maximum tolerable limit of 2 $\mu g \cdot kg^{-1}$ stated in Commission Regulation for edible oils (EC) no. 208/2005.

3. Contamination of sprats by benzo[a]pyrene was lower than maximum tolerable limit, which is equal 5 $\mu g \cdot kg^{-1}$, for smoked fish. However, in case of whole canned fish products (sprat and oil together), only for one investigated canned food benzo[a]-pyrene's level exceeded the limit mentioned above.

REFERENCES

Barranco A., Alonso-Salces R.M., Bakkali A., Berrueta L.A., Gallo B., Vicente F., Sarobe M., 2003. Solid-phase clean-up in the liquid chromatographic determination of polycyclic aromatic hydrocarbons in edible oils. J. Chromatogr. A, 988, 33-40.

Cejpek K., Hajšlová J., Kocourek V., Tomaniová M., Cmolík J., 1998. Changes in PAH levels during production of rapeseed oil. Food Addit. Contam. 15 (5), 563-574.

Changrasekhar T.C., Kaveriappa K.M., 1985. A process for reduction of benzo[a]pyrene content in smoked oil sardine. In: Spoilage of tropical fish and product development. Ed. A. Reilley. FAO Fisher. Rep. 317, 262-266.

Discussion paper on polycyclic aromatic hydrocarbons contamination. 2005. Codex Committee on Food Additives and Contaminants (CCFAC). 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.

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

Guillen M.D., Sopelana P., Palencia G., 2004. Polycyclic aromatic hydrocarbons and olive Pomace oil. J. Agric. Food Chem. 52, 2123-2132.
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.
Kishikawa N., Wada M., Kuroda N., Akiyama S., Nakashima K., 2003. Determination of polycyclic aromatic hydrocarbons in milk samples by high-performance liquid chromatography with fluorescence detection. J. Chromatogr. B 789, 257-264.
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.
Lawrence J.F., Weber D.F., 1984. Determination of polycyclic aromatic hydrocarbons in some Canadian commercial fish, shell-fish, and meat products by liquid chromatography with confirmation by capillary gas chromatography-mass spectrometry. J. Agric. Food Chem. 32, 789--794.
Moret S., Conte L.S., 2000. Polycyclic aromatic hydrocarbons in edible fats and oils: occurrence and analytical methods. J. Chromatogr. A 882, 245-253.
Moret S., Piani B., Bortolomeazzi R., Conte L.S., 1997. HPLC determination of polyaromatic hydrocarbons in olive oils. Z. Lebensm.-Untersuch. Forsch. A 205, 116-120.
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.
Okuda T., Naoi D., Tenmoku M., Tanaka S., He K., Ma Y., Yang F., Lei Y., Jia Y., Zhang D., 2006. Polycyclic aromatic hydrocarbons in the aerosol in Bejing, China, measured by aminopropylsilane chemically-bonded stationary-phase column chromatography and HPLC/ fluorescence detection. Chemosphere 65, 427-435.
Opinion of the Scientific Committee on food on the risk to human health of polycyclic aromatic hydrocarbons in food (expressed on 4 December 2002). 2002. European Commission. Brussels, Belgium.
Philips D.H., 1999. Polycyclic aromatic hydrocarbons in the diet. Mut. Res. 443, 139-147.
Šimko P., 2002. Determination of polycyclic aromatic hydrocarbons in smoked meat products and smoke flavouring food additives. J. Chromatogr. B, 770, 3-18.
Stołyhwo A., Sikorski Z.E., 2005. Polycyclic aromatic hydrocarbons in smoked fish – a critical review. Food Chem. 91, 303-311.
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 Composit. Anal. 18, 857-869.

ZANIECZYSZCZENIE KONSERW RYBNYCH WIELOPIERŚCIENIOWYMI WĘGLOWODORAMI AROMATYCZNYMI

Streszczenie. Zgodnie z zaleceniem Komisji Europejskiej 2005/18/EC z 4 lutego 2005 roku niezbędne są dalsze badania poziomów 15 WWA (wytypowanych przez Komitet Naukowy ds. Żywności UE) w produktach spożywczych. Celem pracy było zbadanie

kontaminacji konserw rybnych wędzonych w zalewie olejowej przez 15 WWA. Materiałem doświadczalnym były szproty wędzone w oleju dostępne na rynku warszawskim. Badaniom poddano zarówno szproty, jak i oleje pochodzące z tych konserw. Wykazano, iż skażenie olejów pochodzących z analizowanych konserw było istotnie statystycznie wyższe od kontaminacji szprotów z tych samych konserw.

Słowa kluczowe: wielopierścieniowe węglowodory aromatyczne (WWA), konserwy rybne, HPLC-FLD/DAD

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