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DEVELOPMENT OF METHODOLOGY FOR CONTROL OF POLYCYCLIC AROMATIC HYDROCARBON CONTENT IN FOOD

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The assumption that benzo(a)pyrene is the most appropriate marker for all PAHs is questionable. In the research that was performed by the European Food Safety Authority (EFSA), the summary concentration of PAHs including benzo(a)pyrene was 20 times higher than that of benzo-(a)pyrene itself. In the routine analyses, the concentration of some other PAHs is more than two times higher than that of benzo(a)pyrene. The aim of the current research was to find a better marker for the reliable characterization of PAHs.

Key words: *polycyclic aromatic hydrocarbons, benzo(a)pyrene, marker, correlation.*

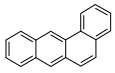
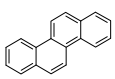
INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are common environmental pollutants. They promote the formation of carcinogenic molecules in the living organisms. The compounds are persistent in the environment. PAHs are formed during the incomplete burning of coal, oil, gas, wood, garbage or other organic substances such as tobacco and charbroiled meat.

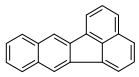
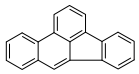
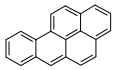
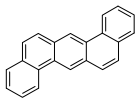
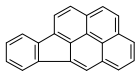
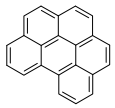
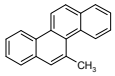
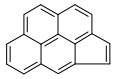
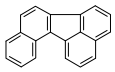
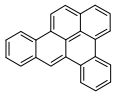
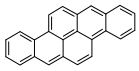
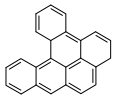
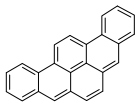
Scientific Committee on Food has suggested to use benzo(a)pyrene as a marker of occurrence and influence of the carcinogenic PAHs in food, based on examinations of PAH profiles in food and on the evaluation of the carcinogenicity study of two coal tar mixtures in mice [1].

In approximately 30% of all the samples, other carcinogenic and genotoxic PAHs were detected despite the absence of benzo(a)pyrene [1]. This is the reason why the suitability of benzo(a)pyrene as a marker for all PAHs is controversial. In this study, relative ratios and correlations between 15 PAHs (Table 1) were analyzed experimentally and the evaluation of benzo(a)pyrene as a most suitable marker to PAHs was done.

Table 1. The chemical structure of the 15 priority polycyclic aromatic hydrocarbons and their abbreviations used

Compound	Abbreviation	Formula
1	2	3
Benz(a)anthracene	B(a)A	
Chrysene	CHR	

End of Table 1

1	2	3
Benzo(k)fluoranthene	B(k)F	
Benzo(b)fluoranthene	B(b)F	
Benzo(a)pyrene	B(a)P	
Dibenz(a,h)anthracene	D(a,h)A	
Indeno(1,2,3-c,d)pyrene	I(1,2,3-c,d)P	
Benzo(g,h,i)perylene	B(g,h,i)P	
5-Methylchrysene	5-MCHR	
Cyclopenta(c,d)pyrene	CP(c,d)P	
Benzo(j)fluoranthene	B(j)F	
Dibenzo(a,e)pyrene	D(a,e)P	
Dibenzo(a,h)pyrene	D(a,h)P	
Dibenzo(a,l)pyrene	D(a,l)P	
Dibenzo(a,i)pyrene	D(a,i)P	

All these 15 PAHs show clear evidence of mutagenicity/genotoxicity in somatic cells in experimental animals *in vivo*. Thus, Scientific Committee on Food has reasoned that these compounds may be regarded as potentially genotoxic and carcinogenic substances for humans and therefore may represent a priority group in the risk assessment of long-term adverse health effects following dietary intake of PAHs [1].

In order to protect the public health and to keep contaminants at levels which are toxicologically acceptable, the Commission Regulation (EC) No 1881/2006 has accepted in the EU maximum levels for certain contaminants in certain foodstuffs, including oils and fats, as well as has processed foodstuffs in which

drying and smoking procedures might cause high level of contamination [2]. Maximum acceptable levels of benzo(a)pyrene in foodstuffs in the EU are summarized in Table 2.

Table 2. Maximum acceptable levels of benzo(a)pyrene in certain foodstuffs

Products	B(a)P maximum levels, μg/kg fresh weight
Oils and fats (excluding cocoa butter)	2.0
Smoked meat and smoked meat products	5.0
Smoked fish and smoked fish products	5.0
Meat of fish, other than smoked fish	2.0
Bivalve molluscs	10.0
Baby foods for infants and young children – processed cereal-based food	1.0
Infant milk and follow-on milk	1.0
Dietary food for special medical purposes intended specifically for infants	1.0

EFSA Panel on Contaminants in the Food Chain has explored whether a toxic equivalency factor (TEF) approach in the risk characterization of the PAH mixtures in food could be applied [1]. They have concluded that the TEF approach is not scientifically valid because of the lack of data from oral carcinogenicity studies on individual PAHs, their different modes of action and the evidence of poor productivity of the carcinogenic potency of PAH mixtures based on the currently proposed TEF values (Table 3).

Table 3. Toxic equivalency factors (TEF) of different PAH's [3–5]

Compound	TEF	Compound	TEF
Dibenzo(a,l)pyrene	10	Benzo(k)fluoranthene	0.1
Dibenzo(a,h)pyrene	10	Benzo(j)fluoranthene	0.1
Dibenzo(a,i)pyrene	10	Indeno(1,2,3-c,d)pyrene	0.1
Dibenzo(a,e)pyrene	1	Cyclopenta(c,d)pyrene	0.1
Benzo(a)pyrene	1	Chrysene	0.01
Dibenz(a,h)anthracene	1	Benzo(g,h,i)perylene	0.01
Benz(a)anthracene	0.1	5-Methylchrysene	not defined
Benzo(b)fluoranthene	0.1		

To simplify the problems related to PAH variety and their different concentration levels, already in 1973 some countries have accepted benzo(a)pyrene as a marker to evaluate the presence of PAH in foodstuffs, despite the fact that benzo(a)pyrene involves only 1–20% of the total PAH carcinogenicity [5].

Summarized literature data and EFSA recommendation for indicator assessment of PAHs content were chosen for the current studies (Table 4) followed by different systems of recommended PAHs sum as markers.

Based on the currently available data relating to the occurrence and toxicity of PAHs, a system of 4 substances (PAH 4) and a system of 8 substances (PAH 8) are concluded as more suitable indicators of PAHs.

Table 4. Polycyclic aromatic hydrocarbons as recommended potential indicators in EU

PAH 1	benzo(a)pyrene
PAH 2	benzo(a)pyrene and chrysene
PAH 4	benzo(a)pyrene, chrysene, benz(a)anthracene and benzo(b)fluoranthene
PAH 8	benzo(a)pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene and indeno(1,2,3-c,d)pyrene

EXPERIMENTAL

Reagents and materials

Cyclohexane (*Pestiscan*), N,N-dimethylformamide (HPLC grade), methanol (Super Gradient), sodium chloride (ACS) were purchased from *Acros*, ethanol – from *J.T. Baker*, sodium sulfate (ACS) from *Fluka*, potassium hydroxide from *Avsista* and silica solid phase extraction (SPE) tubes (500 mg) were obtained from *Phenomenex*. Deionized water was obtained with a MilliQ filter system.

Mixture of 15 PAH standards (PAH mix 170): benz(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, cyclopenta(c,d)pyrene, dibenz(a,h)anthracene, dibenzo(a,e)pyrene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, dibenzo(a,l)pyrene, indeno(1,2,3-c,d)pyrene, 5-methylchrysene and deuterated standard benzo(a)pyrene-D12 were purchased from Dr. Ehrenstrofer. The standard mixture of PAHs consisted of solution in acetonitrile with concentration of 50 ng/µl and the concentration of deuterated benzo(a)pyrene-D12, chrysene-D12, benz(a)anthracene-D12, benzo(b)fluoranthene-D12, benzo(k)fluoranthene-D12, indeno(1,2,3-c,d)pyrene-D12, benzo(g,h,i)perylene-D12, dibenzo(a,i)pyrene-D12 dissolved in cyclohexane was 10 ng/µl. Standard solutions were stored at 4 ^{o}C.

Sample preparation

The sample preparation procedure was elaborated according to Larsson (1982) [6] with some changes made in order to adapt it to the gas chromatography–mass spectrometry (GC-MS) detection method. 25 g of sample were placed into a round-bottomed flask, and then 12 g of potassium hydroxide and 100 ml of ethanol were added. After sample mixing, 25 µl of PAH internal standard solutions with concentration of 10 ng/µl and 125 µl of PAH mix 170 with concentration of 1 ng/µl were added to it, and the mixture was subjected to alkaline treatment with potassium hydroxide and ethanol followed by heating for 2 h (40 ^{o}C) under reflux, and filtered. The filtered solution was transferred to 500 ml separating funnel, 100 ml of water and 100 ml of cyclohexane were added. The funnel was shaken and the layers were separated. The ethanol/water phase was transferred into 250 ml separating funnel and shaken with another 50 ml of cyclohexane. The ethanol/water phase was discarded and the cyclohexane phases were combined. The cyclohexane solution was washed successively with water, with 50 ml of methanol/water (4:1) and with 2×50 ml of water. The cyclohexane extract was shaken with 50 ml of N,N-dimethylformamide/water (9:1) solution. The layer of N,N-dimethylformamide/water solution was transferred into 250 ml separating funnel, 50 ml of 1% NaCl solution were added and PAHs were extracted with 75 ml of cyclohexane. The cyclohexane phase was dried over anhydrous sodium sulfate and concentrated by rotary evaporator under reduced pressure (40 ^{o}C, 235 mbar). The extract was applied to silica SPE

column previously conditioned with cyclohexane (5 ml). The flask was rinsed with cyclohexane (3 ml), and the PAHs were eluted with 6 ml (2×3 ml) of cyclohexane. The collected fraction was evaporated under a light stream of nitrogen at 40 °C, dissolved in 50 µl of cyclohexane and transferred into a GC vial.

Gas chromatography using mass selective detector (GC-MS)

A Hewlett Packard Model 6890 gas chromatograph equipped with a Model 5973 mass selective detector was employed for analyses. Operating conditions were as follows: *Varian Factor Four* capillary column (30 m × 0.25 mm) with stationary phase film thickness of 0.25 µm; helium carrier gas flow rate 1 cm^3/min; injector and detector temperature 280 °C; temperature program: 120 °C (1 min), 120→250 °C (15 °C/min), 250 °C (13 min), 250→280 °C (20 °C/min), 280 °C (1 min), 280→300 °C (35 °C/min), 300 °C (20 min). The total calculated run time was 45.74 min. The ionizing voltage was 1941 V. The sample volume for the GC-MS analysis was 1µl. The data were acquired by operating the MS in selected ion monitoring mode. Peak spectra were compared to the mass spectra of PAH standards. We have not succeeded in the separation of B(b)F and B(j)F when using this methodology. These compounds were determined together, as a sum (Figure 1). The report of PAH standard solution chromatogram is given in Table 5 and Figure 2.

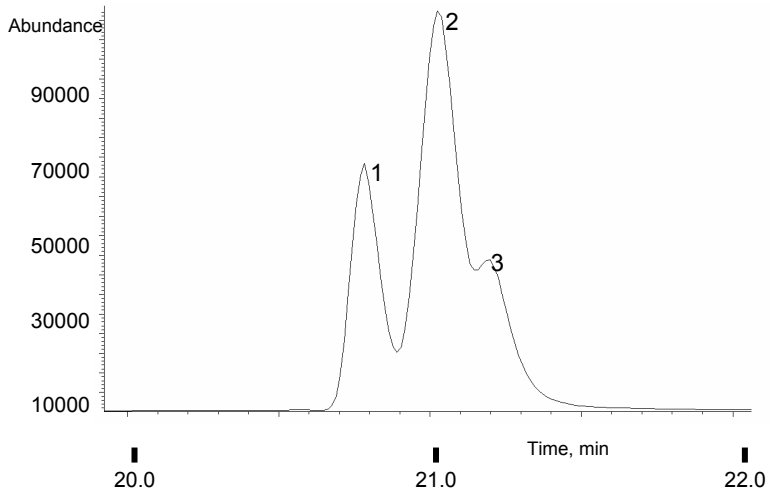


Fig. 1. PAH standard solution chromatogram: *1* – benzo(b)fluoranthene-D12, *2* – benzo(k)fluoranthene-D12 and benzo(b+j)fluoranthene, *3* – benzo(k)fluoranthene.

Benz(a)anthracene-D12 was used as an internal standard for determination of cyclopenta(c,d)pyrene and benz(a)anthracene; chrysene-D12 – for chrysene, 5-methylchrysene and benzo(b+j)fluoranthene. Benzo(k)fluoranthene-D12 was used as internal standard for benzo(k)fluoranthene; benzo(a)pyrene-D12 – for benzo(a)pyrene; indeno(c,d-1,2,3)pyrene-D12 – for indeno(c,d-1,2,3)pyrene and dibenz(a,h)anthracene; benzo(g,h,i)perylene-D12 – for benzo(g,h,i)perylene, and dibenzo(a,i)pyrene-D14 – for dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene and dibenzo(a,h)pyrene.

Table 5. Chromatographic data of standard solution (5 ng/g)

Item	Compound	Retention time, min	Quantification ion	Response value, units	Concentration, ng/g
Internal standards	Benz(a)anthracene-D12	14.31	240	174951	10.00
	Chrysene-D12	14.45	240	161698	10.00
	Benzo(b)fluoranthene-D12	20.75	264	97926	10.00
	Benzo(k)fluoranthene-D12	21.00	264	98584	10.00
	Benzo(a)pyrene-D12	23.47	264	106404	10.00
	Indeno(1,2,3-c,d)pyrene-D12	28.07	288	172603	10.00
	Benzo(g,h,i)perylene-D12	29.04	288	149501	10.00
	Dibenzo(a,i)pyrene-D14	37.65	316	33462	10.00
Target compounds	Cyclopenta(c,d)pyrene	14.40	226	113923	5.00
	Benz(a)anthracene	14.41	228	110429	5.00
	Chrysene	14.56	228	99103	5.00
	5-Methylchrysene	16.80	242	50295	5.00
	Benzo(b+j)fluoranthene	20.98	252	74965	5.00
	Benzo(k)fluoranthene	21.17	252	58553	5.00
	Benzo(a)pyrene	23.63	252	65315	5.00
	Indeno(1,2,3-c,d)pyrene	28.16	276	91438	5.00
	Dibenz(a,h)anthracene	28.29	278	84076	5.00
	Benzo(g,h,i)perylene	29.15	276	76500	5.00
	Dibenzo(a,l)pyrene	34.68	302	24558	5.00
	Dibenzo(a,e)pyrene	37.03	302	29338	5.00
	Dibenzo(a,i)pyrene	37.94	302	9798	5.00
	Dibenzo(a,j)pyrene	38.44	302	8012	5.00

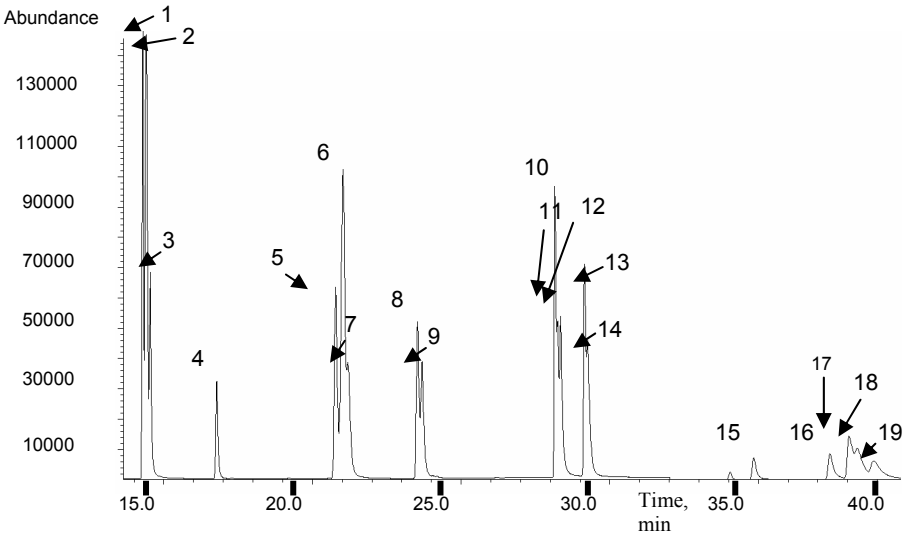


Fig. 2. PAH standard solution chromatogram: *1* – benz(a)anthracene-D12, *2* – cyclopenta(c,d)pyrene, benz(a)anthracene and chrysene-D12, *3* – chrysene, *4* – 5-methylchrysene, *5* – benzo(b)fluoranthene-D12, *6* – benzo(b+j)fluoranthene and benzo(k)fluoranthene-D12, *7* – benzo(k)fluoranthene, *8* – benzo(a)pyrene-D12, *9* – benzo(a)pyrene, *10* – indeno(1,2,3-c,d)pyrene-D12, *11* – indeno(1,2,3-c,d)pyrene, *12* – dibenz(a,h)anthracene, *13* – benzo(g,h,i)perylene-D12, *14* – benzo(g,h,i)perylene, *15* – dibenzo(a,l)pyrene, *16* – dibenzo(a,e)pyrene, *17* – dibenzo(a,i)pyrene-D14, *18* – dibenzo(a,i)pyrene, *19* – dibenzo(a,j)pyrene.

RESULTS AND DISCUSSION

Choice of markers by correlation coefficient

Benzo(a)pyrene is the most widely investigated substance of all PAHs. Other PAHs also possess remarkable carcinogenicity and genotoxicity (Table 6). In the routine analyses, the content of some other PAHs in the foodstuffs is more than two times higher than that of benzo(a)pyrene.

Table 6. Toxicity of polycyclic aromatic hydrocarbons

Compound	Carcino-genicity potential	Bio-logical activity	Geno-toxicity	Carcino-genicity
Cyclopenta(c,d)pyrene			+	+
Benz(a)anthracene	+	TI	+	+
Chrysene	+	TI	+	+
5-Methylchrysene			+	+
Benzo(b)fluoranthene	++	C, TI	+	+
Benzo(k)fluoranthene	0	0	+	+
Benzo(a)pyrene	+++	C, TI	+	+
Indeno(1,2,3-c,d)pyrene	+	TI	+	+
Dibenz(a,h)anthracene	+++	C, TI	+	+
Benzo(g,h,i)perylene	0	CC	+	–

Note: + to +++ Active, CC = Carcinogen with B(a)P, TI = Tumor initiator, C = Complete Carcinogen , 0 = Inactive.
"+" positive, "–" negative

In the current studies, 110 fish products and 23 oil samples were analyzed to establish PAH concentrations in different foodstuffs. From all the evaluated samples, 10 of 23 oil samples exceeded maximum acceptable level of PAHs (2 μg/kg). Benzo(a)pyrene was detected in all oil and fish samples.

In Table 7, all evaluated correlation coefficients between individual PAHs and sum of 15 PAHs are summarized. All data were evaluated by *Microsoft Office Excel 2003* software.

Table 7. Correlation coefficients between contamination by individual compound and the sum of 15 PAHs, maximal and average concentrations of analyzed oil samples (n = 23)

Compound	Correlation between individual compound content and summary content of PAHs	Maximal concentration, ng/g	Average concentration. ng/g
Cyclopenta(c,d)pyrene	0.77	7.34	2.14
Benz(a)anthracene	0.77	9.68	2.82
Chrysene	0.58	11.49	3.81
5-Methylchrysene	0.03	2.01	0.37
Benzo(b+j)fluoranthene	0.70	9.21	2.41
Benzo(k)fluoranthene	0.50	4.72	1.28
Benzo(a)pyrene	0.96	8.13	2.44
Indeno(1,2,3-c,d)pyrene	0.81	6.62	1.73
Dibenz(a,h)anthracene	0.46	1.67	0.38
Benzo(g,h,i)perylene	0.95	8.57	2.05

The highest concentrations of investigated PAHs in oil samples were found for chrysene and benz(a)anthracene, and they essentially exceeded the found content of benzo(a)pyrene (Table 7). Correlation coefficients were higher for benzo(a)pyrene and benzo(g,h,i)perylene, and therefore it becomes possible to affirm that these compounds (benzo(a)pyrene and benzo(g,h,i)perylene) might become potential indicators for oil samples.

The average values of chrysene and benz(a)anthracene content in oil samples were higher than that for benzo(a)pyrene. According to our results, a similar tendency was observed also for fish samples. Benzo(a)pyrene was concluded to be not a suitable marker for chrysene and benz(a)anthracene. This is an acceptable explanation why chrysene can be a more suitable marker for the evaluation of PAH contamination in the oil and fish samples.

After evaluation of the correlation coefficients between sum of PAHs and two component sum in oil samples, the best ones are presented in Table 8.

Table 8. Correlation coefficients between PAH 2 (summary content of two compounds) and summary content of 15 PAHs in oil samples (n = 23)

Compounds	R^2
Benz(a)anthracene+benzo(g,h,i)perylene	0.97
Chrysene+indeno(1,2,3-c,d)pyrene	0.95
Chrysene+benzo(a)pyrene	0.95
Chrysene+benzo(g,h,i)perylene	0.94
Chrysene+benzo(b+j)fluoranthene	0.94

As one can see from our data in Table 8, correlation coefficients between 15 PAH sum and PAH 2 in oil samples are satisfactory only in five cases. Experimentally all possible PAH 2 combinations and their correlation with 15 PAH sum were evaluated. Chrysene, benz(a)anthracene and indeno(1,2,3-c,d)pyrene were found to be the most suitable markers for the evaluation of oil contamination.

Table 9. Correlation coefficients between individual PAH content and summary content of 15 PAHs in fish products, maximal and average concentrations of analyzed fish product samples (n = 110)

Compound	Correlation coefficients	Maximal concentration, ng/g	Average concentration, ng/g
Cyclopenta(c,d)pyrene	0.93	37.73	4.70
Benz(a)anthracene	0.986	33.85	4.12
Chrysene	0.95	36.94	4.06
5-Methylchrysene	0.75	3.64	0.64
Benzo(b+j)fluoranthene	0.97	12.89	1.25
Benzo(k)fluoranthene	0.87	9.01	0.76
Benzo(a)pyrene	0.97	16.08	1.56
Indeno(1,2,3-c,d)pyrene	0.88	10.30	0.59
Dibenz(a,h)anthracene	0.48	1.24	<0.10
Benzo(g,h,i)perylene	0.86	10.99	0.61

The results of analyses of 110 fish samples have shown than only 10 samples have exceeded the maximal acceptable level for PAH (5 μg/kg). The correlation analysis between content of individual PAHs and the sum of 15 PAHs in fish samples was evaluated, and results are summarized in Table 9.

The highest concentrations of PAHs have been observed for chrysene, benz(a)anthracene and cyclopenta(c,d)pyrene. The highest value of correlation coefficient (R^2 = 0.98) was reached with benz(a)anthracene, but for benzo(a)-pyrene, cyclopenta(c,d)pyrene, chrysene and benzo(b+j)fluoranthene high correlation coefficients also were found.

After evaluation of correlation coefficients between sum of PAHs and two component summary amount in fish product samples, the best results are collected in Table 10.

Table 10. Correlation coefficients between PAH 2 (two compound sum) and 15 PAHs summary content in fish product samples (n = 110)

Compounds	R^2
Benz(a)anthracene+benzo(a)pyrene	0.993
Benz(a)anthracene+benzo(b+j)flouranthene	0.992
Benz(a)anthracene+benzo(k)fluoranthene	0.991
Benz(a)anthracene+indeno(1,2,3-c,d)pyrene	0.991
Benz(a)anthracene+benzo(g,h,i)perylene	0.990

As one can see from data in Table 10, the highest correlation coefficients were found in five PAH 2 cases. Therefore as stable markers for the fish product samples benz(a)anthracene as well as benzo(a)pyrene, benzo-(b+j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-c,d)pyrene and benzo-(g,h,i)perylene may serve.

Markers option by sum of PAHs

In this research, all analyzed foodstuffs were divided in three groups – meat products (n = 15), fish products (n = 104) and oils (n = 29). To find the best marker for PAHs, correlation between total PAH content and content of benzo(a)pyrene, chrysene as well as new potential indicators of PAH 2, PAH 4, PAH 8 (see Table 4) was evaluated. The correlation results are presented in Table 11.

Table 11. Assessment of correlation coefficients between individual PAHs, new potential indicators of PAH 2, PAH 4, PAH 8 and total PAH content in different foodstuffs

Sample group (number of samples)	Correlation coefficients				
	benzo(a)pyrene	chrysene	PAH 2	PAH 4	PAH 8
Oil (29)	0.94	0.97	0.994	0.9989	0.990
Meat (15)	0.98	0.95	0.98	0.989	0.995
Fish (104)	0.96	0.95	0.97	0.984	0.981
Sprats in oil (70)*	0.96	0.96	0.98	0.989	0.985

* from total fish samples

As shown in Table 11, PAH 2, PAH 4 and PAH 8 have higher correlation coefficient values than those of benzo(a)pyrene or chrysene, as an individual markers. Benzo(a)pyrene, which was for a long time used as a marker for total

PAH content, can be substituted by PAH 4 or PAH 8. On the other hand, PAH 2 has slightly lower correlation coefficient values. Behaviour of PAH 4 and PAH 8 as markers is very similar, but slightly higher correlation coefficients are characteristic of PAH 4 for oil and fish products. It is necessary to note that in the case of PAH 8 the total content of benzo(b)fluoranthene and benzo(j)-fluoranthene was evaluated due to insufficient resolution of chromatographic peaks of these two compounds.

All the results of PAH 4 obtained mass concentrations in the analyzed foodstuffs are summarized in Table 12.

Table 12. Analysis results of PAH 4 as a marker for total PAH sum (average value, median value, maximum value and percentile) in the different sample groups

Sample group (number of samples)	Mass concentration, µg/kg			95% percentile
	average value	median**	maximum value	
Oil (29)	6.22	2.20	43.7	31.0
Meat (15)	10.6	2.03	59.7	37.3
Fish (104)	10.3	4.13	79.8	35.0
Sprats in oil (70)*	10.7	3.95	79.8	69.7

* from total fish samples

** the median is the point in an ordered frequency distribution that cuts the distribution in half:half; half of observations fall above this point and half below it.

Using PAH 4 as an indicator, the highest content of total PAHs was observed for the fish products (79.8 µg/kg); for the meat and oil samples these mass concentrations were lower. The median mass concentrations of total PAHs in meat and oil products are similar, but fish products contain two times higher content of PAHs.

After evaluation of 95% percentile, maximum acceptable concentration for PAH 4 as marker assumed be 30 µg/kg in oil samples, but in smoked meat and smoked fish samples this concentration amounted to 35 µg/kg. Canned fish samples contain higher contamination level with PAHs, and maximal acceptable concentration for PAH 4 as marker should be 70 µg/kg.

CONCLUSIONS

The current investigation has shown that individual PAHs some other than benzo(a)pyrene are more suitable as single markers or in combinations with other markers in analysis of foodstuff contamination by PAHs. Benzo(a)pyrene, chrysene, benz(a)anthracene, cyclopenta(c,d)pyrene occur to be the most perspective as single markers. The obtained results show that combined markers (benz(a)anthracene in combinations with other PAHs) are very perspective substances for toxicity studies. Sum of four individual PAHs (PAH 4) can be a suitable marker for evaluation of polycyclic aromatic hydrocarbon content in different foodstuffs. Maximal acceptable concentration for oil samples could be 30 µg/kg, for smoked meat and smoked fish samples 35 µg/, and for canned fish samples 70 µg/kg.

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REFERENCES

1. Scientific Opinion of the Panel on Contaminants in the Food Chain on a request from the European Commission on Polycyclic Aromatic Hydrocarbons in Food. EFSA J., 2008, 742.
2. Commission Regulation (EC) No 1881/2006, December 19, 2006. *Offic. J. E. U.*, L 364/5-24.
3. Seidel, A., Tsai, W. T., Mi, H. H., Chang, Y. M., Yang, S. Y., Chang, J. H. (2007). Polycyclic aromatic hydrocarbons (PAHs) in bio-crudes from induction-heating pyrolysis of biomass wastes. *Biores. Technol.,* 98, 1133–1137.
4. Zuin, V. G., Montero, L., Bauer, C., Popp, P. (2005). Stir bar sorptive extraction and high-performance liquid chromatography–fluorescence detection for the determination of polycyclic aromatic hydrocarbons in Mate teas. *J. Chromatogr. A,* 1091, 2–10.
5. Šimko, P. (2002). Determination of polycyclic aromatic hydrocarbons in smoked meat products and smoke flavouring food additives. *J. Chromatogr. B,* 770, 3–18.
6. Larsson, B. K. (1982). Polycyclic Aromatic Hydrocarbons in Smoked Fish. *Z. Lebensm. Unters. Forsch.,* 174, 101.

OPTIMĀLĀ MODEĻA IZVEIDE POLICIKLISKO AROMĀTISKO OGĻŪDEŅRAŽU SATURA RAKSTUROŠANAI PĀRTIKAS PRODUKTOS

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K O P S A V I L K U M S

Policikliskie aromātiskie ogļūdeņraži (PAO) ir viena no lielākajām organisko savienojumu klasēm, kas pazīstami kā kancerogēni savienojumi. Pārtikas piesārņošana ar PAO var notikt gan pārtikas produktu apstrādes laikā (karsēšana, grilēšana, kūpināšana, žāvēšana u.c), gan arī izejvielu ekspozīcijas laikā, uzņemot PAO no apkārtējās vides.

Pieņēmums, ka benzo(a)pirēns ir labs indikators visiem PAO ir apšaubāms. PAO summas līmenis, ieskaitot benzo(a)pirēnu, piesārņotos pārtikas produktos ir vairākas reizes augstāks nekā benzo(a)pirēna koncentrācija. Šī pētījuma mērķis bija atrast labāku indikatoru policiklisko aromātisko ogļūdeņražu analīzei pārtikas produktos. Tādēļ tika izanalizētas relatīvās attiecības, korelācijas starp PAO saturu un izvērtēts, vai benzo(a)pirēns tiešām ir piemērotākais indikators piesārņojuma ar policikliskajiem aromātiskajiem ogļūdeņražiem izvērtēšanai. Kā PAO marķieru varianti tika izvērtētas arī summas PAO 2, PAO 4 un PAO 8.

СОЗДАНИЕ ОПТИМАЛЬНОЙ МОДЕЛИ ДЛЯ ХАРАКТЕРИСТИКИ СОСТАВА ПОЛИЦИКЛИЧЕСКИХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ В ПИЩЕВЫХ ПРОДУКТАХ

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Р Е З Ю М Е

Полициклические ароматические углеводороды представляют собой один из самых крупных классов канцерогенных веществ. Загрязнение пищевых продуктов полициклическими ароматическими углеводородами может произойти как во время приготовления продуктов (жарки, грилирования, копчения, сушения и т.п.), так и из окружающей среды при хранении.

Предположение, что бензо(а)пирен – самый хороший индикатор содержания полициклических ароматических углеводородов, сомнительно. Суммарный уровень полициклических ароматических углеводородов, включая бензо(а)пирен, при загрязнении продуктов в несколько раз превышает количество самого бензо(а)пирена.

Цель данного исследования – найти наиболее подходящий индикатор для определения количества полициклических ароматических углеводородов в загрязненных продуктах. Задание – проанализировать отношения и корреляцию между содержанием полициклических ароматических углеводородов в пище, а также оценить пригодность использования бензо(а)-пирена в качестве индикатора для анализа этого класса соединений. Как варианты суммы индикаторов были успешно проверены суммы 2, 4 и 8 полициклических ароматических углеводородов.

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