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Polycyclic aromatic hydrocarbons (PAHs) in carbon black

The subject of the study was selected carbon black used in rubber technology. The paper presents the results of investigations of fifteen PAHs listed by EPA in carbon black by HPLC-FLD: Naphthalene (Nap), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (Fl), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k) fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenzo(a,h)anthracene (DahA), Benzo(g,h,i)perylene (BghiP), Indeno(1,2,3-cd)pyrene (Ind).
The total concentration of 15 PAHs varied between 60.78–165.88 mg/kg. Benzo(a)pyrene, the most carcinogenic polyarene, was detected in extracts of all tested carbon black at levels ranging from 0.03 mg/kg to 3.37 mg/kg.
Key words: polycyclic aromatic hydrocarbons, PAHs, carbon black, liquid chromatography with fluorescence detection, HPLC-FLD

Wielopierścieniowe węglowodory aromatyczne (WWA) w sadzach technicznych

W artykule przedstawiono wyniki badań zawartości wielopierścieniowych węglowodorów aromatycznych (WWA) w wybranych sadzach technicznych, dostępnych w handlu na polskim rynku, powszechnie stosowanych do produkcji gumy. Badania węglowodorów WWA prowadzono techniką wysokosprawnej chromatografii cieczowej z detekcją fluorescencyjną (HPLC-FLD). Przeprowadzono oznaczenie stężenia piętnastu WWA, spośród szesnastu znajdujących się w wykazie US EPA (Amerykańskiej Agencji Ochrony Środowiska), w tym: naftalenu, acenaftenu, fluorenu, fenantrenu, antracenu, fluorantenu, pirenu, benzo(a)antracenu, chryzenu, benzo(b)fluorantenu, benzo(k)fluorantenu, benzo(a)pirenu, dibenzo(a,h)antracenu, benzo-(g,h,i)perylenu i indeno(1,2,3-cd)pirenu.
Ogólna zawartość WWA stwierdzonych w badanych sadzach technicznych była zróżnicowana i przyjmowała wartości w zakresie od 60,78 do 165,88 mg/kg. We wszystkich ekstraktach badanych sadzy technicznych wykryto obecność benzo(a)pirenu, zaliczanego do najbardziej rakotwórczych poliarenów, w ilości od 0,03 do 3,37 mg/kg.
Słowa kluczowe: wielopierścieniowe węglowodory aromatyczne (WWA), sadza techniczna, chromatografia cieczowa z detekcją fluorescencyjną (HPLC-FLD)

1. Introduction

Carbon black is a powder material produced by the incomplete combustion of liquid or gas petroleum products. Depending on the method of production there are several kinds of carbon black such as acetylene, channel, furnace, thermal or lamp black. Descriptions of these methods can be found in a specialist literature [1, 2, 3]. Carbon black particles consist primarily of carbon atoms. Moreover, there are small amounts of

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such elements as hydrogen, oxygen, sulfur or nitrogen. Comprehensive information on the microstructure of carbon black can be found in many Donnet's publications [4, 5]. Commercial carbon black contains varying amounts of by-products, in particular aromatic compounds. Typical compounds most commonly identified in extracts of carbon black are polycyclic aromatic hydrocarbons (PAHs), nitro derivatives of PAHs (nitro-PAHs) and sulfur containing PAHs. The concentration of PAHs in carbon black is varied and depends on the raw material used for their preparation and technological parameters of production [6]. In solvent extracts of carbon black PAHs such as benzo(g,h,i)perylene, cyclopenta(c,d)pyrene, fluoranthene, coronene and pyrene are marked. Among PAHs found in the extract of carbon black, these compounds are marked most frequently at highest level. Toxicological studies confirmed that all PAHs are regarded as potentially carcinogenic but attention of scientists is focused especially on compounds containing more than four fused aromatic rings. There is sufficient experimental data showing that benzo(a)pyrene has mutagenic and embryotoxic properties. According to International Agency for Research on Cancer (IARC), on the basis of evidence gathered from experimental animal studies, solvent extract of carbon black is considered as carcinogenic [7].

The purpose of this work was the identification and quantification of PAHs by liquid chromatography – fluorescence detection (HPLC-FLD) method in several kinds of carbon black. Determination of PAHs content in raw materials, especially in carbon black, is important in the design of rubber products such as products for food contact. But there are no specific requirements as to the presence of PAHs in them [8]. Therefore, they should be verified in accordance with the current state of knowledge.

2. Materials and methodology

The subject of the research was technical carbon blacks used in the manufacture of rubber, available on the Polish retail market. The study examined five carbon blacks receiving different methods (furnace, thermal and lamp) as well as different manufacturers. Four carbon blacks of German production (marked by the US ASTM standard): N-330 (furnace), N-550 (furnace), N-772 (furnace), N-990 (thermal) and one of Russian production marked as P-803 (lamp).

In this work are used certified standard solution with 16 Certified Reference Materials (PAHs): acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)-perylene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene. Mass concentration of each compound in the mixture was 500 μg/ml.

The scope of the research included determination of the content of 15 PAHs in selected technical carbon blacks. It was designated only 15 PAHs, as acenaphthylene cannot be indicated with FLD detector.

The equipment used for the implementation of work included:

1. High-performance liquid chromatograph (HPLC) Agilent 1260 Infinity by Perlan Technologies company, having five modules: a gradient pump for four components; autosampler, column thermostat; DAD detector – spectrophotometer operating in the ultraviolet and visible light; FLD fluorescence detector – spectrophotometer using photoluminescence phenomenon, working with the system for data collecting and processing – with the ChemStation operational software.
2. A steel chromatography column HPLC, filled with silica modified gel, with octadecyl groups of low polarity – type ZORBAX Eclipse PAH, 4.6 mm x 150 mm, 35 μm dedicated for the determination of PAHs by Agilent company.

In the lack of testing procedures for examine the contents of PAHs in carbon blacks, was developed own Laboratory method in accordance with ISO 1407 standard and PN-EN ISO 17993 standard. Methodology applied for the study, consisted of the following stages:

- Extraction of PAHs using Soxtec apparatus with *n*-hexane solvent;
- Extracts clean-up onto the SPE column cartridge containing 500 mg of silica gel by eluting solvent mixtures of methylene chloride and *n*-hexane;
- PAHs trace amounts preconcentration;
- Qualitative-quantitative PAHs determination by HPLC-FLD.

Qualitative analysis of PAHs was based on the signal of fluorescence detector (FLD) (as recommended by the PN-EN ISO 17993) on the basis of:

1. Comparison of the retention times in the chromatogram of the sample to values the retention times of standard compounds in the chromatogram of the reference registered under the same test conditions. Recovery of PAHs was at 94÷136% level. The limit of PAHs detection at a level higher than 0.02 μg/ml.
2. Comparison of fluorescence emission spectrums of the compounds in the test sample with spectra of reference compounds having compliant retention times recorded in the same test conditions.

Quantitative analysis of 15 PAHs compounds were made using the calibration curve based on the fluorescence detector (FLD) signal.

3. Results and discussion

Examples of the chromatograms obtained during the determination of PAHs in the examined technical carbon blacks using HPLC-FLD shown in Fig. 1.

Results of 15 PAHs extracted from carbon black are shown in Table 1.

Table 1. Results of PAHs extracted from carbon black

Tabela 1. Wyniki oznaczeń zawartości WWA wyekstrahowanych z sadzy technicznych

Individual PAHs	Structure of PAHs (total rings)	Concentration of PAHs (mg/kg)				
		N-330	N-550	N-772	N-990	P-803
Naphthalene (Nap)	2	0.09	ND	ND	ND	ND
Acenaphthene (Acp)	3	ND	ND	ND	ND	ND
Fluorene (Flu)		ND	ND	ND	ND	ND
Phenanthrene (PA)		1.76	2.41	4.71	1.32	0.49
Anthracene (Ant)		0.02	0.10	0.19	0.04	0.05
Fluoranthene (Fl)	4	11.71	8.70	25.19	3.22	6.46
Pyrene (Pyr)		54.09	68.64	114.34	15.31	38.02
Benzo(a)anthracene (BaA)		ND	ND	0.05	0.02	ND
Chrysene (Chr)		ND	ND	0.17	0.11	0.44
Benzo(b)fluoranthene (BbF)	5	ND	ND	0.74	0.39	1.16
Benzo(k)fluoranthene (BkF)		ND	ND	0.09	0.09	0.18
Benzo(a)pyrene (BaP)		0.10	0.03	3.37	2.65	2.89
Dibenzo(a,h)anthracene (DahA)		ND	ND	ND	ND	ND
Benzo(g,h,i)perylene (BghiP)	6	1.41	0.31	15.04	33.50	39.98
Indeno(1,2,3-cd)pyrene (Ind)		ND	ND	1.99	4.13	6.04
Total PAHs		69.18	80.19	165.88	60.78	95.71

ND – no detected

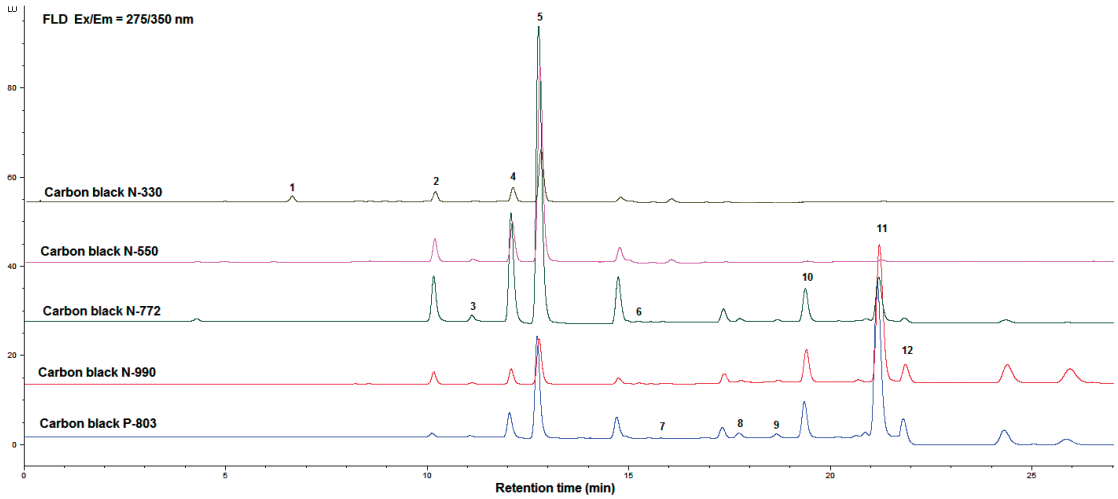

Fig. 1. HPLC-FLD chromatograms of PAHs extracted with hexane in carbon black N-330, N-550, N-772, N-990 and P-803 Identified PAHs: (1) naphthalene, (2) phenanthrene, (3) anthracene, (4) fluoranthene, (5) pyrene, (6) benzo(a)anthracene, (7) chrysene, (8) benzo(b)fluoranthene, (9) benzo(k)fluoranthene, (10) benzo(a)pyrene, (11) benzo(g,h,i)perylene, (12) indeno(1,2,3-cd)pyrene

Rys. 1. Chromatogramy HPLC-FLD węglowodorów WWA wyekstrahowanych heksanem z sadzy technicznych N-330, N-550, N-772, N-990 i P-803

Identyfikowane WWA: (1) naftalen, (2) fenantren, (3) antracen, (4) fluoranten, (5) piren, (6) benzo(a)antracen, (8) chryzen, (8) benzo(b)fluoranten, (9) benzo(k)fluoranten, (10) benzo(a)piren, (11) benzo(g,h,i)perylen, (12) indeno(1,2,3-cd)piren

The total concentration of 15 PAHs varied between 60.78 mg/kg–165.88 mg/kg: N990 (60.78 mg/kg), N-330 (69.18 mg/kg), N-550 (80.19 mg/kg), P803 (95.71 mg/kg) and N772 (165.88 mg/kg).

In N-330 carbon black 7 PAHs content was determined: naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)pyrene, benzo(g,h,i)perylene. The total concentration of these compounds was 69.18 mg/kg. Pyrene concentration (54.09 mg/kg) was highest and the concentration of anthracene (0.02 mg/kg) was lowest.

Concentrations of fluoranthene and benzo(a)pyrene of carbon black N-330 were result consistent with the result obtained by Tsai *et al.* [6] shown in Table 1. In comparison with the results obtained by Tsai *et al.* phenanthrene, pyrene and benzo (g, h, i)perylene concentration were higher. The total concentration of PAHs found was also higher. While the concentrations of anthracene and naphthalene were lower.

For N-550 carbon black 6 PAHs content was determined: phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)pyrene, benzo(g,h,i)perylene. The total concentration of these compounds was 80.19 mg/kg. Pyrene concentration (68.64 mg/kg) was highest and the concentration of anthracene (0.10 mg/kg) was lowest.

Concentrations of pyrene and fluoranthene of carbon black N-550 were result consistent with the result obtained by Tsai *et al.* [6] shown in Table 1. In comparison with the results obtained by Tsai *et al.* phenanthrene concentration was higher. While the concentration of anthracene, benzo(a)pyrene and benzo (g, h, i) perylene were lower. The total concentration of PAHs found was also lower.

Table 2. Comparison of the results of determination of PAHs content in the studied carbon black with the results obtained by Tsai *et al.* [6]
Tabela 2. Porównanie wyników oznaczeń zawartości WWA w badanych sadzach z wynikami otrzymanymi przez zespół Tsai [6]

Individual PAHs	Concentration of PAHs (mg/kg)			
	N-330 (literature data)	N-330 (experimental data)	N-550 (literature data)	N-550 (experimental data)
Naphthalene	7.14	0.09	3.11	–
Anthracene	2.20	0.02	3.58	0.10
Phenanthrene	0.09	1.76	0.19	2.41
Fluoranthene	8.97	11.71	9.38	8.70
Pyrene	8.60	54.09	71.90	68.64
Benzo(a)pyrene	0.16	0.10	0.30	0.03
Benzo(g,h,i)perylene	0.36	1.41	1.30	0.31
Total PAHs	27.52	69.18	89.76	80.19

Then was determined content 11 PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)-anthracene, chrysene, benzo(b)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene) in N-772 carbon black. The total concentration of these compounds was 165.88 mg/kg. Pyrene concentration (114.34 mg/kg) was highest and the concentration of benzo(a)anthracene (0.05 mg/kg) was lowest.

Further the concentration of 11 PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)-anthracene, chrysene, benzo(b)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene) in N-990 carbon black. The total concentration of these compounds was 60.81 mg/kg. Benzo(g,h,i)perylene concentration (33.50 mg/kg) was highest and the concentration of benzo(a)anthracene (0.02 mg/kg) was lowest.

In P-803 carbon black was determined content of 10 PAHs: phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)-pyrene. The total concentration of these compounds was 95.71 mg/kg. Benzo(g,h,i)perylene concentration (39.98 mg/kg) was highest and the concentration of anthracene (0.05 mg/kg) was lowest.

Comparison of analyzed PAHs, taking into account the amount of rings in the molecule is shown in Fig. 2.

Figure 3 shows the concentration of benzo(a)pyrene in hexane extracts of carbon blacks.

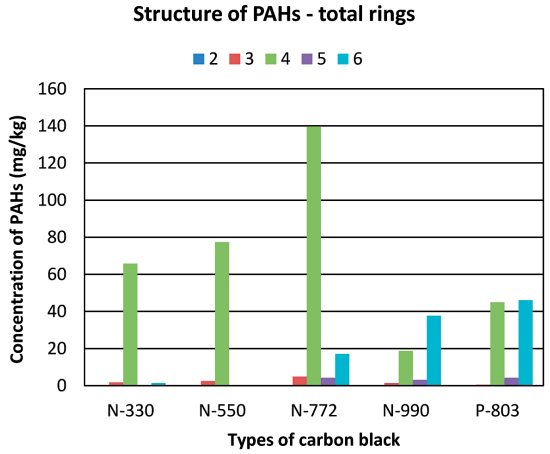

Fig. 2. Comparison of the analyzed PAHs with division into the number of rings in the examined technical carbon blacks
Rys. 2. Porównanie analizowanych WWA z podziałem na liczbę pierścieni w badanych sadzach technicznych

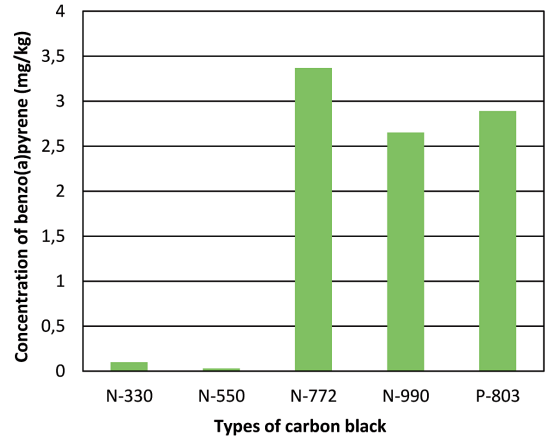

Fig. 3. Concentration of benzo(a)pyrene in carbon blacks
Rys. 3. Stężenie benzo(a)pirenu w sadzach technicznych

Concentrations of benzo(a)pyrene of carbon black N-550 (0.03 mg/kg) and N-990 (2.65 mg/kg) was lower than 0.14–0.29 mg/kg for N-550 and 35.00 mg/kg for N-990 the results obtained by Taylor *et al.* and Zoccolillo *et al.* [9, 10].

4. Conclusion

A decisive impact on the total PAHs content in carbon black N-772, N-330, N-550 had a light PAHs, and thus hydrocarbons two-, three- and four-ring, which accounted for approx. 87.2–99.6% of the total PAHs (Fig. 2).

The high share of heavy PAHs (five- and six-ring) of approx. 67.1% of the total PAHs, was found in carbon black N-990. A comparable proportion of light and heavy PAHs in total PAHs, was found in carbon black P-803.

Benzo(a)pyrene, the most carcinogenic polyarene, was detected in five carbon black extracts at levels ranging from 0.03 mg/kg to 3.37 mg/kg (Fig. 3).

Unfortunately, on the HPLC-FLD chromatograms of the investigated carbon blacks (Fig. 3) not all PAHs have been identified only for 15 PAHs listed under point Materials. Only for these 15 PAHs was known of their retention times for chromatograms HPLC-FLD and we had them characterized fluorescence emission spectra, so that we could conduct their identification and quantification. Due to the lack of specific requirements regarding the presence of PAHs in carbon black in rubber products, whether intended for contact with food or the human body, it cannot judge their toxicity level in the case of processing, the use of the rubber products or impact on the environment and recycling.

In the next phase it is planned to perform the test on the same carbon blacks, with other devices (methods), for verification of the results.

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