

UDC 547.68:662.66

DOI: 10.15372/CSD2020237

Polycyclic Aromatic Hydrocarbons from Coal in the Objects of the Environment

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Abstract

Black coal is formed by a carbon framework originating from metamorphism of condensed polycyclic organic compounds. This framework includes volatile organic substances, as well as a definite amount of mineral admixtures that form ash after coal combustion. The content of individual polycyclic aromatic hydrocarbons (PAHs) in coal depends on the nature of initial plant material that participated in the stages of coal formation, and on thermodynamic conditions of this process. One of the major representatives of PAHs possessing a strong carcinogenic effect is benz(a)pyrene. The group of PAHs compounds also includes phenanthrene, fluoranthene, pyrene, chrysene, which are the major components of emissions during coal production, transportation, storage, concentrating, gasification, coking and combustion, and serve as convenient tracers to evaluate the pollution of the atmosphere, surface waters, and soil. The latter plays the part of a special accumulator into which PAHs get as a result of the global transport of emissions from anthropogenic sources and arrival from natural sources into the atmosphere. Because of this, soil relates to the most representative objects to study PAHs accumulation. The presence of these compounds may play the role of indicators depicting the presence of pollution source. As a rule, PAHs are determined by means of gas and high-performance liquid chromatography.

Gas chromatography in combination with mass spectrometry appears to be the most promising method. To obtain reliable data on PAHs content in various objects, special attention is paid to sample preparation (extraction, purification, concentrating). Methodically correct arrangement of this stage allows excluding a noticeable fraction of the possible error of quantitative determination. The paper presents a review of the methods of PAHs extraction from solid matrices, in particular from fossil coal. It is demonstrated that all ranks of coal may be the sources from which toxic and carcinogenic PAHs enter various environmental objects. A review of the scientific foundations and modern practical methods of PAHs extraction from black coal is presented, the data on the distribution of the representatives of this group of compounds and on the prediction of carcinogenic activity during coal mining, transportation and processing are assessed.

Keywords: black coal, anthropogenic source, polycyclic aromatic hydrocarbons, benz(a)pyrene, carcinogenicity, extraction, gas chromatography, high-performance liquid chromatography

INTRODUCTION

Coal is a complex multicomponent rock of organic origin. Due to the diversity of the natural conditions of coal formation, the composition and properties of fossil coal vary within a broad range [1].

Polycyclic aromatic hydrocarbons (PAHs), persistent ecotoxins, belong to the substances of the 1st class of danger and are present in the organic mass of coal. The content of individual PAHs in coal depends on the type of initial plant

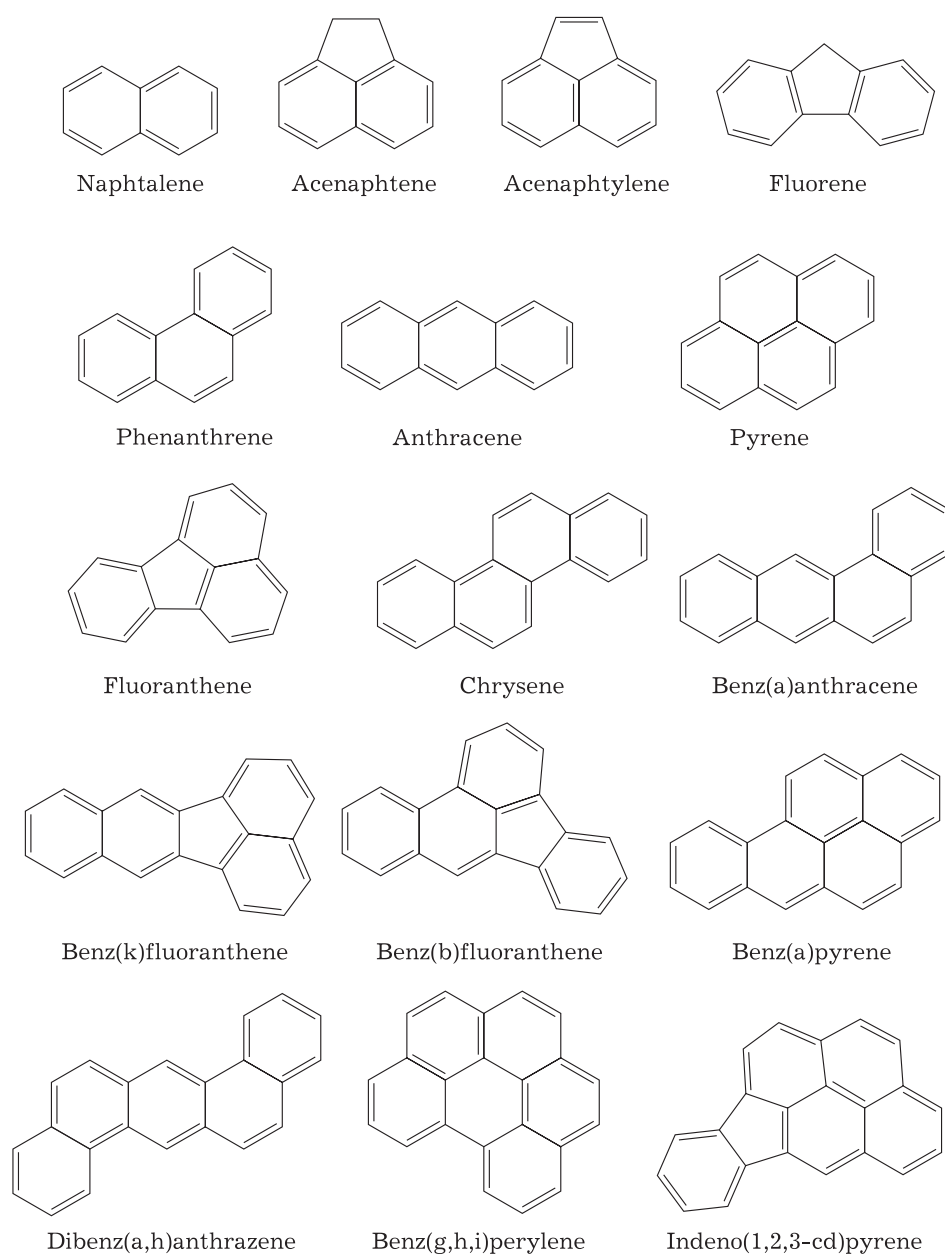


Fig. 1. Structural formulas of priority pollutants belonging to the PAH group.

material that participated in the stages of coal formation, as well as on the thermodynamic conditions of this process. It may reach several hundred or, in some cases, several thousand mg/kg [2, 3]. One of the major representatives of PAH possessing strong carcinogenic action is benz(a)pyrene (BP). The most widespread and stable compounds of this group include phenanthrene, fluoranthene, pyrene, chrysene. The high sensitivity of living organisms to BP defines its use as an indicator of the state of the environment for all PAHs [4].

The structural formulas of the 16 most widespread PAH compounds in environmental objects

are presented in Fig. 1. Table 1 lists the physico-chemical properties of some representatives of PAHs [5].

Coal improvement, combustion, high-temperature treatment are the sources of PAHs emission into the environment [6–8]. Their emission into natural objects is also possible at the stages of mining, storage and transportation of coal.

The global emission of benz(a)pyrene into the environment is more than 20 000 t/year, and 61 % of this amount comes from coal combustion, 20 % – from coke production, 4 % from wood combustion, 8 % – from the open combustion of

TABLE 1

Physicochemical characteristics of some representatives of polycyclic aromatic hydrocarbons (PAHs) [5]

PAH	Number of cycles	Molecular mass, g/mol	Solubility in water, mg/L	Vapour pressure, Pa	Log K_{ow}
Naphthalene	2	128.17	31.0	11.866	3.37
Acenaphthalene	3	152.20	16.1	3.866	4.00
Acenaphthene	3	154.21	3.8	0.500	3.92
Fluorene	3	166.22	1.9	0.432	4.18
Anthracene	3	178.23	$4.5 \cdot 10^{-2}$	$3.40 \cdot 10^{-3}$	4.54
Phenanthrene	3	178.23	1.1	$9.07 \cdot 10^{-2}$	4.57
Pyrene	4	202.26	$1.32 \cdot 10^{-1}$	$5.67 \cdot 10^{-4}$	5.18
Fluoranthene	4	202.26	$2.6 \cdot 10^{-1}$	$1.08 \cdot 10^{-3}$	5.22
Benz(a)anthracene*	4	228.29	$1.1 \cdot 10^{-2}$	$2.05 \cdot 10^{-5}$	5.91
Chrysene*	4	228.29	$1.5 \cdot 10^{-3}$	$1.04 \cdot 10^{-6}$	5.91
Benz(a)pyrene*	5	252.32	$3.8 \cdot 10^{-3}$	$6.52 \cdot 10^{-7}$	5.91
Benz(b)fluoranthene*	5	252.32	$1.5 \cdot 10^{-3}$	$1.07 \cdot 10^{-5}$	5.80
Benz(k)fluoranthene*	5	252.32	$0.8 \cdot 10^{-3}$	$1.28 \cdot 10^{-8}$	6.00
Dibenz(a,h)anthracene*	6	278.35	$0.5 \cdot 10^{-3}$	$2.80 \cdot 10^{-9}$	6.75
Benz(g,h,i)perylene*	6	276.34	$2.6 \cdot 10^{-4}$	$1.33 \cdot 10^{-8}$	6.50
Indeno(1,2,3-cd)pyrene*	6	276.34	$6.2 \cdot 10^{-2}$	$1.87 \cdot 10^{-8}$	6.50

Note. Log K_{ow} is separation coefficient in the system octanol – water.

* These compounds are classified by the Environment Protection Agency of the USA as possible carcinogenic substances for humans [5].

forests and agricultural crops, 1 % – from the emissions of motor transport, and only 0.09 and 0.06 % come from the combustion of oil and gas, respectively [4].

Surface waters function is a special accumulator of PAHs, which get there as a result of global transport of emissions from anthropogenic sources and from natural emission into the atmosphere [9–12]. Because of this, the soil is the most representative object to study PAH accumulation. The presence of these compounds may play the role of an indicator depicting the presence of pollution sources [13–16]. Different mechanisms of anthropogenic arrival of coal as a source of PAHs into the environment are considered in [9]. These mechanisms involve aerial emission of unburnt coal particles, coal improvement and washing, discharge from the tailing dumps of the wastes of coal improvement, coal transportation, shipping, leaks and discharge from storage sites, emergency escapes, as well as natural erosion of coal strata.

PAH CONTENT IN COAL, SOIL, ATMOSPHERIC AIR, AND WASTE WATERS IN THE ZONES AFFECTED BY COAL MINING AND PROCESSING ENTERPRISES

The authors of [2] studied the distribution of PAHs in 50 coal samples from 11 coal basins of the world. It was demonstrated that the environ-

mental risk from the emission of coal particles is not always connected with coal maturity but also depends on its origin

The petrographic composition of 10 coal samples was studied and a correlation between PAHs content and the maceral composition of coal was revealed in [17]. Higher atomic ratios H/C, O/C and higher aromaticity in the inertinite groups are the major reasons for a positive correlation between inertinite and PAH contents. Metamorphism degree also has a substantial effect on the interconnection between the contents of PAH and maceral groups in coal.

It was established in the studies described in [18] that the high concentrations of PAHs are characteristic of bituminous coal. In addition, the mechanism of phenanthrene sorption and desorption was studied in detail for different coal ranks at different pH and ionic strength of a solution. Phenanthrene was chosen as a model compound of the PAH group because this is one of the most stable compounds. Different coal ranks exhibited different sorption capacities within pH 3–11. Phenanthrene was not detected in desorption experiments, which points to its irreversible sorption on initial coal samples. In [19], 15 coal samples from brown coal to anthracite were studied. The concentrations of priority PAHs vary within the range 0.035–11 mg/kg of coal (per the air-dry

state) or 0.038–12 mg/kg of carbon and vary with coalification degree reaching a maximum in the case of highly volatile bituminous coal (vitrinite reflectance $R_o = 0.50$ – 0.90 % or 80–85 mass % of carbon). Thus, the total content of 16 PAHs in lignite is 1.0 to 1.2 mg/kg, for sub-bituminous coal – from 0.25 to 1.6 mg/kg, for highly volatile bituminous coal – from 4.4 to 11 mg/kg, for anthracite – 0.035 mg/kg. Investigations carried out for 8 black coal samples with carbon content 65–90 % revealed the presence of PAHs in the concentration of 1.2–28.3 mg/kg for different types of coal. It was determined that bi- and tricyclic PAHs are recovered from coal series under investigation and most probably may enter the environment during coal preparation and transformation [20].

The concentrations of 16 PAHs were determined in 14 samples of Chinese and American coals of different ranks [21]. The obtained results showed that total PAH content varied within the range 0.31–57.60 mg/kg of coal (per air-dry state) and was dependent on coalification degree; the value was the highest for bituminous low-sulphur coal with carbon content 82.2–88.9 %. High-molecular PAHs dominated in low-rank coal, while low-molecular PAHs dominated in high-rank coal. In addition, the authors suppose that coal is one of the sources of PAHs accumulation in the environment.

We studied the distribution of PAHs in 9 samples of coal at different stages of metamorphism [22, 23]. It was demonstrated that the maximal total amount of 14 PAHs is observed for coal of K rank (0.363 mg/kg) and KS (0.432 mg/kg) ($R_o = 1.185$ and 1.310 %, respectively). For other coal samples, the total PAHs content is within the range of 0.035–0.215 mg/kg.

PAHs content in the samples of soil collected in the zones affected by coal mining and processing facilities in China was studied in [24, 25]. Investigations showed that the total concentration of 16 PAHs (determined as $\Sigma 16$ PAHs) in the surface ground may reach 5.642 mg/kg (with respect to the dry substance). A positive correlation was established between PAHs content in initial coal, fly ash, solid particles (PM 1–2.5 and PM 2.5–10) and PAHs in soil. It was shown that emissions from heat and power stations and the processes involving incomplete coal combustion belong to the major factors affecting PAHs content in soil [26].

The authors of [27–29] pay special attention to the problem connected with PAH content in the particles suspended in atmospheric air. It was shown on the basis of the data obtained that

more than 80 % of PAHs are confined to the particles less than 2.5 μm in diameter (PM 2.5). Thus, the total concentration of 16 high-priority PAHs in the atmospheric air of industrial regions in China was determined to vary from 7.5 to 18.3 ng/ m^3 .

Waste waters and wastes from mining facilities are subjected to regular chemical pollution with toxic metals and PAHs. In [30], the authors studied organic compounds in formation waters of coal beds used for methane production in Australia. The presence of PAHs was revealed in 27 % of water samples in the concentration <1 $\mu\text{g}/\text{dm}^3$. PAHs identified in well waters contain naphthalene, phenanthrene, chrysene and dibenzo(a,h)anthracene.

As a result of various emissions into the environment, coal dust often occurs in marine bottom deposits. The largest amount of coal in the marine environment is observed in the direct vicinity of storage houses, shipping facilities in coal-producing countries and in the countries importing coal; around the territories where coal wastes are stored; along sea routes and in the regions accepting disposed tailing related to coal mining. The sources of distribution of coal particles in the sea environment are considered in detail in [9], and the toxic effect of coal dust on aquatic organisms is described.

S, it is evident that anthropogenic contribution to the problem of environmental pollution with PAHs is substantial. The toxicity and stability of PAHs, as well as their broad occurrence in the environment, provide the necessity of permanent control of these compounds in the atmospheric air [31, 32], in natural waters [33–36], soil [37, 38], vegetation cover [39, 40].

STANDARDIZATION OF PAHS IN ENVIRONMENTAL OBJECTS

Polycyclic aromatic hydrocarbons are priority pollutants both in the list of the European Community (EC) and in the list compiled by the Environmental Protection Agency of the USA (EPA). Control for 16 compounds related to the PAH group must be controlled in environmental objects. The norms that are under development within the activities of the International Organization for Standardization and the EC imply additional broadening of the list of compounds to be determined [41]. In the Russian Federation, maximum permissible concentrations (MPC) for benz(a)pyrene have been established practically for all environmental objects: atmospheric air –

0.1 $\mu\text{g}/100\text{ m}^3$, soil – 0.02 mg/kg, surface water – 5 ng/dm³, bottom sediments – 0.02 mg/kg. Standardization of the content of benz(a)pyrene in the soil is substantially different in Russia and abroad (Table 2).

With respect to this group of compounds, the measures of State regulation are taken in the area of environmental protection [43], therefore, the necessity arises to expand and upgrade the analytical methods of the ecological control of natural objects. Monitoring of PAHs in environmental objects is a very urgent problem requiring efficient and at the same time available procedure of qualitative and quantitative determination of these ecotoxics.

At present, there are procedures accepted for ecological control that allow the determination of all the 16 priority PAHs in the atmospheric air, industrial emissions, water objects, soils, but only the concentrations of benz(a)pyrene and naphthalene in these objects are standardized. So, imperfect regulation leads to ambiguous evaluations of the level of carcinogenic compounds in environmental objects.

METHODS OF PAHS DETERMINATION IN SOLID SAMPLES, COAL AND THE PRODUCTS OF ITS PROCESSING

Separation of the major 16 PAH compounds sufficient for quantitative analysis is achieved by using either capillary columns in gas chromatography (GC) or high-performance columns in high-performance liquid chromatography (HPLC) [44].

To optimize analysis procedure, and to obtain high-quality results, the majority of analytical procedures contain the stage of preliminary isolation (separation) of PAHs from other groups of accompanying substances that are present in the samples. The methods that are most frequently used for these purposes include low-pressure liquid chromatography in the system “liquid – solid” or “liquid – liquid” involving adsorption mechanisms (for example, using silica gel or aluminium oxide) or mixed approaches (for example, adsorption and exclusion using sephadex).

Preliminary purification of samples for the determination of PAHs allows avoiding the influence of fully nonpolar compounds (for example, aliphatic hydrocarbons), moderately and strongly polar compounds (for example, phenols polyatomic alcohols, acids), high-molecular compounds. The resulting purified extracts may contain alkyl derivatives of PAHs, biphenyls, aromatic derivatives of dibenzodioxane and dibenzofuran, and some other compounds. Since the separating potential of columns in HPLC and GC is limited, the reliability of compound identification may be additionally enhanced by using highly selective detectors. Detectors are to provide the determination of compounds under analysis with sufficient sensitivity [44, 45].

The most promising method is gas chromatography in combination with mass spectrometry (GC-MS) [46, 47], which employs two analytical methods: high-efficiency capillary chromatography and mass spectrometry. The combination of

TABLE 2

Comparative data on the standards of benz(a)pyrene content in soil in Russia and abroad, mg/kg [42]

Country	Standard	Categories of objects and recommendations
Russia	0.02	Soils of residential areas, agricultural lands, zones of sanitary control of water supply sources, territories of resort zones and separate establishments
Kazakhstan	0.02	Soils of residential areas, agricultural lands, zones of sanitary control of water supply sources, territories of resort zones and separate establishments
Belarus	Not standardized	Phenanthrene content in peat soil is standardized: 1.5 mg/kg
Denmark	0.1	Recultivation or remediation measures are recommended if the content exceeds 1.0 mg/kg (cleanup level)
the Netherlands	0.052	Content of 7 mg/kg and higher is defined as ecotoxicological risk (Ecotoxicological Serious Risk Concentration – SRCeco for soil)
Germany	2–12	Playgrounds for children – 2 mg/kg; residential areas – 4 mg/kg; parks and recreation zones – 10 mg/kg; industrial objects – 12 mg/kg
USA	0.7–100	Soils of playgrounds for children and agricultural lands – 0.7 mg/kg; soils under temporary or permanent coating – 0.7 mg/kg; soils of woodland parks and green zones – 100.0 mg/kg
Finland	2–15	Soils of playgrounds for children and agricultural lands – 0.7 mg/kg; soils under temporary or permanent coating – 0.7 mg/kg; soils of woodland parks and green zones – 100.0 mg/kg

these two methods allows one to carry out efficient separation of the components and their qualitative and quantitative analysis. The identification of the analytes is performed over the mass spectra from the database, using the data on retention indices [48, 49]. Unlike HPLC, this method allows the separation of numerous components in the object under investigation within a relatively short time for analysis, which gives qualitative and quantitative information on the composition of the sample.

At the stage of sample preparation, the isolation of PAHs from solid matrices is most frequently carried out by extraction with organic solvents (benzene, toluene, acetone, methanol, hexane, diethyl ether, acetonitrile, dimethylsulphoxide, dichloromethane, chloroform or their mixtures) in the Soxhlet's apparatus or in an ultrasonic bath. Extraction in the Soxhlet's apparatus allows achieving a high degree of the recovery of target compounds from 90 to 100 % with the help of rather simple equipment. However, this procedure requires a substantial consumption of solvents (250–300 mL) and requires much time (16–24 h). In the case of ultrasonic extraction, PAH recovery proceeds within a short time interval (10–20 min) with a low consumption of solvents (15–30 mL) but with a lower recovery degree (75–85 %). There are also some other methods of PAH extraction from solid samples which may be used to recover PAHs from coal [50–59].

Microwave extraction is based on the isolation of analyzed compounds from solid samples using organic solvents in the microwave field. Organic solvents and the sample are heated under the action of microwave radiation, which accelerates the extraction of the compounds to be analyzed [51].

Supercritical fluid extraction is characterized by the efficiency comparable with the efficiency of extraction in the Soxhlet's apparatus. To extract the substances, the mixture of components to be separated is brought in contact with gaseous extractant (CO_2) at the critical temperature and pressure. The supercritical medium as a solvent possesses the advantages of gases (high diffusion coefficient, rather low viscosity) and liquid solvents (high density and dissolving ability). The dissolving ability of the fluid may be altered by varying pressure and temperature, which allows one to obtain the fractions enriched with various components. An indisputable advantage of this method is the ease of solvent removal at low temperatures, which does not cause the loss of unstable analytes [55, 56].

Liquid extraction under pressure involves PAH extraction from the solid sample by the solvent at increased pressure (10–20 MPa) at high temperature (50–200 °C). Increased solvent temperature accelerates extraction and causes an increase in the degree of substance recovery from the samples under analysis, while increased pressure keeps the solvent in the liquid state [2, 59].

Extraction by hot water (above 100 °C) under pressure allows one to extract lipophilic organic compounds including PAH. This method does not require the use of organic solvents, which makes it more ecological in comparison with other extraction methods [57].

Among all the methods presented, the most available method is ultrasonic extraction with organic solvents. In [60], we determined PAH content in coal from the Kedrovsko-Krokholevskoye deposit of the Kuznetsk coal basin using various organic solvents (hexane, dichloromethane, toluene) as extractants. Benz(a)pyrene was detected in coal samples. Its concentration was 0.003–0.005 mg/kg in hexane extracts and 0.018–0.032 mg/kg for extraction with dichloromethane and toluene. The maximal concentrations in coal samples were detected for phenanthrene: its content was an order of magnitude higher in comparison with other compounds.

Development of the scientific foundations and practical methods for the isolation of PAHs from black coal of the Kuzbass and investigation of the distribution of the representatives of this group of carcinogenic compounds in the region is an urgent direction necessary for the prediction of carcinogenic danger from coal mining, transportation and processing, in particular for the evaluation of the possible degree of global ecological danger for the region.

The investigation was carried out with financial support from RFBR and the Department of Education and Science of the Kemerovo Region within the framework of research project No. 20-45-420020/20.

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