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# Determination of Polycyclic Aromatic Hydrocarbons in Coal from the Kuznetsk Coal Basin by Means of GC/MS and GC/GC-FID

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## Abstract

Results of the investigation of polycyclic aromatic hydrocarbons (PAHs) content in fine coal powders prepared according to a special procedure within size classes (-0.2+0.1) mm, (-0.1+0.063) mm, (-0.063+0.04) mm, (-0.04) mm for ten different coal ranks (B, D, G, Zh, K, KS, OS, SS, T, A) from the Kuznetsk coal basin are presented. The qualitative and quantitative PAHs content in coal samples was determined by means of GC-MS using a SCION SQ SELECT instrument (Bruker, USA). The maximal ∑14 PAHs content is observed for A rank coal (224.3 mg/kg), KS (201.9 mg/kg) and T (197.8 mg/kg), and the minimal ∑14 PAHs content is detected for B rank (2.2 mg/kg) for the size fraction (-0.04) mm. The concentration of benz(a)pyrene, which is a strong carcinogen, is within the range of 0.026–103.1 mg/kg in coal samples under investigation. At the same time, the fraction of benz(a)pyrene is less than 45% of the total amount of detected PAHs, and it is less stable to the effect of the environment than other PAHs. The most stable component in PAHs series is phenanthrene, which was detected in the series of studied coal samples of different fractions (0.061–43.7 mg/kg). Phenanthrene may be considered a PAHs of priority, and it may be used as a reference compound to evaluate the influence of coal mining and processing on the environment. The group composition of hydrocarbons in coal extracts was determined by means of two-dimensional gas chromatography with flame ionization detection.

## 1. Introduction

Black coal is a solid combustible sedimentary rock formed from the residues of dead plants as a result of biochemical, physicochemical, chemical and physical alterations [1]. Due to the substantial diversity of natural conditions for coal formation, the composition and properties of fossil coal vary within broad ranges. The carbon framework, formed as a result of the metamorphism of condensed polycyclic organic compounds, includes volatile organic substances and a definite amount of mineral impurities, which form the ash during coal combustion. The concentrations of individual polycyclic aromatic hydrocarbons (PAHs) in coal depend on the nature of the initial plant material that participated in the stages of coal formation, as well as on the thermodynamic conditions of this process.

Ecological monitoring in the zones affected by the enterprises engaged in coal mining, processing and transportation encounters the problems connected with the revelation of the sources of

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environmental pollution with toxic substances. One of the major factors causing pollution of atmospheric air, surface waters and soils due to the operation of coal enterprises is coal dust, or pulverized coal, which may contain a broad range of organic compounds, such as biomarkers (hopanoids and steranes), 16 PAHs of priority, alkylated PAHs, sulfur-containing aromatic compounds, etc. In this connection, the determination of toxic organic compounds in black coal dust and in environmental objects is urgent.

Ecological studies connected with the determination of the structure of organic compounds from the organic mass of coal and those entering environmental objects with coal particles remain highly relevant. Researchers in different coal provinces of the world continue the search for marker compounds to determine the sources of environmental pollution with coal matter.

Thus, the authors of [2] report on the concentrations of total extractable hydrocarbons, 16 PAHs pollutants of priority, 27 alkylated PAHs and sulfur-containing aromatic compounds, as well as separate biomarkers (hopanoids and steranes) in 15 coal types along the metamorphism series from lignite to anthracite. Organic compounds were extracted with dichloromethane at room temperature. The total concentration of extracted hydrocarbons was varying from 8.2 to 2500 μg/g of coal (dry mass) with the maximal yield for highly volatile bituminous coal samples. PAHs concentrations were varying from 35 to 11 000 ng/g of coal (dry mass) or from 38 to 12000 ng/g of carbon and depended on coal rank, reaching a maximum for highly volatile bituminous kinds. The distribution of extractable PAHs changed depending on coal rank. The authors state that solid coal particles in the soil and sediments cannot be universally represented by a single set of diagnostic parameters. The yield of biomarkers, hopanoids and steranes also varied depending on coal rank, reaching a maximum for highly volatile bituminous coal samples, and was low in comparison with PAHs. The obtained results were used by the authors to determine the source of soil contamination because solid coal often occurs together with other sources of hydrocarbons in soils and sediments [2].

PAHs concentrations were determined in four dated cores collected from mud depocenters in the southern part of the Brazilian continental shelf since from 1925 to 2017 [3]. The total concentrations of PAHs varied from 44.69 to 305.43 ng/g and were close to each other in the analyzed cores. The historical accumulation of PAHs was connected with different periods of the development of cities in coastal regions and depicted the history of coal mining and consumption in the southern region of Brazil. The authors conclude that the relative decrease in PAH sum, observed since 1990 in the majority of cores, may be connected with a multiple decrease in the industrial use of coal, as well as with the measures that have been taken in the area of environmental regulation of coal mining and consumption [3].

The authors of [4] studied the extracts of 18 anthracite samples from the Xing-tai coal field (China) by means of gas chromatography. The chromatograms of saturated compounds reveal monomodal or bimodal contour of the peaks corresponding to n-alkanes, as a rule, from *n*-C10 to *n*-C31, which leads to two ranges of $\sum$(C1–C21)/$\sum$(C22–C34) values. The ratios pristane/*n*-C17 and phytane/*n*-C18 are similar for the majority of coal samples, while the samples with different Pr/Ph ratios could be formed as a result of different oxidation-reduction conditions during sedimentation. PAHs with higher thermodynamic stability (including 2-methylnaphthalene, 2,6- and 2,7-dimethylnaphthalenes, 2- and 3-methylphenanthrenes, 2,6- and 2,7-dimethylphenanthrenes) dominated in the samples. Dibenzothiophenes and benzonaphthothiophenes were also identified in the samples; their presence is connected with the conditions of coal formation [4].

Sulfur-containing polycyclic aromatic hydrocarbons (SPAHs) have been extensively investigated as the major source of PAHs possessing the function of biological markers and indicators of coal maturity. SPAHs content is especially high in high-sulfur coal. Coal samples with extra-high sulfur content from the Kheshan deposit (Southern China) were studied by means of gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) [5, 6]. Seventy kinds of sulfur-containing polycyclic aromatic hydrocarbons were identified. The largest value of the ratio of total SPAHs content to PAHs reached 89.22 wt.% in coal and 83.07 wt.% in sieved samples. So high SPAHs values are due to the high sulfur content, sedimentation conditions and thermal evolution of the organic matter [5, 6].

For the purpose of determining the mechanisms of lignite formation during coalification and establishing biomarkers, experiments on the sequential thermal dissolution of Baiyinhua lignite in cyclohexane, methanol and ethanol at 300 °C were carried out as described in [7]. Biomarkers detected by means of gas chromatography-mass spectrometry were divided into the following classes of compounds: *n*-alkanes, isoprenoid alkanes, *n*-alkenes, long-chain alkyl benzenes, polyarenes, *n*-alkanones, alkyl-substituted cyclopentanones, and alkyl-substituted cyclopent-2-enones.

The characteristics of the maceral composition of the extractable organic matter in coal from the Yueliangtian mine in Guizhou, Southwestern China, were analyzed using optical microscopy, gas chromatography (GC), and gas chromatography-mass spectrometry (GC-MS) [8]. Extraction was performed with methylene chloride in a Soxhlet apparatus for 36 h, and the yield of the organic matter was 1.01%. The low ratio of saturated hydrocarbon fraction to the aromatic fraction and the distribution of *n*-alkanes provide evidence that coal-forming plants are mainly terrestrial higher plants. More than 100 compounds of PAHs class were elutriated and identified, with phenanthrenes and naphthalenes comprising the major fraction. Thermodynamic stability plays an essential part in the transformations of molecular structures during coal formation, so relatively high concentrations of 2-methylnaphthalene, 2- and 3-methylphenanthrenes, 2,6- and 2,7-dimethylphenanthrenes in comparison with their corresponding isomers are detected in the extracts [8].

The authors of [9] evaluated the contributions of various anthropogenic sources of pollution to the distribution of PAHs in the coastal regions of Canada. The samples of surface sediments and cores were investigated. The samples from urban areas were detected to contain high concentrations of biomarkers (tricyclic terpane, hopane and sterane), as well as alkylfluoranthene/pyrene and benz(a)anthracene/chrysene, and the majority of initial PAHs. The ratios of these alkyl-substituted PAHs with several substituents point to the fact that the samples of sediments in the northern part of the Strait of Georgia, which is the closest to the Comox coalfield, are permanently under technogenic action of the coal matter.

Coal wastes formed as a result of mining activities at the Doru coalfield in Portugal were analyzed by means of GC-MS to identify and provide a quantitative determination of 16 PAHs compounds. The authors suppose that the organic fraction of coal wastes contain PAHs of petrogenic and pyrolytic origin. Phenanthrene, the most widespread PAHs compound, is detected in the studied samples, along with fluoranthene and pyrene. The potential impact of coal wastes on the environment is connected with the income of these PAHs into soil, sediments, ground and surface waters, and biota [10].

The authors of [10] developed and tested a GC-MS procedure for the quantitative determination of 51 alkyl-substituted and 16 non-substituted compounds of PAHs class in soil samples collected from four coal mines. Dichloromethane was used as an extragent. Results showed that the concentrations of alkylated PAHs in soil were much higher than the concentration of 16 PAHs. The average content of polycyclic aromatic compounds was 24543 μg/kg (10606–36414 μg/kg). Among then, the content of alkylated PAHs was 26810, 25090, 16301 and 7059 μg/kg, respectively, while the total average value was 18 815 μg/kg, which is 3.3 times more than the average value for 16 PAHs (5728 μg/kg). The authors state that soil contamination with alkyl-substituted PAHs is widespread in the regions of coal mining and deserves attention [11].

The distribution of 16 PAHs in coal mined in China and the factors affecting this distribution were analyzed in [12]. Results showed that the average concentration of PAHs in the samples of raw coal was 10.540±7.973 μg/g, and PAHs with low molecular mass had the largest content, comprising 44% of the total PAHs concentration. The highest 16 PAHs content was observed in bituminous coal, then in lignite, and the lowest one was detected in anthracite. Analysis of the factors shows that the content of carbon, volatile substances, the ratios H/C and O/C have a substantial effect on PAHs content in raw coal [12]. Those studies were carried out by the authors to substantiate the sources of groundwater pollution with PAHs at the territories of abandoned coal mines.

The authors of [13] carried out experiments to study the factors that affected the recovery of sixteen priority PAHs from coal samples and coal-containing argillite sampled from the Khuay-Bay coal deposit (China). Different extraction times, solvents and methods were used. The authors concluded that (1) coal composition, including H/C and O/C ratios, is an essential factor for the distribution of PAHs in coal; (2) the total amount of priority PAHs increases with an increase in extraction time; ultrasonic extraction for 30 min and extraction in Soxhlet apparatus for 24 h are suitable; (3) $CS_2$ is efficient for the recovery of low-molecular PAHs, while $CH_2Cl_2$ is more suitable for extraction of high-molecular PAHs (both compounds are excellent extraction solvents in comparison with hexane); (4) both Soxhlet and ultrasonic extraction showed similar profiles of PAH concentration, but the ultrasonic method is less efficient [13].

In the studies described in [14], the samples of atmospheric aerosol were collected at the coal burning works in Linfen (China) during the episode of severe air pollution in winter 2017. PAHs, *n*-alkanes, hopanes and steranes were identified in the samples. The diurnal level of PAHs varied within the range 0.5–1.6 $\mu g/m^3$ (1.1±0.3 $\mu g/m^3$ on average), which was 1–2 orders of magnitude higher than in other large cities in China [14].

We have demonstrated previously that coal of any rank may be the source of toxic and carcinogenic PAHs entering various environmental objects, reviewed the scientific foundations and modern practical methods of PAHs extraction from black coal, presented the data on the distribution of the representatives of this group of carcinogenic compounds [15–19], as well as on the predictions of carcinogenic danger during coal mining, transportation and processing. The granulometric and morphological composition of fine coal dust was investigated [20].

The goal of the present work was to determine the qualitative and quantitative content of PAHs class compounds in pulverized coal samples in the metamorphism series within size particle classes (-0.2+0.1) mm, (-0.1+0.063) mm, (-0.063+0.04) mm, (-0.04) mm for subsequent evaluation of the effect of coal mining, transportation and processing on environmental objects.

## 2. Experimental

### *2.1. Objects of investigation and their characterization*

The series of natural coal samples from the Kuznetsk coal basin at different stages of metamorphism from brown coal to anthracite are considered in the work. To evaluate the toxicity of fine coal systems and to determine the fraction of the most dangerous classes, coal samples under investigation were ground to the particle size classes, mm: (-0.04); (-0.063+0.04); (-0.1+0.063); (-0.2+0.1).

The data of technical, elemental and petrographic analyses of initial coal samples, the procedure of making fine coal powders, as well as the results of the investigation of their granulometric and morphological composition, are described in detail in [20].

## 3. Methods of PAHs determination in coal

### *3.1. The procedure of coal sample preparation for PAHs content determination using chromatographic methods*

The PAHs release from solid matrices is most frequently carried out using extraction with organic solvents (benzene, toluene, acetone, methanol, hexane, acetonitrile, dichloromethane, chloroform, and their mixtures) in Soxhlet apparatus or an ultrasonic bath; The methods of PAHs extraction from solid samples that can be applied to extract PAHs from coal include supercritical fluid extraction, liquid extraction under pressure, microwave extraction, extraction with hot water [21–24].

The reliability of the results of PAHs content determination in different objects depends on the sample preparation stage. It is this stage that brings the maximal error into quantitative analysis. According to the literature data, the most complete degree of PAHs recovery from solid samples is achieved with dichloromethane (DCM) used as the extragent, so it was decided to use this solvent at the current stage.

To determine the compounds of PAHs class in the samples under investigation, a weighted 1.0 g portion of coal and 20 mL of the organic solvent DCM were placed in a conical flask 50 $cm^3$ in volume, with a tight stopper, and extraction was carried out in the ultrasonic field with the working frequency of 35 kHz and power 200 W. Ultrasonic treatment was carried out at a temperature of 25–30 °C for 20 min. After that, the extract was passed through a white ribbon filter with a layer of drying agent, which was sodium sulfate ($Na_2SO_4$), 2.0–2.5 cm thick. After filtration, the extracts were purified with a chromatographic column filled with aluminium oxide $Al_2O_3$, followed by washing with 15 $cm^3$ of dichloromethane. The samples were evaporated, and the solvent was exchanged for acetonitrile (for HPLC investigation) or hexane (for GC-MS) to the final volume of 1 $cm^3$. Thus prepared extracts were stored at a temperature of – (12–20) °C.

For analysis by means of two-dimensional gas chromatography, the samples dissolved in dichloromethane were slowly evaporated after the wet salt state and then dissolved in 400 μL of carbon disulfide.

### *3.2. High performance liquid chromatography (HPLC)*

The qualitative and quantitative composition

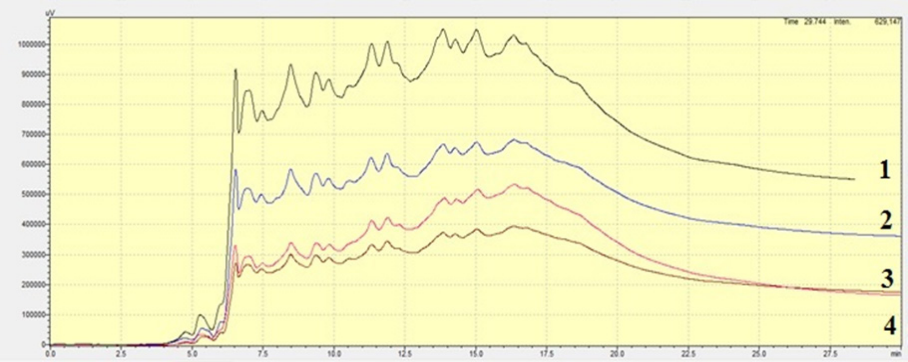


Fig. 1. Chromatograms of the coal samples of K rank with different particle size fractions, recorded by means of HPLC: 1 – (-0.04) mm; 2 – (-0.063+0.04) mm; 3 – (-0.1+0.063) mm; 4 – (-0.2+0.1) mm.

of PAHs in the organic extracts of coal samples was studied by means of HPLC using an LC-20AD Prominence instrument (Shimadzu, Japan) equipped with a spectral fluorescence detector RF-20A and a spectrophotometric detector with diode matrix SPD-M20A at the analytical column Hypersil ODS C18 10 µm (125 × 4.6 mm) under the following conditions: gradient mode; elution rate 0.8 $cm^3$/min; sample volume introduced into the chromatograph 10 $mm^3$; column temperature 40 °C.

The basic calibration solution of the components under determination was prepared from the standard samples SOP 0101-03-0117-03 (Ekokhim, St. Petersburg). Determination was carried out using the following standard PAHs compounds: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benz(b)fluoranthene, benz(k)fluoranthene, benz(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene.

PAHs identification was carried out based on absolute retention times according to calibration, with confirmation from the UV spectra, which excluded the errors in compound identification and the quantitative determination of their concentrations. The quantitative determination of PAHs was hindered as a consequence of the incomplete separation of the chromatographic peaks and matrix effects. The problem of incorrect assignment of the peaks is partially solved by using the diode matrix detector, which allows identification based on the UV spectra of the compounds to be determined. However, the reliable and highly accurate quantitative determination of PAHs in so complicated matrices remains an incompletely solved problem.

For example, one can see in the chromatogram of K rank coal samples of different particle size fractions shown in Fig. 1 that PAHs content increases with a decrease in coal particle size, but it does not appear possible to provide a quantitative determination of these compounds. This method can be used only for the qualitative determination of PAHs in coal extracts.

### *3.3. Gas chromatography-mass spectrometry*

Determination of the qualitative and quantitative composition of PAHs was carried out by means of GC-MS with a SCIONSQ SELECT instrument (Bruker, USA) with a nonpolar capillary column BR-5MS (5% diphenyl-, 95% dimethylpolysiloxane) 30 m × 0.25 mm × 0.25 µm, with a quadrupole analyzer and electron impact ionization under the following conditions: carrier gas (helium) flow rate 1 $cm^3$/min; splitless; initial column temperature and exposure time: 70 °C for 4 min; the column temperature program: heating from 70 to 210 °C at a rate of 10 °C/min, exposure at 210 °C for 4 min; heating from 210 to 260 °C at a rate of 4 °C/min; the final exposure (at a temperature of 260 °C) for 4 min; injector temperature 275 °C; interface temperature 275 °C; sample volume introduced into the column not less than 1 µL.

Scanning was performed over the ions with masses corresponding to the masses of PAH molecular ions; identification was confirmed with the help of the NIST mass spectral library (Table 1). This method provided the complete separation of the chromatographic peaks and quantitative identification of the aromatic compounds.

A chromatogram of coal samples of K rank from different particle size fractions is shown in Fig. 2. Results on the concentrations of PAHs compounds depending on the rank of coal under analysis and the grain size class are presented in Table 2 and Fig. 3.

**Table 1**

Compounds under determination and chromatographic parameters

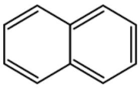
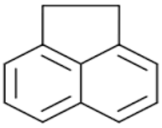
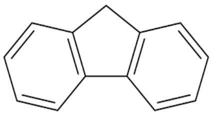
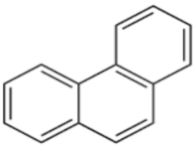
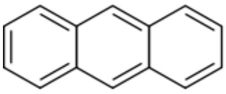
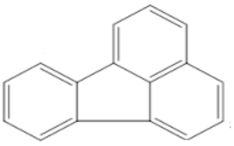
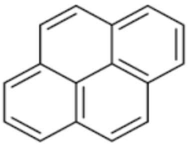
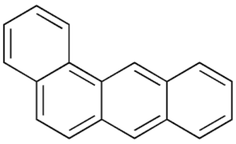
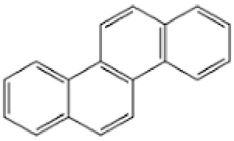
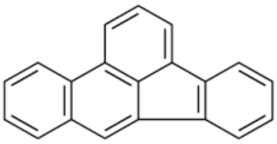
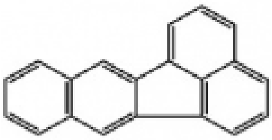
| No. | Compound | Structural formula | Basic ion, m/z | Confirmation ions, m/z | Retention time, min |
|---|---|---|---|---|---|
| 1 | Naphthalene |  | 128 | 127, 129 | 10.0 |
| 2 | Acenaphthene |  | 152 | 151, 153 | 14.3 |
| 3 | Fluorene |  | 166 | 165, 166 | 15.6 |
| 4 | Phenanthrene |  | 178 | 176, 179 | 17.9 |
| 5 | Anthracene |  | 178 | 89, 179 | 18.0 |
| 6 | Fluoranthene |  | 202 | 101, 203 | 21.9 |
| 7 | Pyrene |  | 202 | 101, 203 | 22.9 |
| 8 | Benz(a)anthracene |  | 228 | 114, 229 | 29.6 |
| 9 | Chrysene |  | 228 | 114, 229 | 29.8 |
| 10 | Benz(b)fluoranthene |  | 252 | 253, 126 | 35.4 |
| 11 | Benz(k)fluoranthene |  | 252 | 253, 125 | 35.6 |

**Table 2**

Content of PAHs compounds in coal samples from the Kuznetsk coal basin, of different grain size classes (1 – grain size class (- 0.04) mm, 2 – grain size class (-0.063+0.04) mm, 3 – grain size class (-0.1+0.063) mm, 4 – grain size class (- 0.2+0.1) mm)

| PAHs concentration, mg/kg | Coal rank | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Brown (B) | | | | Long-flame (D) | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| naphthalene | 0.91 | 1.02 | 0.44 | 0.60 | 5.15 | 6.07 | 4.27 | 5.77 |
| acenaphthene | 0.05 | 0.05 | 0.04 | 0.02 | 0.11 | 0.11 | 0.06 | 0.09 |
| fluorene | 0.00 | 0.02 | 0.01 | 0.01 | 0.71 | 0.53 | 0.35 | 0.44 |
| phenanthrene | 0.08 | 0.09 | 0.06 | 0.04 | 3.86 | 2.57 | 1.75 | 2.23 |
| anthracene | 0.00 | 0.00 | 0.00 | 0.00 | 1.14 | 0.75 | 0.46 | 0.62 |
| fluoranthene | 0.09 | 0.09 | 0.06 | 0.03 | 8.76 | 5.68 | 3.49 | 4.47 |
| pyrene | 0.50 | 0.42 | 0.29 | 0.19 | 5.54 | 3.58 | 2.04 | 2.83 |
| benz(a)anthracene | 0.13 | 0.28 | 0.23 | 0.08 | 4.93 | 3.17 | 0.21 | 1.94 |
| chrysene | 0.31 | 0.54 | 0.40 | 0.32 | 5.90 | 3.83 | 0.39 | 2.44 |
| benz(b)fluoranthene | 0.00 | 0.04 | 0.00 | 0.00 | 0.58 | 0.36 | 0.00 | 0.20 |
| benz(k)fluoranthene | 0.00 | 0.24 | 0.14 | 0.15 | 1.93 | 1.56 | 0.12 | 0.97 |
| benz(a)pyrene | 0.12 | 0.70 | 0.51 | 0.35 | 11.12 | 6.62 | 0.62 | 4.90 |
| dibenz(a,h)anthracene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| benz(g,h,i)perylene | 0.00 | 0.00 | 0.00 | 0.00 | 4.43 | 1.05 | 0.00 | 0.54 |
| ∑14PAHs | 2.20 | 3.47 | 2.18 | 1.79 | 54.15 | 35.88 | 13.76 | 27.45 |
| PAHs concentration, mg/kg | Gas (G) | | | | Fat (Zh) | | | |
| naphthalene | 112.09 | 63.62 | 28.25 | 24.41 | 15.63 | 0.14 | 0.76 | 0.46 |
| acenaphthene | 0.67 | 0.41 | 0.13 | 0.12 | 0.39 | 0.00 | 0.00 | 0.00 |
| fluorene | 1.33 | 0.57 | 0.20 | 0.19 | 1.39 | 0.01 | 0.00 | 0.02 |
| phenanthrene | 9.79 | 5.10 | 1.75 | 1.71 | 17.42 | 0.11 | 0.06 | 0.21 |
| anthracene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| fluoranthene | 1.18 | 0.86 | 0.30 | 0.33 | 2.50 | 0.04 | 0.03 | 0.12 |
| pyrene | 1.19 | 0.97 | 0.34 | 0.36 | 5.87 | 0.08 | 0.06 | 0.18 |
| benz(a)anthracene | 0.04 | 0.32 | 0.00 | 0.00 | 12.28 | 0.81 | 0.05 | 0.05 |
| chrysene | 0.05 | 1.41 | 0.02 | 0.02 | 12.24 | 1.38 | 0.22 | 0.26 |
| benz(b)fluoranthene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| benz(k)fluoranthene | 0.00 | 0.62 | 0.00 | 0.00 | 0.83 | 0.74 | 0.63 | 0.71 |
| benz(a)pyrene | 0.03 | 0.94 | 0.00 | 0.00 | 4.54 | 2.23 | 1.31 | 0.85 |
| dibenz(a,h)anthracene | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| benz(g,h,i)perylene | 0.00 | 0.00 | 0.00 | 0.00 | 0.71 | 0.11 | 0.16 | 0.00 |
| ∑14PAHs | 126.37 | 74.82 | 30.99 | 27.14 | 73.79 | 5.66 | 3.28 | 2.86 |
| PAHs concentration, mg/kg | Coke (K) | | | | Coke low-caking (KS) | | | |
| naphthalene | 2.66 | 1.29 | 0.76 | 0.49 | 28.54 | 11.59 | 4.52 | 2.90 |
| acenaphthene | 1.72 | 0.33 | 0.16 | 0.10 | 9.21 | 2.16 | 0.90 | 0.71 |
| fluorene | 3.90 | 0.77 | 0.46 | 0.25 | 9.53 | 1.77 | 0.77 | 0.60 |
| phenanthrene | 23.02 | 5.24 | 3.24 | 0.197 | 43.73 | 8.01 | 4.00 | 2.74 |
| anthracene | 3.60 | 0.77 | 0.65 | 0.41 | 4.01 | 0.72 | 0.34 | 0.24 |
| fluoranthene | 0.94 | 0.00 | 0.00 | 0.00 | 3.58 | 0.87 | 0.49 | 0.34 |
| pyrene | 2.73 | 0.93 | 0.59 | 0.35 | 8.85 | 1.77 | 1.00 | 0.70 |
| benz(a)anthracene | 1.81 | 0.74 | 0.02 | 0.00 | 26.83 | 1.82 | 1.05 | 0.91 |
| chrysene | 3.89 | 2.32 | 1.32 | 0.40 | 29.46 | 2.56 | 1.66 | 1.57 |
| benz(b)fluoranthene | 0.00 | 0.00 | 0.00 | 0.00 | 0.93 | 0.14 | 0.00 | 0.00 |
| benz(k)fluoranthene | 0.86 | 1.32 | 1.31 | 0.49 | 5.02 | 1.53 | 1.35 | 1.51 |
| benz(a)pyrene | 1.07 | 1.55 | 1.42 | 0.45 | 19.88 | 5.56 | 2.07 | 2.15 |
| dibenz(a,h)anthracene | 0.00 | 0.00 | 0.00 | 0.00 | 3.82 | 0.78 | 0.61 | 0.98 |
| benz(g,h,i)perylene | 0.00 | 0.00 | 0.11 | 0.00 | 8.48 | 1.30 | 1.30 | 2.07 |
| ∑14PAHs | 46.20 | 15.26 | 10.04 | 4.89 | 201.86 | 40.58 | 20.06 | 17.41 |

Continuation of Table 2

| PAHs concentration, mg/kg | Coal rank | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Heavy caking (OS) | | | | Low-caking (SS) | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| naphthalene | 40.34 | 15.09 | 5.79 | 1.15 | 5.38 | 0.20 | 3.99 | 0.10 |
| acenaphthene | 15.46 | 3.49 | 1.75 | 0.81 | 5.88 | 1.37 | 1.79 | 0.70 |
| fluorene | 9.79 | 1.70 | 0.87 | 0.54 | 5.95 | 1.41 | 0.93 | 0.60 |
| phenanthrene | 42.05 | 7.86 | 4.00 | 2.69 | 36.85 | 10.08 | 6.41 | 4.15 |
| anthracene | 4.42 | 0.75 | 0.36 | 0.25 | 2.48 | 0.55 | 0.31 | 0.18 |
| fluoranthene | 2.06 | 0.51 | 0.27 | 0.24 | 3.02 | 0.87 | 0.51 | 0.40 |
| pyrene | 5.39 | 1.16 | 0.62 | 0.46 | 6.13 | 1.77 | 1.05 | 0.70 |
| benz(a)anthracene | 21.16 | 5.26 | 2.60 | 1.95 | 19.74 | 6.61 | 2.10 | 1.47 |
| chrysene | 21.80 | 5.45 | 2.96 | 2.28 | 21.54 | 7.69 | 4.02 | 1.97 |
| benz(b)fluoranthene | 0.00 | 0.00 | 0.00 | 0.00 | 0.76 | 0.21 | 0.00 | 0.00 |
| benz(k)fluoranthene | 3.32 | 1.82 | 0.82 | 0.52 | 5.09 | 1.50 | 0.53 | 0.40 |
| benz(a)pyrene | 9.80 | 4.90 | 2.17 | 2.03 | 18.84 | 5.79 | 3.23 | 2.56 |
| dibenz(a,h)anthracene | 4.54 | 2.24 | 1.34 | 0.97 | 5.38 | 1.46 | 0.46 | 0.29 |
| benz(g,h,i)perylene | 6.48 | 3.19 | 1.99 | 1.52 | 16.23 | 4.79 | 1.57 | 1.15 |
| ∑14PAHs | 186.60 | 53.42 | 25.56 | 15.43 | 153.27 | 44.30 | 26.89 | 14.67 |
| PAHs concentration, mg/kg | Lean (T) | | | | Anthracite (A) | | | |
| naphthalene | 0.05 | 0.13 | 0.04 | 0.03 | 0.24 | 0.02 | 0.27 | 0.03 |
| acenaphthene | 0.12 | 0.25 | 0.04 | 0.03 | 0.88 | 0.03 | 0.00 | 0.03 |
| fluorene | 1.36 | 0.36 | 0.14 | 0.13 | 2.00 | 0.36 | 0.12 | 0.15 |
| phenanthrene | 20.74 | 4.40 | 2.17 | 2.06 | 19.20 | 5.27 | 2.38 | 1.79 |
| anthracene | 0.15 | 0.01 | 0.00 | 0.00 | 0.12 | 0.01 | 0.01 | 0.01 |
| fluoranthene | 3.46 | 0.92 | 0.45 | 0.41 | 2.99 | 0.97 | 0.45 | 0.31 |
| pyrene | 8.11 | 20.5 | 1.04 | 0.90 | 7.85 | 2.46 | 1.12 | 0.81 |
| benz(a)anthracene | 26.44 | 1.84 | 0.49 | 0.00 | 25.87 | 4.89 | 0.00 | 0.00 |
| chrysene | 35.46 | 7.99 | 2.46 | 2.07 | 37.58 | 10.14 | 3.43 | 1.78 |
| benz(b)fluoranthene | 0.41 | 0.10 | 0.00 | 0.00 | 0.42 | 0.15 | 0.06 | 0.00 |
| benz(k)fluoranthene | 1.90 | 3.94 | 4.93 | 4.34 | 2.56 | 1.02 | 5.91 | 4.96 |
| benz(a)pyrene | 85.70 | 29.64 | 13.82 | 11.25 | 103.13 | 39.65 | 17.19 | 12.37 |
| dibenz(a,h)anthracene | 3.46 | 0.72 | 0.23 | 0.00 | 4.15 | 1.90 | 0.29 | 0.00 |
| benz(g,h,i)perylene | 10.38 | 4.37 | 2.29 | 1.08 | 17.33 | 11.60 | 2.84 | 1.61 |
| ∑14PAHs | 197.76 | 56.72 | 28.08 | 22.29 | 224.31 | 78.46 | 34.06 | 23.85 |

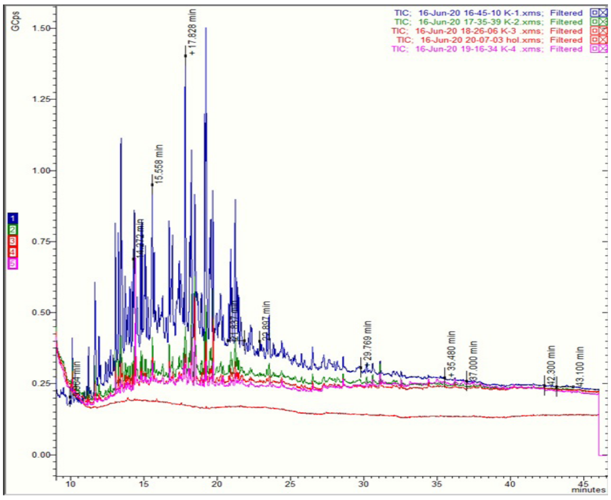


Fig. 2. Chromatograms of K rank coal samples of different size fractions, recorded by means of GC-MS: 1 – (-0.04) mm; 2 – (-0.063+0.04) mm; 3 – (-0.1+0.063) mm; 4 – (-0.2+0.1) mm.

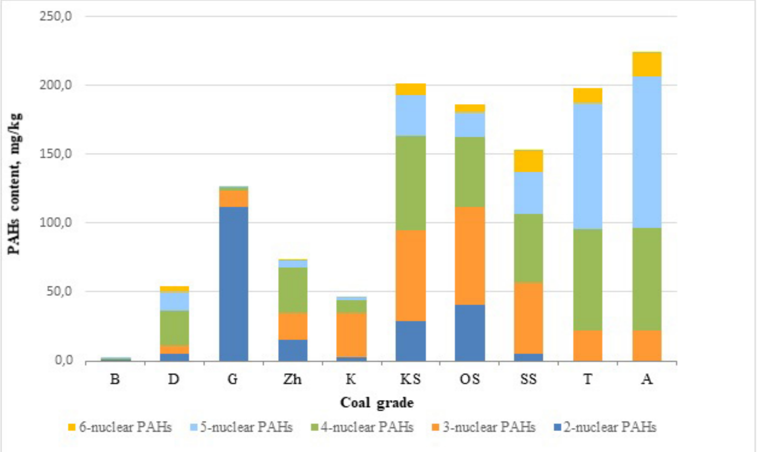


Fig. 3. PAHs content in the studied coal samples of the grain size class (-0.04) mm.

### *3.4. Two-dimensional gas chromatography*

One of the novel methods of modern chemical analysis is two-dimensional gas chromatography, which allows achieving additional possibilities, both for research tasks and for a number of practical problems, in comparison with classical one-dimensional chromatography. The mixture is separated over two parameters by using two columns with principally different phases, which provides a several times increase in the power and information content of separation. The analytical problem of the analysis of coal extracts required the application of high-temperature gas chromatography.

The application of two-dimensional gas chromatography allowed the group analysis to obtain valuable data on the content of different classes of PAHs in the samples under investigation. Unlike one-dimensional chromatography, where under definite conditions it is impossible to take account of the contribution from minor isomers and homologues of PAHs, two-dimensional chromatography allows taking into account the whole sum of PAHs belonging to a definite class. To solve the formulated analytical problem, high-temperature two-dimensional gas chromatography was used. The resolution of this method allows complete separation of different groups of compounds.

The following combination of columns was used: nonpolar first-measurement column – VF-5ht UltiMetal (5%-phenyl) 95%-polydimethylsiloxane, 30 m * 250 μm * 0.1 μm, Agilent Technologies (USA); medium-polarity second-measurement column – DB-17HT (50%-phenyl)-methylsiloxane, 5 m * 250 μm * 0.15 μm, Agilent Technologies (USA). The temperature program of separation was the same for all analyses. The starting temperature was set at 40 °C for 2 min, with subsequent temperature rise at a rate of 3 °C/min to 340 °C. Then the temperature was maintained at 340 °C for 20 min, and then the final temperature of 360 °C was reached at a rate of 3 °C/min.

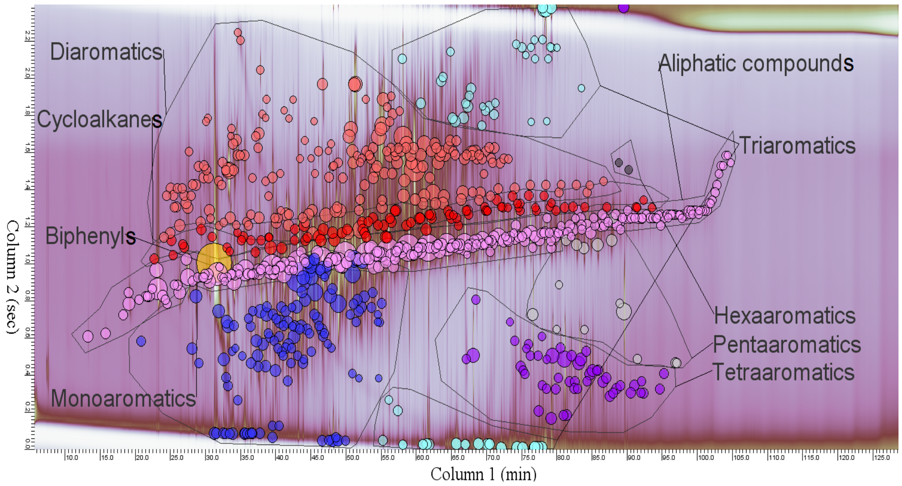


Fig. 4. Chromatogram of the sample of Zh rank coal of the grain size class (-0.04) mm recorded by means of GC/GC-FID.

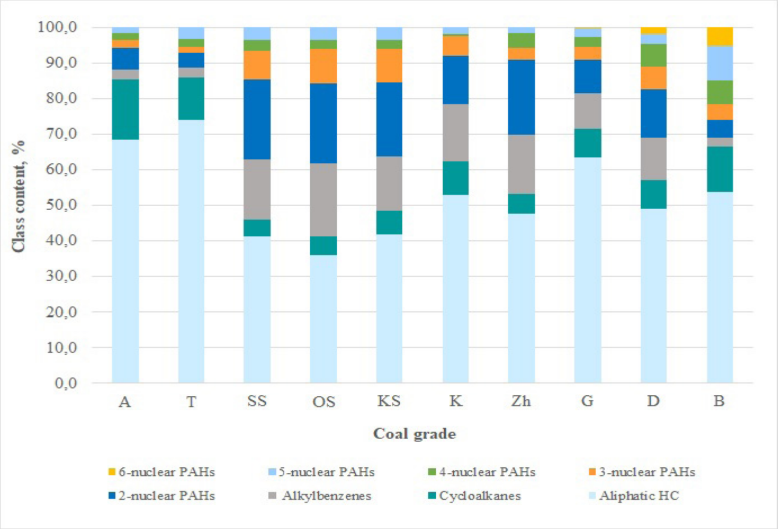


Fig. 5. Distribution of organic compounds in coal samples of different ranks for grain size class (-0.04) mm, recorded by means of GC/GC-FID.

The rates of carrier gas flows were: for the first-measurement column (He) 0.9 mL/min, for the second-measurement column ($H_2$) 35 mL/min. The modulation period was 2.4 s. The injection time was 0.1 s. Biphenyl was used as an internal standard to calculate the group composition. Per one sample, 10 μL of 0.01 g/L biphenyl solution were added.

An example of resulting separation may be seen in Fig. 4; the diagram of the distribution of organic compounds in the extracts obtained from coal samples at different metamorphism stages, of grain size class (- 0.04) mm is presented in Fig. 5.

These samples contain a broad range of PAHs (from 2-nuclear to six-nuclear PAH compounds), which poses definite limitations in choosing the analytical method because such a diversity of chemical classes of compounds may lead to a reversal effect. A Reversal occurs if a compound is retained at the second column longer than modulation time, therefore it is superimposed on the separation of previous modulations. This is why some groups under analysis turn out to be enclosed in each other.

Unfortunately, we were to make a compromise between the resolution capability and reversal of the groups under analysis, because an attempt to avoid reversal completely causes a dramatic worsening of the resolution. The method demonstrated satisfactory resolution, which allowed us to achieve the necessary results. These results are shown as diagrams in Figs. 4 and 5.

One can see in this chromatogram that the high-temperature two-dimensional gas chromatography allowed the separation of the groups of PAHs compounds from each other and from aliphatic hydrocarbons with good selectivity. The group of alkyl benzenes is located in the left lower part, and then PAHs groups follow each other (with an increase in the number of aromatic rings in the molecule) with a shift along the diagonal to the right and upward. The reversal effect takes place as described above so that the group of 2- and 6-nuclear PAHs runs across the group of aliphatic hydrocarbons. For this reason, additional efforts were necessary for the correct distinction between the classes of chemical compounds and for the correct evaluation of the relations between PAHs groups.

## 4. Conclusion

Results obtained in the investigation show that coal samples of different ranks contain polycyclic aromatic hydrocarbons, and the distribution of these compounds differs, depending on coal rank and grain size class. Hydrocarbons with large molecular mass (5- and 6-muclear PAHs) prevail in coal ranks at high degrees of metamorphism. For all coal ranks, the total content of 14 representatives of the PAHs class (∑14 PAHs) increases substantially with a decrease in the grain size class of the fraction under investigation, which is connected with an increase in the surface area of coal in contact with the extragent, that is, with more complete extraction. So, it may be assumed that coal dust with the high content of the particles of small grain size classes would be a source from which PAHs enter environmental objects.

The maximal ∑14 PAHs content is observed for coal samples of the following ranks: A (224.3 mg/kg), KS (201.9 mg/kg), and T (197.8 mg/kg), while the minimal content of ∑14 PAHs is detected in B rank (2.2 mg/kg) for the grain size class (-0.04) mm. However, these kinds of coal exhibit different kinds of PAHs distribution: for coal of A and T ranks, the prevailing compound is benz(a)pyrene, its content is 103.1 and 85.7 mg/kg, respectively, while for coal of KS rank phenanthrene dominates (43.23 mg/kg). For other coal samples, the content of ∑14 PAHs is within the range 5.66–186.6 mg/kg. The highest fluoranthene content (3.5 to 8.8 mg/kg, depending on the grain size class) was detected in coal samples of D rank, in contrast to other ranks. The maximal naphthalene content is characteristic of coal of G rank: from 24.4 for the fraction (-0.2+0.1) mm to 112.1 mg/kg for fraction (-0.04) mm. Dibenz(a,h)anthracene has been identified only in coal samples of KS, OS, SS, T, and A ranks.

The content of benz(a)pyrene, a strong carconogen, in the studied coal samples is within the range 0.026–103.1 mg/kg. At the same time, the fraction of benz(a)pyrene is less than 45% of the sum of detected PAHs, and this compound is less stable against the influence of the environment than other PAHs. The most stable structure in the PAHs series is phenanthrene, which has been detected in the series of coal samples of different fractions (0.061–43.7 mg/kg). Phenanthrene may be considered as the PAHs of priority, and it may be used as a reference compound to evaluate the impact of coal mining and processing on the environment.

A broad range of organic compounds has been identified in the studied samples by means of high-temperature two-dimensional gas chromatography (aliphatic, aromatic, polycyclic hydrocarbons, cycloalkanes), which indicated the complications connected with the use of HPLC to analyze the extracts of coal samples that are multicomponent matrices, the method is suitable only for the qualitative determination of PAHs compounds in these samples.

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