Adsorption method for determining the texture characteristics of Kuzbass fossil coals of the metamorphism series

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Abstract. The presented work is devoted to the study and development of a technique for measuring the parameters of the porous structure of fossil coals in Kuzbass by the adsorption method on an ASAP 2020 analyzer "Micromeritics". The conditions for sample preparation of samples were selected, which make it possible to record reproducible isotherms of low-temperature adsorption-desorption of nitrogen (77K) by the studied samples of fossil coal of various grades. The obtained isotherms of low-temperature adsorption-desorption of nitrogen were used to determine the textural characteristics of Kuzbass fossil coals by various methods (the specific pore surface area was calculated using the Brunauer-Emmet-Taylor (BET) method; the volume of micropores was determined using the comparative t-Plot method; the mesopore volume was determined using the method of Barrett-Joiner-Halenda (BJH). The obtained values of the textural characteristics of Kuzbass coals of the metamorphism series make it possible to reveal their macro- and microstructural features, to obtain information on the adsorption properties of coal, and can also be used to optimize coal use processes, such as the extraction of methane from coal seams, gasification, combustion, liquefaction, beneficiation, production of metallurgical coke.

1. Introduction
Fossil coal belongs to materials with a porous structure [1-3]. The structure of coals is an irregular polymer-like matrix consisting of structural elements of different nature: aromatic, aliphatic, heterocyclic fragments and carbon clusters between them [4-7]. According to the classification system of the International Union of Pure and Applied Chemistry (IUPAC), pores are usually divided into three categories: micropores (< 2 nm), mesopores (2-50 nm), macropores (> 50 nm) [8-10]. The characteristics of the pores, including their shape, size and distribution, affect the adsorption capacity of coal. Currently, more and more attention is attracted by information on the adsorption properties of coal, therefore, the study of the porous structure of coals is of great scientific importance for understanding the macro- and microstructural features of coal matter. The practical significance of these studies lies in their necessity for assessing the methane content of coal seams, for understanding the characteristics of methane migration in the pores of coal, and for optimizing coal utilization processes, such as extraction of methane from coal seams, gasification, combustion, liquefaction, enrichment, and metallurgical coke production. The amount of methane absorbed by coal under
certain conditions is associated with the physical structure of the coal substance - a highly porous natural sorbent [11-13].

To study the porous structure of coals, modern research methods are used, including gas adsorption [14], mercury porosimetry [15], small-angle neutron scattering [16] and small-angle X-ray scattering [17, 18], $^{129}$Xe NMR analysis [19]. The method of low-temperature nitrogen adsorption is widely used, which makes it possible to study nitrogen adsorption isotherms at a liquid nitrogen temperature of 77 K in the range of relative pressures from 0.005 to 0.991.

It should be noted that GOST does not exist for determining the specific surface area and parameters of the porous structure of fossil coals. According to the literature data, for the study of the porous structure of coal by the method of low-temperature nitrogen adsorption, the experimental conditions were determined by the scientists based mainly on their own experience. For example, in [2], the pore structure of medium-metamorphosed coking coal from Shanxi province (China) was analyzed and the duration of degassing at a temperature of 150 °C was 8 hours. In work [20], 27 samples of American coals were studied and degassed at 130 °C for 12 hours. Coal samples that were investigated in [21] were evacuated at 105°C for more than 6 hours. In [22], the characteristics of 24 coals were studied. Samples of lignin and low-grade bituminous coal weighing 3 g were heated to 110-120 °C for 12 hours, and samples of high-grade bituminous coal and anthracite - up to 150 °C for 12 hours. The authors of [3] investigated the porous structure of the coals of the Usinsk deposit of the Pechora coal basin and the thermal vacuum training of the samples was carried out at a temperature of 150 °C.

Different conditions for sample preparation (temperature and time of degassing) before studying the porous structure of coal, the method of low-temperature adsorption of nitrogen, necessitate the study of the effect of these conditions on the results of determining the characteristics of the pores of coal, as well as the choice of optimal experimental conditions.

In this work, the study of the parameters of the porous structure of fossil coals was carried out using analytical and research equipment - analyzer ASAP 2020 "Micromeritics". The main parameters of the porous structure are - total volume (the sum of the pore volumes of all varieties, cm$^3$/g); the limiting volume of the sorption space, which is the sum of the volumes of the sorbing pores (V$_{micro}$ + V$_{meso}$, cm$^3$/g); pore size (width, diameter, nm), which can be used to judge the adsorption properties of coal.

To determine the textural characteristics of fossil coals on the ASAP 2020 analyzer "Micromeritics", the methods for measuring the porous structure of carbon sorbents and semi-cokes, given in [23, 24], were used. However, the conditions for measuring nitrogen adsorption-desorption isotherms indicated in these works are not acceptable for studying the porous structure of fossil coals due to the high temperatures of sample preparation. In this regard, it was necessary to adapt the existing methods for measuring the parameters of the porous structure of fossil coals on this analyzer, in particular, to choose the temperature and time of preliminary preparation (drying) of the test samples, as well as the temperature of their subsequent degassing in the port of the device.

To determine the temperatures of preliminary preparation (drying) and degassing of the studied samples of fossil coals, thermogravimetric analysis was applied, carried out in an inert atmosphere in the temperature range of 20 - 900 °C with a heating rate of 10 °/min.

The analysis of the obtained thermograms showed that the loss of mass by the samples associated with the release of moisture is observed in the temperature range 70-110 °C, depending on the degree of coal metamorphism. In the temperature range of 120-200 °C, the weight loss is insignificant, and at higher temperatures (300-850 °C), the bulk of the weight loss occurs in the samples under study, due to the destruction of carbon-carbon bonds with the release of volatile products and the formation of a coke body. According to the revealed features of thermogravimetric analysis, it was accepted: drying of coal samples at a temperature of 105 ± 5 °C, and degassing in the port of the device at 110 °C.

2. Technique for measuring the parameters of the porous structure
In the presented work, the study of the parameters of the porous structure of fossil coals was carried out on an ASAP 2020 "Micromeritics" analyzer. At the first stage of the work, a sample was taken (according to GOST R ISO 18283-2010) with a particle size of 0.2 - 0.5 mm. Since, before measurement, the samples are necessarily degassed in vacuum when heated and at the same time no toxic or contaminating substances should be released, therefore the test sample must be in an air-dry state. To do this, the coal samples were dried in a drying oven at 105 ± 5 °C to constant weight.

At the next stage of the work, it was necessary to select a weighed portion of a semi-coke sample, which would make it possible to record reproducible nitrogen adsorption-desorption isotherms. According to the operating instructions for the device, the sample should be taken as follows: the minimum required amount of an unknown sample is 1 g (if the specific surface area of the sample is more than 150 m²/g, then the minimum amount is 0.2 g, if the specific surface area exceeds 300 m²/g, then the minimum amount 0.1 g); maximum amount of sample - 3 – 7 g (depending on the bulk density of the material).

According to the literature [2,3, 20-25], the specific surface area of fossil coals is no more than 10 m²/g. Therefore, in order to determine the mass of a sample of fossil coals, necessary for the registration of nitrogen adsorption-desorption isotherms, a series of measurements of the parameters of the porous structure was carried out with a sample mass m = 1.5 ± 0.1 g; 2.0 ± 0.1; 2.5 ± 0.1; 3.0 ± 0.1 g; 3.5 ± 0.1 g. As a result of the measurements, it was found that to register reproducible nitrogen adsorption-desorption isotherms and calculate reliable parameters of the porous structure, it is necessary to use a sample of coal weighing m = 3.0 ± 0.1 g.

Next, a sample of coal was weighed on an analytical balance directly in the sample ampoule intended for the study. Then the ampoule with the test sample was placed in the preliminary preparation port and degassed in vacuum at a temperature of 110 °C (the heating rate was - 10 °C/min) for 12 hours to a residual pressure of at least 5 × 10⁻³ mm Hg. (The degassing temperature was also selected based on the data of thermogravimetric analysis of fossil coal samples).

At the next stage of work, after the completion of degassing, the ampoule with the test sample was re-weighed on an analytical balance. After that, the ampoule with the test sample was installed in the measuring port of the device, and the following parameters were indicated to register the nitrogen adsorption-desorption isotherm:

- the value of the mass of the sample in the ampoule;
- interval of relative pressures: adsorption branch 0.010-0.995 with a step of 0.025, desorption branch - 0.995-0.010 with a step of 0.025;
- the need for rapid degassing and leak testing;
- pressure and time of degassing;
- measurement of free volume;
- measurement of the saturation pressure of the sample (P₀) during the analysis;
- the time to reach equilibrium is 30 seconds;
- filling the ampoule with nitrogen after measurements;
- parameters of the study report

Three parallel measurements of one sample were carried out to establish the convergence of the results. The specific surface area of the samples under study was obtained from the analysis of the adsorption-desorption isotherms of N₂ at -196 °C (77 K). The nitrogen adsorption-desorption isotherms were measured in the range of equilibrium relative vapor pressures from 10⁻¹ to 0.995 P/P₀. Then, from the nitrogen adsorption-desorption isotherms obtained by the coal samples, their textural characteristics were determined. The specific pore surface area was calculated using the Brunauer-Emmett-Taylor (BET) method. Micropore volumes were determined using the comparative t-Plot method. Mesopore volume was determined using the Barrett-Joyner-Halenda (BJH) method. The average pore diameter was estimated by the formula Dav = 4V_ads /S, according to the BET method. The mesopore volume was calculated from the mesopore size distribution (BJH method).

The measurement error is 5-7%.
We used brown coal from the Kaychakskiy open-pit mine of the Tisulsky deposit, located in the Kemerovo region. A sample of coal with a particle size of 0.2–0.5 mm was prepared from the initial coal by successive grinding and quartering and dried in air. For analytical studies, an analytical sample with a particle size of less than 0.2 mm was prepared from it. Characteristics studies were carried out in accordance with the standards ISO 602–74, 562–74 (technical analysis) and ISO 625–75 (elemental composition). The investigated characteristics of the coal from the Tisul deposit are presented in Table 1.

### 3. Results and discussion

As a result of studying the porous structure of fossil coals using an ASAP 2020 "Micromeritics" analyzer, the main parameters of their porous structure were calculated, obtained on the basis of three parallel measurements of nitrogen adsorption-desorption isotherms for each sample under study: specific pore surface area ($S_{BET}$, m$^2$/g), the total pore volume ($V_\Sigma$, cm$^3$/g), the volume of micro- ($V_{micro}$, cm$^3$/g) and mesopores ($V_{meso}$, cm$^3$/g), as well as the average pore diameter ($D_{pores}$, nm), which are presented in Table 1.

| Sample No. | Sample* | $S_{BET}$, m$^2$/g | $V_\Sigma$, cm$^3$/g | $V_{micro}$, cm$^3$/g | $V_{meso}$, cm$^3$/g | Relative content of micro - and mesopores, % | $V_{micro}/V_\Sigma$ | $V_{meso}/V_\Sigma$ | $D_{pores}$, nm |
|------------|---------|--------------------|----------------------|-----------------------|----------------------|---------------------------------------------|------------------|------------------|------------------|
| 1          | Coal of B grade | 3.1 | 0.0052 | 0.0001 | 0.0051 | 2 | 98 | 6.5 |
| 2          | Coal of LF grade | 1.35 | 0.0025 | 0.0002 | 0.0023 | 8 | 92 | 7.4 |
| 3          | Coal of G grade | 1.07 | 0.0018 | 0.0001 | 0.0017 | 5 | 94 | 6.6 |
| 4          | Coal of F grade | 0.74 | 0.0017 | 0.00001 | 0.0015 | 6 | 88 | 7.8 |
| 5          | Coal of WC grade | 0.63 | 0.00126 | 0.00005 | 0.00121 | 4 | 96 | 7.7 |
| 6          | Coal of L grade | 0.99 | 0.0015 | 0.0001 | 0.0013 | 7 | 87 | 5.9 |

**Note.** *grades of coal: B - brown, LF – long-flame, G – gas, F – fat, WC – weakly caking, L-lean*

According to the data obtained, it can be said that the formation of porous space in fossil coals of a series of metamorphism occurs mainly due to mesopores (more than 87%). The contribution of micropores to the total pore volume is practically absent (less than 8%). The highest content of mesopores (~ 98%) was determined in a sample of coal of grade “B”. In addition, there is a tendency towards a decrease in the values of the specific surface area and pore volumes of fossil coals with an increase in the degree of metamorphism to the “WC” grade coal, for the “L” grade coal there is a slight increase in both the pore volume and the specific surface area. The values of the specific surface area of the studied bituminous coals are in the range of 0.5-1.5 m$^2$/g, for brown coal the specific surface area is more than 3 m$^2$/g. It should be noted that the total pore volume, measured by the method of low-temperature nitrogen adsorption for all obtained coal samples, does not exceed 5.5 liters per ton of coal.
Figure 1 shows reproducible nitrogen adsorption-desorption isotherms by a sample of B grade coal from three parallel measurements, which confirm the correctness of the selected sample preparation conditions.

Figure 2 shows the adsorption-desorption isotherms of nitrogen for the studied fossil coals No. 1, No. 2 and No. 5. Using the obtained isotherms of low-temperature adsorption-desorption of nitrogen, using the software of the ASAP-2020 analyzer "Micromeritics", using the BJH method, the mesopore size distributions in the samples of the studied coals of the metamorphic series were calculated (Figure 3).
Adsorption isotherms characterize the porous structure of a material and make it possible to determine a number of its properties. The highest adsorption capacity for nitrogen in the region of low relative pressures is possessed by coal sample No. 1, which indicates higher values of the specific surface area in comparison with other samples. The appearance of nitrogen adsorption isotherms by samples of all fossil coals can be attributed to type IV isotherms according to the IUPAC classification [8-10], which indicates the presence of mesopores in their structure (Table 1).

It should be noted that all isotherms exhibit capillary-condensed hysteresis loops, the appearance of which can be used to judge the pore shapes and the type of porous structure of the samples under study [26]. On the presented adsorption - desorption isotherms of nitrogen by samples of fossil coals, the hysteresis loops according to the IUPAC classification can be attributed to type H3, which indicates the presence of slit-shaped pores consisting of plane-parallel particles.

![Figure 3. Distribution curves of mesopores in coal samples No. 1-6 (the numbers of distribution curves correspond to the numbers of coals in Table 1).](image)

According to the presented mesopore distribution curves (Figure 3), it can be noted that for all fossil coals the formation of the mesoporous space occurs mainly due to small mesopores with a diameter of 30-50 Å (with a maximum on the pore size distribution curves - 40 Å). Coal sample No. 1 has a wider pore size distribution due to the contribution of mesopores with a diameter of 50-80 Å, which is confirmed by the large volume of mesopores for this coal sample.

The results obtained from the study of the porous structure of fossil coals make it possible to reveal their macro- and microstructural features, as well as to obtain information on the adsorption properties of coal. This information can be used to optimize coal utilization processes, such as coal bed methane extraction, gasification, combustion, liquefaction, beneficiation, metallurgical coke production.

4. Conclusion

To determine the parameters of the porous structure of coals of a series of metamorphism by the method of low-temperature nitrogen adsorption on the ASAP 2020 "Micromeritics" analyzer, the conditions for sample preparation were selected, which make it possible to record reproducible nitrogen adsorption-desorption isotherms and to obtain the values of the texture characteristics of coals
(specific surface area, total pore volume, micro- and mesopore volume), which can be used to determine the areas of their further application.

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