# GEOLOGY

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# METHOD FOR DETERMINING THE ULTIMATE SORPTION CAPACITY OF COAL MATTER BY EPR-SPECTROSCOPY

**Purpose.** Improving the method for determining the ultimate sorption capacity of coal matter using EPR-spectroscopy (electron paramagnetic resonance) by adjusting the proportionality coefficient between the ultimate sorption capacity of coal and the concentration of paramagnetic centers and the conjugation coefficient in accordance with the degree of coalification.

**Methodology.** The ultimate sorption capacity of the matter was estimated by EPR-spectroscopy, based on the content of paramagnetic centers (PMC) in coal, which are able to come into physical (sorption) interaction with molecules of paramagnetic gas  $(O_2)$  when the pressure increases. Processing of the research results was carried out by methods of mathematical statistics.

**Findings**. Analysis of long-term results for determining the ultimate sorption capacity of coal matter by EPR-spectroscopy was carried out. The analysis testified about the need to adjust the proportionality coefficient  $\beta$  between the ultimate sorption capacity of coal and the concentration of paramagnetic centers  $N^a$  and the conjugation coefficient  $K_{sc}$ , depending on the coal rank metamorphism. The values of the proportionality coefficient  $\beta$  by hard coal ranks for the yield of volatile components  $V^{daf}$  and the reflectivity of vitrinite  $R^\circ$  were calculated. Appropriate changes were made to the express-method for estimating the ultimate sorption capacity of coal by the EPR method.

**Originality.** It is proved that the proportionality coefficient  $\beta$  between the ultimate sorption capacity of coal and the concentration of paramagnetic centers  $N^a$  and the conjugation coefficient  $K_{sc}$  is not a constant value, but changes (decreases) with the degree of metamorphism. It is established that this relationship is satisfactorily characterized by the sigmoid model, whose inflection (on the graph) is confined to the gas and fat ranks of coals (volatile-matter yield is  $\approx 29 \%$ ) and is caused by the second main jump of coalification during a cardinal change in the molecular structure of coal, associated with the completion of the intensive decomposition of the polymer-lipoidin component in the coal matter.

**Practical values.** The express-method was improved for estimating the ultimate sorption capacity of coal by the EPR-method, which differs by specified proportionality coefficients according to ranks in the series of coalification.

Keywords: coal matter, EPR-spectroscopy, concentration of paramagnetic centers, conjugation coefficient, sorption capacity

Introduction. At the present time, one of the main problems in the national economy of Ukraine is the energy supply, first of all, of its own hydrocarbon raw materials. Limited energy resources and their uneven placement in the world raised the issue of energy security to the level of the most important tasks faced by any state. A number of conditions are necessary for the successful implementation of energy independence. It includes the availability of their own resources and strategic reserves. Ukraine belongs to the number of countries in the world that have reserves of all types of energy resources (oil and gas, natural gas, coal, peat, uranium, etc.), but the degree of availability of reserves, their production, and use are not the same, and in total, they do not create the necessary level of energy security. The stable operation of the coal industry is inextricably linked with the need to solve the problem of mine methane in coal-gas fields. Methane is the main component of gases in coal fields, and since almost the entire coal-bearing strata of rocks are saturated with methane, the production of coal in coal mines during their operation and after the completion of coal-face work is

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constantly accompanied by the methane emission. The problem of coal methane combines three aspects and lies in its extraction from the depth to create a safe environment for coal production, reducing the number of harmful effluents of greenhouse gases into the atmosphere, and further utilization of methane gas as energy or chemical raw material.

Under these conditions, the study on the genesis of coal gases and the scientifically grounded perception of the processes ongoing in fossil organic matter provides an opportunity to determine the hydrocarbon (gas) potential of carbonized organic matter, and to assess the prospects for the production of coal methane, which promotes the solution in a number of social, technical and energy problems in the country.

Practical experience in the development of gas-saturated coal beds and the results of scientific research indicates the imperfection of the existing views regarding the formation of the coal-gas system. First of all, this is due to the insufficient study on the processes that take place in the system under the impact of geomechanical, technogenic, and other factors. The absence of the necessary information reduces the accuracy in the evaluation of the properties and geomechanical state of the coal bed, resulting in an increase in the volume and cost of activities necessary to enhance the security of mining operations, i.e. a significant rise in the price of energy carriers production.

Two opposing hypotheses regarding the origin of methane in coal beds prevail in the literary sources: the biogenic one, which links the methane emission with the processes of metamorphism of coal matter, and the abiogenic one, which assumes the methane flow and other gases into the coalrock massif through deep fault zones from the mantle (asthenosphere, basement).

In recent years, several new hypotheses concerning the mixed forms of methane origin were formulated. According to them, a large number of sources of hydrocarbons emergence and deposit formation mechanisms are recognized depending on the geological conditions and thermodynamic environment in the massif. According to the sedimentary-inorganic hypothesis, methane is a product of the synthesis of deep hydrogen and sedimentagenous carbon, which occurs in the surface areas of the Earth. This hypothesis allows explaining the emergence of gas and oil deposits in sedimentary rocks, because it assumes the inflow of only hydrogen from the depths of the Earth but not finished hydrocarbons, which is more realistic. Low-energy reactions, the joint of hydrogen atoms to unsaturated hydrocarbon structures (hydration), are thermodynamically permissible in the conditions of a mountain massif. According to the dualistic (abiogenic-biogenic) theory of genesis, natural gaseous hydrocarbons were formed from inorganic and organic ascending hydrocarbon substances under the impact of a deep high-temperature fluid by the harsh physical, physicochemical and geological conditions of the earth's crust.

The two latter hypotheses are compromise ones and let us explain the diversity of gas and oil fields located in sedimentary rocks. But none of the existing theories explains the change in the elemental composition of fossil organics in the coalification process, that is, does not link the loss of hydrogen by coal in the process of coalification transformations with the genesis of mine methane. Furthermore, it is difficult to explain the huge volumes of methane that are released during sudden outbursts or feeders by these theories. Therefore, the nature of coal methane, the processes of emission, migration, and accumulation of hydrocarbon gases in the coal-rock massif remain unexplained completely, and the study on the conditions and mechanisms in the formation of gaseous hydrocarbons from the solid phase remains an urgent and important task.

Despite the fact that all current models of methane formation in coal beds are phenomenological ones, they all have the right to exist and, to one degree or another, participate in the formation of gaseous hydrocarbon reserves in the coal-rock massif. Among others, the most probable assumption seems to be that methane of coal bed was formed as a result of structural transformations in the coal matter at the molecular level during coalification. In particular, according to the biogenic hypothesis, the main mass of methane in coal beds was formed in the process of regional metamorphism at the pre-inversion stage in the development of the Donetsk basin at the maximum values of temperature and pressure. The statement that a large part of methane was formed in exactly that period and has survived to the present day is based on the direct dependence of the methane content of coal on the degree of metamorphism, which corresponds to the thermodynamic conditions that existed in the mountain massif at different depths. Therefore, the most common concepts about the genesis of coal methane lie in the fact that its formation is controlled in the earth's crust by thermodynamic conditions and is directly related to the coalification process of fossil organic matter in dispersed and concentrated form. That is, the primary source of methane carbon in the entire series of metamorphism is the organic matter of coal.

Solving the problem of effective methane usage in coal fields depends on studying the conditions of its distribution in the coal-bearing strata [1]. Parameters linked to the state of the "coal-gas" system and characterizing the form and quantity of gases in coal-gas fields (natural gas content, gas capacity, gas saturation, outburst hazard of coal beds, and others) are

largely determined by the sorption properties of coal. Knowledge of the gas sorption characteristics of coal not only helps to explain the mechanism of increased extraction of methane from coal beds but also provides an important basis for simultaneous coal and gas extraction [1]. The experimental study on gas sorption provides a scientific ground for the practical evaluation of methane emission in coal beds (CBM) and CO<sub>2</sub> depositing in the coal bed [2]. In particular, the characteristics of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O adsorption play an important role in predicting the yield of CBM and the potential of geological CO<sub>2</sub> sequestration in the areas of research on methane extraction with increased CO<sub>2</sub> content and CO<sub>2</sub> binding [3].

The research on gas sorption properties of coal is conducted in all coal-mining basins of the world, in particular in the USA, Canada [4], China [5, 6], Australia [4, 7], India [2], Indonesia [8], South Africa [9], Poland [10, 11], and other countries.

It is established that the chemical composition of the adsorbent, porosity, structure of the pore space (distribution of pores by size), temperature, pressure, humidity, and the degree of coal metamorphism are the main characteristics affecting the adsorption capacity of gas in coal beds [5]. The volume of micropores is positively correlated with adsorption capacity – micropores have the largest specific area and are the main regulators of gas adsorption [6].

In work [2], it is also noted that the depth of occurrence, the molecular size of gases, relatedness of gas to coal, density, porosity, the coal rank, etc. are the main factors determining the adsorption capacity of coal. The work [4] describes the fact that the most important factors affecting the sorption capacity are also the type and content of mineral substances (ash-content), while the maceral composition of the coal matter is of limited importance.

At the same time, some researchers note the leading role of exactly the degree of coalification of the coal matter on its sorption capacity. In work [12], the dominant impact of the degree of coalification on the sorption capacity, in comparison with other factors, was estimated at 89 %; in work [13] the determining role of metamorphism, using a multiple regression model, was recorded in 86 % of the cases.

On the demand of regulatory documents in force in Ukraine, when determining the volumes of coal gases during hard coal extraction, it is obligatory to define the sorption capacity of the coal matter [14, 15]. Currently, the evaluation of sorption properties is carried out mainly by the "volumetric method". The duration of one determination reaches up to 30 days (without sample preparation), which makes such an analysis time-consuming and expensive. As a result, mass measurements of the sorption properties of the coal matter are practically not performed at coal mining enterprises. Therefore, there is an urgent need to develop a methodology for evaluating the sorption properties of coal, which is grounded on modern structural methods for researching the matter at the molecular level. To study such complex objects as hard coal, it is necessary to use appropriate physical (structural) techniques that allow you to research changes in the matter at the atomic-molecular level with the smallest deviation from the original state of the matter. The use of modern physical techniques allows conducting research at the level of constituent parts of the organic mass of coal, i.e. considering the coal matter as a set of structural elements, chemical compounds, to the interaction of which the transformation processes are reduced.

Spectrometry of the electron paramagnetic resonance is a powerful tool for obtaining information on the molecular structure and supramolecular organization of carbonaceous organic matter. Solid-state spectroscopy is based on the observation of interatomic bonds in specific compounds and is a synthesizing method that provides a causal relationship between the composition and structure of a matter and allows one to formalize its properties.

The EPR (electron paramagnetic resonance) method makes it possible to quickly determine the ultimate sorption

capacity of coal, that is, the maximum amount of gas that a solid substance can adsorb without changing its molecular and supramolecular structure.

The purpose of the research is to improve the method for determining the ultimate sorption capacity of coal matter by EPR-spectroscopy by adjusting the proportionality coefficient between the ultimate sorption capacity of coal and the concentration of paramagnetic centers and the contingency coefficient according to the degree of coalification.

Method. Coal is an extremely complex natural formation, which needs to be researched with regard to the processes of coalification, that is, changes in its structure and chemical composition over time. Research on processes of coal matter transformation at the atomic-molecular level can be effectively implemented only on the basis of fundamental ideas about the structure and properties of carbonized organic matter. In this regard, the main tasks of experimental and theoretical research on structural transformations in coal matter are to establish the interrelationships between the structure and properties of coal and to identify patterns of changes in its structural parameters during coalification by comparing the results of the research on molecular coal structure by non-destructive physical methods. According to the currently dominant energy theory, a coal bed is considered a kind of gas reservoir. The gas content of the formations and the current methane emission and other fluids are mainly explained by the sorption properties of the coal matter. But the phase state of methane in coal beds and the mechanisms of its emission in mines remain insufficiently studied. At the same time, practical experience shows that the coal-rock strata of the Donbas are saturated with methane, which, according to existing ideas, is located in the fractured-porous structure of coal in the sorbed and free states.

Information about the forms of methane presence in coal is not only scientific, but also of great practical importance, since the nature of bonds in the coal-methane system determines the stability of the system, and, therefore, the choice of the degassing procedure of coal beds and methane extraction. The research on criteria that make it possible to reliably describe the processes of coal methane sorption, as well as quantitatively estimate the kinetic parameters of interphase interaction when baric conditions change, provides an opportunity to solve a number of urgent tasks related to the reliable prediction of mining and geological conditions in coal-rock massif and methane content of coal beds, in particular.

It is believed that methane can be in a free, sorbed state or in the form of a solid solution in a coal-rock massif. That is, there are three forms of gas-solid phase interaction: adsorption (intermolecular interaction), absorption (penetration of gas molecules into a solid substance without chemical interaction with the formation of a solid solution), and chemisorption (chemical interaction of a gas and a substance). With an increase in pressure, the sorption capacity of coal increases, and decreases with an increase in temperature (at 150–200 °C it is lost). The sorption properties of coal also increase with an increase in the degree of coalification. When conducting research on sorption processes related to the gas content of coal beds and gas dynamic phenomena, they mainly mean physical sorption or adsorption, that is, the process is completely reversible within the limits of accuracy and time of a laboratory experiment.

Adsorbed gas is a single phase (a condensed layer) that has the properties of a two-dimensional gas, whose molecules are held on a solid surface accessible to sorbate molecules. As the temperature rises in the coal-gas system, the number of adsorbed molecules increases. Sorbate molecules form a sorption layer that covers the entire surface available to them.

The increase in gas concentration at the interface of two phases – gaseous (sorbate) and solid (sorbent) – occurs under the action of intermolecular forces, unbalanced on the surface of the sorbent. A field of sorption interaction is formed at the phase interface. It is believed that most of the gas in coal beds is exactly in the adsorbed state.

Despite a large number of current theories of sorption, the question about the nature of the methane-coal interaction remains open, primarily because methane is genetically related to hard coal. Moreover, due to the large heterogeneity of the coal matter, its multi-component structure, heterogeneity, and metastability, the sorption interaction in the coal-gas system must be considered in the context of the change in the state of the sorbent (coal).

The essence of the research technique by the EPR method is to register the process in the transition of the system from a stable state under normal conditions to another stable state after the disturbing action by pressure. The properties of a matter are judged by the kinetic characteristics of the coal-gas interaction process. The ultimate sorption capacity of hard coal is estimated based on the content of the matter of paramagnetic centers (PMCs) in the molecular structure, capable of coming into physical (sorption) interaction with molecules of paramagnetic gas at increased pressure.

Evaluation of the sorption capacity of coal matter by the EPR method is carried out on specially prepared coal samples made from a mine trench sample. For this purpose, mine samples are dried at a temperature not higher than 75 °C and dispersed according to granulometric grain-size classes. The grain-size class of 0.10-0.16 mm particles is chosen as a reference for conducting research and measurements, as it is the most enriched with micro components of the vitrinite group.

Previous studies have proven the decisive role of fragments of the molecular structure with conjugation systems in the formation of the sorption properties of coal. Therefore, the conjugation coefficient is one of the main parameters in the structure of coal, which characterizes the set of structural and energetic properties, as well as the peculiarities of the reactivity of cyclic structures with a system of conjugated bonds, which include all structural units with sp<sup>2</sup>-hybridization of bonds. The technique to research the sorption capacity consists of four stages: selecting coal samples and preparing samples for measurements, estimating the concentration of the paramagnetic centers, estimating the conjugation coefficient, processing the measurement results, their analysis, and calculating the ultimate sorption capacity.

**Results.** The use of physical methods of coal matter research, and, in particular, electron paramagnetic resonance (EPR), makes it possible to surely trace the consequences of the external factors impact on the structure of the matter at the atomic-molecular level. PMCs of coal are defects of the electronic structure, unpaired electrons (free radicals), and failures of system conjugate, which arise under the impact of thermal or mechanical factors.

The method of electron paramagnetic resonance (EPR-spectroscopy) is based on the effect of resonance absorption by a matter of the energy of an ultrahigh-frequency (UHF) electromagnetic field while simultaneously acting on a study sample by the constant magnetic field. The method allows studying the properties of objects at the molecular level. The ultimate sorption capacity of hard coal (Q, t/m<sup>3</sup>) is the sorption capacity of hard coal by the ultimate gas saturation pressure, at which the maximum possible physical gas-coal interaction occurs without mechanical destruction of the latter.

Earlier in 1991, the IGTM of the NASU in Ukraine developed and tested a method for determining the ultimate sorption capacity by the EPR method. The developed method of testing is an algorithm for researching the paramagnetic properties of coal in a system with gas by changing the pressure. The sorption properties of the matter are judged by the kinetic characteristics of the coal-gas interaction. The ultimate sorption capacity of a substance (Q) is estimated based on the content of paramagnetic centers (PMCs) in coal capable to come into physical (sorption) interaction with molecules of paramagnetic gas ( $O_2$ ) when the pressure is increased according to the formula

$$Q = \beta \cdot N^a \cdot K_{sc},$$

where Q is ultimate sorption capacity;  $\beta$  is the proportionality coefficient;  $N^a$  is concentration of paramagnetic centers;  $K_{sc}$  is the contingency coefficient.

During the research, the numerical value of the proportionality coefficient  $\beta$  for a specific coal field was determined as a result of a comparative analysis of the data obtained by the EPR method and the volumetric method for determining the sorption gas capacity.

The accuracy of determining the maximum sorption capacity can be affected by: mining and geological conditions (presence of tectonic disturbances), time after sampling, storage conditions of the selected material, state and composition of coal matter (reflectivity, volatile-matter yield, oxidation-recoverability), the petrographic composition of the coal sample, which should be taken into account when choosing a coefficient  $\beta$ .

Long-term experience (up to 30 years) of the practical application of the mentioned method, using a large number of measurements (about 2000), proved that the proportionality coefficient  $\beta$  is not a constant value, even within one coal field. While defining the sorption capacity of the coal matter and comparing the data of laboratory tests by different methods, including the volumetric method, it was noticed that the proportionality coefficient  $\beta$  was a variable value and significantly depended on the degree of coal coalification, which was completely consistent with the above-mentioned data of works [5, 14].

To assess the closeness of this relationship, a correlationregression analysis of the proportionality coefficient  $\beta$  and the volatile-matter yield was carried out as an indicator of the degree of metamorphism. The proportionality coefficient  $\beta$  was calculated based on the results of determining the paramagnetic characteristics (concentration of paramagnetic centers  $N^a$  and conjugation coefficient  $K_{sc}$ ) by the EPR-spectroscopy and determination of the sorption capacity by the volumetric method. Fig. 1 shows a graph of the approximation of this dependence by a straight line. The set dependence is characterized by the coefficient of determination, which is equal to 0.56. More satisfactorily, the dependence of the proportionality coefficient  $\beta$  on the volatile-matter yield is characterized by a sigmoid model, whose graph is shown in Fig. 2. For this model, the coefficient of determination is higher and is 0.64. The graphs also show confidence intervals with a significance level of 5 %. According to the experimental data, almost all points (except for two) turned out to be within the defined area.

It is worth noting that the second main jump in coalification, applied to the fifth limit of coal metamorphism, is of special scientific and practical interest, characterized by a volatile yield of 29 % and a reflectivity of  $R_{\text{max}} = 1.24$ . This stage may reflect a radical change in the molecular structure of coal, associated with the completion of intensive decomposition of the polymer-lipoidin component of coal and scattered organic matter under the action of growing thermal impact. The obtained results fully confirm the existence of a qualitative transformation of the coal substance in this range of coal transformation. The corresponding inflection in the graph (Fig. 2) proves this fact.

That is, the sigmoid model of the specified dependence is more realistic in its physical essence, which corresponds to the restructuring of the internal structure of the coal matter at this stage of coalification ( $V^{daf} \approx 29\%$ ). The gradual nature of changes in the properties of coal, linked with the restructuring of its internal structure in the process of metamorphism, is also noted in the work (Giulmaliev A. M., Golovin G. S., Gla-

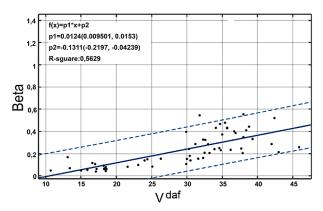


Fig. 1. Linear model of dependence of proportionality coefficient  $\beta$  on volatile-matter yield  $V^{daf}$  (95% of confidence interval is indicated by a dotted line)

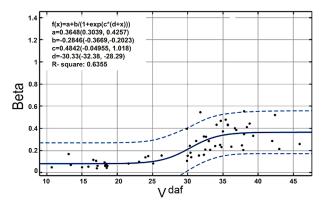


Fig. 2. Sigmoid model of the dependence of the proportionality coefficient  $\beta$  on the volatile-matter yield  $V^{daf}$  (95% of the confidence interval is indicated by a dotted line)

dun T. G., 2003), which is devoted to the research on the relationship between the structure and properties of coal. This fact was proved by the authors of the work (Giulmaliev A. M., Golovin G. S., Gladun T. G., 2003) by three different laboratory methods – based on the data of nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR), and radiography.

The results of the conducted research made it possible to improve the express-method for determining the ultimate evaluation of the sorption capacity of hard coal by the EPR spectroscopy based on new methodological solutions and many years of practical experience in using the methodology and a large amount of experimental data. The collected data allowed establishing the limits of values of the proportionality coefficient  $\beta$  on each rank of coal for the mines of the Donetsk basin. The specified values of the coefficient  $\beta$  in accordance with the indicators of volatile yield and reflectivity of vitrinite are given in the Table.

**Conclusions.** It is found that the proportionality coefficient  $\beta$  between the ultimate sorption capacity of coal and the concentration of paramagnetic centers  $N^a$  and the conjugation coefficient  $K_{sc}$  is not a constant value, but decreases with the degree of metamorphism. This relationship is characterized by a sigmoid model, the inflection on the graph of which is confined to the gas and fat ranks (29 %) and is due to the second

Table

The value of the proportionality coefficient  $\beta$  by coal ranks

Rank of coal	D	G	Zh	K	PS	Р
Indices $R^{\circ}/V^{daf}$	$\frac{0.40 - 0.80}{35 - 50}$	$\frac{0.50-1.00}{33-46}$	$\frac{0.85 - 1.20}{28 - 36}$	$\frac{1.21-1.60}{18-28}$	$\frac{1.30-1.90}{14-22}$	$\frac{1.60-2.59}{8-18}$
The proportionality coefficient, $\beta$	0.300-0.260	0.265-0.210	0.220-0.170	0.175-0.130	0.135-0.100	0.110-0.075

main jump in coalification during a cardinal change in the molecular structure of coal, connected with the completion of intensive decomposition of the polymer-lipoidin component of coal matter.

The express-methodology for estimating the ultimate sorption capacity of hard coal by the EPR technique is improved, which is characterized by refined proportionality coefficients by ranks in the range of coalification. The methodology is oriented to estimate the ultimate sorption capacity of hard coal in order to determine the volume of coal gases during coal mining, predict the emission hazard of coal beds, and estimate greenhouse gas emissions into the Earth's atmosphere.

A significant advantage of the proposed method is its rapidity and manufacturability. The duration of determining the sorption capacity of one sample does not exceed an hour, taking into account control measurements, data processing, and calculation, which results in a low cost of analysis.

Further improvement of the methodology for determining the ultimate sorption capacity of hard coal by the EPR-method in its practical application, will consist in taking into account other factors. When choosing the proportionality coefficient, it is also advisable to take into consideration, among other things, the time after sampling, mining and geological conditions (presence of tectonic disturbances), technical analysis data (oxidation-recoverability), the petrographic composition of the coal sample.

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## Методика визначення граничної сорбційної здатності вугільної речовини методом ЕПР-спектроскопії

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Мета. Удосконалення методики визначення граничної сорбційної здатності вугільної речовини методом ЕПР-спектроскопії (електронного парамагнітного резонансу) шляхом коригування коефіцієнту пропорційності між граничною сорбційною здатністю вугілля й концентрацією парамагнітних центрів і коефіцієнтом спряженості відповідно до ступеня вуглефікації.

Методика. Гранична сорбційна здатність речовини оцінювалася методом ЕПР-спектроскопії, виходячи зі вмісту у вугіллі парамагнітних центрів (ПМЦ), здатних вступати у фізичну (сорбційну) взаємодію з молекулами парамагнітного газу ( $O_2$ ) при підвищенні тиску. Обробка результатів досліджень виконувалась методами математичної статистики.

**Результати.** Проведено аналіз багаторічних результатів визначення граничної сорбційної здатності вугільної речовини методом ЕПР-спектроскопії. Аналіз засвідчив необхідність коригування коефіцієнту пропорційності  $\beta$ між граничною сорбційною здатністю вугілля й концентрацією парамагнітних центрів  $N^a$  і коефіцієнтом спряженості  $K_{sc}$  у залежності від ступеня метаморфізму вугілля. Розраховані значення коефіцієнту пропорційності  $\beta$ по марках кам'яного вугілля для показників виходу летких компонентів  $V^{daf}$  і відбивної здатності вітриніту  $R^{\circ}$ . До експрес-методики оцінки граничної сорбційної здатності кам'яного вугілля методом ЕПР внесені відповідні зміни.

Наукова новизна. Доведено, що коефіцієнт пропорційності  $\beta$  між граничною сорбційною здатністю вугілля й концентрацією парамагнітних центрів  $N^a$  і коефіцієнтом спряженості  $K_{sc}$  не є сталою величиною, а змінюється (зменшується) зі ступенем метаморфізму. Установлено, що цей зв'язок задовільно характеризується сигмоїдною моделлю, перегин на графіку якої приурочений до марок ГЖ (вихід легких речовин ≈ 29 %) та обумовлений другим основним стрибком вуглефікації під час кардинальної зміни молекулярної структури вугілля, пов'язаної із завершенням інтенсивного розпаду полімерліпоїдинової складової вугільної речовини.

Практична значимість. Удосконалена експрес-методика оцінки граничної сорбційної здатності кам'яного вугілля методом ЕПР, що відрізняється уточненими коефіцієнтами пропорційності за марками в ряду вуглефікації.

**Ключові слова:** вугільна речовина, ЕПР-спектроскопія, концентрація парамагнітних центрів, коефіцієнт спряженості, сорбційна здатність

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