Study of inertinite components by IR spectroscopy

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Abstract. The paper presents the results of a study by IR spectroscopy of inertinite concentrates isolated from humus coals of various stages of metamorphism. It was revealed that in the studied samples there is a rather significant intensity of absorption bands characteristic of aromatic structures (D3040, D1620, D900-750 cm⁻¹). To characterize the chemical maturity of inertinites, we used the parameter D3040/D2920 (the ratio of the optical densities of CH unsaturated and CH aliphatic bonds). It was found that the D3040/D2920 parameter increases with an increase in the vitrinite reflectance. The data obtained showed that the components of the inertinite group are characterized by a reduced number of aliphatic groups and a more developed spatial polyconjugation system.

1. Introduction
Fossil coals are a complex composite system consisting of organic microcomponents in the form of macerals and mineral inclusions. Organic macerals of coals are combined into three groups: gelified (vitrinite and semivitrinite), inertinite (fusinite, semifusinite), and lipoid (liptinite and alginate) [1, 2].

Coal macerals differ in chemical composition and technological properties. For example, macerals of the vitrinite group are characterized by an increased content of oxygen, inertinite - carbon, liptinite - hydrogen. A characteristic feature of vitrinite components is their ability to transform into a plastic state when heated without air access. Macerals of the inertinite group do not possess this property. Therefore, when evaluating coals used for coking, the main attention is paid to determining the amount of vitrinite and its quality indicators. For a long time, such close attention was not paid to the quality of inertinite, however, the content of this maceral in coals of various deposits ranges from 10 to 70%. For example, the content of inertinite in the coals of the Kuznetsk Basin is on average 30–40%, but sometimes it can reach a value of about 60% [1, 3]. Due to the fact that the maceral composition of coals determines their consumer value, technological and physical-mechanical properties, information on the properties of individual groups of macerals associated with the peculiarities of their molecular structure is of great importance. The current trend in the study of coals is the use of various instrumental physicochemical research methods, among which IR spectroscopy occupies a special place [4-10]. The method of IR spectroscopy has a fairly high sensitivity to the elements of the chemical structure and the manifestation of intermolecular interactions of the organic mass of coal.

This paper presents the results of studying inertinite concentrates of coal by IR spectroscopy. The task was to reveal the features of the chemical structure inherent in inertinite.

2. Results and discussion
Inertinite concentrates from coals of various stages of metamorphosis were isolated by visual selection of opaque ingredients with their subsequent layering in a mixture of carbon tetrachloride and benzene with a density of 1.40 and 1.45 g/cm³. For the study, a fraction of 1.40 - 1.45 g/cm³ was selected, since the largest amount of inertinite (fusinized components) is concentrated in it [1, 3, 11]. The obtained samples for research were crushed to a particle size of less than 0.2 mm and then dried for 2 hours at a temperature of 105 °C.

The technical analysis of the isolated fractions was carried out using standard methods. The composition of organic matter was determined by elemental analysis. Petrographic analysis was carried out on an automated complex for assessing the grade composition of coals of the SIAMS-620 system (Russia) in an oil immersion environment. The microcomponents were counted automatically at a magnification of 300 times in reflected light.

IR spectra were recorded in the range 4000-550 cm⁻¹ with a resolution of 4 cm⁻¹ using an Infralum FT-08 IR - Fourier spectrometer (Simex) equipped with a diffuse reflection attachment. When studying the structure of such complex objects as fossil coals, the use of the diffuse reflection method allows obtaining additional information through the use of samples in a minimally disturbed state. The IR spectra were processed using the software supplied with the spectrometer. The calculated optical densities of the bands were normalized to the 1460 cm–¹ band [12, 13].

The characteristics of the studied inertinite concentrates are shown in Tables 1 and 2.

| Sample code | Petrographic parameters, % | Vitrinite reflection index | Metamorphism stage |
|-------------|----------------------------|----------------------------|-------------------|
| Vt | St | I | ∑LC | Ro, % | σRo |
| 74 | 30 | 4 | 66 | 69 | 0.61 | 0.045 | I |
| 69 | 31 | 7 | 62 | 67 | 0.85 | 0.101 | II-III |
| 50 | 23 | 14 | 63 | 73 | 1.00 | 0.121 | III |
| 36 | 17 | 14 | 69 | 78 | 1.27 | 0.249 | IV |
| 30 | 26 | 12 | 62 | 70 | 1.38 | 0.245 | IV |
| 48 | 22 | 18 | 60 | 72 | 1.60 | 0.504 | IV-V |
| 32 | 2 | 1 | 97 | 98 | 2.10 | 0.705 | V |

Analysis of the above data shows that inertinite concentrates were isolated from coal from stages I to V of metamorphism, the vitrinite reflectance index (R_o, r) in which varied from 0.6 to 2.10%. Each investigated coal sample contains more than 60% inertinite (I). The maximum content of this component is determined in sample No. 32. The ash content of inertinite components is less than 10%. With an increase in the stage of metamorphism (an increase in the R_o, r index) in the studied samples, the yield of volatiles and atomic ratios H/C and O/C decrease (Table 2).

| Sample code | Technical analysis, % | Elemental composition, % per daf | Atomic ratio |
|-------------|-----------------------|----------------------------------|--------------|
| Wdaf | Adaf | Vdaf | C | H | (O + N + S) | H/C | O/C |
| 74 | 6.6 | 8.4 | 36.9 | 77.5 | 5.2 | 17.3 | 0.81 | 0.17 |
| 69 | 1.2 | 2.5 | 27.7 | 85.1 | 4.9 | 10.0 | 0.69 | 0.09 |
| 50 | 0.5 | 8.3 | 22.5 | 89.4 | 4.6 | 6.0 | 0.62 | 0.05 |
| 36 | 0.5 | 0.8 | 21.4 | 88.6 | 4.5 | 6.9 | 0.61 | 0.06 |
| 30 | 0.5 | 1.1 | 19.6 | 89.2 | 4.2 | 6.6 | 0.57 | 0.06 |
| 48 | 1.5 | 4.9 | 16.2 | 87.9 | 3.5 | 8.6 | 0.48 | 0.07 |
| 32 | 1.0 | 9.6 | 9.7 | 90.7 | 3.2 | 6.1 | 0.42 | 0.05 |

The features of the molecular composition of the organic mass of the studied inertinite concentrates have been established by the method of IR spectral analysis. As for ordinary coals, in the IR spectra of each sample (Figure 1, Table 3), several frequency absorption regions can be distinguished, cm⁻¹:
3100-3600 - stretching vibrations of hydroxyl groups in phenols and carboxylic acids; 3100-3000 - stretching vibrations of CH-bonds of aromatic rings; 2800-2950 - stretching vibrations of CH bonds in saturated aliphatic structures; 1650 - skeletal vibrations of aromatic rings, C=O bonds in ketones, aldehydes, quinones; 1350-1470 - bending vibrations of methyl and methylene groups; 1000-1300 - vibrations of bonds in various oxygen-containing groups; 700-900 - out-of-plane deformation vibrations of Car-H bonds. However, the intensity of the bands in the IR spectra is different. For the studied samples, a sufficiently significant intensity of absorption bands is noted, characteristic of aromatic structures (3040, 1620, 900-750 cm⁻¹), which increases with an increase in their stage of metamorphism. For example, the intensity of the absorption band in the region of 3040 cm⁻¹ increases with an increase in the vitrinite reflectance (Ro, r) (Figure 2).

Table 3. The relative intensity of the absorption bands normalized to the band at 1460 cm⁻¹

| Sample code | 3400 | 3040 | 2920 | 1620 | 1260 | 1030 | 875 | 800 | 750 |
|-------------|------|------|------|------|------|------|-----|-----|-----|
| 74          | 2.75 | 0.06 | 1.59 | 3.48 | 0.96 | 0.66 | 0.82 | 1.11 | 0.68 |
| 69          | 1.34 | 0.40 | 1.67 | 2.34 | 0.88 | 0.48 | 1.19 | 1.09 | 0.87 |
| 50          | 0.54 | 0.45 | 1.22 | 1.33 | 0.52 | 0.57 | 0.95 | 1.01 | 0.99 |
| 36          | 0.48 | 0.58 | 1.07 | 1.96 | 1.02 | 0.25 | 1.53 | 1.27 | 1.51 |
| 30          | 0.42 | 0.62 | 1.13 | 1.61 | 1.14 | 0.26 | 1.73 | 1.71 | 1.40 |
| 48          | 1.78 | 0.90 | 1.08 | 3.22 | 1.36 | 1.04 | 1.54 | 1.74 | 1.92 |
| 32          | 1.30 | 1.30 | 0.79 | 4.07 | 1.11 | 1.35 | 2.45 | 2.47 | 2.73 |

The main macromolecular structure of organic matter in coal is a combination of condensed aromatic carbon layers (the nuclear part of the structure) and chains of greater or lesser complexity that connect them (disordered part). The dimensions of each of the constituent parts of the macrostructure and its share in the determination of the general structure depend on the degree of coal metamorphism [2, 9, 14, 15]. The structural features of the inertinite group components are manifested in an increase in the D(3040)/D(2920) parameter, which reflects the development of the polyconjugation system during metamorphism and changes unidirectionally with the vitrinite reflection index (Figure 3). It can be said that the development of the polyconjugation system with an increase in the stage of metamorphism is mainly a consequence of a decrease in C-H aliphatic bonds, absorbing at 2920 cm⁻¹ and an increase in unsaturated C-H bonds of aromatic structures, the absorption band of which is in the region of 3040 cm⁻¹.
Figure 1. IR spectra of inertinite concentrates isolated from coals of various stages of metamorphism: 1 - sample No. 74; 2 - sample No. 36; 3 - sample No. 32

Figure 2. Relationship of the spectral parameter $D_{3040}$ with the vitrinite reflectance of coals

Figure 3. Dependence of the spectral parameter $D_{3040}/D_{2920}$ on the reflection index of vitrinite in coals

3. Conclusion
Analytical methods of analysis were used to characterize samples of inertinite concentrates isolated from coals of various stages of metamorphism by means of their stratification in a mixture of carbon tetrachloride and benzene with a density of 1.40-1.45 g/cm$^3$. Each investigated coal sample of contained more than 60% inertinite (I). The ash content of inertinite components is less than 10%. The structural features of inertinites were observed in IR spectra by bands with optical frequencies $D_{3040}$, $D_{2920}$, $D_{1650}$, $D_{900-700}$ cm$^{-1}$. It was determined that in the studied samples there is a rather significant intensity of absorption bands characteristic of aromatic structures (3040, 1620, 900-750 cm$^{-1}$), which increases with an increase in the stage of metamorphism. To characterize the chemical maturity of inertinites, we used the $D_{3040}/D_{2920}$ parameter (the ratio of the optical densities of CH of unsaturated and CH of aliphatic bonds), which made it possible to reveal the patterns of changes in the structural parameters of lean components in the series of metamorphism. It was found that the $D_{3040}/D_{2920}$ parameter increases with an increase in the vitrinite reflectance. The data obtained showed that the components of the inertinite group are characterized by a reduced amount of aliphatic groups and a more developed spatial system of polyconjugation of aromatic structures.

4. References

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