Comparative study of demineralized coals by IR spectroscopy

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Abstract. The article presents the results of a study of the influence of ash content of coal on the qualitative characteristics of their IR spectra. Comparative analysis of the IR spectra of the initial and demineralized bituminous coals showed that the mineral components present in their composition in the form of silicates, clay minerals, and carbonates limit the resolution of the method in the range <970 cm⁻¹, since their characteristic peaks are superimposed on the lines from organic matter of coal. Treatment of coals with mineral acids leads to a decrease in their ash content by 5-8 times, which results in an increase in the content of conventional organic matter in demineralized samples. This, in turn, leads to an increase in the optical density of absorption bands in the entire range of the study and, therefore, allows them to be identified more reliably.

1. Introduction

The current trend in the study of the structure of coals and coal products is the use of instrumental physicochemical research methods, among which IR spectroscopy occupies a special place [1-4]. Coal, as a solid, is a complex dispersed system consisting of three main parts: organic matter, moisture and mineral components, which interact to determine the overall physicochemical properties of the system [1, 5]. It should be noted that mineral components can limit the resolving power of the IR spectroscopy method, since they significantly increase the absorptivity coefficient in the samples and their characteristic reflections can be superimposed on the lines from the organic mass of coals.

The purpose of this study is to study the influence of the ash content of bituminous coals on the qualitative characteristics of their IR spectra.

2. Results and discussion

As objects of research, commercial samples of coal were used, selected according to GOST 10742-71 at coal mining enterprises of Kuzbass. Analytical samples of coals (air-dry state, particle size <0.2 mm) were studied. Technical analysis of coals was carried out using standard methods. The composition of the organic matter of the coals was determined by elemental analysis. Ash residues were obtained at 815°C according to GOST 11022-95. Microanalysis of ash-forming elements was carried out using a JSM-6390 LA “JEOL” scanning electron microscope with a JED-2300 X-ray spectrum analyzer as an analytical attachment.

IR spectra of coal samples in the form of tablets with KBr were recorded on an Infra-lum-FT-801 Fourier spectrometer in the range 550-4000 cm⁻¹. When determining the optical density of the bands, a straight line drawn between the maximum transmission in the region of 650 and 1800 cm⁻¹ was taken as the baseline. Then the optical density of the bands was normalized to the band at 1460 cm⁻¹ [6, 7].
For comparative analysis of the IR spectra, the studied coals were demineralized with mineral acids. To do this, 10 g of coal was treated with heating in a water bath (for 30 min), first with 100 ml of 10% hydrochloric acid, and then for the same time with 3% hydrofluoric acid [9]. After decantation, the carbon was transferred to a filter and washed with distilled water until neutral. Then the carbon filter was dried to constant weight in a drying oven at 60 °C. The weight loss of the samples was used to judge the amount of dissolved mineral impurities. The ash content of demineralized coals was determined by a standard method.

The characteristics of the studied samples of coals are given in Table 1. From the given data it can be seen that the original coals are high-ash. Samples No. 1 and No. 3 have the highest ash content (over 20%). According to the elemental analysis data, coal sample No. 1 is characterized by the highest atomic ratio H / C, coal samples No. 2 and No. 3 have the lowest value of this parameter.

| Coal sample code | Technical analysis, % | Elemental composition, % per daf | Atomic ratio |
|------------------|-----------------------|----------------------------------|--------------|
|                  | Wd | Ad | C  | H  | (O + N + S) | H/C | O/C |
| 1                | 1.3 | 20.6 | 88.5 | 4.8 | 6.7 | 0.65 | 0.06 |
| 1*               | 1.5 | 4.0 | 88.3 | 4.9 | 6.8 | 0.66 | 0.06 |
| 2                | 1.0 | 19.8 | 89.1 | 4.6 | 6.3 | 0.62 | 0.05 |
| 2*               | 1.5 | 2.4 | 88.8 | 4.8 | 6.5 | 0.64 | 0.05 |
| 3                | 1.1 | 20.0 | 89.9 | 4.5 | 5.6 | 0.60 | 0.05 |
| 3*               | 1.5 | 4.2 | 89.3 | 4.5 | 6.2 | 0.60 | 0.05 |

- demineralized coal samples

Treatment of coals with mineral acids led to a decrease in their ash content. Acid demineralization had the greatest effect on sample No. 2. The ash content in this sample decreased by almost 8 times and amounted to 2.4%. It should be noted that after the treatment of coals with hydrochloric and hydrofluoric acids, no significant changes are noted in the elemental composition of their organic matter. However, in samples No. 1 and No. 2, a slight increase in the H / C atomic ratio is observed at an almost unchanged O / C ratio.

It is known that mineral impurities in coals are mainly represented by clay minerals (they account for an average of 80-60% of the total amount of mineral substances contained in coals, they are represented by illite, sericite, montmorillonite, kaolinite, less often halloysite is noted); iron sulfides (pyrite, marcasite and melkovite), carbonates (calcite, siderite, dolomite, and ankerite) and quartz [9, 10]. It should be noted that the clay minerals contained in coals are hardly soluble in mineral acids. Carbonate minerals dissolve most easily in mineral acids [11, 12].

The chemical composition of the ash samples of the studied coals is shown in Table 2. It can be seen that the ash residues contain all the main compounds of ash-forming elements. At the same time, silicon dioxide predominates in the ash composition of all coals.

All coal samples are medium-alumina (Al2O3 content in ash is within 15-28%). In all samples, the Al2O3 / SiO2 ratio is rather low (0.43-0.52), therefore, it can be assumed that the mineral part in the studied coals contains large amounts of quartz and siliceous rocks compared to clayey ones. In the ash residues of coal samples No. 1 and No. 2, the ratio CaO + MgO - Fe2O3 / CaO + MgO + Fe2O3 has negative values (- 0.06 and - 0.85, respectively), which is typical for coals in which sulfide mineralization prevails over carbonate.
Table 2. Chemical analysis of the ash of the studied coal samples.

| Coal sample code | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | TiO₂ | Na₂O | K₂O | P₂O₅ | SO₃ |
|------------------|------|-------|-------|-----|-----|------|------|-----|------|-----|
| 13               | 53.7 | 22.9  | 8.3   | 5.8 | 1.5 | 1.1  | 0.7  | 1.0 | 0.3  | 4.7 |
| 13*              | 77.3 | 14.7  | 0.9   | trace | 0.1 | 4.0  | 2.4  | trace | 0.2 | < 0.1 |
| 19               | 36.2 | 18.9  | 38.3  | 1.0 | 2.0 | 0.7  | 0.6  | 0.8 | 0.7  | 0.8 |
| 19*              | 64.3 | 18.1  | 4.7   | 0.2 | 0.2 | 9.1  | 1.3  | trace | 0.7 | < 0.1 |
| 8                | 56.2 | 26.1  | 4.2   | 3.8 | 2.7 | 1.2  | 0.3  | 1.1 | 0.6  | 3.8 |
| 8*               | 80.6 | 9.1   | 2.1   | trace | 0.1 | 5.7  | 1.8  | trace | 0.2 | < 0.1 |

* - demineralized coal samples

After the treatment of coals with solutions of mineral acids in the composition of their ash residues, the content of oxides of calcium, magnesium and iron decreased significantly while the content of Al₂O₃ decreased to a lesser extent. Ash-forming silicon compounds, which are in the composition of the mineral part of all coals, did not undergo dissolution.

The results of the IR spectral analysis of the original coals and those subjected to demineralization are shown in Figures 1, 2 and 3. The IR spectra of the studied coal samples can be conditionally divided into three frequency regions <970, 970-1880 and >1880 cm⁻¹.

The first region (<970 cm⁻¹) contains vibration bands of a number of groups of aromatic, aliphatic, and naphthenic structures. These are the well-known four groups of bands of out-of-plane deformation vibrations of the C=H bonds of aromatic rings at 745-890 cm⁻¹. All the studied samples are characterized by varying intensity of vibrations of all four types of C=H groups. However, it should be noted that it is not possible to carry out a sufficiently reliable qualitative and quantitative processing of the spectra due to the partial superposition of the bands of the C=H groups of the bands caused by the vibrations of the structural elements of mineral impurities present in the coals. For example, the main absorption bands present in all spectra are rather intense bands at 1030 cm⁻¹. Since the Si – O bond is common for all silicates and clay minerals, it can be assumed that the absorption bands in the region of 1030–960 cm⁻¹ are mainly due to the stretching vibrations of Si – O [13]. Clay minerals show similar spectra to silicates, and, in addition, a band of clay minerals appears at 914 cm⁻¹, which may indicate the presence of kaolinite in coals [13].

After demineralization in the IR spectra of all coals, the intensity of the band at 1030 cm⁻¹ decreases (it takes the form of a shoulder) as well as the intensity of the bands in the range of 1030-960 cm⁻¹. Consequently, in the IR spectra of coals, it is possible to clearly identify groups of bands of out-of-plane deformation vibrations of the C=H bonds of aromatic rings. In the second region (970-1880 cm⁻¹), a band can be distinguished in the range of 1160-1350 cm⁻¹ with a maximum of 1260 cm⁻¹, caused by the vibrations of oxygen-containing groups mainly phenoxy groups C=OH. The band at 1161 cm⁻¹ is due to vibrations of oxygen-containing groups, predominantly of the ether (ester) type. There are also quite intense peaks of bending vibrations in various aliphatic structures at 1380 and 1450 cm⁻¹. The band at 1613 cm⁻¹ is formed by peaks of stretching vibrations of carbon-carbon bonds in aromatic rings. In demineralized coal samples, the intensity of this band is slightly increased. The third region > 1880 cm⁻¹ is mainly associated with stretching vibrations of OH - groups at 3440 cm⁻¹. In this case, the region of stretching vibrations of CH bonds in aliphatic and naphthenic fragments (2850-2920 cm⁻¹) is clearly distinguished. Absorption in the region of 3000 - 3100 cm⁻¹ with a maximum at 3040 cm⁻¹ refers to the vibrations of aromatic CH - bonds and remains practically unchanged in demineralized coal samples.
3. Conclusion
A study of the influence of the ash content of coal on the qualitative characteristics of their IR spectra has been carried out. Comparative analysis of the IR spectra of the initial and demineralized bituminous coals showed that the mineral components present in their composition in the form of
silicates, clay minerals, and carbonates limit the resolution of the method in the range <970 cm\(^{-1}\), since their characteristic peaks are superimposed on the line from organic matter of coal. Treatment of coals with mineral acids leads to a decrease in their ash content by 5-8 times, which results in an increase in the content of conventional organic matter in demineralized samples. This, in turn, leads to an increase in the optical density of absorption bands in the entire range of the study and, therefore, allows them to be identified more reliably.

4. References

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