

Optical characteristics of water extracts from the Kuznetsk Basin coals of various metamorphic states

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A study of the optical characteristics of aqueous extracts of coals of various metamorphic states was carried out. Both the absorption and luminescence spectra show a decrease in the intensity of the recorded signals with increasing coal metamorphism. We identify UV absorption with a maximum of 202 nm as the absorption of nitrate ion and luminescence with a maximum of 440 nm with the presence of humic compounds. The clear difference in intensities opens up the possibility of quantitative estimates of soluble nitrogen (by absorption) and of humic compounds (by luminescence) in coals when analyzing aqueous extracts of coals of various metamorphic states.

Keywords: coal, metamorphism, absorption spectrum, luminescence spectrum, nitrates, humic compounds.

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Introduction

Coal is a complex mixture of chemical elements and compounds [1–3]. The main parameter defining the consumer properties of coal is the calorific value that depends on the content of the main organic components of coal C, H, O, N and S [1–5]. Coals also contain mineral components general content of which is defines as the ash content of coal [5,6]. Trace elements may distribute among the organic and mineral components of coals [3,5]. For example, uranium occurs in mineral inclusions — uranium-thorium-containing minerals (zirconium, pyrochlore, monazite, etc.) and also in the organic fraction (as metalorganic compounds). Organic elements may also bind in minerals.

After coal combustion, large part of trace elements remain in solid waste (for example, specific concentration of radioactive elements in ash is 5 to 7 times as high as in the feed coal) [3,5]. Three quarters of the annual fly ash production remain in the surface of dykes and dumps or in abandoned mines and quarries. Potential pollution of ground water poses the main environmental problem [7–10].

The previous research used the optical absorption method to find that mine water contain a large amount of nitrate ions [11]. Increase in the nitrate content in water bodies (springs) was observed near coal mining sites [11]. Environment nitrate and nitrite contamination occurring during coal mining and processing, and application of humic fertilizers produced from nitrates and nitrites calls for the development of nitrate and nitrite content control methods [12,13]. The study proposes the approach to determining these substances by optical methods when

investigating the absorption and luminescence spectra of water extracts of coals of various metamorphism grades.

Methodology

Samples and study methods

Coals with ≤ 3 mm particles from the collection of Institute of Coal Chemistry and Material Science SB RAS were examined. The coals are stored in a tightly sealed plastic container because coal has high capacity of absorbing air moisture, etc., that can affect the physical and chemical properties of specimens and validity of the research data [5]. A work coal sample was taken from them and put into a smaller plastic container in order to prepare in future work samples of water extracts for each of the coals. For the chosen work samples from a metamorphism series, there were exhaustive references to mines and proximate analysis data (see the table).

To prepare the work samples, accurately weighed coal (10 g of feed coal) was placed into a clean plastic container, 100 ml of distilled water was added and the sample was held in a sealed container in ambient conditions during several days. Water used to prepare water extracts was held in the same container at the same time.

After the hold time, absorption spectra were measured on at least 3 parallel samples of clear water from the extract filtered from coal suspension. Measurements were conducted in a quartz cell (1 cm) washed with distilled water after each measurement. Luminescence was examined in the same cell. For processing of results, the spectrum of water

Results of the proximate analysis of analytical coal samples

Sample, coal grade	Sample index	Wa, %	Ad, %	Vdaf, %
№27, grade B, Kaichaksky mine	B	11.8	10.1	53.1
№72, grade D, Kamyshansky mine, Severo-Taldinskoe deposit, bed73	D	7.6	6.2	44.5
№64, grade DG, V.D. Yalewski mine, bed 52	DG	5.7	4.7	42.6
№40, grade G, Kirov mine, Polenovsky bed	G	1.2	3.3	40.4
№15 grade Zh, Tikhov mine, bed №23	Zh	0.8	7.8	33.3
№10 grade K, „Uchastok Koksovy“, inner bed II	K	0.6	4.9	21.3

Note.: Wa — moisture of analysis sample, Ad — ash content, Vdaf — volatile yield.

used for dissolution was subtracted from the measured spectrum.

Equipment

Absorption spectra were measured in the range of 190–1400 nm (Shimadzu-3600 spectrophotometer). Absorbance D is measured in the range of 0–6 with an accuracy of 0.001. Optical absorption spectra of the samples were recorded with the optical absorption layer length (cell thickness) of 1 cm, spectral gap width of 1 nm and scanning rate of 210 nm/min.

To determine the concentration, calibration solutions were prepared from standard sodium nitrate and humic compound specimens using distilled water for dilution. Zero line was adjusted without solutions. Measurements were performed on blank (background) samples made from pure distilled water used as a diluting solution. Absorption spectrum of the solvent was subtracted from the measured spectrum to calculate the absorption spectra of the examined compound. To determine the main absorption properties, the measured spectra were plotted in coordinates: absorbance at an absorption layer thickness of 1 cm (decimal absorption coefficient in cm^{-1}), wavelength nm.

Luminescence and luminescence excitation spectra were measured using the „FLUORAT-02-PANORAMA“ spectrofluorometer. A xenon high-pressure flashlamp that provides short-pulse ($1 \mu\text{s}$) excitation was used as a light source for the analyzer. Analyzer wavelength range was 210–860 nm. The instrument contains two monochromators for luminescence excitation and recording. A part of the light was reflected from the beam-splitting plate and delivered to the light receiver of the additional reference channel that was used for luminescent channel correction. To improve the validity of results, besides the signal correction for the reference channel signal, the method of data averaging over the given number of flashlamp flashes. To perform the measurements with the maximum signal-to-noise ratio, a time interval was chosen (measuring gate) — the time during which signal intensity

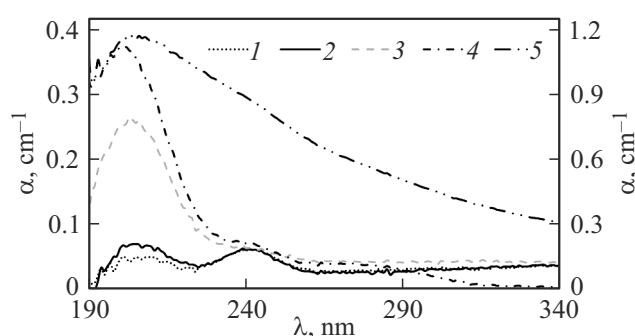


Figure 1. Absorption spectra of water extracts of coals of different metamorphism grades in 10 days after sample preparation. 1 — K; 2 — Zh; 3 — DG; 4 — D; 5 — B (right axis).

information is accumulated (measurements were performed at a gate length of $4.95 \mu\text{s}$, gate delay is $0.95 \mu\text{s}$). Since the excitation was performed to the absorption region, absorption correction was used. All measurements were performed at room temperature. Scattered radiation enters the fluorometric channel and impairs recording of weak luminescence signals, moreover, Raman scattering bands are always recorded in the water spectrum, which was considered in the spectrum analysis.

Findings

Absorption spectra, determination of nitrates

The first absorption spectrum measurement was performed after holding water extracts of samples during 10 days in sealed containers in normal conditions in a dark room (Figure 1), the second measurement was performed after holding during another 10 days (Figure 2).

Structured absorption with the peak at 202 nm (FWHM $\sim 1 \text{ eV}$) and weaker absorption with the peak at 245 nm are observed in the UV range in Figure 1 and 2. Comparison of Figures 1 and 2 shows that UV absorption with the peak at 202 nm weakly depends on the holding time, and absorption in a longer wavelength range became almost

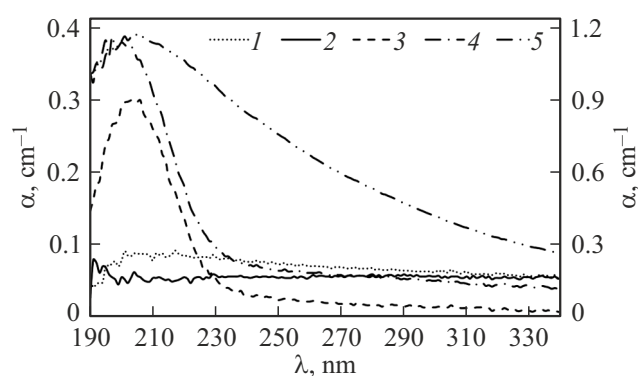


Figure 2. Absorption spectra of water extracts of coals of various metamorphism grades in 20 days after sample preparation. 1 — K; 2 — Zh; 3 — DG; 4 — D; 5 — B (right axis).

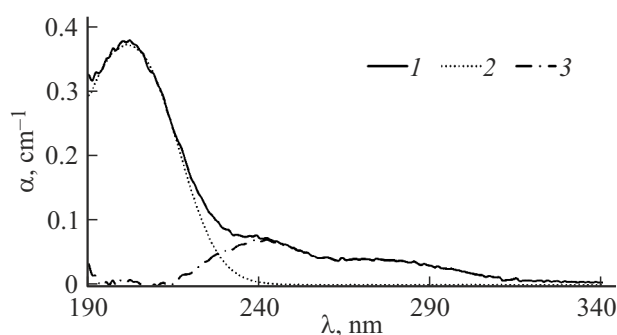


Figure 3. Absorption spectrum of the coal sample: 1 — D; 2 — sodium nitrate with a concentration of 2.4 mg/l; 3 — difference spectrum, where non-identified absorption bands 245 and 275 nm are recorded.

unstructured and is not outlined against the increasing scattering background.

Figure 3 shows the absorption spectrum of sample D after 10-day holding, absorption spectrum of the sodium nitrate standard with a concentration of 2.4 mg/l NO_3^- and spectra difference. Absorption with a peak at 202 nm in the water extract of sample D can be definitely assigned to absorption of nitrate ion with a concentration of 2.4 mg/l [12,13]. It should be emphasized that the ion nitrate concentration indirectly contains information on the concentration of soluble metal nitrates that are active in the absorption spectra.

The difference spectrum (Figure 3) contains bands with absorption peaks at 245 and 275 nm similar to those observed in samples Zh and K (Figure 1), that are not reliably identified and are probably driven by the presence of soluble aromatic compounds in the samples [2,11].

Optical absorption spectra taking into account the molar absorption coefficient were used to define the concentration of NO_3^- in water extracts and to calculate the nitrate ion concentrations to the soluble nitrogen concentration in coal samples of various metamorphism grades. The soluble nitrogen concentrations were compared with the nitrogen

concentrations defined by the elementary analysis method (Figure 4) [2,3,5].

The elementary composition of coal samples was analyzed using the Flash 2000 CHNS/O automatic analyzer. Operating principle of the analyzer is based on sample combustion, combustion gases flow through an oxidation-reduction reactor system, separated in a chromatographic column and are detected by thermal conductivity. Nitrogen content was calculated to the total coal weight. Figure 4 shows the dependence of the nitrogen concentrations on the metamorphism grade in water extracts of coals determined from the optical measurements with the NO_3^- concentration calculated to N (%) and measured during the elementary analysis of coals with N (%) content in coal [5].

The data shown in Figure 4 suggests that the increase in the metamorphism grade leads to the decrease in the content of water-soluble nitrogen (probably associated with the ash part of coal) and the growth of nitrogen content that is determined during sample combustion (elementary analysis of coal and is likely assigned to its organic matrix).

For young slightly metamorphized coals, almost all nitrogen is in the form of water-soluble impurities, and for metamorphized coals, nitrogen is in the form of insoluble inclusions into the organic matrix.

luminescence, determination of humic compounds

Typical fluorescence spectrum of water is associated with dissolved organic matter (DOM) [14–16]. The water luminescence spectrum usually consists of two overlapping bands: UV bands with the peak at 300–350 nm and visible region luminescences with the peak at 400–450 nm [14–16]. The first of these bands is usually assigned in the literature to the fluorescence of protein compounds, the second emission band is mainly associated with the presence of humic compounds in water [14–17]. Humic matter (humic and fulvic acids) are assigned to the group of natural aromatic compounds with large amount of functional groups. Complex and variable composition suggests that humic substances are molecular assemblies with a wide set of properties. Humic substances have high biological activity which is attractive for production of feed additives and fertilizers [18–20].

Figure 5 shows the luminescence spectra of bidistilled and household water with excitation 254 nm. Weak luminescence typical of DOM is observed.

Figure 6 shows the luminescence excitation spectra with a peak at 440 nm and luminescence with excitation 254 nm of water extracts of coals B and Zh.

It can be seen that luminescence intensities of water extracts of samples determined by the presence of humic compounds (~ 440 nm) differ by an order of magnitude with typical drop of luminescence intensity as the metamorphism grade increases.

The following Figure 7 shows the similar results for the water extract of grade DG coal and humic compound standard. Sodium humate in solution at low concentrations

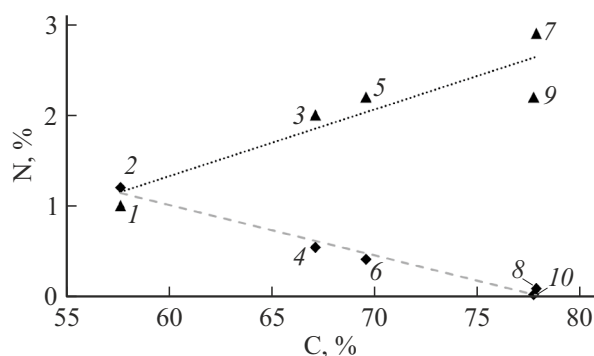


Figure 4. Nitrogen concentration (%) variation in metamorphism series B (1,2), D (3,4), DG (5,6), Zh (7,8), K (9,10): elementary analysis results (1, 3,5,7,9) and determination of water-soluble nitrogen from optical measurements (2,4,6,8,10). Concentrations in % are calculated to the total coal weight.

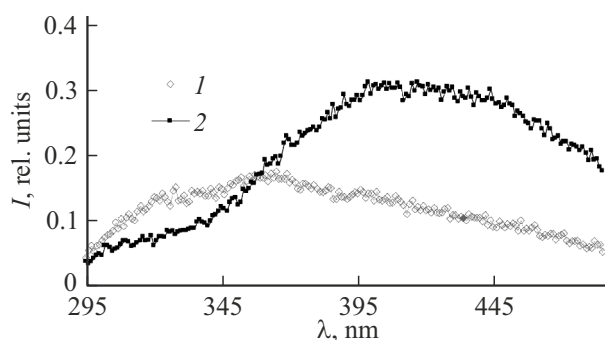


Figure 5. Luminescence spectra of bidistilled (1) and household (2) water with excitation 254 nm.

~ 10 mg/l does not produce large associates and its luminescence depends linearly on the concentration in a particular concentration range.

The observed identity of spectra (Figures 6 and 7) suggests that the recorded luminescence of water extracts is mainly attributed to the luminescence of humic compounds and in the presence of calibration spectra of humic compounds may be used to determine their concentration in coals.

Generally, the luminescence spectra of water extracts of coals show a picture identical to the absorption spectra: drop of the luminescence intensity as the metamorphism grade grows (luminescence intensity of coal (B) is higher than that of coal (Zh) by an order of magnitude).

Conclusion

The studies demonstrate visible difference in both absorption and luminescence intensities of water extracts of coals with decreasing signal intensities in the metamorphism series.

UV absorption of water extracts with high degree of reliability may be assigned to absorption of water-soluble ni-

trates with access to quantitative evaluation of water-soluble nitrogen in coal samples [12,13]. At low nitrate concentrations (~mg/l), an absorption band of NO_3^- with a peak at 202 nm, molar extinction coefficient ϵ 9540 l/mol·cm is observed in the UV range. At concentration ~ 1 g/l, a long-wavelength absorption band of NO_3^- 302 nm whose molar extinction coefficient is $\epsilon \sim 71$ l/mol·cm is reliably recorded. In the 202 nm absorption band, in the absence of other impurities that absorb in this range, nitrate ion content in water may be measured at concentrations in the range of 0.3–100 mg/l, and for the 302 nm absorption band — higher than 50 mg/l. Positions of peaks and FWHM of the NO_3^- bands are stable and weakly depend on the cation. FWHM of the 4.1 eV (302 nm) band is 0.42 eV, and of the 6.14 eV (202 nm) band is 0.94 eV. Therefore, the UV absorption spectroscopy of water solutions (extracts) is used to define reliably the concentrations of nitrate ions in water in a wide concentration range.

Similarly for nitrates, the molar extinction coefficient in the 210 nm band is 7800 l/mol·cm, and the molar extinction coefficient of NO_2^- in the 355 nm band is ~ 23 l/mol·cm. In the absence of other impurities absorbing in this range in the 210 nm band, nitrate ion content may be measured beginning from the concentrations of 0.3 mg/l to 100 mg/l, and in the 355 nm band it may be measured from 20 mg/l. However, determination of low concentrations of nitrites is a more challenging task because they are not stable compounds in water and transform into nitrates against the background of which measurements of low concentrations of nitrites is hindered due to the proximity of absorption bands, lower molar extinction coefficient and phenol absorption in the same range.

Longer wavelength weak absorption observed in the water extracts of coals with peaks at 245 and 275 nm that was not reliably identified by us may be probably associated with aromatic impurities of the anthracene coal fraction [2,3,5]. It is more strongly pronounced in the absorption of metamorphized coals when the concentration of nitrates decreases.

In the luminescence spectra of the water extracts of coals, decrease in the luminescence intensity is recorded as the metamorphism grade of coal grows. The observed luminescence with the peak at 440 nm in 254 nm excitation is defined mainly by the presence of humic compounds in the water extracts of coal, i.e. compounds of aromatic nature [14–16]. The content of water-soluble aromatics in coals decreases as the metamorphism grade grows in the same way as in water-soluble nitrates.

The observed luminescence with a peak at 440 nm may be used for quantitative determination of humic compounds in coal. Concentration of humic compounds in brown coals is an order of magnitude higher than that in coals of higher metamorphism grades, which defines the use of brown coals for production of complex granular gumate fertilizers [18–20]. Production of humic fertilizers and agents is based on the property of humic acids to form water-soluble salts (with Na^+ , K^+ , NH_4^+). Position of peaks

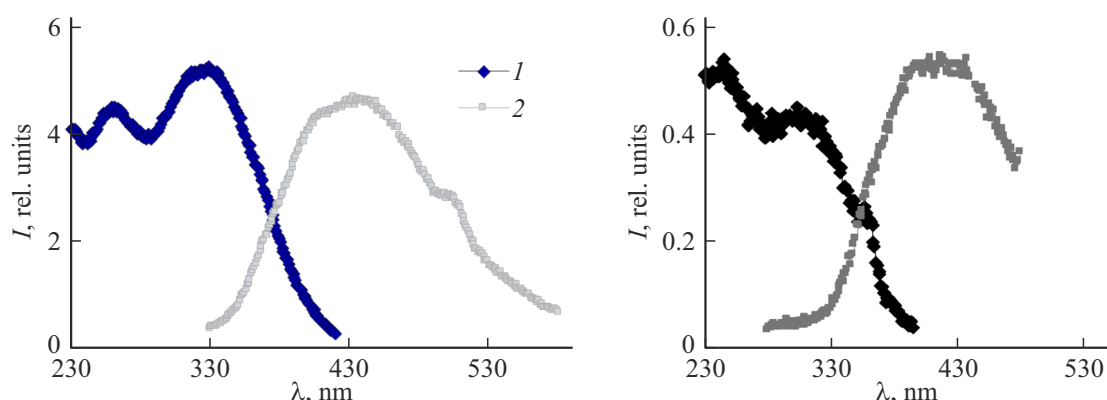


Figure 6. luminescence excitation spectra 440 nm (1) and luminescence with excitation 254 nm (2) of water extracts of grade B (left) and grade Zh (right) coals.

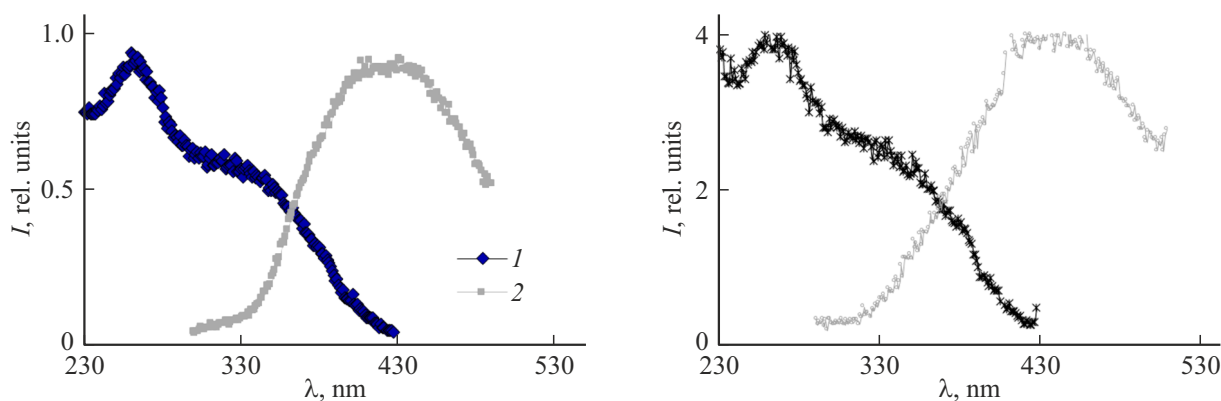


Figure 7. luminescence excitation spectra 440 nm (1) and luminescence with excitation 254 nm (2) of the water extracts of grade DG (left) coals and of humic compound standard (right).

and shapes of the fluorescence bands of humic compounds may inherently depend on their composition and probably used (with reliable calibration) for quantitative evaluations and classification of the types of humus. The work on quantitative determination of water-soluble humic salts that requires reliable standard samples is planned for future.

The experimental result (Figure 4) that shows the decrease in the water-soluble nitrogen content and growth of the insoluble nitrogen content in its organic matrix as the metamorphism grade increases in series B → Zh is the most interesting from our point of view. For slightly metamorphized coals, almost all nitrogen is in the form of water-soluble impurities, and for metamorphized coals, nitrogen is in the form of insoluble inclusions into the organic matrix.

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Conflict of interest

The authors declare that they have no conflict of interest.

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