

Luminescence of coals excited by a pulsed electron beam

I.YU. Liskov, B.P. Aduiev, G.M. Belokurov, Z.R. Ismagilov*

Federal Research Center for Coal and Coal Chemistry SB RAS, Kemerovo, Russia

**ndr999@gmail.com*

Abstract. The paper presents the spectral and kinetic characteristics of the glow of coals from the Kuznetsk basin: brown, long-flame gaseous, gaseous and coke when excited by a pulsed electron beam (240 keV, 25 ns, 20 J/cm²). The glow that occurs in coals as a result of exposure at a temperature of $T = 300$ K has a luminescent character. The glow intensity increases in 50–100 ns with a subsequent decrease in ≈ 500 ns. The luminescence spectra of coals are presented at the moment of reaching the maximum luminescence intensity. Against the background of broadband luminescence, a number of narrow bands associated with the luminescence of polycyclic aromatic hydrocarbons are observed in all coals.

Keywords: electron beam, luminescence, coal, polycyclic aromatic hydrocarbons.

1. Introduction

Coals are natural resources, and establishing the individual composition of a particular grade is a difficult task. It is known that during the combustion of coals, the so-called polycyclic aromatic hydrocarbons (PAHs) are found in the environment, most of which are carcinogens and therefore can pose a serious danger to human health [1]. In this regard, reliable methods are needed to control the presence of PAHs in various organic objects, including coals, including both detailed analysis and express methods. At present, the methods of gas chromatography (GC) [2] and high performance liquid chromatography (HPLC) [3] are mainly used to determine PAHs in organic objects and samples taken from the environment surrounding harmful production. Analytical methods for extracting individual representatives of PAHs in Kuzbass coals of various degrees of metamorphism and the environment polluted by them are presented in [4–7]. These techniques include the step of ultrasonic extraction of these compounds in various organic solvents and their analysis by HPLC. The dominant representatives of PAHs extracted from the organic part of used coals are carcinogenic benzo[a]pyrene and 3-nuclear phenanthrene [4, 5]. These methods have their own advantages and disadvantages. The main disadvantage of the above analytical methods is the need to use the preliminary isolation of the PAH fraction from complex samples. In general, this research methodology is lengthy and laborious.

The procedure for determining PAHs in the composition of coals and other compounds can be greatly simplified using measurements of the optical luminescence spectra of organic objects excited by X-rays. This method was proposed in [8, 9].

It should be noted that, at the initial stage, the authors of [8, 9] carried out the procedure for separating the studied objects in order to isolate single or several groups of PAHs and identify them by chromatography. Next, the authors used the X-Ray excited optical luminescence (XEOL) method. To do this, following the work of Shpolsky [10], an aliquot of PAH concentrate in n-heptane was frozen to a crystalline state at $T = 90$ K and XEOL was measured, in the spectra of which PAH emission lines were clearly distinguished. Comparing chromatographic measurements with XEOL measurements, the authors of [8, 9] identified the emission of individual PAH luminescence bands. If a sufficient number of such measurements are carried out, then it is possible to compile a library of PAH luminescence lines and, without further resorting to complex chromatographic measurements, identify the presence of PAHs by the XEOL method in various objects, which will significantly reduce the analysis time.

Despite the simplification of XEOL measurements relative to chromatographic methods, sample preparation in the XEOL method is, nevertheless, a relatively complex procedure, and measurements are carried out at low temperature ($T = 90$ K) [9].

To carry out studies to determine the content of PAHs in the composition of coals, it is of interest to use a powerful pulsed electron beam using a technique for recording optical luminescence spectra with a high temporal resolution. In this case, the procedure associated with sample preparation is greatly simplified in comparison with XEOL [9]. The high intensity of the electron beam will make it possible to analyze objects at room temperature. Measurement of the spectral-kinetic characteristics of the luminescence of coals in real time is of independent interest, since it provides information on the conversion of the energy introduced into the samples of coals. Such information is currently not available.

The purpose of this work is to study the spectral and amplitude-time characteristics of the emission of coals from the Kuznetsk Basin when excited by a nanosecond electron beam. In this case, special analytical preparation of the samples under study is not required. The experiments were carried out at a temperature of $T = 300$ K. When identifying the PAH luminescence bands in the luminescence spectra of the studied coal grades, the results of determining the position of the spectral bands of various PAHs obtained in [8, 9] by the XEOL method were used.

2. Samples and Method

The samples of coals of the following grades B (brown), LFG (long-flame gas), G (gas) and C (coke) were used in the experiments. The samples were ground in a ball mill and sifted through a sieve with a mesh size of $d = 63$ μm . Further, the coal was stored in a closed container without air access. The technical analysis of coals is given in Table 1. Before the experiment, using a hydraulic press, tablets of the corresponding grade of coal with a size of $\varnothing 17 \times 4$ mm were made. The density of the samples was 1.35 g/cm³.

Table 1. The results of the technical analysis of the analytical sample of coal grades B, LFG, G, K after grinding

Coal grade, deposit, particle size	Technical analysis			
	W^a , %	A^d , %	V^{daf} , %	C^{daf} , %
B , Kaychak deposit, ≤ 63 μm	10.7	9.3	51.3	61
LFG , Sokolovskoe deposit, ≤ 63 μm	4.0	4.6	40.2	79
G , Leninskoe deposit, ≤ 63 μm	2.9	26.4	38.0	81
C , Kiselevsko-Prokopyevskoye deposit, ≤ 63 μm	1.0	4.9	21.2	90

W^a – moisture content, A^d – ash content, V^{daf} – yield of combustible volatile substances, C^{daf} – carbon content.

To measure the spectral and kinetic characteristics of the luminescence of the samples, an experimental complex was used, which was described in detail in [11]. The GIN-600 electron accelerator with an effective electron energy of 240 keV, a pulse duration of $\tau \approx 25$ ns, and an energy density output to the sample of 20 J/cm² was used as a source of sample luminescence excitation. The sample was placed in the vacuum chamber of the electron accelerator at an angle of 45° to the optical axis of the recording system and 45° to the direction of the electron beam. The main elements of the recording system are the Spektr-1 polychromator coupled with the CX-1A photochronograph. The glow arising when the sample was irradiated with a single electron pulse was focused by a lens onto the entrance slit of the polychromator, unfolded into a spectrum in the form of a strip, which was projected onto the photocathode of the electron-optical converter (EOC) of the photochronograph. The latter scanned the spectrum in time in the form of a glow on the output screen of the image intensifier tube, which was read by the CCD-matrix and transferred to a computer for further processing. The file is a matrix in which the brightness of the glow at each point is proportional to the luminescence intensity at a specific wavelength at a fixed point in time. After carrying out the appropriate calibrations for the vertical elements of the matrix, it is possible to construct the luminescence spectrum of the sample at a given time, and for the horizontal elements, the kinetic regularity of the luminescence at a given wavelength. The spectral range

recorded during irradiation with a single pulse is 350–650 nm. The recorded time interval is determined by the applied sweep of the photochronograph and can vary in the range (0.5–3000) μ s.

The temporal and spectral resolutions are set by the size of the entrance slit and can reach 2 ns and 10 nm with dimensions of 0.1×0.1 mm (along mutually perpendicular axes). In our case, the minimum time resolution is determined by the duration of the electron beam pulse $\tau_i = 25$ ns.

3. Experimental results and discussion

When carrying out measurements, it turned out that under the experimental conditions ($T = 300$ K, no special sample preparation as in [8, 9]), the glow of coal samples is relatively weak even at the maximum electron beam density. To increase the intensity of the registered glow of the samples, the entrance slit of the polychromator was increased. As a result, the time resolution was 35 ns, and the spectral resolution $\Delta\lambda = 15$ nm. Kinetic dependences for all studied grades of coals have the same character. For example, Fig.1 shows the kinetic dependence of the glow of LFG grade coal under the action of an electron beam at a wavelength of $\lambda = 450$ nm.

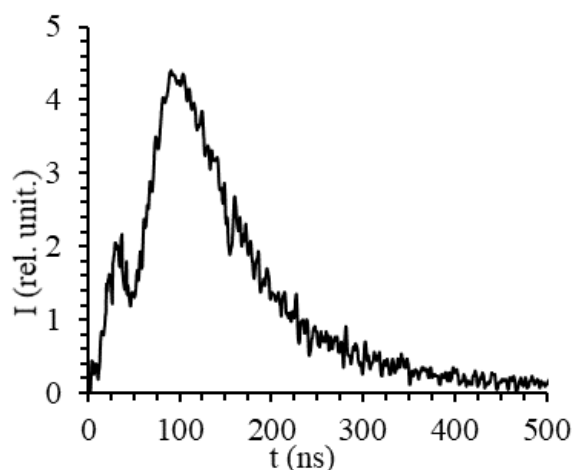


Fig.1. Kinetic dependence of the glow at a wavelength of $\lambda = 450$ nm of LFG coal under the action of an electron beam.

The luminescence spectra of samples of coals B, LFG, G and C at the moment of time corresponding to the maximum intensity of the luminescence are shown in Figs.2–5.

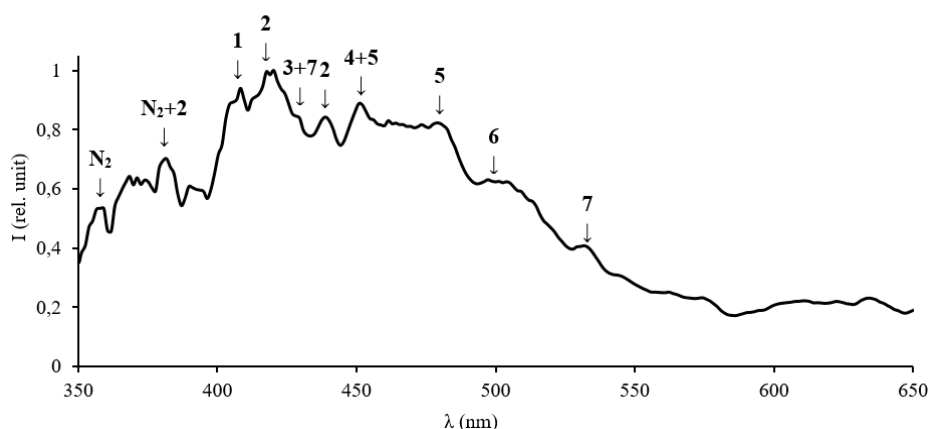


Fig.2. The luminescence spectrum of grade B coal at the time corresponding to the maximum glow intensity of 1) 1,2 benzo[a]anthracene, 2) 3,4-benz[a]pyrene (1,2-benzpyrene), 3) benz[g,h,i]perylene, 4) 3,4,8,9-dibenzpyrene, 5) perylene, 6) phenanthrene, 7) fluoranthene.

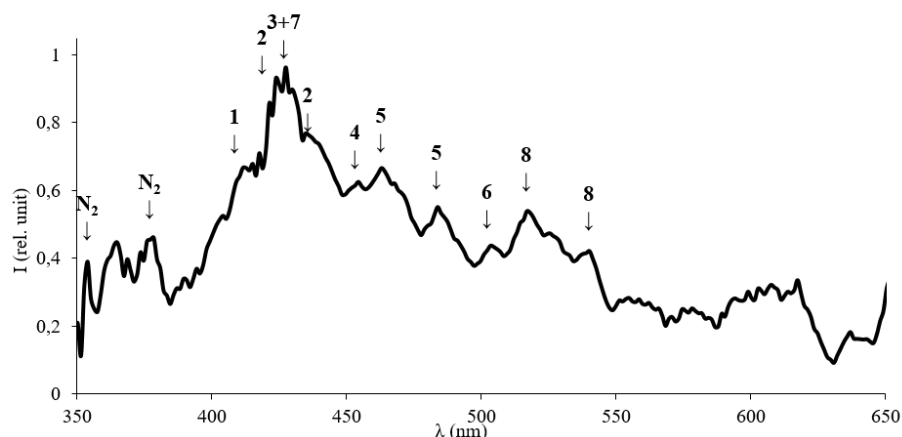


Fig.3. The luminescence spectrum of grade LFG coal at the time corresponding to the maximum glow intensity of in Fig.1. 1) 1,2 benzo[*a*]anthracene, 2) 3,4-benzo[*a*]pyrene (1,2-benzpyrene), 3) benzo[*g,h,i*]perylene, 4) 3,4,8,9-dibenzpyrene, 5) perylene, 6) phenanthrene, 7) fluoranthene, 8) 4,5-benz[*e*]pyrene.

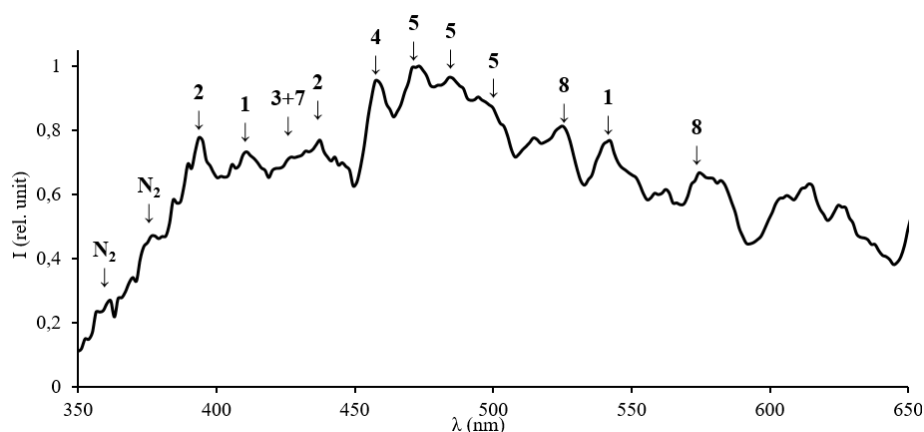


Fig.4. The luminescence spectrum of grade G coal at the time corresponding to the maximum glow intensity of 1) 1,2 benzo[*a*]anthracene, 2) 3,4-benz[*a*]pyrene (1,2-benzpyrene), 3) benz[*g,h,i*]perylene, 4) 3,4,8,9-dibenzpyrene, 5) perylene, 6) phenanthrene, 7) fluoranthene, 8) 4,5-benz[*e*]pyrene.

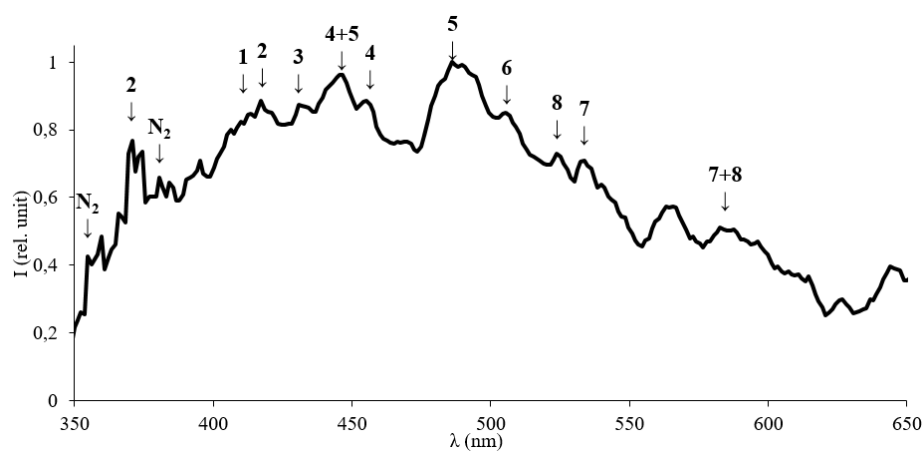


Fig.5. The luminescence spectrum of grade K coal at the time corresponding to the maximum glow intensity of 1) 1,2 benzo[*a*]anthracene, 2) 3,4-benzo[*a*]pyrene (1,2-benzpyrene), 3) benz[*g,h,i*]perylene, 4) 3,4,8,9-dibenzpyrene, 5) perylene, 6) phenanthrene, 7) fluoranthene, 8) 4,5-benz[*e*]pyrene.

At the front of the kinetic dependences of the glow in all the studied coal grades, a step can be distinguished at $t \approx 35$ ns, which coincides with the time resolution and, therefore, corresponds to the end of the electron pulse. This is followed by an increase in the intensity of the glow over time $\tau = 80\text{--}90$ ns, followed by a decrease over time <500 ns. The kinetic dependences of the glow at other wavelengths have a qualitatively similar character.

At this stage, the following interpretation of the observed kinetic dependences of the glow can be given. It is known that when non-metal compounds are excited by an electron beam, electron-hole pairs are generated at the first stage [12] (in the case of coals, these can be free electrons and positively charged radicals). Some electrons are born near the genetic partner and quickly recombine with it through an excited state with the emission of luminescence quanta already during the irradiation pulse [12]. Some of the electrons go a considerable distance from the genetic partner. In this case, diffusion of charged particles must be present for meeting and recombination, which can lead to an observed increase in the glow intensity over a time of $\sim 50\text{--}100$ ns. The decrease in luminescence in the simplest case is associated with intracenter luminescence decay.

To study the mechanism of migration and dissipation of the energy introduced by the electron beam, more detailed studies are needed, for example, the measurement of the temperature dependence of the spectral-kinetic characteristics of the luminescence of samples. Measurements of this kind are of great interest and can provide information on chemical reactions in coals that occur under the action of a pulsed electron beam, and require a separate work.

Consider the glow spectra of coals, provided in Figs.2–5. Despite the low spectral resolution, a significant number of narrow bands can be distinguished in the spectra, which are superimposed on a wide emission band. Using the information from [8, 9] obtained by the XEOL method, we identified the bands, which in Figs.2–5 are indicated by arrows with the corresponding number. The deciphering of the bands is given in the captions to the figures. In addition, general information about the detected PAHs in various coals is presented in Table 2. As follows from Figs.2–5 and Table 2, in all the studied coals, luminescence was detected under the action of an electron beam, associated with a number of PAHs, most of which are carcinogens. The discrepancy between the measured luminescence bands and the literature data $\Delta\lambda = \pm 3$ nm fits into the measurement error using the photochronograph.

Table 2. PAH emission bands

PAH	B	LFG	G	C	Literature data [8, 9]
1,2-benzo[<i>a</i>]anthracene	409	411	411	410	410
3,4-benzo[<i>a</i>]pyrene	382-391,418-	365, 420,	395, 437	370, 385-	368, 385-395, 416-420, 435-440,
(1,2-benzo[<i>a</i>]pyrene)	420, 442	435		395, 417	542, 547
benzo[<i>g,h,i</i>]perylene	427	427	427	429	427
3,4,8,9-dibenzpyrene	452	453	458	447, 454	448, 455
perylene	452, 480	470, 484	470, 484	444, 485	444, 450, 470, 475, 483
phenanthrene	497-504	503	507	507	500-515, 511
fluoranthene	535	427	428	534, 589	427, 536, 542-543, 588, 596
4,5-benzo[<i>e</i>]pyrene		540, 524	524, 574	525, 584	383, 389, 524, 540, 573, 586, 591

The broad emission bands are associated with larger organic aromatic compounds, the spectra of which were observed in [13] upon excitation of photoluminescence in coal tars.

4. Conclusions

1. Spectral and kinetic characteristics of the luminescence of coals of the Kuznetsk Basin of grades B, LFG, G, and C were measured for the first time under the influence of a pulsed electron beam.

2. The glow is characterized by an increase in intensity in the time interval of 50–100 ns and a decrease over a time of <500 ns.

3. In the luminescence spectra, a number of narrow bands associated with the luminescence of polycyclic aromatic hydrocarbons in the composition of the studied coals are superimposed on a wide band.

4. The proposed method for detecting PAHs can be used as an express method for determining the presence of PAHs in coals and other organic objects.

Acknowledgement

The work was carried out within the framework of the state task of the FRC CCC SB RAS (project 121031500513-4, supervisor Aduiev B.P.) using the equipment of the Center for Collective Use of the FRC CCC SB RAS).

5. References

- [1] Kim K.H., Jahan S.A., Kabir E., Brown R.J., *Environment international*, **60**, 71, 2013; doi: 10.1016/j.envint.2013.07.019
- [2] Krylov A., Lopushaskaia E., Alexandrova A., Konopelko L., *Analitika*, **3**(4), 06, 2012; https://www.j-analytics.ru/files/article_pdf/3/article_3270_755.pdf
- [3] Basova E.M., Ivanov V.M., *Moscow University Chemistry Bulletin*, **52**(3), 163, 2011; doi: 10.3103/S0027131411030035
- [4] Zhuravleva N.V., Potokina R.R., Ismagilov Z.R., Khabibulina E.R., *Chemistry for sustainable development*, **23**(2), 117, 2015; doi: 10.15372/KhUR20150202
- [5] Zhuravleva N.V., Khabibulina E.R., Ismagilov Z.R., Potokina R.R., Sozinov S.A., *Chemistry for sustainable development*, **24**(3), 355, 2016; doi: 10.15372/KhUR20160310
- [6] Zhuravleva N.V., Potokina R.R., Ismagilov Z.R., Khabibulina E.R., *Chemistry for sustainable development*, **22**(5), 445, 2014; https://sibran.ru/en/journals/issue.php?ID=162398&ARTICLE_ID=162399
- [7] Zhuravleva N.V., Khabibulina E.R., Ismagilov Z.R., Efimova O.S., Osokina A.A., Potokina R.R., *Chemistry for sustainable development*, **24**(4), 509, 2016; doi: 10.15372/KhUR20160411
- [8] Woo C.S., D'Silva A.P., Fassel V.A., Oestreich G.J., *Environmental Science & Technology*, **12**(2), 173, 1978; doi: 10.1021/es60138a003
- [9] Woo C.S., D'silva, A.P., Fassel, V.A., *Analytical Chemistry*, **52**(1), 159, 1980; doi: 10.1021/ac50051a037.
- [10] Shpol'Skii E.V., *Journal of Applied Spectroscopy*, **7**(4), 336, 1967; doi: 10.1007/BF00607232
- [11] Aduiev B.P., Belokurov G.M., Grechin S.S., Liskov I.Y., *Russian Journal of Physical Chemistry B*, **10**(5), 796, 2016; doi: 10.1134/S1990793116050158.
- [12] Aluker E.D., Lusi D.Y., Chernov S.A., *Electronic excitations and radioluminescence of alkali halide crystals*. (Riga: Zinatne, 1979).
- [13] Li C.Z., Wu F., Cai H.Y., Kandiyoti R., *Energy & Fuels*, **8**(5), 1039, 1994; doi: 10.1021/ef00047a006