Comparative analysis of optical properties of coals by petrography and spectroscopy methods

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Abstract. This paper reports determining the grayscale intensity of macerals in the coal lump polished sections oriented along and across the layering of three main groups of sub-bituminous, high volatile bituminous, low volatile bituminous coals. All measurements have been performed in white, red, yellow, green, blue light. The influence of all selected factors and most of their combinations on grayscale intensity is reliable; the most pronounced effects are established for the optical filter color and the maceral type. Comparative analysis of the grayscale intensity data array with the spectra of full reflectance in the visible region and the coefficient of diffuse reflection in the white light of fine powders of the same samples has been carried out. Green light yields a very dark image of vitrinite and liptinite with the grayscale intensity approaching zero. In two of the six samples, the reflectance level of inertinite in yellow light is significantly higher than the grayscale intensity of white light. This anomaly is associated with a hypsochromic shift in the inertinite maximum absorption. The approach used is an alternative method for quantifying the relative changes in reflectivity and position of the diffuse spectral minimum without applying a microspectrometer.

1. Introduction

The main indicator of the degree of metamorphism of coals is their reflectivity (R_o) [1]. This indicator depends on a series of technical, technological, and geological factors. Thus, when comparing data from 22 laboratories in 14 countries, the measurement error of 0.03–0.11 % in this indicator was revealed in one laboratory, and, in different research centers, it was 0.12–0.54 % [2].

Since the regulatory documents on the measurement of R_o recommend determining it on vitrinite in the briquettes of polished sections or polished sections of coal lumps in monochromatic incident light, it remains unclear which color of lighting is optimal in the study of not only vitrinite but although macerals. To answer this question, it is necessary to know the differences in the reflection spectra of all macerals of coals of different grades.

The task can be solved using a microspectrometer. Thus, the dispersed characteristics of some optical properties of vitrinite in a series of coals were investigated using a microscope-photometer. It has been found that the values of optical parameters for vitrinite increase towards the blue region of the visible spectrum and increase for all wavelengths due to coalification [3]. White Light Reflectance Spectrometry makes it possible to register the dispersion of R_o wavelengths, to assess significant differences in the spectra of macerals for coals of different grades. Especially informative is the ratio of the reflection coefficient of red and green wavelength in bituminite macerals [4]. However, such studies are quite rare while the necessary equipment is not widespread in petrographic laboratories. This is evidenced by the limited number of publications on this topic.

Given the complexity of the R_o measurement technology, an alternative grayscale intensity (GI) indicator was proposed earlier, the use of which simplifies and accelerates routine petrographic measurements [5]. The present study expands this concept towards color measurements.

The aim of this work is to improve the procedure of determining GI in polished sections of coal lumps on the cut and bedding surfaces based on the macerals from the three main groups (vitrinite, liptinite, inertinite) in natural incident light and by using yellow, red, blue, and green light filters.

2. Methods

As objects of research, the following samples of coals were used: sub-bituminous (SB), high-volatile bituminous (HVB), and low-volatile bituminous (LVB). For each rank, two sections of coal lumps were made with polished surfaces oriented along the cut (Across) and layering (Along).

Vitrinite (Vt), liptinite (L), and inertinite (I) were examined by reflective optical microscopy with a 20^x lens on sample surfaces. The experiments were conducted in white incident light, as well as using 4 optical filters (red, yellow, green, and blue) at the same microscope camera settings. To measure GI at micro image points, the Jmicrovision free software was used [6]. This indicator is not a complete replacement for R_o but can be considered as a quantitative assessment of the relative changes in the reflectivity of coals.

To exclude the effect of multiple comparisons in the statistical treatment of the array of data obtained on GI (26 measurements of each variant of the experiment), multifactorial linear analysis of variance (ANOVA) was used. In total, 4 factors were analyzed: Rank, Bedding, Macerals, and Color with levels corresponding to the categories of predictors. The normality of the distribution was assessed by the Shapiro-Wilk test; the homoscedasticity of the group variances was checked by the Levene criterion.

The full (diffuse and mirror) reflectance spectra of finely dispersed coal powders were obtained in the range of 400–830 nm using a Specord M40 spectrophotometer (Carl Zeiss, Jena), equipped with an integrating sphere for reflectance measurements according to a recommendation from [7]. The diffuse reflection coefficient of white light (R_{dif}) from the leveled surface of the coal powders was measured at 10 points by a pre-calibrated Reflectance Meter (ISO 2469: 1994).

3. Results and discussion

The energy of the incident beam of light on the surface of any opaque object is distributed between reflection and absorption. This is the real and imaginary part of the response due to the electronic structure of the substance [8]. Not all the electromagnetic energy of the absorbed photons is dissipated as heat. Part of it can be spent on molecular excitation followed by spontaneous radiation. However, the intensity of luminescence for coals is small. In general, the brightness of the reflected light is inversely proportional to the level of its absorption by the substance.

At an angle to the surface equal to the angle of incidence, the polished samples are dominated by the mirror component visible in the microscope. According to the optical scheme of the microscope, the light falls normally to the surface under study, and only a mirror reflection at the same angle can be observed in the eyepiece. The brightness of diffuse reflection in a conventional microscope is problematic to assess but it also characterizes the molecular structure of the substance. To measure the diffuse component, a matte non-shiny surface of the sample or fine powders is required.

The coefficient of diffuse reflection of the white light of coal powders statistically significantly increases in the process of coalification (Figure 1). In addition, in high-ranking coals, there are differences in the results of measurements along and across the layer. The influence of both factors and their combinations is reliable at the F Fisher criterion for Rank – 214.0, Bedding – 9.8, and Rank×Bedding – 6.1.

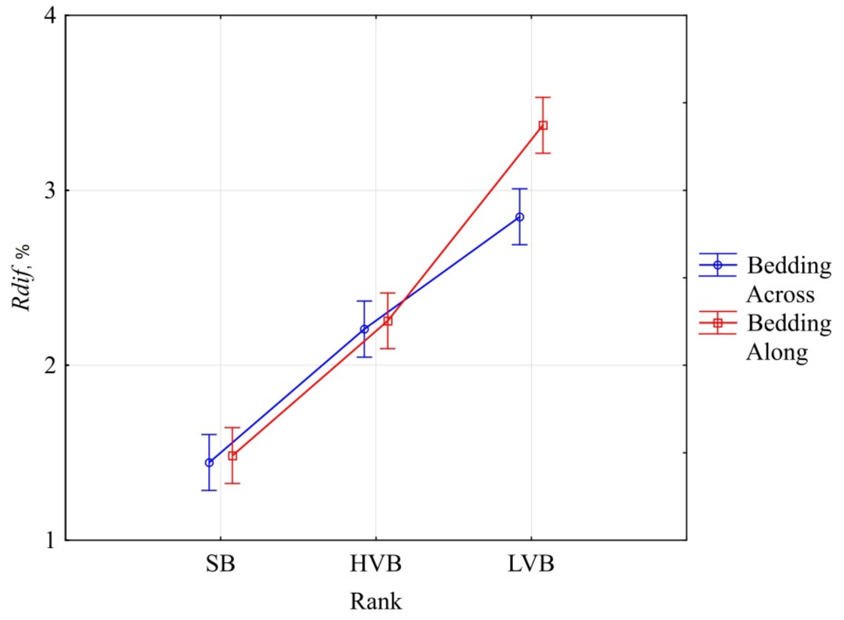


Figure 1. Dependence of the diffuse reflection coefficient on the degree of coalification and orientation relative to layering

The spectra of full reflection of all samples accept a similar shape with a single global minimum (Figure 2). This shape of the spectrum is characteristic of carbon materials [9]. In the wave range of 400–650 nm, the total reflection coefficient (R_{full}) increases with the increasing rank of coals. The value of the wavelength of the global minimum is important for analyzing the degree of carbon conjugation but its direct determination is difficult due to noise distortion. The diffuse shape of the spectral peak with high accuracy and low redundancy of the model can be approximated by a cubic polynomial in the following form: $R_{full}(\lambda) = a\lambda^3 + b\lambda^2 + c\lambda + d$, where λ is the wavelength; *a, b, c, d* are the desired polynomial parameters. Then it is easy to find a minimum as the roots of the equation $dR_{full}(\lambda)/d\lambda=0$ in the predefined determination domain.

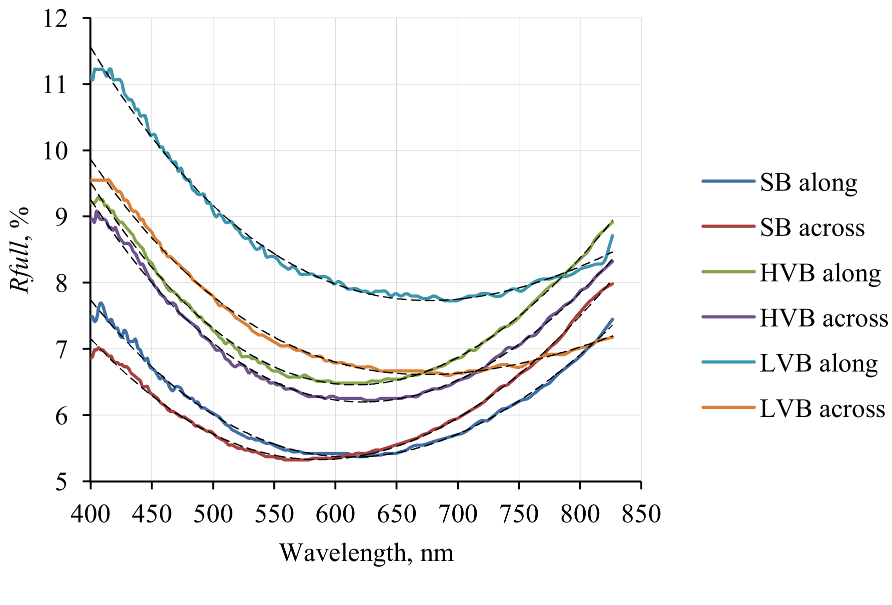


Figure 2. Spectra of coal complete reflectance and their approximation

The average and minimum values of R_{full} naturally increase as a result of coalification (Table 1). R_{full} for layering in all ranks exceed those in the cut. R_{dif} with a correlation coefficient of 0.97 also varies symbatically. The bathochromic shift is likely due to an increase in the size of the conjugate carbon systems, which leads to the appearance of shared π electrons and an increase in the electrical conductivity of coals. The shape of the spectra of high-rank coals becomes less symmetrical relative to the minimum due to increased absorption in the near-infrared region. In the model, this is manifested by a twofold increase in coefficient *a*.

Table 1. Characteristics of spectral curves and their models.

Sample	Minimum		Mean		Model parameters			
	λ, nm	R_{full}, %	R_{full}, %	R_{dif}, %	a, x10^{-8}	b, x10^{-5}	c	d
SB along	612	5.36	6.21	1.48	-2.27	8.99	-0.085	28.7
SB across	586	5.33	6.08	1.44	-1.53	7.76	-0.075	25.8
HVB along	615	6.46	7.54	2.25	-2.52	10.7	-0.104	35.4
HVB across	622	6.20	7.26	2.21	-2.64	10.6	-0.101	34.5
LVB along	676	7.74	9.01	3.37	-4.48	12.9	-0.113	39.0
LVB across	673	6.62	7.68	2.85	-4.66	12.5	-0.105	34.9

Coal petrographic observations at the micro-level allow us to consider various aspects of the reflectivity of coal macerals. Since the R_{full} value of the powders of coal samples is highly dependent on the choice of wavelength, it can be assumed that the mirror reflection from the surface of the polished sections of coal lumps has a similar spectral characteristic. Light microscopes, traditionally used in petrographic studies, are not equipped with microspectrometers and do not make it possible to register a full-fledged reflection spectrum. However, it is possible to use a set of color filters to obtain conditionally monochromatic incident light. We used 4 optical filters with measured transmission spectra (Figure 3). Note that the spectrum of the green filter takes a classical shape, close to the parabola; the spectrum of the yellow filter effectively cuts off the blue region $\lambda<515$ nm. The red and blue filters produce spectra of complex shapes, which partially transmit green lighting.

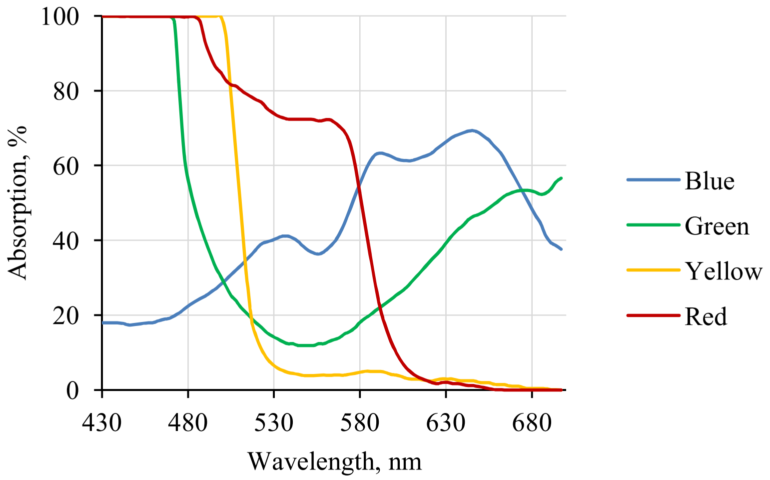
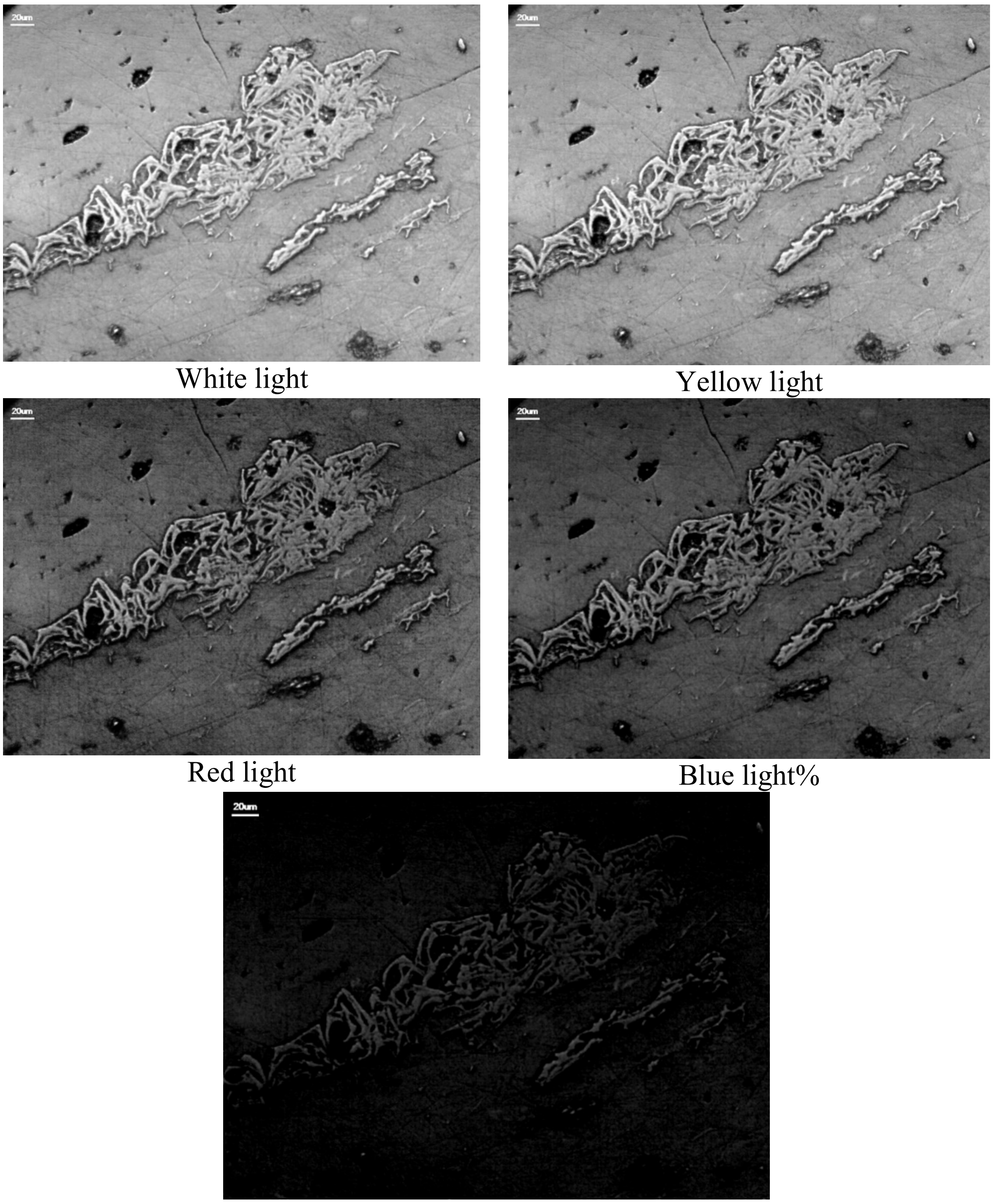


Figure 3. Transmission spectra of color light filters of the microscope.

Our experiments have shown that the same fragment of the micro image of the surface of a polished section of coal lump, obtained when illuminated with white, yellow, red, blue, and green light, demonstrate different brightness (Figure 4). Visually, the images in white and yellow light are identical, as are the images in red and blue light. The green light filter produces the darkest picture; only the lightest maceral – inertinite – is clearly visible with its use. Given the shape of the bandwidths of optical filters, our findings are consistent with spectral data where the maximum absorption and, accordingly, the minimum reflection captures the yellow-green and red region of the spectrum.

Since liptinite was not detected in the LVB coal rank, and GI is determined only on inertinite in green light, it is impossible to fill in the complete matrix of the plan of the 4-factor experiment at all possible levels. Therefore, the task was divided into 3 parts. ANOVA1 takes into account all macerals, colors except green and 2 rank coals. ANOVA2 uses all the ranks of coals, there is no liptinite and green light. In ANOVA3, only inertinite is analyzed for all colors and ranks of coals. The successful choice of factors and their levels is indicated by reliable F-criteria of two and three combinations of predictors. The biggest effects on GI are exerted by macerals and lighting color (Table 2). They are an order of magnitude greater than the influence of the rank of coals. However, given the combinations of factors, the rank of the coal is of great importance in combination with macerals (ANOVA1) and sample orientation (ANOVA2).

For the vitrinite of coals of all ranks, the differences in the average values of GI in red and blue light (Figure 5) are unreliable in both directions (for layering and cross-spread). Excluding green light, the biggest differences are observed between yellow and red or blue light.



White light | Yellow light

Red light | Blue light%

Green light

Figure 4. Characteristic microimages of coal when using various optical filters.

Table 2. Effects of the influence of factors and their combinations on the average value of GI.

	ANOVA1	ANOVA2	ANOVA3
Rank levels	SB, HVB	SB, HVB, LVB	SB, HVB, LVB
Maceral levels	Vt, I, L	Vt, I	I
Factor Rank (1)	**158.2**	**691.5**	**341.7**
Factor Bedding (2)	**78.1**	**18.7**	**33.9**
Factor Macerals (3)	**1988.6**	**2779.9**	–
Factor Color (4)	**3415.6**	**2752.9**	**1621.8**
Rank*Bedding	**14.0**	**52.3**	**39.2**
Rank*Macerals	**118.6**	**13.9**	–
Bedding*Macerals	**35.4**	**19.1**	–
Rank*Color	**29.1**	**19.9**	**16.6**
Bedding*Color	**41.9**	**7.2**	1.9
Macerals*Color	**13.0**	**42.0**	–
Rank*Bedding*Macerals	**13.2**	**14.3**	–
Rank*Bedding*Color	**9.7**	**7.8**	**6.6**
Rank*Macerals*Color	**13.6**	**7.5**	–
Bedding*Macerals*Color	**4.6**	0.8	–
1*2*3*4	1.3	**4.5**	–

Note: Bold indicates F-criteria that are reliable at the significance level p<0.05

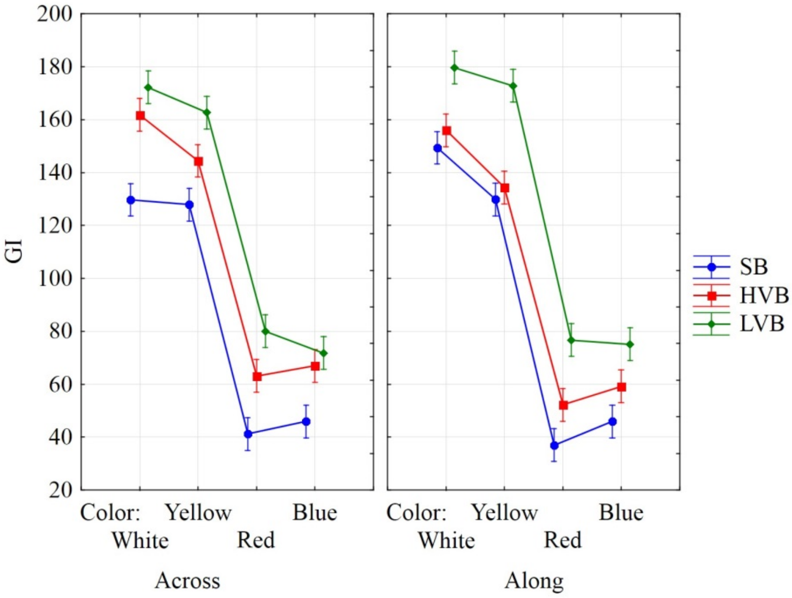


Figure 5. The influence of factor levels on the average values of GI for vitrinite (whiskers – 95 % confidence interval).

In inertinite, the dependence of GI on the color of the filter correlates, in general, with a similar indicator for vitrinite (Figure 6). However, for two coals of rank LVB, in terms of layering, and rank SB, across the layering, abnormally large values of GI in yellow light are observed significantly exceeding the level of reflection in white light. This is possible only if the inertinite in the examined samples has strong maximum absorption in the blue region of the spectrum. Then, in the absence of an optical filter, white light, including a poorly reflecting blue area, would not produce the expected increase in brightness. A similar anomaly in blue light is not observed because the selectivity of the blue optical filter is not high enough. It partially transmits red and even more green light. If an effective blue optical filter was used, along with an increase in GI in yellow light, there would be a corresponding decrease in GI in blue light. The detected maximum absorption is not observed in the

R_{full} spectra of the corresponding samples because the proportion of inertinite in the material composition of the studied coals is small compared to vitrinite.

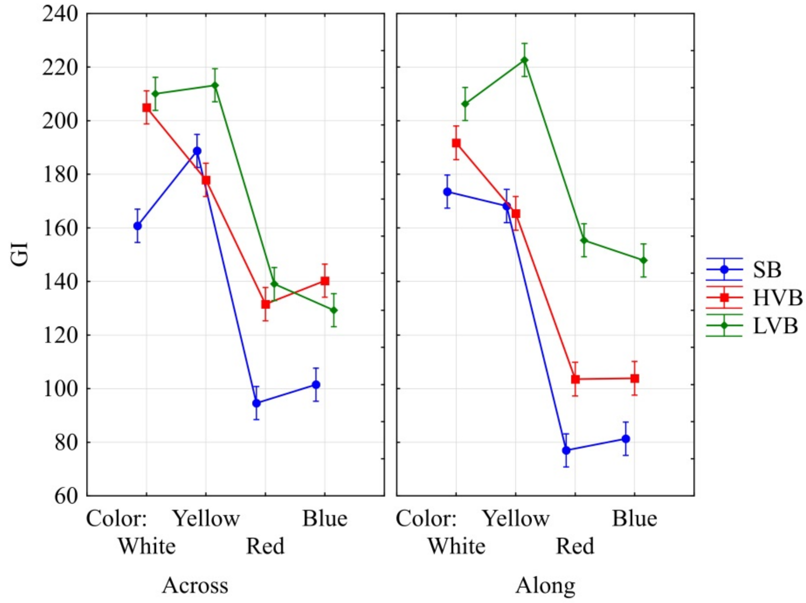


Figure. 6. Influence of factor levels on the average values of GI for inertinite.

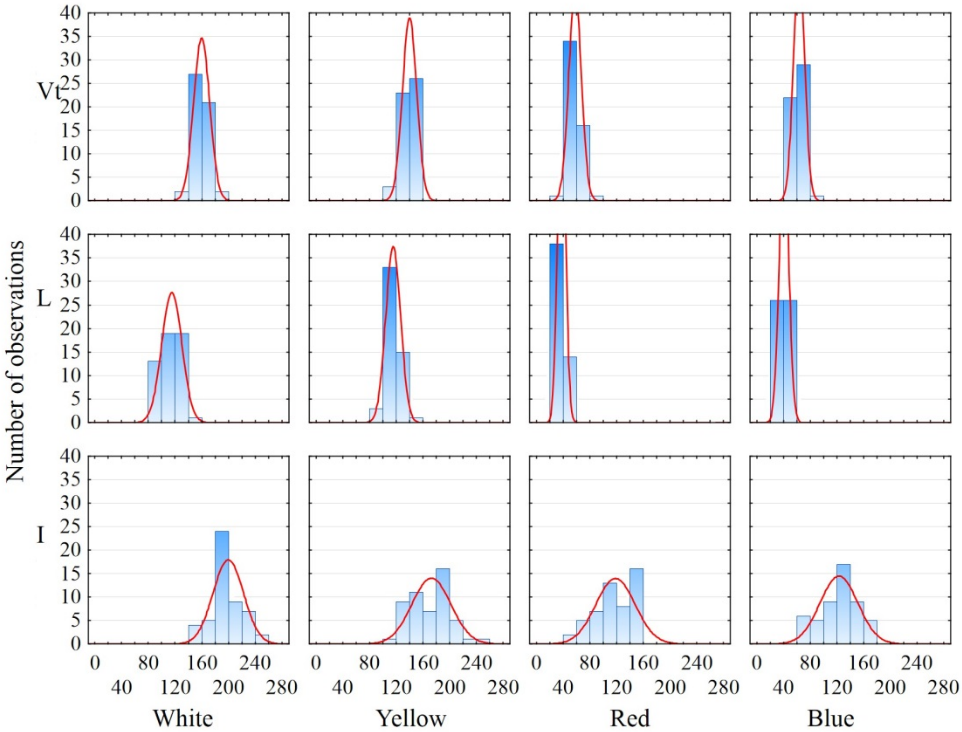


Figure. 7. Categorized GI histograms for HVB coal rank depending on factor levels.

The heterogeneity of GI for inertinite compared to other macerals is confirmed by the large width of the histogram and the shape of the envelope, different from the normal distribution (Figure 7). In the yellow and red light of inertinite, two modes can be traced. Sharp changes in R_o recorded in the inertinites of coals cause a multimodal distribution of their reflectivity [10]. At the same time, the variability of the brightness level of vitrinite and liptinite is small.

In green light, GI for vitrinite and liptinite tend to zero; similar indications of inertinite range from 20 to 60. It is obvious that in order to conduct research in green light, it is necessary to use a brighter light source. However, the light from a high-power lamp can make simultaneous measurements on inertinite inaccessible. That is, at low brightness, the entire inertinite with liptinite can be black, and, at large, all inertinite can be white. To resolve this issue, it is possible to use a camera with 16-bit digitization of the analog signal from the photosensitive sensor, which yields 65,536 instead of 256 gray gradations.

4. Conclusions

The influence of all selected factors Color, Macerals, Rank, Bedding, as well as most of their combinations, on GI is reliable. They are listed in order of significant reduction in effect. A significant dependence on the color of lighting is due to the differences in the absorption spectra of the macerals of the studied coals. This can also explain the detected anomaly of strong reflection of yellow light by inertinite in some samples of coals.

The use of highly selective band optical filters in the microscope allows us to draw conclusions about the shape of the reflection spectrum in the visible region, which is associated with electronic transitions in the molecular structure. Due to the low characteristicity, the spectra are approximated by a cubic polynomial, and the position of the diffuse global minimum can be estimated by GI in the reflection of the corresponding color. This approach is an alternative to the use of expensive microscopes with built-in microspectrometers.

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