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Relationship between coking coal quality and its micro-Raman spectral characteristics

Rafał Morga [a,*], Iwona Jelonek [b], Krystyna Kruszewska [b]

[a] Silesian University of Technology, Faculty of Mining and Geology, Institute of Applied Geology, Akademicka 2, 44-100 Gliwice, Poland
[b] University of Silesia, Faculty of Earth Sciences, Będzińska 60, 41-200 Sosnowiec, Poland

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ABSTRACT

Micro-Raman spectroscopy examination of 20 samples of coking coals (R_r = 0.84–1.43%) was performed. Spectral parameters were correlated with the basic rank and technological properties of coals.
The G band FWHM and the A_G/A_{ALL} ratio decrease with the volatile matter content (V^{daf}) decrease and the all maceral reflectance scan (R_{scan}) value increase. The correlations between these parameters are stronger than those, between the G band FWHM and the A_G/A_{ALL} ratio, and the mean random vitrinite reflectance (R_r). Coking properties are weakly related to the Raman spectral characteristics of coal. Based on the Raman parameters G band FWHM and the A_G/A_{ALL} ratio, it may be possible to evaluate the volatile matter content (V^{daf}) and the all maceral reflectance scan (R_{scan}) value for coking coals.

1. Introduction

In the last years many studies on coals and their individual macerals emerged, in which Raman spectroscopy was applied (Chabalala et al., 2010; Guedes et al., 2010, 2012; Kelemen and Fang, 2001; Konchits et al., 2012; Kostova et al., 2012; Li et al., 2006; Marques et al., 2009; Morga, 2011a,b, 2013; Nestler et al., 2003; Quirico et al., 2005; Rodrigues et al., 2011a,b; Sonibare et al., 2010; Tselev et al., 2014; Ulyanova et al., 2014; Wagner, 1982; Żerda et al., 1981). Some works focused on determination of microstructural alteration of coal or coal macerals under heat treatment (Bar-Ziv et al., 2000; Chabalala et al., 2010; Dong et al., 2009; Gong et al., 2009; Li et al., 2006; Morga, 2011a, 2013; Oboirien et al., 2010; Rodrigues et al., 2011a,b; Sheng, 2007; Wang et al., 2014). Dun et al. (2014) studied influence of a magmatic intrusion on coal microstructure and observed significant changes in relative intensity of Raman bands with the transition from bituminous coal to anthracite. Potgieter-Vermaak et al. (2011), followed by Morga (2011a), discussed application of Raman spectroscopy in examination of coals, chars and cokes.

In few of these studies Raman spectral characteristics were rel ated to the coal rank (Guedes et al., 2010; Kelemen and Fang, 2001; Konchits et al., 2012; Marques et al., 2009; Quirico et al., 2005; Sonibare et al., 2010; Ulyanova et al., 2014). However, these investigations were usually performed on a small number of samples, representing broad rank range, and thus allowing determination of general trends but limiting the statistical approach.

Kelemen and Fang (2001) found a decrease in the Raman G band FWHM with the increasing rank of coal. Quirico et al. (2005) reported that for the maturity range $1\% < R_r < 5\%$ the spectral parameters that correlated best with R_r were: the G band FWHM (which decreased), I_{D1}/I_G ratio (which decreased, and afterwards increased) and the position of the D1 band (which shifted to the lower wavenumbers with R_r increase). Marques et al. (2009) observed the R_{MAX} RIS axis to correlate best with micro-structural parameters of high-rank coals and graphites. The G band FWHM decreased with the R_{MAX} increase. Guedes et al. (2010) found a decrease in the G band FWHM, a shift of the D1 band position and an increase in the I_{D1}/I_G ratio with increasing mean random reflectance of vitrinite in coals ranging from sub-bituminous to anthracites. Sonibare et al. (2010) communicated a slight decrease in the G band FWHM and an increase in the I_{D1}/I_G ratio with increasing rank of Nigerian sub-bituminous to bituminous coals. Konchits et al. (2012) observed a non-linear increase in the I_{D1}/I_G ratio (calculated from the integral D1 and G band intensities), reflecting an increase in the coherent domain size (L_a), with the decrease in the volatile matter content (V^{daf}) in coals from the bituminous coal–anthracite range. Finally, Ulyanova et al. (2014) suggested that the D1 band position, which shows nearly linear shift to the lower wavenumbers within the whole metamorphism range, can play the role of coal type indicator.

The purpose of this study was to determine relationships between the basic rank and technological properties of coking coals and their micro-Raman spectral parameters, and to propose a new way of coal quality assessment based on micro-Raman examination.

* Corresponding author. Tel.: +48 32 237 21 11.
E-mail address: rafal.morga@polsl.pl (R. Morga).

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Table 1
Selected optical, chemical–technological and petrographic properties of the studied coals.

Sample	R_r[%]	R_{scan}[%]	V^{daf}[%]	A^d[%]	SI	b[%]	V[%]	L[%]	I[%]	MM[%]
1 (US)	0.84	0.88	36.50	8.00	6.0	21	59.0	12.0	24.6	4.4
2 (US)	0.85	0.92	33.30	7.10	7.0	18	55.6	11.2	30.0	3.2
3 (US)	0.86	0.95	32.88	5.73	5.0	2	52.6	14.0	31.0	2.4
4 (US)	0.86	0.92	34.90	4.80	7.0	25	50.2	16.0	30.8	3.0
5 (US)	0.86	0.85	30.98	8.40	6.0	25	58.0	7.6	29.4	5.0
6 (US)	0.86	0.94	35.60	7.70	6.0	5	53.4	11.0	32.4	3.2
7 (US)	0.92	1.14	29.99	4.00	4.5	0	33.8	8.6	56.6	1.0
8 (SC)	1.04	1.04	31.30	9.60	8.0	143	66.8	8.4	23.4	1.4
9 (US)	1.05	1.32	25.60	4.20	5.5	66	27.8	13.4	57.6	1.2
10 (KE)	1.06	1.20	24.90	6.60	7.5	148	73.8	0.2	22.2	3.8
11 (US)	1.06	1.11	27.30	6.60	7.5	145	68.2	5.0	20.2	6.6
12 (CO)	1.08	1.11	29.80	8.70	7.0	71	55.0	3.0	36.4	5.6
13 (US)	1.14	1.37	24.50	4.50	4.0	47	48.2	4.2	41.0	6.8
14 (US)	1.22	1.42	24.71	6.51	7.5	130	66.2	2.0	25.2	6.6
15 (BC)	1.31	1.50	21.78	8.60	7.5	107	68.6	0.2	25.2	6.0
16 (US)	1.33	1.53	22.88	5.82	8.0	82	57.4	0.6	35.2	6.8
17 (US)	1.34	1.49	21.15	5.45	7.5	33	38.8	8.8	46.8	5.6
18 (RF)	1.37	1.36	19.60	6.10	8.0	30	79.8	0.4	18.8	1.0
19 (US)	1.42	1.50	24.76	5.45	6.0	65	40.4	11.6	45.2	2.8
20 (US)	1.43	1.45	27.94	5.82	6.0	50	70.0	3.4	25.8	0.8

Explanation: US: Upper Silesian Coal Basin (Polish and Czech part); SC: Shoal Creek deposit (USA); KE: Keystone deposit (USA); CO: Colombian coal; BC: Blue Creek deposit (USA); RF: Red Fox deposit (USA).
R_r: mean random reflectance of vitrinite; R_{scan}: all maceral reflectance scan; V^{daf}: volatile matter content; A^d: ash content; SI: swelling index; b: dilatation, V: vitrinite content; L: liptinite content; I: inertinite content; MM: mineral matter content.

2. Method

Research was carried out on 20 samples of coals (R_r = 0.84–1.43%) collected mostly in the Upper Silesian Coal Basin of Poland and Czech Republic (15 samples) and representing Upper Carboniferous (Pennsylvanian). Individual coal samples came from the Shoal Creek, Keystone, Blue Creek and Red Fox deposits in the USA (Pennsylvanian), and from Columbia (Upper Cretaceous/Tertiary). Selected physical, chemical–technological and petrographic properties of these coals are summarized in Table 1.

The petrographic analysis as well as the mean random vitrinite reflectance (R_r) and the all maceral scan (R_{scan}) measurements were carried out in reflected white light using Carl Zeiss Axio Imager M2m microscope combined with an automated scanning stage point counter. Before measurements the microscope was calibrated against a YAG (Yttrium–Aluminium–Granat) (R_r = 0.901%), GGG (Gadolinium–Gallium–Granat) (R_r = 1.718%), Cubic Zirkonia (R_r = 3.130%) and an optical black (zero) standards. Maceral analysis and reflectance measurements were taken in immersion oil (n_o = 1.518 at 23 °C), in accordance with the ISO standards ISO7404–3 (2009) and ISO 7404–5 (2009), respectively. The all maceral reflectance scan analysis was performed in the following way: random reflectance measurements were taken, using point counter, in 1000 points on polished grain mounts, on all macerals that fell under the measuring cross. Then the mean value was calculated. Other aspects of the measuring procedure were the same, as in case of vitrinite reflectance measurements.

Micro-Raman spectral analysis was carried out using a Renishaw inVia spectrometer (excitation line λ_0 = 514 nm) on 30 coal grains in each sample (with the exception of mineral matter), chosen at a regular distance. The streamline mode was applied, which allows collecting the spectra from the area of a strip and taking into account coal inhomogeneity. The measurement area was 10 μm × 2 μm. Spectral range was 800–2000 cm^{-1}, and spectral resolution 2 cm^{-1}. The spectrometer was calibrated using an internal silicon standard (peak position: 520 cm^{-1}). The calibration was also checked after finishing measurements. During each measurement 10 acquisitions of 5 s were co-added. Then the spectra were summed up, and a final spectrum was obtained, representative for a whole coal sample, which was interpreted. Curve-fitting procedure was performed within the range of 1000–1800 cm^{-1} with the use of GRAMS 32 software, following the method presented by Sadezky et al. (2005), which is frequently applied in examination of coals of similar rank, their individual macerals, and also chars and cokes (Gong et al., 2009; Morga, 2011a,b, 2013; Sheng, 2007; Smędowski et al., 2011; Ulyanova et al., 2014; Zickler et al., 2006). Four Lorentz curves (D2, G, D1 and D4 bands) and one Gaussian curve (D3 band) were assumed (Fig. 1). The band assignments were discussed by Beny-Bassez and Rouzaud (1985), Beyssac et al. (2003), Cuesta et al. (1994), Green et al. (1983), Jawhari et al. (1995), Nemanich and Solin (1979), Reich and Thomsen (2004), Sadezky et al. (2005), Schwan et al. (1996), Tuinstra and Koenig (1970), and followers. They were also summarized by Morga (2011a,b, 2013). Methodological aspects of Raman spectroscopy examination of carbonaceous material, highlighted by Beyssac et al. (2003) and Lünsdorf et al. (2014), were respected. Goodness of fit was checked by χ^2 test. Based on that, position of the Raman bands and their width (FWHM) were

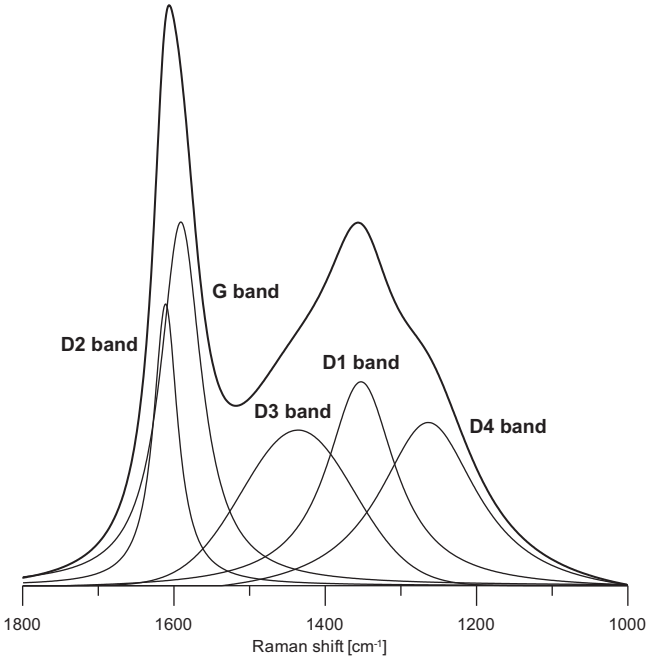

Fig. 1. Deconvolution of a Raman spectrum of a coking coal analyzed in this study.