



Simple procedure for an estimation of the coal rank using micro-Raman spectroscopy



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ABSTRACT

An alternative way for an estimation of coal rank, based on micro-Raman spectroscopy, is presented. Raman spectra and mean random reflectance percentage ($\%R_r$) were measured from 170 vitrinite grains, with $\%R_r$ in the range from 0.18 to 4.67, representing 35 coals within a broad range of rank (peat to anthracite). The spectral region between 850 cm^{-1} and 1840 cm^{-1} of the Raman spectra was fitted with two Lorentzian functions and a linear inclined baseline. It was found that the width of the graphitic band (G near 1580 cm^{-1}) and both width and position of the disordered band (D near 1340 cm^{-1}) monotonously decreased with the increase of $\%R_r$ of the grains. Due to the high reproducibility of these parameters, when calculated from Raman spectra obtained on different spots of the same grain, as well as the clearly pronounced Raman parameters–reflectance dependences, they can be used for an estimate of the coal rank. The correlation between Raman parameters and random reflectance of the vitrinite grains was expressed with empirical formulae.

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1. Introduction

Coal rank reflects the degree of coalification that the organic matter has been subjected during burial. It can be optically determined by measuring the mean random reflectance percentage ($\%R_r$) of vitrinite grains (ISO 7404-5, 2009), establishing a mean value that correlates to the coal rank (Taylor et al., 1998; Thomas, 2013). Rank is an important parameter to decide the application of the coal in industry (Hook, 1977). It correlates strongly to volatile matter content and calorific value of the coal as well as to other chemical parameters that reflect the changes taking place in the coal molecular structure during maturation (Pusz et al., 2014; Thomas, 2013).

It has been shown that Raman spectroscopy can be utilized to gain information on the structural order of carbonaceous materials (Angoni et al., 1992; Baldan et al., 2007; Bernard et al., 2010; Beyssac et al., 2002, 2003; Bustin et al., 1995; Cuesta et al., 1994; Ferrari, 2007; Ferrari and Robertson, 2000; Johnson et al., 1986; Lahfid et al., 2010; Liu et al., 2013; Nakamizo et al., 1974; Rodrigues et al., 2013; Sadezky et al., 2005; Tuinstra and Koenig, 1970; Zaida et al., 2007). The history of different approaches to coal analysis with Raman spectroscopy has been reviewed by Potgieter-Vermaak et al. (2011). Raman spectroscopy has

been used to estimate coal rank (Guedes et al., 2010; Kelemen and Fang, 2001; Liu et al., 2013; Marques et al., 2009; Nestler et al., 2003; Quirico et al., 2005; Ulyanova et al., 2014; Valentim et al., 2010; Zerda et al., 1981) and to track maturity changes in coals or kerogens after some additional thermal treatment (Bernard et al., 2010; Chabalala et al., 2011; Green et al., 1983; Johnson et al., 1986; Li et al., 2006a,b; Liu et al., 2014; Sheng, 2007; Zaida et al., 2007; Zhang et al., 2011; Zhou et al., 2014), high pressure application (Bustin et al., 1995), anisotropic stress (Urban et al., 2003), or metamorphic transformation (Bonal et al., 2006; Lahfid et al., 2010; Rahl et al., 2005; Wopenka and Pasteris, 1993).

The first-order Raman spectra of most carbonaceous materials are dominated by two prominent features similar to those of disordered graphite: the “G-band”, due to Raman allowed E_{2g} vibrations of the carbon rings in the plane of the graphite sheets, and the “D-band”, due to the A_{1g} breathing mode allowed only at the broken borders of the graphene planes (Ferrari and Robertson, 2000). The D-band becomes more intense with the increase of crystallographic disorder, i.e., with the decrease of the size of the microcrystallites (Ferrari and Robertson, 2000; Reich and Thomsen, 2004; Tuinstra and Koenig, 1970).

The assumption of only two main bands (G and D) in the first-order spectrum of coals and chars has been made by several authors (Bustin et al., 1995; Green et al., 1983; Kelemen and Fang, 2001; Liu et al., 2014; Pusz et al., 2014; Quirico et al., 2005). Others use a third band between D- and G-bands (Johnson et al., 1986; Li et al., 1996), either on the

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high frequency side of the G-band (Rodrigues et al., 2013; Wopenka and Pasteris, 1993), or on the low frequency side of the D-band (Nestler et al., 2003; Zerda et al., 1981) in the fitting procedure. Angoni (1992) used three to four Lorentzian or Gaussian functions for coke and three for coals. Cuesta et al. (1994) used 4 functions “principally in order to improve fittings in the deconvolution of spectra”, while Zaida et al. (2007) describe the instability in the fit parameters of the minor bands (non-G or non-D). According to several authors (Bernard et al., 2010; Beyssac et al., 2003; Chabalala et al., 2011; Lahfid et al., 2010; Sadezky et al., 2005; Sheng et al., 2007; Ulyanova et al., 2014; Urban et al., 2003; Valentim et al., 2010; Zhou et al., 2014), Raman spectra of carbonaceous material contain up to five vibrational modes that can be adjusted with five Gaussian or Lorentzian functions. Next to the above-mentioned G- and D(D1)-bands, three additional vibrations due to disorder in the crystal lattice were included: the D2 vibration, centered $\sim 1620\text{ cm}^{-1}$, related to disorder inside the graphite planes (E_{2g}); the D3 vibration, centered around 1500 cm^{-1} , due to defects outside the plane of aromatic layers like tetrahedral carbons; and the D4 band, centered around 1200 cm^{-1} , attributed to disordered graphitic lattice (A_{1g} symmetry) or ionic impurities. These additional bands can be clearly seen in some highly ordered carbonaceous materials like anthracite and graphite (Bernard et al., 2010; Rodrigues et al., 2013; Tan et al., 2004). Guedes et al. (2010) used 6 lines to fit the Raman spectra of coals; however, their fit does not include the D2 vibration mentioned by Sadezky et al. (2005) or Chabalala et al. (2011). Several authors utilized as many as 10 different lines between 1200 and 1800 cm^{-1} to fit the spectra from chars of brown coal (Li et al., 2006a,b; Zhang et al., 2011) or biomass (Keown et al., 2007).

Correlations have been established between Raman bands (position, width, intensities, area ratio, peak distance) and some characteristics of the samples, e.g., maximum temperature of metamorphism (Lahfid et al., 2010; Wopenka and Pasteris, 1993), heat treatment temperature (Green et al., 1983; Johnson et al., 1986; Nakamizo et al., 1974), or deformation pressure (Bustin et al., 1995).

Many authors report a correlation of the Raman fitting parameters to vitrinite reflectance (Guedes et al., 2010; Kelemen and Fang, 2001; Liu et al., 2013; Marques et al., 2009; Quirico et al., 2005; Valentim et al., 2010; Zhou et al., 2014). Few papers investigate large numbers of natural coal samples (Cuesta et al., 1994; Guedes et al., 2010; Kelemen and Fang, 2001; Nestler et al., 2003; Quirico et al., 2005; Zerda et al., 1981), or others have samples in a different R_f range (Marques et al., 2009). While the reported data are consistent with our measurements, the plots found in the literature do not show the trend as clearly, as the data presented in this work. The aim of this work was a general quantitative correlation between some of the parameters of the micro-Raman spectra and the vitrinite reflectance ($\%R_f$). We would like to emphasize that we present only positions and widths of the Raman lines because they practically do not depend on the scattering geometry. Even though the area ratio of the D-band/G-band is the most common parameter illustrating the structural order of coal an carbonaceous material (Ferrari, 2007; Pusz et al., 2014; Tuinstra and Koenig, 1970), the intensities of the D- and G-bands (as well their ratio) will be strongly dependent on the scattering configuration and the crystalline grain orientation (Tan et al., 2004). Wopenka and Pasteris (1993) name the D-band width as a maturity indicator of coals, but neither area ratio nor intensity ratio of the D- and G-bands. Therefore, we limit our investigation to the dependences of the position and the width of the D- and G-bands to the vitrinite reflectance.

Concerning the number of the bands proposed to compose the Raman spectra, we found that when the parameters of many lines were left to vary, the fitting procedure resulted in parameter values that were not unique. Depending on the order in which the parameters were allowed to vary, the results converged to different values. Instead of developing more complex fitting models to adjust sub-components to the main bands, we fitted them with two Lorentzian functions and an inclined linear baseline. All obtained spectra converged with this fit, even though the adjustment to the data points was not perfect. When the fit parameters of

the Raman bands of all vitrinite grains were plotted against the respective $\%R_f$ value, a systematic behavior of the widths and positions was observed. Functional dependences, describing analytically the empirical dependences, were proposed for the correlation between $\%R_f$ and the Raman parameters G-band width, D-band position, and D-band width.

2. Materials and methods

Vitrinite grains from 35 different coals ranging from lignite to anthracite were analyzed. All samples were embedded in resin, petrographically polished and ultrasonically cleaned following standard procedures (Bustin et al., 1989). Only polished coal samples were used because of the requirements for reflectance measurements ($\%R_f$).

The vitrinite reflectance of 170 grains was measured with 546 nm wavelength in oil immersion with an optical microscope (Leica DM 6000 M). This equipment is regularly calibrated with standards (YAG, Gd-Ga-garnet, cubic zirconia, and diamond) and shows a very linear calibration. For each measurement, the calibration was checked with a YAG garnet, and a black glass was used to correct the internal reflectance of the microscope. The procedure was performed according to ISO 7404-5 (2009); however, a minor modification was introduced: instead of measuring the reflectance of 100 different vitrinite grains of the same coal to establish the coal rank as stated in ISO 7404-5, 20 measurements were made from different spots on each of the 170 selected vitrinite grains to determine $\%R_f$ of the grain, and not the mean value of the coal. The measurements showed that each vitrinite grain was very homogeneous in respect to its $\%R_f$.

Table 1

Coal sample identification, number of vitrinite grains measured in the sample, minimum and maximum $\%R_f$ values of the vitrinite grains of this sample, provenance of the coal, reference with detailed description (when available).

ID	No.	$\%R_f$	Provenance	Ref.
04	4	0.18–0.22	Hambach (Nordrh.-Westf.), Germany	a
05	6	0.22–0.30	Garsweiler, (Nordrh.-Westf.), Germany	a
09	6	0.27–0.32	M&S Coal, Sask., Canada	a
10	5	0.32–0.37	Bienfait, Sask., Canada	a
16	5	0.46–0.54	Obed Mountain, Alb., Canada	a
24	5	0.56–0.74	Phalen Mine, NS, Canada	a
33	6	1.04–1.14	Malaysia	a
37	6	1.09–1.39	Westar Mining, BC, Canada	a
40	6	1.40–1.45	Aldenhoven, (Nordrh.-Westf.), Germany	a
42	5	1.46–1.58	Aldenhoven, (Nordrh.-Westf.), Germany	a
43	6	2.10–2.47	Aldenhoven, (Nordrh.-Westf.), Germany	a
44	5	2.72–2.73	Ibbenbüren, (Nordrh.-Westf.), Germany	a
45	6	3.11–4.57	Groundhog Coalfield, BC, Canada	a
ST 07-114	3	2.61–2.97	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-117	3	1.95–2.07	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-118	3	1.48–1.66	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-128	3	0.58–0.68	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-155	3	0.79–0.88	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-166	3	0.86–0.94	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-174	4	0.93–1.19	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
ST 07-186	3	0.81–0.87	Sta. Terezinha borehole CBM001-ST-RS, Brazil	b
07-058	15	3.10–4.67	Anthracite, Vale do Rio Doce company, Brazil	
C 05-103	2	0.74–0.75	Forro, Barro Branco coal seam, SC, Brazil	c
C 05-113	2	0.75–0.77	Coringa (BB), Barro Branco, SC, Brazil	c
UN-ICA	6	0.76–0.90	Unknown, Brazil	
UN-ICB	7	1.36–1.56	Unknown, Brazil	
UM 04/26	5	0.85–0.95	Round robin ICCP samples	
UM 1/4	5	1.26–1.36	Round robin ICCP samples	
63-88	3	1.16–1.22	Cadomin-Luscar coal Field, Alb., Canada	
61-88	3	0.58–0.65	Cadomin-Luscar coal Field, Alb., Canada	
IC 06-90	6	0.66–0.77	Minto, NB, Canada	
08-174	5	0.60–0.84	Coal blend, Jorge Lacerda powerplant, SC, Brazil	
09-120	5	0.47–1.65	Coal blend, Jorge Lacerda powerplant, SC, Brazil	
08-104	5	0.48–0.49	Coal blend, São Jerônimo powerplant, RS, Brazil	
08-105	5	0.47–0.51	Coal blend, São Jerônimo powerplant, RS, Brazil	

a Described in Table 1 of Kalkreuth et al. (1991).

b Described in Table 5 of Kalkreuth et al. (2013).

c Mentioned in Fig. 8, locations 10 and 12 (Kalkreuth et al., 2010).

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