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

Ruth Hinrichs a,⁎, Matthew T. Brown b, Marcos A.Z. Vasconcellos c, Miroslav V. Abrashev c,d, Wolfgang Kalkreuth a,b

a Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, PO Box 15001, 91501-970 Porto Alegre, RS, Brazil
b Programa de Pós-Graduação em Geociências, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, PO Box 15001, 91501-970 Porto Alegre, RS, Brazil
c Instituto de Física UFRGS, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, PO Box 15051, 91501-970 Porto Alegre, RS, Brazil
d Facultad de Física, University of Sofia, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria

⁎ Corresponding author at: IG-UFRGS, PO box 15001, 91501-970 Porto Alegre, RS, Brazil. Tel.: +55 51 3108 7144; fax: +55 51 3108 7302.
E-mail address: ruth.hinrichs@ufrgs.br (R. Hinrichs).

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) were measured from 170 vitrinite grains, with %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, 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.

© 2014 Elsevier B.V. All rights reserved.

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) 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; Tuanstra 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; Uyanova 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 E₂g vibrations of the carbon rings in the plane of the graphite sheets, and the “D-band”, due to the A₁g 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 microcrystallitles (Ferrari and Robertson, 2000; Reich and Thomsen, 2004; Tuanstra 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
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 Zaid 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; Lahfidi 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 at 1620 cm$^{-1}$, related to disorder inside the graphite planes ($E_g$); 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 metamorphosis (Lahfidi et al., 2010; Wopenka and Pasteris, 1993), heat treatment temperature (Green et al., 1983; Johnson et al., 1986; Nakamizo et al., 2001; Nestler et al., 2003; Quirico et al., 2005; Zerda et al., 1981), or others have samples in a different R 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 ($R_v$). 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 a carbonaceous material (Ferrari, 2007; Pusz et al., 2014; Tuijnra 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 $R_v$ value, a systematic behavior of the widths and positions was observed. Functional dependences, describing analytically the empirical dependences, were proposed for the correlation between $R_v$ 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 ($R_v$).

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 IS 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 IS 7404-5, 20 measurements were made from different spots on each of the 170 selected vitrinite grains to determine $R_v$ 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 $R_v$.

### Table 1

<table>
<thead>
<tr>
<th>ID No.</th>
<th>$R_v$</th>
<th>Provenance Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>04</td>
<td>0.18–0.22</td>
<td>Hambach (Nordr.-Westf.), Germany</td>
</tr>
<tr>
<td>05</td>
<td>0.22–0.30</td>
<td>Garoweiler, (Nordr.-Westf.), Germany</td>
</tr>
<tr>
<td>09</td>
<td>0.27–0.32</td>
<td>M&amp;S Coal, Sask., Canada</td>
</tr>
<tr>
<td>10</td>
<td>0.32–0.37</td>
<td>Bienfait, Sask., Canada</td>
</tr>
<tr>
<td>16</td>
<td>0.46–0.54</td>
<td>Obud Mine, Alb., Canada</td>
</tr>
<tr>
<td>24</td>
<td>0.56–0.74</td>
<td>Phalen Mine, NS, Canada</td>
</tr>
<tr>
<td>33</td>
<td>1.04–1.14</td>
<td>Malaysia</td>
</tr>
<tr>
<td>37</td>
<td>1.09–1.39</td>
<td>Westar Mining, BC, Canada</td>
</tr>
<tr>
<td>40</td>
<td>1.40–1.45</td>
<td>Aldenhoven, (Nordr.-Westf.), Germany</td>
</tr>
<tr>
<td>45</td>
<td>1.56–1.58</td>
<td>Aldenhoven, (Nordr.-Westf.), Germany</td>
</tr>
<tr>
<td>46</td>
<td>2.10–2.47</td>
<td>Aldenhoven, (Nordr.-Westf.), Germany</td>
</tr>
<tr>
<td>44</td>
<td>2.72–2.73</td>
<td>Tobenbüren, (Nordr.-Westf.), Germany</td>
</tr>
<tr>
<td>45</td>
<td>3.11–4.57</td>
<td>Groundhog Coalfield, BC, Canada</td>
</tr>
<tr>
<td>ST 07-114</td>
<td>2.61–2.97</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-117</td>
<td>1.95–2.07</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-118</td>
<td>1.48–1.66</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-128</td>
<td>0.58–0.68</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-155</td>
<td>0.79–0.88</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-166</td>
<td>0.86–0.94</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-174</td>
<td>0.93–1.19</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>ST 07-186</td>
<td>0.81–0.87</td>
<td>Sta. Terezinha borehole CBM001-ST-RS, Brazil</td>
</tr>
<tr>
<td>07-058</td>
<td>3.10–4.67</td>
<td>Anthracite, Vale do Rio Doce company, Brazil</td>
</tr>
<tr>
<td>C 05-103</td>
<td>0.74–0.75</td>
<td>Forro, Barro Branco coal seam, SC, Brazil</td>
</tr>
<tr>
<td>C 05-113</td>
<td>0.75–0.77</td>
<td>Coringa (BB), Barro Branco, SC, Brazil</td>
</tr>
<tr>
<td>UN-ICA</td>
<td>0.76–0.90</td>
<td>Unknown, Brazil</td>
</tr>
<tr>
<td>UN-ICB</td>
<td>1.36–1.56</td>
<td>Unknown, Brazil</td>
</tr>
<tr>
<td>UM 04-26</td>
<td>0.85–0.95</td>
<td>Round robin ICP samples</td>
</tr>
<tr>
<td>UM 1/4</td>
<td>1.26–1.36</td>
<td>Round robin ICP samples</td>
</tr>
</tbody>
</table>

$R_v$ is mentioned in Fig. 8, locations 10 and 12 (Kalkreuth et al., 2010).
In Table 1, the coal samples are noted with the same names as in the preceding references studying these samples, the number of vitrinite grains measured in the sample is stated (No.), the minimum and maximum %Rf values measured on the vitrinite grains of these coals are given to show the range of reflectance in the sample, the provenances of the samples are described briefly, and references for detailed geological and chemical characterization (when available) are indicated.

The vitrinite reflectance was measured with 546 nm wavelength in oil immersion with an optical microscope (Leica DM 6000 M). The equipment is regularly calibrated with standards (YAG, Gd-Ga-garnet, cubic zirconia, and diamond) and has a very stable calibration. The calibration was checked at each session with a YAG garnet, and a black glass was used to correct the internal reflectance. 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, 20 measurements were made from different spots on each of the 170 selected vitrinite grains to determine %Rf of the grain. The obtained %Rf values showed that each vitrinite grain was very homogeneous in respect to its reflectance.

The micro-Raman spectra were obtained on these selected grains using a laboratory-assembled spectrometer with a He-Ne laser (Coherent). The Rayleigh scattered light was rejected by a holographic notch filter (Kaiser). The inelastically scattered light was dispersed with a 600 g/mm holographic diffraction grating in a 0.5 m focal length spectrometer (Acton research) on an LN-cooled CCD camera (Princeton) (further details can be found in Vasconcellos et al., 2007). The 632.8 nm line of the He-Ne laser was used for excitation. An objective X50 was used both to focus the incident laser beam onto a spot with ~2 μm diameter and to collect the scattered light. Special care was paid to reduce overheating effects and thermal damage of the illuminated spot. It was found that vitrinite grains with lower random reflectance value were more sensitive to the laser power. For that reason the laser power on the sample surface was reduced to 0.7 mW (harmless value for all grains). The signal-to-noise ratio (SNR) of the spectra proved worse than the SNR of spectra obtained with higher power but sufficiently high to handle them mathematically. The spectrometer was calibrated using the Raman band at 1332 cm⁻¹ of a diamond standard. The spectral slit-width of the spectrometer was about 3 cm⁻¹. From each of the investigated grains, at least 3 Raman spectra in the range 150–1840 cm⁻¹ were measured at different spots. The possible effects of laser-induced sample degradation were checked by comparing consecutive spectra and no significant changes in the shape of the spectra were detected (Zickler et al., 2006).

The spectral region 850–1840 cm⁻¹ of the spectra was chosen for the fit. This spectral window seemed broad enough to allow the fitting software to estimate the linear baseline (Rahl et al., 2005). When the spectra of a same grain were fitted separately, the uncertainties of the G-band position was around 2 cm⁻¹, of the D-band position around 3 cm⁻¹, of the G-band width around 2 cm⁻¹ and of the D-band width around 10 cm⁻¹ (these uncertainties are smaller than the size of the symbols that will be used in the plots). A representative spectrum, consisting of the sum of three spectra of each grain was fitted with two Lorentzian functions and an inclined linear baseline with a Levenberg–Marquardt algorithm (Microcal™ Origin).

3. Results and discussion

3.1. The fitting procedure

An optical micrograph of sample 09-120 and the Raman spectra obtained from three grains with different random reflectance values are shown in Fig. 1. It can be noted that, as the reflectance value of the grain increases, both D- and G-bands become narrower and the position of the D-band shifts to lower frequencies, as had been observed by other authors (Guedes et al., 2010; Nestler et al., 2003).

A selection of several Raman spectra from vitrinite grains belonging to the whole investigated range (%Rf is given on each spectrum) is shown in Fig. 2. Again, the above-mentioned dependence is clearly visible. A large broadening of both bands in the spectra from grains with very low %Rf values can be seen.

To analyze these dependences quantitatively, we started mathematical treatment of the spectra. The first choice to be made is the analytical function that describes the line shape. In Raman spectra of perfect crystals, an allowed band (a result of the inelastic scattering of the light by phonons of the crystal) must have a Lorentzian shape, described with three parameters: position (frequency), width (full width at half maximum [FWHM]), and area (integral intensity). The natural width of the band depends on the finite phonon lifetime (i.e., on the temperature) and for the bands in the Raman spectra of coals it is much larger than the instrumental line width. In disordered crystals, the defects (impurities, random local elastic stresses, the finite and different size of the grains, etc.) additionally broaden the band, and if the effects of disorder dominate, the shape of the band becomes Gaussian. Usually, the two effects for the broadening are comparable, leading to a complex shape of the Raman band, frequently modeled as the sum of a Lorentzian and a Gaussian (pseudo-Voigt profile). This increases the number of the parameters describing the line because it is necessary to obtain the percentage of contribution of the Gaussian and the Lorentzian functions. In many papers that report a fit with a pseudo-Voigt function, the percentage of each curve to the total is not explicitly stated (Beyssac et al., 2003; Guedes et al., 2010), or else indicated as percentage 100% L + G (Chabalala et al., 2011), implying de facto a Lorentzian fit. Ferrari and Robertson (2000) claim that the Lorentzian fit is normally

![Fig. 1. (a) Optical micrograph of the sample 09-120 containing several vitrinite grains (their percentage of random reflectance %Rf is given); (b) the Raman spectra obtained from these grains (the spectra are shifted vertically for clarity).](image-url)
used for disordered graphite, and some authors explicitly state the use of a Lorentzian function to fit the Raman band in carbon materials (Angoni et al., 1992). Lahfid et al. (2010) report satisfactory convergence with 5 Lorentzian functions. To reduce the high number of free parameters in such a 5-line fit, Ferrari and Robertson (2000) suggest a mathematical manipulation with no physical meaning: the utilization of an asymmetric Breit–Wigner–Fano (BWF) function with a negative coupling factor for the G-band, to account for the low frequency intensities of the use of multi-line fit, which is unsatisfactory for the spectra of vitrinite grains with %R, values as low as 0.18 (Fig. 4b).

It has to be kept in mind that the choice to fit the spectra with only two Lorentzian curves implies that the fit parameters obtained for both bands cannot be attributed to vibrational modes of specific groups (Keown et al., 2007; Li et al., 2006a,b; Zhang et al., 2011) because each of them accounts for several disorder-induced additional modes of the coal lattice. In this way, the fit parameters, although without deep physical meaning, describe in unique way the grains with different %R, value and are promising empirical quantitative attributes of the vitrinite grains.

3.2. Correlation of Raman line parameters with %R,

The fitting procedures with two Lorentzian curves described in Section 3.1. converged for all vitrinite spectra with %R, between 0.18
and 4.67, without any restriction of the fitting parameters or further manual intervention. The resulting fit parameters of the G-band positions and widths and the D-band positions and widths are plotted against the average $%R_r$ of each grain in Fig. 5. The uncertainties of the values on the abscissa and the ordinate axes are of the size of the data symbols used in the plot.

The areas of the G- and D-bands obtained from the Lorentzian fit were not considered relevant because the assumption of a linear background is a simplification that ignores the possible existence of additional bands. However, the line positions and widths seemed unaffected by this assumption.

The G-band positions are in the same range as those reported for coals in the literature (Beyssac et al., 2003), while other authors have found values as high as 1600 cm$^{-1}$ for subbituminous coal (Cuesta et al., 1994; Quirico et al., 2005). Our D-band range (corresponding to the main influence of the D1 band of the literature) lies ~30 cm$^{-1}$ below the range reported by Beyssac et al. (2003) and ~35 cm$^{-1}$ below those from the coal samples in Cuesta et al. (1994), which was expected because a different laser wavelength was used to obtain their spectra and the position of the D-line is known to depend strongly on the excitation wavelength (Ferrari, 2007; Matthews et al., 1999; Reich and Thomsen, 2004). Guedes et al. (2010) measured the Raman spectra with a 632.8 nm laser from vitrinites of 9 coals and compared the fit parameters with the vitrinite reflectance. The data are not directly comparable with those from this paper because their spectra were fitted with 6 lines and the reflectance was averaged over the bulk coal.

---

**Fig. 4.** Raman spectra from (a) a vitrinite grain with $%R_r$ 1.65 and (b) a vitrinite grain with $%R_r$ 0.18. Both spectra were fitted with two Lorentzian functions and linear inclined baseline. (Inset: Parameter values obtained from the fit, see text). The notations used for line parameters are: $y_h$ and $y_i$—y-intercept and slope of the baseline; $A$, $w$, and $x_c$—area, width, and position of the lines (G and D). The dashed line shows the fit of the D-band (plus baseline), while the dotted line shows the fit of the G-band (plus baseline).

---

**Fig. 5.** Raman parameters from 170 vitrinite spectra plotted against the average $%R_r$ of each grain; (a) G-band position, (b) G-band width, (c) D-band position, and (d) D-band width. The displayed numbers are the parameters of the analytical approximations of the dependences ($y_0$, $A_1$, $t_1$, $A_2$, and $t_2$ are parameters of the exponential double decay function, see text below).
However, G-band widths and D-band positions of the Raman spectra against \%R_r show the same tendency as observed in Figs. 5b and c. Considering the Raman parameters obtained by their fit, Bonal et al. (2006) states that one of the most sensitive spectral maturity tracers is the width of the D-band. Even though these authors fit the G-band with a BWF asymmetric line, the tendency of the Lorentzian fitted D-band is the same. All of the plots obtained for the parameters against \%R_r look very smooth and show a correlation with the \%R_r value. We attribute the low spread of the data to the acquisition of \%R_r and Raman spectra on the same grains of the sample surface, reducing the fluctuation of the averaged spectral parameters that were discussed by Quirico et al. (2005). Only the G-band position (Fig. 5a) does not depend strongly on the reflectance value, the other parameters show a definite dependence.

Because of the fact that the accuracy of the position and width of a Raman band is about 1 cm\(^{-1}\), it appears that using these dependences and the position of the D-band and the width of the G- and D-band, the \%R_r value of the investigated grain can be predicted with a reasonable accuracy, while not as precisely as with the direct optical measurement (Quirico et al., 2005). We tried to find simple analytical functions describing the Raman line parameter—reflectance dependences with a minimal number of free parameters. Polynomials up to fourth degree (5 parameters) do not describe these dependences well. However, a double decay function (also with 5 parameters) appears to be very suitable:

\[
y = y_0 + A_1 \exp(-x/t_1) + A_2 \exp(-x/t_2),
\]

The steep decrease of the functions for low reflectance values was obtained with small decay constants (\(t_1\)), while at higher reflectances the function is governed by large decay constants (\(t_2\)).

We will now discuss the applicability of these empirical dependences. At the first glance the determination of the Raman line widths will depend on the instrumental function of the Raman spectrometer. However, as the widths of the D- and G-bands are much larger than the typical spectral slit-width of the spectrometers (about 3 cm\(^{-1}\)), this makes their values instrument-independent and therefore the dependences universal.

It is known that the D-band position depends on the laser wavelength (Ferrari, 2007; Ferrari and Robertson, 2000; Matthews et al., 1999; Reich and Thomsen, 2004). Considering that the dependences described here were obtained with the 632.8 nm line of a He-Ne laser, this implies that they can be used only for Raman spectra obtained with this wavelength. However, the laser-wavelength dependency of the D-band is well characterized and the line positions can be corrected for the expected wavenumber difference.

Another presentation of the three dependences (\%R_r in logarithmic scale versus Raman line parameters) gives direct connection between the value of these parameters and the rank of the coal (Fig. 6).

It can be seen that the parameters have low spread in the high rank region, while below 0.5 \%R_r the data scatter significantly.

4. Conclusions

1 Raman spectra and random reflectance values were measured from the same points of large number of vitrinite grains representing numerous coals within a broad range of rank.

![Fig. 6. \%R_r in logarithmic scale against Raman parameters; (a) G-band width, (b) D-band position, and (c) D-band width. Rank according to Taylor et al. (1998).](image-url)
2 It was found that the fit of the Raman spectra with 5 Gaussian curves was mathematically unstable and was not suitable for the Raman spectra of the coals investigated in this work. Therefore, the Raman spectra were fitted in a simple way using two Lorentzian curves and linear baseline.

3 In the range 0.18–4.67 of $\Delta R$, the G-band width, D-band width and D-band position correlated well with the reflectance value. These empirical dependences were presented analytically with double function dependencies. The dependences can be used as an alternative way to estimate the coal rank using Raman spectroscopy.

Acknowledgments

Financial support of the Brazilian funding agencies Capes, Finep, CNPq, and Fapesp is gratefully acknowledged. M.T. Brown acknowledges CNPq MSc grant (130005/2009-6). M.V.A. thanks the Brazilian agency CAPES (project no. BEX7607-13-0).

References


