



## Micro-Raman spectroscopy of collotelinite, fusinite and macrinite

A. Guedes<sup>a,\*</sup>, B. Valentim<sup>a</sup>, A.C. Prieto<sup>b</sup>, S. Rodrigues<sup>a</sup>, F. Noronha<sup>a</sup>

<sup>a</sup> Centro de Geologia e Departamento de Geociências, Ambiente e Ordenamento do Território da Faculdade de Ciências, Universidade do Porto, 4169-007-Porto, Portugal

<sup>b</sup> Departamento de Física de la Materia Condensada, Cristalografía y Mineralogía Facultad de Ciencias, Universidad de Valladolid, 47011-Valladolid, Spain

### ARTICLE INFO

#### Article history:

Received 26 March 2010

Received in revised form 1 June 2010

Accepted 9 June 2010

Available online 23 June 2010

#### Keywords:

Raman spectroscopy

Coal

Macerals

Rank

Petrography

### ABSTRACT

The Raman spectra and the Raman parameters have been correlated with changes in the structure of carbon materials, and most of the studies have revealed different development of the Raman spectrum.

In the present study micro-Raman spectroscopy was conducted on coal bulk samples and on individual coal macerals (collotelinite, fusinite, and macrinite) from a set of Penn State Coal Bank coals of increasing rank to study the variation of their spectral parameters with rank, and considering coal heterogeneity.

The spectral parameters that better correlate with the increasing coal rank, for the coals studied are the full width at half maximum of graphitic band (G: at  $\sim 1580 \text{ cm}^{-1}$ ), the position of disordered band (D: at  $\sim 1350 \text{ cm}^{-1}$ ), and the integrated intensity ratio of the D band to G band (ID/IG). With increasing coal rank a narrower G band, a shift of D band to lower wavenumber, and an increase of integrated intensity ratio ID/IG are observed.

For each coal, the Raman parameters obtained on fusinites and macrinites are similar and differ from those obtained on coal bulk samples and collotelinites.

The variation of the Raman parameters with rank is very well reflected on the analyses of collotelinites.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Coals are sedimentary rocks, resulting from peat coalification during its burial history, and composed of organic and inorganic matter. Therefore, when characterizing coal two characteristics must be considered: its rank (coalification degree) and its composition. The complexity of coal becomes more evident at microscopic level since the organic constituents of coal include the maceral groups (huminites/vitrinites, inertinites, and liptinites), and the individual macerals in those groups (Taylor et al., 1998). The coalification process of organic matter has been from many years the subject of numerous studies, and it was found that during this process the structural chemistry of coal is progressively modified, for example the organic matter becomes progressively more ordered to a certain extent (Bend, 1992; Carpenter, 1988; Davidson, 2004; Given, 1984; Hatcher and Clifford, 1997; van Krevelen, 1993).

One of the used means of studying changes in the structure of organic matter during coalification and graphitisation includes Raman spectroscopy. Several authors have correlated the Raman spectra and Raman parameters with changes in the structure of carbon materials, and most of the studies have revealed different development of the first- and second-order Raman spectra for organic matter in rocks

with varying degrees of coalification or graphitisation (Beysac et al., 2003; Bustin et al., 1995; Cuesta et al., 1994, 1998; Ferrari and Robertson 2000, 2001; Green et al., 1983; Guedes et al. 2005; Jawhari et al., 1995; Rouzaud et al., 1983; Sadezky et al., 2005; Tuinstra and Koenig, 1970; Yoshida et al., 2006; Zerda et al., 2000). Other authors have already applied this technique to conclude about the maturity of coals and other organic matter (Kelemen and Fang, 2001; Nestler et al., 2003; Quirico et al., 2005, 2009; Rantitsch et al., 2005) carrying out Raman analysis in bulk samples.

However, coal bulk analyses provide only general information not considering coal complexity and heterogeneity, and the impact of each coal component to the final result. However, coupling optical microscopes to analytical equipment based on photons and electrons beams, such as micro-probe, micro-FTIR, and micro-Raman, enables direct characterization of selected macerals (e.g. Bustin et al., 1996; Marques et al., 2009; Mastalerz and Bustin, 1993a,b, 1995, 1997; Ward and Gurba, 1999; Wilkins et al., 2002).

Micro-Raman spectroscopy (MRS) of coal allows obtaining the Raman spectrum of a very small volume of material, with a lateral resolution higher than  $1 \mu\text{m}$ . Since the technique uses a microscope it permits to carry out punctual analysis in specific components such as the macerals. Although Raman spectroscopy was carried out by Zerda et al. (1981) in maceral concentrates, MRS was used by Wilkins et al. (2002) measuring liptinite, vitrinite and inertinite fluorescence intensities and, by Marques et al. (2009) in vitrinite from high rank coals. A detailed summary concerning the analysis of coal by Raman spectroscopy is given in Potgieter-Vermaak et al. (2010).

\* Corresponding author. Tel.: +351 220402489; fax: +351 220402490.  
E-mail address: [aguedes@fc.up.pt](mailto:aguedes@fc.up.pt) (A. Guedes).

The present work aims to study the evolution of Raman spectra and Raman parameters on coal bulk samples and individual coal macerals (collotelinite, fusinite, and macrinite) from a set of Penn State Coal Bank coals of increasing rank, considering coal heterogeneity. The MRS analysis of individual coal macerals, in particular of collotelinite would allow for the correlation of these data with collotelinite reflectance.

## 2. Materials and methods

Nine Penn State Coal Bank coals were used in this study (Table 1) corresponding to a set of vitrinite-rich (>79 vol.% vitrinite on a mineral matter free basis) coals of increasing rank from Low rank A (sub-bituminous coal) to High rank A (anthracite A) (ISO, 2005).

Raman analyses are performed with air objectives and the contrast is lower than using oil immersion objectives. Therefore, shape and distinct reflectance were important reasons for choosing collotelinite, fusinite, and macrinite. Another important factor is that collotelinite and fusinite are, respectively, the most representative macerals of the vitrinite and inertinite macerals groups. Macrinite has the advantage of being easily identified with air objectives, and is still a poorly understood maceral.

The Raman experiments were performed on polished sections prepared for organic petrography (ISO 7404-5, 2009) using a JOBIN-YVON LABRAM spectrometer. A He–Ne laser was used giving a monochromatic red light of 632.8 nm at a power of 2 mW, with an approximated irradiance on the sample of 200 kW cm<sup>-2</sup>. Raman spectra were measured with a density filter to avoid thermal decomposition of samples by the laser.

The ×100 objective (0.95 numerical aperture) lens of an Olympus optical microscope was used to focus the laser beam on the sample and also to collect the scattered radiation. A highly sensitive CCD camera was used to collect the Raman spectra. Extended scans from 1000 to 1800 cm<sup>-1</sup> for the first-order Raman spectrum and from 2500 to 3500 cm<sup>-1</sup> for the second-order Raman spectrum were performed on each sample.

Micro-Raman analyses were both conducted in grains of bulk coal samples and in specific macerals: collotelinite, fusinite, and macrinite. For each bulk sample five different grains were analysed and for polished samples five collotelinite, fusinite and macrinite macerals, totalling twenty analyses, were carried on each sample. Coal macerals were identified, in the polished sections using the incident light microscope coupled to the Raman spectrometer, on the basis of their optical properties and morphology according to the ICCP classification and redefinition (ICCP, 1963, 1971, 1975, 1998, 2001; Sýkorová et al., 2005), and Hower et al. (2009).

In order to determine the precise frequencies, bandwidths and the relative intensities of the bands, the spectra were deconvoluted.

Adequate fits to the experimental data were obtained using a mixed Gaussian–Lorentzian curve-fitting procedure in a Labspec program of Dilor–Jobin Yvon. All the analytical and calculation procedures were conducted according to Beyssac et al. (2003).

### 2.1. Raman spectra

Raman spectroscopy is an important tool for material characterization. Its utility in the characterization of solids is due to its high sensitivity to the lattice vibrations and properties of the crystal. On studying carbon material it is known that the two crystalline forms of carbon, diamond and graphite, are characterized by two Raman bands at 1332 cm<sup>-1</sup> and 1581 cm<sup>-1</sup>, respectively (Nemanich and Solin, 1979; Wang et al. 1994). Since Raman spectrum is quite sensitive to lattice order breakdown Raman spectroscopy should provide information about graphite and the disordered carbon present.

In the first-order Raman spectrum of graphite, the E<sub>2g2</sub> vibration mode (polyaromatic structures) with D<sub>6h</sub><sup>4</sup> crystal symmetry occurs at around 1580 cm<sup>-1</sup> (G band). For poorly organized material, additional bands appear around 1150 cm<sup>-1</sup>, 1350 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, and 1620 cm<sup>-1</sup>. The 1350 cm<sup>-1</sup> band (D band) is known as the disorder or defect band. The origin of this band has been related to disorder allowed zone edge modes of microcrystalline graphite due to the presence of impurities, structural defects and tetrahedral carbon and its disorder is reflected by a shift in the position and by a shoulder at 1620 cm<sup>-1</sup>. Its intensity has been reported to be inversely proportional to the graphite grain size.

Both the 1150 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> bands appear only in very poorly organized carbonaceous material. Last, the 1620 cm<sup>-1</sup> band forms a shoulder on the G band. In perfect graphite, this component is absent while in very poorly organized material, the two bands cannot be resolved and then a single broad band occurs at around 1600 cm<sup>-1</sup> (Beny-Bassez and Rozaud, 1985; Beyssac et al., 2002, 2003; Lee, 2004; Tuinstra and Koenig, 1970; Wopenka and Pasteris, 1993). In the second-order spectrum several features appear around 2400 cm<sup>-1</sup>, 2700 cm<sup>-1</sup>, 2900 cm<sup>-1</sup> and 3300 cm<sup>-1</sup>, attributed to overtone or combination scattering (Nemanich and Solin, 1979). The most visible one, near 2700 cm<sup>-1</sup>, splits into two bands in well-crystallized graphite. According to Lespade et al. (1984), this splitting occurs when the carbonaceous matter acquires a triperiodic organization. The Raman parameters of these bands, frequency, full width at half maximum (FWHM) and intensity, are very sensitive to structural disturbances by electronic configuration sp<sup>2</sup>–sp<sup>3</sup> changes in the carbon bonds (C–C) and consequently their presence are used to estimate the structural properties of the carbon material. An important summary of the deconvolution of the Raman spectrum and the assignments of the different Raman bands is given in Li (2007).

**Table 1**  
Origin, rank, proximate, ultimate and petrographic analysis of coals.

Origin	Sample	Storage	% R <sub>r</sub>	Rank (ISO 11760, 2005)	Moist.		Volatile matter	C				O diff.		V		L
					wt.%	wt.% (db)		H	N	St	wt.% (daf)	wt.% (daf)	I	Vol.% (mmf)		
Penn State Coal Bank	Decs-24	Argon	0.42	Low A	13.20	13.39	47.14	76.26	5.30	1.32	6.38	10.74	90	7	3	
	Decs-18		0.50	Medium D	6.81	12.25	46.93	79.08	5.80	1.44	4.80	8.89	86	6	8	
	Decs-23		0.69	Medium C	2.00	9.44	43.53	81.95	5.63	1.49	4.27	6.66	79	14	7	
	Decs-12		0.81	Medium C	2.40	10.25	40.13	83.32	5.69	1.37	1.25	8.37	83	9	8	
	Decs-14		0.95	Medium C	1.46	10.52	36.42	85.20	5.46	1.45	2.01	5.87	89	8	3	
	Decs-3		1.19	Medium B	1.10	5.37	28.73	87.37	5.88	1.74	0.69	4.32	94	6	0	
	Decs-19		1.60	Medium A	1.01	4.60	19.19	89.87	4.90	1.14	0.78	3.31	90	10	0	
	PSOC-1515		2.30	High C	2.44	29.17	11.92	88.07	3.91	1.13	0.82	6.07	91	9	0	
	Decs-21		4.22	High A	3.99	11.15	5.08	90.33	4.01	0.80	0.57	4.30	87	13	0	

R<sub>r</sub>: vitrinite mean random reflectance; V, I, L: vitrinite, inertinite, liptinite.

Download English Version:

<https://daneshyari.com/en/article/1753740>

Download Persian Version:

<https://daneshyari.com/article/1753740>

[Daneshyari.com](https://daneshyari.com)