CARACTERIZATION OF COAL MACERAL GROUPS BY MICRO-RAMAN SPECTROSCOPY

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Resumo

Uma caracterização rápida e não-destrutiva da organização estrutural do material carbonoso pode ser conseguida através da espectroscopia micro-Raman, uma vez que podem ser obtidos espectros de áreas micrométricas. Uma aplicação óbvia desta técnica é a caracterização pontual de macerais do carvão. As análises de espectroscopia micro-Raman efectuadas em diferentes grupos macerais do mesmo carvão revelam, para além da presença dos habituais picos aos 1580 cm^{-1} e 1350 cm^{-1} no espectro de primeira ordem, dois picos de fraca intensidade: um próximo dos 1170 cm^{-1} nos macerais do grupo da inertinite e outro aos 1470 cm^{-1} nos macerais de vitrinite e liptinite. Os diferentes grupos macerais apresentam várias diferenças no espectro de primeira ordem, um estreitamento do pico 1580 cm^{-1} e seu deslocamento para números de onda mais elevados da vitrinite para a liptinite e inertinite; um deslocamento do pico 1350 cm^{-1} para números de onda mais baixos da vitrinite para a liptinite e para a inertinite, conjuntamente com o seu estreitamento na inertinite e um ligeiro aumento da razão entre a intensidade dos picos 1350/1580 da vitrinite para a inertinite e para a liptinite.

Abstract

A fast and non-destructive characterization of the local state of carbonaceous material may be achieved with a micro-Raman spectrometer, since spectra from micrometric areas can be recorded. Therefore, this technique can obviously be applied for characterization of coal macerals. Raman spectral analysis performed on different coal maceral groups of the same coal reveals not only the presence of the usual peaks at 1580 cm^{-1} and 1350 cm^{-1}on the first-order Raman spectrum, but also the presence of two additional weaker peaks, one around 1170 cm^{-1} in inertinite and another around 1470 cm^{-1} appearing in vitrinite and liptinite. Differences of the first-order spectrum of the different macerals include a shift of the 1580 cm^{-1} peak towards higher wavenumbers accompanied by its narrowing from vitrinite to liptinite and inertinite; a shift of the 1350 cm^{-1} peak towards lower wavenumber from vitrinite to liptinite and to inertinite together with a small narrowing in the inertinite and a slight increase in the 1350/1580 peak intensity ratio from vitrinite to inertinite and to liptinite.

Introduction

The usefulness of Raman spectroscopy in characterizing the state of structural order of carbonaceous materials, kerogen, coals and graphite was already been demonstrated (Tuinstra e Koenig, 1970; Lespade et al., 1984; Pasteris & Wopenka, 1991; Wopenka & Pasteris, 1993; Bustin et al., 1995); however the punctual characterization of specific coal macerals by this technique is unknown.

Several Raman parameters have been used to characterise the structural ordering of carbonaceous material: the frequency and width of the 1580 cm^{-1} band, the ratio of the intensities of the 1350 cm^{-1} and 1580 cm^{-1} peaks, the width of 2700 cm^{-1} band in the second order spectrum, among others (Tuinstra e Koenig, 1970; Lespade et al., 1984; Pasteris & Wopenka, 1991; Wopenka & Pasteris, 1993; Bustin et al., 1995).

The first-order Raman spectrum (recorded from 1200 to 1700 cm^{-1}) of well-crystallised pure-carbon graphite has one band at ~1582 cm^{-1} (O peak). The second-order spectrum (recorded from 2350 to 3350 cm^{-1}) shows a feature near 2700 cm^{-1} (S peak). Progressive disorder in graphite is reflected in the first-order Raman spectrum by a broadening and shifting of the 1582 cm^{-1} band to higher wavenumbers due to the development of a shoulder around 1620 cm^{-1} and an additional band near 1350 cm^{-1} (D peak) (Pasteris & Wopenka, 1991; Wopenka e Pasteris, 1993).

O peak at about 1580 cm^{-1} (E_{2g} mode) is due to the C-C vibrations in an aromatic structure and the D peak (~1350 cm^{-1}) corresponding to different types of structural defects.

The ratio of the intensities of the 1350 cm^{-1} and 1580 cm^{-1} peaks (ID/IO) has been related to the crystallite size L_a and its decreasing is generally sensitive to a cristallinity increase. The 2700 cm^{-1} peak appears only in the final stages of the graphitisation process and is related to three-dimensional ordering (Lespade et al., 1984).

The purpose of this study is to describe the Raman spectra obtained on vitrinite, liptinite and inertinite of the same coal and also to compare the Raman parameters between the studied maceral groups.

Analytical method

Micro-Raman spectroscopy was performed on polished blocks in vitrinite (collotelinite), liptinite (spores) and inertinite (fusinite) of a high volatile bituminous coal (see tables 1 and 2), using a Labram Dilor- Jobin Yvon-Spex spectrometer attached to an Olympus microscope. The excitation was done with 633 nm lines of a He-Ne laser with an output of 20mW.

The points were chosen from the most representative and homogeneous parts of the different macerals and each one was scanned from 1200 to 1700 cm-1 for the first order Raman spectrum. Here we characterised the O peak at about 1580 cm^{-1} and the D peak around 1350 cm^{-1}. The Raman parameters such as the frequency and width of the 1580 cm^{-1} band, the ratio of the intensities of the 1350 cm^{-1} and 1580 cm^{-1} peaks were obtained from the resolution of the first order Raman spectrum using a mixed Gaussian-Lorentzian function and the Labspec program of Dilor-Jobin Yvon.

In tables 1 and 2 the characteristics of the coal studied are presented.

Table 1 –Vitrinite mean random reflectance value (Rr%) and coal maceral groups, mineral matter free (%, volume)

Rr	Vitrinite	Liptinite	Inertinite
0.6	41	4	55

Table 2 - Proximate and ultimate analysis

Proximate (d^1, % wg; daf^2, % wg)			Ultimate (daf^2, % wg)				
Ash^1	Volatile matter^2	Fixed carbon^{2,3}	C	H	N	S	O^3
14.14	34.72	64.93	77.03	4.99	1.74	0.84	15.4

^{1}d– dry; ^{2}daf – dry ash free; ^{3}by difference.

Results

The main spectral results from the different maceral groups are shown in Figures 1-3 and in Table 3. All the spectra reveal the presence of the usual peaks at 1580 cm^{-1} (O peak) and 1350 cm^{-1} (D peak) on the first-order Raman spectrum, however two additional weaker peaks appear, one around 1170 cm^{-1} in inertinite (Fig. 3) and another around 1470 cm^{-1} vitrinite and liptinite (Figs. 1, 2). These latter two peaks are associated with the disorder effects and the later was associated by Mernagh et al. (1984) with the effect of exposure to the laser and attributed to C-O vibrations of surface carboxylates or related oxidized species. No second-order features were observed in the three maceral groups.

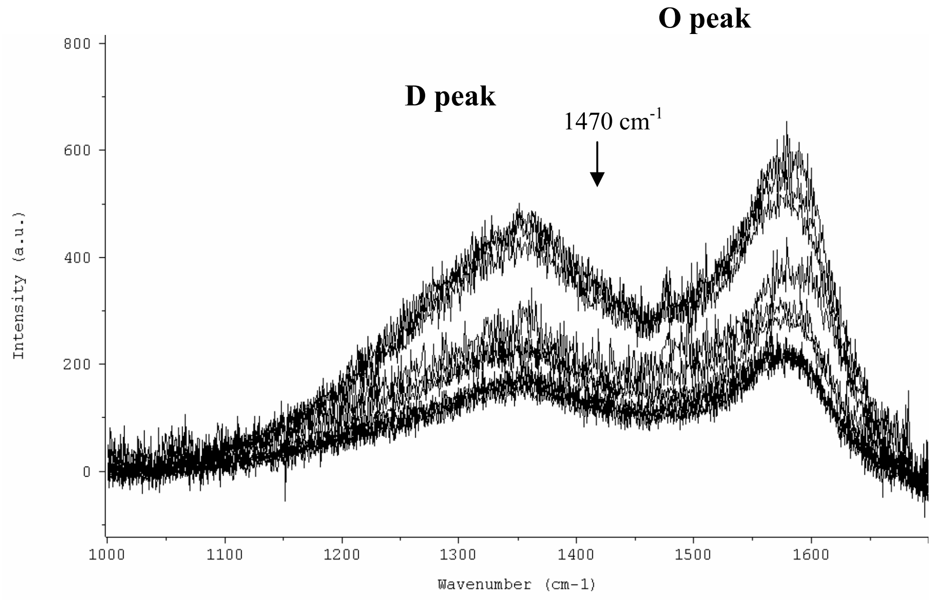

Fig. 1: Raman spetrum obtained on vitrinite.

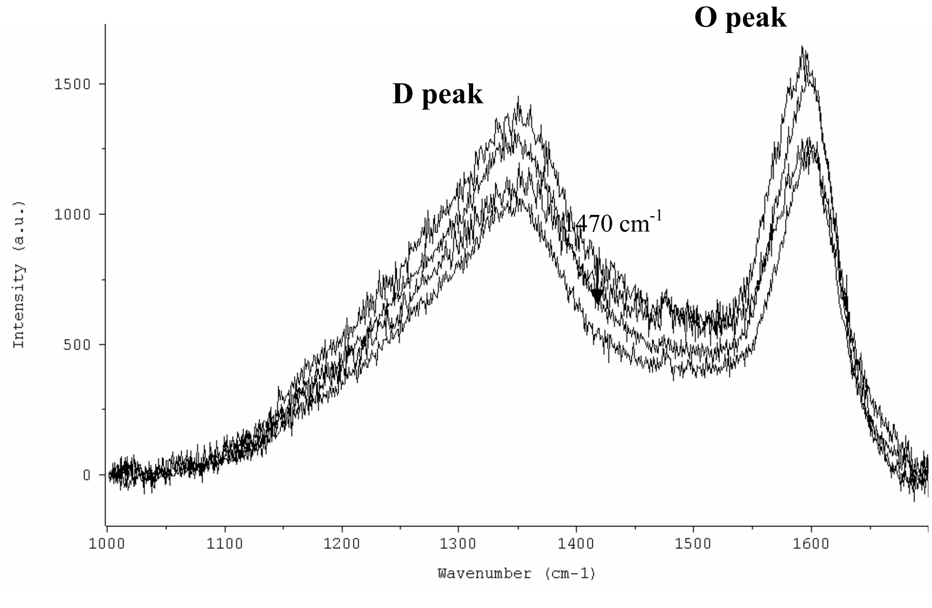

Fig. 2: Raman spetrum obtained on liptinite.

Differences in the first-order spectrum between the different maceral groups include a shift of the 1580 cm^{-1} peak toward higher wavenumbers accompanied by its narrowing from vitrinite to liptinite and inertinite (Tab. 3 and Fig. 4), and a shift of the 1350 cm^{-1} peak toward lower wavenumber from vitrinite and liptinite to inertinite together with a small narrowing in inertinite (Tab. 3 and Fig. 5). The ratio of the intensities of the 1350 cm^{-1}

and 1580 cm^{-1} peaks (ID/IO) show a slight increase from vitrinite to inertinite and to liptinite (Fig. 6). The same trend is observed for the ratio of the integrated intensities of the 1350 cm^{-1} and 1580 cm^{-1} peaks (SD/SO) (Fig. 7).

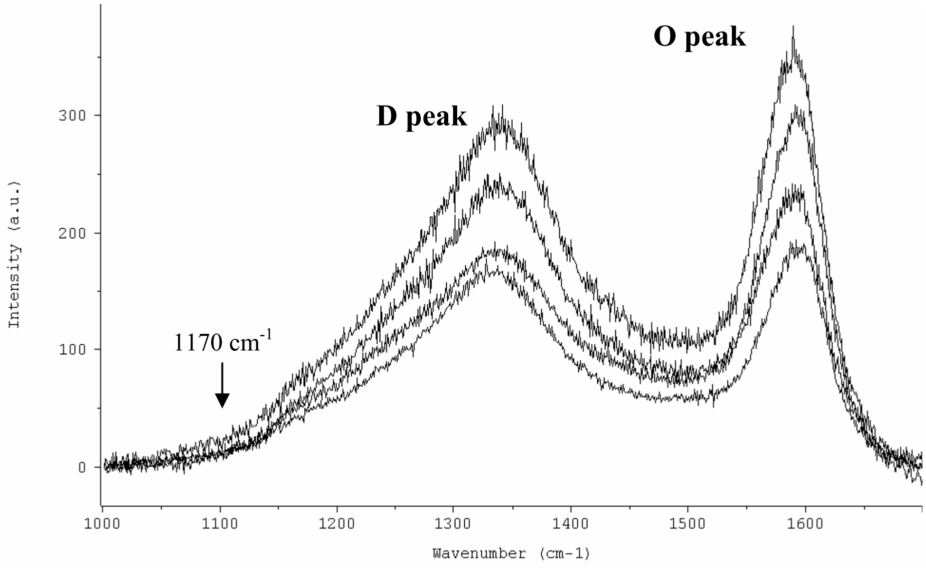

Fig. 3: Raman spetrum obtained on inertinite.

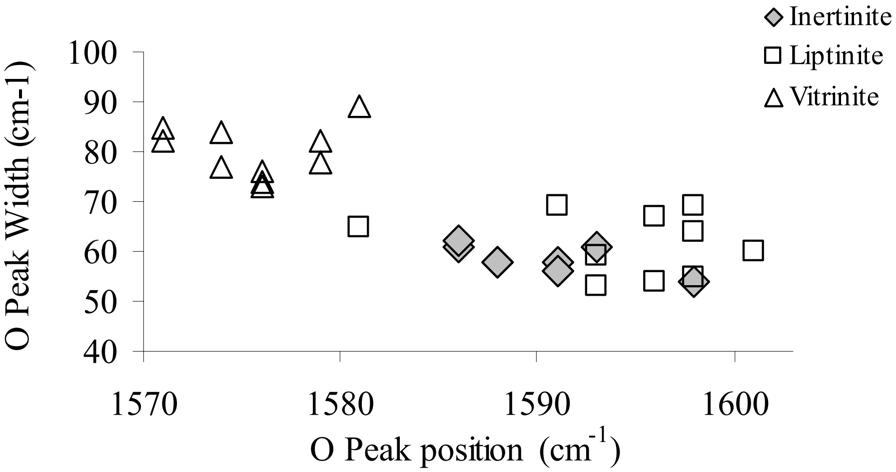

Fig. 4: Peak position vs. peak width (FWHM) of O peak of the different maceral groups.

Table 3 –Raman parameters (mean values)

		ν	I	W	S
Vitrinite					
Peak	n	10	10	10	10
	Min	1344	137	207	39023
1350	Max	1351	443	213	130099
	Mean	1350	266	218	77230
	STDV	4	126	20	36173
	n	10	10	10	10
	Min	1474	18	36	1108
1470	Max	1481	92	74	54957
	Mean	1477	51	55	9067
	STDV	2	22	14	16288
	n	10	10	10	10
	Min	1571	195	73	20679
1580	Max	1581	529	89	62376
	Mean	1576	312	80	36523
	STDV	3	131	5	15515
Liptinite					
Peak	n	10	10	10	10
	Min	1337	164	202	46145
1350	Max	1349	1213	227	379056
	Mean	1346	738	212	185934
	STDV	4	390	31	126306
	n	10	10	10	10
	Min	1474	12	3	56
1470	Max	1486	115	188	304171
	Mean	1477	55	70	35395
	STDV	3	34	73	94651
	n	10	10	10	10
	Min	1581	203	53	19078
1580	Max	1601	1498	69	121494
	Mean	1595	863	62	75609
	STDV	6	488	6	38464
Inertinite					
Peak	n	10	10	10	10
	Min	1170	4	21	116
1170	Max	1178	12	53	865
	Mean	1173	9	40	511
	STDV	2	3	10	248
	n	10	10	10	10
	Min	1324	92	159	21620
1350	Max	1339	299	190	79424
	Mean	1335	214	189	57289
	STDV	4	64	14	18040
	n	10	10	10	10
	Min	1586	97	54	8432
1580	Max	1598	396	62	37016
	Mean	1590	271	58	24110
	STDV	4	89	3	8243

n: number of analysis; ν: wavenumber (cm^{-1}); I: Raman intensity; W (FWHM): width at half maximum; S: integrated intensity.

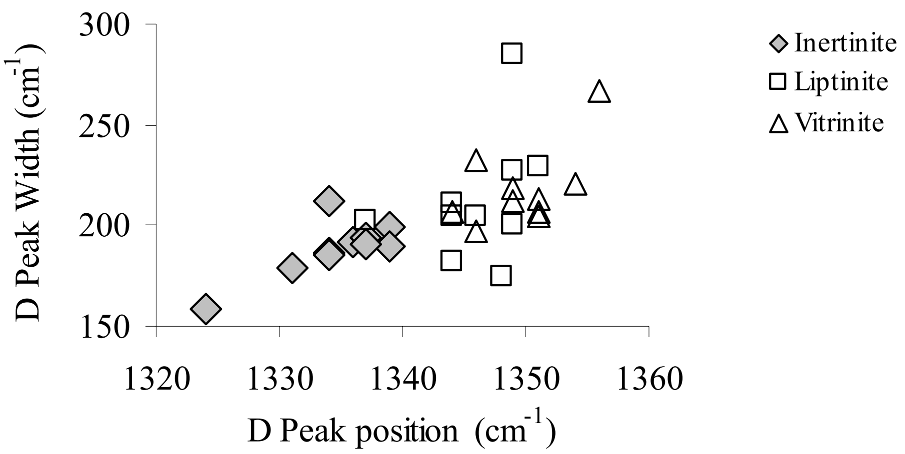

Fig. 5: Peak position vs. peak width (FWHM) of D peak of the different maceral groups.

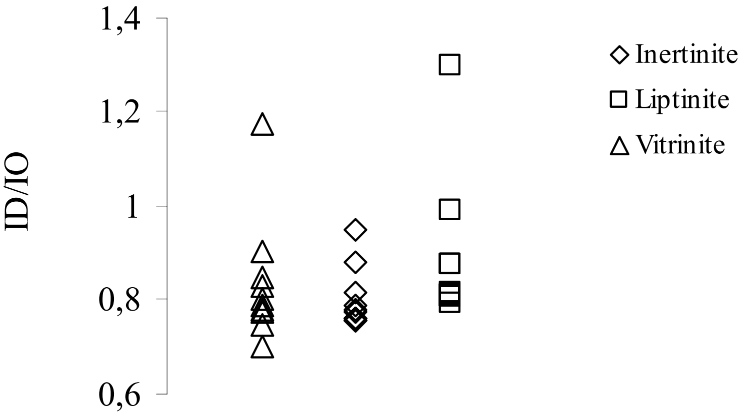

Fig. 6: Intensity ratio of D peak to O peak of the different maceral groups.

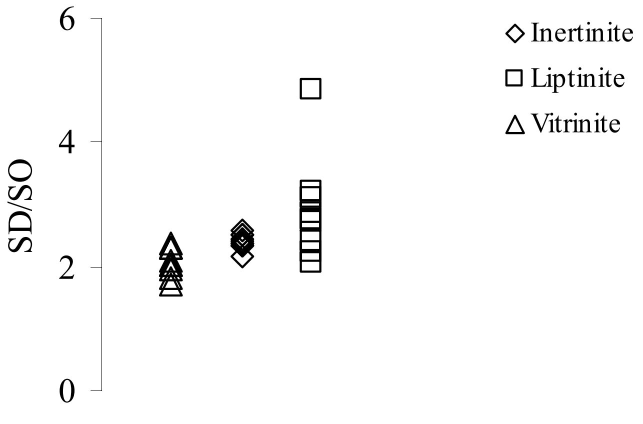

Fig. 7: Integrated intensities of D peak to O peak of the different maceral groups.

Conclusions

Raman spectral analysis performed on vitrinite, liptinite and inertinite macerals of the same coal reveals not only the presence of the usual peaks at 1580 cm^{-1} and 1350 cm^{-1}on the first-order Raman spectrum, but also the presence of two additional weaker peaks, one around 1170 cm^{-1} in inertinite and another around 1470 cm^{-1} in vitrinite and liptinite.

No second-order features were observed in the three maceral groups.

Differences of the first-order spectrum of the different maceral groups include a shift of the 1580 cm^{-1} peak toward higher wavenumbers accompanied by its narrowing from vitrinite to liptinite and inertinite; a shift of the 1350 cm^{-1} peak toward lower wavenumber from vitrinite to liptinite and to inertinite together with a small narrowing in the inertinite, a slight increase in the 1350/1580 peak intensity ratio from vitrinite to inertinite and to liptinite. Similar values of integrated intensities of the 1350 cm^{-1} and 1580 cm^{-1} peaks ratio were obtained for the different maceral groups.

Acknowledgements

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