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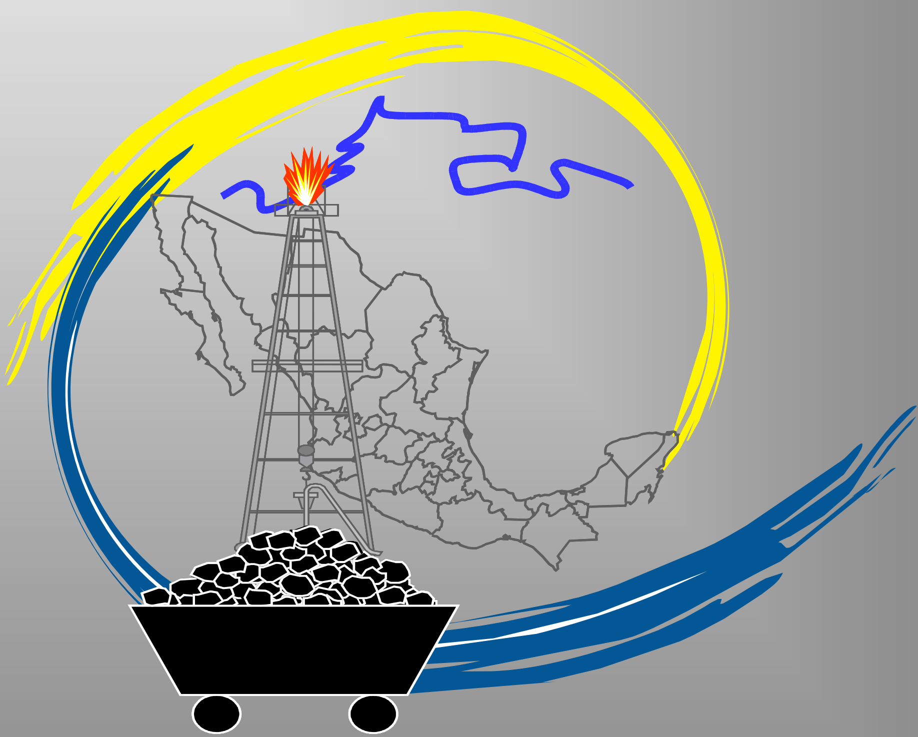

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APPLICATION OF ATTENUATED TOTAL REFLECTANCE MICRO-FOURIER TRANSFORM INFRARED (ATR-FTIR) SPECTROSCOPY TO THE STUDY OF COAL MACERALS: EXAMPLES FROM THE SABINAS BASIN, MEXICO

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ABSTRACT

Attenuated total reflectance micro-Fourier transform infrared (ATR-FTIR) spectrometry has been successfully used to characterise coal macerals, in particular telocollinite in coals from the Sabinas Basin, Mexico. The results show that ATR-FTIR is very sensitive to the increasing aromaticity of the telocollinites, and thus is a very useful tool to study the evolution of aromatic and aliphatic functional groups with maturation of telocollinite, and also to differentiate and characterize the various macerals in coal samples.

RESUMEN

La reflectancia total atenuada micro-Fourier (ATR-FTIR) en espectrometría ha sido utilizada con éxito para caracterizar macerales de carbón, en particular en telocollinita en carbones de la Cuenca de Sabinas, México. Los resultados muestran que el ATR-FTIR es muy sensible para incrementar la aromaticidad de las telocollinitas, y por lo tanto es una herramienta muy útil para estudiar la evolución de los grupos aromáticos y alifáticos con la maduración de la telocollinita, y también para diferenciar y caracterizar las variedades de macerales en muestras de carbón.

INTRODUCTION

Fourier transform infrared (FTIR) spectroscopy has been used for some decades to investigate a range of different materials, generally non-destructively. This is because the infrared spectrum can provide crucial information on the molecular structure of organic compounds, in particular the functionalities such as aromatic and aliphatic groups, carbonyl and hydroxyl. Application of infrared spectroscopy to coal characterization did not really take off until the early 1980s with the advent of interferometric spectrometers (Brown et al., 1981; Painter et al., 1981). The recent development of infrared microscope, as well as processing techniques, renewed the interest for the study of macerals (Sobkowiak and Painter, 1992; Mastalerz and Bustin, 1993, 1995, 1996; Pradier et al., 1996). One recent development in FTIR techniques is the incorporation of an attenuated total reflectance crystal (ATR) into the objective of an FTIR microscope (Reffner et al., 1991). The ATR crystal is brought into contact with the sample while the FTIR spectrum is collected, allowing spectra with improved signal-to-noise ratio to be obtained, compared to conventional micro-FTIR techniques (transmission and reflection). The ATR method applied to coal is that standard polished block samples can be used without further sample preparation (Thomasson et al., 2000). The spectrum obtained by reflectance micro-FTIR from a polished block sample is a reflectance spectrum and is considerably distorted in comparison to an absorption spectrum. Previous workers have attempted to correct this distortion by applying a mathematical procedure (Figure 1; Kramers–Krönig transformation; Mastalerz and Bustin, 1996). ATR does not require this type of correction, although it should be noted that band intensities differ from those in a true absorbance spectrum because of the relationship between penetration depth and wavelength that exists in ATR spectroscopy (Harrick, 1967). This effect in ATR-FTIR spectra can be easily corrected with software because the intensity of the bands is directly related to the wavelength of the IR light (Thomasson et al., 2000). Finally, the true spatial resolution (25 to 30 μm) is similar to that obtained by conventional micro-FTIR methods (Chan and Kazarian, 2003).

In this paper, we report the application of ATR-FTIR to the organic characterization of Sabinas coals directly in polished samples.

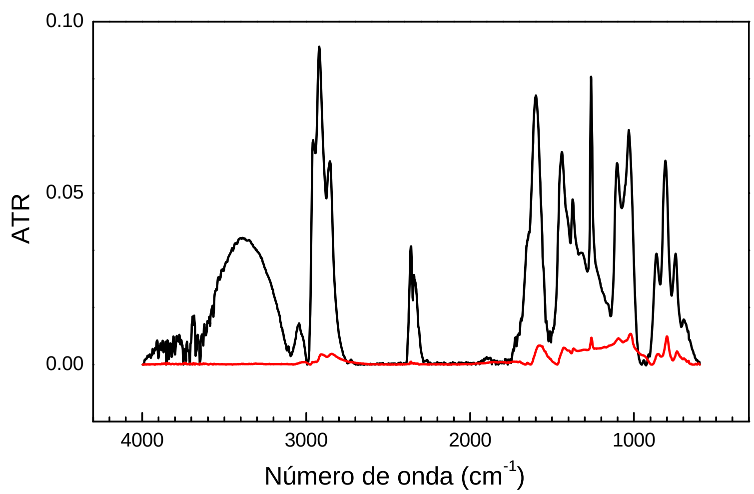

Figure 1. ATR-FTIR vs reflection micro-FTIR spectra of telocollinite for 2 samples from Mine VI strata of the Sabinas Basin. Black: ATR- FTIR spectra; Red: reflection micro-FTIR spectra.

EXPERIMENTAL

A Hyperion Bruker FTIR spectrometer, equipped with an Olympus microscope incorporating an attenuated total reflectance (ATR) objective, was used to collect spectra for the samples examined in the study. In this study, the FTIR spectra were obtained in ATR mode from polished sections, following similar procedures to those described by Thomasson et al. (2000). Polished sections of coal blocks were mounted on the microscope stage, and set in a horizontal orientation. After visually selecting the desired area for analysis, the ATR crystal was moved into place and the sample stage raised so that contact was made with the polished surface of the coal sample. The ATR-FTIR spectra were recorded on equipment by the accumulation of 125 scans with a spectral resolution of 4 cm^{-1} over the range of 4000-650 cm^{-1}, which gave good signal-to-noise ratio. Background spectra of air were collected for every sample immediately before the collection of the sample single-beam spectrum.

Six different samples have been recollected in three different strata in the mine work I, II and VI within the Sabinas coal basin.

RESULTS AND DISCUSSION

Among those 22 spectra collected on the six different macerals, at least 19 spectra were collected from telocollinite and 3 spectra from other macerals (Figure 2 and Table 1; fusinite). Whenever possible, the spectra were only collected from areas consisting of "pure" macerals, without intimate admixture of any other macerals or minerals in the area under investigation.

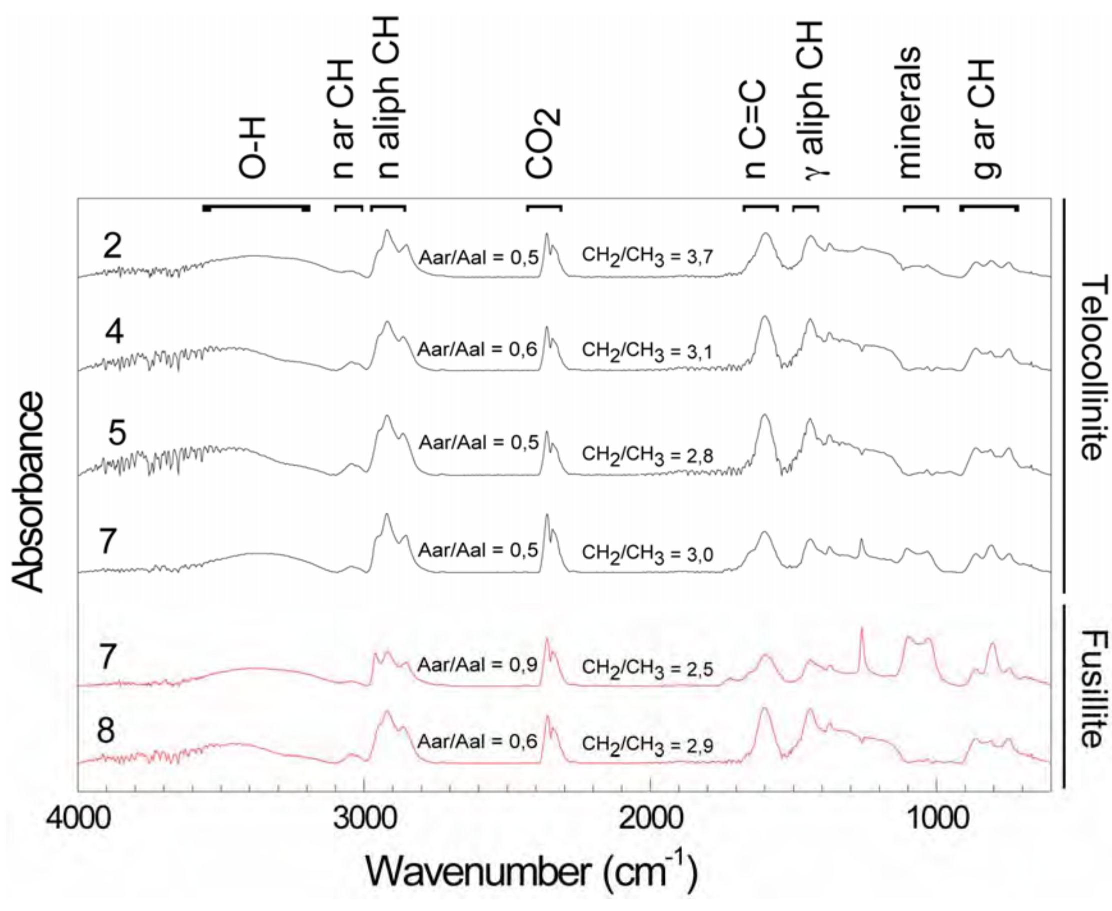

Figure 2. ATR-FTIR spectra of telocollinite (TC) and fusinite (FUS) for Mine I to VI samples from the Sabinas Basin.

The ATR-FTIR spectra reveal strong aliphatic bands (3000-2800 cm^{-1} and 1450-1380 cm^{-1}), with a lower aromatic contribution (3060, 1600 and 900-700

cm^{-1}), and the presence of an amount of C=C (1650-1550 cm^{-1}). As well the presence of oxygen in the structure is highlight by the OH groups (3600-3100 cm^{-1}), but no carboxyl band (C=O 1650-1750 cm^{-1}) is identified.

Table 1. Structural parameters deduced of ATR-FTIR measurements.

Mine	*Spectra*	*CH_2/CH_3*	*Aar/Aal*	*C=C (area)*
Mine II strate 1	2A-1	3,7	0,5	6,3
Mine II strate 1	2A-2	3,6	0,5	6,4
Mine II strate 1	2B-1	3,5	0,5	6,7
Mine II strate 1	2B-2	3,5	0,6	4,9
Mine II strate 1	2B-3	3,7	0,6	5,8
Mine II strate 1	2C-1	3,5	0,5	6,5
Mine II strate 2	4A	3,1	0,6	6,7
Mine II strate 2	4B	3,0	0,6	6,7
Mine II strate 2	4C	3,3	0,6	6,4
Mine I strate 1	5A	2,7	0,5	6,6
Mine I strate 1	5B	2,9	0,5	6,6
Mine I strate 1	5C	2,8	0,6	7,4
Mine VI, strate 2	6B	2,7	0,6	5,4
Mine VI, strate 2	6C	2,6	0,6	5,1
Mine VI, strate 1	7A	3,0	0,5	5,5
Mine VI, strate 1	7B	3,0	0,6	5,9
Mine VI, strate 1	7C	2,5	0,9	4,4
Mine VI, strate 3	8A	2,9	0,6	6,8
Mine VI, strate 3	8B	3,0	0,6	6,8
Mine VI, strate 3	8C	3,1	0,6	6,5

The methyl to methylene ratio can be considered as an estimate of the length of aliphatic chains of coal and a branching index (Ibarra et al., 1994). The CH_2/CH_3 parameter, which is related with length aliphatic chains, was obtained by deconvolution of the region from 2750 to 3200 cm^{-1} containing 2922 and 2854 cm^{-1} bands attributed to stretching asymmetric of CH_3 and CH_2 groups, respectively. When this parameter is higher, it is possible to infer that aliphatic chains bounding aromatics rings are longer, since a coal with a high concentration of CH_3 has a compact structure with less space between aromatic clusters. The CH_2/CH_3 parameter for the telocollinite and fusinite ranges, respectively, from 2.6 to 4.4 and from 2.5 to 3.1. Another parameter that is related to the aromatic factor and with a grade of maturity of coals is $Area_{aromatic}$/ $Area_{aliphatic}$ ratio (900-700 cm^{-1} / 3000-2815 cm^{-1}). The aromatic ratio for the telocollinite and fusinite ranges, respectively, from 0.5 to 0.7, and from 0.6 to 0.9. The C=O structures tend to decrease with increasing coalification, and they practically disappear at the stage of bituminous coal (Ibarra et al., 1996). The band intensity and the variation range of the different structural parameter are comparable in each type of samples. In comparison with the spectrum of telocollinite, the absorbance of fusinite for the same coal has the following characteristics: (1) less stronger absorbance of aromatic CH stretching at 3046 cm^{-1} relative to the aliphatic CH stretching at the region between 3000 to 2700 cm^{-1}, and (2) much stronger absorbance in both the

1020 cm^{-1} and 870 cm^{-1} bands. The stronger absorbance of fusinite at 878 cm^{-1}, compared with the telocollinite of the same coal, could be attributed to an increase in isolated aromatic H in the fusinite.

SUMMARY

The ATR-FTIR technique has been proven to be a simple, fast and effective method to study the FTIR spectra of coal macerals in situ and independently. Micro-FTIR has the advantage that it avoids the difficult and time-consuming procedures for “pure” maceral separation. In comparison with other micro-FTIR techniques, ATR-FTIR has many advantages: (1) sample preparation is reduced as a polished block (2) ATR-FTIR presents a better signal-to-noise ratio and sensitivity without spectral distortion. ATR-FTIR is also proved to be a sensitive tool to evaluate the variations of aromatic and aliphatic functional groups in telocollinites associated with coal maturation processes, indicating the sensitivity of the aromaticity of vitrinite macerals to rank advance. The absorbance intensity of the aromatic C–H groups shows a clearly increasing trend with coal rank, apparently at the expense of the aliphatic functional groups.

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