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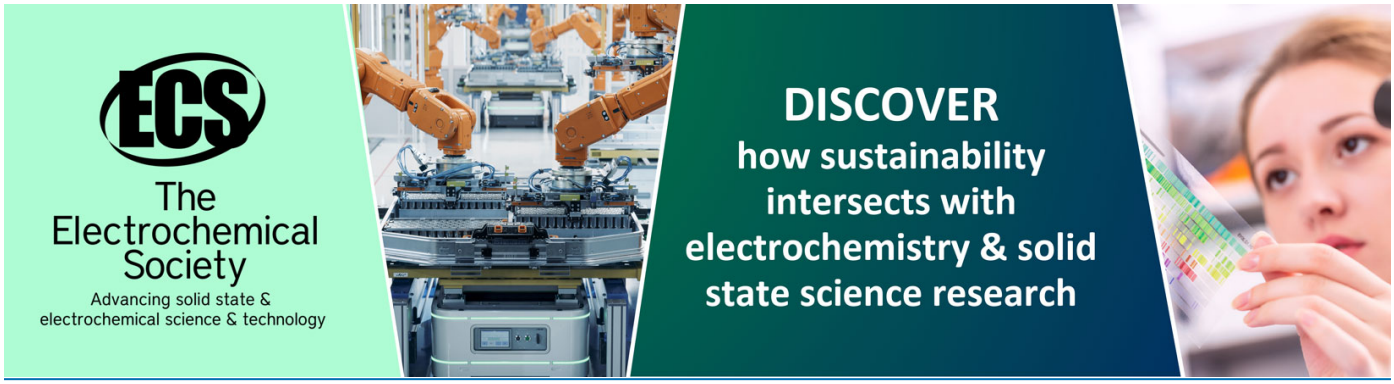

Comparison of photoacoustic and attenuated total reflectance for the qualitative analysis of a bituminous Colombian coal by Fourier transform infrared spectroscopy

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Abstract. A Colombian coal from La Loma, Cesar, Colombia, field was characterized by Fourier transform infrared photoacoustic spectroscopy. Spectral analysis was focused on the mid-infrared, where previous publications have shown remarkable changes in the coal structure. Instrumental parameters of the infrared spectrometer were investigated for optimal spectra acquisition. Optimal parameters are a mirror velocity of $0.16\ \mathrm{cm/s}$, a number of scans of 512, and a resolution of $2\mathrm{cm}^{-1}$. Results of Fourier transform infrared photoacoustic spectroscopy were compared with Fourier transform infrared attenuated total reflectance for validation. Both techniques can be implemented with a minimum sample preparation. Finally, vibrational modes of the functional groups were identified.

1. Introduction

Coal is a hydrocarbon resource with a highly complex chemical structure. Fourier transform infrared (FTIR) spectroscopy has been widely used for the analysis of coal and coal chars, providing insights into molecular structure, mostly the functional groups [1,2]. The analysis of the infrared spectra of the coal allows understanding the possible use of raw samples and expected products of the coal conversion processes [3]. When working on complex solid samples, FTIR spectroscopy can be coupled to attenuated total reflectance (ATR) or photoacoustic spectroscopy (PAS). In the ATR mode, an infrared beam is totally reflected at the boundary between the ATR crystal and the sample. In the PAS experiment, the sample absorbs a modulated infrared beam and transforms it into heat by nonradiative deexcitation processes; it gives rise to periodic temperature oscillations within the sample which produce pressure oscillations to the gas surrounding the sample. These pressure oscillations are detected by a microphone as an acoustic wave that is converted into an electrical signal and then into the corresponding spectrum.

Diverse analyses of Colombian coal have been carried out by using ATR [4,5] and PAS [6,7]. However, the application of FTIR-PAS to Colombian coal and coal char has not been very common. A set of instrumental parameters for an optimal PAS spectra acquisition that allows us to obtain structural information of coal is completely lacking.

Previous investigations have compared different FTIR techniques for a variety of samples e.g. pharmaceutical compounds [8], semisolid fats and edible oils [9], and polymers [10,11]. However, to the knowledge of us, only Orrego-Ruiz (2008) compared FTIR techniques implemented on Colombian coal; he found that PAS has a better spectral repeatability for studying coal than ATR [12]. In the present

study, we investigated the instrumental parameters for optimal spectra acquisition. We aimed to characterize coal by FTIR-PAS and to validate PAS results with ATR.

2. Experimental description

A coal sample was collected from La Loma (Cesar) field, Colombia, according to standard practice ASTM-D2234 (American Society Testing and Materials) [13]. The sample was pulverized, sieved and dried. The particle size, D_p, was $0.5\text{mm} < D_p < 1.0\text{mm}$. Proximate (moisture, volatile matter, ash, and fixed carbon), ultimate (carbon, hydrogen, and nitrogen), and sulfur analyses were performed in accordance with ASTM procedures [14–16]; the corresponding data are reported in Table 1. Based on the ASTM D388 classification [17], this sample is a high-volatile C bituminous coal: the volatile matter content is greater than 31% the fixed carbon is less than 69%, and its gross calorific value is between 10500 and 13000 BTU/lb.

Table 1. Proximate and ultimate analyses of the studied coal.

Proximate analysis					Ultimate analysis				
%Ash	%VM	%FC	RH	CV (BTU/lb)	C	H	O	N	S
6.77	40.84	52.39	10.87	12541	71.67	6.22	19.69	1.57	0.85

Abbreviations: VM – Volatile Matter, FC – Fixed Carbon, RH – Relative Humidity, CV – Calorific value.

Before the spectroscopic analysis, the coal was grounded to overcome problems of heterogeneity and dried at 363K overnight to avoid spectral perturbations at 3400 and 1630cm^{-1} due to the adsorbed water.

FTIR-PAS spectra were run on grounded coal by using a Thermo Scientific Nicolet iS50 FTIR Spectrometer equipped with a photoacoustic cell (PAC) MTEC 300. The PAC was purged by helium gas for 120min, to minimize CO_2 and H_2O vapor interference in the spectra, and then sealed. Helium flow rate about $9\,\text{cm}^3/\text{s}$ was established in the PAC. Carbon black was used for collecting the background spectra. Coal was kept in a stainless-steel cup and placed in the PAC. Spectra were recorded on the range from 400 to 4000cm^{-1} at a resolution of 2 or 4cm^{-1} and 32, 64, 128, 256, 512 or 1024 scans. Mobile mirror velocity in the Michelson interferometer was of 0.16 or $0.32\,\text{cm}/\text{s}$.

FTIR-ATR spectrum was measured by using the same spectrometer. Before scanning the sample, the ATR diamond crystal was thoroughly cleaned and dried to minimize the memory effect; a background spectrum was taken with the empty crystal and stored in the computer. The coal sample was pressed against the ATR crystal for measurement to ensure close and complete contact. Spectrum was recorded by the accumulation of 512 scans with a spectral resolution of 2cm^{-1} over the range from 400 to 4000cm^{-1}.

3. Results and discussion

In the current study, we found that the best conditions for the acquisition of the FTIR-PAS spectra for pulverized coal according to the signal-to-noise ratio are: the lowest mirror velocity: $0.16\,cm/s$; the highest resolution: $2cm^{-1}$; and number of scans: 512. We determined these optimal conditions after experimenting with different instrumental parameters. The choice of instrumental operating conditions is often crucial for obtaining quality spectra.

The signal-to-noise ratio is a useful quantity to describe the quality of an analytical method. The signal (S) has the information related to the analyte and the noise (N) has the unrelated one. The noise is defined as standard deviation of a signal's measured values and the signal is the average of those measurements; this assumes that the signal is relatively constant over the period for which these measurements have been taken. Since some noises are originated from effects related to thermodynamics and quantum mechanics, it is impossible to obtain data without noise. Although a very large S/N ratio is desirable, it may be prohibited due to the cost in time and other resources. For this reason, an acceptable S/N ratio becomes the goal. A better S/N ratio allows detecting weaker analyte signals.

Details about factors affecting the signal-to-noise ratio in FTIR spectroscopy can be found elsewhere [18–21].

We calculated the signal-to-noise ratio in the $1800 - 2000\text{cm}^{-1}$ range, where signals assignable to functional groups do not appear (spectral background). Figure 1 shows how the S/N ratio is influenced by the instrumental parameters: mirror velocity, resolution, and number of scans. We found that the lowest mirror velocity provided a smoother spectrum; something predictable. The relation between the mirror velocity and the photoacoustic signal is the following: a high velocity implies that the time of interaction between the radiation and the sample is short and hence the photoacoustic intensity is low; the lower the mirror velocity, the higher the signal. Regarding the resolution, we can point out that selecting the highest resolution (2cm^{-1}) separate the spectral band of interest from the nearby overlapping bands, allowing to identify weak peaks or shoulders. Data of the signal-to-noise ratio display that in general when the number of scans increases, the signal-to-noise ratio becomes better. We chose a number of scans of 512 for the highest accuracy.

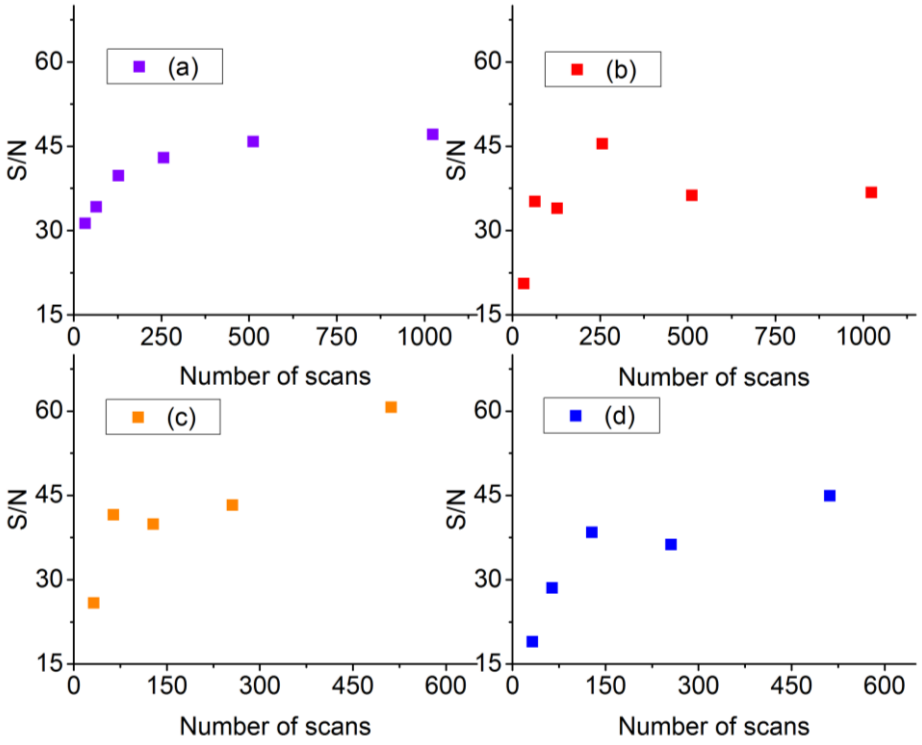

Figure 1. Variation of signal-to-noise ratio with spectrometer parameters: mirror velocity (v), resolution (R), and number of scans. (a) $\text{v} = 0.16\,\text{cm/s}$ and $\text{R} = 4\text{cm}^{-1}$. (b) $\text{v} = 0.32\,\text{cm/s}$ and $\text{R} = 4\text{cm}^{-1}$. (c) $\text{v} = 0.16\text{cm/s}$ and $\text{R} = 2\text{cm}^{-1}$. (d) $\text{v} = 0.32\,\text{cm/s}$ and $\text{R} = 2\text{cm}^{-1}$.

Spectra of coal obtained from FTIR-PAS and FTIR-ATR techniques with the optimal parameters are compared in Figure 2; the frequencies of characteristic coal bands are labeled. Both spectra are broadly comparable and have similar functional groups. They show characteristics vibrational bands of the coal: aromatics bending modes ($900 - 700cm^{-1}$ region), aliphatic bending modes ($1450cm^{-1}$ and $1380cm^{-1}$ bands), and aliphatic and aromatics stretching modes ($3100 - 2800cm^{-1}$ region). The absorption bands were assigned based on comparison with patterns reported in the literature [1–3,6] and are shown in Table 2. Although the FTIR-ATR spectrum is smoother than the FTIR-PAS spectrum, the latter also allows identifying the bands in the mid-infrared region whose frequencies can determine the relevant functional groups of coal.

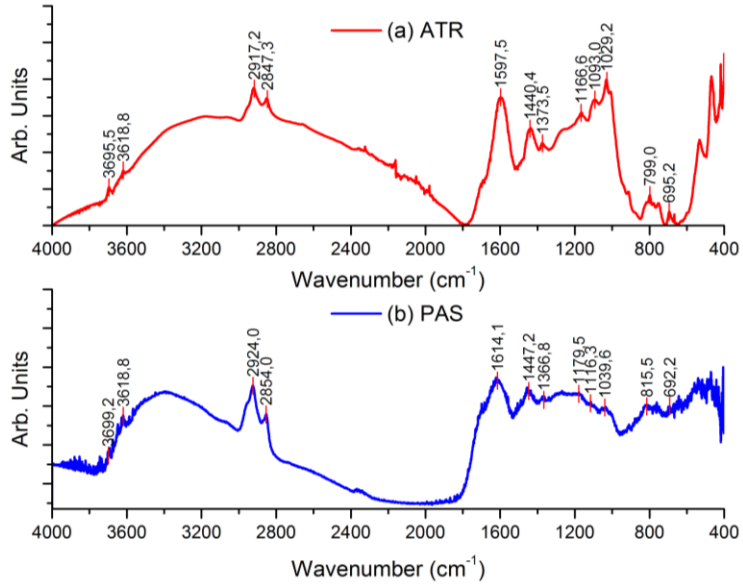

Figure 2. Spectra of coal sample from (a) FTIR-ATR and (b) FTIR-PAS measurements at a mirror velocity of $0.16\,\mathrm{cm/s}$, 512 scans and a resolution of $2\mathrm{cm}^{-1}$.

Table 2. Band assignments on infrared spectra of coal.

Wavenumber (cm^{-1})	Band assignment	Wavenumber (cm^{-1})	Band assignment
$3700-3615$	O-H in silicate mineral	$1615-1590$	$(C\text{-}H)_{ar}$ poly-aromatic system
$3600-3100$	-OH stretching	$1460-1445$	$(C\text{-}H)_{al}$ bending
$3100-3000$	$(C\text{-}H)_{ar}$ stretching	$1375-1365$	$(CH_3)_{al}$
$3000-2800$	$(C\text{-}H)_{al}$ stretching	$1300-1100$	Phenolic deformation C-O (stretching) and -OH bending
$2980-2960$	$R\text{-}CH_3$ asymmetric stretching	$1180-1025$	Si-O- stretching
$2925-2916$	R_2CH_2- asymmetric stretching	$925-670$	$(C\text{-}H)_{ar}$ out of plane bending
$2855-2845$	RCH_2- symmetric stretching	$860-750$	Aromatic rocking HCC

Previous studies showed results about infrared characterization by PAS and ATR that we consider important to remark. Yang and Irudayaraj (2000) concluded that PAS is very powerful for analyzing solids and low-moisture samples while ATR is a confirmed method for high-moisture samples [9]. Orrego-Ruiz found that PAS has a better spectral repeatability for studying coal than ATR [12]; in general, lesser relative standard deviation (RSD) values were obtained for PAS than ATR after determined the RSD for spectra of the same coal sample in the $4000-650\mathrm{cm}^{-1}$ range, the aliphatic region ($3000-2800\mathrm{cm}^{-1}$) and the aromatic region ($900-700\mathrm{cm}^{-1}$).

Taken together, our study investigated the effect of some instrumental parameters on the infrared spectroscopic analysis in the case of PAS mode. As compared with ATR, PAS also allows a reliable identification of the chemical functionalities of coal. Future studies can be addressed towards the analysis of the structural transformations of the Colombian coal in the conversion processes.

4. Conclusions

The potential of Fourier transforms infrared photoacoustic spectroscopy (FTIR-PAS) for the structural analysis of Colombian coal was proved in this study. The instrumental parameters (mirror velocity, resolution, and number of scans) were varied to obtain spectra with an acceptable signal-to-noise ratio (S/N). PAS results were compared with ATR results to perform a validation. It was demonstrated that both techniques are powerful for the characterization of this kind of opaque and dark samples, allowing to obtain structural information of Colombian coal reliably.

Acknowledgements
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