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Characterization of Soil Humic Substances Using Mid-infrared Photoacoustic Spectroscopy

Changwen Du, Zhongqi He, and Jianmin Zhou

Abstract Fourier transform infrared photoacoustic spectra (FTIR-PAS) have been applied to characterize soil humic substances, i.e., humic acid (HA), mobile humic acid (MHA), and recalcitrant calcium humate (CaHA) from Leonardite soil. Conventional transmittance infrared spectra and FTIR-PAS spectra of these humic substances were collected. The FTIR-PAS spectra were significantly different from the transmittance spectra. Totally, the absorption bands of transmittance spectra in the wavenumber range of 2,000–3,800 cm^{-1} were significantly broader than that of FTIR-PAS spectra, but the absorption bands in the wavenumber range of 1,000–1,800 cm^{-1} were obviously narrow than that of FTIR-PAS spectra. The band height of both aliphatic and carboxyl groups in the FTIR-PAS spectra was lower than that of transmittance spectra; however, the ratios of these two band were similar, and the ratio can be used to show the capability of water repellence of humic substances. All the results indicated that FTIR-PAS technique could provide a simple and fast method for quantifying of functional groups in soil humic substances.

Keywords Humic substances • Photoacoustic spectroscopy • Aliphatic group • Carboxyl groups • Characterization

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Introduction

The structure of soil humic substances can be investigated using various spectroscopic methods. Infrared spectroscopy is a relative simple, yet important, technique (He et al. 2006; Mao et al. 2008). Usually, infrared transmittance and reflectance spectroscopy were used to characterize soil humic substances; however, the pellet preparation is time-consuming for transmittance spectra, and the signal is not stable enough due to varied sample particle size for reflectance spectra. Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS), which based on photoacoustic theory, was recently used in soil science (Du and Zhou 2011), and FTIR-PAS spectra can be obtained nondestructively and without any sampler pretreatment on solids samples (Du and Zhou 2009; Du et al. 2010), which permits an alternative option for fast characterization of soil humic substances.

Materials and Methods

The Leonardite humic acid (HA) was purchased from the International Humic Substance Society (IHSS), and the Leonardite mobile humic acid (MHA) and calcium humate (CaHA) samples were prepared in the lab from the Leonardite soil provided by IHSS (Mao et al. 2008). For transmittance measurements, KBr pellets were prepared by mixing 2 mg of humic substance with 200 mg of KBr using a mortar and pestle and applying 5,000 kg to the powder for 2 min. For each sample, 32 successive scans covering the 500–4,000 cm^{-1} range were recorded and averaged. The photoacoustic spectra of humic substances were recorded using a spectrophotometer (Nicolet 380, Thermo-Scientific, USA) equipped with a photoacoustic cell (Model 300, MTEC, USA). After placing the sample (about 200 mg) in the cell holding cup (diameter 5 mm, height 3 mm) purging the cell with dry helium (10 mL min^{-1}) for 20 s to minimize interferences due to water vapor and impurities, the scans were conducted in the wavenumber region of 500–4,000 cm^{-1} with a resolution of 4 cm^{-1} and a mirror velocity of 0.32 cm s^{-1} , and 32 successive scans were recorded and averaged. The software of Matlab 7.0 and Peakfit 4.12 were used in the analysis of spectral data; for the photoacoustic spectra, the only preprocessing consisted of a smoothing filter (second-order Savitzky-Golay filter with a 25-point window) (Savitzky and Golay 1964).

Results and Discussion

FTIR-PAS absorption bands of HA can be observed in the 500–4,000 cm^{-1} interval, and around 750, 1,000, 1,500, and 3,400 cm^{-1} (Fig. 1a); transmittance absorptions can be observed in 1,000–4,000 cm^{-1} , and around 1,200, 1,600, and 3,200 cm^{-1} . There is significant difference in the spectral appearance between PAS spectra and transmittance spectra.

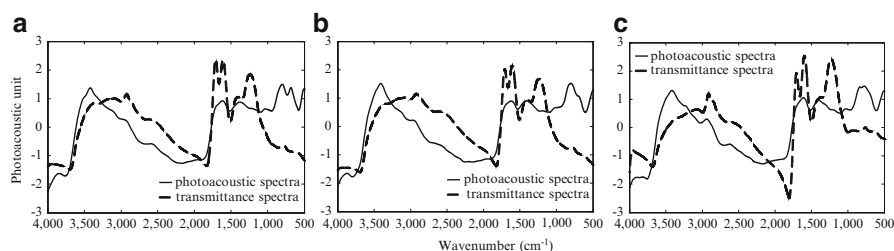


Fig. 1 Fourier transform infrared photoacoustic spectra of Loenardite HA (a), MHA (b) and CaHA (c) versus transmittance spectra of Loenardite HA (a), MHA (b) and CaHA (c)

Table 1 Typical bonding structures of humic substances identified by infrared spectroscopy

Band range (cm^{-1})	Vibration mode
3,500–3,200	O–H stretch, N–H stretch
3,150–3,000	C–H stretch
2,970–2,820	C–H stretch
1,725–1,720	C=O stretch
1,650–1,630	C=O stretch, other vibrations
1,650–1,540	Asymmetric COO^- stretching
1,450–1,360	Symmetric COO^- stretching
1,465–1,440	C–H bend
1,250–1,200	C–O stretch, O–H bend
1,170–950	C–O stretch

A broader band can be observed in transmittance spectra in the region of 2,000–4,000, while the absorption band in the region of 500–2,000 is broader in PAS spectra. FTIR-PAS spectra of Leonardite HA feature the following absorption bands (Fig. 1b): $3,480 \text{ cm}^{-1}$ (O–H stretching of various functional groups); $2,925$ and $2,850 \text{ cm}^{-1}$ (aliphatic C–H group stretching); $1,720 \text{ cm}^{-1}$ (C=O stretching of carboxyl groups); $1,650 \text{ cm}^{-1}$ (aromatic C=C stretching and COO^- -symmetric stretching); $1,508 \text{ cm}^{-1}$ (amide II band); $1,450 \text{ cm}^{-1}$ (aliphatic C–H deformation); $1,424 \text{ cm}^{-1}$ (amide III band); $1,130 \text{ cm}^{-1}$ (C–OH deformation of aliphatic OH); a broad band at $1,225 \text{ cm}^{-1}$ (C–O stretching and O–H deformation of carboxyl and C–O stretching of aryl ethers and phenols); and $1,040 \text{ cm}^{-1}$ (C–O stretching of polysaccharides). The MHA spectrum appearance is very similar to HA spectrum in the wavenumber range of $1,000$ – $4,000 \text{ cm}^{-1}$. However, the fingerprint absorptions (500 – $1,000 \text{ cm}^{-1}$) are significantly different, which implies that the general structure of MHA is similar to that of HA, but the substituent groups attached in the general structure significantly varied. The absorption of aliphatic group (ca $2,900 \text{ cm}^{-1}$) in CaHA (Fig. 1c) is stronger than that in HA and MHA spectra, which means that CaHA may have a strong capability of water repellence. More specific assignments of absorption band are showed in Table 1.

The spectral appearances of HA, MHA, and CaHA are close (Fig. 1), but still there numerous minor differences hidden in the spectra among different humic substances. Peak fitting analysis of the humic substance spectra was conducted, and 21 bands were separated from FTIR-PAS spectra of HA, MHA, and CaHA (Fig. 2).

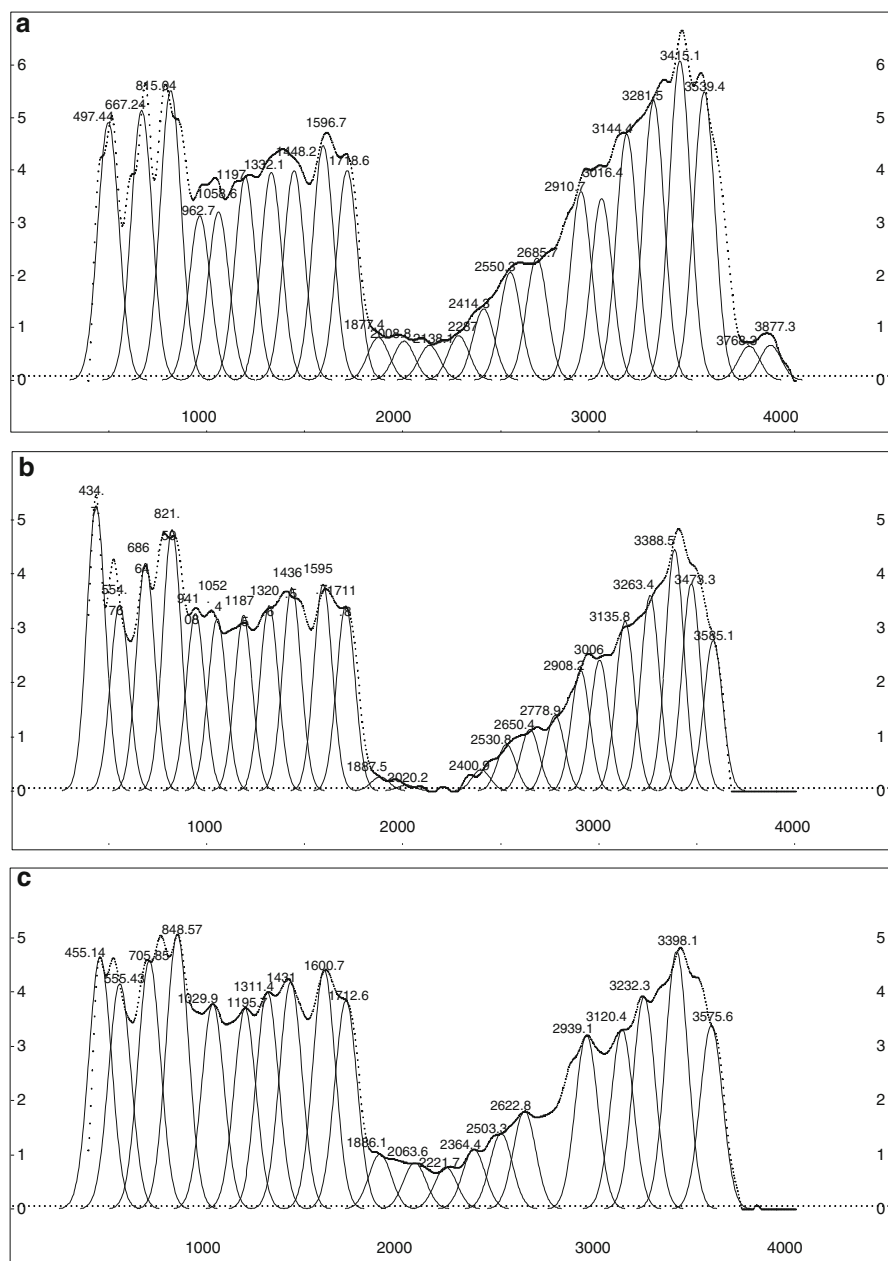


Fig. 2 Peak fitting analysis of FTIR-PAS spectra of humic substances (**a**, HA; **b**, MHA; **c**, CaHA). Gaussian deconvolution method was involved in the peak fitting

Though the number of separated bands is the same, the absolute and relative intensity of each band is significantly different. The height of aliphatic band (ca $2,905\text{ cm}^{-1}$) for HA, MHA, and CaHA are 3.62, 2.32, and 3.22, respectively, and the height of carboxyl band (ca $1,711\text{ cm}^{-1}$) for HA, MHA, and CaHA are 4.01, 3.45, and 3.81, respectively; therefore, the ratios of aliphatic to carboxyl band are 0.90, 0.67, and 0.85, respectively. Thus, water repellence of HA is the strongest, followed by CaHA, and MHA is the weakest. The results indicated that the technique of FTIR-PAS could provide a simple and fast method for quantification of functional groups in humic substances.

This preliminary work demonstrated the potential application of FTIR-PAS for the characterization of humic substances. When compared to conventional absorption spectroscopy, this new technique of FTIR-PAS has several advantages summarized below: (1) No sample preparation is required for PAS studies, and in situ studies can be performed. (2) Unlike conventional spectroscopy, scattering does not pose a problem with PAS, since losses due to the scattering and reflection do not produce PA signals. This aspect makes PA particularly attractive when studying strongly scattering samples. (3) The infrared photoacoustic method is capable of being used to study the mechanism of non-radiative de-excitation, which is not possible when using conventional techniques. (4) Photoacoustic spectroscopy is suitable to study high-absorbing sample, such as humic substances. (5) The PAS spectra can be obtained in a short time, which allows for rapid and efficient evaluation of humic substances. However, the disadvantage of FTIR-PAS is that there may be strong influence due to water.

In the further research, the specific spectral assignments of humic substance should be made and confirmed.

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