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Mid-infrared attenuated total reflectance spectroscopy for soil carbon and particle size determination

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ABSTRACT

In soil analysis mid-infrared spectroscopy (MIR) is not as widely used as visible and near infrared spectroscopy (VisNIR), mainly due to (1) the need for sample preparation and (2) strong absorption leading to spectral distortion and total absorption. In this study we used attenuated total reflectance (ATR) as a sample presentation technique to obtain MIR spectra of neat soil samples to overcome the two aforementioned drawbacks. A set of diverse soil samples (N = 270) were scanned with a Fourier Transform IR spectrometer (4000 to 400 cm^{-1}) on its diamond ATR crystal. The objective was to investigate the usefulness of ATR spectra in determining clay, sand, organic and inorganic C using partial least squares regression. Results showed that inorganic C and clay can be predicted very well with ATR, with validation R^2 around 0.94 and Ratio of Performance to Deviation (RPD) around 4.0. Sand can be predicted satisfactorily also, with $R^2 = 0.88$ and RPD slightly lower than 3.0. Organic C is predicted with $R^2 = 0.77$ and RPD > 2.1. Compared to the results of VisNIR models, significantly higher accuracy was obtained for clay, sand, and inorganic C, and a slight improvement was obtained for organic C. In our opinion, MIR-ATR can be a promising and powerful tool for soil characterization. It combines the advantages of both VisNIR (minimum sample preparation and high analysis throughput) and diffuse reflectance MIR (better model performance). Finally, as evidenced in our "leave-whole-field-out" experiment, the models developed with ATR spectra performed better on dissimilar samples and might have a larger scope of application than VisNIR.

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1. Introduction

Visible and near infrared spectroscopy (VisNIR, 350 to 2500 nm) is much more widely used than mid-infrared spectroscopy (MIR, 4000 to 400 cm^{-1}) for soil characterization and property determination. There are several advantages to work using VisNIR. First, it is more sensitive but less expensive optics and photonics are available for instrumentation and measurement. Second, *in situ* application and onsite deployment are possible. Third, minimum sample preparation is needed. Although some still argue that absorption bands (mainly overtones and combinations) in VisNIR are weak and poorly resolved, rapid advancement in computation and multivariate modeling capabilities make it very efficient to extract relevant information from VisNIR spectra.

There are continuous and growing interests in using MIR for soil characterization. Some early work focused on qualitatively relating spectral bands to soil chemical groups including clay minerals and humic acids (Baes and Bloom, 1989; Nahin, 1955; Nguyen et al., 1991; Niemeyer et al., 1992). Later on when Fourier Transform instruments

became widely available, researchers investigated the use of DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) of either diluted or undiluted samples for quantitative analysis of many soil properties including clay, water potential, carbon content, CEC, and pH (Janik and Skjemstad, 1995; Janik et al., 1995, 1998; McCarty et al., 2002; Viscarra Rossel et al., 2006). More recently, there is a new trend in using MIR to quantify soil organic C and its various fractions (Bellon-Maurel and McBratney, 2011; Bornemann et al., 2005, 2008; Reeves, 2010; Zimmermann et al., 2007). This is due to the importance of organic C in soil quality and sustainability, and soil's great potential to sequester atmospheric C to mitigate global warming.

MIR involves fundamental vibrational bands of functional groups that are very strong. Many regard this as an advantage because absorption bands can be distinctively associated with certain chemical groups. However, it also has undesirable consequences. First, absorption bands are usually so strong that band distortion, or in some extreme cases, total absorption, occurs. Therefore for quantitative analysis, samples need to be diluted in an IR transparent substrate (such as potassium bromide, KBr) so that measured absorbance unit is within the linear range of Beer's Law (or other reflectance theories such as Kubelka–Munk Law). This makes sample preparation tedious, and it becomes the major reason deterring MIR in many applications. This problem is partially addressed by applying multivariate analysis such as partial

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least squares regression on DRIFTS of undiluted samples (in which band distortion or total absorption does occur). The argument is that multivariate analysis can effectively correct this nonlinearity problem and yield satisfactory results.

Attenuated total reflectance (ATR) as a spectroscopic sample presentation technique has been widely used in many areas including food, agriculture, and environmental science (Oliveira et al., 2006; Wilson and Tapp, 1999; Yang et al., 2005). A great advantage of ATR is that it requires minimum sample preparation. The only requirement is that samples be brought into intimate contact with the ATR crystal, easily achievable for liquids, gels, pastes, films, and powders. Despite its common use in other areas, ATR has not raised much attention among soil spectroscopists. Only a few papers applied the ATR technique for soil analysis, primarily focusing on soil identification and nitrate determination (Jahn et al., 2006; Linker et al., 2005, 2006). In the review article by Reeves (2010), ATR was briefly mentioned as a potential non-DR method for soil C analysis.

In this article, we reported on using the ATR technique to obtain MIR spectra of soil samples with a Fourier Transform (FT)–IR spectrometer. Because of the property of the evanescent field (explanation in the next section), ATR spectra are free of spectral distortion or total absorption. The absorption intensity is usually within the linear limit of Beer's Law, making ATR spectra more suitable for quantitative analysis. The objective of this study was therefore to investigate the usefulness of ATR spectra to predict soil particle size and organic and inorganic C, an effort that has not been reported in the literature. In addition, we also wanted to compare the performance of models based on ATR spectra with previously published models based on VisNIR reflectance spectra.

1.1. A brief introduction on ATR spectroscopy

When electromagnetic (EM) radiation travels from an optically dense medium (with refractive index n_1) to an optically rare medium (with refractive index n_2) to an optically dense medium (with refractive index n_1), total internal reflection occurs at the interface when the incident angle θ is greater than the critical angle determined by $\theta_c = \sin^{-1}(n_2/n_1)$. At the interface, a non-propagating wave known as evanescent wave penetrates into the rare medium with an effective penetration depth, d_p:

$$d_p = \frac{\lambda_1}{2\pi\sqrt{(\sin\theta)^2 - (n_2/n_1)^2}} \tag{1}$$

Where λ_1 is the wavelength of the EM radiation in the denser medium; and θ, n_1 and n_2 are as previously defined.

Because of this phenomenon, the technique is also known as evanescent field spectroscopy. Just like transmission or reflectance spectroscopy, the evanescent field (assuming polychromaticity) will be selectively absorbed by the rare medium according to its interacting chemical groups. The totally reflected energy reaching the detector, therefore, is only a portion of the incident energy. This produces a reflectance spectrum (so called attenuated total reflectance, or ATR) that is characteristic of the chemical constituents of the rare medium.

For IR radiation, the evanescent field only penetrates into the rare medium a few microns. This depth is the limit within which the EM radiation effectively interacts with the sample, and is analogous to the path length of EM radiation in transmission spectroscopy. Beer's Law states that $A = \alpha l c$, where α is molar absorptivity, l is path length, and c is concentration. Because many substances are strong absorbers in MIR (large α), it is quite common that total absorption occurs (where A is no longer proportional to c) in transmission or reflectance modes because path length l is large (on the order of millimeters for IR radiation). ATR solves this problem neatly by reducing the effective path length to the order of microns, making the absorption intensity usually well below the linear limit of Beer's Law. This advantage eliminates the need to dilute the sample and

makes quantitative correlation between spectra and chemical constituents more desirable. Detailed discussion on the theory of ATR, and how the absorbance unit of ATR compares to that of transmission and reflectance spectroscopy can be found in Mirabella (2006). Fig. 1 illustrates the measurement principle of the ATR technique, and how soil samples were measured with the FT-IR spectrometer in this study.

2. Materials and methods

2.1. Soil samples

Soil samples used in this study were collected from six fields in Erath County and Comanche County of Texas, in May 2004. The sample set consisted of 72 soil cores cut into 270 samples. The selection of the fields and the coring locations in each field were intended to represent the large variability in soil properties across the landscapes. As a result, 21 soil series by USDA-NRCS were included in the sample set; and the parental material ranged from alluvium, sandstone, shale, to limestone. We are interested in particle sizes (clay and sand) and organic and inorganic C contents. Soil samples were dried in an oven at 44 °C for two days, ground, and passed through a 2-mm sieve before lab analysis. The reference analytical method for particle sizes was the pipette method (Gee and Or, 2002), with an accuracy of $\pm 1\%$ clay. Total C was measured using the dry combustion method (Nelson and Sommers, 1996); and inorganic C was measured using the modified pressure calcimeter method (Sherrod et al., 2002). Organic C was derived by subtracting inorganic C from total C. The accuracy of organic and inorganic C was estimated to be ± 0.7 g kg^{-1} and ± 0.4 g kg^{-1}, respectively. A more detailed description about this sample set can be found in Waiser et al. (2007). Fig. 2 shows the boxplots of the four soil properties by field, clearly showing the great variation in the samples among the six fields.

2.2. MIR-ATR measurement

The soil samples were scanned with a Thermo-Nicolet 6700 FT-IR spectrometer (Thermo Scientific, Madison, Wisconsin) to acquire the ATR spectra in the MIR range (from 4000 to 400 cm^{-1}). Soil samples were first finely ground in an agate mortar before spectral measurement. About 60–80 mg of soil was placed on the spectrometer's Smart Orbit accessory and pressed against an ATR crystal with a constant force of 200 N (Fig. 1). The ATR crystal is a single-reflection diamond crystal with an incidence angle of 45°. Other important configurations of the spectrometer are as follows: beam splitter — CsI (Cesium Iodide); detector — thermo-electrically cooled DTGS (deuterated triglycine sulfate) CsI; spectral resolution — 4 cm^{-1}; spectral sampling — 1.92 cm^{-1}; optical (moving mirror) velocity — 0.632 cm s^{-1}; purge gas — none; and signal processing — automatic atmospheric suppression. The background spectrum was taken every 60 min with atmosphere as background.

2.3. Data analysis

The ATR spectrum of four representative samples was selected for visual assessment. Major absorption peaks in the ATR spectra were identified and associated with the soil properties of interest (clay, sand, organic and inorganic C) based on the published information. Further, simple correlation was made between these major absorption peaks (based on absorption depth) and the associated chemical constituents.

Partial least squares regression (PLSR) was used to correlate the ATR spectra with the soil property data. Several spectral pretreatment methods including Savitzky–Golay smoothing were attempted but they did not improve the model accuracy substantially. Therefore, the original ATR spectra were used. The sample set was split into a calibration set (2/3 of the samples) for model development and a validation set (1/3) for model assessment. For calibration, a total of 15 latent factors were considered, and the optimal model size was selected with the first local minimum of the root mean squared error of cross validation.