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Application of FTIR Spectroscopy to Agricultural Soils Analysis

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1. Introduction

Soil is a very complex medium that contains minerals, organic matter, micro-organisms, air and water. Soil is one of the most important factors for agriculture and some soils are deemed more fertile than others. Soil fertility is directly related to factors such as nutrients concentrations or availability, organic matter content, acidity, moisture, etc., as well as to agricultural practice such as till vs. no-till (Desbiez et al. 2004) (Sá et al. 2009). Ensuring soil fertility is a basic requirement for any form of sustainable agriculture, yet in practice this seemingly trivial goal is very difficult to achieve due not only to the complexity of the soil medium itself, but also due to the complexity of the soil-crop-air interactions and to the fact that some processes require years before having any visible impact. Various recent studies have shown that soil fertility is declining in many farmlands due mainly either to inadequate farming practices (Gobeille et al. 2006), insufficient fertilization, in which case the soil reserves are depleted, or over-fertilization that results in pollution to the groundwater or toxic accumulation of chemicals in the soil. Avoiding such under- or over-fertilization is the chief goal of the so-called *precision fertilization* concept, which aims at delivering exactly the amount of nutrients required to sustain optimal growth of the crop. One of the main obstacles to the application of the precision fertilization concept, or the more general *precision farming* concept, is soil heterogeneity. Hence, although it is technically possible to perform a wide range of analyses and derive a soil fertility or health index such as the one proposed by Idowu et al. (2008), most of the required analyses are time-consuming, which in practice makes it impossible to map the soil properties of a field with the required spatial and/or temporal resolution. The need for fast and cheap methods that would enable the analysis of a large number of samples has been stressed in numerous studies (Viscarra Rossel&McBratney 1998b) and infrared spectroscopy has long been recognized as one of the most promising techniques (e.g. McCarty&Reeves 2006; Mouazen et al. 2007; Cécillon et al. 2009). As in other applications, the initial works were conducted mainly in the near-infrared (NIR) range for which instruments were readily available. Technological achievements in the mid-infrared (mid-IR) range during the last decade have made this spectral range much more attractive and an increasing number of soil studies are conducted using this spectral range. Although there is no doubt that near-infrared spectroscopy can be very useful for some analyses, several comparative studies have shown
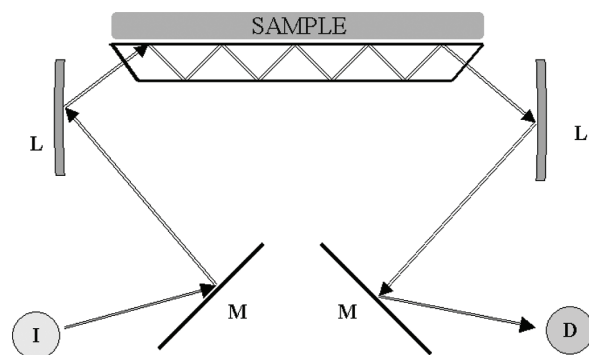
Fig. 3. Attenuated total reflectance (ATR) configuration. I denotes the incoming light (from the interferometer), D denotes the detector, L and M are lenses and mirrors. Reproduced from (Etzion et al. 2004)

crystal surface for a short distance known as the *evanescent field*. If a sample is applied directly onto the surface of the ATR crystal, some of the IR radiation (i.e., the evanescent wave) is absorbed by this sample, so that the sample absorbance spectrum can be obtained. The evanescent wave decays exponentially with the distance from the surface of the crystal. The depth of penetration of the evanescent wave d_p is defined as the distance from the crystal-sample interface at which the intensity of the evanescent wave decays to 37% (1/e) of its original value, and is given by

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\left[\sin^2\theta - \left(n_2/n_1\right)^2\right]}} \tag{2}$$

where λ is the radiation wavelength. The penetration depth and the total number of reflections along the crystal can be controlled to some extend either by varying the angle of incidence of the radiation (θ) or through the selection of the crystal material. The penetration depth is typically less than 10 μm, so that very good contact between the sample and the crystal is critical in order to obtain reliable and reproducible results.

The first use of ATR for soil analysis was reported by Ehsani et al. (2001), who attempted to determine nitrate concentration using ATR spectra of dry soil samples. This study demonstrated the difficulty of obtaining adequate contact between the soil and the ATR crystal, but also showed how the results could be greatly improved by using a soil paste or slurry. Such an technique was further developed by Shaviv et al. (2003), Linker et al. (2004), Linker et al. (2005) and Borenstein et al. (2006) who used samples consisting of soil pastes close to water saturation. Since nitrate is highly soluble in water and is not fixed in the soil matrix, all the nitrate is present in the liquid phase of the soil paste, which has several advantages. First, since the paste moisture content is less than 1 g [H_2O]/g [soil], the nitrate concentration in the liquid phase is higher than in the dry soil. Second, much better contact is obtained between the ATR crystal and the liquid phase than could be obtained between the ATR crystal and the dry soil. Finally, the original moisture of the soil sample has no influence on the measurement. However, water exhibits very strong absorbance bands in the mid-IR range, which may distort or hide bands of interest. This is illustrated in Figure 4 which shows the spectra of de-ionized water, de-ionized water with 1000 mg[N]/kg[water] nitrate, and a paste of sandy soil with 870 mg[N]/kg[water] nitrate. Distortion and shift of

the spectra can be observed, especially in the regions indicated by circles. The magnitudes of these changes are comparable with the size of the nitrate signal and would cause significant inaccuracies if straightforward estimation of nitrate was performed. Therefore an accurate water subtraction procedure such as the one developed by Linker et al. (2004, 2005) should be applied to the spectra prior to the quantitative analysis.
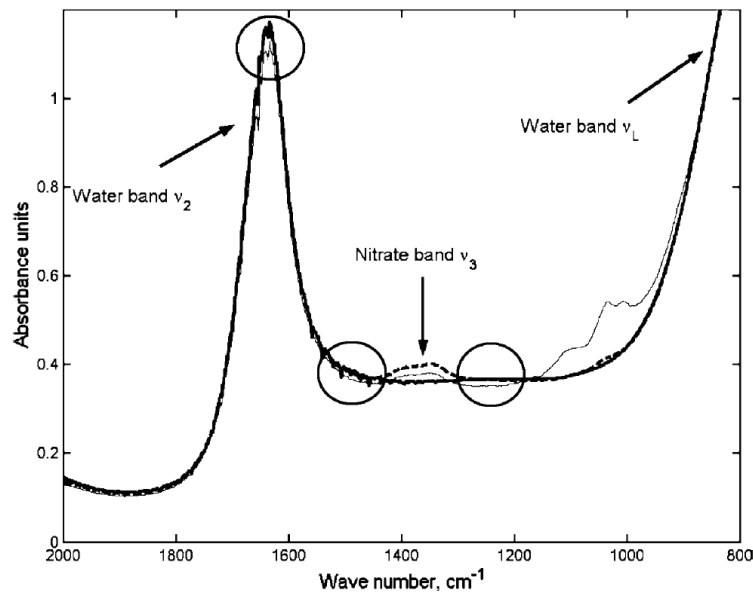

Fig. 4. Spectra of de-ionized water, de-ionized water with 1000 mg[N]/kg[water] nitrate, and a paste of sandy soil with 870 mg[N]/kg[water] nitrate. The circles indicates the regions in which shifts and distorsions of the spectra are most clearly visible. Reproduced from Linker et al. (2005).

2.3 Photoacoustic spectroscopy

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) differs from the previous methods in the sense that it relies on complete absorption of the incoming radiation by the sample. The sample is placed in a sealed enclosure that is purged with He to avoid atmospheric interferences and to which is connected a highly sensitive microphone which records the pressure waves that result from the local heating induced by the absorbed radiation (McClelland et al. 2002) (Figure 5). The recorded spectrum depends on the absorption properties of the sample, its thermal diffusivity, and the thermal penetration depth. Therefore, photoacoustic spectra are more difficult to interpret than reflectance ones and there is no one-to-one correspondence between the spectra obtained with both techniques. Also, photoacoustic spectra are much more prone to measurement noise. Nonetheless, since this method can be used with highly absorbing samples without any pretreatment, it is well suited for soil samples analyses and its use has been reported in several recent studies (Du et al. 2008a, 2008b, 2009b).

3. Data processing

Due to the large amount of data generated by FTIR spectrometers and the complexity of the spectra, it is imperative to use chemometrics procedures to analyze the data. A detailed
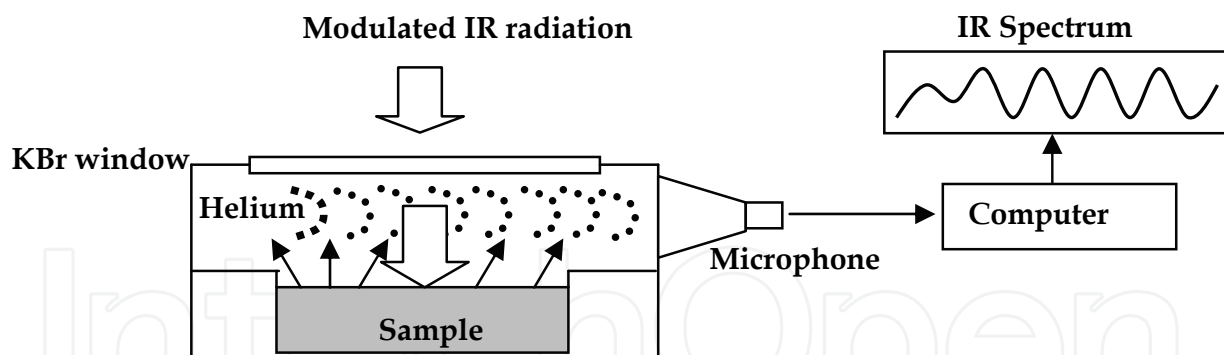
Fig. 5. Schematic description of FTIR photoacoustic spectroscopy. Reproduced from Du et al. (2008a).

description of such procedures can be found in various textbooks such as Brereton (2003) or Chau et al. (2004). Partial Least Squares (Wold et al. 2001) is the procedure most commonly used for quantitative determination of one or several soil components (see for instance the excellent compilation table in Viscarra Rossel et al. (2006)). PLS is an easy-to-use straightforward procedure that is available in standard statistical and chemometrics softwares, which probably explains its popularity. The main limitation of PLS is that it assumes linearity of the data, but the good results reported in most soil studies show that this does not appear to be too restrictive an assumption when analyzing soil spectra. Exceptions to this generally linear behavior were reported for instance by Janik&Skjemstad (1995) and Janik et al. (2009), especially at very high concentrations. However, Janik et al. (2009) reported that in those cases where PLS was not capable of providing a good prediction model, adding a non-linear element in the form of a neural network did not improve the results significantly.

The *a priori* assumption of linearity can be avoided altogether by using procedures such as wavelet decomposition and neural networks. An example of such a procedure is depicted in Figure 6. In this procedure, wavelet decomposition is used to compress the data and obtain a low-dimensional representation of the spectra. Although wavelet decomposition by itself does not produce a compressed representation of the original data, data reduction can be achieved by eliminating the wavelet coefficients that do not contain valuable information. Various approaches have been reported in the literature for selecting the most relevant coefficients, such as eliminating all "small" coefficients using for instance either thresholding (Kai-man Leung et al. 1998; Ehrentreich 2002), entropy (Kai-man Leung et al. 1998), mutual information (Alsberg et al. 1998), maximum likelihood (Leger&Wentzell 2004), or genetic algorithms (Depczynski et al. 1999), or retaining only the coefficients with the highest variance (Trygg&Wold 1998) as depicted in Figure 6. Once data compression has been achieved, the remaining coefficients can be used as input variables for a neural network that creates a non-linear mapping between these inputs and the property (or properties) of interest. The neural network can also be replaced by a simpler linear regression as in Viscarra Rossel&Lark (2009), in which case a hybrid model that contains both linear and non-linear stages is obtained.

Since the wavelet transform decomposes the signal into components at different scales (or loosely speaking, components of different widths), it is a very powerful tool for resolving overlapping bands and separate the bands of interest from the background and interferences. For instance, Jahn et al. (2006) used such an approach to distinguish between the strongly-overlapping absorbance bands of nitrate and calcium carbonate in the ATR spectra of calcareous soils (Figure 7).

4.2 Determination of soil moisture

Water in itself is essential for plant growth and its presence in the soil influences numerous properties such as the availability of oxygen and nutrients, microbial activity, swelling and shrinking of clays or soil stability. Since the methods traditionally used to estimate water-related soil properties are time consuming, much research has been devoted to the development of alternative methods. In particular, very good results have been reported for some of these properties using near-infrared spectroscopy under laboratory conditions (Mouazen et al. 2005, 2006; Viscarra Rossel&McBratney 1998a) and encouraging results have been reported for in-situ field measurements (Mouazen et al. 2005). A summary of the main results obtained with mid-IR DRIFT spectroscopy is presented in Table 2. With the exception of Dataset #1 in Tranter et al. (2008), mid-IR spectroscopy was capable of estimating to some extent water retention at -10kPa and -1500kPa, with R^2 values ranging from 0.64 to 0.81 and from 0.66 to 0.89, respectively. However, the study of Bertrand et al. (2002) clearly shows that KBr dilution of the samples or high $CaCO_3$ concentration deteriorate the results. Although this has not been specifically verified, the very poor results obtained by Tranter et al. (2008) on Dataset #1 were most probably due to the fact that the spectra were recorded from intact soil cores rather than from grounded samples as in all the other studies. Regarding moisture of air-dried and oven-dried soil, the few results available are very good, unless the soil has a high $CaCO_3$ concentration.

4.3 Soil characterization

The soil physical structure affects various physical, chemical and biological processes such as for instance water infiltration and retention or root penetration and proliferation. With this respect, clay is the component most often studied by mid-IR spectroscopy, although some studies also attempted to estimate sand or silt content (McBratney et al. 2006; Viscarra Rossel et al. 2008). For clay, R^2 values of 0.85 or more were reported by Janik&Skjemstad (1995), Viscarra Rossel et al. (2008) and Viscarra Rossel&Lark (2009). Reasonably good results were reported by Janik et al. (2009), Canasveras et al. (2010) and Janik et al. (2009), with R^2 value of 0.84 and 0.82, respectively, but lower R^2 values (0.74-0.79) were reported by Bertrand et al. (2002), McCarty&Reeves (2006), Minasny et al. (2009) and McBratney et al. (2006). No explanation has been offered to explain such a variability of the prediction performances. In addition to the previous DRIFT studies, Du et al. (2007) reported very good results ($R^2>0.90$) using photoacoustic spectroscopy and Du et al. (2008b) further showed that this method can be used to differentiate between different types of clays. Another important soil component that can be estimated by mid-infrared spectroscopy is carbonate. In this case the results are much more consistent, with R^2 values of 0.95 or more reported in the studies of Janik&Skjemstad (1995), Bertrand et al (2002), Canasveras et al. (2010) and Du et al. (2008b). Linker et al. (2006) and Du et al. (2008a) showed that the spectral information related to carbonate and other soil constituents can be used to discriminate between soils, and Linker et al. (2006) further showed that such a automatic discrimination can improve the estimation of nutrients such as nitrate.

5. Current challenges and emerging applications

5.1 Spectral libraries and model transferability

The results presented in the previous Section clearly demonstrated that mid-IR spectroscopy can be used to determine accurately a series of soil characteristics and properties under
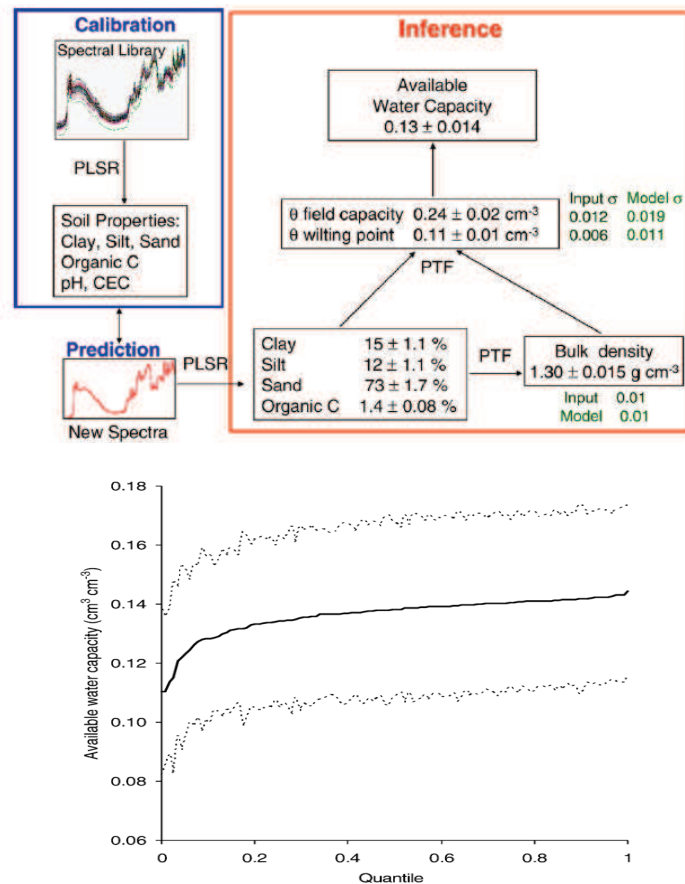
Fig. 8. Top frame: Schematic description of the combination of mid-IR spectroscopy and inference models as suggested by McBratney et al. (2006). Bottom frame: Quantiles of the available water capacity estimated according to the inference scheme. Reproduced from McBratney et al. (2006).

primordial importance (Viscarra Rossel&McBratney 1998b) and considerable research efforts have been devoted to the development of fast, fully automated and geo-referenced measurement systems (Sibley et al. 2009; Mouazen et al. 2007; Christy 2008; Adamchuk et al. 2004, 2005; Sinfield et al. 2010). Among the spectroscopy-based methods, the use of NIR has been investigated more actively, mostly due to the lower price and higher robustness of the equipment. Indeed, in their review paper Sinfield et al. (2010) concluded that the "the FT-IR ATR technique, while very accurate and fast, makes use of expensive and delicate equipment (e.g., moving mirror in interferometer) which is not readily amenable to an on-the-go setting" but that development of sensors based on a limited set of wavebands, as suggested by Linker (2004) and Jahn et al. (2006), could "enhance the potential to apply reflectance based approaches in the field by limiting the sophistication of requisite equipment". At any rate, considerable improvements are still required before large-scale implementation could be considered.

5.4 Monitoring of N isotopes
Nitrogen, either naturally present in the soil or added as fertilizer, may undergo a series of complex transformations. These transformations are interdependent and depend on a large number of variables, so that isolating specific processes or pathways is very challenging. One of the methods used to study these processes consists of enriching the soil with stable

[15]N isotopes and monitoring the concentration of ^{15}N in the by-products of the various reactions (Stevens et al. 1993; Stevens&Laughlin 1994; Baggs 2008). Such studies require the quantification of ^{14}N and ^{15}N, which is done by isotope ratio mass spectrometry (IRMS). However, expensive and laborious preparation of the samples is required to convert the N species into forms suitable for the IRMS measurements and the method can not realistically be used to analyze a large number of samples during an experiment. Du et al. (2009a) showed how mid-infrared spectroscopy could provide a much faster and cheaper alternative for N-isotope tracing, albeit with much lower accuracy than IRMS. The method is based on the observation that since the mid-infrared range corresponds to the fundamental vibrations of a molecule, which depend on the atoms' mass, the absorbance bands of ^{14}N-based and ^{15}N-based compounds are slightly shifted relative to each other, so that the concentration of each species can be estimated. This spectral shift between ^{14}N-NO_3 and ^{15}N-NO_3 is shown in Figure 9.
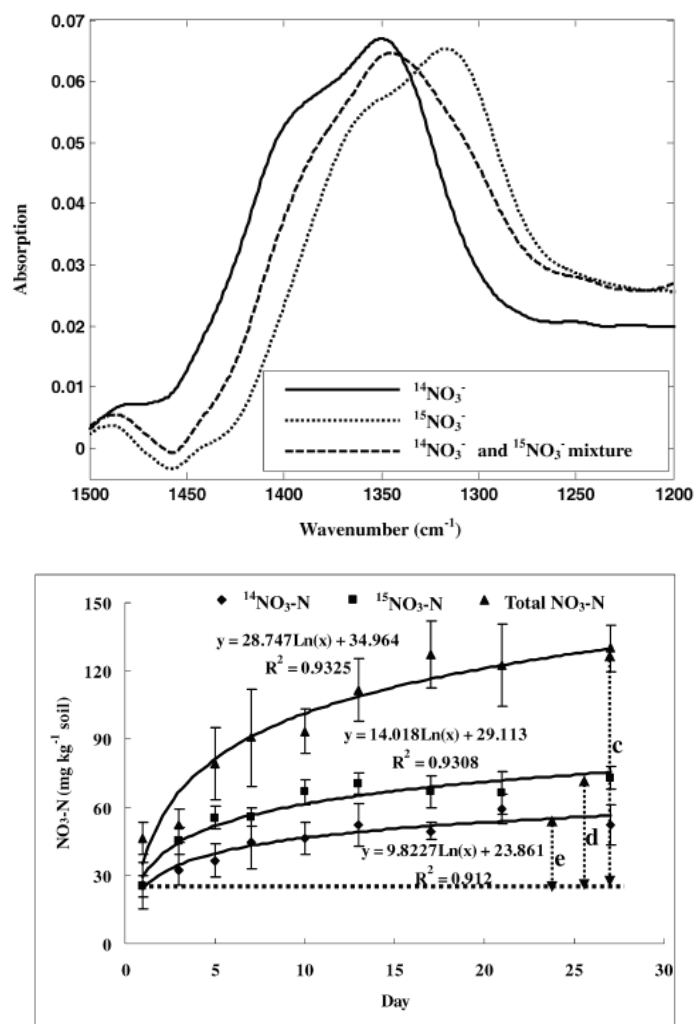

Fig. 9. Top frame: FTIR-ATR spectra of ^{14}N-NO_3 and ^{15}N-NO_3 in water. Bottom frame: Nitrate formation during an incubation experiment as estimated from FTIR-ATR measurements. Nine sub-samples were analyzed at each sampling point. ''c'' is the total amount of nitrate formed. ''d'' and ''e'' are the formed ^{15}N-NO_3 and ^{14}N-NO_3, respectively. Reproduced from Du et al. (2009a).

Using PLS regression models calibrated using saturated soil pastes spiked with ^{14}N-NO_3 and ^{15}N-NO_3, Du et al. (2009a) were able to estimate the ^{14}N-NO_3 and ^{15}N-NO_3 concentrations in a non-calcareous soil with determination errors of less than 6 mg[N]/kg[dry soil], which enabled them to monitor separately the formation of ^{14}N-NO_3 and ^{15}N-NO_3 during an incubation experiment (Figure 9). Although the measurement uncertainties reported in Figure 9 may seem rather large, the low cost and short time required for the FTIR-ATR measurements would make it possible to perform and average more measurements than as done in the study of Du et al. (2009a), and thus reduce the measurement uncertainties. After further validation of the approach with other soils, including with calcareous soils in which the carbonate absorbance band overlaps the nitrate absorbance band and interferes with nitrate determination (Linker et al. 2004, 2005, 2006), and extension of the method to monitoring soil NH_4 and/or NO_2 species, this method would provide a very powerful and cheap tool for studying soil nitrogen transformations.

6. Conclusion

The abundant studies conducted in the mid-IR range have demonstrated the potential that this technique holds for rapid and inexpensive soil analysis. A major advantage of spectroscopy techniques in general and mid-IR in particular is that several properties can be determined from a single spectrum, which greatly reduces the costs of analysis compared to conventional laboratory techniques. In addition, the measurement is very rapid so that a large number of samples can be easily screened or measurements could be conducted "on-the-go", at least in principle. However, several problems still need to be solved before this technology could be upgraded from the research laboratory into routine analyses. The most pressing issue appears to be the standardization of the FTIR and conventional procedures used to analyze the samples, which would make it possible to consider the establishment of spectral libraries similar to those existing in other FTIR fields. Such libraries would provide the basis necessary for developing robust chemometrics models, based either solely on mid-IR spectra or combining mid-IR spectra and pedotransfer functions, valid not only at the local but also at the regional scale.

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