

How to minimise loss in spectral quality when going from laboratory to field measurements using a portable FTIR instrument?

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Abstract

Fourier transform infrared (FTIR) spectroscopy in the mid infrared region has great potential for soil monitoring, but in field applications are still relatively sparse and there are several issues to overcome with *in situ* measurements. Field condition soil samples, unlike the dried-milled ones analysed in the lab, are subject to inhomogeneity, non-ideal particle size and variable moisture, reducing the quality, reproducibility and representativity of the spectra. In this study, two versions of a hand held FTIR instrument were used to test different sampling methods on two sets of field condition soils from Scotland and Sweden, ranging from mineral to organic soils. The instruments allowed for both diffuse reflectance and Diamond Attenuated Total Reflection (DATR) measurements. For comparison, soil spectra of the “best practice” dried and milled soil equivalent were used to determine how well spectra being recorded were representing the soil. In general, the DATR appeared to perform better than the diffuse reflectance, particularly when it came to measurement of field condition soil. The major problem for the diffuse reflectance approach was difficulties in getting enough energy (signal), especially for in-field measurements and dark organic soils. There were also issues with using diffuse reflectance on neat samples of highly organic soils as the intensity of the spectra often resulted in less differentiated peaks. Water obscured parts of the spectrum of field condition soil, however, the smearing of soil on to the DATR appeared to help achieve more representative spectra by allowing a better contact. Letting the soil dry for a short period after smearing on the soil also resulted in reduced water peaks.

Introduction

There is increasing interest in using FTIR spectroscopy in the mid infrared (MIR) region (4000 to 400 cm⁻¹) to characterise soils. Spectra in the mid infrared region give an overall chemical profile of the soil samples encompassing both the organic matter and the full mineralogy represented. The spectra can be used to visualise changes in the soil, interpreted to determine components present and used, in conjunction with chemometrics, for prediction of a range of soil properties. This non-destructive approach has huge potential for soil monitoring, being faster, cheaper and more environmentally friendly than many alternative wet chemistry analyses (Tinti et al., 2015). However, producing representative and reproducible soil spectra with high quality requires thorough sample preparation including drying and milling (Robertson et al., 2013) and to date the technique has not been widely used for in field measurements. Relatively recently, suitable handheld instrumentation has become available, but there are many issues to be overcome with *in situ* or field-based measurements, where drying or milling is not possible, in order to achieve reproducible and representative spectra.

Ideally, particle size for FTIR analysis should be <2 µm (clay size fraction). Larger particle sizes will result in sloping baselines, poor resolution of mineral peaks and “loss” of minerals in the spectrum due to reflection (e.g. by large quartz particles) rather than absorption of the infrared light (e.g. Le Guillou, et al., 2015). They may also result in spectra with poor signal to noise ratio. The heterogeneous nature of non-milled soil samples makes it difficult to get representative and reproducible spectra as different aspects of the soil might be represented to different extents each time. Different sampling accessories have different depths of penetration and sampling areas, so methods may need to be altered, possibly with averaging of different numbers of spectra, to reduce the effects of heterogeneity. This may also change depending on the nature of the soil.

Another problem with *in situ* or field-based measurements is water, which is strongly absorbing in the MIR region and at worst, water bands can virtually obscure all the bands arising from the soil. As with large particles, water films can also result in significant surface reflection reducing the quality of the MIR spectra (Soriano-Disla et al., 2014). Obviously if the moisture varies then the extent of the water bands will also

vary. If the water content is not too high, then this variability might not cause problems for qualitative interpretation of spectra but will cause issues for building chemometric models to predict soil properties.

In this study, different sampling methods on field condition soils were compared with “best practice” laboratory measurements in order to study the effect of particle size and soil moisture on the quality, reproducibility and representativity of the soil spectra. The study was done on a range of soil types and aimed to determine how to achieve the best possible spectra.

Materials and Methods

Datasets

Development work was carried out on a small sub-set of 15 well-documented Scottish soils from the National Inventory of Scotland (NSIS) dataset, which had a large variation in organic matter content (from 1%C to 47%C). High quality FTIR spectra (DATR) of dried-milled samples of these soils were already available in an NSIS spectral dataset (Robertson et al., 2013). Measurements in this study were made on three different treatments of the soil. The first group was of fresh soil samples which had been stored at 4°C, the second was the fresh soil samples after drying at 30°C for approximately 2 days, and the third group were corresponding samples of the soils which had been previously dried and sieved through a 2mm sieve. During method development work the MIR spectra of the “best practice” milled soil equivalent were used for comparison to determine how well spectra being recorded were representing the soil. Subsequently measurements in field and lab measurements on fresh soil samples were also made on 80 Swedish soils, from four fields, with variable organic matter content (from 2%C to about 25%C).

Sampling Accessories

Two handheld FTIR instruments, an Agilent 4100, and the newer Agilent 4300, were used in the development work (Agilent, Santa Clara, CA, USA). The instruments each had exchangeable sampling heads, allowing both diffuse reflectance measurements and ATR measurements (DATR, ZnSe range 4000 to 650 cm^{-1}) to be tested. The diffuse and DATR sampling options produce very different looking spectra, and both have perceived advantages and disadvantages.

The diffuse sampling head has a bigger sampling area and frequency range with greater penetration depth than the ATR. It is generally regarded to be easier for sampling (although this may not necessarily be the case as seen from results). Diffuse spectra of neat soil are too intense which leads to inversion of parts of the spectra, creating artefactual bands and making interpretation difficult (Nguyen et al. 1991). It does however allow small overtones and combinations to become evident which can be useful, particularly in calibration models. Diffuse reflectance spectra of each different soil treatment were recorded in the same way, with a coarse silver cap being used for reference/background measurements. A small metal powder sampling puck with two different sizes for sample presentation was used, and five replicates were recorded for each soil and sample type (where possible) (Figure 1a).

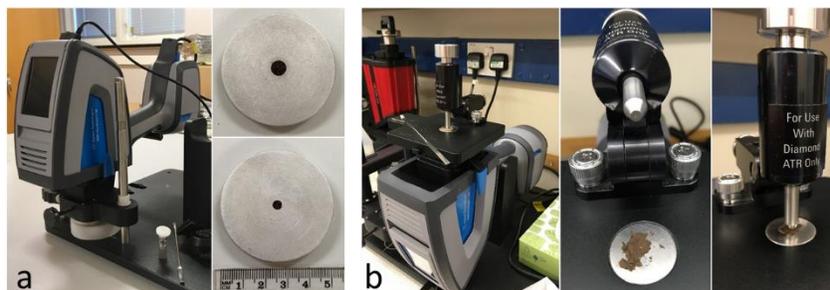


Figure 1. Laboratory setup for a) diffuse reflectance measurements with two powder sampling puck sizes, and b) DART measurements using a small field clip.



Figure 2. In-field measurements using ATR pressing the instrument on to the soil for contact. Also visible are some of the holes from the soil samples that were taken for laboratory measurements.

The DATR sampling area is only approximately 1 mm in diameter and the depth of penetration for the beam is about $2\mu\text{m}$ (wavelength dependent) which has been perceived as a major drawback for soil analysis, particularly given the heterogeneous nature of soil in the field. Due to the depth of penetration, a good contact is also needed between sample and sampling window for the DATR accessory. A small field clip was used to ensure good contact between the sample and the window (Figure 1b). For the fresh soil samples, analysis was carried out by smearing the soil onto the DATR window. Just pressing the sampling window down on the soil sample was also tried, e.g. in the in-field measurements (Figure 2). As for the diffuse, five replicates were recorded for each soil and sample type on the Scottish soils (where possible). In the measurements on the Swedish soils, 10 replicates were recorded for the in-field and lab measurements. So far, only DATR measurements have been done on the Swedish soils.

Results and Discussion

In assessing the results, we considered the quality of spectra produced for the two different sampling methods for each of the soil treatments. Factors considered included the ease of measurement, replication, noise, interference from water and relationship to “best practice” spectra of the soils.

DATR Method

Replication of spectra recorded using the DATR were often much better than might have been expected, given the small sampling area. The fresh soil generally gave better reproducibility than the fresh-dried or dried-sieved samples and were often less noisy. However, that was at the expense of having bands due to water obscuring parts of the spectrum. Allowing the fresh soils to dry for 5 or 15 minutes on the DATR and re-recording produced spectra which showed the same features as the fresh dried samples, but often less noisy, and with better replication. Although variable water in the soils samples undoubtedly creates a problem, it does appear that moisture in the soil allows a better contact with the DATR and produces more representative spectra. It was also found that, for the dry soils, a field clip to ensure good contact was important as pressing into the sample was unreliable. This was also true for the in-field measurement where pressing the instrument on to the soil resulted in weak signals and more variable spectra (Figure 3). Though most of the soils tested gave reasonable replication, and this seemed to be particularly the case for the highly organic soils, there were some samples where individual replicates differed substantially. For one soil with 7%C the replicates varied considerably, with one spectrum essentially just representing a grain of sand. In these cases, further work would be needed to determine how many replicates should be averaged to give a representative spectrum. Figure 4 shows two examples of some of the laboratory measured MIR spectra from one organic (47%C) and one mineral soil (4%C) of the Scottish soils.

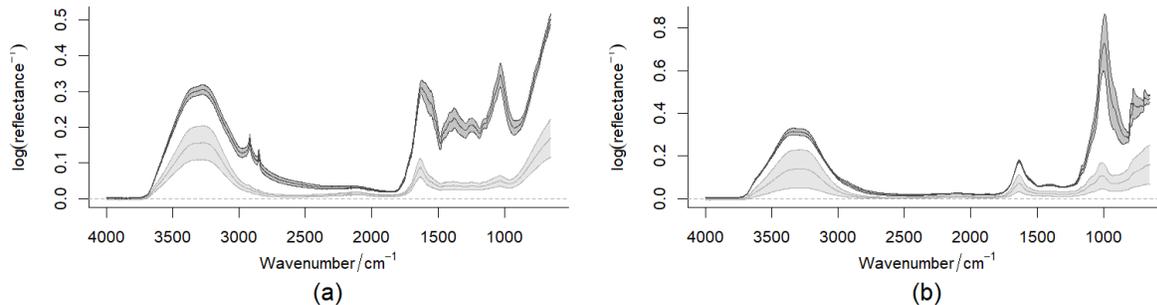


Figure 3. Mean +/- standard deviation of 10 laboratory ATR measured MIR spectra of fresh soil samples (dark grey) and 10 in-field ATR measured MIR spectra (light grey) from two Swedish soils; a) organic soil, and b) mineral soil.

Comparing the DATR spectra of non-milled soils to those of the “best practice” spectra shows that they are noisier, their baselines can slope more, and they have poorer resolution of many mineral peaks. This results in them showing reduced representation of minerals such as quartz and feldspar. Results do show a relative enhancement of the clay mineral and organic matter bands which may be beneficial, as these components are often related to soil properties being studied or measured.

Recording spectra using the DATR accessory was very straightforward and not affected by conditions. This makes recording spectra in the field relatively easy and may also make the methods more transferable from instrument to instrument. It was observed that less noisy spectra were obtained when using the newer Agilent 4300, on the same soil samples.

Diffuse Method

For some of the dry soil samples the appearance of the diffuse spectra un-milled treatments were not that different from diffuse spectra of milled samples and although a bit noisier the replication was reasonable. However, recording the spectra was more difficult than for the DATR method, and involved more trial and error. The diffuse spectra of neat soil have a very different appearance to those recorded using DATR (which are “Transmission like”) and show inversions of the strongest bands, often silicate or carbonate bands (Nguyen et al., 1991) which can make them harder to interpret but may not be such an issue for quantitative work. In fact, the strength of the spectra and enhancement of SOM and clay mineral bands are often regarded as beneficial. There are issues with using diffuse reflectance on neat samples of highly organic soils or peats as intensity of spectra mean that they often show very few discernible differences and can't be readily discriminated (Harrison et al., 2006) in the way that DATR or transmission spectra can be.

Although the diffuse method could be effective on dried soils, it generally seems to be far more problematic for use on field condition soils or for in-field measurement. There are issues with positioning, danger of getting soil into the instrument and difficulty in getting an appropriate reference/background measurement. The major problem for the diffuse reflectance approach, however, seemed to be the difficulty in getting enough energy (signal) for in-field measurements which may be due to it being too wet and too dark. For the fresh dark organic soils, only a portion of the small sample cup could be “presented” to the instrument otherwise the energy was too low for measurement. One effect of presenting a smaller portion of the soil for diffuse reflectance measurement was that the spectra starts to resemble ATR spectra (weaker signal and no longer inverted).

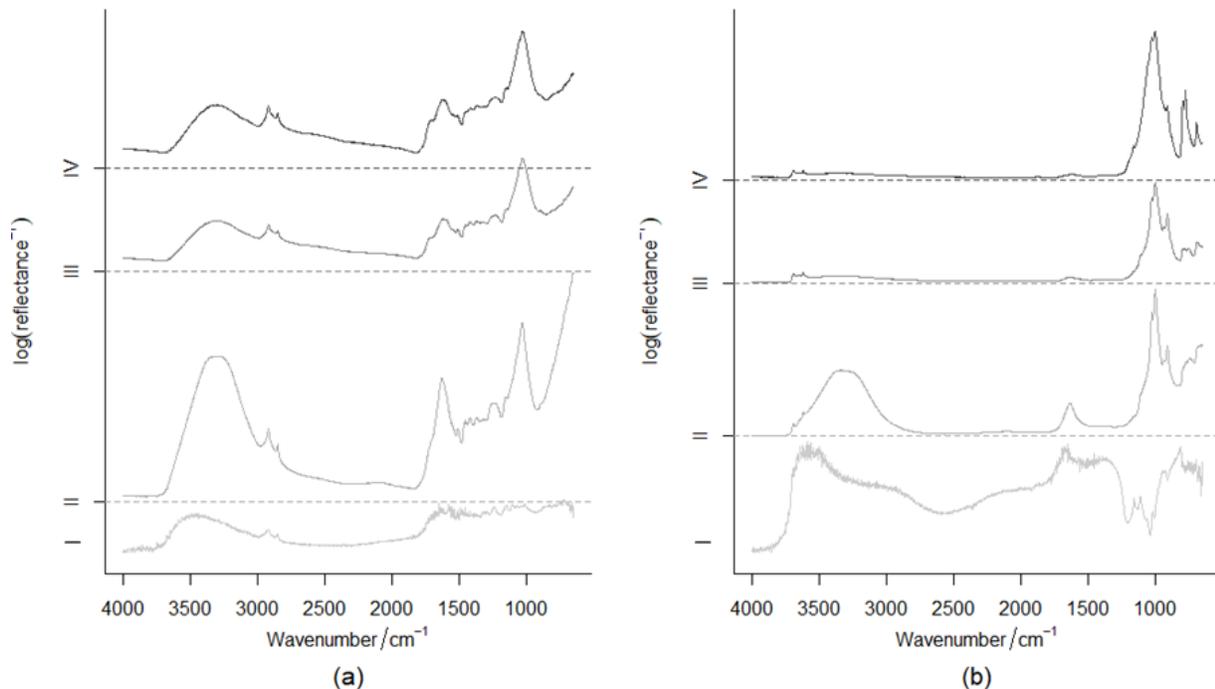


Figure 4. Laboratory measured MIR spectra from two Scottish soils; a) organic soil, and b) mineral soil. I) are fresh samples measured using diffuse reflectance. II to IV are measured using DATR on II) fresh, III) dried, IV) dried and milled soil samples.

Summary

In general, the DATR proved easier to use and appeared to perform better than the diffuse reflectance, particularly when it came to measurement of field condition soil. The major problem for the diffuse reflectance approach was difficulties in getting sufficient signal for fresh soil or measurements in the field. The strong intensity of the diffuse reflectance spectra resulted in inversions of the strongest bands, but measurements on the dried non-milled soil was for some samples still quite reproducible. There were, however, issues with neat highly organic soils, which showed less differentiated peaks when using diffuse reflectance compared with DATR.

For the DATR measurements, the crucial step was to ensuring good contact and using a field clip was essential for dried samples. Soil moisture helped, as fresh soil generally gave better reproducibility than the fresh-dried or dried-sieved samples and were often less noisy. Although, at the expense of having bands due to water obscuring parts of the spectrum. A method of smearing the soil onto the DATR window was easy to do and allowing the fresh soils to dry for a short period on the DATR produced spectra showing the same features as the fresh dried samples, but often less noisy, and with better replication.

For particle size, there may not be many means of changing the spectra, but an awareness of differences compared with milled samples is needed. Minerals (other than clay minerals) are underrepresented in the un-milled spectra, and mineral bands may be poorly resolved, but relative proportions of SOM and clay minerals are enhanced. Sloping baselines can also occur.

For some soil types, especially with coarse texture, averaging of multiple scans may be needed to overcome the heterogeneous nature of the soil and get representative spectra, but for most of the soils included in this study replication appeared quite good.

Acknowledgements

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