

## **A Robust FTIR Database for Scotland**

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### **Abstract**

Using Fourier Transform Infrared Spectroscopy (FTIR) a spectral database of Scotland's soils has been produced using an Attenuated Total Reflectance (ATR) sampling method. Vital to the generation of high quality IR spectra of soil is sample preparation, in particular milling. Here we evaluated a number of milling procedures not only applicable to FTIR analysis, but which also enabled mineral analysis using X-ray powder diffraction spectroscopy (XRPD). The robust spectral database produced allowed comparison between recently sampled and legacy samples, the development of calibrations with soil properties and provides a sound basis for the development of field based FTIR methodologies.

**Keywords:** *FTIR, soil, MIR, ATR, XRPD*

### **Introduction**

FTIR (Fourier Transform Infrared) spectra in the mid infrared (MIR) region (4000 to 400  $\text{cm}^{-1}$ ) of mineral and soil samples give an overall chemical profile of the sample. The spectra can be recorded using a range of different sampling methods: Transmission; Diffuse Reflectance (DRIFTS) and Attenuated Total Reflectance (ATR). ATR is a straightforward method which avoids the need for the sample preparation of transmission methods and produces spectra that have a number of advantages over those recorded by DRIFTS. These include ease of interpreting the absorption bands arising from the fundamental vibrations in this spectral region, and the quality of correlations between spectra and soil properties. Both DRIFTS and ATR spectra can also be recorded in the field.

In order to produce an FTIR spectral database for Scotland's soils an ATR sampling method was selected. To ensure the ATR spectra were as representative and reproducible as possible, it was critical that a sample preparation protocol was developed which produced samples with the optimal particle size, whilst avoiding problems of contamination or degradation of the samples. The first aim of this study was to achieve this. The samples in the Scottish dataset were also being analysed by X-ray powder diffraction (XRPD) for mineralogy and, in order to ensure accurate correlations between the IR spectra and the quantitative mineralogy, the second aim was to produce a shared sample preparation method for the two techniques. This preparation procedure was primarily focussed on the milling and drying of the soil sample prior to analysis.

A high quality and diverse FTIR database for soils, such as this, provides not just an excellent basis for the development of calibrations between FTIR spectra and soil properties, but also a sound platform for the development of future field-based FTIR methodologies. The final aim of this work was to produce a robust spectral database suitable for this, and also for assessment of changes in soils over time.

## Materials and Methods

### Sample Preparation trials

For the milling protocol a small set of 12 samples representing a range of soil types, from organo-mineral soils, with limited soil organic matter to highly organic soils, with limited mineral content were selected. For each milling procedure tested, 2 replicates were run. All methods tested involved wet milling (in water or alcohol) due to the known danger of degrading the samples by the heat generated by dry milling [Russell, 1974]. The methods compared were hand milling, ball milling using a Retsch mill with tungsten carbide or agate balls and milling with a McCrone mill with corundum or agate barrels. Drying methods were also compared, with the samples either being spray dried or air dried. Milling time was also varied.

For the milling trials FTIR spectra of the milled soils were recorded on a Bruker Vertex 70 FTIR spectrometer using a DATR accessory in the range from  $4000\text{cm}^{-1}$  to  $400\text{ cm}^{-1}$  (ATR and baseline corrected) and compared with each other and with spectra of the un-ground soils.

### FTIR spectral database

FTIR analysis was carried out, as described above, on a spatial dataset of soils sampled on a 20km grid throughout Scotland (see Fig 1), as part of the National Soil Inventory of Scotland (NSIS) [Lilly et al, 2010]. Samples were from 183 different sites, top horizons of a pit profile. Where <10 cm deep, a second horizon was also included giving a total of 224 samples in the dataset. Both recently sampled (NSIS2, 2007-2009) and legacy samples (NSIS1, 1978-1988) were analysed. Scottish soils have a great diversity and the dataset had % C values ranging from 1- 50% [Aalders et al, 2009].

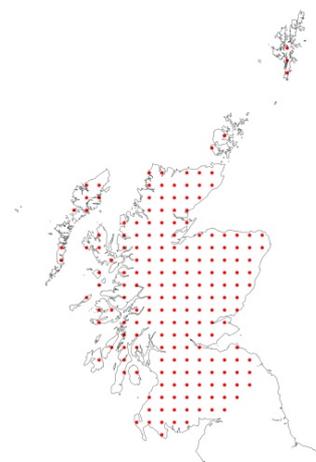


Fig 1 Location of NSIS grid points, each 20 km apart

## Results

### Sample Preparation trials

Some methods showed contamination in the IR spectra and XRPD patterns. This was the case for the Retsch milling with agate balls and McCrone milling with corundum barrels, where the IR spectra were contaminated with visible silica and corundum bands. These methods were eliminated as unsuitable on this basis.

Retsch milling with tungsten carbide balls appeared to alter the Soil Organic Matter (SOM) profile in the IR spectra, particularly where there was low clay mineral content in the soil.

There was an alteration in the 1800 – 1300  $\text{cm}^{-1}$  region which may be consistent with free carboxylic acid being converted to the carboxylate. There also appeared to be a loss of intensity of kaolinite bands. In addition, this method gave spectra with a sloping baseline and some poorly resolved mineral peaks, indicative of particle size not being sufficiently reduced. As expected, this was also found for hand milled samples.

Spray drying of the samples also seemed to alter the SOM profile in the IR spectrum, but was the preferred option for XRPD analysis. Spray drying also provides samples with randomised orientation, ideal for XRPD [Hillier, 1999], but which show different relative intensities for kaolinite bands in IR spectra compared with “normal” oriented samples.

McCrone milling with the agate barrels (12 minutes milling in water) followed by air drying and lightly grinding (in isopropyl alcohol) with the mortar and pestle gave the best results for the FTIR spectra. The organic matter pattern most closely resembled that of the unmilled soil, the particle size was appropriate and there was no evidence for contamination with silica. This was the protocol adopted for the FTIR spectra for the Scottish Soil Spectral Database. The samples for XRPD shared this preparation method up to the drying stage, when they were spray dried

#### FTIR spectral database

High quality FTIR spectra were achieved for the Scottish Soil Spectral Database and they were shown to be highly reproducible and representative by comparisons between spectra of recently sample and legacy soils from the same sites. (See Fig 2) It is therefore possible to look at change over time.

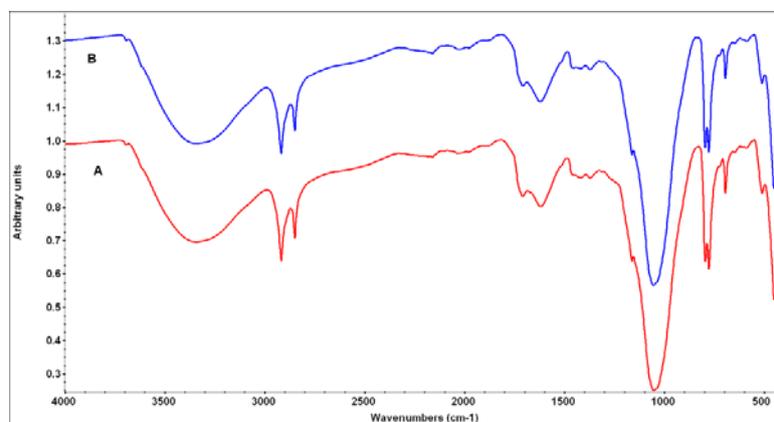


Fig 2 IR spectra of A) a legacy sample and B) a recent sample from the Windyhills site (NJ 800 400)

Successful calibrations have also been achieved for a number of soil parameters, including Soil Bulk Density, and comparisons can now be made between the IR spectra and the mineralogy from the XRPD data.

#### **Discussion**

A huge amount of information is contained in the FTIR “chemical profile” of soil, encompassing fundamental vibrations of both the organic and mineral aspects. The spectrum of each individual soil sample can therefore be interpreted and the nature of the soil determined. However an IR spectral database of well characterised soils also presents considerable opportunities for relating the spectra to soil properties and producing calibrations for different soil attributes. This gives the potential for extensive non-destructive analysis to be carried out in a single measurement. It also allows, for example, the comparison of soils sampled 30 years apart from the same location, a high priority in this laboratory following the re-sampling of the National Soil Inventory for Scotland. It is essential that the spectra recorded are representative and reproducible if reliable information is to be acquired. It can be argued as to whether using lab based FTIR to examine soil is proximal sensing (McBratney et al, 2011), however, establishing the best practice in the lab must also be considered key to moving it out into the field and developing robust methodologies for *in situ* FTIR analysis. Therefore this work not only has the intrinsic value associated with the lab based analysis but in addition can inform the development of field based analysis.

Sample preparation has many potential pitfalls which can alter IR spectra and their subsequent interpretation. Particle size should ideally be  $<2\mu\text{m}$  to avoid problems with sloping baselines, noisy spectra and poorly resolved mineral peaks [Russell, 1974]. Orientation of samples can affect the spectra too, particularly the relative intensity of absorption bands. Milling is required for soil samples to bring them into the ideal particle size range but any milling process will introduce some contamination, and may introduce other unexpected physical and chemical changes. Ball milling with the Retsch mill, dissipates a lot more energy than the roller milling of the McCrone mill and hence contamination is visible from the agate with Retsch but not McCrone (although the corundum barrels are not as durable and therefore lose material even with the McCrone). The combination of the energy dissipated by the Retsch mill and the presence of both clay minerals and tungsten carbide (possible catalyst) may be responsible for the alteration of the SOM pattern. Spray drying involves flash heating to over  $100^{\circ}\text{C}$  and alteration in the SOM profile of soil samples has been noted previously for heating of SOM in presence of clay minerals (Russell et al, 1974) and may be the cause of changes seen in the spray dried samples.

A protocol was devised, here, to avoid the problems discussed above and give spectra of the desired quality. The protocol was shared between samples for FTIR analysis and for XRPD analysis, up to the final drying stage, ensuring direct links between the IR spectra and mineralogy data. The protocol was then applied to the NSIS samples, both legacy and resampled. For many of the samples there has been essentially no change between the FTIR spectra from legacy and resampled soils and the spectra can be almost exactly overlaid. Although not the initial intention, this can be regarded as a very effective validation of the whole chain of processes for NSIS sampling and analysis.

The NSIS soils are available, in their original state, from the Scottish soils archive for use in the next step for developing field based analysis, where the effects of particle size and moisture are likely to be the biggest challenges. Although the “best practice” milling protocol cannot be applied in the field the detailed interpretation of what is present in a given soil, from the lab based spectra, will be invaluable in development of reliable methodologies in the field. A sample which has been previously studied under ideal

conditions can then be looked at under non-ideal conditions with a much greater understanding.

## **Conclusions**

A shared protocol for soil preparation for FTIR analysis and XRPD analysis was developed which allowed high quality data to be recorded for both, and hence the IR spectra and quantitative mineralogy to be directly linked. Using the protocol a robust FTIR spectral database for Scotland's soils was produced, for both legacy and recent samples, which allows change over time to be investigated. It also provides an excellent basis for developing field based methodology.

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