

The Potential of Mid-IR for On Site Determination of Soil Carbon.

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OBJECTIVE

The objective of this study was to determine the feasibility of using Fourier transform mid-infrared (mid-IR) diffuse reflectance spectroscopy (DRIFTS) for the site analysis of soils.

PART 1-BARC, BELTSVILLE, MD

MATERIALS

Sixty seven soil cores (0-30 cm) were taken from a 20 hectare site at the Beltsville Agricultural Research Center (BARC) known as OPE3. Cores were taken from locations based on a previous mapping of carbon values in order to obtain a wide range of carbon concentrations as possible. Each core was sectioned into three sub-sections, 0-10 cm, 10-20 cm and 20-30 cm, resulting in a total of 201 samples. After scanning in a field moist state (neat), sub-samples were dried at 50°C for 72 days and sifted through a 2 mm sieve. Sifted material was then ground in scintillation vials with 3 steel bars on a SampleTek vial rotator.

METHODS

Samples were scanned (neat, dried and sieved; and dried, sieved, and ground) in the mid-IR on a Surface Optics Corporation model SOC-400 portable Fourier transform infrared (FTIR) spectrometer (Figure 1) from 4000 to 400 cm⁻¹ at 8 cm⁻¹ resolution using a rotating sample cup (approximate path 2 mm in width around an 8 mm diameter circle) and in the near infrared (NIR) on a NIRSystems model 6500 scanning monochromator from 400 to 2498 nm (25,000 to 4003 cm⁻¹) with data collected every 2 nm at a 10 nm bandwidth. Dried and sieved; and dried, sieved, and ground samples were also scanned using a Digilab (now Varian) FTS-7000 Fourier transform spectrometer equipped with a Pike AutoDiff autosampler (static cups from 10,000 to 4000 cm⁻¹ at 4 cm⁻¹ resolution (NIR) and from 4000 to 400 cm⁻¹ at 4 cm⁻¹ resolution (mid-IR).

The total carbon content of each sample was determined by combustion on an Elemental Analysensysteme vario MAX CNS elemental analyzer.

Partial least squares (PLS) calibrations were developed for soil C using SAS Ver. 9.12 PLS. A total of 30 different spectral pre-treatments were tested including multiplicative scatter correction and 1st and 2nd degree gap derivatives (1, 2, 4, 8, 16, 32 and 64 data-point gaps) with all spectra mean centered and variance scaled. Two types of calibrations were examined: One, using all 201 samples in a one-out cross validation (Figures 3 and 4); and Two, randomly splitting the samples into 151 calibration samples and an independent test set of 50 samples. This was performed 25 times and the average results shown in Table 1 and Figures 5 and 6.

RESULTS AND DISCUSSION

Figure 1 demonstrates the SOC-400 being operated under ambient conditions. Efforts have demonstrated that the instrument can be operated outdoors either from an inverter connected to a car battery or from AC power with no need for a dry, CO2 free air purge or any additional cooling.

The results in Figure 2 show the average mid-IR spectra obtained from non-dried (neat) samples, and those dried, and dried and ground. As shown, non-ground, dried samples produce similar spectra to ground samples, except that the overall absorbance is higher due to the larger particle size. However, the presence of moisture in non-dried samples causes considerable spectral differences.

The results shown in Table 1 and Figures 3-4 show:

- For dried samples, results with a portable FTIR spectrometer (SOC-400) were equal to those achieved with a research grade, bench top laboratory instrument (FTS-7000).
- Results achieved with research grade Fourier transform near infrared (FTNIR) spectrometer were equal to those achieved with a similar grade, scanning monochromator.
- While results for dried samples were the same for the research grade and portable FTIR spectrometers and for the scanning monochromator and FTNIR spectrometer, the same can not be said for neat samples (field moist).
- While results were similar for neat samples between the scanning monochromator and SOC-400 when using a one-out cross validation using all the samples as a calibration set (Data not presented), the results using data from the scanning monochromator were considerably better when an independent test set was examined. This indicates that the calibration from the scanning monochromator was more robust.
- Further efforts with larger sample sets will be needed to more fully evaluate the effect of moisture on mid-IR calibrations for soil C.
- From these results, it appears possible to develop accurate and robust calibrations for soil carbon using neat samples and NIR spectra, but more work is needed to determine whether robust mid-IR calibrations for neat samples can be developed.
- Based on more recent efforts, air drying in the sun and crumbling appears to be sufficient sample preparation for the development of accurate and robust calibrations for soil carbon, although the greatest accuracy is achieved with ground samples.
- What is removed (or not) by sieving has the potential to greatly affect the sample scanned, versus the sample tested by combustion; or the sample scanned in the field (non-sieved), versus the sample scanned in the lab (sieved) and could present problems for on-site analysis.



Fig. 1. SOC-400 portable mid-IR spectrometer in use.

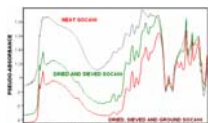


Fig. 2. Average mid-IR soil spectra for neat, dried and sieved, and ground soils taken on a SOC400.

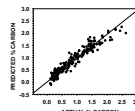


Fig. 3. SOC-400 dried calibration (2 DP av., 1-out, no test set)

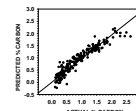


Fig. 4. SOC-400 neat calibration (1 DP av., 1-out, no test set)

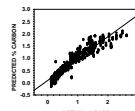


Fig. 5. SOC400 dried test set results (1 DP av.), from 25 random runs.

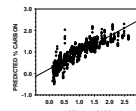


Fig. 6. SOC400 neat test results (1 DP av.), from 25 random runs.

Table 1. Calibration Results From 25 Runs Using 25% (n=50) of Samples as a Randomly Generated Test Set

SAMPLES SCANNED NEAT									
DP	CV	RMSE	R ²	RMSEP	R ²	RMSEP	R ²	RMSEP	R ²
1	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
2	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
4	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
8	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
16	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
32	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
64	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
SAMPLES SCANNED DRIED AND SIEVED									
1	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
2	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
4	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
8	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
16	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
32	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
64	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
DIGILAB (VARIAN) FTS-7000 FTIR									
1	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
2	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
4	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
8	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
16	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
32	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
64	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
SOC-400 PORTABLE FTIR									
1	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
2	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
4	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
8	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
16	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
32	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93
64	151	0.20	0.93	0.18	0.93	0.18	0.93	0.18	0.93

DP=Data points averaged
 MSC=Multiplicative scatter correction
 RMSE = Root mean squared deviation
 T = Test set.

PART 2-CIMMYT, MEXICO

METHODS

In the second part of this study, the SOC-400 was taken to the International Maize and Wheat Improvement Center (CIMMYT) in Mexico to further test the use of mid-IR and to examine the potential problems of using such technologies in developing countries. This was part of a USAD project which also involved testing other technologies such as Laser Induced Breakdown Spectroscopy (LIBS) and Inelastic Neutron Scattering (INS) for the determination of soil C. In this study, 8 samples from the site were collected in a preliminary visit and added to the 201 samples from part 1 to develop a calibration for use on site.

The field experiment in Mexico was conducted 30 April – 3 May 2007 on a 17-year old crop rotation, tillage, residue study located at CIMMYT at 2240 m above sea level. Briefly, the plots sampled consisted of maize (*Zea mays* L.) and wheat (*Triticum aestivum* L.) grown in monoculture or in rotation, with conventional or no tillage methods, and with or without crop residue removal after harvest. 16 treatments were sampled (32 plots total). A composite soil sample made of 12 sub-samples per soil depth (0-5, 5-10, 10-20, and 20-30 cm) was taken from each of the 22 x 7.5 m plots (Due to soil conditions, only half the 20-30 sections were obtained). A portion of each sample was processed near the plots and analyzed for C concentration by mid-IR and LIBS (Entry permits for the INS were not obtainable). The remaining sample was air dried and sent to the KS St. Univ. lab for analysis by combustion.

Samples were scanned both neat and after drying in the sun. Due to the high clay content, grinding in a mortar and pestle was necessary prior to scanning the sun-dried samples. Calibrations developed using the 209 samples previously discussed were then used to determine the C values of the 112 new samples.

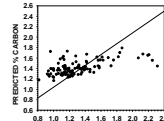


Fig. 7. Prediction results for 112 dried CIMMYT samples using calibration from Beltsville.

As shown in Fig. 7, the results using the calibration developed using 201 samples from Beltsville and 8 Mexican samples performed very poorly with samples generally being predicted near the field mean C concentration (based on combustion data of all samples).

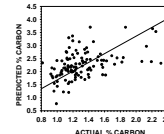


Fig. 8. Prediction results for 112 non-dried CIMMYT samples using calibration from Beltsville.

As shown in Fig. 8, the results for non-dried samples were also very poor. In addition, the non-dried calibration tended to over predict the C values.

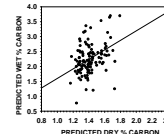


Fig. 9. Non-dried versus dried sample prediction results for 112 CIMMYT samples using calibrations from Beltsville.

The results in Fig. 9 show that there are no relationship between the predicted values using dried and non-dried samples.

In an effort to improve the calibrations, 10% (11 samples) of the CYMMIT samples were selected based on spectral diversity and used to develop new calibrations. This was done by first finding the best spectral pre-treatment by predicting the 19 samples from Mexico (11 new and 8 prior samples) using the Beltsville samples. A new calibration was developed using that pre-treatment and all 220 samples. This calibration was then used to predict the remaining 101 CYMMIT samples (Fig. 10). As seen, while better, the results were still poor.

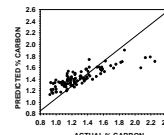


Fig. 10. Results for 101 samples from CYMMIT using calibration based on 201 Beltsville samples and 19 CYMMIT samples.

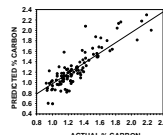


Fig. 11. Best results for 101 samples from CYMMIT using calibration based on 201 Beltsville samples and 19 CYMMIT samples determined by using CYMMIT samples as a test set.

Finally, the 101 remaining samples from CYMMIT were used as a test set to find the best calibration for predicting them. As shown in Figure 11, such a calibration was found and results were much better. However, this required knowing the C values in advance and only demonstrates that accurate calibrations are possible, but not how to find them.

CONCLUSIONS

- Efforts both at Beltsville and at CYMMIT in Mexico have demonstrated that on-site determination of C in soil using mid-IR spectroscopy is possible.
- Efforts have demonstrated that calibrations/predictions can be developed on-site using sun-dried and moist ground samples.
- Results have also demonstrated that mid-IR spectroscopy can be performed using a portable mid-IR spectrometer without the need for a purge to remove CO₂ and moisture. The replacement of the KBr beam splitter with a ZnSe beam splitter would make the instrument moisture resistant even when off.
- Results have also demonstrated that calibrations based on samples not from the country of interest are likely to be problematic, thus making efforts on small areas with diverse soils difficult.
- More efforts are needed to determine the best calibration for future samples using a minimal number of samples from the future site.
- Difficulties in importing and exporting the instruments indicate that such considerations could make the use of these technologies in developing countries difficult even though no practical problems were found in the use of the portable mid-IR spectrometer (SOC-400) once at the location.