

COMPARISON BETWEEN MID-INFRARED AND NEAR-INFRARED FOR SOIL ANALYSIS

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Abstract

This study describes the predictive performance of calibrations using 500 New Zealand soils for total nitrogen (TN) and total carbon (TC) using near-infrared (NIR) and mid-infrared (MIR) instruments. The soils were collected from all over New Zealand and included a wide range of different soil types, and covered a range of TN and TC values.

The NIR spectra were attained using the 2 mm fraction of soil scanned on a Brüker Matrix. The MIR spectra were attained using the fine-ground fraction and scanned on a Brüker Alpha MIR unit.

There was little difference between the predictive performance of the two techniques. Near infrared had the advantage that fine grinding of the soil was not necessary.

Introduction

The use of infrared absorption measurements for the analysis of soil has increased dramatically in the past decade. This is mainly due to the increase in computing power to enable the building of calibrations using complex chemometric methods. Infrared can be split into three subgroups, near-infrared (NIR), mid-infrared (MIR) and far-infrared (FIR). Far infrared is a relatively new technique and is under current investigation for its ability to measure soil properties. The first two techniques (NIR and MIR) are used commercially for measuring soil tests, such as organic matter (SOM), total nitrogen (TN) and total carbon (TC).

Near-infrared (NIR) and mid-infrared (MIR) technologies utilise the light adsorbing properties of the soil to form calibrations against wet chemical data. Near infrared is usually denoted as the electromagnetic spectrum between the wavelengths of ~750 and ~2500 nm in wavelength (~13500 to ~4000 cm^{-1}) where as MIR is between ~2500 and ~23500 nm (~4000 to ~450 cm^{-1}). Mid-infrared has primary vibrational adsorptions, where as NIR measures overtones of these, and higher energy primary vibrations. Due to the complex matrix of soil, both techniques have convoluted peaks due to the large variety of absorbing molecules. Thus both techniques require chemometric methods to build multivariate calibrations.

New Zealand has traditionally favoured NIR, whereas Australia MIR. Traditionally MIR has been used for the qualitative analysis of pure organic compounds, where a peak correlates with a specific functional group in a compound of interest. Initial soil MIR research had the samples diluted with KBr as the strong absorbance in the MIR wavelength range creates very broad peaks which were difficult to assign for qualitative analysis. However, even with dilution with KBr convolution and overlapping of peaks occurs. With the development of multivariate calibration techniques researchers have found that dilution with KBr was not necessary for quantitative analysis.

The following table shows some of the TN and TC calibrations built in the past by researchers on both NIR and MIR instruments.

Table 1: Predictions of total carbon and total nitrogen in the literature for NIR and MIR

| Test | Method | λ (nm) ¹ | Fraction ² | Range ³ | SEP / RMSEP ⁴ | R ² | RER ⁵ | Number | Reference |
|--------------|--------|--------------------------------|-----------------------|--------------------|-----------------------------|----------------|------------------|--|----------------------------------|
| | | | | | | | | N _{calib} / N _{valid} | |
| TC (g/kg) | MIR | 2500– 25,000 | Fine Ground | 0.98 – 104 | 3.4 | 0.98 | 30.3 | 177/60 | McCarty et al. (2002) |
| TC (g/kg) | NIR | 1100– 2498 | Fine Ground | 0.98 – 104 | 5.4 | 0.87 | 19.1 | 177/60 | McCarty et al. (2002) |
| TC (%) | NIR | 1100– 2498 | Fine Ground | 0.61-3.4 | 0.09 | 0.95 | 31 | 120/59 | Reeves et al. (1999) |
| TC (%) | NIR | 400 - 2500 | <8 mm | 0.13- 28.6 | 0.8 | 0.87 | 36.2 | 30/119 | Chang et al. (2001) |
| TC (%) | NIR | 400- 1700 | <2 mm | 0.5-12.2 | 1.3 | | 9 | 228/71 | Rajendram et al. (2005) |
| OC (%) | MIR | 400- 4000 | Fine Ground | 0.2-6.6 | 0.26 | 0.92 | 25 | 94/268 | Minasny et al (2009) |
| TN (%) | MIR | 2500– 20,000 | Fine Ground | | | 0.88 | | | Janik and Skjemstad (1995) |
| TN (%) | NIR | 1100– 2500 | <2 mm | 0.04- 0.23 | 0.01 | 0.92 | 19 | 72/48 | Dalal and Henry (1986) |
| TN (%) | NIR | 1100– 2300 | Fine Ground | | | 0.94 | | 180 x-val | Reeves and McCarty (2001) |
| TN (%) | NIR | 1100– 2498 | Fine Ground | 0.06- 0.28 | 0.007 | 0.96 | 31 | 120/59 | Reeves et al. (1999) |
| TN (%) | NIR | 400 - 2500 | <8 mm | 0.02 – 1.65 | 0.06 | 0.85 | 27 | 30/119 | Chang et al. (2001) |
| TN (%) | NIR | 400- 1700 | <2 mm | 0.01- 1.62 | 0.14 | | 11 | 228/101 | Rajendram et al. (2005) |
| TN (%) | MIR | 400- 4000 | Fine Ground | 0.01- 0.45 | 0.02 | 0.94 | 22 | 90/252 | Minasny et al (2009) |

¹ Wavelength range of instrument.

² Fraction type soil used in measurement.

³ Range of reference values (length of calibration)

⁴ RMSEP = Root mean square prediction (error statistic explained in more detail later).

⁵ RER = Range error ratio (Range / RMSE)

This study describes the development of calibrations using 500 New Zealand soils for total nitrogen and total carbon using NIR and MIR instruments. The soils include a wide range of different soil types, and cover a range of total nitrogen and total carbon values. This study reports the relative predictive abilities of NIR and MIR and their ease of use for soil analysis of TN and TC.

Methods

Five hundred soils from around New Zealand, including a range of soil types and a range of TC and TN values were used in this study. The soils were dried at 38°C, and ground through a 2 mm sieve. A Retsch planetary ball mill was used to fine grind the soil samples. Total nitrogen and carbon were analysed on the fine ground fraction of soil using an Elementar varioMAX CN combustion analyser. The following table shows the statistics and distribution for the reference data:

Table 2: Reference Wet Chemistry Statistics

| | Range ¹ | IQR ² | Mean | Standard Deviation of Population (SD) ³ | SEL ⁴ |
|--------|--------------------|------------------|-------|--|------------------|
| TN (%) | 0.09 - 1.85 | 0.33 | 0.602 | 0.267 | 0.020 |
| TC (%) | 0.69 - 34.06 | 3.87 | 6.824 | 4.397 | 0.214 |

¹ Range of reference values, used in error statistic: RER

² IQR = Inter-quartile range, used in error statistic:

³ Spread of reference values, used in error statistic RPD

⁴ SEL= Standard Error of Laboratory, standard deviation of replicates of reference wet chemistries.

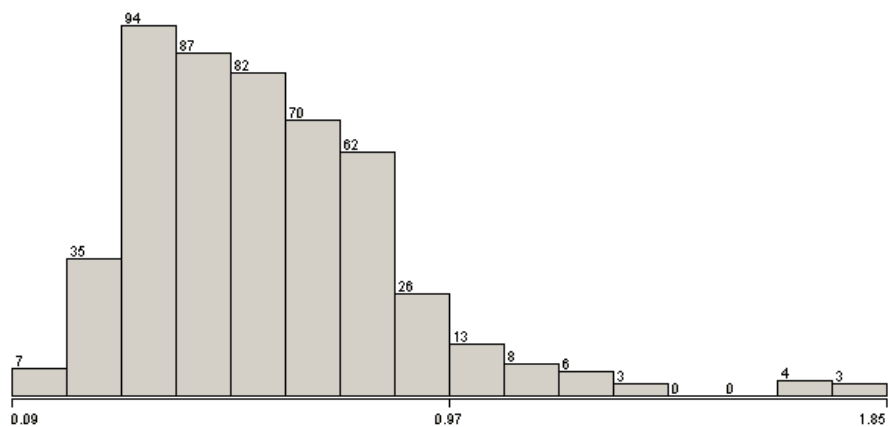


Figure 1: Distribution of total nitrogen (%) reference values

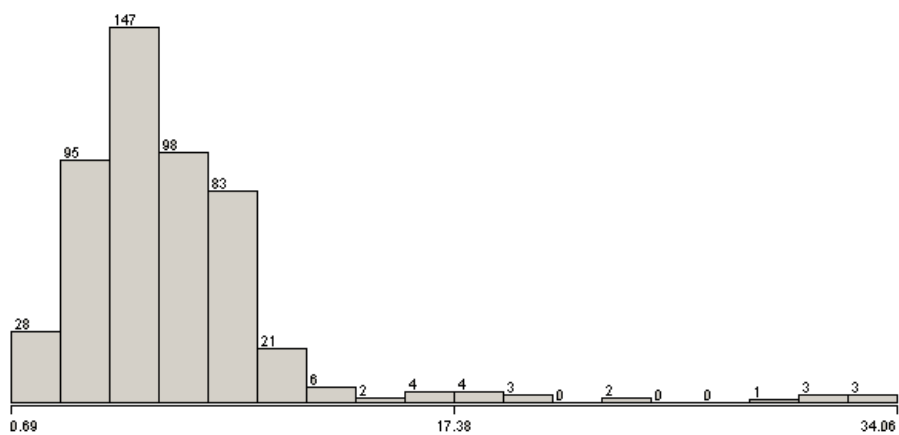


Figure 2: Distribution of total carbon (%) reference values

The NIR spectra was attained using the 2 mm fraction of soil and scanned on a Brüker MATRIX™-F duplex with Q-410/A scanning head, with a scanning range of 12,800 - 3600cm⁻¹. The instrument carried out 124 scans (23 seconds analysis time) and used a Spectralon[®] tile as the background, which was rescanned every 10 minutes (20 samples).

The MIR spectra was attained using the fine-ground fraction and scanned on a Brüker Alpha MIR unit with a scanning range of 375 - 7,500 cm⁻¹. The instrument scanned for 2 mins (120 spectra collected) and used a gold tile as the background which was rescanned every 10 mins (5 samples). For both instruments, the acquired scans were averaged to give the final spectra for each sample.

Studies previously performed at Hill Laboratories had shown that the 2 mm fraction gave comparable calibration statistics and performance with fine ground fractions using the NIR Brüker MATRIX™-F. This was believed to be due to the wide viewing area that the MATRIX™-F (approximately 15 mm diameter) had on the sample surface. Whereas with MIR; fine-ground samples are needed as the viewing area is much smaller. NIR operating with a shorter wavelength and having less absorbance than MIR penetrates the sample further, giving a much larger sample volume analysed. Hence MIR needs to be further ground to achieve a representative sample.

Chemometrics

The data was analysed using a number of chemometric methods and pre-treatments for comparative purposes. A good chemometric method for one spectral technique may not be good for another; and this makes it difficult to compare instruments, whilst keeping the experimental procedures as similar as possible.

Pre-processing of the data included centring the data around a mean of 0 (Centre), and using a partial least squares filter (PLS) with 20 and 25 components (PLS-20 and PLS-25). Bootstrap bagging used by Viscarra Rossel (2007) with 10 iterations, and a first order derivative used by Minasny et al., (2009) were also modelled.

Algorithms used were multivariate linear regression, Gaussian processors and M5. The most complicated model built used a stacking of predictions method, where 3 different predictions of the instance using 3 different algorithms (centred-PLS-Linear regression, centred-PLS-gaussian processors and centred-PLS-multilayer perceptron) and an overall algorithm (M5 rules) to bring those predictive values into one final prediction (the overall method denoted – ‘Stack’).

An in-house modified version of Weka Software was used to create the calibrations and determine the calibration statistics. Cross-validation is a good way to determine predictive abilities of methods in pilot-type studies, and thus a good method for comparing different instruments using the same data set. The standard ten-fold cross-validation was used in this study (Witten and Frank, 2005).

Calculations that compared the wet chemistry reference data to the predicted data for initial assessments of each chemometric model. The R² was calculated as a regression equation between the two sets of data, and a measure of error; Root Mean Square Error (RMSE) was calculated.

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_i - x_i)^2}$$

The range error ratio (RER), the ratio of predictive deviation (RPD) and ratio of performance to inter-quartile range (RPIQ) were also calculated. The different terms estimate the usefulness of the prediction, where the overall range, inter-quartile or the spread of the reference values, defined in terms of a standard deviation (SD), are determined as ratios against the error of prediction.

RER = Reference Range / RMSE

RPD = Reference SD / RMSE

RPIQ = Inter-quartile Range / RMSE

Williams (1987) gives guidance as to what the RPD values mean in terms of predictions with 0 to 2.3 being very poor, 2.4 to 3.0: poor, 3.1 to 4.9: fair, 5.0 to 6.4: good, 6.5 to 8.0: very good and 8.1+ being an excellent calibration for feed samples. Chang et al. (2001) suggested the following of RPD values for soil calibrations; good > 2.0, reasonable 1.4 -2.0 and not reliable <1.4. Williams (1987) also offers some advice for the interpretation of RER values, where above 10 is a useful screening tool, and above 20 the model is essentially quantitative.

Due to the 'skewness' from normality of the population of TN and TC values (following more of a log type distribution), the RPIQ statistic was also calculated as proposed by Bellon-Maurel et al. (2010). The statistic should follow similar advice to RPD but better suited to data that does not fit a normal distribution.

Results and Discussion

All 500 soils were included in the MIR and NIR calibrations. There appeared to be little difference between the two instruments in the predictions of TC and TN for the 500 soils (Tables 3 and 4). In general all calibrations had an RER ratio around or greater than 20, and RPD > 2. The best chemometric method for both instruments was the stacking method with volume weight (VW) included as a predictor variable. Figures 3 and 4 show the best calibration curves for TN using MIR and NIR respectively. Figures 5 and 6 show the best calibration curves for TC using MIR and NIR respectively.

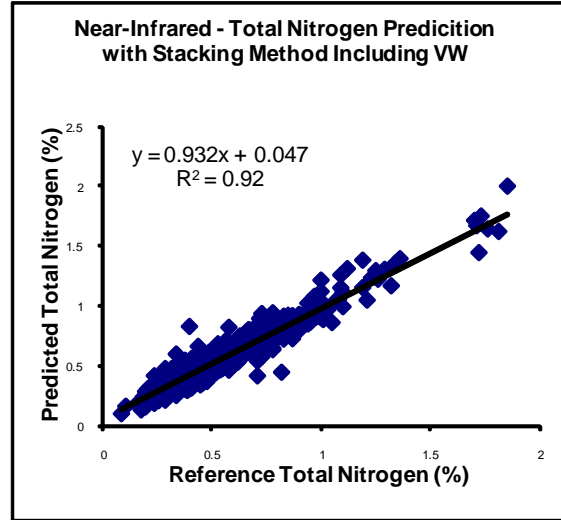
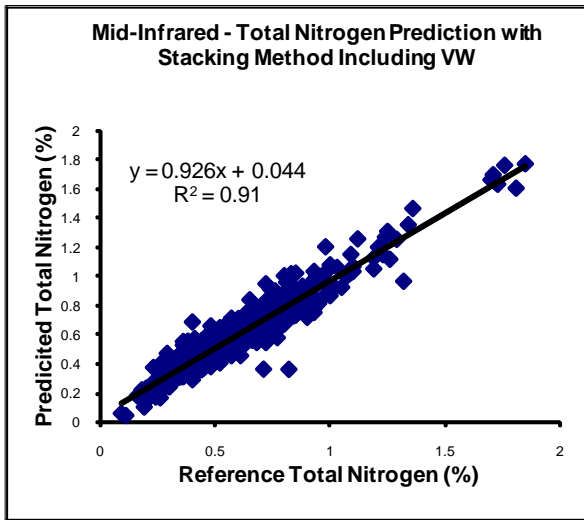
However, the MIR spectra were determined using the fine ground fraction, whereas the NIR spectra were determined using the 2 mm fraction. The extra step of fine-grinding samples contributes extra cost for samples analysed on the MIR, making the NIR substantially more cost effective.

Table 3: Results of total nitrogen calibration statistics using NIR and MIR with different chemometric methods

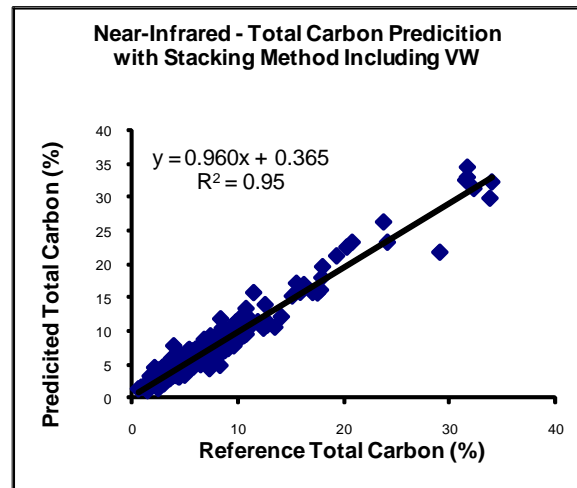
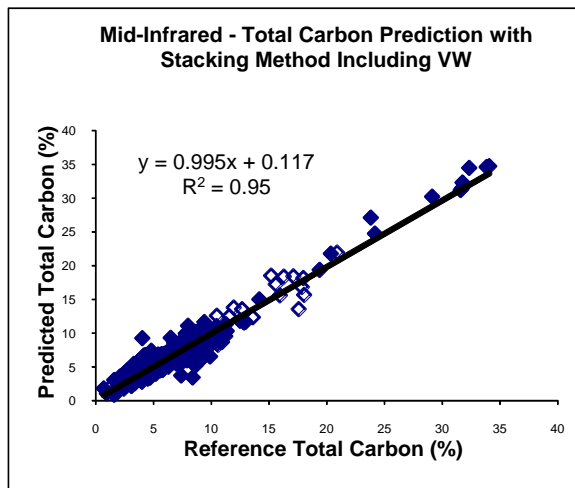
| TN (%) | | NIR | | | | MIR | | | | |
|-----------------------------------|------|----------------|------|-----|------|------|----------------|------|-----|------|
| Chemometric Method | RMSE | R ² | RER | RPD | RPIQ | RMSE | R ² | RER | RPD | RPIQ |
| Centred- PLSR-20 | 0.11 | 0.84 | 16.2 | 2.5 | 3.1 | 0.09 | 0.89 | 19.6 | 3.0 | 3.7 |
| Centred- PLSR-25 | 0.10 | 0.85 | 16.8 | 2.6 | 3.2 | 0.10 | 0.87 | 18.4 | 2.8 | 3.5 |
| Bagged-Centred-PLSR-20 | 0.11 | 0.83 | 16.0 | 2.4 | 3.0 | 0.09 | 0.89 | 20.2 | 3.1 | 3.8 |
| Bagged-Centred-PLSR-25 | 0.11 | 0.84 | 16.7 | 2.5 | 3.1 | 0.09 | 0.88 | 19.3 | 2.9 | 3.6 |
| First Order Derivative - M5 Rules | 0.13 | 0.75 | 13.1 | 2.0 | 2.5 | 0.13 | 0.78 | 13.8 | 2.1 | 2.6 |
| Centred -PLS-20-Gaussian | 0.10 | 0.88 | 17.5 | 2.7 | 3.3 | 0.10 | 0.88 | 18.5 | 2.8 | 3.5 |
| Centred - PLS-25-Gaussian | 0.11 | 0.87 | 16.6 | 2.5 | 3.1 | 0.11 | 0.86 | 16.5 | 2.5 | 3.1 |
| Stack | 0.09 | 0.90 | 20.7 | 3.1 | 3.9 | 0.08 | 0.90 | 20.7 | 3.1 | 3.9 |
| Centred-PLSR-20 + VW | 0.10 | 0.87 | 18.5 | 2.8 | 3.5 | 0.08 | 0.90 | 20.8 | 3.2 | 3.9 |
| Centred-PLSR-25 + VW | 0.09 | 0.88 | 19.2 | 2.9 | 3.6 | 0.09 | 0.89 | 19.6 | 3.0 | 3.7 |
| Stack + VW | 0.08 | 0.91 | 22.1 | 3.4 | 4.1 | 0.08 | 0.91 | 22.3 | 3.4 | 4.2 |

Table 4: Results of total carbon calibration statistics using NIR and MIR with different chemometric methods

| TC (%) | | NIR | | | | MIR | | | | |
|-----------------------------------|------|----------------|------|-----|------|------|----------------|------|-----|------|
| Chemometric Method | RMSE | R ² | RER | RPD | RPIQ | RMSE | R ² | RER | RPD | RPIQ |
| Centred- PLSR-20 | 1.70 | 0.85 | 19.7 | 2.6 | 2.3 | 1.26 | 0.92 | 26.4 | 3.5 | 3.1 |
| Centred- PLSR-25 | 1.62 | 0.87 | 20.6 | 2.7 | 2.4 | 1.30 | 0.91 | 25.6 | 3.4 | 3.0 |
| Bagged-Centred-PLSR-20 | 1.72 | 0.85 | 19.4 | 2.6 | 2.2 | 1.24 | 0.92 | 27.0 | 3.6 | 3.1 |
| Bagged-Centred-PLSR-25 | 1.64 | 0.86 | 20.3 | 2.7 | 2.4 | 1.26 | 0.92 | 26.6 | 3.5 | 3.1 |
| First Order Derivative - M5 Rules | 2.11 | 0.78 | 15.8 | 2.1 | 1.8 | 2.03 | 0.81 | 16.4 | 2.2 | 1.9 |
| Centred - PLS-20-Gaussian | 1.71 | 0.88 | 19.5 | 2.6 | 2.3 | 1.41 | 0.92 | 23.6 | 3.1 | 2.7 |
| Centred - PLS-25-Gaussian | 1.84 | 0.87 | 18.2 | 2.4 | 2.1 | 1.30 | 0.91 | 25.6 | 3.4 | 3.0 |
| Stack | 1.19 | 0.93 | 28.0 | 3.7 | 3.2 | 1.06 | 0.94 | 31.4 | 4.1 | 3.6 |
| Centred-PLSR-20 + VW | 1.53 | 0.88 | 21.8 | 2.9 | 2.5 | 1.19 | 0.93 | 28.1 | 3.7 | 3.3 |
| Centred-PLSR-25 + VW | 1.45 | 0.89 | 23.1 | 3.0 | 2.7 | 1.20 | 0.93 | 27.7 | 3.7 | 3.2 |
| Stack + VW | 0.97 | 0.95 | 34.3 | 4.5 | 4.0 | 1.01 | 0.95 | 33.2 | 4.4 | 3.8 |



Figures 3 & 4: Predictions of Total Nitrogen with MIR and NIR using the Stacking Method (& VW)



Figures 5 & 6: Predictions of Total Carbon with MIR and NIR using the Stacking Method (& VW)

Conclusion

Near-infrared and mid-infrared calibrations with the instruments used gave comparable results for the analysis of total carbon and total nitrogen for New Zealand soils. The spectra for MIR appeared simpler and possibly easier to manipulate with chemometrics. However, the main difference between the two spectral options was the difference in the direct cost of analysing each sample. The potential saving in cost and time through not having to fine-grind the samples gives an advantage to NIR techniques. Further work into the relative differences between NIR and MIR, using Australian soils and different instruments is planned.

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