Measurement of Soil Mineralogy and CEC Using Near-Infrared Reflectance Spectroscopy

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Abstract:

Measurements of soil properties by cation-exchange capacity (CEC) and X-Ray diffraction (XRD) are often time consuming and expensive processes. Near-infrared reflectance (NIR) spectroscopy can be used to create calibration models based on CEC values and XRD mineralogy. These calibrations can then be utilized to predict both cation exchange capacities and mineral composition of soil samples in near real-time without the need for additional costly and time consuming laboratory measurements. NIR has the added benefits of providing a field portable, non-destructive sample measurement. Multiple soil properties can also be simultaneously predicted via a single spectrum. Quantitative calibrations for NIR analyzers are developed using statistical methods that relate measured NIR reflectance to the material properties of interest. This poster examines the quantitative determination of soil mineralogy based on XRD determined kaolinite, montmorillonite and mica abundances, and swelling clays determination by CEC measurement with multivariate calibrations using NIR spectroscopy.

Background:

Measurement of soil mineralogy and composition:

- Traditional assays - XRD, QEMSCAN, ICP or other chemical assays.
- NIR quantitative – must have a large number of samples representing the mineral diversity and a multivariate model must be created.
- NIR qualitative or semi-quantitative; Does not require submission of samples to traditional chemistry analysis, based on peak matching or unmixing.

Partial Least Squares Regression (PLSR) is an ideal tool for dealing with the tremendous diversity and complexity of the soils used to generate each calibration.

60-90 samples required for a feasibility study, 120-180 samples for a starting model and 180+ samples for a robust calibration model.

Figure 1, ASD LabSpec 2500 and Muglight sample accessory

Procedure:

Soil spectra with corresponding reference XRD kaolinite, montmorillonite, mica and CEC data that had been produced by the National Soil Survey Center in Lincoln, Nebraska were used for this evaluation. Spectra were collected on dried sieved samples using ASD LabSpec® 2500 spectrometers with a wavelength range of 350 to 2500 nm. The total organic carbon content of the CEC samples used in this study ranged from 0.0-0.49%. Spectra were collected on dry, sieved samples using the ASD muglight sample accessory.

Following the data collection in ASD's Indico Pro software, the spectra were then converted to ".spc" spectral file format as absorbance Log(1/R) for model development using GRAMS IQ 9.1, Thermo Fisher Scientific, Waltham MA.

Chemometric models were developed using the Partial Least Squared (PLS1) algorithm which is used to create a model with one constituent (ex: kaolinite) at a time. These single models can then be combined into a single calibration model capable of simultaneously predicting multiple constituents following collection of a single spectrum. Models were optimized to remove gross spectral and concentration outliers. Additionally, all constituent models were validated using an independent test set that had not been included in the calibration model.

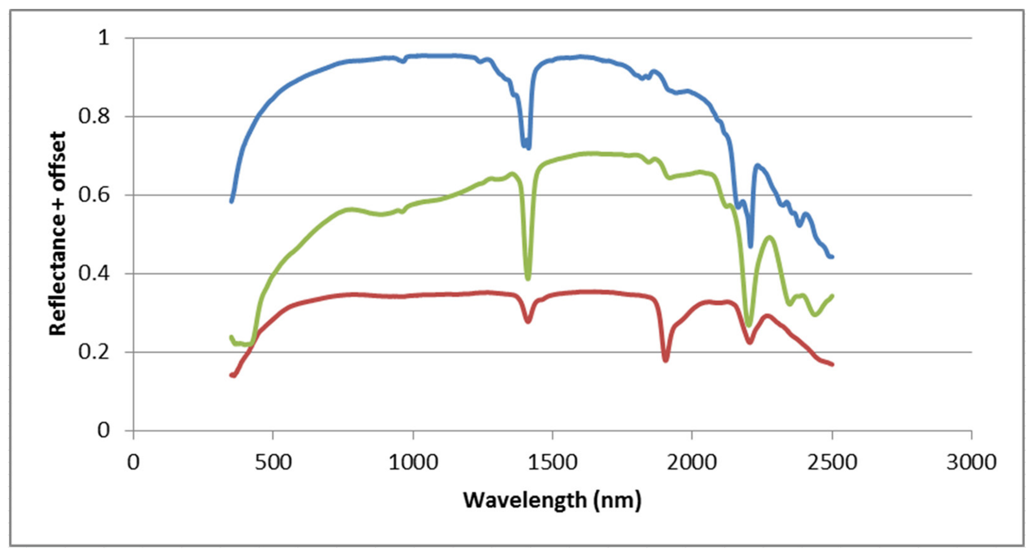

Figure. 2, Typical reflectance spectra for kaolinite (blue), mica/muscovite (green) and montmorillonite (red)

Results:

	Calibration					Validation			
Constituent	n	n outliers	Factors	RSQ	SECV	n	RSQ	SEP	RPD
Kaolinite	395	15	9	0.80	8.36	98	0.81	8.04	2.32
Montmorillonite	251	5	6	0.73	12.99	60	0.69	13.88	1.76
Mica	327	10	15	0.74	7.70	79	0.69	8.84	1.79
CEC	111	2	4	0.75	4.32	26	0.80	3.79	2.22

Table 1, Model summary

Kaolinite

The kaolinite data set modeled very well with an RSQ = 0.80 and SECV = 8.36. The test set statistics were very comparable and also produced the best RPD value among the four different calibrations. RPD is the ratio of performance deviation (standard deviation of the test set reference values divided by the SEP), which is another measurement of the effectiveness of the calibration. Soils researchers have previously established guidelines for RPD: where RPD > 4 is excellent and RPD ≥ 1.75 marks the lower threshold for quantitative models. The RPD of 2.32 for kaolinite is indicative of a successful quantitative calibration.

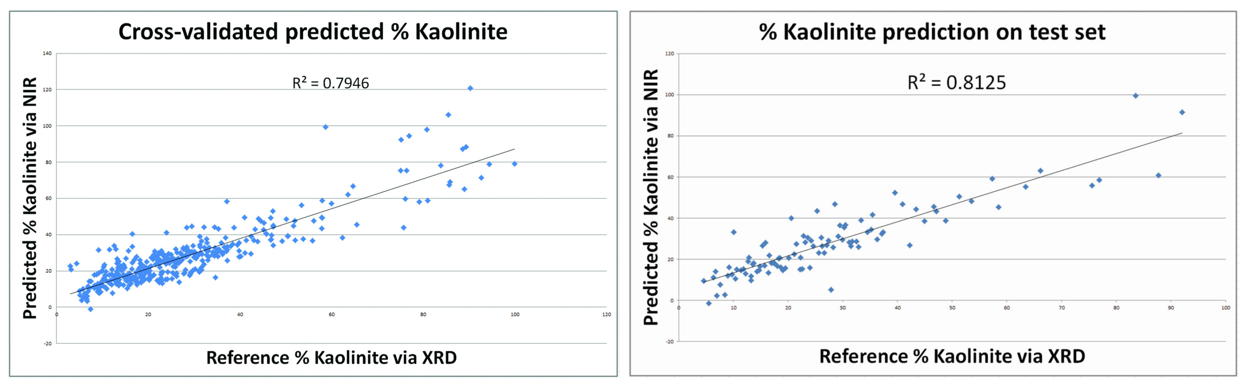

Figure 3, Kaolinite model and test set prediction

Montmorillonite

Montmorillonite is the most common smectite mineral. In soils, it aids in water retention. However, due to the high swelling potential of sodium montmorillonite it is seen as problematic by structural engineers. The montmorillonite data set modeled well with an RSQ of 0.73 and SECV of 12.99. The test set statistics were also comparable with an RSQ of 0.69 and SEP of 13.88, which indicates that the model validated well. The relatively lower RPD of 1.76 for montmorillonite is an indication that this calibration should still be considered as useful for quantitative predictions.

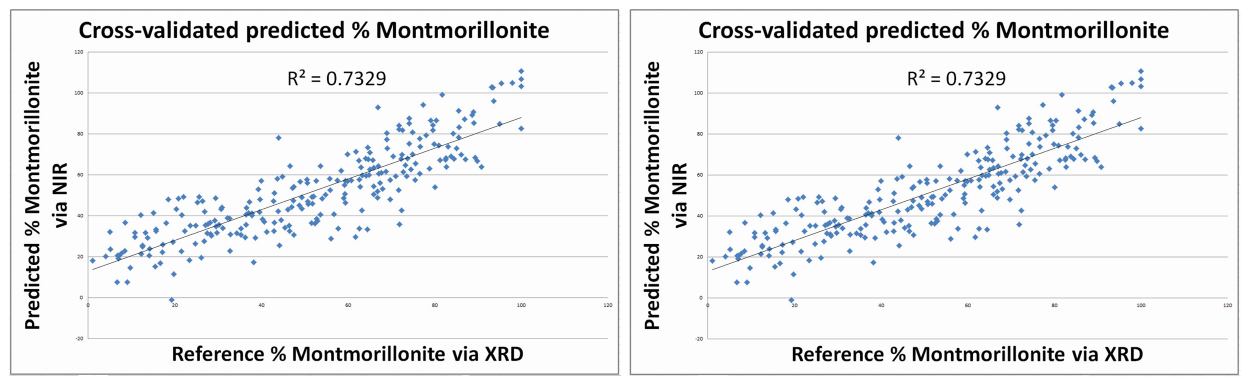

Figure 4, Montmorillonite model and test set prediction

Mica – (Muscovite)

The mica data set modeled well with an RSQ = 0.74 and SECV = 7.70. The test set statistics were also comparable with RSQ = 0.69 and SEP = 8.84, which indicates that the model validated well. The RPD of 1.79 for mica is above the 1.75 threshold and so this is an indication that this calibration would be useful for quantitative predictions.

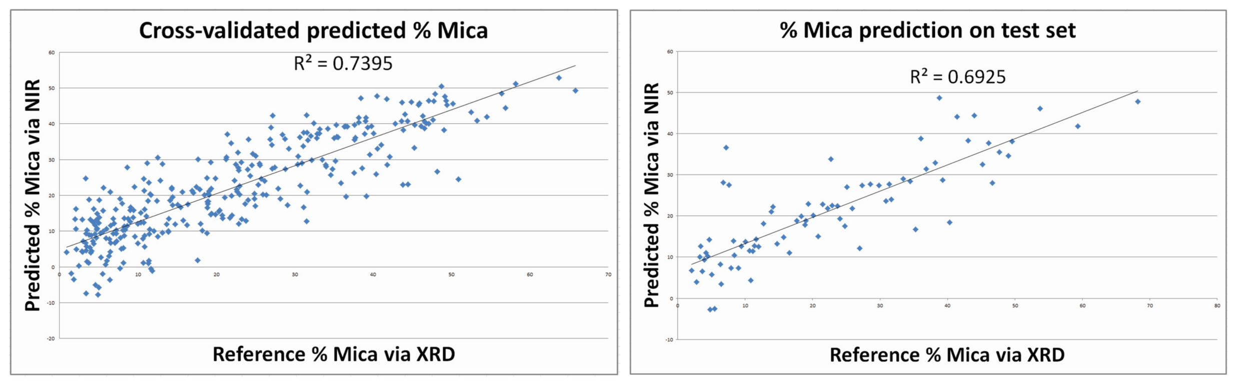

Figure 5, Mica model and test set prediction

Cation Exchange Capacity (CEC)

The CEC assay is a measure of exchangeable cations and is used as an indicator of overall soil fertility and also for estimating soil swelling potential. Primarily CEC is influenced by smectite group minerals, but other clays such as vermiculite, kaolinite, chlorite and illite also contribute to CEC values. Additionally, soil carbon also contributes to CEC values. To avoid CEC interactions related to the presence of soil carbon we used a soil organic carbon threshold value of 0.4%. Use of this threshold allowed for modeling the portion of CEC directly related to soil mineralogy. The CEC data set modeled very well with an RSQ = 0.75 and SECV = 4.32. The test set statistics were very comparable with RSQ = 0.80 and SEP = 3.79. This model produced the second best RPD value among the four different calibrations with RPD of 2.22. This calibration would also be useful for quantitative CEC predictions. In order to apply this calibration appropriately an organic carbon model would also need to be developed to determine carbon content.

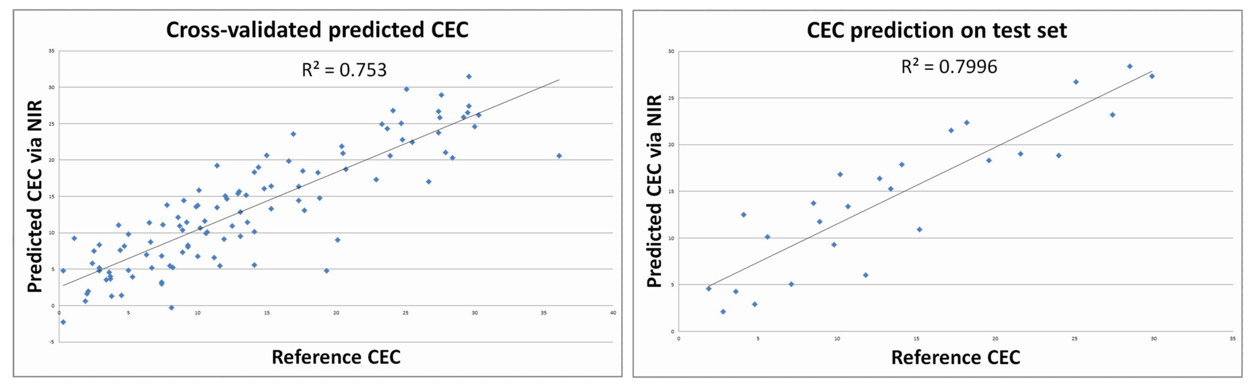

Figure 6, CEC model and test set predictions

Conclusion

We were able to successfully develop and validate NIR models to quantitatively predict soil mineralogy and CEC in naturally occurring samples. The samples used in this study were dried and sieved but future work should investigate the creation of soil models on field moist samples. The creation of soil mineral models could be used to properly fertilize soil and could be potentially useful for the determination of soil stability by construction trades. The analysis speed of NIR, coupled with its low per sample cost should allow this technology to be widely used to replace traditional reference analyses.