Application of short-wave infrared (SWIR) spectroscopy in quantitative estimation of clay mineral contents

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Abstract. Clay minerals are significant constituents of soil which are necessary for life. This paper studied three types of clay minerals, kaolinite, illite, and montmorillonite, for they are not only the most common soil forming materials, but also important indicators of soil expansion and shrinkage potential. These clay minerals showed diagnostic absorption bands resulting from vibrations of hydroxyl groups and structural water molecules in the SWIR wavelength region. The short-wave infrared reflectance spectra of the soil was obtained from a Portable Near Infrared Spectrometer (PNIS, spectrum range: 1300~2500 nm, interval: 2 nm). Due to the simplicity, quickness, and the non-destructiveness analysis, SWIR spectroscopy has been widely used in geological prospecting, chemical engineering and many other fields. The aim of this study was to use multiple linear regression (MLR) and partial least squares (PLS) regression to establish the optimizing quantitative estimation models of the kaolinite, illite and montmorillonite contents from soil reflectance spectra. Here, the soil reflectance spectra mainly refers to the spectral reflectivity of soil (SRS) corresponding to the absorption-band position (AP) of kaolinite, illite, and montmorillonite representative spectra from USGS spectral library, the SRS corresponding to the AP of soil spectral and soil overall spectrum reflectance values. The optimal estimation models of three kinds of clay mineral contents showed that the retrieval accuracy was satisfactory (Kaolinite content: a Root Mean Square Error of Calibration (RMSEC) of 1.671 with a coefficient of determination (R²) of 0.791; Illite content: a RMSEC of 1.126 with a R² of 0.616; Montmorillonite content: a RMSEC of 1.814 with a R² of 0.707). Thus, the reflectance spectra of soil obtained from PNIS could be used for quantitative estimation of kaolinite, illite and montmorillonite contents in soil.

1. Introduction
It has long been recognized that the composition, particle size, degree of consolidation, and aggregate arrangement of clay minerals are closely related to the major physical and chemical properties of soil. Kaolinite, illite, and montmorillonite are the most common soil forming clay minerals. These clay minerals formation processes are largely dependent on the parent rock material, specific climatic, and site conditions [1]. They are used and their value recognized in swelling behaviour, soil fertility, soil
self-purification capacity, heavy metal-adsorption, and so on. All the three kinds of clay minerals are
distinct in diagnostic absorption bands resulting from vibrations of hydroxyl groups and structural
water molecules in the SWIR wavelength region [2]. With the rapid development of spectroscopic
techniques, SWIR spectroscopy technique is attractive for detecting layer-silicates, sulfates, and
carbonates, because the vibrations of the interatomic bonding in these minerals are active in the region.
The degree of crystallinity and compositional variations of minerals can also be gained by this
technique. For these reasons, the objective of this study was to investigate the capability of SWIR
spectroscopy to accurately quantify the contents of kaolinite, illite and montmorillonite in soil.

2. Material and methods

2.1. Soil sample collection and preparation
A total of 55 soil samples were collected from a length of 1250 meters of the profile at 5 cm to 30 cm
depths from Xi Lin District of Yi Chun City in northern China. The soil of the studied area was mainly
composed of primary minerals, such as quartz, feldspar; secondary minerals, such as kaolinite,
montmorillonite, illite and other clay minerals; and carbonates, small amounts of organic matter,
etcetera. All soil samples were air-dried at room temperature and then passed through a 20 mesh sieve.
Each sample was divided into two groups. Group A was scanned by PNIS at wavelengths from 1300
to 2500 nm with a spectral sampling interval of 2 nm. Group B was sent to the laboratory for chemical
analysis. The samples of Group B were analyzed for 23 elements and major oxides including Ag, As,
Au, Cu, SiO$_2$, Al$_2$O$_3$, CaO, etcetera, and the concentration value of those elements and oxides were
obtained. After that, based on those concentration values and the geography condition of the studied
area, the contents of kaolinite, illite, and montmorillonite were estimated as the observed values using
quantitative calculation of clay minerals content of soil [3].

2.2. Data processing

2.2.1. First derivative reflectance
The aim of spectral pre-processing is to avoid the influence of undesirable interference factor on the
spectral measurement such as optical path length variation, light scattering, particle-size effects, and
surface roughness. In this paper, we proposed to use first-order derivative spectrophotometric method
in order to enhance the hidden features of the reflectance spectra, overcome the spectral overlapping,
and reduce some noise. A first difference transformation of the reflectance spectrum (FDR) (Figure.1)
can be derived from the following Equation (1) [4]:

$$ FDR = \frac{1}{\Delta \lambda} (R_{(\lambda(j+1))} - R_{(\lambda(j))}) $$

where $R_{(\lambda(j+1))}$ is the reflectance at the $j+1$ waveband, $R_{(\lambda(j))}$ is the reflectance at the $j$ waveband, and
$\Delta \lambda$ represents the difference in wavelengths between $j$ and $j+1$.

2.2.2. Continuum removal
Absorption-band parameters, such as the position, depth, width, and asymmetry of the feature, have
been devoted to quantitative estimation composition of samples from the laboratory reflectance data.
The absorption-band position is known as the band having the minimum reflectance value over the
wavelength range of the absorption feature. The absorption-band position can be calculated from
continuum removed spectra [5]. The continuum is a convex hull fitted over the top of a spectrum
utilizing straight-line segments that connect local spectral maxima. Continuum removal is a mean of
normalizing reflectance spectra to allow the comparison of individual absorption features from a
common baseline (Figure. 2). After the continuum removal, absorption-band position values are
calculated from SWIR spectra to estimate soil properties.
2.3. Statistical modeling

In order to evaluate the regression prediction, we split the 55 field sample points into two subsets. One contained 40 sample points for the calibration of the regression models; the other contained 15 samples points, for the purpose of validation. Statistical approaches were used to search the consistent relationships between the spectral information of soil and the contents of kaolinite, illite and montmorillonite in soil.

2.3.1. Regression modeling

PLS perform regression on orthogonal variables which physical meaning is not straightforward, however, MLR may be better, because it utilizes the original variables in the model and is, therefore, simpler and easier to interpret. MLR is fit for a few, correctly selected spectral variables, because the collinearity within the variables means that the method exists stability problem, but PLS regression can handle data with multi-collinearity in independent variables, which can also be more numerous than observations [6]. Overall, in order to foster strengths and circumvent weaknesses, we decided to comprehensively use both MLR and PLS. Finally, three schemes were used in the evaluation optimal equations of the reflectance spectra of social samples for estimating the kaolinite, illite, and montmorillonite contents in soil:

Scheme 1: Spectral libraries collected in the field and the laboratory are common data sets used by the hyperspectral remote sensing community. Enter-MLR (In this approach, the Enter-MLR procedure was used for selecting of the most relevant variables) and PLS methods were employed to model the relationship between soil reflectance spectra and three kinds of clay mineral contents in soil. The soil reflectance spectra refers to the spectral reflectivity of soil (SRS) corresponding to the absorption-band position (AP) of kaolinite, illite, and montmorillonite representative spectra from the USGS spectral library.

Scheme 2: For clay minerals in soil, the location of absorption features is controlled by their chemical composition. Accordingly, stepwise multiple linear regression (SMLR) and SMLR-PLS methods were used to establish the equation between the SRS corresponding to the AP of soil spectral and all three kinds of clay mineral contents in soil.

Scheme 3: Considering the influence of some non-absorption characteristic factors on the clay mineral contents calibration models of the relationship between the contents of kaolinite, illite, and montmorillonite and soil overall spectrum reflectance values, were developed by using SMLR and SMLR-PLS methods.

2.3.2. Prediction accuracy

Several statistical parameters were performed to evaluate the predictive quality of a model, the
prediction performance was evaluated on both predicted and observed values of kaolinite, illite, and montmorillonite contents in soil, using the coefficient of determination (\( R^2 \)) and the root mean square error of calibration (\( \text{RMSEC} \)) and the root mean square error of validation (\( \text{RMSEV} \)). Acceptable models should have high \( R^2 \), low \( \text{RMSEC} \) and \( \text{RMSEV} \) and small differences between \( \text{RMSEC} \) and \( \text{RMSEV} \). \( \text{RMSEC} \) and \( \text{RMSEV} \) were calculated from Equation (2):

\[
\text{RMSEC} = \text{RMSEV} = \left( \frac{1}{m} \sum_{i=1}^{m} (\mu_i - \hat{\mu}_i)^2 \right)^{1/2}
\]  

(2)

Where \( \mu_i \) is the observed value (calibration or validation model), \( \hat{\mu}_i \) is the model-predicted value (calibration or validation model), \( m \) is the number of observations. With regard to the PLS method, both robustness and predictive power of the model are assessed using \( Q^2_{\text{cum}} \). When \( Q^2_{\text{cum}} \) is larger than 0.5, the model is considered to have a good predictive ability.

3. Results and discussion

Robust regression models were obtained for all three kinds of clay mineral contents with the first derivative transformation of the reflectance spectra of soil.

3.1. The optimal prediction model of the kaolinite content

The calibration methods provided different prediction accuracy of the studied kaolinite content in soil. The model was applied to establish the relationship between soil kaolinite content and soil overall spectrum reflectance values through the SMLR method (Model 6). This model suffered from serious collinearity problems which made it an invalid model. Table 1 summarizes the prediction results of kaolinite content obtained in the five models. All of the five models were statistically significant. Although the models based on the SRS corresponding to the AP of kaolinite representative spectra from USGS spectral library using Enter-MLR (Model 1) and PLS methods (Model 2) showed acceptable \( R^2 = 0.779, 0.691 \), respectively. In both Model 1 and Model 2 because \( \text{RMSEV} \gg \text{RMSEC} \), they were not robust enough to be considered as the acceptable tools for predicting the kaolinite content in soil. In terms of model stability, calibration model based on the SRS corresponding to the AP of soil spectral using SMLR (Model 3) did not perform as well as Model 4 based on the SRS corresponding to the AP of soil spectral using SMLR-PLS. Meanwhile, Model 4 had the poorest \( R^2 \) value of five models; therefore, neither Model 3 nor Model 4 can be used in the prediction of kaolinite content. Among the five models, the most accurate measurement of the kaolinite content was done with soil overall spectrum reflectance values in Model 5 which employed the SMLR-PLS method. Here, this prediction accuracy was identified as good. This model by soil overall spectrum reflectance values using SMLR-PLS method was considered to provide possible quantitative prediction of kaolinite content (Figure 3).

| Model  | \( R^2 \) | \( \text{RMSEC} \) | \( \text{RMSEV} \) |
|-------|-----------|-----------------|-----------------|
| Model 1 | 0.779 | 1.655           | 2.941           |
| Model 2 | 0.691 | 1.956           | 3.191           |
| Model 3 | 0.766 | 1.700           | 2.443           |
| Model 4 | 0.681 | 1.986           | 2.264           |
| Model 5 | 0.791 | 1.671           | 2.228           |

3.2. The optimal prediction model of the illite content

Based on the three modelling schemes mentioned in Section 2.3.1., we built models especially for predicting the illite content. The calibration model of illite content based on the soil overall spectrum
reflectance values using SMLR method (Model 6) had serious collinearity problem; so the Model 6 had no statistical significance. To analyse the statistical significance of the generated prediction model, five different calibration models were constructed for the prediction of illite content:

Enter-MLR (Model 1) and PLS methods (Model 2) were applied to model the relationship between the illite content and the SRS corresponding to the AP of illite representative spectra from USGS spectral library; illite content measured with the SRS corresponding to the AP of soil spectral using SMLR (Model 3) and SMLR-PLS (Model 4); soil overall spectrum reflectance values using SMLR-PLS method (Model 5). The evaluation indexes of these five models are summarized in Table 2. From the table we could see that the highest correlation between the predicted and the observed illite content ($R^2 = 0.820$) occurred in Model 3; however, the great gap between $RMSEC$ and $RMSEV$ values indicated that this model was too unstable to estimate the illite content. In general, Model 1, Model 2, Model 4, and Model 5 all showed acceptable $R^2$ s which were $0.584, 0.558, 0.687$, and $0.616$, respectively. Model 5 had the least differences between the $RMSEC$ value and the $RMSEV$ value; hence, we considered Model 5 as the optimal model for predicting the illite content in soil (Figure 4).

Table 2. Statistics of the prediction of the illite content in the 5 models.

| Model | $R^2$ | $RMSEC$ | $RMSEV$ |
|-------|-------|---------|---------|
| Model 1 | 0.584 | 1.172 | 1.861 |
| Model 2 | 0.558 | 1.209 | 1.935 |
| Model 3 | 0.820 | 0.770 | 2.715 |
| Model 4 | 0.687 | 1.034 | 2.121 |
| Model 5 | 0.616 | 1.126 | 1.621 |

3.3. The optimal prediction model of the montmorillonite content
The cumulative variance of the dependent variable explained by the PLS components and determined by cross-validation ($Q^2_{cum}$), for the calibration models based on the SRS corresponding to the AP of montmorillonite representative spectra from USGS spectral library with PLS method (Model 2), the SRS corresponding to the AP of soil spectral using SMLR-PLS (Model 4), soil overall spectrum reflectance values using SMLR-PLS method (Model 5), were all less than 0.5, demonstrating that these models no significantly high robustness and good predictive ability and couldn’t be applied to estimate montmorillonite content in soil. The collinearity in Model 6 seriously affected the diagonal elements thereby, influenced the result of calibration model of montmorillonite content. Therefore, Model 6 should be discarded. Table 3 shows the statistics of the prediction of montmorillonite content. The $R^2$ and the difference between $RMSEC$ and $RMSEV$ in Model 1 were 0.707 (Figure 5) and 0.857 respectively, indicating that Model 1 had a good predictive ability and robustness compared to the Model 3 which was based on the soil overall spectrum reflectance values using SMLR-PLS method. Hence, Model 1 could be used to estimate the montmorillonite content.

Table 3. Statistics of the prediction of the montmorillonite content in Model 1 and Model 3.

| Model | $R^2$ | $RMSEC$ | $RMSEV$ |
|-------|-------|---------|---------|
| Model 1 | 0.707 | 1.814 | 2.671 |
| Model 3 | 0.588 | 1.365 | 2.689 |

4. Conclusions
This study focused on the usage of SWIR by evaluating several different methods to obtain the optimal prediction models of kaolinite, illite, and montmorillonite contents in soil. The best prediction models of kaolinite and illite contents were both based on the soil overall spectrum reflectance values using SMLR-PLS method. The optimal prediction result of the montmorillonite content was obtained by modelling the relationship between the montmorillonite contents and the SRS corresponding to the
AP of montmorillonite representative spectra from USGS spectral library with Enter-MLR method. By examining the statistics of model stability and model effectiveness (RMSEC, RMSEV, and R²), we can see that models could be built for predicting the clay mineral contents from soil in the SWIR region. The model could be used for clay mineral content prediction in regional and baseline studies. People could recalibrate the model by adding a few local samples and use it for detailed ecological and farm level studies within the Xi Lin district or the nearby soil landscape, which has similar features with Xi Lin district.

5. References

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