

Spectral feature characterization and nitrogen content prediction in soils with different particle sizes and moisture contents

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Abstract: The objective of this research is to analyze the influences of light source incidence angle, fiber height, moisture content, and particle size on loamy mixed soil spectra. Nitrogen (N) content calibration and cross-validation models at different moisture contents and particle sizes were obtained using partial least squares (PLS) analysis. Spectral data were collected using a spectrophotometer. Fiber height of 100 mm and light source angle at 45° were chosen to obtain the sharpest spectra without apparent scattering effect. The results show that moisture content and particle size strongly influenced the absorbance of the spectra, and a better N prediction model was obtained when the particle sizes were in the ranges of 0.5–1.0, 1.0–2.0 and 2.0–5.0 mm, with the correlation coefficients (r) of 0.819, 0.815 and 0.818, and standard errors of prediction (SEP) of 2.29, 2.41 and 2.42 mg/kg, respectively. Poor N prediction model was obtained when the soil was kept in its natural moisture content with r of 0.575 and SEP of 3.275 mg/kg, compared to the performance of dried soil samples with r of 0.815 and SEP of 2.425 mg/kg.

Keywords: spectral feature, prediction model, soil moisture, nitrogen content, near infrared reflectance spectroscopy, partial least squares

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1 Introduction

Near infrared reflectance (NIR) spectroscopy is a technique that is used to analyze the diffuse reflectance radiation regarding chemical constituents in the materials^[1-3]. It has been adopted in agriculture, as well as other disciplines, as a rapid and accurate technique that has the ability to analyze many constituents at the same time. There have been several attempts to assess soil properties in previous studies. Lee et al. estimated chemical properties of Florida soils using the spectral reflectance^[4]. Brown et al. used visible and near-infrared diffuse reflectance spectroscopy for soil C prediction in Montana^[5]. Brown et al. applied visible and near-infrared

diffuse reflectance spectroscopy to predict soil content, including organic and inorganic C^[6]. Waiser et al. valued soil clay content with visible near-infrared diffuse reflectance spectroscopy^[7].

Spectral features of soil materials in the NIR (750–2500 nm) spectral region are associated with vibration modes of functional groups that are overtones or the combination of vibration bands of light atoms with strong molecular bonds, for example, chemical bonds that contain H attached to atoms such as N, O, or C^[8]. It may be possible to measure soil constituent such as moisture, organic C, and N using the NIR technique. Each soil property especially of minerals has distinct spectral fingerprints in the NIR region because of relatively strong absorption of the overtones and the combination modes $[\text{OH}]^{-1}$, $[\text{SO}_4]^{-2}$ and $[\text{CO}_3]^{-2}$ ^[9,10]. The large particle size (>1.6 mm) used by Krisnan et al. may at least partly account for the failure to predict organic matter by reflectance technique in the NIR region^[11]. Wetzel concluded that particle size, shape, and the voids between them could affect the path length, and thereby influence absorbance^[12]. Dalal and Henry had studied the reflection energy from soils and they agreed that particle size,

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moisture content and organic matter affected the reflection of radiant energy^[13]. They also found that the reflectance increased exponentially with the decrease of particle size up to 0.4 mm. Berntsson et al. estimated the effect of sample size when analyzing powders with diffuse reflectance near-infrared spectrometry^[14]. Khanna et al. developed the angle indexes for soil moisture estimation, dry matter detection and land-cover discrimination based on NIRS^[15]. All those references indicated that the quality of an infrared spectrum strongly depends on the method of sample preparation including its particle size, moisture content and optical interface between the samples and infrared instrument, but there is no definite conclusion about the influence of particle size and moisture content on loamy mixed soil.

The objective of this research work was to analyze the influences of particle size and moisture content on loamy mixed soil spectra. Besides, prediction models for nitrogen (N) content at different moistures and particle sizes were obtained to study the influences of these properties on N prediction, as well as to investigate the

future applications of NIR spectroscopy as a rapid measurement technique in the field.

2 Materials and methods

The experimental site was located in Hangzhou, Zhejiang (120°11' E, 30°28'N). Figure 1 shows the location of the soil samples. The soil was classified as loamy mixed active thermic Aeric Endoaquepts (Granule is up to 50%, and contains a few gravels) according to Zhejiang soil classification. Measurements were taken at 30 sample plots, at a depth of 0–20 cm and grid interval of 2 m using the normal grid method with a GPS receiver (AgGPS 132, Trimble, Inc., USA). Soil samples were collected using a soil sampling auger. A composite sample was obtained by mixing five soil samples of equal volume, one of which was obtained from the central plot and the remaining four separated 1 m away from each other. Total of 30 soil samples were collected and analyzed in this research. The collected soil was divided into two groups (A and B), and each group was placed in a bag properly close to vacuum.

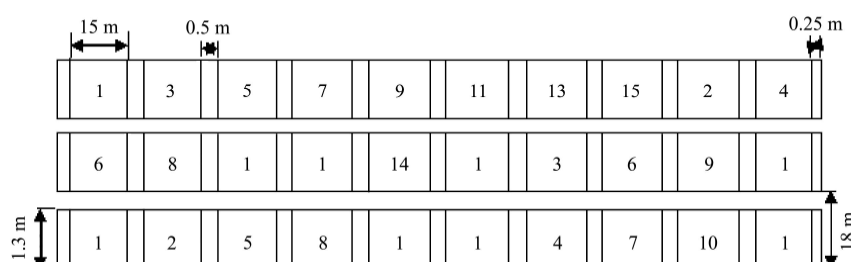


Figure 1 Location of the soil samples

Group A was tested for total N using the Kjeldahl method at the Soil Science Laboratory in Zhejiang University. The range of the N content was from 59.93 to 76.00 mg/kg with the average of 68.05 mg/kg and standard deviation (SD) of ± 3.95 mg/kg.

Group B was analyzed using the NIR spectroscopy technique. Spectral data collection was performed with a spectrophotometer (ASD, FieldSpec Pro FR (350–2500 nm)/ A110070). Soil samples were set in a petri dish with the surface flushed. Absorbance spectra were completed from 350–2500 nm, and the wavelength increment was 2 nm. Absorbance spectra were taken over the central area of the petri dish at three positions by rotating the sample approximately 120° between each position. Twenty scans were performed at each of the three positions. All spectra recorded were checked visually and averaged using ViewSpec pro version 2.14 and exported to multivariate analysis software, The Unscrambler 9.5 (CAMO ASA, Norway).

Prediction models for N content at different moistures and particle sizes were also analyzed in this paper to study the influence of these properties on N prediction. Spectra of total 30 soil samples in different moisture contents and particle sizes were analyzed, and N content calibration and cross-validation models at different moisture contents and particle sizes were also obtained using partial least squares (PLS) analysis.

3 Results and discussion

3.1 Spectral features at different fiber heights and light source incidence angles

To investigate the possible applicability of NIR spectroscopy on site, the spectra of five samples were recorded at different heights over the soil surface to analyze the influence of fiber height on spectral features. To perform this analysis, the optical fiber was attached to a tripod and placed 50, 100, 150 and 200 mm above of the sample surface. The spectra of five samples each at

different heights from the light source were recorded using the same equipment and scanning procedure described above. Figure 2 shows the mean absorbance spectra of the samples at different fiber heights. It can be seen that the absorbance spectral patterns were similar for different heights. They followed the same geometrical behavior, starting with high absorbance and decreasing with the increase of wavelength. There were two major absorption peaks around 1400 and 1900 nm. A slightly smaller absorbance with smaller effect of scattering can be seen at the height of 50 mm, while the absorbance spectra were almost the same when the heights were 150 and 200 mm. Most of the time, 100 mm showed the highest absorbance, probably due to the specific experimental setup. After applying a smoothing correction, this spectrum was found to be the most representative. Although the difference was not considered as great when heights were 50, 150 and 200 mm, 100 mm was used as the standard height for later experiments.

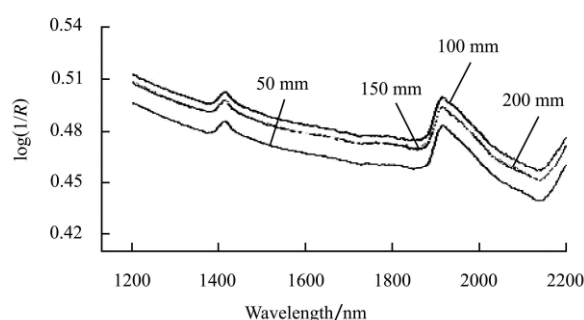


Figure 2 Mean absorbance spectra at different heights

Spectral features in different light source angles, that is, the quantity of light, was also analyzed. The spectra of five samples were recorded at three different light source angles at 20°, 45° and 60°. To measure the angle of the light source, a T ruler was placed perpendicularly to the table surface (the NIRS equipment is also on this table) as the reference, and the angle was measured using a protractor. Each spectrum, including that of the Teflon standard measured prior to each reflection spectrum, was recorded as an average of 60 scans. The absorbance spectra of five samples were recorded consecutively in a light source position, and then the angle was changed and carefully measured repeating the same procedure until completing the measurements (Figure 3). It could be found that the three spectra followed the same geometrical characteristics with an obvious difference in the absorbance values among them. The highest and sharpest absorbance spectrum was obtained at 45°. The spectrum recorded at 60° showed a slightly higher

absorbance than the spectrum recorded at 20° with a transpose of both spectra at 1870 and 2097 nm, which mainly could be caused by scattering in the spectra. All three angles could be used in prediction performance with NIR spectroscopy. Therefore, 45° was chosen as the standard light source angle for later experiments.

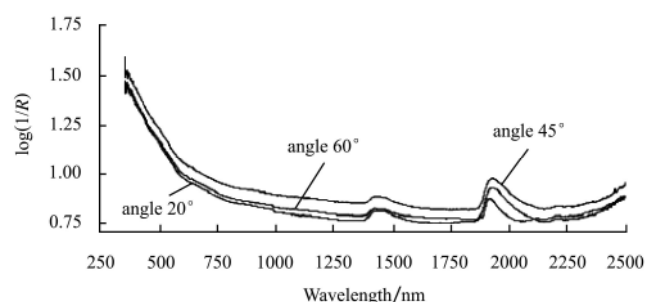


Figure 3 Mean absorbance spectra of the samples at three different angles of light source.

3.2 Spectra features at different soil moisture contents

To analyze the soil spectral features in different moisture conditions, three samples were taken randomly from the population, sieved to <2 mm and divided into two sub samples (each original sample, two sub samples). One sub sample was dried at 40°C, while the other was kept in plastic bags properly sealed to vacuum until the first sub sample was dried and ready to be scanned. Once the first sub sample was ready, the absorbance spectra of both sub samples were recorded (Figure 4). Figure 4 shows the spectral features of the dried and humid soil samples (the average water content of humid soil samples was 16.06 %). All samples analyzed had similar shape in the visible and near-infrared absorbance spectra. The humid soil had high optical density in the visible light region, and two major absorption peaks (around 1400 and 1900 nm) in the near-infrared region. High absorbance could be observed in samples without drying treatment with two prominent peaks in 1400 and 1900 nm obviously related with the presence of water, as well as other minor peaks along the spectrum from 2000–2500 nm, especially near 2500 nm. The high optical density is mainly caused by the high moisture content.

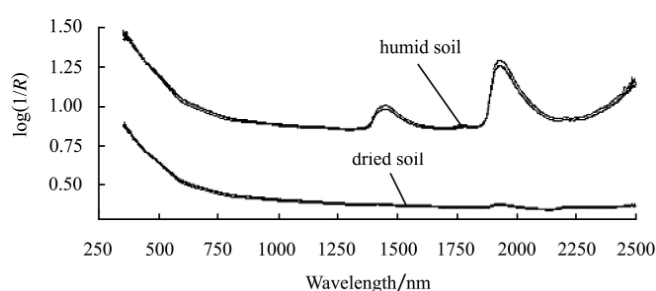


Figure 4 Mean absorbance spectra of humid soil and dried soil

3.3 Spectra features at different soil particle sizes

To analyze the particle size influence on the spectral features, all samples were air-dried (40°C) and subjected to two different analyses. Firstly, the optical density [$\log(1/R)$] spectra of three soil samples manually crushed, and three sieved to <2 mm were compared. Secondly, the mean optical density spectra of five samples previously sieved to five different particle sizes (<0.25 mm; 0.5–1.0 mm; 1.0–2.0 mm; 2.0–5.0 mm, and >5.0 mm) were analyzed. For the first analysis, three soil samples were taken randomly from the population and manually fluffed without sieve, and then the scan was performed. Once the scanning was completed, the three samples were gently crushed in an agate mortar, sieved to <2.0 mm, and placed in a petri dish again for a second scan. During the second analysis, five samples, also randomly selected, were sieved to <0.25, 0.5–1.0, 1.0–2.0, 2.0–5.0 and >5.0 mm, to form five sub samples. These sub samples were scanned following the same procedure previously explained for the first experiment (Figure 5 and Figure 6).

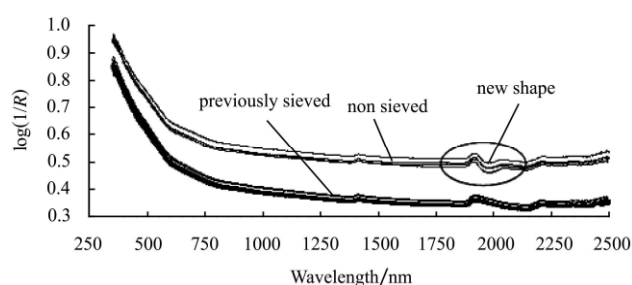


Figure 5 Mean absorbance spectra of three samples, sieved and non-sieved.

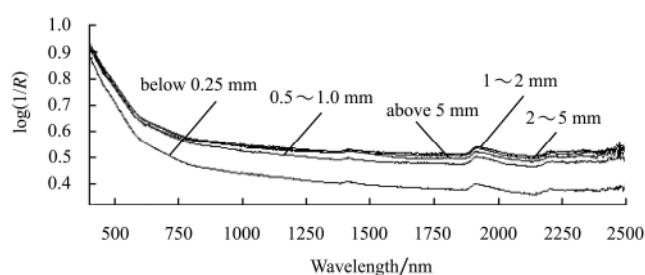


Figure 6 Mean absorbance spectra of five samples sieved to five different particle sizes.

In Figure 5, the spectra of the three samples manually crushed show the same shape in the visible region (400–800 nm), but a prominent descending appears in the near-infrared region, which makes the spectral shape different. Also these samples had higher absorbance than those of the samples sieved to <2 mm. This is a consequence of the particle size, shape, and the voids among them. The arrangement of particles affects the path length and thereby influences absorbance^[11]. On the

other hand, it also demonstrates that in addition to the chemical constituents of a material, near-infrared spectra are also influenced by the physical structure of a material.

Figure 6 shows the mean spectra of five samples previously sieved to five different particle sizes. All of the spectra followed the same shape in the visible and near-infrared region showing a decrease of absorbance with the decrease of particle size. A slight overlapping can be observed among the spectra recorded in samples with the particles sizes of 1.0–2.0, 2.0–5.0 and >5.0 mm, which means that there are no significant differences in the compositions. The spectra representing samples with particle sizes between 0.5–1.0 and <0.25 mm showed less optical density due to a consequence of a decrease in size and the voids between them.

3.4 Influence of soil moisture content on N prediction

To study the capability of NIRS to predict N content in a loamy mixed soil without any dried treatment, 30 samples were sieved to <2.0 mm, and their absorbance spectra were obtained. After that step, each sample was put back in the corresponding original bag, and shaken up to homogenize the mixture again. Later, all samples were sieved again and stored in containers for at least 24 h at 40°C until reflectance was measured.

Soil is a heterogeneous mixture of various chemical compounds, and thus a unique spectral response for soil properties is by no means certain. One method of evaluating the spectral response for a soil property is to study the relationship among wavelength, optical density, and the values of the soil property. As a result, the most important techniques for NIR are how to extract quantitative information from them. Various calibration methods have been used to relate near-infrared spectra with measured properties of materials. Principal components regression (PCR), partial least squares (PLS) regression, stepwise multiple linear regression (SMLR) and artificial neural networks (ANN) are the most commonly used multivariate calibration techniques for NIRS. PLS is usually considered for a large number of applications in chemical analysis and is widely used in multivariate calibration, for it takes the advantage of the correlation relationship that already exists between the spectral data and the constituent concentrations. It performs the decomposition on both the spectral and concentration data simultaneously^[4]. This causes spectra containing higher constituent concentrations to be weighted more heavily than those with low concentrations. It is a good alternative to the traditional multiple regression analysis and PCR. PLS regression analysis was applied in this research, and leave-one-out

cross-validation was done on the calibration set to determine the optimum number of factors (F) for the PLS regression calibration^[16-18]. The best calibration is the one with the lowest root mean square error of prediction (RMSEP), standard error of prediction (SEP), the standard error of calibration (SEC), and the highest r (coefficient of correlation) but also a small difference between SEC and SEP^[19]. The SEC, SEP and RMSEP were defined previously^[10].

The NIR spectroscopy potential to predict N content was carefully analyzed both with and without previous drying treatment of the samples (Figure 7 and Figure 8). It will help to determine if NIR spectroscopy can be applied on site. The calibration and cross-validation

results of PLS models were calculated when the F was 6. The SEC (2.264 mg/kg) and SEP (2.425 mg/kg) of the dried soil samples were adequately lower than those of the humid soil samples ($SEC=3.061$ mg/kg and $SEP=3.275$ mg/kg). This is basically an effect of the soil moisture content on the absorbance spectra which causes the light scattering and changes light path lengths that may be partially but not entirely removed by spectral data pretreatments. The results show the r and $RMSEP$ of the dried soil samples (0.815 and 2.384 mg/kg respectively) are both desirable to validate the PLS model, which are better than those of the humid soil samples ($r=0.575$ and $RMSEP=3.220$ mg/kg).

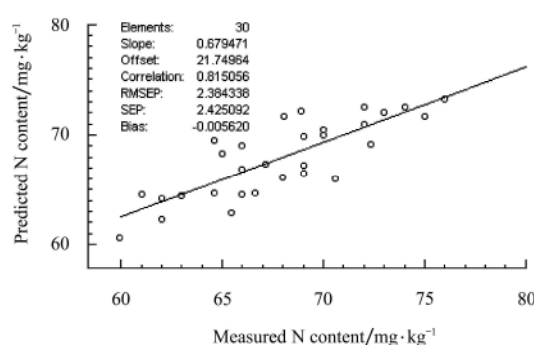
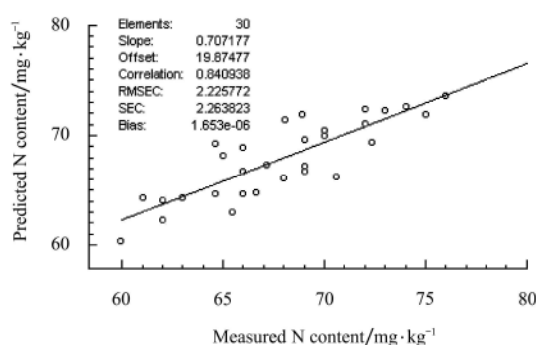


Figure 7 Nitrogen, calibration and cross-validation results using soil samples previously dried

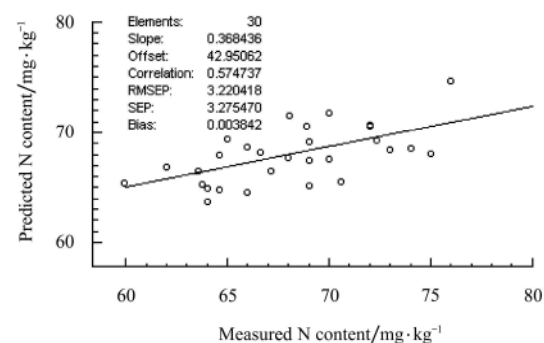
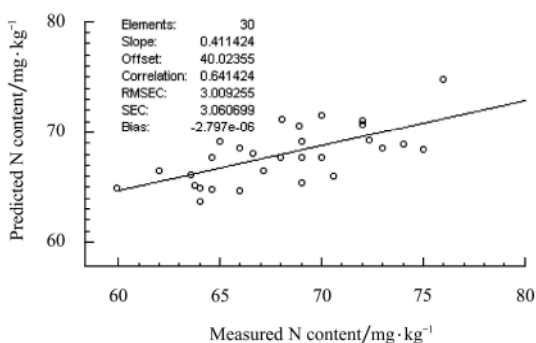


Figure 8 Nitrogen, calibration and cross-validation results using soil samples with their original water content

3.5 Influence of soil particle size on N content prediction

In order to study the influence of soil particle size on N content prediction, 30 samples passed through different sieves (<0.25 mm; $0.5-1.0$ mm; $1.0-2.0$ mm; $2.0-5.0$ mm and >5.0 mm) were placed in the containers and stored for at least 24 h at 40°C until reflectance was measured. Absorbance spectra were performed using the same equipment, and the statistical analysis was the same as described above.

Based on the results, NIR spectroscopy can be used to predict N content with seven factors when the particle sizes vary from $0.5-1.0$; $1.0-2.0$ and $2.0-5.0$ mm with r

of 0.819, 0.815, 0.818; SEC of 2.117 mg/kg, 2.264 mg/kg, 2.297 mg/kg, and SEP of 2.265 mg/kg, 2.425 mg/kg, 2.414 mg/kg, respectively. A slightly better result was obtained when the particle size was between $0.5-1.0$ mm, but there were no significant differences among them. For these three specific cases, the discrepancy should have little effect on the NIR spectroscopy predictions as long as the procedures are consistent. Less reliable models were found when the particle size was <0.25 and >5.0 mm, with r of 0.636 and 0.757, SEC of 3.463 mg/kg and 2.619 mg/kg, and SEP of 3.712 mg/kg and 2.775 mg/kg, respectively (Figure 9, 10, 11, 12, 13). This is basically an effect of the particle size on the absorbance spectra which

causes the light scattering and changes light path lengths, or an effect of sample physical properties that may be partially but not entirely removed by spectral data

pretreatments. Thereby, increasing or decreasing considerably particle size decreased NIRS accuracy.

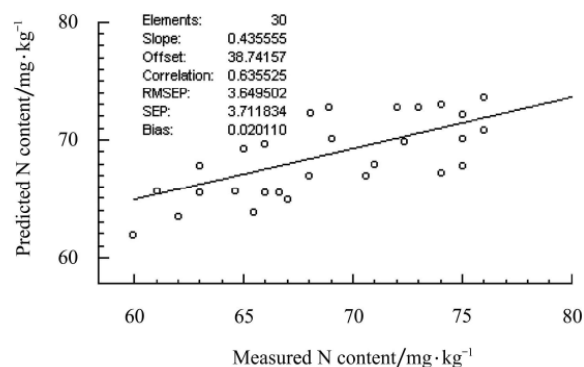
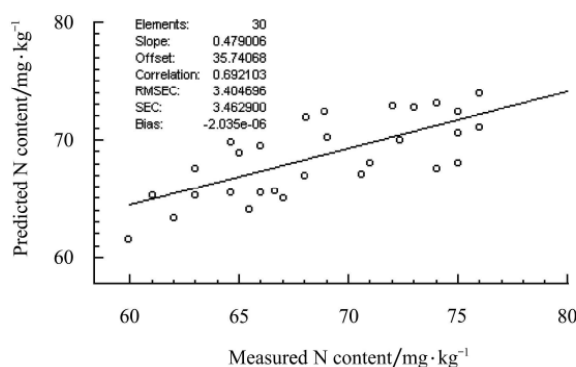


Figure 9 Nitrogen, calibration and cross-validation results in soil sieved to <0.25 mm

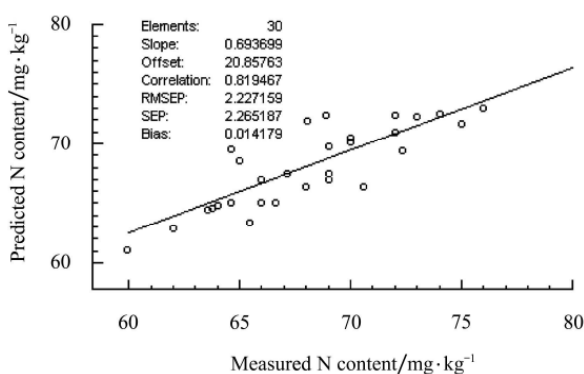
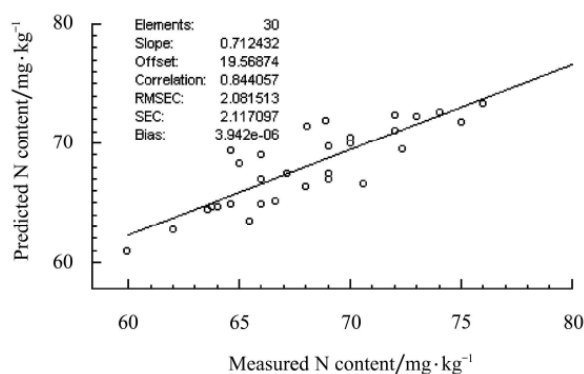


Figure 10 Nitrogen, calibration and cross-validation results in soil sieved to <0.5–1.0 mm

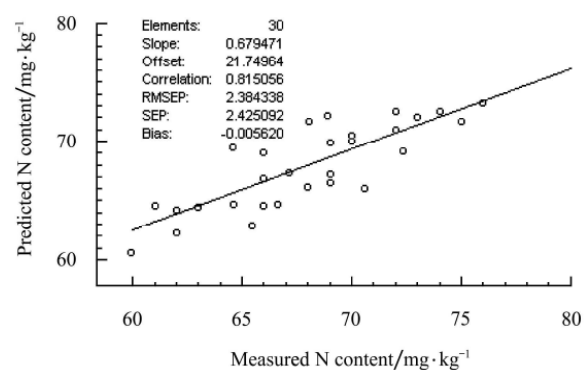
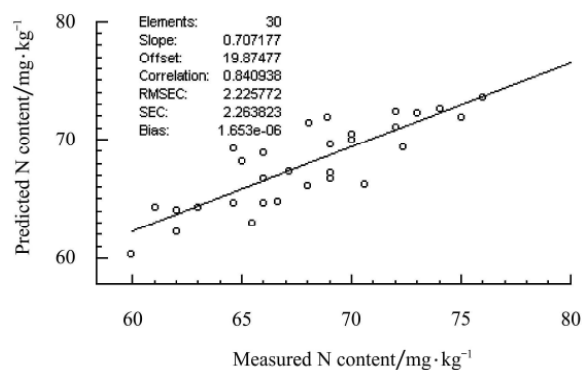


Figure 11 Nitrogen, calibration and cross-validation results in soil sieved to 1.0–2.0 mm

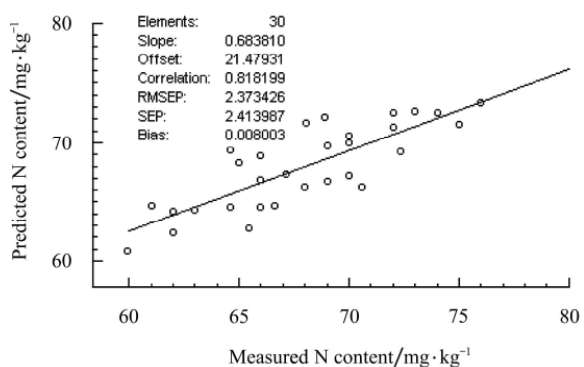
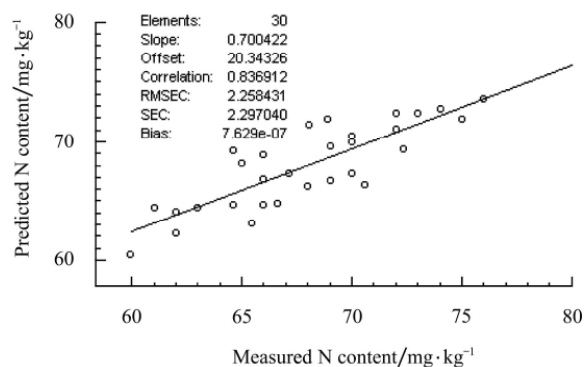


Figure 12 Nitrogen, calibration and cross-validation results in soil sieved to 2.0–5.0 mm

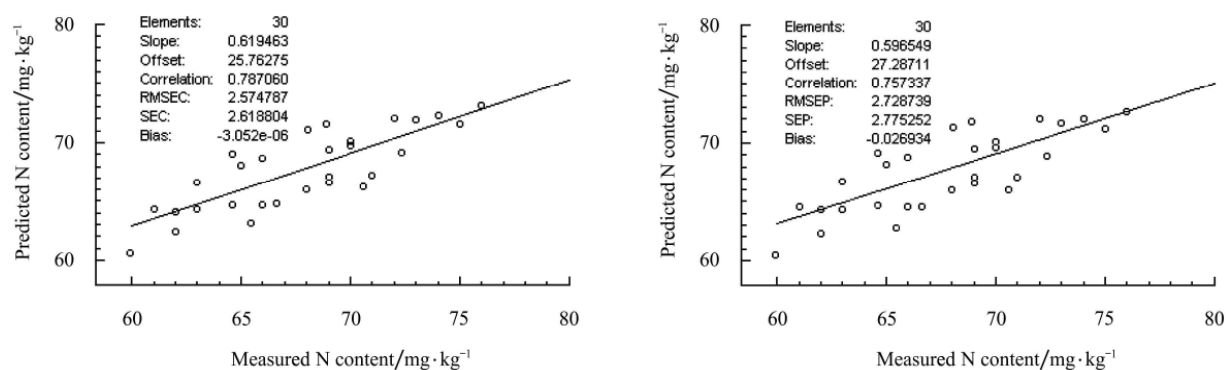


Figure 13 Nitrogen, calibration and cross-validation results in soil sieved to >5.0 mm

4 Conclusions

1) Fiber height of 100 mm and light source angle at 45° were chosen, which presented the sharpest spectra without apparent scattering effect in all heights and angles used.

2) Higher absorbance and different spectra shape were found when the samples were gently hand crushed than when the samples were sieved to <2 mm. On the other hand, absorbance decreased notably with the decrease of particle size. NIRS can be used to predict N content when the particle sizes vary from 0.5–1.0, 1.0–2.0 and 2.0–5.0 mm with r of 0.819, 0.815, 0.818, and SEP of 2.265 mg/kg, 2.425 mg/kg, 2.414 mg/kg, respectively.

3) Poor N content prediction was obtained when the soil was kept in its natural moisture, which was basically because the response of near spectra to water content could mask or affect other constituent prediction. In this analysis, NIR spectroscopy appeared to be better when the model was built using dried soil than humid one.

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