An Alternate Method for Fourier Transform Infrared (FTIR) Spectroscopic Determination of Soil Nitrate Using Derivative Analysis and Sample Treatments

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Abstract This study aimed at examining effective sample treatments and spectral processing for an alternate method of soil nitrate determination using the attenuated total reflectance (ATR) of Fourier transform infrared (FTIR) spectroscopy. Prior to FTIR measurements, soil samples were prepared as paste to enhance adhesion between the ATR crystal and sample. The similar nitrate peak heights of soil pastes and their supernatants indicated that the nitrate in the liquid portion of the soil paste mainly responded to the FTIR signal. Using a 0.01-M $CaSO_4$ solution for the soil paste, which has no interference bands in the characteristic spectra of the analyte, increased the concentration of the nitrates to be measured. Second-order derivatives were used in the prediction model to minimize the interference effects and enhance the performance. The second-order derivative spectra contained a unique nitrate peak in a range of 1,400–1,200 cm^{-1} without interference of carbonate. A partial least square regression model using second-order derivative spectra performed well ($R^2=0.995$, root mean square error (RMSE)=23.5, ratio of prediction to deviation (RPD)=13.8) on laboratory samples. Prediction results were also good for a test set of agricultural field soils with a $CaCO_3$ concentration of 6% to 8% ($R^2=0.97$, RMSE=18.6, RPD=3.5). Application of the prediction model based on soil paste samples to nitrate stock solution resulted in an increased RMSE (62.3); however, validation measures were still satisfactory ($R^2=0.99$, RPD=3.0).

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1 Introduction

As the interest in precision agriculture (PA) and the maintenance of a safe and healthy environment increases, so does the need for direct and fast monitoring methods for nutrients in soils (Shaviv et al. 2003; Linker et al. 2005; Linker et al. 2006). Nitrate is one of the inorganic fertilizers required for implementation of PA (Linker 2004), and there are many researches on the link between intensive agriculture and nitrate pollution (Al-Darby and Abdel-Nasser 2006). In response to the demand for direct and rapid measurement techniques, several promising sensing devices for nitrate have been developed, including ion selective electrodes, ion sensitive field effect transistors, and near- and mid-infrared spectroscopy (Linker 2004). In particular, it has been shown that the Fourier transform infrared spectroscopy (FTIR) applied to the mid-infrared (MIR) portion of the spectrum has some key advantages: simple preparation of samples without chemical processing such as extraction, short measurement time, and a variety of field applications. Moreover, specific spectral signatures of many chemicals of interest, including nitrate, have been identified in the MIR range and make a unique calibration curve possible (Ehsani et al. 2001). Attenuated total reflectance (ATR) of FTIR has been used for measurement of liquid, paste, and powder samples. A paste type of soil sample has been applied to ATR-FTIR measurements to mimic real field conditions (i.e., moist soils) and to increase the adhesion between a sample and the ATR crystal which holds it. Although a paste type of sample enhances the signal quality by improved adhesion, there still remains the problem that some soil constituents, e.g., calcium carbonate, diminish the accuracy of calibration model because of interference with the nitrate band in the MIR range. Alternative calibration models such as partial least square regression (PLSR), principal component regression, and artificial neural network combined with waveband optimization such as wavelet analysis, stepwise regression, and principal component analysis decomposition have been devised for determination of soil nitrate, to take this interference into account (Linker, 2004; Linker et al., 2005; Jahn et al., 2006). Nevertheless, if the amount of interferences in soils is enough to hide a nitrate band, it might be difficult to identify and quantify nitrate in the FTIR spectra.

For an alternate method of soil nitrate determination using ATR-FTIR spectroscopy, the present study examined effective sample treatments for measuring spectra of nitrate and spectral processing which minimizes interference effects and discriminates nitrate without additional interference correction. The available portion of nitrate in the soil paste was correlated to spectral measurement, and possibility of using an extractant such as a $CaSO_4$ solution for nitrate in the soil paste was examined for the increase of the nitrate concentration to be spectrally measured. The derivative analysis was investigated as a spectral processing to enhance prediction performance by minimizing the interference effect.

2 Materials and Methods

2.1 Materials

Farmland soils (FS) mixed with nitrate (as explained below) were used to determine available nitrate and to calibrate the FTIR measurement model. To validate the model, pure kaolinite (KS), three kinds of typical agricultural field soils (AFS) from the Netherlands, namely sand (AH), clay (WA), and peat (ZE), as well as stock solutions of nitrate were used. Soils were dried and passed through an 85-μm sieve. A saturated soil paste was prepared for spectroscopy by adding solution to soil samples (ratio 0.8) in order to increase adhesion between a sample and the ATR crystal. Soil samples initially contained nitrate as shown in Table 1. They were mixed with nitrate solution having concentrations from 10 to 1,280 mg [N] kg^{-1} [dry soil] when preparing paste samples in order to make a calibration. The nitrate stock solution was produced by dissolving KNO_3 in deionized (DI) water. Nitrate in soils was extracted with 0.01 M $CaSO_4$ solution for measurement of the initial concentration (Griffin et al. 1995). Analytical-reagent grade of chemicals and triple-distilled water were used throughout.

2.2 Apparatus

The concentration of nitrate in the stock solution and soils was measured using ion chromatography (Dionex, ICS-2000, USA). Absorbance signals of solution and soil paste samples were measured using a FTIR spectrometer (JASCO, FT-IR 4000, Japan) equipped

Table 1 Characteristics of the soil samples used for nitrate calibration and validation

Soil sample		Soil type	Moisture (%)	pH	Organic matter (%)	C (%)	CaCO$_3$ (%)	Initial NO$_3$–N (mg kg^{-1})
FS[a]		Sandy loam	0.17	6.8	5.63	3.27	0	0.04
AFS[b]	AH	Sand	0.5–0.95	5.3–5.5	2.9–4.8	1.31–2.47	0.1	0.1–90
	WA	Clay	2.07–2.88	7.2–7.4	4.9–10.4	13.5	6.2–8.4	8.2–48.6
	ZE	Peat	6.3–9.7	5	46.3–56.7	23.3–27.6	0.2	0.7–29.5

[a] Farmland soil

[b] Agricultural field soil

with a ZnSe horizontal ATR crystal and a triglycine sulfate detector. The average of 50 successive scans was recorded over the range from 4,000 to 700 cm^{-1} with a resolution of 4 cm^{-1}.

2.3 Available Nitrate for FTIR Measurement

To obtain information on available nitrates in soil pastes during FTIR measurements, farmland soils which had been mixed with nitrate at concentrations of 547, 776, and 1,600 mg [N] kg^{-1} [dry soil] were used. The pH of nitrate solutions (KNO$_3$) for the sorption experiment was adjusted to approximately pH 4 because acidic soils have been shown to retain NO$_3^-$ (Cahn et al. 1992; Vinten and Smith 1993) even though nitrate is considered to be mobile in saturated soil–water systems (Roy and Krapac 2006). Two-gram samples of air-dried and sieved FS soil and 2 mL of nitrate solution were added to 15 mL plastic centrifuge tubes. Samples were agitated for 24 h with irregular stirring and then dried in the oven at 50°C for 12 h. Paste samples of the nitrate-sorbed soil were prepared by mixing with two kinds of solutions, DI water and 0.01 M CaSO$_4$ solution, and with different soil to solution ratios, 0.8 and 1, to compare the amount of nitrate dissolved in each combination. In order to measure nitrate in the supernatant separated from a soil paste, paste samples were centrifuged for 20 min at 3,000 rpm.

2.4 Quantification of Nitrate

2.4.1 Sample Preparation

In order to quantify soil nitrate with FTIR spectra, saturated soil pastes were prepared from soils with added nitrate (0, 10, 23, 48, 104, 146, 189, 383, 414, 543, and 1,120 mg [N] kg^{-1} [dry soil]). For

interference correction in the calibration, CaCO$_3$ was used because of its known absorbance band near the nitrate band in the 1,550–1,200 cm^{-1} range. The calcium carbonate was added to FS samples with the amount ranging from 0% to 25%. DI water and 543 mg [N] kg^{-1} [dry soil] nitrate solution were added to the soil sample mixed with CaCO$_3$. The KS, AFS, and nitrate stock solution were used to validate the calibration model. Properties of these soils are described in Table 1. The soil pastes for validation were made by adding nitrate solution with concentrations ranging from 13 to 1,280 mg [N] kg^{-1} [dry soil].

2.4.2 Spectral Treatment

Prior to calibration, measured spectra were manipulated to reduce spectral interferences and to enhance nitrate bands. The absorption signal was normalized based on the water peak band, after which water spectra or spectra of soil paste including 0 mg [N] kg^{-1} [dry soil] nitrate were subtracted, resulting in a unique absorption peak of nitrate. The spectral processing was applied to the 1,550–1,200 cm^{-1} interval including the bands of nitrate and some interferences (Linker 2004; Linker et al. 2005). Then, the processed spectra were smoothed according to the Savitzky and Golay (1964) method by means of a 21-point smoothing filter, and their first- and second-order derivatives were obtained from polynomials fitted to the smooth curve.

2.4.3 Calibration Model for Nitrate

Nitrate was determined by multivariate calibration using partial least squares (PLS) regression. Both the subtracted spectra and their derivatives were used for a calibration model. The calibration set included

spectra of 17 FS samples containing NO_3 and $CaCO_3$ and 58 artificial signals which synthesized by mixing nitrate and carbonate spectra, subtracted from the FS samples, as a function of each concentration. Spectral intensity was correlated with a concentration of NO_3 and $CaCO_3$ to select the bands with high correlation between them. The regression model was applied to the spectral interval chosen by correlations with NO_3. In order to quantify the performance of calibration model, several measures comparing the estimated value (Y') and measured value (Y) were calculated by leave-one-out cross-validation (LOOCV) and test set-validation. The root mean square error (RMSE) is the measure of absolute estimation error:

$$RMSE = \sqrt{\frac{\sum (Y' - Y)^2}{n}} \qquad (1)$$

The regression coefficient of determination (R^2) and ratio of prediction to deviation (RPD) are measures of the strength of statistical correlation between measured and predicted values. The RPD is a measure of the discriminating power of the calibration, calculated as the ratio of the standard deviation of the measured value of a soil property in the prediction set (SDV) to the RMSE:

$$RPD = SDV/RMSE \qquad (2)$$

RPD values above 2 are considered satisfactory, and values above 5 are excellent (Williams 2001).

3 Results and Discussion

3.1 Spectral Characterization of Nitrate

The FTIR spectra of soil paste samples scanned in the 4,000–700 cm^{-1} range are displayed in Fig. 1. Water showed strong absorption bands at 3,340, 2,116, and 1,636 cm^{-1} and at the end of the observed range. In the range of 1,180–900 cm^{-1}, spectra of soil pastes include fingerprints of minerals, attributed to Si–O–Si stretching and C–O stretching vibrations, as interpreted by a FTIR spectral library (IR Mentor Pro 6.5, Bio-Rad Laboratories, USA). The spectra of solution and soil paste samples were interpreted according to the characteristic IR absorption bands for nitrate and its interferences as reported in the literature; these are summarized in Table 2. The strongest absorption band

at 1,350 cm^{-1}, attributed to asymmetric N–O stretching (ν_3), was used for quantitative determination of nitrate. In the observed range from 1,550 to 1,200 cm^{-1}, carbonate contains a strong peak (ν_1) at approximately 1,420 cm^{-1}, which interferes with the nitrate peak (1,350 cm^{-1}). Although the nitrate and carbonate peaks can overlap, their peaks in Fig. 1 are not symmetric; in addition, nitrate has a different peak position than carbonate. Therefore, the spectrum slope directions are different, and so in turn are the derivatives (Shaviv et al. 2003).

3.2 Available Portion of Nitrate for FTIR Measurement

In order to determine the nitrate portion to be spectrally measured in the soil paste sample, absorption peak heights were compared between soil pastes and their supernatants (Fig. 2). For soil paste samples containing 547, 776, and 1,600 mg [N] kg^{-1} [dry soil] nitrate, the spectral response showed a similar intensity between paste and supernatant separated from the soil paste, allowing for measurement and signal processing errors. This result indicated that the spectral response of nitrate in the paste samples to FTIR measurement is mainly the portion of nitrate extracted from the soil to added solution, and hence, the solution added to make the soil paste is important for accurate determination of nitrate concentration in soils.
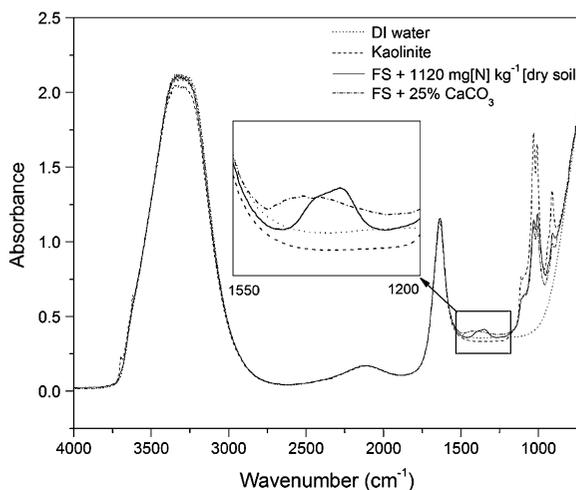
Fig. 1 The FTIR spectra of distilled water, KS paste, FS paste including 25% $CaCO_3$, and FS paste after addition of 1,120 mg [N] kg^{-1} [dry soil] NO_3

Table 2 Assignment of the principal MIR absorption bands in the spectra of soil paste

Vibration mode assignments	Absorption peak (cm^{-1})		
	Literature	This work	Signal degree
Nitrate (NO$_3^-$)			
Symmetric stretch ν_1	1,042[a], 1,046[b], 1,048[c], 1,050[d]		Weak
Out-of-plane bend ν_2	815[a], 816[b], 825[c], 833[d]		Medium, sharp
Asymmetric stretch ν_3	1,300[b], 1,330[a], 1,350[e], 1,384[f,c], 1,385[d], 1,390[g]	1,350±5	Very strong
In-plane bend ν_4	715[d], 719[d,c], 746[b]		Very weak
Carbonate (CO$_3^{2-}$) in bulk CaCO$_3$			
Symmetric stretch ν_1	1,436[b]	1,420±5	Very strong
Out-of-plane bend ν_2	714[b]		
Asymmetric stretch ν_3	878[b]		
In-plane bend ν_4	1,082[b]		

[a] Goodman et al. 2001

[b] Al-Hosney et al. 2005

[c] Vivekanandan et al. 1995

[d] Verma and Deb 2007

[e] Shaviv et al. 2003

[f] Grube et al. 2006

[g] Ehsani et al. 2001

Although nitrate is soluble and difficult to adsorb by soil surfaces except under acidic conditions (Vinten and Smith 1993), water has disadvantages in nitrate extraction due to its low ionic strength, which can cause dispersion and result in cloudy filtrate (Griffin et al. 1995). In samples where 0.01 M CaSO$_4$ solution was added, soil pastes containing 547 and 776 mg [N] kg^{-1} [dry soil] nitrate had a similar intensity of nitrate peak to samples with added water (Fig. 2). However, the sample containing 1,600 mg [N] kg^{-1} [dry soil] nitrate showed that CaSO$_4$ solution led to a higher intensity of nitrate peak than for the sample with added water. The main absorption peaks of CaSO$_4$ around 660 and 600 cm^{-1} provided no interferences to nitrate bands (Verma and Deb 2007).

The extraction effect of added solution on nitrate in soil paste was confirmed with ion chromatography (IC) analysis. Figure 3 shows the percentage of dissolved
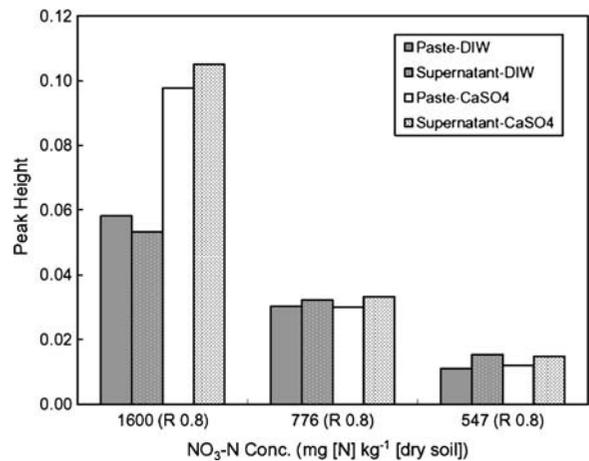
Fig. 2 Comparison of nitrate peak height between soil paste samples and the supernatant separated from the soil paste for three different levels of added NO$_3$–N

nitrate in solution of the paste compared in terms of initial concentrations of soil nitrate, ratio of soil to solution, and added solution. At a concentration of 776 and 547 mg [N] kg^{-1} [dry soil], DI water and CaSO$_4$ solution extracted similar amounts of nitrate from soils, and the amount of nitrate in supernatants was 40–70% of the initial concentration in soil paste. At a concentration of 1,600 mg [N] kg^{-1} [dry soil] NO$_3$, 98% of the initial concentration of nitrate in the soil was dissolved in supernatant by 0.01 M CaSO$_4$ solution, but the percentage of dissolved nitrate in DI water significantly decreased. This high extraction effect might result from the larger ionic strength of
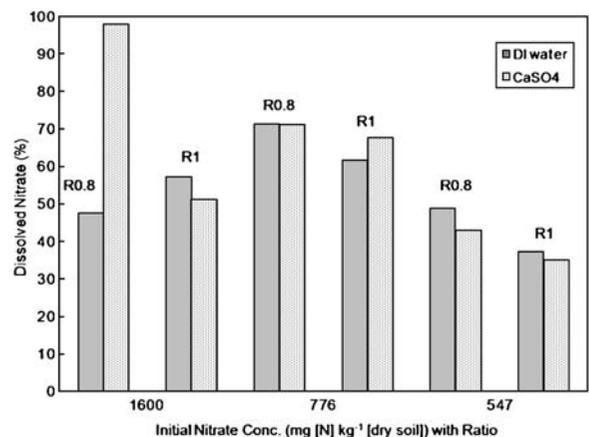

Fig. 3 Comparison of the dissolved nitrate portion (%) in the supernatant separated from the soil paste for DI water and 0.01 M CaSO$_4$ solution at different soil-to-solution ratios (R)

the sulfate solution. Although the increase in the amount of solution was expected to dissolve more nitrates from soils, leading to similar nitrate concentration in the supernatant as the higher soil-to-solution ratios, the samples with a ratio of 0.8 showed higher nitrate concentrations in the supernatant compared to samples with a ratio of 1.

3.3 Quantitative Determination of Nitrate

3.3.1 Quantitative Peak Identification of Nitrate

Figure 4 shows the nitrate peak resulting from asymmetric stretching vibration (ν_3) in the 1,550–1,200 cm^{-1} range as a function of NO_3–N concentrations from 10 to 1,120 mg [N] kg^{-1} [dry soil]. As mentioned, $CaCO_3$ (which is used for neutralizing soils in arable lands) had an interference band around 1,420 cm^{-1}. Spectra of soil pastes including 0–25% $CaCO_3$ as well as 543 mg [N] kg^{-1} [dry soil] nitrate were compared; see Fig. 5a. The sample containing 1% $CaCO_3$ showed almost the same spectral response to the sample with no $CaCO_3$. Calcium carbonate interfered with nitrate peaks at concentrations above 3%. The interference peak of $CaCO_3$ in Fig. 5b was derived by subtracting spectra in Fig. 5a from spectra including 543 mg [N] kg^{-1} [dry soil] nitrate and 0% carbonate. To reduce this interference, derivatives of spectra were calculated. Figure 6 shows that, while the first-order derivatives have different intensities related to the $CaCO_3$ levels in samples, the second-order derivatives include no spectral differences
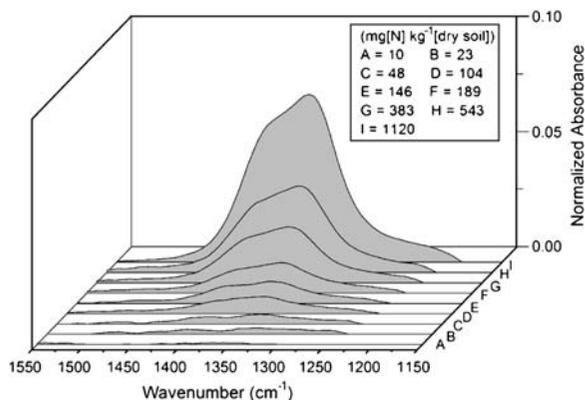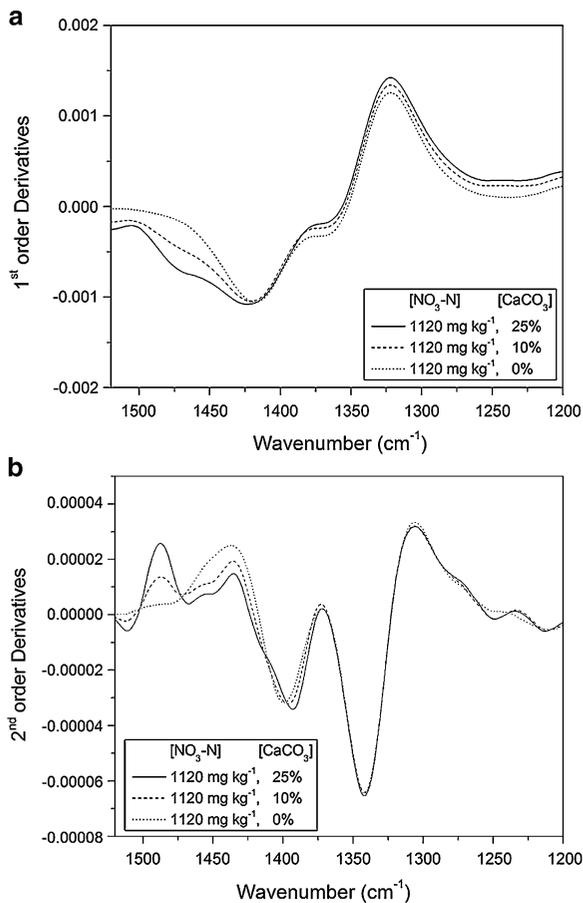

Fig. 4 The spectra of soil pastes, normalized by water spectra and subtracted with the spectrum of FS sample containing 0 mg [N] kg^{-1} [dry soil] nitrate as a function of NO_3–N concentrations
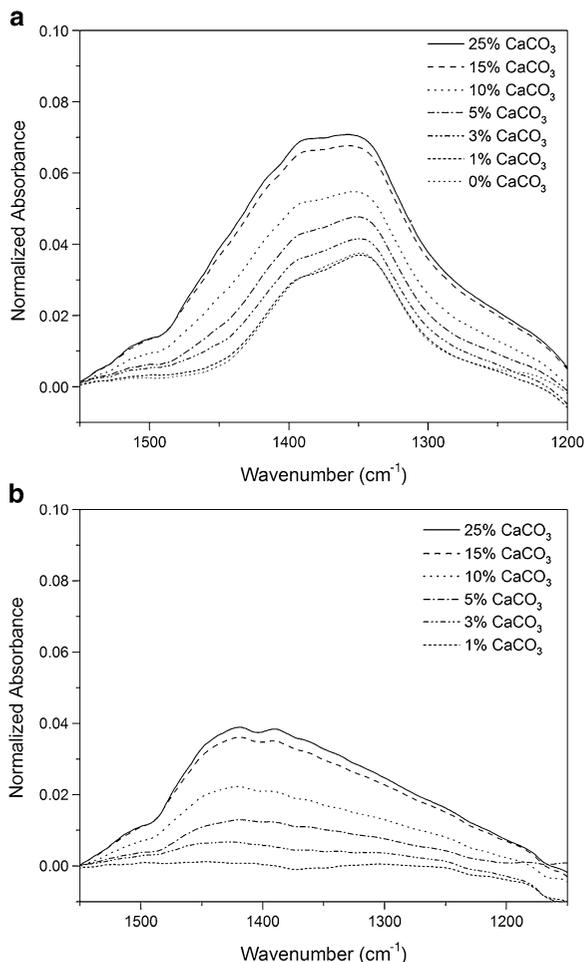
Fig. 5 The processed spectra of samples including calcium carbonate ($CaCO_3$): a Spectra of FS samples containing $CaCO_3$ and 543 mg [N] kg^{-1} [dry soil] nitrate. b Spectra that the signals in a were subtracted with spectrum of FS containing 543 mg [N] kg^{-1} [dry soil] nitrate without carbonate
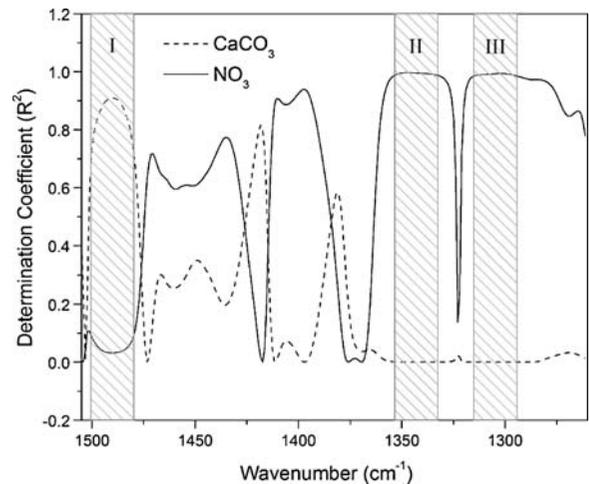
caused by $CaCO_3$ in a range of 1,375–1,275 cm^{-1}. The coefficient of determination (R^2) between second-order derivatives and wave number is displayed in Fig. 7. Nitrate had a high correlation in the ranges II and III where $CaCO_3$ had no correlation. This shows that soil nitrate can be determined without considering interferences of calcium carbonate by using second-order derivatives. On the other hand, $CaCO_3$ showed a strong correlation with second-order derivatives in range I, within which NO_3 showed no correlation. The second-order derivatives in this range can be used in estimating the $CaCO_3$ concentration with decreasing interference by NO_3.

Fig. 7 Determination coefficient (R^2) of second-order derivatives in terms of NO_3 and $CaCO_3$ in the range of 1,500–1,200 cm^{-1}

Fig. 6 The first-order derivatives (**a**) and second-order derivatives (**b**) of spectra for samples including 25%, 10%, and 0% $CaCO_3$ and 1,120 mg [N] kg^{-1} [dry soil] NO_3 after normalization and subtraction of the FS spectrum containing 0 mg [N] kg^{-1} [dry soil] nitrate

3.3.2 Cross-Validation of PLSR Calibration Model

Partial least square regression was performed in a range of 1,550–1,200 cm^{-1} using 58 artificial signals, obtained by mixing nitrate and carbonate spectra derived from the FS samples, as well as the 17 FS samples containing NO_3 and $CaCO_3$. The results of LOOCV for these models are shown in Table 3. The high coefficient of determination (R^2=0.995) was achieved by high performance of selected wave number areas associated with second-order derivative spectra. Both performance quality measures suggest high reliability (RPD=13.8, RMSE=23.5). There was a linear relation between cross-validation predicted and measured NO_3–N concentrations (Fig. 8).

3.3.3 Prediction of Soil Nitrate

The cross-validated calibration model was applied to the KS samples, the three AFS samples, and the nitrate stock solution. Prediction statistics are summarized in Table 4. The parameters for prediction quality, R^2, RMSE, and RPD, showed high performances of the PLSR model as a direct determination method for a nitrate in both solution and soil paste, with little performance difference among soil types. For the validation set, a prediction performance plot is shown in Fig. 9. All three sample sets showed a very high coefficient of determination (R^2), 0.969 (AFS), 0.992 (KS), and 0.989 (stock solution), and their ratio of prediction to deviation was in the reliable range (RPD>2). Prediction results for agricultural field soil which includes clay soil containing 6–8% $CaCO_3$ indicated that calibration model using second-order derivatives avoided the interference caused by carbonate. Moreover, the second-order derivatives showed no difference in signals by mineral composi-
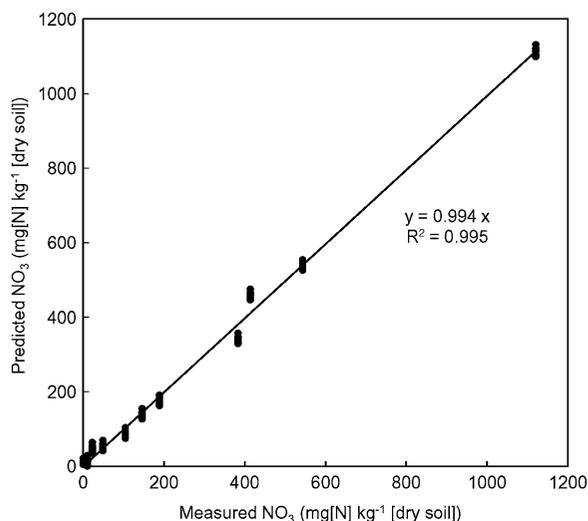
Table 3 PLS regression fit of the training set

n^{a}	SDE^{b}	R^2	RMSE	RPD^{c}
76	23.66	0.995	23.51	13.76

[a] Number of samples

[b] Standard deviation of estimate

[c] Ratio of prediction to deviation

Fig. 8 Predicted against measured NO_3–N concentrations in terms of leave-one-out cross-validation of PLS calibration

Fig. 9 Measured vs. predicted NO_3–N concentrations from PLSR calibration model for the validation sample set, nitrate stock solution, and KS and AFS paste samples where nitrate solution was added
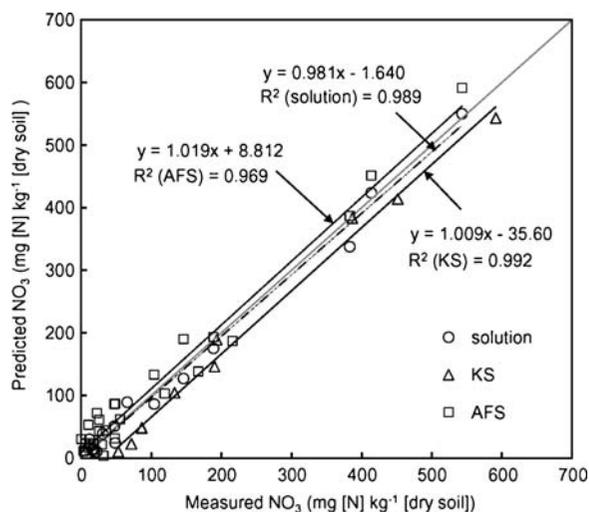
tion in the observed wave number area. Both solid and liquid sample phases could be predicted by this model, even though solution samples had a higher $RMSE_{solution}$ value (=62.3) than soil paste samples ($RMSE_{AFS}$=18.6, $RMSE_{KS}$=36.5).

4 Conclusion

This study focused on examining the alternate method for FTIR spectroscopic determination of soil nitrate using sample treatments and spectral processing in order to increase the prediction performance for soil nitrate. Soil paste was used to improve the contact between sample and ATR crystal. By comparing the nitrate peak intensity of soil pastes and their supernatant, it was shown that the nitrate dissolved in soil solution of the paste mainly responded to the FTIR signal. To increase the nitrate portion in soil pastes

Table 4 Prediction performances for kaolinite (KS), three kinds of typical agricultural field soils (AFS), and nitrate solution

Sample	n	SDE	R^2	RMSE	RPD
KS	11	186.60	0.992	36.49	5.17
AFS	28	53.22	0.969	18.60	3.47
Solution	15	172.51	0.989	62.25	2.97

which are measured by FTIR spectroscopy, using 0.01 M $CaSO_4$ solution for a soil paste provided a high performance at a higher concentration of initial soil nitrates (1,600 mg [N] kg^{-1} [dry soil]) and showed a similar result to the DI water (40–70%) for the samples with relatively lower levels of nitrate. This indicates that the 40–70% nitrate in soil pastes, which is the same amount to that in supernatant, can be measured from FTIR spectra and that using extraction reagents such as $CaSO_4$ can provide enhancement of nitrate estimate from soil paste samples using FTIR spectroscopy with increased concentration of nitrate in soils.

For the better performance of calibration, a procedure was developed which included interference correction and signal processing to derive unique signal characteristics of nitrate. FTIR spectra in a range of 1,550–1,200 cm^{-1} provided the unique nitrate peak; however, absorbance peaks of interferences, $CaCO_3$, and minerals, remained in this range after processing to eliminate the water and mineral peaks and overlapped the nitrate peak. Spectra transformed to second-order derivatives contained unique nitrate peaks in the range of 1,400–1,200 cm^{-1}; further, overlapping peaks of $CaCO_3$ and NO_3 disappeared in these spectra. PLS regression model using second-order derivative spectra gave high prediction quality (R^2=0.995, RMSE=23.5, RPD=

13.8). Agricultural field soils, kaolinite, and nitrate solution were used as validation tests. All gave good results for the prediction of nitrate. In particular, performance results of AFS including 6–8% $CaCO_3$ (R^2=0.97, RMSE=18.6, RPD=3.5) confirmed the use of second-order derivative spectra without interference correction procedures. Even though application of the prediction model based on soil paste samples to nitrate stock solution showed increased RMSE (62.3), validation parameters were still satisfactory (R^2=0.99, RPD=3.0). In summary, applying the second-order derivatives to PLSR calibration can be recommended for its simple procedure and a high quality of prediction for soil nitrate while minimizing the interference by $CaCO_3$ and soil types.

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