Determination of Clay and Other Soil Properties by Near Infrared Spectroscopy

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ABSTRACT

The feasibility of using near infrared (NIR) spectroscopy for rapid non-destructive prediction of clay and other soil properties was investigated. Soil from all regions of Denmark was used to develop universal NIR spectroscopic calibrations. Samples were packed in a rectangular sample cell with a surface area of 60 cm^2 and the cell was moved during measurements using a transport module. Reflectance was measured in the 400- to 2500-nm range and instrument calibration was performed by partial least square (PLS) regression. The accuracy and robustness of NIR equations for determination of clay was dependent on the calibrated concentration range, the spectral regions used for calibration and the spectral pretreatment procedure. The optimal narrow range calibration for clay (1–26% clay) gave prediction errors of 1.7 to 1.9% while the prediction error for the optimal broad range calibration (3–74% clay) was estimated as 3.4%. The estimated true accuracy was 1.5 to 1.7% (1–26% clay). By comparison, the reproducibility standard deviation of the reference method was 1.3%. For C, silt, and sand, the prediction errors were 0.42, 4.6, and 5.5% respectively. The ratios between analyte variation range standard deviation and prediction error were 3.1 (1–26% clay), 4.7 (3–74% clay), 2.4 (C), 2.0 (silt), and 2.4 (sand). The results demonstrate that NIR spectroscopy is a potential technique for rapid and cost-effective determination of clay in soils. The technique may also be useful in prediction of other particle-size fractions. The investigated technique was less suitable for determination of total C in Danish soil samples.

S$_{\text{OIL PROPERTIES}}$ such as clay and organic matter are important factors for soil fertility, and are used, for example, in models predicting the optimal allocation of fertilizers. The development of precision agriculture, where allocation of fertilizer is optimized to reduce costs and environmental impacts, requires a finely meshed knowledge of how these properties vary in the individual fields to obtain the economic and environmental advantages of the technology. The content of organic matter is normally determined from C analysis using an automated elemental analyzer. These instruments are rapid and have a relatively high analyzing capacity. Clay and other particle-size fractions, on the other hand, are classically determined by sedimentation procedures using for example, hydrometer readings. These methods are lengthy, space consuming, and laborious. A more rapid and inexpensive method would therefore be valuable in obtaining the information required for precision agriculture.

Studies using NIR spectroscopy for texture analysis have been published for artificially (Couillard et al., 1996) and naturally composed soil samples (Ben-Dor and Banin, 1995; Couillard et al., 1997; Malley et al., 2000; Chang et al., 2001; Stenberg et al., 2002; Cozzolino

and Morón, 2003). The reported uncertainties are generally high, but also in many cases related to broad variations in the properties. High uncertainties may reduce the applicability of the technique for precision farming on individual farms. In Denmark there are also legal limits on the permitted levels of fertilizers, depending on defined texture classes and the crop grown. Nine classes are defined on the basis of the relative composition of the soil with respect to clay and fine sand. In practice, the most important shift in maximum allowed allocation of fertilizers occurs at a clay content of 10%. Such legal limits may require the application of critical differences (CDs) for routine methods if the routine methods are less accurate than the reference method. A CD is the minimum distance to the legal limit, which can be accepted for results obtained by a routine method without confirming the result by a reference method. The CDs depend on the accuracy of the analytical technique used. To obtain maximum benefit of the NIR technique, the accuracy of the method must be optimized.

Danish soils were mostly formed in glacial sediments of Weichselian and Saaleian ages. Clayey tills dominate in Eastern Denmark, giving loamy soils (generally 10–25% clay), while mostly sandy tills, glaciofluvial sediments, and windblown sands are found in Western Denmark, resulting in sandy soils (generally <10% clay). Extensive marine terraces with sandy and silty soils are also found in the northern part of the country.

The objective of this project was to investigate the possibility of developing universal and robust calibrations useful for precision farming in Denmark, and to investigate the effect of different parameters on the overall accuracy.

MATERIALS AND METHODS

Soil Sampling

Soil samples from all regions of Denmark were used for calibration and validation. The sampling depth was approximately 20 cm and several subsamples were taken from each field and mixed before collection of the laboratory sample. The samples originated from four sampling sets. Set 1 consisted of samples selected by a stratified sampling procedure from a large population of samples to obtain an even distribution across the country (Fig. 1). The clay content in this sample set was restricted to <26%. These samples were obtained from the Danish Agricultural Advisory Center (Skejby, Denmark). Set 2 consisted of samples selected by a stratified sampling procedure from a large population of samples to obtain an

Abbreviations: ANN, artificial neural networks; CD, critical differences; CV, cross validation; MLR, multiple linear regression; MSC, multiplicative scatter correction; NIR, near infrared; PLS, partial least square; RMSECV, root mean square error of cross validation; RMSEP, root mean square error of prediction; SD, standard deviation; SD$_r$, repeatability standard deviation; SD$_t$, total standard deviation; SEP, standard error of prediction; SEP$_{\text{true}}$, true prediction accuracy; SNVD, standard normal variate transformation combined with Detrend).
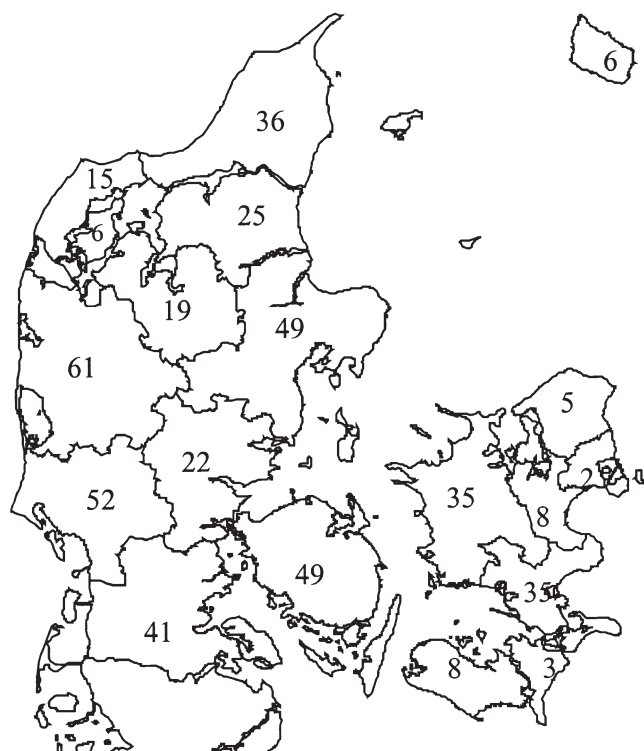
Fig. 1. Geographic distribution of samples in sample Set 1. The number of samples within each county is shown.

even distribution with respect to clay content. The clay content ranged up to 74%. These samples were obtained from the Danish Institute of Agricultural Sciences (Tjele, Denmark). The samples in Groups 1 and 2 were collected over a period up to the Year 2002. Set 3 consisted of a subset of samples selected from incoming laboratory samples in 2002. Samples were selected to obtain an even distribution across clay content in the range 0 to 26% and between regions of Denmark. Samples in Set 4 were collected in the same way but from incoming samples in 2003. The variation ranges of the sample sets are listed in Tables 1 through 3.

Before soil analysis, samples were dried at 55 $\pm$ 5°C for 24 h and crushed through a 2-mm sieve.

Spectral Measurements

The samples were equilibrated to room temperature (20–24°C) and carefully mixed before NIR measurement. A subsample was poured into a modified Coarse Sample Cell NR-7080 with a 35 by 165 mm^2 sampling area (Foss, Hillerød, Denmark) and measured on a NIRSystems 6500 instrument equipped with a vertical transport module (Foss). The commercial sample cell was modified to reduce the sample volume without reducing the sample area and to avoid turbulence during filling, which could cause non-representative segmentation of the sample material. This was done by fixing a 4-mm plate to the back wall, resulting in a sample thickness of 13 mm.

Table 1. Clay content of samples determined by reference method.

Sample set	Number of samples	Clay, %			
		Mean	Min	Max	SD
1	471	10	2.0	26	5.3
2	228	19	2.8	74	16
3	32	12	2.0	24	7.0
4	139	9.4	1.0	26	5.6

Table 2. Total C content of samples determined by reference method.

Sample set	Number of samples	Total C, %			
		Mean	Min	Max	SD
1	471	1.7	0.06	5.4	0.80
2	228	1.5	0.06	5.6	1.2
3	32	n.d.†	n.d.	n.d.	n.d.
4	139	1.7	0.12	6.0	1.0

† n.d., not determined.

Reflectance measurements were performed in the wavelength ranges 400 to 700 nm (visible light) and 700 to 2500 nm (NIR region) with 2 nm between collected data points. Before each sample measurement, 25 reference scans were taken on a ceramic standard supplied with the instrument (Foss), and 40 photometric scans were then collected and averaged on each sample. Two measurements including refilling of the sample cell were performed on each sample under repeatability conditions.

Reference Analyses

Reference analyses were performed using the official Danish standard methods for soil analysis authorized by the Danish Ministry of Food, Agriculture, and Fisheries (Danish Plant Directorate, 1994). The texture method is based on an ASTM method (American Society for Testing Materials [ASTM], 1954) with hydrometer readings of soil suspension after 5-min, 10-min, 4-h, and 18-h sedimentation, and finally sieving through a 200-μm mesh sieve. The fractions determined were coarse sand (200–2000 μm), fine sand (20–200 μm), silt (2–20 μm), and clay (<2 μm). Total C was determined by dry combustion using a LECO CN-2000 instrument (LECO Corp., St. Joseph, MI). The reference analyses on sample Sets 1 and 2 were performed by different laboratories authorized by the Danish Ministry of Food, Agriculture, and Fisheries. Their results were harmonized by running ring trials and official inspections. The reference analyses on sample Sets 3 and 4 were performed in the authors' laboratory by duplicate analyses with single determinations performed on different days (intralaboratory reproducibility conditions).

Spectral Transformations and Calibration

Data were treated with WINISI version 1.04 software (Infrasoft International, Silver Spring, MD). Spectral homogeneity of samples was tested before calibration. Samples with a global H based on a Mahalanobis distance (Mark and Tunnell, 1985) of more than 3.5 were deleted. Calibration was performed by PLS regression on mean spectra with and without scatter correction using multiplicative scatter correction (MSC) (Geladi et al., 1985) or the standard normal variate transformation combined with Detrend (SNVD) (Barnes et al., 1989). Additional pretreatment was performed by derivative treatments (Næs et al., 2002). Wavelengths separated by 8 nm were used in the calibration. First and last data points in the 400- to 1100- and 1100- to 2500-nm ranges were not used. Calibration was performed using six cross-validation (CV) segments. In CV, calibration models are subsequently developed on parts

Table 3. Silt and sand contents of samples in sample Set 1 determined by reference method.

Parameter	Number of samples	Mean	Min	Max	SD
Silt, %	471	21	1.7	54	9.0
Sand, %	471	65	30	95	13

Table 4. Prediction errors for clay obtained on sample Set 1 with equations developed on sample Set 2 (3–74% clay, n = 228) and sample Set 2 restricted to samples with <26% clay (n = 174).

Derivative treatment†	Scatter correction	Wavelength range used for calibration	Calibration on sample Set 2			
			3–74% clay		3–26% clay	
			RMSECV‡	SEP§	RMSECV‡	SEP§
		nm	%			
0,10,10,1	None	408–2492	3.4	3.3	2.0	2.1
1,10,10,1	None	408–2492	3.4	3.1	1.9	1.9
2,10,10,1	None	408–2492	4.8	4.7	2.5	2.5
1,10,10,1	SNVD	408–2492	4.0	4.1	2.4	2.8
1,10,10,1	MSC	408–2492	3.7	4.0	2.1	2.7
1,10,10,1	None	1108–2492	3.7	3.5	1.9	2.1

† In the general WINISI notation for derivative mathematical treatment, the terms (x, y, z, w) are described by: x, derivative number; zero means no derivative treatment; y, gap over which the derivative is calculated; z, first smoothing; the number represents the smoothing of points; w, second smoothing; one means no smoothing.
‡ Root mean square error of cross validation.
§ Standard error of prediction.

of the data and tested on other parts. One outlier elimination pass was accepted. A relatively conservative criterion based on a T-value (residual/RMSECV) of 3.0 was used. The number of PLS factors selected was equal to the fewest factors giving the lowest RMSECV.

Statistics

The standard error of prediction (SEP), which expresses the accuracy of NIR results corrected for the mean difference between NIR and reference methods (bias), was calculated by the following formula:

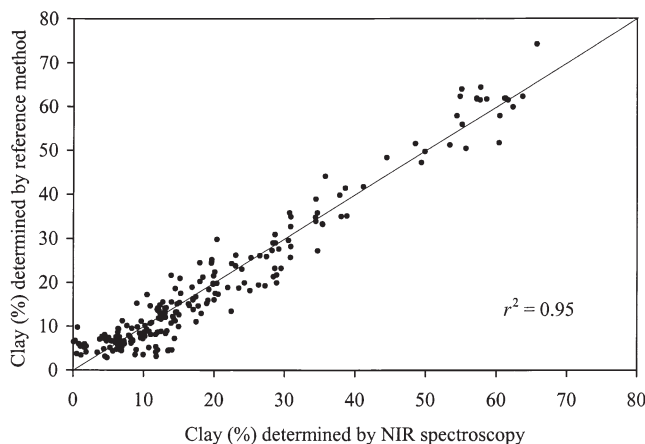$$\text{SEP} = \sqrt{\frac{1}{N-1}\sum(x_i - y_i - \text{bias})^2}$$

where $x_i - y_i$ = difference between results obtained by routine method (x_i) and reference method (y_i) on sample i.

$$\text{bias} = \frac{1}{N}\sum(x_i - y_i) = \bar{x} - \bar{y}$$

N = total number of samples in the test.

The root mean square error of prediction (RMSEP) was calculated from the differences between NIR and reference results:

$$\text{RMSEP} = \sqrt{\frac{1}{N}\sum(x_i - y_i)^2}$$

Fig. 2. Clay results obtained by cross validation on sample Set 2. Calibration was performed in the wavelength range 408 to 2492 nm after first derivative treatment of spectra.

RMSEP includes SEP and bias in a single term, and the relation between the two terms is given by $\text{RMSEP}^2 \approx \text{SEP}^2 + \text{bias}^2$. When the bias is insignificant, the RMSEP tends toward SEP with increasing data number. Generally, RMSEP gives a more realistic estimate of the prediction capability of a calibration than SEP. The SEP and RMSEP terms are calculated on a test collected independently of the calibration samples.

The root mean square error of cross validation (RMSECV) was calculated by the same formula as for RMSEP. The difference is that the RMSECV was calculated from CV on the calibration set and not on an independent test set.

True prediction accuracy (SEP_{true}) was estimated using the formula $\text{SEP}_{\text{true}} = \sqrt{\text{SEP}^2 - \text{SD}_t^2}$ where SD_t is the total standard deviation of the final reference result.

Samples with global H values above 3.5 were not included in the calculation of the statistical terms.

The SD_r (i.e., the variability of independent single results obtained by the same operator, using the same apparatus under the same conditions on the same test sample and in a short interval of time), the reproducibility standard deviation SD_R (i.e., the variability of independent single results obtained by different operators in different laboratories) and the intra-laboratory reproducibility standard deviation $\text{SD}_{R,\text{intra}}$ (i.e., the variability of independent single results obtained on the same test sample in the same laboratory by different operators under different experimental conditions) were determined in accordance with ISO standard 5725-2 (International Organization for Standardization [ISO], 1994).

RESULTS AND DISCUSSION
Near Infrared Spectroscopy

Near infrared spectroscopy has been used successfully for many years in forage and food analyses. The technique mainly measures overtones and combination bands of fundamental vibrations of O–H, N–H, and C–H bonds in the mid infrared region. Use of NIR spectroscopy for determination of inorganic parameters may not seem appropriate. However, experience has shown that useful calibrations for inorganic parameters may be obtained if indirect relationships to organic components in the sample material exist, or if the analyte induces other spectral changes, for example, band shifts.

Instruments operating in the NIR region (700–2500 nm) must be calibrated before they can be used. Because of the complex nature of NIR spectral data, the instru-

Table 5. Ratio of standard deviation (SD) to prediction errors for clay obtained on sample Set 1 with equations developed on sample Set 2 (3-74% clay, n = 228) and sample Set 2 restricted to samples with less than 26% clay (n = 174).

Derivative treatment†	Scatter correction	Wavelength range used for calibration	Calibration on sample Set 2			
			3–74% clay		3–26% clay	
			SD/RMSECV‡	SD/SEP§	SD/RMSECV‡	SD/SEP§
		nm				
0,10,10,1	None	408–2492	4.7	1.6	2.7	2.5
1,10,10,1	None	408–2492	4.7	1.7	2.8	2.8
2,10,10,1	None	408–2492	3.3	1.1	2.1	2.1
1,10,10,1	SNVD	408–2492	4.0	1.3	2.2	1.9
1,10,10,1	MSC	408–2492	4.3	1.2	2.5	2.0
1,10,10,1	None	1108–2492	4.3	1.5	2.8	2.5

† In the general WINISI notation for derivative mathematical treatment, the terms (x, y, z, w) are described by: x, derivative number; zero means no derivative treatment; y, gap over which the derivative is calculated; z, first smoothing; the number represents the smoothing of points; w, second smoothing; one means no smoothing.
‡ SD determined by reference method. RMSECV is the root mean square error of cross validation.
§ SD determined by reference method. SEP is the standard error of prediction.

ment must be calibrated on a series of natural samples representative of the population to be measured. The calibration may be performed using different techniques, for example, multiple linear regression (MLR), multivariate algorithms such PLS, or artificial neural networks (ANN). Multivariate algorithms are often used to compress the dimension of the problem and to reduce multicollinearity in NIR data. Spectra are normally preprocessed before calibration to remove or reduce effects not related to the chemical absorption of light. Often used treatments are MSC, SNV, SNVD, and first or second derivatives. The optimal transformation and other pretreatments of spectra, for example, smoothing, must be determined from trials. Several techniques may give equivalent results. Another important issue is selection of the optimal number of factors in multivariate calibrations. If too few factors are used, an under-fitted solution is obtained, which means that the model is not large enough to capture the important variability in the data. If too many variables or factors are used, an over-fitted solution may be obtained where much of the redundancy in the NIR data is modeled. The optimal number can be determined by plotting RMSECV versus the number of factors. Typically RMSECV is large for small numbers of factors and decreases as the number increases, before it increases again when the number becomes too large. Generally, the best solution is the one giving the lowest RMSECV with the fewest factors.

Outliers may be related to NIR data (X-outliers) or errors in reference data or samples with a different relationship between reference data and NIR data (Y-outliers). A homogeneous calibration set of spectrally similar samples is required to obtain a robust prediction model. This can then also form the basis of an outlier detection system. X-outliers should thus be removed before calibration. One way to identify X-outliers is by using the principle of Mahalanobis distance applied on PCA reduced data. In the present study, an H value of 3.5 based on the Mahalanobis distance was selected for identification of outliers.

When calibration equations have been developed, they must be validated on an independent test set, preferably sampled after the calibration period. The use of cross validation in the calibration process, where subsequent parts of the calibration set are reserved for validation, may give a good estimate of the uncertainty of the method when the calibration samples are properly selected. However, the potential risk is that cross validation may underestimate the ruggedness of the calibration and the predicted uncertainty because cross validation samples are taken from the pool of samples used for calibration.

Near infrared methods in routine use must be validated continuously against reference methods to secure steady optimal performance of calibrations and observance of accuracy. The frequency of checking the NIR method must be sufficient to ensure that the method is operating under steady control with respect to system-

Table 6. Clay results obtained on the independent sample Set 3 by different calibration equations developed after first derivative treatment of spectra.

Samples used for calibration	Wavelength range	RMSECV†	Validation on sample Set 3			
			RMSEP‡	SEP§	SD/SEP¶	T-outliers
	nm		%			%
Sample Set 2, <26% clay	408–2492	1.9	2.2	2.2	3.2	0
	1108–2492	1.9	2.4	1.8	3.9	2
Combined sample Sets 1 and 2, <26% clay	408–2492	1.8	1.9	1.9	3.7	0
	1108–2492	1.8	2.1	1.9	3.7	0
	400–600, 1350–1600, 1850–2400	1.8	1.7	1.7	4.1	0

† Root mean square error of cross validation.
‡ Root mean square error of prediction.
§ Standard error of prediction.
¶ SD determined by reference method.

Table 7. Clay results obtained on the independent sample Set 4 by different calibration equations developed after first derivative treatment of spectra.

Samples used for calibration	Wavelength range	RMSECV†	Validation on sample Set 4				
			RMSEP‡	SEP§	SD/SEP¶	T-outliers
	nm		%				%
Sample Set 2,	408–2492	1.9	2.3	2.3	2.4	<1
<26% clay	1108–2492	1.9	3.1	2.2	2.5	2
Combined sample Sets 1 and 2,	408–2492	1.8	2.0	1.9	2.9	<1
<26% clay	1108–2492	1.8	2.6	2.0	2.8	4
	400–600, 1350–1600, 1850–2400	1.8	1.9	1.9	2.9	<1

† Root mean square error of cross validation.
‡ Root mean square error of prediction.
§ Standard error of prediction.
¶ SD determined by reference method.

atic and random deviations from the reference method. The running validation must be performed on samples selected randomly from the pool of analyzed samples. However, it may be necessary to resort to some sampling strategy to ensure a balanced sample distribution over the entire calibration range, for example, segmentation of content range and random selection of test samples within each segment. The results may be assessed using control charts.

The use of NIR methods is generally limited to samples in the population covered by the calibration set with respect to sample material characteristics and analyte content. Samples coming from outside this population (Denmark in the present study) may not fit the calibration, although the clay content falls within the calibrated range. Thus the system must be able to detect X-outliers and samples falling outside the content range. The H value may be used for detection of X-outliers. When the H value exceeds the warning limit (e.g., 3.5) there is a risk of increased uncertainty of the NIR result. The risk increases with increasing H value.

Calibrations developed on a certain instrument cannot always be transferred directly to an identical instrument operating under the same principle. It may be necessary to perform bias and slope adjustments to calibration equations. In some cases it may even be necessary to standardize the two instruments against each other by mathematical procedures before calibration equations can be transferred.

Use of NIR spectroscopy is advantageous for several reasons. The technique is fast, that is, all parameters calibrated may be determined within approximately 2 min., including packing of sample cell and measurement. The technique is nondestructive, that is, the sample material may be reused for other purposes. The technique is more cost-effective than classical analytical methods when many samples are analyzed because it is rapid, requires a minimum of laboratory space and does not use chemicals. Cost-effectiveness is important in precision agriculture because considerably more samples have to be collected from fields to gain the full benefit of the concept. The drawback of the NIR technique is the calibration and validation steps, which are relatively resource demanding.

Clay

To investigate the optimal spectral pretreatment, calibration models were developed on the smaller sample Set 2 and tested on the larger sample Set 1. In this way the models were stressed to show the robustness of different calibration procedures. The optimal spectral pretreatment proved to be first derivative treatment without any scatter correction (Table 4). This pretreatment has also been used in other studies (Ben-Dor and Banin, 1995; Malley et al., 2000; Chang et al., 2001; Stenberg et al., 2002). The same conclusion was reached if samples containing more than 26% clay were deleted from sample Set 2 before calibration. With this spectral treatment, an extension of the wavelength region 1108 to 2492 nm to include the 408- to 1092-nm region appeared to improve the accuracy slightly. These two regions require different detectors (typically PbS and Si, respectively). Depending on the instrument model, only the longer wavelength region may be available. Figure 2 shows the correlation between the NIR method and the reference method obtained by CV on sample Set 2 consisting of samples with 3 to 74% clay.

An F test on SEP values showed that the broad range calibration (3–74% clay) was significantly less precise than the narrow range calibration (3–26% clay) when tested on sample Set 1 consisting of samples containing 2 to 26% clay (Table 4). The SD/RMSECV ratios for
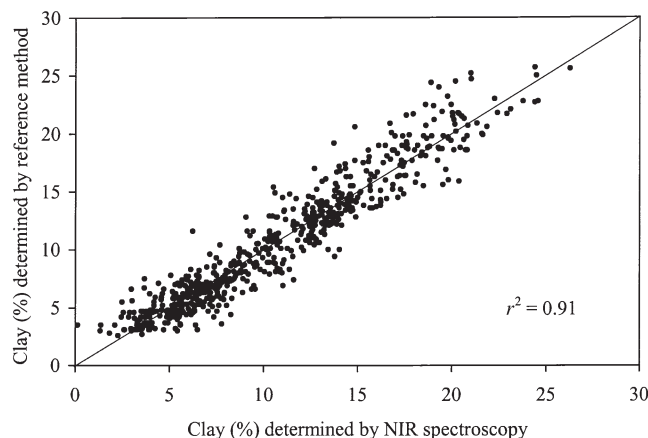
Fig. 3. Clay results obtained by cross validation on samples containing <26% clay from sample Sets 1 and 2. Calibration was performed in the wavelength range 408 to 2492 nm after first derivative treatment of spectra.
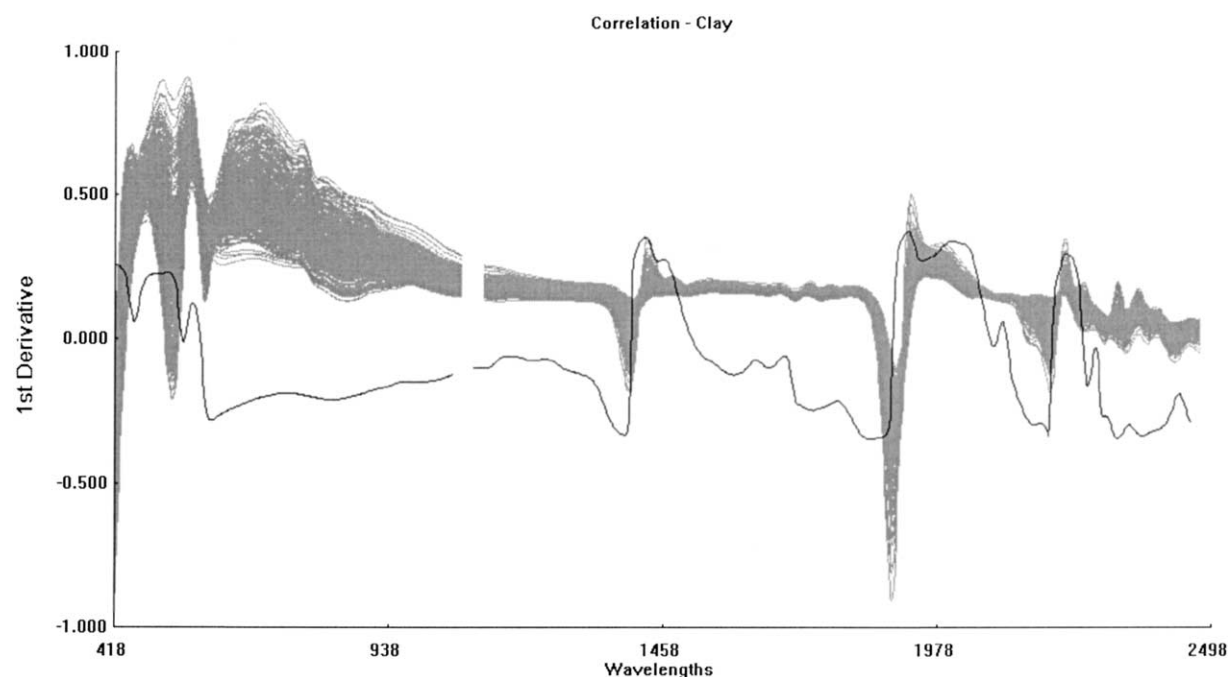
Fig. 4. Spectral profiles of samples in sample Set 1 after first derivative treatment together with the correlation plot showing the correlation between wavelengths and clay content. The *y* axis shows the correlation coefficient.

the broad and narrow calibrations were 4.7 and 2.8, respectively (Table 5), which shows that both calibrations have prediction capability for the respective ranges. However, the corresponding SD/SEP values for sample Set 1 were 1.7 and 2.8. These figures demonstrate that proper calibration ranges relevant for the practical purpose must be selected to obtain maximum benefit of the analytical technique. In practice, the 0 to 26% clay range is much more important in Denmark than the >26% range because most soils fall within this range and because legal limits for fertilizer allocation are set within this range.

Samples of sample Sets 1 and 2 containing <26% clay were combined, and calibration equations were developed after first derivative treatment of spectra. The optimal number of PLS factors was 14 for calibration in both the 408- to 2492- and the 1108- to 2492-nm ranges. Fewer than 2% of the samples were deleted as outliers according to the T > 3.0 criterion. The equations were tested on sample Sets 3 and 4, which were fully

independent of the calibration sample set and were collected at least in the year after collection of the calibration samples. The results were compared with corresponding results obtained by the equations developed on sample Set 2 restricted to samples with <26% clay. The SEP values showed that a more accurate calibration was obtained with the large sample set containing more than 600 samples (Tables 6 and 7). It was also confirmed that the accuracy, and especially the ruggedness, were better when the calibration included the 408- to 1092-nm range (the RMSEP and SEP were lower and the difference between SEP and RMSEP was less). Figure 3 shows the correlation between the NIR method and the reference method obtained by CV.

The importance of different wavelength regions can be assessed by correlation plots. Figure 4 shows the spectra of sample Set 1 after first derivative treatment and the corresponding correlation plot for clay. Positive correlations were seen in the 400- to 600-nm range (violet to yellow colors), 1350- to 1600-nm range (mainly

Table 8. Prediction errors for C obtained on sample Set 1 with equations developed on sample Set 2 (3–74% clay, *n* = 228) and sample Set 2 restricted to samples with <26% clay (*n* = 174).

Derivative treatment†	Scatter correction	Wavelength range used for calibration	Calibration on sample Set 2 3–74% clay		Calibration on sample Set 2 3–26% clay	
			RMSECV‡	SEP§	RMSECV‡	SEP§
		nm	%			
0,10,10,1	None	408–2492	0.56	0.48	0.58	0.45
1,10,10,1	None	408–2492	0.55	0.44	0.60	0.49
2,10,10,1	None	408–2492	0.51	0.49	0.59	0.54
1,10,10,1	SNVD	408–2492	0.54	0.50	0.59	0.57
1,10,10,1	MSC	408–2492	0.49	0.49	0.60	0.48
1,10,10,1	None	1108–2492	0.57	0.47	0.64	0.48

† In the general WINISI notation for derivative math treatment, the terms (*x*, *y*, *z*, *w*) are described by: *x*, derivative number; zero means no derivative treatment; *y*, gap over which the derivative is calculated; *z*, first smoothing. The number represents the smoothing of points; *w*, second smoothing. One means no smoothing.
‡ Root means square error of cross validation.
§ Standard error of prediction.

Table 9. Ratio of standard deviation (SD) to prediction errors for C obtained on sample Set 1 with equations developed on sample Set 2 (3–74% clay, n = 228) and sample Set 2 restricted to samples with <26% clay (n = 174).

Derivative treatment†	Scatter correction	Wavelength range used for calibration	Calibration on sample Set 2			
			3–74% clay		3–26% clay	
			SD/RMSECV‡	SD/SEP§	SD/RMSECV‡	SD/SEP§
		nm				
0,10,10,1	None	408–2492	2.1	1.7	2.1	1.8
1,10,10,1	None	408–2492	2.2	1.8	2.0	1.6
2,10,10,1	None	408–2492	2.4	1.6	2.0	1.5
1,10,10,1	SNVD	408–2492	2.2	1.6	2.0	1.4
1,10,10,1	MSC	408–2492	2.4	1.6	2.0	1.7
1,10,10,1	None	1108–2492	2.1	1.7	1.9	1.7

† In the general WINISI notation for derivative math treatment, the terms (x, y, z, w) are described by: x, derivative number; zero means no derivative treatment; y, gap over which the derivative is calculated; z, first smoothing. The number represents the smoothing of points; w, second smoothing. One means no smoothing.
‡ SD determined by reference method. RMSECV is the root mean square error of cross validation.
§ SD determined by reference method. SEP is the standard error of prediction.

O–H and N–H bands) and the 1850- to 2400-nm range (mainly O–H, N–H, and C–H bands). If calibration on the combined sample set was allocated to these regions, the performance was unchanged or slightly better in comparison with the full spectral range (Tables 6 and 7). The optimal number of PLS factors was 13. None of the ranges could be omitted without an increase in SEP or the number of T-outliers detected. The calibration developed on the segmented wavelength range was preferred because maximum accuracy and robustness could be obtained with fewer data points and fewer PLS factors. The performance of this calibration was characterized by a weighted mean SEP of 1.9 and a corresponding SD/SEP of 3.1. SD/RMSECV ratios of 2.3, 1.7, 2.6, and 2.7 have been reported in the literature for soil samples from Canada (Malley et al., 2000), the USA (Chang et al., 2001), Sweden (Stenberg et al., 2002), and Uruguay (Cozzolino and Morón, 2003).

The SD_r of the NIR measurements was 0.6%. Because this is considerably less than the SEP values, the accuracy of NIR spectroscopy could not be improved significantly by performing double measurements instead of single measurements.

The SD_R of the reference method was 1.3% in the range 2 to 23% clay as estimated from official ring trials. The $SD_{R,intra}$ was estimated at 1.1% from reference analyses of more than 180 samples. By comparison, the $SD_{R,intra}$ of NIR measurements was 0.7% (1–26% clay content), which means that the NIR method was more reproducible than the reference method.

The results showed that predictions of clay content in the range up to 26% could be performed with an SEP of 1.7–1.9%. Because this term also contains impreci-sion from reference analysis, the true accuracy was better than expected from the SEP. When corrected for a $SD_{R,intra}$ of 1.1%, the true accuracy was estimated as 1.5 to 1.7%.

The PLS calibration equation developed on the segmented wavelength regions 400 to 600, 1350 to 1600, and 1850 to 2400 nm using first derivative treatment of spectra and with performance data shown in Tables 6 and 7 has been used in the routine analysis of soil samples since 2002.

Other Parameters

As noted above, the content of organic matter is also an important soil property. Calibration models were constructed for determination of the total C using the same strategy as for clay. The accuracy obtained was relatively insensitive to the mathematical treatment of spectra applied or to the wavelength range selected (Tables 8 and 9). When calibration was performed on the combined sample set of sample Sets 1 and 2, an RMSECV of 0.40 was obtained with an SD/RMSECV ratio of 2.4. The optimal number of PLS factors was 12. When the calibration was tested on sample Set 4, an SEP of 0.42 was obtained after removal of T-outliers (Table 10). These figures may not be alarming. However, the number of T-outliers detected was relatively large, which indicates that it may be difficult to obtain a robust calibration for determination of total C. This may also be revealed from plotting reference data versus predicted results (Fig. 5 and 6). The plots show a nonlinearity trend (upward inflection of curves) and increased prediction errors at higher C contents. From an analyti-

Table 10. Carbon results obtained on the independent sample Set 4 by calibration equations developed on the combined sample Sets 1 and 2 after first derivative treatment of spectra.
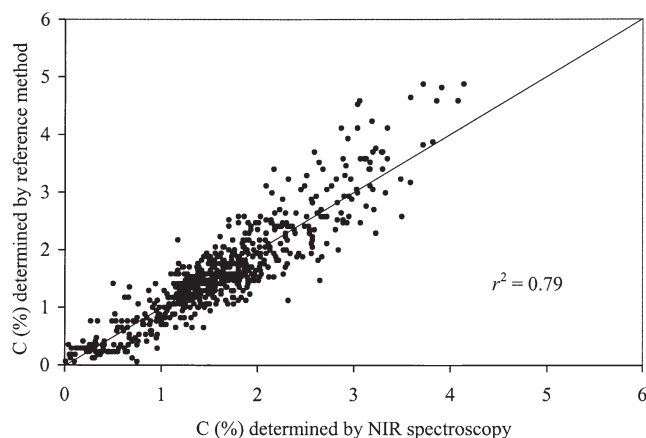
Wavelength range	RMSECV†	Validation on sample Set 4			
		RMSEP‡	SEP§	SD/SEP¶	T-outliers
nm		%			%
408–2492	0.40	0.43	0.42	2.4	4
1108–2492	0.40	0.48	0.44	2.3	5

† Root mean square error of cross validation.
‡ Root mean square error of prediction.
§ Standard error of prediction.
¶ Standard deviation (SD) determined by reference method.

Fig. 5. Results obtained for total C by cross validation on combined sample Sets 1 and 2. Calibration was performed in the wavelength range 408 to 2492 nm after first derivative treatment of spectra.

cal viewpoint, the use of NIR spectroscopy seems less feasible for determination of total C, at least when a universal calibration model for Danish soil samples is the goal. A similar conclusion was reported by Stenberg et al. (2002) for determination of organic C in Swedish soil samples. In their study, the poorest performance was obtained on soils with low clay content. The SD/RMSECV ratios were 1.3 for soils with 0 to 15% clay and 2.3 for soils with 15 to 30% clay. An indication of a similar effect of clay was observed in the present study for determination of total C. When samples in the combined calibration set were split up into a group containing 2 to 14% clay ($n = 504$, SD = 0.90 for total C) and a group containing 14 to 26% clay ($n = 139$, SD = 0.98 for total C) the SD/RMSECV ratios were 2.2 for the first group and 3.2 for the second group. In the study of Chang et al. (2001) a SD/RMSECV ratio of 2.8 was reported for total C in soil samples collected from four Major Land Resource Areas (USA). In the study of Malley et al. (2000), a SD/SEP ratio of 2.6 was obtained for organic C in Canadian soils samples. In both cases the variation in C content was considerable higher than in the present study on Danish soil samples.

Silt and sand data were only available on sample Set
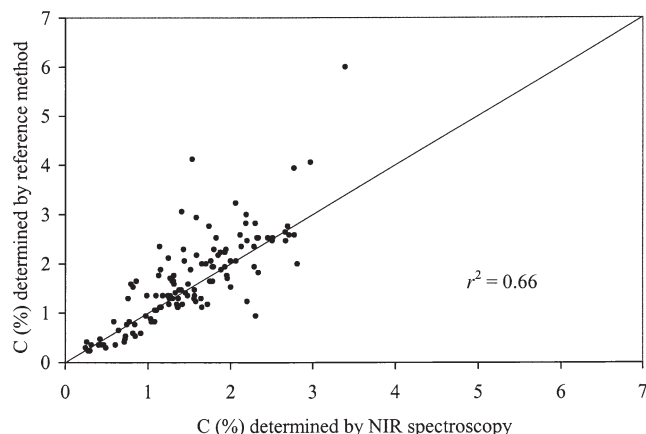
Fig. 6. Validation results obtained for total C on the independent sample Set 4 using calibration model developed on combined samples Set 1 and 2 (wavelength range 408 to 2492 nm, first derivative treatment of spectra). T-outliers were not removed.
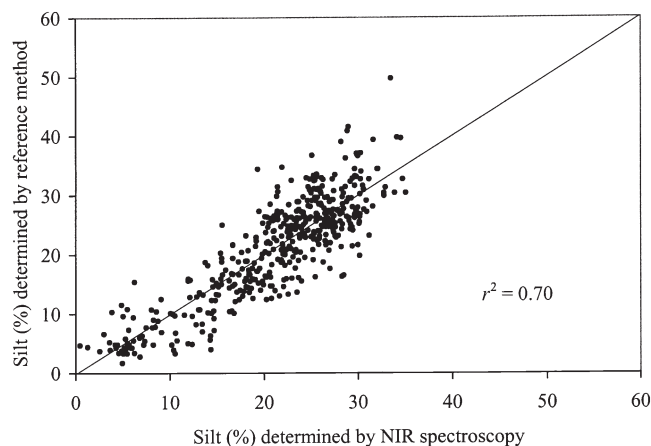
Fig. 7. Silt results obtained by cross validation on sample Set 1. Calibration was performed in the wavelength range 408 to 2492 nm after first derivative treatment of spectra.

1 (Table 3). When calibration was performed on this sample set using the same combinations of derivative treatments, scatter corrections, and wavelength ranges as shown in Table 4, RMSECV values in the ranges 4.6 to 5.2% for silt and 5.5 to 5.8% for sand were obtained. The optimal number of PLS factors was 11 in both cases. The corresponding SD/RMSECV ratios were 2.0 and 2.4 in the best cases. These are within the range of the ratios 2.5 and 2.3 for silt and sand obtained by Chang et al. (2001) on soils from four Major Land Resource Areas (USA), 1.3 and 1.7 obtained by Malley et al. (2000) on Canadian soils, and 2.2 and 1.9 obtained by Cozzolino and Morón (2003) on soils from Uruguay. It was not possible to improve results by calibration on wavelength segments with highest correlation to silt and sand. Plots illustrating the correlation between reference and predicted data are shown in Fig. 7 and 8. If the sand fraction was split up into a fine sand fraction (20–200 μm) and a coarse sand fraction (200–2000 μm), the RMSECV values were 5.6 to 6.8% for fine sand and 7.4 to 8.3% for coarse sand. The corresponding SD/RMSECV ratios were 2.0 and 2.2 in the best cases.
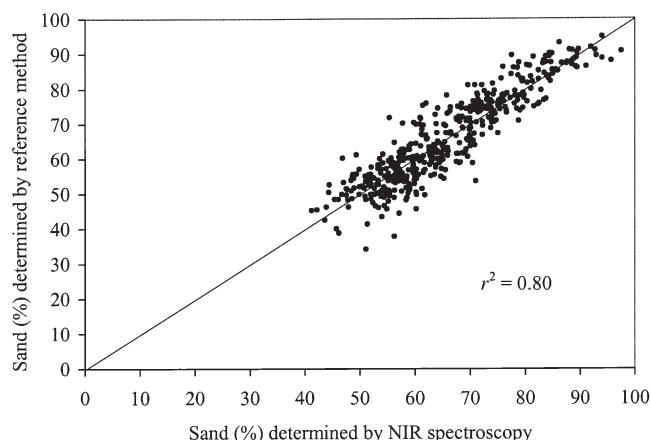
Fig. 8. Sand results obtained by cross validation on sample Set 1. Calibration was performed in the wavelength range 408 to 2492 nm after first derivative treatment of spectra.

CONCLUSION

A detailed knowledge of field variations in soil properties and especially clay and C contents is important in precision agriculture. To gain the full benefit of this technique, low cost analyses must be available. Spectroscopic measurement techniques generally have this potential, at least when the sample numbers are sufficiently high.

A NIR calibration model for determination of clay in soil was developed and tested in practice. The model showed ruggedness, linearity, and stable prediction error over the calibrated content range (2–26% clay). The uncertainty of the method was <40% higher than the reproducibility standard deviation of the reference method for clay contents below 26%. As seen in many other cases, the prediction error was dependent on the content range calibrated. When the range was extended to 2 to 74% clay, the estimated prediction error increased to 3.4%. However, an SD/RMSECV ratio of 4.7 demonstrated a high correlation between NIR spectral data and reference data, which shows that the technique may also be useful in a broad range classification of samples. To obtain the maximum benefit of the technique, the calibrated range should thus fit the purpose.

Calibration models were also developed for determination of total C in soil. The performances of these models were less convincing than for clay. Nonlinear relationships seemed to be present, and the prediction errors were clearly dependent on the total C content. For the soils investigated, NIR spectroscopy seems not to be an obvious alternative to the combustion technique, which is relatively rapid and cost-effective. The variability in published results on C determination indicates that the performance of NIR spectroscopy is dependent on the soil profiles investigated.

Calibrations were developed for determination of silt and sand contents in soils. The calibrations were not tested to the same extent as the other calibrations, but cross validation experiments did not show serious linearity problems or content dependent residuals. The SD/RMSECV values obtained indicate that the performance of NIR spectroscopy for silt and sand determination would be poorer than for determination of clay.

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