Nondestructive determination of chemical composition and classification of soils by near infrared spectroscopy

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Introduction

Modern agronomic techniques dramatically influence soil fertility. Accurately and timely information about soil composition is essential for precision farming and environmental research. This requires determination of wide range of soil components. Determination of soil properties using standard chemical procedures is complex, time-consuming and expensive. Near infrared spectroscopy (NIRS) could provide a possible alternative. NIRS is a rapid and non-destructive analytical technique that related near infrared radiation with a chemical and physical properties of materials. Several studies have already shown successful application of soil reflectance in the visible-near infrared region for predicting soil characteristics like organic matter, total N, total C and some macro and microelements content.[1-7]

The objective of this study was to investigate the usefulness of near infrared spectroscopy for determination of various constituents in agricultural soils and for classification of soils according to their humus and nitrogen content.

Material and methods

A total of 71 samples from Stara Zagora region taken from the 0-40cm layer were collected. Soil types of the samples were leached smolnitza, leached cinnarmonic forest, alluvial deluvial, alluvial deluvial meadow and meadow cinnarmonic.

All samples were analysed for humus, available nitrogen, phosphorus, and potassium content by conventional chemical methods.[8] Heavy metals (Co, Cu, Ni, Pb, Zn and Mn) content was measured for 30 of the samples by means of ICP-AES spectrometry.[8]

NIR spectra of all samples were obtained by InfraAlyzer 450 filter-type spectrophotometer within the range of 1445-2348 nm. Two or three measurements were carried out for each soil sample using independent sampler cell fillings and then averaged to give one spectrum per sample. Calibration equations for quantitative determination of tested parameters were derived by multiple linear regression. Two-third of the samples were used as calibration set, and the remaining samples as independant validation set for for humus, available nitrogen, phosphorus, and potassium content determination.

For qualitative classification, soil samples were divided into 3 groups according to their humus or nitrogen content – poor, moderate and well supplied. The classification of the samples was performed using soft independent modelling of class analogy (SIMCA). SIMCA develops models for each class based on factor analysis, i.e. principal components that describe the variations of the spectral data. Once each class has its own model, new samples could be classified to one or another classes according to their spectra. Samples from calibration set were used to develop SIMCA models for respective classes. The obtained models were tested using samples from independent validation data sets.

Results and discussion

The results for the range, mean values and standard deviation of humus, available nitrogen, phosphorus, and potassium content of respective soil samples in the calibration and the validation sets are presented in Table 1. Calibration and validation statistics of obtained equations for these parameters are summarised in Table 2.

Table 1. Range, mean and standard deviation (SD) of humus, available nitrogen, phosphorus and potassium content in examined samples.

Parameter	Calibration set (n=48)				Test set (n=23)			
	min	max	mean	SD	min	max	mean	SD
N, mg/kg	4.7	56.0	18.22	15.29	4.7	51.42	17.54	15.59
P_2O_5, mg/100g	1.3	75.0	14.99	15.50	1.7	61.2	13.77	15.66
K_2O, mg/100g	6.0	60.0	21.99	12.80	6.0	58.0	21.50	13.10
Humus, %	1.38	5.38	3.33	1.10	1.80	5.13	3.37	1.19

Table 2. Statistical data of the calibration equations and validation statistics for prediction of humus, available nitrogen, phosphorus and potassium content in examined samples.

Parameter	Calibration set (n=48)			Test set (n=23)		
	SEC	R	SD/SEC	SEP	r	SD/SEP
N, mg/kg	3.99	0.961	4.51	4.64	0.945	3.36
P_2O_5, mg/100g	4.59	0.912	3.37	4.94	0.904	3.17
K_2O, mg/100g	3.89	0.950	3.29	5.57	0.885	2.35
Humus, %	0.27	0.965	4.02	0.24	0.975	4.99

The correlation coefficients between the measured and predicted values for humus, available nitrogen and phosphorus content were greater than 0.9 for both calibration and test set. The best accuracy of determination was obtained for humus and nitrogen content. Standard error of calibration (SEC) for available nitrogen content determination was 3.99 mg/kg, correlation coefficient R - 0.961, and standard error of prediction (SEP) for independent validation set of samples 4.64 mg/kg, The respective values for humus content determination were SEC=0.27%, R=0.965, and SEP=0.24%. The ratio SD/SEC and SD/SEP was bigger than 3 for humus, nitrogen and phosphorus content. These values were considered adequate for accurate determination. Figures 1, 2 and 3 graphically illustrate the relationships between determined and NIR spectroscopy predicted values of nitrogen and humus content determination. Useful calibrations were developed for potassium content determination, as well (Figure 4).

The best accuracy of determination of humus and available nitrogen content was not surprising, because these parameters were connected with organic components of the soil. Main sources of nitrogen in the soil are nitrogen-contained organic compounds. Humus is a complicated colloid system, containing clay mineral matrix, humic acids and fulvic acids. These compounds contained aliphatic hydroxyl O-H, aromatic and aliphatic C-H, carboxyl COOH, N-H etc. groups (Naidja et al., 2002). The spectral basis of predicting of soil humus and nitrogen content would be absorption of C-H, C=O and O-H groups.

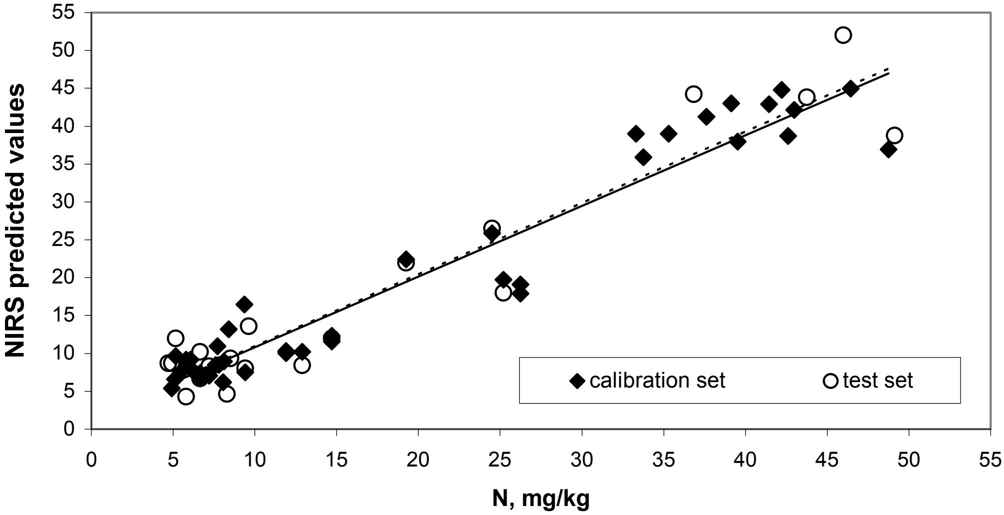

Figure 1. Relationship between actual and NIRS predicted values of soil nitrogen content.

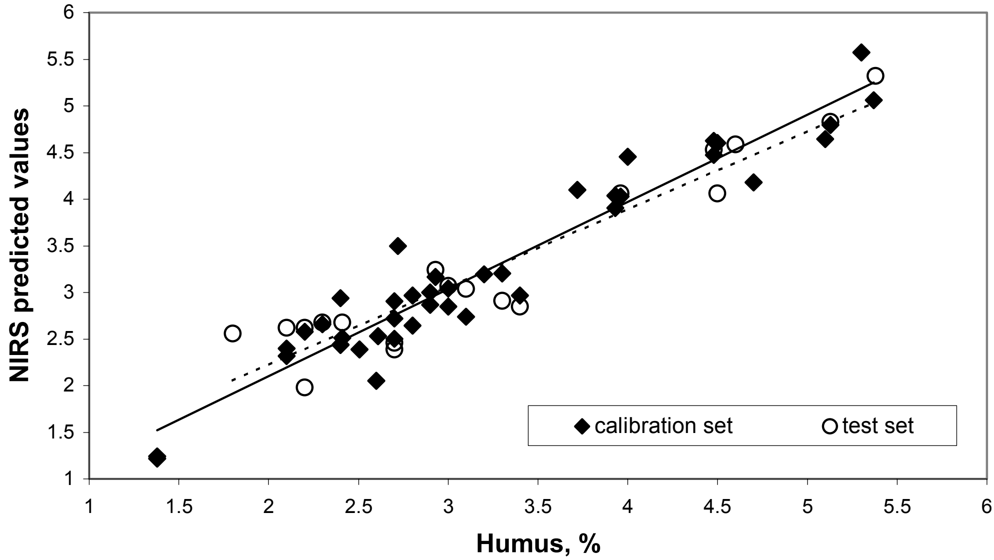

Figure 2. Relationship between actual and NIRS predicted values of soil humus content.

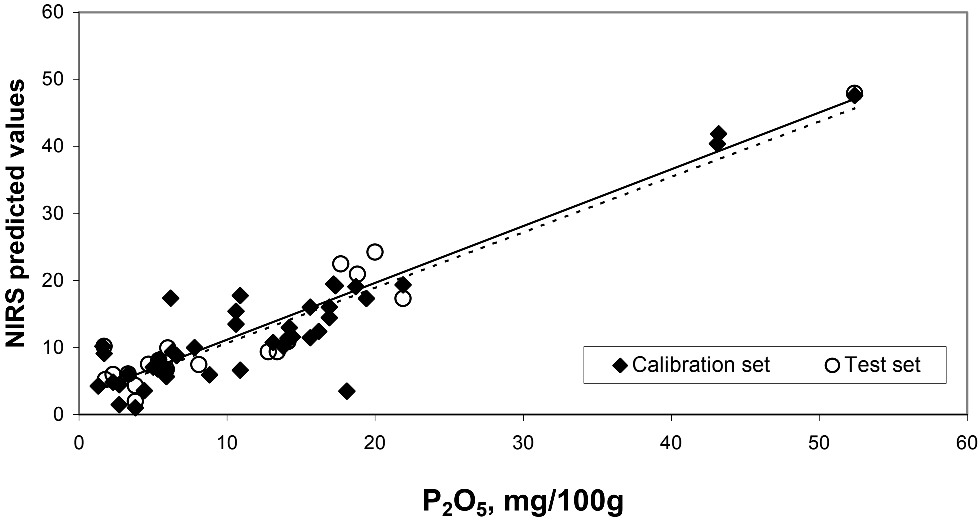

Figure 3. Relationship between actual and NIRS predicted values of soil available phosphorus content.

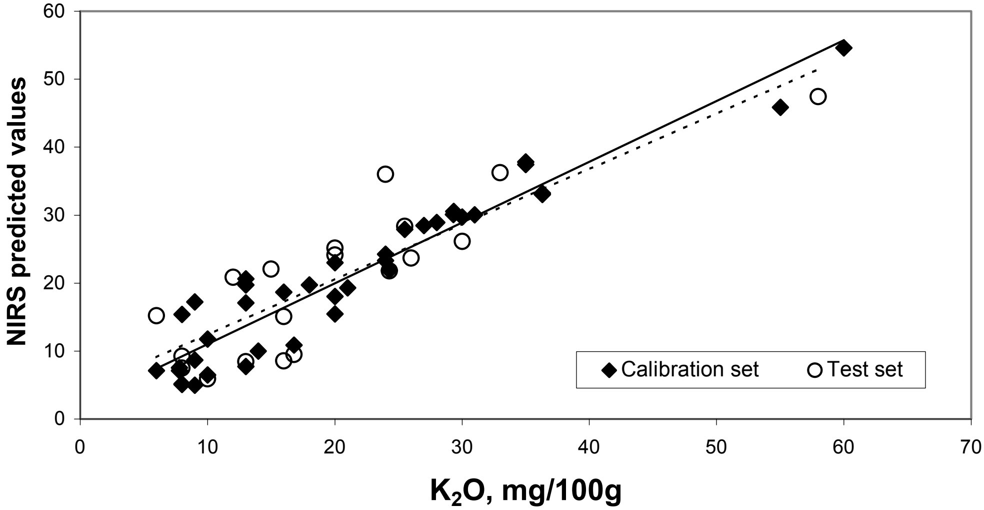

Figure 4. Relationship between actual and NIRS predicted values of soil available potassium content.

The used spectral information in calibration equations for determination of nitrogen and humus content confirmed this suggestion. For example in the equation for humus content were included spectral data at 1445, 1722, 1778, 1940, 2100 and 2190nm. The NIR absorption at 1445nm might be connected with absorption of aromatic combination C-H band; at 1722 and 1778 with C-H first overtone; at 2100nm with O-H/C=O combination; and at 2190nm with CH_2/C=C combination vibration, respectively.[9] It might be concluded that the determination of humus content in soil by NIR spectroscopy was connected with their absorption in the NIR region.

Useful calibrations were developed for Ni, Co, Pb and Cu content, as well (Table 3). Although metals do not have spectral features eithin the NIR region, the basis of prediction of heavy metals could be their correlation with organic substances or clay. These results showed that NIRS is a promising method for non-destructive determination of some heavy metals in soils.

Table 3. Range, mean and standard deviation (SD) of heavy metal content and statistical data of the calibration equations.

Parameter	min	max	mean	SD	SEC	R	SD/SEC	CV, %
Cu, $mg.kg^{-1}$	13.1	58.3	36.29	12.42	3.87	0.951	3.21	10.66
Zn, $mg.kg^{-1}$	55.4	128.0	74.48	13.33	5.47	0.850	2.44	7.34
Mn, $mg.kg^{-1}$	176	983	618.1	189.3	84.88	0.892	2.21	13.77
Co, $mg.kg^{-1}$	11.9	19.0	13.75	1.96	0.38	0.982	5.13	2.76
Ni, $mg.kg^{-1}$	25.3	37.7	29.71	3.46	0.62	0.984	5.58	2.09
Pb, $mg.kg^{-1}$	14.1	32.3	21.21	5.12	1.26	0.968	4.08	5.92

Soil samples were divided into 3 groups according to their humus or nitrogen content for qualitative classification – poor, moderate and well supplied. The classification of the samples was performed using soft independent modelling of class analogy (SIMCA). The obtained classification accuracy of models would allow differentiation of soil samples into 3 groups (Table 4).

Table 4. Results of SIMCA classification of soil samples, according to their nitrogen or humus content.

	Calibration set (n=47)		Test set (n=24)	
	Correct classification	Non-correct classification	Correct classification	Non-correct classification
According to N content	46	1 2.13%	20	4 16.67%
According to Humus content	44	3 6.38%	21	3 12.50%

Conclusion

The obtained results clearly indicated that near infrared reflectance spectra of soils contained a information about soil properties. NIRS had the potential to predict some soil components rapidly and without sample preparation and could be used for characterisation of agricultural soils.

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