Near-infrared reflectance spectroscopy as a fast method for simultaneous prediction of several soil quality components

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The initial NIRS calibrations were performed for the content of humus, organic and total carbon (C_{org}, C_{Dumas}), total nitrogen ($N_{Kjeldahl}$, N_{Dumas}), and several humus substances (HA1, HA, FA1, FA) using 71–205 soil samples of rather heterogeneous origin, collected in 2003. Various calibration procedures were evaluated based on mathematical treatment of reflectance data (use of derivatives, gaps, smoothing), a set composition of calibration samples and wavelength range. NIRS calibrations developed for soil quality components display a good to very good accuracy in the prediction of the humus, C_{org}, C_{Dumas}, N_{Dumas} with the correlation coefficient between reference and predicted data of unknown soil samples R^2_p 0.907–0.921, good performance for FA prediction (R^2_p 0.882) and satisfactory for the prediction of HA1, HA, FA1 and $N_{Kjeldahl}$ (R^2_p 0.601–0.787). Results confirm that with a larger number of representative samples, NIRS can be used as a rapid method to predict simultaneously several soil quality components. No sample weighing is required. The method enables to prevent errors during processing and to reduce analytical costs and time. Chemical-free analysis is safe for the laboratory staff and the environment.

Key words: NIR reflectance spectroscopy, carbon, nitrogen, humic substances, soil

INTRODUCTION

The introduction of near-infrared reflectance spectroscopy (NIRS) into the analytical world as an accepted technique began with the work of Karl Norris in the early 1960s [1]. NIRS is used globally for food and feed analysis. The method was first developed and widely used for rapid analysis of water, oil and protein in grains or seeds and for a rapid and accurate determination of the chemical composition and feeding quality of forage [1, 2, 4–6]. NIRS has also been used to quantify and identify such compounds as chlorophyll, glucosinolates, fatty acid profiles and other components in rapeseed [3, 7, 8]. The use of near-infrared reflectance spectroscopy to evaluate soil properties has started to receive more attention in recent years. The method is used for predicting organic C, total N, macro and micro elements [9–11].

NIR forms part of the electromagnetic spectrum in the wavelength range 780 nm to 2500 nm (Fig. 1).

Absorption bands relating to many chemical bonds, such as C-H, N-H, O-H, S-H, C=O and C=C, are found in the NIR region. The NIR spectrum shows overtone and combination bands of these groups. The absorption bands in the NIR region are broad and overlap, which means that the conventional univariate calibration techniques using only one wavelength per component for evaluations cannot be applied in the cases of overlapping bands [1, 12]. Calibration is required to correlate the spectral response of each sample at individual wavelengths
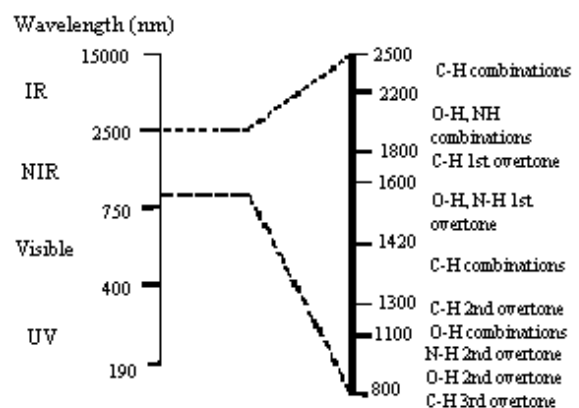

Fig. 1. Principal types of NIR absorption bands and their locations [5]

to known chemical data from laboratory analyses. Near infrared reflectance spectroscopy (NIRS) utilises reflectance signals resulting from bending and stretching vibrations in molecular bonds between carbon, nitrogen, hydrogen, and oxygen. The usual way of employing NIR spectroscopic data to predict the analyte values is to construct a calibration model in the form of a regression equation, which can then be used to predict unknown samples from NIR measurements. This means that it is necessary to relate optical data to the information obtained in a chemical laboratory and referred to as reference analysis [1, 12]. The operating principle is that constituents like protein, oil, starch, fibre, and moisture have molecular bonds that stretch and bend causing absorbance at certain wavelengths of infrared radiation in a linear proportion to the amount of constituent present. An equation that relates log 1/R (log of 1/reflectance) values at selected key wavelengths to chemistry values enables a calibration to be developed provided sufficient samples have been scanned to represent the full range of constituents. Calibration is achieved by collecting spectra from a large population of samples typical of those to be tested in future [12]. It is important to update calibrations with new samples added each crop year and also to represent a wide range of environmental conditions.

Determination of nitrogen content in the soil is important due to the vital relation of this nutrient to plant nutrition and growth as well as to the formation of yield and its quality. Nitrogen fertilisation needs to be optimised to avoid the leaching and runoff of nitrogen from soil and to reduce the productivity costs. Soil organic matter (SOM) is a complex mixture, which influences a number of soil properties and nutrient cycling and is itself influenced in kind and amount by land-use, soil type, climate and vegetation [13]. SOM is usually classified into nonhumic and humic materials [14]. Humic materials are only a portion, but they are a major portion of organic matter in most soils and waters. They are known as "transformed SOM", having lost, during the humification process, both

their morphological resemblance to the structures from which they were derived and their cell structure. Humus content and composition are regarded as integral parameters for soil fertility and variable ecological processes and are a source of information for the early diagnosis of soil degradation [15]. The ratio of humic to fulvic acids varied to some extent depending on a crop rotation [16]. There exists a great variety of methods for the estimation of both humus content and its fractional composition; the selection of method depends on researchers' tasks, available facilities, methodological conventionality and experience [17]. Conventional methods demand time, are labour-intensive, and costly. Research of ecological and sustainable agriculture requires a large number of soil analyses to be carried out. Near-infrared spectroscopy (NIRS) can significantly reduce the time spent on laboratory analyses. The method offers a number of advantages for qualitative and quantitative analysis: no sample preparation, no waste, reduced costs, fast measurements and analysis, high accuracy and the ease of use. The objective of this study was to develop equations and to assess the ability of NIRS to predict some chemical properties of various soils of Lithuania.

EXPERIMENTAL

Materials. The database of NIR spectra was composed of different soil samples collected in 2003 from various areas of Lithuania. The greatest number of samples were collected from the experimental fields of the Lithuanian Institute of Agriculture (LIA) or research stations of the institute. For chemical analysis and NIRS scanning, the visible roots and plant residues were removed. The soil was ground up with an IKA micromill, sifted through a 0.25 mm sieve, and analyses were done on air-dried samples. Nine of the sixteen chemical properties of soil samples included in the database are presented in Table 1.

Analyses by reference methods. Humus content was determined by the Tyurin method modified by Nikitin and calculated by multiplying C_{org} content by

Table 1. **Calibration sample set characterisation**

	Humus	C_{org}	C_{Dumas}	$N_{Kjeldahl}$	N_{Dumas}	HA1	HA	FA1	FA
n	205	127	111	91	111	85	71	71	71
Mean	2.182	1.311	1.154	0.141	0.098	0.070	0.422	0.086	0.572
Min	0.736	0.427	0.107	0.058	0.038	0.010	0.299	0.016	0.412
Max	7.010	4.066	2.113	0.412	0.178	0.333	0.685	0.482	0.886
CV %	37.57	41.31	31.36	45.29	27.98	76.68	17.99	69.01	21.51

n – a number of samples, Mean, Min and Max – values of component, and CV –coefficient of variation.

1.724; humus fractional composition by the Tyurin method modified by Ponomariova–Plotnikova. For humus fractional composition, solutions of different NaOH concentrations were used for extraction: 0.1 M NaOH; 0.02 M NaOH (hot extraction) also 0.05 M H_2SO_4 (for decalcination) at a soil solution ratio 1:20. The extracted humic substances were then separated into humic and fulvic acid fractions by acidifying the extract to pH 1.3–1.5 using 0.5 M H_2SO_4 at 68–70 °C, and humic acids were separated by filtering. The separated humic acids were re-dissolved in 0.1 M NaOH solution. Some humic and fulvic acid solutions of each fraction were evaporated, oxidised and organic carbon content determined using the same procedures as for soil samples. The following humic acid fractions were identified: HA1 – "mobile"; HA2 – bound with calcium; HA3 – strongly bound with soil clay minerals; the fulvic acid fractions: FA1a – the so-called "aggressive" fulvic acid fraction; FA1 – "mobile" fraction; FA2 – bound with calcium; FA3 – bound with soil clay minerals. The total amount of N was measured by the Kjeldahl method, using a FOSS Tecator Kjeltec system with 1002 Distilling Unit, C and N by dry combustion method (C_{Dumas}, N_{Dumas}) using a Vario EL III CNS-autoanalyser, Elementar Analysensysteme, Hanau, Germany. For the modified Dumas nitrogen and carbon determination, the sample is combusted at around 1150 °C in an oxygen atmosphere. The nitrogen compounds will be converted into nitrogen oxides and N_2 and carbon compounds into CO_2. After catalytic post-oxidation, drying and cleaning of the carrier gas, all nitrogen oxides are reduced to molecular nitrogen at a reducing agent (*e.g.*, copper or tungsten) and transported by the carrier gas to the thermoconductivity cell (TCD) for quantitative determination of nitrogen and carbon contents. The computer calculates automatically the percentage of nitrogen and carbon.

NIRS scanning. All the soil samples for calibration and prediction sets were scanned on a NIR Systems monochromator model 6500 (Perstorp Analytical, USA) equipped with Spinning Module, using a small ring cup (Ø 4.7 cm). In this instrument, light from the source lamp is collimated before entering the entrance slit and impinging on the diffraction grating. From the grating the light emerges from the exit slit passing through an order sorting filter before illuminating the sample along the normal at 90° to the sample surface. Reflected light is measured by Si and PbS detectors set at 45° to the macroscopic sample plane. These detectors measure the visible and NIR scanning 16 scans of the tile, 16 scans of the sample and again 16 scans of the reference tile. Detector response is coupled to an optical encoder attached to the grating rotor so that photometric responses can be related to wavelength. The reflectance spectral data as log 1/Reflectance values (log 1/R) collected covered the range 400 to 2498 nm and were recorded at 2-nm intervals.

NIRS calibration. Absorbance values log1/R were used for the data transformation. Pre-treatment of the spectral data, calculation of equations were performed in the framework of the ISI-NIRS2 software Version 3.10, Intrasoft International, USA. The interfering effect was minimised by SNV and detrending D (SNVD) transformation, and cross-validation was used to avoid overfitting. We studied the effect of calibration sample set composition and different math treatment of calibrating spectra on calibration, validation and prediction statistics. Each of the math treatment mode is described by four digits, *e.g.*, 2, 6, 4, 1. The first number (2) is the order of the derivative function, the second (6) is the gap over which the derivative is calculated, the third (4) is the smooth, *i.e.* the number of data points in a running average, and the fourth (1) is the second smooth. Calibration equations were developed using a modified partial least squares (MPLS) regression, which uses all the spectral information.

RESULTS AND DISCUSSION

Spectral properties of different soil samples. Figures 2 and 3 show the soil spectral reflectance curve for
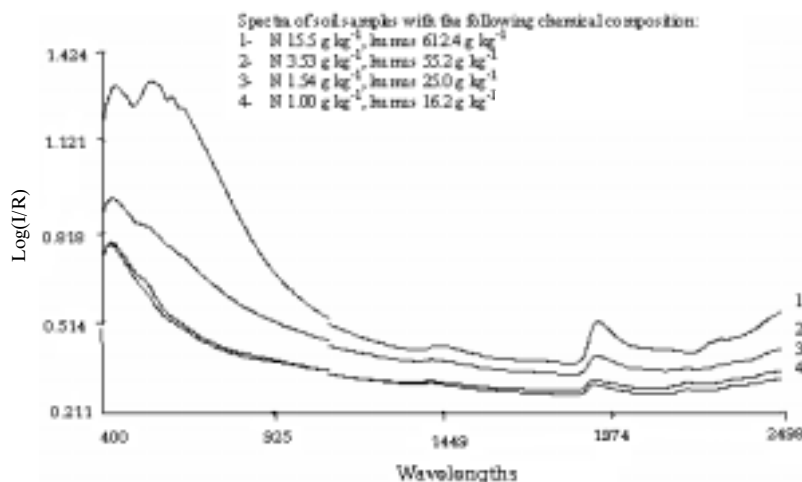

Fig. 2. Original NIR reflectance spectra of four kinds of soil samples of different chemical composition. Mathematical treatment 0, 0, 1, 1; scatter correction – none
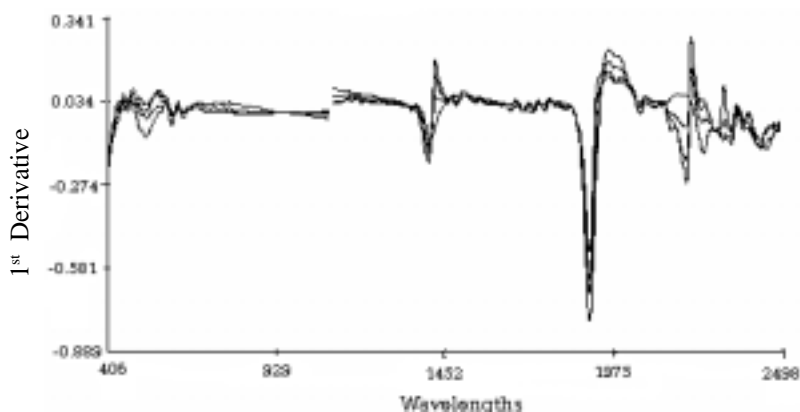
Fig. 3. NIR spectra of four kinds soil samples (as in Fig. 2) with the application of spectral data derivatisation by 1, 4, 4, 1 and of scatter correction SNVD

four individual soil samples with different chemical composition. The raw (log 1/R) spectra of all soil samples had similar shapes with the strongest absorbtion in the visible range and small peaks around 1410 and 1920 nm (Fig. 2). At 2200 a low peak is seen, too.

Absorbance in the visible range 400–700 nm depends on the colour of samples. The segment of 400–1100 nm contains little information about chemical bonds and therefore is rarely used for the development of calibration equations [18]. As the amount of N and humus increases, the overall reflectance tends to increase. Particle size and the structure of a sample can cause spectral differences unrelated to the chemical composition, and the statistics of accuracy of equations developed by using the raw log/1R is often unsatisfactory [3]. The first step for minimisation of the effect of particle size in calibration is subjecting the calibration file to various pre-treatments of the spectral data [1]. These transformations usually include scatter correction that may use standard normal variate procedures for minimisation of the interfering effect and mathematical derivative transformations. Figure 3 shows the first derivative plots of reflectance for different soil types. There is a discontinuity at 1100 nm where there is a change from one detector to another in the instrument. The first derivative spectra show that there are six regions of the spectrum that exhibit distinct absorption features and variability among the samples: 400–560 nm, around 1400, 1900, 2200, 2300 and 2400 nm. The plots appear to be very much similar to several prominent peaks in the NIR region, but some differences between spectra of soil samples are clearly seen in the region of 2000–2500 nm. The regions around 1400 and 1900 nm are related to water and hydroxyl absorption. The absorption features between 2000 and 2500 nm are rela-

ted to components of organic matter [19]. Thus, the spectra are rich in information about the samples, but the information has to be extracted statistically by calibration.

Prediction of humus content. Effect of the calibrating sample set on the robustness of equations.

NIR spectral information cannot be used to determine analyte concentrations directly because of the way in which near infrared radiation passes into, through, and is reflected from, the sample. Rather, analyte concentrations, or other characteristics of the sample are predicted from the relationships that have developed between reflectance and reference data, *i.e.* from prediction equations. The calibration is used to predict the concentrations of unknowns, assuming that the unknowns are in the same sample population as the samples used in the calibration set. The arrangement of these samples' spectra in respect of centred calibration set according to global Mahalanobis distances GH is provided in Fig. 4.

Display of samples of the prediction set against the library file of calibration set determines how close to the population of samples included in the calibration set they may be. One can see that the sample population in the prediction set according to spectra principal components is close to the samples in the calibration set. There are a few samples (rimmed in Fig. 4) that are not covered by the prediction set. These are the soils under perennial pastures with a humus content over 5%. By the chemical composition and data variability the samples in the prediction set are also close to those of calibration set (Tables 1, 2), and thus meet statisti-
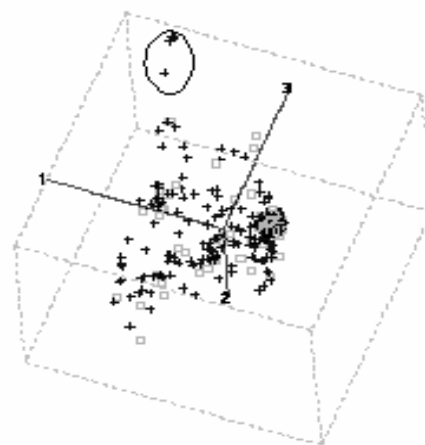

Fig. 4. Display of samples of the prediction set (?) against the library file of calibration sample set (+)

cal requirements for the groups of control samples used to measure the accuracy of equations. Seeking the accuracy and reliability of the analyses by the developed equations, various MPLS calibration models have been calculated for the samples of the calibration set, using different optical data pre-treatment, wavelength range or composition of the calibrating sample set. Statistical indicators of the primary calibration equations for the best prediction of total C, N, humus and several parameters of humus composition are presented in Table 3. NIRS calibrations developed for soil quality components display a good–very good accuracy in the prediction of the humus, C_{org}, C_{Dumas}, N_{Dumas} with the correlation coefficient between reference and predicted data of unknown soil samples, good performance for FA prediction and satisfactory for the prediction of HA1, HA, FA1 and $N_{Kjeldahl}$.

When adjusting a math treatment model of calibrated optical data with wavelength range and especially with the composition and volume of the database, the statistics of the accuracy of the developed equations was changed. The best-analysing equations of all those developed for most parameters were equations for whose calculations we used all recorded spectra of 1, 4, 4, 1 transformation, *i.e.* 400–2500 nm or only a restrictedly narrowed VIS zone, *i.e.* 700–2500 nm and the data base expanded according to possibilities. We succeeded in developing equations with very good statistical parameters in calibration, *i.e.* with small standard errors SEC and correlation coefficients RSQ. However, a control sample group was best analysed not necessarily by these equations. Thus, checking the accuracy of equations in the prediction is an imperative and an inevitable stage of the work. Some factors affecting the accuracy of the developed equations for the prediction of humus content will be discussed here. The first step in calibration is subjecting the calibration file to various mathematical treatments of the data [1]. Table 4 presents statistical data of equations developed by calibration of differently modified spectra. Statistical data on the accuracy of calibration and cross-validation equations when applying various methods of calibrated spectra mathematical treatment were different: standard errors ranged between 0.127÷0.163 and 0.173÷0.212, respectively, and the respective correlation coefficients varied within the range 0.896÷0.941 and 0.836÷0.96. The same effect of the mathematical calibrated spectra treatment method was manifested in the accuracy of the prediction of an unknown sample set. It is most expedient to calculate an equation for humus value determination in the soil by applying derivative 1 to optical data. Cross-validation and prediction errors indicated no advantage for the raw spectra (0, 0, 1, 1) or 2, 4, 4, 1 math treatment. The choice of the derivative can depend on the analyte, on the object, sample preparation and other peculiarities [3, 20, 21]. In each particular case of equation development various math treatment combinations must be tested.

In the course of this work when the database was still being accumulated, equations were developed using sample sets differing in numbers and representativeness. The scope of the calibrated data base, the accuracy of the analyses done by reference methods are decisive factors while developing accurately analysing equations for practical use. The larger the variation of chemical

Table 2. Prediction sample set characterisation

Quality parameter	n	Value			CV%
		Min	Max	Mean	
Hum	62	0.728	3.86	2.074	29.70
C_{Hum}	48	0.442	2.239	1.255	25.90
C_{Dumas}	24	0.251	1.826	1.059	36.87
$N_{Kjeldahl}$	36	0.060	0.240	0.134	29.55
N_{Dumas}	24	0.035	0.157	0.090	33.11
HA1	33	0.010	0.109	0.056	40.89
HA	28	0.300	0.564	0.433	14.64
FA1	28	0.020	0.111	0.073	40.27
FA	28	0.437	0.849	0.581	21.86

n – a number of samples, Mean, Min and Max – values of component, and CV – coefficient of variation.

Table 3. Calibration and prediction statistics of the equations for the prediction of some soil properties

Soil quality component	Calibration		Cross-validation		Prediction			
	SEC	RSQ	SECV	1-VR	SEP	Bias	Slope	R^2_p
Humus	0.114	0.949	0.162	0.897	0.183	0.044	0.993	0.916
C_{org}	0.051	0.966	0.073	0.932	0.107	0.039	1.118	0.914
C_{Dumas}	0.105	0.910	0.132	0.861	0.117	0.022	0.898	0.921
$N_{Kjeldahl}$	0.009	0.968	0.013	0.932	0.026	–0.006	0.806	0.601
N_{Dumas}	0.008	0.890	0.011	0.825	0.009	0.000	1.022	0.907
HA1	0.013	0.868	0.015	0.827	0.011	–0.001	1.145	0.787
HA	0.025	0.868	0.035	0.743	0.031	0.004	0.893	0.771
FA1	0.013	0.833	0.019	0.618	0.017	–0.005	0.854	0.716
FA	0.041	0.890	0.050	0.838	0.043	–0.001	0.976	0.882

Table 4. **Effect of calibrated optical data math treatment on the accuracy of humus content equations. Wavelength range 1100–2500 nm, calibration set characterisation in as Table 1**

Math treatment	Statistical indicators of the accuracy of equations							
	Calibration		Cross-validation		Prediction			
	SEC	RSQ	SECV	1-VR	SEP	Bias	Slope	R^2_p
0 0 1 1	0.163	0.896	0.179	0.876	0.245	0.046	0.881	0.853
1 2 2 1	0.133	0.937	0.201	0.857	0.216	0.046	0.925	0.879
1 4 4 1	0.135	0.936	0.173	0.896	0.215	0.061	0.914	0.889
2 4 4 1	0.127	0.941	0.212	0.836	0.256	0.046	0.926	0.825

Having analysed errors between the data obtained by the laboratory method and by NIR spectroscopy, we identified the errors exceeding the desirable ones while investigating small humus changes in the soil (Fig. 5, rimmed). It is not clear at which accuracy the equation will analyse the soil properties that have formed under different meteorological conditions. Soil samples were accumulated for just one year, while it is known that soil organic matter transformation processes are especially dependent on the year's weather conditions, especially moisture content, water logging of soil and similar factors.

composition values of the samples included in the data base, the more universal equation, i.e. the one that could accurately analyse more varied samples, can be created. According to the coefficients of correlation between optical and laboratory data in calibration and cross-validation, *i.e.* RSQ and 1-VR, all equations developed for the estimation of humus content in the soil are sufficiently reliable, even if these coefficients decline when the database is increased (Tables; A1, A2, A3).

Therefore we are convinced that it is necessary to further supplement the database for at least one more year and if possible continually, and to include at least 10–20 samples annually. AOAC documents (*AOAC: Official Methods of Analysis* 989.03, 1990 74–76) indicate that at least four rules must

Table 5. **Calibration and prediction statistics for the prediction of humus content using different sample sets for calibration. Math treatment 1, 4, 4, 1; wavelength range 1100–2500 nm**

Calibration sample set				Calibration		Cross-validation		Prediction			
	n	Mean	CV%	SEC	RSQ	SECV	1-VR	SEP	Bias	Slope	R^2_p
A1	61	2.641	59.18	0.074	0.996	0.216	0.977	1.046	0.546	0.368	0.582
A2	93	2.305	47.28	0.128	0.958	0.194	0.904	0.588	0.275	0.573	0.620
A3	205	2.182	37.58	0.135	0.936	0.173	0.896	0.212	0.059	0.909	0.897
B	201	2.091	24.10	0.132	0.934	0.117	0.881	0.206	0.055	0.900	0.906

Humus range: in A1, A2, A3 – 0.738–7.010; B = A3, after elimination of samples with humus content > 4%. n – a number of samples, and CV –coefficient of variation.

However, for practical use, *i.e.* analysing the control samples, initial equations developed from a low-volume database are less reliable. This is suggested not only by correlation coefficients but also by standard errors in the prediction. A close correlation (0.90–0.91) between the values obtained by the Tyurin method and with a NIRS-6500 instrument was identified when larger databases were used for the development of equations (A3, B). Standard errors in the prediction by these equations were 0.21. When analysing by reference methods it is aimed to achieve even smaller errors of humus determination. In order to develop a universal equation, the database needs further improvement. Pasture soils very high in humus content (>4%) are analysed inaccurately even by the equations developed on the basis of A3 or B databases.
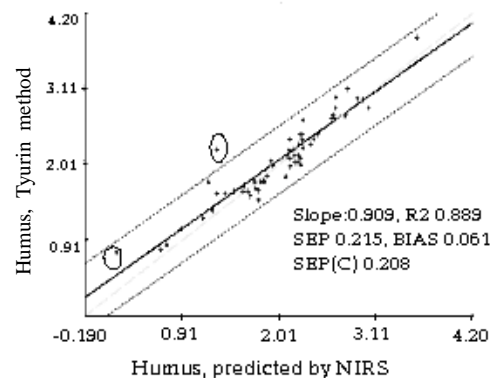

Fig. 5. Relationship between humus values in the group of control samples (prediction) determined by the Tyurin method (*y*) and with NIRS-6500 spectrometer (*x*). Equation database A3 (see Table 5)

be obeyed in calibration: samples of calibrated database must adequately represent sets of analysed samples; calibration sets should have a wide range and even distribution in composition [1]. Construction of a calibration set involves balancing the cost of obtaining a widely representative database, against the desirability of having a calibration set containing representatives of all the samples that are likely to be analysed by the prediction equation.

Literary sources often indicate that spectral data of a 1100–2500 nm interval are used for the development of equations. Park et al. [21], Butkutė [3] have investigated the possibilities of other optical data intervals of calibration to increase the accuracy of equations. Statistical data of calibration of the equation for the assessment of humus content in the soil in the cases studied were good when calibrating optical data of various interval (wavelength) (Table 6).

accurately analysing equation was obtained when we calibrated optical data of 1, 4, 4, 1 treatment of all recorded spectra. In this way, elimination of the 400–1100 nm segment, which is most frequently suggested in the literature, did not give any positive results for the improvement of the equation. Figure 6a describes the relationship between the data of the temporary analytical file (in × axis) developed during the calibration process, *i.e.* data base, in this particular case B3, analysed by the equation under development and the data determined by the Tyurin method (in *y* axis) and stored in the database.

In Figure 6b we see the graphical values of the laboratory and optical data correlation coefficients as a function from the wavelength of spectrum, when calculating equations in the whole range of the recorded spectrum, *i.e.* 400–2500 nm. When calculating the equations by MPLS method, the values of coefficients unambiguously show the significance of a corresponding wave for explaining the variation of humus content in the samples. Actually, as we can see in the plot of wavelength correlation with soil humus content (Fig. 6 b), the coefficients in the first interval, *i.e.* in the visible zone (400–780 nm) are not close to zero.

The correlation especially high is at the wavelength 700 nm. This means that elimination of this spectrum segment while developing an equation for humus determination is useless. In the future, the equations should be further revised by rejecting segments

Table 6. **Calibration and prediction statistics using different wavelength range for the development of equations for the prediction of humus content. Math treatment 1, 4, 4, 1; calibration sample set A3 (see Table 5)**

Wavelength range nm	Statistics of equations							
	Calibration		Cross-validation		Prediction			
	SEC	RSQ	SECV	1-VR	SEP	Bias	Slope	R^2_p
400–2500	0.114	0.949	0.162	0.897	0.183	0.044	0.993	0.916
700–2500	0.119	0.943	0.158	0.900	0.195	0.060	0.975	0.908
1100–2500	0.135	0.936	0.173	0.896	0.212	0.059	0.909	0.897

The calibrated wavelength had some effect on the accuracy of the equations developed for the determination of humus content in the soil. A more

segment while developing an equation for humus determination is useless. In the future, the equations should be further revised by rejecting segments
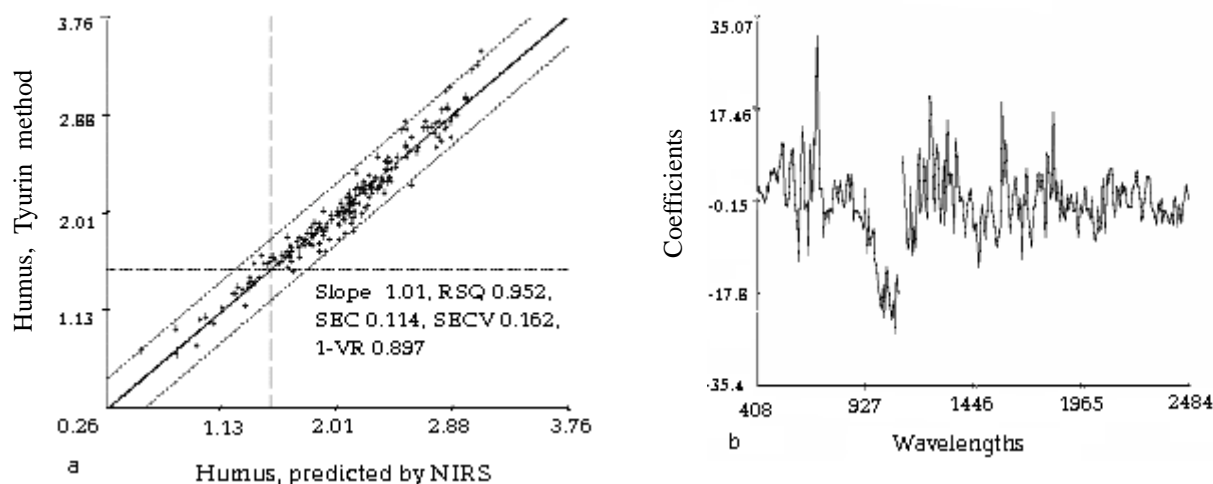

Fig. 6. *a* – correlation between the humus values determined by the Tyurin method (*y*) and predicted by NIRS-6500 (*x*) in cross-validation; *b* – plot of wavelength correlation with soil humus content. Math treatment 1, 4, 4, 1, wavelength range 400–250 nm, database A3 (Table 5)

with particularly low correlation coefficients (800–1100 nm). In Russia, using a filter spectrometer, equations for the determination of humus content, humic to fulvic acids ratio were developed on the basis of NIR absorption at 750 nm [22]. In this work the general equation is presented, in which reflection coefficient at 750 nm is given as a function of a set of variables: content of humus, calcium carbonates, nonsilicate iron and the content of carbon in humic and fulvic acids. However, at this point both individual and generalised equations are valid only for a narrow set of soils.

The results presented in this paper are just preliminary. They demonstrate that the equations developed on the basis of the database accumulated within a year enable to group soils according to humus and nitrogen content, to judge about humus type, and are suitable for agronomic soil assessment. To make the NIRS method more universal and applicable for a precise quality assessment of different soils, it is necessary to supplement databases for individual parameters for the development of equations, to take into account and more comprehensively investigate the effect of compatibility of different calibration factors on the accuracy and precision of equations.

CONCLUSIONS

1. NIRS calibrations were performed for humus, organic and total carbon (C_{org}, C_{Dumas}), total nitrogen ($N_{Kjeldahl}$, N_{Dumas}), and several humus substances (HA1, HA, FA1, FA) content using 71–205 soil samples of a rather heterogeneous origin, collected in 2003. The primary NIRS calibrations developed for soil quality components display a good and very good accuracy in the prediction of the humus, C_{org}, C_{Dumas}, N_{Dumas} with the correlation coefficient between the reference and the predicted data of unknown soil samples R^2_p 0.907–0.921, good performance for FA prediction (R^2_p 0.882) and satisfactory for the prediction of HA1, HA, FA1 and $N_{Kjeldahl}$ (R^2_p 0.601–0.787).

2. Various calibration procedures were evaluated based on the mathematical treatment of reflectance data (use of derivatives, gaps, smoothing), a set composition of calibration samples, and wavelength range. The best fit for the prediction of humus content, based on the standard error of cross-validation (SECV) and the standard error of prediction (SEP), was obtained when using for the equation development full spectra (400–2500 nm) with a first derivative math treatment and a database expanded as far as possible.

3. The results confirm that with a larger number of representative samples, NIRS can be used as a rapid method to predict simultaneously the content of humus, organic and total carbon (C_{org}, C_{Dumas}), total nitrogen ($N_{Kjeldahl}$, N_{Dumas}), and several humus substances (HA1, HA, FA1, FA etc.) in the soil. No sample weighing is required. The method enables to prevent errors during analysis processing, to reduce analytical costs and time. Chemical-free analysis is safe for the laboratory staff and the environment.

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ARTIMOSIOS SRITIES INFRARAUDONŲJŲ SPINDULIŲ SPEKTROSKOPIJA – GREITAS METODAS VIENU METU NUSTATYTI KELETĄ DIRVOŽEMIO KOKYBĖS RODIKLIŲ

S a n t r a u k a

Sukurtos pirminės lygtys dirvožemio humuso, organinės ir bendrosios anglies (C_{org}, C_{Dumas}), bendrojo azoto ($N_{Kjeldahl}$, N_{Dumas}) ir humuso sudėties rodiklių (HR1, HR, FR1, FR) kiekiams įvertinti spektrometru NIRS-6500, naudojant 2003 m. sukauptas duomenų bazes, susidedančias iš 71–205 skirtingų dirvožemio mėginių. Ištirta kalibruojamų optinių duomenų matematinio transformavimo *(Math treatment)*, bangų intervalo *(Wavelength range)*, duomenų bazės apimties įtaka kuriamų lygčių tikslumui. Priklausomai nuo kalibravimo sąlygų ir dirvožemio kokybės rodiklio sukurtos skirtingo tikslumo pirminės lygtys: humuso, C_{org}, C_{Dumas}, N_{Dumas} kiekiams nustatyti – gero ir labai gero tikslumo su koreliacijos koeficientais tarp duomenų, nustatytų referentiniais metodais ir sukurtomis lygtimis R^2_p 0,907–0,921; gero tikslumo – bendrajam fulvorūgščių kiekiui FR nustatyti (R^2_p 0,882); patenkinamai analizuojančios – HR1, HR, FR1 ir $N_{Kjeldahl}$ kiekiams įvertinti (R^2_p 0,601–0,787). Sukurtosios lygtys analizuoja tiksliai tam tikrame reikšmių intervale, tačiau jos nėra universalios. Papildžius duomenų bazes reprezentatyviais mėginiais ir jų pagrindu sukūrus lygtis, artimosios srities infraraudonųjų spindulių atspindžio spektroskopija (AIRA) gali būti sėkmingai taikoma keliems dirvožemio kokybės rodikliams nustatyti simultaniškai kaip greitas ir pigus metodas, kuris gali pakeisti gana brangius ir imlius laikui cheminius dirvožemio analizavimo metodus. Analizuojant AIRA spektroskopija išvengiama paklaidų, susijusių su svėrinio paėmimu bei kitomis sudėtingomis analitinėmis procedūromis, nereikalingi reagentai, todėl analizė šiuo metodu yra saugi aplinkai ir laboratorijos personalui.