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Near-Infrared Analysis as a Rapid Method to Simultaneously Evaluate Several Soil Properties

E. Ben-Dor* and A. Banin

ABSTRACT

The near infrared analysis (NIRA) approach was studied to examine its capability for predicting spectral feature soil properties from the reflectance curves in the near infrared (NIR) region (1-2.5 μm) of arid and semiarid soils. High-resolution diffuse reflectance spectra (3113 spectral points) in the NIR region were recorded for 91 soil samples from Israel. Six soil properties (clay content, specific surface area, cation-exchange capacity, hygroscopic moisture, carbonate content, and organic matter content) were measured by routine methods employed in soil laboratories. An empirical model to predict each property from its spectral signature was developed by adapting the NIRA technique. Several data manipulations were used to obtain optimum performance. The optimum performance of all properties was found to be between 25 and 63 spectral points. Strong support for the NIRA capability was provided by its ability to examine most of the spectral assignments. A slight bias was observed for the prediction of both organic matter and hygroscopic moisture, suggesting that more attention in the prediction of these constituents is required. It was concluded that NIRA is a promising method for rapid and nonrestrictive analysis of soil materials, and further study of the synergism between NIRA and soil materials is recommended.

NEAR-INFRARED ANALYSIS is a laboratory approach that analyzes the diffuse reflectance radiation with regard to a material's chemistry (Stark et al., 1986). This methodology was developed 25 yr ago for rapid analysis of moisture in grains (Ben-Gera and Norris, 1968). Today, NIRA is well accepted and widely used in many other disciplines (Davies and Grant, 1987; Norris, 1988). This method is known for its rapidity, convenience, simplicity, accuracy, and ability to analyze many constituents at the same time (Stark et al., 1986). In

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addition, the method does not require highly developed operator skills or a large amount of sample materials, and the analysis is nonrestrictive (Wetzel, 1983). Basically, the NIRA method assumes that a concentration of a given constituent is a linear combination of several absorption features. The method is empirical, and no physical or chemical factors or assumptions are really needed.

The spectral features of soil materials in the NIR (1-2.5 μm) spectral region are associated with vibration modes of functional groups. These modes are combinations and overtones of the fundaments in the IR spectral region. Soil minerals have distinct spectral fingerprints in the NIR region because of relatively strong absorption of the overtones and the combination modes of the OH, SO₄, and CO₃ groups (Hunt and Salisbury, 1970). Organic matter also has distinct fingerprints that relate to several functional groups (e.g., carboxyl, hydroxyl, and amine) in the organic compounds (Bowers and Hanks, 1965; Al-Abbas et al., 1972).

Both minerals and organic matter in soils were studied using the NIRA approach. Ben-Dor and Banin (1990a) pointed out that the concentration of carbonates could be predicted by NIRA in arid soils if the soils were preheated to 600°C for 8 h prior to the spectroscopic measurements. They concluded that by this pretreatment, the strong absorption features of the OH groups (both in the organic matter and in the clay minerals) are removed and the CO₃ groups are enhanced. Ben-Dor and Banin (1990b) used the NIRA strategy for chemical determination of clay minerals. They found that total Fe, Al, Mg, and silica can be predicted from a group

Abbreviations: NIRA, near-infrared analysis; NIR, near infrared; SSA, specific surface area; CEC, cation-exchange capacity; HIGF, hygroscopic moisture; OM, organic matter; MRA, multiple regression analysis; SEC, standard error of calibration; SEP, standard error of performance; AE, analytical error; CPV, coefficient of prediction variation.

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addition, the method does not require highly developed operator skills or a large amount of sample materials, and the analysis is nonrestrictive (Wetzel, 1983). Basically, the NIRA method assumes that a concentration of a given constituent is a linear combination of several absorption features. The method is empirical, and no physical or chemical factors or assumptions are really needed.

The spectral features of soil materials in the NIR (1-2.5 μm) spectral region are associated with vibration modes of functional groups. These modes are combinations and overtones of the fundaments in the IR spectral region. Soil minerals have distinct spectral fingerprints in the NIR region because of relatively strong absorption of the overtones and the combination modes of the OH, SO₄, and CO₃ groups (Hunt and Salisbury, 1970). Organic matter also has distinct fingerprints that relate to several functional groups (e.g., carboxyl, hydroxyl, and amine) in the organic compounds (Bowers and Hanks, 1965; Al-Abbas et al., 1972).

Both minerals and organic matter in soils were studied using the NIRA approach. Ben-Dor and Banin (1990a) pointed out that the concentration of carbonates could be predicted by NIRA in arid soils if the soils were preheated to 600°C for 8 h prior to the spectroscopic measurements. They concluded that by this pretreatment, the strong absorption features of the OH groups (both in the organic matter and in the clay minerals) are removed and the CO₃ groups are enhanced. Ben-Dor and Banin (1990b) used the NIRA strategy for chemical determination of clay minerals. They found that total Fe, Al, Mg, and silica can be predicted from a group

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calibration and validation stages. clared the preferred equation for predicting samples from the At that point, the corresponding calibration equation was deuntil a relatively high prediction performance was obtained. results (measured). This stage was run for each constituent calculated results (predicted) were compared with the chemical corresponding prediction equation produced in Stage 1. The concentration of each constituent was calculated using the the spectra that provided the prediction equation. Then the

Statistical Analysis

sample and the selected spectral parameters as follows: equation between a constituent concentration Cp in a given The MRA procedure selects a best multiple correlation

$$C_p = b_0 + b_1 L_1 + b_2 L_2 + b_3 L_3 + \dots + b_k L_k$$
[1]

calculated according to Davies and Grant (1987) as follows: tions were calculated using Eq. [1] and the SEC was then or second A"). Predicted values of the constituent concentradata (R), absorption data (A), or their derivatives (first R', A', at wavelengths 1, 2, ..., A and could be either reflectance u, L_1, L_2, \ldots, L_n are the values of the spectral parameters for the spectra readings in various selected wavelengths 1 to where b_0 is an intercept, $b_1, b_2 \dots b_k$ are weighting factors

$$SEC = \sqrt{\frac{N^{c} - u - 1}{\sum_{N^{c}}^{u=1} (C^{u} - C^{b})_{s}}}$$
 [5]

is the number of the samples in the calibration stage, and n is is the predicted value on the basis of the spectral analysis, $N_{\rm c}$ where C_m is the value measured by the chemical analysis, C_p

calculated as follows: the calibration stage (validation stage). The SEP was then concentration in another set of soil samples not involved in The calibration Eq. [1] was used to predict the constituent the number of terms in the prediction equation.

 $ZEP = \sqrt{\frac{N_{p-1}}{\sum_{i=1}^{N_{p}} (C_{m} - C_{p})^{2}}}$

and (iii) the regression coefficient (r2) is unity. is unity, (ii) the intercept of the regression line (b) is zero, the null hypotheses are (i) the slope of the regression line (a) accept the regression line as a 1:1 line. The assumptions of validation results. It uses three null hypotheses to reject or used to examine the regression line $(C_m = aC_p + b)$ of the A bias test, adopted from Miller and Miller (1988), was where M_p is the total number of tested samples in this stage.

of the chemical analysis was calculated as follows: To allow better comparison with the SEP values, the AE

 $AE = \sqrt{\frac{\sum_{j=1}^{N_1} \sum_{j=1}^{N_2} (X_{ij} - C_{mi})^2}{N_1 - 1}}$

is that it has spectral absorption features in the MIR region

of the NIRA approach for analysis of a given constituent

not correlated with any of the other five soil properties

correlation of clay content. Carbonates (Group III) are

and HIGF), either directly or indirectly throughout the

related to the adsorption properties of soil (SSA, CEC,

HIGF). Organic matter (Group II) is also moderately

soil and which affect the adsorption properties (CEC and

which constitute some 70% of the clay portion of the

for the most part contributed by smectite clay minerals,

Amiel (1970) pointed out that in Israeli soils, SSA is

all related to the clay content and its SSA. Banin and

any of the other properties). Properties in Group I are

which consists of CaCO3 content (does not correlate with

A lates with Group I; 0.412 < r < 0.665); and Group III,

Group II, which consists of OM only (moderately corre-

closely correlated among themselves with r > 0.643);

consists of clay content, SSA, CEC, and HIGF (all

Three essential groups can be observed: Group I, which

correlation between all the examined soil properties.

moisture (1.4 and 1.9 µm) and to the crystal lattice in

These features are attributed to the OH groups of soil

the compressed spectra (at ≈ 1.4 , 1.9, and 2.2 µm).

sentative soil spectra as well) are evident throughout all

essential absorption bands (which appear in the 11 repre-

of spectral bands from 3113 to 25. Nonetheless, three

ened by the compression process, decreasing the number

B-7. It is apparent that some spectral features are weak-

Figure 2 presents the compressed spectra of Sample

on which to present the spectral compression process.

that accurately represents the entire population (Table

ever, we further selected an additional soil sample (B-7)

are a good representative of the entire population. How-

(Table 1), it can be concluded that the 11 soil samples

Judging from the chemical range of the whole population

be systematically examined (chemically and spectrally).

adequate conclusions, the whole soil population must

samples. For a broader point of view and for more

samples and does not necessarily apply to other soil

discussion is limited only to the 11 representative soil

K-2, P-2, and S-5; Hunt and Salisbury, 1970). The above

He oxides can be observed at ≈ 1.05 µm (e.g., B-1,

soils, some absorption features that may be assigned to

C-2, W-1, O-2, S-5; low: E-1, A-4, W-1). In some

intensity at ≈ 2.3 µm and the CaCO3 content (e.g., high:

C-2, W-1, and S-5) as well as between the absorption

SSA, and HIGF content (e.g., high: A-4, H-2, P-2; low:

sity at ≈ 1.4, 1.9, and 2.2 µm and the Clay content,

A rough correlation occurs between the absorption inten-

cal data from the 11 soils for each of the six properties.

µm; Gaffey, 1986). Table 1 provides some of the analyti-

very active in the MIR region (major peak at ≈ 2.33

calcite mineral (and hence in calcite-enriched soils) is

2.2 µm; Hunt and Salisbury, 1970). Also, the CO3 in

and i.9 μ and the crystal lattice water (at ≈ 1.45 and

are the OH groups in both the adsorbed water (at ≈ 1.4

components in the NIR region to have strong absorption

soil clay minerals (2.2 µm).

Table 2 presents a matrix of the linear coefficient

An important prerequisite for successful application

Replication J, Cmi is the mean of Sample i, and M is the total Where X_{ij} is the direct chemical measurement of Sample i in

number of the entire replications for a given property.

RESULTS AND DISCUSSION

uted to some of the soil compounds. The most likely consist of spectral information that can be easily attribare given in Fig. 1. It is apparent that all of the spectra most of the soil groups within the examined population Reflectance spectra of 11 soil samples that represent

Spectral Measurements and Compression

Spectral Measurements

recorded under similar spectroscopic and geometric conditions. ported relative to a BaSO4 standard spectrum, which was sample preparation procedure. The soil reflectance was repacked into a stainless steel sample holder, using a standard rick Co., Ossining, NY). The soil powders (<0.355 mm) were diffuse reflectance attachment (DEA-dimensional model, Harflectance was measured by a praying mantis bi-directional and 1.8 nm for the higher wavelength (2.5 µm). Diffuse reresolution between 0.8 nm for the lower wavelength (1 µm) wavelength mode, this resulted in a variation of the spectral spectral points across the 1- to 2.5-um spectral region. In the spectral resolution value of 8 $\mbox{cm}^{-1},$ which produced 3113bands. For the current measurements, we used a constant region and has the capability of producing up to 6000 spectral a high optical resolution of 1 cm⁻¹ throughout the spectral Madison, WI) optimized to the VIR (1-2.5 µm) region. It has by an Alpha Centauri FTIR spectrophotometer (Mattson Co., The spectral reflectances of the soil powder were recorded

Spectral Compression

calculation across the original reflectance-wavelength bands. value of each new band was obtained by using a simple average and their paired reflectance values. The wavelength-reflectance the new band spectrum consisted of 3113/G original bands was divided into G bands (G = 25, 30, 63, 310). Each of carried out as follows. The original spectrum (of each sample) a smaller number of bands. The compressing procedure was was compressed computationally to a new spectrum containing The original spectrum consisting of 3113 spectral bands

Spectral Analysis

known samples. requires both calibration and validation stages to analyze unstage is extremely critical. The complete NIRA procedure Because MIRA is basically an empirical method, the validation the validation stage, where the previous stage is validated. tion stage where the prediction equation is developed and (ii) The MIRA methodology requires two stages: (i) the calibra-

Calibration Stage

samples in the validation stage. was used to determine the concentration of unknown validated each of the MRA stages. The result, a multiterm equation, the spectral parameters (R, A, or their derivatives) and for under a MRA procedure. This procedure was run for each of coefficient of correlation were further selected for examination and their corresponding wavelengths providing the highest run. Twenty-five bands (six for the G=25 compressed bands) log(1/R)] or their derivatives [R',A',A"]) of every band was and the spectral response (reflectance [R], absorption [A = procedure between the concentration of a given constituent directly from the 91 soil samples. A simple linear regression This procedure consisted of a subgroup that was selected

Validation Stage

samples were mathematically manipulated exactly as were in Stage 1. For that purpose, the spectra of all the validation process were used to validate the calibration equation produced Unknown samples that were not used in the calibration

of smectite minerals by using the NIRA strategy without

semiarid regions of Israel. The properties were selected spectral feature properties of soil from the arid and the MIRA technique to simultaneously measure various pose of this study was to examine the capability of ceived much attention in the soil science field. The purtermed a "giant" method (Davies, 1987), it has not repromising tool in many other disciplines as well, and Although the NIRA method was found to be a very properties that are spectrally active in the NIR region. less constituents in soils via an intercorrelation with soil methodology can be used to predict some spectral feature-(1994, unpublished data) were able to show that the NIRA ing for soil applications. Recently, Ben-Dor and Banin constituents and feel, also, that the method is very promismethod is very promising for the prediction of these chemically treated subsets). They concluded that the relatively homogenous soil group (12 soils with their the MIRA capability to predict organic C and M in a tation and the data handling. Morra et al. (1991) studied method if further consideration is given to the instrumenthat the MIRA technique can be used as a routine testing lian soils using the MRA technique. They concluded C, total N, and soil moisture can be predicted for Austrasoils. Dalal and Henry (1986) pointed out that organic also been predicted by using the NIRA procedure in Organic matter and its compounds (C and N) have any pretreatment.

WYTERIALS AND METHODS

properties selected were clay content, SSA, CEC, HIGF,

estimating the agricultural productivity of soils. The

because of their importance in soil classification and

OM, and CaCO₃ content.

Soil Sampling

carried out using the fine soil samples (<0.355 mm). sieve. All chemical and spectroscopic determinations were (quantitatively) by agate mortar to pass through a <0.35-mm through a <2-mm sieve. Subsamples were further ground \approx 1 m². The soils were air dried and gently crushed to pass the Ao horizon of the soils (upper 5 cm) within an area of of Israel. The samples ($\approx 5-10 \text{ kg}$) were collected mostly from soils were selected to cover the arid and semiarid climate zone Ninety-one soil samples that represent 12 groups of Israeli

Chemical Analyses

to assure accuracy. tions (except of CLAY) consisted of three or more replications gasometric method according to Nelson (1986). All determinaaccording to Ben-Dor and Banin (1989), and CaCO3 by the according to Gardner (1986), OM by a loss-on-ignition method measurements before and after heating to 105°C for 24 h soil surface according to Thomas (1986), HIGF by gravimetric saturation and subsequent displacement of Na cations onto the adsorption (Rathner-Zohar et al., 1983), CEC by quantitative and Bauder, 1986), SSA by ethylene glycol monoethyl ether Clay content was obtained by the hydrometer method (Gee

BEN-DOR & BANIN: RAPID METHOD TO EVALUATE SOIL PROPERTIES

of smectite minerals by using the NIRA strategy without any pretreatment.

Organic matter and its compounds (C and N) have also been predicted by using the NIRA procedure in soils. Dalal and Henry (1986) pointed out that organic C, total N, and soil moisture can be predicted for Australian soils using the NIRA technique. They concluded that the NIRA technique can be used as a routine testing method if further consideration is given to the instrumentation and the data handling. Morra et al. (1991) studied the NIRA capability to predict organic C and N in a relatively homogenous soil group (12 soils with their chemically treated subsets). They concluded that the method is very promising for the prediction of these constituents and feel, also, that the method is very promising for soil applications. Recently, Ben-Dor and Banin (1994, unpublished data) were able to show that the NIRA methodology can be used to predict some spectral featureless constituents in soils via an intercorrelation with soil properties that are spectrally active in the NIR region.

Although the NIRA method was found to be a very promising tool in many other disciplines as well, and termed a "giant" method (Davies, 1987), it has not received much attention in the soil science field. The purpose of this study was to examine the capability of the NIRA technique to simultaneously measure various spectral feature properties of soil from the arid and semiarid regions of Israel. The properties were selected because of their importance in soil classification and estimating the agricultural productivity of soils. The properties selected were clay content, SSA, CEC, HIGF, OM, and CaCO₃ content.

MATERIALS AND METHODS

Soil Sampling

Ninety-one soil samples that represent 12 groups of Israeli soils were selected to cover the arid and semiarid climate zone of Israel. The samples ($\approx 5-10 \text{ kg}$) were collected mostly from the A_0 horizon of the soils (upper 5 cm) within an area of $\approx 1 \text{ m}^2$. The soils were air dried and gently crushed to pass through a <2-mm sieve. Subsamples were further ground (quantitatively) by agate mortar to pass through a <0.355-mm sieve. All chemical and spectroscopic determinations were carried out using the fine soil samples (<0.355 mm).

Chemical Analyses

Clay content was obtained by the hydrometer method (Gee and Bauder, 1986), SSA by ethylene glycol monoethyl ether adsorption (Rathner-Zohar et al., 1983), CEC by quantitative saturation and subsequent displacement of Na cations onto the soil surface according to Thomas (1986), HIGF by gravimetric measurements before and after heating to 105°C for 24 h according to Gardner (1986), OM by a loss-on-ignition method according to Ben-Dor and Banin (1989), and CaCO₃ by the gasometric method according to Nelson (1986). All determinations (except of CLAY) consisted of three or more replications to assure accuracy.

Spectral Measurements and Compression

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Spectral Measurements

The spectral reflectances of the soil powder were recorded by an Alpha Centauri FTIR spectrophotometer (Mattson Co., Madison, WI) optimized to the NIR (1-2.5 µm) region. It has a high optical resolution of 1 cm⁻¹ throughout the spectral region and has the capability of producing up to 6000 spectral bands. For the current measurements, we used a constant spectral resolution value of 8 cm⁻¹, which produced 3113 spectral points across the 1- to 2.5-um spectral region. In the wavelength mode, this resulted in a variation of the spectral resolution between 0.8 nm for the lower wavelength (1 µm) and 1.8 nm for the higher wavelength (2.5 µm). Diffuse reflectance was measured by a praying mantis bi-directional diffuse reflectance attachment (DEA-dimensional model, Harrick Co., Ossining, NY). The soil powders (<0.355 mm) were packed into a stainless steel sample holder, using a standard sample preparation procedure. The soil reflectance was reported relative to a BaSO₄ standard spectrum, which was recorded under similar spectroscopic and geometric conditions.

Spectral Compression

The original spectrum consisting of 3113 spectral bands was compressed computationally to a new spectrum containing a smaller number of bands. The compressing procedure was carried out as follows. The original spectrum (of each sample) was divided into G bands ($G=25,\ 30,\ 63,\ 310$). Each of the new band spectrum consisted of 3113/G original bands and their paired reflectance values. The wavelength-reflectance value of each new band was obtained by using a simple average calculation across the original reflectance-wavelength bands.

Spectral Analysis

The NIRA methodology requires two stages: (i) the calibration stage where the prediction equation is developed and (ii) the validation stage, where the previous stage is validated. Because NIRA is basically an empirical method, the validation stage is extremely critical. The complete NIRA procedure requires both calibration and validation stages to analyze unknown samples.

Calibration Stage

This procedure consisted of a subgroup that was selected directly from the 91 soil samples. A simple linear regression procedure between the concentration of a given constituent and the spectral response (reflectance [R], absorption $[A = \log(1/R)]$) or their derivatives [R',A',A'']) of every band was run. Twenty-five bands (six for the G = 25 compressed bands) and their corresponding wavelengths providing the highest coefficient of correlation were further selected for examination under a MRA procedure. This procedure was run for each of the spectral parameters (R, A), or their derivatives) and for each of the MRA stages. The result, a multiterm equation, was used to determine the concentration of unknown validated samples in the validation stage.

Validation Stage

Unknown samples that were not used in the calibration process were used to validate the calibration equation produced in Stage 1. For that purpose, the spectra of all the validation samples were mathematically manipulated exactly as were

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the spectra that provided the prediction equation. Then the concentration of each constituent was calculated using the corresponding prediction equation produced in Stage 1. The calculated results (predicted) were compared with the chemical results (measured). This stage was run for each constituent until a relatively high prediction performance was obtained. At that point, the corresponding calibration equation was declared the preferred equation for predicting samples from the calibration and validation stages.

Statistical Analysis

The MRA procedure selects a best multiple correlation equation between a constituent concentration C_p in a given sample and the selected spectral parameters as follows:

$$C_p = b_0 + b_1 L_1 + b_2 L_2 + b_3 L_3 + \dots + b_{\lambda} L_{\lambda}$$
 [1]

where b_0 is an intercept, b_1 , b_2 ... b_{λ} are weighting factors for the spectra readings in various selected wavelengths 1 to n, L_1 , L_2 , ..., L_n are the values of the spectral parameters at wavelengths 1, 2, ..., λ and could be either reflectance data (R), absorption data (A), or their derivatives (first R', A', or second A''). Predicted values of the constituent concentrations were calculated using Eq. [1] and the SEC was then calculated according to Davies and Grant (1987) as follows:

SEC =
$$\sqrt{\frac{\sum_{i=1}^{N_c} (C_m - C_p)^2}{N_c - n - 1}}$$
 [2]

where C_m is the value measured by the chemical analysis, C_p is the predicted value on the basis of the spectral analysis, N_c is the number of the samples in the calibration stage, and n is the number of terms in the prediction equation.

The calibration Eq. [1] was used to predict the constituent concentration in another set of soil samples not involved in the calibration stage (validation stage). The SEP was then calculated as follows:

SEP =
$$\sqrt{\frac{\sum_{i=1}^{N_p} (C_m - C_p)^2}{N_p - 1}}$$
 [3]

where N_p is the total number of tested samples in this stage. A bias test, adopted from Miller and Miller (1988), was used to examine the regression line $(C_m = aC_p + b)$ of the validation results. It uses three null hypotheses to reject or accept the regression line as a 1:1 line. The assumptions of the null hypotheses are (i) the slope of the regression line (a) is unity, (ii) the intercept of the regression line (b) is zero, and (iii) the regression coefficient (r^2) is unity.

To allow better comparison with the SEP values, the AE of the chemical analysis was calculated as follows:

AE =
$$\sqrt{\frac{\sum_{i=1}^{91} \sum_{j=1}^{N_t} (X_{ij} - C_{mi})^2}{N_t - 1}}$$
 [4]

Where X_{ij} is the direct chemical measurement of Sample *i* in Replication *j*, C_{mi} is the mean of Sample *i*, and N_i is the total number of the entire replications for a given property.

RESULTS AND DISCUSSION

Reflectance spectra of 11 soil samples that represent most of the soil groups within the examined population are given in Fig. 1. It is apparent that all of the spectra consist of spectral information that can be easily attributed to some of the soil compounds. The most likely

components in the NIR region to have strong absorption are the OH groups in both the adsorbed water (at ≈ 1.4 and 1.9 μ m) and the crystal lattice water (at \approx 1.45 and 2.2 μm; Hunt and Salisbury, 1970). Also, the CO₃ in calcite mineral (and hence in calcite-enriched soils) is very active in the NIR region (major peak at ≈ 2.33 µm; Gaffey, 1986). Table 1 provides some of the analytical data from the 11 soils for each of the six properties. A rough correlation occurs between the absorption intensity at ≈ 1.4 , 1.9, and 2.2 μ m and the Clay content, SSA, and HIGF content (e.g., high: A-4, H-2, P-2; low: C-2, W-1, and S-5) as well as between the absorption intensity at ≈ 2.3 µm and the CaCO₃ content (e.g., high: C-2, W-1, O-2, S-5; low: E-1, A-4, W-1). In some soils, some absorption features that may be assigned to Fe oxides can be observed at $\approx 1.05 \, \mu m$ (e.g., B-1, K-2, P-2, and S-5; Hunt and Salisbury, 1970). The above discussion is limited only to the 11 representative soil samples and does not necessarily apply to other soil samples. For a broader point of view and for more adequate conclusions, the whole soil population must be systematically examined (chemically and spectrally). Judging from the chemical range of the whole population (Table 1), it can be concluded that the 11 soil samples are a good representative of the entire population. However, we further selected an additional soil sample (B-7) that accurately represents the entire population (Table 1) on which to present the spectral compression process.

Figure 2 presents the compressed spectra of Sample B-7. It is apparent that some spectral features are weakened by the compression process, decreasing the number of spectral bands from 3113 to 25. Nonetheless, three essential absorption bands (which appear in the 11 representative soil spectra as well) are evident throughout all the compressed spectra (at ≈ 1.4 , 1.9, and 2.2 μ m). These features are attributed to the OH groups of soil moisture (1.4 and 1.9 μ m) and to the crystal lattice in soil clay minerals (2.2 μ m).

Table 2 presents a matrix of the linear coefficient correlation between all the examined soil properties. Three essential groups can be observed: Group I, which consists of clay content, SSA, CEC, and HIGF (all closely correlated among themselves with r > 0.643); Group II, which consists of OM only (moderately correlates with Group I; 0.412 < r < 0.665); and Group III, which consists of CaCO₃ content (does not correlate with any of the other properties). Properties in Group I are all related to the clay content and its SSA. Banin and Amiel (1970) pointed out that in Israeli soils, SSA is for the most part contributed by smectite clay minerals, which constitute some 70% of the clay portion of the soil and which affect the adsorption properties (CEC and HIGF). Organic matter (Group II) is also moderately related to the adsorption properties of soil (SSA, CEC, and HIGF), either directly or indirectly throughout the correlation of clay content. Carbonates (Group III) are not correlated with any of the other five soil properties studied here.

An important prerequisite for successful application of the NIRA approach for analysis of a given constituent is that it has spectral absorption features in the NIR region

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values of a representative soil sample (B-7) that represents these 11 soils and the chemical range of each property within the whole Table 1. The analytical values (measured) of 11 representative soils within the whole population examined. Also given are the chemical

<i>L-</i> 8	16.24	3.90£	51.43	0.3	94.€	87.21
Ksnget	4.1-65.3	10.9-425.3	1.4-62.1	6,111-02,0	62.61-60.0	€. <i>₽</i> 7-0
ş- <u>s</u>	9·L	38.5	Z.T	LI.I	20.1	18.2
Z-d	6'6\$	7.822	\$.T\$.	67'7	61.1	2.22
K-2	38,9	116.2	14.8	3.19	78.2	6.82
7-0	24.6	£.971	8.£2	69.€	2.30	£ 17L
I-W	7.21	0.18	6.01	1.34	78.0	1'91
1-1	9.08	p.68I	31.4	11.12	2,42	9.8£
₹-H	2,13	425,3	5.12	10.14	₽£.2	2.81
≯- V	9,84	2.855	£.09	11.63	29.2	4.8
i-a	4.65	8.961	19.25	89.4	16.4	6°IÞ
ź-ɔ̈	1.01	0.08	12.89	۵۲.۲	1.02	£.04
E-1	13.9	48.5	4.8	1.12	17.1	8.1
, _	%	. 8 _{− 1}	cusof kB_{-1}		%	
aldmes	content	ASS	CEC	HIGE	МО	content
Soil	Clay					CaCO,

† Chemical range of the whole soil population (n = 91).

contain many and varied functional groups (Bowers and chemical complexity of organic matter in soils. They modes can occur. This situation occurs because of the wavelength because many combinations and overtone to specifically assign an absorption mode to a particular throughout the entire NIR region. However, it is difficult In Group II, organic matter is spectroscopically active using the NIRA strategy (Ben-Dor and Banin, 1990b). lated with the chemical composition of smeetite minerals These bands have been found to be quantitatively corre-.(0791, vrudsiles and shunt and Salisbury, 1970). bands and to OH in crystal lattice at 1.3- to 1.45-µm

extracting hidden information from the diffuse soil recated analytical method such as NIRA can be used for cal range (0-2.6% of C). This suggests that a sophistiwere able to predict the OM content despite a low chemiless, by using the MIRA strategy, Dalal and Henry (1986) the OM functional groups in the soil mixture. Nevertheand carbonates) and because of low absorption rates of components (e.g., hygroscopic and crystal lattice water This is because of a strong mask provided by other soil groups of organic matter (Baumgardner et al., 1970). tion of the absorption features related to the functional of soils below 2% does not permit simple spectral detec-Hanks, 1965). Furthermore, the organic matter content

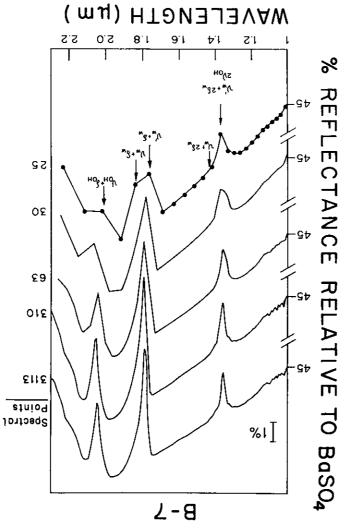
features in the NIR, corresponding to CO3 radicals at In Group III, carbonates have significant absorbance flectance spectrum.

cal values $(n = 91).\dagger$ of the study soils. The correlation was obtained using the chemi-Table 2. Linear coefficient of correlation (r) between the properties

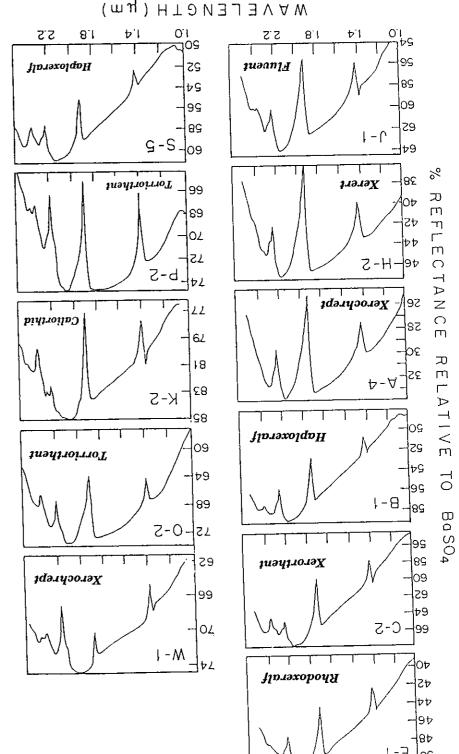
Gronp III	П qиотД		I quo	1Đ		
CaCO	МО	HIGE	CEC	VSS	Clay	
291.0	*2I4.0	**£79 0	** <i>L9L</i> `0	** \$ 28.0	Ţ	Clay
8£0.0 —	**I12.0	** p 08.0	**£26.0	I		VSS
070.0 -	** \$99 °0	**6LL'0	Ţ			CEC
£90.0	*S72.0	I				HICE
680.0	I					WO
Ţ						CaCO

⁼ hygroscopic moisture; OM = organic matter. *, ** Significant at the 0.05 and 0.01 levels of significance, respectively \dagger SSA = specific surface area; CEC = cation-exchange capacity; HIGF

are assigned to OH in free water at 1.4- and 1.9-µm Absorption bands in the MIR region for phyllosilicates



measured spectrum (G = 3113). \mathfrak{S} , was varied by mathematical manipulations of the originally a representative soil sample (B-7). The number of spectral bands, Fig. 2. The effect of compressing the original reflectance spectrum of



to the USDA classification system. Fig. 1. Reflectance spectra of 11 representative soil samples. Each of the soils corresponds to a different soil group and is classified according

combinations and overtones of the OH fundamentals. active throughout the MIR region because of several certain phyllosilicates. The OH groups are spectrally mineral surface. The amount of OH is rather specific to of both the crystal lattice and water adsorbed on the

discussed below. (Murray, 1988). All three groups satisfy this condition, as

in soil. Hydroxyl groups in all phyllosilicates are part face properties) are highly correlated to the clay minerals In Group I, clay content, SSA, CEC, and HIGF (surBEN-DOR & BANIN: RAPID METHOD TO EVALUATE SOIL PROPERTIES

Fig. 1. Reflectance spectra of 11 representative soil samples. Each of the soils corresponds to a different soil group and is classified according to the USDA classification system.

WAVELENGTH (μm)

2.2

1.8

(Murray, 1988). All three groups satisfy this condition, as discussed below.

In Group I, clay content, SSA, CEC, and HIGF (surface properties) are highly correlated to the clay minerals in soil. Hydroxyl groups in all phyllosilicates are part

of both the crystal lattice and water adsorbed on the mineral surface. The amount of OH is rather specific to certain phyllosilicates. The OH groups are spectrally active throughout the NIR region because of several combinations and overtones of the OH fundamentals.

2.2

1.8

368

367

Table 1. The analytical values (measured) of 11 representative soils within the whole population examined. Also given are the chemical values of a representative soil sample (B-7) that represents these 11 soils and the chemical range of each property within the whole population.†

Soil sample	Clay content	SSA	CEC	HIGF	ОМ	CaCO ₃ content
	%	m² g-1	cmol _c kg ⁻¹		% ————————————————————————————————————	
E-1	13.9	48.5	8.4	1.12	1.27	1.8
C-2	10.1	80.0	12.89	2.70	1.02	40.3
B-1	39.4	196.8	35.61	4.68	4.91	41.9
A-4	46.6	338.2	60.3	11.63	5.65	8.4
H-2	61.2	425.3	51.4	10.14	5.34	18.5
J-1	50.6	189.4	31.4	11.12	2.42	38.9
W-1	12.7	81.0	10.9	1.34	0.87	16.1
0-2	24.6	176.3	23.8	3.69	2.30	74.3
K-2	38.9	116.2	14.8	3.19	2.87	58.9
P-2	59.9	228.7	27.5	4.49	1.19	55.2
S-5	7.6	38.5	7.2	1.17	1.05	18.2
Range‡	4.1-65.3	10.9-425.3	1.4-62.1	0.20-11.63	0.09-13.23	0-74.3
B-7	45.91	306.2	51.43	6.0	3.46	12.78

† SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter. ‡ Chemical range of the whole soil population (n = 91).

Absorption bands in the NIR region for phyllosilicates are assigned to OH in free water at 1.4- and 1.9-um

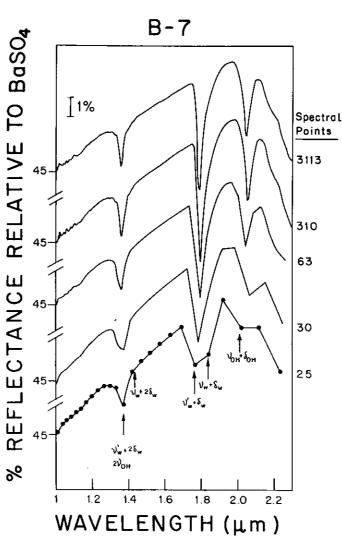


Fig. 2. The effect of compressing the original reflectance spectrum of a representative soil sample (B-7). The number of spectral bands, G, was varied by mathematical manipulations of the originally measured spectrum (G = 3113).

bands and to OH in crystal lattice at 1.3- to 1.45-µm and 2.1- to 2.35-µm bands (Hunt and Salisbury, 1970). These bands have been found to be quantitatively correlated with the chemical composition of smectite minerals using the NIRA strategy (Ben-Dor and Banin, 1990b).

In Group II, organic matter is spectroscopically active throughout the entire NIR region. However, it is difficult to specifically assign an absorption mode to a particular wavelength because many combinations and overtone modes can occur. This situation occurs because of the chemical complexity of organic matter in soils. They contain many and varied functional groups (Bowers and Hanks, 1965). Furthermore, the organic matter content of soils below 2% does not permit simple spectral detection of the absorption features related to the functional groups of organic matter (Baumgardner et al., 1970). This is because of a strong mask provided by other soil components (e.g., hygroscopic and crystal lattice water and carbonates) and because of low absorption rates of the OM functional groups in the soil mixture. Nevertheless, by using the NIRA strategy, Dalal and Henry (1986) were able to predict the OM content despite a low chemical range (0-2.6% of C). This suggests that a sophisticated analytical method such as NIRA can be used for extracting hidden information from the diffuse soil reflectance spectrum.

In Group III, carbonates have significant absorbance features in the NIR, corresponding to CO₃ radicals at

Table 2. Linear coefficient of correlation (r) between the properties of the study soils. The correlation was obtained using the chemical values (n = 91).

		Gı	Group I			Group III	
	Clay SSA		CEC	HIGF	ОМ	CaCO ₃	
Clay	1	0.824**	0.767**	0.643**	0.412*	0.162	
SSA		1	0.923**	0.804**	0.511**	-0.038	
CEC			1	0.779**	0.665**	-0.070	
HIGF				1	0.575*	0.063	
OM					1	0.059	
CaCO ₃						1	

^{*, **} Significant at the 0.05 and 0.01 levels of significance, respectively.

† SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter.

Table 5. The optimal equations for predicting each of the soil constituents. Also given are the suggested wavelength assignments.

validation sets and their corresponding chemical range. Also given is the number of samples in the calibration and

apacity; HIO	ation-exchange	o =	DEO ; ceou	surface a	SSA = specific
£.88-0	£.47-0	Lt	77	III	CaCO3, %
77.01-60.0	£2.£1-60.0	25	68	II	% 'WO
12.9-95.0	69.11-02.0	99	35	Ţ	HICE' %
1.32-62.1	1.4-60.3	99	35	I	CEC, cmol, kg-1
10.8-369.0	£.254-9.01	9\$	32	I	SSA, m² g⁻¹
£. č 3-£.3	4.1-61.2	99	32	I	Clay, %
range	range	§^N	‡	Group	Property†

 $N_{\rm v} = N_{\rm u}$ where of samples in the validation stage.

sentative calibration set that is chemically matched with of prediction of the CaCO3 content of soils is improved. calcite minerals are enhanced and the MIRA capability by preheating the soil to 600°C, the CO3 groups of lattice and hygroscopic mineral sources) are diminished and Banin (1990a) pointed out that it masking OHs (from 1.6, 1.7, 2.2, 2.3, and 2.5 µm (Gaffey, 1986). Ben-Dor

consistency occurs between the two sets in all of the each set. From Table 3, it can be seen that a positive and the validation sets and the number of samples in Table 3 gives the chemical range of both the calibration numbers) for both the calibration and the validation sets. testing group contained different samples (both types and groups were employed for the MIRA examination. Each different groups of properties, three independent testing (Norris and Williams, 1984). Because we identified three the validation set and with a large number of samples

set were selected to indicate the optimal data manipulation criteria of lowest SEP and highest r2 of the validation both the expanded and the compressed spectra. The data manipulation procedures (R, R', A, A', and A") in sets for each soil property group and changed only the and identity of samples in both calibration and validation tions to a manageable set, we kept constant the number lation (Murray, 1988). To keep the number of combinapriori information is available regarding the best manipudata manipulations to obtain optimal prediction. No a (actually requires) many combinations of samples and Basically, the MIRA approach is empirical, allows examined properties.

bias of the validation results were inspected to better for obtaining the best analytical performance. Also, the

Statistical parameters from the calibration, validation, (manipulation and wavelength assignments). estimate the prediction power of the selected routine Table 3. Categorizing of the soil properties into three groups.

HOLH : Wickers:	a sanedaxs-noiti	න = ე	BD : E	ere ezetru	is affiaens = AZZ
€.89-0	£.47-0	Ltr	77	III	% (¿OO£
07.01-60.0	£2.£1-60.0	25	68	II	% 'We
12.9-95.0	6.11-02.0	99	38	Ţ	IIGE' %
1.23-5.1	1.4-60.3	95	38	I	EC, emol, kg ⁻¹
0.698-8.01	£.254-9.01	9\$	32	I	24° m, 8 ₋₁
€.29-€.9	4.1-61.2	95	32	1	% , yal
Validation range	Calibration range	§^N	‡'N	Group	toperty†

hygroscopic moisture; OM = organic matter.

better enhance spectral signals that relate to the examined bands into a new (low-resolution) spectral band may spectra. Averaging several raw (high-resolution) spectral recommended for better utilization of the soil reflectance more, in some cases, low spectral resolution is strongly The NIRA technique requires the selection of a reprelimitation for predicting these soil properties. Furtherings suggest that spectral resolution is not necessarily a manipulation and 25 to 3113 spectral bands. These findperformance of the CaCO3 was obtained by using the R was obtained between any given resolution. The highest whereas for the CaCO3 property, no significant difference mance using 30 spectral bands and R' manipulation, manipulation. The OM property shows the best performance was obtained using 63 spectral bands and A'

of a highly compressed spectrum loses its natural peaks leads to oversaturation by absorption of water. The shape extinction coefficient of free water molecules (HIGF) CEC. One possible explanation for this is that the high wavelengths in the equations for clay content, SSA, and selected by NIRA for HIGF are quite different from the bands and A' manipulation. Moreover, the wavelengths for HIGF (part of Group I) occurred with 25 spectral chemical correlation discussed above. The best prediction observations support the group selection based on the with OH in both crystal lattice and surface water. These optimal performance. The wavelengths are associated and A' spectra) and selected wavelengths resulted in the CEC, a similar mathematical manipulation (63 bands for each of the properties. For clay content, SSA, and Table 5 shows the best prediction equations determined constituent.

Group I (clay content, CEC, and SSA), optimal perfor-

bands) using A" manipulation. In the other properties of

obtained within the low spectral resolution (25 spectral

with one property (HIGF), optimal performance was

necessarily yield the best validation results. Moreover,

the high-resolution spectra (3113 spectral bands) do not

given in Table 4. It was found that for all soil properties,

and analytical stages of the optimal combinations are

correspond to both humic substances (and their compo-In Group II (OM), the spectral assignments might which is closely related to water content. and hence apparently provides peak undersaturation,

951.0

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Analytical

old one. It statistically examines the difference between to examine a new analytical method as it relates to an and Miller (1988) test. This test was originally designed the validation sets was performed by using the Miller outliers. An examination to evaluate possible bias within compensate for reducing the sample sets by omitting 0.126-0.175, Table 4), no recalculations were done to detection for rapid laboratory measurements (CPV = for all six properties was within reasonable limits of tion accuracy. However, because the prediction accuracy from the calibration-validation set may increase predicfew outliers. Murray (1988) noted that removing outliers of the points fell in the vicinity of the 1:1 line with a of the six examined properties. For all properties, most sured) at the calibration and validation stages for each Figure 3 shows plots of Cp (predicted) vs. Cm (mea-

generally cause soils to be more reflective in the MR

any specific absorption band. Large amounts of CaCO3

within the spectrum continuum (albedo) rather than in

of CaCO3 in this case is based largely on the position

SEP. This leads us to the conclusion that the prediction

the compressed spectra resulted in practically the same

obtained using the reflectance (R), and analyses of all

the spectrum. Furthermore, the optimal prediction was

hm) are typically located in nonabsorption regions of

bands. The two selected wavelengths (1.6473 and 1.4825

the calibration are not those characteristic of carbonate

nents) and surface properties (as obtained from the chemi-

30 ¥,

₹9

spectral points

Mathematics

† SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter.

1,01

4.87

2.892

Constant

In Group III (CaCO3), the wavelengths entered into

(as in the visible spectrum).

cal correlation in Table 2).

MO

HIGE

CEC

VSS

Clay

075

the functional properties are more likely similar to fres similar to humic substances, whereas in the second group group, the functional properties of OM are more likel representing less decomposed OM soils. In the fire (ii) a group of soils that consists of 4 to 14% OM OM, representing greatly decomposed OM soils, an tion stages: (i) a group of soils that consists of 0 to 49 two essential groups with regard to the OM decompos We believe that the soil population in our study represent any constituent is an inherent limitation of the procedure closed sample population for the MIRA procedure for pointed out that the necessity of using a well-defined or

group was used (Morra et al., 1991). Morra et al. (1991

C) was found to be possible only if a homogenous so

organic C and N contents of organic matter (0-10% of

of OM and HIGF properties. The MIRA prediction of

that further research is needed to improve the predictio

therefore, did hold some bias. These results may sugges

were significantly different from the ideal 1:1 line and

The regression line parameter a for OM and HIG

the 0.01 significance level) and therefore held no bias

level (clay content, CEC, and CaCO $_3$ even matched $_3$

o significantly match the 1:1 line at the 0.05 significanc

only clay content, SSA, CEC, and CaCO3 were foun

level. However, based on the test of a and b parameters

not significantly differ from 1 at the 0.05 significanc

statistical significance. The r2 values for all properties d

b, and r^2 (taken from the validation stage) along with their

regression line $(C_{\rm p}=aC_{\rm m}+b)$ and the parameters a

the regression and ideal 1:1 lines. Table 6 presents th

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91/06"1 £160°7

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EEEE.S

Wavelength (A)

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70.0

02.0 -

02.0

\$1.0 -

PE'0 -

61.0 -

8.72-

4.46 —

8.16

7.89 -

Z.EEI

p.281 -

0.802

9.164-

£.8£\$1 -

434.0

1,541 -

2,102 -

0.724

9.922

£.6

8.25

L'ZSI

6.£8

(vg) jubioutieos

Weighting

p.78

24.3

No assignments involved

v. + 26. water

26л-он + 26л-он 26л-он + 26л-он 26л-он + 6, 26л-он 26л-он

но-8м82 + но-8м0

Suggested

Zu., water

oc∙n byeuoן

OC-N- SIMMES

in the validation stage; r* = Linear coefficient of correlation; SEP = Standard error of performance; N_a = Number of samples in the analytical stage; CPV = Coefficient of prediction variation (SEP/[Max-Min]); AE = Analytical error; CAV = Coefficient of analytical variation (AE/[Max-Min]).

\$\frac{1}{2}\$SA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter. 1 N° = Number of samples in the calibration stage; R' = Multiple coefficient of correlation; SEC = Standard error of calibration; N' = Number of samples

7L'9

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SEC

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91.0

K,

35

35

Table 4. Statistical parameters of the calibration, validation, and analytical stages.†

٤9

Bands

moiteluqineM

HICE

CEC

VSS

Ргорену‡

 $[\]ddagger N_c = Number$ of samples in the calibration stage.

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Table 3. Categorizing of the soil properties into three groups.

Also given is the number of samples in the calibration and validation sets and their corresponding chemical range.

Group	N _c ‡	N _v §	Calibration range	Validation range
I	35	56	4.1-61.2	6.3-65.3
I	35	56	10.9-425.3	10.8-369.0
I	35	56	1.4-60.3	1.3-62.1
I	35	56	0.20-11.63	0.39-9.21
II	39	52	0.09-13.23	0.09-10.70
III	22	47	0-74.3	0-68.3
	I I I I II	I 35 I 35 I 35 I 35 II 39	I 35 56 I 35 56 I 35 56 I 35 56 II 39 52	Group N _c ‡ N _v § range I 35 56 4.1-61.2 I 35 56 10.9-425.3 I 35 56 1.4-60.3 I 35 56 0.20-11.63 II 39 52 0.09-13.23

[†] SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter.

1.6, 1.7, 2.2, 2.3, and 2.5 μ m (Gaffey, 1986). Ben-Dor and Banin (1990a) pointed out that if masking OHs (from lattice and hygroscopic mineral sources) are diminished by preheating the soil to 600° C, the CO₃ groups of calcite minerals are enhanced and the NIRA capability of prediction of the CaCO₃ content of soils is improved.

The NIRA technique requires the selection of a representative calibration set that is chemically matched with the validation set and with a large number of samples (Norris and Williams, 1984). Because we identified three different groups of properties, three independent testing groups were employed for the NIRA examination. Each testing group contained different samples (both types and numbers) for both the calibration and the validation sets. Table 3 gives the chemical range of both the calibration and the validation sets and the number of samples in each set. From Table 3, it can be seen that a positive consistency occurs between the two sets in all of the examined properties.

Basically, the NIRA approach is empirical, allows (actually requires) many combinations of samples and data manipulations to obtain optimal prediction. No a priori information is available regarding the best manipulation (Murray, 1988). To keep the number of combinations to a manageable set, we kept constant the number and identity of samples in both calibration and validation sets for each soil property group and changed only the data manipulation procedures (R, R', A, A', and A'') in both the expanded and the compressed spectra. The criteria of lowest SEP and highest r^2 of the validation set were selected to indicate the optimal data manipulation for obtaining the best analytical performance. Also, the bias of the validation results were inspected to better

estimate the prediction power of the selected routine (manipulation and wavelength assignments).

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Statistical parameters from the calibration, validation, and analytical stages of the optimal combinations are given in Table 4. It was found that for all soil properties, the high-resolution spectra (3113 spectral bands) do not necessarily yield the best validation results. Moreover, with one property (HIGF), optimal performance was obtained within the low spectral resolution (25 spectral bands) using A" manipulation. In the other properties of Group I (clay content, CEC, and SSA), optimal performance was obtained using 63 spectral bands and A' manipulation. The OM property shows the best performance using 30 spectral bands and R' manipulation, whereas for the CaCO₃ property, no significant difference was obtained between any given resolution. The highest performance of the CaCO₃ was obtained by using the R manipulation and 25 to 3113 spectral bands. These findings suggest that spectral resolution is not necessarily a limitation for predicting these soil properties. Furthermore, in some cases, low spectral resolution is strongly recommended for better utilization of the soil reflectance spectra. Averaging several raw (high-resolution) spectral bands into a new (low-resolution) spectral band may better enhance spectral signals that relate to the examined constituent.

Table 5 shows the best prediction equations determined for each of the properties. For clay content, SSA, and CEC, a similar mathematical manipulation (63 bands and A' spectra) and selected wavelengths resulted in the optimal performance. The wavelengths are associated with OH in both crystal lattice and surface water. These observations support the group selection based on the chemical correlation discussed above. The best prediction for HIGF (part of Group I) occurred with 25 spectral bands and A' manipulation. Moreover, the wavelengths selected by NIRA for HIGF are quite different from the wavelengths in the equations for clay content, SSA, and CEC. One possible explanation for this is that the high extinction coefficient of free water molecules (HIGF) leads to oversaturation by absorption of water. The shape of a highly compressed spectrum loses its natural peaks and hence apparently provides peak undersaturation, which is closely related to water content.

In Group II (OM), the spectral assignments might correspond to both humic substances (and their compo-

Table 4. Statistical parameters of the calibration, validation, and analytical stages.†

	Spectra		Calibration			Validation				Analytical		
Property‡	Manipulation	Bands	N _c	R^2	SEC	$\overline{N_{v}}$	r²	SEP	CPV	N _a	AE	CAV
Clay	Α'	63	35	0.76	8.6	56	0.56	10.3	0.174	91	48	0.065
SSA	A'	63	35	0.84	37.7	56	0.70	50.2	0.140	91	4.0	0.010
CEC	A'	63	35	0.82	6.72	56	0.64	8.46	0.139	91	1.2	0.020
HIGF	\overline{A}''	25	35	0.58	1.9	56	0.62	1.55	0.175	91	0.22	0.019
OM	R'	30	39	0.69	1.63	52	0.55	1.34	0.126	91	0.30	0.023
CaCO ₁	R	25-3113	22	0.70	12.9	47	0.69	11.6	0.169	91	1.3	0.017

[†] N_c = Number of samples in the calibration stage; R^2 = Multiple coefficient of correlation; SEC = Standard error of calibration; N_v = Number of samples in the validation stage; r^2 = Linear coefficient of correlation; SEP = Standard error of performance; N_s = Number of samples in the analytical stage; CPV = Coefficient of prediction variation (SEP/[Max-Min]); AE = Analytical error; CAV = Coefficient of analytical variation (AE/[Max-Min]). ‡ SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter. 8 Estimated value.

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Table 5. The optimal equations for predicting each of the soil constituents. Also given are the suggested wavelength assignments.

Property†	Mathematics spectral points	Constant (b_0)	Weighting coefficient (b_{λ})	Wavelength (λ)	Suggested assignment
				μm	<u>.</u>
Clay	A'	59.7	121.9	2,3333	$v_{Mg-OH} + 2\delta_{Mg-OH}$
	63		83.9	2.1857	$v_{Al-OH} + 2\delta_{Al-OH}$
	55		152.7	2.0973	$2v_{Al-OH} + 2\delta_{Al-OH}$
			35.8	1.9046	$v_w + \delta_w$
			9.3	1.8703	$v_w + \delta_w$
			226.6	1.4720	$v_w + 2\delta_w$
SSA	A'	268.2	457.0	2.3333	$v_{Mg-OH} + 2\delta_{Mg-OH}$
	A' 63		- 201.2	2.0973	$2v_{Al-OH} + 2\delta_{Al-OH}$
			- 143.1	1.9423	$v_w + \delta_w$
			434.0	1.8700	$v_w + \delta_w$
			- 1538.3	1.4033	$v_w + 2\delta_w$
			- 491.6	1.3560	2υ _{Al-OH}
CEC	A'	73.4	208.0	2.3333	$v_{Mg-OH} + 2\delta_{Mg-OH}$
	63		- 185.4	2.0973	$2v_{Al-OH} + 2\delta_{Al-OH}$
			87.4	2.0157	$2v_{Al-OH} + 2\delta_{Al-OH}$
			133.5	1.4313	$v_w + \delta_w$
			- 65.7	1.4119	2υ _{Fe-OH}
			94.8	1.3219	2υ _{Al-OH}
			- 34.4	1.0641	
HIGF	A'	5.1	24.3	2.3620	₽w
	25		-27.8	2.1202	$2v_{Al-OH} + 2\delta_{Al-OH}$
OM	R'	10.1	-0.19	2.3883	υ _{C-N'} amines
	30		- 0.34	2.0165	υ _{C-N′} phenol
			- 0.15	1.9410	$v_w + 2\delta_w$ water
			0.50	1.5849	υ _{COOH} amino acids
			- 0.20	1.4122	2υ _w water
			0.07	1.0429	
CaCO ₃	R	- 74.4	12.0	1.6473	No assignments
-	25-3113		- 10.6	1.4825	involved

† SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter.

nents) and surface properties (as obtained from the chemical correlation in Table 2).

In Group III (CaCO₃), the wavelengths entered into the calibration are not those characteristic of carbonate bands. The two selected wavelengths (1.6473 and 1.4825 µm) are typically located in nonabsorption regions of the spectrum. Furthermore, the optimal prediction was obtained using the reflectance (R), and analyses of all the compressed spectra resulted in practically the same SEP. This leads us to the conclusion that the prediction of CaCO₃ in this case is based largely on the position within the spectrum continuum (albedo) rather than in any specific absorption band. Large amounts of CaCO₃ generally cause soils to be more reflective in the NIR (as in the visible spectrum).

Figure 3 shows plots of C_p (predicted) vs. C_m (measured) at the calibration and validation stages for each of the six examined properties. For all properties, most of the points fell in the vicinity of the 1:1 line with a few outliers. Murray (1988) noted that removing outliers from the calibration-validation set may increase prediction accuracy. However, because the prediction accuracy for all six properties was within reasonable limits of detection for rapid laboratory measurements (CPV = 0.126-0.175, Table 4), no recalculations were doné to compensate for reducing the sample sets by omitting outliers. An examination to evaluate possible bias within the validation sets was performed by using the Miller and Miller (1988) test. This test was originally designed to examine a new analytical method as it relates to an old one. It statistically examines the difference between the regression and ideal 1:1 lines. Table 6 presents the regression line $(C_p = aC_m + b)$ and the parameters a, b, and r^2 (taken from the validation stage) along with their statistical significance. The r^2 values for all properties do not significantly differ from 1 at the 0.05 significance level. However, based on the test of a and b parameters, only clay content, SSA, CEC, and CaCO₃ were found to significantly match the 1:1 line at the 0.05 significance level (clay content, CEC, and CaCO3 even matched at the 0.01 significance level) and therefore held no bias. The regression line parameter a for OM and HIGF were significantly different from the ideal 1:1 line and, therefore, did hold some bias. These results may suggest that further research is needed to improve the prediction of OM and HIGF properties. The NIRA prediction of organic C and N contents of organic matter (0-10% of C) was found to be possible only if a homogenous soil group was used (Morra et al., 1991). Morra et al. (1991) pointed out that the necessity of using a well-defined or closed sample population for the NIRA procedure for any constituent is an inherent limitation of the procedure. We believe that the soil population in our study represents two essential groups with regard to the OM decomposition stages: (i) a group of soils that consists of 0 to 4% OM, representing greatly decomposed OM soils, and (ii) a group of soils that consists of 4 to 14% OM, representing less decomposed OM soils. In the first group, the functional properties of OM are more likely similar to humic substances, whereas in the second group, the functional properties are more likely similar to fresh litter and vegetation.

 $E_{\rm c} = N_{\rm c}$ Number of samples in the calibration stage.

 $[\]S N_v = \text{Number of samples in the validation stage}$

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.(1xs) o does not differ from 0 (see text). that \mathbf{r}^2 does not differ from unity, a does not differ from 1, six soil properties in the validation stage. Also significant is coefficient of correlation, a = slope, and b = the intercept) of Table 6. The regression parameters of the validation sets (r' =

q	v	L ₃	Property†
**96'S	**9L'0	*95.0	СІяу
*8.52	**18.0	∗ 69'0	ASS
**05.8	**89.0	* 1 *9'0	CEC
**66'l	95.0	* 2 9.0	HIGE
** <u>58.0</u>	99.0	*12.0	MO
**ZÞ.T	**87.0	*L9`0	CaCO,

 \dagger SSA = specific surface area; CEC = cation-exchange capacity; HIGF = hygroscopic moisture; OM = organic matter.

*, ** Significant at the 0.05 and 0.01 probability levels, respectively

field, soil survey, and remote sensing). evaluation of soil properties in the laboratory and in the

SUMMARY AND CONCLUSIONS

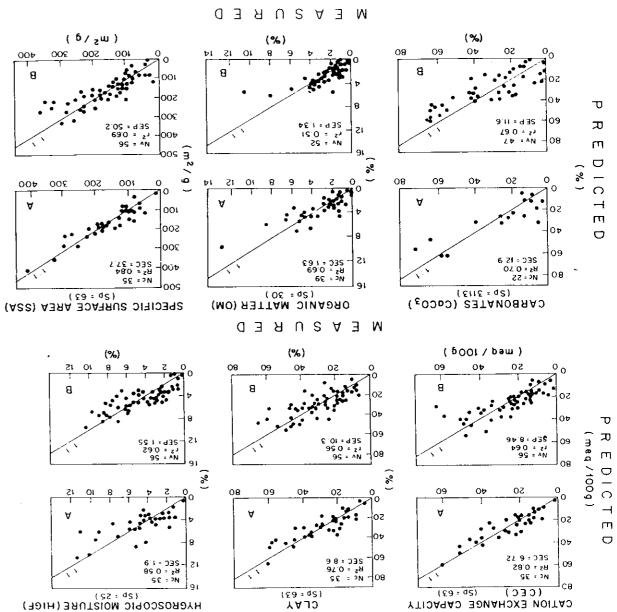
recommended. of the MIRA approach in the soil science field is strongly this study are likely to be good. Further study and use neous population, the NIRA achievements presented in large number of samples within a relatively heteroge-However, for rapid, nonrestrictive measurements of a will never replace the traditional analytical methods. lation. It should be remembered that the MIRA approach calibration samples for a given soil constituent and popuined. Results can be improved by selecting appropriate the method was required for each of the properties exam-MIRA measurement and analysis. Careful utilization of in the preparation and handling of these properties for of OM and HIGF, suggesting that great care is needed MIRA prediction. A slight bias occurs in the validation scopically explained, providing strong support for the lengths entered into the calibration equations are spectrospectra yields better validation results. Most of the wave-Compressing high-resolution spectra into low-resolution validation stage enable selection of the best manipulation. A low SEP and a high coefficient of correlation (r2) in the be examined to select the optimal prediction equation. sorbance, and derivation. Many manipulations should tions such as spectral compression, conversion to abspectral data by using several mathematical manipulaoriginal spectral data have to be converted into new soils is possible by using the NIRA technique. The of clay content, SSA, CEC, HIGF, OM, and CaCO3 in Simultaneous and rapid, nonrestrictive determination

organic matter and clay content to the multispectral radiance of Al-Abbas, H.H., P.H. Swain, and M.F. Baumgardner. 1972. Relating

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SEP = standard error of performance; SEC = standard error of calibration). prediction equation given in Table 5 (N. = number of samples in the calibration stage; N. = number of samples in the validation stage; Fig. 3. Plots of the predicted (Cp) vs. measured (Cn) values at the (A) calibration and (B) validation stages for each property, using the optimal

ments were acquired. HIGF content was performed and the spectral measurethat occurred between the time that the analysis of the result of change in atmosphere (such as relative humidity) The significant bias of the HIGF property may be a

for many applications in the soil science field (e.g., rapid NIRA approach as an applied and promising technique the MIRA method is quite sufficient. This may rank the and laboratory measurements, the accuracy obtained by and 0.126-0.175, respectively). However, for rapid field to the CPVs used in the validation stage, 0.010-0.065 lytical variation for the independent analytical analyses analytical measurements (compare the coefficients of anaindicates better detection and higher accuracy for the experimental errors of the independent analyses (Table 4) A comparison of the SEPs obtained by MIRA with the

correct OM composition) could yield more accurate reof the OM decomposition stage in soil (and hence the no bias analysis, it is speculated that careful consideration both low and high OM content. Because they performed Henry's (1986) results shows, apparently, some bias in was not reported). Careful examination of Dalal and C/N ratio, which may shed some light on this issue, tion stage in most of the soil samples was similar (the prediction was possible probably because the decomposiapproach within the low-OM range (0-2.6% of C). Their to predict soil organic C and N in soil using the NIRA As mentioned before, Dalal and Henry (1986) were able the two populations and, hence, significant bias occurs. chemical range (0.09-13.23%) is not consistent within As a result, the prediction of the OM across a wide

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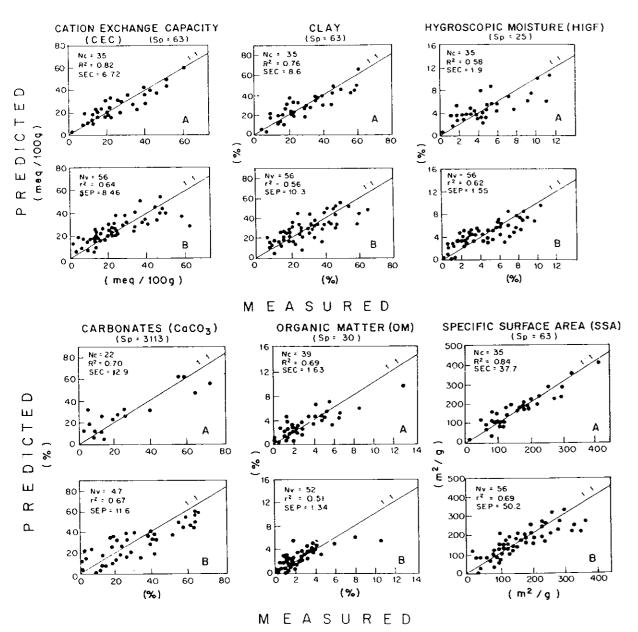


Fig. 3. Plots of the predicted (C_p) vs. measured (C_m) values at the (A) calibration and (B) validation stages for each property, using the optimal prediction equation given in Table 5 (N_c = number of samples in the calibration stage; N_v = number of samples in the validation stage; SEP = standard error of performance; SEC = standard error of calibration).

As a result, the prediction of the OM across a wide chemical range (0.09-13.23%) is not consistent within the two populations and, hence, significant bias occurs. As mentioned before, Dalal and Henry (1986) were able to predict soil organic C and N in soil using the NIRA approach within the low-OM range (0-2.6% of C). Their prediction was possible probably because the decomposition stage in most of the soil samples was similar (the C/N ratio, which may shed some light on this issue, was not reported). Careful examination of Dalal and Henry's (1986) results shows, apparently, some bias in both low and high OM content. Because they performed no bias analysis, it is speculated that careful consideration of the OM decomposition stage in soil (and hence the correct OM composition) could yield more accurate results

The significant bias of the HIGF property may be a result of change in atmosphere (such as relative humidity) that occurred between the time that the analysis of the HIGF content was performed and the spectral measurements were acquired.

A comparison of the SEPs obtained by NIRA with the experimental errors of the independent analyses (Table 4) indicates better detection and higher accuracy for the analytical measurements (compare the coefficients of analytical variation for the independent analytical analyses to the CPVs used in the validation stage, 0.010-0.065 and 0.126-0.175, respectively). However, for rapid field and laboratory measurements, the accuracy obtained by the NIRA method is quite sufficient. This may rank the NIRA approach as an applied and promising technique for many applications in the soil science field (e.g., rapid

Table 6. The regression parameters of the validation sets $(r^2 = \text{coefficient of correlation}, a = \text{slope}, \text{ and } b = \text{the intercept})$ of six soil properties in the validation stage. Also significant is that r^2 does not differ from unity, a does not differ from 1, and b does not differ from 0 (see text).

Property†	r ²	a	<u> </u>
Clay	0.56*	0.76**	5.96**
SSA	0.69*	0.81**	23.6*
CEC	0.64*	0.68**	8.50**
HIGF	0.62*	0.56	1.99**
OM	0.51*	0.66	0.82**
CaCO ₃	0.67*	0.78**	7.42**

- *, ** Significant at the 0.05 and 0.01 probability levels, respectively.
 † SSA = specific surface area; CEC = cation-exchange capacity; HIGF
- † SSA = specific surface area; CEC = cation-exchange capacity; = hygroscopic moisture; OM = organic matter.

evaluation of soil properties in the laboratory and in the field, soil survey, and remote sensing).

SUMMARY AND CONCLUSIONS

Simultaneous and rapid, nonrestrictive determination of clay content, SSA, CEC, HIGF, OM, and CaCO1 in soils is possible by using the NIRA technique. The original spectral data have to be converted into new spectral data by using several mathematical manipulations such as spectral compression, conversion to absorbance, and derivation. Many manipulations should be examined to select the optimal prediction equation. A low SEP and a high coefficient of correlation (r^2) in the validation stage enable selection of the best manipulation. Compressing high-resolution spectra into low-resolution spectra yields better validation results. Most of the wavelengths entered into the calibration equations are spectroscopically explained, providing strong support for the NIRA prediction. A slight bias occurs in the validation of OM and HIGF, suggesting that great care is needed in the preparation and handling of these properties for NIRA measurement and analysis. Careful utilization of the method was required for each of the properties examined. Results can be improved by selecting appropriate calibration samples for a given soil constituent and population. It should be remembered that the NIRA approach will never replace the traditional analytical methods. However, for rapid, nonrestrictive measurements of a large number of samples within a relatively heterogeneous population, the NIRA achievements presented in this study are likely to be good. Further study and use of the NIRA approach in the soil science field is strongly recommended.

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