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Soil quality — Determination of carbon and nitrogen by near infrared spectrometry

Qualité du sol — Dosage du carbone et de l'azote par spectrométrie dans le proche infrarouge

ICS 13.080.10

ISO/CEN PARALLEL PROCESSING

This draft has been developed within the International Organization for Standardization (ISO), and processed under the **ISO-lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five-month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 17184 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

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Soil quality — Determination of carbon and nitrogen by near-infrared spectrometry (NIRS)

1 Scope

This International Standard specifies method for the determination of carbon and nitrogen in soils by direct measurement of sample spectra in near-infrared spectral region. The spectra are evaluated by a suitable calibration model derived from the results obtained by reference methods.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11464:1994, *Soil quality — Pre-treatment of samples for physico-chemical analyses.*

ISO 10694:1995, *Soil quality — Determination of organic and total carbon after dry combustion (elemental analysis).*

ISO 14235:1998, *Soil quality — Determination of organic carbon by sulfochromic oxidation.*

ISO 11261:1995, *Soil quality — Determination of total nitrogen — Modified Kjeldahl method.*

ISO 13878:1998, *Soil quality — Determination of total nitrogen content by dry combustion (elemental analysis).*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

Working document CEN/TC 327/WG 2 Animal feeding stuff — Guidance for the application of near-infrared spectrometry

3 Principle

Soil samples are measured by reflectance near-infrared spectroscopy (NIR). Diffuse reflectance NIR spectroscopy offers a nondestructive means for measurement of soil properties based on reflectance spectra of illuminated soils. Spectral data are evaluated by a suitable calibrating model derived from the measurement of a sufficient number of representative soil samples with known content of carbon and/or nitrogen determined by reference methods. Calibration equations reflect the relationship between the constituents of the sample and NIR spectral information. The soil samples and the set of calibrating samples for the NIR measurement are prepared in the same way.

NOTE 1 NIR is a very fast non-destructive and environmentally friendly analytical technique if compared to the standard chemical methods used as reference methods.

NOTE 2 Soils generally have similar reflectance spectra in the 1100 nm to 2500 nm range. The absorption peaks for soils in the near-infrared region are difficult to assign to specific chemical components.

4 Apparatus

4.1 Near-infrared instrument

Instrument based on measurement of reflectance spectra in the near-infrared region (wavelength range from 900 nm to 2500 nm is usually applied). The instrument should be equipped with a suitable measurement cell for pulverised solid samples. The instrument should measure sufficiently large sample volume to eliminate any significant influence of inhomogeneity of the sample. The software must allow instrument tests, calibration, sample measurement and data evaluation.

NOTE Resolution of the instrument should be equal or better than 8 nm. Wavelengths of spectra recorded in higher resolution can be averaged to reduce spectra noise and there is a danger of over fitting of the calibration model.

5 Procedure

5.1 Preparation of samples

Soil samples have to be prepared by the same way as soils used for the instrument calibration. Any difference in sample preparation can influence the measurement. Sample preparation shall insure a good homogenisation of the sample.

NOTE 1 Sample preparation according to ISO 11464, particle size < 2 mm, is generally used. Air dry or oven dry samples can be used for analysis. The method is not suitable for samples with water content higher than 10 %.

NOTE 2 Oven drying of samples is recommended for samples with high specific surface area that are susceptible to changes in water content due to fluctuations in air humidity.

5.2 Instrument calibration

5.2.1 General

A suitable set of uniformly prepared soil samples is measured by NIRS. The spectra and the results of the content of carbon and/or nitrogen determined by a reference method are used for calculation of the calibration model. Calibration should include enough samples to cover most of the possible spectral variability encountered during routine analysis and to predict the composition of unknown samples accurately. The calibration sample set shall be selected to gain an evenly distributed coverage of the property range.

The NIR spectra represent cumulative information about the chemical and physical properties of a sample. Influence of physical properties of a sample (e.g. particle size), are reduced by mathematical corrections as derivatives, standard normal variate (SNV), multiplicative scatter corrections (MSC) or other. There are several possible ways for development of calibration equations and no specific procedure can be given. The choice shall aim at minimising the calibration error. The most frequent methods applied in the development of calibration equations are: PCR (principal component regression), PLS (partial least square regression), LWR (locally weighted regression), SMLR (stepwise multiple linear regression) and ANN (artificial neural network regression). From these methods only ANN method can give calibration for the whole concentration range for carbon and nitrogen in soils but ANN method is applicable only for more than 500 calibration samples. For other statistical methods splitting of the concentration range into two calibrations (see ANNEX A) was found to be the best solution. Removal of outliers from the calibration set usually reduces the robustness of the calibration and should be avoided.

For samples from different locations and soil types a minimum of 60 to 100 calibration samples is required. A smaller number of calibration samples can be used for sample sets with lower variability such as samples from a defined location.

NOTE 1 Transformations of the reference measurements or the spectra using e.g. log or square root transformed reference measurements may help to reduce the calibration error.

NOTE 2 Calibrations developed on a certain instrument cannot be always transferred directly to an identical instrument. It may be necessary to perform bias and slope adjustments to calibration equations. In many cases it will be necessary to standardize the two instruments against each other before calibration equations can be transferred. Standardization procedures can be used to transfer calibrations between instruments of different types provided that samples are measured in the same way and that the spectral region is identical.

NOTE 3 If the reference method is unbiased and a good linear calibration model is achieved, increasing number of calibration samples averages out errors in the reference method. Therefore, the lack of repeatability in the reference method can be compensated for by using high number of calibrating samples.

5.2.2 Validation of the calibration model

5.2.2.1 General

There are two main methods for validation of the calibration model – cross (internal) validation and external validation. Cross validation (5.2.2.2) is used to determine the number of factors used for PLS by determining a minimum RMSECV. The number of factors shall be as small as possible to avoid overfitting of the calibration model. An external (5.2.2.3) validation shall be used to determine the calibration error since cross validations tends to underestimate the calibration error.

In all cases if a new calibration is developed on an expanded calibration set, the validation process should be repeated. The calibrations should be checked whenever any major part of the instrument (optical system, detector) has been changed or repaired.

Next to the initial validation NIR calibrations should be validated on the regular basis against reference methods to secure optimal performance of calibrations. The frequency of checking depends mainly on the number of changes in sample population. The number of samples for the continuous checking should be sufficient for the statistics applied. The validation exercise is valid only for the range and the sample types used in the validation.

The prediction ability of the calibration model is given by the correlation coefficient (R) and the root mean squared error of prediction (RMSEP) that is in case of cross validation called also root mean squared error of cross validation (RMSECV). These characteristics should be reported with the results. If the difference between two parallel measurements is higher than RMSECV or RMSEP the results may not be valid and should be investigated further.

5.2.2.2 Cross validation

The set of calibration data is divided into K groups, each group has n/K individual samples. A single group of the K groups is retained for validation of the model and the remaining $K-1$ groups are used as training (calibration) data. This step is repeated for all K groups. At the end of cross validation each sample is measured once for validation and the set of measured predicted values is used for calculation of RMSECV (root mean square error of cross validation).

NOTE 1 For $K = n$ the method is called leave-one-out cross validation (LOOCV). A single observation is used as the validation data, and the remaining observations as the training (calibration) data.

NOTE 2 NOTE 2 $K = 10$ is commonly used

$$RMSECV = \sqrt{\frac{\sum_{i=1}^n (y_i^* - y_{i,ref}^*)^2}{n}}$$

$y_{i,ref}^*$ is the prediction concentration;

y_i^* is the concentration of calibration sample;

n is the number of calibration samples.

5.2.2.3 External validation

Two independent and representative sets of samples are necessary for external validation: one set is used for calibration and the other for validation. The differences between predictions and the known reference values are used to calculate root mean squared error of prediction (RMSEP).

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (y_i^* - y_{i,ref}^*)^2}{n_t}}$$

$y_{i,ref}^*$ is the prediction concentration;

y_i^* is the concentration of calibration sample;

n_t is the number of validation samples.

5.2.2.4 Correlation coefficient

The correlation coefficient (R) expresses the correlation between laboratory reference values and values predicted from the NIR measurement.

$$R = \frac{\sum_{i=1}^{N_K} (x_i - x_{av})(y_{i,NIR} - y_{NIR,av})}{\sqrt{\sum_{i=1}^{N_K} (x_i - x_{av})^2 \sum_{i=1}^{N_K} (y_{i,NIR} - y_{NIR,av})^2}}$$

Y_{NIR} is the predicted concentration;

x_i is the reference concentration of the calibration sample;

$Y_{NIR,av}$ is the average concentration of Y_{NIR} ;

x_{av} is the average concentration of x_i ;

N_K is the number of calibration samples.

5.3 Sample measurement

A sub-sample is transferred to the sample cup and the surface is leveled. The spectrum of the sample is scanned following the instrument manual. The number of scans or the dwell time on each wavelength should be large enough to reduce the noise of the measurement to an insignificant level and should be part of the calibration definition. The windows are cleaned between the individual measurements (by a soft brush).

NOTE More measurements of the individual sample after moving the sample cell between the individual measurements is recommended to minimize the influence of sample inhomogeneity.

Test of the suitability of the calibration model for an individual sample should be done after the spectra measurement. This is necessary because calibrations developed for a certain population of samples may not be valid for samples outside this population, although the analyte concentration range is unchanged. Principal component analysis (PCA) or cluster analysis are usually used for this purpose. If the sample does not pass

the test (that means that the sample does not fit into the population of the samples used for calibration and/or validation) it cannot be determined by the NIR method unless the calibration model is changed. (These samples are usually used for improvement of the calibration model.)

If the calibration model is found to be suitable for the measured sample, the spectrum is evaluated according to the validated calibration model. At least one control sample should be measured before and after an uninterrupted series of sample analyses to check instrument hardware stability and to detect any malfunction. The recorded day-to-day variation should be plotted in control charts and investigated for significant patterns or trends. The wavelength/wavenumber accuracy, precision, photometric response and instrument noise should be checked according to the recommendations of the manufacturer.

6 Test report

The test report shall contain the following information:

- a) a reference to this International Standard;
- b) identification of the reference method used for calibration;
- c) complete identification of the sample;
- d) the results of the determination;
- e) root mean square error of cross validation (RMSECV) or root mean square error of prediction (RMSEP) and regression coefficient (R) of the calibration equation;
- f) any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.