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Soil quality – Determination of carbon and nitrogen by near-infrared spectrometry (NIRS) (ISO 17184:2014)

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The European Standard EN ISO 17184:2014 has the status of a Swedish Standard. This document contains the official version of EN ISO 17184:2014.

Denna standard är framtagen av kommittén för Karaktärisering av avfall, mark och slam, SIS/TK 535.

EUROPEAN STANDARD

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EUROPÄISCHE NORM

EN ISO 17184

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English Version

Soil quality - Determination of carbon and nitrogen by near-infrared spectrometry (NIRS) (ISO 17184:2014)

Qualité du sol - Dosage du carbone et de l'azote par spectrométrie proche infrarouge (SPIR) (ISO 17184:2014)

Bodenbeschaffenheit - Bestimmung von Kohlenstoff und Stickstoff durch Nahinfrarotspektroskopie (NIRS) (ISO 17184:2014)

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Foreword

This document (EN ISO 17184:2014) has been prepared by Technical Committee ISO/TC 190 “Soil quality” in collaboration with Technical Committee CEN/TC 345 “Characterization of soils” the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2014, and conflicting national standards shall be withdrawn at the latest by November 2014.

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Endorsement notice

The text of ISO 17184:2014 has been approved by CEN as EN ISO 17184:2014 without any modification.

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

1 Scope

This International Standard specifies a method for the determination of carbon and nitrogen in soils by direct measurement of sample spectra in the 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 documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

3 Principle

Soil samples are measured by reflectance near-infrared (NIR) spectroscopy. Diffuse reflectance NIR spectroscopy offers a non-destructive 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 the same way.

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

NOTE 2 Soils generally have similar reflectance spectra in the 1 100 nm to 2 500 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, based on measurement of reflectance spectra in the near-infrared region (wavelength range from 900 nm to 2 500 nm is usually applied). The instrument should be equipped with a suitable measurement cell for pulverized solid samples. The instrument should measure sufficiently large sample volume to eliminate any significant influence of inhomogeneity of the sample. The software shall allow instrument tests, calibration, sample measurement and data evaluation.

Resolution of the instrument should be equal to 8 nm or better.

NOTE Wavelengths of spectra recorded in higher resolution may be averaged to reduce spectra noise and there is a risk of over fitting of the calibration model. Instruments with lower resolution may be used if their performance is verified for intended purposes.

5 Procedure

5.1 Preparation of samples

Soil samples shall be prepared the same way as soils used for the instrument calibration. Any difference in sample preparation may influence the measurement. Sample preparation shall ensure a good homogenization of the sample.

Sample preparation according to ISO 11464, particle size < 2 mm, is generally used. Air-dried or oven-dried samples can be used for analysis. The method is not suitable for samples with water content higher than 10 %. Oven drying 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 NIR spectroscopy. 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), is reduced by mathematical corrections as derivatives, standard normal variate (SNV), multiplicative scatter corrections (MSC), etc. 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 methods most frequently 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). Among these methods, only ANN methods can give calibration for the whole concentration range for carbon and nitrogen in soils but ANN methods only apply with more than 500 calibration samples. For other statistical methods, splitting of the concentration range into two calibrations 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 It is possible that calibrations developed on a certain instrument may not always be transferred directly to an identical instrument. It may be necessary to perform bias and slope adjustments to calibration equations. In many cases it is 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 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 (see 5.2.2.2), and

— external validation (see 5.2.2.3).

Cross validation (see 5.2.2.2) is used to determine the number of factors used for PLS by determining a minimum RMSECV (root mean square error of cross validation), and when not enough samples are available for external validation. The number of factors shall be as small as possible to avoid over fitting of the calibration model. An external validation (see 5.2.2.3) shall be used to determine the calibration error since cross validations tend 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 a regular basis against reference methods to ensure optimal performance of calibrations. The frequency of checkings depends mainly on the number of changes in the 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 for 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) which is also called root mean squared error of cross validation (RMSECV) when using cross validation. 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. One 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. When cross validation is completed, each sample is measured once for validation and the set of measured predicted values is used for calculation of RMSECV.

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 are used as training (calibration) data.

NOTE 2 $K = 10$ is commonly used.

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

where

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

y_i^* is the concentration of calibration sample;

n is the number of calibration samples.