

STUDY OF THE NEAR INFRARED REFLECTANCE SPECTROSCOPY PERFORMANCES FOR THE DETERMINATION OF SOIL PARAMETERS USEFUL FOR THE FERTILITY DIAGNOSIS

The aim of our study is to provide a fertility diagnosis as close as possible to the field truth

- (i) for use in routine by the laboratories of the Walloon REQUASUD network,
- (ii) without extra-cost for those laboratories and/or for the farmers and
- (iii) which meets the current agronomic and environmental requirements.

Nowadays, the main issues which have to be considered are :

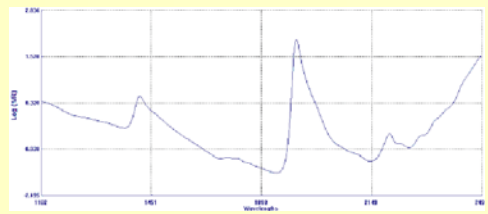
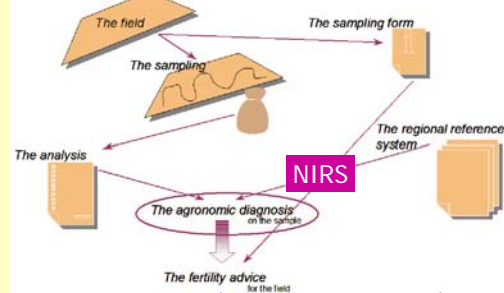
- (i) the acquisition of the cation exchange capacity (CEC) and clay content of the analysed samples (those parameters aren't done in routine even if they are the keys to enter the regional reference system and to give the agronomic diagnosis on the sample),
- (ii) the research of alternative methods for determining the COT content to replace the Walkley-Black procedure which uses chemical reactants.

The NIRS technique is known to be a physical non-destructive, rapid, reproducible, and low cost method, for predicting several soil properties simultaneously (Brunet & al., 2007). It's why this study assessed the ability of the NIRS to predict the total organic content, the CEC and the clay content of the soil samples analysed in Walloon Region.

The NIRS principle

NIRS is an analytical technique that characterizes materials according to their reflectance in the wavelengths ranging between 800 and 2500 nm. Spectral signatures of materials are defined by their reflectance (R), or absorbance (log 1/R), as a function of wavelengths. Under controlled conditions, the signatures are due to electronic transitions of atoms and vibrational stretching and bending of structural group of atoms that form molecules and crystals. The fundamental vibrations of most soil materials can be found in the mid-infrared region, with overtones and combinations found in the near-infrared region. (Brown & al., 2006)

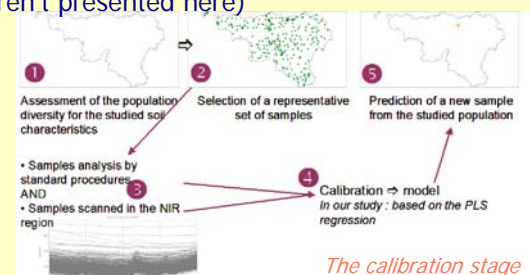
The steps leading to the fertility advice



A soil near-infrared spectrum: the soil fingerprint

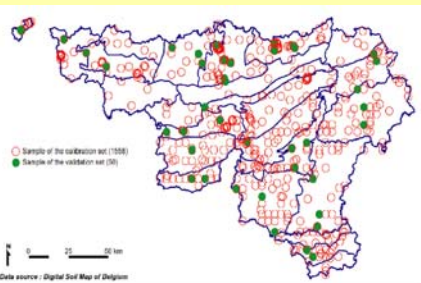
The methodology followed to build the NIRS model and to allow routine use – application for the determination of the CEC

1. Evaluation of the soil characteristics of the population diversity. The population is the Walloon soils for the CEC measurement. (results aren't presented here)
2. Setting-up a representative samples set.
3. Analysis of those samples according to the standard procedures (Metson method – NF X 31-130 for the CEC).
4. Splitting those samples between a calibration and a validation set.
5. Elaborating a sample presentation procedure for the spectrometer.
6. Scanning in replicate all the samples following this procedure.
7. Elaborating a predictive model (selection of the best pre-treatment and selection of the best local model).
8. Evaluation of the repeatability and reproducibility of the method (results aren't presented here)



The calibration stage

Steps 2, 3 & 4 : localization and characterization of the calibration and validation samples sets



	Calibration set CEC (cmol(+)/kg)	Validation set CEC (cmol(+)/kg)
Average	14.3	18.9
Standard deviation	8.04	9.09
Minimum	0.6	7.8
First quartile	9.8	12.7
Median	12.9	15.5
Third quartile	10.4	22.0
Maximum	91.6	60.0
Number of samples		
All	1198	50
Crop	530	22
Grass land	148	3
Forest and others	520	25
Top soil	574	50

To set up the validation set, we conducted a statistical analysis based on the following criteria: land use, top soil/subsoil and soils criteria according to the Walloon Digital Soil Map. We randomly selected the samples in each defined class proportionally to the number of data in those classes.

Step 7 : elaborating a predictive model

Several models were evaluated in this study. To compare the results and select the most accurate model, some criteria were used: the RMSECV (root mean square error of cross validation), the RMSEP (root mean square error of prediction) and the r^2 -value (determination coefficient). RMSECV and RMSEP indicate the error in absolute values. We also express them in percentage of the mean of the calibration or validation set, calling them $RMSECV_m$ and $RMSEP_m$.

First, a so-called "global model" was built. It means that all the calibration samples were used to construct a new model and to predict the soil characteristics of a new sample. The number of PLS components was chosen to be at the minimum RMSECV by dividing the calibration set by 10. The RMSEP was evaluated by using the validation set of 50 samples. The global model was tested using 15 pre-treatments for each soil characteristic including (i) the use of the first (1441) and second (2861) derivatives of near-infrared reflectance data in order to remove a part of the particle size influence (Chang & al., 2001); (ii) the standard normal variate (SNV) to obtain a standard deviation of one and to reduce light scatter effects caused by particle size effects; (iii) the de-trend (D) to remove the linear and quadratic curvature of each spectrum (Stenberg & al., 2005) and (iv) the effect of multiplicative scatter correction (MSC) to remove a part of the particle size effect.

	0111	1441	2861	SNV D 0111	SNV D 1441	SNV D 2861	SNV 0111	SNV 1441	SNV 2861	D 0111	D 1441	D 2861	MSC 0111	MSC 1441	MSC 2861
Nb. PLS factors	13	13	10	15	12	10	14	14	10	14	12	11	14	13	11
RMSECV (cmol(+)/kg)	3.7	3.6	3.5	3.7	3.6	3.8	3.7	3.7	3.7	3.6	3.6	3.5	3.8	3.9	3.8
R^2_{cv}	0.66	0.72	0.72	0.66	0.68	0.68	0.64	0.68	0.68	0.69	0.71	0.73	0.62	0.64	0.65
RMSEP (cmol(+)/kg)	7.7	7.2	6.99	7.1	7.2	7.0	7.3	7.0	6.9	7.4	7.1	6.9	6.8	6.6	6.5
$RMSECV_m$ (%)	27.3	25.7	25.5	27.0	26.8	26.5	28.1	26.6	26.6	25.7	25.4	28.3	28.3	27.7	27.7
$RMSEP_m$ (%)	40.7	38.3	37.0	37.8	38.0	37.0	38.9	37.2	36.9	39.4	37.8	36.3	36.1	34.7	34.3

Steps 5 & 6 : elaborating a sample presentation procedure and scanning the samples

The procedure is elaborated for the calibration stage but also for routine use. It should, therefore be easy to perform and give the same results regardless of the sample, the laboratory, or the technician.

We worked with 2 mm sieved, dried samples placed in a quarter cup (pictures above). Several ways of filling up those cups were tested and we selected the easiest and most robust one as proved by an ANOVA analysis.

All samples were scanned using a FOSS NIRSystem 5000 model. Samples were scanned from 1100 to 2500 nm by 2 nm steps. Spectra were computed as absorbance (log 1/Reflectance). Each sample was scanned in duplicate and the spectra were averaged and recorded in the spectra data base (SDB - where all Y and X_λ of each sample from the calibration set are recorded).



The loading plot – MSC 2861 - factor 1

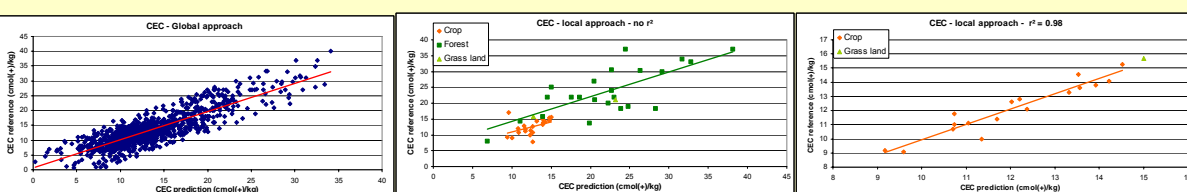


Second, we selected the pre-treatment giving the minimum $RMSEP_m$ to be used in our local approach.

This approach means that a new model is built for every new sample to be predicted for the studied soil characteristics.

For each prediction, the most correlated samples are selected among the spectral data base (SDB) and a model is built thanks to those selected samples. Third, before applying this local approach in routine, a batch processing has to be done to select the optimal number of samples and number of PLS factors and to choose the optimum determination coefficient between the sample to be predicted and the samples to be selected in the SDB. Based on the validation set and thanks to this batch processing, we tested 5300 possibilities (50 to 260 maximum samples selected in the SDB; 6 to 22 maximum PLS factors; 3 to 11 maximum PLS factors to be removed; no determination coefficient or a r^2 -value of 0.95, 0.96, 0.97, 0.98 and 0.99).

	Global	no r^2	$r^2 = 0.95$	$r^2 = 0.96$	$r^2 = 0.97$	$r^2 = 0.98$	$r^2 = 0.99$	Crop no r^2	Crop $r^2 = 0.95$	Crop $r^2 = 0.96$	Crop $r^2 = 0.97$	Crop $r^2 = 0.98$	Crop $r^2 = 0.99$
Max. nb. samples	1198	50	140	50	50	50	70	50	140	50	50	50	70
Max. Nb. PLS factors	11	20	22	8	8	10	18	20	22	8	8	10	18
Max. Nb. PLS factors to remove	/	5	3	5	5	5	5	5	3	5	5	5	5
Nb. predicted samples	50/50	47/50	40/50	38/50	25/50	18/50	14/50	22/22	20/22	20/22	19/22	17/22	15/22
RMSEP (cmol(+)/kg)	6.5	4.1	3.1	3.1	0.8	0.4	0.4	2.2	1.2	1.2	1.2	0.7	0.8
R^2_p		0.73	0.79	0.76	0.90	0.92	0.87	0.21	0.61	0.66	0.63	0.82	0.75
$RMSEP_m$ (%)	34.3	21.8	16.2	16.5	4.3	1.9	2.0	17.6	10.0	9.4	9.3	5.7	6.2



Conclusions and perspectives

NIR spectroscopy can be used as a rapid analytical technique to simultaneously estimate several soil characteristics (TOC, clay contents and CEC) with acceptable accuracy in a very short time.

The local approach gives the best results and those results are improved by applying a determination coefficient higher than 0.95 between the sample to predict and the selected samples coming from the SDB.

Results also show that the crop soil samples are well predicted, better than those of forest or grass land, even if a r^2 -value is used.

For a routine use, the optimal approach should be an iterative one. First the technician applies the best local model (r^2 -value of 0.98) on the sample to be predicted. If the sample is well-predicted, the iteration is finished. If it doesn't work, the second model, with a r^2 -value of 0.97, is applied and so one until the application of the last model (no r^2 -value), given a less accurate result. At this stage, if still no-prediction is obtained, meaning that the sample spectrum is too far away from the spectra recording in the SDB, the CEC value must be evaluated according to the standard procedure (in our study, it would have been the case for 3 samples out of 50).

Brown D.J., Shepherd K.D., Walsh M.G., Mays M.D. & Reinsch T.G. (2006). Global soil characterization with VNIR diffuse reflectance spectroscopy. *Geoderma* 123, 273-290.
Brunet D., Barthès B.G., Chotte J.L. & Feller C. (2007). Determination of carbon and nitrogen contents in Alfisols, Oxisols and Ultisols from Africa and Brazil using NIRS analysis: Effects of sample grinding and set heterogeneity. *Geoderma*.
Chang C.W., Laird D.A., Mausbach M.J. & Hurburgh C.R. (2001). Near-infrared reflectance spectroscopy - Principal components regression analyses of soil properties. *Soil Science Society of America Journal* 65, 480-490.
Stenberg B., Jonsson A. & Börjesson T. (2005). Use of near infrared reflectance spectroscopy to predict nitrogen uptake by winter wheat within fields with high variability in organic matter. *Plant and soil* 269, 251-258.