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Soil analysis using visible and near infrared spectroscopy

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Summary

Visible-near infrared diffuse reflectance (vis-NIR) spectroscopy is a fast, non-destructive technique well suited for analyses of some of the essential constituents of the soil. These constituents, mainly clay minerals, organic matter and soil water strongly affect conditions for plant growth and influence plant nutrition. Here we describe the process by which vis–NIR spectroscopy can be used to collect soil spectra in the laboratory. Because it is an indirect technique, the succeeding model calibrations and validations that are necessary to obtain reliable predictions about the soil properties of interest, are also described in the chapter.

Key words: diffuse reflectance spectroscopy, vis-NIR, clay, organic matter, calibration, validation

Introduction

Interest among researchers in the use of visible-near infrared (vis–NIR) diffuse reflectance spectroscopy in soil science has increased over the past two decades (Stenberg et al., 2010) because there are many advantages with using the technique. It is non-destructive, requires a minimum of sample preparation and does not involve any (hazardous) chemicals. The measurements only take a few seconds and several soil properties can be estimated from a single scan. Moreover, the technique allows for flexible measurement configurations and *in situ* as well as laboratory-based measurements (Viscarra Rossel et al., 2006).

Reflectance spectra in the visible (400–780 nm) and near infrared (780–2500 nm) region are the result of interactions between the radiating energy and the bonds in molecules of soil constituents. In the visible region, the high energy of the radiation causes transitions of electrons between molecular orbits with different energy levels (Miller, 2001). With lower radiation energy, corresponding to longer wavelengths, the absorption of energy occurs due to vibrations in molecular bonds. Absorption in the NIR region is due to overtones and combinations of fundamental vibrations in the mid-infrared region. The energy quanta absorbed are bond specific, but are also affected by the chemical matrix and environmental factors such as type of functional group, neighbouring molecules and hydrogen bonds (Miller, 2001). This allows for identification of a range of molecules which may contain the same type of bonds. The same molecule can give rise to several overtones and combination bands over the NIR region with decreasing intensity and increasing overtone order. Because of this, the NIR region is characterised by few, broad, overlapping absorption features. The diffuse reflectance of the soil is also influenced by soil physical properties related to particle size and surface structure, as well as water films on the soil surface.

Due to the lack of specificity and the fact that a spectrum consists of many highly correlated neighbouring wavelengths, multivariate calibration techniques are commonly used to correlate the spectra with the targeted soil properties (Martens and Naes, 1989). To create calibration models,

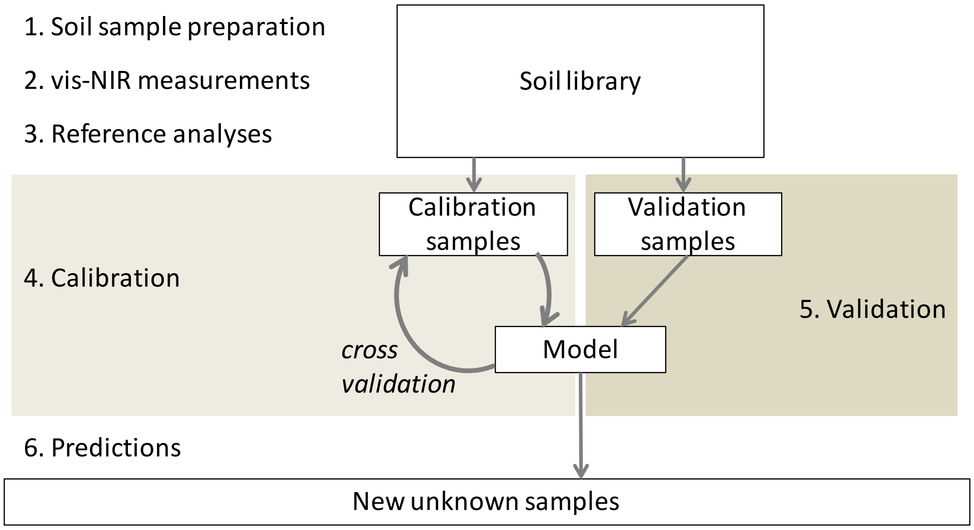

Figure 1. Procedure for developing vis-NIR prediction models.

calibration samples analysed using conventional laboratory methods are also needed. When the calibration models are established, new samples only need to be analysed using vis-NIR and the calibration models are used to predict the targeted soil properties. A schematic of the main steps in the procedure from soil sample preparation to prediction is presented in Figure 1.

The vis-NIR region contains useful information on the organic and inorganic content in the soil and both clay minerals and soil organic matter (SOM), both of which are essential constituents of the soil, have well recognised absorptions features in this region. Water has strong influences on the spectra with some dominating specific absorption bands near 1400 and 1900 nm along with weaker bands in other parts of the spectra (Liu et al., 2002). In addition, with a water film on soil particles, scattering is more forward directed and moist soils appear darker than dry ones (Twomey et al., 1986). The mineral part of the soil generally accounts for half the soil volume (Schulze, 2002), and has pronounced features in the vis-NIR spectrum, both in terms of surface properties affecting the degree of scattering and by absorption. Absorptions in the visible region are primarily associated with iron-containing minerals such as haematite and goethite which show strong absorption bands between 400 and 660 nm (Sherman and Waite, 1985) (Figure 2). Both minerals also show absorption bands near 900 nm (880 and 930 for haematite and goethite respectively) but have almost no absorption features at longer wavelengths (Clark et al., 1990). The absorption by clay minerals in the NIR region is mostly related to absorbed and structural water and Mg-, Al-, and Fe–OH bonds in the mineral crystal lattice. Absorption bands in the 2200–2500 nm region, due to combination vibrations involving O-H stretch and metal-OH bend, are evident for several minerals with slightly different peaks depending on metal and mineral (Figure 2). Absorption bands at 1400 nm and 1900 nm are also apparent in a number of minerals to varying degree and are related to absorbed and structurally bound water. Smectite, for example, has a very pronounced absorption band near 1900 nm due to combination vibrations of water bound in the interlayer lattices as hydrated cations and water adsorbed on particle surfaces (Figure 2) (Bishop, 1994). Carbonates also have several absorption bands in the NIR region, the strongest being near 2300 nm (Clark et al., 1990).

Soil organic matter has clear but broad absorption bands in the visible region (Figure 3a) dominated by chromophores and darkness of the organic matter (Ben-Dor et al., 1999). In the NIR region the absorption is related to stretching and bending of NH, CH and CO groups (Ben-Dor et al., 1999).

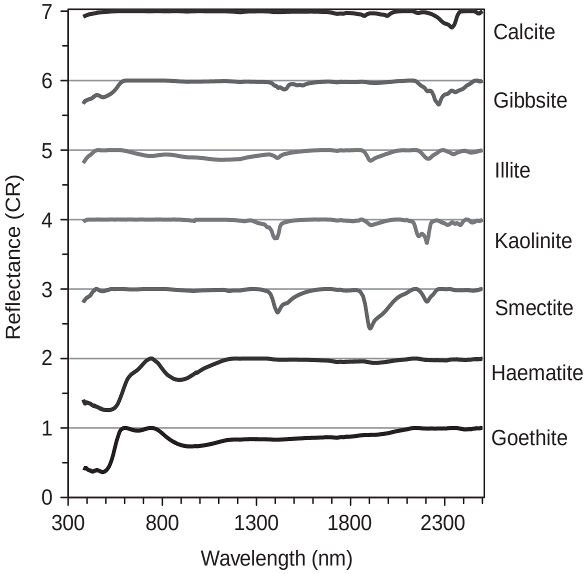

Figure 2. Continuum-removed spectra of common soil minerals offset by 1 unit, from Stenberg et al. (2010).

A number of absorption bands in the 1100-2400 nm region has been identified as important for SOM and total N calibrations, however they are often weak and may not be readily apparent to the naked eye. Viscarra Rossel and Behrens (2010) present a summary of important fundamental absorptions and their occurrence in the vis–NIR and some examples of the effect of SOM on NIR spectra for different soils are presented in Figure 3. Stenberg (2010) identified some of these as especially important.

Both clay and SOM content are important for the soil structure and thereby soil aeration and water holding capacity which are factors strongly affecting plant growth. They influence plant nutrition through their possibility to adsorb cations and take part in the transformation of nutrients to plant available forms through weathering and through direct and indirect influences on the microbial soil fauna. However, plant nutrient salts are by themselves not expected to absorb in the vis–NIR region and correlations found to vis–NIR are often weak (Stenberg et al., 2010). Nevertheless, good correlations can sometimes be achieved (e.g. Dunn et al., 2002; Malley et al., 1999; Mouazen et al., 2006; van Groenigen et al., 2003), possibly through local co-variations with properties that do absorb in the vis–NIR.

In this chapter, we describe the process by which vis–NIR spectroscopy is used to collect soil spectra in the laboratory (Figure 1). Apart from the actual measurement, which is rather simple and fast, we also discuss quality assessment and normalisations of the spectra. Further, we discuss the steps involved in the creation and assessment of a calibration model (Figure 1), which requires most of the work and efforts to secure relevant and reliable predictions of the soil properties of interest. As mentioned in the beginning, vis-NIR spectroscopy allows for *in situ* measurements, and research and development are continuing to facilitate measurements in the field, thus minimising the need for taking soil samples (Christy, 2008; Mouazen et al., 2005; Sudduth and Hummel, 1993; Viscarra Rossel et al., 2009). Although this chapter describes the procedures for laboratory measurements, many of the aspects will also have relevance for outdoor measurements.

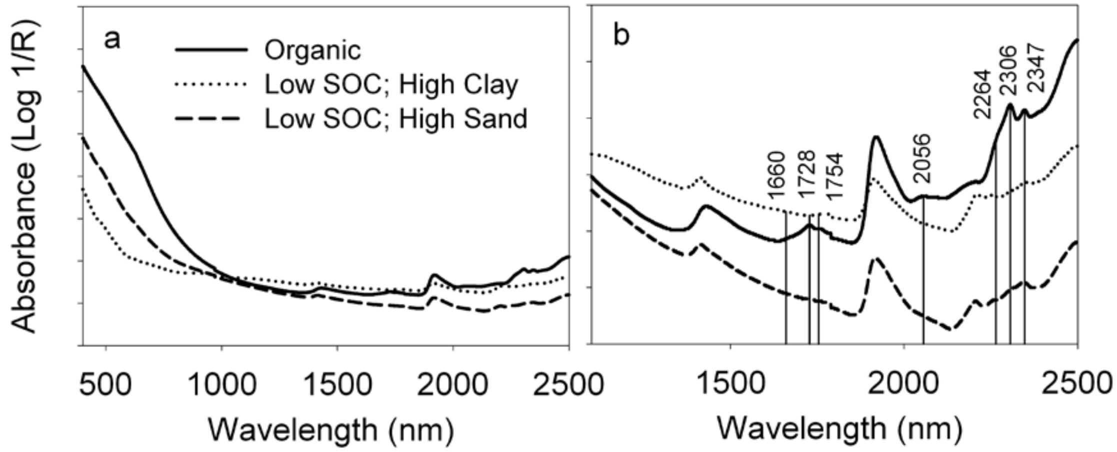

Figure 3. (A) Soil vis–NIR 400–2500 nm spectra and (B) the region 1100–2500 nm showing the spectra of three soils: an organic agricultural soil with 40% SOC and two with 1% SOC of which one has 87% sand and 4% clay, and the other 12% sand and 44% clay. Drop lines in (B) indicate wavelengths typical of organic matter (from Stenberg et al., 2010).

Materials

Instruments

A variety of vis-NIR spectrophotometers from several manufactures exists today, and these provide a number of different solutions for light dispersion, detectors and sample presentation configurations. What instrument to choose is largely dependent on the application and basically there is a trade-off between price and performance.

- Resolution and noise
  For scientific purposes, an instrument with high resolution, 10 nm or better, is favourable; however there is a direct trade-off between resolution and noise. (see Note 1)
- Spectral range
  Similarly, a wavelength range covering both visible (400–780 nm) and the entire NIR region (780-2500 nm) is recommended for scientific purposes, to make sure that as much of the important wavelength bands as possible is included (see introduction).
  If, however the instrument is to be used for a very specific purpose, the need for full vis-NIR spectra may not be necessary.
- Flexibility
  - Possibilities for measurements outside the laboratory
    Different requirements regarding robustness and handling apply depending on whether the instrument is only intended to be used in the laboratory, or if it might be used for outdoor measurements.
  - Special requirements regarding sample presentations
    Will the instrument be used for several very different sample types?
    For out-door or on-line measurements flexibility regarding sample presentation is often a priority and a fibre optic for spectra collection is preferred. For these situations a post-dispersive instrument is advisable as shielding of ambient stray light is not crucial. (see Note 2)

Standardized references

Most instruments include all necessary accessories, but depending on type they can be specific to suit that particular instrument or they can be more general. In any case, make sure that you have the following:

- A standardized white reference, for example Spectralon®, which is inert, stable and has a very high diffuse reflectance in the visible and near infrared: Some instruments have a built in white reference, others need an external one.
- Dark current correction/dark reference is made without the emitting light source, representing 0 reflectance to correct for background electronic noise from the spectrometer. This is often done by using a shutter, but for some instrument-sample configurations an external dark reference might be needed.

(see Note 3)

Methods

Soil sample preparations

- Use air or oven dried soil (see Note 4).
- Grind soil to < 2 mm particle size (see Note 5).

Measurement

Each instrument often has its own sample presentation setup and compatible sample containers. That is, the general recommendation is to follow the instructions for the specific instrument. However, presented below are some general aspects to consider.

- Sample presentation and handling
    - Soils are heterogeneous - therefore, it is very important to measure a representative part of the soil sample and a configuration that allows for a large part of the sample to be scanned is favourable. If the sampled area is very small the use of replicate spectral sampling is recommended.
    - Make sure that the sample is thoroughly mixed in the sample container.
      Do not shake the sample to get an even surface because this will stratify the sample, with the smaller particles moving down towards the bottom of the container. If an even surface is required, instead use a tool to carefully flatten the sample surface.
    - Pack the containers the same way for all samples. Try to use the same volume of soil and to use the same amount of pressure (Williams and Norris, 2001)
    - If the same container is to be used for several samples it is important to clean it between samples, however, avoid using water or alcohol/organic solvents.
    - If the measurement window has direct contact with the soil, it is important to also clean this between samples. Again, avoid using water or alcohol/organic solvents but wipe it clean using a dry dust free tissue.

- White and dark reference
  Depending on instrument, this may be done automatically, however for some instruments it needs to be done manually. This is a crucial step, and to ensure good quality spectra this needs to be done thoroughly and regularly.
    - The white and dark reference should be taken every 10 minutes. In many instruments the dark reference is taken automatically when a white one is taken.
    - If a configuration where an external white (and dark) reference is used it is important that the configuration is the same as that used for the sample measurements.

    - If it is possible to monitor the spectrum of the white reference, this should represent 100% reflection at all wavelengths across the 400-25000 nm range.
- If the measurements are done in such a way that other light sources than that related to the measurement might influence the results, minimize or standardize all other light sources during measurements – e.g. fluorescent light, ambient light from windows, etc.

Pre-treatment of the spectra

- Average spectra of repeated vis-NIR scans on the same soil sample to avoid using false replicates in further analyses. This will also increase the signal-to-noise ratio.
- Transform the measured reflectance to apparent absorption through log(1/reflectance) to enhance the linearity between the measured absorbance and the concentration of the chemical of interest. (see Note 6)
- To enhance the more chemically related peaks and reduce effects such as baseline shifts and overall curvature, it is often recommended to employ some additional pre-processing transformation of the spectra. Numerous techniques exist and most spectroscopy-dedicated software contains a collection to choose from (e.g. Viscarra Rossel, 2008). Unfortunately it is not possible to recommend one single or combination of treatments that would work best for all soil data sets (Stenberg et al., 2010) and the benefit of using any is project specific. Because of this it is recommended to test a few different transformations on a representative calibration set. (see Note 7 and 8)

Reference soil analyses

- The calibration statistics can never be better than the quality of the chemical reference analyses. That is, errors related to the traditional chemical analysis to which the spectra are correlated will be included in the calibration model.
- Make a statistical analysis of the soil data before using it for calibration.
    - Check for abnormalities, possible analysis errors and/or outliers. This should be done for both the reference and the spectral data. However, outlier detection and the removing of outliers should be done very restrictively.
    - To plot the data distributions is a good way of examining the data.

Calibration and validation

There are many different algorithms that can be used to calibrate soil vis–NIR spectra to predict soil properties. They include multiple linear regression (MLR), principal component regression (PCR) and Partial least squares regression (PLS) as well as data mining techniques like artificial neural networks (ANN), multivariate adaptive regression splines (MARS) and boosted regression trees (Viscarra Rossel and Behrens, 2010). They all have merits and disadvantages and we will not make specific recommendations on which technique to choose, but the linear ones are more straight forward and most commonly used. At the same time, the use of data mining is increasing, especially for large diverse data sets where data mining is indicated to perform slightly better than linear analyses (Viscarra Rossel and Behrens, 2010) Rather, we will give some general recommendations on what to think about when choosing calibration samples and how to validate your model.

Calibration set

- The calibration set should cover all possible and relevant variation that is present in the data for which it is meant to be used. That is, if the model is intended to be used for soil samples all over a country, the calibration samples should, as far as possible, include all existing soil types. On the other hand, if the model is intended to be used at a local scale, the calibration samples should capture that variation, and there is no point including soil types that are not present which might actually worsen prediction results.

- The number of calibration samples needed depends on the variation to be covered. As a general rule, the more calibration samples the more robust the calibration model. One hundred to 200 calibration samples might be at the lower limit for a model intended to cover a large geographical area with many and diverse soil types (Shepherd and Walsh, 2002). As few as 25 calibration samples can result in good predictions at the farm or field scale, though it is at the very limit (Wetterlind et al., 2007). The number of calibration samples needed also depends on the target variable. Calibrations for directly measured soil properties with a strong influence on the vis–NIR spectra such as clay could result in good prediction models with rather few calibration samples, whereas indirectly measured soil properties, such as plant nutrients that rely on co-variations with properties that absorb in the vis–NIR, often needs more calibration samples (Wetterlind et al., 2010).
- When developing a soil spectral library from scratch, soil sampling strategy is very important to capture the variation needed for a good calibration set, independent of scale (Gruijter et al., 2006; Wetterlind et al., 2010; Viscarra Rossel et al., 2008).
- Depending on the project you might have a (large) number of vis-NIR scanned samples from where a calibration sample set should be selected. Selecting the calibration samples based on their vis-NIR spectra is a good way to capture as much as possible of the variation in the larger data set. Ideally, the distribution of the calibration set should be a flat even distribution which can be achieved using e.g. the Kennard and Stones uniform mapping algorithm (Kennard and Stone, 1969).

Validation

- To make a true estimate of the prediction performance of a calibration a truly independent validation set is necessary. This means that this set should be sampled and analysed independently from the calibration set and has no influence on the calibration procedure. Ideally, the validation samples should not even have been sampled at the same time as the calibration samples or at least not with the same strategy.
- If no separate validation set has been collected during the soil sampling and the validation samples are to be selected from the total number of samples, we recommend the following:
    - For field and farm scale analyses:
      If the data consist of a number of soil profiles with several horizons it is recommended that all the samples in a profile follow each other, either in the calibration or in the validation set, since the different horizons in the same profile cannot be considered as independent.
    - For regional or global scale analyses:
      Avoid sample sets with geographical sample clusters, within which dependence between samples can be assumed (e.g. multiple samples from individual field trials or farm soil mapping samples clustered at individual farms or fields). If clustered data are to be used it is recommended that all samples from one cluster follow each other either in the calibration or in the validation set to avoid overoptimistic predictions (e.g. Brown et al. (2005)).
- During the calibration an internal validation (before validating the model using an independent validation set) is applied. Depending on calibration method this serves to find the optimum number of components (e.g. PCR, PLSR), to find the best wavelengths to use, or for adjusting and tuning of the calibration model. For this, cross validation or bootstrapping is often recommended. In cross validation, one or more samples are systematically kept out of the

calibration and are predicted using that calibration. This is done for all samples which means that all samples will have been used for both calibration and for validation. The same considerations as applied for the selection of an independent validation set should be applied to the cross validation (see above).

- There is no hard rule regarding what ratio is preferable between the number of calibration and validation samples. However, 2/3 calibration samples and 1/3 validation samples is rather common and can be suggested as a bench mark.

Model assessment

- There are several numerical measurements describing the performance of the predictions. We recommend the use of the root mean squared error (RMSE), bias (or mean error) and standard deviation of the error distribution (SDE) to account for accuracy and imprecision of the predictions, and the ratio of performance to deviation (RPD) for assessments across units:
    - RMSE $= \sqrt{\frac{\sum_{i=1}^{N}(\hat{y}_i - y_i)^2}{N}}$
    - Bias (mean error) $= \frac{\sum_{i=1}^{N}(\hat{y}_i - y_i)}{N}$
    - SDE $= \frac{\sum_{i=1}^{N}(\hat{y}_i - y_i - Bias)^2}{N-1}$
    - RPD $= \frac{standard\ deviation}{RMSE}$

    where $\hat{y}$ is the predicted value and y is the measured value for sample i, with N number of samples.
- Relate the result to what the model it is intended for. Are the estimated prediction errors good enough for the intended implementation?
- When assessing the model, plotting the results (predicted versus measured) is often very helpful.
    - Are there signs of nonlinearity? (This might be improved by using nonlinear data mining calibration techniques).

Software

There are several commercial software packages specially developed for analysis and calibrations of spectral data providing easy to use functions for spectral analyses and calibrations. Many manufacturers provide their instruments with specific software or have close collaborations with commercial software developers to facilitate exporting and importing of measured spectra and sometimes allowing for real-time predictions. Alternatively, most of the analyses and calibration tools can also be found in commercial, shareware and freeware software (Viscarra Rossel, 2008) and in open source environments such as the R-project (R Development Core Team, 2010).

Notes

1. The signal-to-noise ratio can be improved by a longer integration time (the time interval during which energy is collected), a stronger light source or a higher degree of spectra averaging (number of readings averaged to one collected spectrum). To what degree these are configurable by the user is instrument and sample presentation device dependent.
2. ‘Post dispersive’ means that the sample is subjected to a white light source and dispersed into the separate registered bands after reflectance. That means that only a small part of the energy in the stray light, that corresponding to each registered band, influences the spectrum.
3. Vis-NIR calibrations are largely instrument specific, and even moving or sharing calibrations among instruments of the same type can lead to reduced prediction capacity (Pimstein et al.,

2011; Williams and Norris, 2001). Pimstein et al. (2011) propose the use of a common standard in combination with a common protocol to facilitate sharing and moving calibrations between instruments. In their study, washed and bleached sand (90% quarts) performed well as such a standard.

4. The two steps in the soil sample pre-treatment are similar to common standard pre-treatments for many chemical and physical analyses, which has practical advantages.
   It is possible to make good calibrations also on moist soils. Actually there are examples where calibrations on field moist samples have been beneficial (Fystro, 2002) etc.) and standardised remoistening has led to substantial improved performance of clay and SOC calibrations (Stenberg, 2010). However, typically calibrations on dry soil in the lab perform better compared to those on field moist soil. This is mainly due to the higher degree of standardisation and the fact that broad water bands near 1400 and 1900 nm tend to override adjacent absorption bands.
5. The crushing and sieving of soils removes stones and larger plant residues and also forms a basis for representative sub-sampling. Further grinding and sieving will lead to a more constant particle size, which will have an effect on spectra (Ben-Dor and Banin, 1995; Dunn et al., 2002). However, there are few and contradictory reports in the literature comparing the prediction performance based on differences in grinding or sieving procedures (e.g. Barthes et al., 2006; Fystro, 2002; Russell, 2003). Grinding of soil particles increases the overall reflectance and the effect is especially large for clay as aggregates are crushed. However, this effect can be more or less eliminated by a pre-treatment step of the spectra discussed in section 2.4 Pre-treatment of the spectra.
6. This is recommended because soil spectra also are affected by structural properties of the sample, causing non linear light scattering. This means that some of the light that is not measured as reflectance is not directly related to absorbance but is scattered. Other equations that can be used are for example the Kubelka-Munk transformation (1-reflectance)^2/(2×refelctance)) and the Dahm equation (Dahm and Dahm, 2007).
7. Commonly used transformations include the 1st and 2nd derivative combined with smoothing (Savitzky and Golay, 1964) multiplicative scatter correction (Geladi et al., 1985) and standard normal variate combined with D-trending (Barnes et al., 1989). Other transformations are baseline corrections and different types of normalisations. A method that has gained in interest is wavelet transform (Viscarra Rossel and Lark, 2009) which, among other things, provides means to divide the variation in the spectra into different scales.
8. It is always possible that information is removed together with what is expected to be noise and because of this care should be taken not to overdo this step.
   This step cannot compensate for having very noisy raw spectra, which is why it is important to maximise the signal-to-noise ratio during measurements (see Measurement)

References

Barnes, R.J., Dhanoa, M.S., Lister, S.J., 1989. Standard Normal Variate Transformation and De-Trending of near-Infrared Diffuse Reflectance Spectra. Applied Spectroscopy 43(5), 772-777.

Barthes, B.G., Brunet, D., Ferrer, H., Chotte, J.-L., Feller, C., 2006. Determination of total carbon and nitrogen content in a range of tropical soils using near infrared spectroscopy: influence of replication and sample grinding and drying. Journal of near Infrared Spectroscopy 14(5), 341-348.

Ben-Dor, E., Banin, A., 1995. Near-Infrared Analysis as a Rapid Method to Simultaneously Evaluate Several Soil Properties. Soil Science Society of America Journal 59(2), 364-372.

Ben-Dor, E., Irons, J.R., Epema, G.F., 1999. Soil refelctance. In: A.N. Rencz (Ed.), Remote Sensing for the Earth Sciences: Manual of Remote Sensing. Wiley, New York, pp. 111-188.

Bishop, J.L., 1994. Infrared spectroscopic analyses on the nature of water in montmorillonite. Clays Clay Minerals 42, 702-716.

Brown, D.J., Bricklemyer, R.S., Miller, P.R., 2005. Validation requirements for diffuse reflectance soil characterization models with a case study of VNIR soil C prediction in Montana. Geoderma 129(3-4), 251-267.

Christy, C.D., 2008. Real-time measurement of soil attributes using on-the-go near infrared reflectance spectroscopy. Computers and Electronics in Agriculture 61(1), 10-19.

Clark, R.N., King, T.V.V., Klejwa, M., Swayze, G.A., Vergo, N., 1990. HIGH SPECTRAL RESOLUTION REFLECTANCE SPECTROSCOPY OF MINERALS. Journal of Geophysical Research-Solid Earth and Planets 95(B8), 12653-12680.

Dahm, D.J., Dahm, K.D., 2007. Interpreting Diffuse Reflectance and Transmittance: A Theoretical Introduction to Absorption Spectroscopy of Scattering Materials. NIR Publications, Chichester, UK.

Dunn, B.W., Beecher, H.G., Batten, G.D., Ciavarella, S., 2002. The potential of near-infrared reflectance spectroscopy for soil analysis - a case study from the Riverine Plain of south- eastern Australia. Australian Journal of Experimental Agriculture 42(5), 607-614.

Fystro, G., 2002. The prediction of C and N content and their potential mineralisation in heterogeneous soil samples using Vis-NIR spectroscopy and comparative methods. Plant and Soil 246(2), 139-149.

Geladi, P., Macdougall, D., Martens, H., 1985. LINEARIZATION AND SCATTER-CORRECTION FOR NEAR-INFRARED REFLECTANCE SPECTRA OF MEAT. Applied Spectroscopy 39(3), 491-500.

Gruijter, J.d., Brus, D., Bierkens, M., Knotters, M., de Gruijter, J., 2006. Sampling for natural resource monitoring. Sampling for natural resource monitoring.

Kennard, R.W., Stone, L.A., 1969. Computer aided design of experiments. Technometrics 11(1), 137-&.

Liu, W.D., Baret, F., Gu, X.F., Tong, Q.X., Zheng, L.F., Zhang, B., 2002. Relating soil surface moisture to reflectance. Remote Sensing of Environment 81(2-3), 238-246.

Malley, D.F., Yesmin, L., Wray, D., Edwards, S., 1999. Application of near-infrared spectroscopy in analysis of soil mineral nutrients. Communications in Soil Science and Plant Analysis 30(7-8), 999-1012.

Martens, H., Naes, T., 1989. Multivariate calibration. John Wiley & Sons, Chichester, UK.

Miller, C.E., 2001. Chemical principles of near-infrared technology In: P. Williams, K. norris (Eds.), Near-Infrared Technology in the Agricultural and Food Industries. American Association of Cerial Chemists Inc., Minesota, pp. 19-37.

Mouazen, A.M., De Baerdemaeker, J., Ramon, H., 2005. Towards development of on-line soil moisture content sensor using a fibre-type NIR spectrophotometer. Soil & Tillage Research 80(1-2), 171-183.

Mouazen, A.M., De Baerdemaeker, J., Ramon, H., 2006. Effect of wavelength range on the measurement accuracy of some selected soil constituents using visual-near infrared spectroscopy. Journal of near Infrared Spectroscopy 14(3), 189-199.

Pimstein, A., Notesco, G., Ben-Dor, E., 2011. Performance of Three Identical Spectrometers in Retrieving Soil Reflectance under Laboratory Conditions. Soil Science Society of America Journal 75(2), 746-759.

R Development Core Team, 2010. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.

Russell, C.A., 2003. Sample preparation and prediction of soil organic matter properties by near infra-red reflectance spectroscopy. Communications in Soil Science and Plant Analysis 34(11-12), 1557-1572.

Savitzky, A., Golay, M., 1964. Smoothing and differentiation of data by simplified least squares procedures. Analytical chemistry 36, 1627-1639.

Schulze, D.G., 2002. An introduction to soil mineralogy. In: J.B. Dixon, D.G. Schulze (Eds.), Soil Mineralogy with Environmental Applications. Soil Science Society of America Inc., Madison, WI, pp. 1–35.

Shepherd, K.D., Walsh, M.G., 2002. Development of reflectance spectral libraries for characterization of soil properties. Soil Sci Soc Amer J 66, 988-998.

Sherman, D.M., Waite, T.D., 1985. Electronic spectra of Fe3+ oxides and oxiyhydroxides in the near infrared to ultraviolet. American Mineralogist 70(11-12), 1262-1269.

Stenberg, B., 2010. Effects of soil sample pretreatments and standardised rewetting as interacted with sand classes on Vis-NIR predictions of clay and soil organic carbon. Geoderma 158(1-2), 15-22.

Stenberg, B., Rossel, R.A.V., Mouazen, A.M., Wetterlind, J., 2010. Visible and near infrared spectroscopy in soil science. In: D.L. Sparks (Ed.), Advances in Agronomy, Vol 107. Advances in Agronomy, pp. 163-215.

Sudduth, K.A., Hummel, J.W., 1993. Soil organic matter, CEC, and moisture sensing with a portable NIR spectrophotometer. Transactions of the Asae 36(6), 1571-1582.

Twomey, S.A., Bohren, C.F., Mergenthaler, J.L., 1986. Reflectance and albedo differences between wet and dry surfaces. Applied Optics 25(3), 431-437.

van Groenigen, J.W., Mutters, C.S., Horwath, W.R., van Kessel, C., 2003. NIR and DRIFT-MIR spectrometry of soils for predicting soil and crop parameters in a flooded field. Plant and Soil 250(1), 155-165.

Wetterlind, J., Stenberg, B., Soderstrom, M., 2010. Increased sample point density in farm soil mapping by local calibration of visible and near infrared prediction models. Geoderma 156(3-4), 152-160.

Wetterlind, J., Stenberg, B., Söderström, M., 2007. Farm-soil mapping using NIR-technique for increased sample point density. In: J.V. Stafford (Ed.), 6th European Conference on Precision Agriculture. Wageningen Academic publishers, Skiathos, Greece, pp. 265-270.

Williams, P.C., Norris, K., 2001. Variables Affecting Near-Infrared Spectroscopic Analysis. In: P. Williams, K. Norris (Eds.), Near-Infrared Technology in the Agricultural and Food Industries. American Association of Cerial Chemists Inc., Minesota, pp. 171-185.

Viscarra Rossel, R.A., 2008. ParLeS: Software for chemometric analysis of spectroscopic data. Chemometrics and Intelligent Laboratory Systems 90(1), 72-83.

Viscarra Rossel, R.A., Behrens, T., 2010. Using data mining to model and interpret soil diffuse reflectance spectra. Geoderma 158(1-2), 46-54.

Viscarra Rossel, R.A., Cattle, S.R., Ortega, A., Fouad, Y., 2009. In situ measurements of soil colour, mineral composition and clay content by vis-NIR spectroscopy. Geoderma 150(3/4), 253-266.

Viscarra Rossel, R.A., Jeon, Y.S., Odeh, I.O.A., McBratney, A.B., 2008. Using a legacy soil sample to develop a mid-IR spectral library. Australian Journal of Soil Research 46(1), 1-16.

Viscarra Rossel, R.A., Lark, R.M., 2009. Improved analysis and modelling of soil diffuse reflectance spectra using wavelets. European Journal of Soil Science 60(3), 453-464.

Viscarra Rossel, R.A., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma 131(1-2), 59-75.