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Linearization of MIR-DRIFT soil spectra using the 2518 cm^{-1} carbonate band as internal standard

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Due to front surface reflections and high absorption coefficients of inorganic compounds, MIR DRIFTS spectra of neat soils are nonlinear, even after the application of linearizing transforms such as the log-transform into absorbance units or the Kubelka-Munk transform into KM units. In chemometric data processing, this nonlinearity is taken partly into account by additional PLS factors. A generally applicable linearizing transform seems unlikely to exist. One reason is, that different optical configurations of the diffuse radiation collection accessories result in varying degrees of front surface reflection suppression. However, linearization of spectra employing an internal standard seems a promising approach. In natural soils, carbonate is a frequent constituent at high concentration levels and its 2518 cm^{-1} band is relatively free from spectral interferences due to other compounds. This makes it an ideal internal standard candidate for the determination of an empirical linearization function.

MIR-DRIFTS absorbance spectra of 25 dried and finely ground natural soils were obtained. Total carbon (TC) and total inorganic carbon (TIC) were determined and total organic carbon (TOC) was calculated as the difference between TC and TIC. Using a linear baseline between 2648 und 2408 cm^{-1}, the net height of the 2518 cm^{-1} band was obtained and a univariate regression (TIC vs. band height) was performed. Marked nonlinearity was observed. The absorbance spectra A were transformed into linearized spectra A_L using the exponential function $A_L = (A + a)^b$. The parameters a (optimal value 0.4) and b (optimal value 3.3) were chosen such, that the residual sum of squares of the univariate regression (TIC vs. linearized band height) was minimized.

To estimate the effect of the linearization, PLS models for TOC were created and cross-validated using the original and the linearized spectra. In the 3401-2399 cm^{-1} spectral range, 3 PLS factors were used for each model. The linearized spectra ($RMSECV_L$=0.37, R^2_L=91.1) gave much better PLS models than the original spectra (RMSECV=0.60, R^2=77.2). The latter showed marked nonlinearity curvature in the residuals.

Another calibration for TOC in the range 1000-650 cm^{-1} shows, that the PLS models based on linearized spectra perform better ($RMSECV_L$=0.52; R^2_L=82.7; 6 factors) than PLS models based on the untreated spectra (RMSECV=0.62; R^2=75.5; 5 factors). It is remarkable, that this effect is observed also in this spectral region relatively far away from the 2518 cm^{-1} band used as internal standard. Finally, a TIC calibration in this spectral region clearly shows the advantages of the linearizing approach ($RMSECV_L$=0.26; R^2_L=96.9; 5 factors) over the conventional (RMSECV=0.43; R^2=91.3; 5 factors) method. Two soils were excluded as outliers in all PLS models.

The results suggest, that it is possible to use the carbonate 2518 cm^{-1} band as internal standard for the selection of a linearization function of the type $A_L = (A + a)^b$. The parameters can be easily determined on an individual spectrometer/DRIFTS accessory using soils containing carbonate in varying amounts. The linearized spectra can subsequently be used for building PLS models.