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Extended Multiplicative Scatter Correction Applied to Mid-Infrared Reflectance Measurements of Soil

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Introduction: Scattering artifacts adversely affect infrared reflectance measurements of powders and soils, and extended multiplicative and extended inverse scatter correction (EMSC[1] and EISC[2]) are flexible methods useful for correcting for these artifacts. In this example, EISC was used to correct mid-infrared reflectance spectra of two different soils coated with the analyte dibutyl phosphate (DBP). Details of the application can be found in Ref. 3. The correction employed a robust least squares method to account potential biases due to the presence of analyte. Analyte-free (uncoated) samples were used to determine basis functions for an extended mixture model used in the correction. Corrected spectra resulted in partial least squares models that performed at least as well as second derivative spectra and were more interpretable.[3]

The EISC model is

$$b_R \mathbf{x}_{meas}^T + \mathbf{b}_S^T \mathbf{S}^T + \mathbf{b}_P^T \mathbf{P}^T + \mathbf{b}_Q^T \mathbf{Q}^T = \mathbf{r}^T$$

where $\mathbf{x}_{meas}$ is the negative log of the measured intensity, $\mathbf{S}$ is a matrix of target spectra that are allowed to pass the filter, $\mathbf{P}$ is a matrix of polynomials of the frequency axis, and $\mathbf{Q}$ is a matrix of "background" vectors. Variability associated with $\mathbf{P}$ and $\mathbf{Q}$ are not allowed to pass the EISC filter. The vector $\mathbf{r}$ is a reference spectrum (here it was the mean of spectra measured for analyte-free soil and $\mathbf{Q}$ was the PCA loadings from multiple reflectance spectra from analyte-free soil). The coefficients b_R, $\mathbf{b}_S$, $\mathbf{b}_P$, and $\mathbf{b}_Q$ are determined using least squares (here a robust least squares method was used).

Experimental: Reflectance spectra were recorded at 4 cm^{-1} resolution in the mid-infrared (5200 to 500 cm^{-1}) using a Bruker IFS 66/S FTIR. Soils studied were Quincy Soil that consisted primarily of quartz (SiO_2) sand, and League Soil dominated by montmorillonite clay. Spectra were measured before and after purging with dry nitrogen. After measurements were made on the analyte-free soils, solutions of DBP at different concentrations in a highly-volatile solvent were dripped onto the soils and allowed to dry. Details can be found in Ref. 4.

Results and Discussion: Uncorrected and corrected spectra are shown in Figures 1 and 2 for the League Soil and in Figures 3 and 4 for the Quincy Soil. Ideally, measured analyte-free soil spectra would all lie on top of each other with only white noise as the difference, however this is clearly not observed. The corrected spectra have significantly lower variability. EISC corrected spectra provided quantification results that performed that at least as well as second derivative spectra and were more interpretable,[3] and gave promising results for enhancing detection performance.[5]

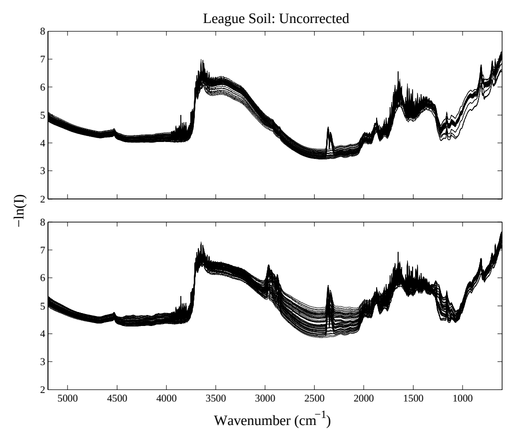

Figure 1: Uncorrected reflectance spectra for League Soil: (top) analyte-free, and (bottom) with DBP analyte.

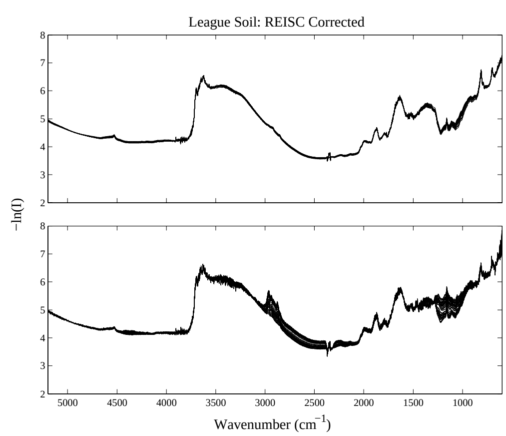

Figure 2:Corrected reflectance spectra for League Soil: (top) analyte-free, and (bottom) with DBP analyte.

Conclusions: EMSC and EISC can be used to remove variability in reflectance spectra. The methods can be viewed as filters that parse the information into e.g., chemically related and scattering related variance. The result can be good models[3,5] with corrected spectra that are easily interpretable. However, some work is required by practitioners to optimize the filter parameters.

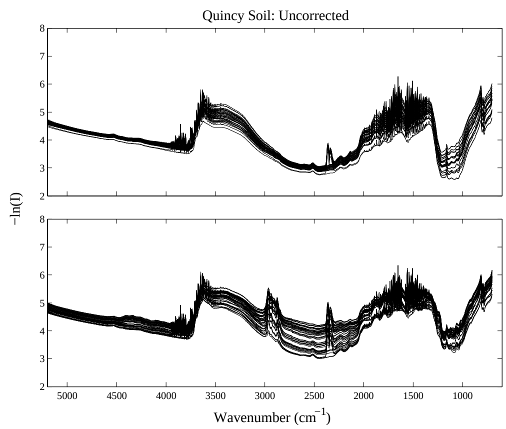

Figure 3: Uncorrected reflectance spectra for Quincy Soil: (top) analyte-free, and (bottom) with DBP analyte.

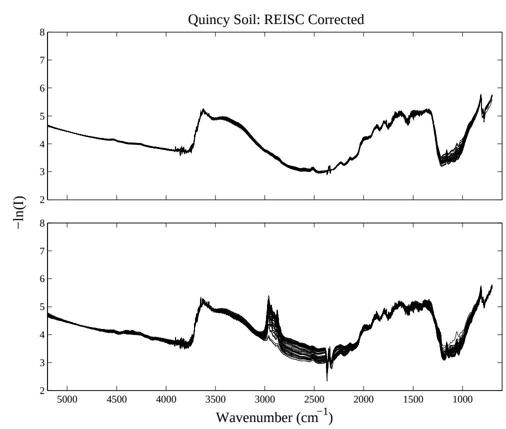

Figure 4: Corrected reflectance spectra for Quincy Soil: (top) analyte-free, and (bottom) with DBP analyte.

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