

CHRYSOTILE DETECTION IN SOILS WITH PROXIMAL HYPERSPECTRAL SENSING AND CHEMOMETRICS

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ABSTRACT

In this work the authors present an innovative methodology, based on proximal hyperspectral sensing and chemometric techniques, aimed at detecting asbestos containing soils. Short Wave InfraRed (SWIR) reflectance spectra of reference samples containing known chrysotile fractions were collected in laboratory. Since the identification of asbestos containing soils depends on the contaminant mass percentage (weight/weight), two supervised multivariate data projection methods were evaluated for asbestos concentration prediction. The first results are reported here, together with advantages and limits of the analytical methods. Orthogonal Partial Least Squares (PLS) regression showed the lowest error in prediction and the highest coefficient of determination in prediction. This technique would support screening activities frequently conducted during environmental assessment and remediation projects.

Index Terms— Hyperspectral sensing, orthogonal partial least squares regression, asbestos, soil contamination

1. INTRODUCTION

Asbestos Containing Soils (ACSs) are frequently found in Naturally Occurring Asbestos (NOA) sites, where asbestos has been mined and asbestos-containing materials produced, installed, or disposed of [1]. ACSs represent a health issue because hazardous fibers may be released in air following natural or anthropic disturbances. Contamination levels are usually measured and compared to guideline values, for choosing the type of management (i.e., disposal vs reuse).

The few standardized methods are based on microscopy, that profit of high resolution and sensitivity, but

require complex procedures [2]. Fourier-Transform InfraRed (FTIR) spectroscopy and X-Ray powder diffraction require sample preparation too and suffer from high Limits of Detection (LOD).

The collection of SWIR reflectance data with hyperspectral sensors and application of chemometric treatments has become a reliable method with a broad range of applications, including assessment of mineralogical composition and pollution levels [3, 4]. When analyzing ACSs, the key issues derive from sample complexity (e.g., interferences) and instrumental sensitivity/resolution, which in turn affect analytical precision and reliability. Often, the LOD and the estimated error make the analytical method less suitable than the available standard techniques.

To overcome such issues, the performance of an innovative method has been assessed on reference ACSs samples and is presented in this work.

2. MATERIALS AND METHODS

Chrysotile fibers extracted in the former Balangero mine (Piedmont, Italy) were milled with ethanol and then dried, while a sample of topsoil collected in Monte Porzio Catone (Latium, Italy) was firstly dried, then hand ground and sieved with a 106 μm mesh-size.

Aliquots were weighed with 0.1 mg resolution and mixed thoroughly by hand to make reference soil samples with known concentration of chrysotile. Each sample was placed on Petri dishes and 25mm-aluminum stubs covered with adhesive carbon tabs were pressed on them. Finally, the stubs were fixed with plasticine into sealed plastic boxes.

The obtained reference samples are listed in Table 1.

Table 1. Chrysotile concentration of reference samples.

Chrysotile conc. (wt.%)	0	0.1	1
Chrysotile conc. (wt.%)	3.5	10	100

Reflectance spectroscopy was conducted with a portable ASD FieldSpec® 4 Standard-Res, in the SWIR region (1000-2500 nm), with a spectral resolution of 10 nm. The instrument was connected to a contact probe with 10 mm spot. A standard calibration procedure was performed before data acquisition. To avoid fibers being released during operations, a borate glass disc was placed between the sample and the contact probe after opening the plastic box. The borate glass was chosen because this material does not significantly absorb in the SWIR spectral region [5].

Twenty spectra were acquired for each sample and analyzed in MATLAB® environment (Ver. 9.10.0. R2021a; The Mathworks, Inc.) with the PLS_toolbox (ver. 8.9.1; Eigenvector Research, Inc.). Splice Correction (SC) was firstly applied to all spectra to eliminate the gaps occurring in the collected data (typically at 1800 nm).

The spectral dataset was randomly split into two parts by using Kennard-Stone (K-S) algorithm. 70% of the spectra was used as training set (calibration and cross-validation), while the remaining percentage (30%) was used as test set (validation). Venetian blinds (VB) method was used as cross-validation for choosing the right number of Latent Variables (LVs) according to an optimal complexity.

Then, two Partial Least-Squares (PLS) regression methods were tested and compared, both consisting in supervised multivariate data projection techniques that are commonly used in predictive models.

The first method is a traditional PLS regression, with Standard Normal Variate (SNV) normalization, Savitzky-Golay (S-G) 2nd derivative (order: 2, window: 33 pt., tails: weighted) and Mean Centering (MC) as pre-processing algorithms [6, 7, 8, 9]. The second method is the orthogonal PLS regression, which instead exploits Orthogonal Signal Correction (OSC) as pre-processing [10, 11].

Root Mean Square Error in Prediction (RMSEP) and the coefficient of determination in prediction (R_p^2) were compared for evaluating prediction performances, while contributes from independent variables were assessed through Selectivity Ratio (SR) and Variable Important in Projection (VIP) scores [12].

3. RESULTS AND DISCUSSION

The raw reflectance spectra averaged according to chrysotile content are shown in Figure 1.

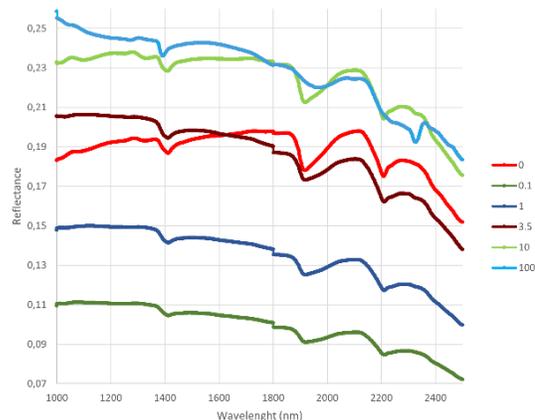


Figure 1. Average raw reflectance spectra.

The absolute reflectance differences between the spectra are caused by minor spacing shifts between the samples and the probe. The average soil spectra are typical of Al-rich clay soils, with absorptions in the first overtone of –OH stretching (1400 nm), the H₂O bending (1900 nm) and the Al–OH combination band (2200 nm) [13, 14]. Chrysotile analytical peak (2330 nm) is easily visible in the 100% asbestos sample, and is less and less observable as the percentage decreases. This absorption is caused by combination of the –OH stretch with the Mg–OH bend and is typical of trioctahedral phyllosilicates [13].

3.1. Partial Least Squares Regression

Spectra pre-processed by SNV, 2nd Derivative and MC are showed in Figure 2. The algorithms enhanced wavelengths at around 1380, 1880 and 2330 nm for chrysotile and at 1400, 1900 and 2200 nm for uncontaminated soil.

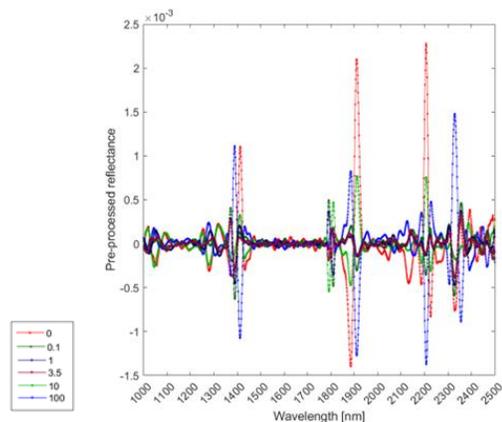


Figure 2. Pre-processed spectra (SNV, 2nd Derivative, MC)

The PLSR results and the related SR and VIP scores are reported in Figure 3a, 3b and 3c, respectively.

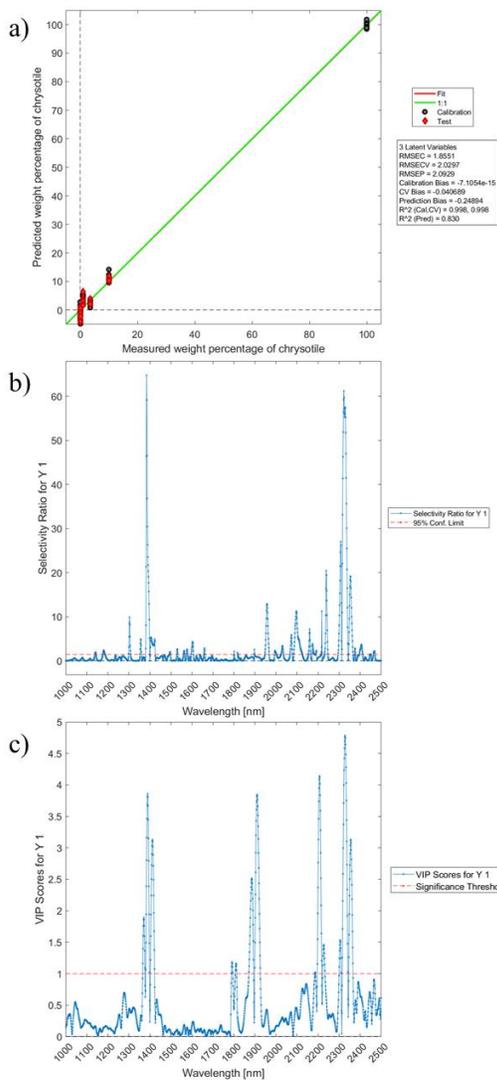


Figure 3. PLSR results (a), SR (b) and VIP scores (c).

The RMSEP with 3 LVs (Fig. 3a) is 2.09 wt.% ($R_p^2=0.83$), which makes this method unsuitable to detect asbestos at concentrations around 1% w/w. The higher SR scores (Fig. 3b) are located at 1380 and 2330 nm, both related to chrysotile [13, 14]. The VIP scores (Fig. 3c) enhanced the same wavelengths, plus 1410, 1880, 1900, 2200 and 2360 nm, that are related to soil constituents (clay minerals) [13].

3.2. Orthogonal Partial Least Squares Regression

The pre-processing algorithms (OSC and MC) enhance the difference between chrysotile and soil spectra (Figure 4).

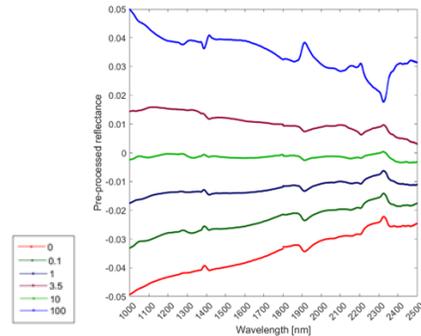


Figure 4. Pre-processed spectra (OSC, MC)

The OPLSR results and the related SR and VIP scores are reported in Figure 5a, b and c, respectively.

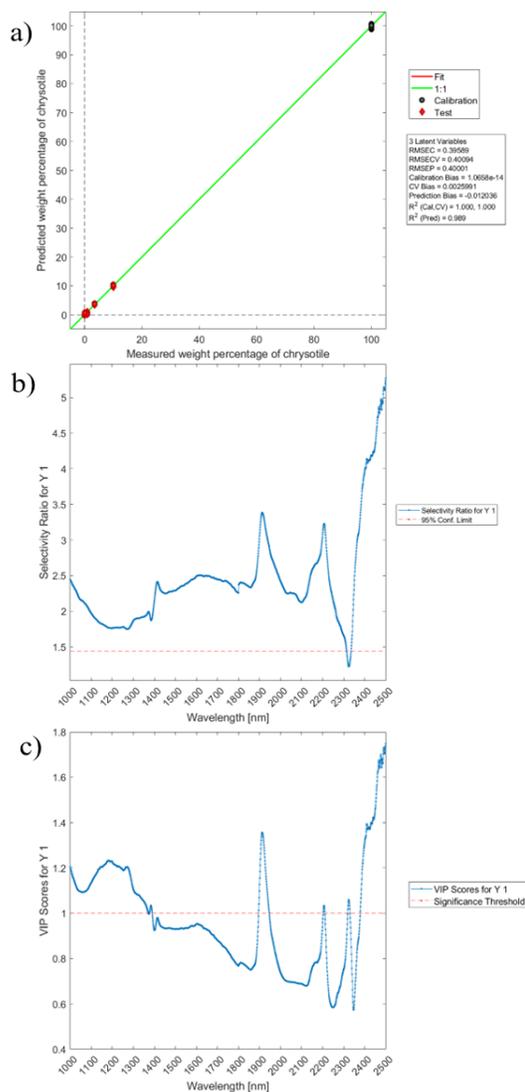


Figure 5. OPLSR results (a), SR (b) and VIP scores (c).

The RMSEP with 3 LVs (Fig. 5a) is 0.40 wt.% ($R_p^2=0.99$) and is significantly lower than the error associated to PLSR. Such performance is still inadequate for assessing soils with low asbestos levels but may be suitable for screening applications in medium/highly contaminated sites.

In this case, the SR enhanced the medium wavelengths (Fig. 5b), while the VIP scores the short ones (Fig. 5c). Both the algorithms highlight peaks at around 1900 (H₂O bending) and 2200 nm (Al–OH combination band). Interestingly, the chrysotile absorption at 2330 nm overcomes the VIP scores significance threshold, while it is the only signal placed under the SR 95% confidence interval.

4. CONCLUSIONS

Two regression methods based on high-resolution reflectance data collected in the SWIR region were evaluated on reference samples of pure chrysotile and asbestos-containing soils in different percentages, to identify spectral differences between sample types and assess the concentration prediction. The performance of OPLSR was better than PLSR, with the same number of LVs (3).

The SR and VIP scores of both regression techniques enhanced wavelengths in the first overtone of –OH stretching, the H₂O bending and the Al/Mg–OH combination bands. Since absorption peaks of hydrated minerals are in these regions, hyperspectral instruments are needed to resolve between different signals, thus detecting asbestos in the sample.

Further studies should be conducted, to lower the prediction error and apply this method for comparing chrysotile concentration with regulatory limit values (usually 0.1% w/w). Such studies should involve a broader sample set.

Since these techniques do not require complex sample preparation, their adoption may reduce the risks of exposure to airborne fibers for technicians. Moreover, the analysis may be performed onsite with handled instruments. Therefore, the presented method may be useful during screening/monitoring activities in contaminated sites.

11. REFERENCES

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