Short-Wave InfraRed Spectroscopy techniques for in-situ discrimination of hazardous mineral fibers in natural and anthropic matrices

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Introduction

Asbestos is a commercial term including six fibrous minerals: one serpentine (chrysotile) and five amphiboles (crocidolite, amosite, anthophyllite, actinolite and tremolite), that have been classified as carcinogens by the International Agency for Research on Cancer (IARC), together with other fibrous minerals (namely erionite and fluoro-edenite). They all occur naturally in several rock types, heterogeneously distributed all over the world, while only chrysotile, crocidolite and amosite can be found in a large number of anthropic Asbestos-Containing Materials (ACMs), such as the famous asbestos-cement sheets [1]. When fibers are not firmly bounded in a matrix, they can be released into the environment, rising up the inhalation risks and related health issues [2].

Early detection carried on field, together with real-time control and monitoring technologies, may be useful to detect ACMs and manage contaminated sites, to prevent human exposures. Among portable instruments, spectrometers are frequently used in many applications [3]. In more detail, Visible (Vis) and Short-Wave InfraRed (SWIR) spectroscopy are adopted worldwide to perform both qualitative and quantitative analysis of almost any material type, including environmental contaminants.

The aim of this study was to test the possibility of using a portable device aided by machine learning techniques to discriminate natural and anthropic materials containing hazardous mineral fibers. Machine learning classifiers were trained and tested using the spectra collected in laboratory to be potentially used in field for assessing asbestos contamination.

Material and Methods

Samples of different ACMs and products were provided by National Institute for Insurance against Accidents at Work (Inail) and were prepared at Inail Research Center of Monte Porzio Catone (MPC - Rome, Italy). The analyzed samples consist of natural occurring asbestos (NOA), erionite, anthropic ACMs and a set of laboratory-made mixtures based on cement/asbestos, soil/asbestos and soil/asbestos-cement.

A FieldSpec 4 Standard–Res field portable spectroradiometer (ASD Inc., Boulder, CO, USA) was used to acquire spectra in reflectance mode. This portable device works in the Visible (Vis) and Short-Wave InfraRed (SWIR) regions, from 350 nm to 2500 nm and has a spectral resolution of 3 nm at 700 nm and 10 nm at 1400/2100 nm and a spectral sampling (bandwidth) of 1.4 nm at 350-1000 nm and 1.1 nm at 1001-2500 nm [4].

Collected data were then analyzed using the PLS_toolbox (ver. 8.9.1; Eigenvector Research, Inc., Wenatchee, WA, USA) and Statistics and Machine Learning Toolbox running in MATLAB environment.

Before proceeding with the calibration of the classification models it was necessary to carry out a data preprocessing. Following initial data preparation, the collected reflectance spectra were reduced from 350 - 2500 nm to 900 - 2500 nm. Splice Correction (SC) was applied in order to eliminate the gaps occurring in the acquired spectra, due to the different detector arrays [4]. The second pre-processing algorithm adopted was the Gap-Segment (G-S) first derivative in order to apply a baseline correction and enhance weak signals in the spectra [5]. Finally, Multiway Center (MC) was applied to obtain a matrix which has a mean of zero for the three given modes (i.e. detector's ranges). The Principal Component Analysis (PCA) was adopted as data exploratory method to detect outliers and select the data to built-up the DA and KNN classifiers.

Different chemometrics techniques were then applied to discriminate the material classes. In more detail, Partial Least Squares-Discriminant Analysis (PLS-DA), Principal Component Analysis-based Discriminant Analysis (PCA-DA), Principal Component Analysis-based K-Nearest Neighbors classification (PCA-KNN), Classification and Regression Trees (CART) and Error Correcting Output Coding Support Vector Machine (ECOC SVM) classifiers were tested. The $Recall_M$, that is the average per-class effectiveness of a classifier to identify class labels, and the *Average Accuracy*, that represents the average per-class effectiveness of a classifier, were adopted to compare the overall performance of the classifiers.

Results and Discussion

The following table shows the performance metrics of different models across three classification phases: calibration, cross-validation, and validation. ECOC SVM and CART consistently displayed optimal performance across all phases, achieving a $Recall_M$ and an *Average Accuracy* equal to 1.00. PCA-KNN demonstrated slightly lower performance, with a $Recall_M$ ranging between 0.98 and 1.00 and an *Average Accuracy* of 1.00, whereas PCA-DA and PLS-DA exhibited comparatively poorer performances, recording a $Recall_M$ between 0.66 and 0.74 and an *Average Accuracy* of 0.95.

Table. Macro-average *Accuracy* and *Recall* of the considered classifiers in classification, cross-validation and validation.

Model	Model phase	Recall M	Average Accuracy
PLS-DA	Calibration	0.74	0.95
	Cross-validation	0.68	0.95
	Validation	0.72	0.95
PCA-DA	Calibration	0.66	0.95
	Cross-validation	0.66	0.95
	Validation	0.70	0.95
PCA-KNN	Calibration	1.00	1.00
	Cross-validation	0.99	1.00
	Validation	0.98	1.00
ECOC SVM	Calibration	1.00	1.00
	Cross-validation	1.00	1.00
	Validation	1.00	1.00
CART	Calibration	1.00	1.00
	Cross-validation	1.00	1.00
	Validation	1.00	1.00

Conclusions

This research demonstrates the practical application of Vis-SWIR portable spectrometers for on-site assessment of asbestos and erionite presence in various matrices, including natural matrices and human-made products. Hand-held spectrometers enable on-site, non-destructive, and cost-effective material analysis, thus facilitating reliable and rapid detection of hazardous minerals and reducing the health risks triggered by the exposure to airborne fibers. Moreover, the utilization of machine learning techniques is a precise and robust methodological approach. Future studies should focus on expanding the spectral library by collecting spectra from more types of natural and human-made materials. Furthermore, an in-depth study is necessary to determine if Vis-SWIR Hand-held Spectrometers are appropriate for use in challenging situations including characterizing Construction and Demolition Waste (CDW), excavated soils and Post-Earthquake Building Waste.

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