HISTORICAL PLASTER COMPOSITION DETECTION USING REFLECTANCE SPECTROSCOPY

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ABSTRACT

Reflectance spectroscopy is a non-invasive method that is based on the fact that a specific object/material provides various reflectances in different wavelengths across the spectral range. It can provide unique information regarding the material composition of the object of interest and has been used in many fields in recent years. Determining composition of historical plaster is very important when defining its individual components and possibly place of origin or even its age. This information can be a key issue for its future repairs that are desired to be done as similar to the original method as possible.

For a precise reflectance spectroscopy material detection, a fine spectral library is needed. Special mathematical methods are used for comparison of measured spectral curve with individual spectral curves stored in the used spectral library. The spectral analysis then shows similarity of the measured curve with the reference ones.

This paper introduces results of the new plaster composition spectral library created by Department of Geomatics, Faculty of Civil Engineering, Czech Technical University in Prague within the Czech Ministry of Culture Project (DF13P01OVV002). This spectral library has been tested on two historical plaster samples.

KEYWORDS

Reflectance spectroscopy, plaster, composition detection, spectral library, QSdata software

INTRODUCTION

Reflectance spectroscopy has been an area of active research and development in many different fields during past decades and its giant potential is becoming more visible with technical development. It provides full reflectance information from across the electromagnetic spectrum in given spectral range. This is done by collecting many (tens to hundreds) narrow, closely spaced spectral bands so that the resulting spectra appear to be continuous curves. Using these data, one can enable the extraction of reflectance spectra that can be directly compared with similar spectra measured in the field or in a laboratory. The number of measured spectral bands is sensor dependent and is not the key issue. It is rather the narrowness and contiguous nature of the measurements.

The percentage of the light hitting a material that is then reflected by that material is called the spectral reflectance. For most materials it varies within wavelength because of different absorption and scattering characteristics over the spectral range. These variations are shown in plots called spectral curves or reflectance spectrums, where wavelength is shown on x-axis and the reflectance on y-axis (see *Figure 1*). Some materials will reflect certain wavelengths of light, while other materials will absorb the same wavelength. These patterns of reflectance and absorption across wavelengths can uniquely identify certain materials.

Specific materials have their spectral curves defined earlier in laboratory and they are stored in spectral libraries. Using these differences and comparison with laboratory measurements one can compare spectral curves in order to detect measured material.
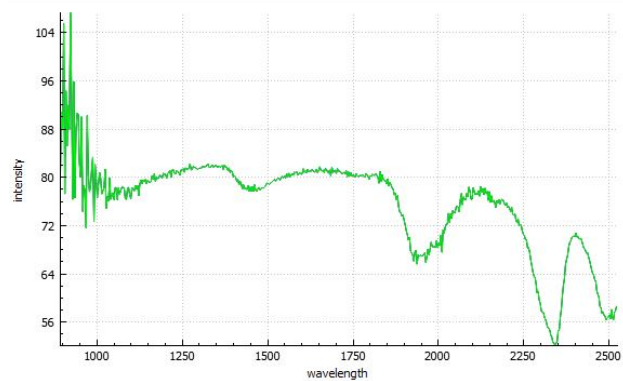
Figure 1 – Example of spectral curve - limestone

INSTRUMENT

Reflectance spectrometers are devices that measure light which is emitted by or reflected from materials and its variation in energy with wavelength. One deals with sunlight or artificial illuminator that is diffusely reflected by measured materials. An optical dispersing element such as grating or prism in the spectrometer splits light into many narrow, adjacent wavelength bands and the energy in each band is measured by a separate detector. Using these detectors, the device can measure many spectral bands as narrow as hundreds of micrometres [1] over a wide wavelength range depending on the instrument.

An Ocean Optics NIRQuest2.5 512 modular spectrometer (*Figure 2*) is at disposal at the department of Geomatics, FCE, CTU in Prague and has been used in this study. It operates in 900 – 2500 nm spectral range where 512 bands are present and it is equipped with an InGaAs detector and cooling. Illumination is ensured by an external source Cool Red (*Figure 3*) that provides adequate light source in mentioned spectral range. An optic fibre then transfers the light into the scanning probe. Reflectance spectrometers give a spectral information about one single point of interest. Data is acquired by enclosing the end of the fibre optics to the object of interest. This device gains data from a single point in form of an ASCII file – wavelength and a corresponding count value.

Figure 2 - Spectrometer NIRQuest

Figure 3- Illumination source Cool Red

A spectroscopic measuring device (*Figure 4*) besides mentioned consists of a laptop with a control software, fibre optics and a measuring probe. The probe is composed of an optical fibre, that transfers information into the spectrometer as well as fibres bringing illumination from external source. End of the probe can be seen in *Figure 5*. A white reference material is a key issue for spectroscopic measurements. After several tests it was found that Spectralon from LabSphere [2], *Figure 6* will be used as a white reference.
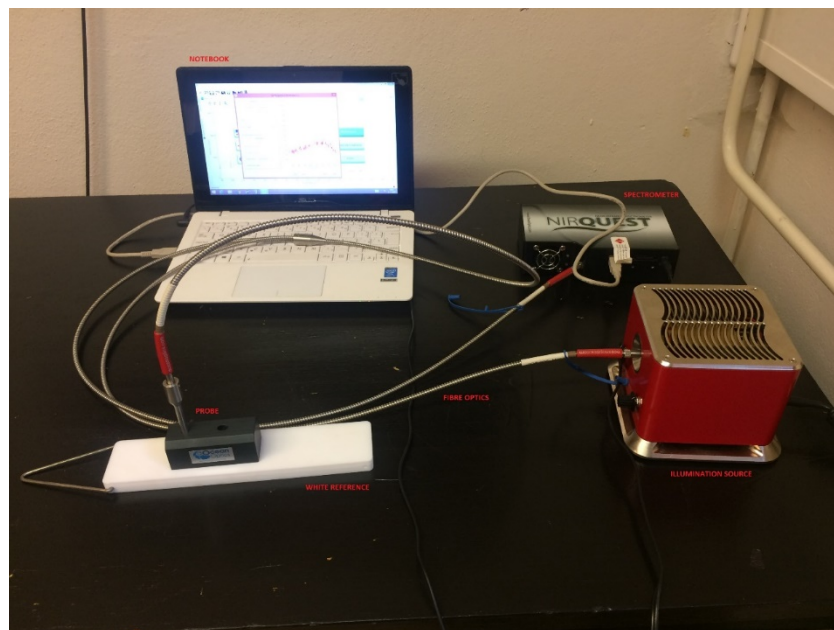

Figure 4 - Reflectance spectrometry measuring device

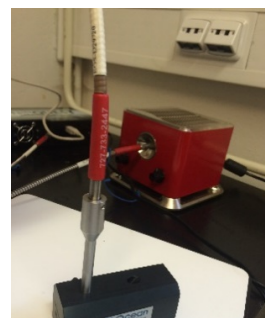*Figure 5 - Probe on the end of fibre optics*

Figure 6 – White reference calibration (Spectralon)

MATERIAL SPECTRAL LIBRARY

In order to analyse various historical samples a unique spectral library had to be created. This was performed in cooperation with Institute of Theoretical and Applied Mechanics, Academy of Science, Czech Republic that provided test samples of 20 most common materials used for plaster production. These samples were carefully prepared and a final set of twenty spectra was recorded. Namely: three different types of sandstone, quartzite, limestone, marlstone, brick, paving stone, five different types of mortar, geopolymer, quart sand, river sand, calcium hydrate, dolomite, gypsum and metakaolin. In order to create convenient etalons curves, many measurements had to be performed and the final spectral curve of each material is an average of 50 individual measurements. Spectral curves of five examples can be seen in *Figure 7.* In case of interest regarding this library, please contact an author via email eva.matouskova@fsv.cvut.cz.
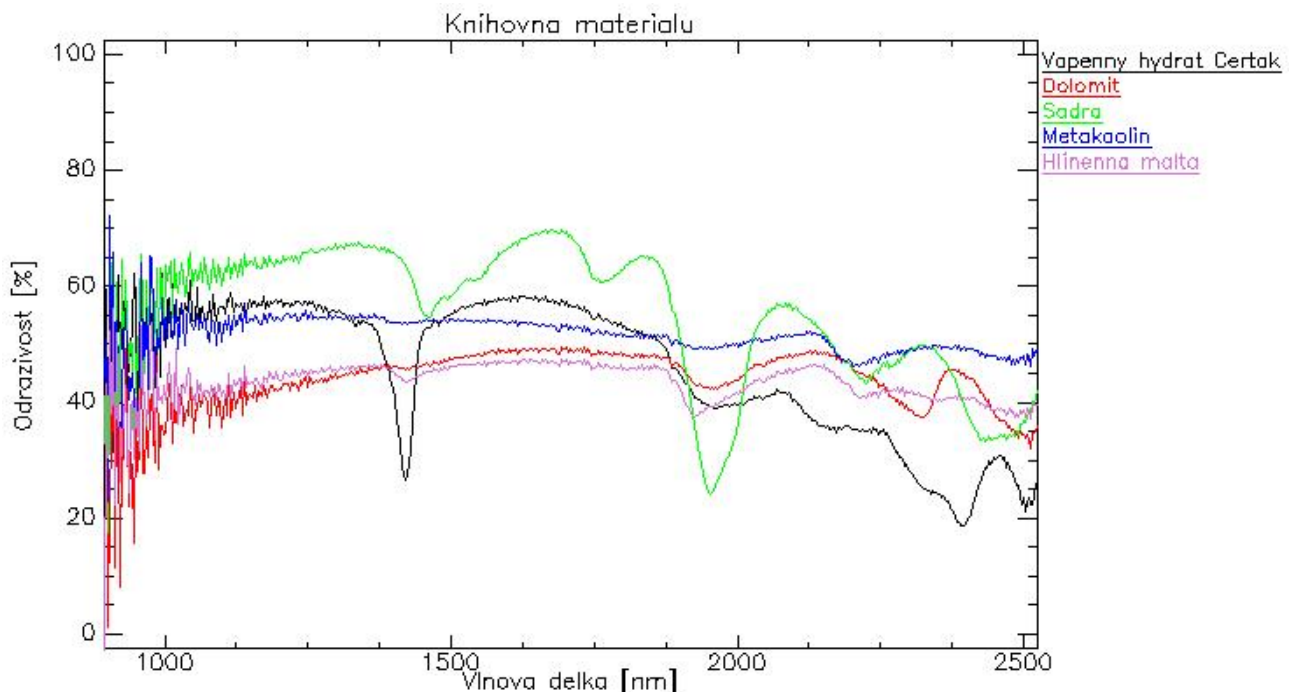
Figure 7 – Spectral curves included in the new library

DATA PROCESSING

The first pre-processing step is the dark and white reference calibration. This can be done by the sensor itself (devices are equipped with a calibration workflow) or manually in processing software. The dark calibration is usually performed by the sensor operating software by subtracting the signal of the sensor (with closed optics) from the object signal. The general-purpose method for the white reference is to use an image processing software. A white reference material is recorded and then it is used as a 100% reflectance. The result will then be a reflectance ranging from 0 to 100% (100% is the reflectance of white reference). After the pre-processing the user can record the reflectance curve of samples of interest.

Final processing can be performed in any suitable software. The key issue is a composition determination that is very complex and provides information about the nature of specific pixel.

Absorption bands or peaks can be analysed in order to discover pixels attributes, other mathematical options can be used. One can mention Spectral Feature fitting that is based on least-squares method [3].

In this analysis a linear unmixing has been performed using the latest version of our spectroscopy analysis software QSdata (v0.9.5). This software has been developed at the Department of Geomatics, FCE, CTU in Prague under the Ministry of Culture Project (DF13P01OVV002) and can be downloaded free of charge from the project website http://lfgm.fsv.cvut.cz/naki/vysledky.html.

SAMPLE ANALYSIS EXAMPLE

When a sample is recorded by the reflectance spectrometer an ASCII text file with wavelengths and corresponding values is stored. One must take into account the calibration procedure of a specific device. Mentioned file is then loaded into the QSdata software and analysis can be performed. Each sample has been measured at least five times and an average has been used in the analysis in order to provide more overall image of the sample of interest. Outlying measurements have been excluded from the average computation.

The final result is then given in the form of table where the most similar etalons are mentioned on the top. A linear combination of active etalons is calculated using non-negative least squares algorithm [3]. The similarity number shows the percentage of each material included in the sample. Samples with similarity number lower than 0,1 are not taken into account due to low similarity and expected calculation error. For more precise percentage determination repetition of the analysis has been performed. With the second analysis etalons with zero similarity have been excluded. The final percentage is then calculated by subtracting a previously defined value so that the final sum is equal to one.

Samples have been provided by the property owners in the Czech Republic. No historic object has been damaged while purchasing these samples, only those found on the ground have been used.
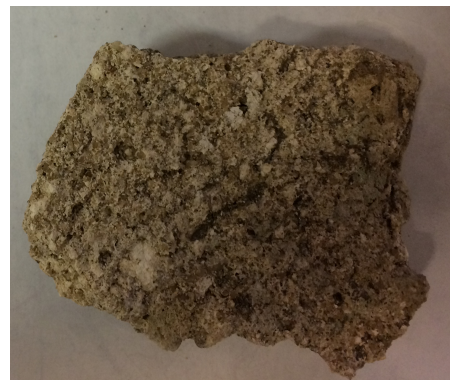

Figure 8 – First analysed sample

Figure 9 – Second analysed sample

The first tested sample (*Figure 8*) consists of 54% hydraulic lime mortar and 46% gypsum (*Figure 10*). Four repetitions of the analysis were performed to obtain this result. *Figure 12* shows the result visualization. The second sample (*Figure 9*) has 49% of hydraulic lime mortar, 37% Božanov sandstone and small ammount cca 4% quartzite (*Figure 11*), with three analysis repetitions. Vizualization is shown in *Figure 13*.

Vzorek4.txt

Similarity	Etalon
0.5943	11-MalHydroVapno
0.5172	18-sadra

Figure 10 – Sample1 - QSdata unmixing outcome

Vzorek2-prumer.txt

Similarity	Etalon
0.6081	11-MalHydroVapno
0.6004	1-piskovec
0.1646	4-kremenec
0.0000	12-MalVapnoMetakaolin

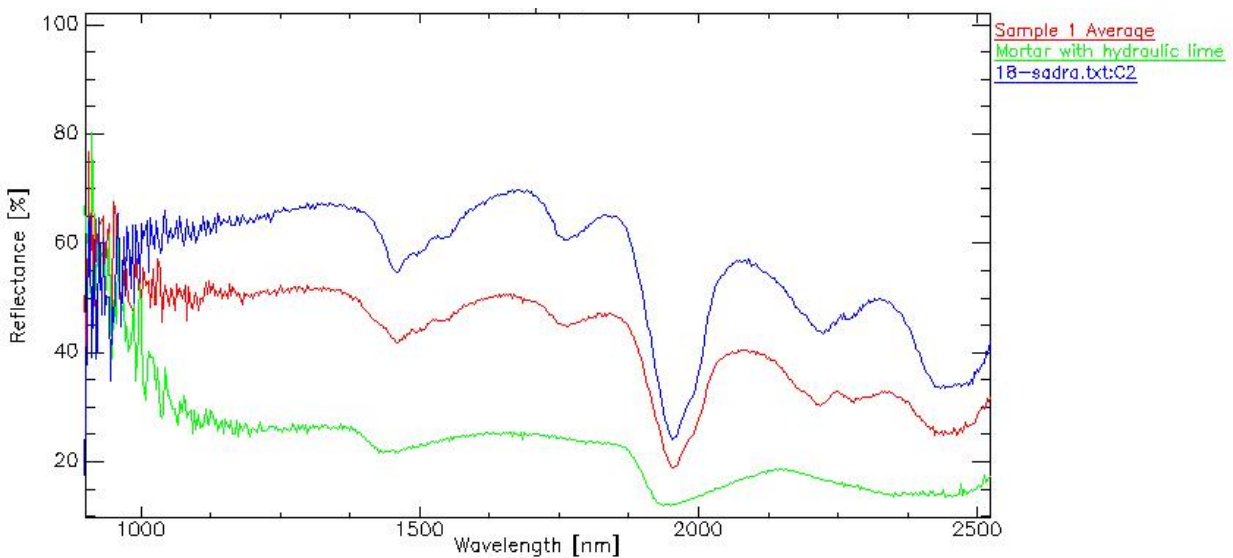*Figure 11 - Sample 2 - QSdata unmixing outcome*
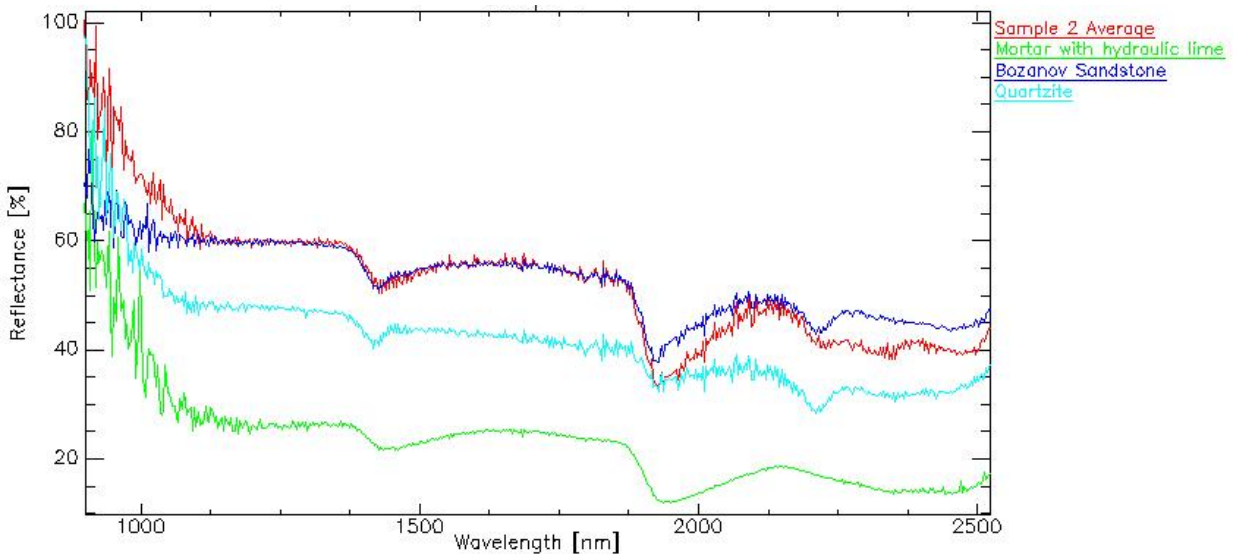

Figure 12 – Sample 1 visualization

Figure 13 – Sample 2 visualization

CONCLUSION

Reflectance spectroscopy has been tested to detect and analyse unknown plaster samples. The latest version (v0.9.5) of newly developed software QSdata has been tested and used for the analysis. Repetition of analysis with excluded low similarity number etalons from previous computations was tested. It was found, that this technique provides fine results, but the percentage of each component has to be recalculated at the end of the analysis. It is desired to include this workflow to the future version of the QSdata software.

Results show that reflectance spectroscopy can provide unique information for a plaster documentation and can help with a composition analysis of samples. Two historical plaster samples have been shown in this paper and their composition has been determined. Further research will be done in this matter to verify the sample material composition and the QS data software will be upgraded in order to visualize results and to provide more user-friendly employment.

The crucial issue of introduced workflow lies in the fact, that the reflectance spectroscopic device is fully mobile and thus can be moved to any location needed and ensures fine non-invasive analysis of the object of interest. The only limitation is the need of electrical power that can be provided by a generator of any kind.

ACKNOWLEDGEMENT

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