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NON-DESTRUCTIVE INVESTIGATIONS OF DIMENSION STONES BY NEAR INFRARED SPECTROSCOPY (NIR)

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Abstract

With the investigation of historical buildings and sculptures a sampling to determine the used dimension stones is only restrictedly possible and often sampling is completely excluded. In these cases, methods are needed that allow an analysis on site. Here is presented an infrared based method of mobile and non-destructive analyses. Besides, a special main focus is the identification of sandstones.

The used portable reflectance spectrometer operates in the near infrared region (NIR) from 1300 to 2500 nm. In this wavelength region all common clay minerals, sulphates, carbonates and other minerals containing OH- and/or H_2O-molecules can be detected. Different clay minerals and/or varieties of clay minerals in connection with their relative contents in sandstones form the NIR spectra in typical manner. In addition also other components like limonite, haematite and amorphous silica influence the spectra. Sandstones which are very similar in colour and texture show therefore in many cases quite typical spectra which can be already distinguished visually and can be absolutely called „spectral identity lines". These identity lines allow identifying the sandstone type (provenance analysis) in many cases. Digital reference libraries with more than 1000 NIR spectra of the most important building sandstones of Germany and adjoining areas were compiled for provenance analyses. The mobile and non destructive NIR spectroscopy was used during the last years successfully in different projects for monument preservation, construction research, archaeology and art history. A special main focus was the investigation of medieval sacred buildings and the investigation of art-historically valuable sculptures.

After a methodical introduction the potentials, but also the limitations of the NIR spectroscopy are presented at some case studies and a perspective about other applications is given.

Keywords: near infrared, identification of sandstones, sacred buildings, sculptor´s works, serpentinite, marble

1. Introduction

Infrared spectroscopy is already more or less standard used for rock and mineral analyses in addition to X-ray diffraction. While these are generally laboratory methods with appropriate technical input, here is presented a mobile method that allows non-destructive investigation of dimension stones for mineral analyses and specifically for the identification of building sandstones.

IR spectroscopy based on activating chemical bonds. By irradiating a mineral mixture, special bonds are activated to vibrate depending on the bond energy (resonance vibration). The energy of the IR spectrum will be reduced accordingly thereby generating an absorption spectrum. The positions of the absorption maxima within the spectral region indicate the types of bonds and, in many cases, identify the mineral containing these bonds. The absorption intensity depends on the amount of the mineral in the sample. According to the Lambert-Beer law quantitative analyses are possible.

In IR spectroscopy three wavelength regions are of interest: near infrared (NIR), mid infrared (MIR) and far infrared (FIR). Because MIR spectroscopy allows the detection of nearly all common minerals, as well as organic material, it is the preferential method in most laboratories. In comparison only special bonds, such as OH, H_2O, CO_2, SO_2 (and therefore only minerals containing these bonds) can be detected by NIR. The number of detected minerals with NIR may be lower (for example quartz and feldspars are mainly not detectable) but all common clay minerals and carbonates characterising sandstones and governing their properties can be determined reliably. Sulphate minerals, as well as mica, limonite and amorphous silica are also detectable. However, the main advantage of NIR is the ability to carry out non-destructive and in-situ analyses by reflection spectroscopy.

The used portable spectrometer operates in the wavelength region from 1300 nm to 2500 nm (NIR). It is supplied with incorporated batteries and may be connected to an external PC or Laptop when not using the on-board hand-held PC. In the following figures IR spectra of four common clay minerals are shown to explain the main features of reflectance spectra produced with the instrument. Principally, reflectance spectra are comparable with absorption spectra. High values of reflectance mean low absorption. Absorbed energy reduces the reflectance and generates absorption bands at distinct wavelengths.

The interpretation of IR spectra provides evidence of the chemical bonds in the sample. Figure 2 illustrates how to interpret the absorption bands to identify chemical bonds. The main characteristic bands to identify kaolinite, smectite, illite and chlorite are labelled in figure 2.

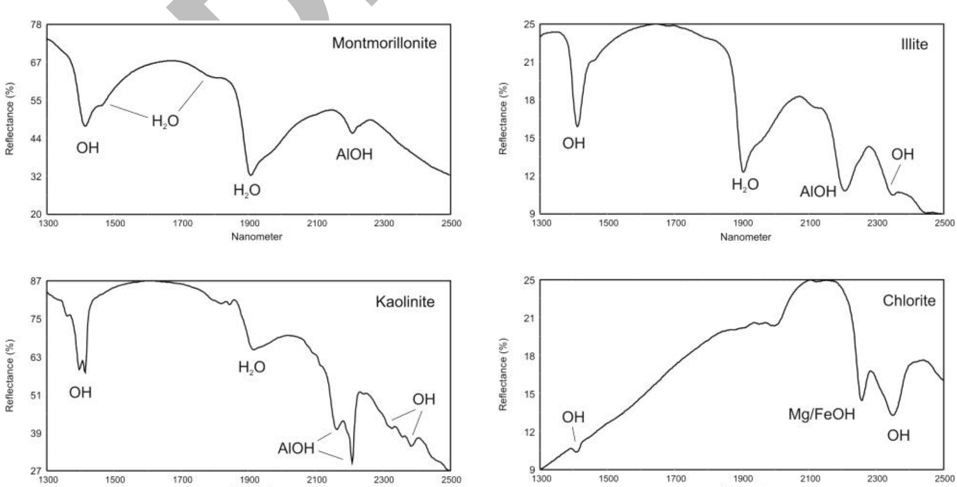

Figure 1. NIR-spectra of important clay minerals in sandstones

Measurements can be performed in-situ without any sample preparation and take less than one minute. The instrument is placed with its optical port directly in front of the sample; the stand-off distance should be less than 5 millimetres. The spectra are measured on a sample area of about 10 mm by 2 mm. Analyses of pulverized samples and granules are also possible.

2. Provenance analysis of sandstones

By irradiating a multi-component sample the produced IR spectrum will show an overlapping of features of each mineral: positions and intensities as well as shape and geometry of each single absorption band. Moreover, infrared spectra of sandstones are formed by all factors influencing diffuse reflectance such grain size, pore size and components with low reflectance. Iron minerals, such as hematite with no characteristic bands in the near infrared, reduce the reflecting energy in red coloured sandstones and cause the attenuation of band intensities. Greenish sandstones, containing chlorite or glauconite, show a typical increasing trend of spectral intensity from shorter to longer wavelengths. Bowitz & Ehling (2008) realized that Sandstones, even if they are very similar in colour and texture, show in many cases quite typical spectra which can be already distinguished visually. They can be absolutely called „spectral identity lines". These identity lines allow identifying the sandstone type (provenance analysis) in many cases. Figure 2 demonstrates how the characteristic clay mineral content of sandstones influences the NIR-spectra.

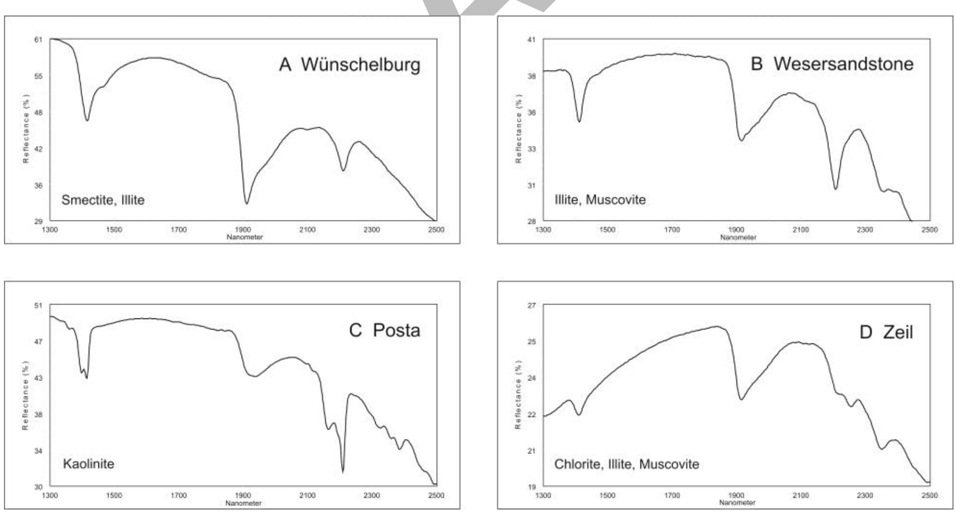

Figure 2. NIR-spectra of different sandstones characterized by their clay mineral content. **A** Silesian sandstone (Wünschelburg), **B** Wesersandstone, **C** Elbsandstone (Posta), **D** Sandstone Zeil

During the last years digital reference libraries with more than 1000 NIR spectra of the most important building sandstones of Germany and adjoining areas were compiled for provenance analyses.

2.1 Sandstones on historical buildings

Mapping of buildings sandstones on historical objects is made difficult by the use of different dimension stones in different times and by the properties of their surfaces which have been changed during the centuries by weathering and other influences. Without additional historical information or analytical investigations provenance analyses of sandstones might be problematic. Mobile NIR-spectroscopy is an important tool to support or to supplement the optical determination.

The St. Nicolai church of Lemgo in Westphalia (Germany) is a former Romanian basilica from the 12th century. In the context of investigations of its construction history dimension stones used in different times have been determined. Beside optical methods, sandstones of the southern portal of the church had been spectroscopic analyzed (see figure 3).

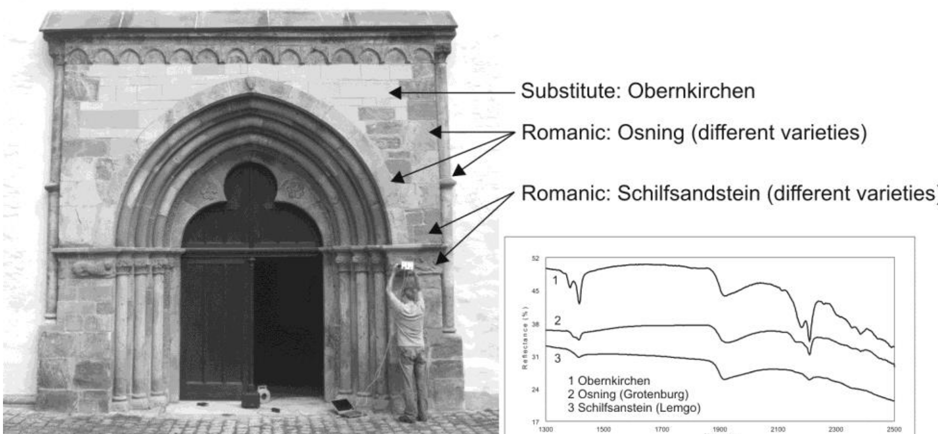

Figure 3. Southern portal of St. Nicolai church in Lemgo (Germany) with NIR-spectra of three used building sandstones

Sandstones of Obernkirchen have been used only to substitute deteriorated material. The original sandstones of the Romanian time are different varieties of Osning-Sandstein (Teutoburger Wald) and Schilfsandstein from different regions in Westphalia. All these used buildings stones can be reliable determined by NIR-spectroscopy (figure 3). Moreover, in some cases a differentiation of varieties and regions is possible. In figure 4 NIR-spectra of some varieties of Osning-Sandstein and Schilfsandstein are plotted exemplary.

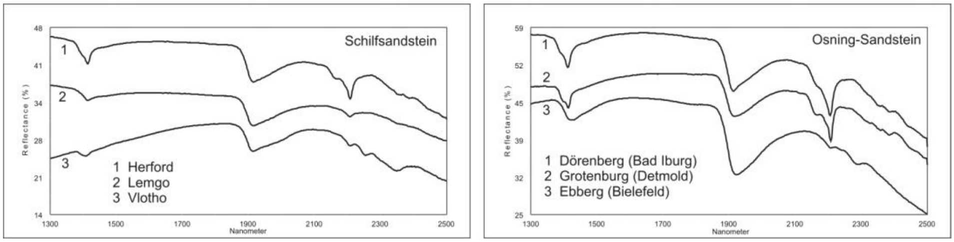

Figure 4. NIR-Spectra of Schilfsandstein and Osning-Sandstein from different regions in Westphalia (Germany) and

2.2 Sculptures made of sandstones

In NE-Germany, today Brandenburg and northern Sachsen-Anhalt, the sandstone from Bernburg on the river Saale (Middle Buntsandstein) was a valued stone of the medieval masons and sculptors. It was an important building stone for the construction of the Magdeburg Cathedral. Beside, many sculptures and other sacral objects had been made of this stone. Sandstones from Bernburg could be detected at more than 50 investigated objects in churches, monasteries and museums. This was only possible by using NIR-Spectroscopy. One example is given in figure 5.

A common problem with the investigation of sandstones used for sculptures and other sculptor's works causes their paintings. In these cases an optical identification of the sandstone is more or less impossible. If a sampling is completely excluded non-destructive analytical methods are needed. NIR-spectroscopy can be applied if a small area of at least 10 mm diameter without painting can be detected on the object.

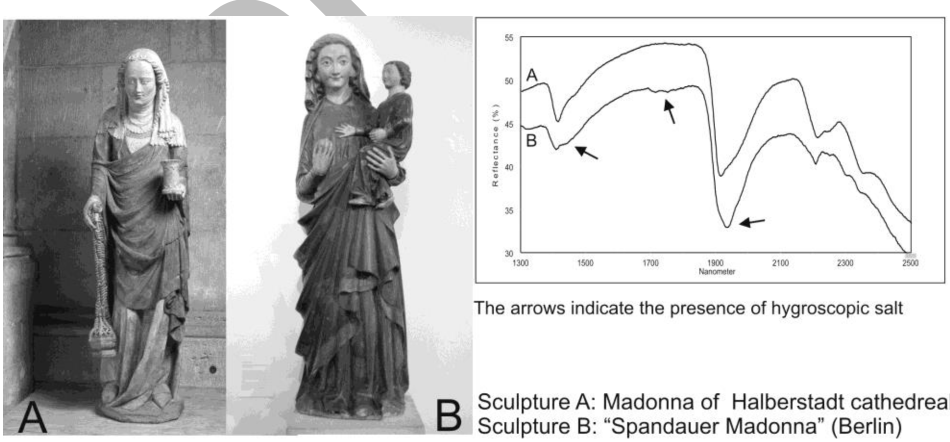

Figure 5. Both medieval sculptures consist of the same sandstone (Sandstone of Bernburg)

The Madonna of Halberstadt had been manufactured about 1380 A.D. by a group of sculptors which works can be traced up to now in seven churches and cathedrals in

Brandenburg and northern Sachsen-Anhalt. All objects of this group are made of sandstones from Bernburg. The “Spandauer Madonna” (about 1300 A.D.) is most likely a sculptor’s work of the masons` lodge in Magdeburg.

Another common feature of objects made of sandstone is the presence of salt, mainly sulphates and chlorides as indicated in figure 4. The ability to detect salts by NIR-spectroscopy might be an additional possible application. But often these salts overlay strongly the spectra of sandstones making an identification difficult or impossible (see chapter 2.3).

2.3 Patina, salts and organics on sandstones

Short wave infrared radiation in NIR region can penetrate the sample maybe two or three millimetres only. Therefore, the property of the surface strongly influences the quality of the spectra. The following figure 6 demonstrates the influence of salts and organics on the surface of the same type of sandstone (Sandstone of Bernburg). Dark patina can absorb infrared radiation and sometimes overlay completely the sandstone´s spectrum as it can be seen in figure 6A. The spectrum of the patina represents mainly organic contaminations. Slight amounts of sulphates or chlorides can be detected without strongly overlapping the sandstone spectra (see figure 6B). The characteristic spectral identity of the sandstone is still conserved. But higher amounts of gypsum (figure 6C) can make the identification of sandstones completely impossible. The same problem is given if organic components of glue and oil (remnants of paintings) are still present on the surface (figure 6D).

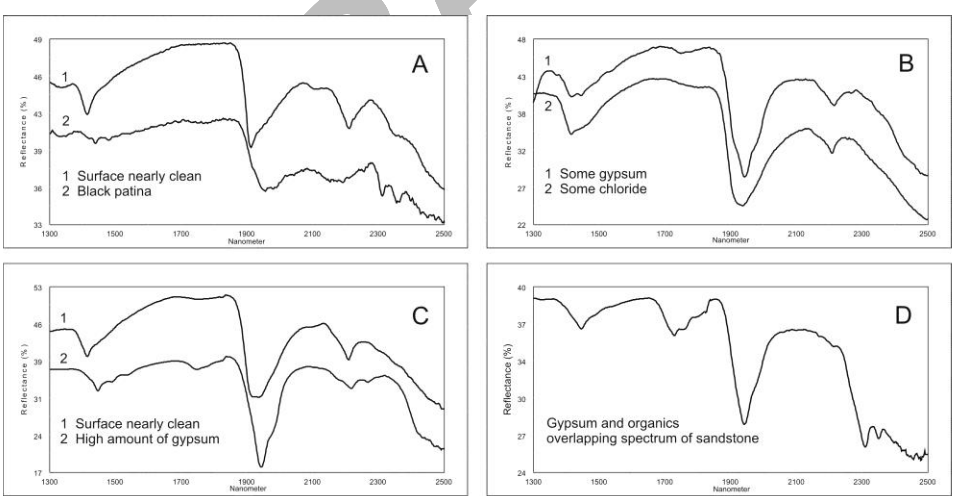

Figure 6. The influence of patina, salts and organics on surface of the same type of sandstone (Sandstone of Bernburg)

3. Perspectives

In the following chapters more possible applications for NIR-spectroscopy are demonstrated with two examples. But it needs more case studies to verify these preliminary results.

3.1 Serpentinite

In the Kaiser-Wilhelm-Mausoleum in Potsdam (Germany) green serpentinites were used for wall covering. As already damages (detoriations) have occurred, it will be searched for replacement stones. Kannis (2009) was concerned with possibility of a provenance analysis and sampled numerous quarries in Liguria (northern Italy). In addition to visual comparisons, he carried out mineralogical investigations using XRD and thin section analyses. After evaluation he found the best matches with samples from the region Bonassola.

In addition spectroscopic analyses by NIR-spectroscopy had been carried out in the mausoleum and at samples from different quarries. Here, too, showed very good matches with the measurements in the mausoleum and samples from Bonassola in comparison to a sample from Deiva Marina near the region of Bonassola (see figure 7). Furthermore, the spectra of the mausoleum showed evidence of hygroscopic salts which could be the cause of damages.

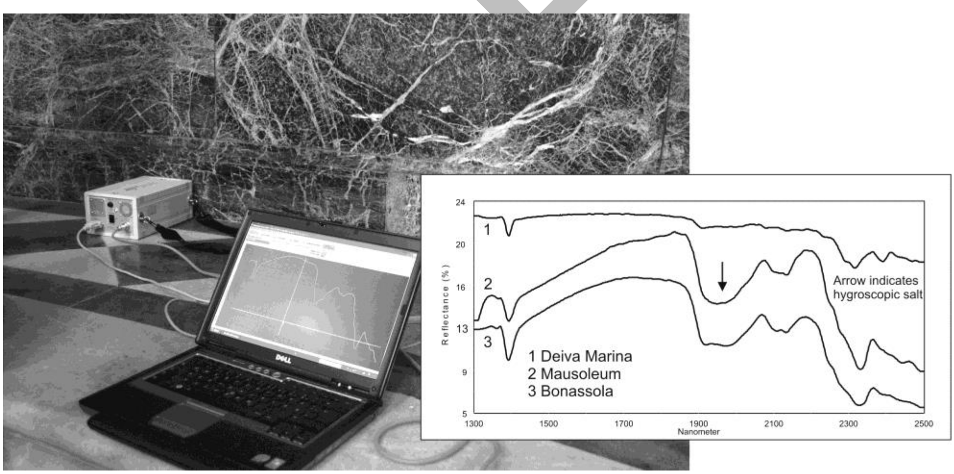

Figure 7. Investigation of serpentinite in the Kaiser-Wilhelm-Mausoleum in Potsdam. Good correlation with a sample of Bonassola. In comparison a sample from Deiva Marina

3.1 Marble

Within a first case study white marbles form different antique quarries in Greece and Turkey have been spectroscopic analyzed to check the possibility of provenance analyses of marbles. First, it was found that even with the non-destructive analysis of marbles calcite and dolomite are to distinguish reliable. Also, the quantitative proportions could be determined. Accessory minerals as mica and clay minerals are detectable (see, figure 8A).

Furthermore, it was observed that pure white marbles, which are identical in geochemistry and mineralogy, show sometimes very different spectral characteristics (figure 8B). The explanation for this and how this phenomenon can be used for provenance analyses must remain subject for further studies.

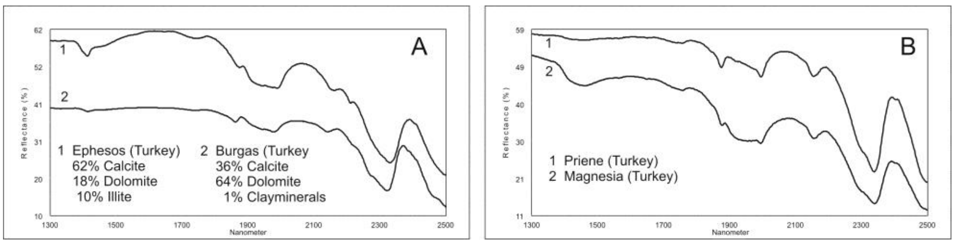

Figure 8. NIR-spectra of marbles from Ephesos and Burgas with analytical results (A). NIR-spectra of pur calcitic marbles from Priene and Magnesia with identical analytical results showing different spectral characteristics

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