Reflectance Spectroscopy as a Tool for Identification of Historic Stone

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Abstract

Within the research of historical stone monuments and artefacts we often encounter the question of determining the original material provenance. The answer to this question is often very complicated due to the frequent impossibility of taking samples for petrographic analysis, which in many cases cannot fully identify the place of origin. It is therefore necessary to pay attention to non-destructive survey methods applicable in the field. For the purpose of non-destructive stone provenance determination, the method of reflectance spectroscopy in the near and mid-infrared spectrum (1000-2500 nm) can be used. It is a very simple and effective method that can be implemented in-situ. This method is based on Earth remote sensing methods and is commonly used for the identification of minerals and soils, but it can also be used for the identification of rocks with a certain experimental set-up and a suitably chosen algorithm for the evaluation of the measured data. For each material, a unique spectral reflectance curve can be defined, which expresses the dependence between reflectance percentage and wavelength. The curve can then be compared with known spectra in a pre-prepared database to find the one that is most similar to the one under study and thus identify the material. The applicability of the method was verified, among other things, in the context of a survey of the historic stone masonry of the southern staircase of St. Vitus Cathedral in Prague, Czech Republic. Obtained results confirm the high potential of this method.

1. Introduction

When studying historical building stones, identifying the original source material often poses a challenge. This difficulty arises mainly because samples needed for traditional analysis (e.g., petrographic, XRD) are often unavailable, and even when they are, these analyses alone may not pinpoint the exact origin. Therefore, it is crucial to employ non-destructive research methods that can be used directly in the field. Reflectance spectroscopy in the near- and mid-infrared spectral range is a straightforward and effective in situ method for non-destructive stone provenance identification. Interdisciplinary collaboration is essential, with experts from various fields contributing to meaningful results. Methods like traceology and archival art history research helps to estimate the age of stone elements. These methods were applied in the research on historical stone masonry of southern staircase of St. Vitus Cathedral in Prague, Czech Republic.

2. Material and methods

2.1 Reflectance spectroscopy

In general, reflectance spectroscopy is a broad term including methods that studies and detects the interaction of electromagnetic radiation with matter. The main principles of reflectance spectroscopy are described in detail by, for example, Clark (1999). As each material reflects and absorbs electromagnetic radiation differently due to changing chemical composition and texture, we can use this method to identify, among other things, the physical and chemical properties of materials (Van der Meer, 2018). Specifically, this method has been used in studies of archaeological sources by, for example, Parish and Werra (2018) and Parish (2016). The destructive techniques of visible and infrared spectrometry, microscopic petrographic analysis, and Raman spectrometry for the purpose of identifying the origin of building stone were used by Hopkinson et al. (2015). In their work, they identified four possible limestone positions in a particular quarry based on petrographic analysis of rock samples from historic masonry and rock samples from quarries, and in conjunction with the results of the spectroscopic methods, they identified one stratigraphic horizon with the most similar rock. In conclusion, they point to the high potential of using these modern survey methods to determine the origin and selection of replacement building stone. Bowitz and Ehling (2008) showcased the significant potential of NIR spectroscopy in identifying historic sandstone.

The use of reflectance spectroscopy in the geosciences is not new, however, it is primarily used for mineral deposit prospecting. A database of spectral reflectance curves of minerals, rocks and other materials is maintained by, for example, the US Geological Survey (USGS, 2017) and NASA (JPL, 2017). These databases are primarily intended for the analysis of remote sensing (RS) data, but some (e.g. minerals) can theoretically be partially used for our purposes after modification. The problem remains, however, that these libraries contain information on rocks and materials occurring in the US that may differ significantly from those found in Europe. It is therefore necessary to use existing libraries with care and to pay careful attention to the location of the data used.

There are possible software solutions for spectral data analysis around the world, most of which are incorporated in existing software solutions for the analysis of remote sensing data. However, these software solutions are not suitable for processing the measured data (lack of calculation of mean, median for multiple measurements of one sample, its statistical characteristics, etc.) and are used primarily for processing image data and their cost is certainly not negligible. Nowadays, there is no simple software solution for users to analyse reflectance spectroscopy data. Data are most often processed using free scripting programs (R-project, 2023) or directly programming

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languages like Python customized to the user's needs. Commercial programs like Matlab (Mathworks, 2023) are also used, where again a tailor-made solution is required.

2.2 Work methodology

As part of our research, we applied the reflectance spectroscopy to investigate a part of the sandstone masonry of the exterior of the southern staircase of St. Vitus Cathedral in Prague (Figures 1 and 2).

Figure 1. St. Vitus Cathedral - material analysis using reflectance spectroscopy.

Figure 2. The studied masonry of the southern staircase of St. Vitus Cathedral with numerical identification of samples.

The studied masonry stone samples were divided into individual groups based on the genetic affinity visual determination and also on their age determination based on the analysis of stone working traces (Cihla et al., 2022).
In order to associate the historic stone sources, we used a set of spectral reflectance curves of the sandstone samples available in our database (Figure 3) and compared the data with each other.
The analysis of the studied samples is carried out using mathematical algorithms that compare the "unknown" curve with those located in the database in various ways to find the best match. Due to the high similarity of the curves of each sandstone in our library, the choice of the algorithm is crucial. In our case, the Spectral Angle Mapper (SAM) algorithm in Matlab (Mathworks, 2023) calculates the spectral angle between two curves proved to be the best solution. The smaller the angle, the more similar the curves are. The analyses were performed in Matlab and ENVI 5.5.

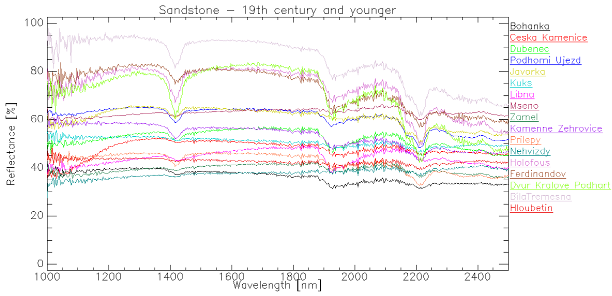

Figure 3. Spectral reflectance curves of selected Czech sandstones quarried from 19th century (Kovářová et al., 2025).

In the Short-Wave Infrared (SWIR) region (1000 - 2500 nm), sandstones display several distinct spectral features primarily influenced by their mineral composition. These absorption bands are linked to various chemical bonds such as OH, H2O, Al-OH, and Mg/FeOH, which are typical for the minerals commonly found in sandstones in varying amounts. The Al-OH absorption band, around 2200 nm, is typically associated with clay minerals like kaolinite and illite. The Mg/FeOH absorption bands, around 2300 nm and 2350 nm, indicate the presence of chlorite and/or serpentine. The potential presence of gypsum and anhydrite is indicated by the SO42- absorption bands around 2100 nm and 2200 nm. Finally, calcite and dolomite can be identified by the CO32- absorption band around 2300 nm (e.g. Bowitz and Ehling, 2008; Zhou et al., 2022; Laukamp et al., 2021).

3. Results and discussion

Based on the traceological analysis, the stone ashlars were divided into three groups, namely: the original, i.e., Gothic, the late 19th century, and the 20th century. Within these groups, blocks were selected (Figures 4 to 6) that represent the same genetic rock type based on visual assessment. These were subsequently analysed using reflectance spectroscopy. The obtained spectral reflectance curves were compared with those in the library, i.e. with 24 Czech sandstones.
Based on the study of written sources, it was certain that our spectral reflectance curves database did not include all the sandstones, arcoses and arcoses sandstones that were used in the construction of the cathedral, especially in the Gothic period (Suchý, 2003; Rybařík, 2016). Suchý (2003) in his work based on the study of the cathedral's accounts, states that mainly Cretaceous quartz sandstones quarried northeast (named Korycany) and east (named Peruc) of Prague were used for the construction of the cathedral at that time. Carboniferous arcosic sandstones to arcoses were then mined west of Prague, with

occasional imports of poor-quality sandstones from Petřín (Prague). Korycany sandstones were quarried in the vicinity of Kostelec nad Labem, Brandýs nad Labem, Zápy, Sluhy and Třískovice. Peruc sandstone was quarried near Horoušany, Carboniferous arcosic sandstone was imported from Kamenné Žehrovice. In the case of Zeměchy, it could have been Carboniferous sandstone (as in the case of Kamenné Žehrovice) imported from Zeměchy by Velvary or opoka from Zeměchy by Louny. However, Zeměchy appears only once in the accounts at that time, suggesting the import of raw material for a specific case, e.g., for sculptural purposes. Due to the absence of spectral reflectance curves for these rocks, we have identified one original "Gothic" block (k21) as a reference and included it in the database for possible comparisons. The results are summarized in Table 1.

Figure 4. A typical example of original building stone from the Gothic period.

Figure 5. A typical example of building stone from the turn of the 19th and 20th century.

Figure 6. A typical example of building stone from 20th century.

For most of the elements studied with our data analysis algorithm, we were able to determine with sufficient specificity the provenance of the sandstone used, or the most likely place of provenance among the first four optically most similar rock types. This procedure allowed us to verify the usability of the method for the given purposes.

In the case of the Gothic stone elements, the SAM algorithm's analysis of the spectral reflectance curves led to the assignment of the three studied elements to a reference block designated as k21, while the results are not entirely clear in the case of block No. 4. Block No. 4 (Figure 5) can be characterized based on visual evaluation as a coarse-grained sandstone to arcosic sandstone, which is visually different from the other Gothic blocks studied. On the basis of the study of Suchý (2003), it can be deduced in this case that it could be, with regard to the partial visual appearance, a sandstone from Žehrovice (the so-called "Žehrovák") or a similar sandstone from Zeměchy, whose spectral reflectance curve, we do not, however, have in our database. Nevertheless, based on the evaluation of the spectral reflectance curves by the SAM algorithm, the block can be optically matched to the k21 block or the Žehrovice sandstone. There is a difference of only one thousandth between the two spectral angles. The first two optically most similar sandstones can be excluded, as these rocks were not imported to Prague in the Middle Ages for the construction of St. Vitus Cathedral (Rybařík, 2016). In order to identify all the Gothic blocks unambiguously, it is necessary to complete the spectra database with the spectra of rocks used at that time. The spectral reflectance curves of blocks 13, 21, 25 and 26 are shown in Figure 6.

Figure 5. The gothic block No. 4.

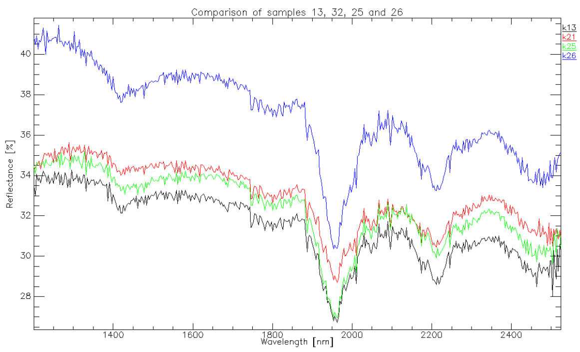

Figure 6. Spectral reflectance curves of blocks No. 13, 21, 25 and 26.

The corner blocks No. 7, 20 and 24 have typical traces of 19th-20th century workmanship. Based on their visual similarity and the evaluation of spectral reflectance curves using the SAM algorithm (Figure 7), we can conclude that these are the sandstones that are visually closest to the Boháňka Sandstone and, in the case of block No. k20, also to the Dubenec and Hořice Sandstones. The Dubenec and Boháňka quarries are located about 10 km away from each other, Boháňka is located about 7 km east of Hořice and Dubenec 17 km east of Hořice. According to Rybařík (2016), Hořice sandstones were used from 1875 during the reconstruction of the cathedral. He also states that sandstones from Hořice (Raiman's quarry, Figure 8) and from Podhorní Újezd, which became the only sandstone used in the construction of the cathedral between 1893 and 1917, were used. Podhorní Újezd is located about 10 km west of Hořice, while Raiman's quarry is located on the eastern edge of Hořice.

Gothic								19th/20th century						20th century			
k4 SAM		k13 SAM		k25 SAM		k26 SAM		k7 SAM		k20 SAM		k24 SAM		k11 SAM		k23 SAM	
Boháňka	0,939	k21	0,938	k21	0,939	k21	0,935	Boháňka	0,936	Žehrovice	0,932	k21	0,936	Hořice staré	0,942	Javorka	0,937
Božanov	0,934	Česká Kamenice	0,934	Česká Kamenice	0,934	Boháňka	0,934	k21	0,930	Dubenec	0,931	Boháňka	0,936	Javorka	0,941	Boháňka	0,936
k21	0,929	Boháňka	0,932	Boháňka	0,930	Česká Kamenice	0,929	Žehrovice	0,930	Bzová	0,930	Česká Kamenice	0,934	Přílepy	0,938	Žehrovice	0,936
Žehrovice	0,928	Kuks	0,930	Kuks	0,930	Božanov	0,925	Česká Kamenice	0,928	Boháňka	0,929	Kuks	0,928	Žehrovice	0,935	Hořice staré	0,933
Krákorka	0,925	Lány	0,927	Lány	0,929	Kuks	0,924	Javorka	0,927	Hořice staré	0,929	Maletín	0,924	Dubenec	0,934	Česká Kamenice	0,930

3.1

Table 1. Ranking of sandstones based on SAM evaluation of spectral reflectance curves (potential sites of provenance indicated by colour, darker shades are more likely, first five sites including SAM values).

The Dubenec sandstone was already used in the 18th century for the construction of the Josefov fortress (Dupis, 2025). From the 1920s onwards, apart from sandstones from Podhorní Újezd, new Cretaceous sandstones were supplied for the construction of the cathedral, namely Mšeno sandstone from Mšené-lázně, Boháňka sandstone from Boháňka in Hořice, Královédvorský sandstone from the municipal quarries in Dvůr Králové nad Labem and Stanovice or Kuks sandstone from Stanovice near Kuks (Rybařík, 2016).

Based on the evaluation of spectral reflectance curves using the SAM algorithm and the above, we can assume that the stone blocks in question are made of Boháňka sandstone. Alternatively, at least based on optical similarity, it can be assumed that the origin of these rocks is east of Hořice. In order to confirm this hypothesis, it would be necessary to complete the spectral reflectance curve database with the curves of all sandstones used in the construction of St. Vitus Cathedral in the past.

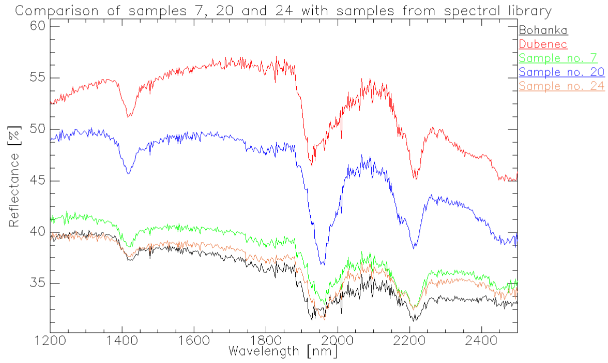

Figure 7. Spectral reflectance curves of blocks No. 7, 20 and 24 and Boháňka sandstone, resp. Dubenec sandstone.

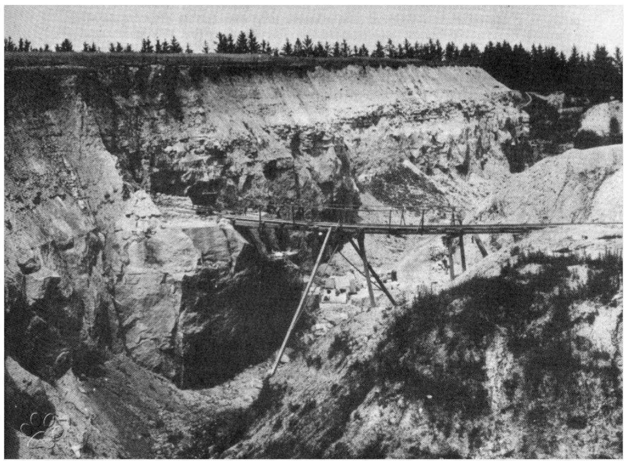

Figure 8. Manual sandstone mining in Raiman's quarry near St. Joseph, 1893 (Jilemnický, 1984).

In the case of the last group of the studied stone blocks, probably from the 20th century, two or three possible source sites can be considered based on the analysis of spectral reflectance curves evaluated using the SAM algorithm. The first possibility is the sandstone from the Javorka quarry, the so-called Bělohrad sandstone, which was mined until 1943 and was restored in 1995 (ČGS, 2025). The other possibility is that it is Boháňka or Hořice sandstone. The difference in the angle of the spectral reflectance curves is negligible (on the order of one thousandth).

3.2 Reflectance spectroscopy limitation

Reflectance spectroscopy has significant potential for identifying the provenance of building and decorative stones. However, like any method, it has limitations, primarily related to the cleanliness of the surveyed surface. Impurities, surface crusts, and restoration treatment can influence the spectral reflectance curves (see Figure 8), complicating stone identification. As it is obvious from the graph, the natural color of the stone, due to the spectral range (1000–2500 nm), plays a less significant role in identification.

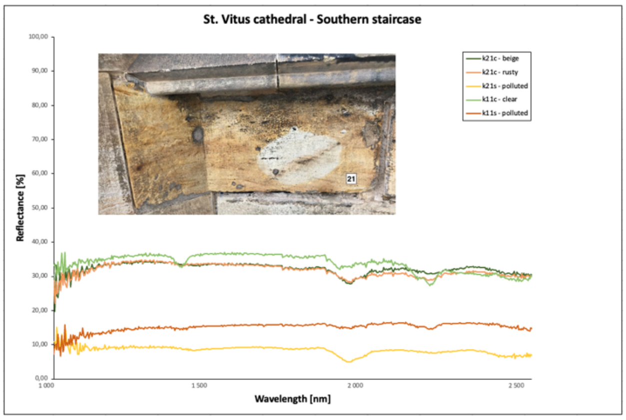

Figure 7. Example of stone impurities impact on spectral reflectance curves, observed at the southern staircase of St. Vitus Cathedral (Kovářová et al., 2025).

Additionally, ongoing weathering processes can alter the rock's mineral composition, e.g., Winkler (1997). Sandstone structures often contain halite and gypsum salt crystals, typical products of weathering processes (e.g. Warke and Smith, 2000). While this negative effect cannot be fully eliminated, it can be partially mitigated by restoration treatments such as masonry desalination (Antepara et al., 2016; Ďoubal, 2017). Similarly, restorers can remove mechanical impurities and crusts from the surface using lasers before provenance identification by reflectance spectroscopy (Siano and Salimbeni, 2010). However, the impact of weathering processes, impurities, and crusts is often insignificant in the interiors of historical buildings or stone collections. One must also consider the possible negative impact of restoration treatments, such as the application of consolidation alkoxysilane coatings, which produce silicon dioxide and silica gel as they age (Xu et al., 2019). These silicon phases affect the spectral reflectance curve, complicating or preventing the identification of the original stone. Lime-based coatings can similarly impede stone provenance determination, as they produce calcium carbonate when aging (Doehne and Price, 2010), affecting the spectral reflectance curve. It is reasonable to expect that other restoration methods producing new mineralogical phases in the stone structure will have similar effects. Therefore, knowing the 'history' of the surveyed stone is crucial when using reflectance spectroscopy, although this is often impossible.

4. Conclusion

In conclusion, the reflectance spectroscopy represents a very perspective method of determining the provenance of historical building stone or artefacts made of it.
Its greatest advantage is its non-destructive character, easy feasibility and the possibility of in-situ use. Disadvantages include the difficulty in processing the data obtained, or the considerable difficulty in comparing spectral reflectance curves using available software, and the possible ambiguity of the results obtained due to small reflectance differences between rock types.
Another limitation of the applicability of the method may be due to the application of restoration agents, e.g. organosilica-based consolidants. Their application causes crystallisation of quartz in the pore space of the rock, the presence of which may affect the measured spectral reflectance curve, making it difficult to assign the proper curve from the database, and the results may be misinterpreted.
In practice, the results obtained can be refined by using other complementary methods, such as X-ray spectrometry (XRF), which is also a non-destructive and in-situ method. At the same time, interdisciplinary cooperation, for example with experts in building history, art history and archaeology in the context of stone use, is appropriate for this purpose. Their knowledge and insights into the use and extraction of natural stone in given historical periods can then help to select the right rock from among those most 'reflectively' similar.

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