

FTIR INVESTIGATION OF PIGMENTS AND BINDER OF PAINTED WALLS IN HERITAGE MONUMENTS

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Abstract. Studies of materials used for works of art and cultural monuments throughout the history contribute to the comprehensive understanding of particular cultures, their technological achievements and customs over time. Investigations of the authenticity of objects and the interventions they may have endured over time keep an important role for their successful restoration and preservation. A three-layer sample of the colored wall decoration from Ottoman Čejvan Čehaja mosque from Mostar, Bosnia and Herzegovina was investigated by FTIR spectroscopy. The plaster was identified as gypsum-lime binder. Inorganic pigments were found in two layers, reddish-brown mixture of Fe_2O_3 and MnO_2 and green pigment recognized as viridian, $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. The upper layer of "golden color" is found to be a physically compact piece of gold foil or leaf whose fixation method meets both the Ottoman and "west" mode of binding. The mode of adhesion by animal glue could be the result of decoration immanent to Islamic culture, but also to reconstruction from the late 19th century during the Austro-Hungarian rule in Bosnia.

Keywords: inorganic pigments; FTIR spectroscopy; heritage; viridian; burnt umber.

1. INTRODUCTION

Čejvan Čehaja mosque, the oldest sacral object from the Ottoman period in Mostar (Bosnia and Herzegovina), was built in 1552. There is no available official data on the restoration of this mosque, although some non-authentic data reveal certain actions on the object in 1895 during the period of Austro-Hungarian rule. The mosque was damaged in 1993 and partially restored in 1996-97 by UNESCO (United Nations, 1997). Along with its cultural and historical significance, the unique architectural landmark of this mosque belongs to the location of the minaret on the left side of the entrance to the building.

Along with other materials, pigments occupy a significant place in the artistic and historical context of painted works and heritage monuments. Identification of particular pigments can give insight into the provenance, dating, authenticity, and extent of material deterioration which have been used in different historical epochs and cultures, as an essential request for a well-balanced approach in restoration and conservation of the monuments. Sampling for analysis is quite specific for this purpose, implying minimum quantities or microsamples and the use of non-destructive methods. FTIR spectroscopy as a fast, sensitive, and inexpensive method for the study of organic and inorganic molecules meets some essential requirements as a mandatory analytical and diagnostic tool in the field of conservation science. This method is especially beneficial in cases of unknown or questionable sample composition. Other methods such as various diffraction techniques and

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in situ modifications are used in specialized laboratories. However, no heritage research is done without infrared or Raman vibrational spectroscopy, often giving the most important and valuable results [1-3].

The aim of this research was the identification of pigments and plaster from the sample obtained from Ćejvan Ćehaja mosque that would allow the use of the same, analogous, or historically admissible materials for further renovation of the building.

2. MATERIALS AND METHODS

For the purpose of inorganic pigments identification, a three-layer sample from Ćejvan Ćehaja mosque was obtained. Infrared spectra were collected on the Perkin Elmer BX FTIR spectrometer (Pekin Elmer, Milano Italy) by KBr method in transmission mode. Along with spectra collected in the region $4000 - 400 \text{ cm}^{-1}$, other regions significant for particular inorganic pigments and plaster have been recorded.

3. RESULTS AND DISCUSSION

A piece of a painted wall containing green, reddish-brown, and "golden" pigments on the plaster layer was investigated by FTIR spectroscopy (Fig. 1). The chemical information gathered by interpreting these spectra could be used by various experts to determine the authenticity of materials from the construction period, previous renovations if any, small interventions, and to plan new procedures.



Figure 1. A sample of a painted wall from Ćejvan Ćehaja mosque, Mostar, Bosnia and Herzegovina.

Plaster

The initial step of this study considered the investigation of the ground. Lime-based lime mortars and plaster have been used since ancient times, even in times of intensive cement use [4-5]. In the spectrum of plaster, the characteristic vibrations of calcium carbonate and gypsum were found (Fig.2.). Carbonate ion is a planar molecule having four normal modes of vibrations, three of which are infrared active. Asymmetric stretching frequency (ν_3) appeared as a broad band centered at 1455 cm^{-1} , out of plane bending (ν_2) at 873 cm^{-1} and planar bending frequency (ν_4) at 716 cm^{-1} [6]. High symmetry in tetrahedral sulfate results with only two fundamental infrared active modes, strong asymmetric S–O stretching (ν_3) found at 1155 cm^{-1} and moderate (ν_4) so-called “umbrella” bending motion of oxygen atoms at 666 cm^{-1} . Although the two sulfate bands are quite strong by themselves, in the presence of carbonate its intensity is somewhat reduced, particularly low-frequency vibration ν_4 . Water molecules in the structure of a crystalline compound, or water absorbed by the surface exhibit characteristic bands in the range $3800\text{--}3200$ and $1700\text{--}1600\text{ cm}^{-1}$, arising from the stretching and bending of O–H bond, respectively. The presence of water from mineral gypsum was confirmed based on strong asymmetric and symmetric vibrations centered around 3470 and 3394 cm^{-1} and bending mode at 1620 cm^{-1} . Out of the plane and in-plane vibrations of water were found at 613 and 460 cm^{-1} [7].

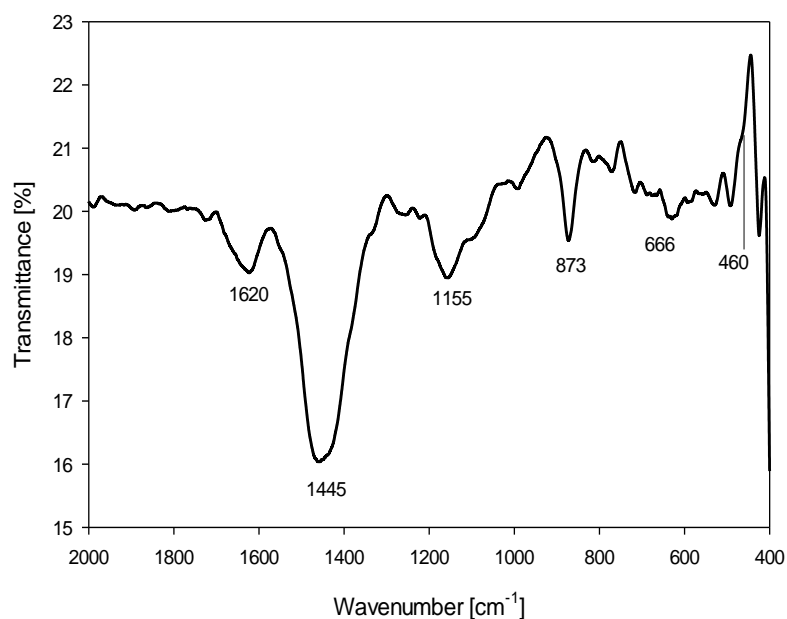


Figure 2. The spectrum of lime-based plaster; the region of characteristic carbonate and sulfate vibrations.

Reddish-brown layer

Natural brown pigments known under the name burnt amber or simply umber since the 16th century [8] mostly contain MnO_2 and Fe_2O_3 in different proportions, sometimes also congaing clay. In this work, the reddish-brown layer was identified to contain a mixture of hydrated Fe_2O_3 and MnO_2 , fillers BaSO_4 and chalk, and a trace of linseed oil as a binder. Ocher, known as earth pigment or hematite, is a natural pigment that can appear in yellow, red, orange, and brown shades. The color of ocher can also be affected by the content of other minerals, very often the clay and manganese oxide minerals that give the ocher a dark color. It

is considered to be the first pigment used by humans in the Middle Stone Age. Almost every prehistoric culture used ochre as a pigment, primarily because of its wide availability. It can be found in many ancient artifacts, colored pottery, also in paintings in caves. In the spectrum of reddish-brown paint in the range $4000 - 400 \text{ cm}^{-1}$ the characteristic vibrations for sulfate and carbonate ions, probably from BaSO_4 and chalk that have been commonly used as fillers, were found (Fig. 3.).

Although the absorption bands of carbonate and sulfate ions are not significantly affected in the case of calcium and barium cations, a discrete shift of these bands toward lower frequencies was observed compared to the ground. In the region $4000 - 600 \text{ cm}^{-1}$ strong and narrow bands at $1141, 1118 \text{ cm}^{-1}$ and moderate bands at 669 and 602 cm^{-1} were assumed to arise from BaSO_4 . Absorptions attributed to CaCO_3 (chalk) at $1420, 874,$ and quite weak band at 713 cm^{-1} are moderate to weak intensity compared to the spectrum of ground with strong absorptions of mostly carbonate-based composition. Absorption at $3548, 3406,$ and 1621 cm^{-1} , attributed to asymmetric and symmetric stretching and bending of water respectively, appeared as narrow and quite well-separated bands indicating the absence of hydrogen bonding found in the spectrum of ground. Traces of organic material, oil binder, were identified based on absorptions at $2942, 2864, 1736,$ and 1685 cm^{-1} [9]. Simple metal oxides absorb in the low-frequency infrared region, mostly below 600 cm^{-1} with low-intensity bands due to bending and wagging mode respectively in decreasing order of frequencies. Stretching vibrations mostly appeared between 750 and 600 cm^{-1} . However, even in the case of mixtures, unlike analytical methods that give the content of individual elements, infrared spectra can provide valuable information about metal oxides in the mixture. This advantage over other analytical methods is especially useful for natural materials which, in addition to the main metal oxides, also contain other elements. The characteristic vibrations attributed to Fe-O stretching in $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ occur in the low-wavelength region of the infrared spectrum. The positions of these absorptions vary depending on the material preparation, size, shape, and internal structure of the particles and could be found in the regions $580 - 520$ and $480 - 420 \text{ cm}^{-1}$ [10-12]. In the spectrum of the reddish-brown sample, we found three bands at $516, 465$ and 424 cm^{-1} that were attributed to Fe-O vibrations in the lattice of hematite.

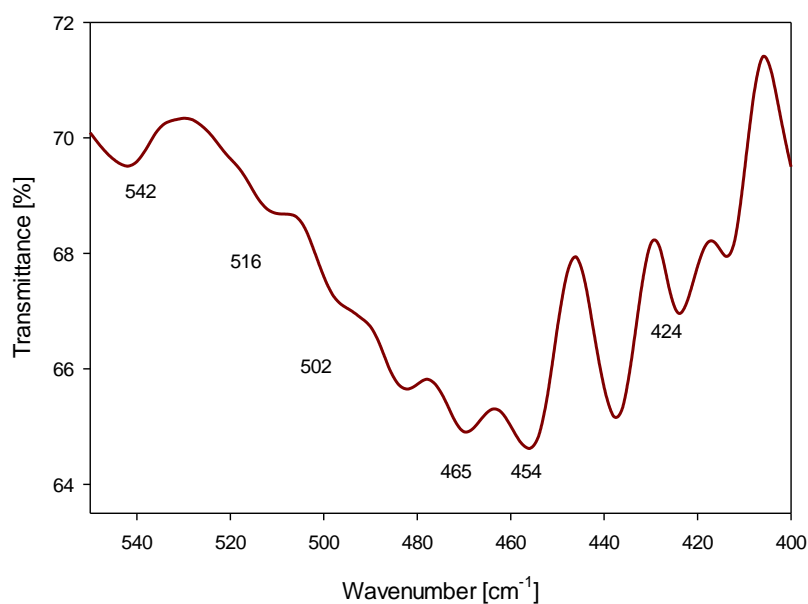


Figure 3. The infrared spectrum of reddish-brown paint

Pyrolusite, a dark brown mineral, has also been used since ancient times. Mn–O vibrations in octahedral $\{\text{MnO}_6\}$ structural units, with ν_3 and ν_4 infrared active modes, appear in the range $650 - 450 \text{ cm}^{-1}$ depending on the different forms and crystal structures [13]. The presence of other ions can also significantly affect the positions of absorption bands due to various interactions and the presence of crystal water or surface adsorbed water. In the spectrum of the reddish-brown sample absorptions at 542 , 502 and 454 cm^{-1} were assigned to Mn–O vibrations of MnO_2 . FTIR spectrum of this paint offers evidence for a mixture of manganese black and hydrated iron oxide. However, no evidence was found for the presence of clay which usually occurs in a natural pigment known as burnt umber. Traditional pigments like MnO_2 and hematite, in red and brown shades, were used as one-component or in the form of natural pigment containing clay. Therefore, it would be questionable whether the reddish-brown pigment is obtained by mixing natural oxides in the desired proportion or corresponds to the burned umber with a minor amount of clay.

Green layer

The most used green inorganic pigments in painted works of art were copper- and chromium-based compounds. There is some confusion about the introduction of chromium(III) oxide under the name "chrome oxide green" and chromium(III) oxide dihydrate ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) known as "viridian" for preparation of paints. Although it has been reported the beginning of its use falls in the middle of the 19th century, there is evidence of its use for painting walls in ancient Chinese culture, dating back to 500 BC [14]. Evidence has also been found in some other works of art from the Roman and Ottoman period [15,16]. The infrared spectrum of green pigment confirmed characteristic frequencies of hydrated Cr_2O_3 (Fig.4.) in the region $700 - 400 \text{ cm}^{-1}$. Absorption at 667 cm^{-1} is attributed to sulfate from plaster, 606 cm^{-1} to water bending, and vibrations at 527 , 471 , 453 cm^{-1} arise from Cr–O vibrations. The presence of water in viridian is also confirmed based on vibrations at 3537 , 3412 , 1620 cm^{-1} ascribed to asymmetric, symmetric stretching and bending mode, respectively.

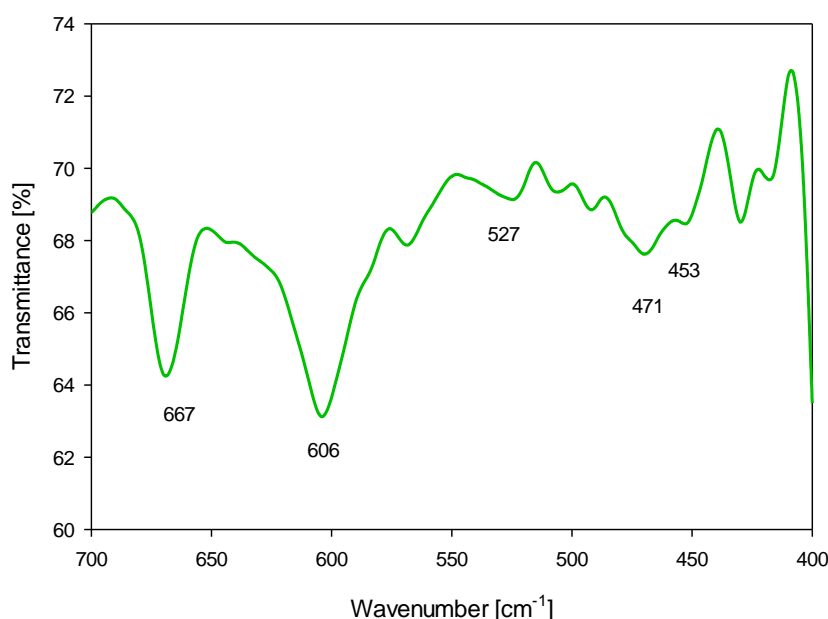


Figure 4. FTIR spectrum of viridian pigment.

Gold layer

The third, physically compact, very thin layer is attributed to the gold leaf or gold foil that is inherent in the Ottoman decoration of sacral objects. The forms of the gold foil and the leaf differ in the thickness varying above or below 10 μm respectively [17]. Application of gold layer on a substrate usually containing gypsum or lime with animal glue as a binder has been a common procedure since ancient times [18-23]. To identify this type of substrate, FTIR spectroscopy is recognized as the method of choice especially in the study of protein structure. The spectrum of adhesive binding substrate for gold coating shows the presence of protein structure identified as collagen from rabbit skin which is often used as adhesive glue [24-27] (Figs. 5 and 6.).

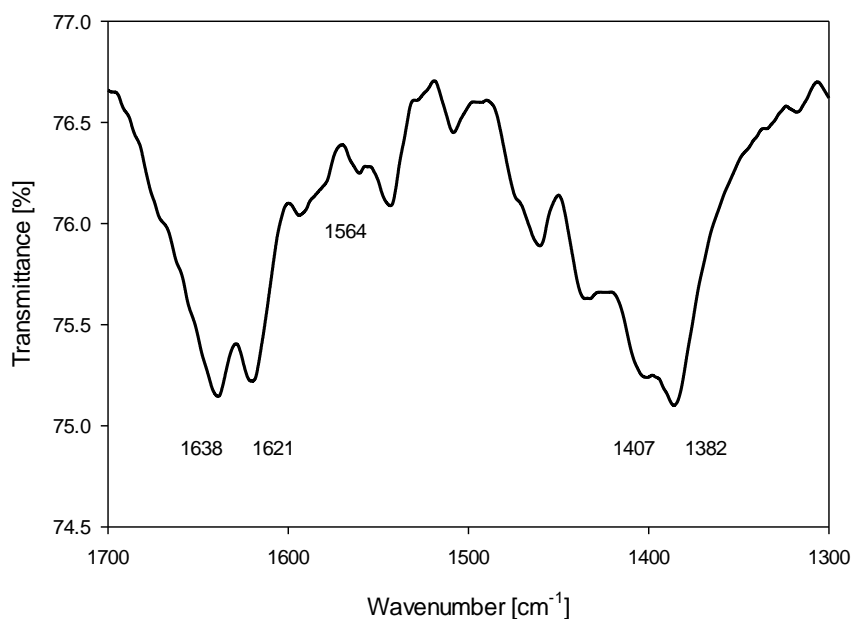


Figure 5. FTIR spectrum of traces adhered to gold in the region of Amide I and Amide II bands.

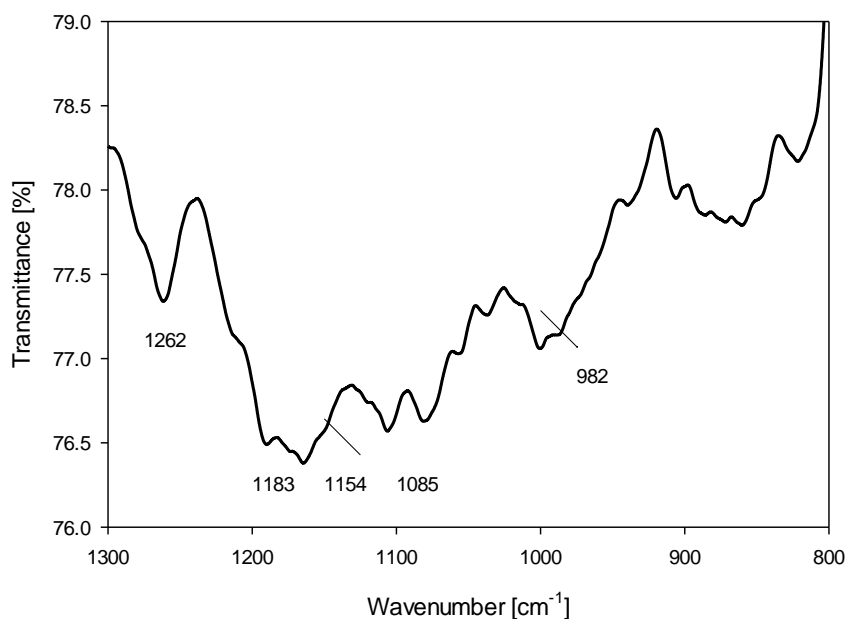


Figure 6. FTIR spectrum of traces adhered to gold in the region of Amide III, gypsum, and carbohydrate moiety.

The spectrum shows Amid A bands at 3418, 3416, 3230 cm^{-1} and Amid B band at 2924 cm^{-1} arising from N–H stretching and C–H stretching, respectively. Amide I band that predominantly originates from C–O stretching is found at 1621 cm^{-1} . A very weak Amide II band at 1564 cm^{-1} was assigned to N–H and C–N stretching. The presence of $\delta(\text{CH}_2)$ and $\delta(\text{CH}_3)$ was confirmed by absorptions found at 1407 and 1387 cm^{-1} , respectively. In the region 1300 – 1180 cm^{-1} , the absorbance at 1262 and 1183 cm^{-1} were attributed to the Amide III band arising from $\nu(\text{C–N})$ and $\delta(\text{N–H})$. The contribution to this band comes from C=O, C–C stretching and C–H wagging making this band extremely sensitive to particular proteins. The intensity of Amide I to Amide III follows the order strong-weak-moderate. At 1085 cm^{-1} absorption was mainly attributed to C–O–C bending coupled with a peptide bond of an amino acid chain. The presence of carbohydrate moiety was confirmed based on C–C stretching absorption at 982 cm^{-1} . Although in the area of the sensitive amide band, evidence of gypsum was found at 1154 cm^{-1} along with the bending mode of water at 1638 cm^{-1} .

4. CONCLUSION

This study of pigments from a mosque in Bosnia and Herzegovina dating back to the 16th century is a pioneering work. FTIR spectroscopy analysis of a three-layer sample obtained from Ćejvan Ćehaja mosque showed that the natural pigments burnt umber and viridian were used. The gold layer was found to be fixed with an adhesive film containing rabbit skin glue and plaster. Since three layers of paints are found in one sample, one over the other, the question of possible major or minor interventions that have not been documented is opened. The fact that the gold layer fixation method meets both, Ottoman and western practice, gives rise to few questions about Ćejvan Ćehaja mosque restoration which are addressed to art historians, architects and scientists working in conservation science.

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