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Bazı Duvar Resmi Örneklerinin Mikro-Raman ile Karakterizasyonu

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Anahtar kelimeler
Raman mikroskopi, Spektroskopi, Pigment karakterizasyonu, Duvar resimleri

Öz

Sinop Balatlar Kilise Kompleksi'nden 15.-20. yüzyıllara tarihlenen toplam 16 duvar resmi örneği Raman mikroskobu ile incelenmiştir. Analiz edilen duvar resimlerinin pigment paleti kalsit, hematit, zincifre, götit, mimetit, lazurit, yeşil toprak ve karbondur. Palet az miktarda pigment içermekle birlikte, aydınlatmayı artırmak için farklı tonlarda bazı pigment karışımları yapılmıştır. Ayrıca, kırmızı kurşun pigmentinin bozunma ürünü olduğu düşünülen pilatnerit minerali tespit edilmiştir.

Micro-Raman Characterizations of Some Wall Painting Samples

Keywords
Raman microscopy, Spectroscopy, Pigment characterization, Wall paintings

Abstract

A total of 16 wall painting samples, which were dated to 15th-20th century, from Sinop Balatlar Church Complex, were investigated by means of Raman microscopy. The pigment palette of the wall paintings analyzed were calcite, hematite, cinnabar, goethite, mimetite, lazurite, green earth and carbon. Although the palette comprises few pigments, some pigment mixtures with different tonalities have been made to enhance the illuminations. Pilatnerite mineral, which is thought to be the degradation product of red lead pigment, was also detected.

1. Introduction

Materials characterization on archaeological artifacts is crucial for the deep understanding of the raw materials and the techniques applied, as well as for employment of the most appropriate conservation procedures.

Over the last few decades Raman spectroscopy has attracted increasing attention in the study of cultural heritage and due to the instrumental improvements it has became the most important analytical tool to study especially pigments and pigment mixture compositions (Bell *et al.* 1997, Burgio and Clark 2001, Smith and Clark 2003, Bellot-Gurlet *et al* 2006, Vandenabeele *et al.* 2007, Clark 2007, Yu and Butler 2015).

The application of Raman spectroscopy for the determination of pigments used in wall paintings is well documented and have provided novel information (Germinario *et al.* 2018, *Ergenç et al.* 2018, Cosano *et al.* 2019, Gil-Torrano *et al.* 2019, Pojana *et al.* 2019). However, despite the increasing importance of the materials characterization in the investigation of archaeological objects, there is a very limited number of research paper concerning the wall paintings found in Anatolia.

The city of Sinop, which lies on a peninsula in the Black Sea, is situated in the northernmost point of Turkey. In the city center of Sinop, there is an ancient building complex called Balatlar Church which was built between the 2nd–3rd centuries as a Roman bath-palaestra complex. The ongoing excavations have revealed that the complex was converted into a church in the 4th-6th centuries and used as a Rum Orthodox Monastery during the Ottoman period (Köroğlu vd. 2014). The church of the Orthodox Monastery (Balatlar Church) displays polychrome wall paintings of the Late Byzantine style with scenes from the Bible and the Old Testament, dating to the Ottoman period (Figure 1).

The main objective of this study was to characterize the pigments and pigment mixtures used in the 15-20. century wall paintings from Sinop Balatlar Church Complex by means of Raman microscopy. For the first time in this study, wall painting samples, dated to the Ottoman period, from the geographical context of the Anatolian Black Sea coast were analyzed.

Figure 1. The monastery walls displaying polychrome wall paintings

2. Materials and Method

Raman microscopy measurements were made with a Bruker SENTERRA Dispersive Raman spectrometer, which is equipped with an Olympus confocal microscope fitted with 10x, 20x, 40x, 50x lenses. In this study, a 20x magnification objective was employed to focus the laser beam onto the samples. The system was equipped with three laser devices operating at 532, 785 and 1064 nm excitation wavelengths. The wall painting fragments were analysed with both 532 and 785 nm laser line excitations and the wavelength of 1064 nm was not used. The analysis were performed directly on the samples, without any preparation, and the signals recorded by a TE-cooled CCD detector. The irradiating laser power and the exposure time has been changed depending on the sample.

All the studies were performed using the facilities of Central Research Laboratory, functioning under Materials Research Center for Cultural Property and Artworks (MerLab) in Mimar Sinan Fine Arts University.

3. Results and Discussions

3.1 Red Color

In red painted samples different hues of color were observed and the spectra of the red samples, showed the presence of two different compounds, hematite and minium. The results of the Raman analysis indicate that hematite dominates in most of the red samples with only one exceptions, Sample Red-8.

The natural pigments obtained from iron are called "ochres" and they have been used since the Palaeolithic. Hematite, iron (III) oxide (α-Fe_2O_3), is the commonest occurring ore of iron and the principal colourant in red, brown and purple iron oxide-based pigments whereas, goethite (α-$FeOOH$) produces yellow (Eastaugh *et al.* 2008).

In the spectra, which are given in Figure 2, the bands at 227 and 495 cm^{-1} were assigned to Fe-O symmetric stretching whereas those at 294, 412, 613 cm^{-1} were assigned to Fe-O symmetric bending. They are all typical of hexagonal structure of hematite (Gutiérrez-Niera *et al.* 2013, Mateos *et al.* 2018, Marić-Stojanović *et al.* 2018, Cosano *et al.* 2019,).

All of the samples contain the characteristic Raman bands of calcite ($CaCO_3$) at 1085 cm^{-1} and 712 cm^{-1} (Mateos *et al.* 2018). The presence of calcite may be caused by the ground layer as well as the intentional addition to obtain a brighter shade (Ling 1991) .

Six of the spectra exibit another strong band at 1008 cm^{-1} typical of gypsum ($CaSO_4.2H_2O$). Gypsum present may be a result from the degradation of calcite by water and sulphur dioxide (SO_2) (Equation 1)(Cosano *et al.* 2019). Possible sources of the sulphur can be listed as, sulphate and sulphur dioxide from the atmosphere, sulphate from the soil, groundwater or rainwater etc. (Rösch and Schwarz 1993). Gypsum may also be an additive to give the paint layer a smoother, brighter finish.

$$CaCO3 + SO2 + 2H2O \rightarrow CaSO4 .2H2O + CO2 \quad (1)$$

Finally, in four of the samples R-1, R-2, R-3, R-4 where a darker tone of red is observed, obtained bands that were assigned to coal.

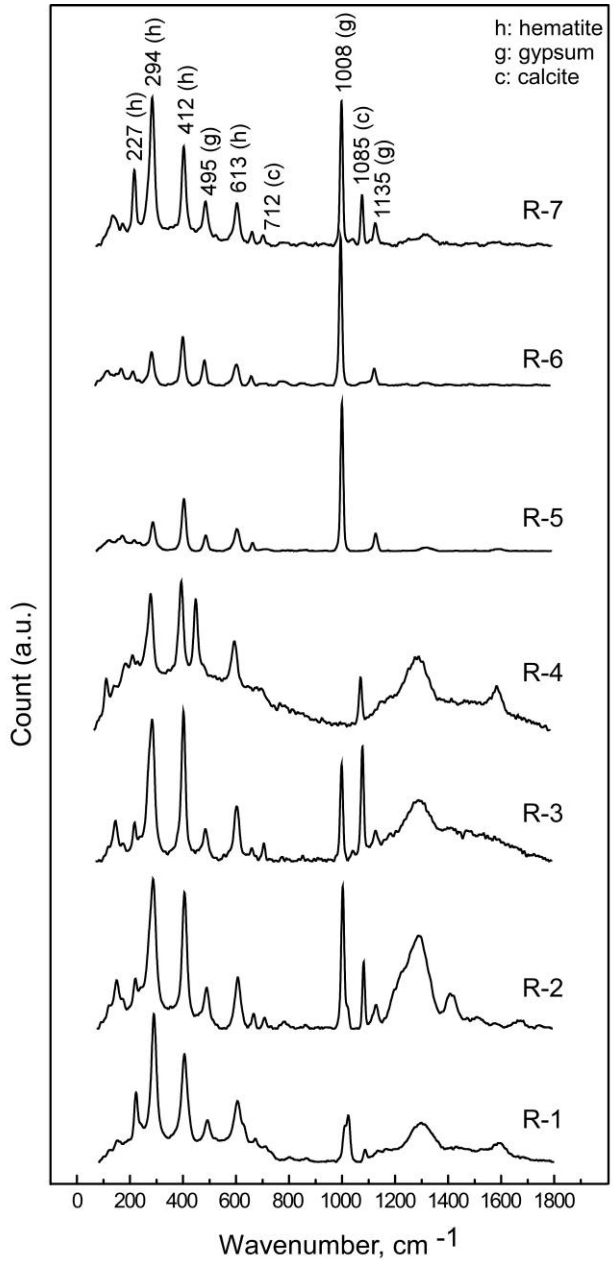

Figure 2. Raman spectra for the red samples (R-1 to R-7)

In sample R-8, cinnabar (HgS), whose characteristic bands appear at a spectral range lower than 400 cm^{-1}, was easily detected due to its strong Raman scattering (Dominguez-Vidal *et al.* 2012, Franquelo *et al.* 2009). The Raman band of the cinnabar are reported in the literature as 72, 88, 108, 256, 282 and 343 cm^{-1}. In this study, Raman bands were observed on Raman shifts of 255, 285 and 344 cm^{-1} as shown in Figure 3 (Gotoshia and Gotoshia 2008, Cheilakou *et al.* 2014).

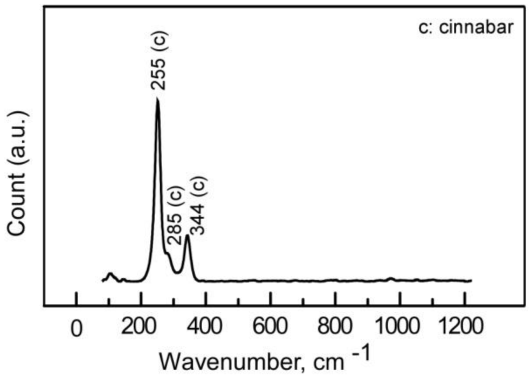

Figure 3. Raman spectrum for the red sample, R-8.

3.2 Yellow Color

Figure 4 shows the Raman spectrum, which is typical for goethite, for the sample Y-1. The strong band at 396 cm^{-1} were assigned to Fe-O-Fe symmetric stretching, 247 cm^{-1} and 667 cm^{-1} to Fe-O symmetric stretching, 300 cm^{-1} to Fe-OH symmetric bending, 548 cm^{-1} to Fe-OH asymmetric bending (Gutiérrez-Niera *et al.* 2013, Mateos *et al.* 2018, Cosano *et al.* 2019).

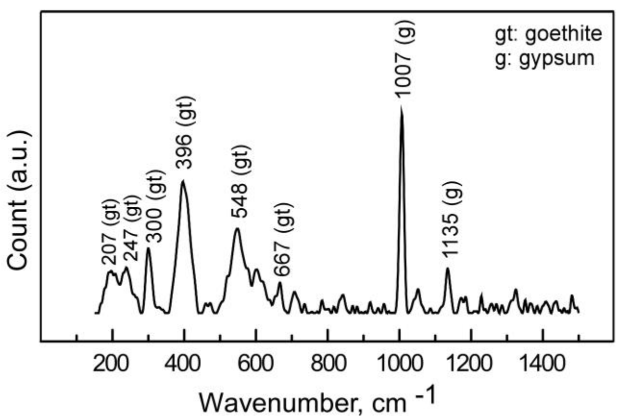

Figure 4. Raman spectrum for the yellow sample Y-1

In the Raman spectra of the other yellow sample Y-2 surprisingly a rare pigment, mimetite ($Pb_5(AsO_4)_3Cl$) was detected by a strong band corresponding to ν1 modes of AsO_4^{-3} at 827 cm^{-1} (Figure 5) although it should be positioned at approximately 810 cm^{-1}. However, the possible reasons of this shift have already been reported as isomorphic substitutions of As^V by P^V, mimetite to pyromorphite ($Pb_5(PO_4)_3Cl$) or isomorphic substitutions of Pb^{II} by Ca^{II}, mimetite to hedyphane ($Pb_3Ca_2(AsO_4)_3Cl$) in the structure (Frost *et al.* 2007, D. Hradil *et al.* 2014).

The use of mimetite in wall paintings was reported by Buisson *et al.* (2014) as a highlighter component of the main figures. Whereas, in some other studies it was mentioned as a degradation product of the pigments orpiment (As_2S_3) and minium (Pb_3O_4) (Janssens *et al.* 2016).

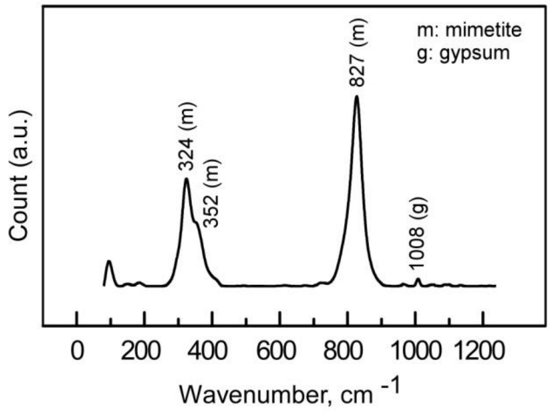

Figure 5. Raman spectrum for the yellow sample Y-2

3.3 Black Color

The Raman spectrum of the black sample Bl-1 is shown in Figure 6. The spectrum contained two strong signals at 1332 and 1596 cm^{-1} that were assigned to coal. The band at 1596 cm^{-1} is labelled "G" and it is due to the E_{2g} vibration mode of C=C bonds with sp^2 hybridization in graphite, while the band at 1332 cm^{-1} is associated with the stretching vibrations of C-C bonds with sp^3 hybridization in diamond (Cosano *et al.* 2019, Mateos *et al.* 2018) .

The color black was usually obtained by burning organic substances. It is called as "smoke black" if the color was obtained from wood or plant, and "bone black" if animal residues were used. Raman spectroscopy is very effective at telling which matter was used, unlike XRD. The presence of the typical band for stretching vibrations of P-O bonds in PO_4^{3-} at app. 960 cm^{-1} indicates the use of animal remains. In this case, the absence of this band pointed out the use of wood or plant residues for obtaining the black color (Mateos *et al.* 2018).

The spectrum also contains typical bans of gypsum.

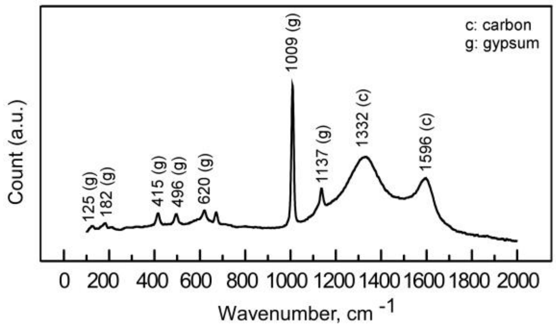

Figure 6. Raman spectrum for the black sample, Bl-1

The other black sample (Bl-2) was taken from a roof figure on the wall painting and the use of black color instead of red was surprising.

The Raman spectrum of this sample is given in Figure 7 and gave a strong band of plattnerite, lead(IV) oxide (PbO_2), at 515 cm^{-1} and a very weak band at app. 420 cm^{-1} (Burgio *et al.* 2000).

The darkening of lead-containing pigments is a widespread phenomenon due to environmental conditions and plattnerite has been reported as a degradation product of lead pigments in air (Miguel *et al.* 2008).

Red lead (lead (II,IV) oxide, minium, Pb_3O_4) was often used in wall paintings and over a long period this pigment may degrade and change into the plattnerite phase (Equation 2) (Kotulanová *et al*. 2009). So, earlier red colours darken and transform into black.

$$Pb_3O_4 + 4H^+ \rightarrow PbO_2 + 2Pb^{2+} + 2H_2O \quad (2)$$

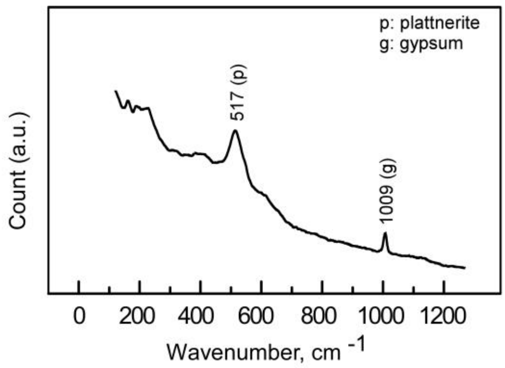

Figure 7. Raman spectrum for the black sample, Bl-2

3.4 Green Color

The green samples gave strong bands (Figure 8) at wavenumbers corresponding to those of green earth pigments, celadonite ($K(MgFe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2$) and glauconite ($(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$. Both minerals belong to the mica group, with a complex chemical structure and due to their crystallographic similarities, most of the Raman vibrations are identical. However, the peak at about 274 cm^{-1} was helpful to discriminate between celadonite and glauconite and suggested the pigment used was celadonite (Baraldi *et al.* 2007, Ospitali *et al.* 2008, Moretto *et al.* 2011).

In the spectra, the low-wavenumber region (100-300 cm^{-1}) is related to the internal vibrations of the MO_6 octahedra, where M is the inter-layer metal atom. Whereas the bands at the region 300-800cm^{-1}, are due to the vibrational modes of the SiO_4 tetrahedra (Ospitali *et al.* 2008, Košařová *et al*. 2013).

The samples also gave characteristic peak of calcite app. at 1085 cm^{-1}.

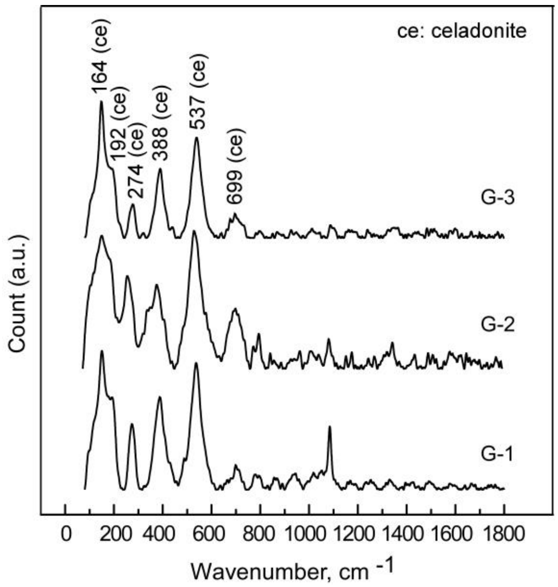

Figure 8. Raman spectra for the green samples

3.5 Blue Color

Only one blue sample (B-1) has been taken from the church and Figure 9 shows the Raman spectrum obtained. The strong peak at 547 cm^{-1} with a shoulder at 583 cm^{-1}, and weaker bands at 260, 1090 cm^{-1} were indicated the pigment used was lazurite ($(Na_8(Al_6Si_6O_{24})S_3)$), the blue component of the mineral lapis lazuli (Bruni *et al.* 1999, Kantha and Singh 2019, Zeng *et al.* 2010, Franquelo *et al*. 2009).

It is reported by Bruni et al. (1999) that among all the pigment particles coloured in blue, only the lazurite lead to the stretching vibration of the S–S bond responsible of the band occurring at approximately 548 cm^{-1}.

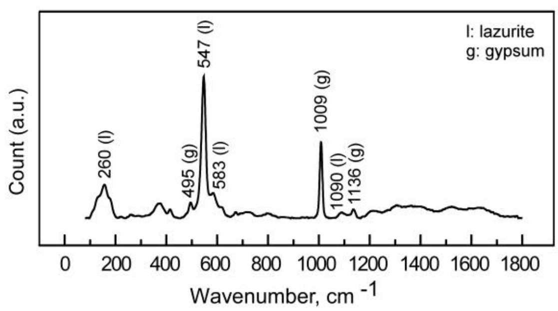

Figure 9. Raman spectrum for the blue sample, B-1

4. Results

16 wall painting samples from Sinop Balatlar Church Complex were characterized in this study by means of micro-Raman spectroscopy.

The predominant pigment colour is red, achieved through the use of hematite and cinnabar in only one sample. Hematite were used either alone or in an admixture with calcite and carbon to produce the desired color hue. Yellow colour were achieved through the use of goethite. For one specimen mimetite, which is a rare mineral, was detected. However, it may be a degradation product of the pigments orpiment and minium. The color black was achieved through the use of wood or plant residues rather than animal remains. All of the green pigments were celadonite and Raman spectroscopy was very useful to discriminate the green earth pigments from each other. Finally, blue pigment was detected as lazurite. The presence of plattnerite is also worth mentioning, suggesting the degradation of minium (Pb_3O_4) due to environmental conditions.

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