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PIGMENTS IDENTIFICATION: COMPARATIVE EXAMINATION OF MATERIALS AND TECHNIQUES IN THE HERMITAGE ASCENSION IN PYTHION OF OLYMPUS, GREECE

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ABSTRACT

Pythion is a settlement of the municipality of Olympus in the regional unit of Larissa. It is located on the southwest side of Mount Olympus, in an amphitheatre position at an altitude of about 725 meters. The word Pythion probably comes from the god Pythian Apollon of Greek mythology. Its oldest name was Selos.

The village remains important during the Byzantine period, a fact that is proven by the Post-Byzantine Hermitages that survive there. These were practised by monks who later manned the monasteries of the area. The best-preserved hermitages are located on the hillside, where the hermitage of the Ascension at the foot and the Holy Cross is a little higher.

The hermitage of the Ascension extends into a spacious cave and includes five irregular spaces. The first two rooms are almost outdoors and served as vestibules of the nave. The access to the temple is made through an arched gate. The chapel consists of a chamber whose side walls have two arched openings that communicate with the interior of the cave. The only murals that have survived are of the archangels Michael and Gabriel which are found in the interior of the gate that leads to the temple and dates back to the 14th century (Gialouri et al., 2014).

The present research study focuses on the analysis of 14th-century mural pigments using spectroscopic non-destructive techniques pXRF and portable Raman.

Keywords: Pigments, Raman, XRF, Identification, Wall Paintings

1.0 INTRODUCTION

Hermitage Ascension is located low at the foot of the hill, inside a spacious cave measuring approximately 10x10m. And in the natural recess formed by the rock in front of it. In these two natural cavities, the hermitage has been created, which consists of five spaces. A long wall closes the opening from the front, while a partition wall divides the recess of the rock and creates two continuous spaces. The first has a width of 5.80m and a depth of 3.80m. And communicates with two entrances to the countryside and the adjoining space. The second space is completely irregular and its dimensions vary from 3 to 6.20m. The long brick side has a blind arch and an arched gate so that it communicates with the interior. These two spaces, which

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essentially constitute vestibules of the temple of Hermitage, are uncovered and only the recesses of the rock and the southwest side of the first space are roughly covered with slates. Thus, uniquely suitable places for the ascetics to rest are created.

The main temple is on a higher level (about 1.60 m.) and one reaches it after passing through the arched gate and climbing six steps. It consists of a chamber, which bears on all its sides, except one, built walls. The floor plan is pentagonal, with sides of 3.50, 3.80, 4.80, 3 and 5.10m. The northern and southern walls have arched openings that communicate the central space with the interior of the cave. The masonry consists mainly of stones and a few porolits.

Some parts of the Ascension appear to have frescoes, but the only ones that are preserved are those depicting the figures of the archangels Michael and Gabriel on the inside of the portal to the naidrium. These wall paintings date back to the 14th century AD. (Gialouri et al., 2014; Adamou, 1997; Nikonanos et al., 1997; Nikonanos et al., 1983).

This research concerns the study of 15 measurements of the catholicon wall paintings and its purpose is the identification of pigments that were used at that period using portable Raman and pXRF spectroscopy. These measurements will help to identify the pigments of that period and comparisons will be made with other studies concerning murals of the same period (Cheilakou et al., 2014; Pelosi et al., 2013).

Figure 1. Hermitage Ascension

2.0 MATERIALS AND METHODOLOGY

2.1 Material

This research examined wall paintings of the Hermitage Ascension which are dated to the 14th century. There is no information about the painter of the wall paintings. It is assumed that he was from the area of Thessaly. The colours that were studied are red, dark yellow, brown, black and green. The conservation status of the wall paintings is not so good.

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2.2 Methodology

All the measurements were performed with non-destructive techniques using the laboratory equipment of Non-Destructive Techniques (NDT) of the Industrial Design and Production Department of the University of West Attica in Athens.

Non-destructive techniques such as portable Raman Spectroscopy and portable X-ray fluorescence analysis were applied in this study. The measurements were taken at the same points in the wall painting so that there is accuracy in the results.

The instrument which was used for Raman Spectroscopy was the portable DeltaNu RockHound with a near-infrared 785 nm excitation source, the resolution of the digital microscope was 5 cm-1, the size of the laser beam was 35μm and the spectral range was from 200 to 2000 cm-1. The advantage of a laser in 785 nm is that reduces the fluorescence interference in compounds through this process (Ganetsos et al., 2020). Alongside, in the XRF method was used the Thermo Scientific portable spectrometer XRF Niton XLp 818 with a 241 Am excitation source and a high-performance thermo-electricity cooled solid-state detector system. The temperature at which the instrument can operate is from 0-50o C and the relative humidity is from 10-90%.

The scientific software Spectragryph was used for the spectra analyses on Raman and XRF spectroscopy (Menges, 2020). The identification of pigments for Raman Spectroscopy was done with the databases of Clark (Bell et al., 1997), Pigments Checker (Caggianni et al., 2016) and e-visart (Castro et al., 2005), for XRF was used Pigments Checker.

Before the main process of pigment identification, Raman spectra were subjected to a pre-processing procedure such as normalization, Savitzky - Golay smoothing and baseline correction (Ferraro et al., 2003).

3.0 RESULTS AND DISCUSSION

The combination of the molecular and elemental analysis of spectroscopic techniques such as portable Raman and pXRF has been useful for the in-situ pigments analysis of wall paintings in the Ascension of Pythion. The colours which were identified in this research work were red, dark yellow, brown, black and green.

Figure 2. Wall paintings under study, the orange dots show the positions where measurements were taken

A table is presented below with all summarized results of colours by XRF.

Colours	Elements by XRF	Estimated Pigments
Red	Fe, Ca, Sr, Mn, K	Red Ochre Fe_2O_3, Calcium Carbonate $CaCO_3$
Dark Yellow	Fe, Ca, Sr, Mn, Sn	Yellow Ochre $Fe_2O_3.H_2O$, Burnt Sienna $SiO_2+Al_2O_3+Fe_2O_3$, Calcium Carbonate $CaCO_3$
Brown	Ca, Fe, Sr, Mn, S	Burnt Sienna $SiO_2+Al_2O_3+Fe_2O_3$, Calcium Carbonate CaCO3, Vine black C
Black	Fe, Ca, Sr, Mn, Cu	Vine black C, Calcium Carbonate $CaCO_3$
Green	Fe, Ca, Mn, Sr	Green earth (Terre Verte) K[(Al,FeIII),(FeII, Mg](AlSi3,Si4)$O_{10}(OH)_2$, Calcium Carbonate $CaCO_3$

Table 1. Summarized results by XRF of the Hermitage Ascension

Observing the results by XRF, it was noticed that the presence of calcium carbonate in all measurements indicates the composition of the substrate. The presence of calcium carbonate confirms that the fresco technique was employed by Byzantine painters, which involves the mixing of pigments with water or lime water followed by their application on damp lime-based plaster (Iordanidis et al., 2011). As the plaster dries, the pigment is pulled onto the surface of the plaster and stabilized by Ca(OH)2 which reacts with CO2 and is converted into CaCO3 (Iordanidis et al., 2011). The elements Mn and Sr in the XRF measurements indicate features of the substrate composition.

The red colour regarding Raman spectroscopy consists of red ochre and calcium carbonate. The red ochre has characteristic Raman bands at 235, 297, 559, and 613 cm-1, and calcium carbonate has Raman bands at 278, 719, and 1085 cm-1.

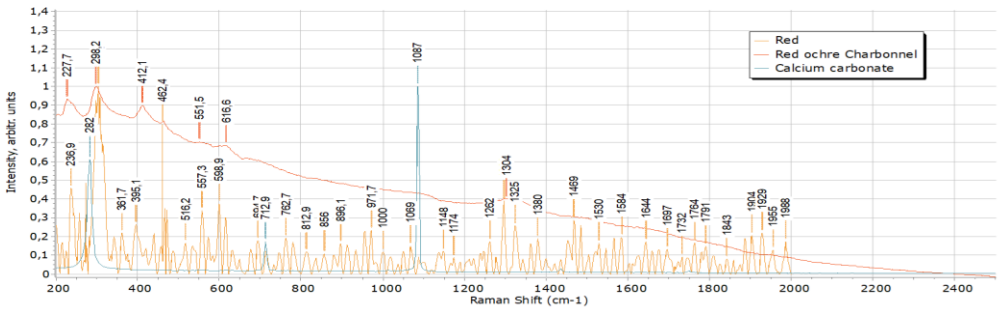

Figure 3. Raman spectra of Red colour in comparison with the e-visart database

The brown colour consists of burnt sienna with Raman bands at 297, 361, 455, 571, 958, and 1225 cm-1, calcium carbonate with Raman bands at 719, and 1085 cm-1 and vine black at 236, 442, 559, 958, 1262, 1327, 1483 cm-1.

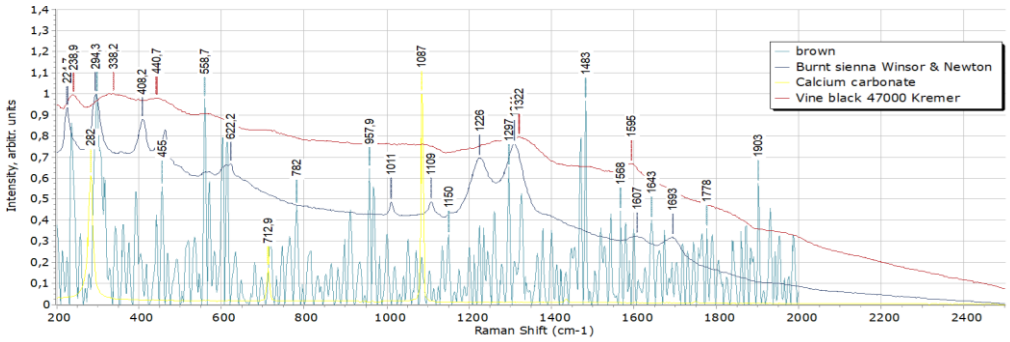

Figure 4. Raman spectra of Brown colour in comparison with the e-visart database

The dark yellow of the wall paintings is made of yellow ochre with Raman bands at 237, 297, 391, 558, 718 and 1086 cm-1, burnt sienna with Raman bands at 297, 454, 570, 959, 1003, 1103, 1225 and 1600 cm-1, calcium carbonate with Raman bands at 718, 1086 cm-1 and vine black at 236, 559, 958, 1086, 1262, 1327, and 1483 cm-1.

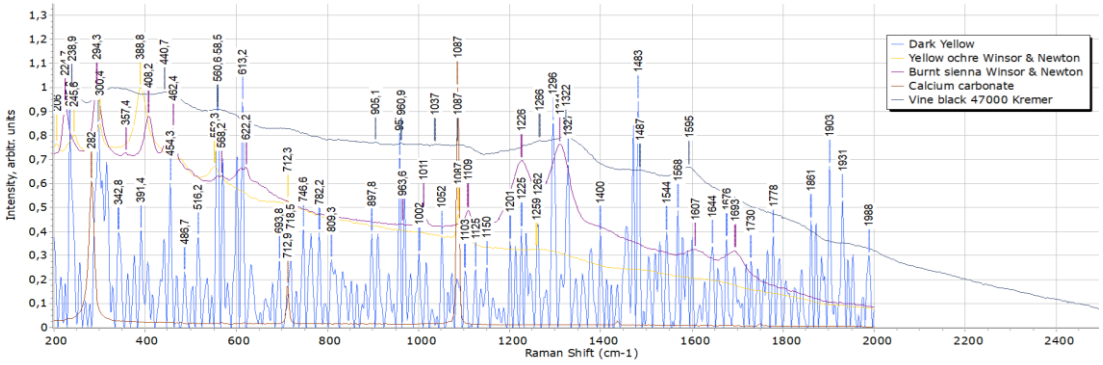

Figure 5. Raman spectra of Dark Yellow colour in comparison with the e-visart database

The black colour comprises of vine black with Raman bands at 239, 557, 912, 955, 1087, 1261, 1325, and 1485 cm-1 and calcium carbonate at 275, 716, 1087 cm-1.

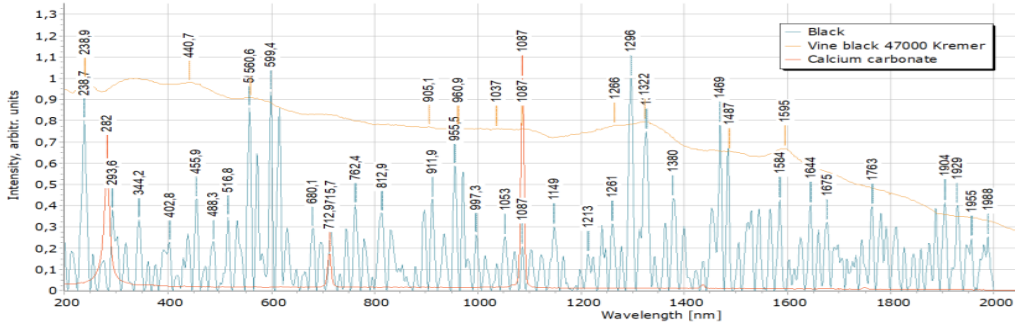

Figure 6. Raman spectra of Black colour in comparison with the e-visart database

Additionally, the green colour identifies as green earth with Raman bands at 598, 954, 1089, and 1294 cm-1 and calcium carbonate at 719 and 1089 cm-1.

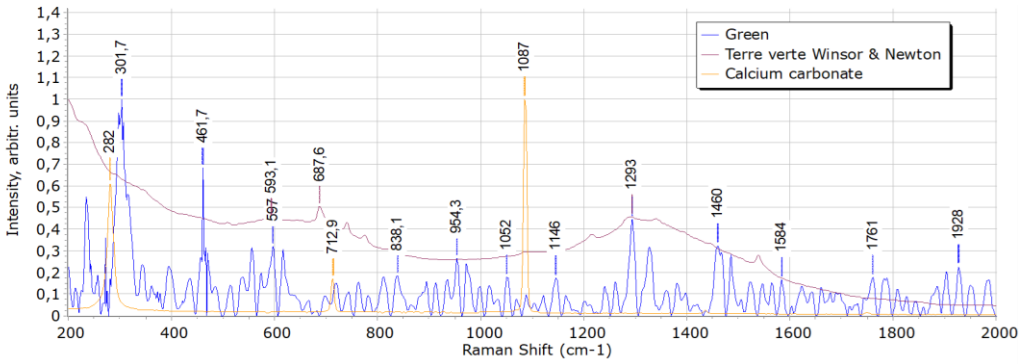

Figure 7. Raman spectra of green colour in comparison with e-visart database

4.0 CONCLUSIONS

The results of the combination of elemental and molecular analysis of spectroscopic techniques such as Raman and XRF make a point of the importance of the complementary techniques in situ measurements of the Hermitage Ascension. The pigments which were used in the Hermitage Ascension were red ochre, yellow ochre, vine black, burnt sienna, green earth and calcium carbonate. Particularly, the red colour consists of red ochre and calcium carbonate, the green colour identifies as green earth (terre verte) and calcium carbonate. The brown colour consists of burnt sienna, calcium carbonate and vine black. The black colour is made of vine black and calcium carbonate and the dark yellow contains yellow ochre, burnt sienna, vine black and calcium carbonate.

The knowledge of the palette of the hermitage Ascension is decisive for the pigments used in that period and crucial for the restoration.

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REFERENCES

ADAMOU G., 1997, Pythion (Sellos) over the Centuries, Pythion: Community of Pythion

BELL I., CLARK R.J.H., GIBBS P.J., 1997, Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD), Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 53, p. 2159-2179

CAGGIANNI, M. C., CONSENTINO A., MANGONE A., 2016, "Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database, Microchemical Journal 129, p. 123-132

CASTRO C., PEREZ-ALONSO M., RODRIGUEZ-LASO M.D., FERNANDEZ L.A., MADARIAGA J.M., 2005, On-line FT-Raman and dispersive Raman spectra database of artists' materials (e-VISART database), Anal Bioanal Chem, p. 248-258

CHEILAKOU E., TRULLINOS M., KOUI M., 2014, Identification of Pigments on Byzantine Wall Paintings from Crete (14 century AD) using Non Invasive Fiber Optics Diffuse Reflectance Spectroscopy (FORS), Journal of Archaeological Science 41, p.541-555

FERRARO J. R., NAKAMOTO K., BROWN C. W., 2003, Introductory Raman Spectroscopy, 2nd edition, USA: Academic Press

GANETSOS T., LUKACEVIC I. MATANIC A., LASKARIS N., MOUZAKIOTOU S., Pigments identification in paintings by J.F. Möcke using Raman spectroscopy: an arts/science project, 7th Balkan Symposium on Archaeometry, 22-25 September 2020, University of West Attica, Athens

GIALOURI A., PLASTARA AIK. MITSATSIKAS M., 2014, the Church of the Panaghia at Pythion in the Municipality of Elassona, 7th Ephorate of Byzantine Antiquities, Larissa

IORDANIDIS A., GARCIA-GUINEA J., STRATI A., GKIMOURTZINA A., 2011, Byzantine Wall Paintings from Kastoria, Northern Greece: Spectroscopic Study of Pigments and Efflorescing Salts, Spectrochimica Acta Part A 78, p. 874-887

MENGES F., 2020, ''Spectragryph – Optical Spectroscopy Software'', version 1.2.15

NIKONANOS N., 1983, The Hermitage of Pythion of Elassona (14th century), Thessalian Calendar, Volume 2th, Larissa

NIKONANOS N., 1997, Byzantine Temples of Thessaly from the 10th Century until the Conquest of the area by the Turks in 1393, Contribution to Byzantine Architecture, Archaeological Resources Funds and Expropriations, Athens

PELOSI C., BARALDI P., AGRESTI G., POGLIANI P., 2013 the Rock Hewn Wall Paintings in Cappadocia (Turkey). Characterization of the Constituent Materials and a Chronological Overview, e-Preservation Science, 10, p. 99-108

