SCIENTIFIC CULTURE
www.sci-cult.com

SCIENTIFIC CULTURE, Vol. 6, No. 2, (2020), pp. 65-72
Open Access. Online & Print

DOI: 10.5281/zenodo.3785044

PIGMENT IDENTIFICATION OF TWO POST-BYZANTINE ICONS OF *THEODOROS POULAKIS* BY PXRF AND RAMAN SPECTROSCOPY: CASE STUDY

Christopoulou, E., Laskaris, N.* and Ganetsos, T.

Department of Industrial Design and Production Engineering,
University of West Attica, Egaleo, Athens, Greece

Received: 15/11/2019
Accepted: 22/02/2020
Corresponding author: Nikolaos Laskaris (n.laskaris@uniwa.gr)

ABSTRACT

Since the late 12th century the Ionian Islands had passed gradually from Byzantine rule to the sphere of influence of Venice. During this long-lasting period, the Ionian Islands became a crossroad of art influenced by both the Eastern and Western styles of religious painting. Additionally, the special characteristics of the "Cretan School" of religious painting had already shaped in 16th c. and under the influence of Venice's art transformed into the 'Creto-Venetial style". As a result, painters of Greek-Orthodox religious painting worked either in the maniera greca, maniera italiana or in a combination of both styles. Several painters of Cretan Origin travelled from Crete up to Venice and through the Ionian Islands for working (e.g. Theodoros Poulakis, Emmanuel Tzanes) or permanent residency (e.g. Stephanos Tzankarolas, Leon Moskos).
This study is focused on two icons of painter Theodoros Poulakis (mid 17th c), kept at the ecclesiastical museum of Kefalonia. Non-destructive analyses with pXRF and portable Raman were carried out in order to identify the pigments used by the artist and therefore to reconstruct his colour pallet. Vermilion and Red Lead for the orange and red colours, lead for white, natural Azurite for blue and nature Malachite for Green are reported.

KEYWORDS: XRF spectroscopy, Raman Spectroscopy, Theodoros Poulakis, Creto - Heptanisian School, post-byzantine period

1. INTRODUCTION

After the fall of the Byzantine Empire (conquest of capital city Constantinople/Istanbul at 1453), the religious painting art continued according to Byzantine styles. The iconographic techniques and materials used by religious painters remain the same, but in a different socio-political context (Konstantoudaki-Kitromilidou, 2012).

During the 15th - 17th c., (same period of the Renaissance and Baroque in the West) the art of religious painting preserves its highly conservative nature. On the other hand, in the Venetian – occupied areas, the social and economic background along with the political expediency of Venetians to left the inhabitants absolute free in the matter of religion, reinforced the development of ecclesiastical art (Moschopoulos, 1990).

The special characteristics of the art of religious painting, which until today is still known as the "Cretan School", had already been shaped since the 16th century. Crete remains one of the most important centers for the flourishing of religious painting (Konstantoudaki-Kitromilidou, 2012). Also, many Greek artists even though were true to their tradition, started to adopt western techniques, which over the time give their art a new style and lead modern historians to characterize it as a "Creto-Venetian style" (Paliouras, 1989).

During that period the Ionian Islands became a crossroad of art. The wave of immigrant painters to the Ionian Islands is steadily increasing, as for many Ionian islands are the intermediate station for the artistic center of Venice. (Leontakianakou, 2006).

After the conquest of Chandakas (1645-1669) by the Ottomans, a large part of the population settled to the Ionian Islands and the rest of Greece. Among them, artists with Cretan origin who stayed permanently at Ionian Islands or worked at times, such as Leon Moskos, Andreas Carantinos, Stephanos Tzankarolas and those who had spent part of their life in the Ionian Islands as the brothers Emmanuel and Constantine Tzanes, Theodoros Poulakis and Markos Bathas. These artists gave fresh motivation and boost to religious painting, creation and cultural development (Paliouras, 1989).

Changing living conditions and adapting to them leads painters to new forms of expression. A large number of these painters are also priests, a fact that explains the conservative tendencies that prevail in painting at this time (Kazanaki-Lapa 1981).

Most of the Cretan artists settled to Zakynthos and Corfu and many others to Venice, along with other craftsmen and famous woodcarvers (Chatzidakis 1987). In Crete, at this time, the level of production of portable panel paintings ('icons') is declining, while the Ionian Islands are emerging as a new arts center for the production of icons.

Therefore, in the Ionian Islands, after the fall of Chandakas, painters who settled there they contributed to the progress of painting sacred portable panel paintings (Leontakianakou, 2006).

The large presence of Cretan painters in Ionian Islands leads, in the second half of 17th c., to a new tendency in painting, with particularities that only occur in this geographical region, the well-known '*Septinsular style*' or '*Heptanisian School*' of religious painting (Paliouras 1989, Chatzidakis 1987).

Theodoros Poulakis was born in Chania of Crete Island around 1620 and died in Corfu (Ionian Islands) in 1692 (Chatzidakis 1987, Chatzidakis and Drakopoulou 1997). He studied in Venice and, as other Cretan painters, settled in Venetian occupied Ionian Islands. In many of his works he follows the tradition of Cretan painters, the older ones (e.g. Klontzas, Damaskinos), his contemporaries (Emmanuel Zanfournari, Emmanuel Tzanes) or he is influenced by Italian works (Vokotopoulos 1990).

As Benaki Museum mention on its online artwork catalogue, Poulakis along with contemporary artist Emmanuel Tzanes "*renewed the vocabulary of late Cretan painting and laid the foundations for the flourishing of Cretan art in the Ionian Islands*" (Benaki Museum catalogue 2020).

Theodoros Poulakis' art is characterized by a strong narrative mood, lively movement, wavy clothes with rich folds and other elements of the time that are copied from Flemish engravings, a fact that gives it a baroque style and a rather cosmopolitan character (Konstantoudaki-Kitromilidou 2012).

2. RESEARCH AIMS

This study aimed at the pigment identification of two icons of religious painter Theodoros Poulakis kept at the ecclesiastical museum of Kefalonia. Results are of high importance for the ascertainment of the colour pallet (pigment variety), materials and, in general, the construction techniques of sacred portable icons applied by religious painters in a geographical region from Crete up to Venice. Also, the second aim of this work is, through the identification of the pigment pallet used by Th. Poulakis to reinforce the possibility of authenticity tests based on materials used.

3. MATERIALS AND METHODS

3.1 Materials

The nunnery of St. Andrew of Milapidia is located in the village of Peratata in Kefalonia, Ionian Islands,

Greece. It is one of the oldest monasteries on the island, founded during the Byzantine era and mentioned in the records of the Latin bishopric of Kefalonia from 1264 (Gkelis 1973). Since 1579 it exists, uninterrupted, as a women's convent with notable nuns such as the Greek-Romanian Princess, Roxani (Konomos 1966, Gkelis 1973).

The ecclesiastical museum, that has several remarkable artworks of ecclesiastical art, was founded 1988 and is housed in the old Katholikon of the nunnery, which is the only architectural part of the old monastery that survived the devastating earthquakes of 1953 (Gkelis 1973). The museum has a permanent exhibition of portable panel paintings of famous religious painters such as Emmanuel Tzanes, Stefanos Tsangarolas and Theodore/Theodoros Poulakis.

In this work, two icons painted by Theodoros Poulakis are studied, the icon of *Assumption of the Virgin Mary* and the icon of *St John Baptist* with scenes of his life (figure 1). Both icons are dated in the second half of 17th century and they are originated from the Church of Assumption at Kyriakata parish of Mantzavinata village of Kefalonia Island (Konomos 1966).

Figure 1. Portable icons of Theodoros Poulakis. a) (left) the Assumption of the Virgin Mary and b) (right) St John Baptist. Yellow dots are the spots were XRF and Raman measurements applied.

3.2 Methods

The method and site of the analyses were in-situ at the ecclesiastical museum of Kefalonia, Greece. The two portable panel paintings that have been studied in this work are shown in figure 1, both dated to the second half of 17th c. The analytical techniques used were XRF and Raman spectroscopies, both portable and non-destructive (Vandenabeele et al., 2004; Bersani and Madariaga, 2012, opoulou 2018, Ganetsos 2019, Liritzis et al 2020; Liritzis and Katsaros 2009).

For the qualitative determination of chemical elements of the examined colour hues, a handheld XRF analyzer Skyray EDX pocket III equipped with a 40kV mini W-Target X-Ray Tube and a Single Collimator of 6mm diameter was used. For the data acquisition from it, a built-in software was used and measurements were saved as Unicode ASCII file format is compatible for further analysis with specialized software. Due to the nature of investigation (only qualitative analysis), a cross-check calibration was applied with pigments of known XRF spectrum supplementary to the built-in shutter calibration.

As for the Raman analysis, measurements were performed with the Rock Hound DeltaNu Raman Spectrometer, which has a near-infrared 785nm laser source, adjusted to 8 cm^{-1} resolution and spectrum range of 200cm^{-1} to 2000cm^{-1}. Before measurements, calibration tests were conducted in ideal pigment samples made for this purpose (Caggiani, Cosentino and Mangone 2016), to ensure the correct Raman shift measurement and operation.

For further analysis, process and evaluation of measurements for both XRF and Raman techniques the scientific software SpectraGryph was used (F. Menges, SpectraGryph-Optical Spectroscopy Software, Version 1.2.14, 2020)

All measured Raman spectra, before the main process of pigment identification were subjected to a pre-processing procedure such as baseline correction, Savitzky - Golay smoothing and normalization (Ferraro Nakamoto and Brown 2003).

4. RESULTS AND DISCUSSION

In figure 1 also the sampling points for each colour hue are presented (yellow dots). In Table 1 the summarized results of XRF analysis and pigments identified by Raman spectroscopy are also shown. Figures 2 to 6 show representative Raman spectrums for different colour along with reference spectrums (Clark and Franks 1975; Bell, Clark and Gibbs 1997; Caggiani, Cosentino and Mangone 2016).

The analysis of both icons with portable XRF reveal elements such as Lead (Pb) for white, lead (Pb) and Mercury (Hg) for red and orange, Iron (Fe) for brown hues and Copper (Cu) for blue and green. In some cases of blue, green and brown spots, traces of Pb were found and are from mixing with nearby lead white.

These results are following previews works. Mastrotheodoros (2016) analyzed another portable icon of St John Baptist painted by Theodoros Poulakis by SEM/EDX and found Lead for white, vermilion (HgS) and red lead (Pb_3O_4) for red and iron-rich ochres for brown. For the blue hues, he found copper (Cu) and from microstructural examination identified it as Azurite ($Cu_3(OH)_2(CO_3)_2$). For the Green, he also found Copper (Cu) and from micromorphological examination identified two different pigments, natural malachite ($Cu_2(OH)_{2(}CO_3)$) and artificial Cu-based green.

In an extensive analysis of blue and green pigments in the post-byzantine period, Mastrotheodoros et al (2020) also mention, in natural blue (azurite) and natural green (malachite), the existence of traces of Barium (probably as Ba-S) and Zn, As associated with minerals such as Adamite [$Zn_2(AsO_4)(OH)$] and Olivenite [$Cu_2(AsO_4)(OH)$] (Mastrotheodoros 2016; Mastrotheodoros et al., 2020).

The results of Mastrotheodoros et al are of high importance to this work for the unequivocal identification of blue and green pigments. The pXRF measurements in their work reveal only the existence of Copper (Cu). Additionally, Raman analysis was performed with 785nm laser leading, as expected, to quite noisy measurements of blue and green (Caggiani, Cosentino and Mangone 2016).

To overcome these limitations, repeated Raman measurements on blue and green were performed in different spots of nearby areas and with several laser power.

As a result of this investigation, for blue a spot of analysis reveals a strong vibration of Ba-S (figure 7) and for green the vibration of Olivenite (figure 8).

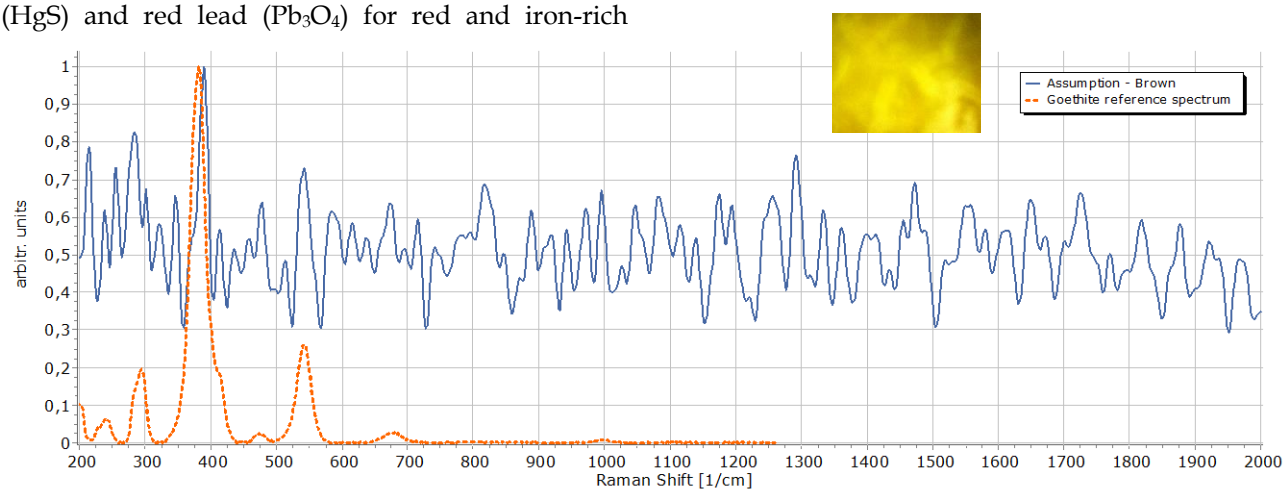

Figure 2. Brown of Assumption (blue solid line) along with reference spectrum of Goethite (red dashed line). Internal image shows the spot of analysis under the microscope mounted on Raman system.

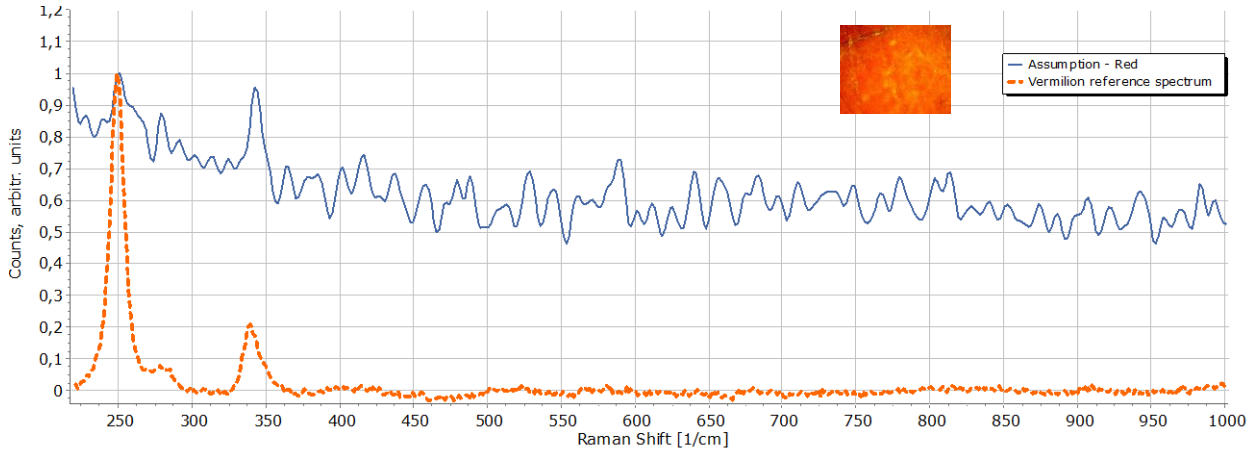

Figure 3. Red of Assumption (blue solid line) and Vermilion reference spectrum (red dashed line) Internal image shows the spot of analysis under the microscope mounted on Raman system.

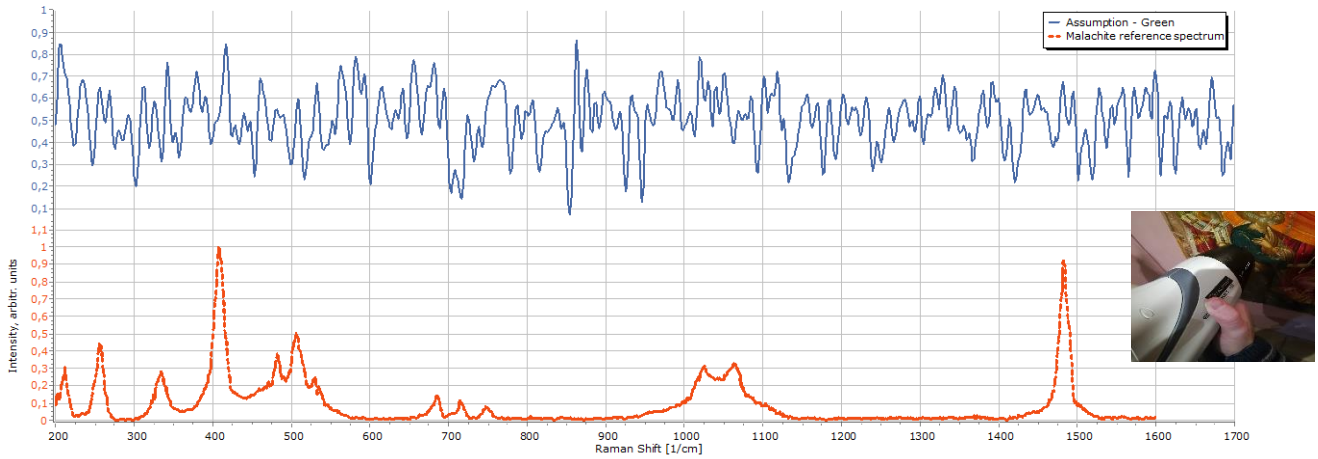

Figure 4. Green of Assumption (blue solid line) and Malachite reference spectrum (red dashed line) Internal image shows the spot of analysis with both Raman and XRF (here with XRF system)

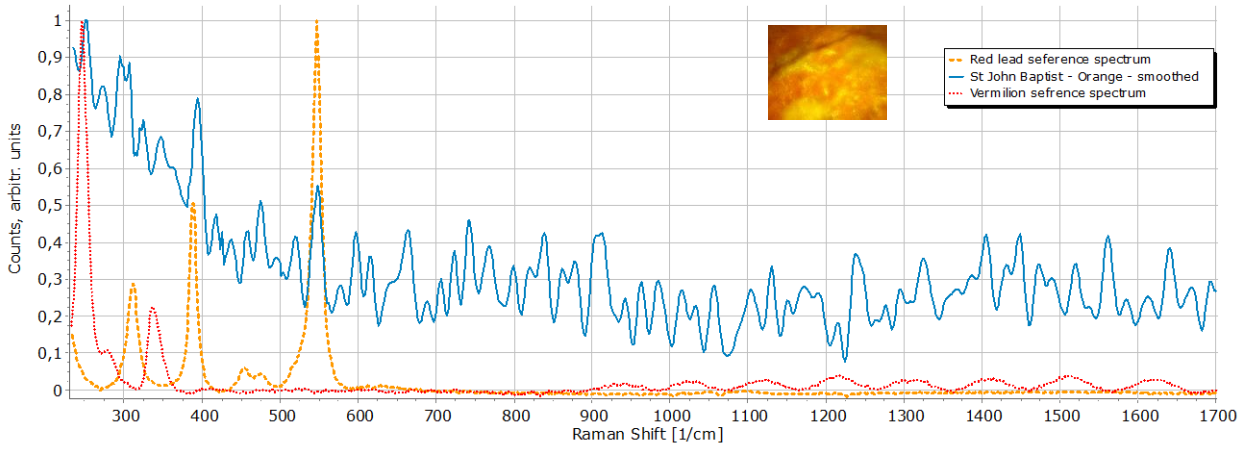

Figure 5. Orange of St. John Baptist (blue solid line) and reference spectra of Red Lead (orange dashed line) and Vermilion (red dotted line). Internal image shows the spot of analysis under the microscope mounted on Raman system.

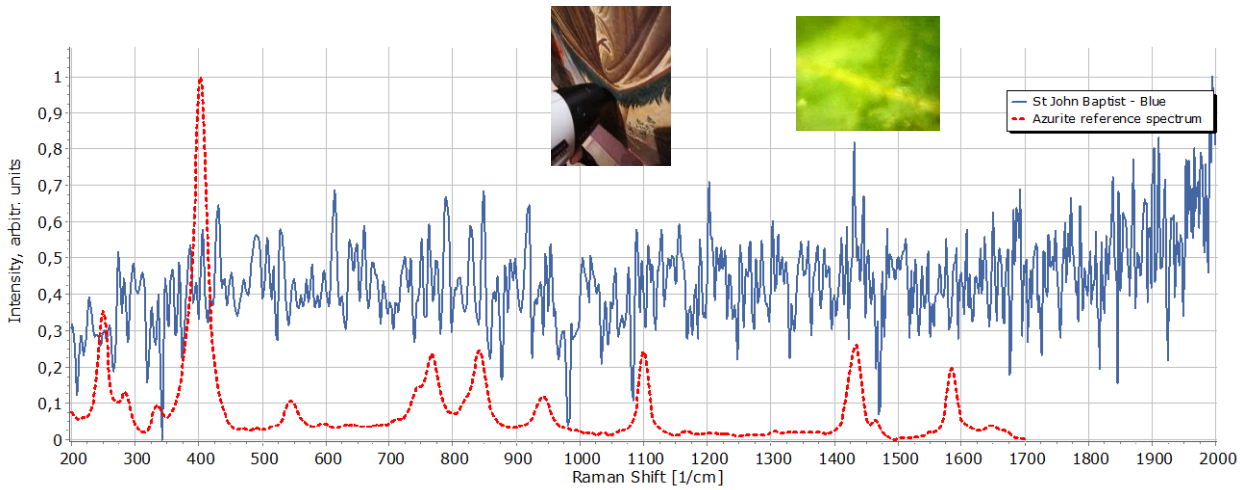

Figure 6. Blue of St. John Baptist (blue solid line) and reference spectra of Azurite (red dashed line) Left internal image shows the spot of analysis with both Raman and XRF (here with XRF system), Right internal image shows the spot under the microscope mounted on Raman system

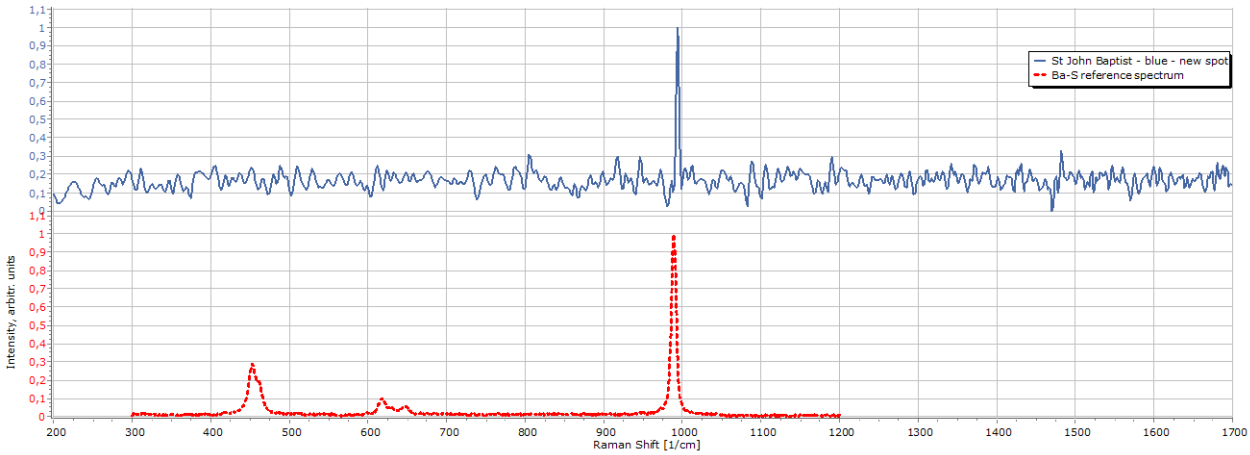

Figure 7. Blue of St. John Baptist (new spot, blue solid line) and reference spectra of Ba-S (red dashed line)

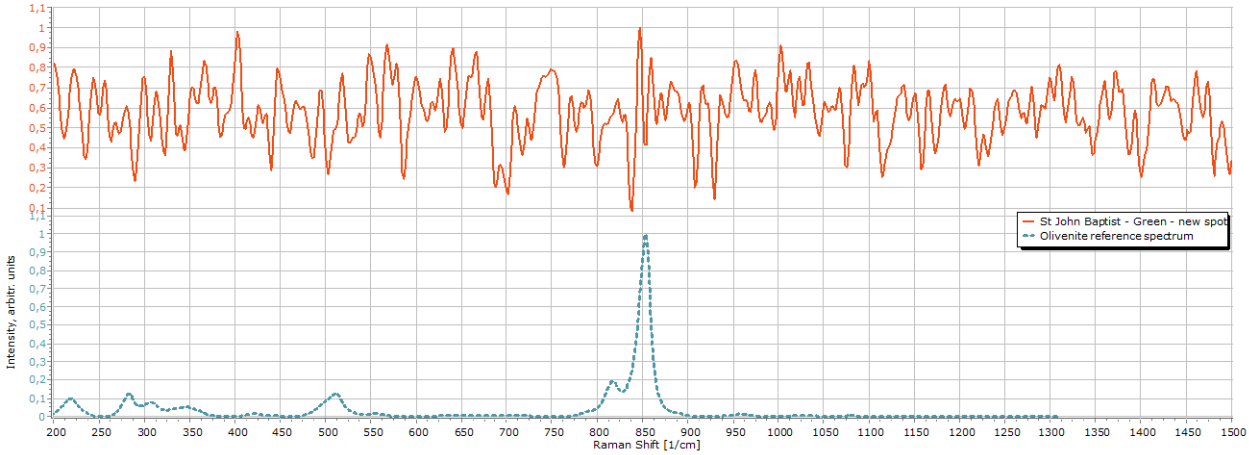

Figure 8. Green of St. John Baptist (new spot, blue solid line) and reference spectra of Oivenite (red dashed line)

Table 1. Summarized Results by XRF and Raman spectroscopies for the two Icons of Poulakis

Colour Hue	Elements by XRF	Pigment identified by Raman
Icon of *Assumption of the Virgin Mary*		
Brown	Fe, traces of Ca	Rich iron ochre – Goethite (FeOOH)
Red	Hg	Vermilion (HgS)
Orange	Pb traces of Hg	Vermilion (HgS) Red Lead (Pb3O4)
White	Pb	Lead White ($2PbCO_3.Pb(OH)_2$)
Green	Cu, traces of Pb	Malachite ($Cu_2(OH)_{2(}CO_3)$)
Icon of *St John Baptist*		
Orange	Pb, Hg	Vermilion (HgS) Red Lead (Pb3O4)
Brown	Fe, Ca, traces of Pb	Rich iron ochre – Goethite (FeOOH)
White	Pb	Lead white ($2PbCO_3.Pb(OH)_2$)
Blue	Cu, traces of Pb	Azurite ($Cu_3(OH)_2(CO_3)_2$)

5. CONCLUSIONS

This study aimed at the pigment identification of two icons of religious painter Theodoros Poulakis kept at the ecclesiastical museum of Kefalonia.

Summarizing the results, painter Theodoros Poulakis in the two studied icons, has used Vermilion and Red Lead for the orange and red colours, Lead for white, natural Azurite for blue and nature Malachite for Green.

Especially the identification of blue and green was achieved by correlating trace elements of natural pigments with Raman characteristic vibrations.

All these pigments are commensurable with earlier works on icons of Theodoros Poulakis, supporting the identification of pallet of the painter for his sacred portable panel paintings.

Author Contributions: All authors have equal contribution to this work.

ACKNOWLEDGEMENTS

This is part of M.Sc. of EC. The Director of Kefalonia Ephorate of Antiquities is sincerely thanked for his permissions and also the conservator of Ephorate Mrs Anna Zafeira for her generous help during the measurements. The authors are grateful to Mr Konstantinos Staveris, Director of the Ecclesiastical Museum of the St. Andreas nunnery in Kefalonia for his help. Finally, the authors are thankful to the anonymous reviewers for their constructive comments.

REFERENCES

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, 12, 2159-2179.

Benaki Museum online catalogue (2020), Collection of Byzantine Art, comments on exhibit No 3007 "archangel Michael by Theodoros Poulakis", https://www.benaki.org/index.php?option=com_collectionitems&view=collectionitem&id=107692&lang=el&Itemid=540&lang=en.

Bersani D., Madariaga, J.M. (2012) Applications of Raman spectroscopy in art and archaeology, Journal of Raman Spectroscopy, vol. 43, issue 11, pp. 1523-1528.

Caggiani, M.C., Cosentino, A., Mangone A., (2016), Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database, Microchemical Journal 129, 123–132.

Chatzidakis M (1987), Greek Painters after the Fall of Constantinople (1450-1830), Volume I, Greek National Research Foundation, Athens (in Greek).

Chatzidakis M and Drakopoulou E (1997), Greek Painters after the Fall of Constantinople (1450-1830), Volume II, Greek National Research Foundation, Athens (in Greek).

Clark, R.J.H., Franks, M.L. (1975) The resonance Raman spectrum of ultramarine blue. Chem. Phys. Lett. 34, 69-72.

Constantoudaki - Kitromilidou M (2012), Portable icon Painting in Crete, Cyprus and Ionian islands after the fall of Constantinople. Main trends and important representatives. Notes for undergraduate students of University of Athens, Department of History and Archaeology, (in Greek).

Ferraro, J. R., Nakamoto K., Brown C. W. (2003), Introductory Raman Spectroscopy,2nd edition, Academic Press.

Ganetsos T., Regkli A., Laskaris N., Liritzis I. (2019), Spectroscopic Study Of Colour Traces In Marble Sculptures And Architectural Parts Of Monuments Of Archaic Period In Delphi, Greece, Mediterranean Archaeology and Archaeometry, vol 19(3), pp 51-61.

Gkelis K (1973), Holy Monastery of Apostolos Andreas Kefallinias, Athens (in Greek).

Kazanaki - Lapa M (1981), Painters of Cania at the 17 the century, Thesaurismata magazine, volume 18 (in Greek).

Konomos N (1966), The Christian Art in Kefalonia, Athens (in Greek).

Liritzis, I., Laskaris, N., Vafiadou A., Karapanagiotis I., Volonakis, P., Papageorgopoulou, C., Bratitsi, M. (2020), Archaeometry: An Overview, *Scientific Culture*, vol6(1), pp 48-98.

Liritzis, I and Katsaros, T (2009) Identification and Characterization of Greek Archaeological Samples with the RockHound. Delta Application Note (http://www.youngin.com/application/Archeological%20Samples.pdf).

Leontakianakou E (2006) From the Cretan school to the Ionian School. Transition from worshipful icon to religious portable icon, Archaeology and Arts Magazine, volume 99, pp 48-54 (in Greek).

Mastrotheodoros G (2016), Pigments and various materials of post - byzantine painting, PhD thesis, University of Ioannina, (in Greek).

Mastrotheodoros G., Beltsios K. and Bassiakos Y. (2020) On the blue and green pigments of post-Byzantine Greek icons, *Archaeometry* (accepted in press), DOI: https://doi.org/10.1111/arcm.12537.

Moschopoulos G. (1990). History of Cephalonia, Vol. 1, Kefalos Publications, Athens (In Greek).

Paliouras A. (1989). The Ionian Islands as a bridge of art between Crete and Venice. In Moschopoulos G. (Ed), Cephalonia. Ecclesiastical Art Vol. 1. General State Archives – Archives of Cephalonia (in Greek).

Panagopoulou, A., Lampakis, D., Christophilos, D, Beltsios, K., Ganetsos, Th. (2018), Technological Examination of Iznik Ceramics By SEM-EDX, Raman, XRD, PLM: A Case Study, Scientific Culture, Vol 4(3), pp 27-33.

Vandenabeele, P. (2004), Raman spectroscopy in art and archaeology, Journal of Raman Spectroscopy, vol. 35, issue 89, pp. 607-609.

Vokotopoulos P (1990), Images of Corfu, Athens (in Greek).