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# Non-invasive pigment identification of post-Byzantine wall paintings from 11$^{th}$ century Monastery of Daphne in Athens (Greece)

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**Abstract.** This work is the first systematic research study to acquire information on the pigments and the painting technique and assess the conservation status of the post-Byzantine wall paintings in the Byzantine Monastery of Daphne (Attica, Greece). A combined non-invasive methodology including Portable X-Ray fluorescence (XRF), portable Fourier Transform Infrared Spectroscopy (FT-IR), multi-spectral imaging (MI) and digital microscopy (DM) was employed *in situ*. The identification of pigments hematite, goethite, green earths, carbon black, calcite, massicot and the creation of the wall paintings by different artists in different time periods were confirmed. MI and DM images gave useful insight into the conservation status of the wall paintings, revealing surface ware with microcracking, loss of color and original material as well as parts of the underdrawing of the painting.

**Keywords:** Non-invasive techniques, XRF, FT-IR, Multispectral imaging, Digital microscopy, post-Byzantine wall paintings, pigments, painting technique.

## 1 Introduction

Historical paintings are regarded as a main part of human culture and one of the oldest forms of artistic expression. The characterization of pigments, binders and materials employed is essential for the understanding of historical value paintings and provides information on the painting techniques, the supply and production of pigments from raw materials as well as community connections. In recent years, the accurate determination of the artwork state and indication of previous undocumented restoration or conservation works contribute to the planning of future conservation procedures [1-4].

Non-invasive techniques are a group of powerful tools with a minimal impact on the artwork, to obtain a large amount of data for the characterization of materials as well as for the diagnosis of damage and the assessment of maintenance interventions. X-ray fluorescence (XRF) and Fourier-transform infrared spectroscopy (FT-IR) are non-invasive, well-established and rapid techniques, allowing analytical information without causing damage to the artwork. XRF provides an immediate determination of the elemental composition of materials as it performs surface and in-depth analysis. The portable FT-IR version is a useful diagnostic tool for organic and inorganic compounds, including binders, pigments and the painting technique. In addition, digital technologies are effective and suitable to produce satisfactory results in representation and visualization [4-10].

The present research work aims at the identification of pigments on post-Byzantine wall painting which are dated back to the 11$^{th}$ Century and originate from the Byzantine monuments of Monastery of Daphne, located in Athens, Greece. The Monastery of Daphne is one of the most important Byzantine monuments of Greece, inscribed in UNESCOs' World Heritage List. Their great archaeological and artistic value did not allow any sampling, settling the need for a strictly non-invasive investigation. Therefore, a combined non-invasive analytical methodology was employed involving portable XRF, FT-IR, MI, and DM to acquire information on the pigments, the painting technique before the restoration of the paintings and assess their conservation status.


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### 1.1 Description of the wall paintings-historical data

The Daphne Monastery is located on the axis of the ancient road that led from Athens to Elefsina, in the area where the traveler Pausanias in the 2$^{nd}$ AD century mentions that there was a building enclosure and within it a temple dedicated to the god Apollo, as well as a stoa or similar building with columns [10, 11]. The main church of the monastery is called "Katholikon" and belongs to the octagonal type. It was built on an original early Christian church dating back to the 6$^{th}$ century AD. The position of the temple was strategically importantas the pagan mystics of the Eleusinian Mysteries passed through this point since ancient times [12].

The wall paintings are related to events in the life of Christ and the Virgin, as well as individual figures of archangels, prophets, saints, martyrs and bishops. The scenes and individual figures are characterized by grace and fluidity of movements, restrained and contemplative expressions on the faces of the saints and love for the natural environment, symmetry and harmony. The lower section of the walls was covered with beautiful marble slabs, which were replaced by wall paintings of mediocre quality in around 1650 [10,13].

## 2 Materials and Methods

### 2.1 *In situ* measurements of wall paintings

In this study, four wall paintings were examined from the Katholikon Church (see Fig.1). The measurement spots were selected with the criterion of the greatest coverage of the color palette and accessibility restrictions imposed by the location of each wall paintings. Color measurements were divided in white, yellow, red, green, blue, orange, brown, pink and black impressions [10].

### 2.2 Portable Digital Microscope (DM)

A Dino-Lite Edge Digital Micro-scope AM7915MZT-EDGE was used for the microscopic observation of the wall paintings. This is 10 cm long and is equipped with an automatic magnification ranging between 10 and 220×, a 5-megapixel resolution sensor, a light polarizer, 8 switchable LEDs, an extended depth of field and an extended dynamic range system. All the images were acquired by DinoCapture 2.0 software.

### 2.3 X-Ray Fluorescence (XRF)

*In situ* measurements were initially performed at multiple spots of all painted areas by a Bruker-AXS Tracer III-V portable XRF spectrometer. The instrument is equipped with a rhodium tube from which X-rays are emitted and a Peltier-cooled, silicon PIN diode detector, operating at 40 kV and 15 μA from an external power source for 200 live seconds using a filter composed of 1 mil titanium (Ti), and 12 mil aluminum (Al). The setting for the X ray tube eliminates the Rh L to assure that the trace elements could be detected in the raw spectrum. Elemental and quantitative analysis were performed using the S1XRF and ARTAX spectra software developed from Bruker-AXS.

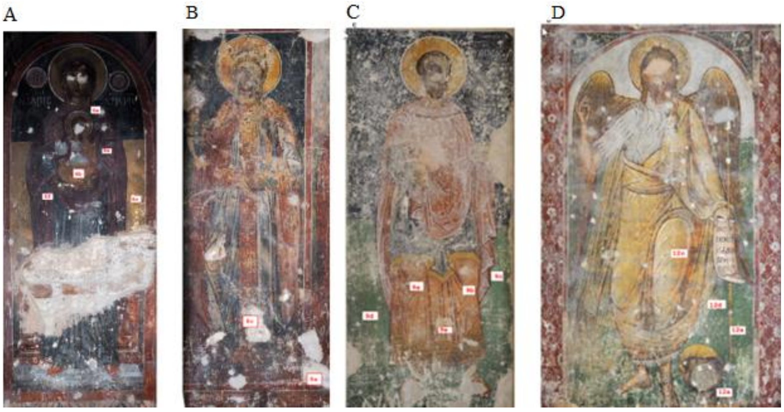


**Fig. 1.** Wall paintings originating from the Katholikon representing A) Virgin (No.6), B) Figures of Holy women (No.8) C) Agios Kosmas (No.9) D) Agios Ioannis Prodromos (No.12) and the relative measurement spots (Photos from the research team record).

### 2.4 Portable Fourier Transform Infrared Spectroscopy (FT-IR)

The Agilent 4300 Handheld FTIR spectrometer was applied for *in situ* measurements of wall paintings. This analytical method provides information on the chemical composition and molecular structure of materials. In paintings, highly informative analytical responses are frequently obtained through FTIR spectroscopy both for organic and inorganic compounds, such as binders, varnishes, and pigments.

### 2.5 Multispectral imaging (MI)

The wall paintings were analyzed by MUSES9-MS spectral camera, that addresses information in a wide spectral range from UV (370 nm) to IR (1000 nm). The camera integrates a spectral band tuning mechanism for selecting or for fully automatic scanning of up to 12 spectral bands. Innovative image filtering allows for the real-time display and side-by-side review of several megapixel-size spectral images. The camera was placed at a height of approximately 1.5 m from each wall painting. Vis and IR images obtained were processed with Adobe Photoshop CC program to correct contrast, tone and other parameters. Due to the lighting conditions in the interior of the monument, as well as accessibility restrictions, it was not possible to take images in the UV spectrum [10].

## 3 Results and Discussion

There are various rapidly developing non-invasive techniques for the analysis and evaluation of artworks. The methodology developed in this work included the following techniques [1,4, 6,10]:

*Step 1 - Visual inspection*. It was applied with the naked eye, providing information about the final stages of deterioration, such as cracks, discolorations.

*Step 2 – In-situ application of DM*. The obtained images provided a high level of detail, acquiring information for the nature and morphology of the varnish and color layers.

*Step 3 – In-situ application of XRF*. The elemental composition allowed the identification of the pigments in the surface layers and the underlying preparation layers (substrate).

*Step 4 – In-situ application of FT-IR.* The analysis offered valuable information on pigment and binding media as well as the painting technique.

*Step 5-In-situ MI.* The images provided information on the conservation state of the wall paintings, including surface damages such as microcracks, loss of color impressions, color fading, detachments, flaking, and losses of original material.

### 3.1 Macroscopic investigation and DM

The examined wall paintings showed considerable damage, which has probably been caused by blows with sharp objects and led to a loss of paint and substrate material. The damage in the region of eyes and face and graffiti with names and words was observed in most wall paintings. The handheld DM was used to capture images with a high level of detail to obtain information regarding the nature and morphology of the varnish and color coatings [10,14]. The application of the color in layers to achieve a lighter tone is evident (see Fig.2). The loss of the painted surface and substrate was observed in all wall paintings. Microcracks in the orange and black colors were also indicated. In several cases, black grains were observed in the paint layer, which were related to carbon dust used to modify the shade.

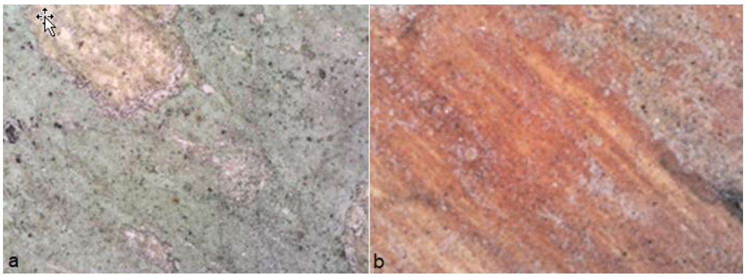


**Fig 2.** Digital image of green color impression of wall painting No. 9 (left) and orange color impression of wall painting No. 8 (right).

### 3.2 XRF analysis

XRF spectroscopy was employed in the characterization of the pigments present in the four wall paintings. The presence of calcium was indicated in white color impressions. The use of lithopone and lead white were excluded due to the absence of zinc, barium and lead [4,8,10].

The black pigments of carbon (such as bone black, carbon dust, etc.) can be indirectly identified due to the absence of other elements. Moreover, the use of black carbon pigments, separately or in mixture, was a common practice in post-Byzantine painting. The use manganese dioxide ($MnO_2$) for black hues was not indicated, as manganese was not detected.

XRF analysis of the yellow color impressions revealed significant concentrations of Fe that indicate the presence of hydrated iron oxide as a primary component of the pigment (yellow ochre) in the form of goethite [$FeO(OH)$] or limonite [$FeO(OH)\cdot H_2O$]. In wall painting No. 9, the same pigment in a mixture with red ochre was apparently applied to achieve darker orange hues. The results of brown colors showed the detection of high concentration of iron and lead (see Fig.3A). Manganese was not present, indicating the pigment is a mixture of yellow ochre with yellow lead oxide (PbO) and carbon [10, 14].

The red impressions of the wall paintings were investigated. In most cases, the high concentrations of Fe detected indicated the use of hematite ($Fe_2O_3$) as the pigment for rendering the red color impression. In the wall paintings No. 8 and 12, the presence of lead leads that the mixture of red ochre with red lead pigment such as minium or white lead carbonate was employed. The dispersion of red pigments on a white substrate (such as calcium hydroxide) conducts to pink shades (see Fig.3B).

XRF analysis of the green color impressions showed high concentrations of iron, while copper was barely detectable. Thus, it appears that copper pigments were not used for the green impressions but probably green earth pigments such as celadonite or glauconite.

The most common blue pigments were azurite, ultramarine and cobalt blue. Sodium was not detected by XRF, thus the use of ultramarine cannot be confirmed. Additionally, its high cost does not align with the specific wall paintings. The absence of copper also rules out the use of azurite. Therefore, the combined use of carbon black, oxides, and calcium carbonate to achieve blue color impressions has been reported extensively [9,10,14].

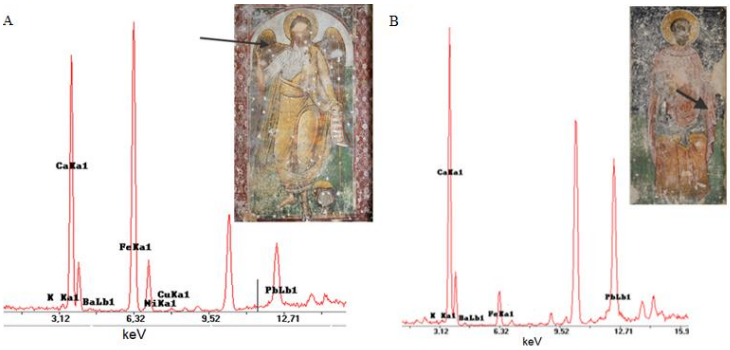


**Fig. 3.** XRF spectra A) Brown color impression of the wall painting No. 12. B) Pink color impression of the wall painting No. 9. The arrows show the points of measurement.

### 3.3 FT-IR spectroscopy

FT-IR spectroscopy is a successful and established technique for characterizing organic materials in historical wall paintings. A representative FTIR spectrum obtained at the point of the red color impression of wall painting No. 6 is shown in Fig. 4. The presence of calcite and clay pyrite compounds was observed, while organic materials were also detected. Thus, in the spectral region of 700 – 1490 $cm^{-1}$, the absorption bands are attributed to the stretching and bending vibrations of carbonate ions $CO_3^{2-}$. These data are also confirmed by XRF analysis, indicating that the *fresco* technique was applied in the construction of the examined wall paintings and calcite was used for white color impressions. The intense absorption bands at 1029 $cm^{-1}$ are attributed to the in-plane stretching vibrations of the equatorial Si-O bonds of kaolinite [9]. The weak bands (2960 -2850 $cm^{-1}$) are attributed to the asymmetric and symmetric stretches for methylene ($CH_2$) and methyl ($CH_3$) groups related to the organic matter. The bands at 892 and 1466 $cm^{-1}$ are attributed to the asymmetric out-of-plane bending and stretching vibrations of $v_2CO_3^{2-}$. The band near 1790 $cm^{-1}$ is attributed to the $v_1+v_4$ combination mode of calcite. The band near 1652 $cm^{-1}$ is attributed to the $v$C=O carbonyl stretching vibrations of the main and secondary amide groups as well as to the in-plane δC-N bending. It is the most characteristic absorption band of proteins in FTIR spectra and is strong evidence for the use of an organic binder (e.g. egg) for the preparation of paints. This is also confirmed in the FT-IR spectra of red, green and blue color impressions in the examined wall paintings. The presence of the bands corresponding to amides II and amides III absorptions (1211 and 1571 $cm^{-1}$ respectively) combined with the peak of the absorption band assigned to $v$C= O vibrations (1692 $cm^{-1}$) in lipid molecules showed the employment of a mixed wall painting technique involving both *fresco* and *secco* [1,4,8,10].

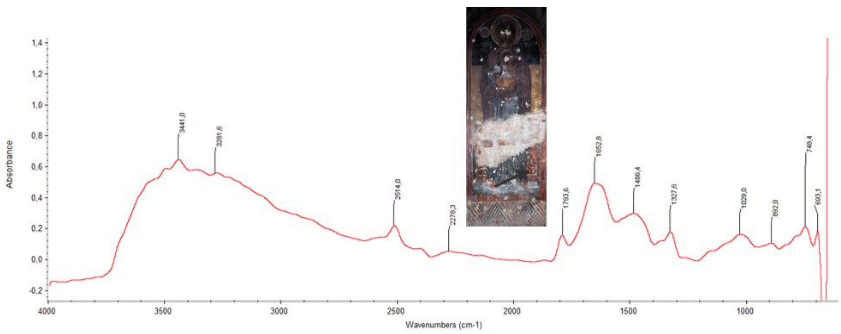


**Fig. 4.** FT-IR spectrum of red pigment in the wall painting No.6.

### 3.4 Multispectral imaging

The obtained Vis and IR images were processed with Adobe Photoshop CC to improve color tone and contrast. The combinations of shots with different filters were also made to highlight features that are not clearly visible in the visible spectrum. In wall painting No. 8, the state of conservation is poor with color surface losses, abrasions and fillings. Combining the Vis image with the IR (with increased contrast) using Photoshop's "Luminosity" mode gave Fig.5b, the scribbles, particularly in the folds of the clothes, are highlighted. From the false-color IR image (Fig. 5.c), the pigments for the yellow color impression on the vestments and halo of the left Saint have potentially similar composition as well as in the red color hues [1, 8-10].

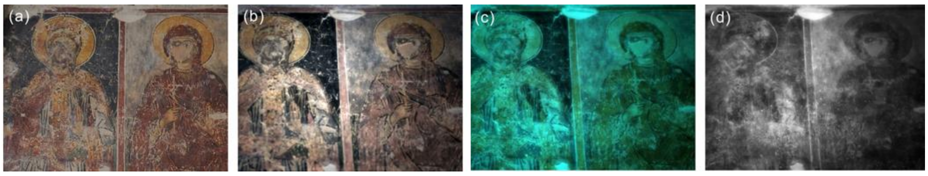


**Fig. 5.** Multispectral images of the wall painting No. 8: (a) Visible (Vis) image, (b) Mixed Vis and IR images (luminosity), (c) false-colour IR image, (d) UV images.

## 4 Conclusions

A non-invasive methodology with portable instrumentation such as XRF, FT-IR, DM and MI was employed for the characterization of post-Byzantine wall paintings (12th Century) of the Monastery of Daphne, Athens. The color palette of the post-Byzantine artists was found to comprise typical *fresco* pigments such as calcite, red and yellow ochre (hematite, goethite). For brown impressions, a mixture of umbra, yellow ochre and massicot was employed. Celadonite or glaucophane was used for green color hues while carbon black, iron oxides and calcite were applied for blue color impressions. The employment of a mixed wall painting technique involving both *fresco* and *secco* was indicated. The wall paintings were created in different time periods by different artists due to the use of various pigments for the same color impression combined with different stylistic characteristics. MI combined with DM and direct visual observation revealed surface damage such as microcrack grids, loss of color impressions, color fading, peeling, flaking, and loss of original material. Finally, the combined non–invasive methodology could be regarded as a valuable tool for the identification of the pigments, the painting technique and the existing state of conservation of the wall paintings.

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