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Non-invasive pigments identification in Macedonian Tomb of Hellenistic period

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Non-invasive pigments identification in Macedonian Tomb of Hellenistic period

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Abstract. The aim of the present research work is the characterization of pigments using non-invasive spectroscopic techniques. Ten samples found at excavations in a funerary monument located in East Macedonia and dated in the Hellenistic Period were investigated. Five powder samples were collected from the painted surface of the caisson ceiling of the tomb and five parts belonged to the painted surface of the detached entablature of the tomb. Due to the high historical value of the samples and their small quantity (granules), they were investigated using X-Ray Fluorescence (XRF) and VIS-Near IR Fiber Optics Diffuse Reflectance Spectroscopy (FORS). The measurements were conducted in every color impression (white, red, yellow, blue, black) of the samples in order to determine the elemental chemical composition and analysis of the spectral reflectance of their pigments. Additionally, the Fourier Transform Infrared Spectroscopy (FTIR) technique was performed to characterize the organic binders and painting technique used. Scanning Electron Microscopy with Energy-Dispersive X-Ray Analysis (SEM-EDX) was also applied to show the architecture, identify image particles and determine elemental analysis. Calcite, cinnabar, red ochre, yellow ochre, Egyptian blue and amorphous carbon were identified. Furthermore, marble was the major component of the architectural surfaces of the tomb. Regarding the painting technique, the detection of a high concentration of calcium and the presence of a protein-binding medium in all samples likely suggests the employment of a mixed wall painting technique involving both *fresco* and *secco*.

Keywords: non-invasive techniques, X-Ray Fluorescence, VIS-Near IR Fiber Optics Diffuse Reflectance Spectroscopy, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis, pigments.

1 Introduction

Color is not only an aesthetic element but also an important characteristic that helps us interpret and understand works of art. Pigments represent a component of high artistic, technical or historical significance in artworks. The chemical and mineralogical characteristics of pigments can provide information on technological knowledge, the painting techniques, the capabilities in the supply and production of pigments from raw materials and ancient community connections, material degradation. Therefore, pigments are indicators of human thinking and technical choices. [1-4].

The application of analytical techniques for the complete characterization of materials and the information gathered from historical and archaeological studies in artworks are crucial in order to apply the proper methods of restoration–conservation. The use of traditional analytical methods to investigate archaeological works is not feasible due to the strict regulations for the protection and preservation of cultural heritage. The uniqueness and value of archaeological artifacts necessitate the application of non-destructive or micro-destructive techniques. Recent technological developments have led to the employment of non-invasive methods for *in situ* elemental analysis, preserving the object or sample untouched and in place during measurements. Among the predominant and well-established methods employed for this purpose are XRF, SEM-EDX, XRD, FORS, FT-IR, and Raman spectroscopy. These techniques provide a wide range of information, including elemental composition, microstructural analysis, and characterization of molecular structures [1, 5-8].

The aim of the present research work is the characterization of pigments using non-invasive spectroscopic techniques. Ten samples found at excavations in a funerary monument located in East Macedonia

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and dated in the Hellenistic Period were investigated. Due to the high historical value of the samples and their small quantity (granules), they were investigated using XRF and FORS. The measurements were conducted in every color impression (white, red, yellow, blue, black) of the samples in order to determine the elemental chemical composition and analysis of the spectral reflectance of their pigments. Additionally, the FT-IR technique was performed to characterize the painting materials (pigments and organic binders) and technique used. SEM-EDX was also applied in one sample in order to show the architecture, verify any possible significant morphological and chemical inhomogeneities among different points, and determine elemental analysis.

2 Materials and Methods

2.1 Samples

Ten samples found at excavations in a funerary monument located in East Macedonia and dated in the Hellenistic Period were investigated (Table 1). Five powder samples were collected from the painted surface of the caisson ceiling of the tomb and five parts belonged to the painted surface of the detached entablature of the tomb of headings. Additionally, the reflectance spectra of pigments in pure powder (supplied by KREMER) were recorded in order to provide a knowledge base on the pigments' spectral features and identify the pigments of the samples.

2.2 X-Ray Fluorescence

A portable XRF Tracer III-V (Bruker-AXS) was used for the non-destructive analysis of samples. It was equipped with a rhodium tube from which X-rays are emitted and a peltier-cooled, silicon PIN diode detector, operating at 40 kV and 15μA 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 ensure that the trace elements can be detected in the raw spectrum. Elemental and quantitative analysis of the XRF spectra were performed using the S1XRF and ARTAX spectra software developed from Bruker-AXS [1,2,9,10].

Table 1. Description of samples collected from the painted surface of the tomb

Sample	Origin	Color impression
df1	Caisson ceiling	Deep red
df2	Caisson ceiling	Deep dark blue
df3	Caisson ceiling	Yellow
df4	Caisson ceiling	Deep blue black
df5	Caisson ceiling	Deep dark blue
D1	Detached entablature	Red
D2	Detached entablature	Blue
D3	Detached entablature	Light Yellow
D4	Detached entablature	Dark brown
D5	Detached entablature	White

2.3 VIS-Near IR Fiber Optics Diffuse Reflectance Spectroscopy

Measurements were also performed on all samples using a portable Ocean Optics, USB4000-VIS-NIR Fiber Optic Reflectance Spectrometer. The instrument features a high-performance 3648-element linear CCD-array detector, installed with a multi-band pass order-sorting filter to cover the 350-1000 nm wavelength range, and a 25 μm entrance slit for optical resolution to 1.5 nm. The instrument is equipped with a QR400-7-VIS/NIR reflection bifurcated probe providing illumination and detection of diffused light from the same direction, an HL-2000 tungsten- halogen light source and a probe holder positioning the QR400-7 at 45° for diffuse reflection in order not to include specular reflectance. The use of this device also allows one to guarantee a correct contact with the surface to be analyzed, to keep constant the sample-to-probe distance (about 4 mm), and at the same time avoiding external light contributions. Diffuse reflectance spectra were referenced against WS-1 Diffuse Reflectance Standard, provided by Ocean Optics, and guaranteed reflective at 98% or more in the spectral range investigated. Diffuse reflectance spectra were recorded in the range of 350-1000 nm. Spectral data treatment was performed with the SpectraSuite software (Ocean Optics) add-on for Origin [1,2,9,10].

2.4 Fourier Transform Infrared Spectroscopy

A ThermoScientific Nicolet 6700 Fourier Transform Infrared Spectrometer (FTIR), equipped with an Attenuated Total Reflectance (ATR) accessory, for the characterization of the pigment's molecular structure. Transmission IR spectra were recorded in the mid-IR spectral region 4000-400 cm^{-1}, at a resolution of 4 cm^{-1} and by collecting 120 co-added scans for each spectrum. The great advantage of the ATR technique utilized is that no sampling preparation is involved, enabling the obtaining the IR spectra of the samples in their native state without any KBr pelletization. Further data processing was carried out using the OMNIC 7.1 Software (Thermo Nicolet) [1, 2, 9, 10].

2.5 Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX)

A FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM), coupled with an Energy Dispersive X-Ray Detector (EDX) was used. During the microstructure analysis, three types of images were shown by the respective detectors: a) the secondary electron (SE) by the Everhart – Thomley detector (ETD), depicting morphology, b) the backscattered electron (BSE) by the Solid State Electron Detector (SSD), showing phase distributions and c) a mixed picture (mix) which was a digital combination of the former images. SEM imaging parameters, selected based on the overall quality of the image, were as follows: 30 kV accelerating voltage, magnifications up to x12000, and detector dead time of 5μs for each single image. The surface elemental composition and the assessment of the bulk elemental composition (derived from measurements on a fresh-cut surface of the fragment) were determined by the EDX detector using spot analysis locally at different selected spots of special interest and surface analysis (mapping) on the whole image. High-resolution images were obtained without gold or carbon coating, thereby enabling imaging of the sample close to its original state without requiring any pretreatment [1,2,9, 10].

3 Results and Discussion

The results obtained from XRF, FORS, ESEM-EDX and ATR-FTIR analysis of the collected microsamples led to the following observations and results regarding the identification of pigments, organic binding media and the technique applied for the construction from the painted surface of the caisson ceiling and the detached entablature of the tomb [11].

3.1 XRF analysis

The first step of the combined methodological approach was the elemental chemical compositions of the entire sample set from the painted surface of the caisson ceiling (df1-5) and the headings of the tomb (D1-5) by portable XRF. Strong peaks of K_α and K_β calcium (Ca) were revealed, indicating the presence of calcite ($CaCO_3$) and the application of *fresco* or *secco* painting technique for the creation of the wall paintings of the caisson ceiling of the tomb. The peaks of lead (Pb) and zinc (Zn) were attributed to impurities in the minerals of the pigments. The detection of K, S, P, Sr and Si were related to the soil [1,9,11].

In Fig 1a, the XRF spectra of the red color impression (df1) showed the presence of a high concentration of Hg, indicating the use of cinnabar (HgS). On the contrary, the red color (D1) from the tomb 's headings showed an intense peak of Fe, leading to the use of red ochre.

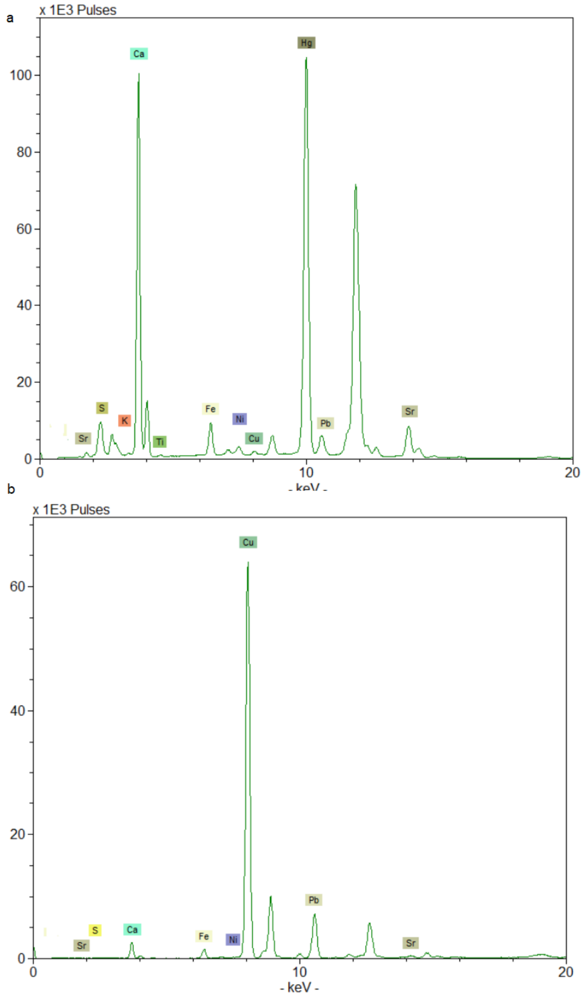

Fig. 1. XRF spectra of a) red color (df1), b) deep blue color (df2) samples.

The elemental analysis of blue color samples (df2, df4, and D2) identified high Cu content as the dominant element with a minor amount of Fe, leading to the use of a Cu-based pigment, such as azurite ($Cu_3(OH)_2(CO_3)_2$) or Egyptian blue ($CaCuSi_4O_{10}$, cuprorivaite). Additionally, the sample df5 with a deeper blue from the other two blue samples showed the presence of Cu and Hg (see Fid 1b).

The XRF results of the yellow color impression (df3) identified high Fe content, suggesting the presence of hydrated iron oxide, possibly in the form of goethite [$FeO(OH)$] or limonite [$FeO(OH)\cdot H_2O$] as the major component. The XRF chemical analysis results of the light yellow and white samples (D2 and D5) revealed the presence of high Ca content, suggesting the presence of calcium compounds. Moreover, in the dark brown color impression (D4), the high Fe content indicated the presence of yellow ochre [1,9,11-13].

3.2 FORS analysis

In the second step of the methodology, Vis-Near IR FORS was employed in all samples with the aim of non-destructive identification and characterization of their pigments. The study was based on the comparative analysis of the diffuse reflectance spectra obtained from the FORS measurements of the colored samples, with appropriate spectral reference databases of pigments developed in the laboratory, as well as reference spectra from the literature [1,9,11-13]. The white impressions were not analyzed as they exhibit a high maximum reflectance. The accurate identification of a pure pigment is based on the spectral characteristics. In ancient Greece, two materials were used for the red color impressions, cinnabar and red ochre. From the comparative spectral analysis of the red color sample (df1), it was observed that the curve presented a sharp positive slope near 600 nm, which is characteristic of cinnabar (Fig. 2a). Regarding the red color sample from tomb headings (D1), hematite was identified due to the sharp positive slope between 525 and 600 nm, a maximum near 760 nm and two absorption bands, a strong one at 485 nm and a weaker in the near-infrared (between 850 and 870 nm).

The diffuse reflectance spectra obtained from the yellow color impressions of the sample (df3) are presented in Fig. 2b. From the comparative spectral analysis, it was observed that the curves presented a typical S-shape, characterized by a positive slope between 500-580 nm and a broad absorption band (minimum) near 660 nm, coinciding with the reference yellow ochre spectral features. In addition, all spectra presented a weak shoulder between 450-480 nm and a broad absorption band near 930 nm which could be attributed to goethite [1-4]. For the light yellow impressions (D3), the reflectance spectra demonstrated a different shape from those analyzed above, implicating a mixture of yellow ochre and calcite. The aforementioned findings are in good agreement with the high Fe concentrations detected by XRF results and confirm the utilization of yellow ochre in the form of goethite for the production of the yellow color impressions [1, 9, 11-15].

The diffuse reflectance spectra obtained from the blue color impression (df2, D2) presented similar spectral features, especially at higher wavelengths, with the reference Egyptian blue curve. The spectra showed an S-shaped curve with two strong absorption bands of about 925 and 730 nm. Moreover, the sample blue color (df5) revealed the use of a mixture of cinnabar and Egyptian blue. The spectral characteristics of sample df4 and D4 didn't show any similarities compared to the reference pigments spectra.

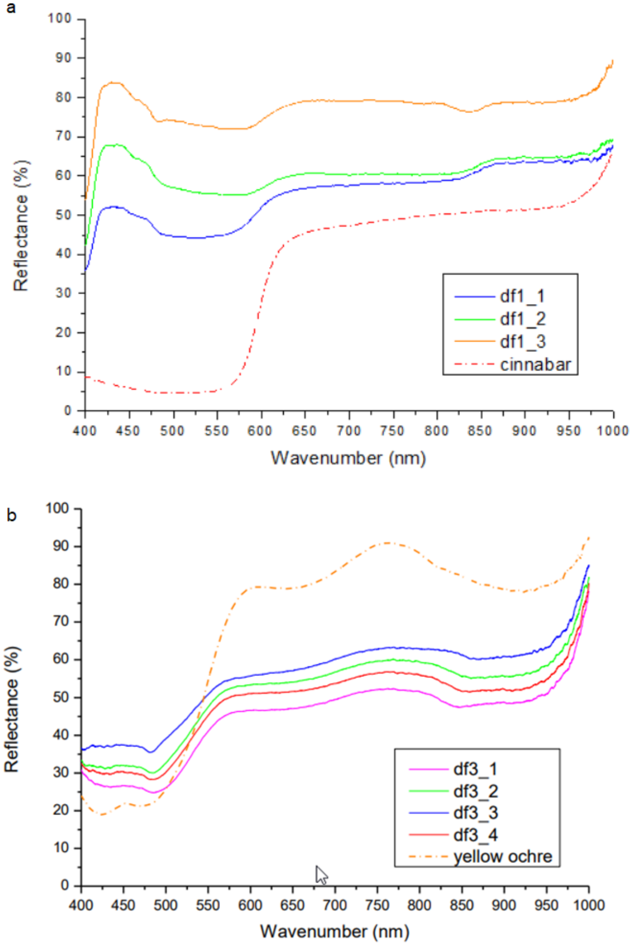

Fig. 2. FORS spectra of a) red color (df1), b) yellow color (df3) samples.

3.3 FT-IR spectroscopy

The third step of methodology employed FT-IR spectroscopy for the characterization of the pigments molecular structure, substrate and environment of all micro-samples. Due to the small amount of some samples, the corresponding FT-IR spectra were not conclusive.

The obtained spectra of the cinnabar sample (df1) presented the peaks at 3621 and 3401 cm^{-1} attributable to hydroxyl groups (Fig. 3). The peaks at 2977, 2921, and 2869 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of methyl and methylene groups νCH_3 and νCH_2, indicating the presence of proteins. The band appearing near 1867 cm^{-1} corresponds to the carbonyl stretching vibrations νC=O. Absorption bands of amides coupled to C=O are at about 1625 cm^{-1} (amide I), indicative of proteins.

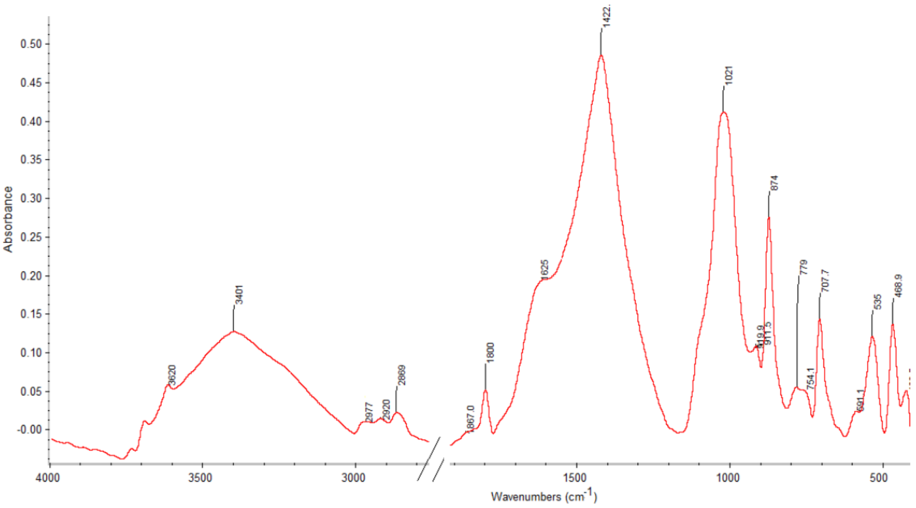

Fig.3. FT-IR spectra of red pigment cinnabar (df1).

The band appearing near 1867 cm^{-1} corresponds to the carbonyl stretching vibrations νC=O. The peaks at 1800, 1422, 874, and 708 cm^{-1} are attributed to calcite. The shoulder at 1100 and the peaks at 1021, 779, 754, 536, 469, and 434 cm^{-1} are attributed to the presence of kaolinite. The peak at 912 cm^{-1} corresponds to the bending vibrations of hydroxyl groups δOH or the bending vibrations δAl-OH of kaolinite. The peak at 591 cm^{-1} is due to the bending vibrations δSi-O, suggesting to the presence of quartz. It is well known that the red pigment cinnabar does not absorb infrared radiation in the range of 4000–400 cm^{-1}.

The FT-IR spectra of the blue pigment (df2) were almost identical to the red pigment, as calcite was the main component of these samples. Absorption bands at 1167, 1052 and 1000 cm^{-1} as well as the peaks at 756, 665, 588, 524, 479 and 420 cm^{-1} are related to Egyptian blue. From the similar FT-IR spectra of deep blue color (df4), it was determined that calcite was present in a higher proportion relative to Egyptian blue (Fig. 4). This indicates that a smaller amount of Egyptian blue was used and an additional pigment was added. Based on the dark color, amorphous carbon is a potential pigment.

In the analysis of yellow ochre (df3), the spectra showed similar characteristics to the other pigments. A distinct peak at 459 cm^{-1} is attributed to hematite or limonite or to the Fe-O bond vibrations of goethite. Additionally, these bands correspond to the bending vibrations of Si-O-Si bonds or the stretching vibrations of Al-O bonds in kaolinite [1,9, 11].

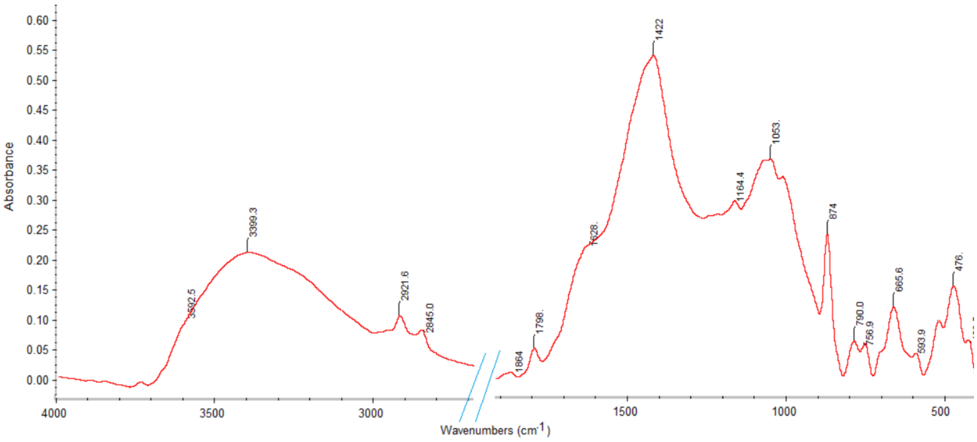

Fig.4. FT-IR spectra of deep blue color pigment (df4).

Based on FT-IR analysis, a combination of *fresco* and *secco* techniques may have been applied in the wall paintings due to the presence of calcite and the proteinaceous material. However, due to the degradation of the original compounds, a limited number of samples, or small sampling areas, complementary methods such as gas chromatography-mass spectrometry (GC–MS) or liquid chromatography-mass spectrometry (LC-MS) are required to determine the type of protein employed [1,9,11-16].

3.4 SEM-EDX

SEM-EDX is generally a useful tool for obtaining an overview of the morphological and elemental characteristics of the sample. The fragment D5 from the tomb headings was analyzed. Three types of images were obtained from the corresponding detectors: the LFD for secondary electrons, the SSD for backscattered electrons, and the mixed image. The chemical elemental composition was determined by the EDX detector using spot analysis at selected points and area analysis over the entire image. The surface layer was quite homogenous among different points.

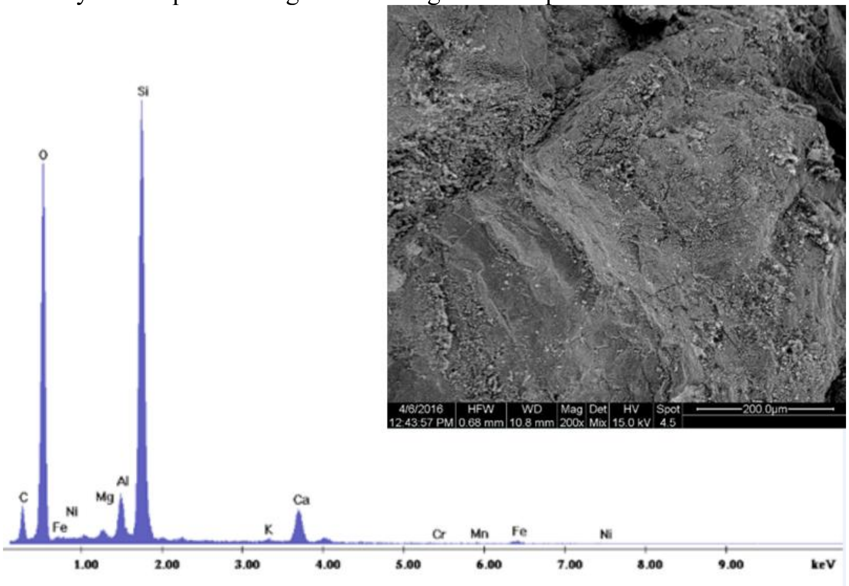

Fig. 5. SEM-EDX analysis on fragment, the EDX spectrum obtained from the area corresponding to Mix image.

The EDX chemical elemental analysis results revealed the presence of high Si content as major component of the sample (Fig.5). The strong intensity of the silicon, oxygen, aluminum, calcium, and carbon peaks in the EDX spectrum, along with the high weight percentages of these elements, lead to the conclusion that the fragment contains aluminosilicate compounds, primarily kaolinite due to the clay and calcite due to the marble [1,9,11].

4 Conclusions

The combination of the chemical elemental analysis results with the molecular information provided by XRF and VIS-NIR FORS, respectively, confirmed that the two spectroscopic methods were complementary, providing accurate identification of the pigments. Calcite, cinnabar, red ochre, yellow ochre, Egyptian blue and amorphous carbon were the applied pigments for the performance of white, red, yellow, blue and black color impressions. Regarding the painting technique, a combination of *fresco* and *secco* techniques was probably employed. Marble was the major component of the architectural surfaces of the tomb.

Finally, the obtained results confirm the combination of non-invasive techniques XRF, FORS, FTIR and SEM-EDX as a valuable, efficient and reliable tool for the investigation of cultural objects regarding the characterization/evaluation of materials, the decay patterns detection and assessment, where sampling is not allowed.

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