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THE STUDY OF BLACK PIGMENTS USED BY ALBANIAN POST-BYZANTINE PAINTERS JANI AND VASILI IN THE XVIII CENTURY

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Abstract. *The study of black pigments used in orthodox church frescoes in southern Albania was conducted using Raman spectroscopy and X-ray fluorescence. These frescoes, painted by the atelier of Jani and his son Vasili from Qestorati, represent artistic expressions that have been preserved since the 18th century. The frescoes belong to The Church of the Monastery of Saint Michael in Nivan, near Gjirokastra (1779), and The Church of Saint Nikolla in Dhrovjan village, Saranda district (1796). The techniques used by painters of the post-Byzantine period have been traced through specific research. Over the years, artists have experimented with modern materials and their combinations. The black pigments used by Jani and Vasili's atelier consist of light elements based on carbon structures, as investigated through Raman and XRF spectroscopy. Their molecular composition corresponds to a graphite structure. Measurements with EDXRF were performed to detect any traces of heavy elements.*

Keywords: *Raman spectroscopy, X-ray fluorescence, pigment, post-Byzantine, frescoes*

1. Introduction

Carbon-based black pigments are a group of dark-colored materials composed by some form of elemental carbon [1], and four groups may be distinguished: graphite, flame carbons, chars, and cokes [2]. Flame carbons comprise any carbon produced in the gas phase that originates from the incomplete combustion of hydrocarbon precursors such as oil and resins [1]. Chars are carbons formed from solid precursors such as wood, bark and stone fruits that remain solid through the carbonization process [1]. Coke is defined as any carbonized product for which the precursor was in a liquid or plastic state immediately before carbonization [1].

Black dyes were produced by burning plant or animal materials and each of these blacks is distinguished by its special properties, which result from physical mixing and the intensity of its coverage or reflection [3].

Ivory black pigment is prepared by burning elephant ivory waste. This pigment has a very strong and deep black color. As a pigment, it is resistant to light, strong, and resistant to atmospheric agents. *Bone black* is black with a reddish tint. The material for its production is the shoulder and thigh bones of sheep, calves, and chicken bones. They are well-cleaned of fat and carefully dried, then finely chopped and carbonized in iron containers without contact with air.

Lamp Black is obtained by burning various oils such as kerosene and naphthalene in large lamps. *Grape black* is a color with a slightly blue tint and is part of the group of plant-derived colors. It is prepared from dried vine branches that are carbonized in large metal containers without being in contact with air. The obtained material is washed with water to remove soluble salts of alkali metals. *The color of the cores* is extracted from the cores of peaches, apricots, cherries, and other trees which, after being carefully washed, are carbonized in closed containers without contact with air. *The black color of the wood* has different shades from black to blue to brownish black. It is produced by carbonizing the wood without having contact with air. *The mineral black* color is a natural earth pigment. It is extracted from several types of clay shales rich in carbon. The pieces of clay shales are carefully crushed in water and the fine powder obtained after sedimentation, after being dried, is used as a pigment. It has an intense black color, is strong, and is resistant to the action of light.

Carbonate compounds found in coal include siderite ($FeCO_3$) dolomite ($CaMg(CO_3)_2$, ankerite ($(Ca,Mg,Fe)CO_3$), calcite ($CaCO_3$) and magnesite ($MgCO_3$) [3]. The identification of carbonaceous material can be easily accomplished by Raman spectroscopy based on characteristic bands of carbon at ~1580 cm^{-1} (G band) and ~1350 cm^{-1} (D band). Nevertheless, it is very difficult to discriminate the source of carbon-based pigments because their Raman spectra are very similar, although differences in band positions, intensities, and bandwidths may be observed after a detailed study of the spectra [1].

Raman spectroscopy has been extensively used as a nondestructive technique to characterize the complex

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microstructure of carbon materials [4] and study carbon based black pigments. This technique has been used to characterize graphitic materials (highly oriented pyrolytic graphite, carbon fibers, glass-like carbons) and carbonaceous nanomaterials (fullerenes, and carbon nanotubes) [5]. The purpose of our study through molecular Raman spectroscopy is to find the structure of graphene in the black pigments used in *The Church of the Monastery of Saint Michael* in Nivan, near Gjirokastra (1779), and *The Church of Saint Nikolla* in Dhrovjan village, Saranda district (1796).

Jani and Vasili were father and son, originally from the Qesarat of Lunxhëria, and developed their artistic activity in the 18th century in the area of Gjirokastra, Saranda, and Himara [8]. From the paleographic inscriptions in Orthodox churches in Albania, the researcher Theofan Popa [8] has concluded that the two iconographers painted about 12 churches from 1758 to 1799 [8]. In their mural painting, the tones of light green and red prevail, among other pigments.

2. Materials and Methods

Restaurateurs from The National Institute of Cultural Heritage extracted four microsamples, two from each church, from black areas in the frescoes of the churches. Respectively there are sample no. 2. "zezë+grund", together with sample number 6. "zezë" from *The Church of the Monastery of Saint Michael* in Nivan (1779), and sample no. 7. "e zeza absid" together with sample no. 10. "e zeza absid 3" from *The Church of Saint Nikolla* in Dhrovjan village, (1796). The compositional analyses were performed in the Department of Analytical Instrumental Methods, Institute of Applied Nuclear Physics, in the scope of the project "Study of the Jani and Vasili atelier from Qestorati, within the framework of 18th-19th century painting" supported from the Ministry of Culture of Albania and University of Tirana.

For this study was used a B&W Tek i-Raman Ex Raman spectrometer with a wavelength of 1064 nm, a laser power of 4.3 mW. Microsamples from black areas of the frescoes were also analyzed by EDXRF spectrometry with Artax 800 spectrometer produced by Bruker. This device is equipped with Rhodium (Rh) anode and operates in direct excitation mode, using a Silicon Drift Detector. During the measurement the generator was operated at 30 kV and 200μA, and the samples being measured for 50s with a dead time of 6%.

As a first step, we performed a visual examination using the Raman Video Micro-Sampling System BAC 151C, which is a compact Raman microscope belonging to the B&WTek portable Raman system. The stratigraphic thicknesses were determined by using the open-source software ImageJ.

Table 1. Samples, dimensions, microscope photos and stratigraphic thickness. The Church of the Monastery of Saint Michael in Nivan (1779)

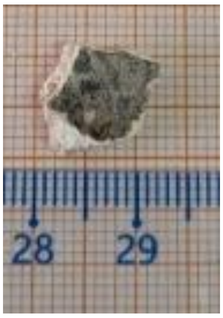
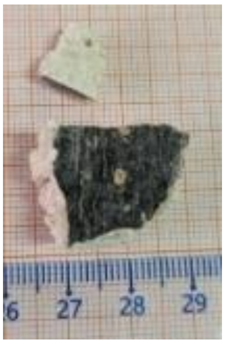
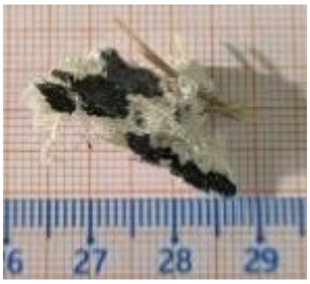
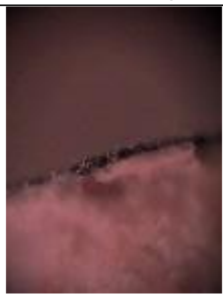
Sample	Picture	Stratigraphic thickness (T)
2. black+preparatory layer		 T=0.015 mm±0.004
6. black		 T=0.016 mm±0.004

Table 2. Samples, dimensions, microscope photos and stratigraphic thickness. The Church of Saint Nikolla in Dhrovjan village, (1796)

Sample	Picture	Stratigraphic thickness (T)
7. black absid		 T=0.016±0.004 mm
10. e zeza absid 3		 T= 0.025 ± 0.004 mm

3. Results and Discussion

Raman spectroscopy is an ideal non-destructive technique for the characterization of a variety of carbonaceous materials because it is sensitive to crystalline and amorphous structures, allowing the study of highly disordered materials, such as carbon-based pigments [6]. The basic structure for analyzing sp^2 bonded carbons is graphite lattice. Only two planar modes with E_{2g} symmetry are active in Raman, modes which are found at peaks at 1582 cm^{-1} dhe 42 cm^{-1}, both for crystalline graphite and for pyrolytic graphite with high-order orientation [4]. The bands present during the analysis of our samples are the D1, D2 E_{2g}, G dhe D' bands.

According to the reference [4] the intensity of the G band for amorphous carbons increases as the photon energy approaches the $\pi - \pi^*$ transition in the sp^2 clusters of carbons, while the D band does not show any noticeable increase. The G band represents the in-plane bonds of aromatic rings with C - C bonds in a stretching vibrational mode with E_{2g} [5]. However, when we have carbons misoriented in sp^2 visible spectral modifications are observed in the G band which broadens, and new bands arise as a result of the reduction of the crystal order.

With increasing wavelength, the peaks tend to shift towards smaller wavenumbers. This argument serves to understand the differences in the spectral data that our study of carbon black pigments has from other studies of the same nature but that have used a laser source with a wavelength shorter than the 1064 nm wavelength. Here we will show a representation of the samples studied as well as the corresponding Raman spectra, along with the main identifying peaks.

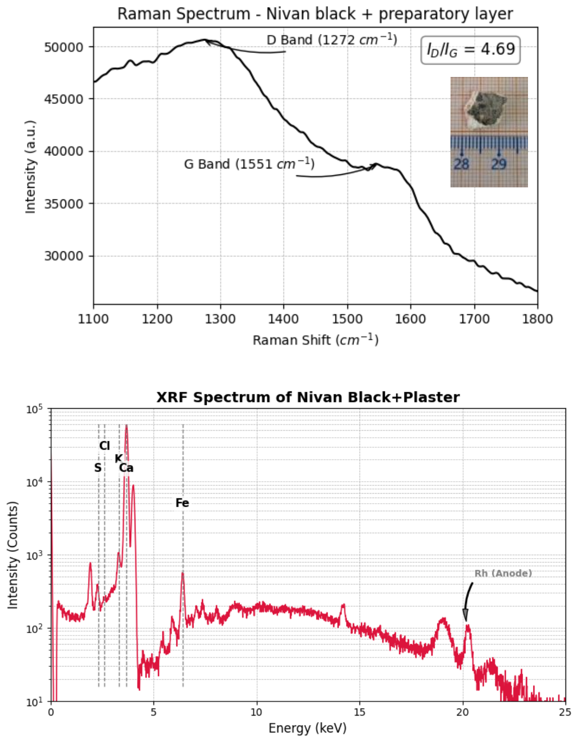


Figure 1. Raman and XRF spectra of 2. Black + preparatory layer, The Church of the Monastery of Saint Michael in Nivan (1779), wavelength of 1064 nm.

In the spectra reported in Figure 1, D band of graphene structure is presented at the wavenumber 1272 cm^{-1} , and the G band at the wavenumber 1551 cm^{-1} , which indicated that it is a **carbon-based** pigment that can be classified of **charcoal origin**. The presence of peaks in the second derivative, namely 281 cm^{-1} , 903 cm^{-1}, 1026 cm^{-1}, 1040 cm^{-1} gives us an additional indication to come to this conclusion.

The detection of minor potassium (K) via XRF is a key indicator for charcoal, reflecting the elemental composition of the original wood source. The accompanying trace sulfur (S) can also be associated with plant materials or the burning process.

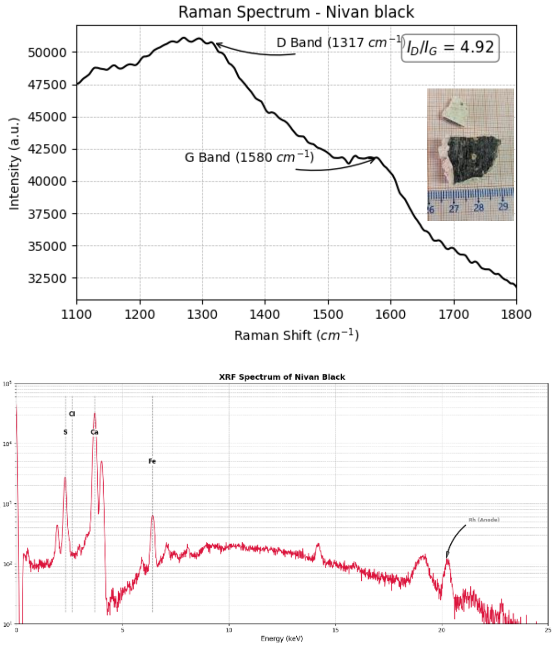


Figure 2. Raman and XRF spectra of 6. black, The Church of the Monastery of Saint Michael in Nivan (1779), wavelength of 1064nm.

Referring to Figure 2, the D band is presented at the wave number 1317 cm^{-1} and the G band at the wave number 1580 cm^{-1}, which is a **carbon-based pigment** that can be broadly classified as **Lamp black** according to [5]. We identify this pigment as lamp black due to the significant presence of sulfur (S) in its XRF spectrum, alongside the notable absence of potassium (K) or phosphorus (P), which are characteristic markers for plant-derived or bone-based black pigments, respectively.

In Figure 3, the D band is presented at the wave number 1297 cm^{-1} and the G band at the wave number 1548 cm^{-1}, which is a carbon-based pigment that can be broadly classified of plant origin, such as grape black, is supported by the significant potassium (K) and chlorine (Cl) peaks detected in the XRF spectrum; these elements are characteristic due to the formation of potassium salts (KCl, K_2CO_3) during the charring of plant matter.

In Figure 4, the D band is presented at the wave number 1317 cm^{-1} and the G band at the wave number 1579 cm^{-1}, which is a carbon-based pigment that can be broadly classified as Grape black according to [5]. For instance, calcium can be present as calcium carbonate, particularly in pigments like vine black which is closely related to grape black.

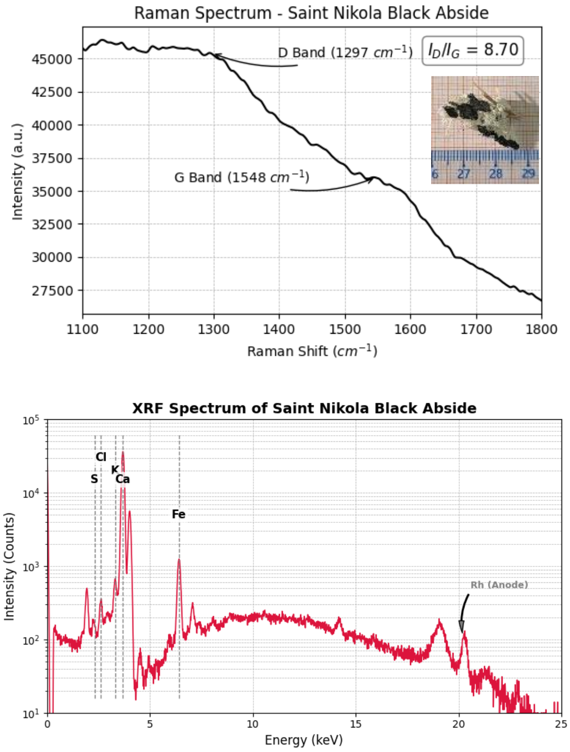


Figure 3. Raman and XRF spectra of 7. black abside, The Church of Saint Nikolla in Dhrovjan village, (1796), wavelength of 1064nm.

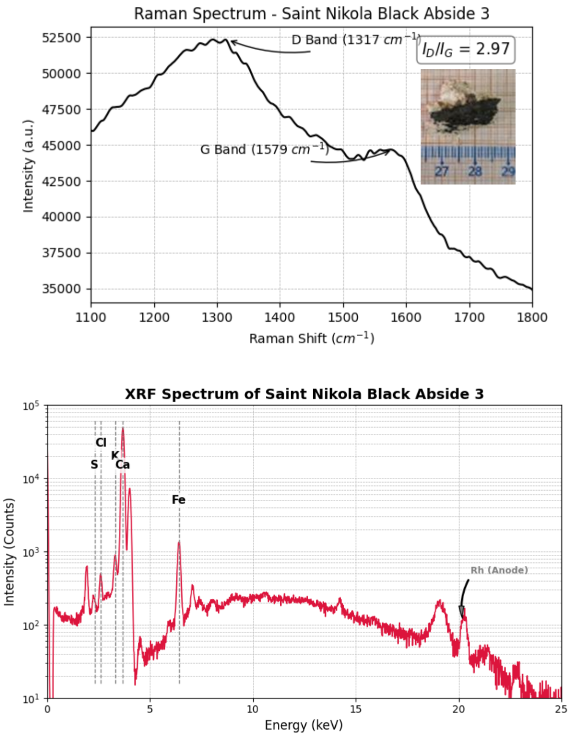


Figure 4. The Raman and XRF spectra of 10. black abside 3, The Church of Saint Nikolla in Dhrovjan village, (1796), wavelength 1064nm.

The energies corresponding to the Raman frequency shifts are the energies associated with the transitions between the different rotational and oscillatory states of the molecule that scatters the radiation. Pure rotational displacements are small and difficult to observe, except for simple molecules in the gaseous state. In liquids, rotational motions are hindered, and discrete rotational Raman lines are not easily found.

Most studies of the Raman effect are concerned with oscillatory transitions, which can be easily observed in gases, liquids and solids, but due to the low molecular concentration in gases, at ordinary pressure and temperature, liquids and substances solid are studied more often.

5. Conclusion

Each spectral evaluation is based on the Raman Spectrometry system, i-Raman EX software library BWID 2.04, reference tables of vibrational modes of chemical bonds, relevant literature, and other previous studies that have been carried out in this field [7], [8]. By analyzing all the spectra from the samples, we conclude that in the bands near 1500 cm^{-1} and 1300 cm^{-1}, we have the presence of some characteristic vibrations of the main structures for the graphite. Therefore, by correlating the characteristic Raman shifts of graphite's D and G bands with the presence of chemical elements ($Z > 11$) and through meticulous analysis of their intensities and relative ratios as observed in the X-ray fluorescence (XRF) spectra we can effectively determine the origin of the carbon black pigment.

In this specific case, the identified black pigments included those originating from **charcoal**, **lamp black**, and plant-derived varieties such as **grape black** or **vine black**. The identification of **charcoal** pigment was based on the detection of potassium (K), sometimes accompanied by small amounts of sulfur (S), as clear indicators of its wood origin. **Lamp black** pigment was distinguished by its significant sulfur (S) signal, coupled with the marked absence of potassium (K) and phosphorus (P) elements that typically characterize other types of black pigments. Plant-derived pigments, such as **grape black** or **vine black,** were recognized by their characteristic high potassium (K) peaks, often along with the presence of chlorine (Cl). Additionally, these samples could exhibit considerable levels of calcium (Ca), particularly in the case of vine black (due to the presence of calcium carbonate), and phosphorus (P) elements originating from the mineral content of the initial plant material from which they were produced.

This case study is just the beginning of the work to fully define the palette of the artists Jani and Vasili from Qestorati who painted the cultural heritage objects of the monastery church of the "Archangels" in Nivan in Zagoria, in 1779, and the old church of "Shën Kolli" in Dhrovjani i Poshtëm in 1796 [9]. It is noted that part of the author's palette was carbon black derived from charcoal and Grape black. Through X-ray fluorescence we understand the presence of materials with high atomic numbers and exclude the possibility of having another composition of the black pigment. Examination with two spectroscopic devices, Raman Spectroscopy and Infrared, is recommended because the analyzes of both complement each other. This study presents an initial overview of the treated issue, which is still being studied in the future.

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