

Optoelectronic investigation of the mural paintings from Drăguțești wooden church, Argeș County, Romania

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This paper presents the first set of investigations on the mural paintings belonging to Drăguțești wooden church (1813-1814 A.D.) that has recently been included into the patrimony of Golești Museum, Argeș County. Conservation of a religious site of this type requires a deep analysis of materials in order to evaluate correctly the murals' state of conservation, but also for identifying the proper intervention materials that must have characteristics similar to the original ones. Aside from photographic documentation, molecular characterization was achieved via Fourier-transform infrared spectroscopy, while functional analysis was performed with X-ray diffraction and elemental identification was performed with the help of X-ray fluorescence spectroscopy and laser-induced breakdown spectroscopy, aiming to obtain as much information as possible about the mortars and the pigments. The results showed the plasters from the intonaco and arriccio layers are similar, based on lime and quartz sand mortars, correlating with the traditional execution technique. Regarding the pigments used, the study revealed that cinnabar could have been used as red pigment, synthetic ultramarine as blue pigment, along with other possible iron oxides. Furthermore, a historical restoration was spotted by the detection of polyvinyl acetate. The study is an essential step towards the future restoration intervention that is of absolute necessity.

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1. Introduction

The wooden church from the old Drăguțești village, from Argeș County, România, was erected in 1813-1814 A.D., belonging to the byzantine era. In the second half of the 20th century, the church was transferred on the premises of the Golești Museum - Argeș County, in order to preserve it. In the entire peasant architecture within the Golești Viticulture and Tree-growing Museum, the Drăguțești church represents one of the main constructions, being the only wooden church, defining for the rural ecclesial architecture of the XVIII-XIX centuries.

The church hosts valuable murals in need of urgent conservation and restoration. Inside the altar, there are four mural fragments extracted and transposed on wooden panels. The murals are believed to have been extracted from the Drăguțești church, since they were inside the church when it was moved in the museum, but there are no documents to attest if they origin from the exterior or interior mural decorations.

The mural paintings are completed presumably using byzantine tradition of painting fresco that requires several layers of plaster.[1]

The mural paintings are in an advanced degradation state, which will require restoration in the near future.

Conservation of a religious site of this type requires a deep analysis of the materials, so that the intervention materials used will be compatible with the original ones.

Thus, advanced optoelectronic techniques have been used in order to gain a complex analysis of the materials and their chemical composition, in order to elaborate a proper

conservation-restoration strategy

2. Experiments

The murals are constructed on a support made from twisted twigs filled with a lime-based plaster rich in aggregates (sand) corresponding to the *arriccio* layer. The murals (Figs. 1-2) are covered with thick adherent deposits layers and present a firm salt crust that reduce the visibility of the iconographic image.



Fig. 1. a) Saint Peter's Vision mural painting, b) D4 sample location.



Fig. 2. a) Solomon and Moses mural painting, b) D1 samples' location

Six mortar samples were collected from the extracted mural paintings from Drăguțești wooden church, 3 from each one. D2-D6 samples have a relatively firm, compact structure, with fine pores that are uniformly distributed. D1 sample has a relatively friable structure. Their structure is a fine micro-granular one, mostly homogeneous. There are different impurities present on the samples' surface, such as adherent dust deposits, dead larvae and oakum traces. D4-D6 samples are pieces detached from the support layer and present surface erosional grooves from the direct contact with the wooden rods backing structure. D3 and D5 include the pictorial layer, also. Information about the samples' locations is listed in Table 1.

Table 1. Sample reference and description

Sample	Description	Location
D1a	mortar fragments from the <i>arriccio</i> layer	Solomon and Moses mural
D1b		
D3	painting mortar fragments from the <i>intonaco</i> layer	
D4, D5	mortar fragments from the <i>intonaco</i> layer	Saint Peter's Vision mural
D6		
	mural painting fragment that contains all the layers	

The mortar samples were subjected to atomic and molecular characterization techniques in order to identify their basic composition. Four methods of investigation were used, selected due to their complementarity, in order to achieve a complex profile of the mortars: Laser Induced Breakdown Spectroscopy (LIBS), X-Ray Fluorescence (XRF), X-ray diffraction analysis (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). All four methods are commonly used for characterization of such types of samples [2]–[5].

Energy-dispersive X-ray fluorescence spectroscopy (ED-XRF) is widely used nowadays and accepted by the cultural heritage community as a non-invasive tool for identification of the elemental composition of materials [6], [7]. Due to the current state of the art in detectors' manufacturing, hand-held XRF equipment can only be used to directly determine the presence of inorganic components, but it can be used to infer the presence of organic components, through the variation of the elemental peaks, as Ferrero and co-workers have concluded [8]. For this study, ED-XRF was employed on mortar samples, with and without polychrome paintings, to gain information about the elemental composition of these samples. XRF analysis was performed with TRACER III from Bruker Elemental, operated at 40 kV tube power and 11 μ A current intensity, 30 s acquisition time. A total of 9 spectra were collected and processed. Elements were identified through Bayesian deconvolution with ARTAX software and data processing was achieved via Microsoft Excel software. The accuracy of the deconvolution was evaluated by comparing the reconstructed spectrum with the acquired one, for each measurement. In order to minimize the effect of X-ray scattering in the sample matrix and to obtain a better comparison, all XRF data were normalized with respect to

the Rh K α line [9], [10].

Laser Induced Breakdown Spectroscopy: The LIBS spectra were recorded using a handheld spectrometer from SciAps that can operate in Argon purge environment. It can be applied directly on the surface of interest; thus, no sampling or sample preparation is required. The laser used for irradiation is a Q-switched Nd:YAG, emitting at 1064 nm, an energy of 5 mJ and a laser spot of 50 μ m. The system is equipped 3 spectrometers that provide a spectral range from 190 nm out to 950 nm. The equipment is manufactured for identification of scrap metals, but it was adapted for applications on Cultural Heritage objects, mainly through software configuration [11], [12]. The system was operated in single pulse mode for identification of the chemical composition of the paint layers and in raster mode (16x16 spots) for mapping the elemental distributions.

Fourier Transform Infrared Spectroscopy: the IR spectra were recorded in attenuated total reflection (ATR) mode with a Perkin Elmer Spectrum Two FTIR spectrometer, equipped with a GladiATR accessory from Pike Technologies. The spectra were collected in the 4000-400 cm^{-1} mid IR at 4 cm^{-1} resolution, by averaging 8 scans. The data were processed using Essential FTIR.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer, with Ni-filtered CuK α radiation ($\lambda=1.5406$ Å), with scan step of 0.05°. The total amount of sample used was approx. 0.8 g of powder. The powder diffraction file (PDF) was used for qualitative identification of the mineralogical composition of the *intonaco* and *arriccio* layers of the mural painting. The analysis of the lime plaster was performed on samples ground to pass through a 45- μ m sieve.

3. Results

Sample D1 consists of a mortar fragment from the support layer of the Solomon and Moses mural painting.

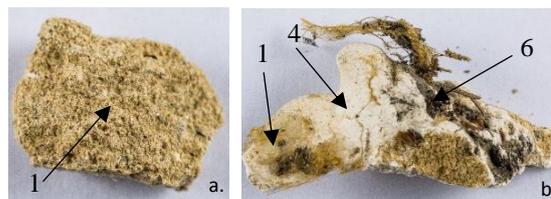


Fig. 3. LIBS areas of investigation on sample D1 from Solomon and Moses mural painting: a. *arriccio* layer, b. white layer

The LIBS analysis on the mortar fragment D1a corresponding to the *arriccio* layer was conducted on two spots of interest, one on each side. The LIBS analysis on the mortar fragment D1b corresponding to the white layer was conducted on 8 spots of interest, but the results were similar and only four were chosen as representative (see Figure 3). In Figure 4 two FTIR spectra are presented, characteristic for two distinct areas of the sample: resin and white basis. The chemical elements and molecules identified by LIBS, XRF and FTIR are described in Table 2.

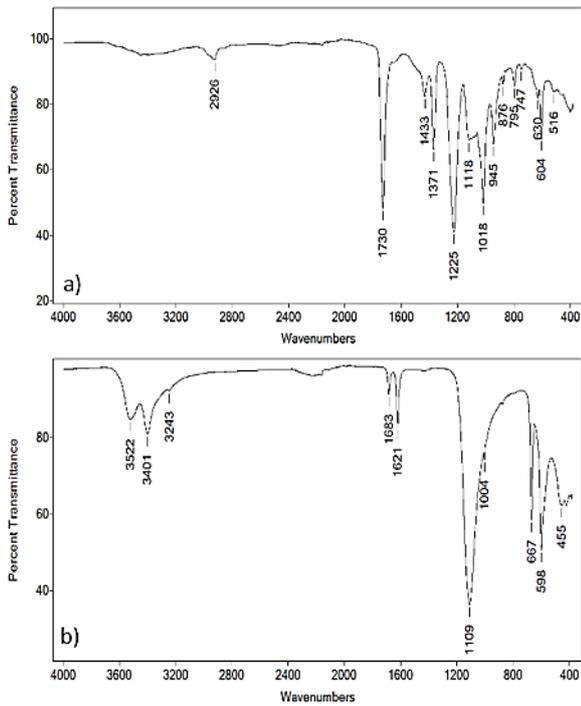


Fig. 4. FTIR spectrum for D1b sample: a) PVA resin and b) white basis (gypsum)

The XRD analysis of sample D1a identified the following mineralogical compounds of the *arriccio* layer: quartz, calcite, muscovite, albite, anorthite, feldspar, clinocllore, ferrohornblende (see Fig. 5).

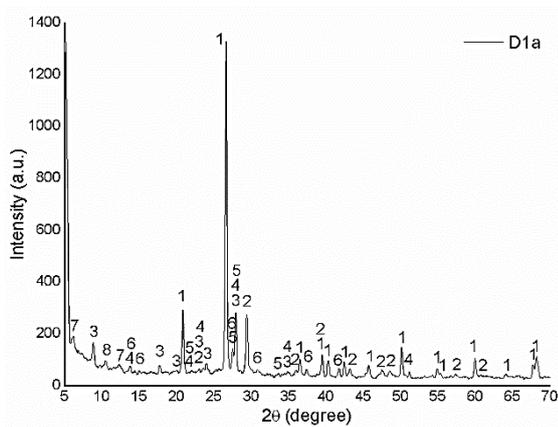


Fig. 5. X-Ray pattern of the sample D1a: 1 – quartz; 2 – calcite; 3 – muscovite; 4 – albite; 5 – anorthite; 6 – feldspar potassian; 7 – clinocllore; 8 – ferrohornblende

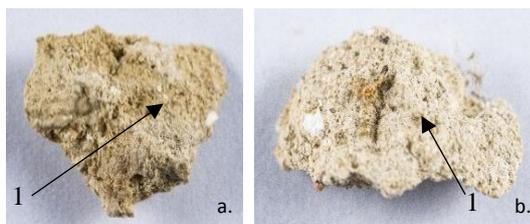


Fig. 6. LIBS spots on the front of the mortar samples from Saint Peter's Vision mural painting: a. D4, b. D5

Sample D4 and D5 represent mortar fragments from the *intonaco* layer of the Saint Peter's Vision mural painting.

The LIBS analyses for samples D4 and D5 were conducted on 2 spots of interest for each: 1 on the front side and 1 on the back side of the piece. The LIBS spots of investigation on the front of the samples are depicted in Fig. 6. A combined representative LIBS spectrum of the two samples is presented in Fig. 7 and the XRF spectrum obtained for the D5 sample is depicted in Fig. 8. The chemical elements and molecules identified using LIBS, XRF and FTIR are described in Table 2.

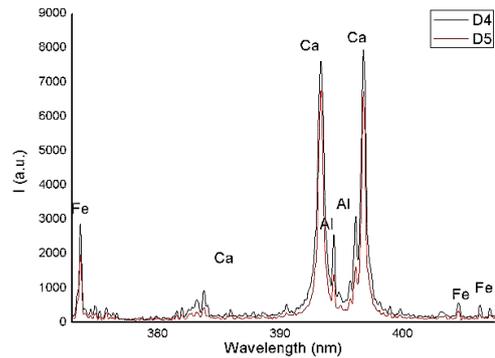


Fig. 7. LIBS spectrum for: D4 (red) and D5 (blue) samples

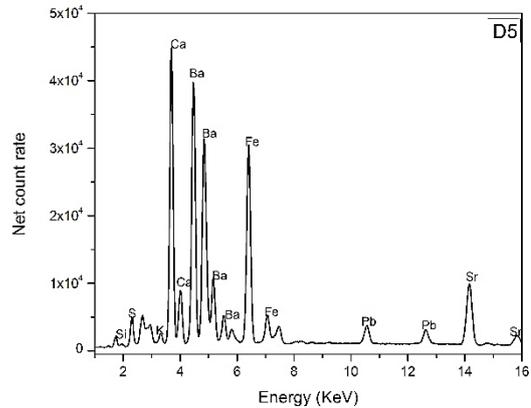


Fig. 8. XRF spectrum for D5 sample

Sample D3 is a mortar fragment from the *intonaco* layer of the Solomon and Moses mural painting.

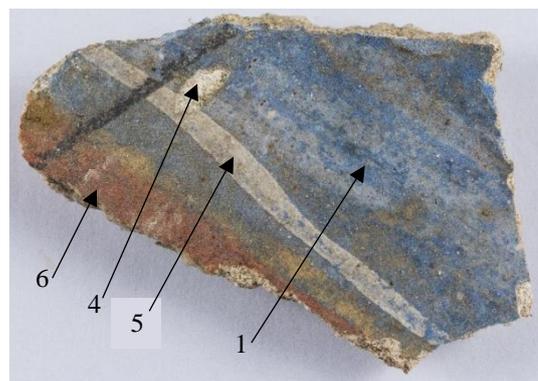


Fig. 9. LIBS areas of investigation on sample D3 from Solomon and Moses mural painting

LIBS analysis on sample D3 was conducted on 9 spots of interest: 7 on the front side and 2 on the back side of the piece. The position of the LIBS spots of investigation is depicted in Fig. 9. A representative LIBS spectrum is presented in Fig. 10 and the XRF spectrum obtained for the D3 sample is depicted in Fig. 11. The chemical elements and compounds are described in Table 2.

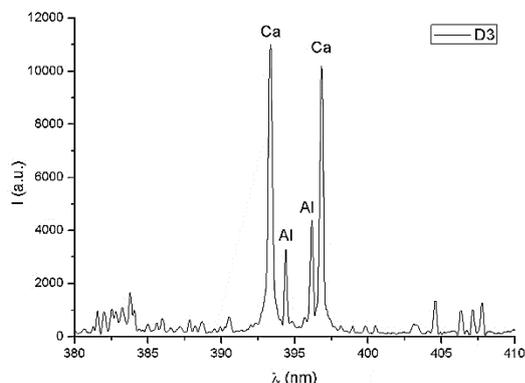


Fig. 10. LIBS spectrum for D3 sample

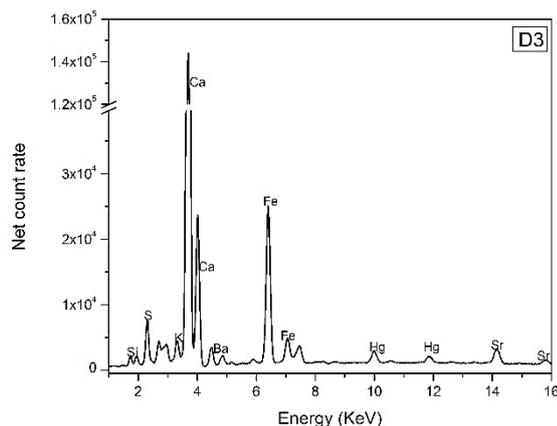


Fig. 11. XRF spectrum for D3 red pigment

Sample D6 is a complex mural fragment from the Saint Peter's Vision mural painting.

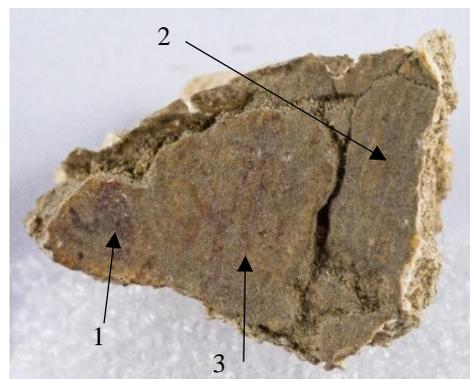


Fig. 12. LIBS areas of investigation on sample D6 from Saint Peter's Vision mural painting

LIBS analysis on sample D6 was conducted on 10 spots of interest: 3 on the front side, 3 on the rear side and 4 on the cross-section parts. The position of some of the LIBS spots of investigation is depicted in Figure 12. The results obtained on the cross-section are similar to the ones obtained for the front and the rear areas, therefore the discussions will consider only 6 points of interest. The chemical elements and compounds that have been identified using the LIBS, XRF and FTIR techniques are described in Table 2.

Several elements have been identified in the acquired spectra, at varying intensities, as listed in Table 2: major elements are listed in bold letters, minor elements are listed in normal letters, and trace elements are listed in italics.

Table 2. Identified elements and vibrational groups

Sample	XRF	LIBS	FTIR
D1	Fe, Ca, Ti, K, Si, Mn, Zr, Sr, Rb, Al, Cu, Cr, S, Zn	D1a	Calcium Carbonate, Silicates, Aluminosilicates, Iron oxides
	Ca, S, Sr, Fe, K, Mn, Ti, Si, Cu, Al	D1b	Gypsum (sulphate naturally hydrated by calcium), Polyvinyl acetate, Silicates (quartz), Iron oxides, Gypsum (traces)
D3 blue	Ca, Fe, Sr, K, S, Ba, Zr, Pb, Hg, Si, Mn, Ti, Zn, Cu, Rb	D3-1	Gypsum, Silicates, Aluminosilicates, Iron oxides, Polyvinyl acetate, Lipid compounds, Protein compounds
D3 white stripe	Ca, Fe, Sr, K, Ba, S, Ba, Hg, Mn, Si, Pb, Ti, Al, Rb	D3-4 D3-5	Calcium Carbonate, Gypsum, Polyvinyl acetate (traces)
D3 red, blue and white	Ca, Fe, S, Sr, K, Ba, Hg	D3-6	Gypsum, Silicates, Aluminosilicates, Iron oxides, Polyvinyl acetate, Lipid compounds, Protein compounds
D3 back	Fe, Ca, Ti, K, Si, Zr, Sr, Mn, Rb, Al, Hg, Cu, S, Zn,	D3-9	Gypsum, Silicates, Iron oxides, Polyvinyl acetate, Lipid

Sample	XRF	LIBS		FTIR
	<i>Cr</i>		<i>Pb, Sm, Mo</i>	compounds
D4	Ca, Fe, K, Ti, Si, Sr, Zr, Mn, Rb, Cu, Al	D4-1	Ca, Al, Li, Na, Ba, Sr, K, Eu, C, Si, Fe, Mg, Ti, Sb, Rb, Pb, Mo, Zn	Calcium Carbonate, Silicates, Aluminosilicates, Iron oxides
D5	Ca, Fe, K, Ti, Si, Sr, Mn, Zr, Rb, Al, Cu, Cr	D5-1	Ca, Al, Li, Na, Ba, Sr, K, Eu, C, Si, Fe, Mg, Ti, Sb, Rb, Pb, Mo, Zn	Calcium Carbonate, Silicates, Aluminosilicates, Iron oxides
D6 pigment	Ca, Ba, Fe, Sr, Pb, S, Cl, Si, K, Cu, Zn, Rb	D6-1	Ca, Ba, Al, K, Li, Sr, Na, Mg, Si, Fe, Ti, C, Eu, Rb, Pb, Cr, Zn	Red: Calcium Carbonate, Gypsum, Silicates, Aluminosilicates, Lipid compounds, Protein compounds, Polyvinyl acetate
		D6-2	Ca, Ba, Sr, Na, Al, K, Li, Mg, Eu, Si, Fe, C, Ti, Rb, Cr, Pb, Zn	Blue: Calcium Carbonate, Gypsum, Silicates, Aluminosilicates, Iron oxides, Lipid compounds, Protein compounds, Polyvinyl acetate
		D6-3	Ca, Al, Li, Na, Ba, Sr, K, Eu, C, Si, Fe, Mg, Ti, Sb, Rb, Pb, Mo, Zn	Calcium Carbonate, Silicates, Aluminosilicates, Iron oxides
D6 back	Ca, Fe, Sr, K, Ti, Zr, Mn, Si, Rb, S, Al, Ba, Cu, Zn	D6-6	Ca, Al, Na, Li, K, Eu, Sr, Mg, Si, Fe, C, Ti, Ba, Cr, Sb	Calcium Carbonate, Silicates, Aluminosilicates, Iron oxides
		D6-7	Ca, Al, Na, Li, K, Eu, Si, C, Fe, Ti, Ba, Cr, Sb	
		D6-8	Ca, Al, Na, Si, Li, K, Eu, C, Mg, Sr, Fe, Ba, Ti, Cr, Sb	

4. Discussions

4.1. Pigments

FTIR data obtained on the pigmented layers highlighted strong contributions ascribed to gypsum (calcium sulphate dehydrate): characteristic bands at 3533, 3402, 1620, 1110, 673 and 601 cm^{-1} . The presence of gypsum can be linked to the ground layer. Although the gypsum can also be identified as a degradation product [13], existing literature [14] frequently mentions the use of gypsum for the preparation layer of 19th century wall paintings executed *a secco*.

In terms of organic compounds, the presence of a polyvinyl acetate (PVA) resin was identified on all investigated pigmented areas, via the strong and sharp bands centred at approx. 1730, 1373, 1225, 1017 and 947 cm^{-1} . This synthetic resin, discovered in 1912 [15] can be linked to past restorations, polyvinyl acetate being used in the conservation of wall paintings before 1935, especially as a consolidant for the transfer of wall paintings to new supports [16].

The use of a protein based binding media can be inferred as indicated by the small but characteristic peaks at 2931, 2852 cm^{-1} (C-H stretching vibrations), and 1644 cm^{-1} (amide I), seen in some of the spectra. The protein content can be linked either with the original painting layer, or with a restoration intervention.

For the blue pigment, the use of synthetic ultramarine can be inferred. Both indigo and Prussian blue can be excluded as no diagnostic IR bands were found within the investigated blue areas. With the exception of iron oxides, no other pigments could be ascribed by FTIR analysis alone.

According to the existing studies [14] the colour palette characteristic for the 18th and 19th century wall paintings in Romanian counties included Prussian blue, indigo, ultramarine, chrome yellow, chrome green, red lead,

vermillion, lead white, zinc white, and various ochres.

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By analysing the distribution of the normalized net count rate of each element, for all spectra, it can be inferred that some elements are related to the mortars and other are related to the pictorial layers. Elements such as Ti, Si, Rb, Zr, which appears as traces in the spectra, all have higher intensities on the mortars as compared to the coloured areas, probably indicators of the terrigenous origin of the raw materials [17]. Other elements, such as potassium, which appears in most spectra as minor or trace element, might be related to pollution deposits on the surface of the samples or the formation of surface salts [18], [19]. One feature appears very clear on the red area of sample D6 – the presence of well-defined Hg lines, which, correlated with slightly more intense S lines, probably indicates the use of cinnabar, red pigment used since ancient times. Cinnabar has been widely used throughout the centuries, due to its high tinting power, in all painting techniques, except for exterior mural painting, because it has low light resistance [14], [20]. Additionally, lead traces were found on samples D3 and D6, on the pigment areas. Lead can come from a large variety of white, yellow, orange, black or red pigments, with different timespans. However, elemental analysis alone cannot positively answer the question of what type of pigment Pb comes from. Ba L lines appear at high intensity on the spectrum of sample D6, on the pigment. Similarly, higher intensities of Ba were noticed on sample D3, on the pigment area. A possible explanation could be that the pigments used contained barium sulphate, often used as filler [14], [21], [22].

4.2. Plasters

FTIR spectra registered on all analysed plaster fragments showed a very similar composition based on calcium carbonate (calcite), aluminosilicate minerals, and iron oxides. The strong absorptions centred at approx. 1400, 872 and 712 cm^{-1} , ascribed to calcite, can be easily seen in all registered spectra. Kaolinite, an aluminosilicate, was identified by its characteristic bands at 3694, 3620, 1005 and 916 cm^{-1} . Peaks at 1162, 798, 778 and 694 cm^{-1} indicate the presence of quartz, a silicon dioxide mineral frequently found with kaolinite. Iron oxides could be inferred via the absorption bands centred at approx. 530 and 470 cm^{-1} [23]. The iron content can also be linked to kaolinite. The distribution of the identified components is quite similar in all investigated fragments, with only sample D1b showing higher amounts of quartz.

X-ray diffraction (XRD) analysis highlighted the fact that the *intonaco* and *arriccio* layers have similar mineralogical composition, being based on lime:

- calcite (CaCO_3) is specific for carbonated binder (lime);

- quartz ($\alpha\text{-SiO}_2$), muscovite ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$), anorthite ($\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$), albite ($\text{Na}(\text{AlSi}_3\text{O}_8)$), feldspar ($\text{K}_{0.5}\text{Na}_{0.5}\text{AlSi}_3\text{O}_8$), clinocllore ($\text{Mg}_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$) and ferrohornblende ($\text{NaCa}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) are specific to the aggregate (sand).

In all samples, quartz is the major component, the intensity of the specific main line ($2\theta=26,64^\circ$) being 1331 a.u. (D1), 1140 a.u. (D3), 942 a.u. (D4). This can imply that the mortars from which the *intonaco* and *arriccio* layers had been made are richer in aggregate and have less binder. Also, the higher intensity of the lines specific for quartz in sample D1 (*arriccio*) as compared to samples D3 and D4 (*intonaco*), can suggest that D1 contains a higher aggregate amount, which correlates with the proportions used by traditional craftsmen for the manufacturing of the *arriccio* and *intonaco* layers. The intensities of the lines specific for the other components in the aggregate are smaller as compared to those of quartz, which is an indicator of the fact that aggregate is quartz sand.

The results obtained by XRD correlate well with those from FTIR, which identified the functional groups characteristic for calcite, silicates and aluminosilicates. The iron oxides found through FTIR have not been observed in XRD, probably due to their low concentration, below the detection limit of the XRD equipment (3%). The only compound found that may contain iron oxides is the ferrohornblende, which is detected very low or even trace amounts.

5. Conclusions

The analytical methods included in the current study are complementary advanced optoelectronic techniques: X-Ray Fluorescence Spectroscopy (XRF), Laser Induced Breakdown Spectroscopy (LIBS), Fourier-Transform Infrared Spectroscopy (FTIR) and Energy-dispersive X-ray

fluorescence spectroscopy (EDX) and provided a complex data package of investigation.

X-ray diffraction analysis in correlation with FTIR analysis shows that plaster from *intonaco* and *arriccio* layers are based on lime and quartz sand mortars. The higher intensities of the quartz-specific lines compared to those of the calcite suggest that the mortars of the *intonaco* and *arriccio* layers are richer in aggregate. The difference in the intensities of the quartz-specific lines from the analysed samples suggests that the *arriccio* layer is richer in aggregate than the *intonaco* layer, which correlates with their traditional execution technique.

The results showed the plasters from the *intonaco* and *arriccio* layers are similar, based on lime and quartz sand mortars, correlating with the traditional execution technique. Regarding the pigments used, the study revealed that cinnabar could have been used as red pigment, synthetic ultramarine as blue pigment, along with other possible iron oxides. Furthermore, a historical restoration was spotted by the detection of polyvinyl acetate. The study provides essential information, directing the future restoration procedures closer towards the minimum intervention principle.

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