

ASPECTS CONCERNING LASER CLEANING OF CONTEMPORARY MURAL PAINTINGS

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Abstract. The current study presents the results obtained using a hybrid setup of correlated complementary techniques that provides a real-time complex data package, with no sampling or sample preparation, by means of quasi-simultaneous analyses with micrometrical precision, dedicated to conservation and restoration of polychrome multilayer mural paintings. The paint layers were subjected to atomic and molecular characterization in order to identify the pigments and the binders, using Laser Induced Breakdown Spectroscopy (LIBS), Fourier Transform Infrared Spectroscopy (FTIR) and Hyperspectral Analysis (HYS). The data were correlated and used for the laser cleaning tests @1064 nm and @532 nm. The laser cleaning was assessed using colorimetry and optical microscopy techniques.

Key words: laser cleaning, LIBS, FTIR, XRF, contemporary art, a fresco, a secco.

1. INTRODUCTION

Each act of creation represents a part of the human legacy and the reminiscence of these acts is gathered into material forms that depend in their morphological structure on the physical composition of the universe. Any act of conservation, preservation or restoration must start from a full understanding of the structure of the cultural good and of the message that they carry. Without this, the path to abuse is open and the results can only be disastrous. The aesthetic and historical prominence of an object has always been related to an accurate identification of the original materials of the heritage entity, thus its authenticity.

The use of radiation as a tool for diagnostic imaging is widely applied for investigation and characterization of the heritage goods, for studies on the degradation of materials and on pathologies in general [1]. However, most of the published studies and researches are focused on the preservation of the historical items, and the current artworks are somehow taken for granted since they rarely pose restorative needs, so far [2, 3].

The current study is focused on assessing the use of state-of-the-art techniques (laser cleaning, LIBS, hyperspectral imaging) on contemporary mural paintings, for a better understanding of the criticalities modern and contemporary art will be

facing and, also, for setting the base for the time when future restoration processed will be needed [4]. The selected paintings are representative, as they embody the devotional murals that are still a trend in Romanian newly built cult sites, therefore proper preservation and restoration protocols must be developed as part of the national conservation management preparedness plan [5, 6].

2. MATERIALS AND METHODS

The artwork investigated is part of a set of mural paintings created by a contemporary artist using modern-day pigments, in *buon fresco*. In this technique, the pigment particles are mixed in water and applied to a fresh lime plaster. Due to the carbonation process by which the pigments are fixed in the plaster, the original colors are preserved for a long time, making it a durable painting technique. Instead, in the *fresco-secco* technique, the painting is done on dry plaster and the colors are prepared using a binder [7].

Numerous studies investigating and evaluating the effect of different laser wavelengths (IR, VIS, UV) on historical pigments and paints were published in the latest centuries, as the field is progressing accordingly to the laser developments [8–10]. Therefore, the first step that has to be made before applying the laser cleaning on an original object consists in identifying the chemical structure of the painting substrates [11]. The paint layers were subjected to atomic and molecular characterization in order to identify the pigments and the binders. The techniques employed were selected due to their complementarity: Laser Induced Breakdown Spectroscopy (LIBS), Fourier Transform Infrared Spectroscopy (FTIR) and Hyperspectral Analysis (HYS).

Laser Induced Breakdown Spectroscopy (LIBS) is a technique popular in modern analytical chemistry applications because it offers multi-elemental analysis inducing a LTE micro-plasma that provides atomic/ionic emission lines spectrum [12–14]. The use of LIBS in Cultural Heritage has attracted attention for many years, in part due to the ability for *in situ* and rapid minimally destructive analysis, multi-element analysis, depth-profiling, and compatibility with other techniques. Several reviews have focused specifically on LIBS in art, archeology, and cultural heritage [15–18].

The spectra were recorded using a handheld spectrometer from SciAps in *stratigraphy* mode, applied directly on the surface of interest, thus no sampling or sample preparation was required. The laser used for irradiation is a Q-switched Nd:YAG solid state laser that emits at the fundamental wavelength (@1064 nm), at a maximum 20 Hz repetition rate, and a pulse duration of 8 ns (FWHM). The energy used for the acquisition is 5 mJ and the laser spot diameter was 50 μm . 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. The system has a camera incorporated that facilitated the focus of the laser beam for the interrogation of specific interest areas.

Fourier Transform Infrared Spectroscopy (FTIR) enhances the LIBS atomic/ionic data adding molecular information, therefore providing a complete spectral identification and discrimination at molecular and atomic/ionic level. 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.

Hyperspectral analysis was selected for two purposes: to map the paintings, corroborated with the LIBS data and to evaluate the laser cleaning process (acquisitions were made before and after LC) [19, 20]. The portable and noninvasive hyperspectral imaging system used is: HySpex SWIR 384 produced by Norsk Elektro Optikk AS. The spectrometer – included in the body of the camera – a state of the art Mercury Cadmium Telluride (HgCdTe or MCT) sensor (Liang, 2012) is equipped with a cooling system which ensures a constant temperature of -150K , a characteristic that provides low background noise, which enables a low background noise, high dynamic range, and optimal SNR level at a maximum speed of 450 fps. In order to obtain the best available resolution, the 30 cm lens were used, which enabled a FOV of 16° across the track – a constraint that imposed multiple acquisitions. Scanning of the surface by means of *push-broom* method was ensured by a motorized translation stage. The particular behavior of the component materials is available in 288 spectral bands, in the spectral range of 950–2500 nm, covering parts of the NIR and SWIR spectra. The hyperspectral system recorded the specific radiance of the investigated materials, meaning the flux that leaves a surface, per unit projected area of the surface, per unit solid angle of direction.

The **laser cleaning** was carried out using a Q-switched Nd:YAG solid state laser from Quanta Systems. The laser has two articulated arms special for *in situ* laser cleaning and it allow us to employ, besides the fundamental wavelength of 1064 nm, three harmonics: 532 nm, 355 nm and 266 nm. The frequency can be selected from 1 Hz to 20 Hz, depending on the type of materials cleaned. The laser beam diameter is 6 mm, the pulse duration is 5–8 ns and the divergency is $< 0.5@1064$ nm. The laser cleaning was made with the IR and VIS wavelengths, depending on the elemental composition of the pigments used in the paint layers, previously characterized using LIBS. The laser maximum energy is 350 mJ for 1064 nm and 280 mJ for 532 nm. The laser cleaning was monitored using colorimetry and optical microscopy.

The **colorimetry** investigations were made using a handheld colorimeter: X-RITE ColorEye XTH from Gretag MacBeth, with $d/8^\circ$ sphere geometrics, spectral range: 360–750 nm, spectral interval: 10 nm and an aperture of 5 mm. The UV-VIS spectra were recorded in the reflectance mode, before and after the cleaning tests,

averaging 5 spots for each pigment area. The CIE $L^*a^*b^*$ color system was used for the evaluation of the color information, taking into consideration the differences in the color axes, but also the total color difference, ΔE . ΔE was calculated using *Formula 1* and it represents the geometric or Euclidean distance between two corresponding points in the color space:

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}, \quad (1)$$

where ΔL^* represents the difference in brightness, Δa^* represents the difference between the red-green coordinates and Δb^* represents the difference between the yellow-blue coordinates [21].

The *microscopy* images were recorded using a portable digital microscope: DG3 from Scalar, mounted on a tripod that allows x - y - z focusing. The microscopic images were recorded at magnifications of 25 \times , 50 \times and 100 \times , before and after laser cleaning in order to evaluate the morphological structure of the layers according to the painting technique under study.

3. RESULTS AND DISCUSSIONS

3.1. ELEMENTAL CHARACTERISATION OF THE PAINTINGS

The polychrome areas were analyzed using complementary methods LIBS and FTIR, in order to obtain both molecular and atomic/ionic identification. The areas of investigation are depicted in Fig. 1.

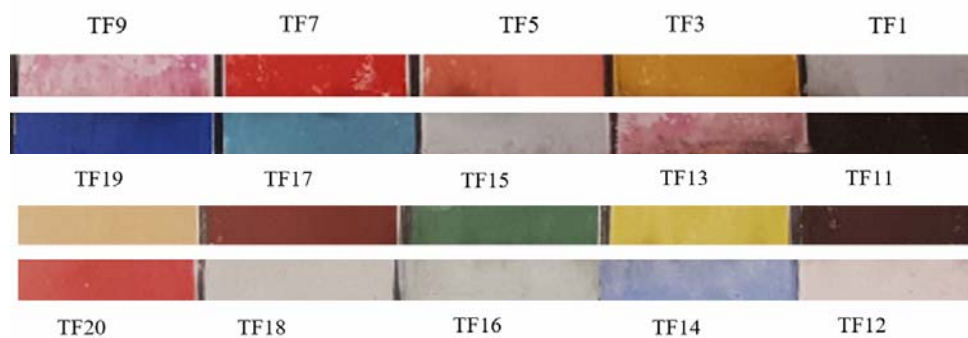


Fig. 1 – The areas of investigation (TF1-TF20).

The results obtained on each specific color area investigated using LIBS and FTIR are presented in Table 1.

Table 1

Synthesis of the results obtained using LIBS and FTIR on the *buon fresco painting*

Area	LIBS	FTIR
F1	Ca, Cd, Ba, Ti, Na, Sr, K, Li, C, Fe, Si, H	titanium white, barium sulfate, calcium carbonate
F2	Ca, Ba, Fe, K, Sr, Na, Li, O, C	black iron oxide, calcium carbonate
F3	Ca, Ba, Fe, K, Na, Sr, Ti, O, Li, C, H	yellow ochre, cadmium-based pigment, titanium white
F4	Ca, Ba, Sr, Na, K, Ti, Fe, O, C, Li, Si	barium sulfate, organic pigment
F5	Ca, Cd, Ti, Ba, Sr, Na, K, Fe, C, Li, O	iron oxides, cadmium red, titanium white, calcium carbonate
F6	Ca, Ba, Ti, Sr, Na, K, Fe, Li, C, O, Si	titanium white, barium sulfate, calcium carbonate
F7	Ca, Cd, Ba, Sr, Na, C, K, O, Li, H, Se	cadmium red, barium sulfate
F8	Ca, Ba, Sr, Na, Zn, K, Fe, C, Al, O, Li, Si, H	ultramarine, iron oxides, titanium white, barium sulfate, calcium carbonate
F9	Ba, Sr, Na, Ti, K, O, C, Fe, Li, Si	iron oxides, cadmium red, titanium white, calcium carbonate
F10	Ca, Na, Al, Ba, Sr, K, Li, Fe, Si, Ti, C, O, H	ultramarine, titanium white, iron oxides, calcium carbonate
F11	Ca, Fe, Ba, K, Sr, Na, Li, O, C, H, Si	ochre, calcium carbonate
F12	Ti, Ba, Sr, Na, K, O, Li, C, Fe, Si, H	titanium white, barium sulfate, calcium carbonate
F13	Ca, Ba, Sr, Na, Ti, Mg, O, C, K, Li, Fe, H, Si	ochre, titanium white, calcium carbonate
F14	Ba, Na, Sr, Ti, K, Al, Mg, Fe, O, Li, C, Si, H	ultramarine, iron oxides, calcium carbonate+ titanium white, barium sulfate, calcium carbonate
F15	Ca, Ti, Fe, Sr, Na, O, Li, K, H, C	iron oxides, titanium white, calcium carbonate
F16	Ca, Ba, Na, Sr, Ti, K, Fe, Li, O, C, H	iron oxides, titanium white, calcium carbonate
F17	Ca, Fe, Sr, Na, C, O, Li, K, H, Si	ochre, calcium carbonate
F18	Ca, Ti, Ba, Sr, Na, O, K, Fe, C, Li, H, Si	ochre, titanium white, calcium carbonate
F19	Ca, Ti, Ba, Sr, Na, Fe, K, Li, O, C	ochre, titanium white, calcium carbonate
F20	Ca, Cd, Ba, Sr, Na, Ti, K, O, C, Li, Fe, Mg, H	cadmium red, barium sulfate

For most of the samples analyzed using LIBS, calcium is the major element identified, followed by iron, titanium and barium. Barium can be linked to mineral

fillers, as confirmed by the FTIR data. The presence of intense Ti and Zn lines suggests the use of titanium (TiO_2) and zinc white (ZnO) pigments. Black iron oxide can be suggested for the black pigments. Sulfur can be correlated with barium, probably as barium sulfate, confirmed by FTIR analysis. Strontium can be correlated to the high amounts of calcium present, as it usually accompanies calcium in natural sulfates or carbonates.

Pigments rich in iron oxides can be attributed to the yellow, ochre and some of the red tones. For the same samples, trace amounts of Mn, Si, K and P can be linked with the impurities present within the earth-based pigments [22, 23]. Cadmium red (cadmium sulfoselenide – CdS , CdSe) pigments were identified for the red hues, while for the green and some of the blue colors copper-based pigments were used [24].

LIBS spectra are mostly drowned in the calcium signal due to the high amount of calcium carbonate absorbed in the painting layers, as confirmed by FTIR that highlighted the presence of calcium carbonate (CaCO_3) in the majority of the painting materials investigated, as can be seen in Fig. 2.

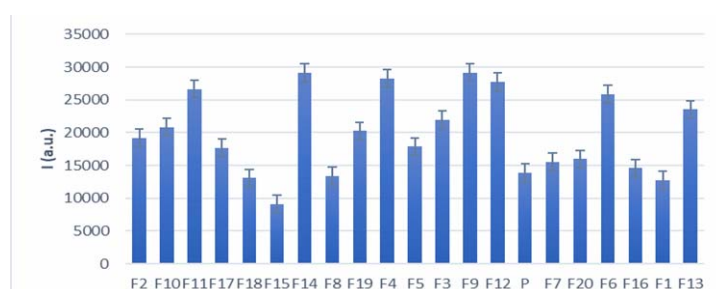


Fig. 2 – Ca distribution through the TF areas.

In order to obtain a clearer view on the distribution of the pigments used and to discriminate different areas that may seem similar at first glance, Principal Component Analysis was applied on the LIBS data and the results are presented in Table 2 and Fig. 3.

Table 2

PCA score data for the main elements investigated

PC 1	PC2	PC3	Score label
89.65%	7.94%	1.13%	
2.33136	1.25319	-0.08372	Ca
-0.34141	0.37073	-0.07645	Al
-0.51474	0.37022	-0.56381	Fe
-0.65969	0.24186	-0.45874	Mg
0.89034	-2.43122	-0.41369	Ba
-0.68753	0.25272	-1.11195	Cd
-0.42968	0.01064	2.30227	Ti
-0.04452	-0.27839	0.78113	Sr

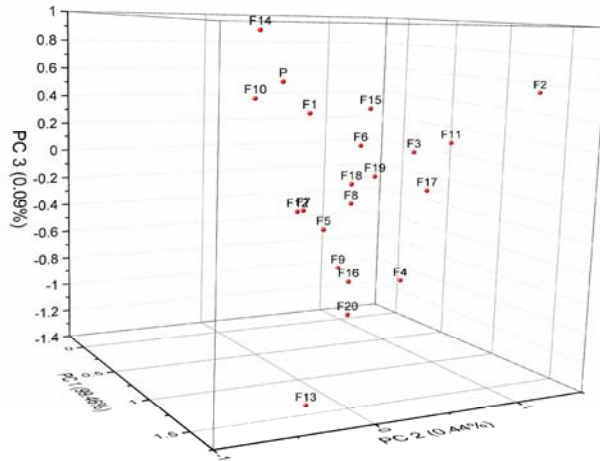


Fig. 3 – LIBS PCA – loading plot.

Hyperspectral Imaging was used in order to achieve a preliminary classification of the elemental distribution on the surface.

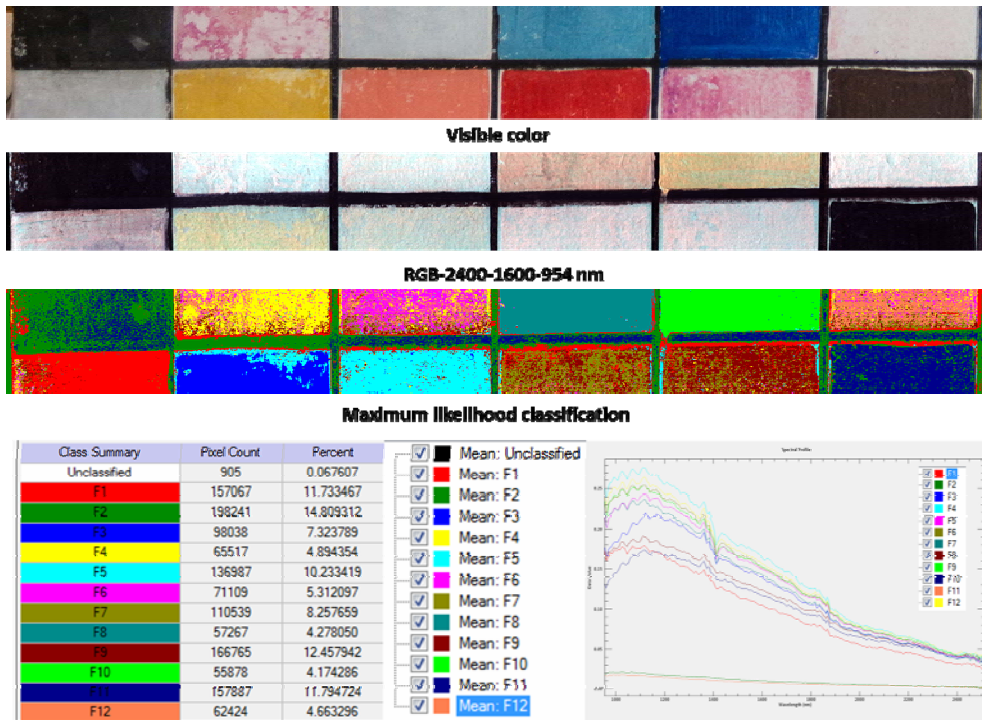


Fig. 4 – Hyperspectral data classification.

Overall, it must be pointed that the spectral variability of the spectral profile is reduced. Most of the pigments display very similar spectra (see Fig. 4). This fact indicates the presence of a major component which in both samples must be attributed to the CaCO_3 (calcium carbonate), which is found in the lime based plaster on which the pigments are carbonated [25], as also depicted by the FTIR and LIBS data.

The data obtained by supervised classification, corroborated with the LIBS elemental analysis, had as result a distribution map that allowed the laser cleaning to be pursued accordingly to each specific area. The ability of the hyperspectral system to characterize all the pixels from an image in terms of spectral profiles was exploited in ENVI, where a series of algorithms have been applied in order to classify and to map the component materials of the samples [26].

In order to extract endmembers Regions of Interest (ROI's) were used, which enabled a better extraction of the spectral profiles in terms of representativeness. For all recordings supervised classification was performed using Maximum Likelihood algorithm [27]. A probability of 0.2% was used in order to differentiate the spectral profiles of each class. If a spectral profile of a pixel would have a greater percent than 0.2 in terms of similarity than it would be attributed to another class.

3.2. LASER CLEANING

Since religious art is under discussion, the main problem affecting the objects in cult locations consists in the greasy candle smoke adherent deposits. Whereas the Cultural Heritage is concerned, any intervention is planned and documented so that the impact on the original substrates is minimum.

Firstly, the ablation thresholds were determined starting at a lower laser fluency and increasing it slowly until the adherent layer started to be removed from the original layers. The ablation rate is strongly influenced by the processing laser beam characteristics (laser spot diameter, laser fluence, laser wavelength, number of pulses and pulse duration), and by the optical and thermal properties of the processed material surface (optical absorption, surface reflectivity, thermal conductance, mass) [28].

The ablation threshold for the paint layers (original) was set accordingly to the pigments present in each specific area (identified in the previous chapter using LIBS and FTIR techniques). The cleaning tests were made using laser radiation at 1064 nm and 532 nm, in order to assess the effects of the laser on the painting layers and the cleaning was monitored and evaluated using colorimetry, microscopy and hyperspectral imaging techniques.

The 20 areas of interest were previously selected based on the distribution of pigments. Each area was divided into 6 subareas of $1.5 \text{ cm} \times 2.5 \text{ cm}$, that were cleaned using 532 nm and 1064 nm at different fluencies above the ablation threshold of the candle smoke adherent layer. Aside for a few problematic areas, the results were mostly similar and TF10 was selected as an example. The microscopy images for the laser cleaning tests are presented in Figs. 5–10.

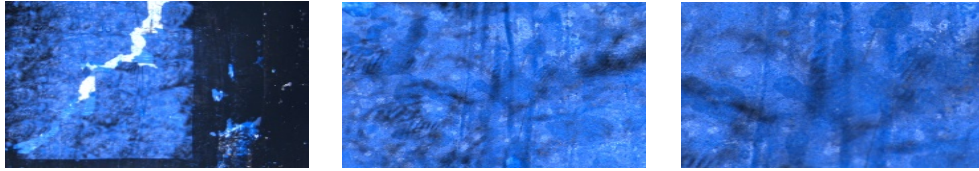


Fig. 5 – TF10A, laser cleaning regime: 532 nm, $F = 0.19 \text{ J/cm}^2$ (left–25×, mid–50×, c. right–100×).

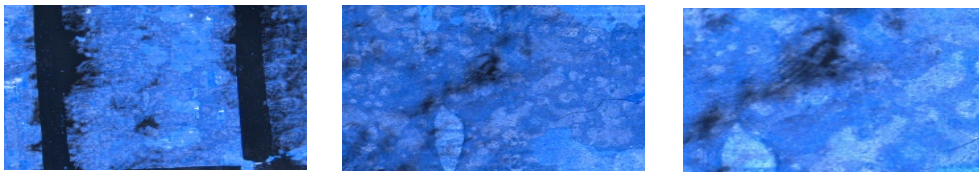


Fig. 6 – TF10B, laser cleaning regime: 532 nm, $F = 0.23 \text{ J/cm}^2$ (left–25×, mid–50×, c. right–100×).



Fig. 7 – TF10C, laser cleaning regime: 532 nm, $F = 0.28 \text{ J/cm}^2$ (left–25×, mid–50×, c. right–100×).

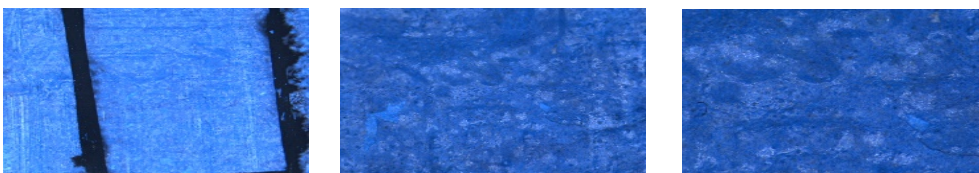


Fig. 8 – TF10D, laser cleaning regime: 1064 nm, $F = 0.32 \text{ J/cm}^2$ (left–25×, mid–50×, c. right–100×).



Fig. 9 – TF10E, laser cleaning regime: 1064 nm, $F = 0.37 \text{ J/cm}^2$, (left–25×, mid–50×, c. right–100×).



Fig. 10 – TF10F, laser cleaning regime: 1064 nm, $F = 0.46 \text{ J/cm}^2$, (left–25×, mid–50×, c. right–100×).

All areas were subjected to colorimetry investigations in order to determine if there are any color alterations that go beneath the human eye's perception. The results of the colorimetric analysis for TF10 are presented in Table 3.

Table 3

CIE L*a*b* data of TF10 of the *buon fresco* painting

	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*
Sample	45.025	3.315	-36.51			
TF10A	39.2	1.66	-32.15	-5.82	-1.65	4.36
TF10B	45.6	0.78	-34.9	0.58	-2.53	1.61
TF10C	42.28	0.76	-33.27	-2.74	-2.55	3.24
TF10D	41.47	1.31	-34.9	-3.55	-2	1.61
TF10E	46.74	-0.61	-30.8	1.72	-3.92	5.71
TF10F	46.44	0.18	-33.5	1.42	-3.13	3.01

Using the colorimeter, the VIS spectra was recorded in reflectance mode and the spectral profiles of the investigated areas depict similar characteristics for every fluency/wavelength combination used, as can be seen in Fig. 11.

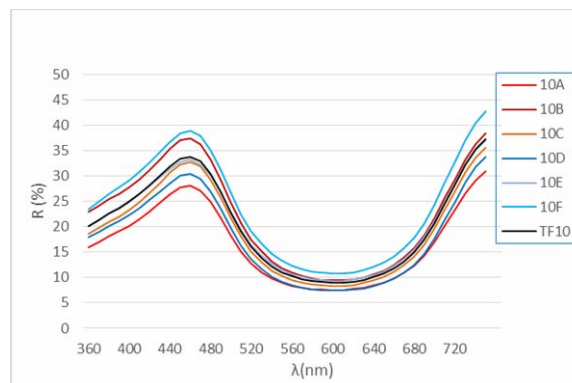


Fig. 11 – VIS spectra of TF10.

On the light color areas (TF1, TF6, TF12, TF14, TF16, TF18) the laser cleaning had good results at both wavelengths, as it was expected taking into consideration the selective vaporization mechanisms involved in the process. The lower fluencies also provided a sufficient cleaning, but required several passes on the surface. In the cases of blue, green, yellow, light brown and two the red areas (TF3, TF7, TF8, TF10, TF11, TF13, TF15, TF17, TF19, TF20), the cleaning efficiency was good, but corroborated with the colorimetry data, it was observed that 532 nm induced slight discolorations and 1064 nm wavelength provided a better cleaning at low fluencies.

There were several problematic areas, two that had flaws in the painting technique and two that had vaporization curves close to the adherent deposits one:

- TF4, TF9 pink – it was a hard area to clean due to the fact that the fresco painting technique was not correct and it presented previously laminations and discolorations; laser cleaning using the 532 nm wavelength provided an insufficient cleaning, but if we pass again on the surface original material is ablated; 1064 nm followed closely the delamination of the paint layer already present and provided a decent cleaning;

- TF2 – dark brown the 1064 nm wavelength induced darkening of the pigment, but 532 nm max fluency offered a good cleaning. 532 nm lower fluencies need several passes on the surface thus, result in affecting the original pigment;

- TF11 – 532 nm wavelength induced a discoloration of the pigment, even at low fluencies, but 1064 nm offers a good cleaning at second and third fluencies.

Hyperspectral imaging results are depicted in Fig. 12. The classification of materials on the samples cleaned with laser indicated a huge potential in the process of monitoring and control of intervention by comparing the similarities and differences of the spectral profiles from reference and intervention areas (see for comparison the spectral profiles before and after laser cleaning).

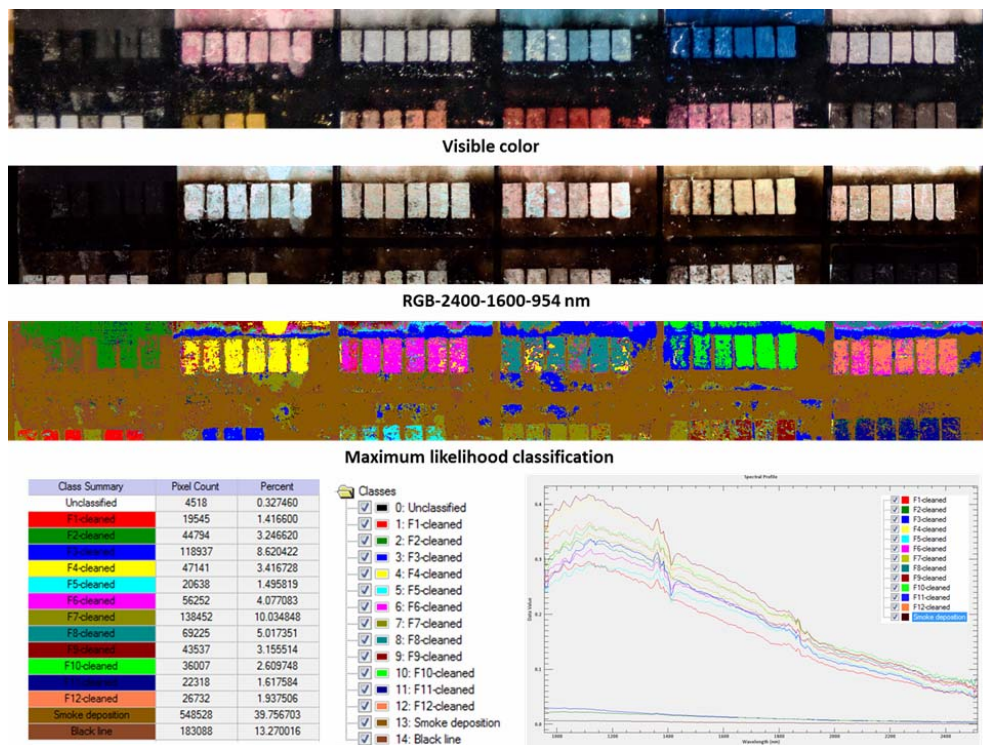


Fig. 12 – Hyperspectral classification based on ROI for the cleaned areas.

Materials with a low intensity of signal, meaning a small value of radiance can be indicated in the case of smoke deposits and the pigment used for contour lines. Also, a spectral profile difference is noticed in the case of blue pigments in comparison with the others.

4. CONCLUSIONS

Contemporary mural painting surfaces were subjected to a complex course of investigation and diagnosis in order to determine the proper laser cleaning regime for removing adherent deposits – candle smoke. Firstly, the characterization of the pigments, binders, underlayers was done using LIBS and FTIR spectroscopic techniques. The FTIR spectroscopy enhanced the LIBS atomic/ionic data adding molecular information, therefore providing a complete spectral identification and discrimination at molecular and atomic/ionic level.

Most of the pigments display very similar spectra due to the presence of a major component attributed to the CaCO_3 (calcium carbonate), traced to the lime based plaster on which the pigments are carbonated. *Hyperspectral Imaging* used in order to achieve a preliminary classification of the elemental distribution on the surface denoted a low the spectral variability. The accuracy of the supervised classification was correlated to the results of LIBS and FTIR spectroscopic investigations which enhanced the discrimination and provided a better understanding in regard to the mapping of materials. This type of complementary approach can be furthermore developed in order to evaluate laser cleaning on different type of materials.

The laser cleaning showed similar results on all areas that were selected, both for 532 nm and 1064 nm, as expected for the selective vaporization mechanism. Best results were obtained on light colors, and dark areas suffered discolorations. There were also some areas with flaws in the painting technique that presented delamination and fragmentation on the paint layers, on which laser cleaning did not obtain the best results although it followed closely the surface and did not add extra stress to it.

Taking into consideration the fact that we are discussing contemporary art, the results of this study will be used for developing a preventive conservation strategy that will serve as a starting point for future interventions.

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