Laser spectroscopy and imaging applications for the study of cultural heritage murals

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ABSTRACT

Laser induced fluorescence (LIF) associated with imaging scanning techniques has already proved to be a powerful diagnostic tool for artworks. The aim is to assess on-site and remote sensing systems and imag- ing measurements on murals in order to detect vulnerability and weathering forms due to the effects of environmental conditions. It also seeks to identify treatments in order to optimize interventions by restorers. Four murals (16–18th centuries) were studied using a LIF prototype remotely operating in reflectance and fluorescence mode. Relevant spectral features are identified using principal component analysis and a spectral angle mapper to assess surfaces using imaging applications. The combination of these methods makes possible to identify bio-crust, fissures and the presence of different treatments.

1. Introduction

Active remote sensing systems, generally known as LIDAR (laser radar), have been included in high resolution scanning devices in order to map the current preservation status of cultural heritage surfaces [1–7]. Conservators are interested to map chemical components and neo-formation due to weathering as well as in the identification of physical damages (surface cracks) occasionally or eventually covered by former restorations [8,9]. Valuable information, especially on rendering with false colors, can be found from the precise location of the image on the surface, regardless of the specific issue.

Laser scanning prototypes, initially developed in remote vision and in metrology devices based on the amplitude modulation technique, have been specifically designed for multispectral applications suitable for the analysis of large surfaces relevant to monumental cultural heritage. Colao et al. [10] demonstrated the application of fluorescence technique to detect retouched crack, unseen by bare eye, on mural *a fresco* painted in Hrastovlje Church (Slovenia). An Italian-Swedish cooperation, investigating Coliseum façade by means of lidar fluorescence technique showed the possibility to locate metal clamps, used as reinforcement structures, and to establish their conservation status by detecting the protective coating added during former restorations [11]. An innovative hyperspectral LIF (laser induced fluorescence) line scanning system was designed and patented at the ENEA laboratory in Frascati [12,13]. The prototype is capable of rapid 2D image acquisition in the visible/UV range, and was developed to investigate the presence of pigments and consolidants, as well as the occurrence of both bio-deterioration and depigmentation on wall paintings.

On-site field campaigns using LIF remote scanning systems were carried out in Andalusia (Spain) in 2010, 2011 and 2012 on 16th to 18th century murals executed using the *secco* technique on gypsum and calcite. The monuments studied were the chapel of Virgen del Buen Aire (Seville, Spain), the church of San Agustín (Marchena, Seville, Spain), the monastery of San Jerónimo (Granada, Spain) and the church of the Santo Cristo de la Salud (Malaga, Spain).

The Chapel of the Virgen del Buen Aire is part of the San Telmo Palace in Seville, which is now the seat of the Andalusian regional government. Construction on the building began in 1682 outside the walls of the city, and the chapel vault was painted by Domingo Martínez in the late 17th and early 18th centuries. The scans were carried out during the second phase of the restoration executed by the Andalusian Institute of Cultural Heritage. The second study, also in Seville, was of the murals in the chapel of San Agustín in the town of Marchena. The old church and convent were built between the 17th and 18th centuries for Augustinian monks. The church ornamentation includes polychrome religious plaster figures, geometric elements, exotic animals and vegetables. The decoration was probably the work of local painters with Latin-American influences. The church of the monastery of San Jerónimo in Granada is another Andalusian mural masterpiece. The stone interior was completely covered with various frescos using secco techniques painted by Juan de Medina in the 18th century. The last example, the church vault of the Santo Cristo de la Salud in Malaga was painted by Alonso Cortés, also on gypsum over the brick and wood structure and using tempera techniques in the 18th century. We know it was restored in 1989 and we scanned different zones of the vault prior to the current restoration carried out by the Andalusian Institute of Cultural Heritage.

Murals are elements of the architecture that cannot be understood if it is isolated of the construction [14], the characterization of murals and the weathering forms are usually studied with traditional techniques [15] though new nondestructive techniques (as IR thermography) enable to assess of damage from distance in real time are been used to see water filtration on roofs that could reduce structural integrity [16]. Structural problems like water filtration or capillarity problems are associated to efflorescences, depigmentations or bio-attack, two former could be detected by LIF, other damages like fractures or fissures could be filled with treatments that could also be detected with LIF. For this reason, these four cases were chosen as sites to demonstrated the potentiality of the LIF system. Thus laser spectroscopy and imaging techniques were used on murals to check deterioration, to assess weathering factors and to discriminate the both the initial painted surface composition and its actual state after successive restorations, through reflectance and fluorescence images.

2. Methods and equipment

The LIF scanner used was designed to collect the entire fluorescence spectrum following UV laser excitation. A quick scanning system was employed in order to remotely obtain both reflectance and fluorescence images.

The fluorescence scans were carried out operating the laser at 266 nm; alternatively reflectance scans were acquired performing a scan with the laser switched off and exposing the sample to the light emitted by a calibrated halogen lamp. The result is a spatially resolved reflectance spectrum, subsequently used to compute the CIE/lab coordinates after calibration against a reference surface. Both systems were used on site and several images were acquired with a millimetric spatial resolution.

For the current measurements it was necessary to ensure that laboratory painted samples did not suffer photo-damage induced by the laser. The maximum laser energy was 1.5 mJ at the output before defocusing through the cylindrical lens, corresponding, at a 5 m distant probed point, to a maximum laser fluence of 0.01–0.02 mJ/cm² which is well below the threshold of 0.1 mJ/cm² established as conservative estimate of for fulfillment for non-destructivity on the considered painted surfaces [5,10].

2.1. LidArt: The line scanner

Our first LIF-scanning system [12] was capable of collecting hyperspectral fluorescence images scanning a surface point by point with 1 mm resolution at about 3 m distance. This equipment was upgraded for applications to large cultural heritage surfaces (e.g. frescos, decorated façades, etc). A compact set-up was built to

increase performances in terms of space resolution, time resolved capabilities and data acquisition speed. The new scanning system uses a diode-pumped Nd:YAG laser source in combination with IV harmonic crystals to generate UV radiation. The system has line focalization which uses a quartz cylindrical lens, an imaging spectrograph (Jobin-Yvone CP240), and a square ICCD sensor allowing for the multichannel spectral resolution [7] (ANDOR iStar DH734, pixel size 13 1m), mounted behind a slit parallel to the laser line footprint during scanning [13].

Rejection of elastic laser backscattering and subsequent high order signals was accomplished by means of a low pass filter at the detector entrance. After acquisition, the fluorescence spectra were corrected for the instrumental spectral response, with the reference radiance emitted by Ocean Optics Mod. DH2000 calibrated source.

The system, installed on a tripod, has a cylindrical shape of about 38 cm dia and 15 cm high with a weight below 25 kg. The current system performances are summarized in Table 1. During the campaigns in Andalusia, typical scan size was 128 pixels wide and 200–600 pixels high, with 250 spectral channels from 200 nm to 800 nm at a nominal spectral resolution of 2.5 nm. With this optical system using a cylindrical lens, a 1.5×5 m² image at 15 m distance was currently scanned in less than 5 min, with a space resolution of about 11 mm. A picture of the LIS scanning prototype in operation during a campaign in Andalusia is reported in Fig. 1.

During all measurement campaigns, the defocusing effects due to chromatic aberrations were limited by operating the system in two different spectral regions: firstly the collection optics was focused on the UV region from 250 to 450 nm, then on the visible spectral region from 450 to 700 nm.

With the laser switched off, the LIF-scanning system was also used, to collect reflectance images based on the availability of a standard light source assuring the operation with an average illuminance of not lower than 10 cd/m^2 . Since these

Table 1

Characteristics of the LIF-scanning system assembled for use during the campaigns in Andalusia.

General features			
Laser operation	1.5 mJ pulsed, 20 ns @ 20 Hz		
Laser sources wavelength	266 nm, 355 nm		
Working range	3-30 m		
Maximum resolution	1.0 mm @ 3 m		
Scanning mirror movements			
Step precision	0.0017°		
Max pixel per row	640 pixel		
Overall time per row ^a	0.2-2 s		
Data acquisition			
ICCD pixel size	25 lm		
Spectral resolution	2.5 nm		

^a Motor actuation and acquisition



Fig. 1. ENEA LIF scanning system operating in the chapel of San Agustín in Marchena. Computer control on the left, the rotating wheel for vertical scanning, on which the laser and the detector are mounted, on the right, above the tripod.

reflectance images were utilized mostly for the precise location of spectral anomalies detected in the fluorescence images, an absolute correction procedure, based on the use of Spectralon reference panels to obtain calibrated reflectance spectra was not adopted.

All the images here reported have been built by extracting the spectral intensities at three pre-selected bands and using them to produce false color RGB images. The band selection is based either on relative maximum intensity from spectral deconvolution or PCA or on channels conventionally placed at 400, 500 and 600 nm (see further Section 2.2). To this respect the importance of remotely collecting by the same instrument and upon the same geometry and resolution, both reflectance and fluorescence maps, mostly relies on the precise location of damage [10]. In fact, to spatially locate a feature that appears only on fluorescence map, even the best calibrated standard photo cannot be used easily, e.g. without photogrammetric and reformatting procedures based on additional markers to be applied onto the scanned surface.

2.2. Calibration, statistical analysis of spectroscopy data and digital image processing

Preliminary experiments were performed prior to measurements in order to collect passive images and LIF signals from different standards (white and black paper, dye-loaded plastic). This calibration shows the potential for remote material identification of monument conditions using data processing software on raw hyperspectral images.

Following on-site measurements, both fluorescence and reflectance spectra are used to produce false color images by combining the three most intense features detected, associated respectively with Red, Green and Blue channels (RGB). Because the band shape and spectral position do not correspond with respective colors the produced images should be more properly called trichromatic, however the common RGB acronym is utilized hereafter also for such RGB-like images. Since spectral features usually contain significant information on the composition of the outer surface layers, classification methods should be applied for automatic image processing and feature extraction. We understand classification as the operation to assign an object to a pre-determinate group, generally fixed. To this aim the object must be characterized by a measurable set defining a multidimensional feature vector. An automatic classification system is composed of a first part where the characteristics are translated and extracted and a second one where the classification algorithm assigns the degree of membership of a class. This mapping can be based on Spectral Angle Mapper Classification (SAM) or Spectral Correlation Mapper (SCM) [17], while statistical analysis such as Principal Component Analysis (PCA) or Linear Discrimination Analysis allows the variance of the samples (pixels) to discriminate differences [18] to be minimized. For our research, two methods were selected in these cases for LIF data processing software: PCA for identification of most significant features with possible correspondence to physical bands and SAM to calculate the 'distance' of the data from a set of reference data, the minimization of such a distance permit to allocate zones with large spectral similitude.

Principal Component Analysis (PCA) is a technique which reduces the dimensionality of data, transforming the original variables into new uncorrelated ones (principal components or factors, PCs) which are linear combinations of the original data and contain the greatest proportion of the total variance. The presence of major physical bands could be inferred from first five PC's, which typically contained more than 70% of the variance (unless otherwise specified). This information allowed us to attempt specific assignments of original spectra based on available data basis which showed clearly respective single bands. Reducing the variables dimensionality by PCA favors the progress of further data analysis since removes smaller spectral features and most of the noise associated with high order components.

The Spectral Angle Mapper (SAM) algorithm is used as mapping tools to broadly define areas with similar spectral content and therefore to document the use of materials used by the artist and by the restoring interventions [19]. According to SAM, the spectral channel intensities are regarded as the coordinate components of vectors in a multidimensional space; given that any two vectors, generate a hyperplane and two directions over it, it is possible to compute the angle between the pixel spectrum and a reference spectrum: the smaller the angle, the greater the similarity between the pixel and reference spectra. A laboratory collection of spectra of consolidants was used to test SAM capabilities for identifying these on murals, after excitation at two different UV wavelengths (266 nm and 355 nm) [10].

Both tools were implemented in the software of the prototype in order to make possible the automatic handling of multispectral images. We used all the spectra as input data; they were organized in a 2D matrix containing the recorded LIF intensities in as many lines as the acquired pixels and as many columns as different wavelengths.

In summary, PCA was run to reduce the dimensionality of the spectra, extracting dominant features. Successively SAM was used to map single spectra, characterized by specific band structure, onto a reference spectrum which could support for its assignment. This method has reported successfully tests on consolidants and binders [5,6,10]. In the case of the former our dataset succeeded in identifying them from the first 3 components upon excitation at 266 nm. In the latter case, it also identified some underlying pigments, and excitation at 355 nm was more effective [6].

The major components can be used for false color mapping following the methodology developed by Vázquez et al. [8,9]. These digital maps show the dominance of a specific color linked to a consolidant. It should be noted that PCA are not necessarily directly related to a specific spectral feature for a single constituent so they do not allow for a direct identification of the anomaly at the surface, nevertheless they do reveal its presence.

2.3. On-site case studies investigated by laser scanning

Four different frescos from the 16–18th century were studied at different angle of incidence and heights during three campaigns carried out in Andalusia (Spain) between 2010 and 2012 (Table 1). The murals studied were produced using *secco* technique on gypsum and calcite, and were studied before or during restoration (Table 2).

The WP1 study was carried out during the restoration process to enable the remote collection of reflectance and fluorescence images from different areas of the fresco walls, while WP2 and WP3 were part of a general examination for diagnosis, and WP4 was carried out prior to restoration.

WP1 LIF scans were performed on vault frescos in two different locations in the central aisle at a distance of 11.2 m (East–West and North–South direction). The WP2 LIF scan monitored the arch at the end of the principal nave, in the middle of the church and at a height of 3.5–5 m.

Five areas of painted wall were scanned for WP3 in a side chapel and at a height between 3 and 5 m. Finally, the highest scan carried out was on the drum of WP4, where we worked on four different areas at 13.5–16 m distances.

3. Results and discussion

The LIF scans of fluorescence spectrum after UV laser excitation and reflectance images obtained during the tests on the four monuments made it possible to detect different chemical and physical features associated to the surface depending on the mural composition and the degree of weathering of its materials.

3.1. Wall paintings of the chapel of Virgen del Buen Aire (Seville), WP1

Preliminary results obtained in the same campaign from another part of the vault showing the Virgin have been already reported as an example of the system performances (consolidant distribution, red and blue pigments mapping) [23].

A WP1 RGB reconstruction (channels at 609 nm, 508 nm, 405 nm, respectively) of the reflectance image remotely collected from the 11 m distant vault is shown in Fig. 2a (upper image).

The reconstruction has high color saturation, with a number of well-defined details that help us to see the angels' faces around the dove of the peace for example. This image allows us to understand the spatial resolution of the images and is useful for overlaying the fluorescence zones separated by SAM.

PCA analysis of the corresponding fluorescence image, collected after laser excitation at 266 nm and focusing the spectral detection range in UV, revealed the presence of significant features at 280 nm, 325 nm, 340 nm, 360 nm and 420 nm (Fig. 2b). Note that first five PCs contained respectively (33%, 10%, 7.0%, 3.0% and 2.6%) of the total variance. SAM allows the identification of areas which could be treated with acrylic products (Fig. 2c), including pixels associated with the fluorescence band at 360 nm (Fig. 2d). The gray scale image shows a well-localized area on the right with a high content of these compounds, indicating the presence of a strongly emitting compound near 360 nm after normalization at 450 nm. This broad yet not uniform distribution on the image lets us assign the feature to a consolidant or protective coating. According to former reference spectra [24] and to our database of consolidants on plaster [10,25], among all the chemicals considered, Paraloid shows the most compatible band shape (the smallest SAM Projection < 10 deg).

Although precise identification and/or discrimination are not immediately possible, it is worth noting extremely accurate localization showing where such a chemical has been used. Moreover, the gray level scale could be due to a qualitative evaluation of the amount of film used since there should be a direct proportion

ID ^a Secco technique description	Stratigraphies show a white primer of gypsum and animal glue, with different layers (3-4) of pigments mixed with linseed oil Pigments: Lead White, Calcium White, Barite, Lead-tin yellow, Chrome yellow (from restoration), Red Earth, Vermilion, carmine from cochineal, Blue smalt, Malachite, Lamp black and Bone black [20]	Stratigraphies show a white primer of gypsum with a layer of pigment. Pigments: Lead White, Calcium White, minium, Prusian blue, malachite and red earth	Stratigraphies show a white primer of gypsum and/or calcite, with different layers of pigments. Three different techniques has been described: tempera technique over gypsum mixed with oil layers, pigments over several layers of calcite, paintings over a primer layer of calcium carbonate, these three techniques could be due to different periods or artists Piements: Calcite. Gvosum. Ultramar blue and iron oxides [21]	Stratigraphies show a white primer of gypsum and animal glue, with different layers (6–7) of pigments mixed with linseed oil Pigments: Lead White, Calcite, Gypsum, Barite, Zinc White, Lithopon, Titanium white (from restoration), Hematite, Red Earth, minium, Prusian blue, Ultramarine, Lamp black and Bone black [22]	
Code	WP1	WP2	WP3	WP4	
Surface (m²)	۲	ы	σ	4	
Height of study (m)	11.0	3.5-6.0	3.0-5.0	13.5-16.0	
Century	17-18th	18th	18th	16–17th	
Location/monument and city	Vault Chapel of the Virgen del Buen Aire (San Telmo Palace, Seville)	Arch of the nave Church of San Agustín (Marchena, Seville)	Painted wall over a door, side chapel Church of San Jerónimo (Granada)	Drum Church of Santo Cristo de la Salud (Malaga)	
Mural painting/author	The Glorification of the Virgin/ Domingo Martínez	Gypsum Ornamentation	Scenes from the life of San Jerónimo/Juan de Media	Images of Virtues and Saints/ Alonso Cortés	a WP-Wall Painting
	Mural painting/author Location/monument and city Century Height of study (m) Surface (m ²) Code ID ^a Secco technique description	Mural painting/author Location/monument and city Century Height of study (m) Surface (m ²) Code ID ^a Secco technique description The Glorification of the Virgin / Vault 17-18th 11.0 7 WP1 Stratigraphies show a white primer of gypsum and animal glue, with different layers (3-4) of pigments mixed with linseed oil Pomingo Martínez Domingo Martínez Chapel of the Virgen del Buen Pigments: Lead White, Calcium White, Barite, Lead-tin yellow, Chrome Yellow (from restoration), Red Earth, Vermilion, carmine from cochineal, Blue smalt, Malachite, Lamp black and Bone black [20]	Mural painting/author Location/monument and city Century Height of study (m) Surface (m2) Code ID* Seco technique description The Glorification of the Virgin Vault 17-18th 11.0 7 WP1 Stratigraphies show a white primer of gypsum and animal gue, with different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments lineed with linseed oil different layers (3-4) of pigments lineed with linseed oil different layers (3-4) of pigments lineed with linseed oil different layers (3-4) of pigments lineed with linseed with linseed oil different layers (3-4) of pigments lineed with linseed with linseed with linseed with linseed with lineed with linseed with linseed with lineed with linseed with lineed with layers (3-4) of pigments lineed with lineed with lineed with layers of pigment layers different layers (3-4) of pigment layer	Mural painting/author Location/monument and city Century Height of study (m) Surface (m) Secco technique description The Glorification of the Virgin/ Vaut 17–18th 11.0 7 WP1 Stratigraphies show a white primer of gysum and animal glue, with different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with linseed oil different layers (3-4) of pigments mixed with layer of pigment. Cypsum Ornamentation Arch of the nave 18th 3-5-6.0 5 WP2 Stratigraphies show a white primer of gysum with a layer of pigment. Cypsum Ornamentation Arch of the nave 18th 30-5.0 9 WP3 Stratigraphies show a white primer of gysum mith a layer of pigment. Cypsum Ornamentation Arch of the nave 18th 30-5.0 9 WP3 Stratigraphies show a white primer of gysum and/or calcie, with different layers of pigments. Strene	Mural painting author Location/moment and civy Century Nurlease (m) Conformation of the Virgin of study (m) Surface (m) Conformation of the Virgin of the Vir

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Table

between film thickness and the intensity of the LIF signal. Fig. 2e shows a binarized image of the studied area in blue and yellow carried out by Vázquez et al. [8] to further document the restoration process. Areas that could have been treated with acrylic products appear in blue, gray areas correspond to pixels that could not be associated to any class within the PCA analysis, and yellow pixels are minimally treated. A close examination of this figure shows that this chemical was used almost everywhere in different amounts, according to the restoration processes carried out by IAPH.

3.2. Wall paintings in San Agustín (Marchena, Seville), WP2

The church of San Agustín (Marchena, Seville), WP2, features original polychrome gypsum decorations, which show weathering from detachment and depigmentation which has increased in recent years. LIF images were collected from the polychrome gypsum on the arch of the central nave at between 3.5 m and 6 m distance, in order to investigate surface detachment and weak cohesion giving rise to depigmentation.

Fig. 3a and b shows the arch under study, (approximate size 0.4×12.0 m). Unlike the previous case, these surfaces decorated with polychrome 3D figures present a new challenge to assess the capacity of LIF equipment to analyze problems associated with cultural heritage vulnerability.

A SAM study was conducted on the spectra collected upon excitation at 266 nm with the endpoint reported in Fig. 3c collected on a depigmented area identified by bare eyes (the front head of the central angel in Fig. 3d), in order to reveal more areas characterized by a clear gypsum emission signature. The most significant result observed in Fig. 3e is related to the SAM mapping ability to show where the gypsum emission band dominates the UV-blue component of different recoded spectra. As confirmed by successive in situ analysis and close observation these areas correspond to a loss of painted surface (Fig. 3d), deposits and increasing deterioration [26]. From Fig. 3e, it can be appreciated that depigmentation not only occurs in sharper areas as the angel hair but also in flat surfaces, as in decorations found in central part of Fig. 3e.

3.3. Murals in the church of the monastery of San Jerónimo (Granada), WP3

A WP3 LIF study was carried out in the church of the monastery of San Jerónimo (Granada), aiming to evaluate the weathering process due mainly to detachment caused by efflorescences and subeflorescences [21]. The scans were performed in a side chapel at a distance of 3-5 m on a mural depicting the life of St Jerome.

Fig. 4 shows an RGB reconstruction of different reflectance images collected from the wall on channels at 609 nm, 508 nm, 405 nm, respectively. The reconstruction shows complete color saturation with a number of well-defined details, such as two different cracks in the sky in the two scanned areas on the right (Fig. 4, area 5 and 4).

While the RGB image helped to detect fractures on the upper part, the presence of efflorescences and subefflorescences in this monument causes the pulverization of the gypsum which dominates LIF signature spectra with a broad band over from 350 to 600 nm in all the main scene, irrispectively from the presence of difference pigments which might originate modulation due to their absorption or emission. Moreover, LIF allowed us to detect differences between the main scene (5) and the left image (1) which could be associated to a larger degradation effect giving rise to a stronger gypsum signature peaked at 400 nm (as in the case observed in Fig. 3b). Note that the double peak structure emerging in the left image seems to indicate a loss of pigments selectively absorbing the near UV emission from the substrate.



Fig. 2. (a) Detail of wall painting of Glorification of the Virgin (chapel of Virgen del Buen Aire, Seville). Reflectance image with RGB reconstruction from 300 lines with spectral channel at 609 nm, 508 nm and 405 nm. (b) Principal Component analysis (PCA) of spectral components of the general image depicted in (a). (c) Absolute fluorescence intensity of the band peaked at 360 nm in a gray scale image, (d) Spectral features of the areas under study (A, B and C). (e) Two color level image based on pixel fluorescence dominated by the band at 360 nm, blue color pixels show a higher concentration of acrylic consolidant than yellow pixels. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this LIF surface study, PCA does not show any evidence of spectral anomalies caused by retouching different pigments or other surface treatments, a part the mentioned double peak struc- ture. All spectra are dominated by the gypsum signature resulting from the main weathering process due to the efflorescences and subefflorescences which caused pulverization of the pigment layer. This weathering form was identified by Cardel and Rodriguez- Gordillo [21]. There is no difference in the PCA analysis of signals

included in the scanned areas shown in Fig. 4b between areas A- C in scan 1 and areas A-E in scan 5. However, it appears that there is some difference between both scans (1 and 5), as scan 1 shows a peak at 390 nm that is a very minor relative maximum in scan 5. Further study is required to identify this difference, based on new database collection allowing us to definitely identify the peak at around 390 nm to a gypsum/calcite layer better than for instance to a former degraded consolidant.



Fig. 3. (a) Studied Arch of San Agustín (Marchena, Seville). In red the area of arch scanned by LIF. (b) Detail of the Arch. (c) Gypsum emission signature found in the church of San Agustín (Marchena). (d) Detail of depigmentation and pulverization of the arch studied (bottom right). (e) Black and white map reporting SAM results, black pixels have strong similarity with the spectrum of gypsum (spectral angle less than 8 deg).

3.4. Murals in the church of the Santo Cristo de la Salud (Malaga), WP4

The WP4 campaign carried out on the mural in Santo Cristo de la Salud (Malaga) covered four lateral rectangles with different orientations with respect to the drum of the vault at a height above 13.5 m.

The RGB reflectance image reconstructed with acquisition at 609 nm, 508 nm and 405 nm is shown in Fig. 5. Unfortunately, in this case the image barely allows us to detect the shape in the drawing or the white border where it is inserted (Fig. 5a).

The PCA analysis of the LIF scan after excitation at 266 nm revealed the presence of bands at 320 nm and 360 nm (Fig. 5b). The band at 320 nm, associated to the variance of component two (PC2), is mainly found in areas A and B in the images and is not present in area C (Fig. 5c).

Areas evaluated with spectral analysis highlighted in Fig. 5a are also depicted in Fig. 5d. The areas recorded as A and B, with a band at 320 nm, have a similar classification using SAM and appear in white while C pixels appear in black as this area presents a different spectral signature.

These bands at 320 nm have been associated with a bio-attack in previous research at this wavelength [27,28]. The main

conservation problem in this church is caused by water filtering into the vault through to the joint between the vault and the exter- nal roof [29]. These areas, covered by soluble salts, re-crystallized calcite and gypsum, with high humidity, were probably affected by a biological attack.

The LIF study associated to digital image analysis based on SAM makes it possible to identify the area that might be associated to the bioattack (Fig. 5d). This map is useful for indicating where samples should be collected and the extent of the damage of the bio-attack and water filtration on the surface.

4. Conclusions

Results demonstrate that laser based on non-destructive remote imaging and laser spectroscopy applications allows valu- able information to be obtained from both reflectance and fluores- cence data of the surface for the study of cultural heritage on painted walls. The LIF-scanning prototype operates at high speed and, thanks to the implementation of the line scanner coupled to the large squared ICCD, has shown its versatility in obtaining valu- able information on the presence and distribution of different



Fig. 4. (a) Scanned areas on the mural of the church of the monastery of San Jerónimo (Granada). RGB reconstruction of the partial image from 300 lines with spectral channel at 609 nm, 508 nm and 405 nm of scanned areas (1–5). (b) PCA of areas 1 and 5 in the mural of the life of San Jerónimo (WP3). From right to left, scan 1 with three areas for study (A–B–C), LIF signature of the 3 highlighted areas (A–B–C), scan 5 with five areas for study (A–B–C–D–E) and the LIF signature of the 5 highlighted areas (A–B–C–D–E). In the first case five PCs contained respectively 35%, 5.0%, 4.0%, 2.8% and 2.8% of the total variance, while in the second case five PCs contained respectively 36%, 4.0%, 3.5%, 3.0% and 2.9% of the total variance.

consolidant treatments (WP1), detachment (WP2 and WP3) and bio-attack (WP4) in four selected case studies of secco paintings characterized by different weathering forms and maintenance conditions. Reflectance maps, contemporary collected, helped in the precise location of specific surface alteration which appeared only in the fluorescence maps.

In particular, traces of former acrylic consolidants, plaster spectral features caused by loss of pigmentation layers and bio-attack areas associated with water filtration were found on frescos on site with remote scanning at a distance of 3–16 m. However, laboratory databases are needed prior to field campaigns in order to understand the spectral features and further studies should be

developed. Moreover, RGB reflectance images allow the detection of weathering in the form of cracks invisible to the naked eye.

This compact LIF-scanning apparatus developed by ENEA for the remote investigation of painted walls will have a huge impact on the analysis of wall paintings through analytical information in 2D images. The speedy remote operating mode and the ability to obtain laser fluorescence signature spectra and RGB images with good sensitivity and selectivity make this set-up very attractive for future research in cultural heritage diagnosis. To this respect it is worthmentioning that former prototypes equipped with much slower point scanners and less sensitive detectors could not reach the same distances and due to tight focusing were



Fig. 5. (a) RGB reconstruction from 300 lines with spectral channel at 609 nm, 508 nm and 405 nm in Santo Cristo de la Salud (Malaga). (b) Principal component analysis (PCA) of the spectral analysis of the general image depicted in (a), first five PCs contained respectively (25%, 5.5%, 4.5%, 3.4% and 3.3%) of the total variance. (c) Spectral signature of areas A, B, C from (a) showing the bio-attack (BA) associated to 320 nm in areas A and B. (d) Gray scale image of the upper part of Fig. 5a. The white area is probably caused by a bio-attack on the painted wall.

potentially more harmful to the investigated surface. The use of digital image analysis, combined with statistical comparison (PCA and SAM), makes it possible to obtain weathering and vulnerability maps of the surface which are invaluable for interventions.

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