Laser-Induced Fluorescence mapping of pigments in *a secco* painted murals

Auxiliadora Gómez-Morón, Rocío Ortiz, Francesco Colao, Roberta Fantoni, Javier Becerra & Pilar Ortiz

Abstract: Laser-induced fluorescence is a remote analysis tool, successfully applied to real-time diagnosis of historical artworks, allowing the observation of features invisible to naked eye, as traces of retouches or presence of modern consolidants. Aim of the present paper is to introduce an historical database of pigments with respective binders and consolidants, realized to support the remote identification and mapping of these materials onto a mural in the least invasive way. To this aim, a monochromatic ultraviolet laser source emitting at 266nm with remote scanning has been used in combination with reflectance. Wall painted models have been built with *a secco* technique according to traditional recipes of XVII century. Digital image analysis, principal component analysis and spectral angle mapping have been carried out on data to get the mapping of two selected pigments, blue smalt and red carmine, in a real mural painting (XVII century). This non-invasive technique allowed us to operate remotely, a distance up to 11 m from the artwork. Results are consistent with traditional microanalysis performed to identity major pigments.

Key words: Laser Induced Fluorescence, *a secco* technique database, surface mapping of pigments, smalt and carmine, non-invasive technique, cultural heritage application

Mapeo de fluorescencia inducida por láser de pigmentos *a secco* de pintura mural

Resumen: La fluorescencia inducida por láser es una técnica de análisis a distancia, aplicada con éxito en tiempo real para el diagnóstico de obras de arte, permitiendo la observación de características invisibles al ojo humano, como rastros de retoques o la presencia de consolidantes modernos. El objetivo de este artículo es generar una base de datos de pigmentos históricos con sus respectivos aglutinantes y consolidantes, realizada para respaldar la identificación remota y el mapeo de estos materiales en un mural de la forma menos invasiva posible. Para este objetivo, se ha utilizado una fuente láser monocromática ultravioleta que emite a 266nm con escaneado remoto en combinación con reflectancia. Se realizaron modelos de pintura mural en técnica *a secco* de acuerdo con las recetas tradicionales del siglo XVII. Análisis digital de imagen, análisis de componentes principales y mapeado de ángulo espectral ha sido llevado a cabo para obtener los datos de mapeado de dos pigmentos seleccionados, azul esmalte y rojo carmín en una pintura mural real (siglo XVII). Esta técnica no invasiva nos permitió trabajar de manera remota, a una distancia de 11 m de la obra de arte. Los resultados son consecuentes con los microanálisis tradicionales llevados a cabo para identificar pigmentos mayoritarios.

Palabras clave: Fluorescencia ultravioleta inducida por láser, base de datos de técnica *a secco*, mapeado superficial de pigmento, esmalte y carmín, técnica no invasiva, aplicación en patrimonio cultural

Introduction

Pigments characterization on different painted artwork surfaces has been already proposed by means of several optical and spectroscopic tools, among which there are reflectance (Acquaviva *et al.* 2008), micro-Raman (Bruni *et al.* 2002) and Laser Induced Breakdown Spectroscopy (LIBS) (Fotakis, Anglos & Couris 1997) techniques, utilized either alone or better in combination. However, their categorization based on invasive character and remote applicability, is the most various. In fact, LIBS and micro-Raman are mostly used in-situ at short distance, being the former micro-destructive and only the latter non -destructive at commonly utilized laser powers. Currently only reflectance is suitable to perform a true non-invasive remote application. The development of additional spectroscopic techniques suitable to remote imaging is therefore advisable.

Laser-induced fluorescence (LIF) resulted a very useful tool in non-destructive analysis in Cultural Heritage (CH) for painted surfaces analysis including pigments with organic binders (Borgia *et al.* 1998; Fotakis *et al.* 1996) and

consolidants (Borgia *et al*. 1998; Fiorani *et al.* 2010). Former researches showed the successful application of this technique to identification of protein based media (Nevin & Anglos 2006; Nevin *et al*. 2006), pigment and acrylic resins (Domingo et al. 2001) and biological degradation (Colao *et al*. 2008; Lognoli *et al*. 2002;). The combination of LIF and Fourier Transform Raman Spectroscopy (FT-RS) was already proposed for pigments and patina investigations (Domingo *et al*. 2001; Oujja *et al*. 2012) and also time resolved operating mode was introduced to carry out specific diagnosis on painted surfaces (Comelli *et al.* 2004; Comelli *et al.* 2011). Fast remote scanning of large surfaces by LIF technique was already demonstrated (Cecchi *et al*. 2000), resulting in the major advantage of the technique whenever in situ measurements or sampling are not feasible. The state of the art on LIF application to material recognition and mapping in murals can be summarized as follows:

- Mapping pigments, whose identification is based on Raman or X-Ray Fluorescence (XFR) in situ measurements at selected points.

- Identifying and mapping consolidants, with support of time resolved LIF data acquisition and occasional combination with Raman in situ measurements at selected points.

- Mapping biodegradation with support of time resolved data acquisition and occasional combination local sampling and bio-chemical analysis for classification.

The equipment employed in this work for LIF (LidArt) is a lidar fluorosensor (optical radar detecting LIF signals (Lognoli *et al.* 2003)) capable to collect and spectrally analyse the fluorescence induced by ultraviolet (UV) laser on remote surfaces. It is suitable to fast process data by means of digital image analysis procedures (Carcagnì *et al*. 2007) for an optimal space-resolved model (Colao *et al*. 2008) on artworks, in which chemical characteristics invisible to the naked eye are highlighted. Its first version, patented in 2007 (Colao *et al*. 2007) and 2010 with improved tools (Caneve *et al.* 2010), has been employed in the Baptistery of Padua (Fantoni *et al*. 2013). In its latter version this equipment allows to scan surfaces in reflectance and fluorescence mode until 30 m distance with a spatial resolution better than 1 cm, collecting respective hyperspectral images.

The huge amount of collected data implies the use of advanced statistical tools and digital image analysis to process the spectra. In this case, grey scale and false-colour images reconstruction, principal component analysis (PCA) (Rencher 2002) and spectral angle mapping (SAM) (Girouard *et al.* 2004; Rashmi *et al*. 2014) have been employed to process the data acquired on the scanned surfaces.

In spite of the large efforts spent to extract and identify significant features from an automatic image analysis, in some cases the complex structure of the examined painted surface can make difficult to select specific spectral features to work with: these are the cases in which it is worthwhile to have at our disposal a series of reference spectra prepared according to historical recipes and restoration procedures. Preliminary studies on LIF of pigments following deep UV excitation were already conducted before the development of lidar fluorosensor systems, considering spectrally (Fantoni et al. 2000) and/or time resolved (Giardini-Guidoni et al. 2000) techniques. Organic molecules, characterized by the presence of conjugated double bonds, metal-aromatics cages, condensed aryl rings, usually have significant fluorescence fingerprints, although their emission wavelength and intensity can be strongly affected by the environmental condition (aggregation state, pH, etc.). This kind of molecules, usually soluble, are prevailing used as colorants in modern products (paints and inks), however a few natural derivatives (e.g. lakes from plants or animals) are well known colorants since the antiquity and are usually classified as organic pigments. Conversely the use of most inorganic pigments, except some of the modern synthetic pigments, date back to very early time in the past, even to the Palaeolithic age (e.g. iron oxides).

In spite of weak luminescence shown by most inorganic pigments alone upon near UV or visible excitation (Burrafato et al. 2004), a set of reference spectra prepared according to historical recipes for wall paintings can be extremely useful to support the identification of original materials and to investigate their distribution. Plaster, historically used binders and modern consolidants are indeed fluorescent upon deep UV excitation; the presence of pigments can give rise to additional bands or characteristic modulations in the detected emission due to selective re-absorption, with a mechanism which implies the pigment acting as a kind of "inner filter" (de la Rie & de la Rie 1982). A LIF database of historical pigments including non-fluorescing or scarcely fluorescing inorganic substances is useful provided that it takes into account these considerations.

The novelty in this paper is based on the realization of a database with LIF spectra of historical pigments, prepared according to traditional receipts, together with their binders in order to assess the possibility to map the distribution of pigments on real artwork painted surfaces, such as the one here considered as case study.

Methods and materials

—*Experimental Apparatus*

The lidar fluorosensor used for this study was already operated to collect hyperspectral fluorescence images of large artwork surfaces (e.g. frescos, decorated facades, paintings on different substrates) upon UV excitation either at 266 nm or at 355 nm (Fantoni *et al.* 2013).

The instrument detected the spectral LIF signature characteristic of different chemical compounds laying on the examined surface, including the effect of their mutual interference in the emission – re-absorption pattern,

thus producing a fingerprint suitable to identify different materials utilized on the surface, as needed in planning restoration. In the present work the instrument was operated at 266 nm, which does give rise to fluorescence for most surface coatings and background plaster.

The sensor is based on an imaging spectrograph (Jobin-Yvon CP240) coupled with an intensified charge coupled device (ICCD - Andor iStar DH734) as light detector. The prototype is able to scan an image of 0.7×2.5 m^2 in less than 2 minutes when placed at 11.2 m average distance from the target.

The optical arrangement was characterized by having the spatial and spectral information on two mutually orthogonal directions imaged on the detector's sensitive area, with about 1 mm spatial resolution at 1 m distance and a spectral resolution better than 2 nm. In the setup used for the present measurements, the overall system specifications are: line scanning, horizontal resolution 640 pixels, 0.1 mrad angular resolution, minimum acquisition time per line 200 ms and field-of-view (FOV) aperture 5.7 deg.

In the utilized laser fluence range (< 0.01 mJ/cm^2) the instrument does not produce any photo-damage on surfaces painted with the *a fresco* or *a secco* technique, as formerly tested in laboratory samples (Colao *et al.* 2008; Raimondi *et al.* 2015). The absence of any photo-degradation on known photo-labile samples (such as white lead paint (Raimondi *et al.* 2015)) in the present database was furtherly checked by optical microscopy inspection after the UV irradiation needed to process LIF signals.

Reference data are acquired by the LIF scanning sensor; the system setup was such to have a spatial resolution of approximately 3x3 mm, and the samples in powder form were put in circular holder with a clear aperture 18 mm approx. In such a way we have not less than 20 spectra simultaneously acquired from the same sample and under the same excitation conditions. The average spectrum is computed as arithmetic mean to increase the S/N ratio.

This lidar fluorosensor can also acquire spectrally resolved reflectance spectra when an appropriate illuminating light is used; from this data a red-green-blue (RGB) reconstructed image in the visible range is produced. To operate in reflectance mode the laser is switched off, a halogen lamp with at less 1000W power is turned on and the optical detector shutter remains opened for the time needed to acquire the image. After calibration, the collected spectra can be used for the computation of standard CIE/lab colorimetric measurements.

—*Operating modes*

During the measurement campaign here reported, the system was sequentially operated in either modes: fluorescence and reflectance mode.

Off line processing of the acquired data is performed to take into account both the wavelength dependent detector efficiency and the spatially dependent collection efficiency. After the calibration we assume to produce images with an efficiency and spatial resolution that are nominally uniform in the entire examined spectral range.

—*LIF Data analysis*

The spectra have been studied by chemometric techniques (PCA) (Rencher 2002) and projection operators (SAM) (Girouard *et al.* 2004; Rashmi *et al.* 2014) and coupled to digital image analysis in order to permit a rapid mapping of the surface by emitted signal similarity.

Major spectral features in LIF spectra are identified by PCA. Although the principal components (PCs) do not possess any direct physical meaning, they can conveniently be described in terms of bands since the overall LIF spectra due to the presence of different surface constituents result from linear combination of PC with appropriate weights (scores).

In the present study PCA is aimed at the identification of prominent spectral features, thus avoiding a manual time-consuming examination of each single spectrum acquired. This procedure has the advantages to be fast and run in a semiautomatic mode, however it has the inconvenience to supply only a global analysis, possibly ignoring the local peculiarities lacking enough statistical significance to be represented in the considered PC. To overcome this drawback, a detailed local analysis can additionally be performed on subsets of the scanned areas, with a separate analysis of the PCs. Once identified, spectral bands are sought for in the acquired LIF spectra, completing the data analysis.

A different method used in the analysis of spectral images, concerns the identification of pixels having a specific spectral content. A typical case is the identification of a given constituent: such task is accomplished either by a band analysis based on spectral deconvolution, or by using spectral mapper algorithms as SAM. This case requires the availability of reliable reference spectra, possibly measured in an analogous matrix in order to account also for interactions among different painted layers. Although the mapper algorithms perform well with a low computational cost, their results based on a partial information are of course less accurate with respect to the complete band analysis procedures, and their application often follows the latter only once major features have been identified.

—*Database models*

Modelling of the wall painting with a secco technique has been performed according to researches carried out by

the Andalusian Institute of Cultural Heritage (IAPH) in the wall painted of Domingo Martínez from the XVII century (Gómez Morón 2008), relevant to the considered case study, and Cenino Cenini´s recipes (Cennini 1859) widely used in the Renaissance and the successive periods until the end of XVIII century. The employ of linseed oil as a medium for mural painting was a common practise during the Spanish Baroque, being described this technique by Francisco Pacheco in his treatise *The Art of Painting* in 1649 (Pacheco 1871).

More than forty plaster models have been built in the laboratory to emulate the surfaces of these murals [figure 1] over a primer layer of gypsum. With this purpose, several bricks have been covered with a mixture of gypsum and sand with animal glue binder. The preparation was done with sand from Guadalquivir River (near to Seville) and gypsum in relationship 1:6. The sand has a fineness of 11.2±3.6 µm. The animal glue (rabbit skin glue) was previously heated with a water bath to acquire a pasty consistency, and then it was added to the mixture gypsum/sand or to the gypsum until saturation

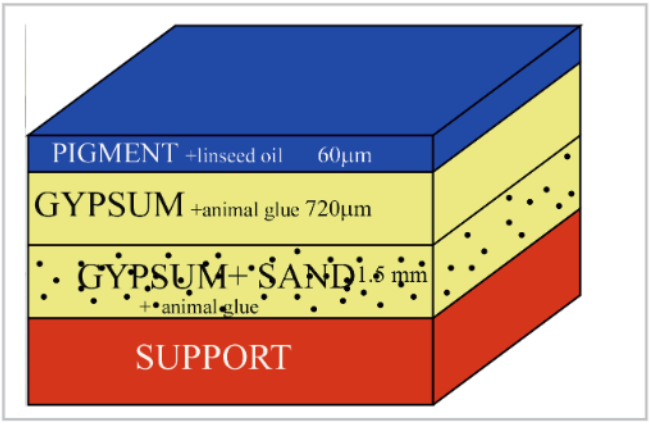

Figure 1.- Laboratory preparation of the plaster for *a secco* painted model scheme of composition and thickness of the plaster respective layers.

in the layer of plaster. The plaster layers were dried a room temperature for two weeks. These layers were the substrate upon which different pigments from KREMER historic pigments [table 1] and products from CTS Srl, have been applied with linseed oil. The colour layer was applied with pigment and linseed oil in ratio 3 (pigment): 1 (linseed). Each model has a surface near 15x5 cm, so it was possible to obtain their LIF signal signature in the considered matrix from the scanned surface. Table I shows the model samples, the mixture compositions and pigments are grouped according to their colours.

The bricks covered by the wall painted models were examined three months after preparation, in order to take into account at least fast aging effects. Note that the binder used, linseed oil in a layer of approximately 60 µm thickness, is known to be fluorescent upon UV laser excitation, giving rise to a spectrum that for the pure sample is slowly changing in intensity and peak position with ageing, where the early effects mostly correspond to blue intensity increase (Miyoshi 1985). For LIF spectral characterization the painted brick has been allocated in a vertical support and scanned at 7 m distance.

All samples listed in Table I showed significant luminescence signal in the examined near UV-visible range, with characteristic modulation (emission or re-absorption) which can be associated to pigments presence in the considered matrix. In order to show examples of the spectra collected, only those relevant to the examined case study (sect. 3.2) are reported in this paper, but the entire data set is available on line as additional material and can be consulted to evaluate the possibility of identifying a single pigment in the presence of others characterized by a similar colour in a real historical sample.

In order to possibly discriminate effects relevant to a specific pigment with respect to those related to

Table 1.- Colour, composition and pigments for Database of a secco technique wall painting models. All materials were applied on plaster, as described in the text, with addition of linseed oil. (*)

Layer color	Common or chemical name (id.#, Kremer order number)
No pigment	Plaster (P1); P1+ linseed oil (P2); P1+ benzyl gel (P22); P1+ tea (P23); P1+ Ammonium citrates (P24, P25); P1+ Paraloid B72 in nitrotoluene -15%- (P26); P1+ DMSO (P27)
White	Lead White (P3, 460009); Calcium White (P4, 58720); Lead Sulfate (P5, 46050); Lithopone (P33, 46100)
Yellow	Lead Tin Yellow (P6, 101009); Orpigment (P35, 10700); Naples Yellow (P17, P32, 431229); Massicot (P36, 43010)
Red/Organge/ Brown	Cinnabar (P7, P21, 10624); Haematite (P8, 48651); Carmine Naccarat made of cochineal (P9, 42100); Red Lead, Minium (P10, 425009); Armenian bole (P28, 40503); Raw Sienna (P11, P12, 40400); Realgar (P31, 10800); Madder Lake (P40, 372141)
Blue	Ultramarine Blue (P13, 45000); Smalt (P14, 10000); Lapis Lazuli (P15, 10500); Azurite (P16, 10200)
Green	Malachite (P18, 10300); Cyprus Green Earth (P29, 17400); Verona Green Earth (P30, 11000); Bavarian Green Earth (P38, 11100); Copper Resinate (P39, 12200)
Black	Manganese Black (P19, 47500); Verdigris (P34, 44450) Ivory Black (P20, 12000); Grape Black (P37, 12015), Furnace Black (P41)

(*) all spectra collected are available online as additional material

its presence in the considered matrix, the spectral acquisitions were repeated over layers of each pure pigment in powder. Samples were prepared by gently and uniformly pressing a few mm thick layer of each pigment powder in order to fill (2 cm^2 x 2 mm) cylindrical holes on aluminium foil used as holders, which were allocate at 7 m from LIF equipment for remote spectra collection. Comments on pure pigments spectra are reported here only for selected samples (ivory and furnace black, azurite and smalt blue, carmine nacarat made of cochineal, madder lake and cinnabar red) relevant to the real case studied in the on-site application.

—*On-site application*

On-site measurements were carried out in the vault of the Chapel Our Lady of Good Air that is part of the Palace of Saint Elmo in Seville, the residence of the president of the Andalusian Government. This Chapel of the XVII century had just been restored by the IAPH, employing different non-destructive techniques for diagnosis and restoration monitoring.

Namely, this work presents the application of LIF database to pigments mapping on the wall paintings the Glorification of the Virgin from Domingo Martinez after its restoration.

Three images acquisitions were performed on the virgin silhouette [figure 2]; table II shows the image acquisition setting in each scan. The wall painting scanned area was about 2.5 m^2, while image size in pixel is 128 pixels in height and a variable number of pixels in width [table II].

Table II.- Image acquisition settings for three scans

Scans	1-2	3
Gate	500ms	500ms
Gain	230	230
Laser current	100A	OFF
Halogen lamp	OFF	2000W
Optical f-number	3	22
Spectral focus	UV-VIS	VIS
Back-ground	No	No
Lines	600	600
Scan width	11000	11000
Distance	11.2m	11.2m

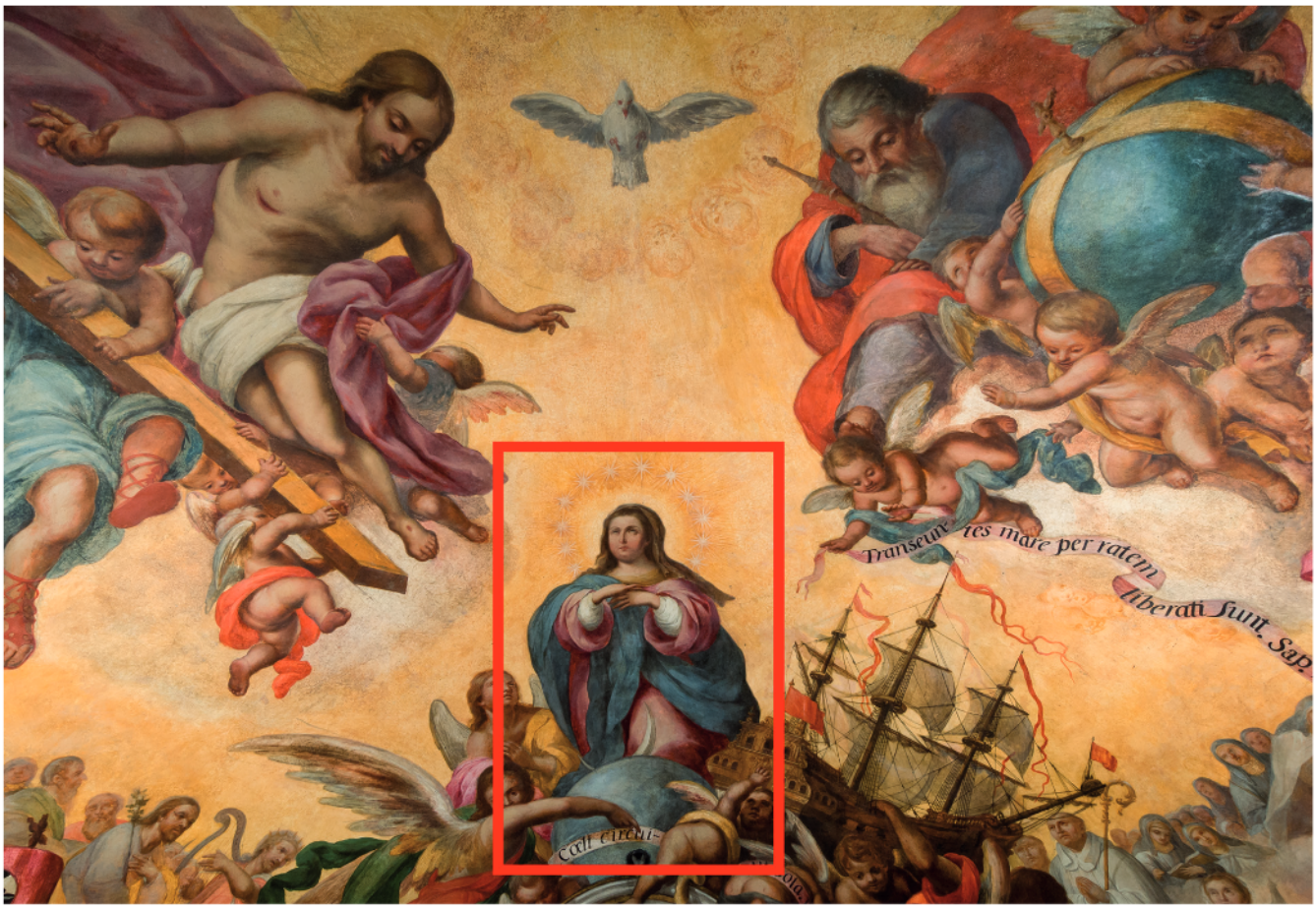

Figure 2.- Scanned zone of the vault of the Our Lady of Good Air (Seville).

— Traditional Analysis

To validate the results obtained, the LIF identification was compared with traditional analysis after the sampling performed following the recommendations of the standard UNE-EN-16085:2014 (AENOR 2014). Micrometer-sized samples were taken to analyse the pigment layers. Sampled specimens were examined by optical microscopy (OM), Scanning electron microscopy/energy dispersive X-ray (SEM-EDX) spectroscopy and X-Ray Fluorescence (XRF) to characterize the substrate; Fourier-transform infrared spectroscopy (FTIR) and gas chromatography with mass spectrometry (GC-MS) were applied to the binder analysis and to detect occasional presence of modern resins used as consolidants.

It is worth mentioning that, twenty-two samples taken in the vaults correspond to less than 1 cm^2 of investigated surface and sampling required the installation of scaffolding, on the other hand the LidArt apparatus allowed to scan quickly near 7 m^2 without any damage to the murals and without any scaffolding.

Results and discussion

—LIF study on laboratory samples

The fluorescence spectra from sample models were collected upon laser excitation at 266 nm. Figures 3 A-F and 4 A-C show the spectra acquired on selected painted plasters, possible references for the case study discussed in the following, and on some involved pure pigments, respectively. The database with all the LIF spectrum of pigments/colorants on plaster with linseed oil has been enclosed as Annex 1.

The spectral emissions, once well distinct features are present, allow for the identification of different pigment/binder mixtures. From sample to sample we observed variations in absolute fluorescence intensity of more than one order of magnitude, however the signal to noise ratio was higher than 20 in all the reported measurements and normalized spectra are plotted.

In case of pigments layered on plaster [figures 3A-F] the fluorescence consists of a broad band centred at 450 nm

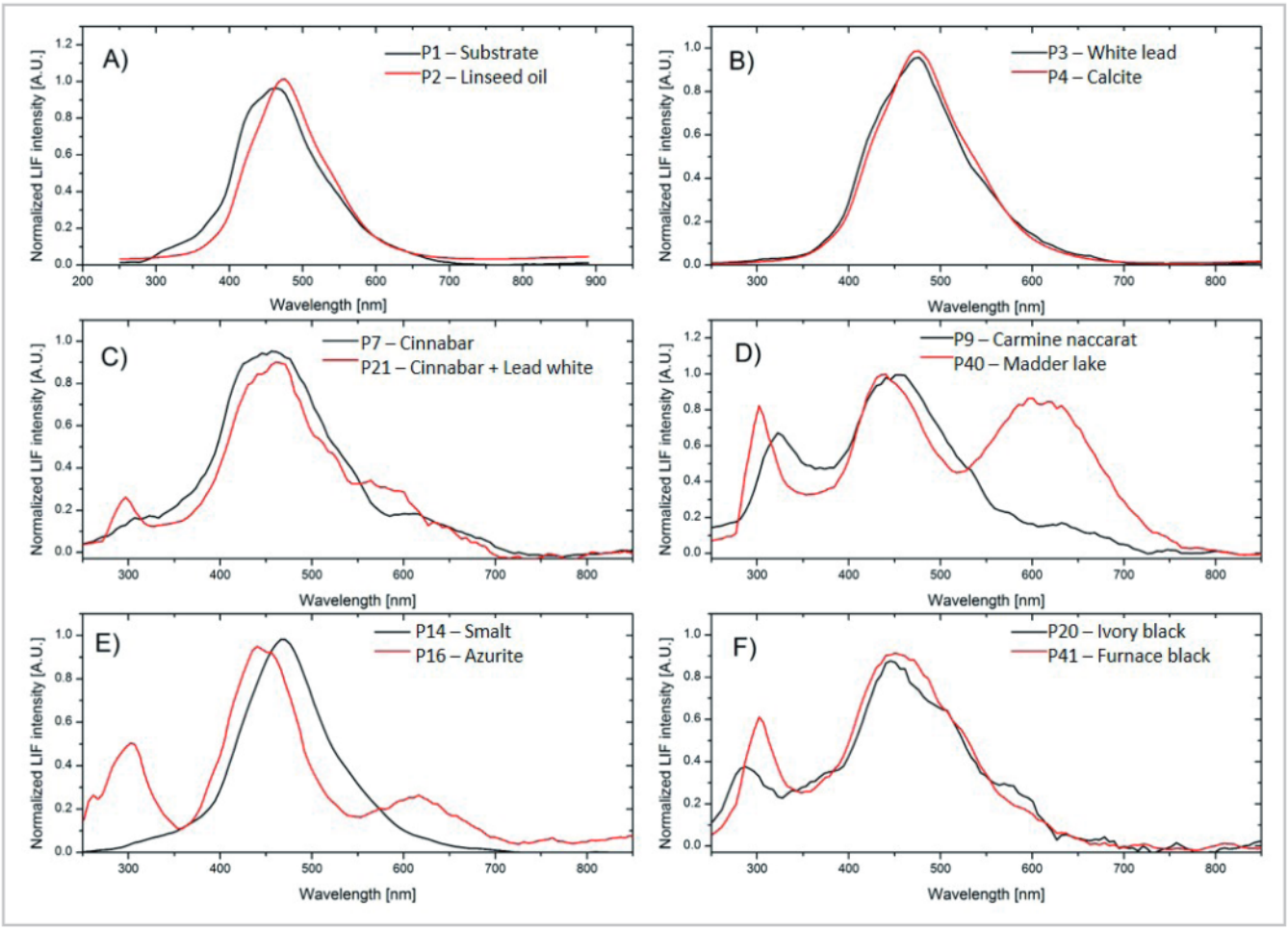

Figure 3.- Normalized LIF spectra of painted substrates: A – substrate samples: alone (P1, black line) and with linseed oil (P2, red line); B - white samples: lead white (P3, black line) and calcite (P4, red line); C - cinnabar samples: alone (P7, black line) and with lead white (P21 red line); D – red samples: carmine naccarat made of cochineal (P9, black line) and madder lake (P40, red line); E – blue samples: smalt (P14, black line) and azurite (P16, red line); F - black samples: ivory black (P20, black line) and furnace black (P41, red line).

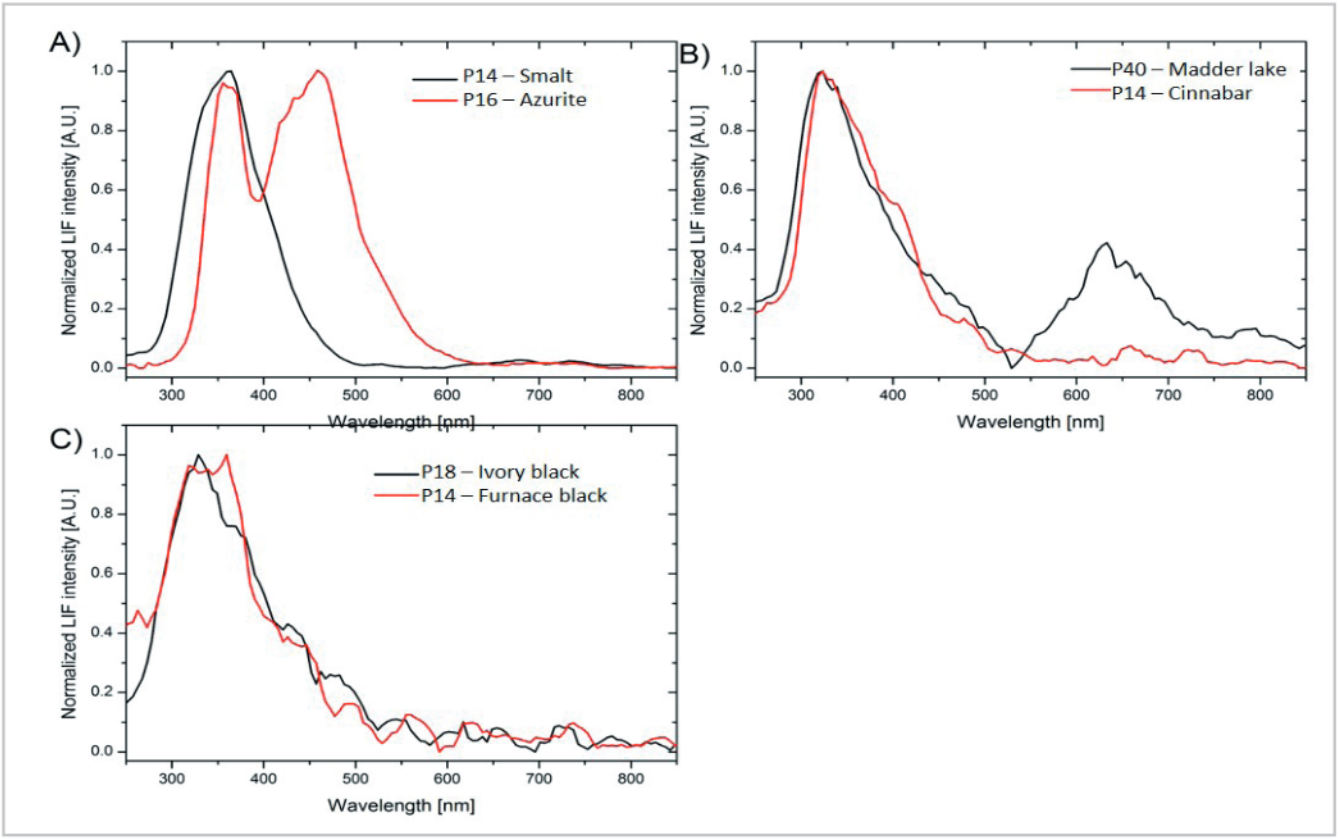

Figure 4.- LIF spectra of pigments in powder form: A – blue pigments: smalt (P14, black line) and azurite (P16, red line); B - red pigments: madder lake (P40, black line) and cinnabar (P7, red line); C - black pigments: ivory black (P20, black line) and furnace black (P41, red line).

and width of 200 nm. The substrate and binding media [figures 3A-B] contribute to the total fluorescence with a broadband emission; in particular the spectrum recorded for the substrate alone (curve P1 in figure 3A) shows an emission peaked at around 450 nm. From this observation we deduce that the main contribution to the emitted band is due to the fluorescence of matrix, that is due to the mixture of substrate (gypsum, quartz and calcite) and binding media (animal glue and linseed oil); over the matrix's band, other spectral emissions are due to the pigments and consolidant components.

As an example, figure 3A shows the difference from the white layer of the plaster alone (P1) and its overlap with the binder, linseed oil (P2); while the effect of the presence of calcite and lead white (P3 and P4) applied with linseed oil on the plaster is shown in figure 3B. In both figures the linseed oil application corresponds to a reduction in the intense plaster UV band peaked at 320-400 nm probably for a selective re-absorption (Verri *et al.* 2008; Simonot, Thoury & Delaney 2011). The presence of the considered white pigments, although causing some attenuation, does not seem to further affect the plaster spectral shape; although the lead white has a characteristic broad emission peaked at 400 nm (Giardini-Guidoni *et al.* 2000) which overlaps to the former.

Differences related to various pigment addition can be observed in figures 3 C-F. As a specific feature some pigments, especially organic pigments such as different types of red, present an additional UV emission band peaked around 300 nm, which is missing for smalt and cinnabar. This band can give a strong indication of the presence of an additional pigment even in small quantity, for instance of lead white to obtain pink from cinnabar red [figure 3C]. The effect of a layer of cinnabar, added either pure or in mix with lead white (curve P7 and curve P21, respectively in figure 3C), is the presence of a characteristic weak band peaked at 610 nm according to Mounier *et al.* (2014), while the addition of white lead give rise to the mentioned UV band and causes some changes in the spectral zone between 450 and 500 nm and a significant reduction of intensity, with the observed increase in signal/noise ratio (SNR).

The spectra of red organic pigments, reported in figure 3D, show distinct features: madder lake samples (P40) has broad bands similar to those describes by Comelli et al. (2011) for madder lake (between 600 and 615 nm), while in carmine nacarat made of cochineal (P9) the intense band peaked at 610 nm is replaced by a significant broad shoulder with a maximum around 635 nm. This emission maximum is identified by Comelli *et al.* (2011) as an anthraquinone-based lake of animal origin, for example, cochineal or kermes. These spectral signatures would allow identifying between some red organic pigments and even its origin, although the remote fluorescence

cannot compete with micro-spectrofluorimetry coupled to chemometrics (Nabais *et al.* 2018) in the identification of manufacturing receipt. The relative intensity recorded on the red band between 610-640 nm is however in both cases larger than for the red band of cinnabar red, which is definitely peaked at a longer wavelength (around 650 nm).

Figure 3E shows the difference of spectral features between two inorganic blue pigments: smalt and azurite. Both pigments originate a broad band, not assigned, peaked between 400 and 500 nm. However, in the case of azurite this band appears blue shifted, it is accompanied by secondary emission at longer wavelengths and there is an emerging UV tail from plaster background. Thus, it will be possible to distinguish smalt from azurite. Discrimination of smalt from other blue pigments would be not so straightforward from LIF spectra alone (see supplementary material).

Figure 3F reports results for black pigments: furnace black (P41 curve) and ivory black (P20 curve). The weak spectra recorded in both cases are dominated by the rather uniform absorption of both pigments in the entire visible range (see again the SNR increase with respect to the plaster curve), the only distinct feature seems to be the most intense tail of UV emission peaked around 300 nm recorded for P41 (furnace black), which might be related to the plaster background, so it is difficult to carry out an identification.

From figures 3C-F we can conclude that each coloured layer, although characterized by a weak overall emission, has a spectral signature, as a fingerprint, resulting from the interaction between layers and components with different absorption/emission behaviour in the considered sample model.

The fluorescence observed from each of the pigments painted on the plaster substrate, closely follows what obtained in the measurements from the corresponding pigment in powder form (pure pigment) reported in figure 4, where it should be noticed the lack of the emission band typical of the plaster substrate.

On the powder pigments, despite the peculiar low SNR, some characteristic signatures appear in the visible at least for the considered blue and red colorants [figures 4A-B]. Note that the observed features are not system artefacts, as checked on Spectralon, a standard material which gave rise only to a flat background. The spectra of blue inorganic pigments, azurite and smalt respectively [figure 4A], present distinct features: the smalt spectrum has a single broad band at peaked 390 nm while the azurite shows a second band with comparable peaked at 480 nm. On the other hand, the black pigments considered appear undistinguishable also from their pure pigment spectra [figure 4C].

The difference between the red pigments: cinnabar and madder lake [Figure 4B] is fully consistent with what observed in case of the same pigments with the binder on plaster, the second band of madder lake peaked at 610 nm emerging very clearly. Two different trends are consistently observed when the spectrum of pure pigments and layers are compared in all analysed samples: on one hand we observe a decrease of the fluorescence emission in the ultraviolet region between 290 and 400 nm on plaster samples, while on the other hand the band at 450-500 nm is modulated because of the simultaneous contributions from pigment emission/absorption and plaster emission. Spectral features emerge clearly on red tail where the plaster contribution is negligible.

These observations suggest that the presence of the substrate alter in a significant way the emitted spectrum related to pigment fluorescence. It is confirmed that an appropriate deconvolution is required to separate the contribution arising from different components, whenever it is possible. Alternatively, a database built with appropriate matrix is necessary to take in account re-absorption and other secondary effects. In fact, strong UV-visible absorption from some pigments may also be responsible for complex features, generating a lack of intensity that cannot be reproduced by a deconvolution based on a simple superposition of positive components.

Summarising, the fluorescence from the plaster alone for a secco technique wall painting, and from the plaster and binder plus pigments, was examined in different experiments, to isolate their spectral contributions in historical matrices. The emission feature of the plaster is an intense band at 450-500nm, and each mixture has an own spectra or fingerprint due to the contribution of different components on the layers. The reference spectra from our laboratory model [figure 3], containing ancient pigments and colorants with their binder on plaster, are proposed to be used as guidelines to select SAM endpoints on on-site wall painted scanned by LIF to discriminate the presence of pigments in the artwork under investigation. A quantitative agreement cannot be expected due to possible differences in the various historical receipts, to long-term aging effects and to possible presence of modern consolidant on the real surface which are known to alter the spectral signatures.

— *LIF database application on-site*

The application of the above described database was carried out on the vault of the Chapel Our Lady of Good Air in Seville (Spain) scanned by our LidArt prototype.

The interpretation of the spectra was simplified by PCA. Five PCs [figure 5A bottom left] show most of the variance of the spectrum in each point analysed of the surface. These PCs have relationship with the main chemical products presents onto the surfaces, they could be considered as a spectral signature (Fiorani *et al.* 2010) containing the spectral information needed to look for at

our pigments-on-plaster database. PCA shows a clear peak at 360nm due to the presence of acrylic products (Paraloid, database P26), as reported in former studies (Fiorani *et al.* 2010; Fantoni *et al.* 2013).

A significant tail on the red, extending above 600 nm in PC3, suggests the widespread presence of a red organic pigment. Other contributions, with signatures between 400 and 500 nm, that are more difficult to understand, require the use of our database with standards on plaster.

With this purpose a spectral analysis was carried out in fixed zones at different points of the images. Spectra collected in the standard database were utilized to perform a two-step mapping procedure based on the SAM algorithm projected onto the entire scanned surface, as described in the following.

The area studied was first digitalized in a false colour fluorescence image [figure 5A, top] in order to evaluate the spatial accuracy of the scans and to achieve an overview of pigments distribution. Internal reference spectra with characteristic signatures are shown in figure 5B-C (bottom). These spectra have been utilized as endpoints for SAM projections on the entire image with the purpose to better identify different areas. Two regions can be clearly identified [figures 5B-C, top].

Figures 5B-C (bottom) report the spectral signature associated to smalt blue peaked at shorter wavelengths [figure 3E curve P14] and carmine naccarat made of cochineal spectra, the latter characterized by the secondary long wavelength structure peaked around 410 nm [figure 3D curve P9]. The omitted fluorescence emission at 610 nm allowed us to discard the use of madder lake. Despite the evident contribution of a red lake of animal origin (i.e. cochineal), the presence of other red pigments, e.g. cinnabar with a weaker but broader red emission, cannot be ruled out with current LIF measurements.

Red and blue pigments maps [figures 5B and 5C top] match greatly with blue and red colours in the image [figure 2]. The first figure shows the use of blue pigment found in the mantle, meanwhile the second one demonstrates the use of red organic pigment mostly in the red robe, though it appeared also used in other zones as part of colour mixtures specially to create some contrast to the background. The possible identification of red organic pigment as lake of animal origin (probably cochineal) is consistent with the wall painting dating, because of the diffusion of the Mexican cochineal in European countries after the discovery of America (Cardon 2007), although it is well known that cochineal lake was previously used in Europe, for example, Polish, Armenian or Ararat cochineals (Eastaugh *et al.* 2004).

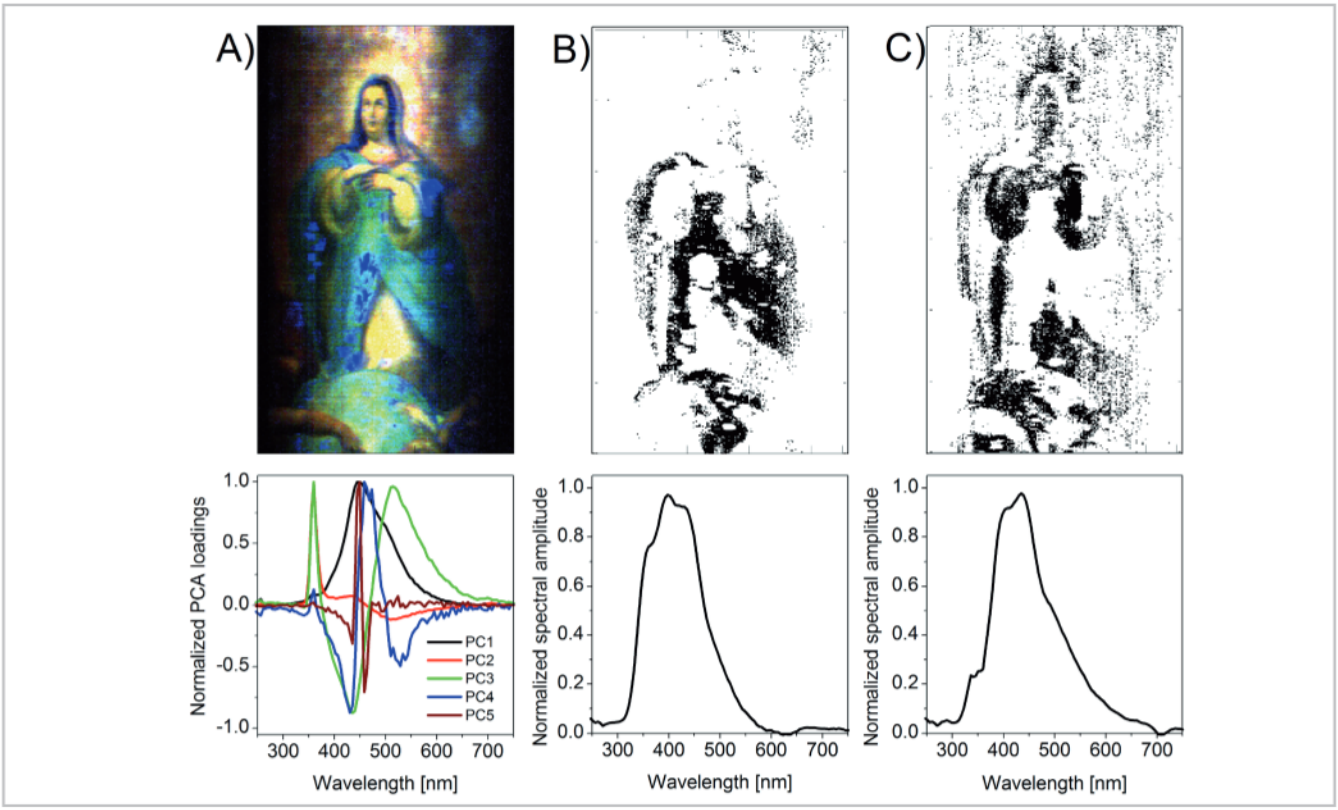

Figure 5.- Results from the fluorescence image analysis performed on the scanned wall painting representing the Glorification of the Virgin. A) top figure - RGB false colour image obtained by combining the fluorescence intensities emitted at 515, 445 and 360 nm; bottom figure - PCA of spectra from image; B) top figure - Similarity image mapping with SAM on blue pigmented areas (mainly blue smalt); bottom graph - endpoint spectrum for SAM; C) top figure - Similarity image mapping with SAM on red pigmented areas (mainly carmine); bottom graph - endpoint spectrum for SAM.

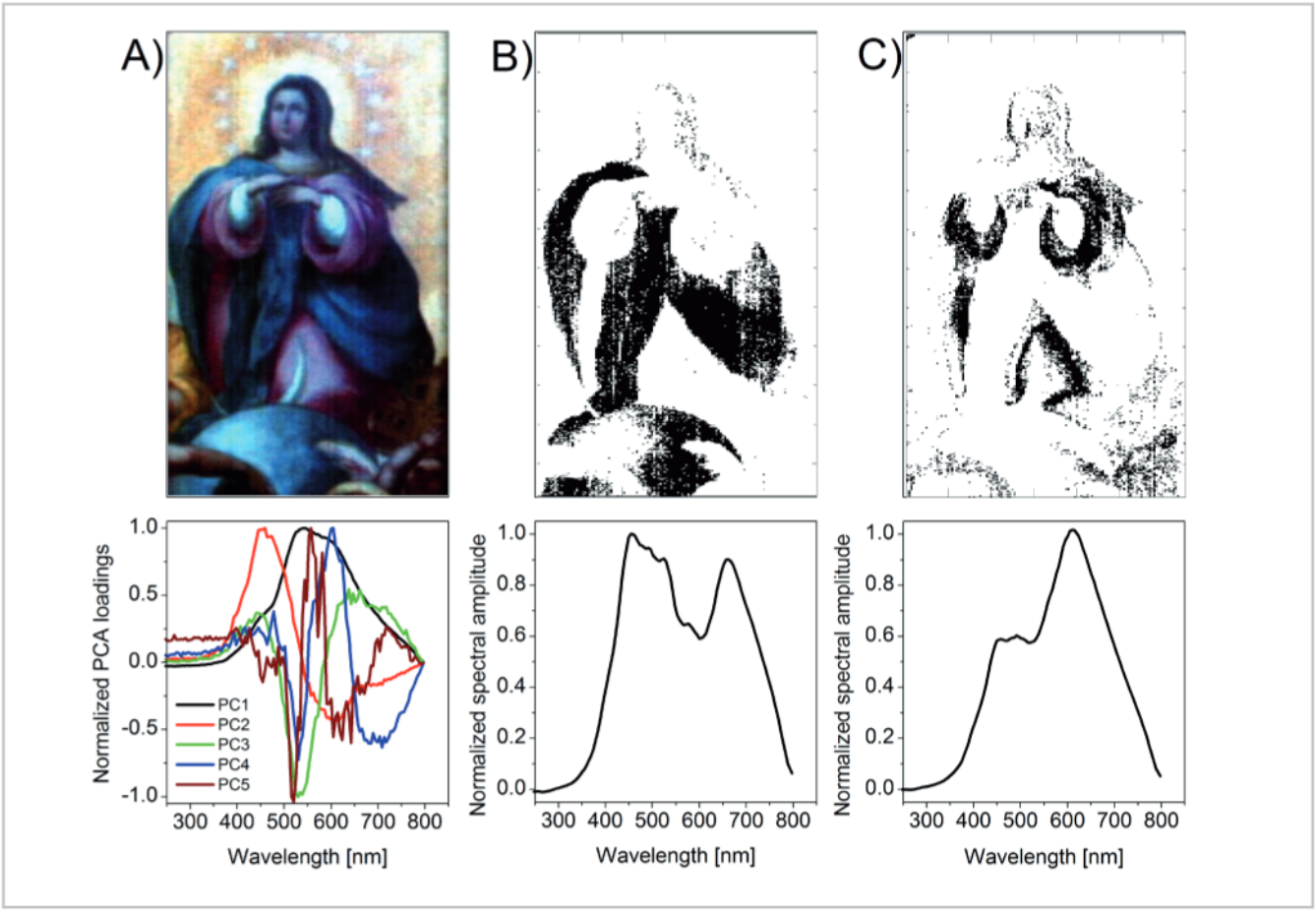

Figure 6.- Results from the reflectance image analysis performed on the scanned wall painting representing the Glorification of the Virgin. A) top figure - RGB image obtained by combining the reflectance intensities emitted at 600, 500 and 400 nm; bottom graph - PCA of the entire reflectance image; B) top figure - Similarity image mapping obtained on the reflectance with SAM on blue pigmented areas (mainly blue smalt); bottom graph - endpoint spectrum for SAM; C) top figure - Similarity image mapping obtained on the reflectance with SAM on red pigmented areas (mainly carmine); bottom graph - endpoint spectrum for SAM.

For sake of comparison the same type of analysis here reported for fluorescence signatures was also performed with reflectance spectra, available from our remote scanning instruments [figure 6]. In this case no detection of acrylic consolidant was obtained from spectral analysis. Furthermore, although it was possible to map most of the red and the blue components where they dominate, no information on the red addition to background was achieved in this case. This observation stresses the power of the proposed method based on fluorescence as a fingerprint of the entire painted outer layers, since the mapping accounts also for the presence of week contributions from the red pigment used.

In order to overcome the scarce selectivity of the spectral features appearing in the fluorescence database for some specific cases, such as for instance the examined black pigments, work is in progress to merge data from fluorescence and reflectance spectra since they are sequentially recorded by our instrument in similar environmental conditions and from the same point of view.

In the selected case study was not possible to identify other pigments in the current database, even by using the combination of fluorescence and reflectance spectra. This is due to the fact that in most of the cases characteristic pigment fluorescence band excited at 266 nm are weak, or even absent, and possibly hindered by matrix effect; in these conditions it is not easy to detect those pigments which are not major components of the examined surface and thus responsible at least for absorption in case of negligible fluorescence.

In summary, the data base has been built with the aim to support pigment identification on real historical surfaces. The considered case study offered the chance to identify three families of major pigment: red, blue and black. Results have been obtained on identification (as carmine and smalt) and mapping red and blue, with better sensitivity than in reflectance for the red carmine.

— *Identification of pigments by traditional techniques*

Traditional techniques have been employed, not only to

design the database, but also to evaluate the accuracy of the results. Conventional micro-analysis and X-rays techniques revealed that the primer wall painted layer was formed by a support of gypsum of different thickness mixed with earths, oxalates, quartz and calcite. Domingo Martinez used a secco technique what was confirmed by GC-MS. The binder analysis revealed the presence of animal glue and linseed oil in the outsider surface, meanwhile traces of resins appeared on the outer surfaces in sporadic zones (Gómez Morón 2008). Since gypsum, quartz, calcite (P4) and animal glue are the basis of our reference models while linseed oil is the binder used to mix the pigments, we expect the best correlation between remote LIF data and results from present *in situ* sampling.

The table III summarises the colour palette of the vault, as deduced from the sampling. Mainly inorganic pigments were found: lead white, smalt blue, red earth, cinnabar, yellow lead and chromium, green malachite (copper hydroxi-carbonate), however the organic compound carmine, possible from cochineal, has been utilized as well in most of the red zones. Relevant for this research was the confirmation of the LIF characterization made for the blue pigment of the mantle and the red pigment of the robe of the Virgin. The smalt blue was determined by SEM-EDX with the presence of silicon, arsenic, potassium, iron and copper [figure 7]. In the case of the robe [Figure 8], a punctual analysis of its stratigraphic section by FTIR identified the use of an organic pigment as red colour.

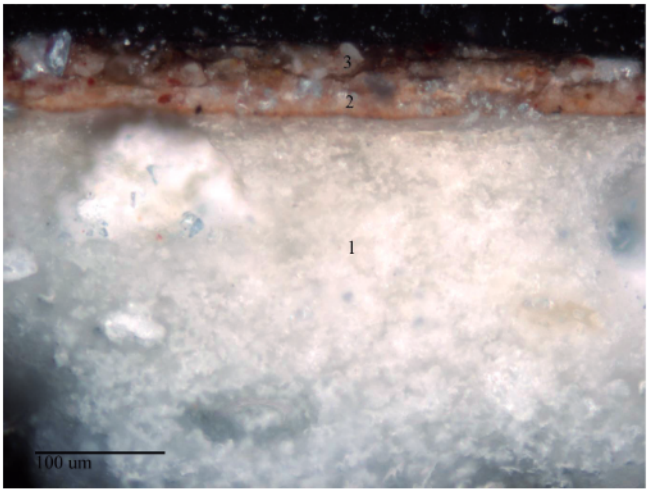

Figure 8.- Stratigraphy of red sample: Plaster composed by gypsum (layer 1), lead white, red earth, calcite, carmine and a few grains of gypsum (layer 2), red layer with the same composition of second layer (layer 3).

Table III.- Colour Palette of the wall painting vault titled "The Glorification of the Virgin"

White	Blue	Red	Ochre, brown, sienna	Green	Black	Metallic
Lead White, Calcite, Barite	Smalt blue	Red Earth, Cinnabar, Carmine (possible from cochineal)	Yellow pigments with lead and chromium (due to a restoration)	Malachite	Lamp Black, carbon	Gold, Silver, Copper

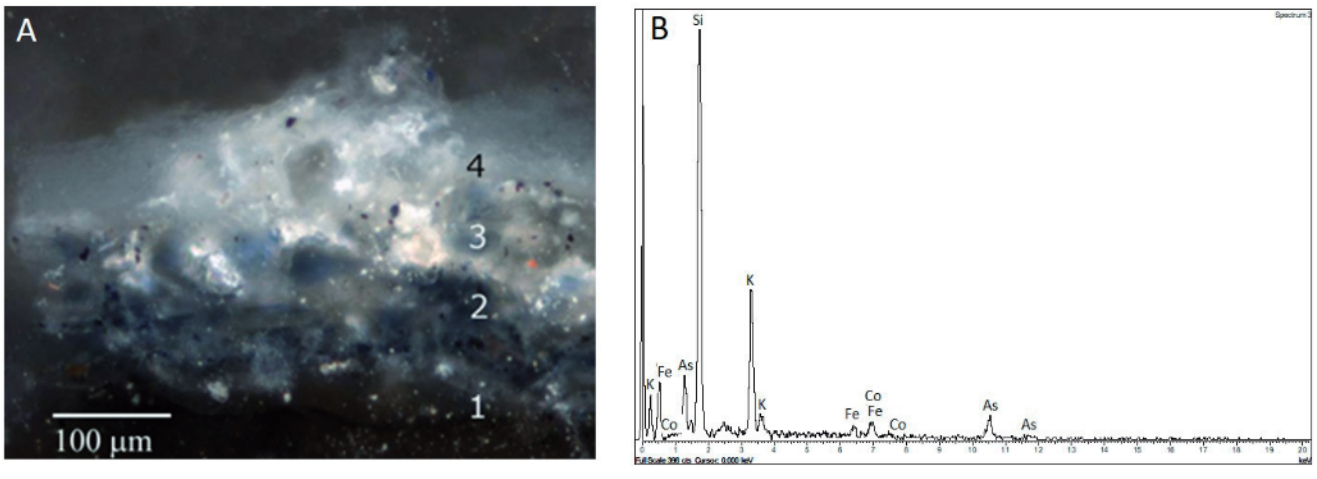

Figure 7.- A-Stratigraphy of blue sample: White primer of plaster (layer 1), Calcite, lead white and blue smalt (layer 2), grains of lead white, calcite and blue smalt (layer 3) in smaller quantities than those identified in layer 2, very thin white layer of calcite (layer 4). B – EDX spectrum where is identified smalt blue (Si, Co, As, K and Fe).

Conclusions

The work here presented supports the use of database according ancient recipes as LIF standards to carry out LIF mapping on painted surfaces. The results show that LIF is a great diagnostic tool, having the ability to perform spectral analysis on-site and with high speed on very large real painted surfaces, also having the possibility to analyse both organic and inorganic pigments even in the case of not well known fluorescence emission bands on pure substances. Most important from the point of view of the conservators, LIF remote imaging is a completely non-destructive analysis. The availability of a validated LIF spectra database allows minimizing samples collection on wall painting following ICOMOS (International Council on Monuments and Sites) recommendations (ICOMOS 2003).

The LIF technique is demonstrated to be an effective diagnostic tool on the considered case study (a XVII century *a secco* mural paint). In fact, based on the historical database built, the assignment of two main pigments (smalt and carmine) was confirmed and their distribution onto the image was obtained, furthermore the capability of mapping the identified red pigment was significantly improved with respect to the reflectance imaging. Note that the distribution on a large area of a specific material achieved by LIF imaging, either original pigment or modern consolidant, is a valuable information for conservation scientists even in the least favourable case of not-straightforward assignment requiring additional in situ measurements or samplings.

Nevertheless, LIF remote imaging still requires further study to complete the database of historical pigments of interest, which have not been formerly investigated with detail upon laser excitation in the UV region. The problem of identifying and/or discriminate contribution for plaster and binders could be possibly solved by using multiple UV/visible excitation wavelengths. Possibilities of combined remote utilization, together with other laser spectroscopies (e.g. Raman) are under investigation to detect by vibrational signatures the presence of characteristic non fluorescent groups at the investigated painted surfaces. Moreover, further studied about ageing and fading must be carried out to complete the database.

ACKNOWLEDGEMENTS

This study has been supported by the agreements IAPH-UPO & UPO-ENEA, José Castillejo (2010) and Technoheritage (2013) grants of Pilar Ortiz and the Project of Excellence of Junta de Andalusia HUM-6775 (RIVUPH).

Part of the data analysis was conducted during the COBRA (Conservation of Cultural Heritage based on Radiations and Enhabling Technologies) Regional project n. 1031 (LR13/2008) funded by Latium Region.

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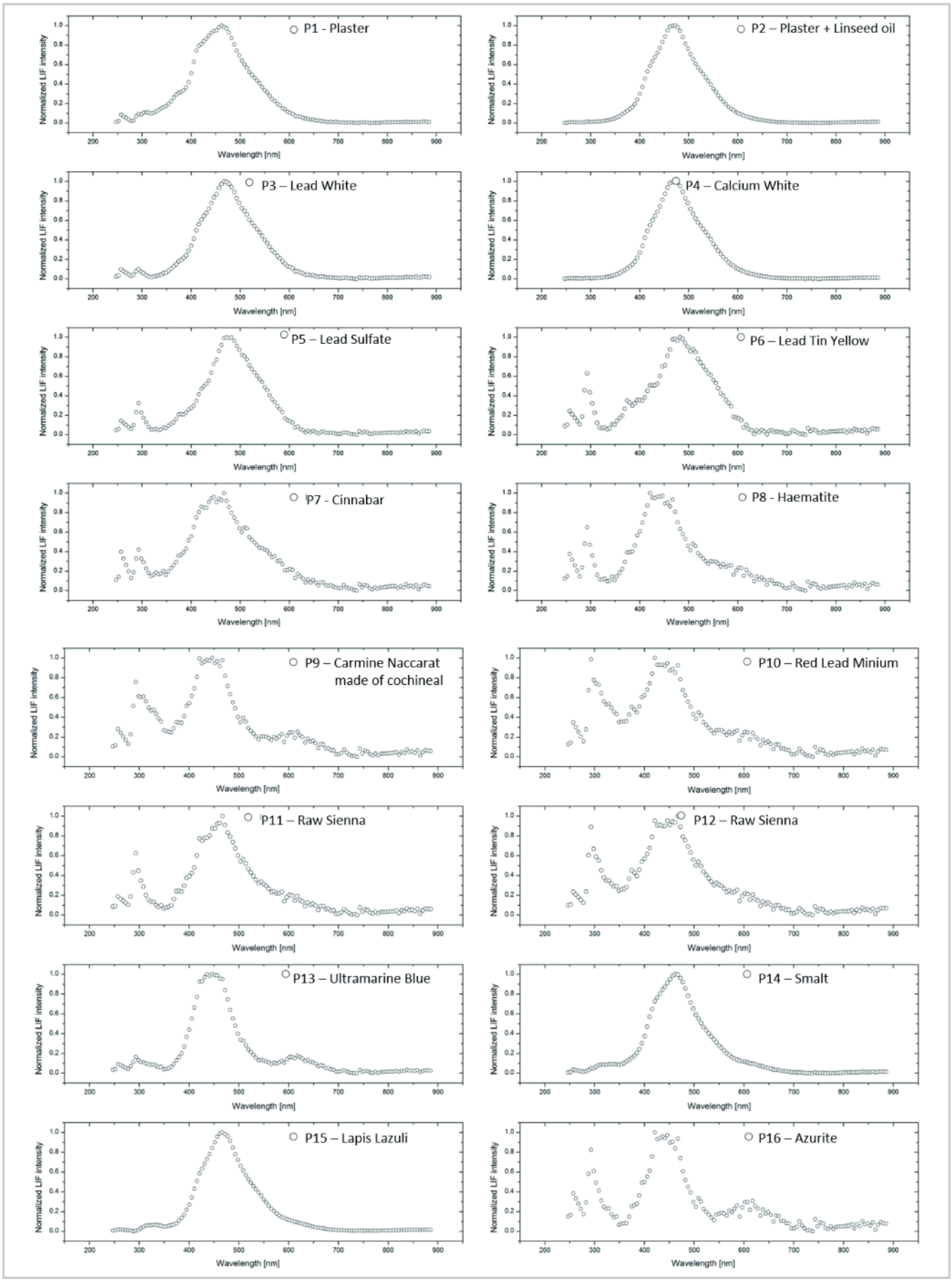
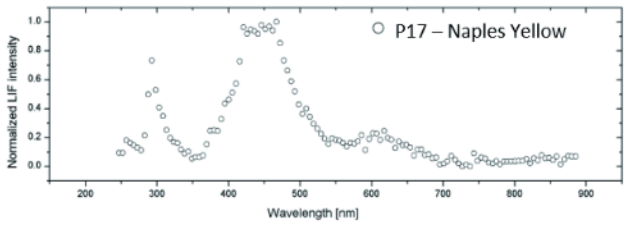
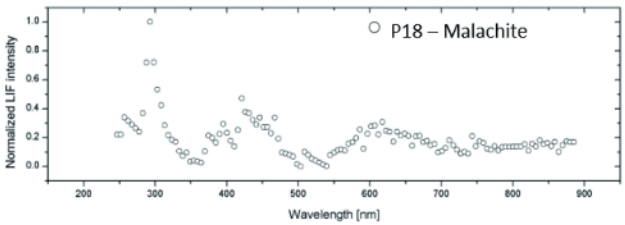
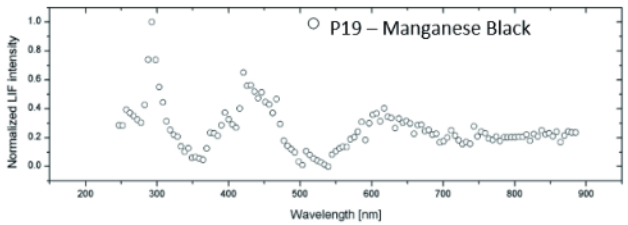
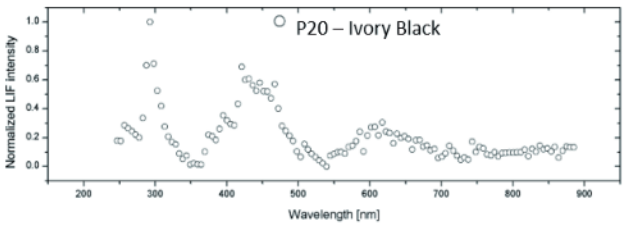
Annex 1.- LIF spectrum of pigments/colorants on plaster with linseed oil. The name of the pigment and the occasional presence of other additives is specified in Table I. Data are normalized on the maximum, an indication on the relative intensity can be derived from SNR (data scattering around the best fit curve).

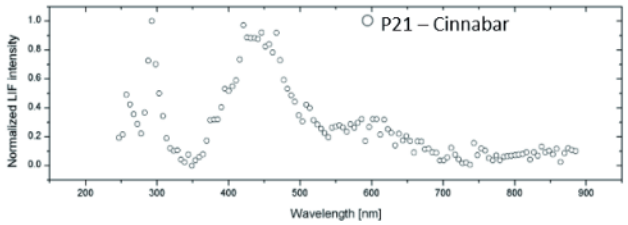


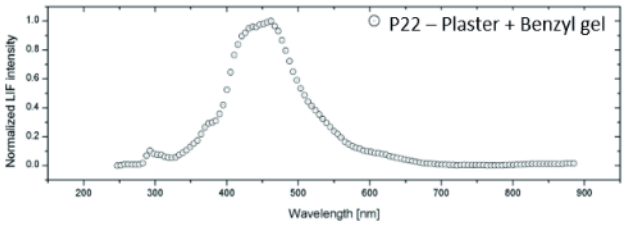

P17 – Naples Yellow
Normalized LIF intensity
Wavelength [nm]

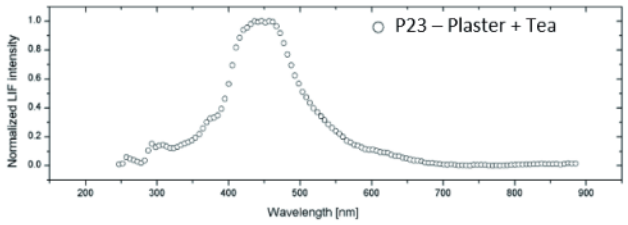

P18 – Malachite
Normalized LIF intensity
Wavelength [nm]

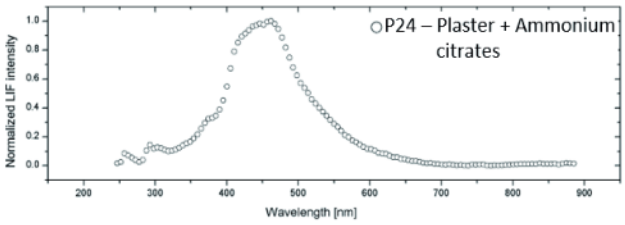

P19 – Manganese Black
Normalized LIF intensity
Wavelength [nm]

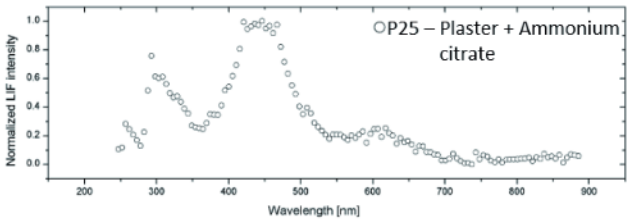

P20 – Ivory Black
Normalized LIF intensity
Wavelength [nm]

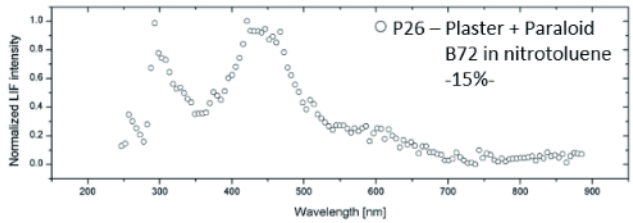

P21 – Cinnabar
Normalized LIF intensity
Wavelength [nm]

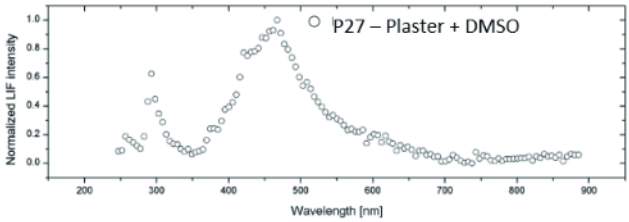

P22 – Plaster + Benzyl gel
Normalized LIF intensity
Wavelength [nm]

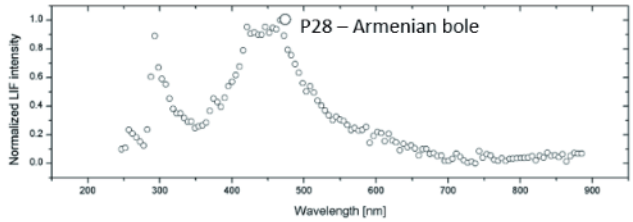

P23 – Plaster + Tea
Normalized LIF intensity
Wavelength [nm]

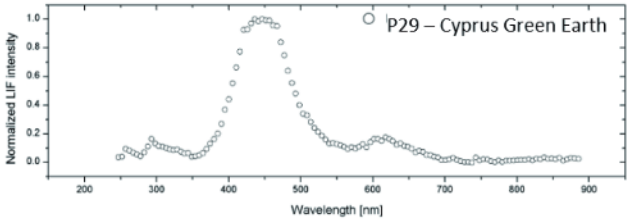

P24 – Plaster + Ammonium citrates
Normalized LIF intensity
Wavelength [nm]

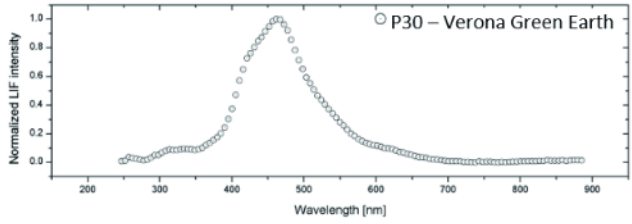

P25 – Plaster + Ammonium citrate
Normalized LIF intensity
Wavelength [nm]

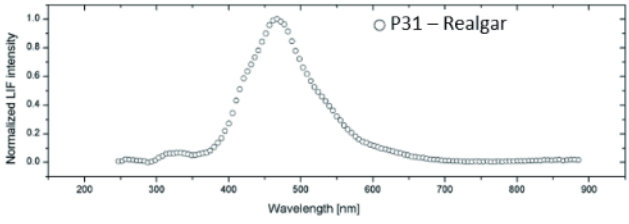

P26 – Plaster + Paraloid B72 in nitrotoluene -15%-
Normalized LIF intensity
Wavelength [nm]

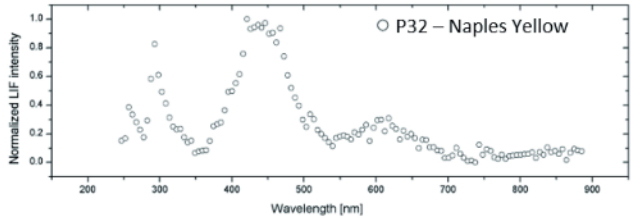

P27 – Plaster + DMSO
Normalized LIF intensity
Wavelength [nm]

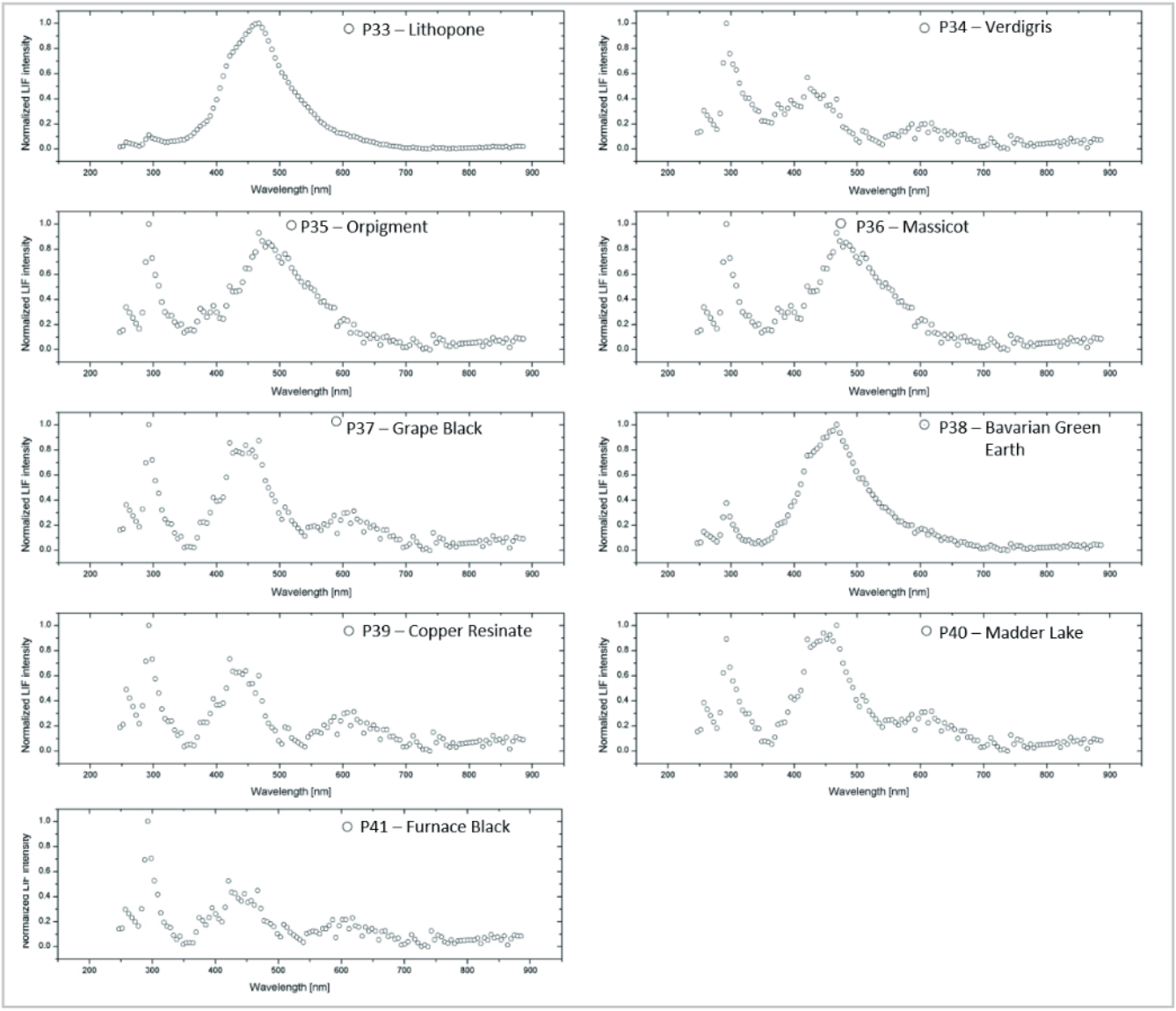

P28 – Armenian bole
Normalized LIF intensity
Wavelength [nm]


P29 – Cyprus Green Earth
Normalized LIF intensity
Wavelength [nm]


P30 – Verona Green Earth
Normalized LIF intensity
Wavelength [nm]


P31 – Realgar
Normalized LIF intensity
Wavelength [nm]


P32 – Naples Yellow
Normalized LIF intensity
Wavelength [nm]



Author/s

María Auxiliadora Gómez-Morón
mariaa.gomez.moron@juntadeandalucia.es
Instituto Andaluz del Patrimonio Histórico (IAPH), Seville, Spain

BSc Chemistry 1989-1994 and Master "Quimilaser. Laser application in Chemistry" 2012 (University of Sevilla). Member, since 2016, of the project "Art-Risk (Artificial Intelligence applied to preventive conservation of heritage buildings)" to investigate and develop a new computerized tool for preventive conservation of heritage in urban centres based on models of artificial intelligence. Art-Risk will be available to organizations and companies dedicated to the restoration and rehabilitation. Member, since 1995, of the research group "Remote Sensing and Geochemistry", with long-term experience in the research line in Archaeometry. Socrates grant at the University la Sapienza, where she worked in the project "Testaccio" (1999). An 18 months training grant at the IAPH (Andalusian Institution for Historical Heritage), from 1.11.1999 to 30.4.2001. A grant for conservation and restoration of cultural heritage at the Institution for Spanish Historical Heritage (2001). Since 2001, she works at IAPH (Andalusian Institution for Historical Heritage), where she takes part in projects such as Giraldillo's restoration and is responsible of the project for application of non-destructive analytical techniques for Historical Heritage. Part time professor at University Pablo de Olavide (Sevilla) since 2009, where she has taught three editions of the on-line course of non-destructive analytical techniques for Historical Heritage.

Rocío Ortiz
rortcal@upo.es
Department Physical, Chemical and Natural Systems, University Pablo de Olavide, Seville, Spain

Graduated in Architecture in 2001, she obtained a Master's degree in Protection of Built Heritage with a project oriented to a case study in Marchena in 2012. In 2014 she earned a Ph.D with European mention in University Pablo de Olavide (Seville).

She is currently working as Professor at the UPO, where she develops research focus on the fields of: Preventive Conservation; Risks and Vulnerability of Patrimony She is also director of the Mater in Diagnosis of the state of preservation of Cutural Heritage and is responsible of the area of crystallography and mineralogy of the same University. Dr. Ortiz's expertise is in diagnosis of Cultural Heritage, management, e-learning, and her scientific works appeared in 30 books, conference proceedings, and journals. Her research projects have been supported by the European Union, national and regional governments, and private organizations. Dr. Ortiz's research interests have focused on risk and vulnerability of Cultural Heritage, GI applied to Cultural Heritage studies, Construction materials, Urban Planning and hazards and innovation in science teaching with the emphasis on cultural heritage diagnosis

Franceso Colao
francesco.colao@enea.it
Department for Fusion and Nuclear Safety Technologies, Division Physical Technologies for Security and Health, ENEA, Frascati, Italy

Specialist in laser applications, signal processing and data acquisition, current interests concern the development of fluorescence lidar for the analysis of pigments, binders and consolidants. Since 1987 he is researcher at ENEA, carrying out research in design and development of remote sensing laser-based systems for atmospheric studies. Known expert in the field of laser spectroscopy and diagnostics, including lidar for atmospheric studies, Raman spectroscopy, visible/UV emission spectroscopy, Laser Induced Fluorescence (LIF). He gained large experience of remote sensing systems for different applications: environmental control of pollutants, and remote diagnostic in the field of cultural heritage. Currently the main activities in the latter field are related to the development of fluorescence lidar, used to monitor the water quality (chemical and biochemical pollution) and the vegetation health (both on phytoplankton species and on green plants), cultural heritage (analysis of pigments, binders and consolidants), application of laser induced breakdown spectroscopy (LIBS) and lidar remote sensing of the statosphere. He was involved in the study of LIBS and its application to the field of laser matter interaction and monitoring of soil and water. He has been responsible for several research projects, among these it is worth of mention the followings: application of LIBS to identification of asbestos' fibres in environmental samples (ISPESL programme 2003-04), development of a LIBS system for extraterrestrial soil analysis (ASI programme 2001-02), study of polar stratospheric clouds by lidar remote sensing (2006, 2017-19), development of a LIBS system for use in hostile environment (MURST programme 2004-07) , development of an integrated system for drug discovery by laser spectroscopy (CUSTOM – EU FP7 2010-2012), development of LIF system for forensic investigation (FORLAB– EU FP7 2011-2013), development of standoff Raman system for prompt identification of explosive substances (NATO project RADEX 2014-16, EXTRAS 2018-20). He has been tutoring of thesis and has given lectures to universities and research centers. The results of his researches have been presented at international conferences and published in peer review journals in more than fifty regulars.

Roberta Fantoni
roberta.fantoni@enea.it
Department for Fusion and Nuclear Safety Technologies, Division Physical Technologies for Security and Health, ENEA, Frascati, Italy

Dr. Roberta Fantoni is the head of the division "Technology Applications for Security and Health" at Fusion and Technology for Nuclear Safety and Security (ENEA). Her role is to coordinate researches in the field of development of applications of ionizing and non-ionizing radiations, including processes and diagnostics based on lasers and particles (electrons, protons) beams for the Industry, Environment, Cultural Heritage and Bio-medicine, and Micro-Nanotechnology. After a degree in chemistry she became a specialist in optoelectronics dealing with laser applications. She is a known expert in the field of laser spectroscopy and diagnostics. Major activities concern applications of the spectroscopic techniques as on-line diagnostics during different process. Recently she coordinated the regional project COBRA dedicated to innovation and technology transfer in Cultural Heritage conservation. Author of 164 scientific papers of peer review papers and 25 book chapters in the field of spectroscopy and laser applications.

Javier Becerra
jbeclun@upo.es
Department Physical, Chemical and Natural Systems, University Pablo de Olavide, Seville, Spain

PhD in History and Humanities: Europe, America, Arts and Language, degree in Conservation and Restoration and MSc Diagnosis of the State of Preservation of the Historical Heritage. Now, Javier is researcher at the Pablo de Olavide University in Seville, Spain. His research activity has focused on a) studies of new conservation-restoration treatments, especially based on nanomaterials b) vulnerability and risk studies in cultural heritage and c) diagnosis, analytical techniques and interventions in cultural heritage. This scientific production has resulted in a patent, 15 journal publications (10 in high impact indexed journals) and 12 book chapters. The results of the investigations carried out have been presented at 10 international conferences with a total of 18 communications. He has collaborated in the diagnosis of samples from national and international monuments (Villa Adriana in Rome, Medina Azahara, archaeological museum of Écija, churches in Seville, contemporary buildings in La Havana, historical buildings

in Oxford and Panama City, etc.) and has participated in analytical reports of national and international artworks requested from institutions such as the Andalusian Institute of Historical Heritage or the Pablo de Olavide University. Finally, his research activity has been recognized with different awards at national and international level.

Pilar Ortiz
mportcal@upo.es
Department Physical, Chemical and Natural Systems, University Pablo de Olavide, Seville, Spain

The research and teaching experience developed has been focused on the diagnosis, preservation and conservation of cultural heritage. For this task, she has collaborated with museums and cultural institutions, such as the IVCR+i, IAPH, Cádiz Museum, Écija Museum, etc. Additionally, I have developed works related to cultural heritage issues in several countries, i.e., the United Kingdom, Belgium, Italy, Romania, Cuba, Peru, Colombia, Panama, etc. Her scientific production can be summarized in 38 publications on indexed journals; 50 books and book chapters, more than 25 attendances to international congresses, chairman and member of scientific committee in several international congresses, etc. She has worked at the University of Amberes (Belgium) as assistant lecturer, invited professor at the University of Oxford (UK), and invited researcher at ENEA (Italy). She has participated in 24 national and international projects, contracts and agreements and has the head researcher in 16 of those projects, highlighting a Project of Excellence of the Junta de Andalucía, a RETOS project of the Government of Spain, an International Cooperation project of the Junta de Andalucía and International Erasmus+. She has opened and leadership important research lines as the application of Lasers techniques for in situ diagnosis in cultural heritage materials, the development of non-destructive techniques for diagnosis of cultural heritage, or the application of risk maps, vulnerability index and artificial intelligence to the preventive conservation of cultural heritage. Dr. Ortiz is member of the International Excellency Campus of the University of Jaén in cultural and natural heritage, of the "Cambio" work group in the International Excellency Campus of the Pablo de Olavide University (UPO), of the Andalusian Council of Cultural Heritage and Dean of the faculty of Experimental Sciences of the UPO.