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REPORT ON LIF MEASUREMENTS IN SEVILLE PART 2: SANTA ANA CHURCH

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Abstract
A scientific cooperation between ENEA UTAPRAD (Frascati) and the Natural Sciences Department of the "Pablo de Olavide" University in Seville, has started aimed at developing and testing innovative diagnostic instrumentation for Cultural Heritage preservation.
Here we report the results obtained in a joint campaign carried on in Seville during February 2010 in the Santa Ana church in Seville (SP). Several wood paintings have been thoroughly investigated by means of Laser Induced Fluorescence scan system along the lines of the Research Project "Non Destructive Techniques" managed by IAPH (Consejería de Cultura de la Junta de Andalucía).The field activities, developed as part of a conservation project carried out by IPAH, were devoted to the determination of retouches, traces of former restorations and detection of chemicals (wax, consolidants, etc.) on the surface under analysis not otherwise documented.

Key words: *Laser Induced Fluorescence, consolidant identification, chemical residuals on painted wood*

RAPPORTO SULLE MISURAZIONI LIF A SIVIGLIA. PARTE 2: CHIESA DI SANTA ANA

Riassunto
Nell'ambito di una collaborazione scientifica fra ENEA UTAPRAD e il Dip. di Scienze Naturali dell'Università di Siviglia "Pablo de Olavide", volta allo sviluppo e alla sperimentazione di strumentazione innovativa per la conservazione di Beni Culturali, si riportano qui i risultati ottenuti in una campagna congiunta eseguita a Siviglia nel febbraio del 2010; in particolare si illustrano i risultati ottenuti nelle scansioni eseguite all'interno della chiesa di Santa Ana su superfici lignee dipinte, nel corso del progetto di ricerca sulle tecnologie non distruttive diretto dallo IAPH, che ha incluso i presenti risultati nel suo progetto di conservazione. La tecnica impiegata ha consentito l'identificazione di aree ritoccate, di ritrovare segni di precedenti restauri (consolidanti) non altrimenti documentate e la rivelazione di sostanze chimiche (residui di cere) sulle superfici lignee esaminate.

Parole Chiave: fluorescenza indotta da laser LIF, identificazione di consolidanti, sostanze chimiche su legni dipinti

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REPORT ON LIF MEASUREMENTS IN SEVILLE. PART 2: SANTA ANA CHURCH

1. Introduction

Along a scientific cooperation already started in 2008 between the ENEA UTAPRAD (Frascati) and the University "Pablo de Olavide" Natural Sciences Department (Seville), aimed at developing and testing innovative diagnostic instrumentation for Cultural Heritage preservation, the first joint campaign with ENEA non destructive laser diagnostic tools has been carried on in February 2010. Specific aim of the campaign was to test remotely the performances of a recently developed LIF (Laser Induced Fluorescence) scanning system on real painted CH surfaces.

The test sites were in Seville, here some fresco's in Virgen del Buen Aire Chapel were selected, while in Santa Ana church wooden painted surfaces were examined. Santa Ana Church and Virgen del Buen Aire Chapel have been investigated along the Research Project of "Non destructive Techniques" managed by IAPH (Consejería de Cultura de la Junta de Andalucía). The experimental activities here reported have been also produced as part of results of a conservation project carried out by IPAH. This report deals with data collected on painted wooden artwork, where traces of former restoration (retouches and consolidants) and of pollution were searched for.

The Santa Ana church, sentimentally considered the Cathedral of Triana, is located in an ancient quarter of Seville on an island between two branches of the Guadalquivir. It was the first Catholic temple built in Seville after the end of Muslim rule in the city in 1248. Alfonso X ordered the beginning of the construction works in 1276. They were finished at the beginning of the 14th century. It is in gothic style although the construction material bricks give a mudejar style. Santa Ana church suffered various reforms, the most important one after the earthquake of Lisbon in 1755.

The building has been renovated recently to give back its original appearance. The interior of Santa Ana offers important artwork:

- the *main altar* and several sculptures from Nufro de Ortega and Nicolás de Jurate from around 1540,
- paintings of the *main altar* from Pedro de Campaña,
- the Stmo. Cristo del Socorro (*Christ*) by Andrés de Ocampo from 1620,
- the *lauda sepulcral* from D. Iñigo López in 1503.

2. Experimental Apparatus

A LIF scanning instrument capable to collect hyperspectral fluorescence images on large areas for applications to Cultural Heritage surfaces (e.g. fresco's, decorated facades, painted wood etc …) has been designed at the ENEA laboratory of Frascati. Based on previous experiences, the system was set up with the aim to increase the performances in terms of spatial resolution, the time resolved capabilities and reduce data acquisition speed.

Major achievements obtained by a critical review of the optical design and of the detector utilized are summarized as follows:

- the scan has been changed from point to line scan mode by using a quartz cylindrical lens and a imaging spectrograph (Horiba CP240);
- the linear array detector, responsible for the multichannel spectral resolution, is replaced with a square ICCD sensor (ANDOR iStar DH734, pixel size 13 μm), mounted behind a slit parallel to the laser line footprint.

This arrangement is characterized by having the spatial and spectral information on two mutually orthogonal directions imaged on the detector, with submillimetric spatial resolution and a spectral resolution better than 2 nm. Additionally time resolved measurements on the nanosecond scale can be performed by controlling the electronic detector gate in a boxcar like configuration.

The overall current system performances are horizontal resolution 640 pixel, 0.1 mrad angular resolution, minimum acquisition time per line 200 ms, FOV aperture 5.7° (corresponding to a scanned line of 2.5 m at 25 m distance). With the latter optics an image of 1.5×5 m is scanned in less than 2 minute at 25 m. The compact arrangement is shown in Figure 1.

The realized instrument is able to measure the spectral LIF signature characteristic for chemical compounds laying on the examined surface. The detection of the emitted fluorescence allows to identify different materials utilized, which is needed in planning any restoration action. Indeed LIF has the ability to reveal the occurrence of retouches, traces of former restorations and consolidants not otherwise reported in the documentation relevant to the artwork, and to identify extraneous materials onto the surface (degraded substances, pollutant, waxes, some kinds of biological attack such as microalgae and fungi).

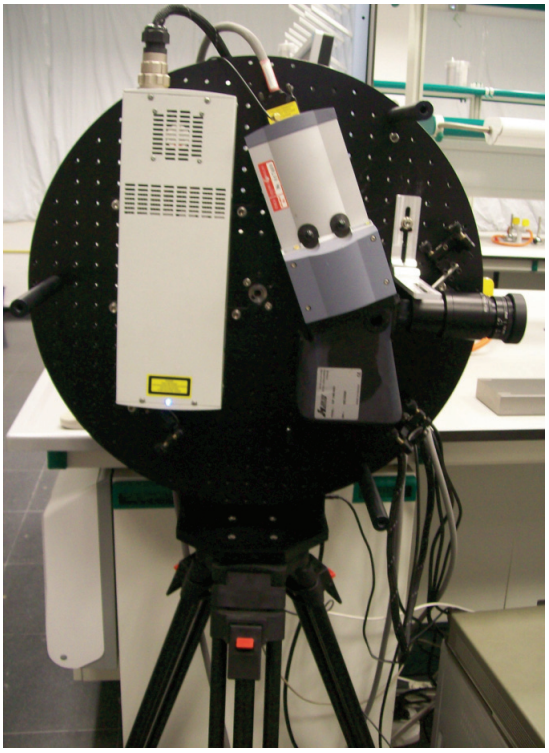

Figure 1 – Compact LIF line scanning, the vertical wheel is mounted on a tripod, vertical scanning is performed by mean of an accurate stepping motor on the back side of the wheel. Transmitting and receiving optics are in the front, the ICCD and the laser on the rear.

2.1 Operating modes

The different focal plane position for UV and VIS, caused by the use of refractive collecting optics make necessary to acquire successive scans, reading a different fluorescence wavelength range, each optimized for a different optical collection. In this way we can obtain a detecting efficiency and a spatial resolution uniform in all the very broad spectral detection interval. Moreover the system has been used for passive reflectance measurements by using a conventional continuous light emitted from a lamp.

During the measurement campaign here reported, the system was sequentially operated in three different modes:

1. the UV region from 250 to 450 nm, and laser on;
2. the VIS region from 450 to 700 nm and laser on;
3. the laser is switched off, a halogen/tungsten lamp is turned on and the optical detector shutter remains opened for a time needed to acquire a reflectance in the visible spectral range.

The latter operating mode permits to use the collected reflectance spectra for the computation of standard CIE/lab colorimetric measurement.

Data analysis

Relevant spectral features of LIF spectra are identified by Principal Component (PC) analysis. Although the PC loadings do not possess any direct physical meaning, they can conveniently be described in terms of bands; since the LIF spectra result from linear combination of PC with appropriate weights (scores), the presence of bands in PC may have a close correspondence on actual emission bands.

As shown in the analysis later reported, a given PC usually has well defined peaks and bands, while sometime exhibits complex shapes and frequent is the case of bands with opposite sign swing. The occurrence of bands in PC is here considered as an indication of the existence of a physical bands which will be searched for in the actual LIF spectra. Few of the PC components are usually considered for band analysis: typically 5 to 8 components are enough to describe the entire spectral data set.

In the present report the PC analysis is devoted to the identification of prominent spectral features, thus relieving from the time consuming examination of the acquired spectra. Advantages of this procedure can be found because it is fast and can run in a semiautomatic mode, however it has the inconvenience to give a global analysis, possibly ignoring those local peculiarities which do not possess enough statistical significance to be represented in the considered PC. To overcome this drawback a detailed local analysis is performed on subsets of the scanned areas, and the PC are analyzed separately. 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. Typical is the case of the localization of a given pigment: such task is accomplished either by a band analysis, or by using spectral mapper algorithms like SAM (Spectral Angle Mapper) or SCM (Spectral Correlation Mapper). Although the mapper algorithms perform well with a low computational cost, their performances are generally lower with respect to the band analysis procedures approach.

3. Santa Ana church

To evaluate the diagnostic potentiality of the hyperspectral LIF apparatus, several scans were performed in the San Ana Church (Seville - Spain) on painted wood of the iconostasis placed behind the main altar. Three different artworks were analyzed: (1) a portion of a decorated column (scans A2 to A8); (2) an angel serving as a basis for a wood pillar (scans A9 to A12), and (3) a representation of "*Telo della Veronica*" (scans A21 to A24). Details of the experimental conditions for each scan are reported in Tables T1 to T3.

Table T1 – Image acquisition settings for scans A2-A8

Scan #	A2	A3	A4	A5	A6	A7	A8
Gate	50 ns	1000 ms	1000 ms	1000 ms	200 ns	200 ns	50 ms
Gain	200	200	200	200	220	220	150
Laser current	100 A	100 A	100 A	100 A	100A	100 A	OFF
Halogen lamp	OFF	OFF	OFF	OFF	OFF	OFF	500 W
Optical f#	2.8	2.8	2.8	2.8	2.8	2.8	22
Spectral focus	UV	VIS-IR	VIS	VIS-IR	UV	UV	VIS
Background	Y	Y	Y	Y	Y	Y	Y
Lines	120	120	120	250	250	250	250
Scan width	256	256	256	256	256	256	256
Distance	3.2 m	3.2 m	3.2 m	3.2 m	3.2 m	3.2 m	3.2 m
Notes	LIF image	LIF image	LIF image Average on 5 laser shots	LIF image	LIF image NO spectral corr. NO bgnd corr.	LIF image Delay 119.25 μs	Reflectance image

Portion of the wood painted backstage of the St. Ana altar. The scanned area is framed by a red line. Real dimensions are approximately 30 cm × 50 cm, image size is 128 × 250 pixels. Left side was not treated, right side was cleaned in by IAPH restorers

Table T2 – Image acquisition settings for scans A9-A12

Scan #	A9	A10	A12	A12_IR
Gate	50 ms	200 ns	1000 ms	1000 ms
Gain	150	200	200	200
Laser current	100 A	100A	100A	100A
Halogen lamp	500 W	OFF	OFF	OFF
Optical f#	2.8	2.8	22	22
Spectral focus	VIS	VIS	UV	VIS-IR
Background	Y	Y	Y	Y
Lines	120	120	120	120
Scan width	256	256	256	256
Distance	3.5 m	3.5 m	3.5 m	3.5 m
Notes	Reflect. image	LIF image	LIF image	LIF image

Portion of the wood painted decoration in the St. Ana church with delimitation of the scanned area. Real dimensions are approximately 30 cm × 25 cm, image size is 128 × 120 pixels.

Table T3 – Image acquisition settings for scans A21-A24

Scan #	A21	A22	A23 UV	A23_IR	A24
Gate	1000 ms	1000 ms	200 ns	200 ns	1000 ms
Gain	220	220	220	200	220
Laser current	100 A	100 A	100 A	100 A	100 A
Halogen lamp	OFF	OFF	OFF	OFF	OFF
Optical f#	2.8	2.8	2.8	2.8	2.8
Spectral focus	VIS	VIS	UV	VIS-IR	UV
Background	Y	Y	Y	Y	Y
Lines	120	120	120	120	120
Scan width	256	256	256	256	256
Distance	6.5 m	6.5 m	6.5 m	6.5 m	6.5 m
Notes	Reflect. image	Reflect. image	LIF image	LIF image	LIF image Erratic Bgnd

Portion of the wood painted backstage of the St. Ana altar with delimitation of the scanned area. Real dimensions are approximately 35 cm × 45 cm, image size is 128 × 300 pixels.

3.1 Analysis of scans A2 – A8

A portion of a decorated wall was used to demonstrate the capabilities of LIF analysis on painted wood. As far as we know the sample under study was made during the XVI century and gave us the opportunity to analyze the fluorescence induced by superficial painted layers. The LIF camera was

placed at 3.2 m distance from the target and the image was scanned with a spatial resolution of approximately 0.003 m. The scan size are 128 pixels width, 120 to 250 pixels height and 250 spectral channels from 250 nm to 800 nm.

Broadband reflectance image

Figure 2 shows a conventional photo of the scanned area a) and the image obtained by operating the sensor in reflectance mode b); the latter image represent the RGB combination of the emission's intensities of the spectral bands centred at 600, 500, and 400 nm respectively for the red, green and blue channels with a bandwidth of 10 nm. The dark and bright regions in Figure 2b correspond to the distinction between cleaned and not cleaned portion of the artwork: the not cleaned part is dominated by lower emission because both the incident light is partially absorbed and the reflectance is attenuated by the superficial layer.

Figure 2 – a) Conventional photo of the scanned fresco surface, b) RGB reconstruction from scan A8 reflectance image.

A close observation of Figure 2b reveals a partial fault on the actuator responsible for the scan movement: indeed in the upper part of the figure a regions is visible with lines vertically swiped. This kind of fault is present also in successive scans, however since the extent of the defective area is small it fortunately does not impair the intelligibility of the image it will be not further considered.

As already pointed out, we remark the twofold usefulness of reflectance image: on one hand it can be used to make a very precisely association between each pixels and their respective position on the actual scanned object (localization capability), on the other hand the use of a special light source, coupled with suitable image analysis data processing and proper calibration, results in spectrocolorimetric information, to complement the LIF diagnostic. The reflectance image is here used just to localize the spectral features measured by LIF technique.

Band identification in LIF spectra

To the purpose of band identification, a PCA is run on scans A2, A4 and A7; five components are considered for band analysis, since they are enough to faithfully describe the entire spectral data set (overall explained variance >85%). The scans A2 and A7 were made using a similar set-up for the receiving optics and are therefore similar; the difference found by comparing Figures 3a and 3c is due to a different setup of the receiving optics: indeed the scan A2 was perfectly focusing the emission in the region 200-350 nm, while in the A7 scan the optics focussed the region 300-500 nm. By contrast the Figure 3b shows the PC analysis when the receiving optics was focussing the 400-650 nm spectral region; the different spectral collection efficiency of these three scans explains the apparent shift towards the red spectral region. Radiometric calibration is necessary to get consistent spectral profiles, however if the analysis is limited to the examination of a single emission band or of a couple of bands not too far apart, we can safely neglect the spectral calibration.

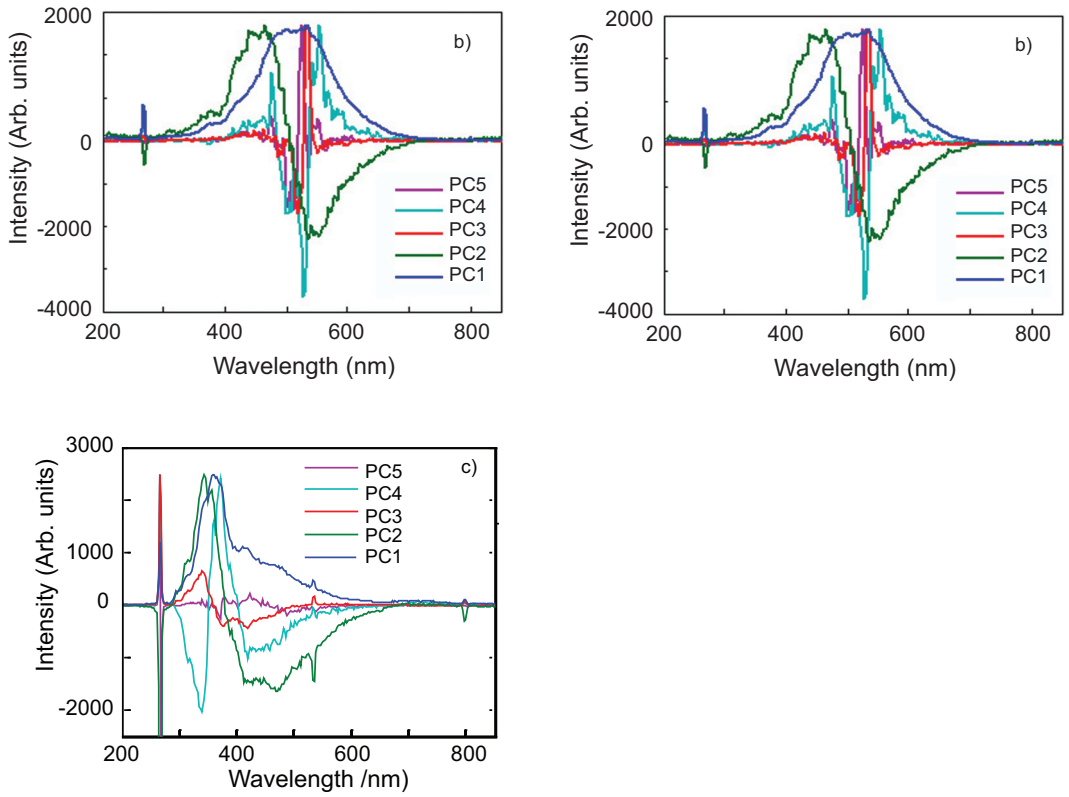

Figure 3 – a) Principal components on A2 scan; b) A4 scan, c) scan A7.

As explained in the previous section, the PC analysis is used to identify spectral prominent features: the observation of PC loadings in Figure 3 allows us to identify the candidates for physical emission bands as listed in Table 4. Once a band is identified, two processing steps are further pursued: firstly a false colour RGB image is built to simultaneously represent different spectral features (see Figures 4, 5 and 6); secondly the image process is refined by single band analysis, i.e. by representing the fluorescence intensity at a given wavelength (see Figures 7 and 9).

Table 4 - Prominent bands identification by means of PCA on scans A2 to A8 with a tentative band assignment

Band [nm]	Description
290-306	This emission bands center has 3464 cm^{-1} spectral shift; Wax, organic compounds
337-342	Dust, carbon layer
368-376	Bio contamination
414-419	Coloured pigment
455-468	Coloured pigment
525-553	Coloured pigment
595-622	Coloured pigment

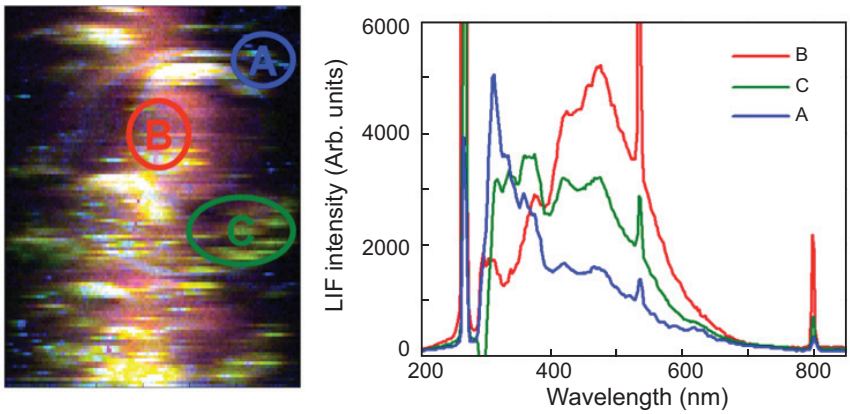

Figure 4 – False colour RGB images built using the bands identified by PC analysis on A2 scan with bands at 468, 380 and 293 nm.

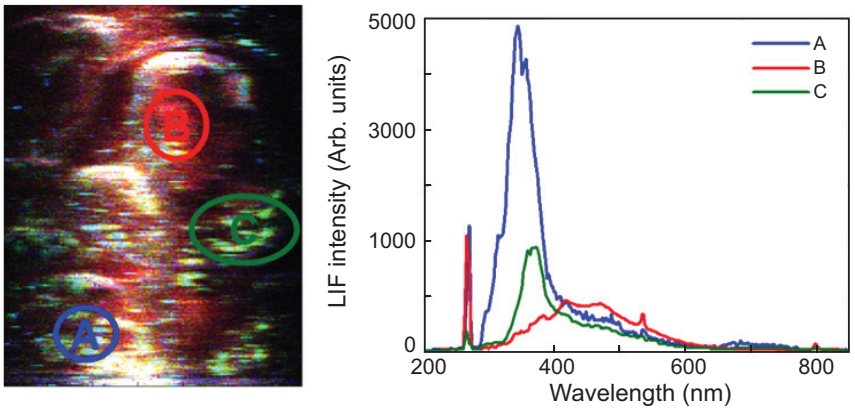

Figure 5 – False colour RGB images built using the bands identified by PC analysis on A7 scan with bands at 468, 380 and 320 nm.

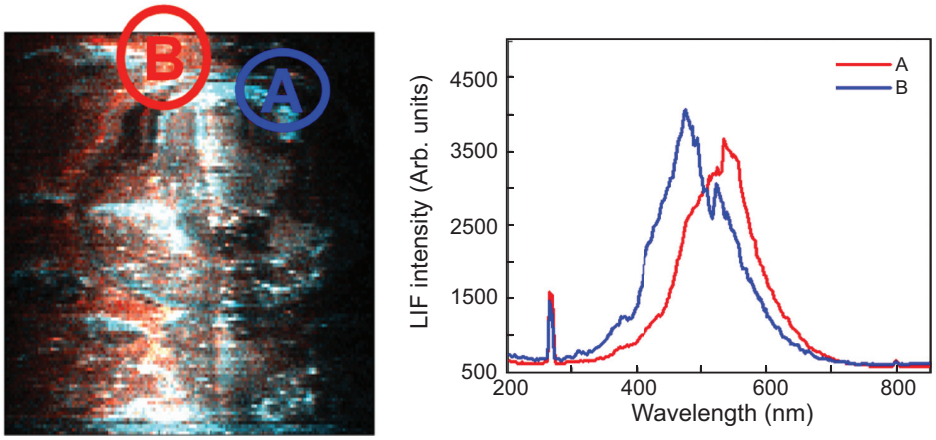

Figure 6 – False colour RGB images built using the bands identified by PC analysis on scan A4 with bands at 580, 460 and 350 nm.

In order to have a highly contrasted RGB image, we used a combination of the prominent bands found by Principal Components analysis; the result is shown in Figures 4 to 6. In spite of the different conditions for the acquisition of scans A2, A4 and A7, all of the images do exhibit a close appearance: as expected the Figures 4 and 5 are remarkably similar indeed the respective experimental set-up is only slightly different; on the other hand Figure 6 shows the largest distinction, still showing an high correlation with Figures 4 and 5.

The right part of Figures 4 to 6 shows the LIF spectra of selected regions, respectively marked with the letters A), B) and/or C). It is possible to observe the appearance of bands of similar relative intensity in the spectra taken in the same regions; a typical example are the spectra marked by letter A) in Figures 4 and 5, however it is also possible to observe a change in the relative intensity due to lack of radiometric calibration. To provide spectrally calibrated fluorescence data is a rather difficult task which can be approached by putting in the scanned area few targets with known spectral response.

As already observed the application of calibration procedure is not possible, however the band ratio analysis still retain a full validity because it is not affected by calibration by more than a dimensionless multiplicative constant, while not disturbing the information related to the spatial distribution of the observed features.

Figure 7 shows a detailed investigation of the fluorescence emission band at 300 nm (F300). Assuming that the band intensity is directly related to the amount of the fluorescent compound per unit area (g/m^2), the occurrences of high intensity emission are marked in dark grey, as shown in the left side of Figure 7b: it is worth noticing that this side corresponds to the not cleaned portion. To explain the observed feature we assume that the F300 band is likely due to smoke particles of candles used in holy functions and accumulated over the years.

The left side has not yet cleaned or treated, and consequently the effects of ageing, exposure to dust deposition is considered responsible for darkening of the colours: this is why this side appears brown.

The points having very high fluorescence in the F300 band are concentrated on the left part of the scanned area, suggesting a relation with superficial organic deposit and aromatic compounds; nevertheless also in the right cleaned portion of the scanned area some regions still have high fluorescence intensity, documenting the impossibility to completely remove the dust traces during the cleaning process. It is interesting to notice that the occurrence of this spots is mainly concentrated on areas with dark colours, as for example in the case of the main character hairs or along the decoration around his face.

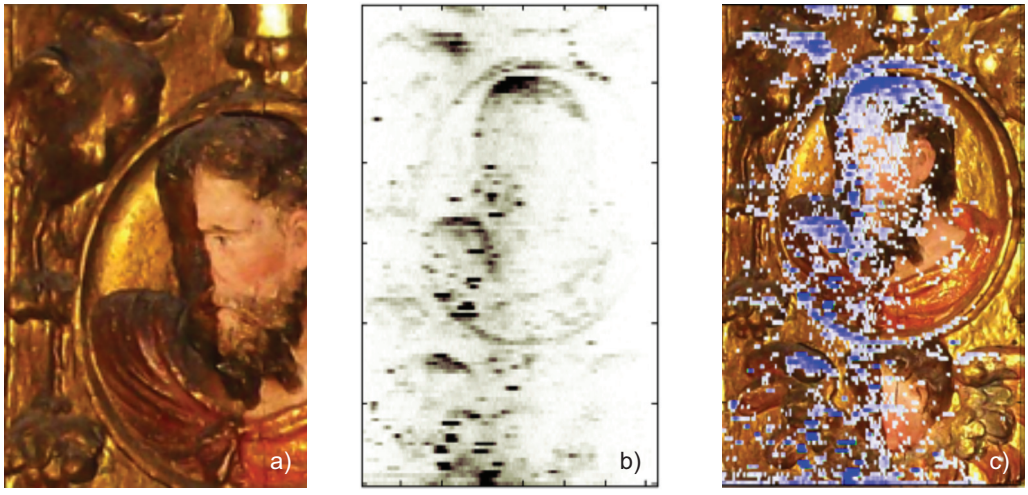

Figure 7 – a) Conventional photos of the analyzed area; b) Image A2 band analysis: the F300 band computed with a bandwidth of 10 nm. Grey levels are used to quantitatively indicate the band intensity; c) The superposition of images a) and b) allows for an easy identification of those portion of the scanned area which are dominated by high intensity on F300 nm band.

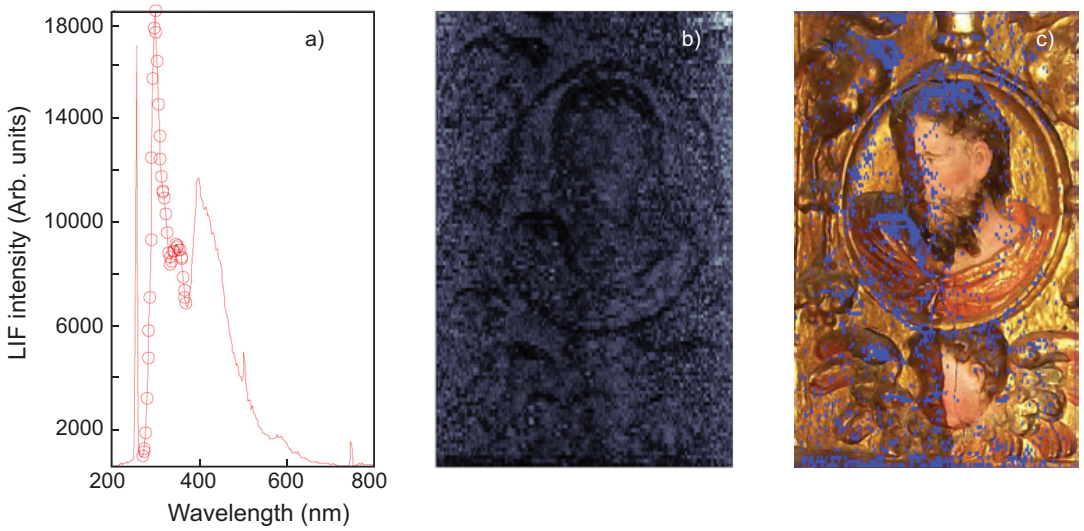

Figure 8 – Image A2 SAM analysis: a) the reference spectrum for the SAM algorithm is the region 270 to 370 nm; b) SAM image c) the SAM image compared with a threshold level 0.17 is superimposed with conventional photo to give evidence of the areas with high similarity with the elected reference spectrum.

The diagnostic capabilities of the LIF are here well exemplified. Actually the conservative treatment was made by visual inspection by skilled restorers; in all the areas characterized by bright colours (e.g. on the main character face and on the little angel face as well) the removal of the superficial dust and contaminants has completed in an optimal way. It was almost complete giving back to the artwork its original contrast by deeply removing dust and wax traces; the counterpart on the LIF signal can be appreciated by observing a strong reduction of the fluorescence emission; however in regions characterized by dark colours (e.g. in the hair, at upper portion of the head) the cleaning has to be softer, because of the roughness of the hair and of the dark colour, these two properties do not allow to differentiate the original part from the dirtiness. As a consequence LIF signal is significantly higher due to dust traces; it is worth notice that it is a common practice to limit the restorer intervention to the minimum on areas not requiring a thorough cleaning.

A different kind of image analysis can be based on the assumption that similarly treated regions do exhibit alike spectral features, therefore the problem of the localization of surface treatment is bring back to the search of spectral similarity. Special techniques have been devised in literature to approach the related problems; here we consider the Spectral Angle Mapper which is based on the computation of the angle between two vectors the first one representing a reference spectrum and a second one corresponding to the spectrum in each point of the scanned area. An interesting result is shown in Figures 8 and 9. In the first case we look for spectral similarity of the F300 band in the UV region, while in the second similarity of the bands in 370 nm – 490 spectral region is sought.

Figure 8a shows the spectrum used as reference endpoint; part b) of the figure reports the SAM

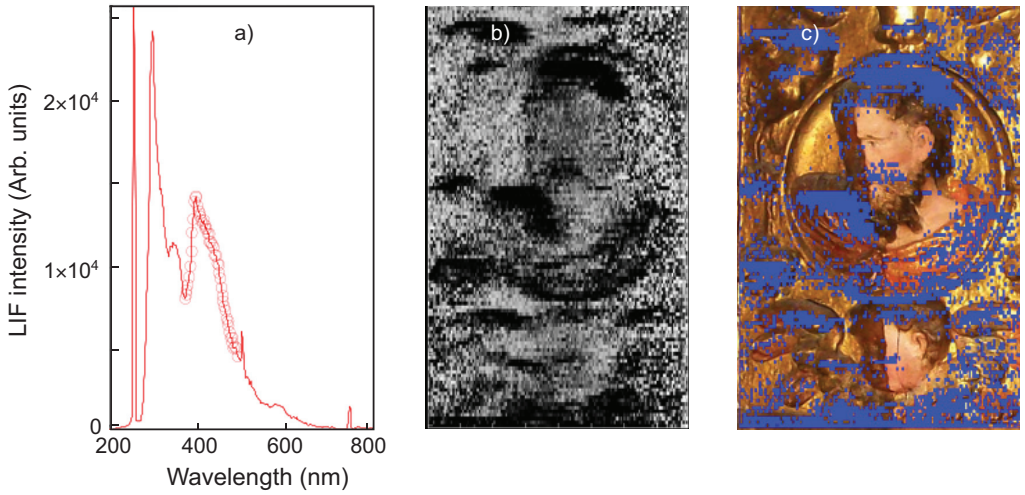

Figure 9 – Image A2 SAM analysis: a) the reference spectrum for the SAM algorithm is the region 370 to 490 nm; b) SAM image; c) the SAM image compared with a threshold level 0.17 is superimposed with conventional photo to give evidence of the areas with high similarity with the selected reference spectrum.

mapping as a grey level image, while in part c) the SAM is transformed in a binary image with a threshold level 0.17, it is given a blue colour and then it is superimposed with the conventional photo to give evidence of the areas with high spectral similarity with the selected reference endpoint. As expected the regions identified by SAM are mainly located in the not cleaned side of the figure and on the indented parts. Indeed in these areas, traces of dust and/or superficial treatments are expected to have higher consistency for the reasons explained before.

As soon as we put our attention in a different spectral region, the SAM analysis gives an alternative view of the same scan as shown in Figure 9. Here the blue region of the spectrum is taken into account since it is expected to be responsible for the fluorescent emission of superficial dust.

Figure 9a shows the spectrum used as reference endpoint; part b) of the figure reports the SAM mapping as a grey level image, while in part c) the SAM is transformed in a binary image with a threshold level 0.17, it is given a blue colour and then it is superimposed with the conventional photo.

Small correlation between images of Figures 8b and 9b can be appreciated, suggesting an independent feature with respect to the previous one.

This experimental finding allows us to conclude that while the band F300 can be related to the presence of wax or other chemical on the surface, the blue region of the spectrum can be associated to superficial dust.

3.2 Analysis of scans A9 – A12

The target for the scans A9 to A12 is a portion of a wood paint decoration. As far as we know the sample under study was made during the XVIII century, giving us the opportunity to analyze the

fluorescence induced by superficial painted layers, and to compare the spectral response with those obtained by the fragments analyzed in the previous section. The LIF hyperspectral sensor was placed at 3.5 m distance from the target and the image was scanned with a spatial resolution of approximately 0.003 m. The scan size are 128 pixels width, 120 to 250 pixels height and 250 spectral channels ranging from 250 nm to 800 nm.

Broadband reflectance image

Figure 10 shows a conventional photo of the scanned area a) and the image obtained by operating the sensor in reflectance mode b); the latter image represent the RGB combination of the emission's intensities of the spectral bands centred at 600, 500, and 400 nm respectively for the red, green and blue channels with a bandwidth of 10 nm.

As previously observed also Figure 10b reveals a partial fault on the actuator responsible for the scan movement, as evidenced by the vertically swiped lines in the lower part of the image.

Again we remark the twofold usefulness of reflectance image: to localize pixels' position on the actual scanned object and to have a spectrocolorimetric information complementary to the fluorescence diagnostic. The reflectance image is here used just to localize the spectral features measured by LIF technique.

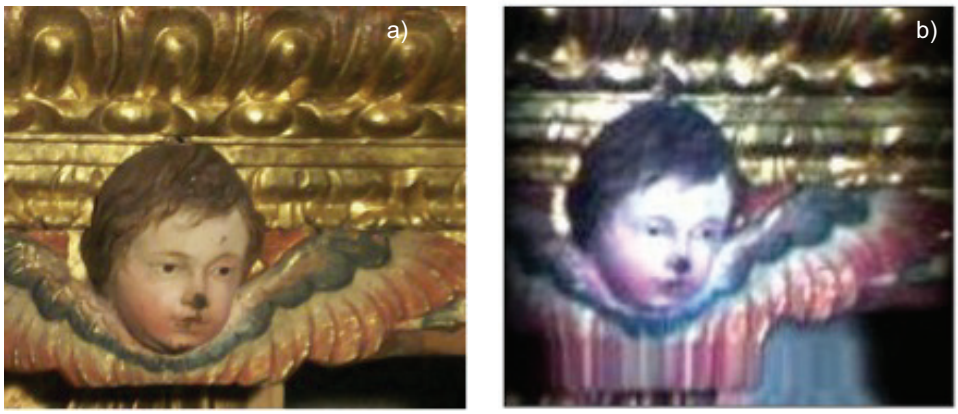

Figure 10 – a) Conventional photo of the scanned fresco surface, b) RGB reconstruction from reflectance image with spectral channel at 600 nm, 500 nm, 400 nm.

Band identification in LIF spectra

To the purpose of band identification, a PCA is run on scans A12_IR and A12 respectively for the visible and UV spectral region, as shown in Figure 11; five components are considered, since they are able to faithfully describe the entire spectral data set (overall explained variance > 85%). During the scan A12 the optical receiver was focusing the emission in the region 300-500 nm, while during A12_IR scan the optics focussed the region 400-650nm; in the latter case we observe a shift towards the red spectral region (see Figure 11b).

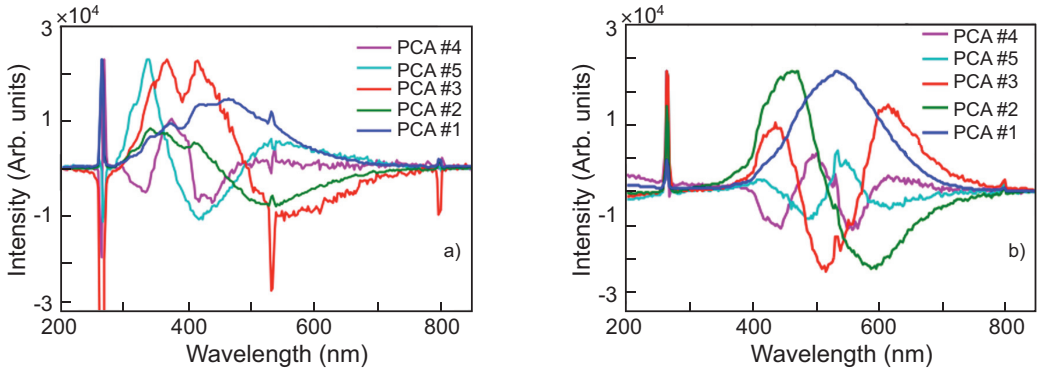

Figure 11 – a) PCA components for A12 scan, b) PCA components for A12_IR scan.

Prominent bands on scans A9 to A12 are the same as those reported in Table 4, with the noticeable exception of the band centred at 290-300nm, since only a small shoulder is now appreciated. To explain the missing of the F300, we consider that, with respect to the sample examined in the previous section, here the cleaning actions possibly resulted in a better removal of superficial layers due to smoother surface. Moreover the position of this item in St.Ana church was different causing a reduced exposition to candles' smoke and to the deposit of ashes and/or dust.

Highly contrasted RGB images are obtained by suitable combinations of the prominent fluorescence emissions; the result is shown in Figures 12a and 12b, where a clear separation appears among areas dominated by independent bands. In spite of the different conditions for the acquisition we notice that images 12a and 12b do exhibit a close appearance.

To further proceed with the spectral analysis, a band analysis is performed by computing the intensity of the specific emission at 340 nm with 10 nm bandwidth. Figure 13a) shows the typical LIF spectrum

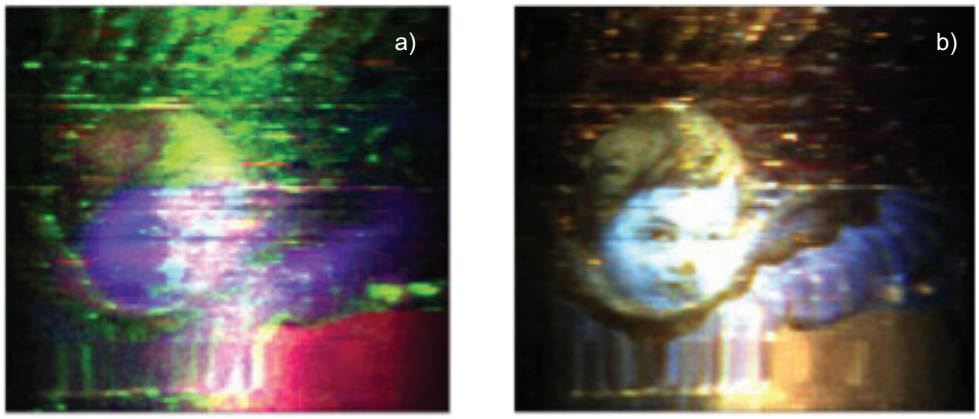

Figure 12 – a) RBG false colour reconstruction from LIF emission at 420, 340 and 550 nm for A12_UV scan; a clear separation appears among areas dominated by independent bands. b) RBG false colour reconstruction from LIF emission at 420, 480 and 580 nm for A12_IR scan; a clear separation appears among areas dominated by independent bands.

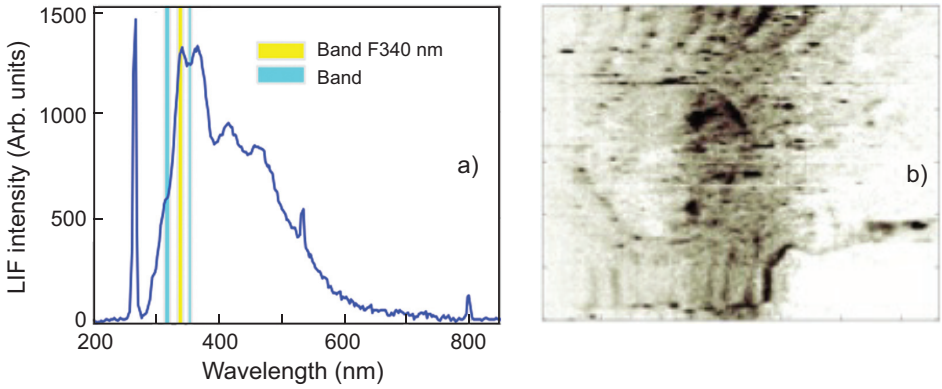

Figure 13 – Typical LIF emission spectrum in areas dominated by F340 band a); background corrected LIF intensity image of the band at F340 b).

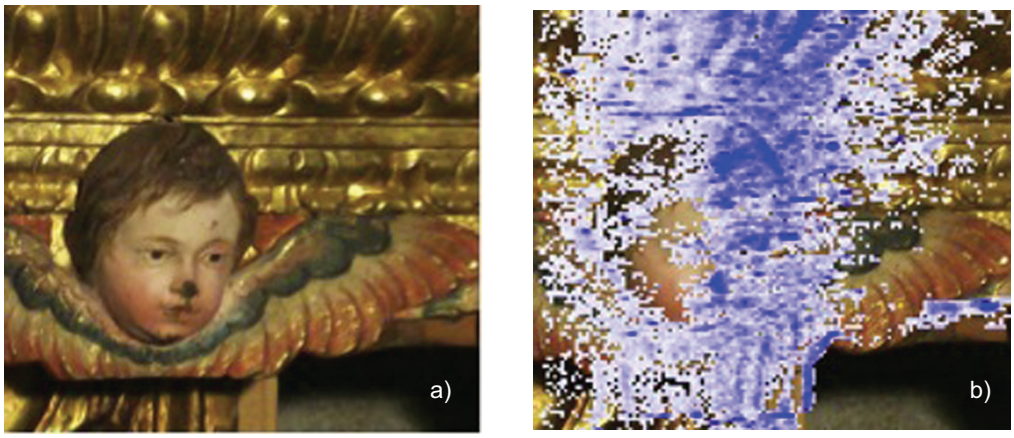

Figure 14 – Superposition of LIF image of the intensity emission band F330 (background corrected), with the conventional photograph.

in areas dominated by the F330 nm band, while in right side we report the fluorescence intensity emission in grey scale. The band analysis is performed in two successive steps: in the first the emission intensity of the selected band is computed, then the contributions from the left tail of the adjacent band at 360 nm is evaluated and subtracted.

It is worth notice some interesting differences with the previous scans; indeed here the fluorescence intensity has smoother spatial variations and is no more changing abruptly in different portions of the scan. This observation allow us to conclude that the cleaning has completed leaving only minor and often negligible traces of superficial deposits and dust.

A precise localization of those areas exhibiting stronger fluorescence is obtained by a superposition with a conventional photograph; the result is shown in Figure 14. To facilitate the comparison the left side (Figure 14a) shows the conventional photograph, while the superposition is shown in the right side (Figure 14b).

3.3 Analysis of scans A21 – A24

The target for the scans A21 to A24 is a portion of a wood paint scene representing the "*telo della Veronica*". This sample gives us further opportunity to analyze the fluorescence induced on superficial painted layers, and to compare the spectral response with those obtained by the fragments analyzed in the previous sections.

As in the first scan set, we have here the simultaneous presence of cleaned and not cleaned portion, thus facilitating the identification of peculiar fluorescence bands in the analysis.

The LIF camera was placed at 6.5 m distance from the target and the image was scanned with a spatial resolution of approximately 0.003 m. The scan size are 128 pixels width, 120 to 250 pixels height and 250 spectral channels ranging from 250 nm to 800 nm.

Broadband reflectance image

Figure 15 shows a conventional photo of the scanned area a) and the image obtained by operating the sensor in reflectance mode b); the latter image represent the RGB combination of the emission's intensities of the spectral bands centred at 600, 500, and 400 nm respectively for the red, green and blue channels with a bandwidth of 10 nm.

Figure 15 – a) Conventional photo of the scanned a wood paint surface, b) RGB reconstruction from reflectance image with spectral channel at 600 nm, 500 nm, 400 nm.

Band identification in LIF spectra

To the purpose of band identification, a PCA is run on scans A23_UV and A23_IR as reported in Figure16; five components are enough to describe the entire spectral data set (overall explained variance >85%). The two scans were made by slightly changing the receiver optics: A23_UV was made by focusing the spectral region 200-350 nm, while in A23_IR scan the receiving optics focussed the region 300-500 nm. By contrast comparing Figure 16 with Figures 3 and 11, we observe that the shift towards the red spectral region is here much less pronounced, as well exemplified by the first PC (blue line).

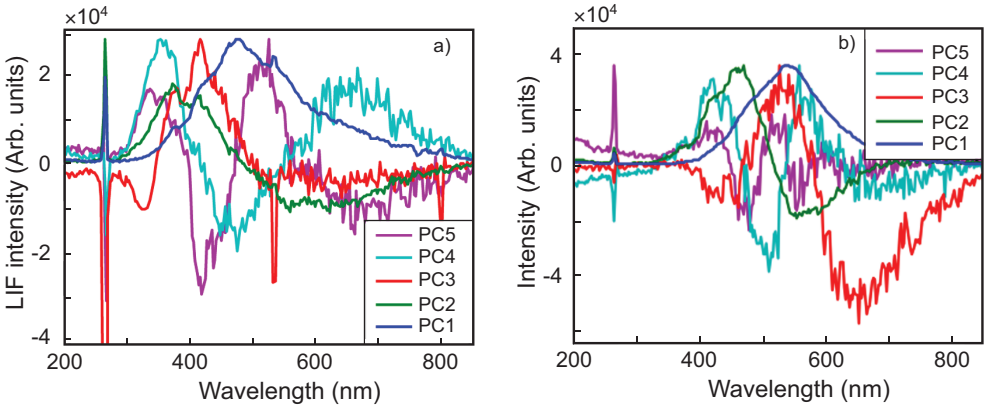

Figure 16 – a) PCA components for A23_UV scan, b) PCA components for A23_IR scan.

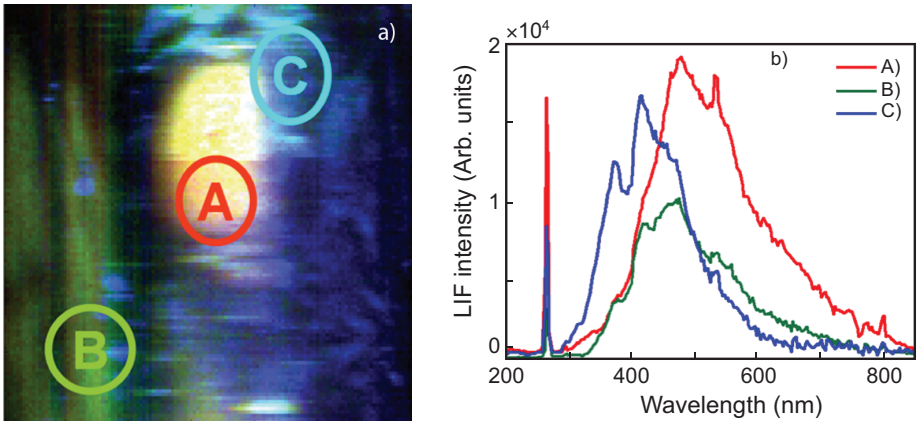

Figure 17 – False colour RGB images built using the bands identified by PC analysis on scan A23_UV with bands at 520, 420 and 340 nm (left side); typical spectrum with intense fluorescence are shown in right side.

From the analysis of the PC loadings it resulted that fluorescence bands are already listed in Table 4. No relevant emission was recorded for the spectral region at 300 nm; on the other hand the band at F340 nm is higher, although it is appreciable mainly in the not cleaned part of the scanned area. Indeed the band centred at 300 nm is hardly visible in the spectrum as documented by Figure 17 (red line spectrum in right side of the same figure). Furthermore the F340 band is higher and dominates all the bluish areas shown in part a) of the same figure; occasionally blue spots appear also in the cleaned part and mostly in indented parts, supporting the conclusion of an incomplete cleaning due to recesses found on the surface.

The superficial dust is assumed to be responsible for the observed band at 340-370 nm; to complete the diagnostic analysis of the scanned surfaces, band analysis and SAM are used for a precise localization of contaminated areas, the results are reported respectively in Figures 18 and 19.

Figure 18 shows the details of investigation of the fluorescence emission band at 340 nm (F340); with reference to the spectrum shown in the left side, we computed the intensity image representing increasing value of the fluorescence by increasing the bluish colour as shown in the right side of Figure 18b. As expected the band intensity is higher in the not cleaned portion of the scanned area.

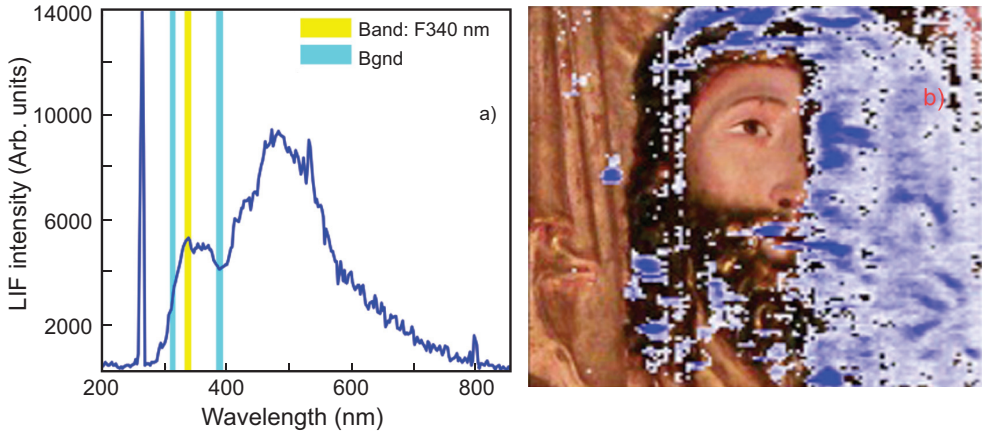

Figure 18 – Typical spectrum with intense fluorescence at 340 nm a), and b) superposition of a conventional photograph with the image of the background corrected fluorescence band at 340 nm.

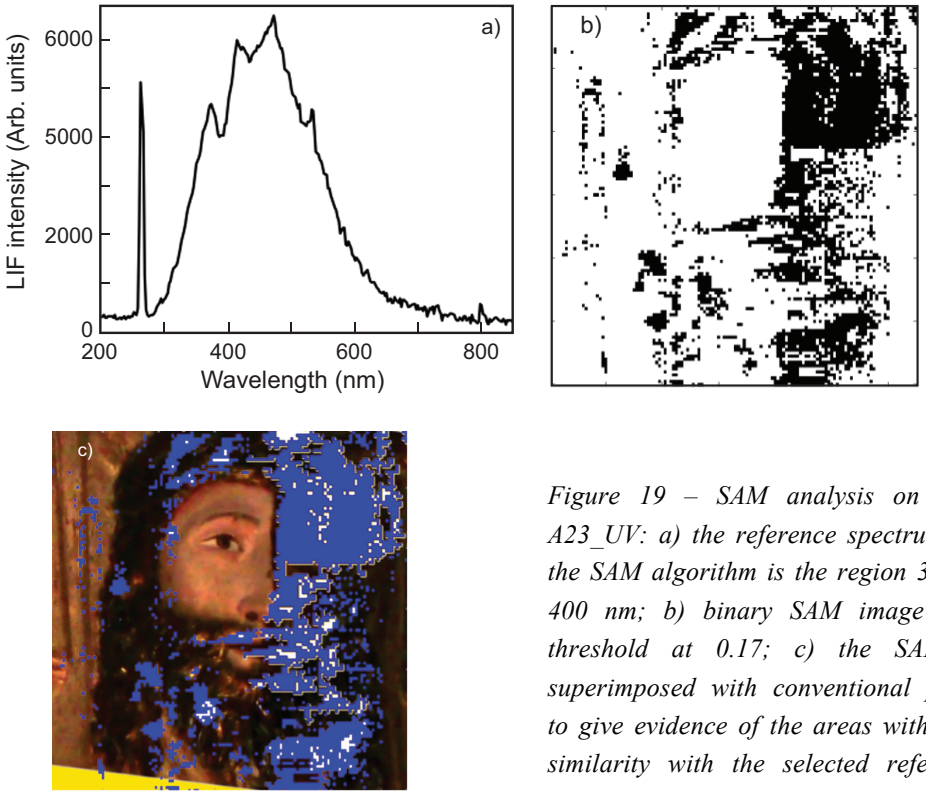

Figure 19 – SAM analysis on scan A23_UV: a) the reference spectrum for the SAM algorithm is the region 300 to 400 nm; b) binary SAM image with threshold at 0.17; c) the SAM is superimposed with conventional photo to give evidence of the areas with high similarity with the selected reference spectrum.

The SAM image analysis is shown in Figure 19, here we search for spectral similarity in 300-400 nm spectral region. Figure 19a) shows the spectrum used as reference endpoint; part b) of the figure reports the SAM mapping as a binary image obtained by using a threshold level of 0.17; finally in part c) the SAM is superimposed with the conventional photo to give evidence of the areas with high spectral similarity with the selected reference endpoint. As expected the regions identified by SAM are mainly located in the not cleaned side of the figure, as well as on the indented parts of the left side of the scanned region. As already pointed out in these areas the traces of dust and/or superficial treatments are expected to have higher consistency.

4. Conclusions

LIF analysis, although still qualitative, resulted to be a powerful tool to assist the restoration of painted wood surfaces exposed to different indoor contamination agents. To obtain quantitative results a twofold laboratory activity should be started, on one side by introducing a reliable calibration procedure, while on the other hand by building a reference database of spectral components uniquely and unambiguous assigned to reference materials. In that way data interpretation be supported by references for comparison, thus increasing the potentiality of the LIF technique as diagnostic tool in the field of cultural heritage conservation and restoration.

References

1. F. Colao, R. Fantoni, L. Fiorani, A. Palucci "Dispositivo portatile a fluorescenza per la scansione spaziale di superfici, in particolare nell'ambito dei beni culturali" Patent RM2007A000278 (2007)
2. L. Caneve, F. Colao, L. Fiorani, A. Palucci "Radar laser portatile per la diagnostica remota di superfici" Patent RM2010A000606 (2010)
3. F. Colao, L. Caneve, A. Palucci, R. Fantoni, L. Fiorani, Scanning hyperspectral lidar fluorosensor for fresco diagnostics in laboratory and field campaigns, Lasers in the Conservation of Artworks (LACONA VII), Ed.s J.Ruiz, R.Radvan, M.Oujja, M.Castillejo, P.Moreno, CRC Press, 149–155, (2008).
4. L. Caneve, F. Colao, R. Fantoni, L. Fornarini, Laser induced fluorescence analysis of acrylic resins used in conservation of cultural heritage, Proceedings of OSAV'2008, The 2nd Int. Topical Meeting on Optical Sensing and Artificial Vision, St. Petersburg, Russia, (2008) pp. 57- 63.
5. Borgia, R. Fantoni, C. Flamini, T.M. Di Palma, A. Giardini Guidoni, A. Mele, "Luminescence from pigments and resins for oil paintings induced by laser excitation", vol. 127-129, pp. 95-100 (1998).
6. F. Colao, L. Caneve, R. Fantoni, L. Fiorani, A. Palucci, "Scanning hyperspectral lidar fluorosensor for fresco diagnostics in laboratory and field campaigns," Lasers in the Conservation of Artworks –M.Castillejo et al. Eds.(2008) pp. 149-155.
7. D. Anglos, M. Solomidou, I. Zergioti, V. Zaffiropulos, T.G. Papazoglou, C. Fotakis, Laser-induced fluorescence in artwork diagnostics: an application in pigment analysis, Appl. Spectrosc. 50, (1996) pp.1331-1334.
8. F. Colao, R. Fantoni, L. Caneve, L. Fiorani, R. Dell'Erba, V. Fassina "Diagnostica superficiale non invasiva mediante fluorescenza indotta da laser (LIF)" sumitted for publication (in Italian).

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