

APPLICATION OF A SCANNING HYPERSPETRAL LIDAR FLUOROSENSOR TO FRESCO DIAGNOSTICS DURING THE CULTURE 2000 CAMPAIGN IN BUCOVINA

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Abstract

A hyperspectral system based on laser-induced fluorescence (LIF) has recently been developed for optical characterizations of surfaces relevant to cultural heritage. This paper describes its field application to frescos diagnostics during an international workshop and the related on-site laboratory held on July 2006 in Bucovina (Romania) within the European program CULTURE 2000. The scanning LIF system demonstrated its capability to supply valuable information on the considered frescos, which were under restoration; in particular, results relevant to biological attacks, current and former restoration methods, and realization techniques, were achieved.

Key words: physical diagnostics on cultural heritage, laser-induced fluorescence, scanning laser systems, frescos, biodeterioration.

1 Introduction

A complex of monasteries, included in the UNESCO World Heritage List [1], is located in Bucovina, Romanian region at the borders with Ukraine and Moldova. They have been built as fortresses between the XV and the XVI century and hold, like a coffer, their precious content: the church at the center of the inner garden, decorated with unique frescos. In fact, those paintings are exceptional in size (they cover all the interior and, in the best preserved cases, most exterior walls) and quality (they are rich of details and gildings, as icons on wood). Nevertheless, these admirable works did not cross the centuries unaffected and require diagnostics and restorations.

From July 16th to 29th, 2006, took place in Gura Humuroului, Bucovina (Romania), the international workshop "Saving Sacred Relics of European Medieval Cultural Heritage" that put together more than one hundred delegates from all over the world, which are experts in different fields linked to the topic: from restoration to conservation of works of art, from icon theology to laser physics. The workshop, funded by the European Union in the framework of the "CULTURE 2000" program [2],

included a theoretical part, with lectures on the artistic and scientific aspects, and a practical part, with visits to monasteries, on-site activities and instrumental measurements. During the workshop different high technology systems such as ground penetrating radar, thermocamera, laser vibrometer, laser range finder, laser-induced breakdown spectrometer, laser cleaner and laser-induced fluorescence (LIF) spectrometer have been used to demonstrate their capabilities in supporting the restorers' work.

This paper describes the application of laser-induced fluorescence imaging technique to diagnostics of frescos performed during the workshop by researchers of the Physics Technologies and New Materials Department - Laser Applications Section, carried on along a research and development line pursued for years [3, 4, 5, 6] and funded on different Italian and European projects.

In a typical LIF measurement, an ultraviolet laser beam is directed on the surface under study where it excites a fluorescent emission, whose spectrum is collected and detected by an optical system. The target point can be accurately varied, scanning a complete image, by moving the beam with a electrically actuated mirror. A portable computer synchronizes laser and mirror so that the instrument can carry out automatic scans on large surfaces. The information on the material at the scanned surface is contained on the fluorescence spectrum that allows to reveal details hidden in a naked eye analysis, related to pigment composition, biological attack and former restoration techniques. LIF technique has the advantage of being fast (a few minutes are required to acquire a 10×10 cm² image), remote (images are recorded at several meter distance) and not invasive (no sample is removed or damaged). The compact instrument realized at ENEA, thanks to its reduced size and weight (see sect. 2) is also suitable to the utilization on scaffoldings whenever high walls or vaults have to be examined.

The sites under study were located in Bucovina. They were:

- the Resurrection Church in the Sucevita Monastery,
- the Saint Nicholas Church in the Popauti Monastery in Botosani,
- the Saint Nicholas Church in Balinesti.

All the sites are currently under restoration.

2 Instrument and method

The compact scanning LIF system used in Bucovina is the natural evolution of a previous instrument developed and tested during former projects [6]. All the mechanical and optical elements (with the exception of the laser – Thomson mod. DIVA and the spectrometer – OceanOptics mod. S2000) have been substituted, thus allowing a size reduction from $101 \times 54 \times 45 \text{ cm}^3$ to $58 \times 43 \times 36 \text{ cm}^3$ (i.e. of more than 63% in volume) and a similar diminution in weight. A picture and the layout of the system are given in (Fig. 1), the specifications for the optical elements are listed in Table 1. The small

the laser pulses reach 5 mJ. The maximum energy was too high for the measurements carried out in Bucovina: according to distance and consistency of the fresco, energies ranging from 0.1 to 1 mJ have been used without focusing the laser beam (1 mm diameter) in order to avoid any surface vaporization. M1 is a high reflecting dielectric mirror, due to the specificity of its coating, the element with the appropriate reflectivity is in turn installed according to the wavelength emitted by the laser. The laser beam reaches the mirror M2 through the hole in the mirror M3. The mirror M2 is mounted on a gimbal support actuated by two stepping motors (MICOS mod. DT-80) driven by

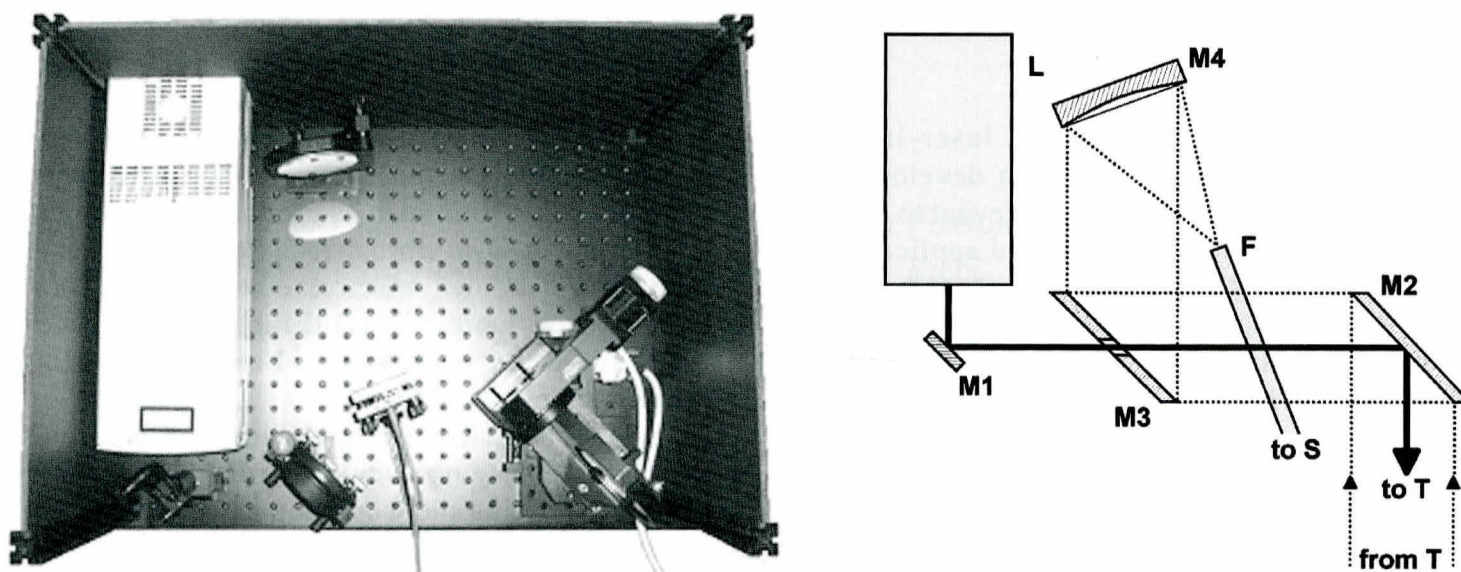


Fig. 1. - Picture from the top (left) and optical layout (right) of the compact scanning LIF system. The optical elements, described in Table 1, are contained in a rigid box (the cover has been removed to take the picture) mounted on a small optical bench.

size and weight allow an easy transport of the system and its operation from scaffolding, in the case of surfaces unreachable within the current maximum range for remote operation (10 m).

After a first doubling crystal (generating the second harmonic at 532 nm starting from the fundamental emission at 1064 nm), either a second doubling crystal or a combining crystal can be mounted alternatively in the same mechanical support inside the laser, generating radiation at 266 or 355 nm, respectively. In both cases

the portable computer, so that the azimuthal and polar angles of the laser beam are accurately controlled. In this way, the target point, i.e. the beam footprint on the fresco surface, can be changed allowing the instrument to scan the surface, with the best resolution corresponding to the laser spot size.

The laser-induced fluorescence coming from the fresco is gathered by the mirrors M2 and M3 and focused by the mirror M4 on the fiber optics F. The mirrors M1, M3, M4 and the fiber optics F are mounted on mechanical

Symbol	Element	Description
L	Nd:YAG laser	λ : 266 or 355 nm (changing the crystal), energy: 0.1 – 1 mJ, repetition rate: 20 Hz
M1	Flat mirror	Coating: dielectric, \varnothing : 25 mm, AOI: 45°, R~99% @ 266 or 355 nm (selecting the mirror)
M2	Motorized flat mirror	Coating: protected Al, \varnothing : 100 mm, R~90% in ultraviolet and visible light
T	Target	Fresco, painted surfaces at different preservation stages
M3	Flat mirror with hole	Coating: protected Al, \varnothing : 100 mm, hole \varnothing : 5 mm, R~90% in ultraviolet and visible light
M4	Concave mirror	Coating: protected Al, \varnothing : 100 mm, f: 250 mm, R~90% in ultraviolet and visible light
F	Fiber optics	Material: quartz, core \varnothing : 910 μm , l: 250 mm, NA: 0.22, T~90% in ultraviolet and visible light
S	Spectrometer	Elements: 2048, range: 200 – 1100 nm, sensibility: 86 photon/count, integration time: 3 ms

Table 1 – Optical elements of the compact scanning LIF system. λ : wavelength, \varnothing : diameter, AOI: angle of incidence, R: reflectance, f: focal length, l: length, NA: numerical aperture, T: transmittance.

supports with micrometric actuators. The light collected by the fiber optics F is sent to the spectrometer S. Finally, the digitized spectrum is transferred from the spectrometer S to the portable computer where a LabView program allows the user to set experimental parameters, to control data acquisition and to perform data analyses.

In the standard protocol selected for operation, the user sets:

- top-left and bottom-right corners of the scanned area,
- azimuthal and polar angle steps,
- number of laser pulses per measurement point,
- shortest and longest wavelength of the spectrum,
- the number of wavelength bands to be acquired.

The wavelength step is a function of the wavelength range, i.e. is derived from the difference between longest and shortest wavelength, divided by the number of wavelength bands. The latter number can be as high as 120, conferring a hyperspectral character to the LIF system.

A first data analysis can be performed on-line thanks to a front-end panel (Fig. 2). A black and white image of the scanned area is provided in the panel. The intensity of each pixel is given by the ratio of the signals (background corrected) at two selected wavelengths (510 and 395 nm in Fig. 2). On the right of the image, the cumulative

spectra are plotted: the yellow one corresponds to the pixel indicated by the two yellow lines on the image, the red one matches to the area inscribed by the four red lines on the image. The user can choose the wavelengths and can move the lines, gaining information on data collected. The yellow and red spectra of Fig. 2 come from two parts of the aureole, and are characterized by different intensities and, especially, by different spectra: paraloid, a protective substance deposited by restorers on the left part of the aureole, fluoresces strongly at about 310 nm while the yellow pigments of the outer border and on the right of the aureole emit more at 510 nm. This example shows the capability of the LIF system to discriminate among various substances present in different areas of the scanned image. On frescos two important emission bands relevant to biodegradation identification correspond to fungi at about 320 – 360 nm (once excited at 266 nm, see Fig. 4) and chlorophyll-a at about 680 nm (once excited at 355 nm [6]).

A more refined data analysis can be performed with a proprietary software (written in MatLab) that produces false color images: R, G and B signal intensities on the screen of the portable computer are proportional to fluorescent emissions at three different wavelengths. A careful selection of these wavelengths allows the user to

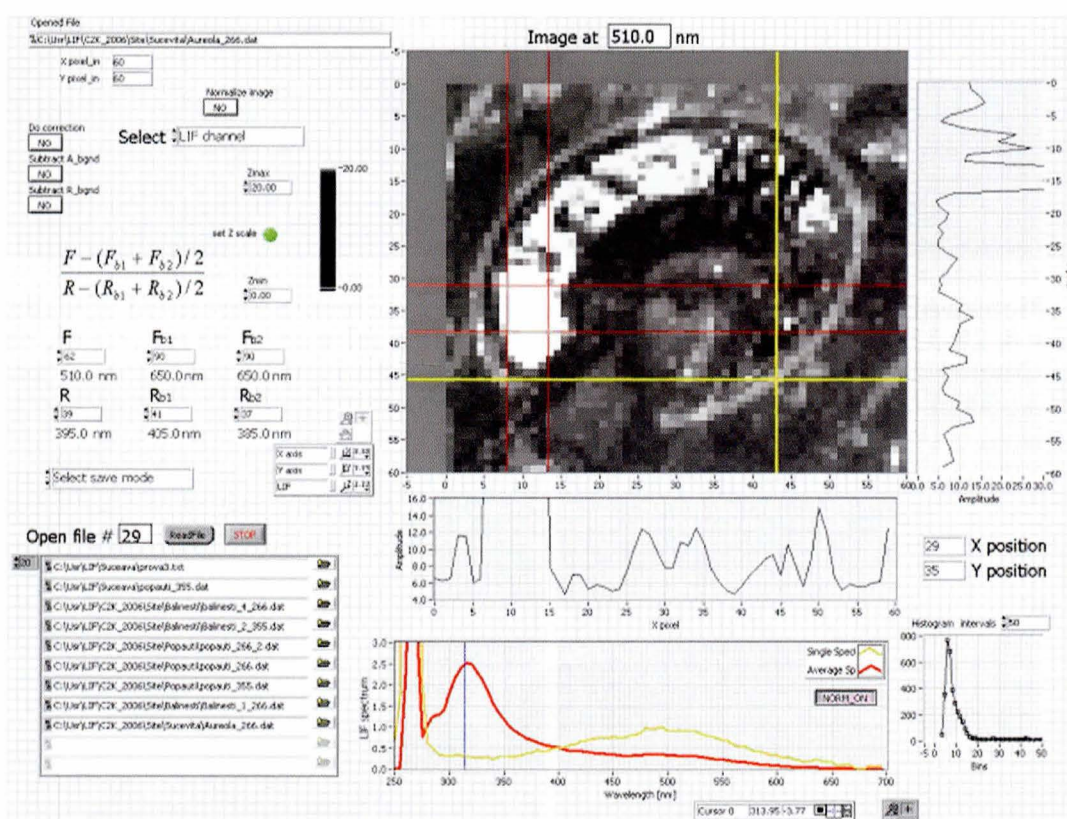


Fig. 2 – Front-end panel for on-line data analyses showing in the top-middle a black and white image of the scan. On the right side of the image, the cumulative histogram of the horizontal rows is displayed. Analogously, under the image, the cumulative histogram of the vertical rows is given. At the bottom of the panel, two spectra are plotted: the yellow one corresponds to the pixel indicated by the two yellow lines crossing on the image, the red one matches to the area delimited by the four red lines crossing on the image.

histogram of the horizontal rows is shown (it is obtained by summing the intensities of the pixels of each row). Similarly, the cumulative histogram of the vertical rows can be found under the image. At the panel bottom, two

identify hidden characteristics of the fresco like pigment composition, biological attack and restoration techniques. More details on this procedure can be found elsewhere [6]. During the present data analysis, the

following bands have been used:

- upon excitation at 266 nm:
 - R: emission at 340 nm, corresponding to fungi or organic compounds,
 - G: emission at 480 nm, corresponding to pigments,
 - B: reflection at 266 nm, corresponding to reflectance/texture;
- upon excitation at 355 nm:
 - R: emission at 680 nm, corresponding to chlorophyll-a,
 - G: emission at 450 nm, corresponding to fungi,
 - B: reflection at 355 nm, corresponding to reflectance/texture.

An example of such analysis is given in (Fig. 3), where

the RGB image obtained upon excitation at 266 nm visualizes the use of paraloid on all the remaining aureole gilding during the restoration.

Another example is given in Fig. 4 where a larger area of the same scene to which Fig. 3 belongs is reported. In this case, data have been collected upon 355 nm excitation, the aureole fluorescence is mostly related to the pigment utilized for gilding, whereas blue features related to fungi emerge at the bottom of the image on Christ's dress.

The LIF system and the Imaging Topological Radar (ITR) [7], a laser range finder developed by researchers of FIM-FIS-LAS, where both used on the same fresco in Sucevița. ITR and the LIF system are in some sense complementary: while the first instrument measures range and NIR (near infra red) reflectance, the second one detects LIF upon

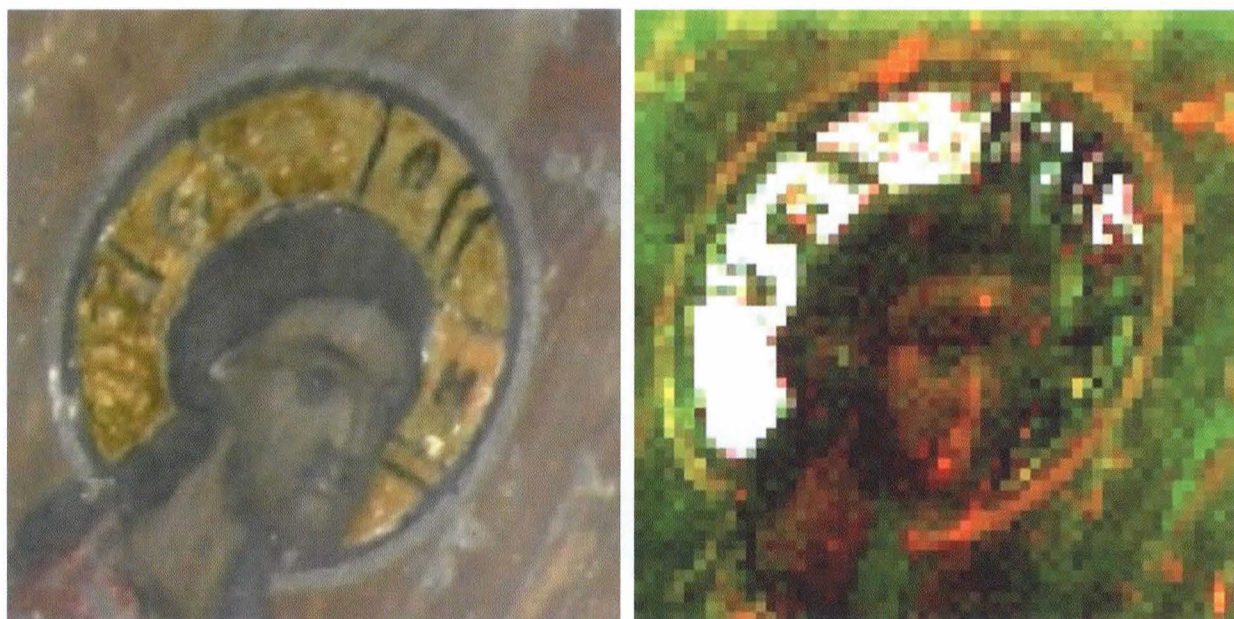


Fig. 3 – Picture of a detail of the fresco “Jesus Heals the Demon-Possessed of Gadarenes” (Matthew 8, 28-33) in Sucevita (left). The corresponding false color image (right), obtained with the scanning LIF system operating at 266 nm, highlights in white the substance deposited on the left part of the aureole (paraloid) to preserve the gilding.



Fig. 4 – Picture of the fresco “Jesus Heals the Demon-Possessed of Gadarenes” (Matthew 8, 28-33) in Sucevita (top). The corresponding false color image (bottom), obtained with the scanning LIF system operating at 266 nm, highlights in dark blue the presence of fungi on the lower part of Christ's dress (circled), conversely the red color of the gilding on the aureole and stars (marked by arrows) does not permit to discriminate the use of paraloid during the restoration.

UV (ultraviolet) excitation. By using the texture collected in both kinds of images or geometrical referenciation of the data acquisition systems [7], the data collected by ITR and the LIF system can be merged in one three-dimensional reconstruction with sub-millimeter accuracy [8]. In this way, damaged areas of a fresco can be localized very accurately by range (revealing the occurrence of plaster detachment) and fluorescence (revealing the presence of biological attack or the use of specific substances for consolidation).

3 Results and discussions

A summary of the data collected by the LIF system during the campaign is given in **Table 2**. In the following, the most relevant results are reported and discussed. As it

on a scaffolding located 5 m above the soil and looking at a niche, thus the scanning beam was not perpendicular to the sampled area. In both the figures, relevant to the upper part of the left absidis, four zones are clearly discernible in the false color images:

- green zones, corresponding to the pigments,
- white zones, corresponding to pigments discoloration,
- red zones, corresponding to the gilding,
- purple zones, corresponding to fungi.

Data collected in Sucevița allowed to demonstrate that paraloid and fungi are clearly distinguishable by their spectra upon 266 nm excitation: their fluorescence peaks are about 30 nm apart (**Fig. 7**). Paraloid spectra are constant throughout the image, while fungi spectra show

Site	Period	Number of sampled areas	Excitation wavelength
Sucevita Monastery	July 21 st – 22 nd , 2006	4	266nm and 355 nm
Popauti Monastery	July 24 th , 2006	1	266nm and 355 nm
Baline ^o ti Church	July 25 th – 26 th , 2006	4	266nm and 355 nm

Table 2 – Summary of the data collected by the scanning LIF system during the on-site campaign.

will be detailed, biodeterioration is mainly due to fungi: chlorophyll-a, easily detectable by the LIF system [6], has not been found, probably because of the low level of natural light inside the churches under study, preventing the development of photosynthetic microorganisms.

3.1 Sucevita Monastery

The data acquired in Sucevita in sample areas 1 and 2 are given in (**Fig. 5**) and (**Fig. 6**). (note that data acquired in

some variability (two examples are given in **Fig. 7**). Nevertheless, the peaks do not move, allowing the clear identification of fungi on the fresco surface.

In summary, all the sampled areas of Sucevita show common features:

- frescos are under low or medium biological attack by fungi,
- aureoles have been protected with paraloid during the restoration, however the protection layer has



Fig. 5 – Picture of the Saint at Christ’s right side in “Christ King” fresco in Sucevita (top). The corresponding false color image (bottom), obtained with the scanning LIF system emitting at 355 nm, highlights: in green, the pigments; in white, pigments discoloration; in red, the gilding; in purple, fungi (main areas of biological attack circled by a yellow line).

sample areas 4 and 3 were already shown in **Fig. 3** and **Fig. 4**, respectively).

In **Fig. 4**, and especially in **Fig. 5**, the geometry of the LIF image is distorted because the system was installed

been applied only where residual gilding was found.



Fig. 6 – Picture of Christ in “Christ King” fresco in Sucevita (left). The corresponding false color image (right), obtained with the scanning LIF system emitting at 355 nm, highlights: in green, the pigments; in white, pigments discoloration; in red, the gilding; in purple, fungi (main areas of biological attack circled by a yellow line).

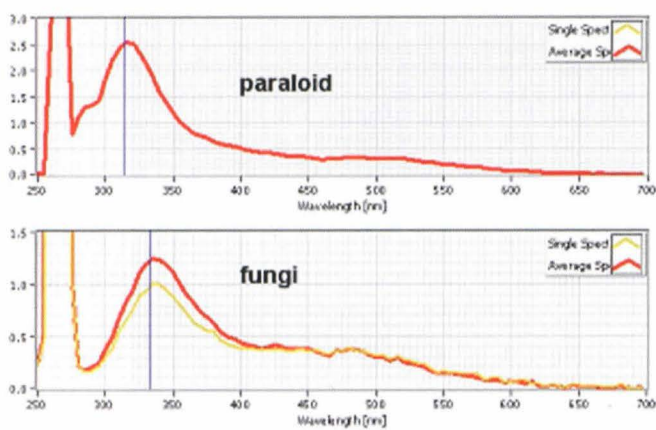


Fig. 7 – Spectra of paraloid (top) and fungi (bottom) of the fresco “Jesus Heals the Demon-Possessed of Gadarenes” (Matthew 8, 28-33) in Sucevita excited at 266 nm. Spectral intensities are given in arbitrary units.

3.2 Popauti Monastery

An example of the data acquired in Popauti is given in (Fig. 8). Part of the sampled area was previously cleaned. Two discontinuities are clearly discernible in the false color image. According to the restorers, they could be explained by successive plaster depositions. The sampled area of Popauti shows that:

- the cleaned part of the fresco is under low or medium biological attack by fungi,
- the non cleaned part of the fresco is under medium or high biological attack by fungi,
- salts efflorescence and pigments discoloration have been detected.

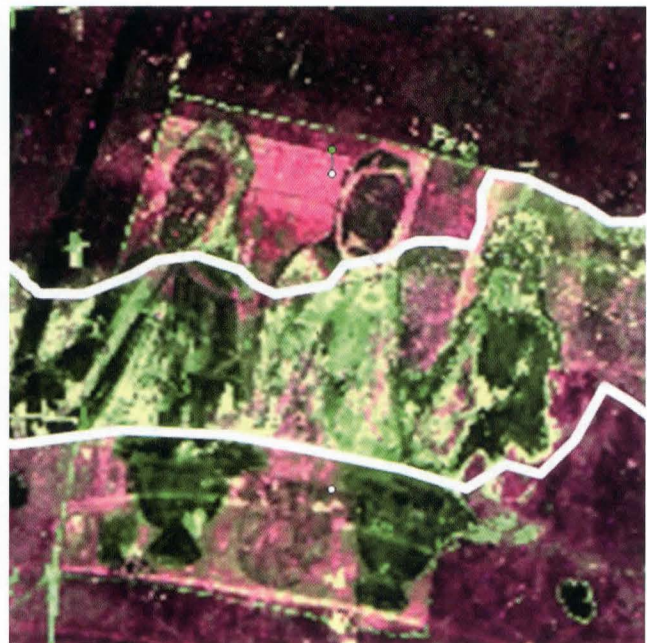


Fig. 8 – Picture of sampled area 1 in Popauti (left). The corresponding false color image (right), obtained with the scanning LIF system emitting at 355 nm, highlights two discontinuities in the fresco marked by white lines.

3.3 Balinesti Church

Four sets of data have been collected in Balinesti, either on complete large painted zones or in small areas selected by the restores to test the efficiency of different treatments. Two sampled areas (1 and 2), corresponding to the latter case, were examined upon excitation at 266 nm and 355 nm, respectively. Results (not shown here) allowed to distinguish:

- a first zone, corresponding to a non treated sector,
- a second zone, corresponding to the sector treated with a biocide,
- a third zone, corresponding to the cleaned sector.

The spectra, similar to those shown in **Fig. 7** in the case of excitation at 266 nm, indicate that biological attack by fungi is high in the non treated sector. They are also present in low concentration in the sector treated with the biocide (the treatment has been carried out few months before the measurements, thus allowing fungi to grow again). Conversely, the cleaned sector is almost free of fungi. No fluorescence band originated from the biocide was detected in either the cases.

In (**Fig. 9**), data relevant to a large image of a saint are shown. The false color image, elaborated after data collection upon excitation at 355 nm, reveals peculiar features: the reddish pigments in the red circles and in the red triangle, indiscernible in the picture, have different

is without pigments. Salts efflorescence, pigments discoloration, gilding and fungi have been detected as well.

Fig. 10 reports data collected on the sampled area 4, a small detail of the queen clothing (see the picture where the complete figure is shown). In this case black and white images collected at different emission wavelength, upon the same excitation wavelength (266 nm) are presented instead of the RGB reconstruction. The black and white images in the fluorescence bands at 480 and 340 nm, are remarkably different: while the first one corresponds to the white pigment (casein and lime, according to the restorers), the second one reveals the pattern of the biological attack by fungi.

In summary, the sampled areas of Balinesti show:

- frescos under biological attack (fungi), ranging from low to high, depending on the restorer intervention (cleaning, treatment with biocide, no treatment, corresponding to low, medium and high attack, respectively),
- salts efflorescence and pigments discoloration,
- differences due to pigments utilized.

4 Conclusions and perspectives

The results presented in this paper demonstrate that LIF

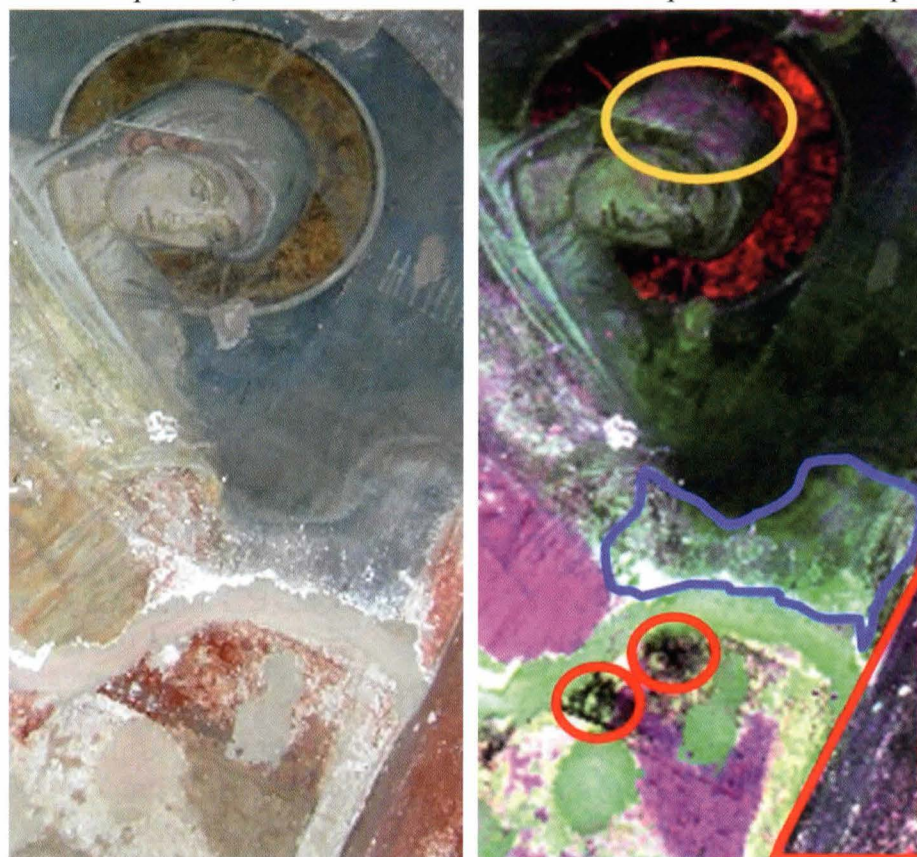


Fig. 9 – Picture of a saint (sampled area 3) in Balinesti (left). The corresponding false color image (right), obtained with the LIF system emitting at 355 nm, highlights: pigment differences (the reddish pigments in the red circles and in the red triangle); salts efflorescence and pigments discoloration (surrounded by a blue line); in red, the gilding; in purple, fungi (main area of biological attack surrounded by a yellow line). The large green areas correspond to plaster without pigments.

fluorescent responses. The big purple spots on the bottom-left part of the sampled area are also relevant to pigment differences. Conversely, green zones appear where plaster

gives information on realization techniques, biological attacks and restoration methods of painted surfaces. In particular, it provides the optical characterization of

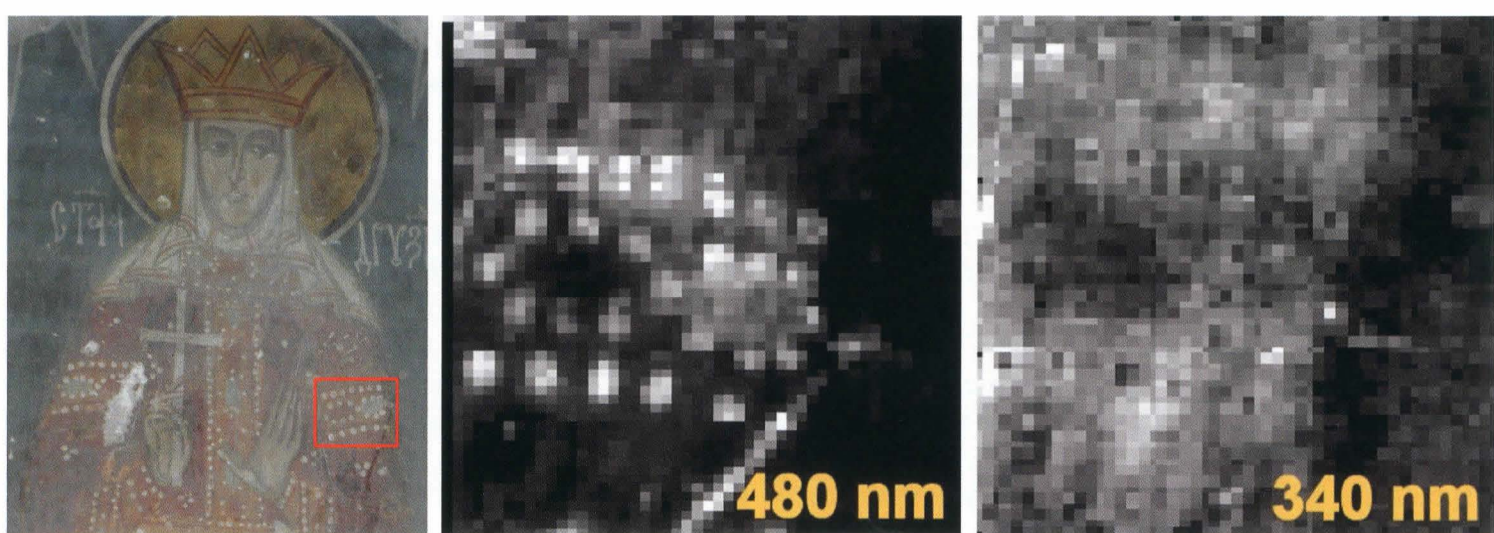


Fig. 10 – Picture of sampled area 4 of Balinesti (left, inside the red box). The corresponding black and white images in the fluorescence bands at 480 nm (center) and 340 nm (right), obtained upon emission at 266 nm, highlight the white pigments (casein and lime) and the biological attack (fungi), respectively.

pigments, fungi and chemicals used in restoration. In other words, it is an effective tool for specific diagnostics of cultural heritage.

LIF offers the advantage of being highly sensitive (e.g. biological attacks are detectable well before being discernible by the naked eye) and completely non invasive (the target is probed remotely by a light beam). Moreover, the LIF system used in Bucovina showed its suitability to a field measurement campaign being compact, lightweight, transportable, rugged, fast and relatively cheap (of the order of 10 k€).

The combined deployment of the LIF system and of the ITR laser range finder allows the restorer to accurately localize biological attacks, frescos detachment and consolidation actions in a three-dimensional model with sub-millimeter resolution. As far as the biological attack is concerned, present data revealed the absence of contamination from photosynthetic microorganisms, and a large presence of fungi which might be identified from their spectral features after growing laboratory cultures for comparison.

Future work on the system includes:

- calibration, in order to provide quantitative measurements, for inorganic (pigments), organic (ligands) and biological materials found on the plaster surface,
- realization of data bases of spectral features for the unambiguous recognition of painting substances (fluorophores, pigments and microorganisms) upon excitation with the commonly available UV laser wavelengths (266 and 355 nm),
- development of algorithms based on principal component analysis (PCA) to effectively extract the most relevant features from the large number of monochromatic images acquired, in order to successfully direct the false color reconstruction.

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