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# Laser-induced fluorescence (LIF) and reflectance measurements of medieval frescoes by Giusto de' Menabuoi in the Padua Baptistery

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## Introduction

Laser-induced fluorescence (LIF) is a powerful remote analysis tool that has been applied successfully to the diagnosis of historical work of arts,<sup>1</sup> allowing the observation of features invisible to the naked eye, such as biological attack<sup>2</sup> and restoration interventions.<sup>3</sup> LIF is fast, remote, non-invasive, sensitive and specific: these advantages have encouraged its application in real-time monitoring of historical frescoes, mosaics, paintings, sculpture, decorated façades and similar objects. The aim of the work described here was to perform remote diagnostics of a fresco by reflectance and laser-induced fluorescence measurements.

The results that are presented were made with the ENEA-patented LIF hyperspectral scanning system, which is capable of collecting fluorescence images by scanning large areas of cultural heritage surfaces. The measurements were obtained during a field campaign carried out in June 2010 on frescoes by Giusto de' Menabuoi in the Padua Baptistery.

Using univariate and multivariate data processing, including false colour imaging, principal component analysis and spectral angle mapping, the presence of surface consolidants was detected and mapped. The results that were obtained will help restorers to define future conservation actions.

## Experimental

The equipment used in the experiments was designed and assembled at the ENEA laboratories in Frascati, Italy: it is based on further development of a point-scan system, by adopting a line-scan configuration.<sup>2,4</sup> The prototype is characterized by its ability to record spatial and spectral information in two orthogonal directions using a charge-coupled detector. Details of the system are as follows: sensor, 640 pixels in the horizontal axis; angular resolution between consecutive lines, <0.1 mrad; spectral resolution, better than 2 nm; minimum

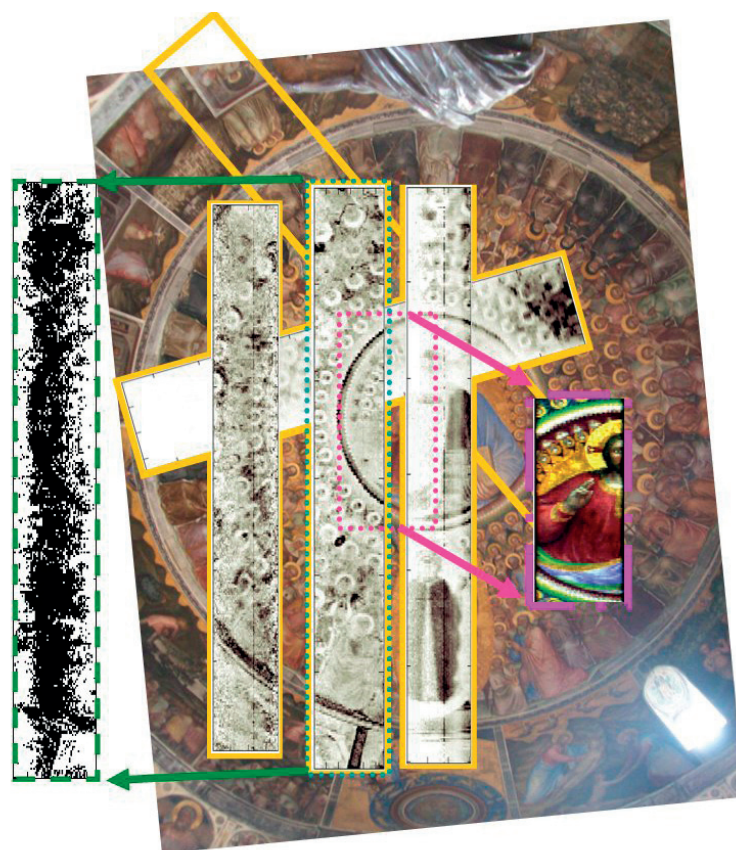
acquisition time per line, 200 ms (typically 1 s); field of view aperture, 5.7°; maximum operating distance, 40 m; and excitation wavelength, 266 nm. The LIF measurements are acquired in full daylight by using a proprietary method to discriminate between the light emitted as a result of laser induction (LIF signal) from diffuse ambient light. It is worth noting that the scanning system can also operate in the passive reflectance mode: in this latter mode the surface under study is illuminated by a 5500 K halogen lamp while keeping the laser off. The reflectance spectrum of each pixel gives relative colour coordinates that can be transformed into standard CIELAB colour space coordinates once the system has been calibrated against a reference sample.

The subsequent data analysis has provided detailed information on the substances used in the area under study. Different data processing methods were applied to the LIF spectra in order to classify regions with specific spectral contents. Typically, the identification of consolidants in an image can be accomplished either by band analysis or by using algorithms such as SAM (spectral angle mapping) or SCM (spectral correlation mapper).

## Results

More than 30 LIF and 10 reflectance scans were performed in the dome and the tambour of the Padua Baptistery. The scanned areas are located about 20 m from the instrument and have a typical dimension of about 1.5 × 10 m. The LIF instrument was used to image non-contiguous and partially overlapping areas on the central dome along an east–west direction (Figure 1), and in the vertical direction on the tambour (not shown). The results presented below are from excitation experiments at 266 nm using the experimental conditions presented in the previous section.

It was possible to extract prominent spectral features from the acquired images by careful examination of the data for



**Figure 1.** Analysis of the 370 nm fluorescence band assigned to Paraloid B72. The greyscale is relative to the LIF signal intensity (yellow border). The inset on the left (green border) represents image mapping using SAM. The inset on right (red border) represents the reflectance image of the Christ Pantocrator, showing a spectral anomaly.

individual spectra; however, a problem arose from the huge number of pixels ( $>10^6$ ) with which it was necessary to deal. Several methods were employed: the first was based on image analysis, making use of averaged spectra for areas that were selected on the basis of anomalies found in the texture that are not visible to the naked eye and are not related to the pictorial image. As an example, in the reflectance scan of the lower part of the right arm of the figure of Christ Pantocrator in the central scan seen in Figure 1 (right inset), a slight stain can be seen that is clearly not part of the figure. While this is easily identified by image analysis, it is difficult to assign it unequivocally to a specific chemical compound or type of deterioration (due to humidity or biological attack). The measurements undertaken here are most relevant in suggesting where additional local analysis using complementary techniques such as X-ray fluorescence (XRF) or micro-diffractometry might be carried out at points around the area that was imaged.

The second approach was based on the use of principal component analysis (PCA) as a semi-automatic tool for identification of prominent emission bands. Principal components (PCs) do not have a direct physical meaning, but they conveniently describe the LIF spectra and the bands identified by PCA usually correspond closely to emission bands. A given PC sometimes exhibits a complex shape and the occurrence of bands in PC provides an indication of where to begin a search for emission bands in the LIF spectra. Although rapid, this procedure could overlook spectral peculiarities with low

statistical significance (less than 4% explained variance). The application of PCA to the measurements permitted a number of spectral bands to be identified in this study and allowed the analysis to be limited to those that are most intense and well resolved spectrally. Thus it is the emissions centred at 290–295 and 360–380 nm that are reported here.

Previous studies demonstrated that spectra collected after excitation at 266 nm are suitable for the classification of resins, since they show specific emission bands for different chemical compounds, while the emission by the substrate does not show any correlation with spectra for consolidants. Based on *a priori* knowledge of the use of acrylic resins as wall painting consolidants in the Padua Baptistery and the similarity between the spectra obtained here and those of pure compounds examined in the laboratory,<sup>5</sup> the use of Paraloid B72 and Movilith 50 seemed most probable. Once the spectral bands were identified, the LIF images that had been acquired were examined to look for these bands in order to complete the data analysis. The aim of this analysis was to map pixels with a specific spectral content, while the intensity of spectral bands formed the basis of quantitative analysis.

As an example, the results obtained in the case of identification of Paraloid B72 are reported. The first method was based on the SAM algorithm and the analysis took into account a reference spectrum of Paraloid B72 previously measured in the laboratory. The result is reported in the left inset of Figure 1 (with a green border). Although the map shows a spectral

similarity almost uniformly across the area, the LIF spectrum of the pure acrylic consolidant overlaps strongly with the spectrum of the substrate (not shown), so the SAM method cannot efficiently separate their respective contributions.

This problem was solved by adopting the band analysis method. The central part of Figure 1 (inset with a yellow border), shows monochromatic image analysis of the relatively narrow UV band at 370 nm that had been assigned to Paraloid B72 on the basis of evidence from PCA. The uncalibrated relative intensity is shown using a greyscale: from very low intensity (white pixels) through higher intensity (grey) to the maximum relative intensity (black pixels). Assuming a linear dependence between the quantitative distribution of a consolidant and the respective band intensity, an almost uniform distribution of the compound can be shown, with high concentrations occurring locally. A similar situation was observed for all the areas scanned in the tambour (images not shown), supporting the hypothesis of widespread use of this consolidant.

## Conclusions

The results show that precise mapping and semi-quantitative determination of consolidants in wall paintings is possible. However, unambiguous assignment still requires additional local measurements with complementary techniques.

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