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Research Article

Remote Multicolor Excitation Laser-Induced Fluorescence Imaging

Rasmus Grönlund,[1] Jenny Hällström,[2] Ann Johansson,[1] Kerstin Barup,[2] and Sune Svanberg[1]

[1] *Atomic Physics Division, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden*
[2] *Architectural Conservation and Restoration, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden*

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Remote laser-induced fluorescence of stone materials was performed with application towards cultural heritage. Fluorescence was induced in targets ~60 m from a mobile lidar laboratory by ultraviolet laser light, either from a frequency-tripled Nd:YAG laser or from an optical parametric oscillator system. Analysis was performed on combined spectra from the different excitation wavelengths and it was noted that important additional information can be gained when using several excitation wavelengths.

1. INTRODUCTION

Laser-induced fluorescence (LIF) can be used to distinguish different areas on surfaces in numerous applications, for example, tissue diagnostics [1]. Laser light illuminating a surface excites the material which reemits fluorescence light when relaxing. Different molecules have different fluorescence features, and thus areas containing different materials give different signals. From stone materials, typically the fluorescence spectra have little features and only small variations occur. The fluorescence usually peaks in the blue/green wavelength region and falls off towards red wavelengths. Variations between materials may be displayed as differences in the slopes and wavelength for the maximum fluorescence. Certain molecules may give more specific fluorescence signals, such as chlorophyll, which shows two sharp peaks in the near infrared [2]. Due to the limited penetration depth of ultraviolet light, only the superficial layer of the target can be investigated.

By studying details in the fluorescence spectra from different parts of a building, it may, for example, be possible to assess surface damage and detect traces of chemicals previously used for restoration purposes, which are often unnoticed in visual inspections. These signals can aid in understanding the effects of earlier restoration techniques and could ultimately form a basis for future maintenance and intervention.

Remote laser-induced fluorescence, also known as fluorescence lidar [3], has earlier been applied by our group to aquatic monitoring [4], studies of vegetation status [5] and surfaces of historical buildings [6, 7]. In these measurements, performed with single wavelength excitation, we have illustrated that chlorophyll-rich areas, regions previously exposed to chemical treatment, as well as different stone types can be demarcated.

Remote fluorescence spectra can be gathered by transmitting a powerful laser pulse onto the target and collecting the induced fluorescence with a telescope and a spectrometer system. To perform measurements at daytime, gating of the detector is usually required to suppress background light. By scanning the laser beam over a target area and recording the fluorescence spectrum in each spot, imaging can be achieved.

In this paper, we present remote fluorescence imaging measurement results from measurement campaigns in both laboratory and field settings. Although much information can be extracted from a single excitation wavelength, the use of two or more excitation wavelengths is demonstrated to add significant information to the analysis, improving the possibilities to discriminate between areas with different fluorescent/physical characteristics. Furthermore, we discuss different analysis methods for extracting useful information from huge fluorescence data sets.

2. EXPERIMENT

Laser-induced fluorescence was used to remotely study stone surfaces. Some measurements were performed in a laboratory environment, while others were performed as field campaigns at cultural heritage sites. By excitation of the material using ultraviolet laser pulses, fluorescence was induced from a distance of about 60 m. The signal was remotely gathered by a telescope and the spectral shape was analyzed. By scanning the laser beam over the building and detecting the fluorescence from each spot, imaging could be performed. When performing measurements on buildings with historical value, it is important to note that the surfaces of buildings are not at all affected by the measurement, which is not the case for many other building investigation methods.

The measurements presented in this paper are from a campaign with brick samples measured in Lund, Sweden, a field campaign at Övedskloster castle in southern Sweden and a field campaign at Coliseum in Rome, Italy. More information on the Övedskloster campaign is presented in [8] and on the Coliseum campaign in [9, 10].

3. MATERIAL AND METHODS

A mobile lidar laboratory [11], which is primarily adapted for atmospheric monitoring by the differential absorption lidar technique, was employed for the experiments. The system has a flexible design and is well suited for monitoring remote fluorescence as has been previously reported [4–7]. The fluorescence lidar transmitter was a frequency-tripled Nd:YAG laser generating radiation at 355 nm in 5-nanosecond-long pulses at a repetition rate of 20 Hz. Typically the transmitted pulse energy was limited to 25 mJ in these experiments. Also, an optical parametric oscillator (OPO) could be used as the excitation source, where the laser wavelength could be selected in a wide range from ultraviolet to infrared. Only ultraviolet wavelengths were used, as fluorescence induction is particularly efficient using these wavelengths, and also due to eye-safety reasons. From the OPO, the transmitted pulse energy was typically 5 mJ. Over a scan, the output integrated over a particular measurement spot was stable to $\sim$20%.

The vertically looking receiving optics was a Newtonian telescope with 40 cm diameter. A 40 cm $\times$ 80 cm folding mirror placed over the telescope in a dome above the vehicle roof can be steered to direct the laser beam onto the desired spot. As the laser beam is coaxial to the field of view of the telescope, the detected radiation is gathered from the correct area. A gated and intensified optical multichannel analyzer, more closely described in [12], detected the fluorescence radiation from 280 to 810 nm with a spectral resolution of $\sim$3 nm. The laser beam expander, which was coaxial with the receiving telescope, was normally adjusted to give a 5-cm-diameter laser spot on the target. For a typical distance of 60 m between the lidar and the target, the diameter of the image spot in the telescope focal plane was $\sim$1.3 mm. The radiation was transmitted through a high-pass filter to suppress the specular reflection and collected using a 600 μm diameter optical fibre connected to the optical multichannel analyzer system. With the computer-controlled folding mirror the lidar was pointed at selected locations for spectral data collection, or scanned row by row over the façades for image generation. A signal integration of 100 laser shots was normally used. To suppress background interference, time-gated detection was used, with a 100 nanosecond gate set to open at the arrival time of the fluorescence pulse.

From each spot investigated a fluorescence spectrum is collected, and as the laser is scanned over an area, a three-dimensional data set is obtained. To extract useful information from this huge amount of data, efficient data processing is necessary. Different aspects of the fluorescence features can be focused on by forming ratios of intensities in different wavelength bands, by performing correlation between spectra or by principal component analysis. In this study, mainly the correlation technique has been used, where a linear correlation between one reference spectrum and all other spectra within the scan is performed. The result is then a single number for each point, between -1 and $+1$, corresponding to the similarity to the reference spectrum, where $+1$ corresponds to identical spectra and -1 corresponds to negatively correlated spectra. A zero value would indicate totally uncorrelated spectra, as would be expected when correlating two sets of white noise. In this way, areas with similar fluorescence features can quickly be found and delineated. Different analysis methods for these types of data are further discussed in [13].

The measurement campaign on brick samples was performed in a laboratory setting. The lidar system was docked to the Physics Department building at Lund University, and the bricks were set up on the roof of a building 60 m away. The measurement was performed using five different excitation wavelengths: 250 nm, 290 nm, 337 nm, 355 nm, and 375 nm. Spectra from the same point, with different excitation wavelengths, can be combined to make it possible to analyze the results, taking all the excitation wavelengths into account simultaneously. This is done by creating an artificial spectrum for each measured spot, by simply assigning one excitation wavelength to the first 1024 data points, another to the next 1024 data points, and so on. If not all 1024 recorded data points contain significant information, some parts can be excluded [11]. Although some features may be appearing only with a certain excitation wavelength, the main advantage is gained when spectra are combined. In this way, all features appear simultaneously and can easily be presented.

In the measurement campaign at Övedskloster, areas on the façade of the building and on the courtyard portal were scanned using 355 nm excitation from the Nd:YAG laser. Different fluorescence features could be observed and much information could be extracted, even though only this one excitation wavelength was used.

During the Coliseum campaign, different areas on the Coliseum façade were scanned. In particular, one area was scanned using two different excitation wavelengths, 355 nm from the Nd:YAG laser and 250 nm from the OPO.

4. RESULTS

As mentioned, the measurements on the brick samples were performed using five different excitation wavelengths. In the analysis, the spectra for the 355 nm excitation have been divided by 5 to compensate for its greater output energy. After combining the spectra, each resulting spectrum has been normalized with respect to its greatest value. The spectra have not been normalized within each excitation wavelength, as the relative intensities hold information that would otherwise be lost. Spectra from six arbitrary spots, each on a different brick sample, have been plotted in Figure 1. By correlating all spectra with an arbitrarily chosen reference spot, different stones could be isolated, as indicated in Figure 2. This was not possible using data from only one excitation wavelength. We note that none of the neighboring pixels is white, the reason for this being that the noise in the different spectra would have to be identical.

One of the areas studied at Övedskloster castle was an ornamental urn on the roof of the main building. This part of the building is very difficult to reach for close-up examination, and thus remote fluorescence imaging is a good method to study such parts. Despite the use of a single excitation wavelength, several aspects of the fluorescence features could be studied, and other examples are given in [7]. It was noted that the spectra from the base of the urn were quite different from the rest of it. In Figure 3(a), a correlation between the spot marked with a red circle and all other spectra in the scan has been performed. The blue pixels correspond to the degree of similarity, and it can clearly be seen that the parts on the base of the urn are similar to each other and different from the rest. A few points on the upper part of the urn appear as similar, but with low correlation values. Figure 3(b) shows the spectra from two points in the scan, marked by the red and cyan circles in Figure 3(a). It is evident that the red spectrum shows a stronger fluorescence towards longer wavelengths.

One area on the Coliseum was scanned using both 250 nm and 355 nm excitation light. In the analysis, the two spectra from each point were combined to yield a combined spectrum containing information from both scans. Figure 4(a) shows the two spectra from a certain point in the scan. The red spectrum indicates the 250 nm excitation and the blue one the 355 nm excitation. In Figure 4(b), the combined spectrum is shown, where data from both excitation wavelengths have been used.

Figure 5(a) shows the area on the Coliseum which has been scanned. In Figures 5(b)–5(d), correlation has been performed with one of the spectra in the scan (marked by an oval) as the reference point. However, in Figure 5(b), only the 250 nm excitation data and in Figure 5(c), only the 355 nm excitation data have been used. In contrast, the result when using the combined spectra is shown in Figure 5(d). The correlation values in the range 0.96–1.0 have been mapped out. Values below 0.96 are not indicated in the figures. All correlation values are relatively high, which is expected, as all spectra are similar and display only subtle differences. Comparing Figures 5(b)–5(d), it is clear that spectra on the block

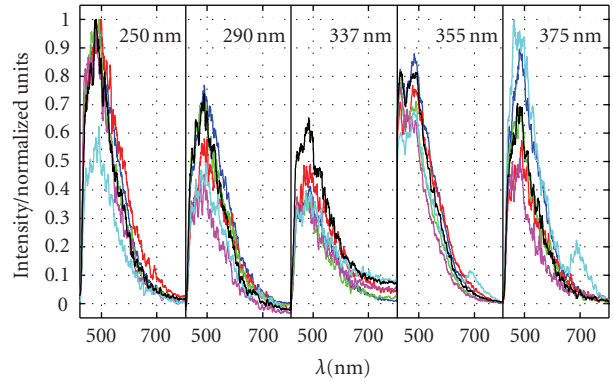

FIGURE 1: Spectra from six different brick samples, measured using five different excitation wavelengths. The spectra have been combined to make analysis of all data possible simultaneously. The different excitation wavelengths are indicated in the figure. Studying the spectra, it is difficult to distinguish them by using only one excitation wavelength, but with the combined spectra differences can be seen. One spectrum contains the characteristic chlorophyll peak at ∼690 nm, but this fluorescence feature can only be seen with the 355 nm and 375 nm excitation.

FIGURE 2: The brick samples measured, with an analysis superimposed. It was possible to delineate one of the brick samples by correlating all spectra in the scan with one spectrum on this particular brick. The white spot corresponds to the chosen reference spectrum and the blue points display the correlation coefficient value. Values below a certain threshold value have not been displayed. The scan was performed over all the bricks and contained 26×22 points, as indicated by the red frame. As can be seen, the points on the particular brick have high correlation values and only a few points in the rest of the scan have values above the threshold.

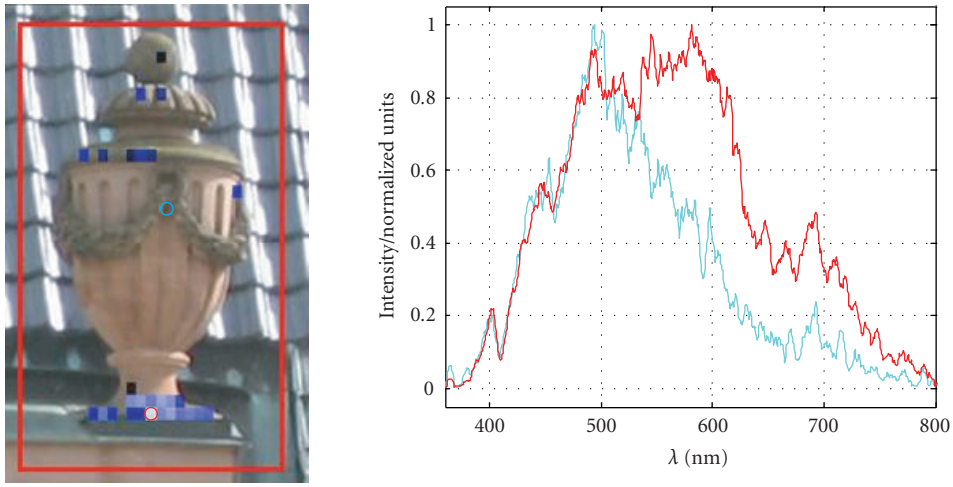

Figure 3: An ornamental urn on the roof of Övedskloster castle. Part (a) shows the correlation between a point on the base of the urn (marked by a red circle) and all other spectra. The frame indicates the measured area. In part (b), the spectra from the selected point and a further point (marked by a cyan circle) are shown, and there is an obvious difference between them. The red spectrum corresponds to the red circle in part (a), and the cyan spectrum to the cyan circle.

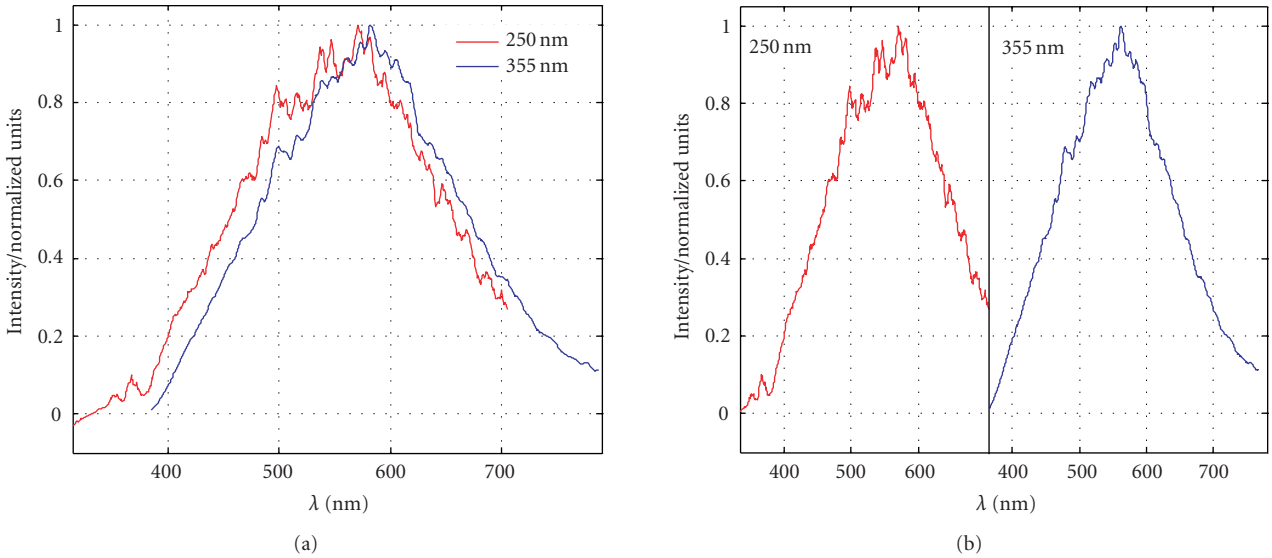

Figure 4: Spectra from a point in a scan on the Coliseum. (a) Shows the two different spectra and (b) shows the combined spectrum. The latter can be used in the analysis to simultaneously use information from both excitation wavelengths.

in the upper part of the pillar and in the bottom line of the scan (corresponding to the edge of a stone further down) are similar. Also, it is seen that these have different fluorescence features than the block between them. It is noted that the correlation using combined spectra discriminates more effectively than the same analysis using only the spectra from one excitation wavelength. In Figure 5(d), only a few points outside the area of interest are above the threshold, and all of them have values within the lower part of the allowed range.

5. DISCUSSION

Our studies show that laser-induced fluorescence is a useful method for studying stone surfaces with application towards cultural heritage. The method is particularly useful when applied remotely, which makes it possible to scan large areas and to reach parts of a building that are not easily accessible to methods that require close-up examination. Further, we would like to emphasize that multicolor excitation

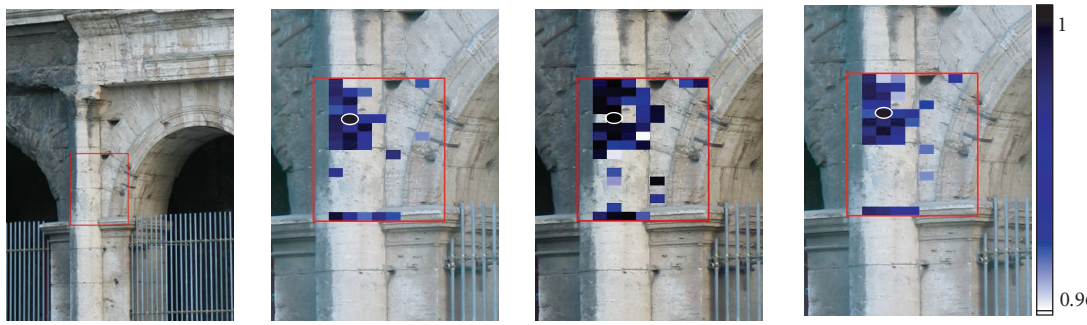

Figure 5: An area on the Coliseum façade, marked in part (a). The close-ups in parts (b)–(d) show correlation between one spectrum (marked by an oval) and all other spectra. In part (b), data from the 250 nm excitation measurement have been used, in part (c), data from the 355 nm excitation have been used, and in part (d), the data from both measurements have been combined. The color scale indicates the correlation value. Note that, since the background stone in light, high correlation values are here demarcated with dark colors, in contrast with Figures 2 and 3. Values lower than 0.96 are not indicated in the figure.

provides more information to the analysis. As different excitation wavelengths are used, different molecules are interrogated or excited to different degrees, thereby causing the observed differences in the radiated fluorescence. As was illustrated in Figures 2 and 5, utilizing the combined data resulting from inducing fluorescence at multiple wavelengths, different regions could be better discriminated and distinguished. The use of correlation analysis was demonstrated to be an efficient tool in extracting relevant information from a large amount of data and by this method it was easy to distinguish areas with similar fluorescence characteristics.

To implement analysis of the fluorescence spectra as a useful tool within the field of cultural heritage, collaborations with building restoration scientists are of utmost importance in the data extraction from fluorescence imaging experiments.

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