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Laser cleaning of 18-th century parchment with polychrome inscriptions

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1. Introduction

This paper reports the laser cleaning of historical parchment, using a non-invasive and non contact investigation method for line up and extra precision. The parchment under investigation, a musical sheet dated 18th c., was improperly used as bookbinding, belongs to a private collection and was kindly offered for study by Ms. Olariu (Private Collection "Alexandrina Olariu", Bucharest).

Traditional chemical and mechanical cleaning procedures using chemical solvents and scalpels respectively, may result to a sample's deterioration and besides it is difficult to discriminate between the surface's and the substrate's ablation. Conventional cleaning methods applied on parchment, using alcohol and water may lead to the hydrolysis of collagen fibers, change of molecular structure of proteins and finally to gelatinization. On the other hand, laser cleaning is a non-destructive, non-contact and selective method to be applied on organic materials, namely on parchment. Its efficiency depends on the object's optical parameters as well as on the laser parameters. However, organic materials are the most sensitive objects on which laser cleaning may be applied, as they are prone to discoloration and degradation induced by photo thermal reactions, which may take place.

Parchment is commonly manufactured from the dermis layer of animal skin after strong alkaline removal of the epidermis and the subcutaneous tissue layers. It mainly consists of collagen fibers. Laser cleaning [1] is a relatively new technique that acquired the attention of many restorers from modern research centers for conservation and restoration, as an outcome of the many advantages envisaged by this non-conventional technique.

Up to now, most of the published studies or investigations concerning laser cleaning are made on inorganic materials (stone, metal), yet an up-growing number of research related to laser cleaning of organic materials are being developed. Due to the fact that in the international literature [2] are so few works dedicated to laser cleaning of parchments we did preliminary studies [3,4] in order to see what are the effects that the laser radiation may induce on collagenous structure before starting work on historical parchments. The aim of these studies was to establish the fluence thresholds adequate to an efficient removal of the dirt layers. The laser used was YAG:Nd Q-Switched that works at fundamental wavelength (1064 nm) as well as at its three harmonics: 532, 355 and 266 nm. The sample were carefully diagnosed before and after cleaning using chemical and physical methods such as FT-IR, NIR, UV-VIS Spectrometry, colorimetry, microscopy and *Micro Hot Table* – for the evaluation of the shrinkage temperature of the collagen fibers. The results of tests were more than satisfactory and concluded that the laser cleaning (applied in correct working regime) induces no harm to the collagenous substrates. The most efficient results were obtained using the 1064 nm wavelength at a fluence starting from 0.5 mJ/cm^2 to 0.7 J/cm^2.

2. Experimental set-up

A major fact that must be considered when cleaning up historical documents is the ink used in its writing. Although the laser regime can be adjusted in order not to affect the ink it is preferable that no radiation should touch the sensible ink substrates. To this aim, we used a laser mounted on a microscope that allows us to follow the letter contour and remove the dirt surrounding it. In order to ensure a precise and safe laser cleaning we developed the cleaning system INOE 2000: gratifying *CLEANART E2094 Eureka Project* [5, 6].

Before the laser cleaning technique was applied, in order to increase the degree of precision, LIF Scanning - as novel investigation and diagnosis technique - was applied in order to map the ink layers and to distinguish them from the dirt layers. In this manner the laser

microscope system could follow closely the original shape of the letters.

This technique is highly recommended by the science conservation community, due to its non-invasive and non-contact features, as well as the high accuracy results introduced.

LIF Scanning is based on Laser Induced Fluorescence Spectroscopy principle, using an UV laser beam to induce the fluorescence process on a precise spot of a surface, so that it can be acquired with a high sensitive spectrometer.

Based on this technique, it was built a LIF scanning device that can irradiate an user-defined area, spot by spot, with high precision (0.0005˚) following the mathematical pattern of a rectangular matrix, starting with the upper-left corner of the area. The portability of this device allows its use in lab and in situ.

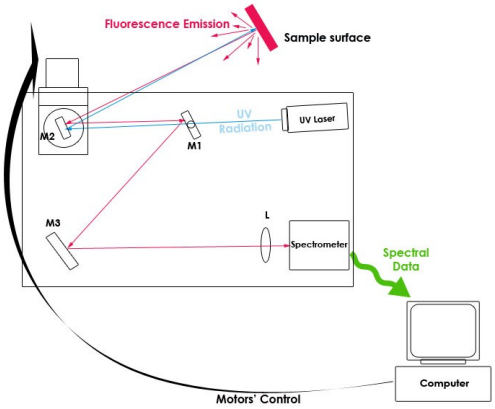


Fig.1. LIF scanning device schematics.

All the synchronized elements of the scanning device are controlled by a computer software interface which allows the operator to set and modify all the scanning parameters: acquisition time, scanning resolution (scanning step length), starting point coordinates, and custom spectra bandwidths.

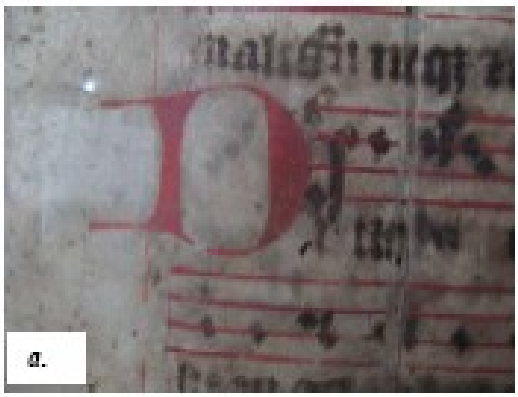
Some of the most important scanning parameters are the custom spectra bandwidths. This allows the operator to set different bandwidths in a single spectrum to be scanned, so that it would fasten the acquisition process and most important, it will improve the interpretation work-time. This method is very useful for the fast-tracking of inquired fluorescence characteristics.

3. Results and discussion

Stain discrimination is a very important feature in obtaining a precise and safe cleaning of the affected artworks. Following this approach, using a non-contact, non-invasive and non-destructive technique based on laser induced spectroscopy we distinguished the diverse types of stains, obtaining a differentiating map of the interest area so we could apply specific laser cleaning regimes accordingly to the type of stains present in each investigated area. Also, this laser induced spectroscopy method was applied after the laser cleaning was accomplished, helping us to notice stain remains untraceable with naked eye, as well as fine definition of the cleaned areas.

3.1 LIF Scanning

There were selected two different fluorescence emission characteristics to be inquired over the Laser Induced Fluorescence Scanning process, corresponding to the red ink and the black ink.



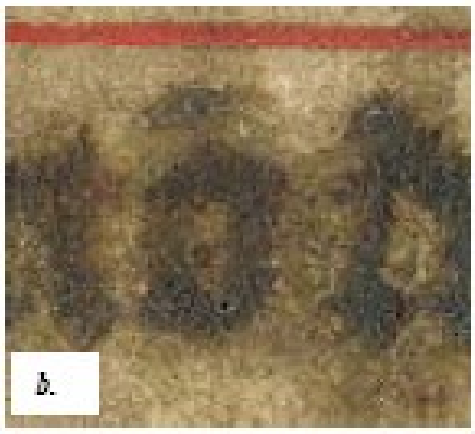


Fig. 2. Areas to be scanned: a.) Area 1- red ink; b) Area 2 –black ink.

In the images below are represented the different spectra and the bandwidth selected for each of them:

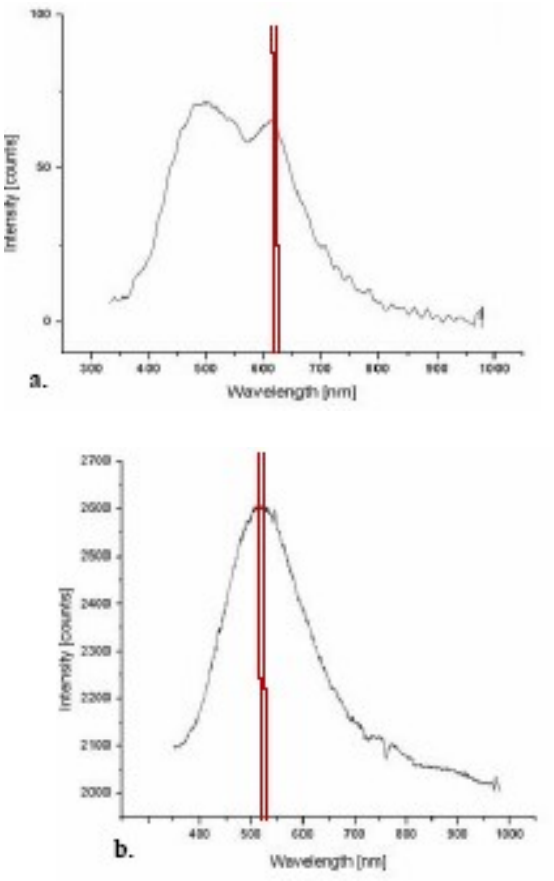


*Fig. 3. Bandwidth selection **a.** Area 1: 612-622 nm, **b.** Area 2: 519 – 529 nm.*

For each spectrum inquired there was also a background spectrum (568-578 nm bandwidth) taken to make the ambient light correction.

As seen in Fig. 2., there were selected some areas for scanning, to highlight the two fluorescence characteristics mentioned above. All the scans were carried out at the same resolution: 0.5 mm/step.

Area 1 was set to 60×40 mm, meaning a 120×80 pixel resolution. This area contains the lower half of the big letter "D" as well as the beginning lines of the stave, from the face A of the parchment. This area should highlight the red pigment used for the letter "D" and the staves' lines, and also the difference between a cleaned and a not cleaned portion of the parchment. Scanning time elapsed was 90 minutes.

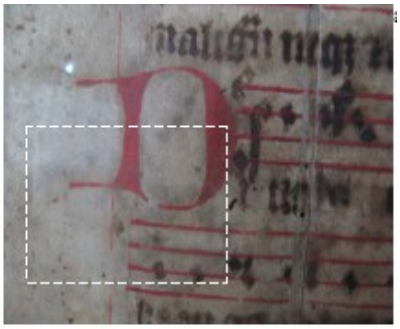
The distance between the sample and the acquisition device was set at 1000 mm. The integration time for the spectrometer was set to 200 ms and the triggering time to 50 ms. So that each scanning step wait time was set to 300 ms.

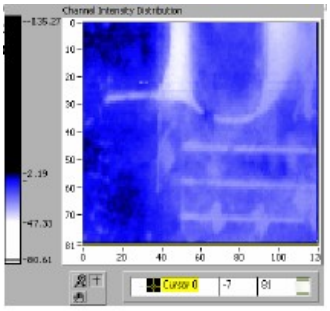
Each area scan results were put in 4 text files: one for each bandwidth and another one for the background spectrum. The files contain the average intensity of the respective bandwidth for each scanned pixel. These files are corrected with the background spectrum bandwidth file and then merged into a single file, with all the adjusted bandwidth intensities on columns, for each area.

The interpretation software has two viewing possibilities: an RGB channel simulation or an intensity distribution graph. The input parameters are: the path of the text file containing the columns with the average intensities for each pixel of a specific area, the pixel resolution, and the number of the column (bandwidth) to be represented by each of R, G and B color channels.

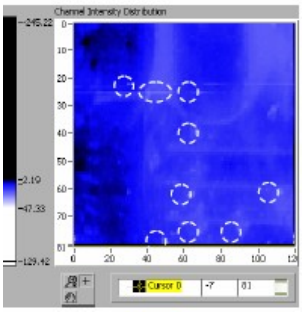
Intensity distribution graphs of a bandwidth, displays a map of the scanned area in that channel. It is used a blue/white color gradient, where the darkest blue represents the lowest intensity of the channel at that point, while the brightest white represents the highest intensity.

The intensity distribution graph of the scanned **Area 1** showed:

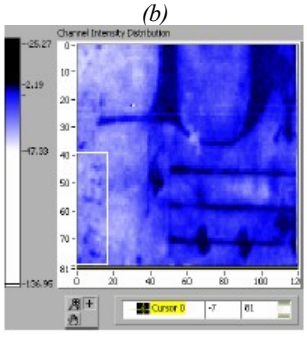




(a)



(b)



(c)

Fig. 5. Scanned Area 1; (a) 612-622nm band (red pigment); (b). 442-452nm band (damaged parchment); (c). 512-529 band (parchment emission).

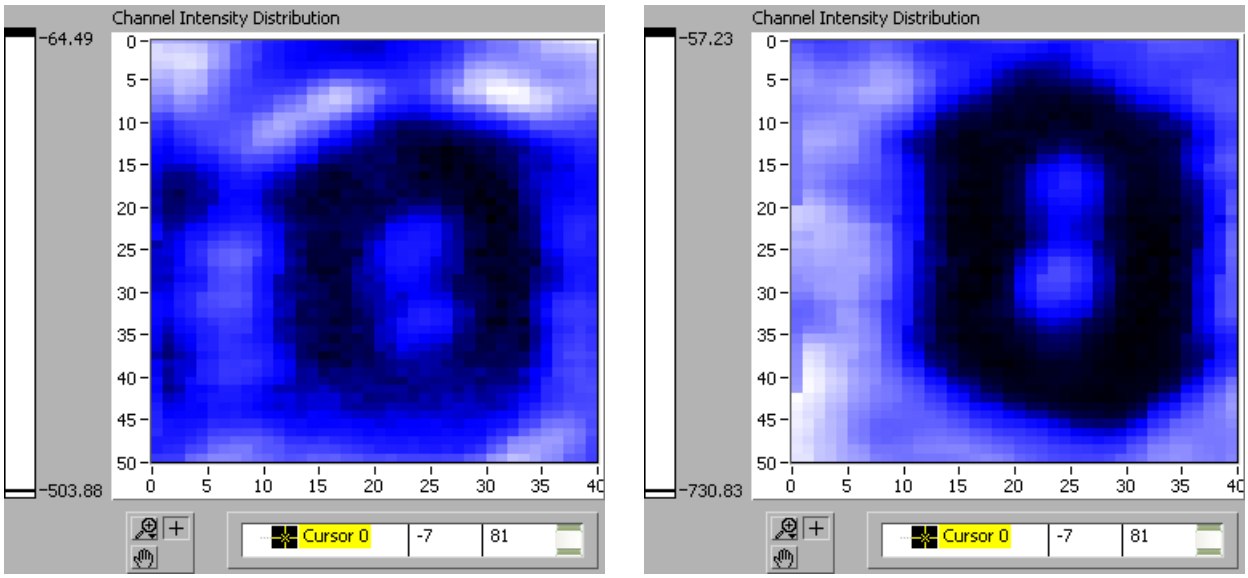
Fig. 5 (a) displays the intensity distribution of the "red pigment" band. It may be observed that even the black color marks on the staves lines are highlighted by this channel but at a lower intensity. The letter "D" is displayed with the highest intensity. The darkest areas suggest that there is no red pigment present. Compared with the real picture of the scanned area there can be seen that those areas were previously cleaned. This could mean that the dirty surface of the parchment contains red pigments at very low intensities (blue color).

Fig. 5 (b) displays the distribution map of the emission fluorescence of the damaged parchment edge that peculiar emission thought to be a biological attack. On this graph there can be clearly observed inside the markings several high intensity emission spots.

Fig. 5 (c) displays the distribution map of the emission of the parchment's fluorescence. With this map one can clearly make the difference between the cleaner and the dirtier areas of the parchment. Here, the areas with higher intensity, represents the cleaner surfaces of the parchment (the left side of the scanned area). In the marked area there can be observed a slight track of a partial text.

The RGB color channels represents the three bandwidths scanned as follows: Red is for the first band 612-622 nm (the red pigment); Green for the second band 442 – 452 nm (the damaged parchment edge) and Blue for the 512 - 529 nm (the parchment fluorescence emission). The RGB picture clearly displays the distribution of all the three channels, especially the Red and Blue.

Area 2 - the scanned area is 8x10 mm with 0.2 mm step length, meaning a 40x50 pixel resolution. Integration time for the spectrometer was set to 800 ms for optimal spectra acquisition. The whole scanning step duration time was set to 900 ms (including triggering time and motor rotation time). The elapsed time for this scan was 40 minutes.



(a) *(b)*

Fig. 5. Scanned Area 2: a. before, b. after laser cleaning.

3.2 Laser cleaning

In order to apply this technique on this historical parchment we have done some tests (Fig. 6) on one of its sides in order to select the proper working regime – fluence thresholds that will give us a good cleaning followed by no induced deterioration to the sensible substrate (see Fig. 7). Laser cleaning follows closely the surface's relief so that removal of the dirt layers doesn't affect the collagen fibers.

Laser working regime: λ = 1064 nm, ν = 20 Hz, laser spot = 0.6 cm^2

Fig. 6. Laser cleaning tests at different energies per laser spot.

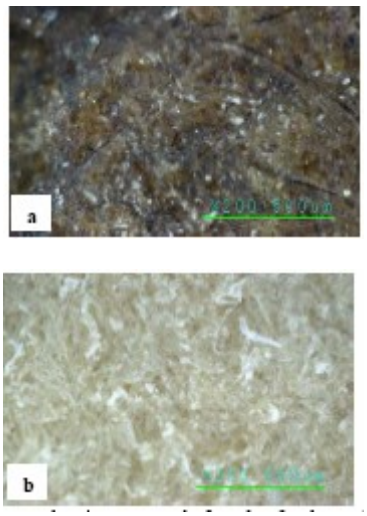


Fig. 7. Microscopic images taken during the laser cleaning tests: ***a.*** *before,* ***b.*** *after laser cleaning.*

After selecting the proper laser working regime, we have chosen 5 areas –with different dirt degrees - where laser cleaning was applied on the parchment. From these five interest areas we have selected two for discussion: one from parchment's face A and another from its face B.

Area 1 (face A) – laser working regime: λ = 1064 nm, E = 335 mJ, ν = 20 Hz, laser spot = 0.6 cm^2, 20 pulses/cm^2, cleaned area: 2 cm × 2.5 cm = 5 cm^2.

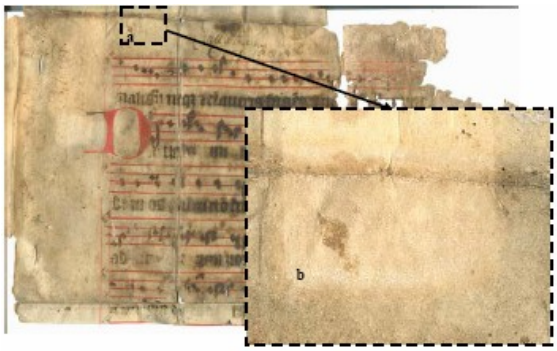
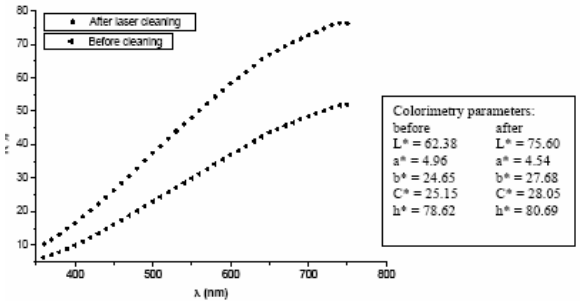


Fig. 8. Laser cleaning of area 2: ***a.*** *before,* ***b.*** *after.*



Graph 1. Colorimetry characteristics of laser cleaned area 2.

Area 2 (face B) – laser working regime: λ = 1064 nm, E = 335 mJ, ν = 20 Hz, laser spot = 0.6 cm^2, 20 pulses/cm^2, cleaned area: 4cm × 3 cm = 12 cm^2.

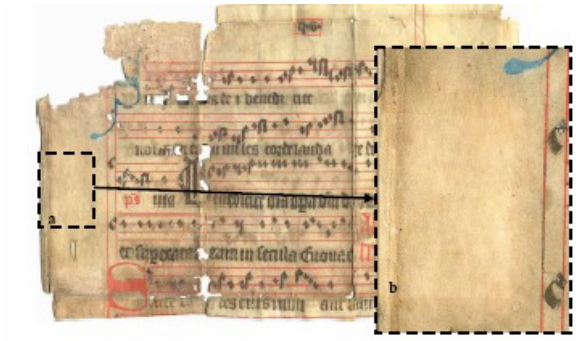
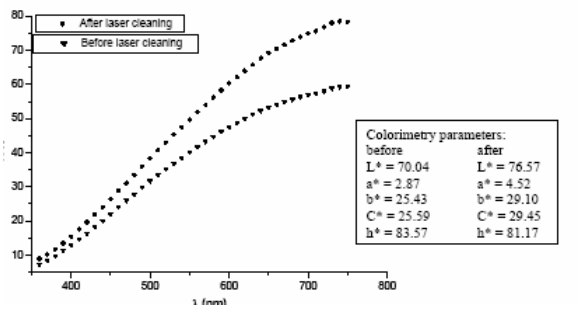


Fig. 9. Laser cleaning of area 5: ***a****. before,* ***b****. after.*



Graph 2. Laser cleaned area 5: colorimetry characteristics.

Micro-precision laser cleaning using a Q-switched YAG:Nd laser mounted on an optical microscope. Laser working regime: λ = 1064 nm, E = 9 mJ, ν = 20 Hz, laser spot = 0.15 mm^2.

Fig. 10. Microscopic laser cleaning of a letter: a. before cleaning, b. after cleaning.

Conclusions

Up to now, still a small amount of research related to laser cleaning of polychrome collagenous artworks has been reported, most of the studies and investigations envisaging inorganic materials (stone, metal).

This paper is the concluding part of an ample study made on the effects that the laser radiation may induce on collagenous structure before starting work on historical parchments. The results were more than satisfactory and proved that the laser cleaning (applied in correct working regime) induces no harm to the collagenous substrates.

LIF technique offers us the possibility to take better decisions regarding the future steps in the object's restoration or conservation.

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