

Challenges in laser cleaning of cultural heritage stained glass

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Abstract. Stained-glass windows play an important role in cultural heritage. Human and environmental factors have subjected these pieces to risks of damage. Mechanical and chemical-based cleaning methods have been used for their restoration and conservation. Additionally, short-pulse lasers have opened new opportunities for safe and controlled cleaning and restoration of these important materials. In this work, ultra-short pulsed lasers were used to clean an artificially applied coating from the surface of a contemporary colorless glass frequently used in the restoration of stained-glass windows. One of the objectives was to explore the applicability of using these types of lasers to safely clean historical stained-glass windows. It was observed that temperature rise and subsequent heat accumulation in the coating layer being removed was sufficient to generate significant thermal stresses on the underlying glass surface leading to damages even when the laser energies are lower than the damage thresholds. Some laser treatments that limit this heat accumulation were designed in this study. For laser systems operating at frequencies in the range of several hundreds of kHz, the option was to work in burst mode, limiting the number of pulses in each burst and selecting an adequate time lapse between two consecutive burst runs. A method to uniformly clean a given surface is proposed in this work. When lower frequencies are available, treatments using frequencies lower than 20 kHz are enough to safely clean the glass. When UV laser radiation is used, optical damage is also an important aspect to be considered. In this case, the cleaning protocol has to deal with both issues, to avoid heat accumulation and chemical damage.



1. Introduction

Stained glasses form an important element in human history. Since stained glasses are multifunctional, they have been utilized both in religious and civil architecture [1, 2]. Exposure to human and environmental factors has subjected these important pieces of human history to damages [3]. The three main types of degradation that have continued to affect these valuable pieces are those of physical, chemical, and organic nature [4, 5, 6]. These degradation factors have led to glass abrasion, cracking, exfoliation of surface layers, corrosion, unwanted patina or crust formation, etc. One of the biggest challenges faced in the conservation of historical stained glasses is the delicate removal of the accumulated crusts [7, 8]. Mechanical, chemical, and laser-based methods have been utilized for their restoration and conservation [9, 10]. Laser technology has increasingly become a unique conservation tool offering possibilities for the safe and controlled cleaning of cultural heritage materials [11].

In a recent work [12], we analyzed and realized that controlling heat accumulation during laser treatment is essential to develop a safe laser cleaning protocol that could be used in stained glass windows. Even if the laser radiation is not absorbed by the glass, the temperature reached in the material that is being cleaned can generate thermal stresses on the glass surface. These thermal stresses are the cause of cracks that may appear during laser treatment. In this context, the use of ultra-short pulse lasers opens new opportunities, because the thermal component of the interaction is lower. Some protocols were proposed to limit the heat accumulation and the maximum temperature reached during the laser cleaning process. When laser operates at high frequencies, higher than 200 kHz, the best option is to use the burst mode [13, 14] limiting the number of pulses in each position at a given series and selecting an adequate waiting time between consecutive series. If lower frequencies are available, a second alternative is to use a continuous beam scanning mode, reducing the frequency to values lower than 20 kHz. The outcomes of this study will pave way for the establishment of a procedure to extend the previously developed cleaning protocols. In the first case, we present how the burst mode can be extended to clean full areas uniformly. In the second case, we explore the possibility of using different wavelengths.

2. Materials and methods

2.1. Experimental

Experiments were carried out using an 800 picosecond (ps) near-IR laser (PowerLine Pico 10-1064, Rofin-Sinar, Germany) with a wavelength of 1064 nm and maximum power output of 8 Watts. The pulse repetition rate can be modified between 250 and 800 kHz and the waist diameter of the laser beam ($1/e^2$ criterium for gaussian energy distributions) is approximately 80 μm , as deduced following the D^2 -method proposed by Liu [15]. The second laser system used was a femtosecond (fs) near-IR laser (Carbide model, Light Conversion, Lithuania) with a pulse duration of 228 fs, a maximum power output of 40 Watts with a wavelength of 1030 nm, and a beam diameter of 100 μm . It was possible to use the third harmonic in the UV range, at 343 nm. The pulse duration was 238 fs and the maximum output power was 11 W. The beam shape was elliptical with $2a=60 \mu\text{m}$ and $2b=45 \mu\text{m}$. The pulse frequency can be modified between 1 kHz and 1 MHz. In addition, this laser offers the possibility of using the Pulse Peak Divider option which makes it possible to reduce the effective frequency of the treatment without increasing the pulse energy. Cleaning protocols were studied using an energy per pulse value of 200 μJ (fluence 2.55 J/cm^2 , irradiance $10^4 \text{ GW}/\text{cm}^2$) at 1030 nm and 55 μJ (fluence 2.59 J/cm^2 , irradiance $10^4 \text{ GW}/\text{cm}^2$) at 343 nm.

Laser scanning was performed using the two different scanning modes previously mentioned i.e., continuous beam scanning and burst. In the beam scan mode, the laser scans the surface at a given speed. By selecting the scanning speed and the frequency it is possible to control the distance between two consecutive pulses. Another important parameter is the distance between two consecutive scanning lines. The burst mode consists of a spot-by-spot scanning process with adjustable laser parameters. The laser system produces a sequence of a defined number of pulses (a burst) controlling the repetition rate [13, 14] in defined positions. It is possible to control the number of pulses in each position, the energy of each pulse, the frequency, and the distance between positions. This surface scanning process is slower

compared to the continuous one because the laser stops at every position. In the case of the n-IR 800 ps laser, treatments were performed in the burst mode in 2 mm x 2 mm regions, with a distance between two positions of 200 μm . When using the femtosecond laser (IR and UV), the scanning parameters were selected in order to maintain the distance between two pulses burst at 10 μm . This ensured that the laser energy was uniformly distributed over the surface being cleaned.

The morphology of the surface was examined using an optical microscope and a confocal microscope (Sensofar PL μ 2300). Optical properties were also characterized before and after laser treatment using a StellarNET Miniature spectrometer. The transmittance and absorption spectra in the UV-Vis-nIR range, in particular, between 300 and 1100 nm, were recorded. An SL1-CAL light source, 0.6 mm in diameter with a cone angle of 25.4° at the output of the optical fiber and specifically configured for irradiance calibrations in the 300-1100 nm range were used. Transmittance tests were carried out with an integration time of 5ms, averaging 100 scans.

2.2. Sample

This work was performed on a contemporary colorless glass (used for restoration) provided by the glass factory of Verreire de Saint-Just located in Saint-Just-Saint-Rambert, in Loire (France). The dimensions of the piece are 4 cm x 1.5 cm x 2 mm (figure 1). The glass surface was covered with permanent ink in order to observe the phenomenology that takes place during the laser cleaning.



Figure 1. Photograph of the colorless glass sample used in this study.

3. Results and discussion

3.1. Laser treatments using an 800 picosecond IR laser system

The sample showed high transparency to this wavelength with transmittance values higher than 85%. This particular laser has a maximum fluence level of 0.49 J/cm² (irradiance 0.61 GW/cm²) with a maximum pulse energy of 24 μJ . It was observed that, by applying the laser treatment directly on an uncoated/unaltered glass surface, no physical damage was induced. The minimum frequency that is available with this laser is 200 kHz. Safe laser cleaning protocols were identified and determined by using the burst mode [12]. It was observed that it was possible to eliminate the permanent ink without deteriorating the glass using series of 200 pulses of 24 μJ at 300 kHz. The distance between positions was fixed to 200 μm . The ink was removed at the center of the positions after applying ten series of 200 pulses with a waiting time of 30 s between two consecutive series. With this laser protocol, it was possible to limit the heating of the glass surface to values lower than 10°C. This level of heating does not deteriorate the surface of the glass.

A protocol was developed to uniformly clean a given area. As can be observed in figure 2(a), when the burst treatment was applied, the ink was removed in a circular region at the center of the incident position in a region of approximately 50 μm in diameter. Afterward, the process was repeated moving the positions by 25 μm in the horizontal direction. This distance was selected because it coincided with the radius of the cleaned regions in the first treatment. This process was repeated six times more, moving every time the positions by 25 μm . After eight treatments, lines of approximately 100 μm thick were uniformly cleaned, as can be observed in figure 2b. To cover the desired area, the process was repeated moving the positions by 50 μm in the vertical direction, using a similar criterium as the one selected for the horizontal treatments. All the process was repeated moving the positions by 100, and 150 μm . A waiting time of 10 s was applied after each laser process. After all the process was completed, there was a full area uniformly cleaned without deteriorating the glass surface, as can be observed in figure 2c.

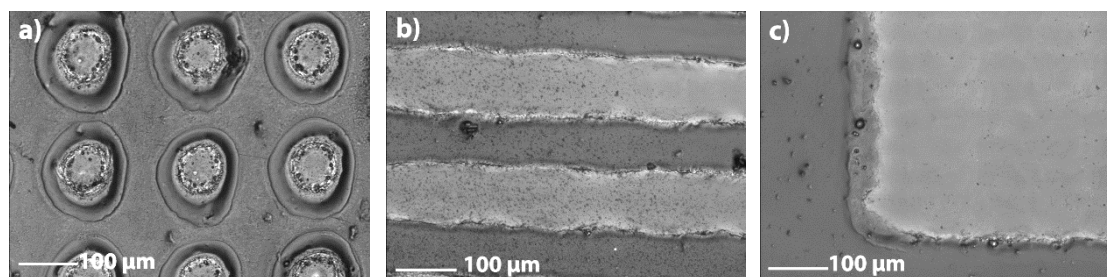


Figure 2. Optical microscope images of the sample surface after the three steps of the cleaning protocol: (a) Single treatment; (b) after the eight treatments that were done horizontally; and (c) after the treatments that were done vertically.

3.2. Laser treatments using a femtosecond laser system

This laser system can work with lower frequencies than the 800 ps laser. In addition, it offers the possibility of using the Pulse Peak Divider option which makes it possible to reduce the effective frequency of the treatment without increasing the pulse energy. In consequence, to control the heat accumulation [14] and the maximum temperature at the surface of the glass it is advisable to reduce the effective laser frequency, as proposed by Weber et al [16]. In our previous work [12] we demonstrated that safe cleaning conditions can be reached when the effective laser frequency is reduced to values lower than 20 kHz.

It is important to have in mind that in historical stained glass, it is highly likely that the material to be removed from the surface of the glass is a patina of gypsum-like compounds. In this case, this laser wavelength is very effective for removing this external layer because this layer has a high absorption level. This layer is often formed due to pollution and environmental contamination. However, once this layer is removed exposing the clean gypsum patina underneath the effectiveness of the fs IR laser treatment is strongly reduced. For this reason, the possibility of using fs UV radiation was also explored. The transmittance spectra of the glass in this work are observed in figure 3(a). This glass exhibited high transmittance values in the UV region, close to 350 nm, but it is expected that these values reduce for lower wavelengths. For this reason, the frequency of the laser treatments with the UV radiation was reduced up to 10 kHz to compensate for possible heat accumulation due to the absorption of the laser energy by the glass [12]. To obtain a uniform energy distribution on the sample surface the distance between two pulses should be lower than the beam radius. To maintain a distance between pulses smaller than the semiaxis of the laser beam dimensions, the laser scanning speed was set at 150 mm/s which gave a 15 μm distance between two consecutive pulses, and the distance between lines was fixed at 15 μm.

Laser treatments did not generate mechanical damage on the glass, but it was observed that there was a gradual darkening of the glass as the laser power was increased. Figure 3(b) shows the aspect of the surface of the glass after having applied the laser treatments with a pulse energy of 16.5 μJ. Similar solarization effects were observed in glasses treated with UV radiation as was reported by Byrne [10] and these effects were associated with photo-oxidation of some of the elements that are present in the glass composition. In consequence, when UV radiation is used, in addition to mechanical damage processes, these chemical damage processes have to be considered as well. Using the D²-method [15] it is also possible to determine the energy threshold that generates this kind of defect. Measuring the size of the laser footprint as a function of the pulse energy we determined that the chemical damage threshold was 5.1 μJ/pulse.

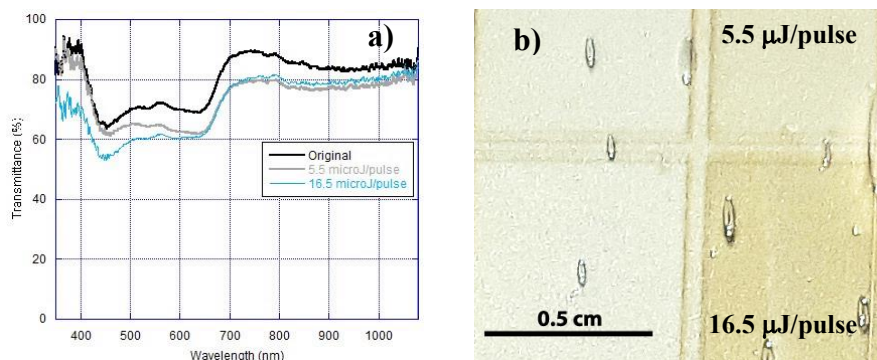


Figure 3. (a) Transmittance spectra obtained before and after performing laser treatments directly on the glass surface. (b) The aspect of the sample surface showing the chemical damage after treatment with the fs UV laser at 10 kHz in the continuous beam scanning mode with a laser speed of 150 mm/s at different pulse energies.

Figure 3(a) also shows the transmittance spectra measured in the glass after performing two laser treatments using energy pulse values just above the chemical damage threshold, 5.5 $\mu\text{J}/\text{pulse}$, and three times higher, 16.5 $\mu\text{J}/\text{pulse}$. With a pulse energy of 5.5 $\mu\text{J}/\text{pulse}$, the glass color started to change and turned brown. This was reflected in the reduction of the transmittance values in the visible range, as can be observed in figure 3(a). When the pulse energy increased, the brown color became stronger, and the transmittance spectra showed a stronger reduction in the 350-650 nm range. This implied that the absorption to the UV radiation increased, reducing the mechanical energy threshold values. Safe cleaning protocols were realized by combining low frequency values that avoided heat accumulation, with pulse energy values lower than the chemical damage threshold.

4. Conclusions

Usually, damage thresholds have to be measured when safe cleaning protocols are to be set. In the case of stained glass, even when pulse energies lower than these thresholds are used, heat accumulation has to be controlled because the thermal stresses that are generated during laser treatment can induce cracks on the glass. Ultra-short pulse lasers offer new possibilities in the development of safe laser cleaning protocols that can be used in the conservation of historical stained-glass windows because the thermal component can be controlled. Several alternatives have been explored in this work to determine these protocols. For the laser systems working with frequencies in the range of several hundreds of kHz, the option was to work in burst mode, limiting the number of pulses in each burst and selecting an adequate time lapse between two consecutive burst runs. In this work, we identified and demonstrated the efficiency of a sequence that allowed uniform cleaning of the desired surface. When the laser system being used offers the possibility of reducing the effective frequency, the best and safe treatments are those performed with lower frequencies. We demonstrated this using a fs laser emitting in the IR or the UV wavelength. Safe and effective cleaning was achieved with frequencies lower than 20 kHz. Also, it has been shown that UV radiation can generate some chemical damage on the glass, depending on the glass composition. The chemical damage threshold was also measured thus showing some laser cleaning protocols that avoid heat accumulation and chemical damage. These treatments were applied to contemporary stained-glass samples in view of further applications to historical stained glass windows.

5. References

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