Laser removal of marker tags from a contemporary graffiti painting

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Abstract. This contribution presents a study on the efficiency of the laser removal of black permanent marker tags from a contemporary graffiti painting. The effect of two wavelengths – 1064 nm and 532 nm, on the marker inks and the graffiti paints was investigated using optical microscopy and colorimetric measurements. Preliminary characterization of the marker inks and the paints by FTIR and XRF analyses was also performed. The results confirm that the materials’ response to laser radiation depends on their particular chemical composition.

1. Introduction
Lasers have found multiple applications in the field of Heritage Science, with laser surface cleaning being one of the most common and well-established procedures. In terms of laser-matter interaction mechanisms, however, some research domains have not been completely investigated; one of them is the contemporary painting materials. Their formulations are often quite complex thus bringing new conservation challenges and concerns that require a comprehensive study [1]. There are numerous problematic aspects associated with the laser cleaning of contemporary artworks. One of the practical issues is the similar composition and properties of overpaints and of pictorial layers which makes the laser removal of overpaints a challenging task as it hinders the selectivity of the process. Another common issue is the light-sensitive nature of the majority of the pigments resulting in paint discoloration upon laser irradiation [2].

The present report investigates the efficiency of the laser cleaning of black permanent marker inks from a contemporary graffiti painting performed by a Q-switched Nd:YAG laser operating at 1064 nm and 532 nm. It represents a common case of a contemporary mural of public interest that has been vandalized by marker tags. A large number studies have been reported on a variety of graffiti paints, although their main focus has been the removal of said paints from different surfaces, not their preservation [3]. This work aims to set an adequate laser working regime guaranteeing efficient removal of the unwanted layer without any detrimental side effects on the pictorial surface. Preliminary characterization of the marker inks and the graffiti paints was done employing FTIR and XRF to highlight the differences and similarities between the materials. This is essential for a better understanding of their behavior and optimization of the cleaning procedure. The cleaning efficiency was evaluated by optical microscopy and colorimetry.
2. Materials and methods

For the study, a model sample representing a multi-color graffiti contemporary mural was prepared. Three different colors of paint (green, pink and silver) with a relatively uniform application on the surface were chosen based on a preliminary investigation of the interaction with the working laser wavelengths. Three different brands of black permanent markers commonly used by street artists were chosen: Faber Castell® (FC) pitt artist pen big brush (containing India ink); Uni-Posca® (UP) (water-based); Royal Talens® (RT)-Amsterdam (water-based acrylic). After application on the graffiti model sample, the marker tags were left to air-dry in laboratory conditions (20 ± 2 °C, 50 ± 10% RH) for two weeks.

To evaluate the laser cleaning efficiency, optical microscopy (Leica DMS 300) and colorimetry (colorimeter X-rite Ci64UV, aperture 8 mm and 4 mm, standard illuminant D65/10°, CIELAB color space, averaging five measurements at different points) were performed before and after the cleaning. FTIR (Perkin Elmer Spectrum Two FTIR spectrometer equipped with a PIKE GladiATR accessory, 4000–380 cm\(^{-1}\) spectral region, resolution 4 cm\(^{-1}\), an average of 16 scans) and XRF (Bruker Elemental TRACER III-SD, Rh-anode X-ray tube, Si-PIN detector, resolution of 190 eV at 10 000 cps) were used to identify the composition of the graffiti paints and the marker inks.

The removal of the marker tags was carried out by a Q-switched Nd:YAG laser (Palladio by QUANTA SYSTEM) operating at the wavelengths 1064 nm and 532 nm, with a pulse duration of 8 ns, a pulse repetition rate up to 20 Hz, and a maximum energy per pulse of 450 mJ at 1064 nm, and 200 mJ at 532 nm. The beam delivery system was an articulated arm. The size of the laser spot on the surface was 0.52 cm\(^2\).

3. Results and discussion

3.1. Chemical characterization of the materials

Small samples of the graffiti paints were mechanically removed from the surface and samples of marker inks applied on glass slides were prepared for the experiment. The results are presented in figure 1. The elemental analysis of the graffiti paints showed large amounts of Ca, Ti and Fe. Traces of Si, S, K, Mn and Cu were also detected. The presence of Ca is justified by the obtained FTIR spectra as well, where major bands of CaCO\(_3\) are noticed (strong broad band in the region 1390 – 1490 cm\(^{-1}\), strong sharp peak at 873 cm\(^{-1}\), weak sharp peaks at 711 cm\(^{-1}\), 1794 cm\(^{-1}\) and 2515 cm\(^{-1}\) [4]). This mineral is usually used as an extender in the formulations of the paints. The presence of Ti most probably stands for TiO\(_2\) which is the most common white pigment used in contemporary commercial paints that also gives them whiteness, brightness and opacity [3]. The XRF analysis showed a major presence of Fe which suggests iron oxide as a part of the pigments’ composition. Si is a trace element in the XRF spectra but in the FTIR spectra, silicate bands are observed as well (broad band between 1000 – 1400 cm\(^{-1}\)). The FTIR spectroscopy provided complementary information about the binder of the paints. The green and the pink graffiti paints showed the presence of p(nBA/MMA) acrylic emulsion binder (C-H stretching band at 2958 cm\(^{-1}\), 2933 cm\(^{-1}\) and 2876 cm\(^{-1}\); C=O stretching band at 1727 cm\(^{-1}\); C=O stretching at 1240 cm\(^{-1}\); C–C stretching at 1148 cm\(^{-1}\); and C-H rocking at 748 cm\(^{-1}\)). The silver paint contains an alkyd binder (C-H stretching band at 2956 cm\(^{-1}\), 2922 cm\(^{-1}\) and 2853 cm\(^{-1}\); C=O stretching at 1733 cm\(^{-1}\); weak peaks at 1603 cm\(^{-1}\) and 1463 cm\(^{-1}\); C-O stretching at 1278 cm\(^{-1}\) [4] [5]).

The pigments in the green and the pink paints could not be identified due to a severe overlapping by the binder’s and the extender’s bands in the FTIR spectra. The XRF could not provide consistent information either. Most probably they are of organic character.

The characterization of the marker inks suggested completely different formulations of the three brands. The elemental analysis identified the presence of Ca in all of them as in RT-Amsterdam it is a major element that was observed in the FTIR spectra as bands corresponding to CaCO\(_3\) (not so pronounced peaks at 1397 cm\(^{-1}\), 1159 cm\(^{-1}\) (shoulder) and 873 cm\(^{-1}\)). Ti and Fe were detected by the XRF analysis as minor elements that suggested the presence of oxides in the ink. The binder of the RT-Amsterdam marker was classified as a styrene-acrylic emulsion. The acrylic copolymer was identified
by assignment of the major bands of C-H stretching (2955 cm\(^{-1}\), 2927 cm\(^{-1}\), 2873 cm\(^{-1}\)), carbonyl stretching (1729 cm\(^{-1}\)), C-O stretching (1232 cm\(^{-1}\)) and C-C stretching (1138 cm\(^{-1}\)) vibrations. The styrene presence was observed by C-H stretching (3105 cm\(^{-1}\), 3087 cm\(^{-1}\), 3060 cm\(^{-1}\) and 3027 cm\(^{-1}\)), aromatic skeletal ring breathing (1602 cm\(^{-1}\)), and C-H out-of-plane bending (759 cm\(^{-1}\) and 698 cm\(^{-1}\)) vibrations [4]. Typically, all water-based emulsion-type permanent markers are composed of styrene-acrylic or styrene–methacrylic copolymers [6]. The FC and UP marker inks exhibited poor absorption in the IR working region and identification of their components was not possible.

Figure 1. FTIR and XRF analysis of the graffiti paints and the permanent black marker inks.

3.2. Laser cleaning and evaluation of the efficiency
Part of the results of the laser removal of marker tags from the graffiti paints is shown in figures 2-4. The FC and UP marker inks were easily removed from the green and the pink paints at 1064 nm. Keeping the fluence close to the damage threshold of the inks, it took several seconds of irradiation exposure to evaporate the marker inks successfully. This observation could be explained by the poor adhesion of the inks to the surface which favors their easy removal and could be related to their chemical composition as well. The microscopic images reveal that the surface relief was preserved and no visual damages were observed (figure 2 – A, B, D and E). On the contrary, the IR wavelength interacted very severely with the silver paint even at very low fluences as the marker inks (FC and UP) and the paint layer were both removed revealing other paint underlayers (figure 2 – C, F). The contrast in the interaction of the three graffiti paints with laser radiation could be explained by the differences in the chemical composition concerning the binders and the pigment particles. In an overview of the use of Nd:YAG laser for different cleaning applications, Siano et al. [7] mention that the acrylic paints show low absorption at 1064 nm because of the deep optical penetration and/or high reflectance. Thus, acrylic-based paints should have a higher damage threshold. Furthermore, this statement is confirmed by the cleaning tests of the RT-Amsterdam acrylic marker. It exhibited a higher damage threshold than the other markers and the needed irradiation exposure was more than 10 s. In figure 2, G-H, the microscopic images of the cleaned areas of the green and the pink paint show the presence of a translucent layer which could be explained with binder residues. In this case, a combination with a chemical solvent could be a possible solution for better results [8]. The different response of the paints to the laser radiation depending on the different nature of their binders has been observed in other researches, too [9], [10]. Further analysis of the laser interaction with such compounds is needed to confirm these conclusions. The removal of the RT-Amsterdam acrylic marker from the silver paint was not successful as well. Moreover, brownish discoloration of the marker tag appeared, which resembles the discoloration effect observed upon IR
irradiation at low fluences of layers with high carbon percentage attributed to the insufficient bulk material removal and thermal dissociation of the carbon particulates [2]. A possible explanation for this effect could be the mixture of the silver paint with black paint rich in carbon in this particular area which is slightly visible on the painting and owes to the complex multi-color technique used by the artist.

In figure 3, the color differences measured in the CIEL*a*b* color space of the cleaned areas are presented. The global color change ΔE*ab is the most important parameter showing the difference between the original surface and the cleaned area. From a conservation standpoint, when evaluating the risks of incompatibility of a certain procedure, if ΔE*ab < 3 the risk is low, if 3<ΔE*ab<5 the risk is medium, and if ΔE*ab>5 the risk is high [11]. On the graphics, the threshold of 3 is visualized with a red dashed line to easily evaluate the incompatibility risks. It could be noticed that only the cleaning of the FB marker ink from the green graffiti paint has low risk. The other areas exhibit medium or high risk. The discolorations could be noticed from the differences in the color coordinates. The decrease in the L* value means darkening of the surface, which corresponds to the microscopic observations. Area (E) reveals significant darkening, too, which could be explained by marker ink residues affecting the calculation. Regarding the silver paint, the increasing of the b* value indicates yellowing of the surface (comparing C-1, F-2 and I) as it is the most pronounced in the area cleaned from the RT-Amsterdam acrylic marker.

![Microscopic images of the laser cleaned areas @ 1064 nm.](image1)

![Colorimetric differences between the original painted surfaces considered as references, and the cleaned surfaces measured in the CIELAB color space.](image2)
Cleaning with the second harmonic of the laser was not as successful. Upon irradiation, the green and the pink paint suffered severe discoloration (not presented) towards a darkening of the surface, which could be attributed to a photo-thermal effect or some chemical modification [2]. A curious result was achieved upon the removal of FB and UP marker inks from the silver paint. The colorimetric measurements showed again discoloration towards darkening and yellowing. On the other hand, the microscopic images demonstrate light cleaning with a lot of marker ink residues as the gloss of the paint is partially preserved. This indicates that the response of the silver paint to the green laser radiation is not as severe, so that and the laser action could be used in combination with other techniques, as suggested above.

Figure 4. Microscopic images and colorimetric measurements of laser removal of FC and UP marker tags from the silver graffiti paint. Working wavelength 532 nm.

4. Conclusion
The efficiency was studied of the laser removal of three black permanent marker inks from the surface of a contemporary graffiti painting. It was noticed that the different materials display different responses to the wavelengths applied (1064 nm and 532 nm) due to the particularities in their chemical composition. It was suggested that the cleaning performance with the IR wavelength depends on the binder compounds. The yellowing effect observed upon cleaning of the silver paint was attributed to insufficient bulk material removal and thermal dissociation of carbon particulates arising from a possible mixture with a black paint rich in carbon in this particular area. The application of the green wavelength caused pronounced discoloration of the green and the pink paints observed immediately after the irradiation, which could be attributed to a photo-thermal effect or some chemical modification. On the contrary, the cleaning of the silver paint showed promising results. Despite the noticeable marker inks residues, the integrity of the paint was partially preserved. This indicated that the response of the silver paint to the green laser radiation is not as severe and the laser action could be used in combination with other techniques, as suggested above.

The reported results would benefit not only the contemporary murals, but can also be extended towards restoration of less complex mortar substrates belonging to traditional built heritage.

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