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ASPECTS OF LASER CLEANING EFFICIENCY FOR CONTEMPORARY ARTWORKS RESTORATION

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The cleaning technique based on the laser ablation phenomenon has been applied in the restoration of valuable objects for over three decades. The effect that it has on contemporary art materials is not comprehensively studied, though. There are several possible side effects that should be considered and carefully monitored when performing laser cleaning. This paper is focused on the interaction of the laser radiation with contemporary art materials as some highlights are put on the induced side effects. A cleaning procedure is also presented followed by an example of an early-stage experiment on laser removal of black permanent marker drawings on a graffiti technique painting. A preliminary investigation of the surfaces from an aesthetical point of view before and after the laser cleaning is done by optical microscopy and colorimetry.

Keywords: laser ablation, restoration, contemporary artworks, side effects, graffiti technique paintings, black permanent marker, optical microscopy, colorimetry.

1. Introduction

The laser applications in the cultural heritage conservation and restoration have more than 40 years of research and development. Starting as a technological transfer from other industrial and research domains, the advances of the laser technologies in this research field have taken a slow but sustainable path. A wide range of new sophisticated and improved powerful techniques and equipment has emerged in order to ensure safe and correct diagnostics and proper treatment of the artworks as well as to meet new conservation challenges.

The complexity of the problems in cultural heritage restoration requires an extensive study of the processes involved in the laser-matter interaction. When the surface of a material is irradiated by a laser beam the interaction may proceed in different ways depending on the laser parameters, the intrinsic properties of the material and the ambient environment (*Table 1*) [1].

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Table 1

Parameters and properties involved in laser-matter interaction

Laser parameters	Material properties	Ambient environment
Wavelength Pulse duration Pulse repetition rate Pulse overlap Beam quality/ beam profile Fluence (energy per unit area)	Optical properties (absorption coefficient) Thermal properties (heat capacity; thermal conductivity; latent heat) Chemical composition Microstructure Degree of polymerization	Air Inert atmosphere Vacuum

The appropriate combination of these parameters is crucial for the applicability of any laser method. The maximum wavelength-absorptivity coupling reduces the possibility the excessive energy to be transformed into thermal load and chemical dissociation. For example, some authors propose the use of a laser source emitting in the UV spectral region for the removal of degraded varnish. This radiation is strongly absorbed by the superficial varnish layer and will have minimal penetration to the sublayers of paints [2]. Pouli et al. [3] demonstrate the "layer-by-layer" model where the etching depth depends on the laser fluence and the effective absorption coefficient of the material, so in-depth control may be achieved using highly absorbed laser radiation. A simple example is given with the removing of aged retouching (mostly of acrylic composition) while revealing and preserving the original painting. The chemical composition and the microstructure of the material (metal, insulator or semiconductor) determine the type of photon-electron interactions, as well as its optical and thermal properties. Also, substances with identical composition but different degrees of polymerization may exhibit different physical properties. The ambient environment is important for the presence of secondary effects following the interaction which may influence the final outcome.

The basic classification of the laser-induced processes is derived from the laser fluence (pulse energy per unit of irradiated surface area [J/cm^2]) and the laser intensity (pulse energy per unit of time per unit of irradiated surface area [W/cm^2]). These two laser parameters define the entire spectrum of processes occurring on the surface during laser-matter interaction. When the laser fluence is sufficient enough an effect called laser ablation determines the interaction. It simply means the ejection of material from the surface of an object as a result of the focusing of high-power laser pulse [4]. It is an irreversible effect which can be induced on optically absorbing materials or in their close vicinity after exceeding certain ablation threshold [1]. This threshold is the minimal fluence necessary for starting the ablation process and it depends both on the laser parameters and the material properties. For homogeneous materials, there are several ablation channels distinguished depending on the pulse duration and the laser intensity/ fluence [5]. However, most of the materials encountered in restoration practice are heterogeneous which assumes that the processes involved in laser-matter interaction are more complex and a combination of ablation mechanisms may be considered.

The most widely applied techniques in the restoration field based on laser ablation are the laser cleaning as a surface intervention and laser-induced breakdown spectroscopy (LIBS) as diagnostic and monitoring technique. Over the years they has been perfected in solving of many conservation and restoration problems either in combination or separately. There is a long-gained experience and collected knowledge about the efficiency of the laser cleaning on various materials and contaminants of objects and monuments mostly with historical meaning, such as stone, metal, painting, paper and parchment, textile, stained glass, wood; removal of dyes, inks, old varnishes, over-paints, biological growth; preserving of patina or other surface coatings. Objects of various shapes and sizes can be effectively treated, such as written documents, archaeological artefacts, sculptures and monuments [1]. A variety of laser sources has been tested in order to establish the most appropriate cleaning protocol for a given case study (LACONA conferences). On the other hand, LIBS has shown to be a simple, fast and straightforward technique for the identification of the chemical composition of any kinds of materials encountered in the conservation-restoration field – organics and inorganics, solids, liquids or gases, etc. enabling stratigraphic analysis as well [6], [7]. It is applied in different configurations, such as double pulse [8], and has demonstrated reliability for in-situ investigation in hostile environments, such as underwater [9]. An important application of LIBS is the evaluation of the efficiency of laser cleaning by real-time monitoring [10] or afterward [11].

The original idea of the laser cleaning consists in selective vaporization of unwanted surface material upon absorption of sufficient amount of laser energy. Its principle is founded on the difference in the absorption of the material to be removed and the material to be preserved. This difference should be large enough to ensure that the unwanted layer absorbs radiation and is ejected while the underlying substrate remains untouched reflecting any further incident radiation. This determines the self-limiting effect of laser cleaning [4]. Still, there are some cases in which the properties of the unwanted material and the original surface are similar and the self-limiting effect is not observed. This requires the use of additional methods for control of the cleaning procedure. Fast scanning of the laser beam over the surface via galvo-scanners and precise motorized two- or three-dimensional positioning stages, or in-process monitoring via different spectroscopic and acoustic techniques are possible solutions [12].

The unique properties of the laser radiation, such as high intensity, monochromaticity, directionality, and coherence lead to some major advantages. The lack of mechanical contact with the surface avoids the need for pre-consolidation and preparation of mechanically fragile objects when surface cleaning is conducted. The monochromaticity defines the selectivity of the laser-matter interaction. Radiation at a certain wavelength that is strongly absorbed by the unwanted superficial layer resulting in its evaporation and that is weakly absorbed by the original material can be used. Moreover, laser cleaning is a flexible technique. The parameters of the laser can be finely tuned so the procedure can be adapted to apply on large spectrum of objects depending on their particular demands. The removal is fully controllable in space and time. The laser processing has nearly sub-micron resolution which makes it highly localized and extremely precise with minimal collateral damage. In some cases, it allows the gradual (layer by layer) and smooth removal of unwanted thickness. The laser intervention allows immediate feedback and monitoring in real-time thus minimizing the risk of irreversible damage to the object. Once the laser irradiation reaches the precious surface the interaction can be immediately stopped. Furthermore, laser cleaning is environmentally friendly as no hazardous chemicals, solvents or foreign atoms are introduced to the surface that may additionally penetrate the original material and cause residual interactions [1].

In spite of all the mentioned advantages of the laser cleaning technique, there are many investigations with respect to the possible induced side effects. Since most of the artwork materials tend to be thermally and light-sensitive [3], it is crucial to take into consideration such effects in order to minimize them. Depending on the laser parameters and the material properties they occur on a different scale. A part of the absorbed energy, upon irradiation with nanosecond and longer pulses, decays into heat which may result in pronounced collateral damage and/or morphological changes. This effect is observed consequent to irradiation at weakly absorbed wavelength, too. Some chemical alterations may result as well from the thermal load or the dissociation of chemical bonds activated by the direct absorption of photons. The structural modifications associated with high-amplitude stress waves produced upon irradiation are crucial, too. Another observed side effect related to the high sensitivity of most of the pigments at laser irradiation is immediate discoloration after treatment [13]. In most of the cases, a considerable number of laser pulses are required for the enhancement of the efficiency of material removal. Hence, there is a possibility of cumulative heating that could result in a larger thermal damage zone. Accumulation of by-products into the substrate is possible, too. The latter may result in a gradual change of the physical and chemical properties of the material.

Thus, it is important to consider that the pulse repetition rate or the pulse overlap should be low enough that the time between successive pulses is sufficient for the complete heat diffusion and to avoid the formation of secondary chemical products. In order to confine and minimize those side effects, it is important to choose carefully the laser parameters correlated with the material's properties. The pulse duration should be short enough to enable the thermal and stress relaxation of the medium (usually in the nanosecond and shorter range). The applied wavelength should be strongly absorbed from the unwanted material as well. The selectivity of the process is determined by the incident fluence, the type of contamination or unwanted layer and its adhesion to the surface. In any case, cleaning should be carried out at the lowest practical fluence so that the more selective mechanisms are at work. Nevertheless, it is important to monitor the extent of such side-effects in order to achieve controlled and safe laser cleaning [1], [4], [14].

Before initiating laser cleaning procedure, it is mandatory to realize, if possible, preliminary tests in order to establish the most suitable working protocol for the given case. As a result, a cleaning procedure could be designed and applied. In the ideal case it would consist of a few steps [12]:

1. Preliminary assessment of the properties of the layer to be removed and the original material (optical properties, physical properties, chemical composition and structure, aging processes, etc.).
2. Laser cleaning:
   - Fine tuning of the laser parameters (spot size, pulse repetition frequency, pulse energy, wavelength, pulse duration, etc.);
   - Determination of the damage thresholds of the unwanted and the original material – setting a safe working range of laser fluences, if the case allows it;
   - Performing laser cleaning – working just above the damage threshold of the unwanted material is always favored in order to ensure the safety of the original layer.
3. Evaluating the cleaning efficiency – examining the condition of the object for any side effects and the presence of residues.

The knowledge of the laser-matter interaction mechanisms and side effects is collected on the basis of experiments on objects, artifacts and artworks mainly with historical significance. Nevertheless, a profound and equivalent awareness of the effect of the laser ablation on modern and contemporary works of art is still scarce. Moreover, most of the materials used in contemporary artists' creations are part of a whole new class of materials emerged within the industrial outbreak of the 20th century and are not thoroughly examined yet. They are easy to reach and to apply, but they are as different from the classic old-fashion materials used by the artists for centuries, in manners of durability, quality of performance, and interaction with the environment. The majority of them tend to degrade in unpredictable ways which endanger the social value of the work itself [15]. During the recent years, the number of laser cleaning investigations of contemporary artworks has been increased but still, those researches are not as systematic and comprehensive.

This paper discusses the interaction of the laser beam with contemporary art materials upon laser cleaning. The aim is to show the essential role of the study towards the understanding and knowing the materials, their interaction with each other and with the laser radiation which will lead to the establishment of suitable restoration protocol. A simple cleaning procedure is demonstrated consisting of an early-stage experiment on laser removal of black permanent marker drawings from a graffiti technique painting. A preliminary investigation of the surfaces from an aesthetical point of view before and after the laser cleaning is done by optical microscopy and colorimetry. The visible aesthetic issues encountered while testing different laser regimes are outlined.

2. Experimental

For the purpose of the research, a multi-color contemporary painting using graffiti technique has been prepared as a model sample. Three different colored parts are chosen on a random basis. Small rectangular areas (1.5x1 cm^2) on them are covered with black felt-tip permanent marker BIC® (Fig. 1).

Fig. 1. Model sample of a graffiti technique painting with black permanent marker drawings

The cleaning tests are performed with a Q-switched Nd:YAG laser operating at wavelengths 1064 nm and 532 nm, with pulse duration 8 ns, pulse repetition rate up to 20 Hz, and maximum energy per pulse 450 mJ at 1064 nm, and 200 mJ at 532 nm. The beam is delivered through an articulated arm. The size of the laser spot is 0.38 cm^2.

In accordance with the proposed cleaning procedure, the chosen areas are observed before and after the laser intervention by means of optical microscopy and colorimetry.

3. Results and discussion

In Fig. 2, microscopic pictures of the original surface, the surface with the black marker and the surface after laser cleaning are shown. The pictures after laser cleaning are taken on the border of the marker drawings and the original painted layer in order to observe the effect of the radiation on both of the materials. On every treated area colorimetric measurements are done on the original and cleaned surfaces. The results are presented in *Table 2*. Since the investigation is in a preliminary stage, the colorimetric values are acquired in a single spot in each area in order to have a basic estimation of the induced color changes. A further systematic examination is planned where the values from multiple points will be averaged for more accurate results.

It is visible that an efficient laser regime is not established as the black marker ink is not removed at all without affecting the graffiti paints. Using the fundamental wavelength (1064 nm) appears to be less effective than the second harmonic (532 nm). With the applied energies at 1064 nm, there seems to be no effect on the black marker (Fig. 2 4(b), 8(b), 12) or if there is, the graffiti paint layer is ablated demolishing the surface beneath (Fig. 2 4(a), 8(a), 12). The reason is that the damage thresholds of the marker and the paints are similar for this wavelength. Such a case is an example of not observing the self-limiting effect. The painting can be monitored during the intervention with spectroscopic and acoustic techniques. If the overpainting layer is tick enough a layer-by-layer working mode can be achieved using fast and precise galvo-scanners [16] or motorized translation stages.

The use of the green wavelength is observed to be less intrusive for the morphology of the surface, but severe discoloration of the graffiti paints is pronounced (Fig. 2 3(a), 7(c), 11(a)). This might be due to photo-induced thermal and chemical alterations or revealing another underpainting layer. In Fig. 2 – 7(a, b), the revealing of different under-layers is noticed. Either way, stratigraphic analyses will be involved for better evaluation.

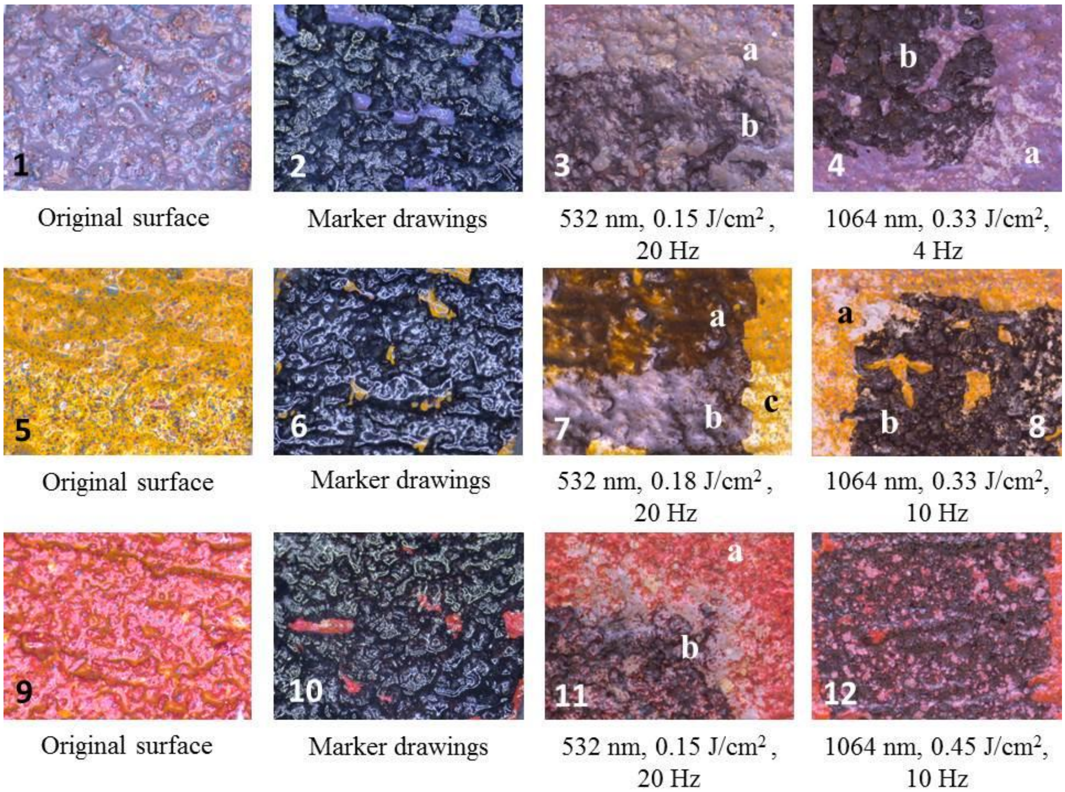

Fig. 2. Optical microscopy images of the investigated areas before and after laser cleaning

Table 2

Colorimetry measurements of the areas before and after laser cleaning in the CIElab system

Area #		L*	a*	b*	ΔE
1	Before	49,33	10,93	0,05	18,62
	After	37,39	-10,44	-1,17	
2	Before	48,57	11,06	-13,52	26,74
	After	27,88	2,76	1,24	
3	Before	69,54	15,57	50,45	
a	After	38,09	1,46	11,89	51,72
b	After	51,43	-0,57	2,96	53,33
4	Before	66.16	17	44.37	56.69
	After	31.01	1.98	2.5	
5	Before	43,35	34,54	20,21	29,90
	After	37,1	9,27	5,51	
6	Before	43,71	32,17	22,03	33,77
	After	31,47	8,04	1,82	

The preliminary colorimetric measurements reveal large differences in the color indexes ΔE between the original and laser-treated areas. At this early stage of the experiment these results support the observations of non-efficient laser cleaning.

The higher damage threshold of the black marker implies the presence of some reflecting additives in the chemical composition of the ink. To verify this, further comprehensive investigation including spectroscopic techniques is planned. Furthermore, other factors influencing the removal efficiency should be considered. These are the adhesiveness of the marker's ink and the roughness of the painting substrate which favors the farther penetration of the ink.

4. Conclusions

During the recent years, the number of laser cleaning investigations of contemporary artworks has been increased but still, those researches are not as systematic and comprehensive. The aim of this paper is to show awareness on the effect of the laser ablation on modern and contemporary art materials stressing out the need for detailed study and monitoring of possible side effects. Moreover, the knowledge and the understanding of the original material, the pollutants and the mechanisms of their interaction with each other and with the laser radiation play an essential role towards the establishment of suitable restoration protocol.

An example of the removal of black marker drawings from painting with graffiti technique is presented as well. The investigation is in a preliminary stage and outlines the aesthetical issues encountered while testing different laser regimes which are related to discoloration and demolishing of the surface. The inefficient laser removal might be caused by several factors: similar properties of the marker and the graffiti paints in terms of damage thresholds; reflective additives in the composition of the marker's ink; strong adhesion of the marker's ink, and surface roughness of the painting's substrate. However, further investigation by means of spectroscopic and stratigraphic analyses is necessary. The use of UV laser radiation for cleaning or a combination with other cleaning techniques is also considered.

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