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Lasers in the Conservation of Artworks

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Laser removal of contaminants from painted surfaces

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Abstract – An analysis of surface ablation by laser exposure of art objects as part of the conservation process indicates that heat diffusion from the site of laser exposure may be minimized by proper selection of wavelength and exposure duration. A model for unwanted material removal with a laser has been developed taking account of the threshold phenomenon of ablation as a function of wavelength, and exposures at 2.94 μm by an Er:YAG laser with short duration pulses is compared with those from a Nd:YAG (1 064 and 532 nm), CO_2 (10.6 μm) and the ultraviolet excimer laser at 193 nm. Thermal diffusion is minimized by taking advantage of the large amount of heat removed by the phase change of water into steam. This model suggests that for bulk removal at strongly absorbed wavelengths, many short pulses are better than continuous exposures. The selection of the Er:YAG laser allows the use of hollow glass waveguides of high flexibility, which are commercially available, as delivery systems. Examples of successful removal are given for contaminants overlying a Madonna's gold leaf halo and the heavy dark accumulation of soot on an unvarnished oil painting, as well as for thick synthetic adhesive on canvas. © 2000 Éditions scientifiques et médicales Elsevier SAS

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1. Introduction

Present laser instruments (mainly the Nd:YAG at various wavelengths) for general art conservation offer many advantages over conventional methods with solvents and scalpels, yet still have many limitations. A particularly critical one is the damage to the material adjacent to that removed or ablated by the laser energy. Laser energy applied to any material immediately produces thermal or mechanical damage to a volume surrounding the impact zone [1, 2]. Part of this is due to scattering [3, 4], but other mechanisms also act on the material. Steam formation, thermal expansion, and acoustic shock waves, with much of their energy in the ultrasonic region, have an effect termed 'physical amplification'.

There may also be a secondary and delayed amplification of the size of the exposure site. This delayed change, in living systems, is a reaction to the physical trauma, and has been termed 'biological amplification' [1, 2]. In art conservation applications, such an effect could result in flaking of the paint that is loosened by thermal expansion, or thermal plasticity of an oil paint with loss of the details of the artist's brush strokes, and is better termed simply 'delayed amplification'. For lasers to be used successfully in art conservation, both immediate and delayed amplification must be avoided or at least minimized.

Following many types of laser exposure, the material evaporates or decomposes when some critical or threshold temperature is reached. At this point the affected region becomes gaseous or is broken up into small enough particles to acquire sufficient kinetic energy to be ejected. However, there is always energy deposition outside of the ablated volume, and following the ablation, some thermal diffusion takes place within this impact volume and into the surrounding material. To minimize the absorption volume and the opportunity for thermal diffusion, it is desirable to limit the laser absorption depth to the thinnest possible surface layer in order to vaporize and remove only the superficial material without disturbing anything underneath. The depth of ablation for each laser exposure can be controlled by variations in the laser power and the time of application to any given spot, as with conventional CO_2 laser removal of surface graffiti [5]. Here the depth of cut is controlled mostly by the speed of the laser beam traversing the surface. Deeper ablations are made by successive applications of the laser beam until the required depth is reached. An analysis of this type of cutting shows that at least three factors are important in limiting thermal damage in the material remaining after ablation, both in the laser exposure site and in the adjacent region: the pattern of energy deposition, which is dependent on the absorption and scattering properties of the material; thermal diffusion from the site of energy deposition; and change of state or vaporization of material elements (usually water, which gives surface cooling by radiation and evaporation). Convection or mixing may also make a contribution if the thermal gradient lasts sufficiently long and the material is sufficiently liquid during the temperature elevation.

Lasers tested for use in fine art conservation have thus far shown significant weaknesses in either immediate or delayed amplification effects. For example, because of its deep penetration, the Nd:YAG laser is rarely suitable for material overlying highly sensitive and important structures to which damage must be avoided at all costs. The use of excimer lasers in the ultraviolet (193 nm) to remove plastics to close tolerances without grossly visible damage in adjacent regions [6–8] suggests that this method may also be helpful in conservation. However, certain features of this type of laser exposure, especially the long-term effects of short wavelength UV and the shock wave associated with ablation, remain to be investigated. This paper reviews laser action in another spectral region, the infrared around 3 μm. It shows the similarities to the ArF excimer laser at 193 nm in precise material removal and compares the possible deleterious implications of each type. As described below, the present method uses the OH bond in water, alcohols and similar small molecules as the chief absorber of the laser radiation. By careful minimization of ablation depth and maximization of absorption, both physical and delayed amplification are effectively eliminated.

2. Pattern of energy deposition

The pattern of energy deposition in material is a function of absorption and scattering. Both of these vary in each material type with wavelength, and together they define the limit for minimizing the volume of energy deposition and the subsequent thermal diffusion. In Er:YAG laser procedures at 2.94 μm, the only important absorber is the OH bond in water and other molecules. Its absorption and scattering properties determine the pattern of energy deposition [9]. The literature is ambiguous as to the exact wavelength for the highest specific absorption of water in the near and mid-IR range [10–15]. However, measurements by Lukashev (pers. comm.) made especially to clarify this issue indicate an absorption peak for pure water at 2.94 μm and a specific absorption depth of approximately 1 micron, corresponding to an absorption coefficient α of 10 000 cm^{-1}. The results of Lukashev's measurements of the absorption of liquid water also indicate that temperature increases result in a shift of the maximum absorption toward shorter wavelengths. Furthermore, it is possible that increases in the water temperature increase the value of the maximum absorption coefficient. Based on these findings, the optimum laser wavelength shifts from 2.94 to 2.70 μm during the pulse so as to allow a better match with the peak absorption of the material as it becomes heated. Within this wavelength range, and for the absorption depths in question, scattering is insignificant. Thus, the pattern of energy deposition is determined by the distribution of molecules containing OH bonds.

In the visible and near IR, water has very low absorption. However, discrete material components such as pigments may absorb heavily, often in a strongly wavelength-dependent way. Molecular (Rayleigh) scattering generally increases in the blue and in the near UV region, while large particle or disjunctive (Mie) scattering is more or less wavelength-independent. To find the rise in scattering and the increased effective absorption of many specific molecular components of the various materials which are to be removed (or, alternatively, left unaffected) in a given laser application in art conservation is laborious and even useless in some cases, as both may have similar or even identical absorption spectra, thus making selective targeting (or avoidance) impossible. In order to circumvent this problem, we select a spectral region where only water and similar compounds have a high absorption, and we add water to the laser exposure zone in sufficient quantities to swamp out any absorption by all other molecules in the contaminating material.

3. Thermal diffusion

The removal of material while minimizing thermal damage to adjacent zones is limited by material absorption characteristics, thermal conductivity, and the time required for heat diffusion in the particular material involved. An analysis similar to that used for photocoagulation of the retina with melanin granules as hot spots [1, 2] shows that the high values of energy input needed for the phase change from water to steam without appreciable thermal diffusion into adjacent materials are reached only when the exposure duration is shorter than the thermal relaxation time. This effect is ultimately limited by the bulk absorption properties of the material at the selected wavelength, as summarized below.

The thermal relaxation time of a given volume of any material is a time short enough to prevent much of the heat to diffuse out. The larger the volume, the longer the time. At 2.94 μm, the free running pulsed Er:YAG laser for each flashlamp excitation has a pulse train of 250 μs, but for each individual 1.5-μs pulse within the train which exceeds the ablation threshold, the thermal relaxation criterion is essentially satisfied. Accordingly, more efficient ablation with the least surrounding thermal damage could be expected to be approached by a pulsed Er:YAG laser. The absorbed energy available for heating with a single 1.5-μs exposure duration would essentially remain entirely right where it is absorbed (in the top few micrometers) long enough to heat and vaporize just the desired portion of the material.

Heat flow can be minimized and temperature peaks for ablation in the absorption site maximized by using short pulses. Even for very short pulses where heat flow is negligible, the greater the absorption depth, the less steep the temperature profile, with correspondingly greater relative amounts of unablated material attaining damaging temperature levels. For this reason, to minimize absorption by adjacent materials, one should select a wavelength with a specific absorption depth as small as possible. To confine the thermal effects to a shallow surface layer, the laser wavelength must be matched closely to the absorption peak of the material in question. A laser at the 2.94-μm absorption peak of water will have the maximum absorption in the shallowest material depth. This offers a great advantage for minimizing thermal absorption outside of the vaporized or ablated zone. From this consideration alone, the best choice in art conservation is to use a laser wavelength of 2.94 μm to decrease both the absorption (ablation) depth and the size of the adjacent damage zone.

4. Delivery systems

Usable delivery systems for the ablative wavelengths in the 3-μm region have been difficult to achieve until recently. Articulated arms with gold- or silver-plated mirrors will give flexibility [16]. However, the mirrors degrade rapidly and are very difficult to keep in alignment for continuous delivery of high-peak-power short pulses. Optical fibers also offer flexibility. For example, in the 2.5–3.2-μm spectral band, comparatively flexible very low loss zirconium (ZrF_4) glass fibers of conventional cladded construction (i.e. core diameter of 50–500 μm) have been tested, but commercially available fibers are quite fragile [17, 18]. Many other types have been suggested: graded index profile fibers [19, 20], germanium oxide glass fibers [21], and 10 % ZrF_4-doped silica glass fibers. Indeed, flexible but somewhat stiff sapphire fibers are also available with high transmission in this spectral region. Although transmission losses of all fiber types in this spectral region are often sizeable owing to bound water and metallic impurities, nevertheless, ZrF_4 glass fibers with an attenuation of 1 dB/m are already available in short lengths. Even these fibers have sufficiently low loss for the 10-m or more transmission length necessary to allow placement of the laser far from the site of the restoration for safety or greater convenience.

In spite of the many advantages of the optical fiber delivery systems, the present day fibers are only suited to experimental use, not daily use without the skilled maintenance required for successful art conservation. Comparatively recently, another solution became commercially available with the development of robust flexible glass or metal tubes internally mirrored with silver. They are capable of carrying usable power levels at 2.94 μm [22, 23]. (The tubes are called hollow glass waveguides (or HGWs) by their manufacturers, though their internal diameter (about 1 mm) is technically too large for waveguide properties.) These HGWs function very well. Most of the power losses in the system are coupling losses. As only a comparatively low energy (20–70 mJ/pulse) is required for successful ablation, the HGWs will withstand the millions of pulses needed for art conservation.

As an additional bonus, the HGWs, as well as the ZrF_4 and sapphire optical fibers, are quite transparent in the visible region of the spectrum. Thus, it would be simple to direct an auxiliary visible laser beam through these fibers to serve as a marker which will remain in precise optical alignment with the invisible infrared beam which is used for art conservation.

5. Applications

The application of the preceding theory to various paintings and other artworks has been a great success. The Er:YAG removes both organic and inorganic residues from paintings without disturbing the delicate underlying color surfaces. To illustrate this the results of laser cleaning tests are presented for five distinct cases: 1) an unvarnished oil on canvas covered with soot; 2) an oil on canvas in which glue penetration from the back has fixed dirt and varnish onto the color surface; 3) the verso of the same painting, which is covered with a thick layer of synthetic adhesive; 4) egg tempera on wood; and 5) the gold-covered punchwork in the halo of a 14th-century-style Madonna, both of which are discolored by aged layers of shellac. In all of these cases, attempts to clean the art with traditional methods proved unsuccessful either because the contaminants were resistant to solvents or because the underlying surfaces were too delicate to withstand the solvent strength required.

5.1. The Er:YAG and its effects on paint surfaces

The work is carried out using the prototype 'Conservator 2940' model Er:YAG laser made by Schwartz Electro-Optics. The light couples directly into a 1.5-m-long 1 000-μm bore HGW (Ceramic and Materials Engineering, Rutgers University), which the conservator holds like a pen. The tip of the HGW is held a few millimeters from the surface, so that the circular impact zone measures approximately a millimeter in diameter. Each laser pulse delivers up to 70 mJ of energy to the target, which is sometimes pretreated with small amounts of water or another OH-rich agent. The water acts as a highly concentrated, highly absorbing stain. As stated previously, the wavelength is carefully chosen to correspond to the strong absorption peak of water, so that the ablation depth is about 1 micron. Thus, the photon energy is deposited in a small volume and causes a highly localized vaporization of water. The pressure rise due to the phase change is explosive and ejects the contaminant from the ablation volume. When using the HGWs care must be taken to prevent the ejecta from clogging the tube; a microscope coverslip placed on the painting works well, attenuating the energy by about 5 % while protecting the HGW from damage. This trick affords the conservator the additional opportunity to examine the ablated contaminant spectroscopically [24].

Because the individual Er:YAG micropulses are shorter than the thermal relaxation time of water-rich materials, the surrounding region is protected from large temperature rises. Most of the photon energy is converted to kinetic energy of the ejected residue so that untargeted areas remain essentially unaffected. In contrast to the ultraviolet excimer laser, long-term (delayed amplification) effects with the Er:YAG are also likely to be minimal. Photons of 193 nm with an energy of over 6 eV each can dissociate OH bonds in most organic molecules, whereas the much softer infrared photons at 0.4 eV can not. Multiple-photon effects do not occur at irradiances of less than $10\ kW/cm^2$ which the Er:YAG typically delivers in this application.

5.2. Cleaning paintings

The technique used to clean paintings with the Er:YAG is relatively independent of the contaminant to be removed. The only parameters which change with each case are the energy per pulse and the OH-bearing agent (if needed) applied before using the laser. The following descriptions of a few sample cases in which paintings have been successfully cleaned illustrate the versatility of the Er:YAG as an art conservation tool.

One of the first paintings treated using the Er:YAG is a latter-19th-century oil on canvas by an unknown American artist, called 'Yacht Race at Dawn'. The surface of this painting was never varnished. Consequently, as it cured, soot, atmospheric impurities, hydrocarbons from kerosene lamps, etc., created a film which became embedded in the paint matrix. In 1996 the painting was restored. The surface was consolidated and backed with new linen canvas. A wide variety of solvents was employed in an attempt to clean the sooty film from the color surface. Where the solvents penetrated underneath the film, leaching and abrasion of the color surface occurred, especially in the grey and black tones. However, removal of the film using solvent combinations proved impossible.

A single pass of 10-mJ laser pulses at a repetition rate of 10 Hz directly onto the untreated surface turned the targeted contaminant into a fine adhesive dust, which was wiped off with a swab moistened with 2 % $NH_4^+OH^-$ solution. *Figure 1* shows the full painting, sections of which have been cleaned with the laser. Partially cleaned details of the painting are shown in *figure 2*. These clearly illustrate that neither the texture of the brushwork nor the fine color details are lost during treatment.

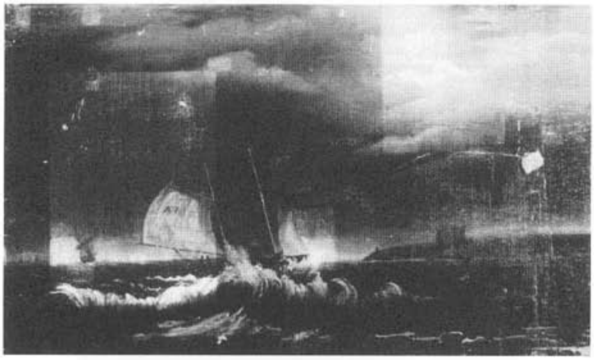

Figure 1. 'Yacht Race at Dawn', by an anonymous American artist. Oil on canvas. Sections of this painting have been cleaned with the Er:YAG.

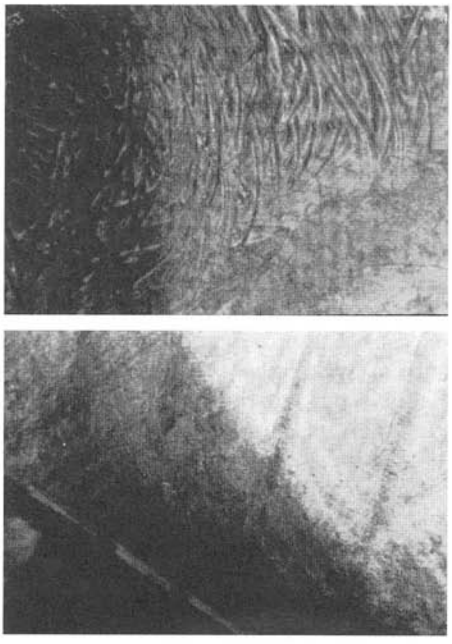

Figure 2. Two micro-details from 'Yacht Race', with the right sides cleaned to illustrate the efficacy of the laser. The top detail shows that the brushstrokes remain intact after cleaning; in the bottom part, fine color detail is left undamaged.

Figure 3. Macro-detail from 'Beatrice Cenci' (oil on canvas), where a central strip has been cleaned.

Our second example is a 17th-century Italian oil on canvas from the circle of Guido Reni, 'Beatrice Cenci'. The verso of this portrait was covered with a thick layer of synthetic resin which had saturated the canvas weave and had penetrated into the paint matrix, fixing dirt onto it. Patches prepared with acrylic resin had been applied to repair tears, and parts of the color surface were overpainted. While the varnish and the overpaint were removed using traditional methods, neither the synthetic resin nor the dirt fixed to the paint surface responded to solvents.

The paint surface was moistened with a small amount of isopropyl alcohol before being exposed to a single pass of 12-mJ laser pulses. The residue of dirt and penetrated resin came away readily with a damp swab. *Figure 3* shows a detail of the painting with a cleaned strip in the center. The verso required more substantial preparation with isopropyl alcohol. Multiple passes of the laser with 20-mJ pulses caused delamination of the resin one layer at a time.

The softened resin was removed from the canvas weave with a scalpel. A small half-cleaned section of the verso is shown in *figure 4*.

The Er:YAG is as effective on delicate surfaces as it is with synthetic adhesives. This is illustrated in the final example, a 14th-century-style Italian 'Praying Madonna' by an anonymous artist. The medium here is tempera on wood with a gold background on bolla. The entire painting was covered with a thick amber shellac varnish with embedded particles of various salts. The surface had been consolidated with traditional colletta glue. Both the tempera and the gold proved very fragile and unable to withstand the solvent strengths required to remove the shellac.

Figure 4. Micro-detail from the verso of 'Beatrice Cenci', half-cleaned. The gummy synthetic resin has been lifted out of the canvas with a scalpel after laser treatment.

Figure 5. Macro-detail of the 'Praying Madonna' (tempera on wood, gold background on bolla). The right side has been cleaned.

Figure 6. Micro-detail of a small punchwork rosette from the halo of the 'Praying Madonna', before (bottom) and after (top) cleaning with the Er:YAG. (See also *figure 5*, bottom edge of halo near veil.) The delicate gold leaf remains unharmed; shellac and salts have been stripped away.

Half of the painting was exposed to a single pass of 10-mJ pulses at a 10-Hz repetition rate. It was found that the absorbing properties of the glue made pretreatment with an OH stain unnecessary. The shellac residue crystallized immediately after exposure to the laser energy, and was easily removed with a swab lightly moistened with ethanol. *Figure 5* shows part of the face and veil. The right side of the detail has been cleaned with the laser. A section of the fragile punchwork halo is visible on the gold background to the right of the veil.

The gilded punchwork was so encrusted with shellac and soluble salts that it was impossible to determine how much of the original surface still remained. The small rosette shown in detail in *figure 6*, before and after cleaning, can be seen in *figure 5* just to the right of the veil. Most of the area surrounding the rosette has become detached from the wood, making it especially vulnerable to damage due to any immediate or delayed amplification effects from the laser. Nevertheless, *figure 6* clearly demonstrates that the delicate gold leaf on the rosette, as well as the integrity of the rosette itself, have not been damaged by the Er:YAG. In general, the gold reflects the incident infrared light and remains intact, while the shellac layers overlying it are cleanly removed.

6. Conclusions

The present paper shows that it is possible to clean paintings in various media safely and effectively with the pulsed Er:YAG laser at 2.94 µm. This wavelength in the infrared is theoretically motivated because it is selectively absorbed by water. The strong absorption ensures that the laser energy is deposited in very superficial layers of small volume, in which high temperature gradients and explosive vaporization ensure that contaminants are ejected from the painting surface while the underlying paint remains unaffected. We show the success of this laser cleaning method with several examples, which also serve to illustrate the versatility of the Er:YAG as a conservation tool. The advantages of the Er:YAG over other lasers which have been considered for use in fine art conservation include: 1) minimal physical amplification effects (compared, for example, to the Nd:YAG); 2) minimal delayed amplification; 3) availability of flexible delivery systems (cf. the excimer); and 4) portability and ease of use. The high precision of the laser pulse delivery to the target areas allows the conservator to maintain fine control over the process. The need for toxic aromatic solvents is completely eliminated.

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