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LASER CLEANING APPLICATIONS FOR RELIGIOUS OBJECTS

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Abstract

Laser clearing is nowadays employed successfully for the removal of unwanted layers of diverse chemical and physical nature from historical and religious monuments and objects. Significant research evolution has been made via close collaboration between scientists, conservators and curators. Several studies have shown that the maximum efficiency of the laser-induced divestment can be obtained in parallel with the safety of the preservable artefact. The examples discussed herein and the numerous case studies presented in the biennial international LACONA conferences demonstrate that in the future laser cleaning may be the leading technique for the preservation of churches, historical monuments and religious objects with great cultural heritage significance.

Keywords: Laser ablation, laser spallation, oxidized and condensed varnishes, encrustation

1. Introduction

Religious expression is usually associated with the erection of churches and monuments bedecked with a variety of artefacts, such as sculptures and icons. These items reflect their historical evidence that is established with age. Such religious monuments and artefacts commonly suffer from uncontrolled climate conditions as well as from their regular use or misuse. Hence their deterioration rate is greater compared to works of art stored and displayed under controlled environments [1]. Therefore, there are several applications and methods reported aiming at their conservation [2, 3].

Among the most significant applications in conservation is considered to be the 'cleaning', that is the removal of contaminants, pollutants and/or damaged protective layers from the original surface of an artefact. 'Cleaning' provides aesthetical improvement of the artefact as well as deceleration of the aging

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process of the original materials [2]. In the present work we will discuss a recent advancement in the multidisciplinary field of 'Lasers in Artwork Conservation (LACONA)' [4-7] that concerns the protective 'cleaning' of religious artefacts. Simplifying the presentation, we consider two types of deterioration layers: (a) surface layers of organic origin such as natural resin coatings/varnishes, usually applied to painted surfaces, e.g. icons; and (b) inorganic dark encrustation formed on the surface of sculptures exposed to the environment. In both cases, there are additional layers of pollutants and sooth resulting in the eventual obscurity of the underlying surface.

Laser technology is commonly employed for the analysis of aged materials, works of art and archaeological artefacts [8-10] and is behind damage assessment techniques such as holographic interferometry [11-13] and monitoring of environmental influences [14]. The vigorously progressive research in 'laser cleaning' is credited to the preliminary work of Asmus and co-workers [15-19], who discovered that lasers can remove black encrustation from aged marble surfaces. Several groups have systematically carried out relevant research and great progress has been made on the laser cleaning of various objects. Papers of comprehensive and ongoing research results, as well as specific case studies for laser cleaning exist in the LACONA international conference proceedings [4-7].

Laser is a light source emitting a beam of monochromatic light that is light of one colour and therefore a single frequency or wavelength. From the extended variety of lasers, two laser types are mainly used for cleaning applications in conservation. The so-called *excimer* laser that fires pulses (light bursts) lasting some nanoseconds – one nanosecond is one billionth of a second – is currently the best option for the removal of aged resin layers [20-22]. On the other hand, *Nd:YAG* laser is the most common type of laser employed for cleaning applications, because of the flexibility provided in terms of pulse duration (ranging between nanoseconds and milliseconds) and wavelength (1064, 532, 355 and 266 nm). There are several examples of Nd:YAG laser cleaning on architectural and archaeological sites [23-28], metal [29, 30] and wood surfaces [31, 32]. Nd:YAG laser has also been employed for the cleaning of wall paintings [33] and has provided efficient removal of black wax stains from an icon surface [34].

A good evaluation of laser cleaning can be provided by online monitoring, using Laser Induced Breakdown Spectroscopy (LIBS) [21, 35-37]. Damage of the object can be prevented using the appropriate laser implementation and cleaning methodology [22]. In the case of inorganic surfaces such as stone and marble, this is facilitated by the so-called self-limiting process [19, 22, 38]. According to this process, while dark encrustation layers are gradually removed, the brighter original surface is eventually uncovered and appears unaffected. On the other hand, laser cleaning of aged resin coatings over photosensitive surfaces, e.g. pigments, is a rather laborious process [20], since there is no clear barrier between the removable and sustainable layers. Therefore, a thin layer of the coating is usually left on the substrate to prevent undesirable penetration of laser photons [21, 22, 39].

This work presents a few examples of laser cleaning applications on religious artefacts and is divided in two sections according to the nature of the removable layers. First we describe the laser ablation of aged and contaminated varnishes from secular icons using an excimer laser. Then, we will discuss the laser induced divestment of encrustation from inorganic surfaces using Nd:YAG lasers.

2. Experimental results

2.1. Laser cleaning of coated painted surfaces

The laser-induced removal of oxidized and condensed resin coatings is carried out with UV-pulsed laser ablation [21, 22]. A comprehensive review on the excimer laser properties is nowadays available [40]. A series of optics under the required configuration [21, 35, 41] are used for the maximum exploitation of the stable excimer laser beam profile (Gaussian versus top hat in the transverse directions). Depending on the laser wavelength, ablation is based on successive photochemical, thermal and photomechanical actions, following the laser-induced electronic excitations of the irradiated surface. These actions lead to ejection of the photo-dissociated material, creating etchings ranging within the sub-micron scale [40, 42, 43]. Laser wavelengths shorter than 248 nm are preferable because they have negligible or no thermal contribution to the irradiated surface. KrF excimer laser provides the most cost-effective ablation of aged varnishes [22] and has been used for the cleaning of aged icons.

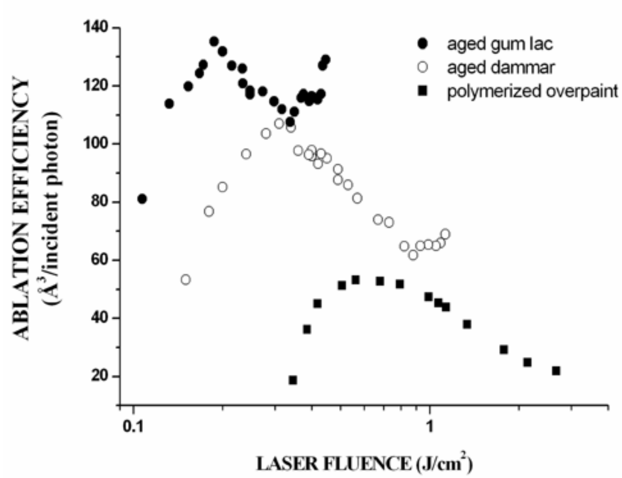

Figure 1. Ablation efficiency of four different complex coatings with a KrF excimer laser. The error is less than 10%.

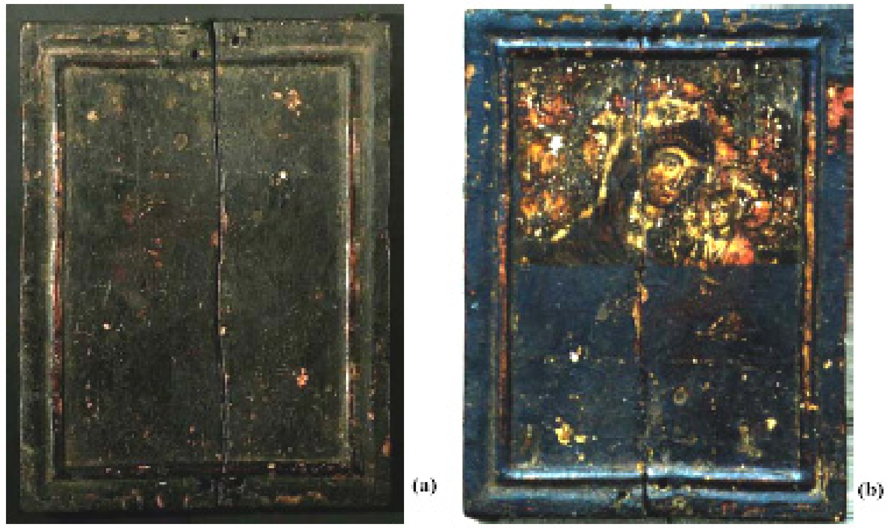

Figure 2. Burnt icon before (a) and after (b) cleaning of the upper half with a KrF excimer laser. The treatment was carried out with a fluence of 0.6 J/cm^2 and 4 scans of 5 pulses per scan.

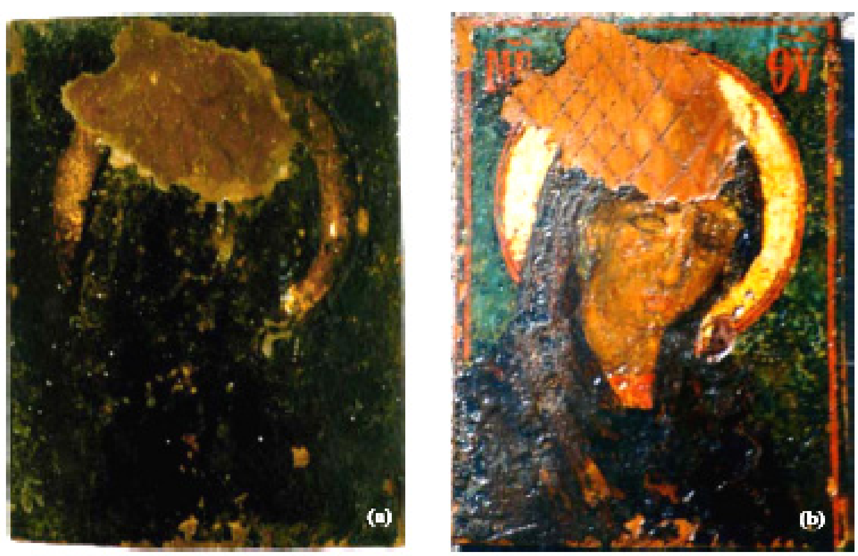

Figure 3. Burnt icon before (a) and after (b) KrF excimer laser ablation. The laser treatment was carried out using a fluence of 0.7 J/cm^2 and 12 scans of a single pulse per scan. Note the cleaning efficiency of the laser on the wooden panel, where the painted part was missing.

The most important factor for the success of the application is the selection of the energy density (fluence), which maximizes the ablation yield per incident laser photon (Figure 1) [21, 22]. Using this particular laser fluence, the risks of laser-induced thermal effects occurring in the low fluence regime and risks of photomechanical defects in the underlying layers, which may take place in the high fluence regime, are considerably reduced [22, 42, 43]. Moreover, ablation with optimal fluences guarantees the lowest possible transmission of laser photons in the underlying valuable surface [20, 22].

Often, religious objects in use are badly preserved because of the lack of precautions with respect to their preservation. There are several cases reported with burning injuries owing to the use of candles or oily vigil lights. Such injuries are difficult to treat from the conservation point of view. For example, in the case of burnt varnished icons, the surface layers of the original aged coating is covered with thick charred layers, which along with the oily fumes and the incorporating melting species of the aged varnish may introduce a high degree of insolubility. Such cases can be comfortably treated using laser cleaning. Two examples of KrF excimer laser cleaning of extremely burnt icons are shown in Figures 2 and 3. In the case of Figure 2 the varnish was completely charred and no other treatment was available but laser cleaning. In the case of Figure 3, there was sparsely some varnish preserved below the charred coating layers, which was removed with solvents after laser cleaning.

Laser cleaning is also employed for the removal of better preserved aged varnishes, which may not be removed by other means. In these cases, the composition of the ablated coating plays a significant role in the success of the process. Excimer laser ablation is affected first by the absorption regulated by the degree of oxidation and subsequently by the degree of condensation of the irradiated substance [42]. During the laser cleaning tests, spin-off findings aside laser cleaning tests showed that both the degrees of oxidation and condensation of aged natural resin films are decreasing depth-wise [39, 44]. As a consequence the degrees of absorption and laser-induced bond-breakage as well as the corresponding ablation yield are reducing with depth [45]. These phenomena are fully established today [20]. Aging converts varnishes from transparent to discoloured films influencing the appearance of the substrate [46]. This transition is caused by the generation of oxidative products via a sequence of cross-linking processes [47, 48]. Because of the stronger deteriorated surface, compared to the bulk of the coating, the underlying surface appears gradually clearer as the varnish thickness is reduced (Figure 4) [39]. The depth-wise decreasing deterioration is also determined in terms of increasing solubility with depth [39].

Finally, the coating is the only barrier that prevents the propagation of the incident UV laser photons in the original underlying material. In case of uncontrolled laser transmission or direct irradiation paints containing inorganic pigments discolour [49]. Although this side effect occurs only in the uppermost layers of the irradiated pigment particles [50], the damage is irretrievable. Therefore, the removable coating must be aged so that to develop the essential high degrees of absorption and condensation. However, the maximum deterioration of natural resin films occurs in a depth up to 15 μm [20, 39, 47], because this is the maximum absorption length of UV ambient radiation in these coatings [20]. This finding and the presence of gradients indicate that the laser cleaning of varnished surfaces should be terminated after the most deteriorated part of the coating is removed. If further cleaning is required, a cautious use of low polarity solvents is recommended, because the remaining film is exponentially more soluble than at its surface. Nevertheless, for many cases a subsequent chemical cleaning should not be necessary, because of the evident enhancement of the appearance of the underlying surface with depth (Figure 4).

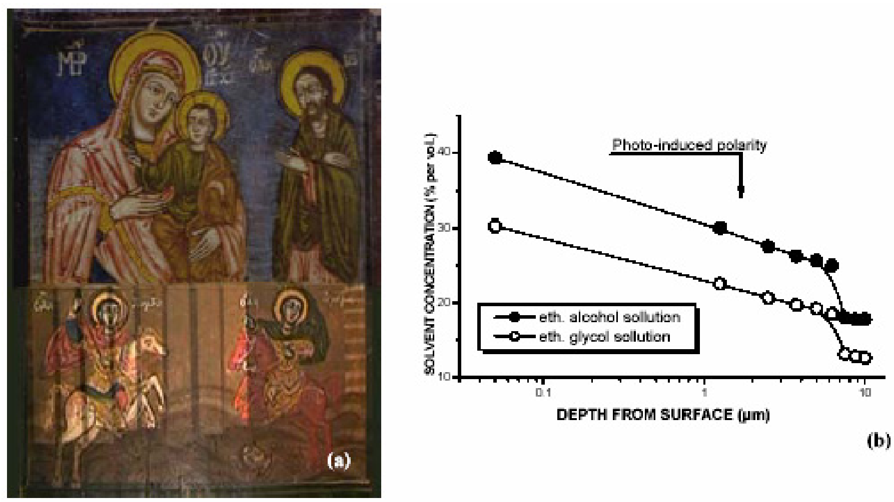

Figure 4. A laser cleaning test of an aged, discolored varnish using a KrF excimer laser: (a) The original varnish was 15 μm thick. Eight laser cleaned areas span a thickness of varnish removal from 1.25μm to 10 μm (left to right). Note the gradual improvement of the appearance of the painted surface; (b) The gradual depth-wise change is also reflected on the reduction of the concentration of solvent required to dissolve the remaining varnish with depth [39].

2.2. Laser cleaning of inorganic surfaces

As discussed above, the Q-Switched Nd:YAG laser is frequently used for controlled cleaning applications to inorganic surfaces, such as marble and stone [16, 19, 37, 51, 52]. In this case the so-called self-limited divestment process protects the underlying surface. This phenomenon has been termed so, because of the lower spallation threshold of the encrustation layers compared to the preservable substrate. Figure 5 shows the spallation rate data from marble and a thick dendritic encrustation [22].

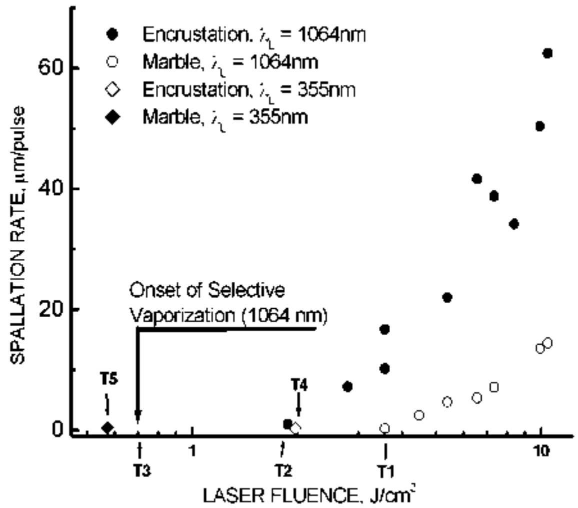

Figure 5. Ablation rate data for a marble substrate covered with dendritic encrustation using a Q-switched Nd: YAG laser under the fundamental wavelength (1064 nm) and the 3rd harmonic (355 nm). Arrows designate the various thresholds described in text.

It is shown that the spallation thresholds of marble and crust at 1064 nm are at 3.5 J/cm^2 (T1) and 1.85 J/cm^2 (T2) respectively. The success of the process depends on the choice of a fluence between the two thresholds (T2 and T1), so that to produce efficient removal of the encrustation without affecting the substrate.

Encrustation is normally overlaid in consecutive layers, which may be separated or mixed. Apparently, the composition of these layers depends on pollutants and the concentration of oxygen in the environment; thus surface encrustation varies between objects in different environments [53]. Regardless of the environment, in the majority of objects the lowest layer of encrustation is similar, mainly consisting of a gypsum (CaSO4·2H2O) film with embedded black carbonised particles and various minerals (Figure 6a) [54, 55]. A suitable use of the Nd:YAG laser enables the selective removal of the black particles from the gypsum layer and allows to maintain or remove part of the gypsum (Figure 6b). This property is based on the absorptivity of 1064 nm laser light, which is up to 4 times higher for the black particles than for the gypsum layer or the substrate [16]. Thus, the high energy deposited in the particles leads to their removal via explosive vaporization [22]. However, upon the 1064 nm laser irradiation the substrate acquires a yellow hue [52, 56]. In short, yellowing is suggested to be a light scattering problem [22, 57]. It is now understood that yellowing is the consequence of the light response in the particle-free porous gypsum film, part of which undergoes chemical change that renders the gypsum to anhydrites and hemihydrates [58].

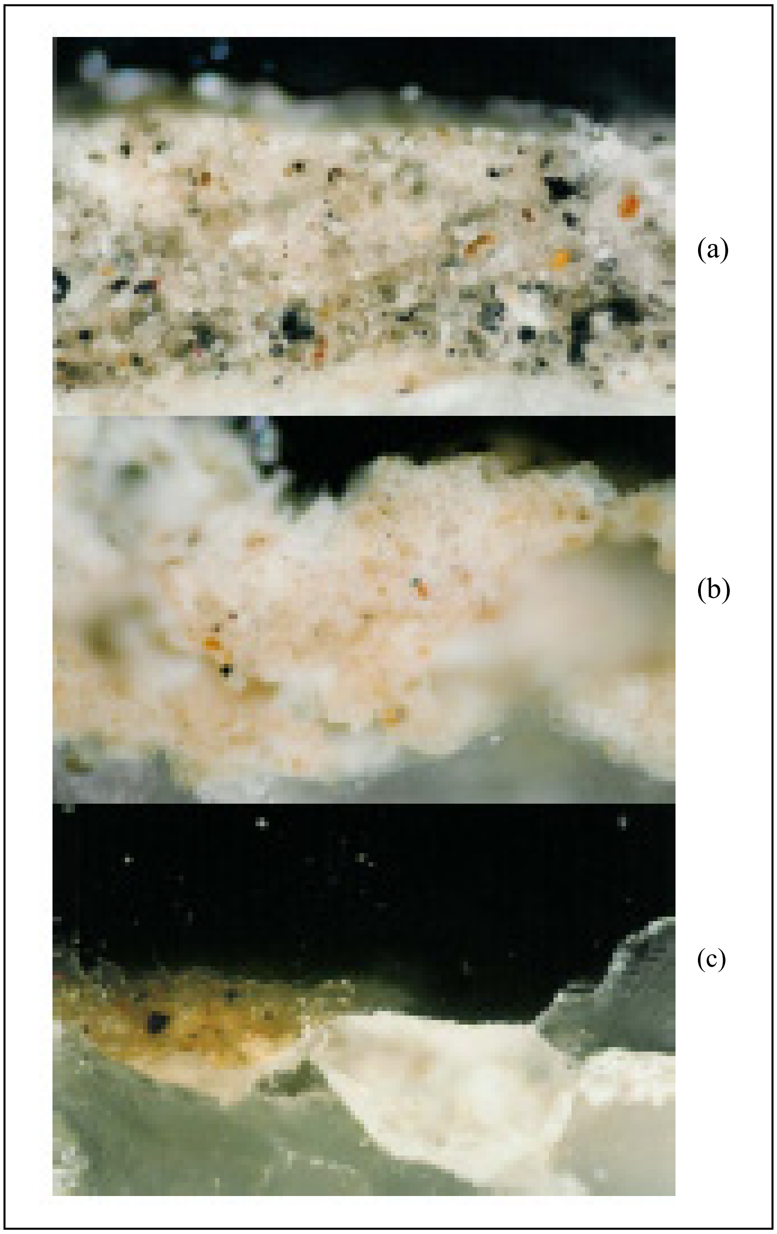

Figure 6. Cross-sections of: (a) CaSO4 (gypsum) encrustation layer with embedded black carbonised particles; (b) the same material after vaporization at 1064 nm after 50 pulses with 0.8 J/cm^2; (c) after controlled spallation with the 3rd harmonic (355 nm) with 0.45 J/cm^2. In (b) note the absence of the black particles, the yellowing of the layer and the porous texture. In (c) it is shown that both the gypsum and the particles are removed, while the underlying marble remains unaffected. All pictures correspond to an area of 500 x 350 μm.

In contrast to this well documented problem due to 1064 nm irradiation, removal of black encrustation with the third harmonic of the Nd:YAG laser (355 nm) does not cause yellowing (Figure 6c). UV reflection imaging has shown that the black carbonised particles and the gypsum-rich layer absorb 355 nm equally [59].

Therefore, at 355 nm the mechanism of selective vaporization is not likely to occur. In such cases, cross-sections have revealed the simultaneous and with no discrimination removal of black particles and gypsum-rich layer down to the substrate (Figure 6c). Thus, at 355 nm the observed reflectance of treated substrates resemble the reflectance of non-treated clean surfaces [22]. However, using the third harmonic there are risks for irradiating the surface since the gypsum layer is readily removed.

In order to overcome yellowing and over-irradiation of the substrate, the simultaneous use of two laser beams of 1064 nm and 355 nm with temporally and spatially overlapped pulses, has been recently introduced [60]. For optimum results the energy densities of the two beams are set to a certain ratio. The optimal fluences for the two laser wavelengths as well as their ratio vary for each case of combination of surface encrustation and substrate. When the power densities of the two laser beams are such that the two divestment mechanisms – explosive vaporization of dark particles and spallation of encrustation – operate in the same depth from the surface, the substrate remains visually unaffected. In other words, we have the optimum cleaning results, without the controversial yellowing effect. This method is now established and it is applied to important archaeological monuments, as for example for the cleaning of the Parthenon West Freeze Marbles [28].

Figure 7. A laser cleaned section from the outdoor decoration of the 12th century church of Panaghia Kapnikarea in the historical centre of Athens (Marakis, 2000) [62]. The application was carried out with the 3rd harmonic of the Nd:YAG laser (355 nm) using consecutive pulses at 0.4 and 0.5 J/cm^2.

Thus, such a powerful cleaning technique can be readily applied to religious objects of inorganic nature. Unfortunately, there are not any examples of the synchronous wavelength cleaning applications to religious related artefacts yet. However the use of the technique for the cleaning of Parthenon West Freeze Marbles [28] is a good measure for the validly of this technique and it is expected that this will be the main laser cleaning method in future applications. Figure 7 shows an example taken by Marakis (2000) [61], showing the laser cleaning of an outdoor decoration detail in the 12th century church of Panaghia Kapnikarea in the historical centre of Athens. Moreover, there is a great potential of laser cleaning applications to other historical and religious artefacts, which are still under investigation. An example is shown in Figure 8, where the 3rd harmonic of the Nd:YAG laser has been used for the cleaning of a 12th century wall painting. Numerous case studies of laser cleaning on religious artefacts can be found in LACONA's literature [4-7].

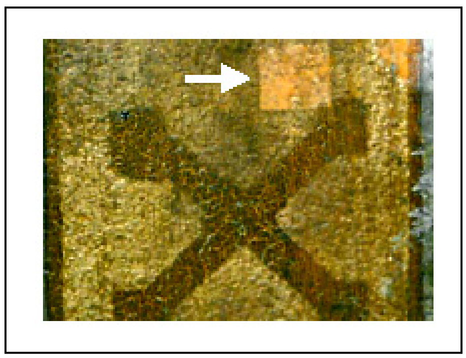

Figure 8. The white arrow points to a lacer cleaned test on an indoor wall painting in the 12th century church of Panaghia Kapnikarea in Athens (Marakis, 2000) [62]. The application was carried out using the 355 nm wavelength of the Nd:YAG laser with a fluence of 50 mJ/cm^2.

3. Conclusions

Lasers can be employed to delicately remove unwanted layers of diverse chemical and physical nature from sustainable surfaces. So far several cases have been studied. It is demonstrated that a maximum efficiency of the laser-induced divestment can be obtained in parallel with the safety of the preservable artefact. Via continuous research and close collaboration between scientists, conservators and curators, laser-cleaning applications in many fields of religious and archaeological conservation are now in a mature stage. Research carries on for the optimisation of the laser cleaning of a few other types of materials and objects.

The examples shown herein and the numerous case studies presented in the international LACONA conferences demonstrate that in the future laser cleaning may be the leading technique for the preservation of churches, historical monuments and religious objects with great cultural heritage significance.

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