Easel paintings on canvas and panel: application of Nd:YAG laser at 355 nm, 1064 nm and UV, IR and visible light for the development of new methodologies in conservation

Joakim Striber¹*, Vanja Jovanović², Maja Jovanović²

¹ Alfa BK University, Palmira Toljatija 3, Belgrade 11000, Serbia
² Central Institute for Conservation, Terazije 26, Belgrade 11000, Serbia
* Corresponding author: striber65@yahoo.it

Abstract
Laser cleaning has been applied in the conservation of objects of cultural heritage since the early 1980s. Nowadays its technology is the object of many scientific studies. Laser can be applied on different objects of cultural heritage, while for objects with specific problems, in some cases, it is even indispensable. However, it has not yet become part of the standard procedure in the conservation studios. Despite the existence of an adequate legal framework and the scientific achievements in this field, the main conservation laboratories in Europe are still insufficiently equipped.

The general objective of this article is to join the efforts of other institutions in promoting the concept of modern approach to heritage conservation, which could be defined as a combination of art, science and technology. Therefore, it presents an equipment that can meet these requirements and is both available and economically acceptable. This equipment was applied in two case studies of the conservation of objects with specific problems.

The subject of research and conservation were two works of art: the painting Portrait of Jelena Milojevic with her daughters from 1922, the work of the Russian painter Valentin V. Volkov, and the Ukrainian icon Holy Mother of God from the 19th century.

Portrait of Jelena Milojevic with her daughters: by observing the results of chemical cleaning tests under the UV light, it was concluded that due to the very high sensitivity of some pigments it was impossible to apply this methodology on such delicate surfaces. The laser cleaning, which had already proved to be an acceptable alternative for chemical cleaning of easel paintings, was the only solution in this case.

Icon Holy Mother of God: the icon was made with a technique of egg tempera in the 19th century in Ukraine. A bronze coating was subsequently added on the aureoles, below which there was a gilding sheet. This sheet was poorly linked to the preparation layer so that any intervention, whether it was mechanical, chemical or laser cleaning, would have caused its removal together with the bronze coating. But when the surface layer was first irradiated at 1064 nm, the added layer of coating was separated from the original layer, which allowed, subsequently, an easy mechanical removal of unwanted layers. Combination treatment of the aureoles using two techniques – laser cleaning and mechanical removal – is faster and more uniform than in the case of treatment by other techniques.

Keywords: easel paintings, laser treatment, mobile equipment, Nd:YAG laser, coating on gold leaf, combined treatment
1. Introduction

To meet all the needs of modern conservation, it is necessary to define only the methods and research techniques whose application to objects of cultural heritage will not undermine the basic principles of conservation. These require that any intervention on an object must not compromise its integrity, in the broadest sense of the word: physical, aesthetic and historical [1].

Easel paintings represent the main challenge of laser cleaning – they are complex, multilayer systems, often very sensitive and difficult to clean. This kind of intervention is of high importance because it is the least reversible invasive intervention, as well as the most usual of all conservation treatments. Cleaning is important in maintaining the aesthetic aspect of easel paintings and prolonging their lifetime by removing potentially damaging environmental pollutants from the surface.

The application of laser technology to the paintings conservation field started in the early 1990s. Despite several works having been reported, including systematic investigations on laser interaction effects induced on pigments and binders, the laser approach was still far from conservation practice. Nevertheless, it was clear that the laser technology had great potential in the development of safer procedures for conservation because of its controllability and reproducibility.

In the case of thinning of varnish on the paintings, a method of laser cleaning with excimer laser was developed, where automatic monitoring of the cleaning process was applied [2]. This permitted an efficient, relatively fast, highly controlled and accurate removal of the varnish layer – only the desired thickness, with precision up to 1mm. However, such systems turned out to be very expensive, immobile and for the time being are not yet commercialised. For these reasons, in most cases where varnish thinning on the paintings is necessary and for which the laser would be optimal if not indispensable method of cleaning, the system is practically inaccessible.

On the other hand, at least 300 Nd:YAG laser systems [3] are presently operative in conservation laboratories and restoration yards all over Europe and abroad. It is a proof that laser cleaning technologies moved from research laboratories to commercial production, and then to restoration work sites. Such a unique case of technological and methodological transfer in conservation of cultural assets was entirely determined by the scientific contribution provided by various research institutions. The latter can still play an important role in order to rigorously extend the exploitation of experimental results and address open cleaning problems.

In general, \( \lambda = 213 \text{ nm} \) and \( \lambda = 355 \text{ nm} \) are very promising wavelengths, giving new interesting results in the field of laser restoration [4–5]. In one part of this work, possibility and efficiency of thinning of varnish on the painting Portrait of Jelena Milojevic with her daughters will be examined using 355 nm wavelength. Laser cleaning proved to be an acceptable alternative for chemical methods of cleaning [6], but in this case it was the only possible solution. A mobile commercial pulse Nd:YAG laser with radiation at 355 nm was used instead of the excimer laser. Monitoring and control of the effects of cleaning was done before, during and after conservation treatment of the easel painting.

Another case of conservation of high risk was the removal of a thick bronze coating layer from a golden leaf, since any intervention of cleaning – mechanical, chemical
In order to analyse the state of conservation and to obtain information about different painting layers, imaging techniques were applied.

**Multispectral analysis**

Using different parts of the light spectra (IR, VIS, and UV) to illuminate the surface of objects, mostly paintings, it is possible to obtain an image of various surface layers: the upmost surface layers can be observed with UV light, while going from UV toward IR region, deeper layers will be visible. This gives the possibility to study the underdrawings or to visualize the composition and condition of paintings. It can aid in the study of the applied artistic techniques, the analysis of colour and pigments and can help to reveal previous restorations.

**UV radiation in painting’s analysis**

The objective of the UV-induced visible fluorescence photography is to localize prior restoration interventions on the painting. This technique can expose the old natural resin varnishes, as these often fluoresce under the UV light while newer varnishes do not. It is also possible to identify overpainting, repairs and floating signatures which usually appear as dark spots in contrast to the original fluorescent areas [7].

**Recording with an infrared camera**

Infrared reflectography (IRR) has become a classic image registration method in the technical examination of art [8]. This technique reveals the presence of preparatory drawings made of carbon black (infrared non-reflective material) and the artist’s process of execution and changes in the composition (*pentimenti*) as well. Infrared spectroscopic imaging could also prove useful in document and forgery analysis, as well...
as in attributions of works of art [9]. In this case InGaAs camera was used in the spectral range from 900 nm to 1700 nm, with filters for 1500 nm, 1600 nm and 1700 nm, each of them having spectral width of 50 nm.

**Laser cleaning**

Regarding laser cleaning of materials that have a very low thermal damage threshold, such as organic fibers, pigments or binders, a certain risk of adverse effects is present [10]. On the other hand, whenever there is a need to clean at micron level, which is often the case with paintings, selectivity, high precision and control of cleaning can be achieved in the process of photochemical ablation [11].

Studies have shown that the dominant mechanism of laser cleaning using UV radiation is a photochemical process [12]. This means that the rise of temperature is very small. UV radiation is strongly absorbed by organic materials, which means that its penetration is only about a few microns [13]. Therefore, the UV radiation is very suitable for thinning of varnish on the paintings, which should remove only a thin layer of material, with high precision. In the case of Volkov’s painting, various techniques have been used to create a new methodology for examination of all phases of the painting process, but also for the monitoring and control of laser cleaning. In this study, a Q-switched Nd:YAG laser Thunder art system for laser cleaning was used at 355 nm.

**State of preservation (Fig. 1)**

The icon was painted using the egg tempera technique. The layer of paint was unstable in zones where cracks are grouped, and it was partially missing in zones of damage of the foundation layer. Colour coating is translucent and in some places covered with spots and stains.

Subsequently applied bronze coatings that were oxidized and darkened by ageing were visible on the aureoles, the ring with the inscription and the vestments of Virgin and Christ.

The gilding on the vestments of Christ and on the Archangel’s icon lamp (in the corners, which is an Old Testament motive – prophet Moses’s vision of the bush that burns, but does not burn out. Judging by the flesh tones and the use of characteristic blue background, this icon was painted in the early 19th century.

![State of preservation of the icon.](image.png)

**1.2 Holy Mother of God**

**Basic information on the object**

The subject of this icon, written in circle: “Sacred face of the Most Holy Mother of God, which is called the burning bush”, is determined by prefiguration presented in corners, which is an Old Testament motive – prophet Moses’s vision of the bush that burns, but does not burn out. Judging by the flesh tones and the use of characteristic blue background, this icon was painted in the early 19th century.

![State of preservation of the icon.](image.png)
Easel paintings on canvas and panel: application of Nd:YAG laser at 355 nm, 1064 nm and UV, IR

central part, lower half) is made of gold leafs, which were thinned in some places due to the inadequate storage conditions.

The final varnish layer was of uneven thickness, probably applied at a later date.

**Optical microscopy – application in the cultural heritage**

A microscopic analysis can give a new perspective on the origin and history of paintings by differentiating between natural ageing effects and changes deliberately instigated as part of the artist's technique. It is also used to study the conservation state of object's surface, and to determine the efficacy of conservation treatment on the surface. In this study, a ViTiny Pro10–3 Portable UV/IR/White Light Digital Microscope was used with Ultra-violet, IR and White LED lighting and 10× to 200× magnification, 2M pixels Lens & CMOS sensor.

**Chemical cleaning**

Solubility test was carried out by using Wolbers mixture of solvents, containing acetone.

**Laser irradiation**

During the laser ablation of material, measurements performed by the laser interferometry technique demonstrate that ablation induced high pressure on the surfaces of analyzed samples, which can provoke the appearance of delocalized defects formation [14].

In case of conservation of the Holy Mother of God, this effect, usually considered as a negative one, was used for safe and efficient cleaning. Laser radiation induced a phenomenon of layer delamination, where connections between the leaf of gold and the bronze coating became weak. When this was combined with subsequent mechanical cleaning, it allowed a quick and efficient removal of the bronze coating, with minor losses of the golden leaf.

3. Results and discussion

3.1. Portrait of Jelena Milojevic with her daughters

During the preview inspection of this painting *in situ*, a number of previous inadequate conservation interventions were noted in the form of darkened paint and retouch, as well as a very thick oxidised varnish layer, which could be clearly seen in the UV fluorescence images. This protective varnish had a yellowish tone – the result of aging and oxidation, and it was covered with a thin layer of surface dirt, which significantly harmed the aesthetic appearance of the work.

The main goal of the treatment, besides stabilization and revitalization of structural layers of the painting, was a selective removal of the thick layer of yellowed varnish and subsequent coatings, in order to reveal the original colors of the painting. The next goal was to apply adequate restoration treatments and bring back the original look and dimension of the painting, which would enable its overall perception.

The fact that the painting changed in the past, required a more detailed research and analysis of this work. Using modern methods such as multispectral analysis, it was possible to make the difference between the original and subsequent interventions on the painting – by the author and by the restorer. Also, selective and controlled removal of the restorer's intervention was successful.

Further tests, in which different parts of light spectra (IR, VIS, and UV) were used, revealed numerous *pentimento*, old retouching, micro-cracks in the varnish, as well as an
advanced process of oxidation of the upper layer of the varnish.

**Multispectral Analysis**

IR reflectography discovered certain changes in the drawing, i.e. corrections that the artist made during the painting process working out the original idea and changing the composition of the painting. Darkened paint, retouch and a very thick oxidised varnish layer were clearly visible in the UV fluorescence images (Fig. 2 to 6).

IR 1600 – Besides visible initial drawing, the changes that the artist introduced during the process of painting are clearly visible on the IR recording: the girl’s elbow is moved upwards while the dark stripes on the dress are covered with textile belt.

UV: UV recording reveals minor retouching and a thick layer of lacquer in the upper left zone (violet fluorescence).

**Microscopic analysis**

Instead of chemical cleaning, the laser cleaning was efficient: by thinning of the varnish craquelures, darkened paint and a thick oxidized varnish layer were eliminated. Following the application of a thin coat of new

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**Fig. 2. VIS** – The final appearance of the surface does not suggest through which phases/changes the painting went during and after the painting process; IR 1600 – Besides the visible initial drawings, the changes that the artist introduced during the painting process are clearly visible on the IR recording: the position of the girl’s arm (elbow is moved upwards) and painting frame (upper left corner) is in further painter’s procedure covered by the vase of flowers; UV – On the UV recording a large retouched area, which extends all the way to the girl’s shoulders (dark zones on the left half of the photo) and several smaller retouched areas in the same zone are clearly visible.

**Fig. 3. VIS** – At the final appearance on the surface of the painting, a thick layer of paint can be seen on the right half of the image and a circular shape appears on the brown drapery; IR 1600 – The IR recording reveals the original appearance of the divan and the drapery (or horizontal position and the track frame rails); UV – The UV recording reveals minor retouching on the hair of the little girl and a thick layer of lacquer in the upper right zone (violet fluorescence).
Easel paintings on canvas and panel: application of Nd:YAG laser at 355 nm, 1064 nm and UV, IR

Fig. 4. VIS – At the final appearance of the painting's surface a thick layer of brown color can be seen, with which drapery over the divan was painted, as well as an inadequate retouch on a dark red curtain; IR 1600 – IR image reveals the original appearance of the right half of the image (the painter has added a dark red curtain, covered part of the divan with draperies and added a brown toy – a doll – in the final stages of painting); UV – UV image reveals the retouched positions on the skin of the woman as well as on the drapery in the right corner and a thick layer of varnish on the right half of the image (violet fluorescence).

Fig. 5. VIS – The final appearance of the surface of the painting does not suggest through which phases/changes the painting has gone during the painting process.

Fig. 6. VIS: The final appearance of the surface image does not suggest through which phases/changes the painting has gone during the painting process; IR 1600 – The IC recording clearly shows that the girl's right leg is rounded (dark drawing) and also that the painter has put the textile belt after he has painted the dresses; UV – UV snapshot reveals minor retouch on the knees of a little girl.

Varnish on the cleaned surface, satisfying aesthetic and visual integrity of paint was obtained.

Optical microscopy was used in order to identify surface variation during the laser cleaning. The microscopy recordings have shown that after laser cleaning, thickness of varnish cracks was reduced and, with the elimination of impurities, the visual unity of the surface was brought back (Figs. 7–9).

Summing the observation of analysis:

- Surface of varnish before cleaning – the uneven aspect of varnish, with very bright or
completely matte surfaces is caused by the advanced stage of its aggregation.

- Surface of varnish after cleaning – after the thinning of varnish by laser, the aggregation of varnish was completely eliminated, and the surface is uniform in thickness and shine.

The process of varnish removal was accompanied by the emergence of light bleaching as a result of the creation of micro-cracks due to the break-off of the polymer chains in the layer. To eliminate this effect and obtain satisfying aesthetic and visual integrity of the paint, it was sufficient to apply a thin coat of new varnish on the cleaned surface.

**Cleaning of the painting: chemical and laser cleaning**

The final decision about the method of thinning of varnish layer was taken after observing the surface of varnish by a digital microscope which provided useful information about the layers and their mechanical structure. The process of laser cleaning of varnish was controlled by visible and UV light. Due to different effects of UV fluorescence on the varnish layer and on the paint layer, it was possible to control the presence of varnish, taking the paint layer as a reference. By combining these techniques, optimal results were achieved both from the
conservation as well as from the aesthetic standpoint.

In order to remove the varnish, Wolbers dissolution test was performed, which is based on different mixtures of polar and nonpolar solvents. Results of this test have shown that by using different mixtures, the protective varnish was removed. Even more, by comparing (the parameter values of the three parameters ($f_d$ = non polar dispersion forces, $f_p$=polar dipole forces, $f_h$=hydrogen bonds), it is possible to determine the nature of that varnish [15]. In the case of painting of Portrait of Jelena Milojevic with her daughters, the best result was obtained by the solution of cyclohexane and ethanol in ratio 40:60 (test Wolbers – CE6: Fig. 14), which indicates that a natural resin was used for preparation of the varnish.

This test has proved, however, that the paint layers which consisted of a pallet of natural, earthy pigments (brown, ochre, red, green) were very unstable, so it was impossible to continue cleaning with these solvents. Partial results were obtained using the concentrated mixture of isopropyl alcohol and distilled water, which was safe but only for bright areas of the picture.

The result pointed the fact that the chemical cleaning of the paint layer was unsatisfactory – most of the pigments being extremely unstable for this treatment, despite the fact that the protective varnish was removed. Because of the impossibility to selectively and partially remove the protective varnish due to difficult control of penetration of solvent into structural layers, this method proved to be inadmissible.

Very high control of laser cleaning, removing layers with thickness between 1 and 100 mm [16], was decisive to use it as a substitute method of cleaning. Using UV laser radiation at 355 nm with 4 pulses/s

in Q-switched regime (pulse duration ~ 10 ns) made it possible to safely remove part of the varnish. Gradual increase in energy resulted in finding the optimal condition of laser cleaning: safely, efficiently and relatively rapidly removing desired thickness of varnish at 80 mJ/cm². Because of the very high absorption coefficient of varnish, UV radiation was totally absorbed by it and at the same time, the paint layer was protected. The process of laser cleaning of varnish was controlled by day light and UV light [17]. As mentioned above, thanks to a different effect of UV fluorescence on the varnish layer and on the paint layer, the presence of varnish was controlled using the paint layer as a reference. Treated surface had a lower fluorescence intensity of untreated surfaces and surfaces without varnish had no fluorescence. The cleaning process is stopped when the treated area satisfied the aesthetic aspect under ordinary light and UV fluorescence confirmed the continued presence of a layer of varnish on that area.

The process of varnish removal was accompanied by the emergence of light bleaching because of the creation of microcracks due to the break-off of the polymer chains in the layer. To eliminate this effect and obtain satisfying aesthetic and visual integrity of paint, it was sufficient to apply a thin coat of mineral spirit on the cleaned surface. The painting after conservation is shown on Fig. 10.

3.2. Holy Mother of God

Chemical cleaning of the gilding (Figs. 11–14)
The liquid bronze coat, which was applied on the gilding in previous interventions, has oxidised during the ageing process and
harmed the aesthetic appearance of the icon. Chemical removal in such cases could be extremely risky, especially when the solubility parameters of the bronze coating and of the mixture used in the original gilding coincide (e.g. when an oil-based liquid bronze is directly applied on a gilding with oil mixture).

Based on the preserved original gilding (the vestment of Christ) and the fact that real gold was used as an element in the painting of the Orthodox art, it was supposed that there is an original gilding underneath the bronze coating layer.

For the abovementioned reasons, it has been decided to remove this bronze coating.
All solvent mixtures containing acetone removed the coating only partially, and the best results were achieved with pure acetone. However, the test results on the bronze coating have shown that the original gilding layer was not reached, and the research was continued.

**Laser irradiation**

In order to find an adequate solution, laser cleaning tests were done (Fig. 15) using infrared wavelength at 1064 nm. Energy of radiation was increased gradually, from 150 to 650 mJ/cm², for 20 pulses per point. However, the coating had not been removed. On the other hand, with a further increase of energy there was a risk that by removing the bronze coating, the gold leaf would be removed, too.

For this reason, energy of 200 mJ/cm² was used, increasing the number of pulses at 200 per point. But, the optimal result was not yet achieved.

However, in a new attempt of mechanical cleaning, it was noted that the bronze coating was easily removed from the surface which was previously irradiated with laser (Fig. 16). It was assumed that these are the surfaces where a delamination, i.e. weakening of linkage between the layers of coating and gold, occurred due to irradiation. Namely, the previous interferometric measurements have confirmed that ablation of material from the object's surface could induce great pressure on that surface, causing stress which induces the effect of delamination.

Laser irradiation was then applied on the remaining surface, with subsequent mechanical cleaning. Removal of bronze coating was fast and efficient, and the process of cleaning was safe for areas on which the gilding was solidly attached to the surface. Microscopic recordings confirm these facts (Fig. 17).

On the areas where the gilding was weakly attached to the surface, cleaning with scalpel could have led to the removal of gilding, so the answer was found in gel or, more precisely, jellified ethanol (Gellano was used for thickening) (Fig. 18). Tests of cleaning with this gel showed that following its application on the bronze coating a gradual, controlled softening was obtained and there was no penetration of solvent in layers underneath. Jellified ethanol was applied to the persistent coating and after a gradual softening the varnish was removed with a wet swab.

The icon after conservation is shown on Fig. 19.
4. Conclusion

_Portrait of Jelena Milojevic with her daughters_  
Paintings are complex, multilayer systems, often very sensitive and difficult to clean. Laser cleaning/thinning of varnish proved to be an acceptable alternative. In the presented case, it was the only possible solution. The results on the removal of degraded layer of varnish and deposits from the easel paintings suggest a potential practical usefulness of Nd:YAG laser’s third harmonic (355 nm) in order to address such problems – it is possible to clean delicate substrates such as paintings or composite structures of polymeric layers (e.g. networks of polymerized resin or polymeric paints, respectively) when bearing in mind some fundamental criteria.

In certain demanding cases, in situ monitoring such as multispectral imaging or other diagnostic methods must be used for controlling the optimum cleaning depth.

_Holy Mother of God_  
This new conservation treatment, combining the laser irradiation and the mechanical cleaning, brings the possibility of developing a new conservation methodology. The phenomenon of delamination of layers is used.
However, in order to develop this new methodology, it is necessary to undertake a series of new experiments and examine the phenomenon of delamination in detail. There are several studies that have been carried out with the aim to study possible negative effects induced by laser irradiation on surfaces of artwork objects, for example separation between surfaces’ layers. This new research goes in the other direction, in order to exploit this effect to improve and facilitate conservation in some specific cases.

References


