

Er:YAG laser: an innovative tool for controlled cleaning of old paintings: testing and evaluation

Paola Bracco ^a, Giancarlo Lanterna ^a, Mauro Matteini ^{a,*}, Kyoko Nakahara ^a, Oriana Sartiani ^a, Adele de Cruz ^b, Myron L. Wolbarsht ^c, Ed Adamkiewicz ^d, Maria Perla Colombini ^e

^a*Opificio delle Pietre Dure (OPD), Florence, Italy*

^b*DeCruz Studios, New York, NY, USA*

^c*Duke University, Durham, NC, USA*

^d*Schwartz Electro-Optics (SEO), Orlando, FL, USA*

^e*Università di Milano Bicocca, Milan, Italy*

Abstract

A cleaning method based on an Er:YAG laser system at 2.94 μm , highly absorbed by OH bonds, was tested for removal of over-paintings, varnishes and patina top-layers from various painted surfaces, including laboratory paint models and old paintings. The aim was to evaluate the efficiency, selectivity and safety of the laser cleaning method using various pulse energies and various OH containing wetting agents to enhance the efficacy and limit the penetration of the laser beam. A large number of paint models were prepared with known characteristics (type and number of layers, thickness, composition) simulating old masters' techniques. A set of diagnostic controls was designed to study the effects of the laser radiation on the surface components, including morphological, optical and chemical examination and analyses. The aim was also to compare the laser method with the traditional solvent based procedures. Thresholds of safe energy were found for each type of surface layer such as varnishes and over-paintings. The results confirmed the suitability of the Er:YAG laser when used by qualified and expert conservators, especially in combination with traditional chemical and mechanical cleaning methods. © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Cleaning; Paintings; Er:YAG laser; Paint models; GC-MS; FTIR; SEM; OH bond

1. Research aims

The cleaning of painted surfaces is among the most critical operations in conservation. It is an irreversible removal of very thin, non-homogeneous layers which alter the aesthetics (deposited materials, old varnishes), falsify the image (retouching or over-painting) or affect the physico-chemical stability (fixatives or adhesives). Extreme selectivity is needed, since the original layers, including any external thin glaze, must be preserved. One of the most important requirements to obtain appropriate results, according to the contemporary criteria for the conservation of polychromed artworks, is to realise a progressively controlled cleaning, based on discretion that only an expert conservator has. Traditional cleaning methods were based on mechanical tools (scalpels), which require great dexterity

and are lengthy procedures, and/or chemical agents (solvents). Several problems of their own: (1) the spatial expansion of solvents, even when dispersed in a gel or soap, is difficult to control, (2) the majority of the efficient solvents is toxic, and (3) many materials to be removed are sometimes insoluble in any solvent tolerated by the paint surface, make mechanical intervention the only alternative. For the above reasons, alternative methods, such as laser exposure, are worth being considered.

A cleaning method for paintings based on an infrared Er:YAG laser (Fig. 1) at the wavelength of 2.94 μm was first presented in a LACONA Conference, Lacona III in Florence [1,2]. This laser generates an infrared radiation strongly absorbed by OH bonds with a correspondingly shallow depth of penetration, a crucial feature when cleaning paintings. The OH bonds can be contained in the extraneous materials on the surface or, when scarce or not present, they can be added by auxiliary hydroxylated liquids (water, alcohol, other liquid mixtures). On this basis, an in-depth experimentation of the actual possibilities of the above-

* Corresponding author.

E-mail address: Matteini@data.it (M. Matteini).

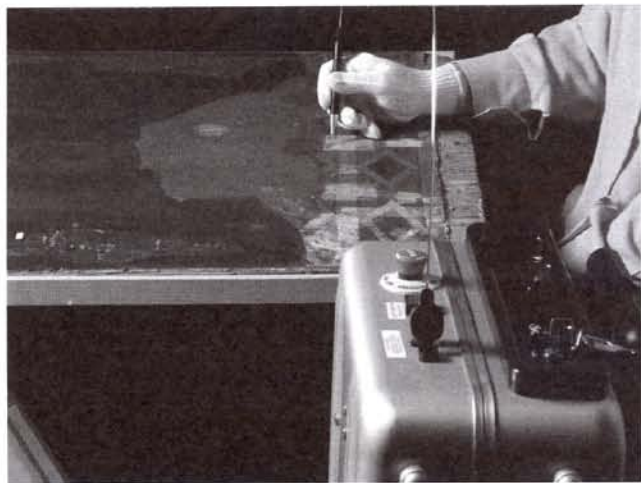


Fig. 1. The Er:YAG laser while operating.

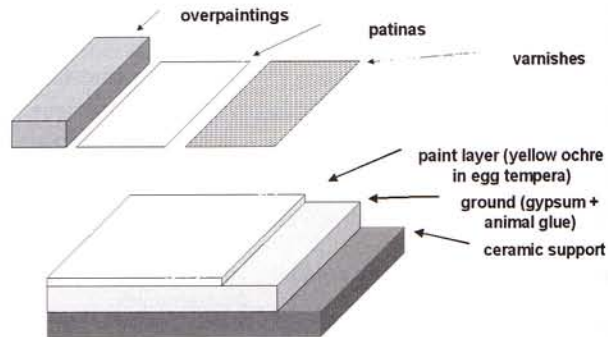


Fig. 2. Layer structure of laboratory pictorial models.

2. Experimental section

2.1. Laboratory painted models and old paintings for testing laser effects

A comprehensive set of laboratory models was prepared. Physically stable ceramic plates (100 × 150 × 4 mm) were coated with a gypsum/animal glue ground layer and covered with paint layers composed of pigments and binders, the former chosen among those potentially sensitive to the Er:YAG laser (Fig. 2).

Top-layers were applied consisting of the following paint categories: natural resin varnishes, oil-resin varnishes, synthetic varnishes/fixatives, artificial patinas, over-paintings (Table 1). In this paper, the authors present the data obtained from yellow ochre/egg tempera paint models coated with the following top-layers:

- mastic or dammar varnishes (natural resins),
- linseed oil/sandarac varnishes (oil-resin mixtures),
- Paraloid B72 (synthetic resin),
- burnt umber in linseed oil (over-painting), lamp black, and
- animal glue (artificial patina).

In fact these models (bold labelled in Table 1) were characterised by very stable and dry film.

All the models were artificially aged by exposure to UV radiation at 365 nm for 45 d at a mean source/sample distance of 45 cm, followed by natural ageing for a long period (over 8 months) at room conditions.

Following the tests on the laboratory models, portions of several old paintings were considered in the experimental

cleaning method was proposed by the Opificio delle Pietre Dure of Florence (OPD) in close collaboration with the US partners.

The efficiency, selectivity and safety of the laser system, as well as the possibility of a progressive removal of surface layers, were tested first on laboratory paint models and then on old paintings by expert conservators of paintings.

Physical and chemical effects were then studied, scientifically investigated and correlated with variable working parameters (fluence, pulse-frequency, number of exposures, auxiliary liquids). The experimental programme has designed the preparation of a set of laboratory paint models which simulate the old painting techniques and on which the cleaning tests should be carried out. The main targets of this project were to be able:

- to have physical systems, specially prepared with known composition and stratigraphy, in order to evidence possible interactions with laser radiation,
- to change the operative laser parameters freely, on expendable models, so that possible energy safety-thresholds could be individuated,
- to take adequate samples, both quantitatively and qualitatively, for the analyses,
- to compare testing and analysis on the laboratory models with specific selected cases of old paintings.

Table 1
Composition of the top-layers of the laboratory models (bold characters indicate materials which were actually tested by laser)

Modern varnishes or fixative (synthetic materials)	Traditional varnishes (natural materials)	Artificial patinas	Over-paintings (with and without interposed mastic varnish)
<i>Paraloid B72</i>	<i>Mastic</i>	<i>Lamp black + animal glue</i>	Naples yellow + linseed oil
<i>Laropal K80</i>	<i>Dammar</i>	<i>Lamp black + whole egg</i>	Naples yellow + casein
<i>Berger's PVA</i>	<i>Shellac</i>	<i>Lamp black + starch</i>	<i>Burnt umber + linseed oil</i>
	<i>Sandarac + linseed oil</i>	<i>Gum arabic + green earth</i>	<i>Burnt umber + casein</i>
	<i>Mastic + walnut oil</i>		
	<i>Boiled linseed oil</i>		

Table 2
Old paintings tested with the laser cleaning method

Support	Author	Subject	Layer to be ablated	Century
Panel	Fra' Paolino	The Holy Family	Thin resinous varnish	XVI
Canvas	Copy from Caravaggio	Christ crowned with thorns	Egg based over-painting	XVII
Panel	Anonymous	Portrait of a man	Recent resinous varnish	XVII
Panel	Anonymous	Virgin and Child	Mineral deposit/varnish	XIII
Canvas	Antonio Veneziano (attr.)	The beheading of the Baptist	Thick proteinic over-painting	XIV

programme, including both panel and canvas paintings, from the period between the XIIIth and XVIIth centuries (Table 2).

2.2. Laser equipment and operative conditions

The 2.94 μm Er:YAG laser ('Conservator 2940®' made by SEO) emits 250 μs duration 'macropulses' consisting of a train of 1–2 μs micro-pulses. The radiation goes directly into a 1.5 m long, 1 mm bore hollow internal mirrored glass guide [3] with a pen-like tip for aiming at specific target sites. The control of energy of each pulse to the millijoule level allows determination of ablation thresholds for each specific material. The macropulse frequency adopted was 15 Hz. The auxiliary wetting liquids used were chosen among OH containing substances (such as water and alcohol) or non-OH containing liquids (light aliphatic hydrocarbons) added with controlled amounts of OH containing substances (glycols). The following formulations were tested: WT (distilled water with 2% Tween 20®), WE (1:1 v/v water/ethanol) and WS (white spirits denatured with 15% di-ethylene-glycol).

In most of the tests, a microscope glass cover-slip was placed on the painted surface to collect the ablated material. The energy levels employed in each application were measured by an oscilloscope.

2.3. Methods of examination of laser effects

Macroscopic and microscopic evaluations of the physico-optical properties of the surface were made before and after laser ablation. Chromatic co-ordinates were measured by a Minolta CM 2000 CIE- L^*a^*b Colorimeter. The morphology of treated and untreated surfaces was studied with optical microscopy (OM), (Zeiss Axioplan Microscope, with 100 W halogen lamp and UV 100 W HBO lamp, 5 \times and 20 \times magnification) and with scanning electron microscopy (SEM) (a Leica-Cambridge S 440 SEM with back scattered electron detector). Further morphological information was obtained from samples taken from the laboratory models. They were embedded in resin, polished into cross-sections,

and observed under OM and SEM. Chemical composition and possible chemical changes were investigated through instrumental analyses on other samples taken from the surface. Three different kinds of samples were collected: untreated surface (A), treated surface (B), and the ablated material condensed on a cover-slip (C). Each sample was analysed by gas-chromatography/mass-spectrometry (GC-MS) (Hewlett-Packard 5980 series II Capillary Gas Chromatograph; 30 m length, 0.25 mm i.d. HP-5 MS fused silica capillary column coupled with a HP 5971A Mass Spectrograph quadrupole detector) and by Fourier Transformed Infrared Spectrometry (FTIR) (Perkin Elmer 1725 Spectrophotometer, KBr 1.5 mm diameter micro-pellets).

3. Results

3.1. Evaluation of laboratory models

The optimal energy thresholds were between 7 and 45 mJ in order to thin top-layer varnishes and remove over-paintings, depending on the material. About 10–12 mJ were necessary to remove a varnish layer of about 15 μm , depending on the underlying layers and the auxiliary liquid used. Relatively thick oil based over-painting (about 30 μm) needed about 40–45 mJ laser pulses and repeated exposures with gradually diminishing energies.

In general, the CIE- L^*a^*b colour measurements showed an increase of light scattering, which is clearly attributable to a higher surface roughness, as normally seen also after traditional cleaning methods. Such an effect can be easily erased when the surface is revarnished according to the normal conservation practice.

The surface varnish layers treated by laser, usually showed a typical morphology like a 'melted' material. Micro-bubble inclusions as well as micro-craters are visible under OM and SEM magnification. This would suggest swelling and partial decomposition of the scarcely polymerised organic materials (probably due to insufficient ageing). This is probably due to insufficient ageing of each layer of paint models, where some solvent residue can vaporise inside the film (Fig. 3).

No chromatic variations of the ablated surface were observed when operating within the lower threshold energy (12 mJ). Supra-threshold energies increased the ablation of the top-layer materials and also affected the paint layer below, by causing brown dots in the ochre pigment. Actually, yellow ochre is a hydrated iron oxide with water molecules in the crystal lattice which are ablated in the case of supra-threshold energies (Fig. 4).

Concerning the auxiliary liquids, the efficiency of laser ablation increases proportionally to the amount of the -OH groups, according to the theory. WT has the greatest effect, being richest in -OH groups; WE causes a more moderate

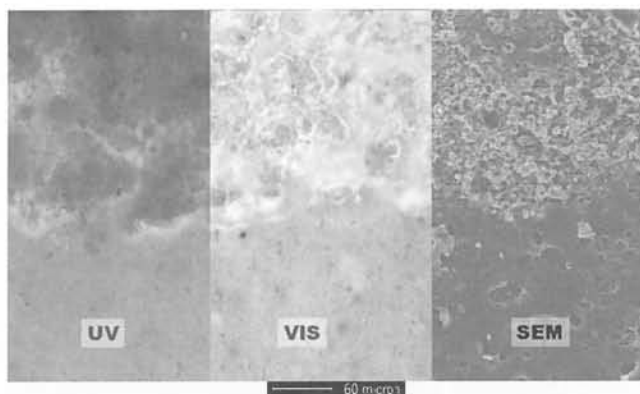


Fig 3 Top-layer of a dammar varnish laboratory model, on the border between an untreated area (lower part) and a treated area (upper part) with 10 mJ laser pulses, dry method (a) UV fluorescence; (b) macro daylight photograph, (c) SEM micro-photograph

effect and WS is the least effective. The morphological observation (OM, SEM) seems to confirm this trend.

All the instrumental analyses generally showed maintenance of the original molecular composition of the organic materials sampled from the treated surfaces. Only minor changes in the composition were recorded by comparing the ablated material with the untreated surfaces.

In particular, GC–MS analysis showed the following results:

- no significant variation in the amino-acidic pattern of the binders in the over-paintings was observed in all the three kinds of samples,
- a decrease of the oleic acid contents was observed in resinous and oil-resinous varnishes, due to its transformation into di-carboxylic acids and epoxy compounds in the ablated material,
- no change in the composition of resinic acids in natural resin varnishes was observed (chromatograms match),

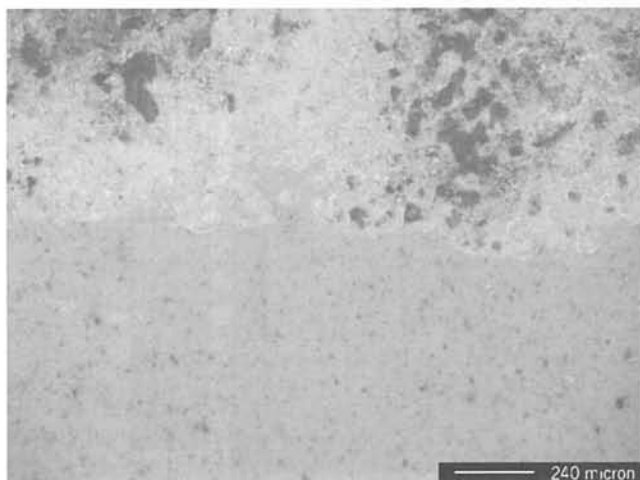


Fig 4 Top-layer of a mastic varnish laboratory model, after exposure to laser energies (upper part) over the safety-thresholds (20 mJ) The photograph shows the rising brown dots in the yellow ochre pigment ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), caused by the ablation of hydration water molecules

except a slight decrease in the amount of the hydroxylic components in the ablated material (Fig. 5, ablated material, fraction between 24 and 28 min), and

- as for the Paraloid based models, only very small amounts of ablated material were collected and identified.

The following observations could be drawn by FTIR spectrometry:

- no change of composition between the treated and untreated surface materials was generally shown,
- minor variations were observed in the relative amounts of several polar substances between the ablated material and untreated surface,
- very small wavelength shifts in the absorption bands of esters were recorded in the ablated material from resin and oil-resin varnishes.

As a conclusion of the experimentation carried out on the laboratory models, we can confirm that the organic painting materials examined generally maintain their chemical composition after laser exposure, in the operative conditions used for the tests. We could also verify that the laser can be used in a gradual and selective way, on the condition that the chosen energy remains near the threshold values.

3.2. Evaluation of old paintings

The first test was carried out on a XVII century oil painting on canvas (copy from a Caravaggio) to remove an egg tempera over-painting on the original colour. The removal of this layer was particularly difficult using chemical and mechanical means. Laser exposures were given at successive intervals with progressively decreasing energy levels (15, 13, and 10 mJ), first wetting the surface with WE and then with WS. In this way, the over-paint could be gradually removed without influencing the original colour layers, as shown in UV photograph where it is possible to observe a gradual fading of the fluorescence (Fig. 6).

On a XIIIth century painting (Virgin and Child), different cleaning methods (laser exposure and solvent cleaning) were separately compared to test the possibility of a gradual removal of aged and dirty varnish and some over-paintings. This painting had been repainted in the XVth century and again later in a very unsightly way. Testing was done on an area of the floor, by removing a thin, grey-coloured surface layer composed of atmospheric deposit incorporated into an old varnish layer on an over-painting. The laser was used without wetting agents at 4 mJ; then, for comparison, a pH 9 gel composed of Carbopol 940® and Triethanolamine (TEA) was used as chemical cleaning agent, followed by washing with an enzyme agent water solution [4] (Fig. 7). Another test was performed on the repainting of the throne drapery to gradually remove, first a brownish varnish layer, then a green over-painting. To eliminate the brownish varnish, one exposure was sufficient with WE at 20 mJ. For

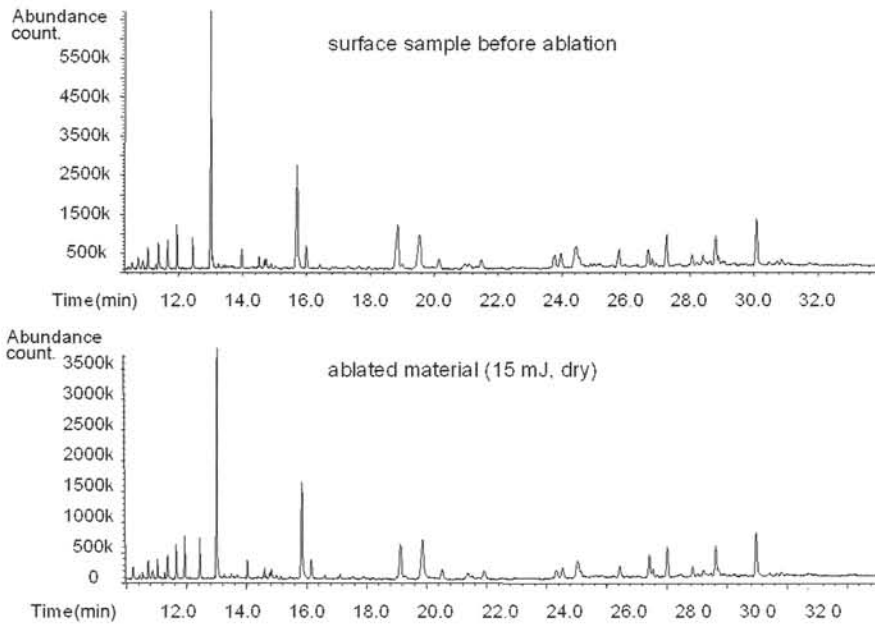


Fig. 5. GC–MS chromatograms of a top-layer dammar varnish laboratory model (*above*: surface sample before ablation; *below*: ablated material (15 mJ, dry)).

sum of applied energy (mJ) in multiple passages

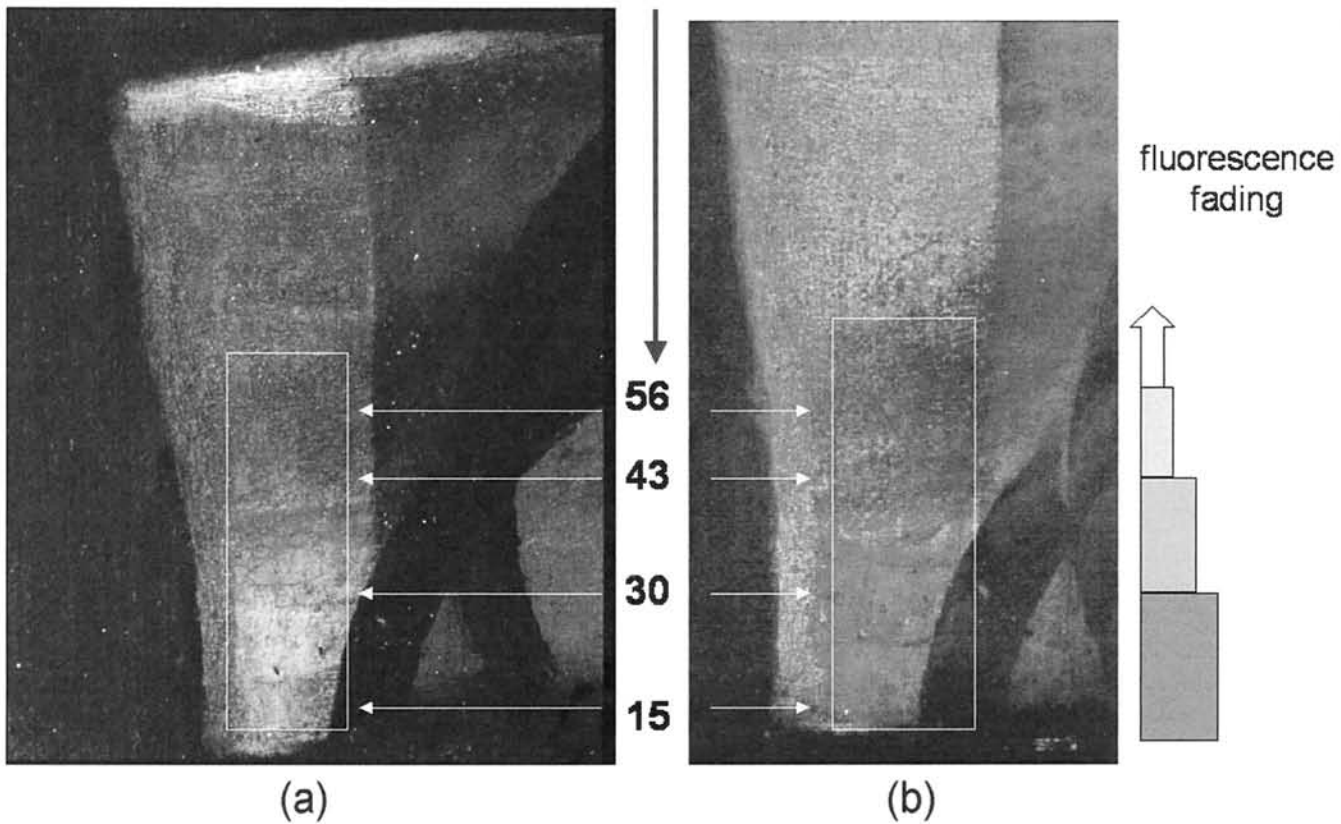


Fig. 6. ‘Christ crowned with thorns’ details showing two cleaning tests: (a) colour photograph after laser ablation; (b) UV fluorescence showing the thinning of the varnish.

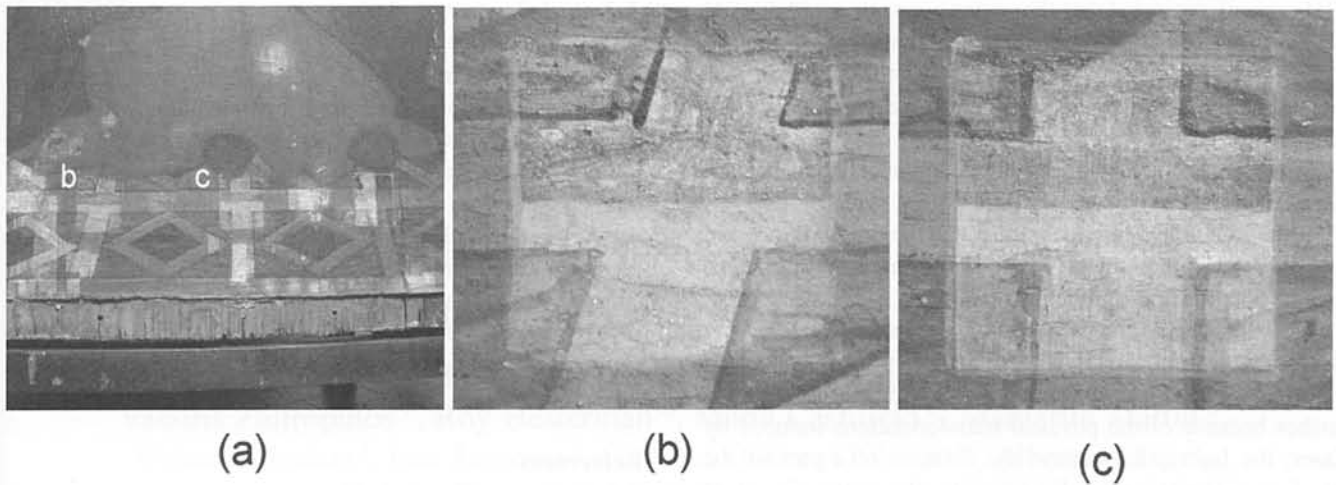


Fig. 7. Virgin with Child, colour photograph comparing details of results between laser cleaning (4 mJ dry) and chemical cleaning (pH 9 aqueous gel) of a thin layer of atmospheric deposits (a) detail of floor; (b) after chemical cleaning; (c) after laser ablation.

the removal of the over-painting, three applications at decreasing energy (from 20 to 15 mJ using WE) were necessary. In comparison, solvent cleaning was first done with a chelating agent (citric acid, Carbopol 940®, TEA, distilled water) at pH 8.5, followed by a solvent gel of ethanol and toluene [5], also resorting to the aid of a scalpel.

The laser cleaning test carried on a XIV century glue tempera painting ('The beheading of S. John the Baptist') showed very satisfying results. It was confirmed that a preliminary laser treatment significantly facilitated the next chemical removal of a thick over-painting. This very thick brown over-painting was thinned and weakened by several laser exposures (at 20, 30 and 40 mJ), followed by chemical treatment with a mild basic gel based on iso-propanol, butyl acetate and TEA. Operating times were noticeably shortened (only a few minutes), compared to the time required using the same solvent alone (over 30 min).

Another test was carried out on a fragment of a XVII century oil painting on panel (portrait of a man). Thanks to the selectivity of the laser, it was possible to remove only the top-layer varnish, leaving the older inner varnish untouched. In this test, pure ligroine was used as a wetting agent. It allowed the conservator to have a clear vision of the surface without influencing the solubility of the material to be ablated. The top-layer varnish irradiated by the laser at 4 mJ was removed by the successive chemical cleaning with a relatively non-polar solvent (5% iso-propanol/ligroine mixture), which is practically ineffective when used alone.

Among all the tests carried out on old paintings, only in one case some problems were observed: in a XVI century oil painting (Fra' Paolino's 'Holy Family'). During preliminary tests on the very thin recent varnish on the sky background, some discoloration (a white effect) of the light blue colour was recorded even at a very low energy (~2 mJ). The cause of this phenomenon seems to be attributable to a probable dehydration of some iron complex

contained in the pale blue pigment, as confirmed by SEM/EDS analysis. The first hypothesis seems to be a Vivianite-like mineral. Nevertheless, more thorough studies (XRD id est) are in progress.

Cover-slips were always used during the tests in order to collect the ablated material for the analyses and prevent the pen-tip from being stuck by the ablated material. It was noticed, however, that it is possible to operate without using cover-slips, as long as relatively low energy is used and the working distance is controlled. It was also observed that in the case of the ablation of not-fully polymerised material (such as in the case of some of the laboratory models), it would be preferable not to use cover-slips because the fused material on the surface could stick to it. Some improvements are expected such as a pen-tip equipped with a holder for interchangeable thin glass protection, so that the shield-effect could be maintained while any direct contact between the glass and the surface would be avoided.

4. Conclusions and future research

The behaviour of the cleaning method based on an Er:YAG laser gave different results depending on the type of painted surface. On laboratory models, some drawbacks were observed due to the incomplete drying of some organic materials. Generally, much more satisfactory results were obtained on old paintings.

The Er:YAG laser cleaning method can be considered effective, selective and safe when used within appropriate energy levels, which are specific for each category of surface layer materials.

The efficiency of the laser pulses is high enough on top-layers OH containing materials. Nevertheless, the use of Er:YAG laser can be extended also to materials with low

OH content, provided that the surface is wetted with an OH containing liquid. Furthermore, the hydroxylated wetting agents help to restrict the penetration of the radiation, and are especially useful when heat sensitive paint layers are present.

After ablation, no significant chemical change in top-layer materials has been observed during testing.

This laser cleaning technique can be used alone but, much better, in conjunction with traditional cleaning methods to obtain a more efficient result.

The 'combined method' (laser exposure followed by solvent or scalpel cleaning) facilitates very significantly the removal of hard and resistant over-paintings and old varnishes because of the physical transformations induced by laser: the laser pulses cause the ablation of a part of the top-layer components, disaggregate the remaining part which, consequently, becomes rougher and softer to mechanical tools and more interactive with solvents. The use of milder solvents or softer mechanical action is allowed and operative times are dramatically shortened. This procedure provides also a higher safety for the conservators (shorter exposure times to toxic solvent) as well as for the paintings (lower penetration, milder and progressive action).

Further investigation should be done on the rest of the laboratory models as well as on a wider range of old paintings. The result confirms the suitability of the Er:YAG laser, when used by well-trained expert conservators.

Acknowledgements

The authors wish to thank Marco Ciatti and Chiara Rossi of the OPD in Florence for their precious collaboration and help in carrying out the experimental programme; Carlo Lalli, Simone Porcinai and Maria Rizzi of the OPD and Alessia Andreotti of Pisa University for their scientific support in the analyses; Fabrizio Cinotti of the OPD for the photographic document; Lillina Di Mucci for the help in editing. One of the authors (MM) thanks the Italian CNR 'Progetto Finalizzato per i Beni Culturali' for research support.

References

- [1] A. De Cruz, Method for cleaning art work, PCT/International application pending, US Patent registration No 5.951778, 2000.
- [2] A. De Cruz, M.L. Wolbarsht, S.A. Hauger, Laser removal of contaminants from painted surfaces, *J. Cult. Heritage* 1 (2000) S173–S180.
- [3] J. Dai, J.A. Harrington, High-peak-power, pulsed CO₂ laser light delivery by hollow glass waveguides, *Appl. Optics* 36 (1987) 5072–5077.
- [4] P. Cremonesi, *Materiali e metodi per la pulitura di opere policrome*, Phase ed., Florence, 1997.
- [5] R.C. Wolbers, *Cleaning Painted Surfaces, Aqueous Methods*, Archetype Publications, London, 2000.