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Laser cleaning of paintings: in situ optimization of operative parameters through non-invasive assessment by optical coherence tomography (OCT), reflection FT-IR spectroscopy and laser induced fluorescence spectroscopy (LIF)

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Abstract

Nowadays the use of laser technology as a highly precise tool for the cleaning of paintings is gaining ground. The development of a non-invasive analytical protocol aimed at thorough assessment of the treated surfaces and real time monitoring of the laser cleaning action is thus becoming imperative. This ensures that no side effects (e.g. discoloration, darkening, blackening) will occur on the painting surfaces due to laser ablation. In the present study the potential of the combined use of optical coherence tomography (OCT) and reflection FT-IR spectroscopy for in situ non-invasive assessment of laser cleaning procedures has been investigated on a historical easel painting donated to science. Specifically, OCT and FT-IR analyses were carried out before and after each cleaning test in order to carefully assess the condition of the painting surfaces upon their irradiation with a KrF excimer laser and evaluate the removal of weathered and/or non-original materials (i.e. waxes, aged natural varnishes, oxalates, deposition/migration compounds). This specific laser radiation, operating in the ultraviolet region ($\lambda = 248$ nm), is highly absorbed by coating materials (i.e. oxidized natural varnishes) and thus high selectivity and control of the cleaning process can be pursued. A systematic integration of the information on the chemical changes of the molecular composition of the painting surface provided by reflection FT-IR spectroscopy with the visualization of the stratigraphical changes by OCT allowed the evaluation of the sensitivity of the painting materials to different operative parameters of the laser treatment, such as laser fluence and number of pulses. In parallel, laser induced fluorescence (LIF) spectroscopic measurements, recorded with the same laser beam at significantly attenuated energy density values, were exploited to provide information on the fluorescence properties of the irradiated varnish surfaces. The combination of the results obtained by OCT and FT-IR complemented with those from LIF measurements are discussed with the aim of developing an efficient methodology for assessing in situ the irradiated painting surfaces after the laser cleaning treatments and, thus, setting the basis for a future monitoring scheme that would ensure optimum cleaning interventions.

Keywords: Laser cleaning, OCT, Reflection FT-IR, LIF, In situ assessment, Non-invasive examination, Easel paintings

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Introduction

A physical method with continuously growing use in the cleaning practice of painting surfaces is laser technology [1, 2]. Laser ablation is a complex process which refers to the interaction of a laser beam with a surface resulting in selective removal of small amounts of material. Provided that the employed laser wavelengths are strongly absorbed by the material, their pulse duration is short and the fluence values are high, layer-by-layer material removal is feasible. Its application as advanced tool for cleaning practices on paintings was introduced in the early 1990s [1, 3] and referred to the removal of aged/hardened varnish coatings, overpaints or soiling. The most exploited laser systems emit in the UV region (e.g. KrF excimer laser at $\lambda = 248$ nm) [1] where the functional groups of the varnishes and of their degradation products are strongly absorbing, while other types of lasers emitting in the infrared (Nd:YAG [4] and Er:YAG [5, 6]) have also been studied.

However, the incontestable benefits of laser cleaning are countermanded by the high sensitivity of the majority of pigments to the laser radiation, which may cause irreversibly damage to the painting materials [7]. The investigation of these unwanted side effects has attracted the interest of the scientific community since the earliest applications of the method. Systematic studies have been performed with the purpose to assess the laser action by multi-analytical approaches [8–18].

These studies, mostly performed on pure pigments and model paints, have contributed to build the knowledge framework in order to investigate the mechanisms responsible for the observable changes and, accordingly, to define operational ranges of laser parameters (i.e. wavelength, fluence, pulse duration, pulse shape, repetition rate and irradiation geometry) for succeeding in effective and safe cleaning of different types of painting substrates. However, due to the high variability of the nature/composition of painting materials, the optimal laser parameters are best defined through preliminary tests on specific areas of the artwork. Hence, the development of non-invasive analytical methods for in situ assessment of laser cleaning of artworks is a priority.

For this purpose, in the present study, a non-invasive approach based on the complementary use of optical coherence tomography (OCT) and reflection FT-IR spectroscopy has been used on an historical easel painting subjected to KrF excimer laser treatments, in order to develop a methodology for in situ assessment of the treated surface, thus enabling optimization of operative laser cleaning parameters. Strengths and limits of the integrated use of OCT and FT-IR were already proved for assessing the progressive removal of unwanted layers from both model paints and historical paintings

by solvent cleaning procedures [19]. Specifically, OCT allowed obtaining the stratigraphic information (i.e. number and thickness of the layers before, during and after treatment, as well as the amount of removed material), while the chemical surface composition was determined through step by step FT-IR measurements. This technique is, in fact, particularly sensitive to molecular properties and chemical changes of painting surfaces and it is very specific for the identification of organic and inorganic components that typically are the target of the laser cleaning treatment; these include soiling materials or patinas formed with natural ageing (that generally contain silicates, sulphates and oxalates) as well as overlaid materials such as aged, natural and synthetic varnishes, overpaints, retouchings, fixatives or adhesives.

Combined measurements by OCT, FT-IR and colorimetry were already used for non-invasive monitoring of laser removal of shellac varnish from the surface of models of artificially aged mural paintings [20]. Furthermore, OCT combined with other optical techniques was exploited to investigate laser cleaning of calcium oxalate layers from historical mural paintings [21].

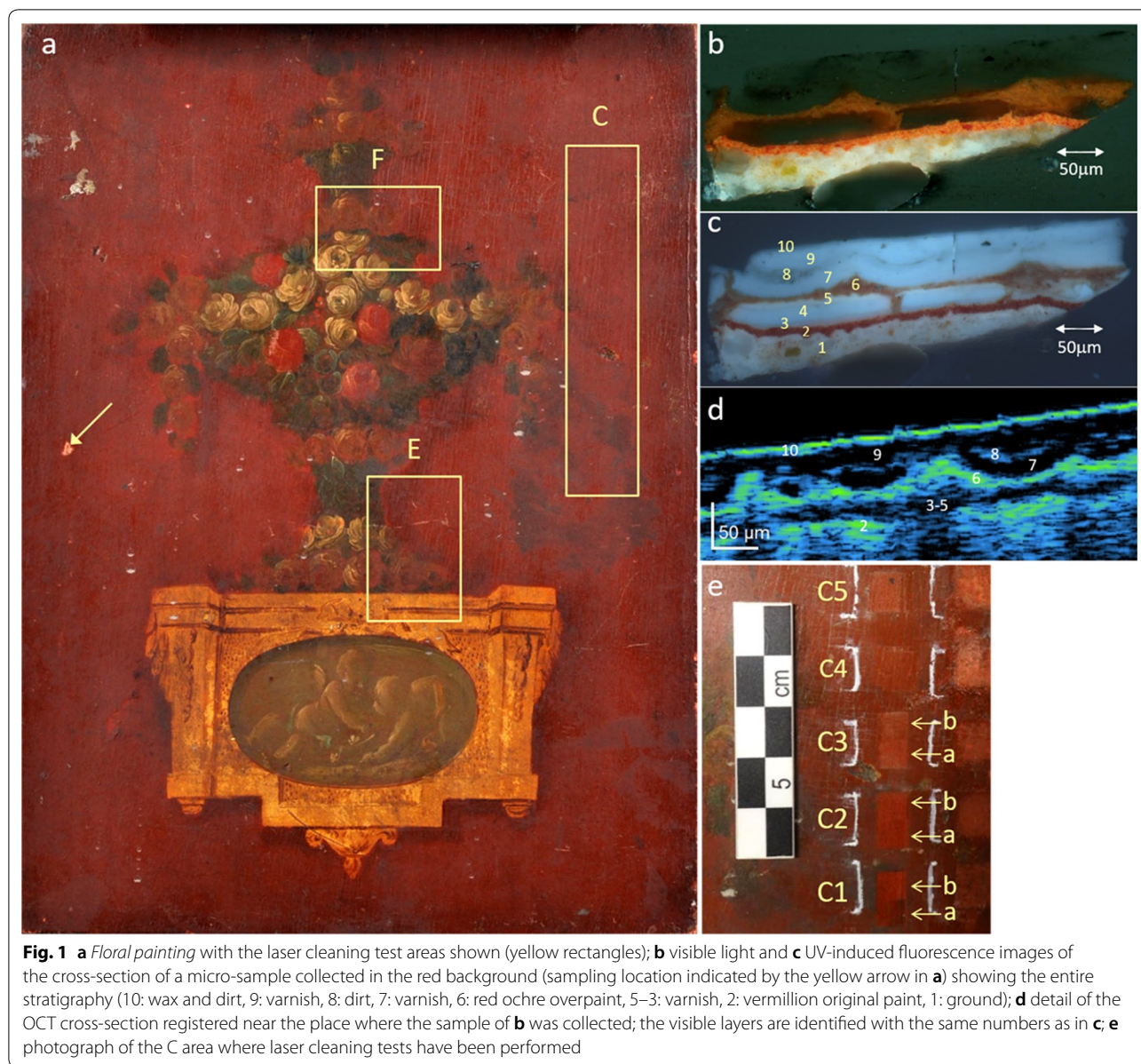
In this study, laser induced fluorescence (LIF) measurements have also been carried out in parallel with reflection FT-IR and OCT analyses, employing the same laser beam used for the cleaning at significantly attenuated energy density values. The aim of the fluorescence measurements was to verify the potential of LIF spectroscopy as a complementary analysis for monitoring the cleaning action that, in principle, can be carried out on-line with the cleaning process, using the same experimental set-up of the laser cleaning workstation.

Materials and methods

Historical easel painting

The historical easel painting investigated herein, entitled *Floral painting* (Fig. 1a), belongs to the Rijksmuseum study collections of Amsterdam and was selected among a set of paintings donated to science within a specific research task (WP7.1a: *Diagnostic Strategies for Assessing the Cleaning of Paintings*) in the framework of the IPE-RION CH project [19, 22].

The *Floral painting* (Fig. 1a) is an oil painting on a panel (20.8×27.4 cm²) realized by an unknown master probably in the 19th century and characterized by multiple thin layers of wax, varnish and a red ochre overpaint. The stratigraphy and material composition were investigated in the first phase of the project, prior to the research described herein. Few samples have been collected from the paintings, and both Vis, UV-induced fluorescence microscopic sample analysis (Fig. 1b, c) and SEM-EDS mapping were performed on the cross-sections, providing detailed information



regarding the stratigraphy of the painting. Specifically, as shown in Fig. 1b–d, the red ochre overpaint layer of rather irregular thickness (layer No. 6) is covered by several organic coatings (shown as layers Nos. 10, 9 and 7) as well as a thin intermediate layer of dirt and silicate deposits (layer No. 8). The overall thickness of these varnish layers (No. 10–7) is in the range of 40–60 μm. Underneath the red ochre overlayer, other organic coatings (mainly varnish resins, Nos. 4 and 5, and a very thin glaze layer, No. 3) are present, with thickness varying from 12 up to 20 μm. Finally a homogeneous in thickness (7–10 μm) layer of vermillion, HgS, (No. 2) is identified, well adhered on a ground layer (No. 1).

Non-invasive assessment of the stratigraphy was performed by OCT in 74 places altogether. Identification of surface coatings was carried out with reflection FT-IR spectroscopy, while information on the used pigments and their distribution was obtained from macro XRF scanning (data not shown). The latter, paired with UV-induced fluorescence imaging, gave insight also into past restoration attempts.

Methods

Excimer KrF laser and cleaning procedure

A workstation, custom-made at IESL-FORTH for the cleaning of flat surfaces such as painted artworks, was

employed. In this workstation the painting was fixed on a rigid support/holder and the laser beam was directed towards its surface via a system of galvanometric driven mirrors. The galvanometric system was controlled using a tailor-made software developed at IESL-FORTH. The laser cleaning was carried out using an excimer KrF laser [LAMBDA PHYSIK, Excimer Laser L.P.X. 200 (210i)] emitting pulses of nanosecond (ns) duration (24×10^{-9} s) in the ultraviolet (UV) spectral region, at 248 nm. The laser beam was focused on the painting surface [17] into a 0.08×1.00 cm² rectangular area. The fluence values (F) employed varied between 0.1 and 1.1 J/cm² and the number of applied pulses (N) ranged from 1 to 50, in order to perform a selective and gradual cleaning procedure.

Optical coherence tomography (OCT)

OCT measurements were performed using a system designed and built especially for the examination of cultural heritage objects [23–25]. It is a Fourier domain OCT instrument utilising near infrared (770–970 nm) radiation and a spectrographic detection. With the power of a probing beam at the object below 0.8 mW and an exposition of a given spot of the object to the radiation for 45 μ s only, and thus fluence of about 30 mJ/cm², it is considered safe, even for sensitive materials [26].

The ability to differentiate thin layers is due to the axial (in-depth) resolution, which equals ca 2.2 μ m (in materials of refractive index equal to about 1.5). Lateral resolution (the ability to differentiate structures occurring close to each other in lateral plane) is about 13 μ m. The distance to the examined object from the most protruding element of the device is 43 mm and the structural information from an area up to 17×17 mm² can be acquired in one measurement. Data collection time for one 2D cross-section (B-scan) is 0.15 s.

OCT tomograms (virtual cross-sections) are presented in false colours. Warm colours correspond to high scatter/reflection of the probing light, whereas cold colours mark areas with low scatter. Transparent media (e.g. clear varnishes, air above the surface of the examined object) or areas located beyond the range of penetration are shown as black.

All tomograms are presented here with light approaching from top: the air above the object is therefore shown in black and the first visible structure is the surface of the painting: usually the air-varnish interface. The varnish is shown in black if it does not scatter the probing light, or in green–blue in case of weak scattering. Below the varnish, the profile of the paint layer is always visible. However, the possibility of imaging the bulk of the paint and of the layers underneath depends on their permeability to near IR radiation. It is worthwhile to note that OCT provides axial distances as optical ones (dependent on

refraction index of the media). However, all OCT cross-sectional images presented herein are corrected for this effect in post-processing and all distances are shown as geometrical. Two kinds of tomograms are shown: vertically stretched for better readability showing overall cross-section spread over 15 mm and not distorted, with the same scales in both directions for detailed inspection of the ablation results. Unless otherwise indicated, the scale bars represent 200 μ m in both directions. The same OCT data was used to render a paint surface before and after laser ablation (Fig. 3a) and by subtraction of two relevant surface profiles to generate maps of removed material (Fig. 3b). In turn data from these maps was used for estimation of the average thickness of removed material with the HWHM (Half Width at Half Maximum) of its distribution (Table 1).

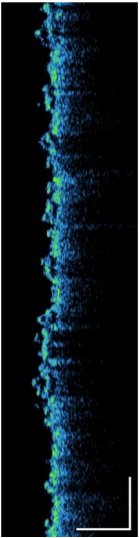
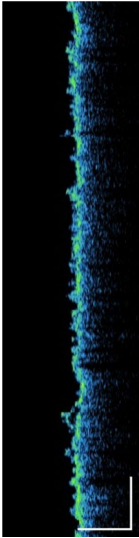
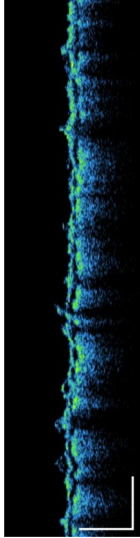
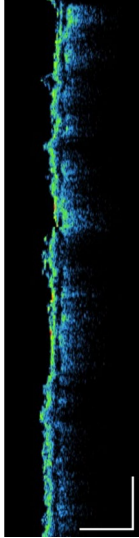
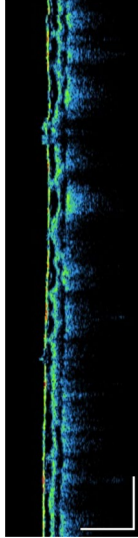
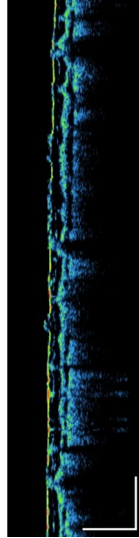
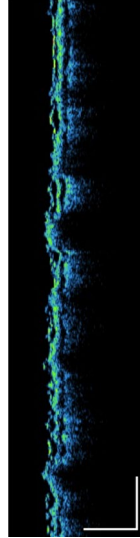
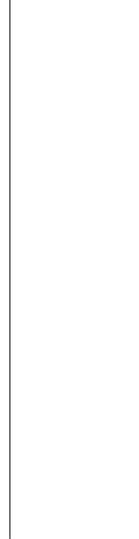
Reflection FT-IR spectroscopy

Non-invasive FT-IR measurements were performed through a portable ALPHA-R spectrophotometer (Bruker Optics, Germany/USA-MA) equipped with an external reflectance module with specular optics (22°/22°). The system consists of a SiC Globar source, a “rock solid”-design interferometer (with gold mirrors) and a DLaTGS detector. Data were acquired from areas of ca. 4 mm diameter, in the spectral range of 7500–350 cm⁻¹, with a resolution of 4 cm⁻¹ and using an average of 186 scans (few minutes of acquisition time). The background was acquired from a flat gold mirror. Data are shown as pseudo-absorption spectra [$\log(1/R)$; R=reflectance]. Reflection FT-IR spectroscopy from a complex and optically thick surface (as that of a painting) generally involves the collection of both diffuse (from the volume) and specular (from the surface) reflection with a variable and unpredictable ratio that basically depends on the roughness of the examined surface as well as on the optical properties of the investigated materials; as a result reflection FT-IR spectra generally show distorted profiles that cannot be properly corrected by software. Nevertheless, they are still able to provide valuable information on the surface chemical composition ([19] and references therein).

Laser induced fluorescence (LIF) spectroscopy

The experimental set-up used in this work employs the laser beam of a pulsed ns KrF Excimer laser (LAMBDA PHYSIK, Excimer Laser L.P.X. 205SD) at 248 nm, which was weakly focused perpendicularly on the surface of the painting (area of analysis of almost 0.01 cm²) and at a fluence of approximately 0.005 J/cm². The fluorescence emission was collected by a fused-silica optical fibre and transferred into a 0.25 m Czerny–Turner imaging spectrograph (PTI Model 01-001AD). The spectrograph is

Table 1 Summary of FT-IR, OCT and LIF data obtained after the laser cleaning tests (series C—Fig. 1a, e) performed on the Floral painting

Area	F = fluence (J/cm ²)	N = number of pulses	Layer examined with FT-IR after cleaning	Cross-section and changes in structure of layers as seen with OCT after cleaning (OCT tomograms cover an area of 2 × 0.5 mm ² , bars represent 200 μm in both directions)	Average thickness of removed material (μm)	Layer examined with LIF after cleaning
C1a	1.1	30	Probably paint layer (noisy spectrum)		65 ± 21	The band at 473 ± 5 nm is reduced in intensity and red shifted to 483 ± 5 nm after cleaning A new band appears at 610 ± 5 nm
C1b	1.1	20	Probably paint layer (noisy spectrum)		69 ± 18	
C2a	0.9	50	Probably paint layer (noisy spectrum)		55 ± 14	
C2b	0.9	40	Probably paint layer (noisy spectrum)			
C3a	0.9	20	Probably paint layer		42 ± 12	
C3b	0.9	10	Natural varnish		30 ± 6	Emission intensity is increased after laser irradiation. No other changes are observed
C4	0.7	25	Natural varnish		19 ± 5	
C5	0.7	46	Probably paint layer (noisy spectrum)		34 ± 10	The main band at 473 ± 5 nm is reduced in intensity and red shifted to 483 ± 5 nm after cleaning A new band appears at 610 ± 5 nm

equipped with a 300 grooves/mm holographic diffraction grating, covering a spectral range of 280 nm with a resolution of 0.4 nm. Fluorescence emission spectra were recorded in the wavelength range 370–625 nm, and background corrected.

Experimental methodology

The analytical investigations through the complementary use of OCT, FT-IR and LIF techniques were performed before and after each laser cleaning test. In particular, reflection FT-IR measurements were carried out at the centre of the treated areas, with the instrument head at 1 cm of distance from the painting surface. The repositioning of the FT-IR spectrophotometer after the cleaning treatments was possible due to the relatively large size of the measuring spot, while for the repeatability of the OCT scans a micrometric precision was required. Images from two video cameras built-in the OCT instrument enabled the precise documentation of the position of examined area before laser cleaning and were used subsequently for its repositioning after treatment.

All the recorded LIF spectra were acquired by accumulation of 300 single-laser shot spectra per area/spot in order to increase the fluorescence signal to noise ratio. For each laser cleaning test, three adjacent areas/spots were analyzed and the mean fluorescence signal is presented.

Results and discussion

Assessing the laser cleaning of paintings by means of OCT and reflection FT-IR

OCT and FT-IR measurements carried out on the red background before the laser cleaning tests provided the local painting stratigraphy and the chemical composition of the surface layers, respectively. In the OCT tomograms (Figs. 1d, 2a,d and 4a) the three surface transparent layers over the overpaint layer were recognized. The red ochre overpaint layer (No. 6) is semi-transparent to OCT probing light and, thus, varnish layers below (Nos. 3–5) are visible as well (Figs. 1d, 2a, c, d, f, 4a, c). It is worthwhile to note that fading “tails” visible below the surface of the opaque paint (No. 2) are the result of multiscattering phenomena in the paint and do not reflect its real structure.

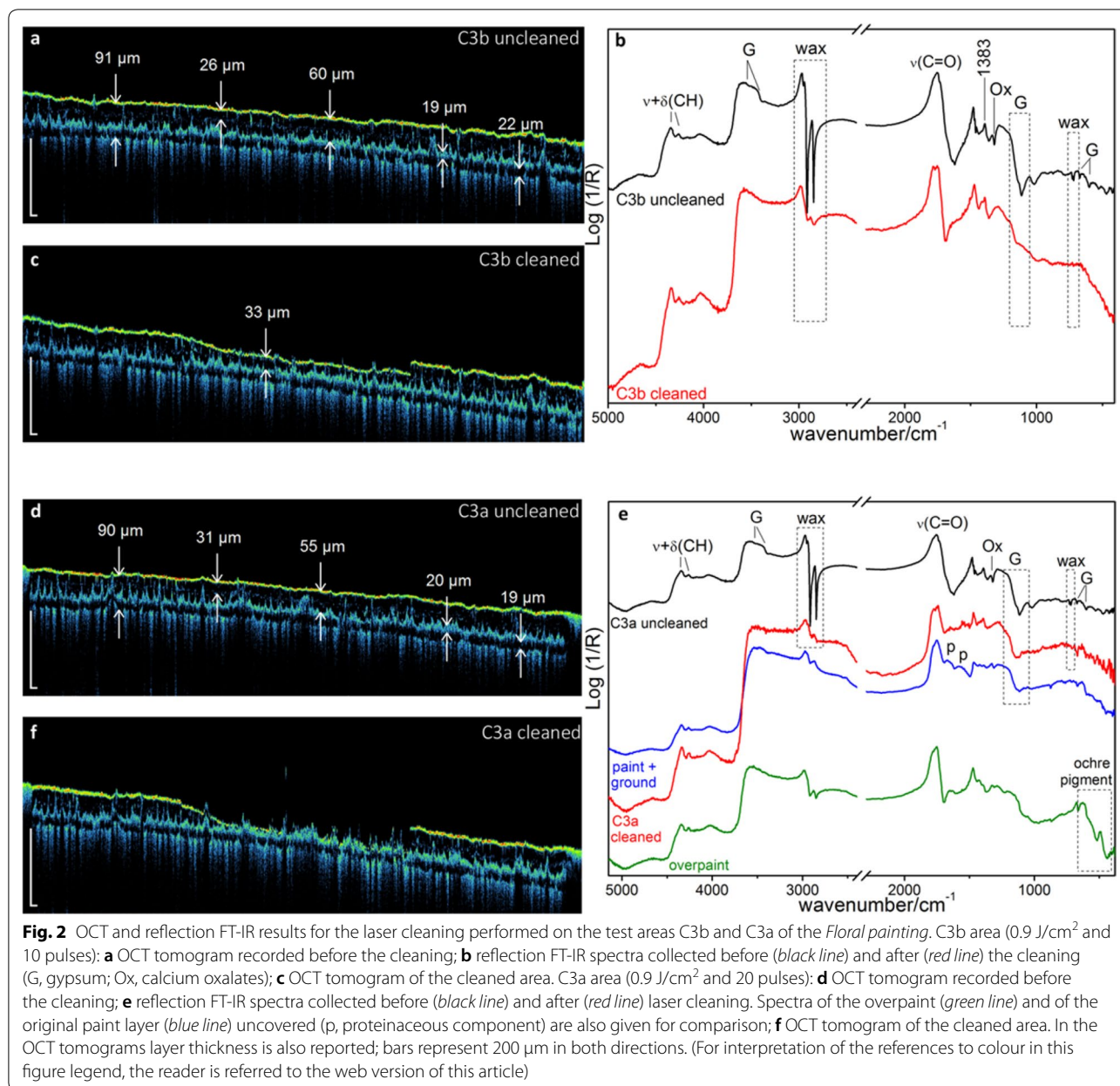
The uppermost layer was attributed to a wax coating identified by FT-IR. In the infrared spectrum collected before the treatment (Fig. 2b—black line), indeed, absorption features of beeswax at 2954 cm^{-1} (asymmetric *stretching* CH_3), 2922 and 2853 cm^{-1} (asymmetric and symmetric *stretching* CH_2 , respectively) and the doublet at 732 and 716 cm^{-1} due to the CH_2 *rocking* mode were observed [27]. Additionally, the band at 1320 cm^{-1} revealed the presence of oxalates [28], probably of

calcium, while the OH *stretching* signals at 3398 and 3555 cm^{-1} and the characteristic SO_4^{2-} vibration modes (ν_3 at 1120 cm^{-1} and ν_4 at 676 – 608 cm^{-1}) indicated gypsum [29] from deposition or migration.

The main goal of laser cleaning on this multifaceted painting was to gradually remove the upper varnish layers until a safe level was reached, with the red ochre overpaint left intact; this safe level was established to consist in maintenance of a “buffer” residual varnish layer over the red ochre overpaint so as to protect it from photochemical oxidation due to laser illumination. Furthermore, additional tests aimed at investigating the removal of the red ochre overpaint layer itself have also been performed. Towards these goals a series of cleaning tests employing different fluence values (F : 0.7 – 1.1 J/cm^2) were executed, resulting into a different ablation depth and thus cleaning level. The cleaning tests were fine-tuned using variable number of pulses (N : 10 – 50) according to the indications provided by the OCT and reflection FT-IR survey carried out before and after each laser application (treated areas shown in Fig. 1a, e).

Table 1 summarises results of one of these series of cleaning tests (C series) providing the relationship between various combinations of F and N and the different cleaning levels, namely reduction or removal of the outermost wax layer and the two upper varnish layers.

From Table 1 it can be seen that the cleaning depth can be regulated by using different laser cleaning parameters. In particular, by adopting the lowest fluence of 0.7 J/cm^2 with 25 pulses (C4 area) a mild cleaning result was obtained, which mainly refers to the removal of the wax layer and partially of the upper varnish layers, corresponding to a total thickness of $19 \pm 5\text{ }\mu\text{m}$. On the other hand, roughly doubling the number of pulses at the same fluence (46 pulses, C5 area) the surface appears over-cleaned, showing a patchy distribution of the residual varnish. The most acceptable outcome for the needs of conservation, intended at removing the varnish layers but leaving the overpaint intact, was reached at laser irradiation fluence of 0.9 J/cm^2 with 10 pulses (C3b area); in this case, removal of wax and partially of the upper varnishes is observed from the comparison between the OCT tomograms acquired before and after the laser treatment (varnish removal is estimated to be $30 \pm 6\text{ }\mu\text{m}$, Table 1 and Fig. 2a, c). These findings were confirmed by the FT-IR profiles collected on the same area before and after the cleaning step. In detail, in the spectrum related to this latter step, red line in Fig. 2b, the infrared features of beeswax disappear, while the varnish is still visible. This latter is clearly distinguished from the underlying oil binder thanks to the identification of the CH_2 asymmetric *bending* mode at 1383 cm^{-1} , which usually appears much more pronounced in the natural varnish spectral pattern



than in the oil one and can be used as a marker band in reflection mode FT-IR spectroscopy [30]. In addition, the infrared analysis allowed us to detect the removal of calcium oxalates ($\nu_s(\text{CO})$ band at 1320 cm^{-1}), and of surface gypsum (from deposition or migration).

For higher number of pulses (C3a with 20, C2b with 40 and C2a with 50), maintaining the same value of $F = 0.9 \text{ J/cm}^2$, a fine modulation could be reached: the thickness of the removed material was increased with increasing N values. From the surface maps generated by OCT data (Fig. 3a) a significant difference in ablation efficiency can be already noticed by doubling the delivered number of

pulses (C3a area, $N = 20$, vs C3b area, $N = 10$); also FT-IR measurements before and after laser cleaning of the C3a area (Fig. 2e) exhibit a significant reduction of the varnish signal, while spectral contributions ascribable to the underneath paint layer start to be visible, as better clarified from the analysis of the C1a area (see discussion below). The same conclusion can be drawn from the map of the removed varnish (Fig. 3b). Close inspection of both images (Fig. 3a, b) reveals that despite the ablation of the varnish, the *craquelure* structure remains intact as it is seen by direct comparison of details in the surface maps (Fig. 3a) and as yellow lines (indicating

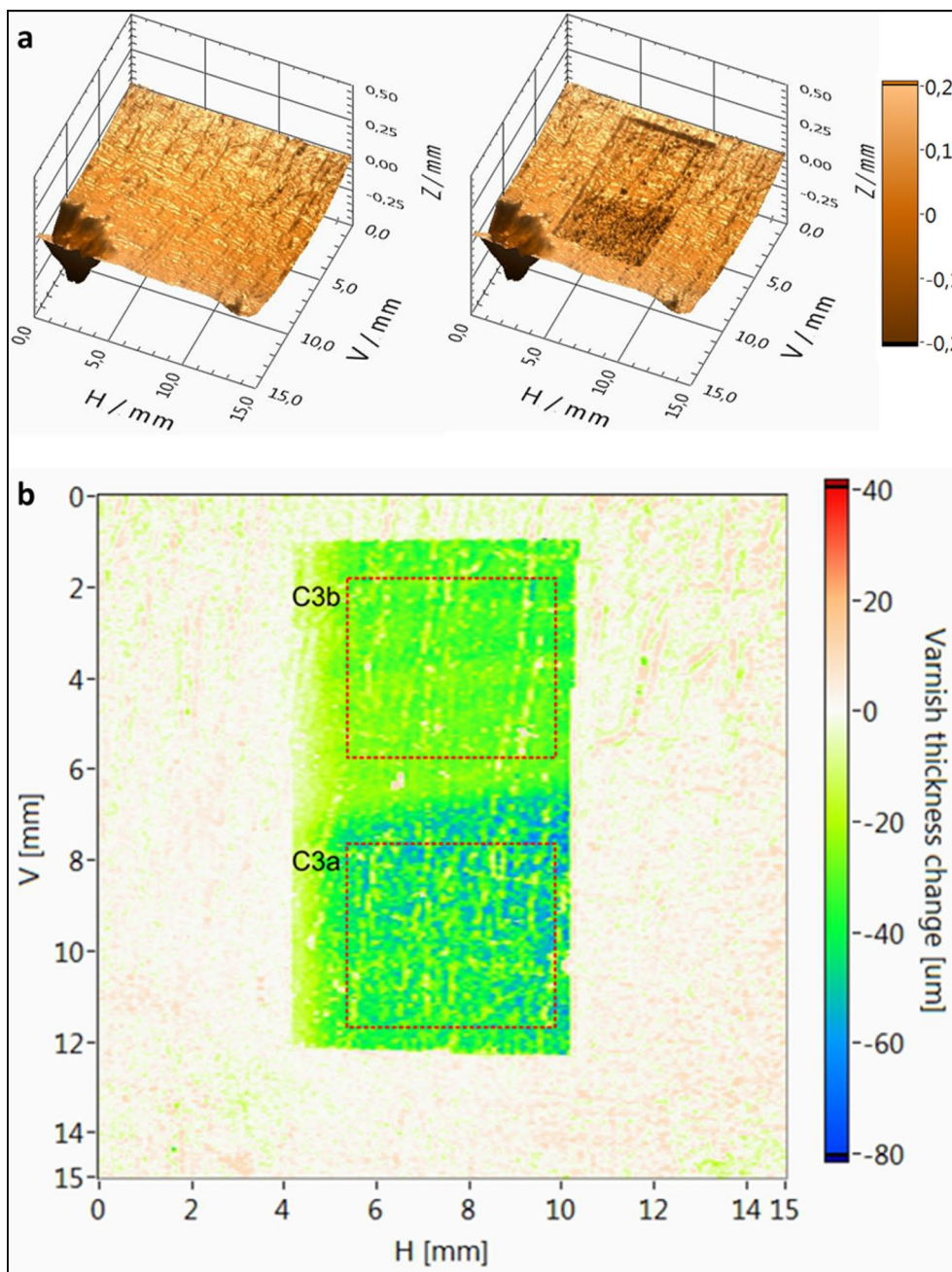
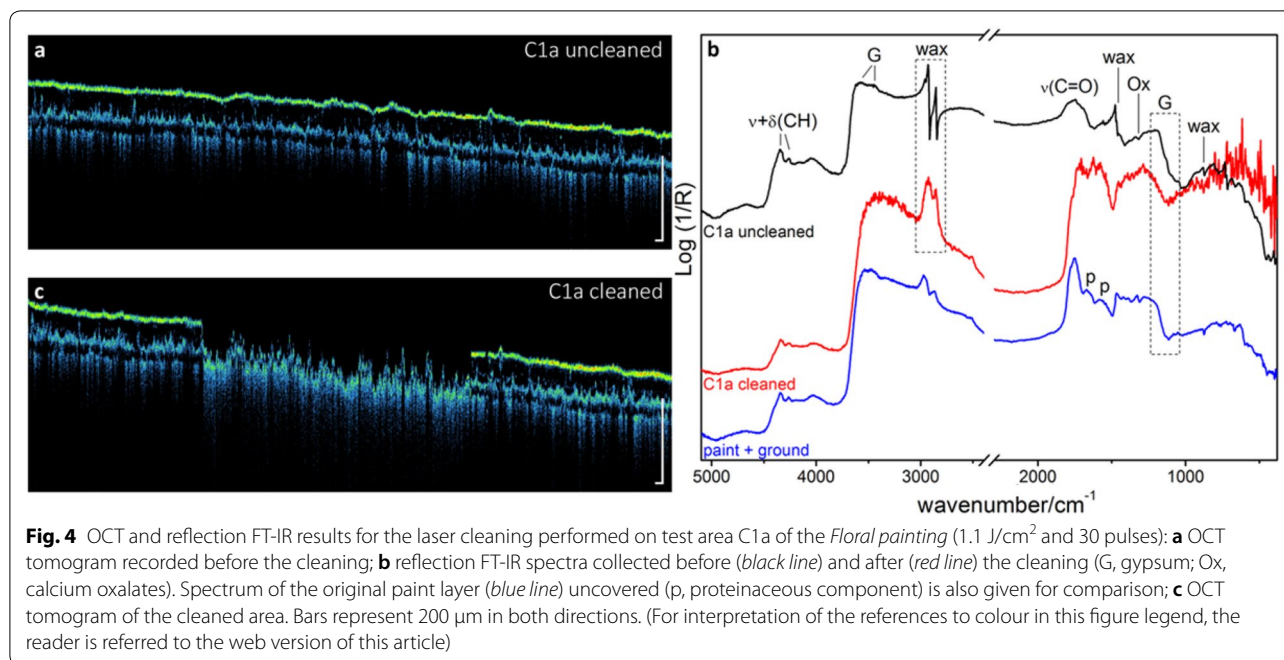


Fig. 3 **a** Varnish surface maps of the test areas C3a and C3b before (left) and after cleaning (right) rendered from OCT data. **b** Map of the varnish thickness change after laser cleaning obtained from OCT data, red rectangles indicate areas used for averaging the thickness of removed material given in Table 1

significantly lower local ablation) in the map of Fig. 3b. This effect is especially visible for the C3b area where the amount of removed material is also more homogenous over the whole area with respect to the C3a area; this should be evaluated as a desirable result from the conservation point of view and confirms the conclusion about

the most acceptable outcome for area C3b, stated above, based on the analysis of the OCT cross-sections and FT-IR data. Areas C2b and C2a (N=40 and 50, respectively), on the other hand, appear over-cleaned; the two upper varnish layers were removed while the overpaint



was partially ablated, as seen by OCT and FT-IR results (Table 1).

At last, in the attempt of revealing the original red vermilion paint layer, for the highest F value tested (1.1 J/cm²) at increasing number of pulses (C1b=20, C1a=30) the red ochre overpaint layer as well as the varnish coatings were removed (Table 1). In Fig. 4a, c OCT tomograms acquired before and after the laser treatment with the most intense operative parameters of this study (area C1a, F=1.1 J/cm² and N=30) clearly show the uncovering of the original red vermilion paint layer, which appears with increased surface roughness. Reflection FT-IR measurements confirmed OCT results: after the cleaning step (red line in Fig. 4b) the diagnostic signals of beeswax and of the surface varnish layers are not visible anymore, while the lipid component of the oil binder is detected (diagnostic bands: C=O *stretching* and $\delta + \nu$ CH modes) along with signals in the spectral region of the amide I and amide II bands (1550–1650 cm⁻¹); these latter possibly come from the underneath ground layer, as also suggested by the permanence of a sulphate band at about 1100 cm⁻¹, despite the fact that the surface sulphate deposits were removed by laser cleaning. Interestingly, the infrared spectrum acquired on the original paint layer uncovered by laser cleaning is particularly noisy, especially at low wavenumbers (red line in Fig. 4b); a similar result was obtained for all the areas where either the red ochre overpaint or the original red vermilion paint were partially uncovered (Table 1). This fact might be explained by a possible irregular action of

cleaning with the specific laser parameters on the treated paint surfaces, which, notably, has been readily revealed by both OCT and FT-IR.

Assessing the laser cleaning of paintings by means of LIF

While the combined use of OCT and reflection FT-IR spectroscopy has proved to be successful in assessing the treated surface at different laser parameters, the possibility of equipping the laser cleaning workstation with a diagnostic modulus for on line monitoring and control of cleaning process is still to be explored. In this perspective, laser induced fluorescence spectroscopy has been evaluated having the definite advantage of being compatible with the optical set up of a laser cleaning workstation (e.g. sharing the same laser source used at different fluence values). The use of UV–Vis–NIR fluorescence spectroscopy (exploited with different type of excitation sources, namely, filtered Xenon lamp, laser, and more recently LED) to analyse and study cultural heritage objects and materials is well established [31, 32]. Its use as a diagnostic tool is recommended in combination with UV–Vis reflection spectroscopy and when organic dyes and/or pigments are present with rather good emission quantum yield [33]. Conversely, fluorescence spectroscopy of organic materials, like varnishes and binding media, does not provide satisfying specificity for their differentiation [32]. Nevertheless, the use of LIF as a tool to assess and monitor the cleaning processes (using conventional [34] as well as laser-based [9, 12, 35,

36] methodologies) can be done on the basis of direct comparison of luminescence spectra before and after cleaning.

The fluorescence intensity (I_F) depends on the amount of energy absorbed at the excitation wavelength and thus, according to the Beer–Lambert law, on the thickness of the remaining film after cleaning ($I_F = Z \cdot I_0 \cdot \Phi_F \cdot (1 - 10^{-\varepsilon cd})$, where Φ_F is the fluorescence quantum yield, Z is the geometrical (collection angle) factor, I_0 is the intensity of the incident probe laser beam, ε is the molar extinction coefficient, c is the molar concentration and d is the optical path length). Therefore, in our study, the reduction of the fluorescence intensity recorded on the laser treated surfaces may be indicative of the thinning of the varnish layer. In parallel, changes to the shape and position of the fluorescence profile can be indicative of a photo-ageing process. Specifically, broadened and red-shifted bands are associated with the presence and formation of new fluorophores (i.e. new C=C bonds show increased fluorescence at longer wavelengths) and can be linked with oxidized and cross-linked products that characterize aged polymers [37]. Finally, the appearance of new bands may indicate signal from underlying materials (e.g. specific emitting pigments in paint layers).

In the case study presented herein, the LIF spectra recorded after each laser cleaning test (red lines in Fig. 5a,

c) are compared with the ones recorded before laser irradiation (reference spectra, black lines in Fig. 5a, c) on the basis of the intensity (I_{\max}) and wavelength (λ_{\max}) of their main fluorescence band (Table 1 and Fig. 5). All spectra are background corrected in order to compare the absolute maximum fluorescence intensity reflecting the chemistry of the exposed surface. Moreover, the spectra are also normalized to their maxima in order to clearly visualize any changes in λ_{\max} (lower part in Fig. 5a, c).

As it can be seen in Fig. 5, all the recorded fluorescence spectra are relatively broad with maxima at ca. 473 nm. In most of the cases I_{\max} appears reduced indicating elimination of the varnish thickness in agreement with OCT and FT-IR analysis. A characteristic example is demonstrated in Fig. 5a (upper part); I_{\max} of the LIF spectra recorded for the area C1a is significantly decreased after cleaning, confirming the elimination of the varnish layer. This is also illustrated in the digital microscope UV-induced fluorescence image recorded (Fig. 5b, lower part), where the area C1a after the laser treatment appears darker due to absence of emitting materials. Comparison of the normalized spectra in Fig. 5a (lower part) leads to the observation of a notable red-shift of the fluorescence maxima ($\Delta\lambda_{\max} \sim 10$ nm) and a new band (shoulder) at ca. 610 nm. This observation was recorded for most of the laser-treated areas except for the C3b (Fig. 5) and C4 ones (Table 1). As

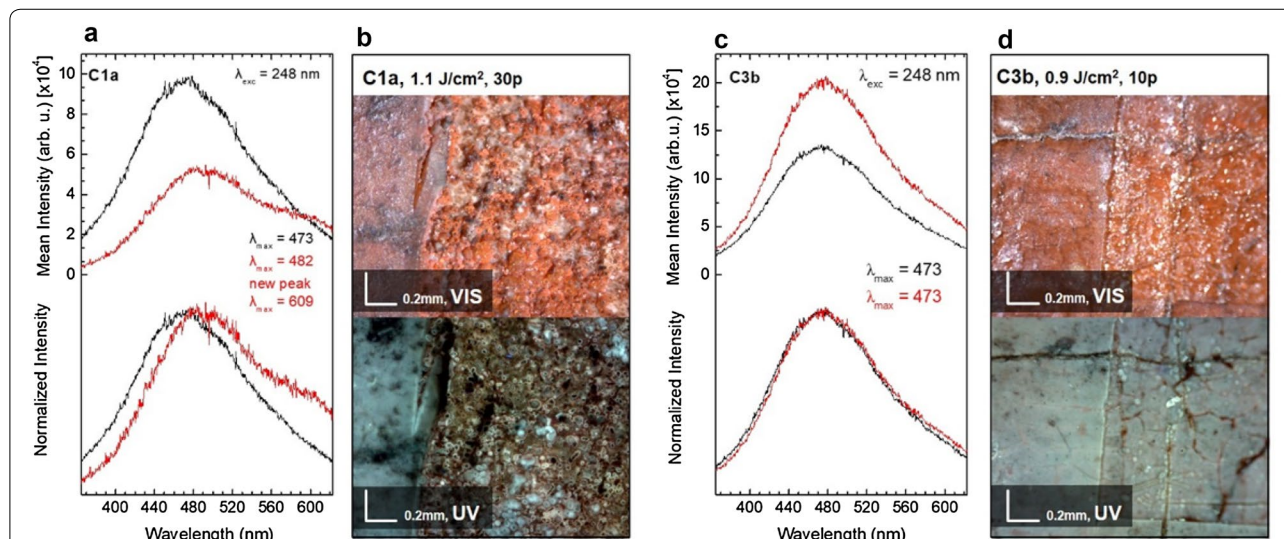


Fig. 5 **a** LIF spectra of test area C1a without (upper) and with (lower) fluorescence intensity normalization. Black line corresponds to the LIF recorded from the untreated/reference surface while red line corresponds to the surface that has been laser cleaned at $F = 1.1$ J/cm² and 30p. **b** Details of the cleaned areas photographed with DINO-lite microscope in the visible (upper) and UV (lower) regions showing treated (right) and reference (left) areas (magnification $\times 200$). **c** LIF spectra of test area C3b without (upper) and with (lower) fluorescence intensity normalization. Black line corresponds to the LIF recorded from the untreated/reference surface while red line corresponds to the surface that has been laser cleaned at $F = 0.9$ J/cm² and 10p. **d** Details of the cleaned areas photographed with DINO-lite microscope in the visible (upper) and UV (lower) regions showing treated (right) and reference (left) areas (All DINO-lite images show magnification $\times 200$)

discussed previously, the red-shift can be correlated to photo-oxidation of the probed layer while the shoulder at ca. 610 nm (Fig. 5a) is tentatively assigned to vermilion (HgS) [14, 32, 38, 39], thus indicating that cleaning may have partially reached the original paint layer (layer No. 2 in Fig. 1c).

In contrast in test areas C3b (Fig. 5c, d) and C4, where FT-IR and OCT analyses have shown partial removal of the outermost varnish layers, the fluorescence spectrum, although maintaining the same profile, presents higher intensity values after the cleaning. No other changes (e.g. λ_{\max} shifting) are observed after laser treatment (Fig. 5c, lower part). This result is interpreted as partial varnish removal up to a layer where photo-oxidation may be present and is also illustrated in Fig. 5d, through the digital microscope images, which both confirm that a varnish layer remains and no paint layer is reached.

Conclusions

Overall, the results presented herein confirm the combined use of OCT/FT-IR spectroscopy to be highly valuable as an analytical tool for in situ assessment of laser cleaning treatments applied on painting surfaces. In particular, the correlation between laser parameters and the change in surface chemical composition and in painting stratigraphy, provided by reflection FT-IR and OCT, respectively, was systematically explored in investigations on a historical painting donated to science. This allowed us to guide the fine tuning of the laser operative parameters in order to meet the requests posed by conservators, demonstrating the potential of laser ablation to remove selectively unwanted surface layers (aged varnish layers and/or overpaints) with high precision and resolution. Furthermore, LIF measurements were also performed as a complementary analysis to OCT/FT-IR investigations. Based on the achieved results, LIF can be considered as an analytical technique with high potential for in situ assessment of cleaned surfaces, as well as for monitoring of laser cleaning processes in painting conservation. The fact that it employs the same (but attenuated) laser beam that is used for the removal of the unwanted layers is an important advantage as regards its use on line with the laser cleaning intervention. It may be also applied with automated scanning laser cleaning schemes for a more straightforward monitoring. Further studies on technical samples and real objects will be performed in order to clarify all issues and develop a reliable analytical methodology that would allow a careful and consistent evaluation of the cleaning level so to be able to reliably control the cleaning process.

Abbreviations

OCT: optical coherence tomography; FT-IR spectroscopy: Fourier transform infrared spectroscopy; LIF: laser induced fluorescence spectroscopy; F: laser fluence (energy density); N: number of applied laser pulses.

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Authors' contributions

PM conducted FT-IR measurements, analyzed FT-IR and drafted the manuscript; MI conducted OCT examinations and interpreted the results; KM conducted the laser cleaning tests; ED and OK performed the LIF measurements and analysed the data; MD contributed to address conservation issues for the historical painting; MS conducted OCT examination and developed software for acquisition and analysis of OCT results; PP supervised the laser cleaning tests and the interpretation of the LIF analysis and drafted the manuscript; PT contributed to the analysis of the OCT results and drafted the manuscript; KJB contributed to address conservation issues for the historical painting; LC conducted FT-IR measurements, analyzed FT-IR and drafted the manuscript; CM supervised the project, the analysis of the FT-IR data and drafted the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets collected during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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