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Optical devices provide unprecedented insights into the laser cleaning of calcium oxalate layers☆

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ABSTRACT

Calcium oxalates are insoluble colorless or whitish salts constituting noble patina, on both natural and artificial stone artworks' surfaces, the presence of which is extremely valued. The oxalates are not considered detrimental to the substrate, however, being often accompanied by other substances such as gypsum, silicates, and pigmented particles. They may form very adherent, relatively thick and colored layers creating disfiguring effects and hindering legibility of the pictorial surface. For this reason it may be appropriate to diminish their thickness, but patina's partial preservation is particularly required calling for extremely gradual and controllable cleaning approach. Thinning of calcium oxalate patina from a detached 16th century fresco (from Sansepolcro) was performed through the use of laser (Nd:YAG and Er:YAG) systems and chemical means (Carbogel loaded 5 wt.% of tetrasodium EDTA). Optical coherence tomography (OCT), providing a non-invasive stratigraphic cross-section of the examined surface, allowed to distinguish the oxalate from the underlying original layers and therefore to have an overview about its distribution, to numerically evaluate patina's thickness range and to provide the information on the amount of the material both removed and left on the artwork's surface. Laser scanning conoscopic microprofilometry allowed for a high-density sampling of the artwork's surface providing a three-dimensional model of the surface pattern. The obtained 3D models were used to estimate the amount of material removed and to compare them with those provided by OCT. The successful exploitation of the proposed exceptional cleaning monitoring methodology may be seen as an innovative and valid support for the restorers in the conservation of mural painting or other surfaces covered by oxalate layers and may pilot more targeted, cautious and respectful cleaning intervention.

1. Introduction

The calcium oxalates are insoluble colorless or whitish inorganic salts formed through mineralization of organic compounds and/or due to the metabolic activities of lichens, fungi in two major crystal structures — monohydrate whewellite or dihydrate weddellite ($CaC_2O_4 \cdot (2)H_2O$) [1]. By themselves are not deleterious, however, they are often accompanied by gypsum, silicates, pigments, carbon particles, etc. whereby generating disfiguring and adherent orange to brown layers (~10–100 μm) that affect and obscure the pictorial surface. In order to improve the artworks' legibility, it becomes necessary to lighten, but at the same time to preserve, a thin patina layer with a protective function over the substrate/pictorial layer. The choice of the most appropriate cleaning methodology is a very demanding task necessitating expertise and matured experience of restorers and conservation scientists who should be possibly assisted by analytical information on the cleaning efficacy, gradualness and selectivity, induced surface morphology and color alterations, and controllability, especially in case of innovative cleaning systems. Chemical information can be obtained by advanced techniques such as Fourier transformed infrared and Raman spectroscopy, gas chromatography, X-ray fluorescence, laser-induced breakdown spectroscopy, and electron microscopy coupled to energy dispersive X-ray spectrometry [2], but the morphological aspect may result of equal importance. In this respect, an instrumental investigation involving different advanced and complementary optical techniques is proposed to monitor the partial reduction of oxalate layers. The outcome of cleaning tests, performed on the 16th century fresco affected by a dark brown oxalate patina, was monitored by optical coherence tomography (OCT), laser microprofilometry, scanning multispectral Vis-NIR as well as traditional reflectance spectrophotometry. OCT is an interferometric technique that returns stratigraphic sections at high spatial resolution of diffusing or semi-transparent objects without any kind of sampling or contact, on the condition of a refractive index spatial variation. It has been

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Table 1
Set-up of cleaning methods.

Cleaning mode	Wavelength	Pulse duration	Modality	Fluence
Laser Nd:YAG (LQS)	1064 nm	100 ns	3 Hz, dry mode	1.7 J/cm^2 (spot ø 3.10 mm, E = 130 mJ)
Laser Nd:YAG (SFR)	1064 nm	40 μs	3 Hz, dry mode	3.3 J/cm^2 (spot ø 2.75 mm, E = 200 mJ)
Laser Er:YAG (Er70)	2940 nm	135 μs	15 Hz, wet mode with isopropanol	7.0 J/cm^2 (spot ø 1 mm, E = 70 mJ)
Laser Er:YAG (Er85)	2940 nm	145 μs	15 Hz, wet mode with isopropanol	7.6 J/cm^2 (spot ø 1 mm, E = 85 mJ)
Chemical (CH)	Carbogel (4%)	30 min contact time	Poultice tetrasodium EDTA (5%)	

introduced into conservation science since 2000 mainly for the non-invasive examination of the stratigraphy of paint and varnish layers. [3–5] OCT has also been shown to be a responsive technique for revealing preparatory underdrawings beneath paint layers owing to its high dynamic range and depth selection capabilities. It can be used for dynamic monitoring of the wetting and drying of different varnishes, varnish removal using solvents, real time laser ablation of varnish layers and tracking of canvas deformation due to environmental changes or in the examination of ancient glass, enamel, ceramics, jade, faience and parchment. [3–12] The OCT capability to probe the material substructure is limited by a combination of scattering and absorbing effects (i.e. material opacity). Since the OCT depth (axial) resolution (Δz) is related to the source wavelength and its spectral bandwidth ($\Delta z \sim \lambda^2/\Delta\lambda$) and the scattering coefficient of a material generally decreases with increasing wavelength, the best OCT probing depth is obtained with longer wavelength sources at the cost of lower axial resolution [8,9,11].

The aim of this work is to demonstrate that OCT technique may provide useful information on thickness and distribution of oxalate patina not only as a preliminary step preceding its thinning, but also in monitoring the cleaning output. This aspect is of utmost importance as preservation of the noble patina is highly desirable since it provides an aged character to the surface with protecting function. The data provided by near infrared OCT were compared with those obtained by optical microscopic measurements on a cross-section obtained by invasive and traditional sampling. Moreover, conoscopic profilometry, another interferometric technique, was used to quantify the removed material from the differences of measured quotas before and after cleaning. [13–21] The aforementioned techniques were used to evaluate the outcome of different traditional and innovative laser-based cleaning methods. The traditional cleaning of oxalates was performed with salts of ethylenediaminetetraacetic acid (EDTA) that form a part of chelate agents. Tetrasodium EDTA (pH = 11.6) binds the calcium ions of oxalate layers through complexation on two amines and four carboxylates, leaving theoretically the calcium carbonate constituting the mural painting intact. However, if high concentration is used (above 6%) or when left to react for prolonged time period, the detrimental effects to the pictorial layer can be provoked. [22] Such traditional method, which is and still may be used in by many restorers, was compared with relatively innovative cleaning methods based on laser ablation. To this aim, first harmonic of Nd:YAG lasers with optimized pulse durations in nanosecond (Long Q-switched, LQS) and microsecond (Short Free Running, SFR) regime, as well as SFR Er:YAG laser, were employed. In spite of initial skepticism about the cleaning control these techniques offered, the optimized temporal regime proved alternative to traditional cleaning methods for Nd:YAG at both laboratory and real-application level [23–27] whereas for SFR Er:YAG only laboratory tests were performed [28]. The previous works describing the Er:YAG laser in cleaning mural paintings involved longer pulses (free-running). [29,30] The optimized pulse duration can prevent the high mechanical stress and at the same time minimize the large instantaneous temperature gradients in the irradiated surfaces [25,26], keeping in mind that shorter high-intensity laser pulses favor pressure effects, while thermal effects dominate with longer pulses. By carefully selecting the pulse energy criteria, the laser can remove encrustations and dirt while leaving the underneath material intact. The investigation of the oxalate layers removal was realized in situ on real artwork as the simulation of artificial oxalate patinas of similar thickness and physicochemical properties as those encountered on real artworks is extremely difficult.

2. Material and methods

2.1. Mural painting description

The mural painting from Sansepolcro (Tuscany, Italy) was realized with a buon fresco technique on the Pesa arc that connects the current city museum with the town hall; the painting dates back to the 16th century. In 1950 it was detached (with strappo technique) and glued on a masonite panel of a 119 × 97.5 × 2.5 cm by the Leonetto Tintori's studio. The fresco is in an advanced deterioration state: it is very fragmented and covered with a relatively thick brownish patina layer recognized to be composed mainly of calcium oxalates, gypsum, carbon and red ochre particles through diagnostic tests performed in the scientific laboratories of the Opificio delle Pietre Dure. The formation of calcium oxalates can be most likely and at least partly linked to the mineralization of animal glue [31] used in the process of detachment and that remained on the fresco surface.

2.2. Configuration of the parameters used for cleaning systems

Table 1 reports all the parameters used for each applied cleaning system. The cleaning methods using Nd:YAG lasers were described elsewhere [31], but are reported here for clarity and comparison. On the other hand, Er:YAG (produced by El.En. S.p.A., Calenzano, Italy) tests were performed in the frame of this work and refer to a laser source with emission wavelength $\lambda = 2940$ nm with a variable pulse duration ($t_d = 40$–150 μs). The laser light beam is led by a hollow fiber producing a 1 mm in diameter spot. The pulse repetition rate can be set to 7, 10 or 15 Hz. Table 1 refers to the measured energy values. The parameters were set so as to achieve the optimal cleaning level obtainable with each specific method in three cleaning steps. This was done through a series of preliminary tests non reported here.

Table 2
Set-up of progressive cleaning steps.

t0	t1	t2	t3
No cleaning (reference)	Single pass of laser irradiation or 30 minutes poultice	Two-passes laser irradiation or 60 minutes poultice	Three passes of laser irradiation or 90 minutes poultice

Fig. 1. Output of cleaning methods (labels described in Table 1) applied on the Sansepolcro fresco (t0 before cleaning and t1–t3 progressive cleaning steps).

To gain insight into the gradualness, the cleaning was broken down into the three progressive cleaning steps with the aid of a grid composed of four 1×1 cm^2 checkboxes as described in Table 2. Progressively proceeding to the next step, the previous box has been obscured so as to obtain three progressive t1, t2 and t3 cleaning steps.

2.3. Instrumental monitoring of cleaning

Monitoring of cleaning was performed with non-destructive, non-invasive and non-contact optical techniques (Vis-NIR multispectral scanner, conoscopic microprofilometry, Optical Coherence Tomography).

2.3.1. Vis-NIR multispectral scanner and reflectance spectrophotometry

The multiVis-NIR scanner acquires the radiation backscattered from the measured surface in many narrow-band spectral intervals. The instrument scans a 1 m^2 surface with a spatial sampling of 4 point/mm in about 3 h, generating 32 monochromatic images in the visible (from 380 to 780 nm) and in infrared region (790 to 2500 nm) with a spectral sampling step of 20–30 and 50–100 nm, respectively. The instrument works at a distance of 12 cm from the paint surface in a 45°/0° configuration according to CIE standards. [32,33] The CIELab values are promptly returned for each point of the surface (for each pixel), in our case nine L*a*b* values were computed for each step of cleaning with a preset size of 10×10 pixels (2.5×2.5 mm). The spectrophotometer Konica Minolta CM-2600d was used for the spectrophotometric survey as well. For each step, nine measurements (3 mm spot diameter), each performed with a series of three light pulses, were made and the average value was calculated for each measure with the respective standard deviation. L*a*b* coordinates were calculated using the CIELab 1976 color-space, using the D65 illuminant with observer at 10°.

The spectrophotometer and multispectral scanner acquire the backscattered radiation in two different configurations, respectively diff/0° (integrating sphere) and 45°/0°. However, using the spectrophotometer's specular component excluded mode the comparison between the two datasets is feasible [34] and it was possible to verify their mutual agreement.

2.3.2. Optical coherence tomography (OCT)

This instrument returns stratigraphic sections at high spatial resolution of diffusing or semi-transparent objects without any kind of sampling or contact. The prototype used for stratigraphic analyses associates confocal microscope optics with the OCT-technique set-up. The spectral width ($\lambda = 100$ nm) of the source at $\lambda = 1550$ nm determines the axial resolution of about 10 μm, whereas confocal operation enables the positioning of the beam focus inside the sample. Our time domain OCT operates with a lateral resolution down to 2.5 μm and with a working distance of the objective from the surface of about 3 mm. The scan rate is 4 Hz and the maximum scanning area is 25×25 mm [35].

2.3.3. Conoscopic microprofilometry

The instrument acquires a collection of vertices over a regular grid, which forms the 3D model of the measured surface. The working distance from the surface is 4 cm, with a dynamics of 8 mm (depth of field) whereas the acquisition frequency is about 400 points/s. The maximum scanning area is 30×30 cm with 1 μm axial and 20 μm lateral resolution. Laser scanning conoscopic microprofilometry provided a topographic map of the artwork's surface pattern, supplying height (z) values, which were used to estimate the amount of the removed patina.

3. Results

The cleaning output of the different techniques is shown in Fig. 1 that shows the RGB image reconstructed through colorimetric procedures from the 16 visible channels acquisitions by Vis-NIR scanner.

3.1. Spectrophotometric measurements

Spectrophotometric characterization is a well-established and traditionally used technique in conservation, above all to draw a comparison in time of the same studied surface allowing to check the trend of the chromatic alteration as an effect of either cleaning or aging. [34,36] Colorimetric measurements enable the analyst to overcome subjective visual perception limitations through scientific quantification of the painted surface, on the basis of the relevant acquired reflectance data. Spectrophotometric measurements were expressed as numerical values

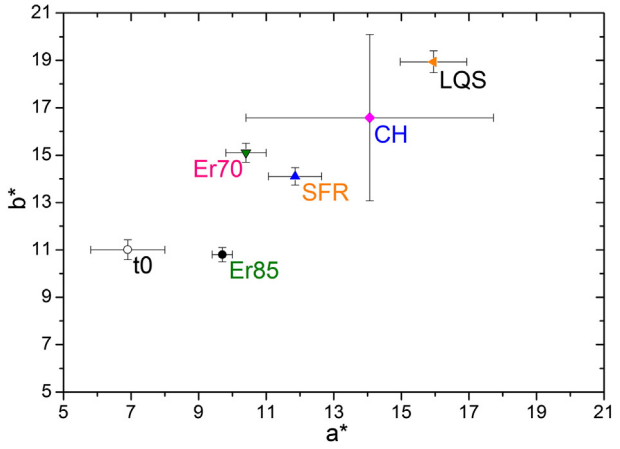

Fig. 2. Plot of a* and b* colorimetric coordinates with their standard deviations as measured on surface before (t0) and after t3 (final) step of cleaning.

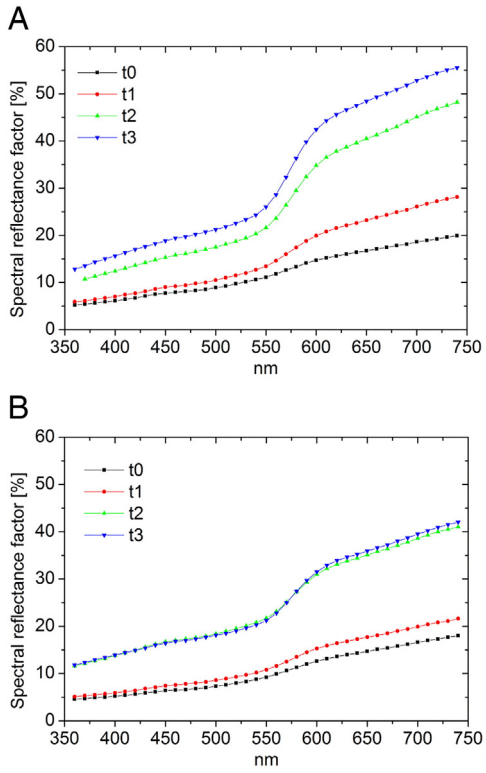

Fig. 3. Reflectance spectra in the visible region for surfaces cleaned with Nd:YAG LQS (A) and SFR (B) as a function of t0–t3 cleaning step.

L*a*b*, as defined by the Commission Internationale de l'Éclairage (CIE). The L*a*b* colorimetric coordinates, computed from the Vis output of the multispectral scanner, confirmed a global increase of a* parameter evidencing a transition of the painting's surface color from brown to a more reddish color, as a function of progressive cleaning for all cleaning methods (Fig. 2). For each system, the plot of a* and b* coordinates related to surface before cleaning (t0) and to the third step of cleaning t3 shows how the surfaces cleaned with Er70, Er85 and SFR systems exhibit both lower a* and b* values, returning a colder shade of pictorial layer as compared to LQS and Carbogel systems that return a warmer tone.

Referring to step t3, we can affirm that all the applied laser cleanings are more homogeneous than chemical. Indeed, the values of the standard deviations relative to a* and b* parameters are higher for chemical ($\sigma > 3$) than for laser cleaning ($\sigma \leq 1$).

Investigating the reflectance factor values in the visible region allowed to gain insight into gradualness of the cleaning techniques. As an example, the reflectance curves obtained on surfaces cleaned with Nd:YAG in LQS and SFR regime are reported in Fig. 3 as a function of cleaning progress. In terms of the spectral reflectance factor changes, an increase especially in the red region is observed. In specific, surface before cleaning exhibits a rather flat reflectance spectrum (t0) that changes its shape as a function of cleaning. This testifies that hematite (α-Fe_2O_3) contained in the pictorial layer was progressively uncovered as judged by the absorptions due to charge transfer mechanism among Fe^{3+} and O^{2-} of iron(III) oxide. [37] A more abrupt change in spectral reflectance factors occurs between t1 and t2 for SFR, suggesting a less gradual cleaning as compared to LQS (gradual increase t1–t3). Moreover, the surface remains darker for SFR (lower spectral reflectance factors) than for LQS after the final step of cleaning.

3.2. Confocal OCT measurements

OCT is an interferometric technique that uses light to capture three-dimensional images from within optical scattering media with micrometric resolution. The output is the so-called tomographic image or tomogram, an image representing a slice or section through a three-dimensional object. An example of tomogram acquired with our OCT device shows the superficial stratigraphy of the mural painting (Fig. 4). In this section, from top to bottom, two signals are clearly detected, due to the scattered light on the air/oxalate patina interface and on the oxalate patina/pictorial layer interface, confirming, thus, the capability of OCT to visualize the distribution of oxalate based patina.

Measurements with our confocal OCT on mural painting patina can provide two types of signals: one related to the measurement with confocal microscope (CF) and the second derived from the interferometric signal (OCT). Being n the refractive index of the patina at λ = 1550 nm (with the approximation of homogeneous system), the real patina thickness (d_r) is given by $d_r = d_{OCT}/n$, whereas from the CF signal $d_r = d_{CF} \cdot n \cdot f(n)$. In the formula of the real patina thickness in the confocal modality, the term $f(n)$ is related to the numerical aperture of the objective, and accounts for the fact that the focus position inside the sample varies with the refractive index of the medium crossed by the radiation, and can be obtained from the Snell's law of refraction.

In our operative conditions, for n ranging from 1.3 to 1.8, $f(n)$ can be considered as constant and equal to 1.1. Therefore by defining an effective thickness $d_{CF}^* = d_{CF} \cdot f(n)$, the real patina thickness can be computed by combining the two signals measured in the same point $d_r = (d_{CF}^* \cdot d_{OCT})^{1/2}$. The real patina thickness of the calcium oxalate before cleaning was then estimated by averaging over 25 measurements, and resulted to be (41 ± 2) μm, achieving a very good agreement with the optical microscopic measurements on a cross-section obtained with the invasive and traditional sampling method (Fig. 4 right).

An important aspect of OCT measurements is not only to provide the information on the thickness before the cleaning but mainly on the thickness of the calcium oxalate patina remaining on the painting surface after the cleaning steps. The importance of such data is linked to the fact that a very thin layer of transparent and inert patina with a protective function should be ideally preserved on the surface. Such result is reported in Fig. 5 as a function of cleaning system and progress so as to show an example of surface that is optimally cleaned (Nd:YAG-LQS), overcleaned (Nd:YAG-SFR) and insufficiently cleaned (chemical poultice).

OCT can go beyond qualitative imaging toward quantitative measurement. The estimate of the patina that remained on the surface is reported in Fig. 6 for all the methods. Relative to the last step of cleaning (t3), it is possible to state that the SFR Nd:YAG and Er85 (with a $d_r \leq 10$ μm) systems caused over-cleaning, keeping in mind 10 μm is our OCT device detection limit. With Nd:YAG laser in LQS regime and SFR Er:YAG laser (Er70) an optimal level of cleaning, with respective

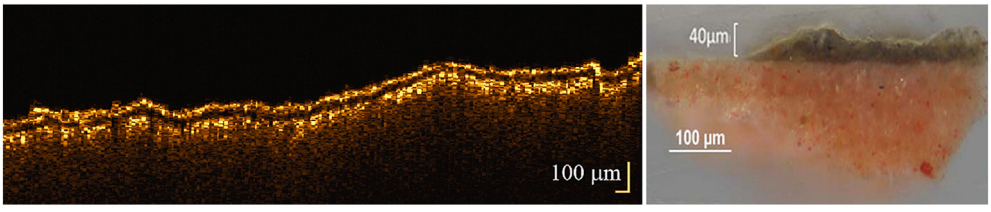

Fig. 4. Mural painting before cleaning: as tomographic section acquired by our OCT device (left), as optical micrope image of cross-section (right).

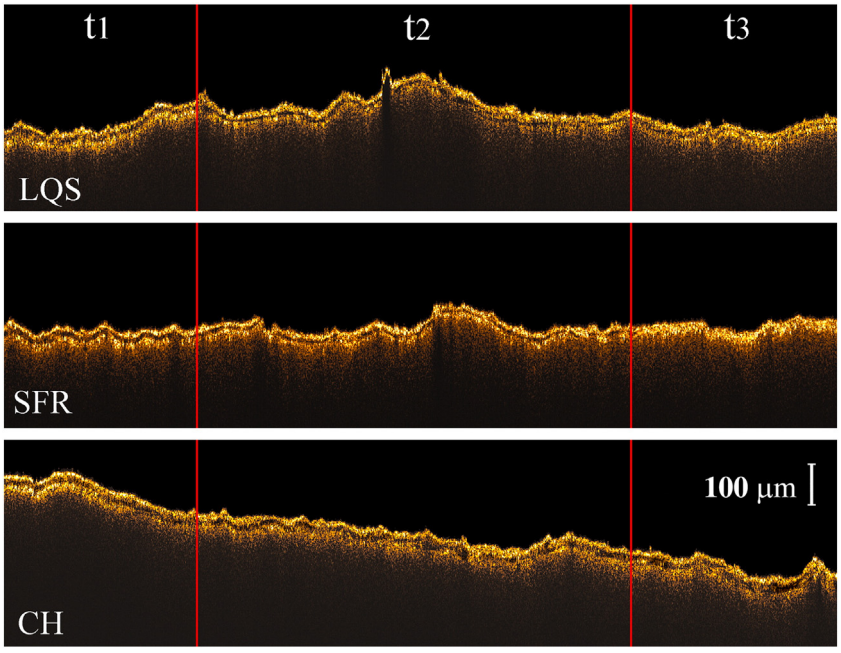

Fig. 5. OCT scans (2 cm long) in the progressively cleaned zones from top to bottom cleaned with Nd:YAG in LQS and SFR regime and chemical poultice.

patina residual thicknesses on the order of d_r ~ 20 μm and d_r ~ 23 μm, was achieved. Conversely, EDTA in Carbogel poultice (d_r ~ 30 μm) did not allow for a sufficient cleaning under employed conditions (90 min contact time, 5% of tetrasodium EDTA in 4% Carbogel). The analytical assessment, based on OCT data, was in agreement with the visual evaluation of the result by the restorer and consents us to state that the optimal cleaning level corresponds to about 20 μm of patina preserved on the artwork surface, in this specific case. The data obtained in intermediate steps t1–t2 provide an insight into the dynamics and gradualness of cleaning process as well as into the etch rate information.

3.3. Conoscopic measurements

Conoscopic profilometry is a scanning interferometric technique that returns 3D models of the acquired surface. This quantitative representation of relief can be used either during the cleaning to monitor morphological variations of the surface, or to compute roughness calculations. The 3D models can be displayed as images, for instance in simulated grazing light that allows the visualization of the finest details of the surface, or as color maps to enhance the different quota areas.

For all systems of cleaning the fresco surface morphology was respected and no noticeable superficial changes in brush strokes were observed. In order to appreciate the dynamics of the removal by laser ablation, images of *z* value differences were generated. Despite the difficulties due to the impossibility to perfectly align the two acquired range maps (before and after cleaning), it is possible to appreciate the dynamics of the removal by laser ablation. As an example, data acquired on the area before and after cleaning with SFR Er:YAG laser system (Er70) is shown in Fig. 7. The quota difference is then displayed in color scale (Fig. 7) and enables to estimate the thickness of removed patina. This latter resulted to be lower than 15 μm in t1, in a range between 15–20 μm in t2 and on the order of 20 μm in t3 step. The obtained data agree with the estimate furnished by OCT. The apparent protrusions and depression (points and stripes) visible in z value difference image are caused by the marks made with calcium carbonate mixed with water to delimit the areas to be cleaned as a part of a common praxis among the restorers. The marks may be removed during the cleaning process and the area is delimited by new marks in roughly same positions. That is why one set of marks appears in a difference image as a protrusion (positive zeta values) and a new set as a depression (negative zeta values).

3.4. Evaluation of cleaning methods

The use of Nd:YAG may be justified by the absorption of its 1064 nm fundamental wavelength by carbon/dark particles present in oxalate patina whereas that of Er:YAG laser by the absorption of 2940 nm wavelength by oxalate and gypsum. The Er:YAG laser system proved effective for the removal of a film of calcium oxalate. This phenomenon is enabled by the coupling of laser radiation ($\lambda = 2.94$ μm) into the –OH groups present in the patina. The removal of the patina was carried out with the laser irradiation in the wet mode (isopropyl alcohol) so as to enhance the absorption and to confine the surface temperature.[38] The irradiation produced a whitening of the surface due to the rupture of the patina. The removal of mechanically compromised patina was then achieved through the use of cotton swab soaked in isopropanol. This combined procedure has the advantage of enabling gradualness and controllability more apparent during early phases of cleaning. Conversely, a drawback that can occur is a non-homogeneous cleaning result. The Er70 system is less effective than Er85 system, however the result for the latter is not satisfactory in

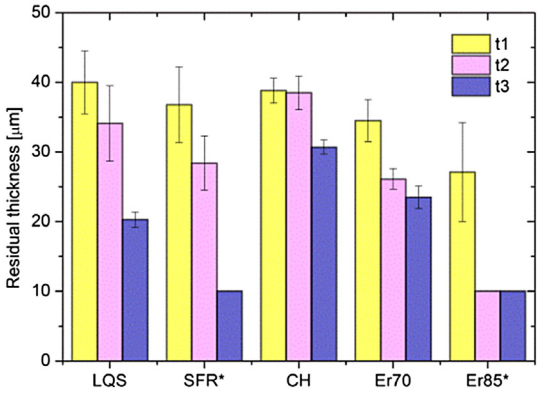

Fig. 6. Patina's residual thickness as calculated from OCT measurements after t1–t3 cleaning steps with five different cleaning methods.

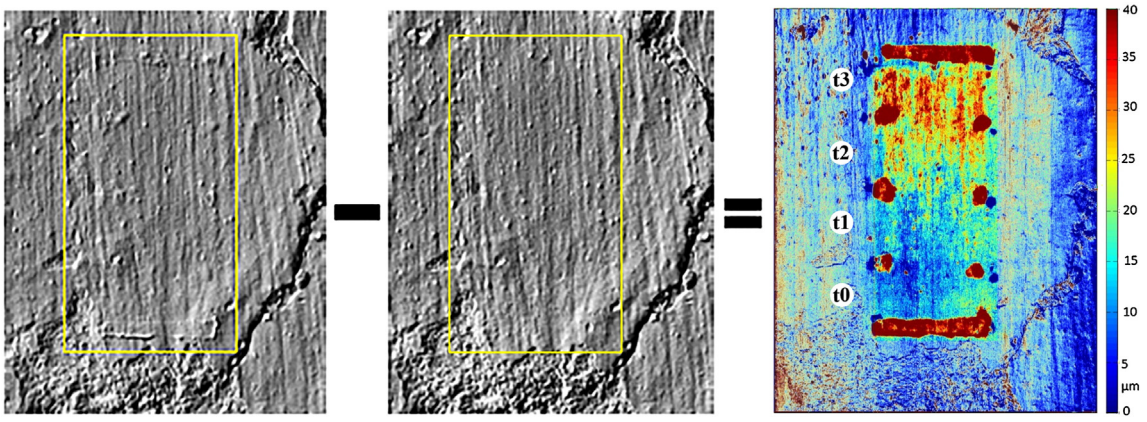

Fig. 7. Estimate of removed material by subtraction of *z* values obtained with conoscopic measurements before (left) and after (middle) cleaning. The differences in *z* values are displayed as color image for Er70 system (right).

terms of conservation: as can be seen from OCT data, the Er85 removal, as well as the SFR Nd:YAG one, was too incisive, leaving a layer of patina too thin on the fresco's surface. This relatively thin layer itself may impart a cold tone color. This hypothesis is valid also for the SFR Nd:YAG laser that yielded slightly over-cleaned and thus cold tone surface. As shown by both the reflectance spectra and OCT measurements, the LQS system proved to be more gradual than SFR Nd:YAG system. Moreover, even if the last cleaning step by SFR Nd:YAG evidenced a patina reduction, the surface color characteristics changed minimally, leaving the surface relatively dark, possibly due to prevalent photothermal effects [25,26]. The removal of material by ablation with the Nd:YAG laser in LQS mode, through prevalently photomechanical mechanism [25,26], is immediate and does not require any additional treatment of the surface. To summarize, the LQS system appeared to be the best cleaning method in terms of efficacy, selectivity and aesthetic results. Finally, action times of EDTA in Carbogel poultice must be carefully tuned and the cleaning requires a continuous visual supervision that is complicated due to the poultice opacity. In this case, the action time on the order of 90 min did not ensure sufficient cleaning. Moreover, the system proved neither gradual nor controlled, nor homogeneous due to the poor adherence of this specific poultice type. However, it returned a surface color close to the LQS system and then close to the result deemed acceptable by the restorer.

4. Conclusion

This work aims at demonstrating the applicability of optical coherence tomography (OCT) in monitoring the thickness and distribution of oxalate layers formed on a detached 16th century mural painting. The findings/outcomes of this work confirm that OCT at 1550 nm ($\Delta\lambda = 100$ nm) is able to detect the scattered light on two interfaces (air/oxalate patina and oxalate/pictorial layer) and whereby to visualize the superficial stratigraphy and thus the patina distribution. The prototype developed at INO and used in this work combines the confocal optical microscope with OCT. This combination, as added value, allows for a more precise estimate of the effective patina thickness thanks to the possibility to calculate the refraction index value at 1550 nm and thus to correct the apparent thickness measurement that would provide OCT or confocal microscopy itself. The data provided by OCT were in good agreement with those obtained by invasive and traditional sampling and observation of a sample cross-section under the optical microscope as well as with those provided by conoscopic profilometry. On the contrary to conoscopic microprofilometry, the OCT results provide information also on the residual thickness and as compared to microprofilometry are more straightforward to obtain.

OCT can go beyond qualitative imaging toward quantitative measurement: a decent depth resolution OCT device (~10 µm) is sufficient to effectively monitor the cleaning process as the optimal cleaning level was found to correspond to ~20 µm patina thickness preserved on the surface. The successful exploitation of the optical methods for monitoring of cleaning may be seen as a valid support for the conservators of mural paintings or other artificial or natural stone substrates that may be affected by oxalate layers. Thus OCT has the potential to become a routine non-invasive tool for scientific conservators allowing cross-section imaging and could pilot more targeted, cautious and respectful cleaning intervention, especially when testing innovative cleaning systems. Ideally, it should be complemented by chemically specific technique such as reflectance Fourier-transformed infrared or Raman spectroscopy.

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