

Color and Colorimetry Multidisciplinary Contributions

Vol. XIX A

Edited by Filippo Cherubini and Andrea Siniscalco



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Vol. XIX A**

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Introduction

The GdC - Associazione Italiana Colore organizes the Color Conference every year, and it reached its nineteenth edition in 2024.

The two-day international event featured three keynote speakers: Phil Green (University of Science and Technology, Gjøvik, NO), Vien Cheung (University of Leeds, UK) and Robin Kingsburgh (York University Toronto, CA).

During the conference, the “Color Award / Premio Colore 2024” was also conferred, which went to the extraordinary painter Valerio Adami.

A special thanks go to the Color Award Commission, in the person of Cristian Bonanomi, Lia Luzzatto, and Lisa Vergelli (author of the winner's presentation text), for their valuable contribution.

Heartfelt thanks to Filippo Cherubini (IFAC-CNR) for his valuable help in managing the conference and to all the session chairs who moderated the speeches: Luca Cogo (Università degli studi di Milano Bicocca), Marcello Picollo (IFAC-CNR), Francesca Fragliasso (Università degli studi di Napoli Federico II), Ingrid Calvo Ivanovic (Universidad de Chile), Alice Plutino (University of Amsterdam), Verena M. Schindler (AIC Study Group on Environmental Colour Design), Alessandro Rizzi (Università degli studi di Milano Statale), Lisa Vergelli (Sapienza Università di Roma), Beatrice Sarti (Università degli studi di Milano Statale).

Thanks also to all the people who contributed to the conference's digital moderation and ensured its success: Paola Bertoletti, Alessandro Bortolotti, Gianluca Guarini, Ivanka Dicheva, Plutino Alice, and Vergelli Lisa.

Final thanks to Konica Minolta, which generously sponsored the conference.

Enjoy the reading.

Andrea Siniscalco

December 2024

Index

COLOR IN MEASUREMENT- COLOR IN DIGITAL	9
Modeling individual differences in color appearance through images' correction	10
Camilla Simoncelli, Michael Webster	
Beware: M. E. Chevreul's chromatic circle may conceal multiple systems	13
A. Malmert, C. Andraud, E. Pouyet	
A perceptual assessment of the chromatic scale of uncertainty in hypothetical virtual architectural 3D reconstruction	21
Fabrizio Ivan Apollonio, Federico Fallavollita, Riccardo Foschi	
Implementing Generative Artificial Intelligence in Lighting and Color Design: Methodologies, Advantages, and Challenges.....	29
Paola Bertolotti	
PBR material: a comparison between rendering for accurate material color reproduction. A case study	38
Gianluca Guarini, Maurizio Rossi	
COLOR AND RESTORATION.....	47
Silent Film Colourisation Process: From Recipes to Film Laboratories	48
Valentina Rossetto, Alessia Buttarelli, Margherita Longoni, Silvia Bruni	
Influence of the binder on the susceptibility of the painting irradiated with a nanosecond pulse Nd:YAG laser at 1064 nm.	56
Kateryna D'Ayala, aura Andrés-Herguedas, Daniel Jiménez-Desmond, Pablo Barreiro Castro, Teresa Rivas, José Santiago Pozo-Antonio	
Visible-induced infrared luminescence (VIL) with monochromatic visible excitation: a preliminary look into various artistic materials and possible future perspectives	65
Mattia Morlotti	
Combination of multiple analytical techniques for a holistic technical study of a 17th-century easel painting	74
Alice Pertica, Chiara Ricci, Mattia Morlotti, Serena Hirsch, Amina Vietti, Daniele Demonte, Marianna Ferrero, Federica Pozzi	
Evaluation of the effects of cleaning with essential oils on the colors of motion picture films	83
Caroline Figueroa Fuentes	
Wrappings and colors for eternity: scientific investigations on the votive animal mummies' manufacture.....	92
Maria Diletta Pubblico, Sofia Ceccarelli	
COLOR AND DESIGN- COLOR AND CULTURE	100
"Who is afraid to sit on a rainbow bench?" Contemporary color solutions for benches and seating units in public spaces - selected issues	101
Justyna Tarajko-Kowalska, Przemysław Kowalski, Agata Kwiatkowska-Lubańska	
COLOR DESIGN FOR SAFETY AND INCLUSION.....	112
D. Freda, F. Valan, P. Paglierani, A. Farini, M. Zaroni, A. Ferraro	

The Enduring Economic Value of Color: Tracing its Multifaceted Impact Across Eras and Industries	122
Alessandro Bortolotti and Riccardo Palumbo	
Kawésqar colour names and their associations: survey results	130
Verena M. Schindler	
COLOR AND EDUCATION- COMMUNICATION / MARKETING	136
Expanding color understanding in the graphic communications classroom through color model comparisons.....	137
Celeste Calkins, Erica Walker	
Demonstrating Metamerism: A Key Concept for Lighting/Color Design Education	146
Maurizio Rossi	
Colour is for Everyone: Teaching interdisciplinary colour foundations.....	154
Robin Kingsburgh	
COLOR AND LIGHTING, COLOR AND PHYSIOLOGY, COLOR AND PSYCHOLOGY	162
The use of color in open-plan office partitions: The effect on workers' circadian response.....	163
Laura Bellia, Federico Contella, Francesca Diglio, Francesca Fragliasso, Ugo Lafranceschina	
Lighting and Colour profoundness, the building up of an initiatory pathway to human need of shadow	172
Richard Caratti-Zarytkiewicz	
RGB illuminant compensation using multispectral information	181
Mirko Agarla, Simone Bianco, Marco Buzzelli, Luca Cogo, Ilaria Erba, Matteo Kolyszko, Raimondo Schettini, Simone Zini	
Metamerism in forensic medicine in imaging aspect	187
Kazim Hilmi Or	
Shades of Perception: Understanding Color Vision Impairments in Multiple Sclerosis.....	196
Teresa L'Abbate, Alessandro Bortolotti, Laura Marzetti and Franca Tecchio	
Color Preferences of University Students in Dormitory Rooms.....	205
Serra Koz, Nilgün Olguntürk	
Colour Meaning Matrix: A Tool for Connecting Concepts to Hue, Value and Saturation.....	214
Ingrid Calvo Ivanovic	
Between the lines: a survey to evaluate how light color gradients affect emotions	222
Andrea Siniscalco, Alessandro Bortolotti	
KEYNOTE SPEAKERS	230
A gamut boundary test chart for extended colour gamut reproduction	231
Phil Green	
Colour association: rational or groundless?	232
Vien Cheung	
Colour is for Everyone: Teaching interdisciplinary colour foundations.....	233
Robin Kingsburgh	

Color in Measurement - Color in Digital

Influence of the binder on the susceptibility of the painting irradiated with a nanosecond pulse Nd:YAG laser at 1064 nm.

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Abstract

This study is part of the vast panorama of laser applications for cleaning artworks with a particular focus on the application of a Nd:YAG laser working at 1064 nm to clean tempera and frescos paintings. Paintings mock-ups were prepared following traditional recipes with green earth, egyptian blue, cinnabar, chromium oxide, ultramarine blue and mars red. Before being irradiated with the laser, the samples soiled with soot were exposed to an artificial ageing in a climatic chamber with exposure to SO₂. For comparative purposes, pigment pellets and references paintings were also irradiated. Surfaces were analysed with stereomicroscopy and colour spectrophotometry for an estimation of physical changes. Moreover, chemical changes were evaluated by Fourier-transform infrared spectroscopy. As result, damage thresholds of paints were higher than those determined for their corresponding pellets. Thus, the binder has a protective character for the pigment. Cinnabar- and mars red-based paints were most sensitive under laser radiation leading colorimetric changes with low fluences, while blue and green paints were laser-resistant. The protective effect of the binder depends on the mineralogical composition of the pigment: cinnabar, mars red and ultramarine temperas showed higher resistance to laser radiation than their fresco counterparts, whereas for the rest of the pigments, the fresco paintings were more resistant. Regarding soiling cleaning, the irradiation with the painting damage thresholds provoked damages on the pictorial layer, so decrease the fluence was necessary, except for the red pigments with both binders. Although the cleaning was satisfactory at naked eye, soiling remain was detected in cavities by means of stereomicroscopy and FTIR.

Keywords: laser cleaning, pigment, soiling, fresco, tempera, conservation, egg yolk.

Introduction

Since 1970's, in which a laser was used for the first time by Asmus to remove dark encrustations on Venetian marble (Asmus et al., 1973), laser ablation as a cleaning method of Cultural Heritage materials has been deeply investigated, mainly for stone (Fotakis et al., 2006; Pereira-Pardo and Korenberg, 2018; Zanini and Bartoli, 2018). Laser factors that mainly condition an effective cleaning of the stones without exerting harmful effects to the forming minerals are: the active medium, the wavelength, the pulse duration and the fluence. Then, in order to optimize the laser cleaning is necessary to determine, before cleaning the undesirable surficial deposit, the effect of the different factors in a step-by-step methodology: 1st to find the interaction of the available laser beams with the reference (without any undesirable substance) to determine the damage threshold; 2nd to determine the fluence necessary to extract the undesirable deposit and 3rd to optimize the laser parameters to extract the deposit on the artwork, avoiding damage. Although less research has been carried out in wall painting comparatively to stone, this step-by-step methodology must be considered to achieve a satisfactory cleaning, considering the compositional complexity of these paintings, specifically tempera wall paintings and fresco paintings. The former are made of an inorganic pigment (cinnabar, malachite, azurite, etc.) and an organic binder such as rabbit glue or egg yolk (Mayer, 1985). Usually, the paint is applied on a substrate of calcium carbonate formed as a result of the carbonation of

portlandite. In fresco painting, pigments are painted onto the outer layer of mortar when it is still wet. This enables the pigments to bond to the surface via a carbonation process, i.e., calcium hydroxide reacts with atmospheric CO₂ to form calcium carbonate.

Among the deterioration forms (EwaGlos, 2016), soiling composed of particulate matter, dirt and pollutants due to traffic emissions and industrial activities, is commonly found on wall paintings, when they are (semi-)exposed outdoors. The paintings components (pigment and binder) with different physical and chemical behaviours show different susceptibilities, making laser cleaning of wall paintings a real challenge.

Regarding the laser cleaning of wall paintings, scientific studies address the effect of different laser systems on pure pigments, simulated tempera mock-ups (using different binders) with/without an undesirable deposits (varnishes, artificial patinas, complex layers of polymers, etc.) or real tempera artwork (Castillejo et al., 2002, 2003; Bracco et al., 2003; Chappé et al., 2003; Oujja et al., 2003, 2013; Pouli et al., 2003, 2009; Andreotti et al., 2007, 2016; Camaiti et al., 2008; Siano et al., 2012). Considering the cited scientific publications, it is necessary, to achieve a satisfactory cleaning of wall painting, firstly to determine the effect of the laser parameters on the painting components and the whole painting without the undesirable substances to determine the damage threshold. Secondly, the mineralogical composition of the pigment and the binder nature must be taken into account in order to understand the behaviour of the paintings under laser radiation.

This study, using a nanosecond (6 ns) pulsed Nd:YAG laser with a 10 Hz repetition rate working with a 1064 nm wavelength, aimed to identify: 1) damage thresholds for pigment and paint mock-ups, considering the effect of the binder (calcite and egg yolk) on the behaviour of the painting under laser irradiation and 2) the effect of the application of these damage thresholds on the soiled mock-ups to identify the role of the soiling-paint interaction on the cleaning effectiveness.

Material and methods

Samples preparation

The selected pigments (supplied by Kremer GmbH) are among the most popular colours in wall paintings, such as red, green and blue. Two pigments were chosen for each, one representing use from the earliest period (cinnabar, green earth and egyptian blue) and the other from modern production since the 18th century (mars red, chromium green and ultramarine).

Pigment-only samples were made into 4 cm diameter aluminium moulds and compacted with a 30-tonne press. Regarding painting, the reproduction of fresco and tempera paintings were made following the Old Master recipes (Pozzo, 2009). Part of the painting samples were contaminated by soot collected from diesel engine car exhaust pipes. It was deposited on the mock-up surfaces before introducing them into a climatic chamber FITOCLIMA 300EDTU with gases exposure. Samples were exposed for 40 days under a relative humidity of 80%, temperature of 18°C and SO₂ concentration of 200 ppm.

Laser system

The laser applied was a Q-Switched (QS) Quanta Ray INDI-series operated at 1064 nm (IR radiation) with a pulse duration of 6 ns and a 10 Hz repetition rate. To improve focalization, a convergent lens with a focal length dependent on the fluence required for each sample was used.

The methodological approach conducted (Fig 1) was based on: firstly, 0.3cmx0.3cm square tests were done on the periphery of each sample to look for the conditions at which minimum damage began to appear. Once identified, this fluence (identified as D) was used to do a 1.2cmx1cm square in the top left side of the tablet (Fig 1.1). Then, to identify the damage threshold, two more squares (1.2cmx1cm) were made decreasing the fluence identified as D: reduction of 10% (identified as D-10% area in the top right of the tablet) and 40% (identified as D-40% area in the down left of the tablet). If the -10% area had no visible damage, it was selected as the damage threshold (Th_p). If -10% showed visible damage and the -40% did not, this was selected as the damage threshold (Th_p). Finally, other square

(1.2cmx1cm) was done increasing D fluence by 40% to ensure a clear damage on the sample (identified as D+40% area in the down right of the tablet).

Secondly, the fluence identified as threshold fluence- Th_p - (-10% or -40%) was used to perform a 1,2cmx1cm square in the paintings (Th_p , Fig 1.2). If physical changes occurred in the paint (mainly darkening or extraction), the fluence was decreased to find the damage fluence of the paints (Th_{EY}/Th_F). The fluence was then increased to find the surface damage fluence (F_{dam}).

Finally, the fluence identified as the damage threshold (Th_{EY}/Th_F) of the paintings was applied to the soiled samples (Fig 1.3). If this fluence was not sufficient to clean the paint or it allowed the removal of the soiling but also the paint layer, it was raised or lowered respectively to achieve the appropriate cleaning playing with the number of scans (1 or 2 scans) to achieve a gradual cleaning.

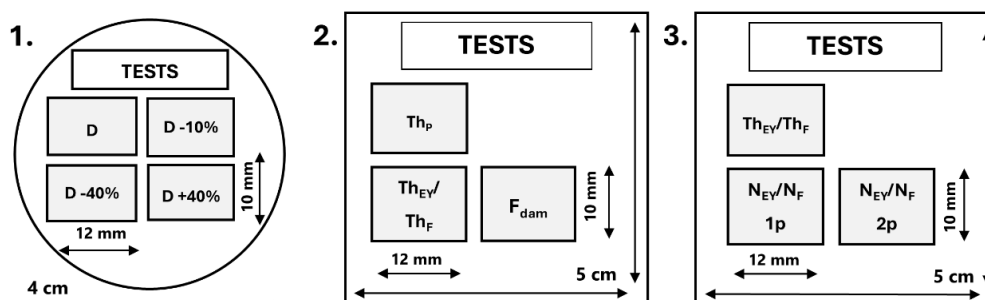


Fig 1 - Methodological approach following in the research based on the application of the laser Nd:YAG at 1064 nm. 1. Pigment tablet. 2. Painting without an undesirable substance and 3. Soiled painting.

Analytical techniques

The following techniques were applied in the samples before and after the laser irradiation:

- A stereomicroscope (SMZ800 Nikon) was used to detect physical changes (textural, structural and colorimetric features) of the samples.
- A Minolta CM-700d spectrophotometer was used to characterise the colour of each pigment tablet and each irradiated area. Measurements were taken in the CIELAB and CIELCH colour spaces. L^* represents lightness, varying from 0 (black) to 100 (white), a^* is a colour position between red (+ a^*) and green (- a^*) and b^* is a colour coordinate between yellow (+ b^*) and blue (- b^*). C_{ab}^* is the chroma or saturation and h represents the hue. Measurements were made in specular component excluded (SCE) mode, for a spot diameter of 3 mm, using a D65 illuminant and an observer angle of 10°. Five measurements were made for each area (reference and irradiated) of each sample. Taking the colour of the tablets before irradiation as reference, the ΔL^* , Δa^* , Δb^* , ΔC_{ab}^* and ΔH^* differences and the colour difference (ΔE_{ab}^*) were calculated following CIE (2007). Values of ΔE_{ab}^* were considered on the basis of the ability to see differences of an unexperienced observer (Mokrzycki & Tatol, 2011).
- Molecular changes in the paintings and soiling remain were determined by a portable Fourier-transform infrared spectroscopy (FTIR) 4300 Agilent with an Attenuated Total Reflectance (ATR) system.

Results and Discussion

The determination of the threshold fluence for the pigments in tablets allowed to establish their susceptibility at the irradiation with the laser QS Nd:YAG operating at 1064 nm. The mineralogical composition influences this interaction the most. Indeed, the more resistant materials, i.e. those to which a higher fluence (Th_p in Tab 1) was applied, were found to be silicate pigments, such as green earth, egyptian blue and ultramarine. Disregarding cinnabar, which had the worst performance, pigments consisting of oxides were found to be more sensitive: chrome green and mars red. The

pigment that reacted worst to laser was cinnabar (a sulphide), because at low fluences ($<0.11 \text{ J/cm}^2$), clear blackening was already observed. Chappé et al. (2003) reported that if a pigment shows a reaction to irradiation with an energy density below 0.04 J/cm^2 , it is defined as 'unsuitable' for laser cleaning. In the present work, however, it was possible to apply a fluence of 0.04 J/cm^2 and obtain a $\Delta E^*_{ab}=1.37$ CIELAB units (Fig 2.CI). The fluences determined were confirmed to be the damage threshold fluences (Th_p) also by means of the ΔE^*_{ab} , which was below 3.5 u. CIELAB, a threshold value according to which an inexperienced eye notices clear differences in colour (Mokrzycki & Tatol, 2011). Only for ultramarine (Fig 2.UL) the $\Delta E^*_{ab}=4.83$ u. CIELAB was higher than 3.5 u. CIELAB, because it was influenced by the L^* component, which can be associated with roughness parameters (López, et al., 2018).

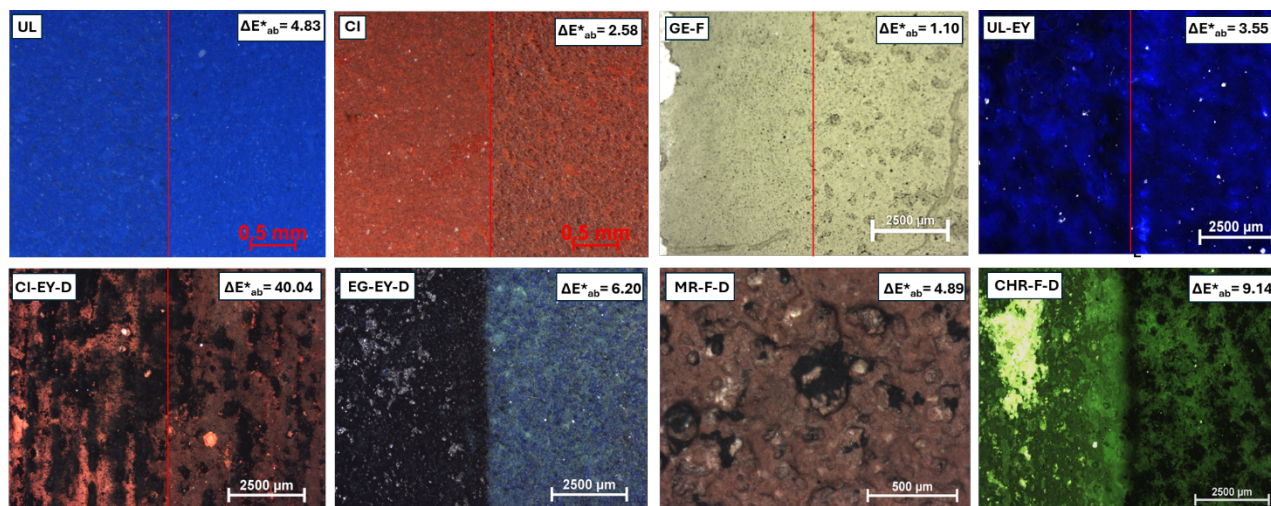


Fig 2-Micrographs of some of the samples used in this research. UL: ultramarine; CI: cinnabar; GE: green earth; EG: egyptian blue; MR: mars red; CHR: chromium oxide; EY: egg yolk; F: fresco; D: diesel soot. ΔE^*_{ab} (CIELAB units) is depicted for each treated surface.

For paintings, with most of the pigments, fluence increases, comparatively to pigment tablets, were required to reach the damage threshold (Th_F/Th_{EY} , tab 1), except for cinnabar and green earth with egg yolk. This was assigned to the protective character on the pigment by the binder, as confirmed by Schnell et al. (2006), applying a Nd:YAG laser at 1064 nm on pigment-only tablets and on paints with linseed oil, casein, gum arabic and lime. In fresco painting, through the carbonation of calcite, the pigment is incorporated into the *intonaco*. As a result of this process, the pigment's resistance seemed to be improved. The resulting calcite after carbonation had a whitish hue that caused low absorption of the laser beam due to its reflection (Cooper, 1998). This characteristic was evident in the two green pigment- and in the egyptian blue-fresco paintings (Fig 2.GE-F). Analogous process happened in tempera painting where egg yolk formed a protective film around the pigment. This protection factor occurred in the mars red and both blue pigments in tempera paints. Concerning ultramarine (Fig 2.UL-EY), tempera paint showed a $\Delta E^*_{ab}>3.5$ u. CIELAB, which could be related to binder degradation (Oujja, et al, 2010). It will be a priority of future studies to investigate this further.

In the case of improper use of the laser with fluences greater than the threshold fluence (F_{dam-F} and F_{dam-EY} ; Fig 1.2): it was possible to ascertain chromatic changes and paint extraction. Specifically, paintings with red pigments turn to black (Fig 2.MA-F-D), while those with egyptian blue with both binders and green earth in tempera painting altered to lighter colours tending to yellow according to positive values of the b^* coordinate.

FTIR allowed to confirm the extraction of the surface carbonation layer after irradiation, particularly in the green earth fresco painting (Fig 3), in which a change in the relative intensity, with a decrease of the 997 cm^{-1} band of the pigment and the increment of 870 cm^{-1} band assigned to $C=O$ of the

calcium carbonate was evident (Fig 3.1). In the tempera paintings (Fig 3.2), changes in the intensity relations occur between the decreasing of the band at 1745 cm^{-1} assigned to carbonyl functional groups of triglycerides and the increasing of the band assigned to C=O stretching from amide I (protein) at 1654 cm^{-1} , which could be due to protein denaturation at $60 - 75\text{ }^{\circ}\text{C}$ (Blume, et al., 2015).

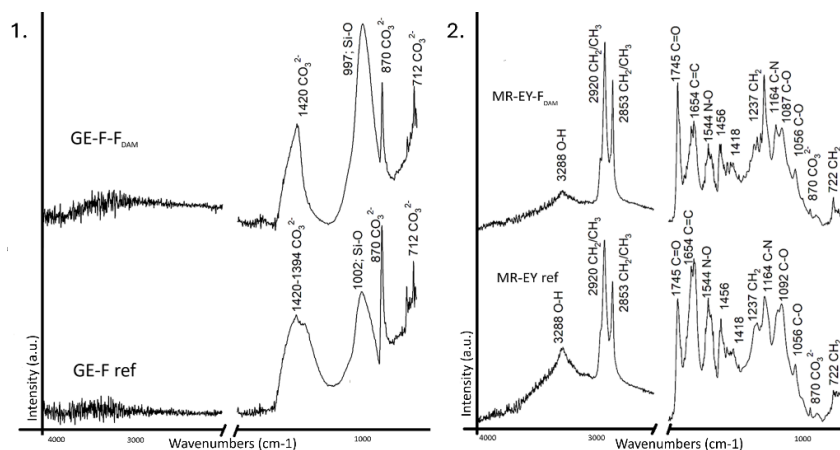


Fig 3 - FTIR spectra of some of the paintings before (ref) and after (F_{DAM}) laser irradiation. 1: green earth-based fresco paintings, 2: mars red-based egg yolk paintings.

Tab 1 - Threshold fluence (J/cm^2) of pigments (Th_P) and paintings (Th_F/Th_{EY}) with ΔE^*_{ab} (CIELAB units)

Pigments	Th_P (J/cm^2)	Th_{EY} (J/cm^2)	Th_F (J/cm^2)
Cinnabar	0.04 $\Delta E^*_{ab}=1.37$	0.04 $\Delta E^*_{ab}=4.37$	0.02 $\Delta E^*_{ab}=2.51$
Mars red	0.15 $\Delta E^*_{ab}=1.89$	0.27 $\Delta E^*_{ab}=1.20$	0.18 $\Delta E^*_{ab}=1.10$
Green earth	1.90 $\Delta E^*_{ab}=3.28$	1.36 $\Delta E^*_{ab}=2.48$	2.35 $\Delta E^*_{ab}=1.24$
Chromium green	0.31 $\Delta E^*_{ab}=1.46$	0.36 $\Delta E^*_{ab}=0.54$	0.97 $\Delta E^*_{ab}=4.31$
Egyptian blue	0.81 $\Delta E^*_{ab}=3.39$	1.94 $\Delta E^*_{ab}=1.96$	2.74 $\Delta E=2.80$
Ultramar	1.74 $\Delta E^*_{ab}=4.83$	2.61 $\Delta E^*_{ab}=3.55$	2.48 $\Delta E^*_{ab}=2.95$

The application of the threshold fluences for each painting (Th_F/Th_{EY}) to remove the soiling produced different effects which can be categorised according to two criteria: i) soiling removal and ii) paint damage.

In terms of soiling removal, for cinnabar-based paintings with both binders and mars red-based fresco, it was necessary to increase the fluence to achieve the necessary fluence for cleaning (N_F/N_{EY}). However, in the cinnabar paintings it was not possible to remove soiling, despite the fluence increase, since remains can still be identified using stereomicroscopy (Fig 2.CI-EY-D) and FTIR. In mars red-based fresco, soiling was removed superficially but remained in the cavities (Fig 2.MR-F-D).

Regarding damage, threshold fluences detected for paintings induced chromatic changes and pictorial layer extraction. With fluences between 0.3 and $2\text{ J}/\text{cm}^2$, chromatic changes and minimal extraction were visible in tempera paintings with green earth and egyptian blue and in chromium green-based fresco (Fig 2.CHR-F-D), while in tempera paintings containing chromium oxide, only minimal

ablation of the paint was visible in those areas where greater roughness was present. With fluences above 2 J/cm^2 , complete extraction of the paint layer was caused in both paintings containing artificial ultramarine and in the green earth and egyptian blue-based frescos. Considering the literature (Cooper, 1998), the extraction of the paint was the result of photothermal ablation with fluences above the threshold, which caused an explosive vaporisation favoured by the soot, i.e. a perfectly absorbent layer of contamination that promoted a sudden temperature rise, generating sufficient forces to overcome the particle's adherence to the surface. However, further studies are needed to investigate the temperatures reached.

During the cleaning, the binder seemed to exert a greater influence than the pigment mineralogy in the interaction paintings-laser. In fact, it was possible to apply higher fluences in the tempera paintings for all paintings with exception of those with chrome green and egyptian blue, which allowed higher fluences with fresco painting. The only pigment for which mineralogy continued to be of considerable importance was cinnabar, which was characterised by a strong sensitivity to laser interaction (Fig 2.CI-EY-D).

The cleaning experienced critical issues in the egyptian blue with both binders, because from the colorimetric analysis, b^* coordinate showed more positive values towards yellow tones in comparison to the reference (Fig 2.EG-EY-D). This yellowing could be due to the light scattering in a thin absorbent layer and the surface roughness as was reported by Vergès-Belmin and Dignard (2003). However, the chromatic changes because of accelerated ageing in the climate chamber cannot be dismissed. So further studies are needed. In general terms, in those samples with satisfactory levels of superficial cleaning, remains found in cavities can jeopardize the cleaning effectiveness, specifically in the mars red (Fig 2.MR-F-D) and chromium green tempera paintings. FTIR spectra revealed (Fig 4) the conspicuous removal of soiling, due to an intensity increase in the $1750\text{--}1200 \text{ cm}^{-1}$ (bands assigned to the protein binder) and a decrease at 1450 cm^{-1} (soot). The paintings in which the cleaning was considered satisfactory by stereomicroscopy and FTIR were those with ultramarine blue and green earth with both binders and the chromium green-based paintings.

The fluence required for cleaning was applied in two areas with one (1p) and two (2p) (Fig 1.3) laser scans to allow the operator to proceed gradually with the soiling removal avoiding damages. However, not for all the paintings was the two-scans square chosen. Specifically for the cinnabar-based paintings and the fresco with the red of mars, 1p squares were chosen because colour changes in the 2p squares were detected, specifically turning to darker shades, with a decrease in the L^* coordinate. It should be noted that the L^* was also influenced by the permanence of soiling on the surface. In order to be more conservative, 1p square was also chosen for the tempera paintings with the blue pigments, because the 2p square in egyptian blue tempera showed yellowing and the 2p squares in ultramarine tempera a slight discolouration, which needs further investigation.

Tab -2- Necessary fluence for cleaning (N_F and N_{EY}) compared with threshold fluence (Th_F and Th_{EY}) of the paintings. Under each fluence it is described the effect of the laser.

Pigments	Tempera (EY)		Fresco (F)	
	$Th_{EY} (\text{J/cm}^2)$	$N_{EY} (\text{J/cm}^2)$	$Th_F (\text{J/cm}^2)$	$N_F (\text{J/cm}^2)$
Cinnabar	0.4 no effects on soot or paint	0.095 1p darkening paint & soot remains	0.02 no effects on soot or paint	0.087 1p darkening paint & soot remains
Mars red	0.27 remains a lot of soot	0.27 2p some soot remains	0.19 no effects on soot or paint	0.25 1p some soot remains
Green earth	1.36 slight painting film extraction	0.6 2p no soot	2.35 painting film extraction	0.24 2p no soot

Chromium green	0.36 slight painting film extraction	0.23 2p some soot remains	0.97 painting film extraction	0.28 2p no soot
Egyptian blue	1.94 chromatic change & painting film extraction	0.44 1p no soot & slight yellowing	2.74 painting film extraction	0.8 2p no soot & slight yellowing
Ultramarine	2.61 painting film extraction	0.44 1p no soot	2.48 painting film extraction	0.3 2p no soot

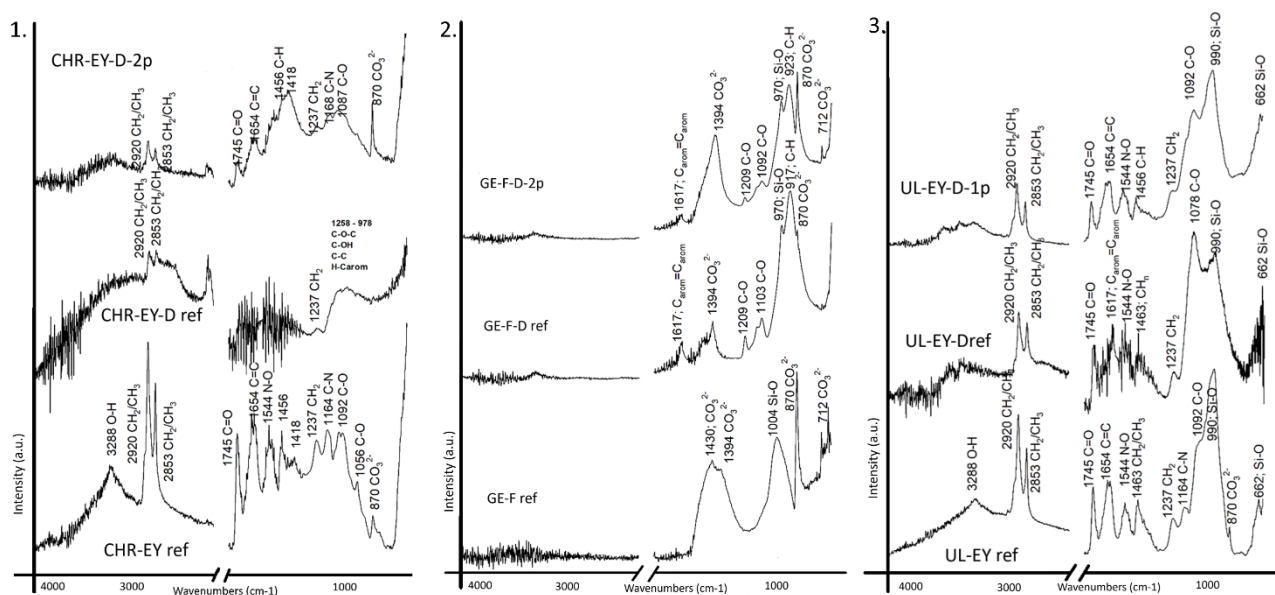


Fig 4 - FTIR spectra of some of the soiled paintings exposed to laser irradiation. 1: chromium oxide-based egg yolk paintings; 2: green earth-based fresco paintings, 3: ultramarine-based egg yolk paintings.

Conclusions

A Nd:YAG working at 1064 nm was applied to remove an artificial soling on fresco and tempera paintings with blue, green or red pigments with different composition. The damage thresholds for the pigment tablets and the paintings considering the effect of the binder (calcite or egg yolk) were determined previously to the cleaning of the soiled mock-ups. The binder does have a protective character for the pigment. Cinnabar- and mars red-based paints were most sensitive under laser radiation leading colorimetric changes with low fluences, while blue and green paints were more laser-resistant. The protective effect of the binder depends on the mineralogical composition of the pigment. In general terms, the paint damage threshold irradiation to the soiled surfaces provoked damages on the pictorial layer, so in order to clean, a decrease of the fluence was necessary achieving satisfactory cleaning.

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