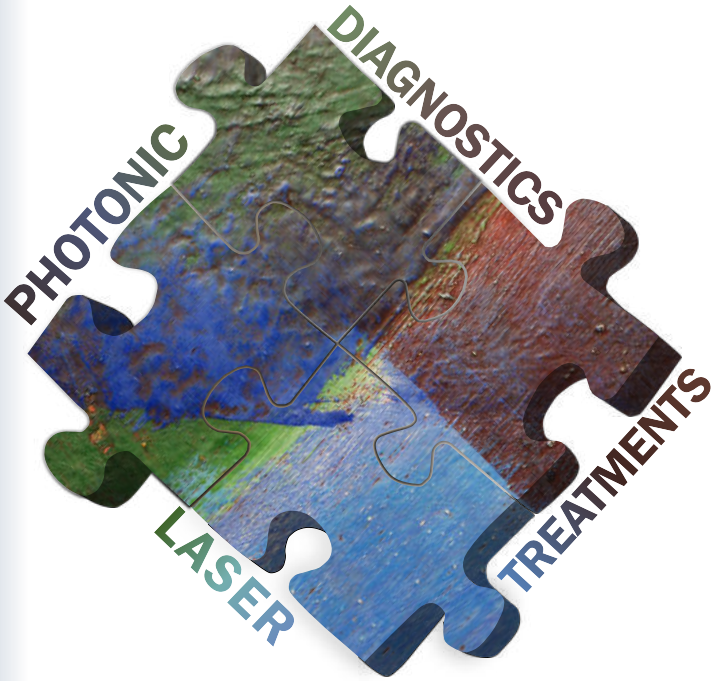
Lasers in the Conservation of Artworks

LACONA XIII

Florence - September 12-16, 2022



Abstract Book

Consiglio Nazionale delle Ricerche

LACONA XIII

13th International Conference on

Lasers in the Conservation of Artworks

Organized by

Consiglio Nazionale delle Ricerche

Istituto di Fisica Applicata "N. Carrara"

with the patronage of Tuscany Region

the collaboration of

Opificio
delle
Pietre Dure

MINISTERO
DELLA
CULTURA

and the sponsorship of

13th International Conference on Lasers in the Conservation of Artworks

Chair

Salvatore Siano

International Steering Committee

John F. Asmus	Center for Advanced Nanotechnology, Department of Physics, University of California, San Diego, La Jolla, CA, USA
Marta Castillejo	Instituto de Química Física Rocasolano, CSIC, Madrid, ES
Martin Cooper	Lynton Lasers Ltd., Holmes Chapel, Cheshire, UK
Vincent Detalle	Centre de Recherche et de Restauration des Musées de France - C2RMF, FR
Abdelrazek Elnaggar	Faculty of Archaeology, Fayoum University Al-Fayoum, EGY
Wolfgang Kautek	University of Vienna, Dep. of Physical Chemistry, Vienna, AT
Austin Nevin	Department of Conservation, Courtauld Institute of Art, London, UK
Johann Nimmrichter	Federal Office of Historical Monuments (Bundesdenkmalamt), Department for Restoration and Conservation, Vienna, AT
Vadim Parfenov	St.Petersburg State Electrotechnical University, RU
Paraskevi Pouli	Institute of Electronic Structure and Lasers – FORTH, Heraklion, EL
Roxana Rădvan	National Institute of Research and Development for Optoelectronics – INOE, Bucharest- Magurele, RO

Matija Strlič	University College London, Inst. for Sustainable Heritage London, UK
David Saunders	International Institute for Conservation, UK
Manfred Schreiner	Inst. of Science & Technology in Art Acad. of Fine Arts, Vienna, AT
Salvatore Siano	Institute of Applied Physics "Nello Carrara" - CNR, Florence, IT
Véronique Vergès-Belmin	Laboratoire de Recherche des Monuments Historiques, Champs sur Marne, FR
Kenneth Watkins	The University of Liverpool, Dep. of Mechanical Eng., Liverpool, UK
Alessandro Zanini	El.En. SpA, Calenzano, IT

International Advisory Committee

Giorgio Bonsanti	Former Professor at the University of Florence and Superintendent of the Opificio delle Pietre Dure, Florence, IT
Klaus Dickmann	Laser Center, Muenster University of Applied Sciences, DE
Costas Fotakis	Emeritus Professor of Physics at the University of Crete and Distinguished Member of the Foundation Organization for Research and Technology (FORTH), Heraklion, Crete, EL
Renzo Salimbeni	Former Research Director at CNR and Director of the Institute of Applied Physics "N. Carrara" - CNR, Florence, IT

Local Organizing Committee

Stefania Agnoletti	Opificio delle Pietre Dure, Firenze, IT
Juri Agresti	Istituto di Fisica Applicata “N. Carrara”- CNR, Sesto Fiorentino, IT

Alessia Andreotti	DCCI-Università di Pisa, Pisa, IT
Anna Brunetto	Restauri Brunetto, Vicenza, IT
Ilaria Cacciari	Istituto di Fisica Applicata “N. Carrara”-CNR, Sesto Fiorentino, IT
Daniele Ciofini	Istituto di Fisica Applicata “N. Carrara”-CNR, Sesto Fiorentino, IT
Francesco Colao	UTAPRAD-ENEA, Frascati, IT
Roberta Fantoni	UTAPRAD-ENEA, Frascati, IT
Raffaella Fontana	Istituto Nazionale di Ottica-CNR, Firenze, IT
Marco Giamello	DSFTA - Università degli Studi di Siena, Siena, IT
Stefano Legnaioli	Istituto di Chimica dei Composti Organometallici-CNR, Pisa, IT
Rachele Manganelli Del Fà	Istituto di Scienze del Patrimonio Culturale-CNR, Sesto Fiorentino, IT
Andrea Azelio Mencaglia	Istituto di Fisica Applicata “N. Carrara”-CNR, Sesto Fiorentino, IT
Austin Nevin	Department of Conservation, Courtauld Institute of Art, London, UK
Iacopo Osticioli	Istituto di Fisica Applicata “N. Carrara”-CNR, Sesto Fiorentino, IT
Silvia Rescic	Istituto di Scienze del Patrimonio Culturale-CNR, Sesto Fiorentino, IT
Cristiano Riminesi	Istituto di Scienze del Patrimonio Culturale-CNR, Sesto Fiorentino, IT
Vincenzo Palleschi	Istituto di Chimica dei Composti Organometallici-CNR, Pisa, IT
Olga De Pascale	Istituto di Nanotecnologia-CNR, Bari, IT
F. Paolo Romano	Istituto di Scienze del Patrimonio Culturale-CNR, Catania, IT

Giorgio S. Senesi	Istituto di Nanotecnologia-CNR, Bari, IT
Francesco Taccetti	Istituto Nazionale di Fisica Nucleare Sesto Fiorentino, IT
Renato Torre	Dipartimento di Fisica ed Astronomia – UNIFI, Firenze, IT
Alessandro Zanini	El.En. SpA, Calenzano, IT

Preface

Since twenty-seven years ago, LACONA "*Lasers in the Conservation of Artworks*" has gathered together researchers from natural and technological sciences, conservators, and restorers of public institutions and private enterprises for discussing about innovation in conservation of cultural heritage based on non-invasive photonic diagnostics and laser treatments. The tradition of the Conference includes the development, validation, and application of dedicated laser systems and methods for controlled material removal, as well as of analytical techniques based on multispectral and hyperspectral imaging, holography, 3D scan, Laser Induced Plasma/Breakdown Spectroscopy, Raman spectroscopy, Laser Induced Fluorescence, and other. These started to be extensively tested and used in material characterization and conservation works during the 1990s, although they were introduced in the present sector well before. Contributions on some of the mentioned analytical techniques were reported along with those on laser treatments (which were introduced fifty years ago) since LACONA I (1995).

With hindsight, we can say that LACONA has contributed to achieve two fundamental goals: 1) to establish an effective technical dialogue among research institutions, conservation centers, museums, and stakeholders of the photonic industry; 2) to take full advantage of the significant synergistic potential provided by the association of portable compositional and imaging diagnostics with conservation treatments based on laser irradiation. Rigorous validations, methodological and thematic insights, and hence innovation were and continue to be strictly dependent on the extent to which such goals are achieved through effective multidisciplinary and multiprofessional symbioses.

LACONA XIII aims at strengthening such a tradition and an important role in knowledge and conservation of tangible heritage. In particular, in line with what has happened from LACONA VI onward, the present edition includes almost balanced numbers of contributions dedicated to photonic diagnostics and laser treatments, respectively. These works, approach optimization studies, experimentation of the most advanced laser sources and sensors, validations, and several important case studies. The participation of new groups and of many young researchers and

conservators, as well as the discussion of new developments and applications are very promising towards the perspective of growing of our community, long life of the Conference, and wide spreading of the photonic approach in cultural heritage and other application fields presenting similar knowledge and laser material treatment problems.

Salvatore Siano

Invited Speakers

Photonic Diagnostics

Photonic Diagnostics of Painted Surfaces

ORAL

Advances in Imaging Diagnostics

ORAL

Laser Treatments

Laser Treatments of Metal Artefacts

ORAL

POSTER

Laser Treatments of Stone Artefacts and Similar

ORAL

POSTER

Laser Treatments of Painted Surfaces

ORAL

INVITED SPEAKERS

Lasers & Light in an Art Museum

Marco Leona

The Metropolitan Museum of Art, New York, USA

Keywords: spectroscopy, imaging, conservation, art history

"*…much interest has been expressed both here and abroad in the possibility of using ultra-violet rays as a means of determining the age and condition of works of art*": thus Joseph Breck, Assistant Director of the Metropolitan Museum of Art introduced James J. Rorimer's 1931 volume on *Ultra-Violet Rays And Their Use In The Examination Of Works Of Art* [1]. Rorimer, a Harvard trained Medievalist who later played a key role in World War II as a Monument Man and eventually became Director of the Met, had been experimenting for three years examining and photographing works of art under UV illumination, all the while corresponding with eminent scientists such as Robert Wood at Johns Hopkins and art curators throughout the United States and Europe. At a time of important collaborations between the Met and chemists in academia, Rorimer's work represents the beginning of photonics – writ large- at the Met. More remarkable however than this early date is the fact that the impetus for the use of photonics tools came from an art curator, albeit one with an extraordinarily wide-ranging curiosity.

Over the years other light-based techniques came into use at the Met, following the pace of development of diagnostic tools in art museums; among them are infrared-reflectography, fluorescence spectroscopy, and eventually Raman spectroscopy and hyperspectral imaging, accompanied by more conservation-oriented techniques such as Micro Fading Testing and Laser Cleaning.

Raman spectroscopy entered our repertory of analytical techniques in 2001, when Silvia Centeno installed the first Raman microspectrometer in a museum in the United States. Since then, Raman has been used in thousands of analyses at the Met. The technique has been used in complex interdisciplinary and multianalytical projects such as the examination and reevaluation of Veronese's *The Choice between Virtue and Vice, Wisdom and*

Correspondence: Marco.Leona@metmuseum.org

Strength, and Mars and Venus United by Love.

Surface-enhanced Raman spectroscopy is now approaching twenty years of research, development, and application in the museum lab. It has emerged as an invaluable microanalytical technique for the ultrasensitive identification of dyes and organic pigments, with several hundred case studies completed.

Circling back to Rorimer's early work, Hyperspectral Imaging is now allowing curators, conservators, and scientists to look together at the object in a new light, rendering, as Rorimer himself said "*the invisible visible*". More important, by returning compositional information in a uniquely visual nature, it permits us to share our scientific work with a broader public in a more direct way.

In recent years, applied photonics at the Met has also involved preliminary experimentations of the laser treatments, whose integration in the conservation practice of most of the museums still represents an exciting open challenge.

This talk will attempt to describe the history of development and application of photonic techniques at the Met and to outline possible future advances, with particular attention to the intersection of science and art, trying to heed Joseph Breck's admonition that none of the aids that science has placed at our disposition *"invaluable as it may be… in helping to establish identity and in recognizing fraud and repairs, is of itself endowed with intelligence. These aids supplement the discerning eye; they do not replace it*".

Acknowledgements

I am indebted to my colleagues at the Metropolitan Museum of Art for their generosity in sharing the results of their work. In particular, Elena Carrara, whose pioneering research on James Rorimer's archive informed my own thinking; Silvia Centeno, whose work in the scientific examination of paintings represents for me the best example of the dialogue between scientists, conservators, and curators; and Elena Basso, who is expanding the reach of the Met's lab to provide support to museums all over New York City under the Network Initiative for Conservation Science program. I am also indebted to the Alfred P. Sloan Foundation and to the Andrew W. Mellon Foundation for their support of the Network Initiative for Conservation Science.

References

[1] James J. Rorimer, Ultra-Violet Rays And Their Use In The Examination Of Works Of Art, The Metropolitan Museum of Art, New York, 1931.

Applied photonics vs. conservation in practice

Austin Nevin

Department of Conservation, Courtauld Institute of Art, London, UK

Keywords: technical study, wall paintings, molecular spectroscopy, easel paintings

Research forms an essential component of the work of conservators and conservation scientists. As part of conservation, analysis aims to document the composition and condition of works of art and to diagnose conservation issues. Conservation is resource intensive, and therefore we need to balance the benefits of adopting low-cost and easily accessible methods for technical imaging, with the use of *in situ* analysis and sampling. Access to increasingly sophisticated portable and laboratory instrumentation based on the use of photonics for imaging and mapping means that today we have more access to more data to inform conservation decisions, and an increasingly nuanced understanding of the complexity of paintings and their stratigraphy on the microscale.

This talk will highlight recent advances in method development for the analysis of easel paintings and wall paintings carried out at the department of Conservation at The Courtauld. Case studies involving the application of technical imaging, fluorescence lifetime imaging, laboratory and in situ methods will highlight how analysis can inform our understanding of chemical and physical changes, and ultimately influence conservation decisions. Examples will range from the analysis and treatment of wall paintings in Rajastan, to the study of 20th Century paintings on canvas. Practical aspects of conservation that rely on the development of new methods for stabilising and cleaning wall paintings, the assessment of risk, and the impact of treatment will be presented. The field of conservation faces multiple challenges related to sustainability, access to training for future generations, and the adoption of greener methods in conservation, which is part of the European Green Deal. This talk will demonstrate how photonics plays a key role in addressing some of these challenges, and advancing the field.

Correspondence: Austin.Nevin@courtauld.ac.uk

LIBS: A POWERFUL ANALYTICAL TOOL FOR THE GEOCHEMICAL DIAGNOSTICS OF STONE ARTIFACTS

Giorgio S. Senesi

CNR - Istituto per la Scienza e Tecnologia dei Plasmi (ISTP), Sede di Bari,
Bari, 70126, Italy

The geochemical fingerprinting of stone artifacts based on mineralogical, petrographical and isotopic data can provide unique information on the geological and geographical origin of materials and help to reconstruct material pathways from sources to artifacts and determine the possible nature and causes of alteration, so providing useful operational guidance for their preservation, restoration and conservation. In particular, for the preservation and restoration of historic buildings, it is essential to characterize the construction and mortar materials, determine their origin, and analyze in detail their alterations.

The improved efficiency and tremendous developments in the analytical capabilities of novel advanced non-invasive, non-destructive or micro-destructive spectroscopic and imaging diagnostic techniques occurred in the last decades have improved enormously the characterization and discrimination of materials and weathering products, so contributing substantially to improve the traditional conservation and restoration approaches with relevant innovation in cultural heritage research providing new solutions and perspectives. In the last two decades, a number of analytical techniques, including elemental and isotopic analyses, Raman, infrared and laser-induced breakdown spectroscopy (LIBS) and X-ray fluorescence (XRF), have been widely used with increasing frequency and variable success in cultural heritage research to identify the major and trace elemental and isotopic composition of stone materials and classify and discriminate them on the basis of their compositional profile of minor and/or trace elements fingerprinting. In particular, LIBS appears an ideal, fast, standoff method to measure a wide variety of elements, including those lighter than silicon (not possible by XRF), which can be employed in a variety of geometries with various distances from the target. Furthermore, the capacity of LIBS to operate in situ makes it

Correspondence: Giorgio.Senesi@istp.cnr.it

particularly attractive for the analysis of large objects, monuments and historical buildings, where the use of mobile or remote sensing instruments offers significant advantages. The four features that distinguish LIBS from traditional laboratory-based analytical techniques are: no or minimal sample preparation requirement, capacity of analyzing both 20-100 μm diameter spots and whole-rocks, providing a LIBS spectrum containing a detailed chemical signature of the sample, and availability of backpack portable and handheld instrumentations that can be used directly in situ as a diagnostic tool not only for stone identification and analysis but also for depth profiling of encrustation grown on stonework and the distribution of environmental pollutants within it. Currently, the availability of reliable analytical instrumentation that can operate directly on site, such as handheld (h) LIBS, is in high demand. The fast data acquisition and minimal sample preparation features of these devices make them very attractive candidates for qualitative and semiquantitative elemental analysis, microchemical mapping and sample selection. Finally, the above-described advantages are expected to facilitate decisions concerning the planning and implementation of restoration treatments.

In this presentation the basics of the LIBS technique for geochemical analysis will be summarized and recent results by various research groups of LIBS applications to mineral chemistry, geochronology and chemical mapping of cultural heritage stone artifacts will be discussed. In particular, the promising role and performance of hLIBS devices for the real-time, on site, routine chemical analysis of a broad spectrum of cultural heritage artifacts, which is as yet only minimally explored, will be illustrated while targeting specific questions of geological interest.

PHOTONIC DIAGNOSTICS

Photonic Diagnostics of Painted Surfaces

ORAL

Mystery of a 17c. Hebrew grammar book - back to the 11th century

P. Targowski[1], G. Żukowska[2], M. Kowalska[1], B. Wagner[3], D. Jutrzenka-Supryn[4], P. Pludra-Żuk[5], M. Opalińska[6]*

[1] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziądzka 5, 87-100 Toruń, Poland
[2] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[3] Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland
[4] Department of Conservation and Restoration of Paper and Leather, Faculty of Fine Arts, Nicolaus Copernicus University in Toruń, Sienkiewicza 30/32, 87-100 Toruń, Poland
[5] Institute for the History of Science, Polish Academy of Sciences, Nowy Świat 72, 00-330 Warsaw, Poland
[6] Institute of English Studies, Faculty of Modern Languages, University of Warsaw, Dobra 55, 00-312 Warsaw, Poland

Keywords: MAXRF, OCT, manuscripts fragments, parchment, Old English

In this contribution, we will present preliminary results of a physico-chemical examination of two parchment strips used as endleaf guards in an early print from the library of Samuel Meienreis – a noble 17th c. townsman from Elbląg (Ger. Elbing) – a city in Royal Prussia, a province of the Polish-Lithuanian Commonwealth [1]. Before his death at the age of 32, Meienreis made several journeys around Europe during which he studied and collected books. From one of his journeys, he brought a copy of a Hebrew grammar published in 1600. The volume, bound in white parchment with a supralibros, is now held at the C. Norwid Research Library in Elbląg. The first parchment strip was discovered during a project carried out for *Fragmentarium*: a multi-year international initiative established to promote research on manuscript fragments and to provide a central platform for publishing the results. [2] The strip, used as a strengthening, was attached to the front cover which has come apart. The strip turned out to be a re-used fragment of a Latin psalter with a continuous gloss in Old English. Comparative analyses enabled us to date it to the 11th century and associate it

*Correspondence: ptarg@umk.pl

with England before the Norman Conquest. In this study, we will present the results of a MAXRF and OCT examination of the front strip. The goal of this analysis was to provide data for further comparative research and to support the decision to uncover another strip concealed under the endpaper at the back of the volume. To that end, we performed the MAXRF examination through paper and compared the results to those of the front strip.

Figure 1. a: front strip, unfolded; b: Fe-Kα map of the front strip; c: back endpaper covering the back strip, folded; d: Fe-Kα map of the back strip (folded) registered through the endpaper.

Subsequently, the decision to uncover the second strip was approved by the conservation team. In this paper, we will discuss the results of this examination and present both parchment fragments. Furthermore, we will outline the evidence which supports the hypothesis concerning the common origin of both strips and their source. Additionally, we will show how the results of OCT profilometry helped us to reconstruct the details of the original manuscript preparation.

References

[1] M. Opalińska, 'A phantom psalter from late Anglo-Saxon England – a new piece of the puzzle', a conference paper presented at the Centre for Medieval Studies, University of Bristol conference From Fragment to Whole: Interpreting Medieval Manuscript Fragments on September 16, 2021

[2] Fragmentarium - Laboratory for Medieval Manuscript Fragments https://fragmentarium.ms - accessed April 18, 2022

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

A COMBINED ND DIAGNOSTIC INVESTIGATION BY DHSPI, SIRT, THZ, NMR, ON GIOTTO FRESCO

V. Tornari[1], M. Andrianakis[1], S. Duchêne[2], W. Nowik[2], D. Brissaud[2], D. Giovannacci[2], M. Küppers3, C. Rehorn[3], B. Blümich[3], G. Ricci[4], G. Artioli[4]*

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, Heraklion 711 10, Crete, Greece
[2] LRMH Laboratoire de Recherche des Monuments Historiques, 77420 Champs-sur-Marne, France
[3] Fakultät für Mathematik, Informatik, Naturwissenschaften, ITMC - Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, Germany
[4] Centro CIRCe e Dipartimento di Geoscienze, Universita` di Padova, Padova, Italia

In this paper the full potential of DHSPI, SIRT, THz and NMR combined application as innovative non-destructive diagnostic techniques for on-field examination of fresco paintings is presented in a study performed on the famous Giotto frescoes in San Antonio Cathedral of Padova, Italy. The project aimed to investigate the enigma represented by the presence of the missing Giotto fresco in the chapel house where the invisible portion of Giotto's original fresco may still be present under the Baroque plaster and need to be resurfaced.

In general, to satisfy this aim, the research project coordinated by the CIRCe Center of the University of Padua, was much wider in implementing various NDT techniques scientifically and technically supported by the instrumentation and staff of the advanced mobile laboratory (MOLAB). In the study a wide range of MOLAB techniques was adopted varied from X-ray fluorescence (p-XRF), fiber optic reflectance spectroscopy (FORS), Raman spectroscopy penetrating radar investigations (GPR) and multispectral reflectometry investigations (by CIBA and CIRCe center of UNIPD), TeraHertz (THz) imaging and spectroscopy (MOLAB-France), nuclear magnetic resonance (NMR-MOUSE by MOLAB Germany) whereas radiocarbon dating (C14) by AMS has been carried out at the (C.I.R.C.E. laboratory, University of Campania " Luigi Vanvitelli ") and microclimatic monitoring of temperature and humidity carried out in the period 2017-2018, by the CNR-ISAC staff. During the

*Correspondence: vivitor@iesl.forth.gr

analytical and diagnostic campaigns, in fact, microclimatic monitoring was also carried out for a period of over a year, as well as the specific measures of capillary humidity in the walls of the room capitulate. These data underline the urgency of a conservative intervention, and will be published separately.

In this paper the main results of techniques and the combined analysis of their data will be described. Starting from surface/ subsurface deformation provided by interferometry (DHSPI, MOLAB Greece), to heat diffusion inside the fresco layers by thermography (SIRT, MOLAB France) combined with relevant in position THZ and NMR in-depth data; aiding under a complimentary methodology to solve the enigma of hidden Giotto painting by curators and to upgrade the importance of complementarity potential of techniques' combination.

The study also highlights the evolution of on-field ND diagnosis from technologies that succeeded to provide efficient portable systems; as techniques are applied on site diagnosis is advancing by the analysis of data resulted from complementary techniques encircling a problem from different aspects till the requested answer, as has been performed on the very important historical frescoes of Giotto from which a specimen of work it is herein presented.

Modern technologies advanced to the state of portability allow combination of diagnostic data to deliver spherical approach in on-field documentation hold the key to a new era for Cultural Heritage documentation, preservation and restoration research and the maintenance strategy.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Non-destructive diagnostic investigations on the architectural layout of the Brancacci's chapel in Firenze

C. Riminesi[1], R. Manganelli Del Fà[1], S. Brizzi[1], R. Manca[1], R. Fontana[2], A. Rocco[3], M. Bertasa[2], E. Grifoni[2], A. Impallaria[2], G. Leucci[1], L. De Giorgi[1], I. Ferrari[1], F. Giuri[1], S. Penoni[4], A. Felici[5]*

[1] National Research Council of Italy, Institute of Heritage Science (CNR-ISPC), Via Cardinale Guglielmo Sanfelice 8, 80134 Napoli, Italy
[2] National Research Council of Italy, National Institute of Optics (CNR-INO), Largo Fermi 6, 50125 Firenze, Italy
[3] Institute of Applied Physics "Nello Carrara", National Research Council of Italy (IFAC-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy
[4] Opificio delle Pietre Dure, Conservation Laboratories, Viale F. Strozzi 1 (Fortezza da Basso), 50129 Firenze, Italy
[5] Soprintendenza Archeologia Belle Arti e Paesaggio per la città metropolitana di Firenze e le province di Pistoia e Prato Piazza de' Pitti, 1 - 50125 Firenze, Italy

Keywords: Photogrammetry, IR Thermography, DHSPI, millimeter reflectometry, georadar, knocking test

The Brancacci chapel, located in the Basilica of Santa Maria del Carmine in Firenze, hosts the Renaissance wall paintings by Masaccio, Masolino and Filippino Lippi. Complementary non-destructive investigations were undertaken to investigate the stratigraphy and the sequence of interventions over the centuries. Some conservation problems needed to be assessed, such as the detachments between mortar and masonry and between painted layer and mortar, in addition to defects, e.g., out of plumb or swelling elements [1]. The strategy adopted for the diagnostic campaign was to survey from large to small scale, and with increasing measurement resolution. The photogrammetric relief (Structure from Motion technique) of the wall paintings for sizing of the out of plumb or swelling elements was first applied. Investigations were then carried on by scanning in depth the masonry: starting from the surface with knocking test and IR thermography, Digital Holographic Speckle Pattern Interferometry (DHSPI), millimeter reflectometry in the microwave and THz range, and georadar investigation were applied to inspect all the thickness of the masonry (60-70 cm) with a resolution from a few microns up to 1 cm. The results of this

*Correspondence: cristiano.riminesi@cnr.it

interdisciplinary and multi-analytical work allowed to deeply analyze the state of conservation of both the wall paintings and the support, and formulate some hypotheses regarding restoration interventions aimed at preserving their integrity.

Acknowledgements

The authors wish to thank Opera per Santa Maria del Carmine in Firenze and the Municipality of Firenze in particular all the staff of the 'Servizio Belle Arti e Fabbrica di palazzo Vecchio' (Resp. Archt. G. Caselli) for valuable and constant support during the organization and execution of the whole diagnostic campaign.

References

[1] C. Rocca, P. Rossin (1991) L'impianto architettonico della cappella Brancacci in Santa Maria del Carmine a Firenze. Rilievo e analisi, Mori Editore Aulla

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Detection of low contrast paintings by post-processing data collected with three laser stimuli elastic channels

M. Francucci[1], M.Guarneri[1], M. Ciaffi[1], R. Fantoni[1], R. Carmagnola[2], G. Adinolfi[2]*

[1] ENEA FSN-TECFIS-DIM, Via E. Fermi 45, 00044 Frascati (RM), Italy
[2] Association Amici delle Tombe Dipinte di Tarquinia, 01016 Tarquinia (VT), 89.4 km, Italy

Keywords: laser scanner, digitalization, image processing, painting, etruscan tombs

One of the major problems affecting the conservation of painted surfaces is the different durability of the pigments related to the environmental conditions, anthropic impact and material aging. The archaeological area of Tarquinia hosts thousands painted Etruscan tombs with different states of conservation. The iconography reveals scenes of everyday life in combination with mythological and religious believes. More specifically, some of the frescoes contain relevant information about the history of the families who populated the tomb itself. However, in several cases the conservation of frescoes is quite poor presenting vanished figures, walls ruined by humidity and degrading agents through the ages or by anthropic inappropriate interventions. ENEA, within the former Regional project COBRA, organized in 2016 a data acquisition campaign addressed to demonstrate the role of innovative laser technologies in the investigation of Etruscan tombs, selecting some important tombs among the least accessible ones, in Tarquinia necropolis. The investigation, based on different laser scanning imaging techniques, concerned mainly their state of health, their allegories with the intent to present an analytical work which could be used for scientific and educational purposes, and the possibility of digital model fruition [1]. In particular, the so called “Tomba della Querciola” was investigated with the mentioned purposes by using the ENEA RGB-ITR prototype of laser scanner with capabilities of native color rendering. This tomb, at the time closed to the public, is a 5x5x3 m^3 room, with a scarce artificial illumination at the entrance and presents paintings

*Correspondence: massimo.francucci@enea.it

on all the four lateral walls. By the use of our three stimuli laser scanner the complete 3D digitalization of the entire room, collecting both colorimetric and structural information, was achieved. In particular, the single high-detailed point-to-point acquisition of the three elastic channels processed with different image-processing techniques, and suitably developed filtering algorithms, permitted to improve the readability of partially lost images. An example is shown in Figure 1, where the filter applied stresses the image profile in a case of partially lost pigmentation. With the support of the archaeological experts, several represented allegories were studied, especially focusing the efforts on the vanished images populating the lower part of the walls.

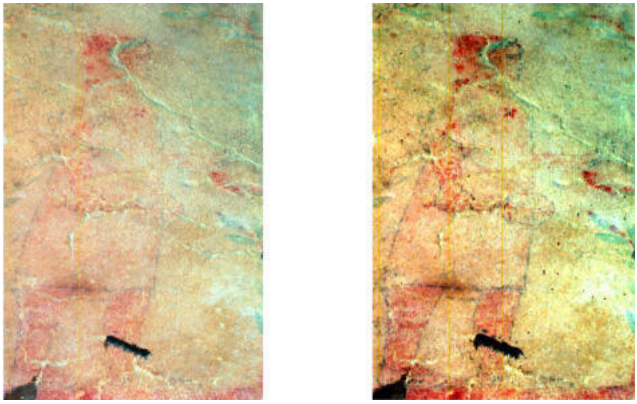


Figure 1 Images of a vanishing detail on a wall of Tomba di Querciola. Left: RGB-ITR image as acquired. Right: post-processed RGB-ITR image with enhanced profile.

Acknowledgements

The financial support of this work has been provided by COBRA Project, Latium Region l.ge 13/2008. The support from Soprintendenza per i Beni Archeologici dell'Etruria Meridionale, is gratefully acknowledged.

References

[1] S. Ceccarelli, M. Guarneri, M. Romani, L. Giacopini, M. Francucci, M. Ciaffi, M. Ferri De Collibus, A. Puiu, G. Verona-Rinati, F. Colao, R. Fantoni, Are the blue daemons really blue? Multidisciplinary study for the colours characterization of the mural paintings inside the Blue Daemons Etruscan tomb, Journal of Cultural Heritage, 47, 2021, 257-264.

Non-destructive methods of analysis applied to the study of Oscar Pereira da Silva paintings

*J. Schenatto**, *M. A. Rizzutto*

University of São Paulo, Nuclear Physics Department, Physics Institute, São Paulo (SP), Brazil

Keywords: Portable equipment, ED-XRF, Raman, Infrared Reflectography, Painting, Oscar Pereira da Silva

The application of analytical techniques, such as Raman spectroscopy, Energy Dispersive X-Ray Fluorescence (ED-XRF) and Infrared Reflectography (IRR) has become increasingly used to study the chemical and physical properties of an object. Also thank to their portability and non-destructiveness, these analytical approaches are very useful for the study of cultural heritage objects. The application of the spectroscopic methods (Raman and ED-XRF) to the study of easel paintings can allow achieving the chemical composition of the pictorial and underlying layers, identify the pigments used in the production of the artwork. Furthermore, the mentioned imaging method (IRR) can reveal drafts, underdrawings and changes made by an artist. The results found through these techniques are important to understand an artist's creation process, and can assist with deciding on appropriate conservation and restoration treatments [1-3].

The objective of the present work was to characterize easel paintings by the Brazilian artist Oscar Pereira da Silva (1867-1939) that belong to the Paulista Museum collection from University of São Paulo, in São Paulo, Brazil. To this goal, the application of the mentioned portable and non-invasive imaging and spectroscopic techniques was proposed. Here, we will present the results obtained in the analysis of the paintings "Fundação de São Paulo" (1907), "Sessão das cortes de Lisboa" (1922), and "O príncipe D. Pedro e Jorge de Avilez a bordo da fragata União" (1922). Oscar Pereira da Silva is known for having painted numerous portraits of famous public figures and several historical settings, with a remarkable creation of nature scenario and an academic style of painting. During the late 19th and early 20th century, the artist helped to

**Correspondence: schenatto@usp.br*

create a narrative about important events to the republic's formation producing various paintings on the subject, including those studied in this work.

The IRR method made it possible to confirm the artist used to execute the preparatory drawing with graphite, as well as that the habit of squaring the canvas to create the scene with correct proportion, since these details were observed also in a previous research. [3] The IRR images also showed the presence of pentimenti in the three paintings and, in "Fundação de São Paulo", an underlying draft was revealed, showing a very similar scene to the one presented in the final work, but with a greater proportion.

In all the objects of study, the pallet determined by Raman and ED-XRF showed iron-based pigments, vermilion, and a variety of white pigments composed of zinc and/or barium, calcium, and lead. In addition, traces of strontium, cadmium, arsenic and copper were identified only in the painting "Fundação de São Paulo". In particular, the present investigation allowed to confirm the use of strontium yellow, azurite blue, and Scheele's green, in agreement with the results of a previous study [3], as well as to reveal other features of the artist's creative process that will be presented and discussed in some details.

Acknowledgements

The financial support of this work has been provided by CNPq (National Council for Scientific and Technological Development). We would like also to thank the collaborators from Paulista Museum for allowing the analytical studies of this artworks.

References

[1] CR Appoloni, F Lopes, and MA Bruno, "Analysis of the painting "Moema" by PXRF, TXRF and Raman Spectroscopy" In Karen Barbosa, "Moema – restauração/restoration", p. 59-78, Comunique Editorial, São Paulo, 2013

[2] C Calza, MJ Anjos, A Pedreira, and RT Lopes, "Analysis of the painting "The first mass in Brazil" (Victor Meirelles) using a portable XRF system", International Nuclear Atlantic Conference – INAC, Associação Brasileira de Energia Nuclear – ABEN, 2007

[3] PHOV Campos, EAM Kajiya, MA Rizzutto, AC Neiva, HPF Pinto, and PAD Almeida, "X-ray fluorescence and imaging analyses of paintings by the Brazilian artist Oscar Pereira da Silva", Radiation Phys. and Chem., 95, 2014

HYPERSPECTRAL IMAGING LEAFS THROUGH THE PICASSO BLUE PERIOD: THE CASE-STUDY COPA BLAVA (BLUE GLASS)

C. Cucci[1], M. Picollo[1], L. Stefani[1], R. Jiménez[2]*

[1] Institute of Applied Physics "N. Carrara", National Research Council (IFAC- CNR), Florence, Italy
[2] Museu Picasso, Barcelona, Spain

KEYWORDS: Hyperspectral imaging, paintings, diagnostics, conservation, Picasso

Following an extraordinary technological maturation, in the last decade Reflectance Hyperspectral Imaging (HSI) has become well established in the field of cultural heritage, and fully available for a variety of applications on artworks, and historical objects [1,2]. As for paintings, HSI technique implemented in the spectral regions from the Visible and Near-IR (VNIR) up to the Short Wave IR (SWIR) ranges, is acknowledged as one of the most effective non-invasive techniques for attaining extensive analysis and documentation of the painted surface and underneath layers. By associating a reflectance spectrum to every pixel of the imaged area, the HSI data-set embeds a huge, though redundant, information. Through algorithms of data-compression, multivariate analysis, and, more recently, methods borrowed from big-data processing domain (DL and ML), HSI data-cubes are processed to provide multiple answers to several conservation issues [3]. Indeed, HSI data are used not only for identification and mapping of pigments, but also for documenting with high-quality images the conservation status. The advantages of HSI are even strengthened by the combination with other non-invasive techniques, like MA-XRF. These potentialities, along with the availability of high-performance mobile instrumentations, have recently initiated a new trend towards a more systematic use of reflectance Hyperspectral Imaging (HSI) in most important museums. Indeed, HSI is often included in multi-analytical protocols to non-invasively analyze masterpieces, a corpus of paintings, an artistic period, etc. [4]. A highly representative example of this novel tendency is the interdisciplinary research project undertaken at the Museu Picasso in Barcellona, whose outcomes are currently shown

**Correspondence: c.cucci@ifac.cnr.it*

in the exhibition “Picasso Blue Project”. This ambitious project aims at re-exploring the Blue Period paintings of the permanent collection under the new light brought by the results of cutting-edge technologies. High attention is paid also to the dissemination of results to a vast public, highlighting the incredible additional value provided by imaging techniques applied to the study of paintings. The present contribution is framed in this wider context and focuses on the analysis of the painting “The Blue Glass” (Copa Blava, 1903). Among other complementary techniques, HSI has been applied for upgrading the earlier documentation on this painting, on which previous RX radiography had revealed the existence of another Picasso creation under the surface. Thus HSI analysis was carried out to provide new high resolution spectral images, which enabled visualization of new hidden details, leafing through the painting from the visible surface up to the inner layers. Also, the study of pigments and their distribution on the surface provided new clues on the Picasso creative process. Starting from the original results obtained on this case-study, the paper will illustrate the general issues faced in the interdisciplinary research of the Blue Project.

References

[1] Cucci, C., Delaney, J. K., Picollo, M., Reflectance Hyperspectral Imaging for Investigation of Works of Art: Old Master Paintings and Illuminated Manuscripts, Acc. Chem. Res., 49 (10), 2016

[2] Cucci, C., Casini, A Hyperspectral imaging for artworks investigation. In: J. M. Amigo (Ed.), Data Handling in Science and Technology (Vol. 32, pp. 583-604). Elsevier, 2020.

[3] C. Cucci, A. Barucci, L. Stefani, et al. . Reflectance hyperspectral data processing on a set of Picasso paintings: which algorithm provides what? A comparative analysis of multivariate, statistical and artificial intelligence methods. Proc. SPIE Optics for Arts, Architecture, and Archaeology VIII. 11784 (2021) 1178404.

[4]. F. Albertin, C. Ruberto, C. Cucci et al. “Ecce Homo” by Antonello da Messina, from non-invasive investigations to data fusion and dissemination. Scientific Reports. 11, 2021

Novel integration of non-invasive imaging techniques for the analysis of an egg tempera painting by Pietro Lorenzetti

A. Dal Fovo[1], S. Mattana[1], C. Ruberto[2,3], L. Castelli[2], R. Cicchi[1], R. Fontana[1]*

[1] Consiglio Nazionale delle Ricerche-Istituto Nazionale di Ottica (CNR-INO), Largo E. Fermi 6, 50125 Firenze, Italy
[2] Istituto Nazionale di Fisica Nucleare (INFN) , Via Bruno Rossi, 1, 50019 Sesto Fiorentino, Italy
[3] Dipartimento di fisica e astronomia, Università degli studi di Firenze, Via Sansone, 1, 50019 Sesto Fiorentino, Italy

Keywords: pigments, FLIM, OCT, MA-XRF, multispectral reflectography

The artistic production of Pietro Lorenzetti, a well-known 14th-century Sienese painter, takes its cues from the masters Duccio da Boninsegna and Giotto and is characterized by an innovative sensitivity to everyday details. The scarce and controversial historical information on the artist's life, as well as the still limited availability of scientific data on the pictorial materials used, has conditioned the critical evaluation of his paintings and the study of the artistic technique.

In this work, we analysed one of the stories of the Altarpiece of the Blessed Humility (Florence, Uffizi Gallery), which takes up the archaic typology of the frontal representation of the Saint in the centre, with the story of his life narrated in small compartments on the sides. This panel painting, currently under restoration at the Opificio delle Pietre Dure, was studied with a non-invasive multi-analytical approach for the compositional and stratigraphic characterization of the pictorial layers using complementary optical imaging techniques, namely VIS-NIR multispectral reflectography [1], XRF mapping [2], and optical coherence tomography [3]. Additionally, here for the first time, a novel portable fibre-based fluorescence lifetime (FL) imaging system was used to discriminate luminescent organic and inorganic pigments based on their different emission lifetimes [4,5]. Innovative data post-processing and integration made it possible to identify the pictorial materials used by

*Correspondence: alice.dalfovo@ino.cnr.it

the artist, to investigate the stratigraphic structure of the internal layers, and to detect retouches dating back to a nineteenth-century restoration not distinguishable to the naked eye.

This study, while confirming the effectiveness of a non-invasive multi-analytical approach and highlighting the potential of the new FL prototype, is a representative example of a fruitful collaboration between the various professionals involved in the study and conservation of works of art.

Acknowledgements

The financial support of this work has been provided by Consiglio Nazionale delle Ricerche (CNR) [Intervention program "CNR4C"] and the Regione Toscana [POR FSE 2014-2020 - Axis A Employment, "GiovaniSì"] as part of the projects SuperTec3D.

Conservators Patrizia Riitano and Sandra Ramat, Dr. Cecilia Frosinini and Dr. Sandra Rossi from Opifico delle Petre Dure are gratefully acknowledged.

References

[1] Striova, J., Dal Fovo, A., & Fontana, R. (2020). Reflectance imaging spectroscopy in heritage science. La Rivista del Nuovo Cimento 43(10), 515-566.

[2] Taccetti, F., Castelli, L., Czelusniak, C., Gelli, N., Mazzinghi, A., Palla, L., ... & Giuntini, L. (2019). A multipurpose X-ray fluorescence scanner developed for in situ analysis. Rendiconti Lincei. Scienze Fisiche e Naturali 30(2), 307-322.

[3] Targowski, P., Iwanicka, M., Sylwestrzak, M., Frosinini, C., Striova, J., & Fontana, R. (2018). Using optical coherence tomography to reveal the hidden history of the Landsdowne Virgin of the Yarnwinder by Leonardo da Vinci and Studio. Angewandte Chemie International Edition, 57(25), 7396-7400.

[4] Dal Fovo, A., Mattana, S., Chaban, A., Quintero Balbas, D., Lagarto, J. L., Striova, J., ... & Fontana, R. (2021). Fluorescence Lifetime Phasor Analysis and Raman Spectroscopy of Pigmented Organic Binders and Coatings Used in Artworks. Applied Sciences, 12(1), 179.

[5] Mattana, S., Dal Fovo, A., Lagarto, J. L., Bossuto, M. C., Shcheslavskiy, V., Fontana, R., & Cicchi, R. (2022). Automated Phasor Segmentation of Fluorescence Lifetime Imaging Data for Discriminating Pigments and Binders Used in Artworks. Molecules 27(5), 1475.

Photonic Diagnostics of Painted Surfaces

POSTER

THE SECRETS OF OLD MASTERS: INVESTIGATING THE PIGMENT MIXTURES AND LAYERING TECHNIQUES IN TWO PAINTINGS BY LUCAS CRANACH THE ELDER AND HIS WORKSHOP

*I.M. Cortea**, *L.C. Ratoiu*, *R. Rădvan*

National Institute of Research and Development for Optoelectronics - INOE 2000, Magurele, Romania

KEYWORDS: painting technique, Lucas Cranach the Elder, hyperspectral imaging, spectroscopy, pigment mapping

Lucas Cranach the Elder (1471-1553) was one of the most important artist of the 16th century German art world, best known for his portraits of German royalty, biblical scenes and mythological subjects. A prolific artist with over 1000 surviving artworks, Cranach headed a large workshop that included among the numerous apprentices, his sons - Hans, and Lucas the Younger. Cranach's continual search for the most efficient techniques enabled the development of a rapid style that facilitated the workshop production. Starting with the mid 1520s hundreds of artworks were produced in Cranach's workshop with many works existing in different variations. After his death, paintings in "Cranach style" and versions of his works were still produced by his studio, giving rise to many problems of attribution [1-3].

In this paper results of an *in situ* technical study carried on two paintings on wood panel assigned to Lucas Cranach the Elder and his workshop are refined and discussed. Preliminary results of a complementary diagnostic investigation were previously presented elsewhere [4]. The two paintings, *Madonna and Child* and *The Beheading of St John the Baptist*, part of the collection of European paintings within the National Museum of Art of Romania, are representative religious themes for Cranach's oeuvre. Both works have undergone several restoration interventions along the years, both at the level of the paint layer and at the level of the wooden support, but only the recent interventions, after the 1950s, are well documented.

Based on the preliminary information obtained via combined handheld X-ray fluorescence (XRF), Fourier transform infrared

*Correspondence: ioana.cortea@inoe.ro

spectroscopy (FTIR), and hyperspectral imaging (HSI), in this paper we aimed to gain further understanding into Cranach's pictorial style by combining HSI mapping techniques with spectroscopic spot analysis. Details regarding the pigment mixtures and layering techniques used by this renowned 16th century master were investigated with various spectral mapping methods that allowed an unprecedented analysis of the artworks. The SWIR hyperspectral data cubes were processed using algorithms such as SAM (Spectral Angle Mapper) or LSU (linear spectral unmixing) with the aim to obtain relevant spatial distribution of the endmembers/pigments on the surface of the painting. HSI mapping has been combined with XRF spot analysis to reconstruct the palette employed and answer specific questions regarding the techniques and materials used in specific areas of the paintings. Despite their complexity, changes in composition were found to be rare within the investigated artworks, revealing a masterful technique that supports Cranach's reputation as a "quick painter".

Reported results show the potential and limits of selected analytical methodology for an in depth characterization of the painting materials and techniques. The proposed methodology highlights the importance of data treatment and presents how classification and spectral unmixing approaches can help in obtaining more relevant interpretation of data. Obtained results contributes to the existing literature about Cranach's pictorial technique, and offer new insights and greater understanding on the artist' working methods and on his workshop practice. Not least, we believe that the findings are of great interest to art historians, conservators and restorers, by offering key information for the restoration procedure and long term conservation strategy of these valuable artworks.

ACKNOWLEDGEMENTS

The financial support of this work has been provided by the Romanian Ministry of Research, Innovation and Digitization under contract no. 18PFE/30.12.2021 and by UEFISCDI under grant no. PN-III-P1-1.1-PD-2019-1099.

References

[1] Heydenreich, G. Artistic exchange and experimental variation: studies in the workshop practice of Lucas Cranach the Elder, Studies in Conservation, 43, 1998, pp. 106-111.

[2] Frank, K. Reconsidering Cranach: Digital Approaches to the Cranach Œuvre, Visual Resources, 31, 2015, pp. 211-215.

[3] Cranach Digital Archive - The research resource. https://lucascranach.org

[4] Cortea, I.M., Ratoiu, L., Chelmuș, A., Rădvan, R., Sfrijan, I. An integrated non-destructive approach for exploring the color palette and painting techniques of Lucas Cranach the Elder. Book of Abstracts - Colloquium Spectroscopicum Internationale XLI & I Latin American Meeting on LIBS, Exhibition and Congress Centre, National and Autonomous University of Mexico, June 9-14 2019, Mexico City, pp. 185.

THE CONTRIBUTION OF SCANNING XRF TO THE INVESTIGATION OF EASEL PAINTINGS: EXAMPLES OF APPLICATIONS FROM THE COURTAULD GALLERY

S.R. Amato, A. Nevin, A. Burnstock*

Conservation Department, The Courtauld Institute of Art, Somerset House, Strand, London, WC2R 0RN, United Kingdom

KEYWORDS: scanning XRF, conservation, easel paintings, Courtauld

In recent years, a range of spatially resolved imaging techniques to examine paintings has become integrated into the arsenal of analytical methods used in many museum laboratories worldwide. An example is scanning XRF, a non-invasive method that provides distribution maps of a wide range of elements in materials used for paintings.

Scanning XRF has recently been used together with conventional methods for technical study to investigate paintings from the Courtauld Gallery, including *Christ and the Woman taken in Adultery*, dated to 1565, one of the three surviving *grisaille* paintings by Pieter Bruegel the Elder, a large-scale *Portrait of Don Francisco de Saveedra*, painted by Francisco de Goya in 1798, and *Le Déjeuner sur l'herbe* by Édouard Manet, a smaller an undated version of the large work of the same title painted by the artist in 1863 and on display at the Musée d'Orsay in Paris.

While the results from the technical exanimation of these paintings have recently been published [1-4], this poster will focus on the contribution of scanning XRF to these studies, providing an opportunity to evaluate the advantages and limitations of this imaging method applied to the study of the selected works.

The results will inform future research into the material composition and the development of compositions of other paintings by Bruegel, Goya and Manet, and by other artists who used similar materials and techniques.

REFERENCES

[1] Burnstock, A., Serres, K., Pieter Bruegel the Elder's Grisaille Paintings, The Hand of the Master. Materials and Techniques of Pieter Bruegel the

*Correspondence: silviarita.amato@courtauld.ac.uk

Elder. Oberthaler, E., Hoppe-Haranoncourt, A., Penot, S., Spronk, R. & Sellink, M. (eds.), Kunsthistorisches Museum Publications in collaboration with Hannibal Publishing, 2019, pp. 82-95.

[2] Burnstock, A., Cross, M., Serres, K., Insoluble Surface Spots, Metal Soaps and Challenges in the Conservation of Goya's Portrait of Francisco de Saavedra, ICOM-CC 18th Triennal Conference Preprints, Copenhagen, 4-8 September 2017, Bridgland, J. (ed), 2017, 1-7.

[3] Amato, S.R., Burnstock, A., Cross, M. et al. Authors, Interpreting techincal evidence from spectral imaging of paintings by Édouard Manet in the Courtauld Gallery, X-Ray Spectrometry, 2018, pp. 1-11.

[4] Amato, S.R., Cross, M., Burnstock, A., et al., Examining Édouard Manet's Le Déjeuner sur l'herbe from the Courtauld Gallery using spectral imaging techinques, 'Tales of the Unexpected': In Paintings Conservation, Kempski, M., Kirby, J., Leanse, V. & Mandy, K. (eds.), London: Archetype Publications, 2020, pp. 98-110.

Response of different wood with multiple thicknesses under thermal excitation by Digital Holographic Speckle Pattern Interferometry (DHSPI) examination

J. Auber-Le Saux[1,2], V. Detalle[1,3], M. Andrianakis[4], X. Bai[1,5], S. Richiero[1,2], N. Wilkie-Chancellier[2], and V. Tornari[4]*

[1] C2RMF, Centre de recherche et de Restauration des Musées de France, 14 Quai François Mitterrand, 75001 Paris, France
[2] SATIE, Systèmes et Applications des Technologies de l'Information et de l'Energie, CY Cergy-Paris Université, CNRS UMR 8029, 5 mail Gay Lussac, 95031 Neuville sur Oise, France
[3] PSL Research University, Institut de Recherche Chimie Paris, Chimie ParisTech, CNRS UMR 8247, 75005 Paris, France
[4] FORTH, Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas (IESL-FORTH), N. Plastira 100, Heraklion 71110, GREECE
[5] Centre National de la Recherche Scientifique (CNRS), Federation de recherche NewAGLAE FR3506, Paris,France

Keywords: heritage science, speckle pattern interferometry, deformation map, preventive conservation, panel painting

Museum curators are developing preventive strategies to control their collection environment (temperature, relative humidity, luminosity, etc.) with aim of better preserving their artworks. The environment control does not include for now any direct material monitoring to follow mechanical modifications or chemical reactions happening with environmental fluctuations. To address this failure, we use a technique based on speckle interferometry: Digital Holographic Speckle Pattern Interferometry (DHSPI) [1-4], which is a non-destructive, contactless, and full-field technique, allows taking images of the surface to detect possible deformation below the micrometre level. This technique could be particularly adapted to control wood panel paintings that represent one of the major parts of cultural heritage artworks. This system of interferometry works like the first step, the reference arm is moved to obtain the images of the painting surface of different phases of interference at the same time to increase the signal-to-noise ratio. Then, we process the images automatically to obtain deformation maps that give the surface movement information and eventually improve the accuracy of the maps.

*Correspondence: vincent.detalle@culture.gouv.fr

In this work, we focus on an instrument designed particularly to monitor wooden panels. But beyond monitoring, as described before, every single slightly change can be detected by the DHSPI, so our purpose is to use this mobile instrument in the museums to help the curators diagnose their panels and alert them before the possible damages happen. To that aim, we used the DHSPI system to measure the deformations response of different wooden samples to detect the defaults that may induce damage with further variations of temperature, humidity, etc. Our experiments were realised by using multiple thermal excitation processes in a controlled environment without any humidity variation. From the experimental results, and the calculated samples' deformation, we deduced a difference between wooden species response and for a given wooden species a response variating with the sample thickness. These results can build eventually a database to know the preserving states of wooden panel paintings and help the curators to adapt the panels' environment with more accurate control. It can also help conservators by giving some defaults, their coordinates and their evolution.

Acknowledgements

This work was supported by the Ecole Universitaire de recherche PSGS HCH Humanities, Creation, Heritage, Investissement d'Avenir ANR-17-EURE-0021 - Fondation des sciences du patrimoine.

References

[1] Tornari, V.; Bernikola, E.; Nevin, A.; Kouloumpi, E.; Doulgeridis, M.; Fotakis, C. Fully-Non-Contact Masking-Based Holography Inspection on Dimensionally Responsive Artwork Materials. Sensors 2008, 8, 8401-8422.

[2] Tornari, V.; Bernikola, E.; Tsigarida, N.; Andrianakis, M.; Hatzigiannakis, K.; Leissner, J. Preventive deformation measurements on cultural heritage materials based on non-contact surface response of model samples. Studies in Conservation 2015, 60, S143-S158, doi:10.1179/0039363015Z.000000000219.

[3] Tornari, V.; Andrianakis, M.; Hatzigiannakis, K.; Kosma, K.; Detalle, V.; Bourguignon, E.; Giovannacci, D.; Brissaud, D. Complimentarity of digital holographic speckle pattern interferometry and simulated infrared thermography for Cultural Heritage structural diagnostic research. Int. J. Eng. Res. Sci IJOER 2016, 2.

[4] Tornari, V. On development of portable digital holographic speckle pattern interferometry system for remote-access monitoring and documentation in art conservation. Strain 2019, 55, e12288, doi:10.1111/str.12288.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Peter Paul Rubens's Death of Hippolytus (1610-12) at the Courtauld Gallery London: How XRF Mapping Shed New Light on Old Questions

K. Stonor[1], C. Richardson[2], S. R. Amato[2], A. Nevin[2], A. Burnstock[2]*

[1] Tager Stonor Richardson, UK
[2] Conservation Department, The Courtauld Institute of Art, Somerset House, Strand, London, WC2R 0RN, United Kingdom

Keywords: scanning XRF, conservation, easel paintings, Courtauld, Rubens

A traditional technical analysis of the *Death of Hippolytus* by Peter Paul Rubens was undertaken by Richardson and Stonor as part of a study of early works by the artist in the Courtauld Gallery's Collection in 2011 [1]. The heavily discoloured varnish and conservation history made the thinly painted work hard to sample and difficult to interpret with surface microscopy, and key art historical questions of the function of the work within Rubens' studio practice, intimately connected to its condition and conservation history, could not be adequately answered. Through dendrochronology and the identification of key pigments, it was possible to confirm that the painting likely dated from Rubens's lifetime, but it remained a tantalizing puzzle.

The painting has been the subject of much debate amongst Rubens scholars, enjoying a good reputation in the late 19th century when Rooses compared it favorably to the well-preserved version on copper now in the Fitzwilliam Museum [2]. At that time the work was in the collection of Abraham Hume and was sold by his descendants in 1923 to a private collection in Berlin. It entered the collection of Count Seilern and is recorded in his catalogue in 1955.

Seilern describes the 20th century restoration of the picture by Isepp, which successfully removed late 18th or early 19th century overpaint [3]. The appearance of the painting prior to restoration is recorded by Cosway in her engraving [4]. After the restoration, Seilern proposed that the painting should be regarded as a *modello* rather than a finished work. Held expressed doubts that the painting belonged in his catalogue raisonné of oil sketches, believing the 'sketchy' appearance was possibly 'due more to its condition than

*Correspondence: Clare.Richardson@courtauld.ac.uk

Rubens intention' [5]. Recently, Gifford has reappraised the work as part of her study of *The Fall of Phaeton* and sees it as sitting comfortably in a chronology of iconography explored by Rubens after his return to Antwerp from Italy (1609-12)[6].

With the advent of scanning XRF, distribution maps of a wide range of elements could be identified non-invasively. The results gave new insights into the creation of the work, as well as a better understanding of its condition, allowing a more informed investigation of the art historical questions around the status of the picture.

References

[1] This work formed part of a Caroline Villers research fellowship at the Courtauld Insititute of Art
[2] Rooses M, L'œuvre de P. P. Rubens; : histoire et description de ses tableaux et dessins,. Anvers: J. Maes; 1886, vol 3 p.109
[3] Seilern, Flemish Paintings & Drawings, London, 1955, p.32
[4] https://www.britishmuseum.org/collection/object/P_1867-0309-448
[5] Held JS, The oil sketches of Peter Paul Rubens : a critical catalogue / Vol.1. Princeton, N.J: Princeton University Press for the National Gallery of Art; 1980, p.333-34
[6] E. Melanie Gifford, "Rubens's Invention and Evolution: Material Evidence in The Fall of Phaeton," Journal of Historians of Netherlandish Art 11:2 (Summer 2019) DOI: 10.5092/jhna.2019.11.2.1

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

The analysis of The Sacred Heart of Jesus by Adolf Herman Duszek (1872-1964) by the application of X-ray radiography and MAXRF techniques

P.K. Śwituszak[1*], P. Targowski[2], J. Olszewska-Świetlik[3]

[1] Doctoral School of Humanities, Theology and Arts - Academia Artium Humaniorum, Nicolaus Copernicus University in Toruń; Collegium Humanisticum, W. Bojarskiego 1, 87-100 Toruń, Poland
[2] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziądzka 5, 87-100 Toruń, Poland
[3] Department of Visual Arts Technology and Techniques, Faculty of Fine Arts, Nicolaus Copernicus University in Toruń, Sienkiewicza 30/32, 87-100 Toruń, Poland

Keywords: MAXRF, X-ray, overpainting, zinc, metal support

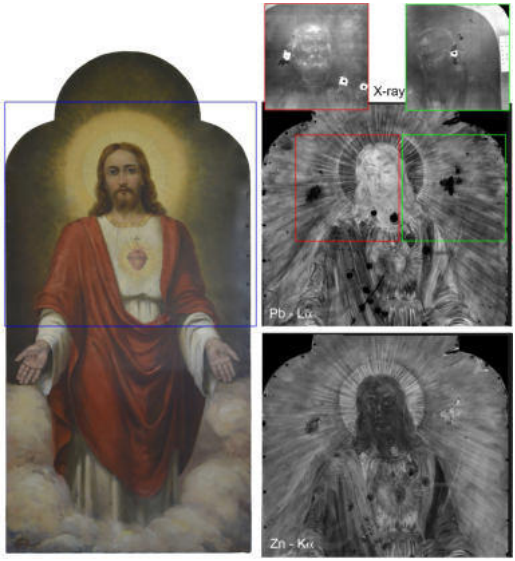
The research involved the application of X-ray radiography and MAXRF analysis to examine a painting entitled The Sacred Heart of Jesus by Adolf Herman Duszek in a non-destructive procedure. The performed analyses led us to the discovery of two other depictions hidden under the currently exhibited one.

A. H. Duszek was a professional Polish artist. He started his artistic career as a Wojciech Gerson's student. Next, he became a part of Munich School where he was developing his skills under Stanisław Grochowalski's supervision. The selected picture constitutes an intriguing example of a painting prepared on a metal, i.e. zinc, support which is extraordinary and unconventional even in the 20th century. We may usually expect that a metal support will be made out of cooper or tin alloys. The image is also interesting because it has been shot through several times. After WWII, the author of the painting, A. H. Duszek, performed its restoration and described this part of its history at the back of it. X-ray radiography and MAXRF techniques allow a detailed analysis of the structure and composition of the multiple layer painting. X-ray radiography is an excellent example of an easily available, time-efficient, and reliable imaging method. It has provided us with the initial evidence for the presence of another image hidden beneath the visible upper layer of the painting. Once the previous layers were identified, the MAXRF analysis was additionally employed to map of elements distribution. What makes this investigation important is the

*Correspondence: paula.swituszak@doktorant.umk.pl

confirmation that both methods are sensitive on slightly different depths. Three chronological layers of the painting have been documented eventually. It became evident that the A. H. Duszek's artwork was painted over the depiction of two saints: St. Peter and St. Paul with the inscriptions written above their heads with the Cyrillic alphabet. Over this painting a primary representation of Jesus was painted by Duszek before WWII. This painting was damaged during the war and restored by Duszek after it. The X-ray radiography also allows us to differentiate the size of the gunshot holes, which proved that the picture was shot through many times with weapons of at least two different calibres. MAXRF maps turned out to be highly informative as far as the state of preservation of the previous paint layers including Duszek's alterations during his restoration and permitted for deciphering of the saint's names.

The case study of *The Sacred Heart of Jesus* by A. H. Duszek gives unexpected results. The investigation proves that zinc support paintings might be examined by X-ray radiography and MAXRF analysis. Both techniques give unique and extremely valuable images and, when combined, they create the comprehensive picture of the complicated structure of the artwork. It has initialised the historical investigation of the object and connects its beginnings not with the Catholic religion but with the Orthodox Christian faith.



Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Wall paintings inspection by the use of Thermal Recovery Maps

M. Rippa[1*], G. Trojsi[2], M.R. Vigorito[2], P. Mormile[1]

[1] Institute of Applied Sciences and Intelligent Systems "E. Caianiello" of CNR, Pozzuoli (Napoli), Italy
[2] Department of Humanities, University Suor Orsola Benincasa, Naples, Italy

Keywords: thermography, wall painting, thermal map, conservation, diagnostics

Nowadays the use of non-invasive techniques to analyze the state of health of works of art represents a common practice. Among the cases of interest for cultural heritage, the structural decay of wall paintings affected by degradation represents an important and complex problem that involves the knowledge of materials, environmental conditions, conservation status and possible causes [1]. For the conservation of wall paintings, an important request is the use of non-invasive diagnostic tools that allow the detection of detachments and a comparison between their state before and after consolidation treatments. Thermography is a contact-less and non-invasive imaging technique and it represents a reliable means of providing a low-cost in situ analysis in different applications fields [2, 3]. In the active approach of this method, the surface of the sample investigated is heated using a controlled external source and the thermal response is recorded through the use of an appropriate infrared camera. The analysis approach carried out for the acquired images is strictly dependent and specific on the nature of the investigated sample. In this work, we report on in situ thermographic analysis performed before and after a restoration work of wall paintings preserved at the University Suor Orsola Benincasa of Naples (Italy) and datable in the XVIII century. We use an active technique based on the application of extended heating times to stimulate areas of the painting under investigation. From the thermal images acquired, we calculate the thermal recovery maps, which allow to detect structural inhomogeneities in the paintings under investigation that can be associated with the presence of detachments and defects. Our results demonstrate as this approach of investigation allows a simple and quick detection of the areas

*Correspondence: m.rippa@isasi.cnr.it

mainly affected by degradation and it can be used to effectively support the restoration works and to evaluate the consolidation results achieved.

References

[1] L. Nodari, L. Tresin, A. Benedetti, M.K. Tufano, P. Tomasin, Conservation of contemporary art: alteration phenomena in a XXI century artwork. From contactless in situ investigations to laboratory accelerated ageing tests, J. Cult. Herit., 35, 2019, pp. 288–296.

[2] X.P.V. Maldague, Theory and Practice of Infrared Technology for Nondestructive Testing, John Wiley & Son, New York, 2001.

[3] M. Rippa, V. Pagliarulo, A. Lanzillo, M. Grilli, G. Fatigati, P. Rossi, P. Cennamo, G. Trojsi, P. Ferraro, P. Mormile, Active Thermography for Non-invasive Inspection of an Artwork on Poplar Panel: Novel Approach Using Principal Component Thermography and Absolute Thermal Contrast, Journal of Nondestructive Evaluation, 40:21, 2021, pp. 1-9.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Study of the most effective analysis procedures using multispectral imaging techniques on ancient Egyptian painted objects

I. Shaheen, N. Hamza*

Grand Egyptian Museum, Giza, Egypt

Keywords: Multispectral Imaging, Reflectance Transformation Imaging, Cartonnage, Coffin, X-Ray Fluorescence, Ancient Egypt

Photonic and digital technologies significantly enhance the characterization potential of art and historical objects. Their promotion and integration within the museum documentation and conservation practices is attractive since they can allow more effective monitoring and maintenance. Here, example applications of the Multispectral Imaging (MSI) combined with X-Ray Fluorescence (XRF) elemental analysis at Grand Egyptian Museum of Giza will be reported, by focusing on the definition of the most suitable protocol allowing for better characterization of the painted objects. In particular, MSI is one of the imaging techniques which is used in preliminary investigations in order to non-destructively identify and study painted layers. The use of MSI to tentatively identify pigments allow rapid and low-cost survey of large areas. It is possible to tentatively identify some historical pigments and discover the invisible paint layers, inscriptions, and underdrawings.

The two selected objects were rich in pigments. The first one was a polychrome anthropoid wooden coffin lid (*GEM No. 22452*) the date back to 21st Dynasty (c. 1070 - 945 B.c.) Late Period, which belongs to the collection of Bab el- Gusus tomb. The second one was a Cartonnage mummy trappings on linen (*GEM No. 8615*), which date back to 27th dynasty, Late Period.

This research illustrates how the MSI system used enabled preliminary identification of the pigments and how its combination with Reflectance Transformation Imaging (RTI) provided additional information. Several tests were carried out in order to evaluate the effectiveness of this approach. Finally, X-ray fluorescence (XRF) spectrometry was for the identification of the pigments.

**Correspondence: Islamshahin29@gmail.com*

SPECTROSCOPIC AND MORPHOLOGICAL ASSESSMENT OF NATURAL AND SYNTHETIC PAINT VARNISHES AGED BY LED LIGHTING

G. Chiarello[1], A. Suzuki[2], G. Magni[3], B. Salvadori[2], C. Cucci[3], C. Riminesi[2]*

[1] University of Ca' Foscari, Dorsoduro 3246, Calle Larga Foscari, 30123 Venezia (VE), Italy
[2] Institute of Heritage Science, National Research Council of Italy (ISPC-CNR) , Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy
[3] Institute of Applied Physics "Nello Carrara", National Research Council of Italy (IFAC-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy

KEYWORDS: terpenoid and sesquiterpene, acrylic copolymer, VIS-UV-IR spectroscopy, confocal microscopy, museum lighting

In recent years, museum lighting has been changed by the progressive replacement of traditional light sources with light emitting diode (LED) technologies and intelligent lighting systems. Nonetheless, the current guidelines for lighting museum objects are still based on previous technologies, thus raising urgent issues for updating the recommended limits for light exposure of photosensitive materials [1,2]. The available normative on lighting indoor exhibitions of cultural heritage is currently under revision. This rapid technological transformation has therefore renewed interest in investigating photodegradation mechanisms in artist' materials, with a special focus on the assessment of impact of LED sources typically used in museum environments.

This study is a contribution framed in a wider project aimed at undertaking systematic studies of light ageing on representative classes of materials of interest in museum collections using LED sources.

The investigation on the exposure effects of terpenoid and sesquiterpene compounds, and acrylic copolymers to the LED lamp have been performed in comparison with accelerated ageing under artificial irradiation (Xenon lamp with filter 310-850 nm). Samples appling triterpenoid (dammar and mastic), sesquiterpene (shellac) and synthetic varnishes (Paraloid B72 e Primal AC33) were realized on laboratory glass slides with thickness of 15-25 micron. Both the light sources were set to expose the sample surface to the same

*Correspondence: giacomochiarello98@gmail.com

total irradiance (40 Mlxh), for 384 h which can be compared to about 65 years of exposure in recommended museum conditions [3-5]. The molecular changes induced by photo-ageing have been investigated by infrared spectroscopy (FT-IR) with ATR module and by UV-VIS transmittance spectroscopy, whilst morphological modifications were evaluated by confocal microscopy. The photo-induced changes in the UV-Vis spectra result in colour changes and, thus, in visible effects, which are considered a key parameter to assess the light impact in museums. In the present study, the different data acquired suggest that LED lighting has a lower impact in terms of spectral changes and morphological effects on examined materials than halogen lamps. The acrylic varnishes appear not to be particularly affected by the ageing process for both the selected lighting sources.

These results, although preliminary, represent a contribution to the wider work needed to fill the lack of knowledge and experimental data on the photo-induced effects of new LED sources on photosensitive materials.The open issues in the experimental protocols and data interpretation will be illustrated and discussed.

Acknowledgements

This work has been carried out under partial financial support of EU-project IPERION HS, Integrating Platforms for the European Research Infrastructure ON Heritage Science (H2020-INFRAIA-2019-1, under GA 871034)

References

[1] CEN/TS 16163:2014 Conservation of Cultural Heritage - Guidelines and procedures for choosing appropriate lighting for indoor exhibitions

[2] CIE 157:2004, Control of Damage to Museum Objects by Optical Radiation ISBN: 9783901906275

[3] I. Osticioli, D. Ciofini, A. A. Mencaglia, S. Siano, Warm white LED lighting in museums: Ageing effects on terpenoid resins assessed through Raman spectroscopy and chemometrics, Strain., 2018, 54:e12255.

[4] S. Bracci, M.J. Melo, Correlating natural ageing and Xenon irradiation of Paraloid B72 applied on stone, Polymer Degradation and Stability, 2003, 80:533–541.

[5] G. Thomson, Annual Exposure to Light within Museums, Studies in Conservation, 1967, 12(1):26-36.

A NEW OPEN ACCESS SPECTRAL LIBRARY OF ART-RELATED MATERIALS AS A DIGITAL SUPPORT TOOL FOR CULTURAL HERITAGE SCIENCE

I.M. Cortea[1], A. Chiroșca[2], L.M. Angheluță[1], G. Seriță[3], R. Rădvan[1]*

[1] National Institute of Research and Development for Optoelectronics - INOE 2000, Măgurele, Romania
[2] University of Bucharest, Măgurele, Romania
[3] University Politehnica of Bucharest, Bucharest, Romania

KEYWORDS: spectral library, open access, art materials, heritage science, spectroscopy

Investigation of art and cultural heritage objects using various analytical methods has become a standard approach in the field of heritage science. Identification of the various constituent materials, such as the identification of components in paint samples, can provide valuable information on the artist's working methods, can support authentication, and can provide important data that can support the conservation/restoration process. Development of databases with high-quality data of the pure substances used as artist's materials is of utmost importance for the identification and characterization of unknown samples.

Within the framework of the postdoctoral research project INFRA-ART [1], an open access spectral library with more than 500 reference samples of materials related to cultural heritage and conservation science has been developed. The spectral collection is freely available online [2], and was designed as a useful digital resource tool for researchers and other specialists in the field of heritage science, art history, conservation, and materials science. The reference materials have been characterized using complementary spectroscopic techniques - Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray fluorescence (XRF). These easily accessible spectroscopic techniques are probably the most commonly used analytical tools in conservation science as they offer a series of advantages such as: relatively low-cost, non- or minimal-invasiveness, and immediate response in terms of results.

The database is an ongoing compilation of spectra that contains

**Correspondence: ioana.cortea@inoe.ro*

at this moment primarily ATR-FTIR and XRF data, and a preliminary dataset of Raman spectra, of the following groups of materials: paint components (natural and synthetic pigments and dyes; glues, gums and binders; resins, balsams and wax); artist color paints (oil paints, watercolor, tempera, etc.), conservations materials (glues, polymeric materials, solvents, etc.) and unclassified materials (mixed pigments, etc). Each sample is associated with a series of identifiers (sample ID, sample type, sample source, origin, description), descriptive data (alternative names, chemical information, history of use), as well as metadata (experimental conditions on data acquisition). The database is keyword searchable and an interactive spectra viewer that allows users to visualize and analyze the spectra of each sample is available. In terms of future development directions, we plan to expand the number of available reference samples, integrate a higher number of Raman data, and develop an analytical tool that will allow peak search for each data type. A summary of the database structure and design, functionality, and use, will be presented in view of dissemination of this new open access digital resource to the scientific community.

Acknowledgements

The financial support of this work has been provided by the Romanian Ministry of Research, Innovation and Digitization under contract no. 18PFE/30.12.2021 and by UEFISCDI under grant no. PN-III-P1-1.1-PD-2019-1099.

References

[1] INFRA-ART postdoctoral research project - Spectral data mining for material identification, chemical fingerprinting and forgery detection of painted works of art, grant no. PN-III-P1-1.1-PD-2019-1099. http://certo.inoe.ro/infraart/

[2] INFRA-ART Spectral Database. https://infraart.inoe.ro/

Heritage Annotator: A Tool for Documenting, Browsing and Exploring Culture Heritage Data

K. Petrakis[1], M. Paterakis[1], D. Angelakis[1], K. Melessanaki[2], K. Hatzigiannakis[2], A. Giakoumaki[2], A. Philipidis[2], P. Siozos[2], S. Sotiropoulou[2], P. Pouli[2], C. Bekiari[1]*

[1] Centre for Cultural Informatics and Information Systems Laboratory, FORTH-ICS, Heraklion, Greece
[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Greece

Keywords: image annotation, documentation, diagnostics, conservation

A vast area of research in Heritage Sciences concerns the documentation of analytical examinations and conservation interventions on heritage objects carried out by different actors. Archaeologists, conservators, engineers, material scientists, curators and restorers of cultural property are enriching on a daily basis the knowledge and information about heritage artefacts. As expected, all this knowledge consists of highly heterogeneous data produced by different procedures. Current practice mostly uses spreadsheets or text files to organize the information. This form offers itself for data analysis and scholarly interpretation however it also poses problems including i) the difficulty for collaborative but controlled documentation by a large number of users, ii) the lack of representation of the details from which the documented relations are inferred, iii) the difficulty to extend the underlying data structures as well as to combine and integrate data from multiple and diverse sources and procedures, and iv) the limitation to reuse the data beyond the context of a particular research activity.

The need to store and identify all this information under a common denominator is more than obvious. The basic idea for the Heritage Annotator is to meet this need by allowing users to directly annotate images of the object whether it is a painting, a sculpture, a building or a work of art in general. This approach creates a clear visual overview of the procedures that have been followed and the location where this information was derived from. The annotation data structure makes use of existing standards for information

*Correspondence: cpetrakis@ics.forth.gr

documentation and publication (CIDOC-CRM), focusing on semantic interoperability and the production of searchable data of high value and long-term validity.

In this paper, we describe the process of documenting on the same digital image of the heritage object, analytical techniques providing different information and presenting different degrees of invasiveness, which implies a hierarchical protocol for their sequential application. Additionally to allow the user to preview and annotate the areas of examination with high accuracy, regardless the scale of operation, a function of dynamic zoom is available. As an example, MultiSpectral Imaging on an area, microRAMAN at micro scale and macroLIBS (Laser Induced Breakdown Spectroscopy) inducing a macro-spot of ablation are presented. The annotation file is linked to the same digital image of the heritage object creating rich structured knowledge which helps scientists from different fields to combine their data and cooperate on curation and conservation.

Acknowledgements

The financial support of this work has been provided by the projects “POLITEIA II” (Advanced analytical, diagnostic, surveying and documentation technologies in Cultural Heritage II, MIS 5002478) and “PROTEAS” (Advanced system for collection and management of analytical data for documentation and conservation of large-scale paintings in an open laboratory, MIS 5069984) which are respectively implemented under the “Action for the Strategic Development on the Research and Technological Sector” and “RESEARCH-INNOVATE-CREATE II” and are funded by the Operational Programme ¨Competitiveness, Entrepreneurship and Innovation¨ (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

References

[1] N. Platia, M. Chatzidakis, C. Doerr, L. Charami, Ch. Bekiari, K. Melessanaki, K. Hatzigiannakis and P. Pouli, ‘POLYGNOSIS’: the development of a thesaurus in an Educational Web Platform on optical and laser-based investigation methods for cultural heritage analysis and diagnosis, Heritage Science 5 (50), 2017.

ASSESSING THE USEFULNESS OF LASER-BASED TECHNIQUES FOR EVALUATING THE BIOCLEANING OF MURAL PAINTINGS

L. Ghervase[1], M. Dinu[1], V. Atanassova[1], I. Gomoiu[2], R. Rădvan[1]*

[1] National Institute of Research and Development for Optoelectronics INOE 2000, Magurele, Ilfov County, Romania
[2] Department of Microbiology, Institute of Biology Bucharest of the Romanian Academy, 296 Splaiul Independentei, Bucharest, Romania

KEYWORDS: laser-induced breakdown spectroscopy, Raman spectroscopy, hyperspectral imaging, biocleaning, mural painting

Mural paintings, especially those found in active religious sites, are often deteriorated by the action of various organic products derived from the daily activities associated with those religious sites, such as oil, candle soot or candle wax, which need to be removed during restoration procedures. Moreover, at times, products related to previous interventions, should also be removed. Products used in removal of surface layers such as aged consolidants or organic deposits, are often powerful substances, which may be harmful for the user. In the search for alternative, more user- and environmentally-friendlier ways of cleaning mural paintings, some approaches based on fungal decomposition have been tested. The present paper aims to evaluate how useful would laser-based techniques, mainly laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy, be for assessing the cleaning efficiency of such approaches. LIBS and Raman were chosen because they both have the advantage of in situ, real-time operation, without the need for any sample preparation. To this aim, several mural painting mock-ups have been created, and covered with specific mural contaminants. The next step was to try to remove the surface contaminant layer, by using a specific protocol based on fungi which were isolated from brackish and hypersaline lakes from Romania and from greasy deposits and candles. These mock-ups have been analyzed using both LIBS and Raman. In order to guide the evaluation process, a rapid initial assessment is performed with hyperspectral imaging. The estimated outcome is that LIBS can be useful for the precise evaluation of the surface deposition layer, while Raman spectroscopy could help identify molecular compounds

**Correspondence: ghervase@inoe.ro*

associated with the contaminants, before and after the treatment.

Acknowledgements

The financial support of this work has been provided by The Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI), grant number PN-III-P2-2.1-PED-2019-0082.

Multi-analytical approach for removal of thick layers of metallic overpaints from a Brancovan iconostasis

M. Dinu[1*], *V. Atanasova*[1], *L.C. Ratoiu*[1], *L.M. Anghelută*[1], *S.R. Polizu*[2], *R. Rădvan*[1]

[1] National Institute of Research and Development for Optoelectronics, INOE 2000
[2] IORUX Restorations

Keywords: laser cleaning, LIBS, HIS, chemical cleaning

The present paper reports a complex casuistry: the restoration of the iconostasis from Sf. Treime Church from Măgureni, România, built in 1694. The iconostasis is covered by a thick layer of bronze paint that was thought to be applied in the restoration made after a fire affected the church. The thick metallic layer demanded a careful documentation and characterization of the stratigraphy, that was attained by corroborating data from hyperspectral imaging (HIS) and Laser Induced Breakdown Spectroscopy (LIBS). For the areas where the thick layer of overpaint and grime was chipped off, digital microscopy and FTIR was performed. Following the tests, it was found that the iconostasis was covered in two rows with paint that imitates silver and gold (liquid bronze). The first lighter metallic paint was probably applied in 1925, following the intervention of the painter Norocea, to give the iconostasis and the new elements introduced a unitary look. The second coating with metallic paint is later, using also metallic gold paint. The cleaning tests were made evaluating several methods, in order to find the proper regime that would help preserve as much as the underlying polychrome layers. Based on the tests, it was decided that the best solution was to use laser cleaning guided by the HIS images for the removal of the metallic paint overlayers and finalize with chemical cleaning.

Acknowledgements

This work was supported by the Romanian Ministry of Research, Innovation and Digitalization, through Program 1 - Development of the National Research-Development System, Subprogram 1.2 - Institutional performance - Projects to finance the excellence in RDI, Contract no. 18PFE/30.12.2021.

**Correspondence: monica.dinu@inoe.ro*

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Novel method to characterise laser-induced damage on paintings during Raman spectroscopy with VIS-NIR Hyperspectral Imaging

A. Suzuki[1,2], Y. Li[1], C. Shing Cheung[1], C. Riminesi[2], H. Liang[1]*

[1] School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, UK
[2] Institute of Heritage Science, National Research Council ISPC-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Florence, Italy

Keywords: monitoring, reversible/permanent damages, VIS-NIR reflectance Hyperspectral Imaging, Thermal Imaging, pigments

Raman spectroscopy is a common analytical technique for the characterization of artists' materials. The safety evaluation of such a laser-based technique is required in order to guarantee non-invasive application on cultural assets. Commonly used sources for Raman spectroscopy are Continuous Wave (CW) lasers from VIS to NIR spectral range with output power range from 0.01 to hundreds of mW with spot sizes ranging from few microns (micro-Raman) to hundreds of microns (portable devices) up to remote Raman systems which exploit spot sizes of a millimetre. Damages/alterations may manifest in different ways and extent and can affect the optical properties, electronic and molecular structure of materials. Alterations in some cases are too subtle to be detected by visual inspection or by monitoring of vibrational spectral changes by Raman spectroscopy during the measurement [1-2].

Therefore, alternative monitoring set-up is necessary for a sensitive detection of damage to guide optimum laser settings to avoid damage.

In this work, a multi-analytical approach focused on the use of imaging techniques for the monitoring of laser-induced degradation on oil-painting mock-ups while performing Raman spectroscopy with CW lasers is presented. The set-up is designed to correlate the time-resolved reflectance changes in the VIS-NIR spectral range with simultaneous thermal monitoring of the surface. This monitoring method is presented for three different red/orange semiconductor pigments (red lead, vermilion and realgar) upon laser irradiation at 532, 785 and 1064 nm.

**Correspondence: maria.suzuki2019@my.ntu.ac.uk*

Transient and irreversible VIS-NIR spectral changes were detected with different combination of intensity, spot size and laser irradiation time. Damage threshold was found to depend strongly on the laser spot size even with no significant photo-thermal effect. Reversible VIS spectral changes seem to appear prior to the occurrence of permanent damage suggesting this method to be a powerful tool to predict damage.

References

[1] Y. Li, C. S. Cheung, S. Kogou, A. Hogg, H. Liang, S. Evans, Standoff laser spectroscopy for wall paintings, monuments and architectural interiors, in Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, 2021.

[2] A. De Santis, E. Mattei, C. Pelosi, Micro-Raman and stratigraphic studies of the paintings on the 'Cembalo' model musical instrument (A.D. 1650) and laser-induced degradation of the detected pigments, J. Raman Spectrosc. 2007, 38, 1368.

Technological and Methodological Advances

ORAL

PHOTOTHERMAL ASPECTS IN PHOTONIC DIAGNOSTICS AND LASER TREATMENTS

J. Agresti, D. Ciofini, I. Osticioli, A.A. Mencaglia, S. Siano*

Institute of Applied Physics "Nello Carrara"- CNR, Sesto Fiorentino (Florence), Italy.

KEYWORDS: light propagation, laser heating, optical absorption, thermal transient, inhomogeneous absorption, IR sensor

The physical description of the laser-matter interaction features represents a crucial step for correctly interpreting the spectral behavior and possible alteration phenomenologies during laser-based photonic diagnostics and conservation treatments of a given artefacts. Despite the strongly non-homogeneous nature of most of the materials encountered in knowledge and conservation of cultural heritage, effective medium approximations can sometime provide useful information for parameterizing and optimizing the characterization or conservation processes. In particular, pulsed or CW laser heating of several materials was modelled and the corresponding results were compared with time resolved temperature measurements using suitable IR sensors, thus extending some results reported in recent works [1-3].

Such an approach, where the actual material is replaced with an homogeneous effective medium, is sometime not suitable within the specific time and spatial scales of interest. Thus, regimes where the finite-size effects of the laser-matter interaction play a fundamental role in the physical processes were also investigated. Particle scattering and absorption of electromagnetic radiation were modelled using various codes (MatLab, Mathematica, and other) and discussed within the framework of laser-based diagnostics and conservation treatments. The effects of localized absorbing particles dispersed in a host matrix as well as the effect of multiple-scattering in dense particulate media were examined. These types of phenomena are responsible for non-homogeneous laser energy coupling and localized heating, melting, evaporation, and pressure generation. Such a modeling was exploited for simulating and comparing the temperature rises in homogeneous and inhomogeneous paint layers and determining safe operative

**Correspondence: J.Agresti@ifac.cnr.it*

irradiances

References

[1] C. Chillè, J. Agresti*, D. Ciofini, A. Mencaglia, I. Osticioli, and S. Siano, Measurement of temperature gradients during Er:YAG laser irradiation of poly(vinyl alcohol), J. Phys.: Conf. Ser. 2204 (2022) 012071.
[2] C. Calvagna, A. A. Mencaglia, I. Osticioli, D. Ciofini, and S. Siano, Probe for Thermally Controlled Raman Spectroscopy Using Online IR Sensing and Emissivity Measurements, Sensors 2022, 22, 2680.
[3] D Ciofini, J Agresti, AA Mencaglia, S Siano, I Osticioli, Temperature sensing during Raman spectroscopy of lead white films in different purity grades and boundary conditions Sensors and Actuators B: Chemical 325 (2020) 128958.

Advances in Compositional Photonic Diagnostics

ORAL

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Development of a hybrid portable instrument performing LED-Induced Fluorescence, LIBS and Diffuse Reflectance for an integrated study of diverse surface layers/deposits on monuments

A. Giakoumaki[1], V. Piñon[1], K. Hatzigiannakis[1], M. Andrianakis, K. Melessanaki[1], P. Pouli[1] and D. Anglos[1,2]*

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology, Nikolaou Plastira 100, 70013, Vassilika Vouton, Heraklion, Crete, Greece
[2] University of Crete, Department of Chemistry, Voutes University Campus, P.O. Box 2208, 70013, Heraklion, Crete, Greece

Keywords: hybrid system, spectroscopic analysis, deterioration, monuments

Monuments are exposed to numerous meteorological and anthropogenic phenomena that lead gradually to the formation and deposition of crusts on their surface such as biodeterioration, atmospheric pollution crusts, corrosion products, patinas etc. Furthermore, the surface of the monuments might present chromatic layers, which can either belong to its architectural characteristics (e.g. wall paintings) or created later on from exogenous factors. As in many cases the deposits might alter aesthetically or even structurally the monument, their complete characterization is essential before deciding on their removal or preservation. This task can be challenging as the compositional diversity of these layers (biological, organic, inorganic) might involve the application of more than one analytical technique, ideally capable to be applied in-situ. These requirements can be met with the use of the hybrid portable instrument that is being developed and can perform three spectroscopic measurements: LED-Induced Fluorescence for the detection and discrimination of biodeterioration, Laser-Induced Breakdown Spectroscopy (LIBS) for the elemental analysis of pigments, metals/ metal corrosion and inorganic crusts and Diffuse Reflectance Spectroscopy for the molecular analysis of pigments and coloured layers. LED-Induced Fluorescence and Diffuse Reflectance are completely non-destructive, while LIBS gives also the possibility of stratigraphic analysis of a multilayered structure.

*Correspondence: agiakoumaki@iesl.forth.gr

In the present study the design, components and performance characteristics of the newly-developed system are demonstrated. Various archaeological objects and fragments from monuments and sites of the city of Athens (stones, ceramics, metals, wall paintings) have been analysed firstly in the lab to test the performance of the system prior to its application in the field. An analysis methodology is developed by selecting the proper experimental parameters for all the techniques involved. The preliminary results show that the hybrid instrument can be proved a valuable tool at the hands of conservators, heritage scientists, archaeologists etc., as it can characterise a wide variety of materials that appear on the surface of monuments in a rapid, portable and effective manner.

Acknowledgements

The financial support of this work has been provided by CALLOS: Conservation of Athens antiquities with Laser and Lidar technologies Open to Science and public (MIS-5056208), an “open innovation in culture” action co-funded by the European Regional Development Fund (ERDF) and national resources through the Operational Program “Competitiveness, Entrepreneurship & Innovation” (NSRF-EPAnEK). The authors are grateful to the Ephorate of Antiquities of Athens, which provided the archaeological objects.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Remote spectroscopic system combined laser-induced breakdown spectroscopy (LIBS), laser-induced fluorescence (LIF), Raman spectroscopy and reflectance spectroscopy for cultural heritage

V. Detalle[1,2,3,], X. Bai[1,2,4], J. Auber--Le Saux[1,4], S. Richiero[1,4]*

[1] Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris, France
[2] Centre National de la Recherche Scientifique (CNRS), Federation de recherche NewAGLAE FR3506, Paris,France.
[3] PSL Research University, Institut de Recherche Chimie Paris, Chimie ParisTech, CNRS UMR 8247, Paris, France
[4] Fondation des sciences du patrimoine/EUR-17-EURE-0021, Cergy-Pontoise cedex, France

Keywords: LIBS-LIF-Raman spectroscopy, reflectance spectroscopy pulsed laser, Heritage science, stratigraphic analysis

The characterization of materials of cultural heritage works of art requires information on both organic and inorganic materials. A system was developed, which combines laser-induced breakdown spectroscopy (LIBS), laser-induced fluorescence (LIF), Raman spectroscopy and reflectance spectroscopy, and allows for remote measurements and complementary elemental and molecular analysis (Figure 1) [1-2]. This opens up exciting prospects for advancing the state of the art by combining complementary techniques in custom-designed mobile or portable hybrid instruments, allowing scientists to efficiently perform multi-analytical investigations with a single instrument including multimodal capabilities [3]. Then, this new system can take specific place in heritage science application for extensive identification and characterization of inorganic and organic materials. It is included in the mobile laboratory of IPERION HS (Integrating Platforms for the European Research Infrastructure ON Heritage Science (H2020)) in order to to support extensive and comprehensive on-site measurements and decision-making [4].

This presentation focuses directly on the design and area of applications of this multi-analytical instrument prototype capable of combining three laser-based spectroscopic techniques working with

*Correspondence: vincent.detalle@culture.gouv.fr, xueshi.bai@culture.gouv.fr

the environmental light with the help of a pulsed laser. Several analysis cases will be presented: stone identification, pigment characterization, stratigraphic analysis in multi-layer systems, such as painting or ceramics. Through these examples, we will describe the advantages and limitations of the instrumentation depending on the material composition. This mobile prototype based on a combination of popular spectroscopic techniques offers atomic and molecular analysis with sufficient sensitivity, rapidity and spatial and temporal resolution to perform in situ stratigraphic measurements.

ACKNOWLEDGEMENTS

This work has been supported by the French Ministry Research Program EquipEx PATRIMEX ANR-EQPX-0034 and by IPERION-CH project funded by the European Commission, H2020- INFRAIA-2014-2015, Grant No. 654028

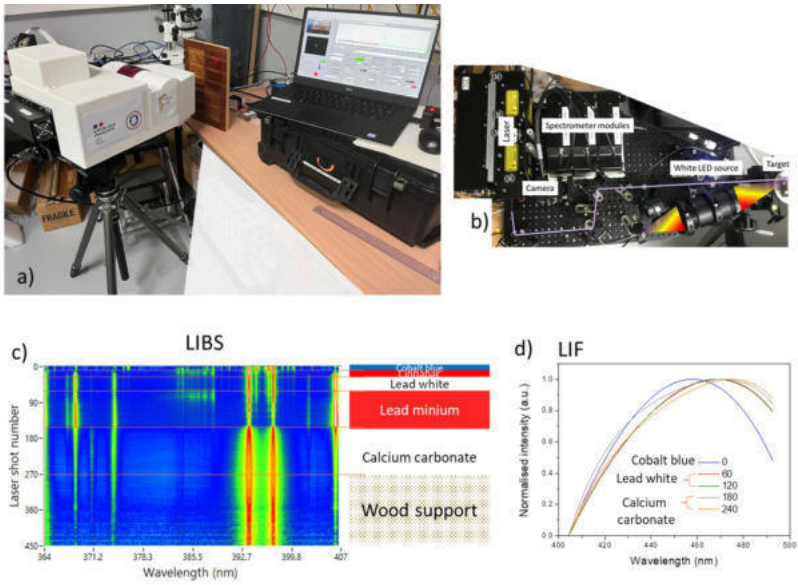


Figure 1. a) Mobile part of the prototype; b) Optical path in the mobile head; c) Depth profile of LIBS spectra represented in false color; d) the integrated fluorescence intensity from the observed spectral range (404-493 nm) after 0, 60, 120 and 180 laser shots from the same spot, respectively.

References

[1] X. Bai, D. Syvilay, N. Wilkie-Chancellier, A. Texier, L. Martinez, S. Serfaty, D. Martos-Levif and V. Detalle, Influence of ns-laser wavelength in laser-induced breakdown spectroscopy for discrimination of painting techniques, Spectrochim. Acta Part B, 134 (2017) 81-90.

[2] X. Bai, M. Oujja, M. Sanz, M. Lopez, C. Koch Dandolo, M. Castillejo, and V. Detalle, Integrating LIBS-LIF-Raman into a Single Multi-Spectroscopic Mobile Device for in Situ Cultural Heritage Analysis, Optics for Arts, Architecture, and Archaeology VII: International Society for Optics and Photonics, Vol.11058 (2019)

[3] D. Syvilay, X. Bai, N. Wilkie-Chancellier, A. Texier, L. Martinez, S. Serfaty, and V. Detalle, Laser-Induced Emission, Fluorescence and Raman Hybrid Setup: A Versatile Instrument to Analyze Materials from Cultural Heritage, Spectrochimica Acta Part B: Atomic Spectroscopy 140 (2018): 44-53.

[4] V. Detalle, X. Bai, E. Bourguignon, M. Menu, and I. Pallot-Frossard, LIBS-LIF-Raman: A New Tool for the Future E-RIHS, Optics for Arts, Architecture, and Archaeology VI: International Society for Optics and Photonics, Vol.10331 (2017)

LASER-DRIVEN PARTICLE ACCELERATION FOR ELEMENTAL CHARACTERIZATION OF ARTWORKS

F. Mirani, A. Maffini, A. Formenti, D. Vavassori, D. Dellasega, V. Russo, M. Passoni*

Politecnico di Milano, Department of Energy, Milano, Italy

KEYWORDS: laser-driven particle acceleration, PIXE, EDX, PAA, NAA, imaging, artworks

In this contribution, the potentials of laser-driven radiation sources for the elemental analysis of materials, with reference to artworks and objects of historical interest, are presented.

In recent years, laser-driven particle acceleration [1] has attracted increasing attention because of its potential application in several fields, including materials science and elemental characterization. It relies on the interaction between ultra-short (10s fs), super-intense ($I > 10^{18}$ W/cm^2) laser pulses provided by high power lasers (from ~10 TW to 1 PW) and targets to accelerate electrons and ions. For instance, when the laser pulse hits the front surface of a μm-thick solid foil, electrons and protons are co-emitted from the rear side. They have broad energy spectra with maximum energies ranging from few MeV up to 10s of MeV depending on the laser power. Moreover, exploiting the interaction with proper converter materials, the accelerated electrons and protons allow generating high energy photons and neutrons. Notably, a unique feature of laser-driven sources, compared with conventional particle accelerators, is the possibility of providing all mentioned radiations with minor variations to the setup. Lastly, using advanced target configurations [2,3] is a viable rout to optimize the laser-target interaction process, thus efficiently accelerate particles with compact 10s TW class systems. Because of their potential compactness and versatility, laser-driven radiation sources may offer an important breakthrough in the field of materials science.

Elemental characterization techniques based on charged particle-induced X-ray emission spectroscopy (PIXE, EDX), photon activation analysis (PAA), fast neutron activation (FNAA) analysis and radiography are well recognized as major tools in materials

*Correspondence: francesco.mirani@polimi.it

science. Among several fields, they find widespread use for cultural heritage studies [4-6]. PIXE and EDX allow performing the surface analysis of solid samples exploiting MeV protons and keV electrons, respectively. On the other hand, PAA and FNAA can be used for bulk analysis of materials via irradiation with 10s MeV energy photons and neutrons, respectively. The commonly exploited particle and radiation sources offer solutions that are, on one hand, adequate to the irradiation aim, but, on the other, can be dependent on the particular application and the specific particle beam needed.

Here we show a numerical and experimental investigation aimed at assessing the feasibility of laser-driven radiation sources for PIXE, EDX, PAA, NAA and radiography. Exploiting Particle-In-Cell and Monte Carlo simulations, we identify the proper target solutions to carry out the mentioned techniques with laser-driven sources [7-9]. Moreover, we identify the ranges for the laser parameters (e.g. intensity and repetition rate) required to achieved the necessary particle energies and fluxes. Then, preliminary proof-of-principle setups for laser-driven material characterization techniques are proposed. This investigation is performed considering artworks characterization case-studies. Lastly, the results of a campaign aimed at proving the experimental feasibility of laser-driven PIXE and EDX are presented [10]. The experiment has been carried out at the Centro de Láseres Pulsados in Salamanca with the 200 TW VEGA-2 laser. These results provide new perspectives toward the development of versatile particle acceleration systems for elemental characterization in cultural heritage studies.

Acknowledgements

The financial support of this work has been provided by the ERC-ENSURE (No. 647554), PoC-INTER (No. 754916) and PoC-PANTANI (No. 101069171) projects.

References

[1] Macchi, A., et al. Ion acceleration by superintense laser-plasma interaction. Reviews of Modern Physics, 85(2), (2013), 751.

[2] Fedeli, L., et al. Enhanced laser-driven hadron sources with nanostructured double-layer targets. New Journal of Physics, 22(3), (2020), 033045.

[3] Prencipe, I., et al. Efficient laser-driven proton and bremsstrahlung generation from cluster-assembled foam targets. New Journal of Physics,

23(9), (2021), 093015.
[4] Verma, H. R. Atomic and nuclear analytical methods. Springer-Verlag Berlin Heidelberg, (2007).
[5] Segebade, C., et al. Principles, methodologies, and applications of photon activation analysis: a review. J. Radioanal. Nucl. Chem., 312(3), (2017), 443-459.
[6] Marchese, N., et al. New generation non-stationary portable neutron generators for biophysical applications of Neutron Activation Analysis. Biochim Biophys Acta Gen Subj, 1861(1), (2017), 3661-3670.
[7] Passoni, M., et al. Advanced laser-driven ion sources and their applications in materials and nuclear science. Plasma Physics and Controlled Fusion, 62(1), (2019), 014022.
[8] Passoni, M., et al. Superintense laser-driven ion beam analysis. Scientific reports, 9(1),(2019), 1-11.
[9] Mirani, F., Calzolari, D., Formenti, A., & Passoni, M. Superintense laser-driven photon activation analysis. Communications Physics, 4(1), (2021), 1-13.
[10] Mirani, F., et al. Integrated quantitative PIXE analysis and EDX spectroscopy using a laser-driven particle source. Science advances 7.3 (2021): eabc8660.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Observation and mitigation of light-induced alterations of lead pigments in their study via Raman microscopy

A. Philippidis[1*], G. Kampouropoulos[2], D. Anglos[1,2]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1385, GR 711 10 Heraklion, Crete, Greece
[2] Department of Chemistry, University of Crete, GR 710 03 Heraklion, Crete, Greece

Keywords: Raman spectroscopy, laser-induced pigment alterations, safe limits, lead pigments

This study investigates the interaction of laser light with lead-based pigments during their analysis by Raman spectroscopy. Five pigments, red lead (Pb_3O_4), lead white ($2PbCO_3 \cdot Pb(OH)_2$), massicot (PbO), lead tin yellow ($PbSn_{1-x}Si_xO_3$), known since antiquity, and lead chromate ($PbCrO_4$) a synthetic pigment (early 19th C) have been examined. Three different Raman spectrometers were used: a mobile one equipped with a diode laser source emitting at λ_{exc}: = 785 nm, and two laboratory microscopes with excitation at λ_{exc} = 473 nm and λ_{exc} = 532 nm, respectively. The pigments were used neat, in powder form, and also dispersed in a binder and coated with a layer of varnish. Key irradiation parameters were examined including laser power, focusing conditions (different objective lenses), time of pigment exposure to the laser beam and excitation laser wavelength (in the visible and the near-infrared region). The main objective of this research has been to establish irradiation regimes and protocols for the safe use of Raman microscopy in the analysis of common pigments widely used by artists. It is of great importance for the analyst to obtain reliable results and maximize signal to noise (S/N) in the Raman spectra and at the same time to ensure that no damage is produced during exposure of the pigment to the laser beam. The five lead pigments presented differences in the interaction with the laser light such as the appearance of new Raman bands or the decrease/increase of Raman band intensities with increasing laser power. In most cases, a visible darkening of the pigment surface appeared above a specific laser power value (visible alteration threshold). It was observed that the presence of a binding medium in the painting layer and/or the existence of a varnish coating decreases/minimizes the extent of alteration for all

*Correspondence: filagg@iesl.forth.gr

pigments examined. Despite this favorable protective effect offered by the binder and the varnish, it is strongly suggested that during Raman analysis laser power density be kept below the pigment alteration threshold values as defined in the case of the neat pigments.

Acknowledgements

Financial support of this work has been provided by project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science) funded by the European Union, H2020-INFRAIA-2019-1, under GA No. 871034) and project SpArch (Spectrochemical Analysis of Archaeological Bioorganic Residues) funded by the Hellenic Foundation for Research and Innovation, Grant HFRI-FM17-TΔE-3542).

References

[1] L. Bertrand, S. Schoeder, D. Anglos, M.B.H. Breese, K. Janssens, M. Moini, A. Simon, Mitigation strategies for radiation damage in the analysis of ancient materials, Trends in Analytical Chemistry, 66, 2015, 128-145.

[2] A. Philippidis, A. Mikallou, D. Anglos, Determining optimum irradiation conditions for the analysis of vermilion by Raman spectroscopy, Eur. Phys. J. Plus, 136, 2021, 1194.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Advances on temperature controlled Raman spectroscopy

I. Osticioli, D. Ciofini, J. Agresti, A.A. Mencaglia, S. Siano*

Istituto di Fisica Applicata "N. Carrara" - CNR, Florence, Italy

Keywords: IR sensor, conservation, pigments, impurities

Raman spectroscopy is a well established analytical technique in many fields of application. In particular, it has become an almost indispensable tool for characterizing paint layers. However, the intrinsic need to use high intensities CW laser irradiation (~0.1-1 kW/cm^2) due to the well-know low efficiency of the Raman scattering could lead to local overheating, spectral alterations, and damage to the paint film. In a previous work, we introduced the approach of temperature controlled Raman spectroscopy [1] based on an IR sensor line, in order to ensure optimum measurement conditions and non-destructiveness. A novel probe was hence proposed (exc. 1064 nm) allowing for automated control of the laser induced temperature rise through a suitable modulation of the incident power, which was integrated in a scanning system [2]. Very recently, a further step ahead was achieved by designing a general purpose Raman probe that can be integrated with several commercial probes [3]. It was built on an integrating sphere hosting three sensing lines for measuring the emissivity (needed for deriving the temperature using IR sensing), temperature rise, and Raman spectrum, respectively. The latter line was achieved by adapting a commercial Raman probe (exc. 785 nm).

Here, besides the way to achieve safe molecular analyses, we used the two systems described above to investigate the photothermal behaviour of pigments, paint layers on different substrates, which is an axtension of what already reported for lead white [4]. At the same time, the systems were exploited in order to study the spectral effects of the temperature rise and to support the interpretation of non-Raman components of the spectrum. More in detail, intense background emissions, often visible in Raman spectra and usually subtracted, were instead studied herein to provide information regarding the chemical composition, the purity grade,

*Correspondence: I.Osticioli@ifac.cnr.it

the microstructure, the thickness and the grain size of the paint layer. Tests were carried out using a set of natural and synthetic pigments. Different brands of the same pigment have been investigated, which exhibited significant differences in spectral features, temperature rises, and background depending on the purity grade and microstructural features of the corresponding paint film samples.

Acknowledgements

The financial support of this work has been provided by EU project IPERION HS, GA n. 871034

References

[1] I. Osticioli, A. A. Mencaglia, and S. Siano, Temperature-controlled portable Raman spectroscopy of photothermally sensitive pigments, Sens. Actuators B Chem. 238 (2017) 772–778.

[2] AA Mencaglia, I Osticioli, D Ciofini, S Siano, Raman spectrometer for the automated scan of large painted surfaces, Rev. Sci. Instrum. 90, 053101 (2019).

[3] C. Calvagna, A. A. Mencaglia, I. Osticioli, D. Ciofini, and S. Siano, Novel Probe for Thermally Controlled Raman Spectroscopy Using Online IR Sensing and Emissivity Measurements, Sensors, pp. 1-13, 2022.

[4] D. Ciofini, J. Agresti, A. A. Mencaglia, S. Siano, and I. Osticioli, Temperature sensing during Raman spectroscopy of lead white films in different purity grades and boundary conditions, Sens. Actuators B Chem. 325, 128958, 2020.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Development of new SERS sensors based on the laser irradiation of the major hydration product of Portland cement

L. Maestro-Guijarro[1], P.M. Carmona-Quiroga[1], S. Martínez-Ramírez[2], S. Sanchez-Cortes[2], M. Castillejo[1], M. Oujja[1]*

[1] Instituto de Química Física Rocasolano (IQFR-CSIC), C/ Serrano 119, Madrid, Spain
[2] Instituto de Estructura de la Materia (IEM-CSIC), C/ Serrano 121, Madrid, Spain

Keywords: SERS, Concrete, Calcium silicate hydrate, Conservation, Laser irradiation

Portland cement concrete is considered, since being adopted by modern architecture in the twentieth century, a 'noble' material, the latest to join the list of built heritage materials.

For correct conservation of cement concrete, including the selection of compatible protective treatments, the determination of constitutents that can influence, cause or be the result of deterioration phenomena is of fundamental importance. However, components found in low concentrations, such as organic aditives, are difficult to detect with the most common concrete research- and industry-driven analysis.

In heritage science, surface-enhanced Raman spectroscopy (SERS) has become a very useful molecular identification technique for the detection of organic molecules at very low concentrations provided by the physical effect known as surface plasmon localization. This effect occurs when the molecule is in close contact with metallic nanostructures upon resonant laser irradiation.

In this work, the first approach for the development of a new "in situ" SERS sensor for Portland cement concrete is presented using a simplified system based on the main product of the hydration of Portland cement, a calcium silicate hydrate (C-S-H). Thereby, C-S-H with and without Ag were synthesized and irradiated by nanosecond ultraviolet and visible laser pulses for the detection of a model organic molecule, rhodamine B in low concentration (10-6 M), a traditional analyte in SERS studies. The results of SERS analysis showed a high amplification of the rhodamine Raman signal in substrates irradiated by laser.

**Correspondence: pcarmona@iqfr.csic.es*

ACKNOWLEDGEMENTS

The financial support of this work has been provided by the SCOCHLAS project (Study and Conservation of Cultural Heritage with Lasers, PID2019-104124RB-100) and the H2020 project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science, GA 871034). The professional support provided by the CSIC 'Open Heritage: Research and Society (PTI-PAIS)' Interdisciplinary Thematic Platform is also gratefully acknowledged.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

COMBINING MULTIMODAL GROUND BASED REMOTE SENSING WITH MACHINE LEARNING FOR MONITORING AND IDENTIFICATION OF SALTS ON HISTORICAL BUILDINGS

S. Kogou[1], Y. Li[1], C. S. Cheung[1], D. Thickett[2], H. Liang[1]*

[1] School of Science & Technology, Nottingham Trent University, Nottingham NG11 8NS, UK
[2] English Heritage, Rangers House, Chesterfield Walk, London SE10 8QX, UK

KEYWORDS: salts, LIBS, Raman, SWIR imaging, machine learning

Soluble salts activity is one of the main factors contributing to the deterioration of heritage buildings. Salt crystallisation, and the consequent damage, have been thoroughly investigated over the years in several laboratory-based studies. This study introduces a new methodology for the in situ and non-invasive monitoring and identification of salts, combining the complementary use of remote sensing techniques with machine learning. The ground-based remote sensing suite of this study consists of short-wave infrared (SWIR) imaging and remote Laser-induced breakdown (LIBS) and Raman spectroscopies. All techniques operated from standoff distances of 3 to 15m. The remote SWIR spectral imaging system covers the spectral range between 1 and 2.5 microns, with a spectral resolution of 5.5 nm and spatial resolution of 125 microns at 4 m. The in-house developed remote standoff Raman system uses as excitation source a 780 nm continuous wave (CW) laser, whose beam is focused to a spot size of ~1 mm on the target at all distances. The in-house developed remote standoff LIBS system uses a laser with an excitation wavelength at 1064 nm. It covers the spectral range between 200 and 900 nm, while its beam focuses down to 1 mm. SWIR imaging has been widely used for the analysis of various types of artworks. However, this study is the first one that introduces the application of remote SWIR imaging in cultural heritage, and more specifically on the examination of historical buildings. The complementary application of remote LIBS and Raman spectroscopies in the analysis of murals has been presented in a recently published study [1]. In our approach, SWIR imaging is used for scanning large wall surfaces. The post-processing of the

*Correspondence: sotiria.kogou@ntu.ac.uk

acquired spectral imaging data, using our machine learning-based clustering method that groups areas of similar spectra [2,3], maps the material variations across the wall. Detailed examination of the mean SWIR spectra for each cluster offers a preliminary identification of salts, also indicating variations in volume concentration. For the precise identification of the salts in their different hydration states, remote LIBS and Raman analysis is then performed on representatives of each cluster areas. The new method is presented through laboratory experiments as well as on site examination of historical buildings.

References

[1] Li, Y., Cheung C. S., Kogou, S. Hogg, A., Liang, H. and Evans, S, Standoff Laser Spectroscopy for Wall Paintings, Monuments and Architectural Interiors. In Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, 17–21 May 2021, ed. J. Bridgland. Paris: International Council of Museums.

[2] Kogou, S., Shahtahmassebi, G., Lucian, A., Liang, H., Shui, B., Zhang, W., Su, B., and Van Schaik, S., From Remote Sensing and Machine Learning to the History of the Silk Road: Large Scale Material Identification on Wall Paintings. Scientific Reports, 10, 2020, 19312.

[3] Kogou, S., Lee, L., Shahtahmassebi, G. and Liang, H., A New Approach to the Interpretation of XRF Spectral Imaging Data Using Neural Networks. X-Ray Spectrometry. 2020

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Deep learning models for MA-XRF imaging Spectroscopy of paintings

A. Busacca[1,2], Z. Preisler[1], R. Andolina[1], C. Caliri[1], C.G. Fatuzzo[1], G.M. Privitera[1,3], D. Zappalà[1], D. Allegra[2], F. Stanco[2], C. Miliani[1], F.P. Romano[1]*

[1] CNR-ISPC, via Biblioteca 4, 95124 Catania, Italy
[2] Mathematics and Informatics Department of University of Catania, Viale Andrea Doria 6, 95125 Catania, Italy
[3] Physics Department of University of Catania, Via Santa Sofia 64, 95123, Catania, Italy

Keywords: MA-XRF, Artificial Intelligence, Machine Learning, Paintings, Imaging

The current advancements of non-invasive imaging methods applied for the study and conservation of cultural heritage have driven a rapid development of novel computational methods. MA-XRF is nowadays well-established and often used for the investigation of paintings in museums and conservation studios. However, MA-XRF scanning generates large datasets that can be challenging and time-consuming to analyze. In the following, we employ machine learning approaches as they allow for identification of non-trivial dependencies and classification across the high dimensional data hence promising a more comprehensive interrogation. We have developed a novel deep learning model for the MA-XRF imaging spectroscopy. The new proposed methodology is based on standard CNN and ResNet type networks and takes advantage of both synthetic as well as experimental data. In this work, the synthetic data are used for training while the experimental ones are used for testing, evaluation, and as a reference. The experimental data are taken from previous MA-XRF in-situ investigations of XRAYLab of ISPC-CNR of Catania performed on artworks painted across a range of art periods to include different typologies of pigment materials, and pictorial techniques [1]. The experimental data are used as a guideline to build a consistent synthetic dataset representing XRF spectra of pigments and their mixtures in real artworks. The synthetic XRF spectra are generated by Monte Carlo simulations based on a Fundamental Parameters

*Correspondence: andrea.busacca@ispc.cnr.it

approach and tuned for the geometry and X-ray source of our MA-XRF setup [2]. Moreover, simulations can be easily generalized for different experimental conditions. The simulations were run with a two-layers painting model representing a preparation layer and mixtures of pigments at the surface. The use of the synthetic data is important because the training is no longer dependent on the classical deconvolution of experimental XRF spectra and allows us to extend the models to work for various measurement settings (i.e., X-ray source parameters, anode material, acquisition time, measurement geometry). We have optimized the network architecture and their hyperparameters to maximize the performance in terms of speed and accuracy but also to limit the size of the network to make the evaluation possible with conventional GPU-based workstations. Finally, we show a comparison of the conventional and AI/ML methodology and present current applications in painting analysis.

References

[1] T. Schoonjans, et al., Spectrochim. Acta B 70(10-23), 2012.
[2] F. P. Romano, et al., J. Anal. At. Spectrom. 32(773-78), 2017.

Advances in Imaging Diagnostics

ORAL

In-depth structural and compositional assessments of aged terpenoid varnish layers

*M. Martínez-Weinbaum[1], L. Maestro-Guijarro[1], P. Carmona-Quiroga[1], S. Siano[2], M. Castillejo[1], D. Ciofini[2], M. Oujja[1]**

[1] Instituto de Química Física Rocasolano, CSIC; C/ Serrano 119, Madrid, Spain
[2] Istituto di Fisica Applicata "N. Carrara", CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

Keywords: Nonlinear optical microscopy, Multiphoton excitation fluorescence, Laser-induced fluorescence, terpenoid varnishes, artificial aging

Varnishes are employed in painted artworks for protection from atmospheric pollution and oxidation and for improving the aesthetic appearance of paintings by providing an even and brilliant surface finish. Varnishes undergo complex and differentiated structural and chemical changes over time depending on their composition and conservation conditions. The present work investigates the degradation due to aging of the outermost layers of varnishes as a function of depth by using nonlinear optical microscopy (NLOM) [1] in the modality of multiphoton excitation fluorescence (MPEF). This totally non-invasive technique has been employed for the determination, with a high axial and lateral resolution, of the affected regions of pictorial varnish layers resulting from various types of degradation [2,3]. In this work, terpenoid varnishes such as dammar, mastic, shellac and sandarac, subjected to various types and degrees of aging, natural, artificial and a combination of the two, were tested. A homemade nonlinear optical microscope, based on a tightly focused pulsed femtosecond laser emitting at 800 nm, was used for the investigation. Single-photon laser-induced fluorescence (LIF) measurements served to determine the degree of surface aging and the optimum NLOM-MPEF operating conditions and helped to interpret the results obtained applying the latter [4]. These results signpost the correlations of the nature of the varnish layer, the initial thickness and the type and extent of aging with the in-depth degradation gradients determined by NLOM-MPEF.

**Correspondence: m.oujja@iqfr.csic.es*

Acknowledgments

This research has been funded by the Spanish State Research Agency (AEI) through project PID2019-104124RB-I00/AEI/1013039/501100011033, by the H2020 European project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science, GA 871034). Support by CSIC Interdisciplinary Platform "Open Heritage: Research and Society" (PTI-PAIS) is acknowledged.

References

[1] A. Dal Fovo, M. Castillejo, R. Fontana, Nonlinear optical microscopy for artworks physics, La Rivista del Nuovo Cimento 44 (2021) 453-498.

[2] G. Filippidis, M. Mari, L. Kelegkouri, A. Philippidis, A. Selimis, K. Melessanaki, M. Sygletou, C. Fotakis, Microsc. Microanal. 21 (2015) 510-517.

[3] M. Oujja, S. Psilodimitrakopoulos, E. Carrasco, M. Sanz, A. Philippidis, A. Selimis, P. Pouli, G. Filippidis, M. Castillejo, Phys. Chem. Chem. Phys. 19 (2017) 22836-22843.

[4] D. Ciofini, M. Oujja, M. V. Cañamares, S. Siano, M. Castillejo, Microchem. J., 141 (2018) 12-24.

Use of Laser Additive Technologies for Restoration of Artworks

V. Parfenov[1], S. Igoshin[2], D. Masaylo[2], A. Orlov[2], D. Kuliashou[3]*

[1] St. Petersburg Electrotechnical University, Department of Photonic, Faculty of Electronics, 197376 St. Petersburg, Russia
[2] Peter the Great St. Petersburg Polytechnic University, Institute of Mechanical Engineering, Materials and Transport, 195251 St. Petersburg, Russia
[3] Center of Prototyping, 197376 St. Petersburg, Russia

Keywords: laser additive technologies; 3D scanning, Cultural Heritage object, restoration, reconstruction

In recent decades, one of the most serious challenge in the preservation of cultural and historical heritage (CH) has been the rapid decay of exterior monuments due to environmental deterioration, especially in large industrial megapolises. However, in addition to poor environmental conditions, sculptures and other CH objects also suffer from natural disasters and vandal attacks, which also result in damage and sometimes total loss. In this context, the question on the need to reconstruct damaged CH objects or to gradually replace them with copies with subsequent transfer of originals to closed museum premises was on the agenda. According to the world practice, today, it is the only opportunity to preserve the most important monuments of the past for descendants, at least their most valuable ones.Innovative 3D laser scanning technology in combination with stone milling machines with numerical software control is attractive way of replicating CH objects. This allows copying sculptural monuments made of natural stone (marble, limestone, granite, etc.). The main advantage of this method is that it is contactless and does not have any negative impact on the original monument. Thanks to this, laser-based contactless copying technology is now widespread in some European countries [1–3]. Ultimately, copying CH objects using natural stone is expensive, and it is not always advisable to use this approach. A different approach can be used to replicate ordinary artifacts and to create copies of lost fragments of works of art for modeling restoration work. Such tasks can be resolved by means of using laser additive technologies.

**Correspondence: restlaser@gmail.com*

In the paper we will present the results of several experimental works devoted to combined use of 3D scanning and laser additive technologies for repairing and reconstructing CH objects in St. Petersburg city. We used stereo-lithography and direct metal laser sintering (DMLS) technologies.

As far as we know, reconstruction of damaged cast iron historical objects using DMLS is a first case study at all of such sort of restoration works using lasers.

References

[1] Fowles, P.S. The Garden Temple at Ince Blundell: A Case Study in the Recording and Non-Contact Replication of Decayed Sculpture. J. Cult. Herit. 2000, 1, S89–S91. https://doi.org/10.1016/S1296-2074(00)00190-4.

[2] La Pensée, A.; Parsons, J.; Cooper, M.; Broadbent, S.; Bingham, R. The Use of 3D Laser Scanning and 3D Modelling in the Realisation of an Artistic Vision; Production of Large Scale Public Art in Tudor Square, Sheffield. In Proceedings of the International Archives of Photogrammetry, Remote Sensing and Spatial Information Sciences, Newcastle upon Tyne, UK, 21–24 June 2010; Volume XXXVIII, pp. 375–380.

[3] Parfenov, V.A. Non-Contact Replication of Marble Sculptures Using Laser Technology, in: Sculpture of XVIII-XIX Centuries in out-Door Environment; St.Petersburg`s museum of Urban Sculpture Publishing house: St.Petersburg, Russia, 2010; pp. 66–69.

A NOVEL PARADIGMA FOR ACCURATE LASER MICROPROFILOMETRY OF POLYCHROME ARTWORKS BASED ON DUAL REFLECTANCE-HEIGHTS SURFACE DATASET

*S. Mazzocato** and C. Daffara

Department of Computer Science, University of Verona, Strada le Grazie 15, 37134, Verona, Italy

KEYWORDS: optical microprofilometry, surface metrology, surface monitoring, conoscopic holography

In this research we explore the use of the optical scanning microprofilometry and surface metrology as a complementary technique for the inspection of the microsurface of polychrome artworks, based on a accurate, reliable model of the texture features at submillimeter scale (order of ten microns). As reported in literature, this technique has proven effective in collecting high resolution and high accuracy microsurface dataset on variegate objects [1], which are being analysed as rendered “raking light” model in support to diagnostic imagery [2] or quantitatively by metrology descriptors [3]. However, it is recognized that a crucial problem in the use of microprofilometry for artwork monitoring is the difficulty to spatially register the microsurface datasets, due to lack of reference in the heights data with respect to the “visually legible” artwork surface. Motivated by this need, we present in this work a novel profilometry workflow that goes beyond the usual paradigma. Beside the quantitative inspection of the microsurface, we demonstrate the use of the raw reflectance values in order to collect other meaningful information of these challenging artworks. In detail, the optical microprofilometer is based on conoscopic holography sensors and micrometric scanning stages that measures the surface heights with a micrometer accuracy, pointwise and in continuous scanning, on the sampling area [1]. Along with the interferometric measurements we exploit the raw data collected by the sensor, i.e. containing the laser intensity values just after the backscattering of the beam from the surface. The joint exploration of these two spatially registered datasets turns to be very useful for cultural heritage applications: on the one hand, the heights map allows to

*Correspondence: sara.mazzocato@univr.it

quantitatively measure the surface topography, on the other hand, the reflectance map carries "some" information about the material texture, e.g. pigments. On this regard, it is worth nothing that the wavelength of the laser beam is 655 nm and the different surface colors absorb or reflect the radiation differently. Thus, the reflectance map can be employed for several applications such as the optimization of the signal collect from the sensor, the visualization of the craquelure of a painting and the color-based segmentation of the different parts of an artwork. The proof-of-concept of the novel microfilometry workflow exploiting a dual reflectance-heights dataset is given through exemplary applications on genuine artworks, from 3D archaelogical objects to 2D ancient paintings.

Acknowledgements

The financial support of this work has been provided by Eu Project SCAN4RECO and POR FESR Project TEMART.

References

[1] N Gaburro et al, A versatile optical profilometer based on conoscopic holography sensors for acquisition of specular and diffusive surfaces in artworks, Proc. SPIE, 10331, 2017, 48–56

[2] J Striova et al, Optical devices provide unprecedented insights into the laser cleaning of calcium oxalate layers, Microchem J, 124, 2016, 331–337

[3] C Daffara et al, Multiscale roughness analysis by microprofilometry based on conoscopic holography: a new tool for treatment monitoring in highly reflective metal artworks, Eur. Phys. J. Plus, 137, 2022, 430

Integrating Thermal Quasi-Reflectography in manuscript imaging diagnostic protocols to improve non-invasive chemical investigation

D. Cimino[1*], *G. Marchioro*[2], *C. Daffara*[1*]

[1] OpDATeCH Optical Devices and Advanced TEchniques for Cultural Heritage Lab, Computer Science Department, University of Verona, Ca' Vignal 2, Strada Le Grazie 15, 37134 Verona, Italy
[2] LaMeDan Laboratorio di studi Medievali e Danteschi, Cultures and Civilizations Department, University of Verona, Viale Università 4, 37129 Verona, Italy

Keywords: thermal quasi-reflectography, mid-infrared imaging, material characterisation, multimodal&multispectral, manuscript.

The awareness of the uniqueness of human beings' art production makes the application of non-invasive diagnostic approaches mandatory. For years manuscript investigation has considered a multi-technique protocol, where UV-Vis-IR imaging is the first fundamental step. Indeed, the resulting image stack can describe the object in its artistic value and production other than its conservation state from the varnish layer down to the underdrawing. Despite that, the lack of chemical information, sometimes estimated by induced-UV fluorescence or false colour processing, requires a further step to be carried out by analytical spectroscopies [1].

The present work introduces a holistic approach which flanks multispectral UV-Vis-IR imaging with Thermal Quasi-Reflectography (TQR) [2], an innovative imaging technique in the medium wave IR range (MWIR, 2.5÷5 μm), whose diagnostic potential is well demonstrated on paintings but still not explored on manuscripts. While reflectography in the near IR provides information related to the layers underneath (e.g. hidden traces and underdrawing), the TQR technique acquires in quasi reflectance approximation the MWIR signal from the artwork surface, directly linked with the chemical composition, highlighting not only organic and inorganic materials, but differences among chemical families as suggested by preliminary tests.

After a proper optimization of the imaging protocol and the source-camera setup, the MWIR range ensures a sharp imaging tool with suitable spatial and contrast resolution since this thermal band

*Correspondence: dafne.cimino@univr.it; claudia.daffara@univr.it

exhibits low optical diffraction and background radiation [3].

Thanks to this multimodal and multispectral protocol carried out in the broader UV-MWIR range, the historical book heritage of Verona (with its spearheads in the Capitular Library and National Archive collections) is being investigated in a collaborative project. The ancient manuscripts can be characterised in their original matters, conservation state, retouching areas, layers overlapping, and hidden writings consequence of ink evanescence, ensuring a holistic non-invasive approach with portable instrumentation.

Acknowledgements

The financial support for this work has been provided by the Capitolare LaMeDan Project.

References

[1] J. K. Delaney, P. Ricciardi, L. D. Glinsman, M. Facini, M. Thoury, M. Palmer, E. R. D. L. Rie, Studies in Conservation, 59(2), 2014, 91-101.

[2] C. Daffara, D. Ambrosini, L. Pezzati, D. Paoletti, Optics Express, 20(13), 2012, 14746-14753.

[3] C. Daffara, S. Parisotto, D. Ambrosini, Optics and Laser in Engineering, 104, 2018, 266-273.

Technological and Methodological Advances

POSTER

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Characterisation and quantification of light elements in archaeological steels by Laser Induced-Breakdown Spectroscopy

S. Richiero[1,2,3], X. Bai[2], P. Dillmann[4], C. Comby-Zerbino[5], B. Mille[2], T. Calligaro[2], V. Motto-Ros[5], F. Téreygeol[4], N. Wilkie-Chancelier[1], V. Detalle[2]*

[1] SATIE, Systèmes et Applications des Technologies de l'Information et de l'Energie, CY Cergy-Paris Université, ENS Paris-Saclay, CNRS UMR 8029, 5 mail Gay Lussac, 95031 Neuville sur Oise, France
[2] Centre de Recherche et de Restauration des Musées de France (C2RMF), 14 quai François-Mitterrand, 75001 Paris, France
[3] Fondation des sciences du patrimoine/EUR-17-EURE-0021, Cergy-Pontoise cedex, France
[4] LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France
[5] Institut Lumière Matière, UMR5306, Univ.Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne, France

Keywords: archaeological steels, light elements detection, LIBS, carbon, phosphorus, mapping

Ferrous alloys related to steel, which is an iron-carbon material, have been ubiquitous on archaeological sites since the Iron Age. Their study helps to provide informations on the lifestyle of ancient populations. An important criterion for characterising ancient alloys is the quantification of carbon (present at levels from 0.02 to 1% approximately) and phosphorus (present at levels of the order of several thousand µg/g). These elements have a direct influence on the mechanical properties. The quantification of these elements allows a better understanding of their production chain, their exchange and use value and possibly their age. Due to the heterogeneous atmospheric conditions in the reduction structures during the ore reduction process, carbon is heterogeneously distributed in ancient alloys. This limits the use of macroscopic or chemical methods that are bulk analysis methods. One possible time consuming method to determine locally the carbon content is metallography by microscopic observation after Nital and Oberhoffer etching taht allow spatialization of carbides. The metallographic method has some uncertainties, as It is not suitable for so-called "non-equilibrium" conditions, i.e. with rapid cooling, which is the case

**Correspondence: sarah.richiero@culture.gouv.fr*

most often in archaeological contexts. Indeed, the structures resulting from rapid cooling (martensite, bainite, widmanstätten) do not allow the use of thermodynamic diagrams necessary for the determination of the carbon content.

In this work, we present The ELEGAN project, started in October 2021, proposes to use the laser-induced breakdown spectroscopy (LIBS) to quantify and locate carbon and phosphorus in steel in order to meet the needs of this type of research.

LIBS instruments are adaptable to different constraints. It is possible to carry out analyses in situ to limit sampling. 3D identification and high resolution mapping, which can be produced in laboratories, are available for quantifying carbon and locating concentration variations while reducing analysis time. The limit of detection of LIBS makes it possible to observe light elements present in an iron matrix and make possible non-equilibrium characterization.

In this study, the first elements consist in the validation of the LIBS quantification by the comparison of these results with those obtained by Laser ablation-induced coupled plasma-mass spectroscopy (LA-ICP-MS) and Nuclear Reaction Analysis (NRA). Then the improvement of LIBS method will be carried out for the applications in archaeological issues.

We will show the first results of LIBS mapping performed on our reference samples. The surface and depth mapping allows us to examine the elemental stratigraphic distribution, to discriminate the carburized zones of the steel and to identify the presence of other elements.

References

[1] X. Bai, H. Allègre, M. Gosselin, P. Dillmann, M. Lopez, F. Téreygeol, V. Detalle, Impact of laser- induced breakdown spectroscopy implementation for the quantification of carbon content distribution in archaeological ferrous metals, Spectrochim. Acta B At. Spectrosc., 172 (2020). 105964.

[2] X. Bai, M. Gosselin, P. Dillmann, F. Téreygeol, H. Allégre, J. Auber-Le Saux, V. Detalle, Quantitative mapping of carbon content in archaeological ferrous metals with laser-induced breakdown spectroscopy, SPIE, (2021).

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Laser Induced Breakdown Spectroscopy (LIBS) to classify different gold leaves shades

F. Surma[1*], *P. Schloegel*[1], *V. Aguilar*[3], *M. Laboure*[2], *L. Rosenbaum*[1]

[1] Epitopos, Strasbourg, France
[2] Mescla, Strasbourg, France
[3] Ecole et Observatoire des Sciences de la Terre, University of Strasbourg, France

Keywords: spectroscopy (LIBS), gilding, conservation, gold leaf, PCA

In cultural heritage, different gold leaves shades can be used: red, orange, green, yellow and white gold depending the context. With time and alterations, the original color can be modified. In order to characterize gildings during the restauration process, Laser Induced Breakdown Spectroscopy (LIBS) has been used to study different shades samples. Gold leaves of different colors were applied on a red ocher base and a wide number of laser analyses were performed on each one. The laser beam is pointed on a surface sample and the high-temperature micro-plasma created is recorded optically. The collected spectrum of light emission gives the intensity of specific wavelengths and then characterizes the composition. It is a semi destructive method (spot of 200 µm) that can be performed on site and which provides the elementary composition of the gilding. Elementary differences appeared on LIBS spectra. Therefore, particular gold (Au), silver (Ag), copper (Cu) and zinc (Zn) emission lines are studied. Statistical analyses such as ternary charts and Principal Component Analysis (PCA) were realized in order to separate chemically gildings. Principal component analysis (PCA) is a process of computing the principal components and using them to perform a change of basis on the data, sometimes using only the first few principal components and ignoring the rest. Thanks to statistical processing, red, orange, yellow, green and white gildings could be chemically classified. Thereby, this approach using LIBS could be performed on site, on altered gildings, to help restorers and gilders in their work.

*Correspondence: fabrice.surma@epitopos.fr

Acknowledgements

The financial support of this work has been provided by Epitopos and Mescla. We want to thanks Carla Laboure, restorer, for samples preparation.

References

[1] Vallet J.- M. , Detalle V. , Guillon O.1, Trichereau B., Mouhoubi K. ,Syvilay D., Bodnar J.-L., Analyses non destructives et in situ des dorures des fresques de Giovannetti à Villeneuve-lez-Avignon (France), Conference paper RIPAM at Marseilles, 2013.

[2] Andreas Ionardis, Javier Garcia-Guinea, Gold gilding and pigment identification on a post-byzantine icon from Kastoria, Northern Greece, Analytical Letters, 46:6, 2013, 936-945.

[3] Aidan Hart, Gilding techniques, aidanharticons.com.

[4] Jose L. Perez Rodriguez, Maria D Robador, et al., Non-Invasive analytical techniques applied to characterize the components of ancient golden medallions, Heritage Science, 4:4, 2013.

[5] Sandu Irina et al., A comparative multi-technique investigation on materiel identification of gilding layers and the conservation state of 7 Portuguese mannerist altarpieces, International Journal of Conservation science, Volume 6, Special Issues, 2015,439-454.

[6] Sandu Irina et al., Gilding techniques in religious art between and west, 14th-18th centuries, International Journal of Conservation science, Volume 6, Issue 1, January-March 2010,47-62.

[7] Sergio Musazzi, Umberto Perini, Laser-Induced Breakdown Spectroscopy Theory and Applications, Springer Series in Optical Sciences, Volume 182, 2014, pages 452 and 320.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

LIBS vs XRF application on underwater heritage: the case study of the silver coins of the frigate "Nuestra Señora de las Mercedes"

I. Donate Carretero[1], M. Oujja[2], M. Martínez-Weinbaum[2], S. Díaz[1], E. García[1], M. Bueso[1], M. Castillejo[2] , M. Martín[1]*

[1] Instituto del Patrimonio Cultural de España, Ministerio de Cultura y Deporte, C/ Pintor el Greco 4, Madrid, Spain
[2] Instituto de Química Física Rocasolano, CSIC; C/ Serrano 119, Madrid, Spain

Keywords: Laser induced breakdown spectroscopy, X-ray fluorescence, Frigate Mercedes, Underwater metallic heritage, Silver alloy.

Underwater cultural heritage entails complex conservation problems. Particularly, metallic artefacts under aerobic marine conditions suffer from severe corrosion that produces thick patinas, in addition to the deposition of concretions of the seabed. The nature of these degradation layers depends on several factors: the original composition of the metallic alloys, along with the minor elements and traces, the metallurgical processes for obtaining metals and manufacturing and the environmental conditions on the seabed [1]. As a consequence, the conservation and study of these metal objects are challenging.

This work presents a comparative investigation using two non-invasive elemental analytical techniques, laser-induced breakdown spectroscopy (LIBS) [2] and X-ray fluorescence (XRF) [3], for chemical characterization of underwater corroded metals.

In this case study, the considered pieces were selected from the treasure of the Spanish frigate "Nuestra Señora de las Mercedes", a ship loaded with funds and products from the Viceroyalty of Peru and sank by the British Army in 1804 off the coast of Algarve in Portugal. In 2007 the treasure was plundered by the commercial company *Odyssey Marine Exploration*, but after a legal battle in a US court it was recovered by the Spanish State [4]. The pieces are six coins ("reales de a ocho") made of 925 sterling silver, belonging to two different Spanish-American mints, Potosí and Lima, and produced between the years 1797 and 1804.

LIBS analyses were carried out in air under nanosecond laser

*Correspondence: inmaculada.donate@cultura.gob.es

excitation at 266 nm and XRF studies were performed in the same areas explored by LIBS, using an X-ray tube with rhodium anode and peak voltage of 50 kV.

The comparison of the obtained results indicates that, while XRF is effective in characterizing the main corrosion products of the surface of the coins, such as silver chloride and bromide, copper chlorides and carbonates, LIBS analysis allows to identify the original composition of the metallic core, including minor elements as Ni, Hg and Co, regardless of the patina components. Therefore, the complementarity of both techniques is demonstrated: XRF helps to answer inquiries associated to the conservation and restoration of the metallic pieces and LIBS can solve questions about their core composition and metallurgical techniques.

Acknowledgements

This research has been funded by the Spanish State Research Agency (AEI) through project PID2019-104124RB-I00/AEI/1013039/501100011033, by the H2020 European project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science, GA 871034). Support by CSIC Interdisciplinary Platform “Open Heritage: Research and Society” (PTI-PAIS) is acknowledged.

References

[1] E. Angelini, S. Grassini, S. Tusa. Corrosion and conservation of cultural heritage metallic artefacts: 12. Underwater corrosion of metallic heritage artefacts. European Federation of Corrosion (EFC) Series. Elsevier Inc. Chapters. 2013.

[2] J. P. Sing, S. Thakur (Eds.). Laser-Induced Breakdown Spectroscopy. 2nd Edition. Elsevier, 2020.

[3] C. Streli, P. Wobrauschek, P. Kregsamer, X-ray Fluorescence Spectroscopy, Applications, Encyclopedia of Spectroscopy and Spectrometry, 1999, pp: 2478-2487.

[4] S.G. Ramirez, C. M. Alonso. El último viaje de la fragata Mercedes. La razón frente al expolio. Un tesoro cultural recuperado. RdM. Revista de Museología: Publicación científica al servicio de la comunidad museológica, 2014, no 61, pp. 89-99.

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Digital holographic interferometry (DHI) to in situ register the dynamic behavior of concrete 20th century building heritage

F.M. Vincitorio[1], G. Bolla[1], A. Flores[1], M. Gomez-Coronel[1], A. Ramil[2], A.J. López[2]*

[1] Facultad Regional Paraná, Universidad Técnica Nacional, Entre Ríos, Argentina
[2] Laboratorio de Aplicacións Industriais do Láser. Campus Industrial de Ferrol. Universidade da Coruña,1547, Ferrol, Spain

Keywords: Digital Holographic Interferometry, Concrete, in situ diagnostics.

In the last 100 years concrete and steel have been the most common building materials, so that they constitute the core of the structures on which the architecture of the 20th century is based. However, historic concrete buildings are at risk, among other things due to the limited understanding of concrete technology until the 1960s which resulted in more sensitive buildings than modern concrete buildings. In order to develop a monitoring system that allows the premature detection of structural problems in concrete, it was implemented a novel scheme of digital holographic interferometry (DHI) for in situ detection. The optical arrangment is based on lens-less Fourier digital holography and comprises a stabilised semiconductor laser source and optical fibre instead of the usual elements in a conventional set up[1]. DHI ensemble was arranged in an ad hoc plastic holder made by 3D printer. This plastic holder, designed entirely in 3D CAD, clamps the optical elements and routes of the optical fibres, to ensure adequate lighting and observation angles for hologram generation and the stability of the optical set up, even in presence of vibrations. This plastic holder allows the device to be attached directly to the specimen to be tested under dynamical excitation conditions. This system was tested on concrete specimens of different composition which were submitted to loads in the range 1000 kg – 28000 kg by using an Amsler hydraulic press. The obtained results, though preliminary, showed that it was possible to measure the radial deformation on normalized cylindrical specimens in the range of 4-10 μm[2]. These results open up new possibilities for the application of DHI in the

*Correspondence: ana.xesus.lopez@udc.es

field of preventive conservation of historic concrete buildings

References

[1] Kumar, R., Dwivedi, G., and Singh, O.,Portable digital holographic camera featuring enhanced field of view and reduced exposure time," Optics and Lasers in Engineering 137, 106359 (2021)

[2] Fabio M. Vincitorio et al. A novel method based on digital holographic interferometry (DHI) to in-situ register the dynamic behavior of concrete 20th century building heritage. Proc. SPIE 11784, Optics for Arts, Architecture, and Archaeology VIII, 117840G (8 July 2021); https://doi.org/10.1117/12.2592112

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

Determination of Camphor Content in Celluloid Bookbindings by Raman Spectroscopy

*V. Knotek**, *N. Šipošová, J. Neoralová, P. Vávrová*

The National Library of the Czech Republic in Prague, Collections Preservation, Development and Research Laboratories, Sodomkova 2, 102 00 Prague 15, Czech Republic

Keywords: Raman spectroscopy, cellulose nitrate, camphor, degradation

Research on bookbindigs from celluloid (cellulose nitrate plasticized by camphor) is a part of national project named "Synthetic materials in the modern library collections". The modern library collections are dated from the beginning of 19th century to the present, and the first semi-synthetic materials appeared in the second half of 19th century. One of the goals of the national project is research and development of non-destructive survey and identification of various types of synthetic materials of bookbinding and their degradation processes and condition. Many books from modern library collection contain synthetic materials as a part of their bookbindings.

The modern library collections contain books with celluloid bookbindings in many types of design, mainly as the imitation of tortoiseshell and nacre. Degradation process of cellulose nitrate involves the release of plasticizer and harmful oxides. The degradation process leads to the decay of the specimen and may also be dangerous for surrounding objects [1].

In this work, samples of commercial imitations of tortoiseshell and nacre made of celluloid were artificially aged in Q-SUN Xenon test chamber and partially extracted by toluene. The content of nitrogen was evaluated by ATR-FTIR spectroscopy [2]. The evaluation of camphor content by ATR-FTIR is problematic due to the formation of carbonyl groups during aging. Therefore, an approximate model for determining the camphor content of celluloid by Raman spectroscopy was developed. A Bruker Bravo handheld Raman spectrometer was used for the measurement.

**Correspondence: vitezslav.knotek@nkp.cz*

Acknowledgements

The authors would like to acknowledge the Ministry of Culture of Czech Republic for financial support within the framework of the Program of Applied Research and Development called NAKI II (project no. DG18P02OVV001).

References

[1] Y. Shashoua, Conservation of Plastics: Materials Science, Degradation and Preservation, Routledge, 2008, pp. 177-180.

[2] S. Nunes, F. Ramacciotti, A. Neves, E. M. Angelin, A. M. Ramos, É. Roldão, N. Wallaszkovits, A. A. Armijo, M. J. Melo, A diagnostic tool for assessing the conservation condition of cellulose nitrate and acetate in heritage collections: quantifying the degree of substitution by infrared spectroscopy. Heritage Science 8 (33), 2020

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

DECAY OF HISTORIC STONE MASONRY DUE TO THERMAL CYCLES AND SALT CRYSTALLISATION: NEW CHALLENGES IN A CHANGING ENVIRONMENT

R.E. Rizzo[1,2], C. Porfido[3,4], I. Butler[2], I. Allegretta[3], R. Terzano[3], O. De Pascale[4], G.S. Senesi[4]*

[1] Dipartimento di Scienze della Terra, Università di Firenze, Firenze, Italy
[2] School of Geosciences, University of Edinburgh, Scotland, UK
[3] Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari "Aldo Moro", Bari, Italy
[4] CNR - Istituto per la Scienza e Tecnologia dei Plasmi (ISTP) - sede di Bari, Italia

KEYWORDS: sedimentary rocks, freeze-thaw cycles, salt crystallization, micro computed tomography (μ-CT), laser-induced breakdown spectroscopy (LIBS)

Many of Italian and Scottish iconic monuments are built using porous sedimentary rocks. Increasing levels of extreme weather events can lead to the increase of degradation of the historic fabric and loss of structural integrity through processes such as increased water penetration, more frequent freeze-thaw cycles and salt-induced decay.

Although geographically distant, the historic buildings in the two cities of Bari (Apulia) and Edinburgh (Scotland) are exposed to similar threats, i.e. both cities are located in the vicinity of sea water that exposes stone masonries to salt-induced decay (chemical weathering). At the same time, climate changes would expose the rock materials to unusual and unprecedented temperature conditions. In particular, temperature variations are responsible for physical damage of stonework of valuable heritage sites. For instance, freeze-thaw cycles in cold climates (Scotland), and expansion-contraction cycles in warm climates (Apulia), are responsible for inducing cracking in the stone masonry of many historical buildings. Furthermore, physical degradation (i.e., thermal cracking) often acts in combination with salt crystallization damage as the cracks caused by thermal damage would allow saline-rich fluids to penetrate in the inner parts of rock materials further exposing them to chemical weathering. Laboratory simulation of thermal and chemical conditions responsible for the degradation of

*Correspondence: giorgio.senesi@istp.cnr.it

historic stoneworks can actively contribute to conservation management plans. The combination of advanced analytical and imaging techniques can provide powerful tools for understanding and evaluating the damages occurring to historic stone materials exposed to the changing climate.

In this study two rock types have been selected and compared, i.e. a limestone (Calcare di Bari) and a sandstone (Binny Sandstone), which are representative and widely used building stones in the two areas of Bari and Edinburgh, respectively. Structural and elemental analytical techniques were combined with advanced analytical tools and modern 3D-imaging methods, i.e. computed tomography (CT) and micro computed tomography (μ-CT), laser-induced breakdown spectroscopy (LIBS), in order to study the degradation processes responsible for the damage of stone masonries in these two cities.

The mechanical damage due to freezing/thawing cycles and crystallisation of NaCl rich brines (salinity of about 3.5% (35 g/l) within these historical stones masonry has been tested and modelled by CT, μ-CT and LIBS, which provided new insights on the weathering processes damaging these stone buildings. In particular, pre- and post-imbibition CT and μCT acquisitions were conducted to visualize and describe salt crystallization patterns both at specimen surfaces and inwardly, moreover, it has been possible to evaluate the occurrence of mechanical damages such as cracks and particles detaching after the testing procedure. The CT 3D-rendering allowed to visualize the spatial distribution of porosity within the selected rock types which allowed to measure the percentage of connected pores representing preferential channels for water/fluid infiltration and percolation responsible for the stones' weathering degradation. Furthermore, the detection, identifications and microchemical mapping of the elemental composition of the mansory rock samples achieved by handheld LIBS analysis in real-time in the field have provided useful additional information on the physical processes that may occur in these stones weathering.

Acknowledgements

The financial support of this work has been provided by Joint Bilateral Agreement CNR/Royal Society of Edinburgh (Scotland) Biennial Programme 2021-2022.

LASER TREATMENTS

Laser Treatments of Metal Artefacts

ORAL

Pulse-Laser-Induced diagnostics of historical and artificial copper patina

A. Giesriegl[1], U. Pacher[1], T. Nagy[1], B. Pichler[2], W. Kautek[1]*

[1] University of Vienna, Department of Physical Chemistry, Vienna, Austria
[2] University of Applied Arts Vienna, Institute of Art and Technology, Vienna

Keywords: copper patina, laser ablation, laser cleaning, diagnostics, LIBS

The history of copper in architecture can be linked to its durability, corrosion resistance, and prestigious appearance. Environmental influences that lead to the formation of patina layers not only affect copper surfaces in architecture but also in microelectronics, medicine and automotive technologies. Corrosion monitoring by the deployment of in-situ nanosecond pulse laser depassivation of protective conversion layers has been addressed in the context [1,2].

In this study, the analysis of destruction and reformation of protecting anodic oxide films such as copper oxides (e.g. cuprite, Cu_2O) and brochantite ($CuSO_4 \cdot 3Cu(OH)_2$) on historical copper roofing sheets from the Belvedere Castle, Vienna, allowed insight into the mechanism of long-term protection on objects of cultural heritage. Surface and layer analyses were employed by scanning electron microscopy and energy dispersive X-ray spectroscopy on both artificial [3] and natural patina on original roofing sheets of the Belvedere Palace built by Prince Eugene of Savoy 1723. The possibilities of laser cleaning and laser-induced stratigraphy were explored for the first time on cuprite and brochantite. In order to explore an alternative to conventional cleaning methods of soiling on patina surfaces, the removal of model soiling was investigated. The cleaning thresholds for these contamination layers were determined. They are orders of magnitude smaller than those of the cuprite and brochantite layers. Thus, the possibility of a laser intervention was demonstrated. Through spectroscopic analyses using Laser-Induced Breakdown Spectroscopy (LIBS) [4], the ablation processes of patina films could be quantitatively monitored. Based on these data, physical-chemical strategies were developed to avoid destruction of

*Correspondence: wolfgang.kautek@univie.ac.at

the metals or oxide layers during a cleaning intervention.

References

[1] T. Nagy, U. Pacher, A. Giesriegl, L. Soyka, G. Trettenhahn, W. Kautek Appl. Surf. Sci. 302 (2014) 184–188.
[2] T.O. Nagy, M.J.J. Weimerskirch, U. Pacher, W. Kautek Z. Physik. Chem. 230 (2016), 1303–1327.
[3] B. Pichler, ICOMOS–Hefte des Deutschen Nationalkomitees 29 (1998) 63-69.
[4] T.O. Nagy, U. Pacher, A. Giesriegl, M.J.J. Weimerskirch, W. Kautek, Appl. Surf. Sci. 418 (2017) 508-516

The use of femtosecond laser pulses in the cleaning of archaeologically corroded iron and copper objects

D. Prokuratov[1,2,3*], *D. Pankin*[4], *A. Samokhvalov*[5], *N. Kurganov*[6,7], *O. Vereshchagin*[8], *R. Balmashnov*[9], *A. Povolotckaia*[4], *A. Shimko*[4], *A. Mikhailova*[4]

[1] The State Hermitage Museum, Saint-Petersburg 190000, Russia
[2] Heritage Science laboratory, ITMO University, Saint Petersburg 199034, Russia
[3] Department of Photonics, Saint Petersburg Electrotechnical University "LETI", Saint-Petersburg 197022, Russia
[4] Center for optical and laser materials research, Saint Petersburg State University, Saint Petersburg 198504, Russia
[5] International laboratory "Laser micro-and nanotechnologies", ITMO University, Saint Petersburg 197101, Russia
[6] Conservation Department, Faculty of Arts, Saint Petersburg State University, Saint Petersburg 199004, Russia
[7] Institute of the History of Material Culture of the Russian Academy of Sciences, Saint Petersburg 191186, Russia
[8] Mineralogical Department, Institute of Earth Sciences, Saint Petersburg State University, Saint Petersburg 199155, Russia
[9] "Lasers & Optical Systems" Co. Ltd. Saint Petersburg 199053, Russia

Keywords: laser cleaning, conservation, ablation, femtosecond pulses

Over the past three decades, laser cleaning has become a successful, widely accepted art restoration technique. It has been proven to be a highly effective and environmentally safe approach with many advantages over traditional restoration techniques. The most significant results were achieved in the field of restoration of stone artifacts. The situation, however, is much more complex with cleaning of metal objects. Despite several successful examples, the procedure remains challenging due to various problems such as localized melting and possible surface discoloration.

Here, we report the results achieved along a 10-years research. The aim of this work was to investigate the possibility of using a laser cleaning technique for the conservation of various cultural heritage objects: archaeologically corroded copper and iron items; the role of laser irradiation parameters (wavelength and pulse duration) was examined.

*Correspondence: denis.prokuratov@gmail.com

Laser irradiation was applied using different wavelengths: 355, 532, 1064 nm, 2.97 and 10.6 μm. Comparison of results for pulse duration of 100 μs, 100, 25, 8, 6 ns, 75 ps, and 100 fs was performed. Laser irradiation of iron corrosion samples was studied in various environments: air, helium, argon atmosphere, water, ethanol, engine oil, and glycerin.

The optical microscopy, Raman spectroscopy, Scanning Electron Microscopy, X-ray photoelectron spectroscopy and X-ray diffraction techniques were used for the surface analysis.

Results demonstrated that the cleaning with micro-, nano- and picosecond pulses did not allow the ablation of iron and copper corrosion layers without changing their color at any irradiation fluence. Only spallation ablation by femtosecond laser pulses allowed performing layer-by-layer cleaning without structural modification of corrosion. Overall, our results indicated that the pulse duration is a much more important parameter in preservation of the surface during laser cleaning of metals than previously anticipated. Therefore, laser cleaning of metal corrosion from the surface of cultural heritage objects requires careful selection of laser energy parameters with particular attention to pulse duration.

The restoration of the amalgam gilded bronze elements and of the enamelled and gilded strips of the Baptismal Font of Siena: remarks on laser ablation in combination with other cleaning methods

S. Agnoletti[1], L. Bartoli[2], M. Baruffetti[1], P. Belluzzo[1], A. Brini[1], A. Cagnini[1], S. Casu[3], E. Della Schiava[3], M. Galeotti[1], A. Mignemi[3], M. Nesi[3] C. Ortolani[1], S. Porcinai[1], E. Tartaglia[1]*

[1] Opificio delle Pietre Dure di Firenze, Laboratori di restauro
[2] El.En SpA, Calenzano, Italy
[3] Individual conservation-restoration enterprises

Keywords: Laser ablation, amalgam gilding, bronze, enamel, cleaning

The Baptismal Font of Siena is a very complex artwork, created between 1417 and 1430 by several artists. This paper refers to the work in progress in Florence, at the Opificio delle Pietre Dure (Laboratorio di restauro del Settore Bronzi e Armi Antiche). The restoration work deals with all the bronze sculptural elements, consisting of six panels (approx. 60x60 cm^2) with the stories of the Baptist, six sculptures of the Virtues (h ca 50 cm), four putti (h ca 41 cm) and the tabernacle door (ca 47x23 cm^2), all decorated by mercury amalgam gilding (also known as fire gilding). In addition, there are 12 enameled and gilded strips (ca 100x4 cm^2). All these bronze elements were executed by different workshops and artists, such as Iacopo della Quercia, Giovanni di Turino, Goro di ser Neroccio, Lorenzo Ghiberti, and Donatello1.

At the moment, the cleaning has been completed only on the Banchetto di Erode panel and on a Virtue (the Hope), both executed by Donatello, and on two other Virtue: the Charity by Giovanni di Turino and the Fortitude by Goro di ser Neroccio.

It is well known that the laser cleaning of gilded bronzes was developed during the restoration of the Gates of Paradise made by Lorenzo Ghiberti and it was subsequently adopted for the restoration of the other doors of the Florentine Baptistery. Since then, LASER ablation has been used for various cases and materials, whether involving or not surface gilding [2-4].

*Correspondence: stefania.agnoletti@cultura.gov.it

In this new case-study, the cleaning of large amalgam gilded surfaces specifically focused on indoor stored artworks characterized by different maintenance substances. The consequent conservation issue concerns the interaction of metal substrate with these substances (such as waxes, oils and varnishes) and with the effects of some drastic cleaning methods operated in the past.

The operative method selected by the conservation team was based on a combined approach to remove altered material from the surface. Particularly effective was a preliminary step based on the treatment with steam and the cleaning with 'oil in water' (OW) emulsions, which allowed to thin the organic layers and to proceed with lower fluence laser cleaning. The choice of the type of laser and the operating parameters, along with the scientific investigations aimed at the characterization of surface materials and the monitoring of ablation, have suggested insights on the effectiveness of some operating solutions.

Particularly interesting were also the twelve distributed along the perimeter of the hexagonal font. This contribution describes the laser cleaning of gilded copper inscriptions and racemes that stand out on enameled backgrounds, combined with investigations and technological studies.

Acknowledgements

The financial support of this work has been provided by Opera Metropolitana di Siena.

References

[1] P. Bacci, Jacopo della Quercia: nuovi documenti e commenti, Siena, 1929; G. Fattorini, Dalla “historia d’attone pel Battesimo” a “le porti di bronzo del Duomo”: Donatello e gli inizi della scultura senese del Rinascimento, in Pio II e le arti. La riscoperta dell'antico da Federighi a Michelangelo, Siena, 2005, pp. 45-81.

[2] S. Siano, R. Salimbeni, The Gate of Paradise: physical optimization of the laser cleaning approach, Studies in Conservation 46 (2001) 269-281.

[3] S. Siano, F. Grazzi, V. A. Parfenov, Laser cleaning of gilded bronze surfaces. Journal of Optical Technology 75 (2008) 419-427.

[4] S Siano, J Agresti, I Cacciari, D Ciofini, M Mascalchi, I Osticioli, AAMencaglia, Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd: YAG lasers, Appl Phys A 106 (2012) 419-446.

A NEW METHOD FOR LASER ABLATION IN UNDERWATER IRRADIATION CONDITIONS OF LARGE BRONZE ARTIFACTS

G. Rotondi[1*], A. Brini[1], F. Cantini[2,3,4]

[1] MIBACT - Opificio delle Pietre Dure di Firenze (OPD), Firenze, (Italy)
[2] Università degli Studi di Firenze, Dipartimento di Fisica e Astronomia, Sesto Fiorentino, (Italy)
[3] Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata Nello Carrara (CNR-IFAC), Sesto Fiorentino, (Italy)
[4] Istituto Nazionale di Fisica Nucleare, Laboratorio di Tecniche Nucleari per i Beni Culturali (INFN -Labec), Sesto Fiorentino, (Italy)

Keywords: laser ablation, underwater irradiation, conservation, gilded bronzes

A group of twenty-eight fragments of bronze statues from the Roman Age, recently underwent a series of conservation treatments, during the internship for the master's degree thesis held at "Scuola di Alta Formazione" (SAF) of Opificio delle Pietre Dure (OPD) in Florence (Italy). These fragments were seized by police from a depot near the Arno River basin and had never been thoroughly investigated or cleaned before.

During the restoration, supported by an extensive diagnostic campaign, an attempt was made to understand the conservation problems of the individual fragments, and to identify for each one the treatment that most respected the nature of the artifact and, at the same time, guaranteed the removal of undesirable materials.

This contribution aims to present a very significant case study of some of the bronze fragments.

Indeed, two fragments (dimensions: 14x58x68 cm and 10x55x48,5 cm; W-L-H), depicting a horse's neck with a mane, and identified as part of an equestrian monument, showed traces of gilding emerging from a thick layer of mineralization and encrusted sandy deposits even before the restoration (Fig. 1A). The bronzes were therefore subjected to cleaning tests by means of laser ablation in order to uncover possible additional gilding remains and evaluate the most suitable methods.

The results of the initial tests (conducted with laser ablation, chemical and mechanical means), discovered an incredibly well-

*Correspondence: giovanni.v.rotondi@gmail.com

preserved leaf-gilding. Some procedures were then evaluated, identifying the combination of preventive application of ion-exchange resins and subsequent laser ablation with a pulsed short free running Nd:YAG laser (λ = 1064 nm), an efficient and easily controllable cleaning system [1,2], as the most suitable treatment. We also observed that laser ablation allowed us to achieve better results in underwater irradiation conditions.

Due to the size and shape of the artifacts (featuring protruding details like the mane)) and the general state of conservation, it was impossible to submerge them completely or apply plastic films on the surface to set up “pockets” (Fig. 2A) filled with deionized water, as done by Mignemi 2009 [3]. This last method offers some additional advantages exploiting cavitation mediated processes [1,4-6].

This paper focuses on presenting another, innovative, approach able to provide the same benefits without exposing the artifacts to prolonged water submersion, applying adhesives to the sensitive foil-gilded surface, or being influenced by the geometry of the artwork. This process also avoided a lot of physical interaction with the artwork, leaving just the removal of the thicker sandy crusts and the cuprite residues to mechanical instruments.

The new method is based on a modified *water tank brush*, (Fig. 2C) in order to obtain a very localised “water bubble” without the need of any containing system applied to the surface. This method has proved to be very effective in the removal of the cuprite layer

Figure 1 – One of the fragments before (A), during (B) and after (C) the conservation treatment.

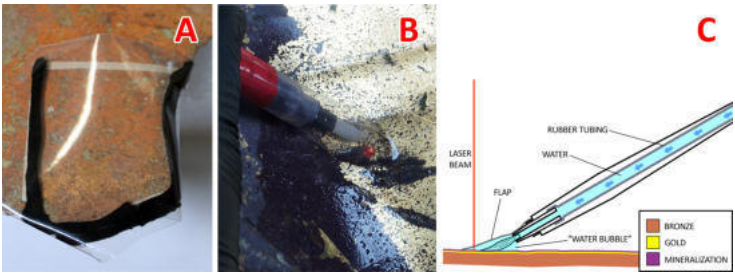


Figure 2 – (A) "Pocket" filled with deionized water (as done by Mignemi 2009 [3]); (B) Modified water tank brush in use during the laser ablation (C) Modified water tank brush diagram.

without affecting the underlying gold leaf, leaving just a few traces of the mineralised deposits (Fig. 1B-C; 2B).

The accuracy of this method was verified by analytical investigation before and after the procedure; it proved to be very selective and simple, yet an efficient approach to the cleaning of leaf-gilded bronzes of various and complex shapes.

Acknowledgements

The authors gratefully thank the management of the OPD, especially Dr. M. Ciatti (Superintendent of OPD), dr. L. Speranza (Director of the conservation of bronzes and ancient weapons OPD), dr. A. Patera (associate director of OPD Scuola di Alta Formazione), and dr. M. Salvini (officer of the Superintendence of Archeology, Fine Arts and Landscape for the metropolitan city of Florence and the provinces of Pistoia and Prato) for making this work possible.

They also wish to thank the staff of the OPD scientific laboratory for their valuable collaboration, and Dr. A. Mignemi for the precious suggestions.

References

[1] Siano, S., Agresti, J., Cacciari, I. et al., Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd: YAG lasers, Appl. Phys. A 106 (2012) 419–446.

[2] Siano, S., & Grazzi, F., Optimised pulse duration for the laser cleaning of oil gilding, Il Nuovo Cimento C 30 (2007) 123-128.

[3] Mignemi, A., Trattamenti di pulitura innovativi basati su tecniche chimiche e laser nel restauro del San Giovanni Battista del gruppo bronzeo

"Decollazione del Battista" di Vincenzo Danti, In: Il contributo degli Schiavoni molisani al restauro e alla conservazione in Europa, 2009, pp. 189-199.

[4] Siano, S., Salimbeni, R., Pini, R., Giusti, A., & Matteini, M., Laser cleaning methodology for the preservation of the Porta del Paradiso by Lorenzo Ghiberti, Journal of Cultural Heritage 4 (2003) 140-146.

[5] Siano, S., Pini, R., Salimbeni, R., & Vannini, M., Imaging and analysis of photomechanical effects induced in water by high-power laser-target interaction, Applied Physics B 62 (1996) 503-510.

[6] S Siano, R Salimbeni, Advances in laser cleaning of artwork and objects of historical interest: the optimized pulse duration approach, Account of Chemical Research 43 (2010), 739-750.

A new approach for the restoration of gilded surfaces : Revealing original decors of the "Bargueño" (16th century) by Er:YAG laser processing controlled by optical coherence tomography (OCT)

S. Courtier[*], *V. Detalle*[*]

Center of Reshearch and Restauration of the museum of France (C2RMF)

Keywords: OCT, laser ablation, diagnostics, conservation, gilding

The restoration of the gilded surfaces of the travel cabinet known as "the Bargueño", dating from the 16th century and originating from the Château de Pau, was carried out in the gilding workshop of the C2RMF by Stéphanie Courtier.

The preliminary study and analysis of the gilded wood and ivory surfaces have revealed the presence of two gildings underneath the oil gilding, made of different techniques and materials according to the composition of the supports. Originally the gilding is mixed, on the wooden parts a water gilding has been observed while on the ivory parts, it was an oil gilding. The oil gilding n° 2 covering all the original mixed gildings was removed during the renovation of the surface. The removal of the original decorations was then considered and led to a reflection on the feasibility of such a removal of two layers with the same binder. It should be noted that the conservation-restoration of original surfaces generally begins with the research of bibliographic sources, the knowledge and understanding of techniques, traces and the materiality of the object. During the restoration of gilded wooden works, cleaning and mechanical and/or chemical removal are commonly performed. These choices of intervention are related to the problem encountered and are influenced by the condition of the original surface. Although the range of tools available to the restorer is nowadays wide, in some cases, the physico-chemical properties of the materials make the choice of a satisfactory method challenging.

Following the Lacona XII congress, presenting the laser in Cultural Heritage Sciences and the current associated research, a study of the feasibility of removal with a pulsed Er: YAG laser (2940

*Correspondence: stephanie.courtier@culture.gouv.fr, vincent.detalle@culture.gouv.fr

nm, µs regime) on gilded ivory mock-ups was considered to overcome the limitations of traditional methods for this specific case of restoration. Indeed, the physical parameters of the laser (coherence, selectivity, energy and high precision) make it an appropriate tool for this kind of application. It allows to physically and/or thermally cleave the layers of interest, without direct contact with the material and with a micrometric or even sub-micrometric precision.

These pulsed laser removals have required a sophisticated work, including the implementation of laser cleaning protocols followed and controlled by Optical Coherence Tomography (OCT). These protocols were developed on representative mock-ups in order to ensure the safety of the laser processing and the preservation of the integrity of the original materials. After the tests on mock-ups and the validation of a protocol, the joint use of Er:YAG and OCT on twisted and gilded columns allowed, with different settings of laser repetition rate and energy, the gradual and controlled removal, at different levels, in the thickness of the gilding. First, the metal foil was ablated, second, the oil layer n° 2 was thinned and third, the oil layer was completely removed.

This work was carried out with Maxime Lopez, in parallel with his thesis work on the removal of oxidized varnishes from the surface of easel paintings by pulsed laser. An innovative technique was thus implemented for the removal of the modern gilding of the “Bargueño”. The laser treatment coupled with OCT was accompanied by analyses under X-ray Fluorescence, under ion beam on AGLAE, by SEM analysis and by ultraviolet and composite absorption Fluorescence (CAF) imaging at the Research Department and the Imaging Department of C2RMF.

We will present in detail the process, the experimental methodology and the result obtain after the restoration work.

References

[1] Maxime Lopez, Xueshi Bai, Dominique Martos-Levif, Alessandro Zanini, Alexandre Semerok, Stéphane Serfaty, Michel Menu, Nicolas Wilkie-Chancellier, Vincent Detalle, Towards a new approach to cleaning paintings: using lasers to remove varnish, Technè, N°50, 2020, 13 p.

[2] Maxime Lopez, Evaluation and development of a laser cleaning tool for easel paintings, intended for restorers, to complement their traditional methods, particularly in delicate cases requiring very high precision., FSP,

2020.
[3] Stephanie Courtier, Broker, laser clearance report, C2RMF/Eros, C2RMF76786/ N°49223, 2019,12p.
[4] Stephanie Courtier, Intervention report on the restoration of the Bargueno, C2RM/Eros, C2RMF76786 /N° 52115, 47p.

Innovative procedure based on ^{18}O isotopes and Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS) analyses for assessing laser interaction mechanisms on copper alloys

E. Di Francia[1], D. Neff[2], S. Grassini[1], R. Lahoz[3]*

[1] Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[2] NIMBE/LAPA-IRAMAT, CEA/CNRS/Université Paris-Saclay, UMR3685, CEA Saclay, bat 637, 91191 Gif/Yvette, France
[3] Instituto de Nanociencia y Materiales de Aragón, (CSIC Universidad de Zaragoza), María de Luna 3, 50018 Zaragoza, Spain

Keywords: scanning laser ablation; copper alloys; re-oxidation; surface interaction mechanisms; ToF-SIMS

The present work describes experimental research related to the study of laser cleaning processes of typical corrosion present on archaeological copper alloys [1,2]. An innovative procedure, involving ^{18}O isotopes and Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS) analyses, was developed to assess the driving mechanisms of laser-surface interactions.

Preliminary studies were carried out on artificially-corroded Cu-based reference samples using a NIR Q-switched Yb:YAG fibre laser operating in the nanosecond pulsed regime. Those tests were performed in a controlled atmosphere of synthetic air enriched with the ^{18}O, a less abundant oxygen isotope naturally present in the atmosphere. The laser cleaning parameters were selected and then, a surface characterisation was extensively performed on laser-treated and non-treated samples [3]. The presence of re-oxidised compounds was detected, and we could discriminate the oxygen originally present in the corrosion layers and the one introduced by the interaction with the laser (generated through reactions with ^{18}O). To assess the interaction, a set of samples treated with different laser conditions were characterised by FESEM-eds and μ-Raman; ToF-SIMS Spectrometry was used to determine the content and distribution of the oxygen isotope through the corrosion layers.

The results show that re-oxidation phenomena can occur and its selectivity depends on the laser conditions. The characterisation

*Correspondence: difrancia.elisabetta@gmail.com

conducted is discussed and a model of the laser-surface-atmosphere interaction is proposed. Finally, the method has been validated during the cleaning of an archaeological bronze coin [4].

Acknowledgements

The authors would like to acknowledge the CSIC Interdisciplinary Thematic Platform "Open Heritage: Research and Society (PTI-PAIS)" for its support and the European Federation of Corrosion (EFC) – EUROCORR Young Scientist Grant Selection Committee 2016, that stimulated and co-funded the initial collaboration that subsequently produced this research.

References

[1] L. Robbiola, C. Fiaud, Apport de l'analyse statistique des produits de corrosion à la compréhension des processus de dégradation des bronzes archéologiques, Rev. d'Archéométrie. (1992). https://doi.org/10.3406/arsci.1992.896.

[2] D.A. Scott, Metallography and microstructure in ancient and historic metals. Getty Conservation Institute, Archetype , Marina del Rey, CA (US), 1991.

[3] E. Di Francia, R. Lahoz, D. Neff, V. Rico, N. Nuns, E. Angelini, S. Grassini, Novel procedure for studying laser-surface material interactions during scanning laser ablation cleaning processes on Cu-based alloys, Appl. Surf. Sci. (2021). https://doi.org/10.1016/j.apsusc.2020.148820.

[4] Di Francia, E. et al. Laser-cleaning effects induced on different types of bronze archaeological corrosion products: chemical-physical surface characterisation. Appl. Surf. Sci. 573, 150884 (2022). https://doi.org/10.1016/j.apsusc.2021.150884

Laser Treatments of Metal Artefacts

POSTER

LASER-ASSISTED REMOVAL OF LACQUER FROM SILVER ALLOY OBJECTS; INVESTIGATION FOR OPTIMUM PARAMETERS AND ASSESSMENT OF THE RESULT

Ch. Bylund-Melin[1,2], S. Golfomitsou[2], E. Dimitroulaki[3,4], K. Melessanaki[3], P. Pouli[3]*

[1] The Nationalmuseum, Stockholm Sweden
[2] Department of Conservation, University of Gothenburg, Sweden
[3] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Greece
[4] Department of Material Science and Technology, Heraklion, Greece

KEYWORDS: lacquer removal, laser ablation, silver objects, gilded silver

The application of lacquers on decorated silver and gilded silver artefacts is a commonly used method to protect them from tarnishing [1]. Due to their reflective surface, the types of coatings used are limited with cellulose nitrates being amongst the most commonly used. Nevertheless, their deterioration with time and environmental conditions is unavoidable and thus cleaning becomes inevitable [2]. The use of these varnishes was very common in Sweden with a number of significant artefacts being covered with aged lacquers that nowadays need to be removed. In this study UV laser irradiation has been investigated as regards its potential to safely remove yellowed and aged cellulose nitrate coatings from silver alloys. Preliminary tests have been performed on artificially aged silver coupons. The silver and gilded silver coupons were tarnished to different levels, coated with cellulose nitrate films of and artificially aged in an environmental chamber with controlled UV, relative humidity and temperature to simulate ageing of the lacquer. This enabled us to carry out experiments to investigate the potential and limitations of laser techniques on such precious surfaces. Different types of lasers emitting in various wavelengths and pulse durations, have been tested [3]. In this communication the cleaning methodology developed based on the results obtained from this study, as well as the thorough surface assessment of the cleaned areas will be presented with emphasis to its applicability to similar cleaning challenges.

**Correspondence: lottabmelin@outlook.com*

Acknowledgements

The financial support of this work has been provided by The Donor Circle of The Nationalmuseum in Stockholm, Sweden and IPERION-HS H2020 project (Integrated Platform for the European Research Infrastructure ON Heritage Science) funded by the European Union, H2020-INFRAIA-2019-1, GA 871034.

References

[1] Luxford, N. and Thickett, D. Preventing silver tarnish - lifetime determination of cellulose nitrate lacquer, Metals 07, Rijksmuseum, Amsterdam, 2007, 88-93

[2] Grissom, C.A., Grabow, N., Smith Riley, C. and Charola, E.A., Evaluation of coating performance on silver exposed to silver sulfide, Journal of the American Institute for Conservation, 2013, Vol. 52:2, 82-96.

[3] B. Taarnskov, P. Pouli, J. Bredal-Jørgensen , Laser cleaning studies for the removal of tarnishing from silver and gilt silver threads in silk textiles, Lasers in the Conservation of artworks VIII, eds R. Radvan, J. Asmus, M. Castillejo, P. Pouli, A. Nevin, CRC Press, Taylor and Francis Group, London, 2011, 67-73

Laser Treatments of Stone Artefacts and Similar

ORAL

Comparison between short pulse and ultrashort pulse laser cleaning of heritage stonework

J. Brand[1,2*], A. Wain[1], A. Rode[2], S. Madden[2], L. Rapp[2]

[1] Centre of Cultural and Creative Research, Faculty of Art and Design, University of Canberra, Bruce ACT 2617, Australia
[2] Department of Quantum Science and Technology, Research School of Physics, Australian National University, Acton ACT 2601, Australia

Keywords: laser ablation, laser cleaning, conservation, granite

Laser cleaning has become a popular technique for the removal of unwanted surface layers in the field of conservation of heritage stonework, for a variety of objects ranging from sculptures to entire buildings and monuments facades. Nanosecond pulsed lasers are widely used, and are already commercially available with portable units deployable on-site. However, those lasers rely on thermal mechanisms of ablation, which generate heat and shock waves that can result in undesirable side-effects on the stones such as increased surface roughness, melting or cracking.

Ultrashort pulse lasers, with pulse duration in the sub-picosecond range, offer a remarkable and efficient alternative to short pulse lasers. The non-linear nature of the interaction with the targeted materials results in a laser-induced removal of unwanted surface layers with very limited heat-related damage, the process called 'cold ablation'.

Here, we compared the removal of graffiti paints commonly found on heritage stonework using an ultrashort (subpicosecond-range, $<10^{-12}$ s) pulse laser and a short (nanosecond-range, $\sim10^{-8}$ s) pulse laser. We demonstrated that both lasers were able to remove the undesirable paints successfully, but melting of biotite and other damage to the stone was clearly induced using the nanosecond pulse laser. We determined the damage threshold laser fluence and showed that, by setting the laser fluence under the threshold, the ultrashort pulse laser allowed to reach a complete removal of paint while preserving the full integrity of the stone surface. This illustrates the potential of ultrashort pulse lasers for the conservation of heritage stonework.

*Correspondence: julia.brand@canberra.edu.au

ACKNOWLEDGEMENTS

This research was supported by the Australian Government through the Australian Research Council's Linkage Project funding scheme (Project LP180100276) and funding provided by Transport for New South Wales.

APPLICATION OF ULTRA-SHORT PULSE LASERS IN THE RESTORATION OF HISTORICAL STAINED-GLASSES

*E.M. Maingi[1,2,3], M.P. Alonso Abad[2], G.F. de la Fuente[2], S. Dubernet[3], R. Chapoulie[3], E. Vally[4], L.A. Angurel[2]**

[1] Área de Historia del Arte, Departamento de Historia, Geografía y Comunicación, Universidad de Burgos, Pº Comendadores S/N, 09001 Burgos, Spain. Unidad Asociada de I+D+i al CSIC "VIMPAC'', Spain
[2] Instituto de Nanociencia y Materiales de Aragón (CSIC-University of Zaragoza), María de Luna 3, 50018 Zaragoza, Spain
[3] Archéosciences Bordeaux laboratory UMR 6034, CNRS, Bordeaux Montaigne University, France
[4] Maison Lorin, 46 rue de la Tannerie, 28000 Chartres, France

KEYWORDS: Ultra-short pulse laser, conservation, cultural heritage, stained-glass, heat accumulation

Stained-glasses form an important element in cultural heritage. However, in addition to human and environmental factors, the composition of the materials, their behavior over time, their interaction with other materials and physical, chemical, natural and biological conditions have subjected these materials to deterioration. In addition to conventional restoration methods, laser technology has increasingly become a unique conservation tool offering possibilities for the safe and controlled restoration of stained glasses. In previous studies, nanosecond lasers have shown their potential in restoration but also their technological limitations and low reliability that could potentially damage the material. Ultra-short pulse lasers are evolving very fast and have opened new possibilities towards the development of safer restoration methods in comparison with traditional techniques. Because of the thermal, mechanical, and chemical properties of glass, specific restoration protocols are required to preserve the integrity of the stained-glasses. In this study, femtosecond lasers were used to establish laser parameters that would allow effective removal of corrosion products from stained-glass surfaces while limiting the maximum temperature reached on the glass surface due to heat accumulation, thus avoiding crack generation due to thermal stresses created during the laser cleaning process. The established laser cleaning

*Correspondence: angurel@unizar.es

methods were successfully applied to remove a calcium sulphate and carbonate contamination layer that had formed on the surface of some historical stained-glasses from the Cuenca cathedral in Spain. These protocols proved effective in the removal of the contamination layer without inducing any damage to the underlying pigments or the glass substrate. The results of the physiochemical modifications after the laser cleaning process were acquired using FESEM-EDS, confocal microscopy, and Raman spectroscopy. The results suggest that ultra-short pulse lasers enable the application of controlled laser cleaning protocols to achieve effective and safe restoration of fragile stained-glasses.

Acknowledgments

This work has been supported by H2020-MSCA-ITN-EJD/ED-ARCHMAT action under the Marie Sklodowska-Curie grant agreement No. 766311 and by Gobierno de Aragón (research group T54_20R).

Laser cleaning of graffiti and cleaning evaluation using FTIR

M. Laboure[2*], F. Surma[1], P. Schloegel[1], V. Aguilar[3], L. Rosenbaum[1]

[1] Epitopos, Strasbourg, France
[2] Mescla, Strasbourg, France
[3] Ecole et Observatoire des Sciences de la Terre, University of Strasbourg, France

Keywords: spectroscopy, laser ablation, laser cleaning, FTIR, graffiti

The removal of graffiti is one of the current challenges for the conservation of buildings. Indeed, it is important to restore the affected area as close as possible to its initial state and to avoid any kind of additional degradation. There are several cleaning techniques, nevertheless, the use of chemical products or sandblasting can alter the stone surface. This study focuses on the removal of homemade graffiti by laser [1-3]. We use the Infinito fiber laser (100 W) from the El.En company at two different average power levels. Eighteen sandstone and marble plates have been sprayed with oil-based and acrylic paint products or markers employed nowadays for street-art. A preliminary analysis using LIBS (Laser Induced Breakdown Spectroscopy) and FTIR-ATR (Attenuated Total Reflectance by Fourier-Transform Infrared Spectroscopy) has been performed to identify mineral and organic pigments and binders on the surface of the plates. The cleaning has been carried out and three zones analysed for each sample (a non-cleaned surface and surfaces cleaned at 50W and 75W average power). A DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) [4-5] acquisition has been performed, keeping the same area of analysis, allowing for a quantitative cleaning evaluation. Samples were studied using a field microscope and a colorimeter, and surface roughness measurements were also carried out.

Acknowledgements

The financial support of this work has been provided by Mescla and Epitopos. The authors would like to thank Meazza society in Mundolsheim for providing the marble and sandstone plaques used for the investigation.

*Correspondence: m.laboure@mescla.eu

References

[1] C. Giusti, M. P. Colombini, A. Lluveras-Tenorio, J. La Nasa, J. Striova, B. Salvadori, Graphic vandalism: Multi-analytical evaluation of laser and chemical methods for the removal of spray paints, Journal of Cultural Heritage 44 (2020) 260-274.

[2] Siano, S., Agresti, J., Cacciari, I. et al. Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers. Appl. Phys. A 106, 2012, 419–446.

[3] Daurelio, G. & Andriani, Sabino & Marano, D. & A.Albanese, & Catalano, The Removal of Sprayed paints on Calcareous Stones : A comparative study of the application of N-Mode, Short Free Running and Q-Switch Nd - YAG beam.. RESTAURO Review - Forum fur Restauratoren,Konservatoren und DenKmapfleger. by VERLAG CALLWEY – Munich, 2007, 400 - 409

[4] Rita Wiesinger, Laura Pagnin, Marta Anghelone, Ligia M. Moretto, Emilio F. Orsega, Manfred Schreiner, Pigment and Binder Concentrations in Modern Paint Samples Determined by IR and Raman Spectroscopy, Angewandte Chemie, Volume 130, Issue 25, 2018

[5] Adele Bosi, Alessandro Ciccola, Ilaria Serafini, Marcella Guiso, Francesca Ripanti, Paolo Postorino, Roberta Curini, Armandodoriano Bianco, Street art graffiti: Discovering their composition and alteration by FTIR and micro-Raman spectroscopy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 225, 2020

Evaluation of femtosecond laser texturing of natural stones for conservation applications in the field of Cultural Heritage

A.J. López[1*], D.M. Freire-Lista[2], A. Ramil[1]

[1] Laboratorio de Aplicacións Industriais do Láser, Campus Industrial de Ferrol, Universidade da Coruña, 15471 Ferrol, Spain
[2] Universidade de Trás-os-Montes e Alto Douro. Quinta de Prados. 5001-801 Vila Real,Portugal

Keywords: Laser texturing, femtosecond, marble, dolomite, wettability

In the field of stone conservation, a common direct intervention seeks to increase the water repellence of objects. To decrease wettability, chemicals are often applied; however, laser texturing, currently used in different technological fields, could be considered as an alternative procedure, thus eliminating exposure to chemicals with varying degrees of toxicity. Due to the versatility of the laser structuring process, research elucidating correlations between the surface topography generated and wetting response of laser-structured materials is still being intensely investigated. These studies are essential in the case of materials, such as natural stone, in which the challenge is their heterogeneity leading to irregular surface absorption of the laser ligth. [1].The objective of this study is to evaluate the effect of femtosecond laser texturing for preventive conservation of the stones used in the main fountains of Paseo del Prado (Madrid, Spain)[2]. The main sculptural sets of Paseo del Prado in Madrid (Spain) were designed by the architect Ventura Rodríguez in 1777. They have a neoclassical style to form part of Salón del Prado, originally with three aligned fountains: Fuente de Cibeles, at the northern end; Fuente de Apolo, at the center; and Fuente de Neptuno, located at the southern end. Cibeles and Neptuno Fountains are built mainly with Montesclaros marble and Fuente de Apolo is built with Redueña dolomite. The historical quarries of the three fountains were located and samples were extracted and cut with the appropriate sizes both for their characterization and for laser structuring. Petrographically, Montescaros is a dolomitic marble and Redueña dolostone is

*Correspondence: ana.xesus.lopez@udc.es

massive, formed by rhombic dolomite crystals, and fossils. Fresh stones were characterized, and a femtosecond pulse laser system from Spectra Physics (1040 nm wavelength and pulse width < 400 fs.) was used for structuring thin sections and polished samples with different texturing patterns. Characterization of the topography of the textured surfaces by means of interferometric microscopy showed differences in the response of both stones to laser structuring. The analysis of the wettability of treated surfaces in terms of contact angle measurements was accomplished, in addition with roughness and colour measurements to evaluate eventual changes in the appearance of the surface and consequently to properly selecting the process parameters that ensure minimal modification.

Acknowledgements

The financial support of this work has been provided by Fundação para a Ciência e a Tecnologia (Lisboa, PT) GRANT_NUMBER: CEECIND/03568/2017.

References

[1] López AJ, Pozo-Antonio JS, Moreno A, Rivas T, Pereira D, Ramil A. Femtosecond laser texturing as a tool to increase the hydrophobicity of ornamental stone: The influence of lithology and texture. Journal of Building Engineering 2022:104176. https://doi.org/10.1016/J.JOBE.2022.104176.

[2] Freire-Lista DM. Geotourism from fuente de cibeles of Madrid. History, building stones and quarries. Cadernos Do Laboratorio Xeoloxico de Laxe 2020;42:69–94. https://doi.org/10.17979/CADLAXE.2020.42.0.7286.

Combined used of Er:YAG and Nd:YAG lasers for the cleaning of marble sculpture from the portico of the Monumental Cemetery of Pisa

A. Sutter[1], C. Di Marco[1], M. Spada[1], A. Trinchetti[1], M. Spampinato[2], A. Manariti[3], A. Andreotti[3], M.P. Colombini[3]*

[1] Opera della Primaziale Pisana (OPA), Piazza Duomo 17, 56126, Pisa, Italy
[2] Spampinato Dr. Marcello private laboratory, analysis of stone and pictorial materials, Traversa III° 15/A, Via di S. Maria del Giudice, 55100 Lucca
[3] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 15, Pisa, Italy

Keywords: laser cleaning, diagnostics, stone conservation, marble reliefs, analytical investigation

The pillars, arches and four-light windows (i.e. quadrifore) in the east side of the Monumental Cemetery of Pisa, Italy, show a severely degraded state of conservation of the stone surfaces (i.e. S. Giuliano's and Apuan's marbles, and Filettole's limestone). The deterioration get worst on the inner side of the gallery, where rainwater infiltrations came inside from a leak in the roof. The stone surfaces, included decorative elements, are affected by an extensive sulphation of the carbonate matrix, swelling and exfoliation phenomena (up to 5 mm in thickness), as well as coherent and incoherent dirt deposits on the surface. Past conservation treatment, particularly the application of fluorinated elastomers as protective layer (applied during the last restoration campaign in the 90s), prevented the natural external migration of soluble salts. The crystallization of the salts, at the interface between the protective layer and the stone surface, increases the deterioration phenomena, particularly in the pillar number four and its figured capital, whose reliefs are strongly compromised. The aim of the first step of the restoration work was to clean the stone surfaces using contactless laser cleaning methods and allow a partial and selective removal of the hydrophobic protective layer, difficult to reach with traditional methods because of the stone disintegration. For this purpose, the single or combined action of two Infrared laser sources with different wavelength and pulse duration were tested: Nd: YAG laser (1064nm and 532nm, 6 ns), and Er: YAG laser (2940 nm, 150 µs, 250 µs, 400

**Correspondence: alessia.andreotti@unipi.it*

μs). In order to select the best working laser parameters, a diagnostic campaign has been carried out. Petrographic and chemical analyses were used for investigating the stratigraphy and identifying the soluble salts. Thin sections of marble samples were studied with a polarizing optical microscope, electron microscope and microprobe (SEM-EDX) to determine the mineralogical composition of the materials and the deterioration products. X-ray diffractometry (XRD) was used for the identification of the crystalline phases. A few samples of the superficial films have been selected with optical microscopy through Vis and UV examinations, for the molecular characterisation of organic materials with the attenuated total reflection (ATR) infrared spectroscopy (IR) and pyrolysis coupled with gas chromatography and mass spectrometry (PY-GC-MS). The water repellence has been tested by means of capillary absorption measurements with contact sponge water absorption tests and static contact angle measurements. Laser tests have been carried out with different fluences as well as a variable number of pulses and in wet or dry condition. The laser test evaluation has been carried out comparing the marble surface before and after the laser treatment. Moreover multispectral investigations by Vis scattered and grazing light and UV light have been performed on larger laser treated area in order to set the best working laser parameters.The optimal cleaning parameters, tested for each type of condition and material to be removed, have been successfully applied for the complete and safe cleaning of the pillar and its figured capital.

Figure 1 - Particular of the deterioration of the capital in Vis diffuse (left) and grazing (right) lighting

Figure 2 - Laser cleanig tests on the pillar surface in Vis lighting (left) and UV fluorescence excited @465nm (right).

Application of Femtosecond UV Laser for Selective Cleaning of Archaeologically Significant Pleistocene Bones

Md. A. Rahman[1,3,6], G.F. de la Fuente[1], J.M. Carretero[2], E.M. Maingi[1,3,5], M.P. Alonso Abad[3], R. Alonso Alcalde[4], R. Chapoulie[5], N. Schiavon[6], L.A. Angurel[1]*

[1] Instituto de Nanociencia y Materiales de Aragón (CSIC - University of Zaragoza), c/ María de Luna 3, 50018 Zaragoza, Spain
[2] Laboratorio de Evolución Humana and Unidad Asociada de I+D+i al CSIC "Vidrio y Materiales del Patrimonio Cultural (VIMPAC)", Departamento de Historia, Geografía y Comunicación, Universidad de Burgos, Plaza Misael Bañuelos S/N, 09001 Burgos, Spain
[3] Área de Historia del Arte and Unidad Asociada de I+D+i al CSIC "Vidrio y Materiales del Patrimonio Cultural (VIMPAC)", Departamento de Historia, Geografía y Comunicación, Universidad de Burgos, Pº Comendadores S/N, 09001 Burgos, Spain
[4] Área de Didáctica y Dinamización, Museo de la Evolución Humana, Paseo Sierra de Atapuerca nº2, 09002 Burgos, Spain
[5] Archéosciences Bordeaux laboratory UMR 6034, CNRS, University Bordeaux Montaigne, France
[6] HERCULES Laboratory, University of Évora, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal

Keywords: femtosecond, UV laser, cleaning, bone, Sierra de Atapuerca

Archaeological bones are extremely vulnerable to contaminants and degrade significantly over time as a result of inorganic mineralization weathering and exposure to environmental pollutants at the burial site. Since the fragile and sensitive surfaces are subject to varying degrees of degradation, cleaning archaeological bones is a challenge that requires solutions based on multidisciplinary scientific approaches. When traditional chemical and mechanical cleaning methods are no longer feasible and short-pulsed laser ablation desorption is not entirely effective, ultrafast femtosecond (fs) pulsed laser technology may provide a viable alternative for cleaning archaeological artifacts. The latter should enable precise control of ablation depth while avoiding unwanted photothermal and photochemical damage. In this study, an Yb:YAG fs laser with Ultraviolet emission wavelength (343 nm) was employed to remove

**Correspondence: ashiqur@unizar.es*

surface contaminants, degradation products, and hardened soil crusts from two significant Pleistocene bones unearthed from Sierra de Atapuerca (Burgos, Spain). The most efficient cleaning parameters, ablation threshold, damage threshold, and operative threshold cleaning values in laser beam scanning mode were identified. Optical Microscopy (OM), Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM-EDS), Fourier Transform Infrared Spectroscopy (FTIR), and X-ray Diffractometry (XRD) were used to characterize the physicochemical properties of the deteriorated bones before and after the laser treatment, while evaluating the degree of damage produced to the original bone surfaces. The study reveals the capability of fs UV laser in the successful conservation of archaeological bones, considering its ability to selectively clean unwanted materials with nanoscale precision, while avoiding heat accumulation, physicochemical transformations, and mechanical damage to the substrate during the controlled laser bone cleaning process.

ACKNOWLEDGEMENTS

Project supported by H2020-MSCA-ITN-EJD/ED-ARCHMAT action funding under the Marie Skłodowska - Curie grant agreement, No 766311 and by Gobierno de Aragón (research group T54_20R).

Laser Treatments of Stone Artefacts and Similar

POSTER

The Flight of Night: Laser Cleaning Coated Plaster

E. Promise

Isabella Stewart Gardner Museum

Conservators at the Isabella Stewart Gardner Museum have used a Q-switched Nd:YAG 1064 nm laser unit to clean marble surfaces in the collection with gratifying results. Success in cleaning stone surfaces has prompted occasional experiments with more delicate materials such as gilded frames. ISGM conservators have found that, in contrast with the parameters for working on marble, using a low energy pulse and increasing working distance to produce a diffuse spot size can, with care, effectively remove a dark layer of soiling from a vulnerable surface. The author used a similar approach to clean heavy grime and soot from a plaster cast with a darkened resin surface while preserving the resin coating.

In late 2018, the author was tasked with treating a plaster object entitled *The Horses of Anahita*, or *The Flight of Night* originally created by William Morris Hunt as a preparatory model for a mural and cast in plaster around 1880. Copies of this plaster cast can be found in several collections across the United States including The Metropolitan Museum of Art, The Art Institute of Chicago, Boston Athenaeum, and the Pennsylvania Academy of the Fine Arts. The level of coating present on each example varies considerably from a bright, white uncoated appearance to a thick, uniform amber tint. The version in the ISGM collection has a patchy, orange-brown brush coat that curators and conservators desired to retain.

Numerous wet and dry cleaning methods were attempted to remove the dark soiling from the plaster cast before laser cleaning was initiated. The author corresponded with colleagues at other institutions with copies of *The Horses of Anahita* in order to ascertain the treatment history of the alternate versions of this object. This resulted in little viable information. Meanwhile, correspondence with laser expert Martin Cooper suggested that cleaning soiling from a resin coating using an Nd:YAG laser may be possible at a very low fluence.

After promising spot tests were carried out on the sides of the object, the decision was made to move forward with laser cleaning.

Correspondence: epromise@isgm.org

Several challenges arose in laser cleaning the coated plaster, which the author will detail in this presentation. However, the results overall were satisfactory. This method largely succeeded in retaining the resin coating with no damage to the underlying plaster, which is an ever-present risk with both mechanical and wet-cleaning methods. Results suggest that further studies of the potential for Nd:YAG lasers to safely clean coated surfaces should be undertaken.

Ultrashort pulse laser cleaning for the preservation of the Sydney Harbour Bridge

J. Brand[1,2 *], A. Wain[1], A. Rode[2], S. Madden[2], L. Rapp[2]

[1] Centre of Cultural and Creative Research, Faculty of Art and Design, University of Canberra, Bruce ACT 2617, Australia
[2] Department of Quantum Science and Technology, Research School of Physics, Australian National University, Acton ACT 2601, Australia

Keywords: laser ablation, laser cleaning, conservation, preservation, granite

The Sydney Harbour Bridge is a heritage-listed bridge located in Sydney, New South Wales, Australia, and celebrates this year its 90th anniversary. The Bridge is made of a steel arch flanked by massive granite-clad pylons on each side of the shore. It is considered a national and international icon, and is a vital part of Sydney's transport infrastructure with more than 200 trains, 160,000 cars and about 2,000 bicycles crossing the Harbour every day. The maintenance of such a structure is a monumental undertaking, and the current conservation work involves sandblasting. Many restrictions and challenges make the process difficult.

Laser cleaning has become a popular technique for the removal of unwanted surface layers in the field of conservation of heritage stonework. Nanosecond pulse lasers are most widely used, and already commercially available with portable units deployable on-site. Those lasers offer various benefits compared to more conventional cleaning methods like sandblasting, such as avoiding the use of abrasives, and eliminating problems of chemical toxicity, corrosive residues, and erosion or loss of surface detail. However, those lasers rely on thermal mechanisms of ablation, which generate heat and shock waves that can result in undesirable side-effects such as melting.

Ultrashort pulse lasers, with pulse duration in the sub-picosecond range, offer a remarkable alternative to short pulsed lasers. The non-linear nature of the interaction with materials result in a process called 'cold ablation', meaning none or very limited heat-related damage.

The Sydney Harbour Bridge is a unique case study for the

*Correspondence: julia.brand@canberra.edu.au

application of ultrashort pulse laser for the conservation of cultural heritage. We explored the cleaning treatment of the Australian Moruya granite, made of quartz, plagioclase, potassium-feldspar, biotite, and hornblende, used in the cladding of the pylons, with a femtosecond pulsed laser. We determined the ablation threshold for removal of rust, dirt and bio-contamination without detrimental effect on the underlaying stone surfaces of the Bridge while keeping the laser energy under the damage threshold of the stone. The effects on the treated surfaces and the cleaning efficiency were assessed using multiple analytical methods including optical and scanning electron microscopy, profilometry, and Raman and FTIR spectroscopy.

We demonstrate efficient cleaning results in a damage-free and abrasion-free treatment, illustrating the advantages of ultrashort pulse lasers for the conservation and preservation of cultural heritage.

Acknowledgements

This research was supported by the Australian Government through the Australian Research Council's Linkage Project funding scheme (Project LP180100276) and funding provided by Transport for New South Wales.

Practical Applications and Advantages of Using Laser Cleaning For Fire Damage Restoration and Conservation of Architecture and Cultural Heritage

B. Dajnowski[1*], *B.J. Morris*[2], *A. Dajnowski*[3], *M. Dajnowski*[4]

[1] G.C. Laser Systems Inc., Forest Park, IL, USA
[2] Northwestern Univeristy, Evanston, IL, USA
[3] The Conservation of Sculpture an Objects Studio, Inc., Forest Park, IL, USA
[4] G.C. Laser Systems Inc., Forest Park, IL, USA

Keywords: fire damage, cleaning, restoration, architecture, buildings

The laser cleaning process is globally becoming a more recognized alternative to various blasting, mechanical, and chemical cleaning methods for fire damage remediation and restoration. The precise control over laser cleaning parameters that allow the process to be sensitive to a wide range of materials and substrates makes a portable and tunable 1064nm pulsed high frequency laser system a very effective tool to have in the toolbox for the conservation and restoration of buildings and objects that have suffered from a fire damage event. The lack of mechanical force or pressure makes the laser cleaning process a particularly appealing option for fragile or intricate surfaces. Effective laser ablation thresholds and examples of appropriate parameters for cleaning materials such as stone, masonry, metals, wood, ceramics, painted surfaces, and other materials will be identified and examined with tools such as high magnification 3D microscopy. Detailed comparisons of the effects of various pulse durations and fluence levels on these materials will be evaluated and the useful applications and limitations of the laser cleaning process for disaster recovery will be explored. Fire damage restoration research, case studies, and actual fire damage laser cleaning projects from North America, Europe, and Australia will be presented.

*Correspondence: Bartek@GCLasers.com

Effects of fs Laser Irradiation on Batalha Monastery Limestone

Y. Ding[1], G.F. de la Fuente[2], L.A. Angurel[2], N. Schiavon[1]*

[1] Hercules Laboratory, University of Évora, Évora, Portugal
[2] Instituto de Nanociencia y Materiales de Aragón (CSIC-Universidad de Zaragoza), Spain

Keywords: femtosecond laser, laser cleaning, in-situ monitoring, stone conservation

Ablation of the biological layers found at the surface of the Batalha Monastery limestone walls in Portugal was carried out by three femtosecond laser harmonics in order to compare their cleaning performance and optimize the stone conservation strategy. Femtosecond laser emission was tested at the following different wavelengths and pulse durations: 1) UV laser emission at 343 nm and pulse duration of 238 fs; 2) green laser emission at 515 nm and pulse duration of 249 fs; 3) near IR laser emission at 1030 nm and pulse duration of 228 fs. The ablation process was monitored by a thermal camera to detect heat accumulation effects caused by the laser irradiation. Several parameters and techniques were used to evaluate the cleaning effect: a) surface roughness change was assessed with a confocal microscope; b) optical microscope and SEM were used to observe the damages to lichens and the substrate morphology after the microbial crusts had been removed; c) mineral and chemical changes induced by laser irradiation of the limestone substrate were investigated by XRD; d) CVI MTT assays illustrated how microbial cell viability was reduced by laser treatment. Results demonstrate that UV and green femtosecond lasers were able to achieve outstanding cleaning results, inasmuch as they removed completely the lichen thallus growing on the stone surface without affecting the substrate, while infrared irradiation was shown to trigger thermal effects giving rise to the risk of chemical alteration and morphology change on the stone. Fragmented remains of lichens and fungus observed beneath the ablated surface demonstrate the difficulty of thoroughly vanishing all endolithic microbes that penetrated deeply within the porosity framework of the substrate. Thus, while the explored femtosecond laser irradiation

**Correspondence: yding@uevora.pt*

was found to be a suitable tool in the conservation of stone monuments and artefacts, periodic laser cleaning schedule needs also to be implemented. It was casually discovered that fs laser irradiation did increase the hydrophobic character of the limestone surface, opening the development of a promising solution for the artefacts' outdoor protection.

Acknowledgements

Financial support of this work was provided by the European Union's Horizon 2020 research and innovation program under the H2020-MSCA-ITN-EJD ED-ARCHMAT, grant agreement No 766311.

Er:YAG laser treatment for biodegradation on 20th-century cement based statues. A possible alternative for biocides?

A. Andreotti[1], M.P. Colombini[1], A. De Cruz[2], G. Ranalli[3], K. Nakahara[4]*

[1] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 15, Pisa, Italy
[2] Conservator Scientist, New York, USA
[3] Università degli Studi del Molise, Pesche, Isernia, Italy
[4] Conservator-Restorer of Cultural Heritage, Florence, Italy

Keywords: laser ablation, diagnostics, conservation, biodeterioration, cement statue

The characteristic wavelength of Er:YAG laser at 2,94 μm which is highly absorbed by -OH bonds is the significant key to the effective removal of biodeteriogens (e.g. lichens, fungi, algae) most of which are polysaccharides. The potentiality of Er:YAG laser treatment for biodeterioration has been preliminarly tested [1]. In this work, the Er:YAG laser treatment to clean the surface of some twentieth-century statues has been efficiently performed. The statues are "Venus", "Girl with vase and basket", and "Nymph"; composed by cement and marble-powder and realized by casts method (Fig.1 a-b). The statues are all conserved in outdoor environment in Florence (Italy) and they have been continuously colonized by biodeteriogens (green alga, black fungi, mosses, etc.), even after traditional chemical-mechanical cleaning. The objectives of this work are the study of Er: YAG laser cleaning on various types of surface biodeteriogens and the monitoring of long-term effects after laser treatment. Furthermore, different tests will be performed and compared with (a) essential oils (EO) from green plants, alone and in mixture; (b) with/without microbial bioprecipitation of new calcite as a bioconsolidation process to reduce surface biosensitivity to future biofouling. Bio-analyses (viable cultivable microbial counts, microbiota and microbiome changes, 19 enzyme profiling, water absorption change, stereo microscope observations) and scanning electron microscopy with energy-dispersive x-ray spectroscopy analyses (SEM-EDX, Fig.1 c–d) were designed, before, during and after sequential laser and EO treatments.

*Correspondence: alessia.andreotti@unipi.it

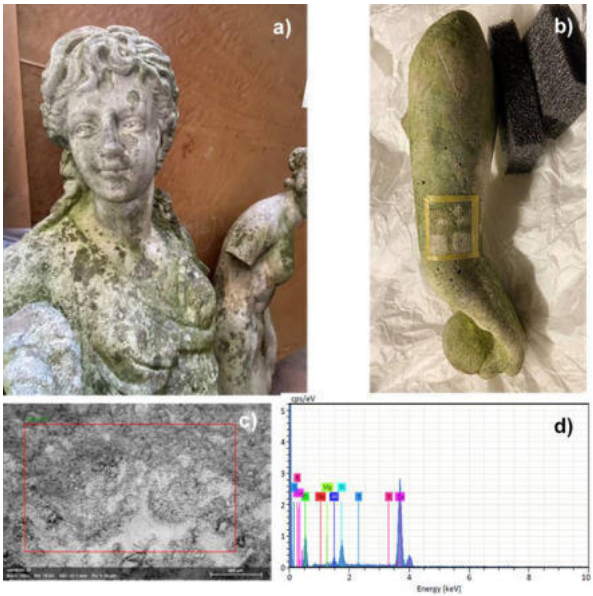


Figure 1 a) "Girl with vase and basket" and the "Venus"; b) detail of preliminary laser tests on the arm of the "Venus"; c) SEM-EDX picture and d) analysis of a surface fragment.

References

[1] A. DeCruz, M.L. Wolbarsht, A. Andreotti, M.P. Colombin, D. Pinna, C.F. Culberson, Investigation of the Er:YAG Laser at 2.94 μm to Remove Lichens Growing on Stone, Studies in Conservation, 54, 2009, pp.268-277.

METHODOLOGY DEVELOPMENT FOR THE SUCCESSFUL REMOVAL OF COEXISTING BIOFILMS AND BLACK CRUSTS ON ARCHAEOLOGICAL STONEWORK USING THE 2-WAVELENGTH LASER CLEANING APPROACH

E. Kourti[1,2*], *A. Giakoumaki*[2], *K. Melesanaki*[2], *P. Pouli*[2]

[1] Aristotle University of Thessaloniki, Faculty of Engineering, Thessaloniki, Greece
[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology, Heraklion, Crete, Greece

KEYWORDS: Laser Cleaning, 2-wavelength ablation, Biodeterioration

Biodeterioration is a rather challenging problem in the field of Cultural Heritage, for both outdoor monuments and archaeological objects. Biofilms on stones and other building materials, which are formed due to the climatic conditions, can be proven not only aesthetically but also structurally damaging and therefore actions must be taken towards their treatment.

In many cases, biological films coexist with other crusts, such as black pollution accumulations of inorganic composition. The use of the fundamental wavelength (1064 nm) of a Nd:YAG laser is a well-established method to remove black crusts from the surface of stone and other building materials, but is not as efficient for the removal of biofilms. In the present study, the 2-wavelength blending laser cleaning methodology, developed and applied for removal of black crusts from the Acropolis marble sculptures [1] has been carefully adopted for the removal of biodeterioration. In this case the fundamental and second harmonic beams of a Nd:YAG laser at 1064 and 532 nm respectively have been employed in spatial and temporal overlapping to remove successfully both black pollution and biological crusts.

The results of this study will be presented with the aim to demonstrate the effective removal of biological formations on stonework using the 2-λ laser cleaning methodology on the basis of determining all operative parameters for effective cleaning (the energy density thresholds for crust removal and stone damage, the defined optimum ratio for the two beams etc.), as well as, careful assessment of the treated surfaces using surface specific and

*Correspondence: elenikourti@arch.auth.gr

imaging analytical techniques.

Acknowledgements

The financial support of this work has been provided by CALLOS: Conservation of Athens antiquities with Laser and Lidar technologies Open to Science and public (MIS-5056208), an "open innovation in culture" action co-funded by the European Regional Development Fund (ERDF) and national resources through the Operational Program "Competitiveness, Entrepreneurship & Innovation" (NSRF-EPAnEK).

References

[1] P. Pouli, E. Papakonstantinou, K. Frantzikinaki, A. Panou, G. Frantzi, C. Vasiliadis, C. Fotakis, The two-wavelength laser cleaning methodology; Theoretical background and examples from its application on CH objects and monuments with emphasis to the Athens Acropolis sculptures, Heritage Science vol. 4 (1), 2016,

LASER REMOVAL OF BIOLOGICAL GROWTHS FROM EARTHENWARE

D. Ciofini[1], V. Mazzotti[2], B. Salvadori[3], D. Magrini[3], R. Manganelli Del Fà[3], J. Agresti[1], D. Pinna[4], C. Riminesi[3], S. Siano[1], I. Osticioli[1]*

[1] Institute of Applied Physics "Nello Carrara" (IFAC) – National Research Council (CNR), Sesto Fiorentino (FI), Italy
[2] International Museum of Ceramics (MIC), Faenza , Italy
[3] Institute of Heritage Science (ISPC)-National Research Council (CNR), Sesto Fiorentino (FI), Italy
[4] University of Bologna, Chemistry Department, Bologna, Italy

KEYWORDS: biodeterioration, laser ablation, spectroscopy, earthenware conservation

In recent years, laser removal of biological growths from stone artefacts has been thoroughly investigated [1-3] and corresponding validations have been reported [4]. Here, the possible extension of the laser approach to the removal of biocolonized earthenware artefacts has been explored. The study was carried out within the framework of the definition of the conservation treatments to be applied to a Roman earthenware *dolium* (large jars) from the garden of the International Museum of Ceramics (MIC) of Faenza (IT). This presented significant biological growths, which needed a preliminary systematic study, thus providing the opportunity to approach such a conservation problem from a general standpoint.

The laser removal of biodeteriogens from earthenware is quite different than removing them from whitish stones. Earthenware exhibits higher optical absorption than the latter, has a pronounced tendency to undergo delamination phenomena, and has a pronounced photothermal sensitivity determined by its iron oxides pigment load. The investigation was hence aimed at exploring the interaction of different lasers with hand-made earthenware artefacts of known composition. These samples were subjected to systematic measurements of bio-characterization, uncovering tests, and damage thresholds, comparison of diversified ablative laser treatments, and then diagnostic assessment of the irradiation effects through microscopy and spectroscopy. As mentioned above, the validation of the latter was carried out on a Roman *dolium*, which

**Correspondence: D.Ciofini@ifac.cnr.it*

had its surface extensively colonized by biological growths mainly including crustose lichens and biofilms. In particular, large thalli of *Circinaria hoffmanniana* were present close by the *dolium* opening. Differently, the surface below the edge was mainly covered by *Verrucaria nigrescens* and *Acarospora gallica*. Finally, in the lower part, the surface was colonized mainly by *Verrucaria nigrescens* and biofilms.

For systematic and validation studies, three laser systems with different wavelengths and pulse durations were used for the tests: LQS (120 ns) and SFR (40-140 µs) Nd:YAG(1064 nm) laser, QS (10-30 ns) Nd:YAG (532nm); laser FR Er:YAG (2940 nm, 150 µs).

Surface assessment before and after laser treatments was achieved using optical microscopy, 3D photogrammetry, and Pulse-Amplitude-Modulated Chlorophyll-Fluorometry (CF-PAM). Moreover, spectroscopic techniques such as FTIR and Raman along with LIBS were employed to evaluate the removal effectiveness.

Best and safe removal was achieved by applying ablative laser irradiation after gentle mechanical action. In particular, for the validation case, a soft bristle brush and water were used to remove about 70% of the bio-colonization. The remaining 30%, represented mostly by fungal component of lichens well anchored to the support was removed using laser irradiation. Best compromise between application times and safety was achieved using long-pulse lasers.

References

[1] I. Osticioli, M. Mascalchi, D. Pinna, S. Siano, Removal of Verrucaria nigrescens from Carrara marble artefacts using Nd: YAG lasers: comparison among different pulse durations and wavelengths Appl. Phys. A 118 (2015) 1517-1526.

[2] M.Oujja, C. Ascaso, S.Pérez-Ortega, V.Souza-Egipsy, R.Forte A.de los Rios, J. Wierzchos, M.V. Cañamares, M. Castillejo, Influence of wavelength on the laser removal of lichens colonizing heritage stone, Appl. Surf. Sci. 399 (2017) 758-768.

[3] T. Rivas, J.S. Pozo-Antonio, M.E. López de Silanes, A. Ramil, A.J. López, Laser versus scalpel cleaning of crustose lichens on granite, Appl. Surf. Sci. 440 (2018) 467-476.

[4] M Mascalchi, I Osticioli, OA Cuzman, S Mugnaini, M Giamello, S Siano, Laser removal of biofilm from Carrara marble using 532 nm: The first validation study, Measurement 130 (2018) 255-263.

Damage analysis to define conservative treatments for a part rescued in the context of a post fire at National Museum, RJ, Brazil

A.L. Castro do Amaral[1*], P.L. Von Seehausen[2], N.C. Ghetti[3]

[1] Museu Nacional/UFRJ, Quinta da Boa Vista s/n, Rio de Janeiro, Brazil
[2] Museu Nacional/UFRJ, Quinta da Boa Vista s/n, Rio de Janeiro, Brazil
[3] Escola de Belas Artes-EBA/UFRJ, Rio de Janeiro, Brazil

Keywords: diagnostic, conservation, 3D photogrammetry, post fire

On the night of September 2, 2018, a major fire struck the National Museum of Rio de Janeiro, located in the Palace at Quinta da Boa Vista, a building of historical importance, former home of the emperors of Brazil in the 19th century, and the oldest scientific Institution in the country. For the past four years, a group of employees from the same Institution has been organized in a Nucleos that is conducting in a salvage excavation in the wreckage of the palace. Among the collections that were rescued, a small Egyptian statuette, dated back to the XVIII dynasty, has catch the attention of the researchers, since it was structurally preserved.

However presenting a considerable damage caused by fire and the collapse of the upper floors of the building, including burning stains, encrustations of exogenous materials, losses and soot deposits. The Laboratory for Processing Digital Image had previously 3D scanned the statuette before the fire, which was used in order to map the various alterations of the. The cavity map of the two 3D models was also prepared, in order to compare the state of conservation before and after the sinister by performing material analyses using X-ray fluorescence (XRF) and micro stratigraphy with the aim of evaluating the possible laser cleaning application for the removal of burn stains, encrustations, soot layer and other substances adhering to the artefact. The results of imagery and compositional analysis are the focal point of this work, which aims to assess the consequences of fire on lithic objects and establish a possible methodology for the conservation and restoration of the statue for its future public exposure.

*Correspondence: ana.amaral@mn.ufrj.br

Laser Treatments of Fibrous and Membranous Material Artefacts

ORAL

Application of laser technology for the cleaning of silk: comparison of different laser parameters and the effects of cleaning on the fibre

N. Brockmann[1*], *A. Sicken*[2], *J. Krueger*[3]

[1] Victoria and Albert Museum, London, United Kingdom
[2] Cologne University of Applied Sciences, Cologne, Germany
[3] Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

Keywords: conservation, silk, laser ablation, scientific analysis, cleaning

The cleaning of aged silk fibres poses a common challenge in the conservation of textiles, since traditional cleaning techniques often yield unsatisfactory results or even harm the objects. In this regard, cleaning objects with laser radiation is a promising addition to the range of available methods. Due to it being contactless, even brittle and touch-sensitive objects with disfiguring or harmful soiling could potentially be cleaned and therefore made accessible for research and presentation. Examples of treatment have sometimes shown spectacular results. Still there is some scepticism concerning the safety of this treatment for textile materials. The technique used on silk fibres had previously been researched [1-2] and it was found - under the given parameters - to be too dangerous. Taking these results into account, the range of examined lasers has been extended in this study, from 532 nm nanosecond laser to 1064 nm nanosecond and 800 nm femtosecond laser, re-evaluating the effect of this treatment on the fibres.

The physio-chemical processes taking place on the silk fibre when cleaning with lasers are complex and still not fully understood. The aim of this project was therefore to bring more clarification about potential effects of those processes on the condition of silk samples treated with a set of different parameters for wavelength, pulse duration, energy density and number of pulses, it also looks at the influence of the presence of soiling on the results. The analysis of potential effects was then carried out using statistical methods and advanced analytics. Scanning electron microscopy, Fourier-transform infrared spectroscopy and colorimetry technology provided the required insights to better assess the effects.

*Correspondence: nora.brockmann@aol.com

In conclusion it was possible to further investigate the practical application of this advanced technology regarding its suitability for textile conservation. Results show that laser cleaning of silk fibres, like most other conventional cleaning techniques, is not completely without risk, but knowing what the possible effects are helps making decisions on whether the benefits of the technique used justify these risks.

Most of the scientific analysis was carried out at the CICS (Cologne Institute of Conservation Sciences). Cleaning samples were made at the BAM (Bundesanstalt fuer Materialforschung und -pruefung) in Berlin, where also helpful discussions with the team, and sharing of their knowledge, supported a deeper understanding of laser technology.

The project is the author's master thesis, supervised by Dr. Anne Sicken (CICS) and Dr. Joerg Krueger (BAM).

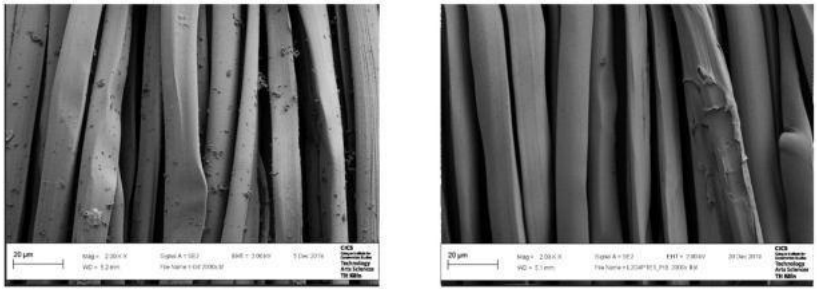


Fig. 1 - Artificially aged and soiled silk fibres (left) and aged silk fibres after cleaning with 1064 nm laser 5 pulses and 1 J/cm² (right).

Acknowledgements

Production of cleaning samples and operating of lasers was supported/carried out by the team of Joerg Krueger, Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin Scientific analysis was carried out (partly together with) Dr. Anne Sicken, Dr. Stephanie Dietz, Dr. Doris Oltrogge, Dr. Christoph Berthold. The financial support of this work has been provided by the “Maria und Otto Heynen – Stiftung”.

References

[1] Karin von Lerber, Untersuchung zur Reiningung ungefaerbter Seide mit Laser, Diplomarbeit, Bern, 2004.

[2] K. von Lerber, M. Strlic, J. Kolar, J. Krüger, S. Pentzien, C. Kennedy, T. Wess, M. Sokhan, and W. Kautek, Laser Cleaning of Undyed Silk: Indications of Chemical Change, Springer Proceedings in Physics 116 (2007) 313-320.

Laser Treatments of Fibrous and Membranous Material Artefacts

POSTER

Study and experimentation for a controlled laser cleaning of feathers

C. Mammoliti[1], R. Genta[2], M. Castellino[3], P. Croveri[4], F. Zenucchini[5]*

[1] University of Turin SUSCOR, via XX settembre, 18, 10078, "Venaria Reale" (TO), Italy
[2] University of Turin, Centro Conservazione e Restauro "La Venaria Reale", via XX settembre, 18, 10078, Venaria Reale (TO), Italy
[3] Department of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Turin, Italy
[4] Chemistry Department, University of Turin, Via P. Giuria, 7, Turin, Italy
[5] University of Turin, Centro Conservazione e Restauro "La Venaria Reale", via XX settembre, 18, 10078, Venaria Reale (TO), Italy

Keywords: ethnography, feathers, laser cleaning, diagnostics, XPS

The present work is aimed on the experimentation and the subsequent application of an analysis methodology for the study of the effects of laser radiation on the surface of macaw feathers present in an ethnographic bow with arrows, from the Museum of Anthropology and Ethnography of the University of Turin.

The bow has been treated with laser because of its fragility and peculiar deterioration [1-3]. The intervention on the artifact was therefore preceded by a careful and detailed experimentation, which allowed developing a protocol based on optical microscopy, SEM, colorimetry, and XPS analyses. The latter, which has rarely been used in conservation of fibrous materials [4], was selected in order to overcome limit of the former techniques [5-7] in characterizing the laser irradiation effects. The traditional techniques of analysis, in fact, do not allow to have an absolute certainty about the safety of such a kind of treatment. Here, we show XPS made it possible to analyze the treated material and to assess the level of damage induced by laser irradiation and then to objectively define the damage threshold. In particular, the latter can be based on the changes observed at the chemical-physical level in the cysteine, sulfur and nitrogen component present in the ornithological material.

Thanks to the experimentation, the ideal operating parameters for the laser treatment of the macaw feathers have been established, leading to the choice of a Nd:YAG laser in Long Q-Switched mode

*Correspondence: Camilla.gr.m@gmail.com

using fluences between 0.50-0.70 J/cm^2 that allowed for effective removal of the deposits and safeguard of the uncovered substrate. The treatment, in fact, did not induce any observable change of the surface microstructure, any variation of the colorimetric coordinates, and any detectable modification of the molecular bonds.

References

[1] Huget, Y. (2011). Le nettoyage et la restauration des plumes: une sélection de méthodes. CRBC. Conservation-Restauration des bien culturels(29), 49-59.

[2] Siano, S. (2006). Principles of Laser Cleaning in Conservation. In M. Schreiner, M. Strlic, & R. Salimbeni (Eds), Handbook on the use of Lasers in Conservation and Conservation Science. Bruxelles.

[3] Dignard, C., Lai, W. F., Binnie, N., Young, G., Abraham, M., & Scheerer, S. (2003). Cleaning of soiled white feathers using the Nd:YAG Laser and traditional methods. In K. Dickmann, C. Fotakis, & J. Asmus (A cura di), LACONA V Proceedings, Lasers in the Conservation of Artworks. 15-18 Sept. 2003, Osnabrück. Springer.

[4] M. Carr, C., & H. Leaver, I. , X-Ray Photoelectron Spectroscopic study of the wool fiber surface. Textile Research Journal, 1986. 56(7), 457-461.

[5] D. Ciofini, G. Rossignoli, I.Tosini, G. Lanterna, S. Siano, Laser ablation treatment of soiled featherworks: The first validation study, J. Cult. Herit. 56 (2022) 118-129.

[6] Pandozy, S., Rivière, C., Brunori, M., Nepote, F., Rivalta, A., Santamaria, U., Morresi, F., Fraticelli, F., Colantonio, C., Brunetto, A. (2014). Sperimentazione sull'uso del laser per la pulitura delle piume presenti nella collezione etnologica dei Musei Vaticani. Aplar 5 Applicazioni laser nel restauro. Atti del Convegno (p. 423-441). Città del Vaticano: Nardini Editore.

[7] Lasers in the Preservation of Cultural Heritage. Principles and applications. London: Taylor & Francis

Laser cleaning feathers: influence of the bio-pigments

M. Bertasa[1,2*], *C. Korenberg*[1]

[1] Department of Scientific Research, The British Museum, Great Russell Street, London WC1B 3DG, United Kingdom
[2] Present Address: National Research Council - National Institute of Optics (CNR-INO), Largo E. Fermi 6, 50125 Florence, Italy

Keywords: feathers, bio-pigments, Nd:YAG, damage and cleaning threshold

Feathers are complex materials that exist in a wide variety of colours. In museum collections, they are difficult to clean as physical contact can disturb their delicate structure [1,2]. Conservators generally use gentle brushing and vacuuming to remove soiling from feathers. As much as possible, the application of water, solvents and surfactants is avoided, unless soiling cannot be removed otherwise. Laser cleaning could be an appealing method for feathers as it is contactless. However, only a few case studies on laser cleaning have been published so far and the reported outcomes have been unclear or contradictory [3-8]. In the present project, systematic cleaning tests were conducted on a range of feathers using a Q-switched Nd:YAG laser emitting at 1064 nm and 532 nm. The feathers tested contained the main bio-pigments found in birds, i.e. melanin, carotenoids and/or psittacofulvins. Dyed, white and iridescent feathers, as well as down feathers, were also included in the study. First, the damage threshold fluence was determined for each type of feather and then laser tests were conducted on feathers artificially soiled with dust or carbon black. The laser was unsuccessful at removing carbon black from any feathers and better outcomes were obtained on feathers soiled with dust. At both wavelengths dust could be removed from white feathers, dyed feathers and yellow feathers containing psittacofulvins. Feathers containing melanin were found to have a much lower damage threshold fluence than other feathers. Also, laser radiation at 532 nm could cause discolouration on pink feathers containing carotenoids at high fluences. Finally, it was not possible to remove dust from down feathers without causing thermal damage. This investigation showed that laser cleaning using a Q-switched Nd:YAG laser can be

*Correspondence: moira.bertasa@ino.cnr.it

used successfully on certain types of feathers to remove dust. However, laser radiation can cause damage to down feathers and feathers containing melanin at low fluences.

Acknowledgements

This research project was made possible thanks to the generous financial support of Ed and Anne Teppo.

References

[1] E. Pearlstein, The conservation of featherwork from Central and South America, Archetype Publications, 2017.

[2] Solajic MR, Cooper, M., Seddon, T., et al. Multidisciplinary investigation of the Amazonian featherwork from the ethnographic collection at the National Museum and Galleries on Merseyside Colourful Feathers. In: Wright M, editor. The Conservation of Fur Feather and Skin 2000. p. 69–78.

[3] Asmus JF., Laser divestment for natural history museum collections. Journal of Cultural Heritage. 2000;1:S259-S62.

[4] Pacaud G, Lemaire J. Le nettoyage au laser d'un jaunissement observable sur des plumes blanches ayant subi un traitement par laser yag de désincrustation. La Lettre de l'OCIM. 2000(67):21-32.

[5] Dignard C, Lai W-F, Binnie N, Young G, Abraham M, Scheerer S. Cleaning of soiled white feathers using the Nd: YAG laser and traditional methods. Lasers in the Conservation of Artworks, Springer; 2005. p. 227-35.

[6] Karantoni E, Ekaterini M. The Influence of Cleaning Methods on Feather Structure: A Comparative Study, CAC - 31ST Annual Conference and Workshop, Jasper, Canada2005.

[7] Pandozy S, Rivière C, Brunori M, Nepote F, Rivalta A, Santamaria U, et al. Sperimentazione sull'uso del laser per la pulitura delle piume presenti nella Collezione Etnologica dei Musei Vaticani. APLAR 5 Applicazioni laser nel restauro, Nardini Editore, 2015.

[8] Colantonio C, Lanteri L, Ciccola A, Serafini I, Postorino P, Censorii E, et al. Imaging Diagnostics Coupled with Non-Invasive and Micro-Invasive Analyses for the Restoration of Ethnographic Artifacts from French Polynesia. Heritage. 2022;5(1):215-32.

Luca Trevisani's printed feathers: a laser case study

A. Di Matteo, G. De Cesare, A. Giovagnoli*

Accademia di Belle Arti (ABAQ), L'Aquila, Italy

Keywords: laser ablation, feather, cleaning of synthetic polymers.

Contemporary artists have no limits in the choice of materials to create their works. The symbolic aspect of objects taken from reality, becomes irreplaceable in expressing the artistic message. Luca Trevisani in his work “Wireless Fidelity”, part of the Maxxi Collection, used printed peacock feathers. Modifying their chromatic aspect, he maintains their symbolic characteristic of writing instrument, in the era that celebrates the speed of communication. The project of this artist is also connected to the modification and development of a highly technological technique that turns an “ancient” natural organic material into modern symbol beyond measure.

The life of his artwork is destined to a difficult conservation for the selected constituent elements, fragile and ephemeral by their constitution, chosen as a deontological reference to nature modified by man. After the interview with the artist, his execution technique was rebuilt. It is focused on making the feather a printing support with inks cross-linked with UV light, on an alkyd preparation and a protective agent for UV radiation.

A model was reproduced and it was subjected to laser irradiation at different wavelengths and pulse durations, to evaluate its resistance and the possibility of offering a valid and safe tool for cleaning the Trevisani artwork in future. Fiber coupled (1200 μm core diameter) QS and LQS Nd:YAG lasers (1064 nm, 15 and 120 ns, respectively) along with FR Er:YAG(2940 nm) laser (El.En. SpA, Calenzano, IT) were tested. The results achieved using the latter were very encouraging and they allow to foresee some interesting application perspectives.

*Correspondence: alessandra.dimatteo@studenti.abaq.it

Femtosecond lasers potential for pressure-sensitive tapes stain's removal from paper-based objects

A.C. Machado[1,2,3*], P.S. Rodrigues[1], E. Vieira[2], L.A. Angurel[3], G.F. de la Fuente[3]

[1] CHAIA Centre for Art History and Artistic Research, University of Évora, Palácio do Vimioso, Largo Marquês de Marialva, 8, 7000-809, Évora, Portugal
[1] CITAR Art History and Artistic Research Centre for Science and Technology of the Arts, Portuguese Catholic University – Regional Centre of Porto, Portugal
[3] INMA Institute of Nanoscience and Materials of Aragón, CSIC – University of Zaragoza, EINA, c/María de Luna 3, 50018, Zaragoza, Spain

Keywords: femtosecond pulsed laser, pressure sensitive tapes, paper, conservation techniques

Laser technology has gained significant attention over the past few decades, as an efficient, precise, and contactless tool for artworks conservation, along with a wider diffusion of applications in physical assessment and diagnoses techniques [1]. However, within the paper conservation field, laser cleaning techniques remain at an experimental level, especially concerning pressure-sensitive tape-damaged paper-based artworks.

Despite their instability, pressure-sensitive tapes have long been used as a convenience aid and were often employed on artworks as a temporary solution for a multitude of purposes, like the fastening of loose parts, tear mends, or picture framing for exhibit purposes.

Conventional conservation procedures are often not entirely satisfactory for minimizing persistent, sticky, and aesthetic obstructive stains from aged tapes on fragile, water-sensitive media. Additionally, they are difficult to control and essentially based on a trial error-based methodology, which results in further damage to the paper matrix and promotes health risks to the paper conservator, further emphasizing the value of research into the effects of laser cleaning on paper supports [2-4].

A Carbide model (Light Conversion) fs-pulsed laser operating at 1030 nm, 515 nm and 343 nm was employed to explore the cleaning of a set of different types of adhesive-stained papers with no patrimonial value. Macro-photography, optical and confocal microscopy, colorimetry, and FT-IR spectroscopy techniques were

*Correspondence: amachado@uevora.pt

used for the documentation and analytical characterization of the samples before and after the cleaning trials. Pulsed fs lasers have shown to significantly improve the cleaning results in comparison to nanosecond pulsed lasers with similar emission wavelengths. In addition, its ability for real-time monitoring of the cleaning progress, along with the possibility for better control of the laser parameters (pulse duration, frequency, pulse energy), is particularly relevant for the cleaning efficiency of challenging heterogeneous adhesive stained areas on fragile paper-based heritage [5-8].

Acknowledgements

The financial support for this work has been provided by FCT for the PhD Scholarship SFRH/BD/143540/2019 and to Government of Aragón (research group T54_20R).

References

[1] Kautek, W., et al. (1998). Near-Ultraviolet Pulsed Laser Interaction with Contaminants and Pigments on Parchment: Spectroscopic Diagnostics for Laser Cleaning Safety, Optics and lasers in Biomedicine and Culture V.

[2] Benedek I., et al. (2009). Handbook of Pressure-Sensitive Adhesives and Products, CRC Press, Taylor & Francis Group, New York.

[3] Dalley, J. A. (1994). Pressure-sensitive tapes: their behaviour and removal, as illustrated by a case study. In: Conservation of Historic and Artistic Work on Paper. Canadian Conservation Inst., Ottawa, Canada. pp. 39-45.

[4] Pereira-Pardo, L., & Korenberg, C. (2018). The use of erbium lasers for the conservation of cultural heritage: a review. J. Cult. Herit. 31. 236-247

[5] Boynukara C. Y., et al. (2021). An investigation of the cleaning performances of femtosecond and nanosecond laser pulses for artificially soiled papers with sizing. Appl. Phys. A127, 127-275

[6] Antonopoulou-Athera, N., et al. (2013). Use of Lasers for Cleaning of Paper Documents and Coins Conference. 6th International Congress, Science, and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin, Athens, vol. 6.

[7] Fotakis, C., et al. (2007). Lasers in the Preservation of Cultural Heritage: Principles and Applications. Taylor & Francis Group. CRC Press.

[8] Scholten, J., et al. (2005). Laser Cleaning of Pressure Sensitive Tapes on Paper (pp. 43–49). In Dickman K., Fotakis C., Asmus J.F. (Ed.). Lasers in the Conservation of Artworks. Springer Proceedings in Physics, vol. 100.

Advanced techniques for conservation and restoration of textile Cultural Heritage objects

M. Dinu[1]*, *C.H. Radulescu*[2], *G. Rosu*[3]

[1] National Institute of Research and Development for Optoelectronics, INOE 2000
[2] National Institute for Research and Development of Textile and Leather INCDTP, Romania
[3] National Museum of Romanian Peasant, Romania

Keywords: textile, laser cleaning, bio-technological tools

Crop refinement has led to an immense change of wild plants during the centuries and the original genetic resources are lost, being replaced by plants with improved crops, quality, resistance to pests and diseases and adapted to the contemporary climate changes. The investigations and analyses reported in the current paper are part of a complex research using biotechnological tools, focused on development of textile reference materials that have the strongest biological and/or technical similarity with the Cultural Heritage objects, for an enhanced restoration and conservation plan. The study analyses three types of bast materials: one is the artefact, another one is a textile material obtained from contemporary fibers and the third one is a textile material regenerated using biotechnological tools applied on ancient bast seeds.

The textile artifacts are part of the traditional costume collections from National Museum of Romanian Peasant. The reference materials, phylogenetically similar or regenerated from old fiber samples, were subjected to artificial ageing protocols and were used either for documented restoration purposes or for studies that had as results new strategies for their preservation. Laser cleaning was evaluated for removal of difficult stains, mostly of organic nature, such as sweat or food residues.

Acknowledgements

This work was supported by the Romanian Ministry of Research, Innovation and Digitalization, through Program 1 - Development of the National Research-Development System, Subprogram 1.2 - Institutional performance - Projects to finance the excellence in RDI, Contract no. 18PFE/30.12.2021 and Project PN-II-PT-PCCA-2011-

*Correspondence: monica.dinu@inoe.ro

3.1-0408/ MYTHOS

References

[1] Hughes-Stamm, S., J. Ashton, K., van Daal, A., Assessment of DNA degradation and the genotyping success of highly degraded samples, In: International Journal of Legal Medicine, 2011, vol. 125, no. 3, pp. 341–348.

[2] W. Kautek, M. Oujja, M. Castillejo,J. Hildenhagen, V. Ljubic, M. Dinu, W. Maracineanu, Walter, R. Radvan, V. Zafiropulos, N. Melniciuc G. Bregar, M Strlic, Laser cleaning and multi-method diagnostics of textile pieces of art. Lasers in the Conservation of Artworks – Proc. of LACONA 7. 371-374. 10.1201/9780203882085.ch59., 2008

Laser cleaning of a Depero wollen cloth futuristic inlay

S. Vegni[1*], A. Piccirillo[2], F. Zenucchini[2]

[1] SUSCOR, University of Turin, Venaria Reale, Italy
[2] Fondazione Centro Conservazione e Restauro "La Venaria Reale", Venaria Reale, Italy

Keywords: laser cleaning, conservation, pills, inlay, futuristic

The object of this essay is a futuristic inlay in polychrome wool cloths, Farfalle in quattro *ellissi*, made by Fortunato Depero in the laboratory founded by him and his wife Rosetta in 1920 in Rovereto.

The provenance of the artwork has been reconstructed thanks to the preliminary study and the interviews with the Spreafico Family, the owners of the work.

Today the inlay is part of the private Spreafico family's collection who arranged the loan at the Museum of Modern and Contemporary Art of Trento and Rovereto – MART.

An interdisciplinary approach has allowed the analysis of cloths and degradation, through scientific analysis, correlating environmental and anthropogenic causes, arriving at a recognition of the deterioration process of the original materials. In particular, the woollen cloth (the constitutive material of the artwork) has caused the particular effect of entanglement of woollen fibrils with the consequent formation of pills that was particularly reactive towards the atmospheric particulate, and the punctual removal of which was carried out by a combined method using Nd:YAG QS LASER equipment in 1064 nm, in conjunction with a surgical microaspiration with NEW ASKIR 30, to solve various conservative issues.

Pilling is the most impacting type of alteration present on the cloth, and even if it has not been removed, the superficial deposits that evidenced its presence have been removed because they created effects of chromatic alteration.

The success of the intervention was possible after the execution tests on mock-ups, to evaluate parameters that led to the choice of instrumentation and operational methodologies. First, the stability of cloths dyes has been evaluated, then their possible toning [1] [2]: studying the effects of variable energies on textiles is one of the

*Correspondence: silvia.vegni@outlook.it

most complex problems that concern the interaction of laser beam with the substances present in the fibres [3]. The effectiveness of the treatment was subsequently assessed based on the level of cleaning of fibres concerning their possible microstructural alteration: the identification of a damage threshold has allowed the operability within a range of fluence and frequency able to meet the needs pursued.

In support of the testing phase, observations were performed under an optical microscope, using scanning microscope (SEM) and by performing colorimetric measurements, comparing them with the original fibres before and after treatments.

Acknowledgments

This work has been carried out during a MA thesis in conservation and restoration of cultural heritage at SUSCOR, University of Turin, by a working group composed by the authors, Roberta Genta, Monica Gulmini, Fabio Belloni, and Luca Avataneo.

References

[1] Milo V., Brunetto A., Frezzato F., Trattamenti di 'luce' su un achrome di Piero Manzoni, APLAR 6 – Applicazioni laser nel restauro, 2019, pp. 459-472.

[2] Watkins K. G., Report on session “Interaction with polycrhromies and discoloration„, Journal of Cultural Heritage, 2003.

[3] Giovagnoli A., et al., Il laser. Pulitura su materiali di interesse artistico – Attività sperimentale, 2009, p. 14.

Laser treatment of soiled cotton fabric

C. Chillè[1*], C. Calvagna[1], G. Rossignoli[2], T. Nagasawa[2], I. Osticioli[1], J. Agresti[1], S. Siano[1], D. Ciofini[1]

[1] Institute of Applied Physics "N. Carrara" - CNR, Sesto Fiorentino (Florence), Italy
[2] Textile Conservation Department, Opificio delle Pietre Dure, Florence, Italy

Keywords: laser treatment, diagnostics, conservation, cotton textile, artificial soiling.

The effectiveness of the cleaning methods to remove soiling and stains from fabric artefacts is often limited by their complex microscopic and macroscopic structures, including fiber bundles, warp, weft, narrow folds, sewing deformations, and other. These structures may sometimes make the complete cleaning of the fabric very challenging and they can easily be damaged. In order to approach such a problem, dry laser cleaning has been investigated along the last decade [1–3], as it can potentially offer the advantage of removing soiling in a contactless and controlled way. However, the reported data cannot be considered exhaustive and significant insights are still needed before the extensive application of the laser approach.

To this goal, here, the effects of pulsed-laser treatments of artificially soiled cotton fabrics were investigated. As a first step, fabric cotton samples were sized with rice-based starch. Then, based on the information supplied by related literature [4], a mixture of carbon black, iron oxides, lime, kaolin, gelatine, and starch was applied as artificial soiling. Afterwards, samples were subjected to accelerated hydrothermal ageing.

Laser tests were hence carried out on the following samples: i) untreated cotton fabric, ii) unaged sized cotton fabric, and iii) aged sized cotton fabric with soiling. Moreover, to evaluate whether standard treatments can favour a more effective laser cleaning treatment, a combination of vacuum cleaning and humidification was also considered prior to laser irradiations. The fundamental wavelength and second harmonics of a Q-Switched Nd:YAG laser(1064 and 532 nm) were used for the experimentation.

Finally, the morphology and chemical composition of the laser irradiated mock-ups were characterized through a multi analytical

*Correspondence: C.Chille@ifac.cnr.it

approach including Vis spectroscopy, calorimetry, optical microscopy, Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS), Raman and X-ray fluorescence spectroscopy (XRF).

Acknowledgements

The work was performed within the project CNR4C-Plas@RT, co-financed by the Tuscany Region (POR FSE 2014-2020, "Giovanisì"), CNR-IFAC, and El.En. S.p.A.

References

[1] Ciofini, D.; Bedeir, A.; Osticioli, I.; Elnaggar, A.; Siano, S. Conservation of ethnographic artefacts: Selective laser ablation of deposits from doum palm fibers. J. Cult. Herit. 2017, 27, doi:10.1016/j.culher.2017.02.012.

[2] Londero, P.; Corda, L.; Ciofini, D.; Giuntini, C.; Leona, M. Laser Cleaning of a First Phase Navajo Wool Chief 's Blanket by Nd:YAG. In Proceedings of the Lasers in the Conservation of Artworks XI, Proceedings of LACONA XI; P. Targowski et al., Ed.; NCU Press, 2017.

[3] Elnaggar, A.; Fitzsimons, P.; Nevin, A.; Watkins, K.; Strlič, M. Viability of laser cleaning of papyrus: Conservation and scientific assessment. Stud. Conserv. 2015, 60, S73–S81, doi:10.1179/0039363015Z.000000000211.

[4] Wolbers, R. The use of a synthetic soiling mixture as a means for evaluating the efficacy of aqueous cleaning materials on painted surfaces. In Proceedings of the Conservation restauration des biens culturels; 1992; pp. 22–29.

Diagnostics and conservation of an archaeological coin purse from Pompeii

E. Gualandris[1], A. Patera[1], G. Lanterna[1], I. Tosini[1], F. Miele[2], J. Agresti[3], D. Ciofini[3] , S. Siano[3], G. Rossignoli[1]*

[1] Opificio delle Pietre Dure, viale F. Strozzi, 1 – Florence, Italy
[2] MANN, Museo Archeologico di Napoli, Piazza Museo, 19 – Napoli, Italy
[3] Institute of Applied Physics "Nello Carrara" (IFAC-CNR), Via Madonna del Piano 10, Sesto Fiorentino, Florence, Italy

Keywords: laser treatment, diagnostics, conservation, linen, excavation

The "coin purse" from the Pompeii excavation is a fabric wrapped around itself in several wrapped, so called because of its cylindrical shape and the presence of round shape elements inside. It is an exceptionally valuable piece of evidence both for its completeness and for the fact that, probably because of the specific conditions under which it was found, it is one of the few finds from the core of organic materials that didn't carbonize.

The object is realized with a beige-colored plant fiber cloth, a plane weave; the textile structure is quite intact. It has two openings: the shape is semicircular on one side, in which nine layers of fabric are clearly visible, and the other one is barely discernible. The dimensions of the purse are 9.5x5.4x3.2 cm. Before the conservation work it weighed 100.40 g, which was excessive to be an empty fabric object. The find was in a poor state of conservation due to a thick deposit of brownish-gray soil distributed over the surface, covering it entirely and compacting the fibers.

Preliminary investigations were carried out to understand the level of degradation and the nature of the materials by false-color IR imaging and UV fluorescence. Furthermore, multi-view X-rays images were collected, which allowed us to investigate the internal part and to identify the presence of five coins. Microfragments of the deposits and some fibers were also taken and analysed by scanning electron microscope (SEM-EDX). FT-IR spectrophotometry characterization of the residual bright green corrosion products was also carried out. From the conservation standpoint, it was considered appropriate to proceed with the dry removal of superficial

*Correspondence: guia.rossignoli@cultura.gov.it

deposits. Preliminary controlled microaspiration was performed, which from the very beginning yielded excellent results as it allowed the fibers to relax and soften, removing deposits that were less adherent to the surface. Afterwards, laser ablation was selected to remove the residual deposits strongly bound to the fabric. Several laser removal tests were carried out on prepared fabric samples, which were artificially aged and soil-stained to simulate the stratification of the present find. Nd:YAG laser systems with different wavelength and pulse duration were investigated and the LQS temporal regime was eventually selected. Laser ablation was performed under a stereoscopic microscope in combination with microaspiration, in order to prevent re-deposition effects. This allowed to achieve a final satisfactory removal result without any relevant undesired effect.

References

[1] Melillo, L. I reperti tessili dall'area vesuviana nel Museo Archeologico Nazionale di Napoli, In: Giulierini, P. et al. (Eds) Miniere della Memoria. Scavi in archivi, depositi e biblioteche, Firenze 2020, pp. 51-61.

[2] Galli, M.; Coletti, F.; Lemorini, C.; Mitschke, S. The Textile Culture at Pompeii Project, In: Busana M.S. et al. (Eds) PURPUREAE VESTES VI. Textiles and Dyes in the Mediterranean Economy and Society, atti del VI Simposio internazionale (Padova-Este-Altino, 17-20 ottobre 2016), Valencia 2018, pp. 276-277.

[3] Gualandris E. Il restauro di due reperti tessili archeologici provenienti dall'area vesuviana, ora al Museo Archeologico Nazionale di Napoli (MANN), OPD school diploma thesis a.a. 2017-2018

[4] Juez F.L.; Diaz Vilches V. Developing Techniques for the Conservation of the Archaeological Textiles Collection held by Antofagasta Museum, Consejo Nacional de la Cultura y las Artes, Gobierno de Cile, Fondart project n. 45112, 2015.

[5] Schirripa Spagnolo G.; Della Ventura G.; Bellatreccia F. Analisi storico-iconografica e accertamenti tecnici su un falso sesterzio di Vespasiano con il tipo del Colosseo nella collezione Maruffi, in Terre, antichità, memorie. La raccolta numismatica Maruffi, Roma 2014, p. 256.

[6] Mazzeo R. Patine su manufatti metallici, in Le patine. Genesi, significato, conservazione, Kermes Quaderni, Firenze 2005, pp. 29-44.

[7] Pappalardo, U. L'eruzione pliniana del Vesuvio nel 79 d.C.: Ercolano, In: Albore Livadie C. et al. (Eds.) Volcanology and Archaeology Volcanologie et archéologie, Workshops Procs., Strasbourg 1990, pp. 197-215.

Laser cleaning of a modified eighteenth-century waistcoat of the Civic Museums of Modena

V. Scaglia[1*], A. Piccirillo[2], C. Ricci[2], F. Zenucchini[2]

[1] SUSCOR, University of Turin, Venaria Reale, Italy
[2] Fondazione Centro Conservazione e Restauro "La Venaria Reale", Venaria Reale, Italy

Keywords: Laser cleaning, conservation, costume, silk, metallic threads

The present work intends to deepen the cleaning treatment carried out during the restoration of a waistcoat coming from the Civic Museums of Modena.

The correct setting of the treatment began through the historical-artistic, technical and material analyses of each artifact's element, which highlighted its original manufacture between 1690 and 1720. The garment was modified through several remodellings, possibly made in the nineteenth century and considered as historical evidences. In detail, the main fabric in silk taffetas, its two internal linings and the rich embroidery that decorates it – made with eight different types of metal threads and sequins – could be from the eighteenth century. The fabrics of sleeves, back, main lining and the inner reinforcement cardboards are all nineteenth-century made.

The dress was therefore heterogeneous from an historical, material, and also conservation perspective: the silk was characterized by large halos and soiling, while metal threads presented a significant silver oxidation.

The entire cleaning treatment was designed specifically in order to remove these alterations, setting two primary aims: on the one hand, preserving every historical evidence without unsewing the tailoring and, on the other hand, respecting the conservative requirements of the multiple materials involved, thanks to a specific cleaning method, developed in order to interact selectively with the surfaces of any elements to be treated and to not affect the complex stratification of the garment.

In the first place, chemical cleaning was experienced by means of rigid gels together with different solutions. The negative results of these tests led to experiment the laser cleaning. The latter was

*Correspondence: va.scaglia@gmail.com

preceded by in-depth research on similar cases taken from the international literature [1-3], allowing to select the most suitable instruments and operating conditions for this peculiar treatment.

A first set of tests was conducted to obtain a chromatic lowering of halos and stains on silk; the second set was performed to remove the oxidation patina of the metallic threads. For each set, both undertaken directly on the artifact, three Laser Nd:YAG instruments were tested (QS at 532 nm, QS at 1064 nm and LQS at 1064 nm) and, in addition, the irradiated portions were monitored through a wide diagnostic support – with stereo and 3D optical Microscope, Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDS) and Colorimeter.

The treatment of the nineteenth-century textiles proved to be completely inefficient, while positive results were obtained on the eighteenth-century silk and metallic threads, leading to complete their cleaning on the whole waistcoat.

References

[1] Shehata N. M., An experimental study on using laser for cleaning metal threads, Journal of Materials Science and Chemical Engineering, volume 8, 2020, pp. 46-63.

[2] Patti M. & Siano S., I tessili, applicazioni laser e altre indagini per i materiali fibrosi, Noventa Padovana: Nardini Editore, 2017.

[3] Degrigny C., Tanguy E., Le Gall R., Zafiropulos V., & Marakis G., Laser cleaning of tarnished silver and copper threads in museum textiles. Journal of Cultural Heritage, volume 4, 2003, pp. 152-156.

Removal of a black varnish coating from a leather cover of 19th century bicycle saddle using Nd:YAG laser

C. Donati[1], D. Ciofini[2], S. Siano[2], G. Rossignoli[1], A. Sidoti[1], S. Agnoletti[1]*

[1] Opificio delle Pietre Dure, Via degli Alfani 78, 50122, Firenze, Italy
[2] Istituto di Fisica Applicata "N. Carrara", CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

Keywords: laser ablation, conservation, leather, varnish.

In the restoration-conservation of historical leather objects the removal of protective organic coatings is a challenging task, as collagen-based materials are subject to degradation with consequent loss of mechanical strength over time. This makes them very sensitive to most of the available wet treatments, strongly motivating the use of less invasive strategies. For this reason, during the conservation intervention of a bicycle of the late Nineteenth Century, we investigated the potential of laser technology to uncover the original leather surface of its saddle cover. In particular, the main goal was to remove a variably thick, very adherent and bonded black alkyd varnish coating, which was applied all over the leather surface after many years from the production of the of the saddle. This coating strongly damaged the underlying leather substrate, because it was very thick and rigid, and made the surface extremely shiny. Moreover, the saddle cover appeared very sensitive to mechanical and chemical stresses. Solvents would have stained the leather, whereas the use of mechanical tools (scalpels, rubbers, needles ecc.) would have led to structural damage and losses of leather fragments.

Before dealing with laser tests, the surface was thoroughly inspected through microscopy examinations. Afterwards, irradiation tests were carried out using two commercial pulsed Nd:YAG lasers with emission at 1064 nm, the EOS 1000 (Long Q Switched, LQS) and the Smart Clean II (Short Free Running, SFR). The former is characterized by an intermediate pulse duration of 120 ns, which enables an efficient photomechanical action minimizing associated thermal effects. Instead, the SFR is characterized by a longer pulse duration (30-140 μs) allowing for a more photothermal and negligible

*Correspondence: caterina.donati97@gmail.com

photomechanical action. Single-shot damage and cleaning fluence thresholds were first determined on the wooden supporting structure of the saddle and then on its leather cover. Different fluences, number of pulses, and pulse repetition frequency were tested in small areas of the wooden saddle structure. Then, the operating parameters that provided the best results were used for extending the cleaning tests on localised spot areas of the black coating on the leather folding on the underside of the saddle.

The tests showed that EOS 1000 LQS laser provided the best cleaning results, in terms of removal effectiveness and respect of the leather surface. Fluences of 0.45-0.6 J/cm2, 1 Hz pulse repetition frequency resulted to be the most suitable irradiation parameters in order to lower the thickness of the protective layer and attenuate its undesired glossy appearance.

Laser Treatments of Painted Surfaces

ORAL

LASER INDUCED PHOTOTHERMAL TEXTURING FOR ENHANCING SOLVENT ACTION IN REMOVAL OF UNWANTED OIL-BASED PAINTS

D. Ciofini[1], L. Giola[2], A. Pavia[2], J. Agresti[1], I. Osticioli[1], S. Siano[1]*

[1] Istituto di Fisica Applicata "N. Carrara" - CNR, Sesto Fiorentino, Italy
[2] Pavia Restauro S.r.l, Rome, Italy

KEYWORDS: laser texturing, photothermal, solubility, swelling, painting.

In this study we investigate on the potentialities of Nd:YAG laser induced photothermal texturing (LIPT) in mitigating the risks associated with solvent exposure, both for the operator and the painting layers, during ablative conservation treatments. Following the demonstration that LIPT can significantly facilitate the mechanical removal of oleoresinous patinations on bronzes [1-2], here, we provide the first analytical evidence that it can also favour the mild solubilization of unwanted paint layers. In particular, we aimed at the removal of unwanted oily overpaints from oil paintings, which is a subject of high concern among painting conservators. Within this field, it is known that polar solvents or their mixtures are routinely used as an effective way of facing with the solubilization of resins or tough old oil films. However, it is also noteworthy that solvent diffusion and its retention can affect the physicochemical properties of the inner paint layers, mainly due to local solubilization effects. Undesired consequences upon solvent material removal can be mainly ascribed to paint swelling, leaching (extraction) and desorption of soluble components, which lead to embrittlement and optical changes (blanching or desaturation) of the treated surface overtime [3]. Therefore, with the aim of reducing the above-mentioned risks, in this study, LIPT and consequent removal by solvent of unwanted oil-based paints is addressed. Here, LIPT is achieved by photothermal phase changes using microsecond Nd:YAG laser. To simulate unwanted oil-based paints, raw and burnt umber oil formulations were applied and studied as a micrometer-thick single layer films over glass substrates and over painted samples. The latter included lead white, chrome yellow, ultramarine blue, Prussian blue, cerulean blue and zinc white, which were mixed

*Correspondence: D.Ciofini@ifac.cnr.it

and thinned with linseed oil, spread out over primed canvas substrates and then exposed to curing and artificial aging. Threshold fluences, laser processing parameters, modification of surface topography, chemistry, wettability and their influence on solubility parameters and solvent action have been thoroughly assessed and quantified by microscopy image analysis, colourimetry, Fourier transform infrared spectroscopy (FTIR), along with droplet and solubility tests [4].

Analytical results showed that with long-pulsed lasers LIPT is achieved at fluences well-below the damage thresholds of the underlying pictorial layers. Laser textured surfaces showed an increased roughness due to the formation of micro-craters and micro-swelling surface structures, whereas no significant modifications of the oil medium were detected through FTIR spectroscopy. Most important, with respect to untreated surfaces, solubilization of laser-textured surfaces was more easily achieved using solvent mixtures with lower polarity. The latter allow removing the LIPT-processed overpaints without any risk of dissolution for the underlying paint layers. The observed shifts in the solubility parameters were mostly due to an improved diffusion and dissolution process of the solvent across the laser-textured film.

Finally, after a thorough analytical campaign including multispectral photography, X-Ray Fluorescence (XRF) Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), and micro-Raman Spectroscopy, the optimized approach combining LIPT and low-polarity solvents allowed approaching for the first time safely and in a controlled way the uncovering of an inedited valuable oil painting on millboard. The painting was found on the back of Luce Balla's Notturno, beneath a dark brown overpainting. The presented method opens new perspectives in the removal of undesired paint layers from paintings, as well as from a variety of substrates.

References

[1] S. Siano, M.L. Nicolai, S. Porcinai, Verrocchio's David: characterization and conservation treatments, In: G.M. Radke et al. (Eds), Verrocchio's David Restored, Giunti, Florence 2003, pp. 97-109. ISBN: 8809032640.

[2] S Siano, J Agresti, I Cacciari, D Ciofini, M Mascalchi, I Osticioli, A.A. Mencaglia, Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd: YAG

lasers, Appl. Phys. A 106 (2012) 419-446.
[3] Baij, L., Buijs, J., Hermans, J.J. et al. Quantifying solvent action in oil paint using portable laser speckle imaging. Sci Rep 10, 10574 (2020).
[4] Cremonesi, P. (2004). L'uso dei solventi organici nella pulitura di opere policrome.

Laser cleaning of the painted frames of the Issenheim altarpiece in Colmar (FR)

A. Brunetto[1], D. Martos-Levif[2], A. Pontabry[3], M. Lopez[2], V. Detalle[2*]*

[1] Restauri Brunetto, Vicenza, Italy
[2] Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris, France
[3] Private conservator, Paris, France

Keywords: laser cleaning, painting, evaluation, OCT, altarpiece Issenheim.

The cleaning treatment of the paintings consists in the gradual reduction or removal of layers of degraded varnishes and overpainting, often distributed in multilayers over the paint layer, without damaging the original material of the painting itself.

The application of the laser technology on the polychromies frames of Grünewald's Issenheim altarpiece painting (1512-16, Figure 1) has demonstrated its effectiveness and safeness tool for unrevealing sensitive paint layers, otherwise not easy to remove with other traditional cleaning techniques. Infact, different layers of repainting have been identified on the original frame. The scientific committee following the work aimed to reveal the original layer. Different chemical compositions of the repainting have induced difficulties to work with classical chemical or mechanical approach. Then, laser cleaning has been evaluated as a possible solution for ensuring this restoration work.

The constituent materials, characterized by micro-stratigraphic investigations, FTIR, have allowed the identification of animal glue and therefore a technique of painting in tempera. The overpaint, probably dating from the beginning of the 20th century, was composed of a layer of oil paint applied on a preparation based on calcium carbonate.

The cleaning tests were perfomed by comparing two laser systems: an EOS Combo Nd: YAG (El. En. S.p.a), with a wavelength of 1064 nm in SFR (30-110 µs) and LQS (100 ns) pulse mode and a Light Brush 2 Er: YAG (El.En. S.p.a), with a wavelength of 2940 nm in Very Short (150 µs) and Short (250 µs) modes.). Tests with Er: YAG lasers were performed with the auxiliary action of a buffer

*Correspondence: vincent.levif@culture.gouv.fr, dominique.martos-levif@culture.gouv.fr

solution or with a mixture of water / alcohol or acetone gels. We will present the scientific methodology occurring during this work, the results obtain after testing the different wavelength and duration modes as well as the evaluation of the laser cleaning with OCT analysis, a diagnostic laser tool, particular interest to examine the stratigraphy and the surface of the paintings.

Acknowledgements

Our thanks to the Musée Unterlinden for the concrete collaboration.

Figure 1. Altarpiece panels of San Sebastiano, the Crucifixion and San Antonio. ©Musée Unterlinden

Waiting for Science to Catch Up to the Problem: The Development and Application of a Custom-Designed Green Laser System to Remove Decades Old Penciled Graffiti on Raw Canvas from Morris Louis' Masterwork, Beta Upsilon

A. Kerr[1], B. Dajnowski[2]*

[1] Smithsonian American Art Museum, Washington DC, USA
[2] G.C. Laser Systems Inc., Forest Park, IL, USA

Keywords: laser ablation, conservation, canvas, painting, cleaning.

In 1989, paintings conservators at the Smithsonian American Art Museum were confronted by the vandalism of Morris Louis' Beta Upsilon, a masterwork painting from his unfurled series (1960-61). Comprised of colored bands of paint flowing inward from the edges on an unprimed canvas, the work was defaced with penciled graffiti lines on the raw canvas that mimicked the unfurling strokes of colors. Testing revealed the solution was not readily at hand at the time. Despite pressure to treat the artwork immediately, conservators persisted in finding the right solution. Laser cleaning was considered as a possible solution, but the correct parameters needed to be identified. Extensive testing was conducted on mockup samples using various pulse durations and wavelengths: 1064nm, 532nm, 355nm, and 266nm. After many years of preparation and testing, it was concluded that the 532nm wavelength was appropriate for this particular cleaning problem. An entirely new laser cleaning system, the GC-532, was designed and built specifically to clean the *Beta Upsilon*. In order to allow great flexibility in laser parameter optimization the new bespoke laser system was built to have the 2nd harmonic 532nm, tunable pulse duration, pulse frequency, and pulse energy, an ultra-high speed hot-spot free circular scanner with tunable RPM, and various focal lens options. The research and testing leading up to the creation of a new purpose built green 532nm pulsed laser system, the process of optimizing laser cleaning parameters, and the cleaning results achieved will be presented. This new laser technology will have future applications in cleaning canvasses and organic materials.

*Correspondence: Bartek@GCLasers.com

Egyptian Limestone Polychrome Statues: Laser Cleaning in Comparison with Traditional Methods

E.A. Furgiuele[1*], *F. Zenucchini*[2], *P. Croveri*[3], *M.C. Capua*[4]

[1] Università degli Studi di Torino - SUSCOR, Turin, Italy
[2,3,4] Centro Conservazione e Restauro "La Venaria Reale" - UniTo, Turin, Italy

Keywords: laser cleaning, egyptian limestone, conservation, restoration

This comparative study between traditional and laser cleaning methods focuses on identifying the best intervention methodology for small limestone sculptures from Heliopolis that hold traces of red ochre, part of the *Museo Egizio di Torino* collection.

The main conservation issues of these artefacts, identified as fertility votive offerings dating back to the VII-III century B.C., were a thick layer of deposit and surface decohesion. These artworks had never been restored before, therefore, the layer adhering to the surfaces was made up mainly of excavated earth material with a thickness and tenacity that differed from sculpture to sculpture. After a thorough characterization diagnostic campaign using non-invasive investigations (XRF and SEM-EDS), original constitutive materials have been identified and a set of preliminary tests on samples were carried out to achieve a gradual, controlled, and selective cleaning. This was possible thanks to the method adopted, mainly through LQS laser, which during the study phase proved to be the best solution between traditional methods and the different types of Nd:YAG lasers tested (Q-Switch, Long Q-Switch and Short Free Running). This method successfully uncovered painted, as well as unpainted, surfaces with minimized risk of damage as compared with standalone mechanical or chemical approaches.

Based on the results obtained from preliminary laser cleaning tests on samples, special attention was given to determine the operative fluences, define a suitable irradiation protocol, and combining it with traditional cleaning systems only when necessary. A constant monitoring through investigation was performed proceeding gradually and resulting in an overall balanced cleaning, achieving a critical aesthetic restitution performed case-by-case.

*Correspondence: eleonora.furgiuele@gmail.com

You Can Clean But Cannot Touch. Graffiti Removal From Prehistoric Pictographs at Hueco Tanks State Park & Historic Site Using Laser Ablation Process

A. Dajnowski[1], T. Tague[2], T. Roberts[3], M. Strut[4], B. Price[5], N.M. Kelly[6], D. Tague[7], K. Sutherland[8], B. Dajnowki[9]*

[1] The Conservation of Sculpture and Objects Studio, Inc., Forest Park, IL, USA
[2] Bruker Safety Committee, Billerica, MA, USA
[3] Texas Parks and Wildlife Dep, Fort Davis, TX, USA
[4] Texas Parks and Wildlife Dep, Austin, TX, USA
[5] Philadelphia Museum of Art, Philadelphia, PA, USA
[6] Bruker Nano Analytics, Denver, CO USA
[7] University of Texas, Richardson, TX , USA
[8] The Art Institute of Chicago, Chicago, IL, USA
[9] G.C. Laser Systems Inc., Forest Park, IL, USA

Keywords: pictograph, laser ablation, graffiti, conservation

The Hueco Tanks State Park & Historic Site, near El Paso, Texas, USA, is culturally and spiritually significant for several Native American Tribes. It has the largest concentration of prehistoric mask pictographs (rock paintings) in North America. This National Historic Landmark, which is also a popular recreational destination, was vandalized numerous times over the past century. The pictographs and rock formations were disfigured by extensive graffiti paint. We employed laser ablation to remove the graffiti without affecting the original pictographs and rock formations. This process has restored the legibility of the pictographs while respecting their sacred legacy.

To inform the laser cleaning treatment, we analyzed the pictographs and graffiti. Because the site is sacred and pictograph sampling was not permitted, non-invasive Raman, XRF, and microscopic analyses were performed in situ. Goethite, hematite, gypsum, copper-containing pigment, quartz, feldspar, and calcium oxalate were characterized. The graffiti paint was sampled and analyzed at the Philadelphia Museum of Art using MFTIR, PY-GCMS, and SEM-EDS. Cellulose nitrate- and alkyd-based paints, formulated with chrome yellow, Prussian blue, iron oxide, burnt umber, zinc oxide, calcium carbonate, and barium sulfate pigment/fillers, were identified.

*Correspondence: adajnowski@csosinc.com

We prepared mockups on local stone samples to simulate the analyzed pictograph and graffiti compositions and to test the laser parameters. Once optimal parameters were determined, they were applied in the field using 1064 nm lasers to safely and effectively remove the graffiti without affecting the original works.

This paper describes the research, preparation, and graffiti removal from the Hueco Tanks pictographs and rock formations using selected laser systems.

CW-LASER THERMAL RESTORATION OF OXIDIZED LEAD WHITE IN MURAL PAINTINGS

T. de Seauve[1], S. Bosonnet[2], O. Grauby[3], A. Semerok[4], V. Detalle[5], J.M. Vallet[1]*

[1] Centre Interdisciplinaire de Conservation et Restauration du Patrimoine (CICRP), 21 rue Guibal, 13003 Marseille, France
[2] Université Paris-Saclay, CEA, Service de la Corrosion et du Comportement des Matériaux dans leur Environnement, 91191, Gif-sur-Yvette, France
[3] Aix-Marseille Université, CNRS – UMR 7325 CINaM, campus de Luminy, Case 913, 13288 Marseille Cedex 9, France
[4] Université Paris-Saclay, CEA, Service d'Études Analytiques et de Réactivité des Surfaces, 91191, Gif-sur-Yvette, France
[5] C2RMF, Palais du Louvre – Porte des Lions, 14, quai François Mitterrand, 75001 Paris, France

KEYWORDS: Laser heating, reconversion, colours, mural paintings, lead white

Red lead and lead white are some of the most ancient and common pigments in mural paintings. However, they tend to blacken with time due to their oxidation to plattnerite (β-PbO_2). The possibility to induce the reconversion reactions for red lead by CW laser heating (Figure 1) was already demonstrated [1]. Minium (Pb_3O_4) and subsequent massicot (β-PbO) formation from plattnerite were achieved (confirmed by SEM-EDS, XRD and micro-Raman) under CW-Ar^+, 810 nm diode and Nd:YAG lasers. As for lead white, another reconversion route, involving PbO, was suggested, given the impossibility to trigger the carbonatation reaction of plattnerite in solid-state conditions [2]. We hereby report our recent advance on the feasibility study of this restauration process. First, the thermal decomposition of plattnerite into both litharge α-PbO and β-PbO, depending on the conditions, was studied in ovens. Massicot being more easily obtained by laser heating, its solid-state carbonatation, or oxy-carbonatation, was studied in CO_2 and CO_2/H_2O atmospheres by TGA and in ovens. The formation of cerussite or hydrocerussite from massicot, an exothermic reaction spontaneous under 300 °C, was not observed during thermogravimetric analysis or oven trials at high temperature (250 – 300 °C). Condensed water

*Correspondence: thea.de-seauve@cicrp.fr

seems to be an important aspect of this reaction, as previous work show [3]. Basing ourselves on this study, we suggest a two-step restauration process, involving (1) a laser heating of β-PbO_2 in order to form β-PbO and (2) an exposition of the wet pictorial layer to a CO_2 flux at temperatures below 100 °C, in order to trigger the carbonatation and oxycarbonatation reactions.

Figure 1. Darkened red lead paint sample after irradiation by a CW top-hat Nd:YAG laser (red part on the right) at 1000 kW m^{-2}. The lighter stains designated by an arrow are due to gypsum. Cracks were present before the treatment.

Acknowledgements

The authors wish to acknowledge the French Ministry of Culture and Communication for financial support and the French Fondation des Sciences du Patrimoine for their financial support to the RECONVERT 2 project.

References

[1] S. Aze et al., Reversion of darkened red lead-containing wall paintings by means of cw-laser irradiation: In situ tests and first application, Lasers in the Conservation of Artworks VIII, 2010, 129.

[2] T. de Seauve et al., Continuous wave laser thermal restoration of oxidized lead-based pigments in mural paintings, Applied Physics B, 127, 2021, 162.

[3] W. Mu et al., Adsorption of CO2 on PbO at ambient temperature, Applied Surface Science, 258, 2011, 950–954.

2D HIGH LATERAL RESOLUTION XRPD MAPPING FOR THE IN-DEPTH CHARACTERIZATION OF CW NIR LASER IRRADIATION TO THERMALLY INDUCE THE CONVERSION OF PLATTNERITE INTO RED LEAD PIGMENT

A. Suzuki[1], I. Osticioli[2], S. Siano[2], C. Riminesi[1]*

[1] Institute of Heritage Science, National Research Council ISPC-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Florence, Italy
[2] "Nello Carrara" Institute of Applied Physics, National Research Council IFAC-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Florence, Italy

KEYWORDS: temperature controlled laser irradiation, micro-Raman spectroscopy, wall paintings, synchrotron radiation, PbO_2

Red lead (*Minium*, Pb_3O_4), one of the earliest manufactured pigments, while naturally aging may undergo various types of discoloration. On wall paintings, in most cases the alteration can be ascribed to the transformation of the lead-based pigment into PbO2, mainly in the ß phase called plattnerite. The set up of restoration methods to effectively recover the darkened paint layer is crucial for the integrity of artworks. One recently proposed restoration method is based on the thermal effect exploited while irradiating with VIS/NIR CW lasers to thermally induce the transformation of lead dioxide into red lead [1]. This method appears to be successful although not yet fully characterized as some open questions remain. How controllable and effective is the conversion? At which temperature the surface has to be treated and which drawback this temperature may cause to the wall painting? How deep could the treatment go into the paint layer? Therefore, in the present work, wall painting mock-ups with plattnerite in casein binder where prepared and several irradiation tests where performed with 785 and 1064 nm CW lasers with the simultaneous monitoring of the surface temperature. The conversion results achieved at different laser intensity and radiant exposure, were characterised using micro-Raman spectroscopy. Furthermore, a thin section of the sample, which exhibited the best result in terms of conversion effectiveness was analysed with 2D high lateral resolution (few microns) X-Ray Powder Diffraction (XRPD) mapping available at ID13 (ESRF synchrotron facility) [2]. The mapping at the micrometer scale of the crystalline

**Correspondence: amelia.suzuki@ispc.cnr.it*

phases provided by these techniques has allowed to shed light on the in-depth distribution (2D map size of 400x400 um^2) of the different lead oxide phases produced by CW NIR laser irradiation of plattnerite.

Acknowledgements

We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities and we would like to thank Manfred Burghammer for assistance in using beamline ID13 (proposal HG-172, pilot of a BAG project supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No 870313, Streamline). Moreover, we are greatful to all the Historical Materials BAG team for the efficient and valuable support during and after beamtime.

References

[1] de Seauve T., Detalle V., Semerok A., Aze S., Grauby O., Bosonnet S., Ginestar K., Vallet J.M., Continuous wave laser thermal restoration of oxidized lead-based pigments in mural paintings, Appied Physics B, 2021,127, 162.

[2] Cotte, M., Gonzalez, V., Vanmeert, F., Monico, L., Dejoie, C., Burghammer, M., Huder, L., de Nolf, W., Fisher, S., Fazlic, I., Chauffeton, C., Wallez, G., Jiménez, N., Albert-Tortosa, F., Salvadó, N., Possenti, E., Colombo, C., Ghirardello, M., Comelli, D., Avranovich Clerici, E., Vivani, R., Romani, A., Costantino, C., Janssens, K., Taniguchi, Y., McCarthy, J., Reichert, H., Susini, J., The "Historical Materials BAG": A New Facilitated Access to Synchrotron X-ray Diffraction Analyses for Cultural Heritage Materials at the European Synchrotron Radiation Facility, Molecules, 2022, 27, 1997.

FINDING A PATH FOR RESOLVING LASER CLEANING PROBLEMS – SELECTED ASPECTS OF THE PRELIMINARY STUDIES AND IMPLEMENTATION PROCESS OF A NEW TYPE OF IR LASER WITH HIGH REPETITION OF PULSES TO CONSERVATION-RESTORATION PRACTICE

A. Faron[1*], *M. Iwanicka*[2]

[1] Doctoral School - Academia Artium Humaniorum, Nicolaus Copernicus University in Toruń, Bojarskiego 1/C 017, 87-100 Toruń, Poland
[2] Department of Conservation and Restoration of Paintings and Polychrome Sculpture, Faculty of Fine Arts, Nicolaus Copernicus University in Toruń, Sienkiewicza 30/32, 87-100 Toruń, Poland

KEYWORDS: laser ablation, diagnostics, conservation, painting

The aim of this work is to present a preliminary study in the field of laser cleaning of easel paintings and gilded heritage objects. Although, till now, some successful similar laser treatments have been performed [1-3], a novelty of this attempt consists in the new type of laser and its parameters, which were not yet reported extensively in the literature. The equipment applied to this work was based on RedEnergy G4 EP-Z Pulsed Erbium Fiber Laser (SPI Lasers, UK) which is characterized by an emission wavelength of 1064 nm, power of 100W and a very high pulse repetition frequency (1kHz – 4 MHz), with pulse time adjustable in the range of 5 ns-2 μs and a very small spot diameter of ca 200 μm. The scan pattern is programmable with adjustable scanning speed of 6–260 cm/s. The conical delivery path offers a significant advantage when cleaning objects with a developed surface. The high and adjustable repetition rate, the relatively low power of a single pulse and the fast scanning on the surface of the object created premises for the expectation of high homogeneity of the ablation process and increased safety of the historic object during the process, in comparison to typical lasers used in the conservation of heritage objects.

As possibilities of implementation of such laser to the conservation of polychrome and gilded works of art were not well reported, there was a need to perform a series of basic tests and trials that led to defining a safe range of parameters for certain materials and painting supports. Dedicated software for fluence

*Correspondence: faron.anna@doktorant.umk.pl

estimation was created, enabling comparison with the experiment conditions reported in the literature.

In this paper, some examples of systematic attempts to clean various polychrome and varnished surfaces will be shown – the first stage of trials was conducted on newly prepared models, the second on 30-year-old naturally aged samples and, finally, on representative heritage objects selected for the laser cleaning. Along with the removal of undesired layers, a monitoring protocol of assessment of the treated surface will be presented. Analyses were conducted before and after the cleaning process to evaluate changes in the particular layers. Examination techniques chosen for the purpose of this study were mostly non-destructive: observation in visible and ultraviolet light, VIS-UV optical microscopy, MA-XRF and optical coherence tomography.

Acknowledgements

The financial support of this work has been provided by Excellence Initiative - Research University programme.

References

[1] Siano S., Osticioli I., Pavia A., Ciofini D., Overpaint removal from easel paintings using an LQS Nd: YAG laser: The first validation study, Studies in Conservation, vol. 60 (1), 2015, pp. 49-57.

[2] Hellen R., Preliminary study into the reduction and removal of naturally aged varnishes from painted surfaces using Er:YAG laser in a two-step cleaning process with solvents, Journal of the Institute of Conservation, vol.43, no. 1, 2020, pp. 79-93.

[3] Brunetto A., Bono G., Frezzato F., Er:YAG laser cleaning of 'San Marziale in Gloria' by Jacopo Tintoretto in the Church of San Marziale, Venice, Journal of the Institute of Conservation, vol.43, no. 1, 2020, pp. 44-58.

Photoacoustic monitoring of UV laser ablation of aged varnish coatings on Heritage objects

E. Dimitroulaki[1,2*], *G. Tserevelakis*[1], *K. Melessanaki*[1], *G. Zacharakis*[1], *P. Pouli*[1]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Greece
[2] Department of Materials Science and Technology, Heraklion, Greece

Keywords: Photoacoustics, laser ablation, monitoring of cleaning, aged varnishes

Varnish coatings undergo degradation mechanisms leading to their deterioration, and thus the removal of their most degraded outer layer becomes imperative. UV laser ablation offers high control and accuracy and is undoubtedly an exceptionally promising cleaning approach, though may be significantly reinforced with real-time monitoring. Up to this point, most monitoring techniques are focused on the exploitation of light and all the information it may provide. However, herein, the investigated implement is the acoustic waves produced during the laser ablation process.

Photoacoustic monitoring was employed in order to investigate its potential in monitoring the ablation process, in the context of real-time comparison of the photoacoustic (PA) signals produced upon material removal by UV light. In this novel technique, an air-coupled transducer capable of recording acoustic waves in the MHz regime, is set in a non-contact geometry close to the object undergoing laser cleaning, in order to detect the PA signals generated upon the laser assisted thinning of varnish. The feasibility of this approach lies on two major indicators; the amplitude of the PA signal, as well as its temporal delay, which are providing us with crucial information that can be exploited to effectively monitor this highly sensitive cleaning process. The results from this study will be substantially explained with a view to the potential of using the photoacoustic method as an effective real-time monitoring method to follow the UV laser cleaning process of polymeric coatings and films.

Acknowledgements

The financial support of this work has been provided by IPERION-

*Correspondence: evdoxia.dimitroulaki@gmail.com

HS H2020 project (Integrated Platform for the European Research Infrastructure ON Heritage Science) funded by the European Union, H2020-INFRAIA-2019-1, GA 871034.

References

[1] O. Kokkinaki, E. Dimitroulaki, K. Melessanaki, D. Anglos, P. Pouli, Laser-induced fluorescence as a non-invasive tool to monitor laser-assisted thinning of aged varnish layers on paintings: fundamental issues and critical thresholds, Eur. Phys. J. Plus, 136, 2021

[2] G. J. Tserevelakis, P. Pouli, G. Zacharakis, Listening to laser light interactions with objects of art: a novel photoacoustic approach for diagnosis and monitoring of laser cleaning interventions, Heritage Science, 8, 2020

[3] A. Papanikolaou, G. J. Tserevelakis, K. Melessanaki, C. Fotakis, G. Zacharakis and P. Pouli, Development of a hybrid photoacoustic and optical monitoring system for the study of laser ablation processes upon the removal of encrustation from stonework, Opto-Electronic Advances, 3, 2020, pp. 190037-1.

In-situ and rapid assessment of Er:YAG laser cleaning on easel paintings by a portable hyperspectral sensor

C. Wang[1,2], Y. Cao[3], F. Tie[1], M. Camaiti[4]*

[1] Key Laboratory of Cultural Heritage Research and Conservation (Northwest University), Ministry of Education, Xi'an, China
[2] School of Cultural Heritage, Northwest University, 710127, Xi'an, China
[3] Institute of Culture and Heritage, Northwestern Polytechnical University, Xi'an 710072, China
[4] CNR-Institute for Geosciences and Earth Resources, 50121, Florence, Italy

Keywords: Photoacoustics, laser ablation, monitoring of cleaning, aged varnishes

Varnish coatings undergo degradation mechanisms leading to their deterioration, and thus the removal of their most degraded outer layer becomes imperative. UV laser ablation offers high control and accuracy and is undoubtedly an exceptionally promising cleaning approach, though may be significantly reinforced with real-time monitoring. Up to this point, most monitoring techniques are focused on the exploitation of light and all the information it may provide. However, herein, the investigated implement is the acoustic waves produced during the laser ablation process.

Photoacoustic monitoring was employed in order to investigate its potential in monitoring the ablation process, in the context of real-time comparison of the photoacoustic (PA) signals produced upon material removal by UV light. In this novel technique, an air-coupled transducer capable of recording acoustic waves in the MHz regime, is set in a non-contact geometry close to the object undergoing laser cleaning, in order to detect the PA signals generated upon the laser assisted thinning of varnish. The feasibility of this approach lies on two major indicators; the amplitude of the PA signal, as well as its temporal delay, which are providing us with crucial information that can be exploited to effectively monitor this highly sensitive cleaning process. The results from this study will be substantially explained with a view to the potential of using the photoacoustic method as an effective real-time monitoring method to follow the UV laser cleaning process of polymeric coatings and films.

**Correspondence: mara.camaiti@igg.cnr.it*

Acknowledgements

The financial support of this work has been provided by IPERION-HS H2020 project (Integrated Platform for the European Research Infrastructure ON Heritage Science) funded by the European Union, H2020-INFRAIA-2019-1, GA 871034.

References

[1] O. Kokkinaki, E. Dimitroulaki, K. Melessanaki, D. Anglos, P. Pouli, Laser-induced fluorescence as a non-invasive tool to monitor laser-assisted thinning of aged varnish layers on paintings: fundamental issues and critical thresholds, Eur. Phys. J. Plus, 136, 2021

[2] G. J. Tserevelakis, P. Pouli, G. Zacharakis, Listening to laser light interactions with objects of art: a novel photoacoustic approach for diagnosis and monitoring of laser cleaning interventions, Heritage Science, 8, 2020

[3] A. Papanikolaou, G. J. Tserevelakis, K. Melessanaki, C. Fotakis, G. Zacharakis and P. Pouli, Development of a hybrid photoacoustic and optical monitoring system for the study of laser ablation processes upon the removal of encrustation from stonework, Opto-Electronic Advances, 3, 2020, pp. 190037-1.

Laser applications in the conservation of archaeological artifacts: polychrome wooden objects from ancient Egypt

F. Zenucchini[1], A. Piccirillo[1], C. Ricci[1], T. Cavaleri[1,2], P. Buscaglia[1,3]*

[1] Center for Conservation and Restoration of Cultural Heritage «La Venaria Reale», Venaria Reale (Turin), Italy
[2] Department of Economics, Engineering, Society and Business Organization (DEIM), University of Tuscia, Viterbo, Italy
[3] Department of Applied Science and Technology (DISAT), Politecnico di Torino, Italy

Keywords: laser cleaning, conservation methodologies, ancient Egypt, polychrome wooden artifacts

Since 2007, the Center for Conservation and Restoration of Cultural Heritage (CCR) “La Venaria Reale” has carried out extensive studies on the application of laser-based methodologies for the treatment of a variety of objects and materials, such as wood, textile, metal, ivory, pigments, stone, wall paintings, and polychrome surfaces.

This work describes some of the main results obtained over the years in the application of different laser sources to the cleaning of ancient Egyptian painted wooden objects, such as wooden sculptures and coffins, with the primary goal of removing superficial blackening and altered synthetic adhesives applied within previous conservation treatments. The 2015 renovation of Turin’s Museo Egizio provided CCR staff with an opportunity to study and conserve several polychrome wooden coffins from the museum’s holdings. In this context, laser cleaning was initially performed on the lid of Nesimendjem’s coffin [1] with successful results. This prompted the team to expand this line of applied research, still underexplored for this kind of artifacts, also encouraged by a longstanding collaboration with Museo Egizio [2]. The project’s following phases entailed a systematic comparison of laser sources commonly used in the cultural heritage field, including Nd:YAG 1064-nm and 532-nm lasers in Q-Switching (QS) and Long Q-Switching (LQS) modes, both alone and in combination with dry cleaning and solvent mixtures. Effectiveness and non-interference of these methodologies were evaluated on artifacts whose constituent

*Correspondence: francesca.zenucchini@centrorestaurovenaria.it

materials displayed a high depolymerization level prompted by their extreme vulnerability - one of the reasons why traditional cleaning methods are often not suitable for these objects.

A selection of optimal laser modes and experimental parameters was supported by a multi-analytical campaign, including the use of portable optical microscopy (OM), X-ray fluorescence (XRF) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS). These analyses aimed not only to characterize the objects' materials and techniques, but also to assess the specific conservation conditions of each artifact and to monitor the cleaning process. Results demonstrate how the target materials located in the most superficial layers, on top of the original painted decorations, could be removed with high spatial control, with no interference from the underlying substrate and no mechanical stress to the treated surfaces. The promising data obtained from this study will hopefully serve as a basis to further optimize the application of lasers in the field of cultural heritage, especially by broadening the current experience in the treatment of polychrome archaeological materials.

Acknowledgments

Initial experiments in the conservation of coffins were performed within the Vatican Coffin Project. The authors would also like to acknowledge El.En Group S.p.A. for the longstanding collaboration and support.

References

[1] Buscaglia, P., Cardinali, M., Cavaleri, T., Croveri, P., Ferraris di Celle, G., Piccirillo, A. & Zenucchini, F., Nesimenjem and the Valley of the Queens' Coffins in H. Strudwick and J. Dawson, eds. Ancient Egyptian Coffins: Past Present Future. Oxford: Oxbow Books, 2018, pp: 83-95.

[2] Amenta, A. 2014 The Vatican Coffin Project in E. Pischikova, J. Budka and K. Griffin, eds. Thebes in the First Millennium BC. Newcastle upon Tyne: Cambridge Scholars Publishing, pp. 483–499.

Laser Treatments of Painted Surfaces

POSTER

A NOVEL TYPE OF IR FIBRE LASER– IMPLEMENTATION IN CLEANING OF PIGMENT-COATED HISTORICAL PAPERS

T. Kozielec[1], A. Zięba[1]; A. Faron[2], M. Iwanicka[3]*

[1] Department of Conservation and Restoration of Paper and Leather, Faculty of Fine Arts, Nicolaus Copernicus University in Toruń, Sienkiewicza 30/32, 87-100 Toruń, Poland
[2] Doctoral School - Academia Artium Humaniorum, Nicolaus Copernicus University in Toruń, Bojarskiego 1/C 017, 87-100 Toruń, Poland
[3] Department of Conservation and Restoration of Paintings and Polychrome Sculpture, Faculty of Fine Arts, Nicolaus Copernicus Universityin Toruń, Sienkiewicza 30/32, 87-100 Toruń, Poland

Keywords: laser cleaning, historical paper, pigment–coated paper, conservation

Pigment-coated papers began to be mass-produced at the turn of the 19th and 20th centuries. The main ingredients of the mixture are white pigments (coating clay, permanent white, chalk, etc.) and binders, mainly natural. Coating the paper with pigment and adhesive mixture in one or more layers significantly improves the smoothness of the paper and its whiteness. Pigment-coated papers can have a variety of surface finishes from matt to high gloss. Due to all these features, the papers are used as an exclusive substrate for prints, leaflets, art drawings, endpapers in bookbinding, etc.

The aesthetic perception of pigment-coated papers decreases in the event of deposition of dirt and products of biological activity on its surface. Contamination can damage the coating layer causing optical and surface texture changes. Commonly used cleaning methods are abrasive, which causes irreversible changes in the appearance of the surface. This is due to physical changes to the surface of the coating or to the presence of abrasive conservation residues such as polyvinyl or latex rubbers, which are very difficult to remove.

Conservators are looking for new solutions to clean the surface of pigment-coated papers. One interesting alternative is the use of a laser that can safely remove contaminants from the paper. A novelty of this paper lies in using a novel type of a fibre laser and its parameters, which were not yet reported extensively in the literature.

**Correspondence: miwanicka@umk.pl*

The setup utilized in this work was based on RedEnergy G4 EP-Z Pulsed Erbium Fibre Laser (SPI Lasers, UK) which is characterized by an emission wavelength of 1064 nm, with pulse length adjustable in the range of 5 ns-2 µs, very high pulse repetition frequency (1kHz – 4 MHz) and average power of 100W. The optical head delivers the laser beam with a spot diameter of ca. 200 µm and with a programmable scan pattern with adjustable scanning speed of 6–260 cm/s. The relatively low energy of a single pulse combined with the fast scanning on the surface of the object, as well as high and adjustable repetition rate gave reasons to suggest a higher homogeneity of the ablation process and an increased safety of the historical papers during this process, when compared to other lasers used in the conservation of heritage objects.

In order to check the effectiveness of the impact of the laser beam on the layer of contamination on pigment-coated papers, a number of tests were carried out on different types of historical pigment-coated papers. A range of fluence, repetition rate and pulse length were tested. Dedicated software was written and employed for fluence estimation.

The cleaning effects were observed before and after artificial ageing, according to the ISO 5630 standard, with the use of optical microscopes (visible raking light, polarized light, UV-induced fluorescence imaging). Reflection Transformation Imaging analysis and colorimetric measurements (L*a*b* CIE R_z) of the paper before and after treatment were performed.

Acknowledgements

The financial support of this work has been provided by Excellence Initiative - Research University programme.

References

[1] J. Kolar, M. Strlič and M. Marinček, “The Effect of Nd:YAG Laser Radiation at 1064 nm on Paper”, Restaurator, volume 21(9), 2000, pp. 9 - 18

[2] L.C.P. Loureiro, M. Sandy, A. Manning, A.I. Seruya, „European Coated Papers 1850-1975: their Identification for Conservation Purposes“, ICOM Committee for Conservation 16th Triennial Meeting Lisbon Portugal 19-23 September 2011, [online] https://www.icom-cc-publications-online.org/1188/European-Coated-Papers-1850-1975--their-Identification-for-Conservation-Purposes [accessed: 22.04.2022].

Lasers in the Conservation of Artworks
LACONA XIII

13th International Conference on
Lasers in the Conservation of Artworks
Florence - September 12-16, 2022

PVC CLEANING VIA DIFFERENT METHODS: COMPARISON OF LASER AND CO_2 SNOW

M. Havlová[1], K. Kocová[1], J. Neoralová[1], L. Mašková[2], D. Novotná[1], P. Vávrová[1]*

[1] National Library of the Czech Republic, Collection Preservation Division, Prague, Czech Republic
[2] The Czech Academy of Science, Institute of Chemical Process Fundamentals, Rozvojová 315, Prague 6, Czech Republic

KEYWORDS: laser, CO_2, PVC, cleaning, modern library collection

In the last couple of decades, new methods for removal of pollution from modern library collection were studied and developed. One of them is a laser ablation, which has become a very promising method for cleaning sculptures, paintings or textiles [1].

Another cleaning method, which was also examined recent years, is using CO_2 snow. This method is also thought to be promising in various areas of conservation and preservation [2].

In this work, we present a comparison of these two different methods and their effectiveness in cleaning soft PVC samples and we compare them to classical mechanical cleaning. First, we tested these methods on clean samples, which were later subjected to accelerated ageing. We measured contact angle, color change, roughness, weight, tensile strength and glass transition temperature of those samples. The results show that laser and CO_2 snow do not affect PVC samples and even do not affect aging of the samples.

The cleaning abilities of a laser and CO_2 snow were tested on samples with artificial dust and artificial sebum soil (palmitic acid). For these samples, we measured contact angle, roughness, color change and weight to determine the performance of these cleaning methods. The results from the removal of pollution are also very promising and they show that these methods are possible alternatives to mechanical cleaning of library collection.

As the last step, these three methods were used for cleaning real PVC samples.

ACKNOWLEDGEMENTS

The financial support of this work has been provided by the

**Correspondence: marketa.havlova@nkp.cz*

Ministry of Culture of the Czech Republic under grant DG18P02OVV048.

References

[1] Ersoy T. et al, Femtosecond laser cleaning of historical paper with sizing, Journal of Cultural Heritage 15 (2014) 258–265.

[2] Feng, X. et al. Development of CO2 snow cleaning for in situ cleaning of CMM stylus tips, Measurement Science and Technology, 28 (2017),15007.

Investigating the impact of laser cleaning on heritage plastics: a case study of cellulose acetate

F. Azolini[1,2*], S. Da Ros[1], K. Curran[1], A. Gibson[1,2]

[1] UCL Institute of Sustainable Heritage, London WC1H 0NN, UK
[2] UCL Medical Physics and Biomedical Engineering, London WC1E 7JE, UK

Keywords: Plastics, Nd:YAG laser, Cleaning, Cellulose Acetate, Artificial Soilings

Since the 20th century, plastics have increasingly become an important part of museum collections. The great variety of compositions (e.g., copolymers, composites, blends, pigments, stabilisers, additives) make plastics a heterogeneous and unpredictable group of materials, the conservation of which is still a significant challenge.

A 2019 UCL survey at Tate and the 2012 EU project POPART showed that dust and ingrained dirt are common causes of damage in plastic collections. Cleaning strategies for plastics are currently limited and not completely effective (e.g. permanence of residues or consequent mechanical damage caused by the cleaning process itself). Recently, some cleaning methods from the NANORESTART and POPART projects have been compared to evaluate their effectiveness at cleaning [1]. Despite the fact that laser systems have been exploited successfully for the cleaning of heritage objects for more than thirty years, their use for cleaning plastics remains relatively unexplored. An initial study from the Victoria and Albert Museum demonstrated successful laser cleaning of adhesives from plastic which opens up the potential to broaden this field of research [2].

Here, we examine the effect of laser cleaning and potential mechanisms for damage on newly moulded samples of cellulose acetate (CA), which is a plastic commonly found in museum collections. The aim of this study was to explore the potential of a Q-Switching Nd:YAG laser (emitting at 1064 nm with a pulse duration of 5 ns, fluences between 130-390 mJ/pulse and pulse repetition rate 1-30 Hz) for laser cleaning. Considering the thickness and appearance of the soil layer compared to the plastic substrate, it was expected that the near-infrared radiation would be preferentially

*Correspondence: francesca.azolini.21@ucl.ac.uk

absorbed by the soil layer, removing it from the underlying plastic. Concerns about heating were mitigated by using a low pulse repetition rate and water-assisted systems. CA mock-ups were synthetised with 20 wt% of diethyl phthalate, with no other filler or colouring agents. Synthetic soils were prepared following published recipes and applied to the CA samples. Some samples were exposed to accelerated artificial ageing cycles for a better incorporation of the soiling particles in the surface layers. Any damage to the plastic caused by the laser, for example physical marks or changes in the optical or polymer properties, and cleaning effectiveness, were detected using optical microscopy, spectrophotometry, ATR-FTIR spectroscopy and FTIR microscopy. The results achieved allowed to define a suitable methodology for applying laser ablation in conservation of the principal plastics that represent a major cause of concern in museum collections. We show the level of cleaning can potentially be controlled by suitably selecting the appropriate laser parameters allowing for selective removal of the soiling layer.

Acknowledgements

The financial support of this work was provided by Engineering and Physical Sciences Research Council [grant numbers EP/R513143/1, EP/T517793/1]. Thanks to UCL Culture and UCL Chemistry who very kindly provided access to staff, facilities, and equipment. Special thanks to Dr Miriam Claudia Policarpo Wright, Dr Jia Khong, Emilia Kingham and Graeme McArthur, whose help and knowledge have been invaluable.

References

[1] Yvonne Shashoua, Margherita Alternini, Gianluca Pastorelli, Louise Cone, From microfibre cloths to poly(vinyl alcohol) hydrogels – conservation cleaning of plastics heritage, Journal of Cultural Heritage 52, 2021, pp. 38-43

[2] Dafni Daskalaki-Mountanou, The use of lasers in the conservation of museum objects made from plastics, V&A blog, 2017.

ASSESSMENT OF NON-THERMAL PLASMA SYSTEMS FOR THE THINNING OF AGED VARNISH ON PAINTINGS

*A. Suzuki[1], B. Salvadori[1], G. Magni[2], L. P. D'Acqui[3], C. Riminesi[1]**

[1] Institute of Heritage Science, National Research Council ISPC-CNR, Florence, Italy
[2] Institute of Applied Physics "Nello Carrara", National Research Council IFAC-CNR, Florence, Italy
[3] Research Institute on Terrestrial Ecosystems IRET-CNR, Florence, Italy

KEYWORDS: FTIR, confocal microscopy, Optical Emission Spectroscopy, terpenoid varnishes, acrylics

Cleaning of aged varnish on paintings is a complex conservation procedure that requires high controllability and selectivity. Varnish cleaning is mainly approached as a step-by-step chemical treatment in order to gradually evaluate the suitable degree of varnish thinning, as often a partial varnish removal is preferred to maintain protection of the painting. Scientific research provided successful alternatives to more traditional varnish cleaning methods in the last decades, such as UV excimer lasers and MIR lasers (Er:YAG). Nevertheless, UV lasers have the potential drawback related to the high-energy photons that could trigger photochemical alteration of the paintings (mainly related to pigments discoloration) while the MIR lasers can induce undesirable strong thermal effects. Therefore, non-thermal plasmas can be a valuable alternative for treatment of polymeric surfaces as it benefits of low controllable temperature (below 70-80°C), extreme surface action with negligible amount of UV radiation and high controllable etching rate (range of 1-0.1 μm/s).

In this work, the etching capability of a Dielectric Barrier Discharge (DBD) Ar atmospheric plasma torch with additional injet admixture of Ar with 2% of O_2, is compared to a radio-frequency (RF) under vacuum oxygen plasma system for the thinning of artificially aged varnish mock-ups. IR-thermography and Optical Emission Spectroscopy were used to characterize both plasma sources in order to set the most suitable operative conditions. The chemical effects have been assessed by Fourier Transformed Infrared Spectroscopy (both in external reflection and in Attenuated Total Reflection mode) and confocal microscopy was used to evaluate the thinning grade and morphological changes. The

*Correspondence: cristiano.riminesi@cnr.it

advantages and drawbacks of both techniques are highlighted for the removal of both natural (dammar, mastic, shellac) and synthetic coatings (Paraloid B72 and Primal AC33) typically present on paintings.

Acknowledgements

This work has been carried out under partial financial support of Tuscany Region (POR FSE 2014-2020) in the framework of PLas@rt project "Innovative techniques for the conservation based on laser ablation and non-thermal plasma method". Confocal microscopy acquisitions were carried out at the Institute of Applied Physics “Nello Carrara”, National Research Council IFAC-CNR, Florence, Italy.

Laser cleaning assessment on two ancient Egyptian coffins: potentialities and limitations of different analytical techniques

C. Ricci[1], F. Zenucchini[1], T. Cavaleri[1,2], A. Piccirillo[1], F. Di Iorio[1], D. Demonte[1], F. Pozzi[1], P. Buscaglia[1,3]*

[1] Center for Conservation and Restoration of Cultural Heritage «La Venaria Reale», Venaria Reale (Turin), Italy
[2] Department of Economics, Engineering, Society and Business Organization (DEIM), University of Tuscia, Viterbo, Italy
[3] Department of Applied Science and Technology (DISAT), Politecnico di Torino, Italy

Keywords: laser cleaning, monitoring, multi-analytical protocol, scientific analysis, ancient Egypt, polychrome wooden artifacts

In recent years, conservators and scientists at the Center for Conservation and Restoration of Cultural Heritage (CCR) "La Venaria Reale" have been faced with the treatment of several wooden coffins from ancient Egypt [1]. In all these cases, preliminary tests were carried out to identify the most appropriate cleaning procedure for the removal of surface deposits and altered synthetic resins applied within previous interventions, some of which remain undocumented. Laser cleaning has shown great promise for most artifacts examined, yielding high spatial control with no mechanical stress to the treated substrate. Nevertheless, the monitoring of the cleaning still poses a major challenge; in this context, a detailed characterization of the ablated materials and a systematic study of the effects of laser radiation on the artifact's surface are just a few of the most crucial, though typically demanding aspects worth investigating. Ideally, the cleaning treatment should be monitored continuously, in real time, or through spot measurements acquired at relevant stages of the process, preferably by means of non-invasive techniques [2,3].

This work presents the laser treatment of two painted wooden coffins from the collection of Museo Egizio, Turin, and a detailed evaluation of the cleaning via scientific analysis. The two objects, which date back to the Third Intermediate Period (22nd - 23rd Dynasties, 946-712 B.C.E.) and to the Late Period (740-655 B.C.E.), were treated by means of Nd:YAG 1064-nm lasers in Q-Switching

*Correspondence: chiara.ricci@centrorestaurovenaria.it

(QS) and Long Q-Switching (LQS) regimes. For both case studies, different analytical techniques were used to examine the coffins before and after treatment, with the main goal of assessing the outcomes of the cleaning process. Among the techniques employed are the following: observation through a portable digital microscope; multispectral imaging, including ultraviolet-induced visible fluorescence (UVF) and visible-induced infrared luminescence (VIL); Fourier-transform infrared spectroscopy (FTIR) of the material removed by laser ablation; examination of layered samples collected at the interface between cleaned and uncleaned areas of the coffins by means of optical microscopy (OM) and scanning electron microscopy (SEM). Potentialities and limitations of each technique will be highlighted and discussed. Though not exhaustive, the multi-analytical approach described here may represent a valuable starting point for the development of a monitoring protocol aiming to optimize the application of laser cleaning to archaeological wooden artifacts.

Acknowledgments

The authors would like to acknowledge colleagues from Museo Egizio for making the artifacts available for scientific studies and for many useful discussions.

References

[1] Cavaleri, T., Buscaglia, P., Caliri, C., Ferraris, E., Nervo, M., & Romano, F. P. (2021). Below the surface of the coffin lid of Neskhonsuennekhy in the Museo Egizio collection. X-Ray Spectrometry, 50(4), 279-292.

[2] Moretti, P., Iwanicka, M., Melessanaki, K., Dimitroulaki, E., Kokkinaki, O., Daugherty, M., Sylwestrzak, M., Pouli, P., Targowski, P., van den Berg, K. J., Cartechini, L., & Miliani, C. (2019). 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). Heritage Science, 7(1), 1-12.

[3] Giumlia-Mair, A., Albertson, C., Boschian, G., Giachi, G., Iacomussi, P., Pallecchi, P., Rossi, G., Shugar, A. N. & Stock, S. (2010). Surface characterisation techniques in the study and conservation of art and archaeological artefacts: a review. Materials Technology, 25(5), 245-261.

Laser irradiation of modern paints and plastics: research of the threshold limits of fluences with different lasers

G. De Cesare[1*], E. Dimitroulaki[2,3], K. Melessanaki[2], P. Pouli[2]

[1] Accademia di Belle Arti (ABAQ), L'Aquila, Italy
[2] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Greece
[3] Department of Material Science and Technology, Heraklion, Greece

Keywords: laser ablation of modern paints, laser ablation of plastics, cleaning of synthetic polymers

Over the past 30 years, significant research efforts have been focused on the study of laser interactions with Heritage materials with emphasis to stonework and encrustations, paintings and aged varnishes, metals and corrosion accumulations to name a few. As a result, a significant level of knowledge and experience has been gained leading to successful laser cleaning interventions. Nevertheless, industrial materials employed in contemporary art, such as synthetic polymers constituents' paints [1] and plastics [2], have not been studied to the same level. Working in this direction, this study aims at the determination of the maximum irradiation tolerance of a series of paint mock-ups [3] with primary colours (Yellow, Red, Green and Blue in characteristic media such as linseed oil, gouache, acrylic and vinylic emulsions on quartz substrates) and plastic supports [4] (polyethylene, polystyrene, polyurethane, polyvinyl-chloride, polyamide). Their sensitivity under laser irradiation is examined with the aim to determine safe working limits upon laser cleaning of contemporary art materials. As a final product of this study, a practical graphical guide, similar to a Teas triangle of solubility areas, is being developed, with the aim of facilitating the conservators of modern art to be able of taking informed decisions before deciding and organising their cleaning interventions.

Acknowledgements

The financial support of this work has been provided by IPERION-HS H2020 project (Integrated Platform for the European Research

*Correspondence: g.decesare@abaq.it

Infrastructure ON Heritage Science) funded by the European Union, H2020-INFRAIA-2019-1, GA 871034) through the FIXLAB TNA activities.

References

[1] G. De Cesare, K. Melessanaki, P. Pouli, J. Domingues, F. Rosi, C. Miliani, and C. FotakisExtended Abstract—Laser Cleaning Applied to Contemporary Paintings: Optimization of Working Parameters, in Proceedings from the Cleaning 2010 International Conference Universidad Politécnica de Valencia and Museum Conservation Institute, Washington D.C. 2013, pp 237-238

[2] De Cesare G., Russo C., Melessanaki K., Pouli P., Lasers application for the cleaning of plastic supports, FUTURE TALKS 2015 Processes. The Making of Design and Modern Art Materials, Technologies and Conservation Strategies, Oct. 28 to 30, 2015 Pinakothek of Modern, Munich, Germany, pp. 181-187

[3] G.De Cesare, P. Iazurlo, P. Biocca, La pulitura laser di vernici sintetiche su una tavolozza acrilico-vinilica: rimozione/resistenza e alterazioni in Convegno APLAR5 - Città del Vaticano, 18-19 settembre 2014

[4] Zaccagnini E., De Cesare G., Pulitura laser su plastiche in lastra: Test di valutazione della soglia di rischio in Convegno APLAR7 - Venezia, 7-8 novembre 2019.

Gradual cleaning of a seventeenth-century polychrome wood sculpture with Er:YAG laser

A. Andreotti[1], E. Cantisani[2], M.P. Colombini[1], A. De Cruz[3], D. Magrini[2], K. Nakahara[4]*

[1] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 15, Pisa, Italy
[2] Italian National Research Council – Institute of Heritage Science, Italy
[3] Conservator Scientist, New York, USA
[4] Conservator-Restorer of Cultural Heritage, Florence, Italy

Keywords: laser ablation, diagnostics, conservation, polychrome wood sculpture

In the last 20 years, various laser technologies have been developed and applied for the conservation of cultural heritage. The cleaning of art works by Er:YAG laser (2,94 μm) has been widely studied since late 1990's [1], and this system has been proved efficient for the cleaning of paintings, particularly for -OH bond rich materials, i.e., for the removal of degraded varnishes as well as of overpaintings [2-4]. This paper describes the application of the Er:YAG laser for the cleaning of a seventeenth-century polychrome wood sculpture, “the Virgin and Child“, (h. ca. 66 cm). This sculpure was originally opulently gilded, but had been totally overpainted together with thick white fillings around the nineteenth century. Heavy conservation intervention often occurred for the wooden polychromed sculptures, due to the deterioration that made the restoration necessary, or for the change of stylistic taste. The decision to remove or not the non-original part is a very critical issue and requires the thorough diagnostics and discussion. A series of diagnostic analyses and laser tests have been performed for a comprehensive understanding of the artistic-technique and the state of conservation of the materials, as well as for controlling the laser cleaning. Cross-sections of scalpel samples and samples collected layer by layer by means of the Er:YAG laser on microscope coverglass allowed us to understand the complex stratigraphy. PY-GC-MS, SEM-EDX analysis (Fig.1a), and XRF analyses, highlighted the challenge of this cleaning work. It has been considered appropriate to remove gradually the overpaints on the clothing of the

*Correspondence: kyoko.nakahara@gmail.com

Virgin in order to uncover the original gilded portion, although it might be extremely degraded (Fig.1b). The pen shaped mirrored glass tube (Ø 1 mm ca.) holder permits easy ablation even in the interior part of the modelling, which is difficult to reach with a traditional scalpel. The thick layers of overpaintings and restoration infillings which heavily disguised the original facial anatomy of the Virgin have been succesfully removed. The mid-infrared Er:YAG laser ablation allowed the selective removal of different layers of multi-colored overpaint and of the thick and resistant past restoration infilling which covered the thin degraded original layers.

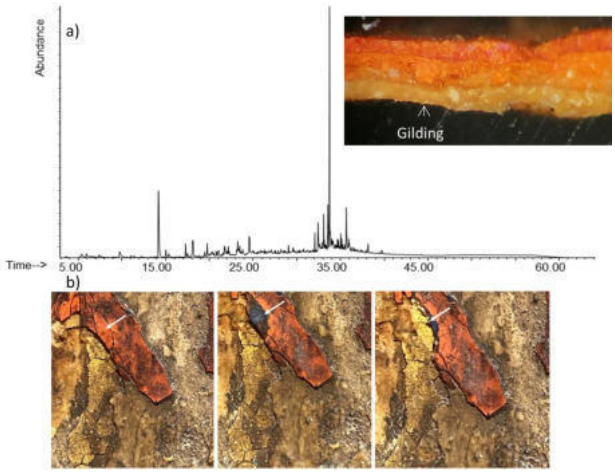


Figure 1 a) Pyrogram and SEM picture of a sample of the clothing of the Virgin; b) Er:YAG laser cleaning test showing the gradual removal of the thick layers of overpaint (red and blue) and infilling.

References

[1] A. DeCruz, et al., The role of lasers in fine arts conservation and restoration, Opt. Photonics News, 10, 1999, 36-40.
[2] P. Bracco, et al., Er:YAG laser: an innovative tool for controlled cleaning of old paintings: testing and evaluation, J. Cul. Herit. 4, 2003, 202s-208s.
[3] A. Andreotti, et al., Diagnosis of materials and effectiveness of Er:YAG laser cleaning as complementary treatment in a panel painting attributed to Lluis Borrassa (fifteenth century) Appl. Phys. A 122, 572 (2016). https://doi.org/10.1007/s00339-016-0100-1
[4] A. Andreotti, et al., Er:YAG laser cleaning of a marble Roman urn, J. Inst. Conserv. 43 (2020) 12-24

Spectroanalytical evaluation of the potential selectivity of laser treatment of oil paintings at 213, 266, and 2940 nm

D. Ciofini[1], M. Martínez-Weinbaum[2], M. Castillejo[2], M. Oujja[2], C. Chillé[1], S. Siano[1], I. Osticioli[1]*

[1] Istituto di Fisica Applicata "N. Carrara" - CNR, Sesto Fiorentino, Italy
[2] Instituto de Química Física Rocasolano - CSIC, Madrid, Spain

Keywords: spectroscopy, laser ablation, diagnostics, conservation, painting

Laser treatments based on the use of far-ultraviolet (Nd:YAG harmonics @213 and 266 nm) and mid-infrared (Er:YAG@2940 nm) solid-state laser sources provide significant advantages in gradual thinning down of varnishes on paintings that have lost their original transparency. The significant potential of both the mentioned lasers in addressing such a conservation problem is favored by the high optical absorption of the organic materials at their wavelengths. The corresponding pros and cons have been thoroughly investigated on a variety of varnish films [1, 2], whereas little has been reported on the effects of direct laser radiation of unvarnished paint layers and then on the discrimination potential of the mentioned lasers in practical conservation treatments.

With these premises, this work aims at characterizing structural and chemical modifications induced by pulsed laser on oil paint films at 213, 266, and 2940 nm, never reported in the literature so far. As either the pigment or the binder exhibits strong laser absorption at the present wavelengths, the sample preparation phase was deemed crucial. The volume ratio of pigment to oil was retained a more meaningful parameter than the the corresponding weight ratio, as it allows to prepare paint films with similar particle packing levels and hence better comparable in laser testing. Thus, homemade oil-pigment formulations were prepared according to two different pigment volume concentrations (PVC), referred to as gloss (low PVC) and matte (high PVC) paints. Lead white, cinnabar, chrome yellow, ultramarine blue, Prussian blue, and zinc white were selected. After grinding and mixing with linseed oil, formulated paints

*Correspondence: d.ciofini@ifac.cnr.it

were spread out in controlled thickness over glass substrates. After 2.5 month-curing under controlled laboratory conditions, the samples were exposed to thermal and light aging.

The fourth (266 nm) and the fifth (213 nm) harmonics of a Q-Switched Nd:YAG laser (15 ns pulses), and a 2940 nm Free-Running Er:YAG laser (160 μs pulses) were used for irradiation tests. After determining exposure limits, laser-induced effects were thoroughly assessed at the fluence threshold by optical microscopy, micro-Raman and T-controlled 1064 nm-excited Raman spectroscopy [3]. Special care was dedicated to the application of safe analytical protocols, as to avoid overheating of the material under analysis, radiation-induced damage, and consequent misinterpretation of the obtained spectral data. Diffuse Reflection FTIR spectroscopy was also used for determining the possible degradation of the oil binder. The adopted spectral analytical approach enabled thorough characterizations of the materials and of the corresponding laser induced effects, which were evaluated by statistical analysis of more than 800 spectral acquisitions obtained over 100 laser-irradiated areas.

Acknowledgments

The financial support of this work has been provided by the H2020 European project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science, GA 871034), by the project CNR4C-PLAS@rt" co-financed by the Tuscany Region and El.En. S.p.A., and by the Spanish State Research Agency (AEI) through project PID2019-104124RB-I00/AEI/1013039/501100011033. Support from CSIC Interdisciplinary Platform "Open Heritage: Research and Society" (PTI-PAIS) is acknowledged.

References

[1] Ciofini, D., Oujja, M., Cañamares, M. V., Siano, S., & Castillejo, M. (2016). Spectroscopic assessment of the UV laser removal of varnishes from painted surfaces. Microchem. J. 124, 792-803.

[2] Oujja M., García A., Romero C., R. Vázquez de Aldana J., Moreno P., Castillejo M. (2011). Phys. Chem. Chem. Phys. 13, 4625-4631.

[3] Osticioli, I., Mencaglia, A. A., & Siano, S. (2017). Temperature-controlled portable Raman spectroscopy of photothermally sensitive pigments. Sens. Actuators B: Chem. 238, 772-778.

TIME-RESOLVED TEMPERATURE MEASUREMENT DURING ER:YAG LASER IRRADIATION OF NATURAL AND SYNTHETIC VARNISHES

C. Chillè[1], J. Agresti[1], D. Ciofini[1], A.A. Mencaglia[1], S. Siano[1]*

[1] Istituto di Fisica Applicata "N. Carrara"- CNR), Via Madonna del Piano 10, Sesto Fiorentino, Florence, Italy

KEYWORDS: Er:YAG laser, resin, laser heating, IR sensor

The use of Free Running (FR) Er:YAG (2940 nm) lasers to remove unwanted materials (e.g. coatings and overpainting) is challenging due to the high sensitivity of the constituent materials to be safely uncovered. The strong optical absorption hydroxyl groups at 2940 nm can lead to diverse photothermal and photomechanical effects within and in proximity of the irradiated volume. In particular, the most significant issue of FR Er:YAG laser irradiation relates heat generation and thermal wave propagation through the underlying layers.

This work aimed to investigate and deepen the development of a time-resolved, non-contact temperature probe allowing for online monitoring of the temperature rise during pulsed laser irradiation. A fast IR photovoltaic detector (bandwidth 2-12 μm and response time < 7 ns) was selected for this study, and the calibration of the setup was carried out using thick poly (vinyl alcohol) (PVOH) films. A 3.6 μm longpass filter was placed in front of the detector to cut off the reflected laser light. The thermal radiation emitted from the surfaces of the laser-heated coating was collected with two Zinc Selenide (ZnSe) lenses system in a 1:1 configuration. The recorded thermal signals were thus converted into temperature values. PVOH polymer, dammar and colophony resins were selected due to their extensive use in the conservation field. Experiments were conducted at different fluences ranging between 0.5-2 J/cm2, using three temporal regimes: FR1 (t_L=164 μs), FR2 (t_L=301 μs), and FR3 (t_L=403 μs). In parallel, a mathematical computation of the temperature rise with the dry irradiated coatings was carried out. The corresponding behaviors of the temperature rises were eventually compared with those measured through the time resolved

**Correspondence: J.Agresti@ifac.cnr.it*

IR measurements.

ACKNOWLEDGEMENTS

The work was performed within the project PLAS@rt (part of CNR4C), co-funded by Tuscany Region (POR FSE 2014-2020, "Giovanisì") and El.En. S.p.A.

Leonardo Beyond Leonardo: laser uncovering of the artist's drawings in the Sala delle Asse, Castello Sforzesco, Milan, Italy

A. Brunetto[1], S. Mazzocato[2], C. Daffara[2]

[1] Restauri Brunetto, Vicenza, Italy
[2] University of Verona - Dept. of Computer Science, Verona, Italy

Keywords: laser uncovering, laser ablation, scialbo, Leonardo, drawing, UV-VIS-IR imaging

The Sala delle Asse of the Castello Sforzesco in Milan represents a significant artistic testimony of the activity of Leonardo da Vinci at the Sforza Court at the end of the 15th century.

The 1950s restoration of the walls of the North corner room uncovered monochrome charchoal and brush drawings, showing tree roots and rocks, until then unknown as they were concealed by the *scialbo* layers. Art historians attributed the discovered drawings to Leonardo on the basis of stylistc analysis.

That first restoration concerned only a portion of the drawing. Most of them, indeed, had still been hidden by the *scialbatura* until recently, when a second intervention on Sala delle Asse was carried out. Researchers were also called to respond with innovative diagnostics on the Leonardo mural paintings [1]. In this framework, in 2017 we were involved in the investigation of the potential of laser treatments for the removal of the scialbo layer covering the drawings of Leonardo.

The laser cleaning procedure was extended on different surfaces of the large room (15x15 m^2). QS, LQS and SFR Nd:YAG lasers (1064 nm) were used together with the VShort and Short Er:YAG laser (2940 nm). For each procedure, the windows of operational fluency and the different adopted methodologies are indicated [2, 3]. The laser intervention brought to light a series of graphic subjects by Leonardo under the removed cloaked layers. In particular, the visible image now reveals the presence of two different drawings, the first one is carbon-based and preparatory to the second one, painted and superimposed.

With the aim of enhancing such features, we performed UV-VIS-

*Correspondence: claudia.daffara@univr.it

NIR imaging in reflectance and luminescence mode, using a CMOS camera and following the international standard, to obtain a high-quality, calibrated and registered images. To separate the drawings, the image stack was processed on a “physical basis”, i.e. by combining the signals according to the surface or subsurface character of the respective in-band imaging modality. UV-reflected probes the materials in the surface, as well as the UV-induced luminescence, while NIR-reflected collects information from surface-subsurface layers, integrated across the radiation path, according to the optical transparency. UV-VIS-NIR spectrometry was performed to acquire the reflectance and the luminescence of the painting materials. The interplane combination of the image stack allowed to enhance the two superimposed Leonardo drawings in separate images.

Acknowledgments

Technical photography was performed by Vittorio Barra, formerly at University of Verona. The authors thank Claudio A. Salsi and Francesca Tasso of the Municipality of Milan, and Michela Palazzo of the Lombardy Region for entrusting us with the restoration work of Leonardo.

References

[1] C. Daffara, S. Parisotto, P.I. Mariotti, D. Ambrosini, Dual mode imaging in mid infrared with thermal signal reconstruction for innovative diagnostics of the "Monocromo" by Leonardo da Vinci, Scientific Reports 11(1), 2021.

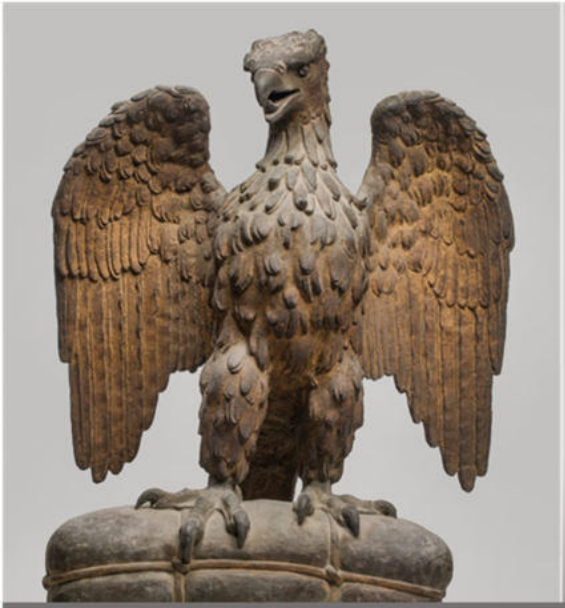
[2] S. Siano, A. Brunetto, A. Mencaglia, G. Guasparri, A. Scala, F. Droghini, A. Bagnoli, Integration of Laser Ablation Techniques for Cleaning the Wall Paintings of the Sagrestia Vecchia and Cappella del Manto in Santa Maria della Scala, Siena. In: Nimmrichter et al. (Eds) Lasers in the Conservation of Artworks, Springer Proc.in Physics, vol 116, Springer, Berlin 2007, pp 191-201.

[3] A. Brunetto, S. Ridolfi, I. Carocci, B. Mazzei, Trattamento di rimozione laser dalle pitture murali di due arcosoli nella catacomba di Domitilla, In: A. Brunetto (Ed), Atti del convegno APLAR 5, Nardini Editore, Firenze, 2017, pp. 245-266.

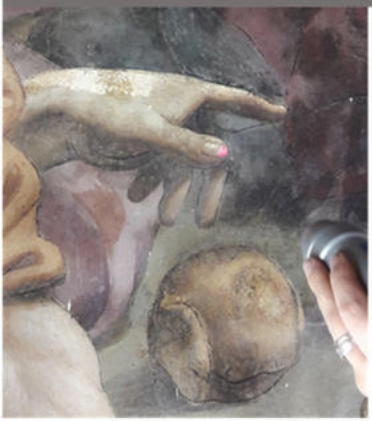
Index of names

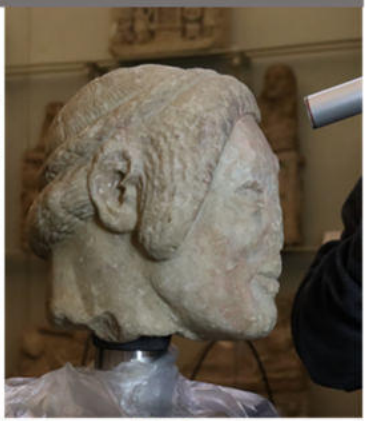
ELEN™
THE FUTURE IN A BEAM

LIGHT FOR ART



LASER SYSTEMS FOR THE CONSERVATION OF ARTWORKS





www.lightforart.com

GC LASER SYSTEMS

G.C. Laser Systems was founded by art conservators to offer laser systems that are specifically designed for art and architecture conservation. Our compact portable and globally patented laser systems offer unmatched precision and control over the level of cleaning for objects ranging from small artifacts to entire historic buildings and have been used in the USA, Canada, Australia, and throughout Europe to clean works of art and cultural heritage structures. We offer laser equipment sales, rentals, training, and technical support worldwide. We have decades of laser cleaning experience and we also specialize in custom project solutions.

Precise control over laser parameters such as pulse duration, pulse frequency, scan speed, fluence, and wavelength are critical for safe and consistent cleaning.

Info@GCLasers.com

Email us and mention "LACONA 2022" for a 20% discount in 2022

 www.GCLasers.com +1(844)-532-1064