# The eleventh conference on Lasers in the Conservation of Artworks (LACONA XI)

# BOOK OF ABSTRACTS

**Tuesday 20$^{th}$ to Friday 23$^{th}$ September 2016**

**Organisers:**

**The Jan Matejko Academy of Fine Arts in Kraków**

**Nicolaus Copernicus University in Toruń**

**The Interacademic Institute of Conservation and Restoration of Art, Warszawa/Kraków**

**The National Museum in Kraków.**

## Contents:

11th Conference on Lasers in the Conservation of Artworks is co-financed by the Minister of Science and Higher Education of Poland (Project No. 581/P-DUN/2016) from the resources allocated for the activities disseminating knowledge.

# Foreword

The eleventh conference on Lasers in the Conservation of Artworks is the latest of the LACONA conference series, initiated more than 20 years ago – in 1995 – by Costas Fotakis and held in FORTH in Heraklion, Greece. It was followed by the LACONA II meeting in Liverpool, UK in 1997, LACONA III in Florence, Italy in 1999, LACONA IV in Paris in 2001, and then Osnabrück, Germany in 2003. The LACONA conference was held in Vienna in 2005, followed by Madrid in 2007, Sibiu, Romania in 2009 and London in 2011. The most recent LACONA X conference was planned in 2013 in Egypt, but due to political disturbances was transferred to Sharjah, UAE and held in 2014. The present edition will be held in Kraków, Poland in September 2016, hosted by the Jan Matejko Academy of Fine Arts. It is co-organized by Nicolaus Copernicus University in Toruń, The Interacademic Institute of Conservation and Restoration of Art in Warszawa and Kraków, and, last but not least, by the National Museum in Kraków.

The early editions of LACONA were devoted mostly to the application of lasers to cleaning of artworks, which, at the time, was an emerging topic. Today, we prefer to talk about "removal of unwanted layers and coatings" to emphasize that this application now goes far beyond simple 'cleaning' and has become – for many classes of objects – a mature procedure, widely accepted within the conservation/restoration community. Nevertheless, its effective and safe application to specific objects remains a subject of extensive study. Also, continual progress in the development of lasers, especially by utilizing the ultra-short pulses provided by compact and less expensive sources, opens new areas of application by placing a broader set of tools in the hands of the conservator/restorer. Another significant feature of recent LACONA conferences is the much broader range of subjects presented, since the application of lasers in the conservation of artworks covers much more than simply 'laser cleaning'. Appropriate restoration procedures are always preceded by examination, and laser techniques – or, more broadly speaking, techniques utilizing coherent light – such as LIBS, Raman spectroscopy, optical coherence tomography and nonlinear or two-photon laser microscopy, feature regularly as significant subjects at LACONA.

A specific aim for the LACONA series has always been to bring together conservation scientists active in the field of developing methods and instruments with practising restorers and conservators who are the most important recipients of these new developments. Without the professional knowledge and experience of the latter it would not be possible to implement any of the results obtained in laboratory research in conservation practice. Therefore, LACONA has always been a unique forum for the exchange of ideas between scientists and practitioners. All these areas of interests are reflected in this year's conference programme, where the two largest sessions are devoted to fundamental research on the removal of unwanted substances with the aid of lasers and to case studies, in which reports of the use of lasers in restoration studios will be presented. These two groups of contributions will be complemented by coherent light-based methods for imaging, documentation and examination of objects and structures as well as laser-based spectroscopic techniques for the analysis of culturally-significant objects and the monitoring of restoration treatments.

During this, the latest, LACONA conference, 43 short oral communications and 15 posters will be presented. The scientific programme will also include five keynote lectures including one that is very special, as it is devoted to the memory of Professor Jan Marczak, the pioneer of laser cleaning in Poland, who was killed in an accident in January 2016. One of the most distinctive restoration campaigns carried out by a team led by Professor Marczak was that in Sigismund's Chapel in the Cathedral Church of Wawel Castle in Kraków. A visit to this site is included in the 'Conservation sightseeing of Kraków' scheduled for Wednesday, Sep. 21st.

For the first time the LACONA conference is preceded by a one-day workshop for about 50 participants, devoted to laser cleaning techniques for various cultural heritage objects. During hands-on sessions, the participants will have an opportunity to work with four different specialized lasers to gain experience and a better understanding of the use of lasers in conservation. This session would not be possible without a kind support from Dr Alessandro Zanini from El.En, Ms Malgorzata Musiela from Restauro and Mr Bartosz Dajnowski from GC Laser Systems Inc.

Finally, this event would never happened without enthusiasm and hard work of the secretary of the organizing committee Dr Małgorzata Walczak, other members of the organizing committee from the Academy of Fine Arts, the National Museum in Kraków, Nicolaus Copernicus University and the Interacademic Institute of Conservation, as well as members of the Permanent Scientific Committee of the LACONA conferences.

Piotr Targowski, Ph.D.
Professor of Physics
Chair of LACONA XI conference

# Permanent Scientific Committee

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**Marcin Sylwestrzak**, Nicolaus Copernicus University, Toruń

# Conference programme

## Tuesday, September 20th, 2016

8:30 **Registration** – Conference site, Academy of Fine Arts, Plac Matejki 13

9:00 **Opening** Page

### Session 1: Developments in laser removal of unwanted substances on culturally-important objects and monuments – chair: **Wolfgang Kautek**

## Session 1 continued – chair: **John Asmus**

## Session 2: Case studies I – chair: **Johann Nimmrichter**

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|---|---|---|
| 16:30 | **The removal of intractable materials with an Erbium:YAG laser at 2.94 mm from ancient tempera painting on panel .**<br>William P. Brown, Adele DeCruz, Alessia Andreotti, Mara Camaiti, Maria Perla Colombini | 38 |
| 16:50 | **Using the new G.C. Laser Cleaning System for cleaning and surface preparation for re-gilding of a large outdoor bronze monument of Alexander Hamilton**<br>Andrzej Dajnowski, Bartosz Dajnowski | 39 |
| 17:10 | **Experiences at the Academy of Fine Arts of Brera: the application of laser-cleaning technology on three case studies of the historical heritage**<br>Elisa Isella, Donatella Bonelli, Silvia Cerea, Francesca Mancini, Veronica Ruppen, Antonio Sansonetti | 40 |
| 17:30 | **Decontamination of biocidal loaded wooden artworks by means of laser and plasma processing**<br>Birgit Angelika Schmidt, Simone Pentzien, Andrea Conradi, Jörg Krüger, Constanze Roth, Oliver Beyer, Annett Hartmann, Bernd Grünler | 41 |

# Wednesday, September 21st, 2016

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| 7:50 | meeting at Wawel Castle Hill in front of the Cathedral |
| 8:00 | **exclusive sightseeing of the Cathedral** including conservation visit to Zygmuntowska and Batory Chappels (laser cleaned) and more |
| 10:30 | **Breakfast and coffee** at conference site |

## Session 3: Miscellaneous topics – chair: **Manfred Schreiner**

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|---|---|---|
| 11:00 | **Investigation of parchment alteration by correlative nonlinear optical microscopy and infrared nanoscopy – *key-note lecture***<br>Gaël Latour, Laurianne Robinet, Alexandre Dazzi, François Portier, Ariane Deniset-Besseau, Marie-Claire Schanne-Klein | 21 |
| 11:40 | **Laser-induced particle desorption and adhesion force investigations**<br>Wolfgang Kautek, Ignacio Falcón Casas, Oskar Armbruster | 42 |
| 12:00 | **LIF-Raman-LIBS analysis of heritage stones with a single set-up using UV pulsed laser excitation**<br>Mohamed Oujja, Mikel Sanz, Esther Carrasco, Marta Castillejo | 43 |
| 12:20 | **Spectral imaging of Dutch gilt leather for improved conservation strategies**<br>Roger M. Groves, Vassilis M. Papadakis, Martine Posthuma de Boer, Tigran Mkhoyan, Bianca van Velzen, Kate Seymour | 44 |
| 12:40 | **Building comprehensive management systems for handling and disseminating information recorded upon laser analysis, diagnosis and conservation**<br>Paraskevi Pouli, Demetrios Anglos, Martin Doerr, Chryssoula Bekiari | 45 |
| 13:00 | **Lunch break** | |

## Session 4: Instrument presentations and announcements – chair: **Martin Cooper**

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|---|---|---|
| 14:00 | **Using a new laser cleaning technology in the USA on works of art and architecture: introducing the GC-1 Laser Cleaning System**<br>Bartosz Dajnowski | 46 |
| 14:20 | **MicroLIBS analysis of archaeological objects: elements analysis and fingerprinting**<br>Lee Drake | |
| 14:40 | **El.En. laser systems for restoration of CH objects**<br>Laura Bartoli | |
| 15:00 | **European Research Infrastructure for Heritage Science (E-RIHS)**<br>Piotr Targowski, Luca Pezzati | 47 |
| 15:20 | **break** | |
| 15:30 | **Introduction to a visit to the Mariacki Church – present conservation project of Veit Stoss altarpiece**<br>Jarosław Adamowicz | |
| 16:00 | **Departure for the Conservation sightseeing of Kraków – part II**<br>including Mariacki Church, Collegium Maius, and Rynek Underground Permanent Exhibition | |

# Thursday, September 22nd, 2016

## Session 5: Coherent light-based methods for imaging, documentation and examination of objects and structures – chair: **Marta Castilleo**

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| 9:00 | **An examination of the complementary use of optical coherence tomography (OCT) and non-linear microscopy – *key-note lecture***<br>Haida Liang, Meropi Mari, George Filippidis, Chi Shing Cheung, Sotiria Kogou, Matthew Hine | 22 |
| 9:40 | **A study in the use of optical coherence tomography to examine depth of penetration into varnish layers ablated by the Er:YAG laser pulse at 2.94 µm**<br>Adele DeCruz, Joseph Izatt, Derek Nankivil, Eva Kielczewski | 48 |
| 10:00 | **Optical coherence tomography and reflection FTIR as complementary tools for examination of varnish layers in Vincent van Gogh's Sunflowers– preliminary results**<br>Magdalena Iwanicka, Costanza Miliani, Ella Hendriks, Marcin Sylwestrzak, Patrizia Moretti, Letizia Monico, Piotr Targowski | 49 |
| 10:20 | **Non-invasive multi-modal analysis of Cave 465 murals in Dunhuang, China**<br>Sotiria Kogou, Haida Liang, Chi Shing Cheung, Andrei Lucian, Bomin Su | 50 |

## Poster session – chair: **Vincent Detalle**

12:10 **Poster pitch** (all posters)

12:50 **Lunch break**

14:00 **Poster session** (all posters) and **coffee** (with posters) – until 16:00

17:00 **Departure to Wieliczka Salt Mine** (from J. Matejko square)

# Friday, September 23rd, 2016

## Session 6: Case studies II – chair: **Véronique Vergès-Belmin**

## Session 7: Laser-based spectroscopic techniques for analysis and monitoring – chair: **Praskevi Pouli**

## List of Posters

### Developments in laser removal of unwanted substances on culturally-important objects and monuments



### Coherent light-based methods for imaging, documentation and examination of objects and structures

## Laser-based spectroscopic techniques for analysis and monitoring



## Other topics

# Key-note lectures

# Final endeavor of “Monument Man”

John Asmus[1*], Vadim Parfenov[2]

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In September 1973 two advisors to the World War II staff of General Eisenhower met for the first time in a hospital room in San Diego, California. George Stout, retired Director of the Gardner Museum of Boston, had led the "Monuments Men" (played by motion picture actor George Clooney) in recovering World War II looted artworks. Professor Walter Munk, (recovering from a skiing accident) was an Associate Director of the Scripps Institution of Oceanography (SIO) and had led the team that forecast the sea conditions for the Normandy invasion sites and selected an optimum date for the Allied landings. At their hospital meeting the pair set in motion events that led to the establishment of the Balboa Art Conservation Center as well as the UCSD Center for Art/Science Studies. That year (after the 1972 SIO discovery of self-limiting laser divestment of stone and metal exterior statuary during a 3D holographic study in Venice) research at the University of California (UCSD) continued to explore laser technology as a promising approach to objects conservation (with the support of Mr. Kenneth Hempel of the Victoria and Albert Museum, London.) On the other hand, Stout was primarily interested in the conservation of paintings and he proposed laser varnish ablation for improved removal of residues from previous cleaning attempts. He utilized an available first commercial solid-state laser (Hughes Company ruby laser model 202, 9/18/62) to demonstrate laser divestment of embrittled oxidized varnish from a painting. The test painting was a Serbian Icon, "Our Lady of Tikvin," (Timkin collection.) Forty years later, this technique of painting cleaning is widely employed, but with lasers that are vastly more suitable in wavelength and pulse duration than Stout’s free-running ruby device. Shortly before his passing in 1978, he (independently with Lord Kenneth Clark, Professor Carlo Pedretti of UCLA, and radio carbon dating discoverer, Professor James Arnold) suggested the virtual (digital) restoration of the Louvre “Mona Lisa" and he arranged for the spectral analysis of its varnish. This final endeavor of George Stout led to the discovery of necklace pentimenti as well as a revelation that Leonardo painted two versions of the “Mona Lisa”, just as is the case of his other celebrated paintings. George Stout concluded his UCSD collaboration by making arrangements with UNESCO for the performance of TEA laser divestment tests on stone specimens from the World Heritage Isis Temple Site at Lake Nasser on the island of Philae.

# The main Polish conservation projects with the use of laser techniques

Roman Ostrowski[1*], Jan Marczak†, Andrzej Koss[2], Halina Garbacz[3], Karol Jach[1], Wojciech Skrzeczanowski[1], Antoni Rycyk[1], Antoni Sarzyński[1], Marek Strzelec[1**], Krzysztof Czyż[1]

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The paper and presentation are dedicated to the memory of Professor Jan Marczak, originator of introduction of laser technique in to the conservation of art works in Poland, whose unexpected accident, fight for life in hospital and final death swamped in sadness all his friends and colleagues.

*Christ Pantocrator*, Tum, relief from 12th century during laser cleaning - (J. Marczak).

The beginnings of research on laser cleaning of monuments in Poland are dated in 1997 – first tests of method on elements of the Tomb of the Unknown Soldier in Warsaw. With the progress in technology of laser devices and increasing experience of team of co-workers, subsequent bigger and major conservation projects were realized. Among them, definitely the most important one in the past was project connected with conservation of Sigismund's Chapel of the Wawel Cathedral in Kraków. Later, lasers were widely used in restoration of architectural and sculptural decoration of the Collegiate Church of St. Mary and St. Alexius from 12th century in Tum and important Polish historical tombs and tombstones at Montmartre Cemetery in Paris. Complex diagnostics of laser cleaning process of metal artworks, funded in the frames of Norwegian/EEA Program was successfully realized in the years 2008-2011. In 2015, the team initiated the long-term project of evaluation and conservation of Wit Stwosz's Altarpiece, the largest Gothic altarpiece in the World and a national treasure of Poland, located behind the High Altar of St. Mary's Basilica, Kraków.

The paper summarizes the main research results, analysed by teams headed by Prof. Jan Marczak and Prof. Andrzej Koss, devoted to the different laser cleaning case studies, and evaluation of art works preservation state using different analytical methods from the area of materials engineering, optoelectronic, optics and lasers.

# Investigation of parchment alteration by correlative nonlinear optical microscopy and infrared nanoscopy

Gaël Latour[1*], Laurianne Robinet[2], Alexandre Dazzi[3], François Portier[4], Ariane Deniset-Besseau[3], Marie-Claire Schanne-Klein[5]

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Parchment was the main writing material in the Middle Ages in Western Europe up to the growth of paper production in the 14-15th centuries. Made from an untanned animal skin it was preserved by liming, scraping and drying the skin under tension. Parchment is very sensitive to water, causing in extreme case the denaturation of collagen, its main constituent, to gelatin. The aim of this work is to demonstrate the interest of using two complementary nondestructive techniques, nonlinear optical microscopy and IR nanospectroscopy, to better understand the mechanisms of degradation.

Nonlinear microscopy is an emerging and promising optical technique for the investigation of artworks. The potential of pump-probe microscopy has been proven for the discrimination of pigments in painting [1] and nonlinear optical (NLO) microscopy based on simultaneous detection of two photon excited fluorescence (2PEF) and second harmonic generation (SHG) has been shown to give insight into the structure and the nature of the components of varnishes (binders, fillers, pigments) [2]. This latter technique performs non-invasive three-dimensional (3D) imaging with micrometer-scale resolution based on an intrinsic optical sectioning. A key advantage is probably its multimodal capability with different modes of contrasts that are directly linked to the structural and chemical nature of the materials. SHG signals are specific for non-centrosymmetric structures, with no counterpart in usual (linear) optical techniques. Fibrillar collagen emits strong SHG signals as widely used in biomedical imaging (cornea, skin…).

In this study [3], we show that SHG microscopy provides structural information of the 3D organization of the fibrillar collagen within parchments. Historical parchments at different states of degradation are investigated going from a well-preserved to a gelatinized parchment. We demonstrate that during degradation SHG signals vanish due to molecular and/or macromolecular modifications. We finally apply this investigation to an historic maritime map from the 17th century [3].

Infrared spectroscopy provides information on collagen secondary structure and is used to characterize the parchment gelatinization. To have a better insight into collagen modifications, analysis have to be performed at the fibers (~1-5 µm) or fibrils (~100 nm) scale, therefore infrared technique with a high spatial resolution is required. We report the first results in parchment fibers analysis at the nanometer scale using nanoinfrared spectroscopy (nanoIR, AFM imaging coupled with IR illumination to collect IR spectra with nanometer scale resolution).

The correlation of both NLO microscopy and nanoIR provides morphological and chemical information at different length scales about collagen degradation. NLO microscopy therefore appears as a powerful tool to reveal collagen degradation in a non-invasive way. It should provide a relevant method to assess or monitor the condition of collagen-based materials in museum and archival collections.

[1] T. E. Villafana, W. P.Brown, J. K. Delaney, M. Palmer, W. S.Warren, M.C. Fischer, Proc. Nat. Ac. Sci. **111** (2014) 1708-1713
[2] G. Latour, J.-P. Echard, M. Didier, M.-C. Schanne-Klein, Opt. Express **20** (2012) 24623-24635
[3] G. Latour, L. Robinet, A. Dazzi, F. Portier, A. Deniset-Besseau, M.-C. Schanne-Klein, Scientific Reports (accepted)

# An examination of the complementary use of optical coherence tomography (OCT) and non-linear microscopy

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As imaging and sensing technology advances with the availability of new lasers and detectors, non-invasive examination of cultural heritage is increasingly being explored for material identification, 3D surface structure and subsurface microstructure visualisation. Non-invasive examination is often the only allowed scientific examination of culturally significant historical objects.

Recent work has demonstrated the potential of non-linear microscopy for depth resolved imaging of materials in cultural heritage such as varnishes, parchment, paint and corrosion layer in metal-based artefacts. The non-linear microscopy modalities employed were multi-photon excitation fluorescence (MPEF), second harmonic generation (SHG) and third harmonic generation (THG). The 3 modalities were found to complement each other. MPEF depends on the intrinsic fluorescence properties of the material. Old varnishes, organic paints and binding media are known to fluoresce. SHG is produced only in non-centrosymmetric molecules and hence providing material information and a unique image contrast. THG is sensitive to refractive index and third order non-linear susceptibility and therefore sensitive to layer interfaces. Since only at the very focus of the laser spot would there be high enough photon intensity to initiate these non-linear effects, the tightness of focus determines the axial resolution. Non-linear microscopy is not affected by multiple scattering and cross-talk due to scattering from out of focus regions. The penetration depth is mostly limited by absorption.

In comparison, Optical Coherence Tomography (OCT) is a more established optical technique for non-invasive imaging of subsurface microstructure of cultural heritage such as old master paintings. OCT imaging is based on a fast scanning Michelson interferometer that uses a broadband laser. The axial resolution is determined by the coherence length of the laser source. It is most sensitive to changes in refractive index and therefore sensitive to the interface between layers. It can detect reflectivity of order 10-9. The penetration depth is limited mostly by multiple scattering and to a lesser extent by absorption.

The aim of this study is to compare systematically the two 3D subsurface imaging modalities for imaging paint and varnish layers used on historical paintings. A set of mockup paint and varnish samples were imaged by both OCT systems at NTU and a non-linear microscopy system at IESL-FORTH. An ultra-high resolution OCT systems at 810 m was used for the thin varnish samples and a long wavelength OCT at 1960 nm was used for the paint samples to measure both the sample thicknesses and their refractive indices. The measured refractive indices are then used to correct the non-linear microscopy images to compare with the OCT images. A study of the potential laser induced degradation due to the high laser intensity required in non-linear microscopy was also conducted.

This work was supported by Laserlab-Europe (EU-H2020-654148)

# Laser based techniques for a multidisciplinary action aimed at the restitutive restoration of S. Costanzo church in Ronciglione (Italy)

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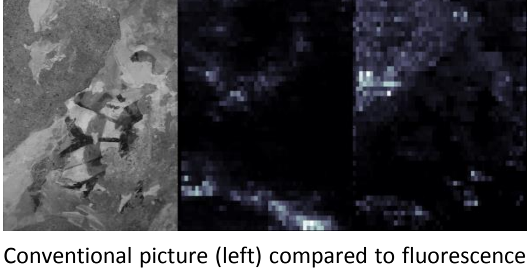
In the frame of the COBRA (Development and diffusion of methods, technologies and advanced instruments for the conservation of Cultural Heritages, based on the application of radiations and enabling technologies) project a multidisciplinary study has been carried out in order to restore the mural painting of the cupola of the S.Costanzo church in Ronciglione (Italy). Large difficulties have been met during the restitutive restoration of the original renaissance fresco decorating the cupola. In fact, two and sometimes three layers of paint, which lays on an extremely crumbled substrate have been detected on the surface, in addition to large, deep and complex degradation forms with the presence of efflorescence. Tests have been conducted in restricted areas, in order to understand the quantity and quality of the fresco decoration. Moreover, pre-consolidation action aimed to give solidity to the plaster also resulted in the consolidation of the upper paint layers, making the operation of cleaning even harder. To solve such a critique situation researchers, restorers and suppliers of lasers for cleaning have collaborated to plan the most appropriate intervention.

Laser based diagnostics have been employed to characterize different surface areas before and after cleaning tests. In particular, ENEA has offered its prototypes of LIF (Laser Induced Fluorescence) and RGB-ITR (Red Green Blue Imaging Topological Radar, an innovative 3D colour laser scanner) and a laser Raman system for both the material and degradation recognition and a micro-structural study. LIF data processing, exploiting the fluorescence emission bands and the images obtained both in reflectance and in fluorescence configuration, allowed for the identification of small areas where the presence of the consolidant is more massive and/or biodegradation effects appear. On the other hand, first analyses of the RGB-ITR data show the possibility to obtain a high-quality, high-resolution 3D colour model of the mural painting for a highly precise digital reproduction of the artwork that allows for the evaluation of the conservation state of the painting and the effects of restoration works and cleaning tests.

The cleaning tests have been performed with both classical methods and lasers made available by El.En. group. Different operative parameters such as pulse duration, repetition rate, energy, have been tested. The removal capabilities have been evaluated thanks to remote fluorescence and colorimetry measurements and local Raman analyses.



Conventional picture (left) compared to fluorescence images at 320 nm (center) and at 700 nm (right).

The laser employed has made possible to overpass the difficulties encountered by other techniques: painting layers have been removed selectively, allowing conservators to bring to light the original surface. The remote colorimetry results obtained by RGB-ITR on areas already treated with chemical approaches show that the colors obtained after the laser cleaning are much more saturated than before the intervention, highlighting the ability of the laser cleaning to remove thin patinas, impossible to eliminate by means of other techniques.

# Oral presentations

# Non-linear microscopies for the assessment of photochemical modifications upon laser removal of varnishes used in paintings

Marta Castillejo[1*], Mohamed Oujja[1], Sotiris Psilodimitrakopoulos[2], Esther Carrasco[1], George Filippidis[2], Alexandros Selimis[2], Aggelos Philippidis[2], Mikel Sanz[1], Paraskevi Pouli[2]

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A challenging issue in the laser cleaning of paintings is the controlled removal of polymerised degraded varnish coatings. By optimization of laser parameters (wavelength, fluence, duration, and number of pulses), and taking advantage of the possibilities of high spatial resolution, accuracy, material selectivity and immediate feedback, it is possible to circumvent the possible side effects on light-sensitive painting materials, including pigments, binders and protective coatings [1, 2 and references therein].

Imaging based on nonlinear optical microscopy (NLM), a technique initially developed in the field of biomedical optics, allows surface mapping and profiling of multi-layer structures (e.g. coatings) and has been proposed as an examination tool for Cultural Heritage studies [3, 4 and references therein]. In NLM imaging, ultrafast laser excitation serves to exploit several nonlinear optical effects that allow high contrast imaging of samples. The common NLM imaging modes of Multi-Photon Excited Fluorescence (MPEF), and Third Harmonic Generation (THG) provide non-destructive accurate determination of thickness within multilayer samples.

In this work we have aimed at determining by NLM the extent and nature of the photochemical damage that could be induced on underlying painting layers by laser removal of varnish coatings, with the final objective of identifying the optimal laser cleaning conditions that produce the minimum collateral damage in painting layers.

The study has been carried out on model samples, where a top varnish (mastic or dammar) layer coats a bottom layer constituted by a doped synthetic polymer (polymetilmetacrilate, PMMA) film, the latter mimicking a paint layer. To determine the in-depth affected region of the doped polymer layer induced by laser ablation of the varnish, we have applied the NLM modalities of THG and MPEF and a number of laser conditions for varnish removal, namely different UV wavelengths and pulse durations. For NLM measurements and ablation studies we have used the experimental set-ups available at the ULF-FORTH Facility in Heraklion. Characterization of the samples by NLM has been complemented by micro-Raman and laser induced fluorescence (using one-photon excitation in a pump and probe configuration) spectroscopic measurements, thus obtaining a complete characterization of the lateral and in-depth chemical and morphological changes following laser removal of the varnish layer.

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme LASERLAB-EUROPE (H2020-INFRAIA-2014-2015, nº 654148). This work is also supported by programs Geomateriales 2 (S2013/MIT-2914) and IPERION-CH (H2020-INFRAIA-2014-2015, nº 654028).

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# Optimization of the laser cleaning of rough surfaces of granitic stones used in the building heritage of NW Iberian peninsula

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Granite is the most common building stone in the NW Iberian Peninsula. As marble, granite exhibits crusts and patinas caused by its interaction with atmospheric agents and with biological activity [1]. Thus, the main conservation intervention is the cleaning. In the last years, laser ablation has been one of the most studied cleaning procedure and it has been proved more complex in case of granite than in other stone materials (i.e. marble) because of its polymineral composition, which leads to different responses under laser irradiation. In previous works, the effectiveness of various laser equipment has been found different considering the coating nature and the granite type, i.e. mineralogy, texture and especially surface roughness [2]. Therefore, it is necessary to carry out a study of the influence of the surface roughness on the laser cleaning effectiveness.

In this paper, an optimization of the process of laser cleaning of different deposits and coatings on granite stones with different finishes was carried out. Samples of a hercynian granite from NW of Spain covered with blue graffiti and gypsum black crust were cleaned using the third harmonic of a Nd:YVO4 nanosecond laser. A careful selection of the irradiation parameters was undertaken in order to achieve an effective cleaning without damaging the granite substrate. Once these conditions were established, larger areas could be treated in order to achieve an effective and safe cleaning with minimal time consumption.

The obtained results will account to a progress in the knowledge in a field of conservation of granite cultural heritage objects.

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# Wavelength-dependent absorption and scattering effects on laser cleaning of a corroded iron alloy European scale armor

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Traditionally, the reduction of thick weathering corrosion from historic iron artifacts has been accomplished mechanically or chemically. For some ferrous surfaces, however, these traditional approaches may be too aggressive, prohibitively time-consuming, may jeopardize associated non-metallic materials, or might create an undesired surface appearance. As alternative methods are explored, laser cleaning has become increasingly popular as a conservation tool for reducing corrosion layers from historic metals. In laser cleaning, the laser pulse fluence can be tailored to remove the iron oxides and other undesired surface material without damaging the underlying metal alloy. For some ferrous surfaces, laser cleaning can prove less invasive to the historic artifact and significantly more time efficient than traditional mechanical methods, thereby increasing the amount of surface that can be cleaned within a realistic time frame. After laser cleaning, the metal surface can still be treated using traditional finishing methods to achieve the desired surface aesthetic and to promote corrosion resistance. This research seeks to optimize laser energy profiles for the reduction of ferrous corrosion products on historic iron alloy surfaces. The study examines how the heavily corroded iron alloy surfaces of a 19th century, European scale armor jazeran (19.49.16) in the collection of the Arms and Armor Department at the Metropolitan Museum of Art, New York can be satisfactorily cleaned using a 10 ns, q-switched Nd:Yag laser operating in the second harmonic (532 nm) even when cleaning is unsuccessful operating at 1064 nm. Through the characterization of the various forms of iron corrosion present on the surface, it is shown that the success of the 532 nm laser cleaning is consistent not only with the green laser's more resonant energy absorption but also with the need for this increased absorption due to lower scattering at 1064 nm. The corrosion layers were analysed by stereomicroscopy, SEM/EDS and Raman, directly on a free scale as well as on corrosion scrapings. The stratigraphy of corrosion layers was ~500 μm thick in total consisting of (from metal surface to top): a red layer of platy lepidocrocite (~5 μm in diameter), a dark layer of magnetite, a bright orange layer of acicular goethite (2-3 □m in diameter), and a translucent organic film (under analysis). These data were used to optimize the optical parameters of the laser energy interaction with the corrosion products for removal to develop more effective and safer laser cleaning profiles for the reduction of ferrous corrosion layers on the historic iron alloy surface.

# Comparison between Er:YAG and Nd:YAG laser for the laser assisted removal of degraded protective from stone

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Nd:YAG laser systems (1064 nm) have been widely applied in the removal of protective layers from stone. Many studies have been conducted both on laboratory model samples and real cases, investigating various laser parameters, including pulse duration length. The ability of the Er:YAG laser (2940 nm) to clean stone has mainly been investigated on model samples and for the removal of natural varnishes [1]. We compared the ablation rate, effectiveness and safeness of the laser-assisted removal of synthetic protectives and consolidants from stones using a Q-Switched Nd:YAG laser with different pulse duration and a Er:YAG laser with a pulse duration of 250 µs. Various limestone and sandstone model samples were selected as being representative of the most common stone artifacts subjected to conservative interventions in the past. The consolidants applied were aqueous emulsions of silanes/siloxanes with a low and medium molecular weight (Pulvistop and Idroblock, Geal S.r.l.; and Hydrophase Acqua, Phase Italia) and a Paraloid B72 solution in acetone. The products were applied by brushing to saturation 5x5x2 $cm^3$ and 10x10x1 $cm^3$ stone samples. Two sets of laboratory models (one for the Nd:YAG and the other for the Er:YAG laser testing) were then submitted to artificial aging procedures: i) in a Solar Box (CO.FO.ME.GRA 3000e, equipped with Xenon lamp, $\lambda$>295 nm) for 400 h at 500 $W/m^2$, and ii) in a climate chamber with -10/+50°C temperature cycles (Challenge 500, Angelantoni). To evaluate the performances of the materials, the surface changing under ageing and the facility in the removal of products, the following multi-analytical approach was chosen:

- preliminary characterisation of the materials and investigation of the physical properties of the model samples; a Pyroprobe EGA/PY-3030D (Frontier Lab) coupled with a gas chromatograph/mass spectrometer (PY-GC-MS, Agilent Technology) and a portable Fourier transform infrared spectroscopy (FT-IR ALPHA, Bruker) were used to characterize the non-aged products. The water repellence imparted to the laboratory models was tested by means of capillary absorption measurements following the UNI EN 15801:2010 standard. Colorimetry data (using a Minolta ChromaMeter CM-700d) were obtained on various spots of the model samples following the UNI EN 15886:2010 standard;
- all the preliminary tests were performed before and after artificial aging;
- after laser removal of the protective/consolidant, the stone surface was investigated by means of capillary absorption measurements and FTIR analysis. The degradation phenomena were investigated using PY-GC-MS, both on the removed material (after Er:YAG laser application) and on the material left on the stone, which was collected by scalpel on a few selected areas. Finally, environmental scanning electron microscopy (ESEM) was used in order to assess the laser removal efficacy in some tested areas.

Our results highlight that the optimization of the different laser parameters leads to the safe removal of materials used for conservation purposes, which over time have led to yellowing or darkening phenomena on stone artifacts.

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# From underground to outer space: new applications for laser cleaning in mineralogy

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Varying the parameters such as pulse duration, fluence, and pulse frequency of conservation lasers can result in successful cleaning of mineralogical materials such as quartz crystals coated with dark orange iron oxide films that were mined from iron-rich clays, and corroded iron meteorites. Quartz is typically desirable for specimen collections and commercial applications as a pure clean crystal. One of the most common methods for cleaning quartz involves using hot acidic solutions such as oxalic acid. Using 1064nm laser pulses may provide a less aggressive alternative for removing the oxide films from the crystals. Meteorites provide scientists with valuable information about the geologic past of our own planet and our neighbors in the Solar System. Iron meteorite samples are often cut and polished to reveal cross sections that display crystalline structures. However, via moisture introduced from the environment, wet polishing methods, inappropriate handling, and exposure to oxygen, the surfaces of these iron-rich samples can easily oxidize due to the formation of various iron oxy-hydroxide-hydrates, sometimes including the further oxidation promoting akaganeite ($Fe^{3+}O(OH,Cl)$). The current method for removing rust from these samples involves additional wet polishing, which introduces moisture that will ultimately react with chlorine contaminants and result in additional surface oxidation. Further, wet polishing involves the removal of a layer of material from the specimen—an irreversible, destructive treatment. The Smithsonian's National Museum of Natural History Department of Mineral Sciences, has a number of meteorite samples that are currently limited in scientific utility due to oxidized surfaces, coupled with the concern that wet polishing could prove too aggressive. The use of 1064nm laser pulses at various durations and fluences is explored as a means to remove the oxide coating from these meteorites without the removal of a significant layer of specimen material and the introduction of additional moisture.

# Laser cleaning of historical postage stamps and stationery

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Laser cleaning of historical postage stamps and stationery can serve as a representative case study of paper substrates which exhibit complex combinations of printed pigment coatings, postmarks and old contaminations. Five historical samples were chosen consisting of three stamps (6 and 9 Kreuzer; Austrian "kk Poststempel" from Teplitz), stamped ink lines on stationery, and a historical Austro-Hungarian stationery. The laser treatment was performed with 532 nm at a pulse length of 5ns. The paper, contamination and ink destruction thresholds were determined by a well-proven systematic methodology [1-5]. The substrate destruction thresholds were about one order of magnitude higher than the removal/ablation of print or contamination providing a large cleaning window. The consequences of the ablation threshold overlaps of print, dirt stains and black ink are discussed.

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# Laser ablation on polychrome stone surface: a protocol for risk evaluation

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The Spanish Institute for Cultural Heritage (IPCE) is developing a research project within the framework of the Research in Conservation National Plan, with the aim to optimize a protocol for risk and efficacy evaluation of restoration treatments on polychrome stone sculptures.

While in recent years methodologies for the assessment of chemical cleaning have been proposed, the formulation of standard procedures for verification of physical systems has lagged behind. This project aims to provide a systemized analytical support which contributes to the planning and optimization of the laser cleaning strategies for polychrome stone sculptures, in accordance with the European reference standards.

Part of the work is the analysis of treatments carried out on the polychrome surfaces of the Portal of Glory in the Santiago of Compostela Cathedral with Q-switched lasers and different wavelengths. The variety of materials and conservation status of the pictorial layers allow for a wide casuistry on which the research project and study of the effects of laser on polychrome surfaces is based.

The methodology developed during preliminary tests on the restoration of the Portal has helped to determine the parameters of suitable cleaning in each case, to verify the safety of each test material on the monument and to establish a control process of the restoration both *in situ* and in the laboratory. To this end, a type of physico-chemical analysis was carried out: X-ray fluorescence (XRF) by energy dispersive X-ray microanalysis (EDXMA), optical microscopy, scanning electron microscopy (SEM), energy dispersive microanalysis X-ray (EDX) and infrared spectrometry (FTIR). In addition, the test areas were characterized by means of optical analysis: surface scanning, spectral reflectance, colorimetry and 3D macro photogrammetry.

The analytical study was mainly based on the assessment of the materials released as a result of the laser ablation and on the textural and compositional characterization of the cleaned surface. The eliminated particles were collected by interposing a sheet of glass between the polychrome surface and the laser beam and were later fixed into adhesive discs of carbon drivers for analysis by SEM-EDX.

The density and typology of the particles released, the composition of the surface after cleaning and the micro-textural changes (porosity, fusion processes, roughness, etc.) were evaluated in relation to the original surface in each of the cases analyzed.

The result of the work has been a comprehensive, objective and scientific evaluation of the risk and efficacy of each laser cleaning treatment used to develop a standard act of protocol applicable in other cases.

# Laser yellowing effect: study of the nanophases created by laser irradiation of natural and model gypsum crusts using transmission electron microscopy (TEM) and electron paramagnetic resonance (EPR) spectroscopy

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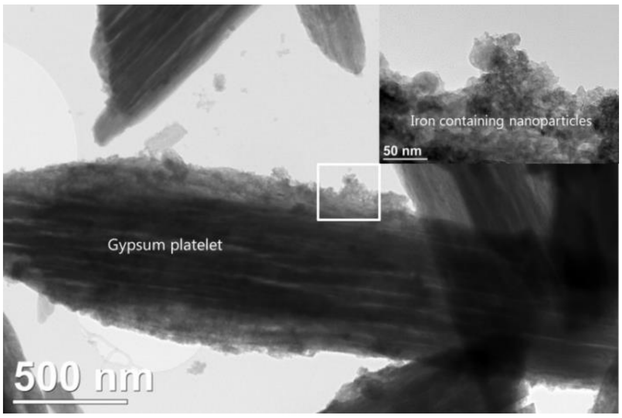
Nd-YAG Q-switched laser devices operating at 1064 nm have been considered in the 1990s as the most promising tools for cleaning stone sculptures, and more particularly for the elimination of indurated black gypsum crusts. However, the spreading of the laser technology has been undermined because of the yellow hue it occasionally conveys to the cleaned surfaces. Especially in France, this yellow effect is considered as a major esthetical issue by the conservators. At the present time this discoloration is still only partly explained: a currently admitted hypothesis states that the iron oxides present in the black crusts would transform, on laser irradiation, into yellow iron-rich nanophase(s) that would re-deposit on the cleaned substrate. To verify this hypothesis, two types of samples were prepared: i) natural black crust fragments collected at the Saint-Denis Basilica in Saint-Denis, France and ii) simplified model crusts composed of a mixture of red hematite α-$Fe_2O_3$ and gypsum $CaSO_4 \cdot 2H_2O$ applied like a coating on a plaster platelet. Natural black crusts and model red crusts were then irradiated using a Nd-YAG QS laser: as a result an instantaneous shift of their colour to yellow was observed. In order to identify the phases created by irradiation, a multi-scale analytical methodology was developed, as the size of the irradiation products vary from some nanometres to some hundreds of micrometres. Optical microscopy and scanning electron microscopy (SEM) have permitted to study the micro-morphology of the products of irradiation whereas transmission electron microscopy (TEM) has enabled observations of the nano-sized products which are very probably responsible of the yellowing. (See figure below: a yellow gypsum platelet covered by iron containing nanoparticles)




The elementary chemical composition of the nanophases was determined by energy dispersive X-ray spectrometry (EDS) and electron energy loss spectroscopy (EELS) coupled with scanning transmission electron microscopy (STEM). In addition, electron paramagnetic resonance (EPR) spectroscopy has been used to ascertain the presence of ferrimagnetic and super-paramagnetic materials in the same samples to aid in the identification of the neo-formed yellow phase(s).

# Laser cleaning of a Navajo wool blanket by Nd:Yag

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While laser cleaning is increasingly used in art restoration, there are relatively few applications on textiles. We demonstrate effective laser cleaning of soot-like deposits on a *Navajo Phase I Chief Blanket*. The cleaning protocol was derived from colorimetric and mechanical testing of reference churro wool cleaned with the second harmonic (532 nm) fundamental (1064 nm), and included samples subjected to accelerated light and thermal aging.

The privately owned (churro) wool blanket dates to 1840-1850. Its classic pattern features broad alternating bands of undyed white and dark brown, punctuated with narrow indigo-dyed bands. Large areas of gray contamination were evident throughout white bands on both sides. Given the minute amount of material required for a visible color change on a substrate of transparent fibers, the contaminant could not be determined by Raman spectroscopy or FTIR. Reflectance spectroscopy revealed the difference in reflectance between white and gray areas to be flat and uniform throughout the near-UV, visible, and near-IR. This is consistent with carbonaceous deposits, which were deemed the most likely contaminants. Laser cleaning was consequently selected to remove the deposits.

Laser cleaning tests were performed on reference material of woven Navajo churro wool. Kremer furnace black was dispersed by sonication in DDI water and airbrushed uniformly onto reference samples until peak reflectivity was reduced by ≈50%. The soiled areas were laser cleaned by a Nd:Yag laser at 5 Hz. Tested parameters included wavelength (532 nm and 1064 nm), pretreatment (moistening with DDI or not), number of pulses per laser spot area (4, 40, and 400), and flux (6, 36, and 66 MW/cm$^2$ at 532 nm and 7.5, 29, and 50 MW/cm$^2$ at 1064 nm). Accelerated light and thermal aging tests of cleaned and uncleaned reference samples were performed to gauge the potential long-term impact of the treatment parameters on the color and tensile properties of the wool fibers. Light aging was performed at 100 kLux for two weeks in an Atlas ci35 fadeometer. Thermal aging was performed at 60 Celsius and 75% RH for three weeks in a Caron 7000-33-1 environmental chamber, approximating 60 years of aging at 20 Celsius and 65% RH. The laser-cleaned and control sample's measured reflectance curves and single-fiber yield strengths were within statistical error of each other both before and after accelerated aging. Pre-wetting reduced cleaning effectiveness in all cases. Irradiation at 1064 nm left a red-brown stain that appeared to be a byproduct of the excited soot.

Irradiation at 532 nm, 35 MW/cm$^2$ and 40-400 pulses provided excellent soot removal with no detectable optical or mechanical changes in the wool fibers. The results provided confidence to apply these parameters to the soiled white (transparent) wool bands of the artwork. This soiling was successfully, though irregularly, reduced overall. Several techniques were developed to enhance the Navajo blanket's cleaning, including tensioning of narrow sections of the soiled bands over small shaped jigs to "expand" the tightly woven structure. Approximately 300 hours were needed including developing the manipulation protocols, but time should be significantly reduced for future treatments.

# Wavelength effects on the laser removal of lichens on heritage stone

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Lasers constitute a promising alternative to more conventional cleaning techniques for certain applications. In fact laser cleaning of stone is a well-established technique in the field of cultural heritage because it allows fine and selective removal of superficial deposits and encrustations. When biodeterioration crusts are present on the stone surface, the laser approach requires a physical parametrization, associated with a diagnosis of the induced effects on the both stone and biodeteriogens [1, 2]. Lichens (symbiotic association of a fungus with a photosynthetic partner, an alga and/or cyanobacteria) develop complex interactions with the rock minerals and, depending on the species, present characteristic morphologies that influence the resistance to the removal treatments.

In this work, granite from Alpedrete (Madrid) quarry front and sandstone from Valonsadero (Soria) were investigated in order to find the conditions for efficient laser removal of lichens crusts. These stone materials have been traditionally used in heritage buildings and monuments in central Spain. The selected samples present superficial areas colonized by different crustose lichens, i.e. Protoparmeliopsis bolcana, P. muralis, Aspicilia viridescens, A. contorta, Candelariella vitelina and Rhizocarpon disporum.

To determine the best laser irradiation conditions, we measured UV-Vis absorption spectra of the lichen crusts diluted in ethanol. A comparative laser cleaning study was carried out on the mentioned samples with nanosecond laser pulses of infrared, ultraviolet and sequences of both wavelengths. To that purpose we used the fundamental (1064 nm), 3rd (355 nm) and 4th (266 nm) harmonics of a Q-switched Nd:YAG laser (pulse duration 17 ns, repetition rate 1-10 Hz) at fluences just below the previously determined ablation thresholds.

A number of techniques were employed to detect morphological and chemical changes on the irradiated surfaces. Stereomicroscopy was used to describe morphological and colour changes. Scanning electron microscopy (SEM) at low vacuum served to analyse the effects on the surface of the lichens, while SEM-BSE of the polished transversal cross sections was applied to assess effects inside the crust and in the lithic substrate. FT-Raman spectroscopy was employed to detect possible structural and chemical changes.

The results obtained indicate that the optimal conditions for laser removal of the lichen crusts are highly dependent of the lichen species treated. For example, in the case of Protoparmeliopsis, sequential 1064-266 nm laser irradiation partially removed the thallus cortex in the vegetative parts of the lichen (areoles). However, the damage inflicted in the apothecia (fungal reproductive structures) was found minimal, possibly due to the highly efficient protective role of their sterile elements. For the other lichens, the optimal cleaning conditions were obtained at 266 nm, which resulted in the partial removal of the cortex and exposition of the algae. In this case the complete removal of fragments of thalli was observed.

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# Towards the understanding of the two wavelength laser cleaning in avoiding yellowing on stonework

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The synchronous use of Infrared (IR at 1064nm) and Ultraviolent (UV at 355nm) wavelengths of a Q-Switched Nd:YAG laser has been shown to effectively tackle the issue of yellow discoloration of the treated surfaces, and thus this methodology is effectively employed in various laser cleaning applications.

In order to further investigate the mechanisms that influence this result, a series of tests were undertaken on simulation samples and real marble fragments with environmental encrustation. Through a number of irradiation tests using a variety of laser parameters (individual use of IR and UV beams, as well as, their sequential and synchronous use in various ratios) the different ablative processes have been investigated. Micro-Raman, LIBS and spectral imaging were among the analytical techniques employed in order to divulge the role of each laser beam and their combination and approach the reason behind the yellowing.

The results of the above studies will be presented with the aim to further describe the two wavelength laser cleaning methodology and its principle, thus elucidating its effectiveness.

# The removal of intractable materials with an Erbium:YAG laser at 2.94 μm from ancient tempera painting on panel

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The deterioration of a 15th century Spanish panel painting by Lluis Borrassa (1365-1425) *Christ before Pilot* was scientifically studied for the first time to devise a method to remove intractable restoration materials from the painting surface.

In a previous restoration, performed in the first half of the 20th century, a pigmented varnish of a dark amber colour was applied on the surface in order to conceal damages to the colours and give uniform tone to the paint losses. Therefore, the painting was in need of cleaning because the dark old varnish obscured the design and colours of the picture. In particular the blue of the Christ figure robes, which appeared black, and required extreme attention to the compromised state of conservation of the pictorial layer composed of lapis lazuli and the delicate binding material.

The overall result of these treatments was that an intractable layer of material was left behind which needed to be carefully removed with a method not affecting the original painting layers, especially the under bound lapis lazuli of the blue robe in Christ's figure.

To understand and to solve such problems, it was fundamental to identify the materials, which have been used by the artist and which were applied by restorers. Moreover, in order to understand the oxidation pattern undergone by the materials themselves extensive identification analysis of the organic and inorganic materials, both original to the painting and those applied in previous restorations, were carried out.

A multi-analytical approach based on VIS-Ultra Violet images, Gas Chromatography-Mass Spectrography (GC-MS), also coupled with a pyrolizer (PY/GC-MS), Fourier transform-infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM-EDX) techniques have been employed, and herein presented. The results showed, among others, the presence of materials such as proteinaceous compounds and polysaccharides. These compounds are ideal products that can be removed by laser ablation at 2.94 µm, and explain the inability to remove the dark incrustation with traditional methods, without damaging the original surfaces.

The acquired new knowledge guided the conservators to choose and test some cleaning methods and finally adopt the appropriate Er:YAG laser cleaning method.

# Using the new G.C. Laser Cleaning System for cleaning and surface preparation for re-gilding of a large outdoor bronze monument of Alexander Hamilton

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The conservation of the Alexander Hamilton Monument by John Angel from the Chicago Park District and Ferguson Monument Fund will be discussed. The monument was installed in 1952 and was re-gilded in 1983.By 2015 over 80% of the gilding had failed and fallen off. Successful gilding of outdoor monuments requires very thorough surface preparation to remove all chlorides and active corrosion products. Inter-granular corrosion is a particular problem that is often difficult to resolve. In order for gilding to last, a bronze has to be as corrosion free as possible. Traditional surface preparation techniques such as media blasting and ultra high-pressure washing carry the risk of causing physical changes to surface topography of the metal and may leave behind active chlorides. In comparison, laser cleaning is more environmentally friendly as there is no contaminated media waste disposal and the precision and control during cleaning is unparalleled. The results of laser cleaning and surface preparation for re-gilding using the new tunable 1064nm pulsed G.C. Laser Cleaning Systems, specifically designed for art conservation treatments, will be presented.

# Experiences at the Academy of Fine Arts of Brera: the application of laser-cleaning technology on three case studies of the historical heritage

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The scientific research regarding conservation of gypsum plaster heritage is quite scarce; cleaning is often a problematic issue on this kind of material due to its water sensitivity and mechanical features. Therefore laser cleaning is often a good option as recent paper reported. [1,2]

The research presented here focused on laser cleaning of three gypsum plaster casts belonging to the collection of Brera Fine Arts academy and dated back to XIX century; recalling the names of the original marble statues, the items are the Flora Farnese, The Velletri Pallas and the Barberini Faun. The three casts were exposed since many decades in the entrance hall of the Academy in a semi-confined environment. Unfortunately, the continuous passage of students soiled the plaster surface with a grey greasy layer localized especially on the lower parts and on the surfaces with a strong horizontal component. It was possible to identify superficial grime and traces of the original patina. Marks of different nature (felt, pen, pencil, scratches) were also present. Cleaning tests were carried out using Thunder Art Nd:YAG able to emit both at 1064 nm and at 532 nm. The effects of laser cleaning were studied with a diagnostic campaign carried out both before and after the cleaning operation. To define the aspects and the nature of the surface, micro samples were sampled and analysed with XRD, XRF, then observed with a scanning electron microscope (SEM), and optical microscopy.

Several tests were carried out on the Flora Farnese, calibrating the fluence in order to match the ablation threshold avoiding any damage (from FL = 1 ÷ 1.45 J/cm² at 1064 nm to FL = 0.5 ÷ 0.7 J/cm² at 532 nm with repetition rate from 6 Hz to 10 Hz) in particular on these surfaces the removal of cement splashes constituted a hard task. A comparison between 1064 nm and at 532 nm tests were performed. Both tests were evaluated with the aid of humidification with free water (applied with brush) and with the use of AgarArt® rigid gel. On the basis of laser-plaster interaction observed on the Flora, the tests on the other casts excluded the IR radiation, because of a yellowing effect. For what regards the cast of the Pallas, one of the low relieves in the wooden support base was involved. The laser cleaning allowed the perfect removal of the outer layers of *scialbo*.

For the cast of the Faun, laser cleaning proved to be the appropriate system to eliminate greasy deposits and dark grey stains visible on the irregular surface, maintaining the original morphology. Hence it was possible to avoid invasive mechanical and chemical systems, minimizing the interaction with the matter and saving working time. The aim of this work is to provide a contribution to the scientific researches by the point of view of a Fine Arts Academy, which is starting to build a database for the conservation products and methods about such a known and used material as plaster, which is not sufficiently studied.

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# Decontamination of biocidal loaded wooden artworks by means of laser and plasma processing

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Many wooden artworks are contaminated by DDT (dichlorodiphenyltrichloroethane) as a result of a surface treatment by means of Hylotox-59©. The liquid preservative was used until the end of the 80s. DDT crystal structures are formed on the wood surfaces by the "blooming" of chlorine compounds. In addition to an aesthetic disturbance, it is assumed that DDT represents a health risk since it is absorbed through the air. Even decades after applying, the toxins in the wood preservatives are still detectable because they are of low volatility in many wood samples.

Contaminated waste wood with natural biocide ageing, gilded and wood carved elements of an old picture frame and wooden samples with paint layers were provided by the Schlossmuseum Sondershausen.

A non-contact procedure by using laser technology appears reasonable, since initially the most heavily contaminated top layer of wood can be treated by this method. Experiments mainly focus on health and safety issues for the operator. The removal of DDT was evaluated employing femtosecond and nanosecond laser radiation and cold atmospheric plasma technique using different working gases (air, nitrogen, and argon).

Before laser application, a chlorine measurement is done by X-ray fluorescence (XRF) analysis as reference. After laser processing, the XRF analysis is used again at the same surface position to determine depletion rates. Additionally, a documentation and characterization of the sample surface is done before and after laser and plasma treatment using optical microscopy. For plasma processing with various systems a chlorine measurement is done by gas chromatographic-mass spectrometry (GCMS) analysis.

For laser treatment a depletion of the chlorine concentration of 55-70% and 75% was achieved for 1064-nm nanosecond pulses and 800-nm femtosecond pulses, respectively. For the application of 30-fs laser pulses, no crystalline DDT residues remain on the sample surfaces. This holds also for the plasma processing with nitrogen as working gas.

After laser and plasma treatment, it shall be recorded in long-term observations, to what extent the remaining DDT residues in the wood possibly efflorescence again.

# Laser-induced particle desorption and adhesion force investigations

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Particle removal by pulsed lasers is of fundamental importance in cleaning technologies and conservation science. In the case of mechanical desorption processes [1,2] adhesion forces have to be quantified. This was realized by scanning force microscopy (SFM). Polystyrene spheres attached to SFM cantilevers served as model particles. Pull-off forces on polymer and silicon substrates in the range of 50-200 nN were detected, which is about one order of magnitude lower than the predictions by theoretical models [3]. Therefore multiple contacts, asperities on the spheres, and humidity have to be considered [4]. These investigations are correlated with particle acceleration measurements induced by surface acoustic waves generated by laser pulses. Thus, an quantitative experimental comparison between the adhesion force and repulsive force caused by the surface acceleration become accessible.

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# LIF-Raman-LIBS analysis of heritage stones with a single set-up using UV pulsed laser excitation

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Laser based analysis of artworks benefits from the development of hybrid instruments where a single laser source serves to excite fluorescence, Raman and laser induced breakdown spectroscopy (LIBS) signals [1, 2 and refs. therein]. With UV excitation it becomes possible to collect LIF spectra of a wider range of materials, thus allowing the combined acquisition of LIF, Raman and LIBS signals with a common excitation wavelength in a single set-up. Here, we present results obtained upon excitation at 355 nm, third harmonic of a Q-switched Nd:YAG laser. The system includes appropriate optics for beam delivery and signal collection, with Notch and cutoff filters to reject laser scattered light, and a spectrograph (300 or 1200 lines/mm gratings) coupled to a time-gated intensified charge coupled device for spectral analysis and detection with temporal resolution. With this system we have collected the three signal modalities from heritage stone samples of alabaster, limestone and marble.

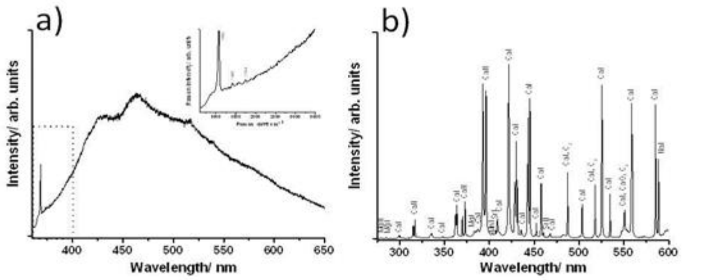


Figure. Spectra acquired on Hontoria limestone upon common laser excitation at 355 nm in a single set-up. a) Raman-LIF spectrum, inset in a) represents the area within the dotted square as a function of the Raman shift, and b) LIBS spectrum with assignment of lines.

As an example, the figure shows spectra acquired on a limestone sample of the Hontoria variety (Burgos Museum, Spain). The LIF and Raman signals are collected together in a single spectrum that consists of two main broad fluorescence bands, centered at 425 and 475 nm, and sharp Raman peaks. The fluorescence bands are assigned to acid-extractable organics and bitumen [3], main limestone fluorophores, while the Raman bands are characteristic of calcium carbonate and correspond to a vibration mode of free $CO_3^{2-}$ (1085 $cm^{-1}$) and organic residues (1445 and 1744 $cm^{-1}$). The LIBS spectrum reveals the elemental composition of limestone, displaying emissions of Ca, Na, Mg, Sr, Mn, $C_2$ (Swan bands) and CaO (Green system).

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# Spectral imaging of Dutch gilt leather for improved conservation strategies

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Gilt leather was one of the most fashionable and costly types of wall hangings in the Western world in the 16th to 18th centuries. Despite its appearance, it is not real gold that creates the golden shine, but typically a silver leaf which is coated with an orange-brown lacquer to obtain a golden lustre. Gilt leather has its origins in North-Africa, and the technique was widely practiced in Southern Europe through the middle ages and Renaissance. By the mid-17th century Dutch gilt leather had a similar fame to Delftware and Dutch paintings. Despite this only a small fraction of the large amounts of gilt leather wall hangings produced in Europe has been preserved. Gilt leather is a layered composite of organic and inorganic materials, including leather, animal glue, silver leaf, varnish, oil paint – materials which fall within different conservation disciplines. The aging of gilt leather is characterized by the specific degradations of each of the applied materials, and the possible interactions between them. Some common conservation treatments practiced in the past, such as oiling the leather, have negative side effects, such as gloss and colour change (darkening) and stiffening of the support. Furthermore, most of the surviving gilt leather decorative sections show traces of surface cleaning, such as abrasion, re-varnishing or the application of other protective coatings.

Hyperspectral imaging has a wide range of applications in astronomy, biology, chemistry, medicine and quality control. Within the domain of art history, archaeology and conservation, hyperspectral imaging has been used since the 1990’s, mostly for the examination of paintings and manuscripts. It has proved a successful tool for revealing things that are invisible to the naked eye, for example varnish layers, overpaints or underdrawings. In this study the research team investigated a collection of gilt leather objects at SRAL (Stichting Restauratie Atelier Limburg, Maastricht) using an imaging monochromator IMSPECTOR V10E (Specim©, spatial resolution 1300 pixels, wavelength range 400-1000 nm, bandwidth 2.8nm). Scanning of selected case study objects was performed with an automated 3D scanning platform, developed at TU Delft. The objective lens enabled imaging of an approximately 100 mm of field of view. The sample was illuminated by 3 tungsten lamps (30W Halogen) at a 45° angle to avoid specular reflections and to ensure that only diffuse scattering caused by the surface roughness and scattering centres underneath the surface were recorded by the camera. The technique is non-invasive and non-destructive to the studied object.

The data was recorded in February 2016 and is currently being analysed using the TIPP software platform, developed at TU Delft. This software platform includes algorithms to perform filtering and un-mixing of hyperspectral data cubes, along with memory management for large data sets and tools for data visualization. Data processing will be performed within the next months, with the objective of mapping areas of surface chemical degradation or change in composition due to earlier conservation treatments. Results will be included in the full paper.

# Building comprehensive management systems for handling and disseminating information recorded upon laser analysis, diagnosis and conservation

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Research laboratories involved in Cultural Heritage (CH) scientific analysis and conservation are often engaging in practical activities and applied campaigns in the context of their outreach to user communities. This enables a strong interaction between researchers, conservation scientists and conservators/restorers of highly interdisciplinary character. As a result, a massive amounts of scientific data may be recorded which require archiving, managing and dissemination. The final interpretation and application of analytical data in CH research and conservation often requires evidence from different methods, disciplines and even about different objects. Since this data cannot be understood without knowledge about the meaning of the data and the ways and circumstances of their creation, it raises the need for a new, systematic information flow and a new kind of information systems which manage data together with metadata about its Digital and empirical (i.e., physical-experimental) provenance and allows for systematic information integration and data reuse.

A collaborative effort between the two Institutes of FORTH; the Institute of Electronic Structure and Laser (IESL-FORTH), and the Institute of Computer Science (ICS-FORTH), aimed at implementing these new possibilities. The Photonics for CH group of IESL-FORTH is developing and applying state-of-the-art laser analysis, diagnosis, and conservation methods and tools, while the centre for Cultural Informatics of ICS-FORTH researches on supporting the entire lifecycle of cultural and scientific information and documentation procedures for the benefit of study, preservation and promotion of CH, focusing in particular on metadata, semantic interoperability, information integration and integrated access. This research brought into light that there is a common basic workflow for all analytical methods in all disciplines with few variations and a few core patterns of evaluation, which extends to a certain degree even into conservation methods. Along these lines a comprehensive management system has been developed encompassing a number of procedures, which facilitates the handling, documentation and management of analytical data and certain conservation methods.

This paper introduces to the current IT situation in these application domains and describes the needs and the requirements for supporting this new emerging common workflow for scientific processes in the CH science field and first implementations.

# Using a new laser cleaning technology in the USA on works of art and architecture: introducing the GC-1 Laser Cleaning System

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The new GC-1 laser cleaning system was specifically designed and built for art conservation applications by Bartosz Dajnowski in 2014, and has multiple patents pending worldwide. The 1064nm high frequency pulsed laser system is highly tunable, compact, and portable. Precise tuning of laser parameters such as pulse energy, fluence, pulse duration, pulse frequency, and scan speed allows for precise control over the level of cleaning that can be achieved on various surfaces and materials. Examples of various levels of cleaning on stone will be presented. The system features a geometrically efficient circular scan pattern that has proven to be extremely effective on projects across the USA such as the laser cleaning of the 3,500 year old Egyptian obelisk in New York's Central Park, cleaning the marble façade of the U.S. Supreme Court, and various works of art and cultural heritage objects. The presentation will feature examples of actual projects from 2014-2016.

# European Research Infrastructure for Heritage Science (E-RIHS)

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The European Research Infrastructure for Heritage Science (E-RIHS) is one of the six new projects which entered the ESFRI Roadmap in 2016, and the only research infrastructure project in the Social and Cultural Innovation section of the Roadmap. E-RIHS will help the preservation of the World's Heritage by enabling cutting-edge research in HS, liaising with governments and heritage institutions to promote its constant development and, finally, raising the appreciation of the large public for cultural and natural heritage and the recognition of its historic, social and economic significance.

At present representatives of sixteen countries (15 from EU and Israel) have submitted the proposal of the project E-RIHS PP to develop in the next three years the preparatory phase of the E-RIHS. It is expected that the E-RIHS will be launched as a standalone research infrastructure in 2021.

The European Research Infrastructure for Heritage Science (E-RIHS) will support research on heritage interpretation, preservation, documentation and management. It will comprise: E-RIHS Headquarters and National Hubs, fixed and mobile national infrastructures of recognized excellence, physically accessible collections/archives and virtually accessible heritage data. Both cultural and natural heritage are addressed: collections, buildings, archaeological sites, digital and intangible heritage. E-RIHS will provide state-of-the-art tools and services to cross disciplinary research communities advancing understanding and preservation of global heritage. It will provide access to a wide range of cutting-edge scientific infrastructure, methodologies, data and tools, training in the use of these tools, public engagement, access to repositories for standardized data storage, analysis and interpretation. E-RIHS will enable the community to advance heritage science and global access to the distributed infrastructures in a coordinated and streamlined way.

The major services to the community, provided now as transnational and virtual access by the two projects IPERION CH and ARIADNE, will be organized on four platforms:

1. MOLAB: access to advanced mobile analytical instrumentation for non-invasive or minimally invasive measurements on valuable, fragile or immovable objects, archaeological sites and historical monuments. The MObile LABoratories will allow its users to carry out complex multi-technique diagnostic projects, allowing effective in situ investigation.

2. FIXLAB: access to large-scale and specific facilities with unique expertise in Heritage Science, for sophisticated scientific investigation on samples or whole objects, revealing micro-structures and chemical composition, giving essential and invaluable insights into historical technologies, materials and species, their context, chronologies, alteration and degradation phenomena.

3. ARCHLAB: physical access to archives and collections of prestigious European museums, galleries, research institutions and universities containing non-digital samples and specimens and organized scientific information.

4. DIGILAB: virtual access to organized knowledge and scientific information in heritage data hubs – including multidimensional images, analytical data and documentation – from large academic as well as research and heritage institutions.

Other forms of scientific activity will be aimed at continuous development of methods and instruments to upgrade the access offer.

The E-RIHS infrastructure web site (under construction): http://www.e-rihs.eu/.

# A study in the use of optical coherence tomography to examine depth of penetration into varnish layers ablated by the Er:YAG laser pulse at 2.94 µm

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To restore the original intent of the artist, art conservation is moving towards an increased use of laser ablation to remove varnish layers, which have become encrusted with contaminants or have been otherwise altered over the years. It is possible to guide the restoration process with imaging modalities that provide information about the varnish layers. In paintings where the encrustation has not rendered the varnish completely opaque, Optical Coherence Tomography (OCT) has the potential to provide details about the structure and thickness of the varnish layer in a non-invasive manner.

OCT has been used, to visualize and quantify the varnish layers of paintings and to verify the success of removing the varnish layer using laser ablation. A free-running Er:YAG (MonaLaser, Orlando, Florida) laser with a central wavelength of 2.94 µm, a reputation rate of 15 kHz and optical power of 1 mW was used to remove the varnish. A spectral domain OCT system with a Michelson topology was constructed using a broadband super-luminescent diode (SLD-371, Superlum, Carrigtwohill, Ireland) with a central wavelength of 840 nm and a 50 nm bandwidth and a line scan CMOS sensor (AViiVA, e2v Inc., Milpitas CA) with a 20 kHz line rate. The OCT system provided an 8.5 µm axial and 7.5 µm lateral resolution, a sensitivity of 105 dB, an imaging range of 0.8 mm (6dB fall off) and a field of view of 5 x 5 mm. Also, Two Bioptigen Envisu (Spectral Domain Ophthalmic Imaging System) systems were used: 1) R3500 2) R2300. The two systems utilize different sources and spectrometer designs, but both permitted visualization of varnish and paint, at different depths

Samples, including pigment, varnish and substrate, approximately 1 mm2 in size, were removed from an oil painting on panel (San Giorgio Maggiore) by Martin Rico (1833-1908) and imaged using Environmental Scanning Electron Microscopy (ESEM). Varnish thickness obtained from OCT was validated by similar measurements obtained from ESEM. In addition, a late 18th century landscape, signed Thomas Gainsborough, was imaged with OCT to compare neighbouring regions before and after laser treatment and to examine the layering of the artist's signature in an effort to determine its authenticity. Varnish layer thickness was 10.8 ± 3.8 µm and 12.7 ± 0.7 µm measured by OCT and ESEM respectively. Complete varnish layer removal was observed in several regions of paintings after laser treatment with occasional residual varnish in regions of significant surface topological variation. Additionally, the presence of over-paint and differences in penetration depth were observed in the OCT cross-sections. Also, laboratory samples have been studied to provide a controlled examination of the varnish surface and paint substrate.

We believe this is the first demonstration of the application of OCT to show that the varnish removed by Er:YAG laser treatment is gradual and can be controlled to remove microns of material without penetrating into the substrate. In conclusion, we demonstrate that OCT may provide a non-invasive technique that provides measurements of the varnish layer and verification of its removal after laser ablation-based conservation.

# Optical coherence tomography and reflection FTIR as complementary tools for examination of varnish layers in Vincent van Gogh's Sunflowers– preliminary results

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"Sunflowers" by Vincent van Gogh, the version painted in January 1889 and now in the collection of the Van Gogh Museum in Amsterdam, is one of the icons of the 19th c. European painting. Detailed understanding of the painting's materials, structure, and state of preservation is crucial towards its safekeeping for future generations. In 2016 systematic and multi-technique examination of the Sunflowers was carried out courtesy of the MOLAB Transnational Access (IPERION CH project). Although the results are still under evaluation, some preliminary conclusions can be drawn and will be presented in this contribution.

One aspect involved examination of the varnish layers present. The aim was to reveal their stratigraphy, thickness and chemical composition, to help determine an appropriate conservation strategy for the painting. The varnish layers were investigated with a portable HR OCT system (built at NCU for the CHARISMA project, 870 nm central wavelength, axial resolution in the varnish = 2.2 µm), a portable FTIR system (ALPHA from Bruker, 7500 $cm^{-1}$ – 400 $cm^{-1}$ spectral range, spectral resolution = 4 $cm^{-1}$) and a HR 3D digital microscope (HIROX KH-7700).

In most places examined, two varnish layers of variable thickness and probably of different composition were found. These layers are separated by a semi-transparent, highly scattering layer. Locally, another semi-transparent deposit was found underneath the bottom varnish layer. Reflection FTIR measurements were able to identify the upper glossy varnish layer as a synthetic resin (showing a rather complicated infrared profile), which was probably applied in the 1960's. In places, the surface of the upper varnish is rendered matt by the local application of a synthetic wax. The bottom varnish present, which must be that applied in 1927 when there is a first record that the painting was comprehensively treated, did not give any visible infrared signals. Using reflection FTIR it was possible to measure the removal of the synthetic varnish during spot cleaning tests made along the edges of the painting, although it was hard to distinguish specific signals that could be ascribed to the uncovered bottom varnish layer, as opposed to the original oil-based paint.

In addition to the overall examination, some fine-scale degradation phenomena disrupting the boundary between paint and varnish (microscopic metal soap protrusions, as well as delamination and/or dissolution of paint) were studied with the HIROX digital microscope and with OCT in order to precisely locate them within the layer build-up of the painting.

The concurrent application of FTIR and OCT techniques was found to provide a valuable tool to support the conservator's evaluation of tests to remove the top layer of synthetic varnish only, leaving the underlying varnish and oil-based paint layers intact.

The complicated structure of the object and its built-up texture made it necessary to develop novel OCT data post-processing techniques in order to provide the conservator-restorer with results in a form convenient for future evaluation and comparison with results obtained with other complimentary techniques.

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# Non-invasive multi-modal analysis of Cave 465 murals in Dunhuang, China

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The Mogao Cave complex near Dunhuang in the Gobi desert is a UNESCO site of great cultural and historical importance. This study is focused on the analysis of the murals in these caves and more specifically cave 465. Cave 465 is of particular interest as it is the only cave in Mogao containing Tantrayana Buddhist iconography in typical Tibetan style and its murals are the oldest of such art preserved outside Tibet. The aim of this project is to understand the painting techniques and materials of these murals, exploring the history of this monument and more specifically the exchange between the Tibetan and Chinese painting culture, as well as to examine the material degradation through the years.

Conventional analytical techniques are usually invasive where samples are collected from the paintings which, apart from being destructive, restricts the information to materials contained in the detached samples and therefore may not even be representative of the artwork as a whole. For this reason, a range of non-invasive imaging and spectroscopic techniques has been applied to examine the murals. The multimodal non-invasive analytical approach introduced here combines coherent light-based imaging and spectroscopic systems, optical coherent tomography (OCT) and Raman spectroscopy, with other techniques such as remote multispectral imaging (PRISMS), as well as X-ray Fluorescence (XRF) and fibre optic reflectance spectroscopy (FORS). This approach enables a holistic analysis of the murals combining the strength and overcoming the limitations of individual techniques.

Optical coherence tomography (OCT) is a non-invasive, non-contact imaging technique capable of three dimensional imaging of subsurface microstructure using a fast scanning Michelson interferometer. OCT has been successfully applied to the non-invasive imaging of historical paintings and other cultural artefacts as, due to its non-invasive nature, it is the only method that can provide cross-sectional microstructure imaging without causing any damage. In this project, OCT imaging was used for the examination of the sequence of paint and drawing applications in high resolution. Given the large scale of the murals, PRISMS was used for their preliminary examination, using the near infrared bands, in order to highlight the areas with underdrawings that should be analysed in details with the OCT system. Moreover, the OCT signal contains absorption and scattering information which provides an extra tool for the characterization of painting materials.

Raman spectroscopy is a non-destructive analytical technique widely used for pigment identification that provides highly specific pigment identification. It is a technique successfully used for the identification of both inorganic and a few organic colorants, but with limitations in the identification of highly fluorescent materials such as aged binders and the majority of organic colorants. In our study this limitation is partially overcome by using high resolution reflectance spectroscopy in the 350-2500 nm range. XRF measurements provide elemental identification. Both pigment identification and the examination of the painting techniques were extended to areas at a distance up to 12 m (e.g. ceiling) using PRISMS data collected from them.

# Laser conoscopic holography for the assessment of the effects of traditional and innovative cleaning treatments of silver

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In the complex procedure for the conservation of a work of art, the effective monitoring of the surface treatment, together with the diagnosis of the state and the characteristics of the degradation, is an important step in order to establish a conservation protocol and, in particular, to define guidelines and hence allow for the conservator to adopt the correct cleaning procedure.

The evaluation of the effects of the cleaning requires that the outermost layer of the artwork be inspected with complementary diagnostic techniques to gain information on both materials and surface morphology.

In this work, following this integrated approach, a custom device based on laser conoscopic holography was jointly used with laboratory microscopy techniques for testing the performance of different mechanical procedures for the cleaning of silver alloy objects.

Tarnishing is the main alteration phenomenon for silver alloy artworks, due to the interaction of silver with sulphur-containing compounds in the environment. Even if this modification does not affect the conservation of the objects, it heavily influences aesthetical features. Thus, one of the most important conservation treatments in this case is the removal of tarnishing.

Many different cleaning techniques are proposed, based on mechanical, electrochemical, chemical and physical methods. The mechanical procedure, based on the use of an abrasive powder suspended in a liquid matrix, is of widespread use due to its simplicity and effectiveness. Here, a dry cleaning process based on the use of erasers is tested and compared with traditional mechanical methods. The proposed procedure is expected to effectively remove tarnishing and produce less morphological alteration of the surface than traditional methods.

Silver alloy mockups were artificially tarnished and cleaned using five different erasers and two traditional mechanical methods (calcium carbonate and sodium hydrogen carbonate suspended in water). The effects of these processes on the surface morphology were studied using optical microscopy and scanning electron microscopy. These techniques were proven effective to detect the single defects locally; however, they cannot provide an objective measure of the average roughness at micrometric scale over the sample.

To this aim, the surface structure was investigated with multiscale profilometry, using scanning conoscopic holography and atomic-force microscopy, in order to inspect the alteration of morphology from microscopic to nanoscopic scales. 3D surface metrology is carried out using ISO-25178 standards areal parameters.

The multi-technique methodology is described, from the information provided by the single method and the limit of the performance to the multiscale integration. As reflective metal is challenging for optical techniques, the effectiveness of the optical profilometry device, based on conoscopic holography and custom setup, is discussed in term of its effective resolution.

Preliminary results are presented, which indicate that the proposed dry cleaning methods are very efficient in removing tarnishing and that produces mechanical damages less or similar to traditional methods. The optical profilometry results are of particular significance since this technique allows an in-situ use and a real monitoring of actual artwork surfaces.

# Effect of aging in starch based adhesives, studied using second harmonic generation imaging microscopy

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Many valuable works of art on papers or even whole books probably would have been entirely lost without a skillful restoration. In paper conservation, adhesives are used to consolidate, fixing, mending, filling of losses, lining, matting and framing or to provide binders, glazes, and varnishes. Specifically, weak or brittle papers or sheets are commonly conserved by backing (lining) them with another sheet of paper. The lining is usually adhered with an adhesive based on starch. The basic principle of lining is minimal intervention. In particular, the adhesive should create less impact on the paper, physically as well as chemically. The lining glue selected should further demonstrate long-term stability and aging characteristics. Stability may be judged by natural or accelerated aging and consequent analysis. The results of such tests and their evaluation are of great assistance in making a final decision on the most appropriate restoration treatment.

Nonlinear imaging microscopy (second harmonic generation (SHG), third harmonic generation (THG) and two photon excited fluorescence (TPEF)) is already well established technique for biological imaging. Recently THG and TPEF have been employed for Cultural Heritage (CH) studies providing exact thickness determination and compositional identification of fresh and aged varnish protective layers, pigments and corrosion layers [1]. In contrast to TPEF, which relies on nonlinear absorption, SHG and THG rely on nonlinear scattering and, thus, are regarded as minimally invasive imaging techniques. While THG primarily appears where there is a change of refractive index, SHG is strong in non-centrosymmetric materials and originates from laser induced 2$^{nd}$ order polarization. The SHG signal is sensitive to the incoming excitation polarization and to the SHG active structures architecture. By rotating the axis of linear polarization reaching the sample and by recording the dependency of the detected SHG signal, it is possible to gain structural information unreachable by common intensity only SHG imaging [2]. Polarization sensitive SHG (PSHG) imaging has been used lately to characterize the molecular architecture of main endogenous sources of contrast in tissues [3,4] and in starch [5].

Here, we use PSHG to compare naturally aged (~7 years) starch based adhesives (flour pastes and starch pastes) samples, with fresh ones. We found that in aged glues, the starches' SHG angle, $\vartheta$ is shifted to higher values, in comparison to the fresh granules. Modifications due to aging on starch, altered $\vartheta$, thus the minimally invasive PSHG optical technique was able to recognize aged from fresh glues.

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# Nonlinear imaging techniques (NLO) for painting investigation

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Nonlinear imaging techniques (NLO imaging), i.e. multiphoton excitation fluorescence (MPEF), second and third harmonic generation (SHG, THG), are high-resolution imaging modalities which may provide non-destructive determination of thickness and composition within multi-layer objects as a function of depth. Initially employed in the field of biomedical optics, these techniques have been only recently applied in artworks analyses, for the identification of corrosion layers in metal-based objects, for the visualization and characterization of wood microstructures and for the study of synthetic glue and varnish protective layers. Some tests have been also conducted on paintings, giving promising results that encouraged further investigations. In fact, since absorption by most materials employed in paintings is low in the near-infrared (NIR), the use of laser light in this spectral region enables deeper optical penetration and makes feasible the examination of underlayers. Besides, using a multimode operation scheme enabling the recording of complementary (MPEF, SHG, THG) images, it is possible to obtain the micrometric surface mapping, as well as the in-depth profiling of thin films on the basis of refractive index changes, variation of optical activity and presence of fluorescence chromophores. Such information are definitely useful for the analysis of painted objects, and can be also crucial for the monitoring of restoring operations, like the cleaning process, that modify surfaces micrometric morphology and coating layers thickness.

In this regard, we present the preliminary results obtained through the application of NLO imaging techniques on a series of single- and multi-layers systems simulating the real egg-tempera wood panel paintings. Each sample shows a sequence of stratifications as follows: wooden support (a “sandwich” structure made of fir and poplar), preparation layer (gypsum and animal glue), underdrawings (lead and tin stylus, natural carbon, iron-gall ink), first pictorial layer (egg tempera with different pigments), second pictorial layer (different lakes) and superficial protective layers (natural and synthetic varnishes, egg, and multi-layer coatings). The variability of paint and protective layers thickness and composition enables the evaluation of the NLO-signals as a function of depth and of chemical make-up. In order to assess the reliability of NLO measurements, data were complemented with other well-established techniques, such as Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Fluorescence (XRF) for the chemical characterization of materials, Optical Coherence Tomography (OCT) and confocal microscopy for the determination of layers thickness, and laser scanning micro-profilometry for the study of surfaces morphology. Colorimetric analyses, i.e. reflectance spectroscopy in the visible region, are also reported in order to chromatically characterize pigments and lakes. Finally, the transparency of the different materials is investigated by means of Scanning Multispectral Infra-Red Reflectography (SMIRR).

This work describes whether and to what extent the NLO imaging techniques prove useful in probing multilayer painted objects.

# Shapes of degradation – Raman spectroscopy for identification of polymers in the cast sculptures from museum collection

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Increasingly large percentages of museum, library, and archive collections are composed of objects that are in part or entirely made from synthetic polymers. Due to the inherent instability of these materials, as well as artistic experiments with additives many heritage objects made from synthetic polymers are degrading at an alarming rate. The lack of conservation expertise lead to the application of inappropriate treatments that have, in some cases, resulted in the increased degradation of objects.

Tadeusz Kantor and Alina Szapocznikow's cast sculptures were the subjects of our research. The aim of this research was to identify polymers used in these museum objects. Firstly a review of historical recipes of polymers prepared by the artists themselves was performed. The polymers and additives composing the body of the sculptures were identified and characterised with portable Raman (785 nm, Inspector Raman, DeltaNu), micro-Raman (514 nm, Jobin-Yvon T64000) and FTIR (IR Affinity-1, Shimadzu). Fillers and inorganic colorants were characterised and identified with XRF (Artax 400, Bruker), and SEM-EDS (ProX, Phenom).

In order to evaluate the state of preservation, non-invasive analysis were performed: VIS, near IR, UV photography and X-ray radiography (Dix-Ray).

The identification of the materials is the first step to make recommendations for the care and display of resin cast and plastic objects in museum collections. Through a better understanding of the materials used and the effect of artist's additives and conservation treatments, it will be possible to propose ways to limit the objects' degradation, advise on their care and display, and help to ensure their continued presence and display in the nation's collection.

# Analytical studies to investigate the safeguarding of the original surfaces upon laser cleaning interventions at the Athens Acropolis monuments

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An innovative laser cleaning methodology is being employed since 2002 to restore the unique marble architectural members of the Athens Acropolis monuments. The cleaning challenge refers to the controlled and safe removal of soot deposits and black crust, products of pollution accumulation, which cover extensive parts of the sculpted masterpieces especially in areas protected from direct rain-washing. Traces of unique painted decoration and tool marks are often hidden beneath these pollution encrustations and their preservation upon cleaning interventions is a major issue. Furthermore, it is important to safeguard the fragile and delicate original surface of the stonework including any historic layer, without any chemical (i.e. formation of by-products) or physical (morphological) alteration.

The novel laser cleaning methodology and system that have been developed for this purpose and combine the simultaneous use of two laser beams (IR at 1064nm and UV at 355nm), are by now well described and known. In this paper, the results of the laser cleaning intervention on the Parthenon West Frieze and the coffered ceiling of the Maidens' Porch in Erechtheion, will be presented with emphasis to the safeguarding of the original surface and its details. Systematic analysis of the laser treated surfaces by means of Optical microscopy, X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Visible - Induced Luminescence imaging (VIL) has confirmed the superiority of the methodology by detecting traces of unaltered/undamaged pigments (Egyptian blue for example), historic protective layers and other details.

# Laser ablation: a moderate micro-sampling of cultural heritage objects for ICP-MS detailed elemental analysis

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is one of modern instrumental methods, which use in elemental analysis of cultural heritage objects has recently noticeably increased. The method requires almost no sample preparation and permits direct analysis of solid samples, availing only minute amount of the material. The micro-destructiveness of ablation processes remains usually within the scale acceptable for art historians, conservators, archaeologists and art curators, therefore the capability to perform multi-elemental, ultra-trace and isotopic analysis can be fully used during studies of cultural heritage objects.

Different scenarios of using laser ablation will be discussed with highlighting their influence on the state of entire objects depending on the analytical protocol developed individually for each case:

(1) ablation from the mechanically taken fragments of analyzed objects;
(2) ablation executed directly from a surface of an object, which fits to a closed ablation cell;
(3) ablation executed in an open cell attached to a surface of an object;
(4) direct laser ablation executed in ambient air;
(5) ablation with use of a portable laser device.

Some constrains are reported on using of LA-ICP-MS for quantification, however apart from just a few limitations it is a method that can be flexibly tuned to collect the desired elemental/isotopic information about various cultural heritage objects. The application potential of LA-ICP-MS will be presented in comparison to other instrumental methods and illustrated by examples of a comprehensive use of this method with (i) SEM-EDS; (ii) XRF; (iii) LIBS and (iv) Raman spectroscopy in analysis of diverse historical objects (pottery, red stoneware, glass beads, coins, wall paintings) towards their provenance and identification of used materials.

# Use of 3D laser scanning for replication and digital restoration of sculptures: most important recent cases studies in St. Petersburg, Russia

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Laser 3-D scanning is powerful measurement technique which can be used for documentation and analytical techniques of any objects. At the moment there is a growing interest in the use of this technology in preservation of Cultural Heritage. Recording in 3D can produce detailed archives of important objects and makes possible digital reconstruction of sculptures and architectural fragments. One more important application is concerned with manufacturing moulds and replicas for replacements of sculptures in case their preservation requirements do not allow them to remain in their original place.

In this paper some of the most important case studies of use of 3D laser scanning for replication and digital reconstruction of out-door sculptures in St. Petersburg city (Russia) are presented. In our works we used a triangulation based scanner made by Konica Minolta (model Vi9I).

One of most important projects was the replication of an out-door marble sculpture "Primavera" (18th century, Italy) from the collection of the State museum-preserve "Tsarskoye Selo".

Fig. 1. The Primavera: : left – original, right - replica

The post-processing of the scanning data resulted in a finished data set of approximately two and half million polygons (approximately 80 MB). Machining was done by using a 7-axis CNC milling machine, which created precise copy from a new block of Carrara white marble. When machining was complete, a small amount of hand finishing was done for removal of small, localised, drill markings. Now the replica of "Primavera" is on display on its historical place in front of the Caterina Palace in town Pushkin near St. Petersburg (see Fig.1). This work was the first case study of non-contact replication of stone sculptural monuments in Russia.

Another important case study concerns the digital reconstruction of zinc sculpture "Eve at the Fountain", which was the XIX-century copy of a marble sculpture by English sculptor Edward Hodges Baily. The mentioned copy was a part of the art collection of Maximilian Joseph Eugene Auguste Napoleon de Beauharnais, 3rd Duke of Leuchtenberg, who had a country estate Sergievka near St. Petersburg. This collection was almost completely lost during Second World War as it was a place of fierce fighting between Soviet and German troops. Fragments of the sculpture were found in the earth in the process of construction works in 2007, but they represent only 7% of total surface of the sculpture. This does not allow one to use conventional techniques of reconstruction of damaged sculptures. We created 3D model of the sculpture using of both scans of found fragments and "sculpturing" procedure carried out using software (RapidForm, Zbrush and KeyShot). The latter allowed us to create a photo-realistic images of a "reconstructed" sculpture that made it possible to create the virtual replica of the lost sculpture, which can be used for its display.

# Archeometric investigations of medieval stained glass panels from Grodziec in Poland

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Stained glass panels were one of the most important and precious features of medieval architecture. During the Middle Ages in Europe glass were generally formed from quartz and ash from beech trunks or from bulk beech trees. Application of such materials were reflected in high amount of silicon, potassium and calcium. Medieval glass technology utilized different materials for gaining specific colour of glass and additional borders, glazings were applied to make impressions on spectators or users of the building.

Information about elemental composition of glass is necessary to determine glass type, technology and provenance of the object. Information about changes in elemental composition due to corrosion processes is usually extremely valuable to settle proper conservation treatment. Many analytical methods can be applied to investigations of glass samples. Scanning Electron Microscope coupled with an Energy Dispersive X-Ray spectrometry (SEM-EDX) enables for measuring content of main elements. Nevertheless information about trace elements content is not accessible for this method. This information usually has significant value for provenance studies of historical glass. One of the methods capable for delivering information about trace elements without sample preparation is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

Investigations were focused on three stained glass panels of Austrian origin, dated on 1425-30. The panels come from Grodziec in Poland and nowadays they belong to the collection of the National Museum in Wroclaw. Elemental composition of bulk glass and external layers of glass samples was determined using SEM-EDX and LA-ICP-MS methods. Morphology of the deteriorated glass were investigated through SEM-BSE images of the cross-sections. Also *LA-ICP-MS* longitudinal concentration *profiles were elaborated.* Corning D and NIST 610 glasses were used as reference materials for LA-ICP-MS analysis.

The applied analytical techniques provided valuable information about the structure of glass and external paint layers and gave insight on the manufacture processes. Results show that the stained glass panels reveal characteristic elemental composition of wood ash glass produced from 1000 to 1400 AD. Almost equal proportions of potassium and calcium oxides indicate that high quality beech wood was applied by manufacturers. Main elements content is similar for almost all investigated glass samples, which means that manufacturers follow strictly the assumed recipe during panels production. Common correlations between elements (i.e. Sr – Ca, Rb i Ba – K, Ti – Al) were detected. Especially concentration of titanium (0,1 – 0,15% by weight) and barium (0,3 – 0,4% by weight) were relatively constant and typical of medieval wood ash glass. Some differences in elemental composition were detected for minor or trace elements which are connected to impurities or colour additives. Several stained glass samples exhibit typical composition of modern glass. Such samples were probably used during conservation treatments in the 20$^{th}$ century.

Additionally, considerable differences between the composition of healthy bulk glass and the deteriorated surface of glass were detected though SEM-BSE images and LA-ICP-MS longitudinal concentration *profiles*. High concentrations of lead, copper and iron were also determined in external layers of glass samples. Results can be connected with decorative paint layers and drawings.

SEM-EDS measurements were supported by the National Science Centre of Poland, decision no. 2012/05/E/HS2/03867. LA-ICP-MS measurements were supported by National Science Centre of Poland from funds granted within post-doctoral internship based on decision no. DEC-2013/08/S/ST4/00560.

# Easel paintings on canvas and panel: application of Nd:YAG laser at 355 nm, at 1064 nm and UV, IR and visible light for the development of new methodologies in conservation

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Although the beginnings of the application of laser technology in the conservation of easel paintings date from the early 1980s, it has not yet become part of the standard procedure in the conservation studios. The reason is a complicated and expensive procedure. This paper aims to present a set of mobile equipment that is applicable for conservation of other materials too, and therefore its acquisition could be more profitable for the institutions of protection of cultural heritage. It will show application of different light sources - the classical and laser radiation, before, during and after conservation treatment of the easel painting. In order to analyse the painting layers, subsequent interventions and retouching, the UV lamp, infrared cameras and a digital microscope with UV, visible and infrared light were used. A commercial Nd:YAG mobile laser system was used for thinning of the varnish. For the monitoring of the cleaning process, the fluorescence was induced on the surface of the painting by the UV lamp.

The subject of research and conservation was the picture "*Portrait of Jelena Milojevic with her daughters*" from 1922, the work of the Russian painter Valentin V. Volkov. By observing the results of the tests of chemical cleaning under the UV light, it was concluded that due to the very high sensitivity of some pigments, it was impossible to apply this methodology on such delicate surfaces. The laser cleaning instead, proved to be an acceptable alternative for cleaning of the easel paintings, but in this case it was even the only solution. Further tests, in which different parts of light spectra (IR, VIS, and UV) were used, revealed numerous pentimento, old retouching, micro-cracks in the varnish, as well as an advanced process of oxidation of the upper layer of the varnish. The final decision about the method of thinning of varnish layer was taken after observing the surface of varnish by a digital microscope which provided useful information about the layers and their mechanical structure. The process of laser cleaning of varnish was controlled by visible and UV light. Due to different effects of UV fluorescence on the varnish layer and the paint layer, it was possible to control the presence of varnish, taking paint layer as the reference. By combining these techniques, optimal results were achieved both from the conservation as well as from the aesthetic

Another case of this study is separation of layers on the icon, using the same laser. The object of study was the icon *Holy Mother of God*. The icon was made with technique of egg tempera in the 19th century in Ukraine. A bronze coating was subsequently added on the aureoles, below which there is a gilding sheet. Gilding sheet was poorly linked to the preparation layer, so that every intervention whether it is mechanical, chemical or laser cleaning had caused its removing, together with the bronze coating. But when the surface layer was irradiated at 1064 nm in Q-switched regime, with low energy that did not cause ablation of material, the added layer of the icon was separated from the original layer as a result of the shock waves on the surface. This allowed, subsequently, an easy mechanical removal of unwanted layers. Combination treatment of the aureoles using two techniques - laser cleaning and mechanical removal, is faster and more uniform than in the case of treatment by other techniques.

# White, yellow and green pigments on Polish artist's palettes in the period 1838-1938

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The 19$^{th}$ century evolution of chemical composition of whites, yellows and other pigments was stimulated by numerous chemical discoveries. Dates of the inventions and patents are well established thanks to the preserved documents, catalogues and literature.

The survey of more than 200 hundred Polish artists' paintings from the years 1838 - 1938 proved significant shifts between the date of invention of the pigment and the moment of its implementation by artists. According to the gathered data the year opening reported period (1838) is the moment when viridian was for the first time used on the painting. A century later (1938), titanium white was implemented by Pankiewicz. Among artists examined within the research were: P. Michałowski, W. Orłowski, J. Matejko, W. Gerson, W. Kostrzewski, W. Szementowski, W. Malecki, W. Pruszkowski, J. Mehoffer, S. Wyspiański, L. Wyczółkowski, J. Chełmoński, W. Weiss, F. Pautsch, J. Malczewski. Such wide range of painters allowed to build chronological database of the dates of the first use of individual kind of pigment, period of its especially intensive exploitation and in some cases of subsequent absence of the pigment on the palette.

Portable XRF and complementary Raman spectroscopy and SEM-EDX analysis (when sampling was possible) allowed to establish some turning points like the first use by Polish artists of zinc white, cadmium yellow, zinc and barium yellow, emerald green and viridian. In the same time minor changes and the technological evolution of pigments were observed: modification of Naples yellow by zinc or tin based admixtures in the second half of the 19$^{th}$ century (in opposition to pure lead antimonite in its first half), or variety of additions to basic lead white changing with time (chalk, barites, zinc white, lithopone or aluminium based compounds). Innovative approach was to confront information on the evolving palette with the results of identification of fillers of the priming. When pigments and priming were recognized together, it significantly strengthened precision and accuracy of the material examination based dating and authentication.

Conducted research started to build panorama both of the turning points and more fluent changes within the practice of use of some pigments and grounds by Polish painters in the period 1838-1938. In some cases it indicated characteristic habits of individual artists.

Gathered data is a solid source for comparative studies for modern Polish paintings of unknown origin. The survey is going to be continued and broadened.

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# Analysis and documentation of historical artifacts using advanced imaging and spectroscopic techniques

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Documentation is extremely vital step that must be carried out in the field of historical objects preservation. They collect complementary information used for the study of artifacts. Photographic imaging was historically the main method used for archeological documentation as well as advanced diagnostic techniques.

An early 20th century Egyptian painting was documented using a combination of digital and computational imaging techniques: multispectral imaging, Reflectance Transformation Imaging (RTI), and lab-made scanning system. These methods were chosen with consideration for the long-term preservation and reuse of the data collected using well-documented and open-source standards.

In parallel spectroscopic techniques, Raman spectroscopy, Laser induced fluorescence, FT-IR and X-ray fluorescence are involved to investigate the used coloring techniques and pigments of the sample. A chromatographic investigation was conducted to identify the used organic pigments that used in that painting. The chromatographic results confirmed the results of spectroscopic techniques that we used. Results suggest that complementary use of different techniques offers a reliable methodology for identification and allow better understanding of the main type of pigments that used in that period of time by Egyptian artists. Further, the study with the support of the high resolution photographs provided additional information on the manufacturing style of the artist and revealed details and decorative elements of the desired objects, which are indiscernible under standard illumination. This study finally gave us a good estimation of the age of the of the paint that had been used in the artwork.

# Simultaneous LIBS and LA-ICP-MS analysis of wall-paintings cross-sections

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The research was devoted to elemental mapping of multilayered historic samples characterized by a high degree of inhomogeneity using two laser-based instrumental methods: (i) LIBS (laser induced breakdown spectroscopy) and (ii) LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry).

Samples were analyzed in the form of cross-sections prepared from tiny blue fragments of mediaeval Nubian wall-paintings embedded in resin and polished in such way that every layer of the mural was visible and available for the analysis.

All experiments were performed using a J200 Tandem LA/LIBS instrumentation (Applied Spectra Inc., Fremont, CA) equipped with a 266 nm Nd:YAG laser. For collection and spectroscopic analysis of the radiation emitted by the laser induced plasma a Bruker Aurora Elite spectrometer was employed. Generated aerosol was analyzed using a Thermo iCAP Qc quadrupole ICP-MS (ThermoFisher Scientific, Bremen, Germany). LIBS and LA-ICP-MS analysis were performed from the same sample area simultaneously in the multiline scan mode (n=11).

Both methods enabled to determine two blue pigments used in Nubian wall-paintings only on the basis of their elemental composition. Egyptian blue (CaCuSi4O10) was identified when Cu, Ca and Si were distributed in the same areas of the analyzed samples. Co-presence of Na, Al and Si indicated the use of lapis lazuli (Na8-10Al6Si6O24S2-4). Low limits of detection characteristic for LA-ICP-MS permitted to observe the distribution of some mineralogical impurities such as Ag, Sn, Sb, Hg, As, Cl in the thin dark blue painting layer, which led to conclude about the use of natural ultramarine instead of artificial one. LIBS provided the information about lighter elements such as O not accessible by applying only LA-ICP-MS mapping.

The finding of lapis lazuli used as a pigment in Nubian wall-painting was quite surprising, because mediaeval Nubia was supposed to be a rather insignificant artistic centre and the price of natural ultramarine in that times was close to the price of gold.

# Identification of contemporary binders by time resolved laser induced fluorescence (TR-LIF) spectroscopy

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Since 1850, a great number of chemical and synthetic materials have been available thanks to the development of modern chemical industry. Moreover, contemporary artists have used most of them in their paintings. Acrylic and vinyl polymers undoubtedly represent the most used binders in contemporary paintings. Despite the great popularity of those polymeric binders in the field of contemporary arts, many artists still prefer to use the traditional ones, as linseed oil and dammar varnish. However, the oil binders, which are produced trough industrial processes, show many different chemical compositions with respect to the ones produced in ancient times. Because of these characteristics, contemporary artworks are often realized with multi-component materials with unknown composition, which may be subjected to an unforeseeable degradation. The use of those multi-component mixtures, whose chemical and physical properties are not well assessed to date, probably represents the major problem arising from contemporary artworks conservation.

Most of the alteration and degradation issues on painted surfaces are related to the binders used. This is the reason why their identification becomes mandatory in order to plan appropriate conservation and restoration strategies. Nevertheless, the complex nature of these multi-component mixtures makes their investigation really complicated by conventional non-destructive diagnostic techniques. In this sense, Laser Induced Fluorescence (LIF) is a non-destructive technique used for the investigation, characterization and preservation of Cultural Heritage, thanks to its peculiar advantages of high sensitivity, non-invasiveness and prompt response. In this work, a great numbers of binders employed in contemporary paintings have been studied by Laser Induced Fluorescence (LIF) spectroscopy. The emission spectra have been acquired irradiating the investigated samples with an UV laser excitation source at 220 nm. Multi-material samples main issue is related to mixing, i.e. assigning the spectral signatures of different constituents. This issue can be overcome by using Time Resolved LIF, which discriminates the emissions from different compounds analyzing the time evolution of fluorescence spectra. Experimental results confirm the capability to isolate specific contributions from the investigated constituents by a TRLIF analysis. The results presented in this work have been classified in a reference database, which is dedicated to the identification of the employed materials for contemporary artworks.

# Assessment of elemental heterogeneity by means of LA-ICP-MS imaging approach in artwork studies

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LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) is an analytical method eagerly used in artwork studies. Beside multi-elemental analysis, this method offers ability for acquiring information about spatial distribution of selected elements over the sample's surface. These advantages of LA-ICP-MS were decisive in undertaking research devoted to analysis of heterogeneous samples, e.g. pottery shards and pigments. The aim of the pottery study was to evaluate the degree of heterogeneity as well as to assess the correlation between samples, which could be used for their provenance determination. Heterogeneity of collected pigments particles was also the aim of pigments analysis focused on searching for coexistence of particular elements.

Analyzed samples included pottery sherds from different excavation sites (e.g. Topaz Gala Depe, Ara Depe, Atsyz Depe) from Sarakhs oasis in Turkmenistan and particles of pigments carefully collected by a conservator on the occasion of exhibition of works painted by Olga Boznańska in the National Museum in Warsaw in 2015.

LA-ICP-MS procedure was optimized separately for ceramics and pigments to allow comparison of important chemical information available for various analytical scenarios:

(a) pottery samples were ablated by using pattern of 11 parallel lines selected to obtain elemental distribution on a relatively large area of each sample and monitoring of transient signals for 42 selected isotopes;
(b) particles of pigments were ablated by using more moderate approach and only 3 lines were defined for micro-sampling step with 36 isotopes taken into account. The interpretation of LA-ICP-MS results of analysis of pigment particles were supported by using Raman spectroscopy and collection of respective molecular information.

Although at first glance the purposes of these analysis differed considerably, in fact they represent general and very flexible possibilities of using LA-ICP-MS in the study of heterogeneous materials.

The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007 – 2013.

# PLEAF spectroscopy of black inks and red seal inks on Chinese paintings

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Plume-Laser-Excited-Atomic-Fluorescence (PLEAF) is a soft laser/material interaction spectroscopic technique that presents advantages for cultural heritage material characterization. The PLEAF principle is based on a two-laser-pulse scheme: the first 355 nm laser pulse induces desorption of a thin layer of material (laser fluences below the damage threshold) and the second 193 nm laser pulse induces fluorescence from the multi elemental and molecular analytes in the desorbed plume. The sample stage design can accommodate samples of different size and shape. Sample preparation is not necessary.

We analyzed Chinese black inks and red seal inks on paper by means of PLEAF. We were able to detect trace elements at the ppb level with spectral averaging. Single-shot analysis gave atto-mol level mass LOD. We sampled five commercial Chinese inks that were applied on two kinds of xuan paper, ten ink/paper combinations in total. We also characterized three commercial Chinese red seal inks on xuan paper. Partial-least-square discriminant analysis unambiguously sorts the various ink-paper combinations. The sampled area is not visibly damaged even under the microscope. The degree of non-invasiveness will be further discussed.

# Raman, chromatography and microscopy studies for wax-sealed documents from some old Romanian pulp and paper factories

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Waxes have been used as adhesives, as painting media, for surface coating purposes, as a component of seals and as a modelling or casting materials and also in conservation practice. The history of detection and identification of waxes can be connected to modern methods of analysis [1]. Waxes are translucent solid substances with mineral, vegetable and animal origin, easy to solubilize. They contain long chain hydrocarbons, acids, alcohols and esters or mixtures of these. Some types of wax components are fully saturated materials with a considerable chemical stability and waterproofing properties.

Most damages in library and archive collections are of mechanic character: cracks, missing pieces or pollution and excessive handling of documents. With wax seals, the loss of fatty acids and non-permanent alcohols causes saponification, so the material becomes both opaque and friable. In this paper the compositional analyses have been achieved by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR), which can provide molecular structural information of wax materials. Also, the composition of degraded wax seals was determined using gas chromatography / mass spectrometry (GC/MS), for evidence of some alkenes with 31, 32, 33 and 35 carbon atoms. The gas chromatography has been used in the detection and identification of small amounts of waxes and greases encountered in old paper conservation. The aspect of degraded wax seals and paper substrates have been identified and discussed by optical microscopy and scanning electron microscopy. All these analytical investigations have been achieved for paper samples from two dissafected pulp and paper factories - Letea and Bușteni (Romania) belonging to industrial patrimony, proving the damaging effect of wax seal for paper documents, in order to optimize the proper solutions for conservation and restoration.

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# LIBS, optical and multivariate analyses of selected 17th century oil paintings from Museum of King Jan III's Palace at Wilanów

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Laser-Induced Breakdown Spectroscopy results of a study of the ground layers investigated in 17th-century oil portraits belonging to the collection of the Museum of King Jan III's Palace at Wilanów, supported by microscopy and statistical analyses are presented in the paper. The unsigned artworks seem to have been painted by artists of King Jan III royal court and that is why there were chosen for examination.

The erudite king, a well-known patron of artists and broadly educated art connoisseur, was also a staunch art collector who looked for works of art in the entire Europe. Unfortunately, after his death, the valuable collection was divided among his heirs and over the years it became more and more dispersed.

After the WWII, continuous efforts have been undertaken to recreate the royal collection. In 2012 we started a new project the aim of which is to collect comparative materials in order to establish and classify differences between the technique and technology of the unsigned portraits of Jan III and his family which were presumably painted in the king's lifetime and which appertained to royal collection.

The aim of the study is to determine the technological structure of the paintings, gather comparative material that would serve to conduct further multidisciplinary attributive research.

The research is carried out with active participation of art historians, conservators and experts in conservation science. Because of the large field and numerous threads to follow, the research will be conducted stage by stage and traditional research methods as well as the most advanced ones, e.g. based on the spectroscopy, will be employed. One of the latter is laser-induced breakdown spectroscopy (LIBS).

During the investigations conducted from 2012 to 2014, we concentrated on comparison of composition of ground layers, essentially on presence of some specific elements like Li, Ba, Ti identified in grounds layers and tried to classify the paintings according the content of them. In parallel, we studied stratigraphy distributions of various elements over ground layers, which allowed us to find similarities and differences among analyzed paintings.

Five oil paintings portraits of king Jan III, queen Marie d'Arquien, and their daughter Teresa Kunegunda were tested using LIBS method and digital 3D microscopy. Results were compared with SEM/EDS and µXRDP data available for some paintings. Obtained results allowed us to find stratigraphy distributions of elements in selected parts of paintings as well as to identify pigments used in tested points. Evident differences and similarities were found in grounds deposited on particular paintings. The analysis was additionally supported by statistical multivariate analysis. Presented results exhibit a scale of micro-destructibility introduced by LIBS.

Finally, presented results showed reasonable agreement with data obtained from other techniques and gave some indications related to workshops and authorship of the paintings.

# Posters

# POSTER P1

## Cleaning performance of femtosecond and nanosecond laser pulses for artificially soiled papers with sizing

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Laser cleaning is becoming of increasing practical use in cultural heritage conservation. The method has significant advantages over more conventional alternatives. Yet, due to strong dependence of performance on variations of materials and laser parameters, it has to be carefully investigated for each novel application. Nd:YAG lasers are used very commonly and efficiently for cleaning of mechanically strong materials such as stones. However, high penetration depth and high laser fluences may become problematic for application in more fragile artifacts such as papers, textiles and parchments [1][2]. At UV wavelengths, laser irradiation can also cause photolysis of cellulose. Furthermore, colour obtained after laser irradiation has to be very close to authentic colour of paper (e.g. colour of clean/uncontaminated parts of a historical document). Side effects such as yellowing or bleaching should be avoided.

Ultrashort-pulsed lasers offer more reliable method to clean delicate materials [3]. At such pulse durations, heat deposition to background material is minimal, eliminating the possibility of deterioration of fiber network. In our recent work on femtosecond (fs) laser cleaning of paper samples with sizing, we determined that the sizing layer provides some degree of protection to the underlying fiber network. As a result, it is still an open question to whether longer (e.g. nanosecond, ns) pulse durations might still be applicable to this particular type of paper material.

In this study, we present comprehensive and comparative experimental results including fs ns laser cleaning of paper samples with various sizing types. Sizing is a protective layer applied to paper surfaces. It prevents water or ink from spreading into paper. Various substances have been used for sizing in Ottoman papers, and we prepared a range of paper samples using various sizing types. The samples were artificially soiled with graphite and graphite - kaolin mixture. For aging, all of the samples were exposed to air at 90 ˚C and 50% relative humidity during 16 days. In laser cleaning treatment, two different methods and lasers were used. In the first method, Yb:Glass fs laser beam (1030 nm) was focused on paper surface by using cylindrical lens (25 mm focal length). Square regions were cleaned through scanning the samples under laser light. Laser power was varied in the range of 100-200 mW. In the second method, Q-switched Nd:YAG ns laser was operated at fundamental wavelength (1064 nm) and second harmonic (532 nm). Laser fluence is varied from 0.24 to 1.24 J/cm$^2$. Each sample was cleaned by means of 10 laser shots. Effectiveness of cleaning was investigated through measurements of colour variations and microscopic observations.

As a result of our evaluations, we conclude that fs laser cleaning is still superior in performance as compared to ns. Yet, the latter might still be of acceptable and significantly lower cost use in certain sizing types.

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# POSTER P2

## Laser cleaning of archaeological artefacts using 1064 nm and 532 nm pulsed laser radiation

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Laser cleaning represents the most important contribution of physics and chemistry to the conservation of cultural heritage and has been studied on different types of materials during the past three decades, and has proved to be superior when compared with other methods [1-5]. Contamination removal using high power pulsed lasers is a very advanced, non-contact, precise and a fast technology. Several objects are affected by particulate contaminants of organic or inorganic nature when exposed to either outdoor or indoor environmental conditions. For a successful conservation and restoration process a complete understanding of the artefacts, contaminants and the cleaning mechanism to be employed is prerequisite. In this study pulsed Nd:YAG laser has been used to demonstrate the laser cleaning of corrosion or patina layers on archaeological corroded objects. A part of contamination was deeply penetrated in the samples and was difficult to remove using conventional cleaning methods in comparison to the laser cleaning method owing to the precision and the localized control. Two different wavelengths i.e. Near Infrared (1064 nm) and Visible (532 nm) were used to ablate the contamination layers from the archaeological materials and cleaning status has been demonstrated for comparative dynamics. The chemical composition of the studied artefacts was determined using laser induced breakdown spectroscopy before and after the laser treatment. The cleaning status has been monitored using optical microscopy and scanning electron microscopy.

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# POSTER P3

## Optical coherence tomography for monitoring of the laser cleaning of ceramic tiles

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Ceramic artifacts from archeological sites suffer from a vast range of deterioration phenomena, some of which are occurring in glaze layers. Such problems, caused mainly by long exposure to environmental factors, are: cracks, delaminations, pitting, all eventually resulting in formation of losses within the glaze. Also surface dirt and old conservation coatings contribute to the complexity of present conservation issues. Cleaning of such objects is both difficult and controversial, since most conservators believe that the corroded glaze layer should not be removed.

The aim of this work was to evaluate the applicability of Optical Coherence Tomography for monitoring of laser removal of unwanted dirt and secondary layers. A group of medieval ceramic tiles with various deterioration problems (both fragments and whole preserved tiles) from the collection of the District Museum in Toruń were chosen.

Optical Coherence Tomography (OCT), the technique of non-invasive imaging of transparent and semi-transparent layers was employed to monitor the state of glazes before, during and after laser cleaning trials. The laser used was Nd-YAG Thunder Art system from LightForArt (El.En. S.p.A.).

In the presentation OCT cross-sectional images of both fragments and preserved historic tiles before, during and after laser cleaning will be shown to examine the process of removal of surface deposits as well as mid-twentieth century conservation coatings. In case of some of the ceramic fragments (donated to science) the destruction of the glaze layer after a few steps of laser cleaning was induced intentionally and then visualized with OCT.

The experiments performed confirmed that OCT is a suitable monitoring tool for laser cleaning of semi-transparent glazes on historic tiles, as well as enabled to define specific risk factors for these objects, such as preexisting cracks or delaminations within the glaze layer.

# POSTER P4

## Thinning of oxalate patina with Er:YAG laser stand-alone and in combination with Agar and Carbogel systems

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In this work, the removal tests of the oxalate patina present on the 15th century mural painting are described. The thinning of oxalate patina is of utmost importance due to its widespread presence on natural and artificial stone substrates. The removal tests were performed either by the laser cleaning or by the combined chemical followed by laser approach. The output of these tests, monitored with optical coherence tomography, profilometry and colorimetric measurements, is discussed and compared.

The laser cleaning tests were accomplished with a short-free running Er:YAG laser (El.En.spa) emitting at 2.94 microns with variable pulse duration. The pigment transformation due to the thermal or photo-oxidation processes under the laser beam is a well-known phenomenon. For this reason, the resistance of red ochre pigment, present also in the fresco, was verified through a series of irradiation tests on laboratory prepared specimens. A very good resistance towards the laser radiation was ascertained under all the tested fluences (3.8-9.4 J/cm2).

As a further step, it was verified that the Er:YAG laser does not allow for the non-contact oxalate expulsion. However, the mechanical disruption of the oxalate patina was achieved. Consequently, the disrupted patina was removed with cotton swab soaked with water or isopropanol. The phenomenon of photomechanical disintegration was enhanced when laser irradiation was performed in presence of isopropylalcohol as a wetting agent. This is due to the efficient coupling of the 2.94 microns laser radiation into the vibrational modes of –OH groups of alcohols. The etch rate, which in this context means the depth of the disrupted layer, was calculated as a function of the applied fluence. The 7.0 and 7.6 J/cm2 fluences proved as the most efficient and time-wise reasonable operation conditions to diminish the 40 microns thick oxalate layer.

The combination of chemical followed by physical cleaning was tested as well. To this aim, two commonly used gels (Agar and Carbogel) were charged with EDTA chelate (5% tetrasodium ethylenediaminetetraacetate) and left to act for 30 minutes. The preliminary action of poultice charged with chelate agent allowed to diminish the laser fluence and to operate at 5.0 J/cm2 with the results comparable to those achieved by standalone laser irradiation.

In conclusion, the preliminary chemical cleaning followed by mild laser ablation appears as beneficial. Moreover, Agar poultice ascertains better adhesion and therefore more homogeneous cleaning results.

# POSTER P5

## The application of optical coherence tomography in a technical study of *The Mellow Pad* by Stuart Davis

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In 2015, the Brooklyn Museum was awarded a Bank of America Art Conservation Project Grant to study the materials and techniques used in Stuart Davis's seminal artwork, *The Mellow Pad* (1945-51). *The Mellow Pad* is Davis's most complex composition. He took six years to complete the painting, working out in excruciating detail his theories of "color-space logic" and finally achieving what he called "the most powerful objective Art realization of my life." The painting has been a highlight of the Brooklyn Museum's American Art collection since its acquisition in 1992.

The primarily non-invasive technical study was undertaken in preparation for the upcoming retrospective exhibit In Full Swing: The Art of Stuart Davis, organized by the Whitney Museum of American Art. Upon request for loan to the exhibit, questions about the painting's condition and stability prompted treatment as well as the Bank of America-funded investigation into its materials.

The investigation focused on narrowing down potential causes for interlayer cleavage and discolored paint. Because of the painting's complexity, non-invasive analytical techniques offered the best opportunity to gain comprehensive knowledge of the materials without excessive sampling. The non-invasive techniques used included optical coherence tomography (OCT), fiber optic reflectance spectroscopy (FORS), x-ray fluorescence spectroscopy (XRF), multispectral imaging, and x-radiography. This range of techniques provided information about the painting's colorants and layer structure, which can be used to tell a more complete story of the painting's development and condition in conjunction with historical records. This poster focuses on discoveries made using OCT, with supporting information from FORS and XRF.

The 810nm ultra-high resolution OCT, with axial resolution of 1.2 µm in paint, scanned three dimensional image cubes of surface topography and subsurface microstructures in areas of interest. Many successful studies of historic paintings and artifacts have been conducted with the instrument from Nottingham Trent University, but The Mellow Pad was its first Modern-Contemporary application. Thus, the study was beneficial in better understanding the painting as well as the analytical potential of OCT. Optical scattering and absorption properties of some colorants prevented capturing a full stratigraphy of the paint layers; however, other aspects of the painting's condition were clarified, sometimes as a result of the same optical properties. Insights into Davis's use of paint mixtures and charcoal, and into restoration materials present, were among the most interesting results.

# POSTER P6

## A study of illuminated manuscripts using optical coherence tomography and non-invasive spectroscopic techniques

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Optical Coherence Tomography (OCT) is a non-contact and non-invasive 3D imaging technique for the examination of subsurface microstructure of materials. OCT has been successfully applied to easel paintings revealing varnish and paint layer stratigraphy, ageing of the varnish, as well as giving the highest resolution and contrast images of underdrawings. In comparison, OCT has not been applied as extensively to illuminated manuscripts. Since sampling is usually not allowed on manuscripts, application of non-invasive imaging and spectroscopic techniques is the only way to examine them. Recently, we used our newly developed ultra-high resolution OCT (UHR OCT) to examine folios in a number of medieval manuscripts in the collection of the Fitzwilliam Museum in Cambridge (UK). The UHR OCT at a central operating wavelength of 810 nm has a resolution of ~1.2 microns in depth (for paint and parchment) allowing the thinnest paint layers to be seen. In this paper, we illustrate how OCT can be used to examine illuminated manuscripts in order to deduce the paint layer thickness and structure, examine the internal microstructure of the parchment and to assist pigment and binding medium identification in combination with visible and near infrared fibre optic reflectance spectroscopy (FORS) and X-ray fluorescence spectroscopy (XRF). XRF identifies elements with atomic number $Z>12$, while VIS/NIR FORS gives molecular information allowing not only the identification of pigments but also of some binding media. The combination of OCT with FORS and XRF is capable, in some cases, of giving depth-resolved material identification.

# POSTER P7

## SERS analysis of Fuchsine and Diamond Green G on Ag nanoparticles prepared by photoreduction

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Micro- or non-destructive identification of synthetic organic dyes employed to color cultural heritage objects such as historical textiles, is a real challenge for conservator scientists. This is due to their inherent high tinting strength and consequent low concentration in the carrying matrix [1]. This fact severely limits the number of analytical techniques that can be efficiently and micro-destructively employed for their detection and unambiguous identification. Surface-enhanced Raman scattering (SERS) has been developed as a micro or non-destructive technique for the characterization of organic dyes in works of art [1]. The application of Ag nanoparticles produced by laser photoreducion [2], lead us to analyze and detect synthetic organic dyes directly “on the fiber” by SERS spectroscopy.

Synthetic dyes meant technological simplifications to the home and industrial textile production. Thus, their use was rather widespread. However, a lack of comprehensive scientific and conservation literature on these molecules could be linked to the fact that the attention on the characterization of contemporary works of art has been made just relatively recently [3].

In this work, wool fibers dyed with two synthetic dyes belonging to the triarylmethane group, Fuchsine and Diamond Green G, were investigated by SERS spectroscopy. None of these dyes could be detected by regular Raman spectroscopy. Therefore, the use of the SERS technique was necessary for their study on fibers.

Ag nanoparticles were prepared and immobilized directly on wool fibers by photoreduction of AgNO3 using a laser/micro-Raman coupled system [4] with excitation at 442 and 532 nm. SERS spectra were carried out directly of the fibers using different wavelengths (442 nm, 532 nm, 785 nm).

Both Ag nanoparticles prepared by photoreduction give rise to intense SERS spectra. However, excitation at 442 nm has the great advantage of form active SERS substrates in 10% of the time needed to prepare them by irradiation at 532 nm. In the case of fuchsine, best results were obtained at 442 and 532 nm, due to the pre-resonant effect at those wavelengths. However, as Diamond Green G absorbs at 623 nm, a pre-resonant effect exits when the SERS spectra at 785 nm.

This work was supported by CSIC (project 201560I029) and Comunidad de Madrid/EU (project GEOMATERIALES 2).

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# POSTER P8

## Stratigraphy by multiple wavelength laser-induced breakdown spectroscopy

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Many modern industrial, medical, and conservation scientific applications require rapid qualitative and quantitative stratigraphic analyses of metal coatings. One promising option to achieve this is Laser-Induced Breakdown Spectroscopy (LIBS). However, a quantitative stratigraphy with a resolution down to the optical refraction limit has not been demonstrated yet.

This study used Nd:YAG lasers emitting at 1064, 532, 355 and 266 nm for the systematic ablation analysis of a Ni-Co alloy layer. The resulting plasma emission data were converted into stratigrams [1] employing the linear correlation coefficient method [2]. These were then used to determine the effective absorption coefficients [3], which were compared to theoretical estimations [4]. This approach allowed a systematic insight into both the influence of heat diffusion in the sample and laser-plasma interactions on the ablation rate.

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# POSTER P9

## Raman spectroscopy and associated techniques used in the pre-screening stage of radiocarbon dating process

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Employing instrumental analysis methods can provide precious information in establishing the processing strategy for initial samples, as well as verifying the final product purity which will be used in radiocarbon dating. RoAMS Carbon-14 dating Laboratory and Physical and Chemical Tests Laboratory (IRASM Radiation Processing Center) currently use, within the Center of Excellence for the Study and Conservation of Cultural Heritage, the following analytical methods: FTIR and FT-Raman spectroscopy, chromatography, mass spectrometry, thermal analysis, color analysis, ESR, TL OSL spectrometry. The present work highlights several case studies in which non-destructive and non-contact vibrational spectroscopy methods (FTIR and FT-Raman) offered additional information in establishing the age of museum materials under suspicion of being contaminated with preserving agents, but also for a series of archaeological materials for which the contamination is mostly due to environmental factors from the post-storage step.

Macromolecular structure characterization was performed by Fourrier Transformed Infrared and Raman spectroscopy using a Bruker Vertex 70 FT-IR spectrometer equipped with a RAM II Raman module (N2 cooled detector). FT-IR was performed in transmission mode with KBr pellets and FT-Raman with a Nd:YAG laser excitation source of 1064 nm.

The present study focuses on using spectrometric techniques to study old osteological materials (raw bone powder and Type I collagen), hair and leather for the pretreatment step. All of these samples were dated at RoAMS in the final step.

This work was partially supported by the project cod: PN 16 42 03 02 and International Atomic Energy Agency Research Contract 18876 under Coordinated Research Project F23032: Developing Radiation Treatment Methodologies and New Resin Formulations for Consolidation and Preservation of Archived Materials and Cultural Heritage Artefacts.

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# POSTER P10

## Guanine - an unexpected organic pigment identified in the polychrome of the wood sculpture using the method of Raman microspectroscopy

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An investigation of polychrome of the wood sculpture Our Lady of Sorrows (1460-1470, Inv. No. P 6041, lime wood, h. 65 cm) was carried out in the chemical-technological laboratory of the National Gallery in Prague. The sculpture represents a late reminiscence of the work of a significant Prague sculptor, so called Master of the Týn Calvary active between 1420 and 1450 in Prague. His influential style spread out the Central Europe and very soon influenced a number of artists. The sculpture is characterized by simplifying of forms and rural style of carving skills.

Samples of the paint layers were taken and a complete chemical analysis was carried out. The cross-sections were prepared and pigments from the layers of polychrome were identified by using Raman micro-spectroscopy. In the sample (flesh tone) of the neck of Virgin Mary an organic interlayer was found between two pink layers containing common inorganic pigments. The comparison of the Raman spectrum of the organic interlayer with a specialized library resulted guanine ($C_5H_5N_5O$). Raman mapping (laser wavelength 780 nm, laser power 13 mW, exposure time 1 s, number of exposures 60, X step size 2,5 µm, Y step size 3 µm) was applied on the area where guanine was identified to see the position of the guanine layer on the cross-section.

Guanine layer has been never described on a polychrome sculpture yet. In this case guanine layer is probably a secondary historical treatment as the origin and time of this treatment is not clear. The layer is preserved fragmentally under repaint containing usual inorganic pigments (lead white, vermillion, chalk). The sample with guanine layer was taken on a boundary of flesh and silvered coat of the Virgin Mary, so it’s possible that guanine was used for retouching the silvering.

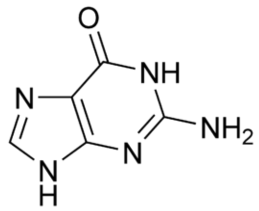

Fig. 1. Guanine

Guanine and little amount of hypoxanthine (3 - 24 %) together form natural pearl essence, the oldest nacreous (pearlescent) pigment. At first this pigment was isolated in the middle of the seventeenth century from fish scales by the French rosary maker François Jacquin. In the eighteenth century pearl essence was applied by coating in fish glue and simulated pearls were produced. Widespread use that occurred in the beginning of the twentieth century led to a development of cheaper synthetic nacreous pigments. At the present day natural pearl essence is used in cosmetics or for coatings [1]. In one case guanine coating was described in the interior of a hope chest from the sixteenth century [2].

Our unique discovery of guanine was enabled by applying the Raman micro-spectroscopy method, an analytical technique of a great use in the conservation science primarily in the field of pigment analysis.

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# POSTER P11

## The forgotten baroque master - authentication investigations of the painting attributed to J. J. Knechtel

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The recovery of the artistic heritage of Joseph Jeremias Knechtel is believed to be an important juncture in the art historical study of Baroque Silesian art. J. J. Knechtel was almost completely forgotten and his works were hardly known by art historians.

Several paintings attributed to Knechtel were subjected to comprehensive investigations within the research project completed by the Cultural Heritage Research Laboratory. The results delivered information about the painting technique and materials employed by the artist. Moreover, the attribution of the painting "Bolko Świdnicki" to Knechtl was confirmed1. Thus, further development of the database created by experts from different fields including art history, chemistry1 and conservation2 became essential in broadening the knowledge of Knechtel's workshop.

Recently, conservation treatments of "Madonna and Child" from the main altar in the church of SS. Simon and Jude Thaddeus in Rudno (formerly Rauden, Lubuskie province, Poland) began, aimed at recovery of the original appearance of the painting. The main image of the altarpiece was signed by Knechtel, but not "Madonna and Child". Stylistic analogy between these two paintings is significant, but due to the lack of signature and former conservation interventions, the attribution to Knechtel was questioned. It is worth mentioning that the artists treated the paintings from the top part of the altar as their commission. Thus, leaving them unsigned was a common practice.

To confirm the authorship of "Madonna and Child", the painting was subjected to comprehensive investigations based mostly on non-invasive and non-destructive physicochemical analyses. UV and IR photography was performed to determine the state of the preservation of the painting and to specify the area for collection of micro-samples. The paint cross-sections were submitted to optical microscopy in order to characterize their stratigraphy. The application of Raman spectroscopy, SEM-EDS point analysis and mapping delivered information about pigments used and their distribution in different layers. Additionally, GC-MS analysis provided complementary information about organic media employed.

The results of the investigations were subjected to the comprehensive analysis together with the data from the developed database and allowed the verification of the attribution of the analyzed painting. Moreover, stylistic analysis of "Madonna and Child" was carried out by an art historian, which further supported Knechtel's authorship of this painting. It belongs to a wide range of representations of the Madonna, originating from the Byzantine depiction of Our Lady Eleusa (Greek: showing mercy).

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# POSTER P12

## Investigation of techniques of gilding and tin-relief decoration in Bohemian panel paintings from the gothic period

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This paper deals with the results of the survey of painting techniques during the Late Gothic period on the Reliefs of the Fourteen Holy Helpers (ca. 1480, Inv. no.: P 3017 – P 3020) and the two wings of the Altarpiece from Kadaň – Birth of the Lord and Adoration of the Magi (ca. 1480, Inv. no.: O 7036 – O 7037), which are both stored in the National Gallery in Prague. The work is focused mainly on the technique of gilding and specific decorative technique of tin-relief (Pressbrokat), which are used in the reliefs, wings and ark itself and, thus, they have to be considered in the mutual context from the material and historical point of view. Hence, this work is a result of the interdisciplinary collaboration among the scientists and art historian.

In the course of the chemical-technological investigation of taken samples, polished sections were prepared on which an individual stratigraphy was observed. Then, the pigments present in the individual colour layers were examined by optical microscopy and by means of specific micro-chemical reactions. To confirm these investigations as well as to non-destructively differentiate a filler material of the relief decoration, a micro-Raman spectroscopy was used as an invaluable tool [1]; the spectra were measured on the individual pigment grains or on the polished sections using the mapping mode. In addition, elemental analysis using a Scanning Electron Microscopy coupled with an energy-dispersive detector and an X-ray Fluorescence were also performed in order to differentiate between both the individual pigments in colour layers and gilding. Finally, binding media were determined by means of a Gas Chromatography coupled with a Mass Spectroscopy.

From the obtained results, it was possible to compare the materials of decorative techniques on the reliefs, wings and ark itself as well as to differentiate between the original technique and later supplements. In addition, more fundamental workshop differences can be traced in the decorative tin-relief technique by considering its material base [2]: on the ark itself and reliefs, the filler material of the pressbrokats was the same (natural chalk), whereas on the wings (especially on the Virgin Mary coat), a red lead bottom layer was also found. Thus, this investigation helped to understand the use of historical techniques and factual details of the workshop practice in the course of the history.

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# POSTER P13

## Terahertz time-domain reflection spectroscopy for moisture tomography in gypsum

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Moisture and soluble salts are two of the major "enemies" of mural paintings, causing their gradual degradation [1]. High levels of moisture within depths of a few millimetres under the wall's surface can cause deterioration or detachment of the fresco painting due to diffusion and eventual evaporation from the surface. The efflorescence phenomenon is also driven by the moisture diffusion through the gypsum. Early detection and mapping of moisture layers under the wall surface is therefore essential in order to treat appropriately the problem in time.

Various methods [1–3] are currently used for moisture detection in walls, none of them though is a tomographic one, meaning that these techniques cannot locate the exact position of the moisture front inside a wall. On the other hand, terahertz time-domain reflection spectroscopy (THz-TDS) could be a natural fit for the in-depth moisture detection due to the unique properties of terahertz electromagnetic waves such as their non-invasive nature and their ability to penetrate through many materials, which are usually opaque in the other parts of the spectrum [4]. The fact that terahertz waves are strongly absorbed by water allows one to achieve high sensitivity detecting even small amounts of moisture, while the pulsed nature of our source enables the ability to acquire in-depth tomographic information.

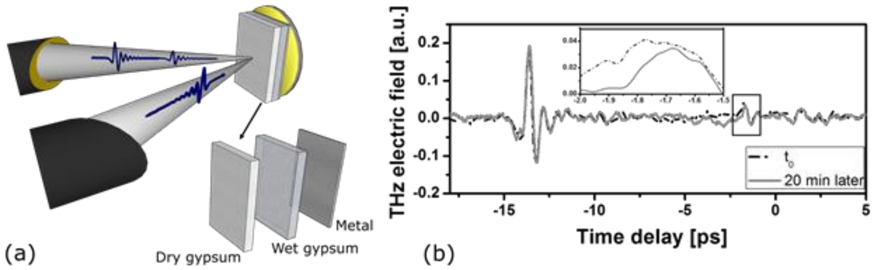


Figure 1: (a) Schematic representation of the studied structure. (b) The reflected THz electric fields.

Here we present our THz-TDS studies demonstrating the detection of the penetrant moisture front in gypsum samples. We observe that it is possible to identify the exact location of moisture in depth of a few millimetres, observing at the same time its temporal diffusion process. Our findings are also supported by theoretical simulations.

THz-TDS could, eventually be used as an early diagnostic technique allowing a targeted restoration procedure and contributing this way to an easier, faster and harmless treatment of mural paintings with high historic and artistic value.

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# POSTER P14

# Materials analyses of pyrotechnological objects from late bronze age Tiryns, Greece, by means of laser-induced breakdown spectroscopy: results and a critical assessment of the method

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Laser-Induced breakdown spectroscopy (LIBS) was employed in the investigation of pyrotechnological materials (metal and ceramic items, glass-based objects, plaster-based materials) from several Late Bronze Age workshop and activity area contexts at Tiryns, Greece. The use of portable instrumentation (LMNT-II+ spectrometer), which could be brought into the study place where all objects were housed, was crucial in order to establish the elemental content or verify the composition of almost all materials analysed. In addition, one important object, a bronze ingot exhibited in the Archaeological Museum of Nafplio, was analysed with the same instrumental set-up on location. In almost all cases, the LIBS analyses led to the preliminary identification of the materials investigated. In most cases, LIBS results sufficed to confirm earlier research carried out or was in agreement with similar analyses published in the literature. The analyses demonstrate that the micro-destructive LIBS technique provides useful preliminary elemental characterisation of most of the pyrotechnological materials while for some, additional work needs to be conducted to obtain conclusive results.. Furthermore, the portability and compactness of the instrumentation allow it to be employed in any workspace with a solid desk, light and electricity access. While the technique remains limited by spot analyses it does open up an immense array of possibilities for routine characterization or speedy screening of different types of artefacts in any storage or museum context. These important methodological and scientific findings are considered prerequisite steps leading towards and aiding in responsible sampling strategies for further analysis.

# POSTER P15

## Multispectral imaging to unveil the drawings and colours of a burnt Minoan wall painting showing a "Female figure in sanctuary/shrine"

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The "Female figure in sanctuary/shrine" is a unique Minoan wall painting which was revealed during excavations at the site of Haghia Triada, Crete, in the early 1900's. The wall painting depicts the lower part of a barefoot female (from the waist and down) and in particular her skirt bearing an exquisite decorative pattern. On the wall painting's background a shrine is illustrated and parts of flower decoration can be barely observed.

The site of Haghia Triada, possibly a royal villa, dated in the Middle Minoan (2200–1500 BC, by Evans) period was destroyed by an extended fire at the end of the Late Minoan IB (1500–1450 BC) period. Due to this incident the majority of the wall painting has been burned and the painted layers of the wall painting have been severely damaged.

The wall painting has been examined using non-destructive imaging techniques in order to determine the extent of damage and investigate the presence of draft-drawings and/or inscribed designs underneath the painting surface. Multispectral Imaging and post-processing of the recorded data using advanced software protocols have allowed the enhancement of drawings and motives hidden beneath the burnt layer, the identification of pigments and thus enabled archeologists, conservators and researchers to get further and important information on the historic era of this unique Minoan masterpiece.

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# Notes