# TECHNART 2025

International Conference on Analytical Techniques for Heritage Studies and Conservation Perugia,  $6^{\rm th}$  –  $9^{\rm th}$  May, 2025



# Book of Poster Abstracts



# SATCULT: CLOSING THE KNOWLEDGE GAP – VOCATIONAL TRAINING ABOUT EO SERVICES IN CULTURAL HERITAGE PRESERVATION

Nicodemo Abate,<sup>1</sup> Dante Abate,<sup>2</sup> Karin Drda-Kühn,<sup>3</sup> Nicola Masini<sup>1</sup>

<sup>1</sup>National Research Council, Institute of Heritage Science, Italy
<sup>2</sup> Eratosthenes Centre of Excellence, Cyprus
<sup>3</sup>Media k GmbH, Germany
nicodemo.abate@cnr.it

Earth observation data can make a fundamental contribution to the protection and conservation of cultural heritage (CH). However, the international scientific community working in the field of CH is still a long way from acquiring a real awareness of the possibilities and knowledge of how to use it, as those involved in the conservation of cultural heritage are not yet qualified to collect and analyse data and adopt preventive measures. This poster presents the potential of the Erasmus+ SATCULT project. SATCULT (Closing a knowledge gap by vocational training about satellitebased services in cultural heritage preservation) is a European project that began on 1 December 2024 and is being developed by a pool of partners from several countries: Germany (MediaK), Italy (National Research Council - Institute for Cultural Heritage Sciences), and Cyprus (Eratosthenes Centre of Excellence). The SATUCULT project aims to: (i) to investigate and record the conditions under which organisations for the protection of cultural heritage can acquire the necessary knowledge through professional training; and (ii) to provide an opportunity to make staff, networks and initiatives in cultural heritage conservation and their training providers aware of the immense potential of Earth Observation data and of the translation of data into concrete actions. In particular, SATCULT is working on: (i) identifying the qualification needs of employees of public and private institutions for the protection of cultural heritage through a Europe-wide survey; (ii) recording good examples of heritage conservation activities based on Earth observation data in a database; (iii) defining the learning content and skills needed to take advantage of the data; (iv) Communication of opportunities at a European level; (v) Creation of a pool of European experts from satellite geo-information services able to support institutions in the protection of cultural heritage.

# INTEGRATING X-RAY FLUORESCENCE AND X-RAY COMPUTED TOMOGRAPHY FOR COMPREHENSIVE ANALYSIS OF HISTORICAL CERAMICS FROM CRACOW DISTRICT

Romisaa Abdelrahman, 1,3 Sebastian Wroński, 1 Michał Wojenka, 2 Lucyna Samek 1\*

<sup>1</sup>AGH University of Krakow, Faculty of Physics and Applied Computer Science, Al. Mickiewicza 30, 30-059 Krakow, Poland

<sup>2</sup>Jagiellonian University, Archeological Institute, ul. Golębia 11, PL 31-007 Kraków, Poland <sup>3</sup>Future University in Egypt (FUE), Faculty of Engineering and Technology, 11835 Cairo, Egypt. Lucyna.Samek@fis.agh.edu.pl corresponding author

This study presents the application of non-destructive analytical techniques, particularly Xray Fluorescence (XRF) and X-ray Computed Tomography (XCT), to characterize archaeological pottery from medieval and early post-medieval periods. Five pottery samples from the Krakow district, Poland, were analyzed to explore their material composition, structural properties, and manufacturing techniques. The XRF analysis revealed detailed chemical compositions, highlighting significant variations in elemental concentrations that reflect diverse clay sources, tempering materials, and firing techniques. Ternary plots of oxide compositions, such as SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>-CaO and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-(Na<sub>2</sub>O+K<sub>2</sub>O), provided a visual representation of these variations, offering insights into the materials and methods used in pottery production during the studied periods. The XCT analysis provided high-resolution, three-dimensional images of internal structures, such as inclusions and voids, enabling further investigation into tempering and preparation methods. Segmentation and void analyses demonstrated variations in clay refinement, inclusion distribution, and porosity, indicating a range of manufacturing techniques from rudimentary to advanced practices. The integration of XRF and XCT results underscored the complementary strengths of these techniques despite their respective limitations, such as challenges in mineral differentiation in XCT and voxel resolution constraints. The findings emphasize the value of combining chemical and structural analyses to comprehensively understand archaeological ceramics. This study advances the methodological approaches for pottery analysis and offers broader implications for archaeological research and heritage conservation.

Acknowledgements: This research project was supported/partly supported by the program "Excellence initiative—research university" for the University of Science and Technology. The subsidy of the Ministry of Science and Higher Education, grant number 16.16.220.842 partially financed this study.

## MIXED IRON BASED INKS: INSIGHTS IN THE ROLE OF CARBON AND HOW IT CAN AFFECT THE INK DEGRADATION MECHANISM

<u>Miriam Alberico</u>,<sup>1,2</sup> Brunella Cipolletta,<sup>1</sup> Maria Francesca Sannino,<sup>3</sup> Manuela Rossi,<sup>4</sup> Gennaro Tortino,<sup>5</sup> Concetta Pironti,<sup>1</sup> Andrea Carpentieri,<sup>1</sup> Antonino Pollio,<sup>3,6</sup> Leila Birolo,<sup>1,6</sup> Alessandro Vergara<sup>1,6</sup>

<sup>1</sup>Dept. Chemical Sciences, University of Naples Federico II, Italy

<sup>2</sup>Dept. Of Classics, University La Sapienza, Italy

<sup>3</sup>Dept. Biology, University of Naples Federico II, Italy

<sup>4</sup>Dept. Earth Sciences, Environment and Resources, University of Naples Federico II, Italy

<sup>5</sup>Restoration Laboratory, Royal Palace of Caserta, Italy

<sup>6</sup>Task Force "Metodologie Analitiche per la Salvaguardia dei Beni Culturali", University of Naples Federico II

miriam.alberico@uniromal.it

The conservation and restoration of paper artifacts play a crucial role in safeguarding Cultural Heritage. A key area of interest is the characterization and study of ink composition to better understand their degradation mechanisms and develop appropriate restoration strategies.<sup>[1]</sup> The interest in the analysis of paper and ink heritage arose from the significant destructive effects observed in the use of inks on parchment and paper substrates, leading to severe corrosion problems resulting in the fragmentation of paper and the formation of holes or gaps. [2,3] Although mixed Carbon-iron-gall based ink have been mentioned in literature, [4,5] their degradation processes remain largely unexplored. Herein, results on both original and laboratory-prepared samples are presented. As relevant case study, the Royal Palace of Caserta stores Luigi Vanvitelli's correspondence, on which a combination of non-destructive (Optical microscopy, ATR-FTIR, Raman micro-spectroscopy) and micro-destructive (GC-MS) diagnostic methods were used to identify the ink as a carbon-iron-based ink, possibly mixed with iron-gall components. In degraded areas, the composition was highly variable in sulphates content and in its metallic counterpart, as well as in organic compounds. The microbiological analysis also revealed the presence of a fungal species, Aspergillus tubigensis. To elucidate the possible degradation mechanisms of mixed carbon iron-based inks, mockups containing combinations of iron sulphate, gallic acid, carbon, arabic gum and linseed oil were prepared. The different mockups will be applied on different supports as glass, paper, and parchment, and will be characterized from a chemical, microbiological and colorimetric point of view prior and after the artificial aging at controlled temperature and humidity.

**Acknowledgments:** This work was financially supported by the Project PE 0000020 CHANGES - CUP [B53C22003780006], PNRR Missione 4 Componente 2 Investimento 1.3—Next Generation EU.

<sup>[1]</sup> S. Caterino, N. Pajer, C. Crestini, Microchemical Journal 2023, 185, 108258.

<sup>[2]</sup> M. J. Melo, V. Otero, P. Nabais, N. Teixeira, F. Pina, C. Casanova, S. Fragoso, S. O. Sequeira, *Heritage Science* **2022**, *10*, 145.

<sup>[3]</sup> H. G. M. Edwards, P. Vandenabeele, P. Colomban, *Raman Spectroscopy in Cultural Heritage Preservation* **2023**, Springer International Publishing, Cham, 215–231.

<sup>[4]</sup> M. Bicchieri, M. Monti, G. Piantanida A. Sodo, Raman Spectroscopy 2008, 39, 1074–1078.

<sup>[5]</sup> M. Aceto, A. Agostino, E. Boccaleri, A. C. Garlanda, X-Ray Spectrometry 2008, 37, 286–292.

# MULTIMODAL ANALYSIS OF CÂNDIDO PORTINARI'S PAINT TUBES AND "SÃO JORGE" MURAL PAINTING

## <u>Itiara Mayra B. Albuquerque</u>,<sup>1</sup> Marcia A. Rizzutto,<sup>1</sup> Jessica F. Curado,<sup>1,2</sup> Eva K. Mori,<sup>1</sup> Pedro De Campos<sup>1,3</sup>

<sup>1</sup>Institute of Physics, University of São Paulo (USP), Brazil

<sup>2</sup>University Center FEI, Brazil

<sup>3</sup>Faculty of Design Sciences, University of Antwerp, Belgium

itiara.albuquerque@usp.br

Cândido Portinari (1902–1962) was one of the most important Brazilian modernist artists, achieving both national and international recognition. He was the creator of the War and Peace panels, installed at the United Nations headquarters in New York. [1] Throughout your life, Portinari, maintained a deep connection with his hometown, Brodowski (SP, Brazil), where he did more than just visit his family home—he turned its walls into his canvases. In this space, he produced several works, including religious-themed murals such as *São Jorge*, the focus of this study. Now a museum, the *Museu Casa de Portinari* preserves not only his murals but also materials used by him, including paint tubes. [2,3] Thus, this study aims to characterize the materials and techniques used by Portinari through spectroscopic and computational analyses applied to the *São Jorge* mural and the paint tubes from the museum's collection.

A series of in situ analyses at the Museu Casa de Portinari was conducted. Including X-ray Fluorescence (XRF) and Raman spectroscopy to identify pigments in the mural and paint tubes collections. Also, various imaging techniques such as visible light photography, ultravioletvisible induced fluorescence and infrared reflectography were applied. As part of the computational approach, the alignment of visible and infrared images will be performed using the Structural Similarity Index (SSIM), followed by the creation of false-colour images. These approaches will support the interpretation of material distribution in the artwork.

Therefore, this study aims to identify the materials present in the São Jorge mural and the paint tubes collection, assessing potential correspondences between the pigments used in the artwork and those found in Portinari's paint tubes. Additionally, computational methods will be applied to refine the selection of spectroscopic analysis points, enhancing both the efficiency and accuracy of material identification. By combining these approaches, this research contributes not only to the study of the artist's creative process and materials, but also to the development of

only to the study of the artist's creative process and materials, but also to the development of methodologies for cultural heritage conservation.

Acknowledgements: Thanks to Museu Casa de Portinari for the partnership. MAR thanks FAPESP (2017/07366-1) and CNPq (302823/2021-2), IMBA CAPES (88882.461730/2019-01) for financial support.

<sup>[1]</sup> J. C. Portinari, SciELO Brasil "Projeto Portinari. Estudos avançados" 2000, 14, 369-400.

<sup>[2]</sup> MUSEU CASA DE PORTINARI, A casa de Portinari, Brodowski: Museu Casa de Portinari, 2022. Disponível em: https://www.museucasadeportinari.org.br/wp-content/uploads/2022/03/a-casa-de-portinari-web.pdf. Access: 08 Aug. 2024.

<sup>[3]</sup>P. Tirapeli, Capela da Nonna: livro digital 2023.

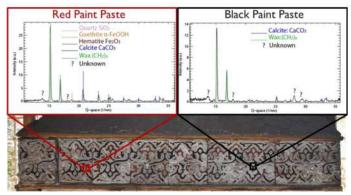
<sup>&</sup>lt;a href="https://www.museucasadeportinari.org.br/wpcontent/uploads/2023/04/livro-capela-da-nonna-digital-4-4-2023-compacto2">https://www.museucasadeportinari.org.br/wpcontent/uploads/2023/04/livro-capela-da-nonna-digital-4-4-2023-compacto2</a>.

# INLAYING PAINT PASTES IN ISLAMIC ARCHITECTURAL BUILDINGS: AN ATTEMPT TO UNRAVEL THIS TECHNIQUE

### Ehab Al-Emam, 1,2,3 Amr Osman, 1 Victoria Beltran, 2,4 Ermanno Avranovich Clerici, 2 Koen Janssens 2,3

<sup>1</sup>Conservation Department, Faculty of Archaeology, Sohag University, 82524, Sohag, Egypt <sup>2</sup>AXIS Research Group, University of Antwerp, Groenenborgerlaan 171, 2020, Antwerp, Belgium <sup>3</sup>ARCHES Research Group, University of Antwerp, Mutsaardstraat 31, B-2000, Antwerp, Belgium <sup>4</sup> Royal Museum for Central Africa, Leuvensesteenweg 7, 3080, Tervuren, Belgium ehab.alemam@uantwerpen.be

Islamic buildings are well known for their intricate decorations that were realized using a variety of techniques and materials. The inlaying technique is a commonly applied decorative process, normally used to execute vegetal motifs and geometric designs in addition to inscriptions. Several approaches are described, to execute this technique; one of these involves filling engravings in stone with inlaying-colored pastes. This inlaying paste technique was prominently employed in the buildings of the *Mamluk Sultanate* in Egypt (1250-1517 AD) where it can be found in many exterior and interior architectural elements.<sup>[1]</sup>



**Figure 1**: XRPD patterns of red and black paint pastes used in inlaying vegetal motifs on marble tiles - the mosque of Prince Qanibay Al-Rammah

In literature, there is no information available (yet) that explains how the craftsmen of this period prepared their colored pastes. To our knowledge, only one study characterized black and red paint pastes that were used in decorating a 15<sup>th</sup> century building in Cairo.<sup>[2]</sup> The aim of this study is to fill the existing gap and gain deeper insight into their preparation procedure thanks to the exact characterization of the inlaying paint pastes collected from two different *Mamluk* buildings, namely, the mosque of *Prince Qanibay Al-Rammah* (1506 AD) and the mausoleum of *Prince Tarabay al-Sharifi* (1504 AD), both in Cairo, Egypt.

Since these paint pastes are mainly composed of (inorganic) pigments and organic binders, this study will focus on relevant analyses to identify these components along with the precise estimation of the relative proportions that allowed the artists to form a workable paste for inlay with them. To this end, several analytical methods were employed such as XRPD, SEM-EDS, XRF, ATR-FTIR and optical microscopy. Additionally, gravimetric analyses were used to collect qualitative and quantitative data on the proportions of the solid particles and the organic component(s). Preliminary investigations showed that the red paint paste is characterized by red ochre while the black paste is a carbon-black based pigment (Fig. 1). The main organic component of both pastes was identified as wax with a possible presence of traces of oil probably used to increase the workability of the paste.

<sup>[1]</sup> A. M. Ali, "Coloured inscriptions on religious buildings in Cairo during the Circassian Mamluk era (784-923 AH / 1382-1517 AD): A visual archaeological study" **2024**, PhD thesis - Faculty of Archaeology - Sohag University.

<sup>[2]</sup> A. M. Bakr, T. Kawiak, M. Pawlikowski and Z. Sawlowicz, Journal of Cultural Heritage 2005, 6 (4), 351-356.

# SMART\*LIGHT FOR HERITAGE SCIENCE: A NEW INVERSE COMPTON X-RAY SOURCE FROM THE NETHERLANDS

### <u>Matthias Alfeld</u>, Gesa Welker, Luís Manuel de Almeida Nieto, Joris Dik, Peter Mutsaers, Jom Luiten

<sup>1</sup>Department of Materials Science and Engineering, ME, Delft University of Technology, the Netherlands <sup>2</sup>Department of Applied Physics and Science Education, Eindhoven University of Technology, the Netherlands m.alfeld@tudelft.nl

X-rays allow for non-invasive and non-destructive analysis, making them ideal for examining cultural heritage objects that must be preserved for future generations. Advanced X-ray techniques like X-Ray Absorption Near Edge Structure (XANES) and X-Ray Diffraction (XRD) provide insights into local chemical environments. When combined with micrometer-focused X-rays, these methods can reveal detailed data about material composition and chemical degradation on a microscopic level. However, these powerful techniques require tuneable, high-intensity, monochromatic X-rays, which are only available at synchrotron sources. Consequently, these techniques can only be applied after a lengthy administrative process and the transport of sample or object over several hundred kilometers.

Inverse Compton Sources (ICS) address this limitation by scattering visible or IR photons off a relativistic electron beam to produce X-rays through the inverse Compton effect, resulting in coherent, tuneable "pink" X-radiation. Smart\*Light, a compact ICS developed at TU Eindhoven, achieved its first X-ray generation in mid-2024. Here, we describe Smart\*Light's cultural heritage and beam characterization endstation, present initial results from beam characterization, and discuss the transformative potential of ICS sources for analysing heritage artifacts from art and archaeology.

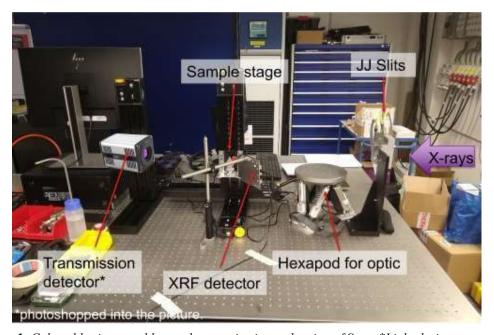


Figure 1: Cultural heritage and beam characterization endstation of Smart\*Light during a stage test.

#### CLASSIFICATION OF EGYPTIAN FUNERARY NETS FROM MA-XRF

Rosario Andolina,<sup>1</sup> Zdenek Preisler,<sup>1</sup> Claudia Caliri,<sup>1</sup> Enrico Ferraris,<sup>2</sup> Costanza Miliani,<sup>1</sup> Eva Luna Ravan,<sup>1</sup> Paolo Marco Riela,<sup>1</sup> Martina Terzoli,<sup>2</sup> Valentina Turina,<sup>2</sup> Francesco Paolo Romano<sup>1</sup>

<sup>1</sup>Istituto di Scienze del Patrimonio Culturale, CNR, Catania, Italy <sup>2</sup>Museo Egizio, Torino, Italy rosario.andolina@cnr.it

Egyptian funerary nets, composed of tubes and beads, were decorative and symbolic elements used in ancient Egypt to adorn the deceased during funerary rituals. Primarily made of faience, a glazed ceramic material often blue or green in colour, these nets could also include other materials such as semi-precious stones, glass, or metals. To classify and study these ancient artifacts effectively, a multidisciplinary approach is essential, bringing together morphological, technological, chemical, and archaeological perspectives. Our study employs modern machine learning approaches to elemental characterization from Macro X-ray fluorescence spectroscopy (MAXRF). Clustering analysis represents a powerful method for identifying compositional patterns in complex samples, such as Egyptian faience. However, its reliability depends on our ability to distinguish intrinsic variations in composition from external factors, such as measurement geometry. The measured intensity of spectral lines depends on the measurement distance due to changes in the solid angle and air attenuation, causing differences in intensity even for identical compositions at different distances. In the absence of correction, this can lead to misclassification of clusters reflecting geometric variations rather than genuine elemental differences, compromising data interpretation. To address this challenge, we extended our previously developed AI methodology for XRF analysis to also predict sample-source distances.<sup>[1]</sup>

This in turn allows us to construct a robust correction making the obtained results independent on the measurement geometry. Using the AI predicted distance, we apply a theoretical correction based on air attenuation and solid angle distance dependence. This novel approach is therefore applied to the analysis of the Egyptian funerary net from Muzeo Egizio showing improved clustering analysis. The results demonstrate the critical role of distance correction in ensuring reliable clustering, highlighting its importance for the accurate interpretation of complex 3D samples in XRF analysis.

Acknowledgements: PNRR projects: 1) H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029, CUP B63C22000730005; 2) CHANGES, "Science and Technologies for Sustainable Diagnostics of Cultural Heritage", PE0000020, CUP B53C22003890006. E-RIHS European Infrastructure of Heritage Science (ERIHS)

<sup>[1]</sup> Z. Preisler, R. Andolina, A. Busacca, C. Caliri, C. Miliani, F. P. Romano, Science Advances "Deep learning for enhanced spectral analysis of MA-XRF datasets of paintings" **2024**, 10(39), 13.

## READING THE UNREADABLE: USING XRF AND NIR REFLECTOGRAPHY TO ACCESS THE HERCULANEUM LIBRARY

#### Lorenzo Angiolini, 1 Rebecca Davenport, 1 Ariadne Marketou, 1,2 Ira Rabin 1

<sup>1</sup>Bundesanstalt für Materialforschung und -prüfung (BAM), Germany
<sup>2</sup>MF Norwegian School of Theology, Religion, and Society; University of Oslo, Norway

<u>lorenzo.angiolini@bam.de</u>

The collection of nearly 1000 carbonized papyrus rolls from Herculaneum, preserved at the Officina dei Papiri in Naples, represents the most substantial find of manuscripts from the Roman period from the 3<sup>rd</sup> century BCE to the 1<sup>st</sup> century CE in Western Europe and the most significant collection of Epicurean philosophy retrieved so far. Their analysis can bring an invaluable contribution to the historical and cultural understanding of ancient Greek and Roman societies. The eruption of Vesuvius in 79 CE contributed to the preservation of the Herculaneum papyri whilst making it impossible to open them without causing irreparable damage. Several non-invasive techniques have been used to access the text in the carbonized papyri without opening them, with very limited success thus far. X-ray-based computed tomography (CT) has been used to "virtually unroll" an entire charred, physically inaccessible Dead Sea Scroll from En-Gedi.<sup>[1]</sup> It is reported that the presence of metals in the ink of this scroll makes it denser than the support, improving the signal-to-noise ratio of the CT scan and greatly enhancing the readability of the text. Studies on fragments of the Herculaneum papyri, similarly to the inks of the Dead Sea Scrolls from the same period, revealed the presence of metal-based inks.<sup>[2]</sup> These findings suggest that metal-based inks were already in use at the time, and that a few of the carbonised Herculaneum papyri may have been written using metal-based inks. XRF analysis combined with NIR reflectography can offer a fast and simple method to screen the Herculaneum collection for papyri containing metal-based inks to build a database of items suitable for CT virtual unrolling. In this work, we present a case study of 3<sup>rd</sup> - 4<sup>th</sup> century CE Hermopolis papyri, demonstrating this methodological approach to the analysis and characterization of metals in inks by means of XRF and NIR imaging, in preparation for our study of the unopened Herculaneum papyri.

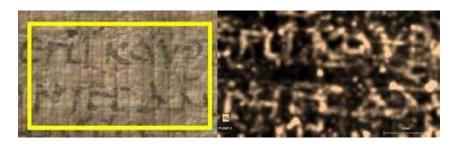


Figure 1: XRF scanned area (left) of a portion of P. Berol. 13267 and the corresponding Fe distribution (right).

Acknowledgements: Sophie Breternitz, Marius Gerhardt and Reinhard Franke

<sup>[1]</sup> W. B. Seales, Sci. Adv. 2016, 2, 1-9.

<sup>[2]</sup> I. Rabin, "Inchiostri nell'antichità" TRACING THE SAME PATH - Tradizione e innovazione nella papirologia ercolanese tra Germania e Italia 2021, Marzia D'Angelo et al. (Ed.), 175-180.

# THE PICTORIAL TECHNIQUE IN CERUTI'S PAINTINGS: A HOLISTIC INTERDISCIPLINARY STUDY BASED ON MULTI-BAND IMAGING DIAGNOSTICS AND WRITTEN SOURCES REVIEW

Nicole de Manincor,<sup>1</sup> <u>Paola Artoni</u>,<sup>2</sup> Lorenzo Mascheretti, <sup>2</sup> Claudia Daffara,<sup>1</sup> Monica Molteni<sup>2</sup>

<sup>1</sup>Computer Science Department, University of Verona, Italy <sup>2</sup>Cultures and Civilizations Department, University of Verona, Italy nicole.demanincor@univr.it

Giacomo Ceruti (1698-1767) enjoyed a considerable success as a painter of genre compositions and as a portraitist. So far, his production has been studied mainly from a traditional art historical perspective and the investigation of his painting technique has been limited to specific instances .<sup>[1]</sup> In the framework of the 'CINABRO' project, <sup>[2]</sup> the LANIAC Centre and the OpDATeCH Lab of the University of Verona performed a systematic diagnostic campaign of Ceruti's *corpus* of paintings with a holistic and interdisciplinary approach, integrating noninvasive diagnostics and art historical methodology (iconographic analysis, general literature review, research into conservation reports and other written sources). Twenty-four paintings by Ceruti, realised over his whole artistic career, were analysed. They were displayed within the monographic exhibition *Miseria e nobiltà*. *Giacomo Ceruti nell'Europa del Settecento* (Brescia, 2023).<sup>[3]</sup>

The diagnostic protocol was designed as a full-field survey with multimodal and multi-band imaging in the VIS-IR spectral ranges, using a CCD camera (up to 1 micron), and an InGaAs scanning camera (up to 1.7 micron). IR False Color mapping was also obtained from the image data and is discussed here, while punctual spectrometry was left to target specific questions concerning the use of blue pigments. The VIS-IR imaging dataset was combined into a web app for better visualization and comparison.<sup>[4]</sup>

Analyses provided significant new information on the supports, Ceruti's *modus operandi* (his sequence of gestures, the way he applied the paint, his habit of wiping the brush on the canvas, the use of cost-saving solutions, such as leaving the ground layer visible *a risparmio*), and changes and *pentimenti* halfway through the process. They also offered insights into the conservation and restoration treatments, which were undisclosed in previous documents. The integration of scientific data with archival, iconographic and art-historical research has allowed to verify the correlation between Ceruti's artistic procedure and the painting norm of his time as outlined in written sources and technical literature, and also notice his more norm-adjacent choices, such as the immediate embracing of Prussian blue before it was commonly employed.

<sup>[1]</sup> F. Nezosi, F. Piazza (edited by), "Ceruti a Gandino" 2023, Scalpendi, Milano, 62-73.

<sup>[2]</sup> CINABRO, "Campaigns of Invasive and Non-invasive Analysis and restoration studies in BRescia On seventeenth century paintings - Joint Projects 2019 - CUP B39C19000100008 – project funded by the University of Verona in partnership with Fondazione Brescia Musei", P. I. Prof.ssa Monica Molteni.

<sup>[3]</sup> R. D'Adda, F. Frangi e A. Morandotti (edited by), "Miseria e nobiltà. Giacomo Ceruti nell'Europa del Settecento" **2023**, Skira, Milano.

<sup>[4]</sup> N. de Manincor et al., "The role of infrared imaging to support art historical interpretation of Giacomo Ceruti's paintings" (print in progress in MetroArcheo2024 proceedings).

# ANALYSIS OF CRACKING OF HISTORICAL GLASS WITH THE ACOUSTIC EMISSION TECHNIQUE

#### Nefeli Avgerou, Łukasz Bratasz, Marcin Strojecki, Sonia Bujok

Jerzy Haber Institute of Catalysis and Surface Chemistry, Poland <a href="mailto:nefeli.avgerou@ikifp.edu.pl">nefeli.avgerou@ikifp.edu.pl</a>

This research examines the phenomenon of crizzling which manifests as the formation of a hydrated layer on the glass surface, and it evolves into a network of microcracks that lead to complete disintegration over time. Aligned with the GoGreen project, the study aims to improve the understanding of glass corrosion processes, particularly focusing on fluctuating relative humidity (RH) levels in accelerating damage.

Current conservation guidelines suggest limiting RH fluctuations to a narrow range of 46-48% to mitigate deterioration. [1] However, these recommendations are based primarily on chemical processes, leaving a significant gap in understanding the physical mechanisms that contribute to damage. This study seeks to bridge that gap by systematically monitoring microcrack development with the Acoustic Emission technique in different replicas of historical glasses exposed to controlled RH variations. Complimentary, measurements of sorption/desorption with the use of the microbalance and observation of the samples surfaces with the HIROX microscope have taken place. Finally, SEM and FTIR analyses are employed to determine the chemical composition of the hydrated layer and to assess whether water is chemisorbed or physisorbed on its surface.

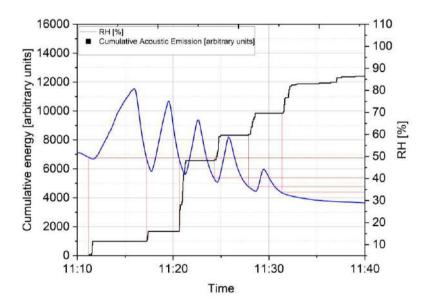


Figure 1: Cumulative AE energy of hydrated layer microcracking in relation with RH%

<sup>[1]</sup> S.P. Koob, N.A. R. Van Giffen, J. J. Kunicki-Goldfinger, R. H. Brill, Studies in Conservation 2018, 63, 146-150.

# FRANCSISZKA THEMERSON'S WHITE PAINTINGS: A CASE STUDY FOR UNDERSTANDING SURFACE PHENOMENA IN MODERN PAINTINGS

#### Donatella Banti<sup>1</sup> and Aviva Burnstock<sup>1</sup>

<sup>1</sup>Courtauld Institute of Art, United Kingdom donatella.banti@courtauld.ac.uk

White paintings have been made by many artists since the beginning of the 20<sup>th</sup> century.<sup>[1]</sup> Franciszka Themerson<sup>[2]</sup> was born in Warsaw in 1907 and arrived in London in 1940. Her paintings from the late 1950s include a predominantly white palette with locally applied monochrome or coloured glazes. This poster focuses on the characterization of the materials used for selected paintings that provides evidence for causes of surface degradation phenomena in some of her paintings, such as powdering and yellowing paint and deep cracks. A characteristic example of some of these issues is provided by *Mother and Child*, painted in 1962, that presents an overall cracking that dominates the composition.



Figure 1: Composite image: a-c. Themerson white paintings from the period 1959-1965; d. Franciszka Themerson in her studio in the 1960s; e. Mother and child, 1962; f.-i. some of the analytical results

A multi-analytical approach was applied to characterize the painting materials including MAXRF,  $\mu\text{-Raman}$  and  $\mu\text{-FTIR}$  imaging. Results so far show that the white pigments include the anatase polymorph of titanium dioxide  $^{[3]}$  and that the cracking may be the result of the relationship between a slow drying medium-rich white underlayer and a dilute application of fast drying superficial paint that has contracted. Further investigation via chromatographic techniques will aim at identifying the specific oil binder. The production of reconstructions to replicate the cracks will also allow us to estimate a time frame for their formation. This will inform a view of the artist's intention and also of how conservators may present Themerson's white paintings and also works made using the same artists' materials that have undergone similar deterioration.

<sup>[1]</sup> T. Barson, "Painting with White", Available at: <a href="https://www.tate.org.uk/visit/tate-modern/display/in-thestudio/painting-white">https://www.tate.org.uk/visit/tate-modern/display/in-thestudio/painting-white</a>

<sup>[2]</sup> N. Wadley, Franciszka Themerson 2019, Ed. Themerson Estate.

<sup>[3]</sup> B. van Driel, "Titanium white – Friend or Foe? Understanding and predicting photocatalytic degradation of modern oil paintings" **2018**, PhD Dissertation (TU Delft), Delft University of Technology.

# CHANGES PROJECT: DISCRETE WAVELET TRANSFORM TO REDUCE SURFACE SCATTERING IN GPR SECTIONS

#### Dora Francesca Barbolla, Lara De Giorgi, Giovanni Leucci 1

<sup>1</sup>Institute of Heritage Science - CNR, Lecce, Italy dorafrancesca.barbolla@cnr.it

Ground-penetrating radar (GPR) is often a fundamental tool for cultural heritage preservation. However, under some conditions, coherent noise can occur in the radargram interfering with the useful signal. Reflections from above-surface objects, such as walls or vaults, and buildings, could be recorded in the radar sections and could hide subsurface reflections linked to the structures of interest. The problem of surface scattering can be addressed by using the Discrete Wavelet Transform analysis which decomposes the signal allowing the recognition of different anomalies coming from different targets.

# CARBON ISOTOPES TO CHARACTERIZE LEAD WHITE GROUND LAYERS OF THE 20TH CENTURY. APPLICATION TO THE PIERRE SOULAGES' PAINTINGS

# <u>Lucile Beck</u>, <sup>1</sup> Pauline Hélou-de La Grandière, <sup>2,3</sup> Chloë Coustet, <sup>4</sup> Ingrid Caffy, <sup>1</sup> Mathieu Thoury <sup>4</sup>

<sup>1</sup>Laboratoire de mesure du carbone 14 (LMC14)/LSCE, Université Paris-Saclay, Gif-sur-Yvette, France

<sup>2</sup>Atelier La Grandière, conservation-restauration de peintures, Nîmes, France

<sup>3</sup>CY Cergy Paris Université, Cergy-Pontoise, France France

<sup>4</sup>CNRS/IPANEMA, Saint-Aubin, France

lucile.beck@cea.fr

Lead white paint was one of the most widely used materials for canvas grounds due to its fast drying ability and strong stability.<sup>[1]</sup> Lead white had also unfortunately two major defaults, its toxicity and its slow manufacturing process.<sup>[2]</sup> For these reasons and up to its definitive banishment in the mid-20th century, industrial methods to produce lead white were frequently modernized leading to various subtypes,<sup>[3]</sup> traditionally studied by X-ray powder diffraction and scanning electron microscopy.<sup>[4,5]</sup> Recent studies <sup>[6,7]</sup> have shown that lead white also carries a <sup>14</sup>C and <sup>13</sup>C isotopic signature that reflects, to the nearest isotopic fractionation, the nature of the reactants used to synthesize the pigment. It is thus possible to trace the lead white production method by measuring carbon isotopes by Accelerator Mass Spectrometry (AMS).<sup>[8]</sup>

This work focuses on <sup>14</sup>C and <sup>13</sup>C AMS measurements of lead white paint ground layers of paintings by Pierre Soulages (1919-2022). It is part of an extensive research project carried out by the painting conservator specialist of the artist, <sup>[9,10]</sup> providing the opportunity for a campaign of chemical analysis of a large corpus of pre-primed canvas. 18 samples were collected from taking margin of paintings produced between 1958 and 1986. <sup>14</sup>C content of linen, and <sup>14</sup>C and <sup>13</sup>C contents of pigment and the oil binder were determined. The results shed light on two main aspects. First, it is possible to compare the date of canvas production given by <sup>14</sup>C dating with the date of completion given by the artist. <sup>[11]</sup> Secondly, by combining the carbon isotope contents of individual component (canvas, oil and pigment), batches of pre-primed canvases were identified. Such a study offers new perspectives on the lead white production after the Second World War and on the practices and interactions of artists and their material suppliers.

Acknowledgements: we acknowledge the LMC14 staff for sample preparation and radiocarbon measurements.

<sup>[1]</sup> A. Stewart, "Official Digest. Federation of Paint and Varnish Production Clubs" **1950**; R. J. Gettens and G. L. Stout, "Painting Materials, A short Encylopaedia" **1966**, 288, Dover Publication, New-York; M. Witlox, L. Carlyle, "ICOM Committee for Conservation 14th Triennial Meeting The Hague 12-16 September 2005" **2005**, 1, 519-528.

<sup>[2]</sup> L. Lestel, Techniques & Culture 2002, 38.

<sup>[3]</sup> I. Bijker, N. Deleu, Y. Darcis, et al., Dyes and Pigments 2025, 235, 1-17.

<sup>[4]</sup> V. Gonzalez, G. Wallez, T. Calligaro, et al., Analytical Chemistry 2017, 89, 13203-13211.

<sup>[5]</sup> C. Coustet, P. Hélou-de La Grandière, I. Bonaduce, et al., in prep.

<sup>[6]</sup> C. Messager, L. Beck, D. Blamart, et al., Journal of Archaeological Science: Reports 2022, 46, 1-10.

<sup>[7]</sup> I. Bijker et al., submitted to this conference.

<sup>[8]</sup> L. Beck et al., Radiocarbon 2024, 66, 1041-1053.

<sup>[9]</sup> P. Hélou-de La Grandière, "Metal Soaps in Art's Book" 2019, Springer Ed., 393-412.

<sup>[10]</sup> P. Hélou-de La Grandière et al., Recherche et Restauration: histoires, pratiques et perspective 2023, 113-128.

<sup>[11]</sup> L. Beck et al., accepted to Radiocarbon 2025.

## GLAZE CERAMIC INTRODUCTION AND CONSUMPTION IN THE GARB AL-ANDALUS

#### Massimo Beltrame, <sup>1</sup> Elena Salinas, <sup>3</sup> Susana Gòmez Martínez, <sup>2</sup> José Mirão <sup>1</sup>

<sup>1</sup>Hercules Laboratory, University of Evora, Portugal <sup>2</sup>CEAACP, University of Coimbra, Portugal <sup>3</sup>School of Arabic Studies, CSIC, Spain massimo@uevora.pt

GC-CIGA<sup>[1]</sup> is new research project recently granted by the Portuguese Science and Technology Foundation to the University of Évora (Portugal) in collaboration with the School of Arabic Studies (CSIC-Spain). The main goal of the project is to explore the diffusion of glaze technology in the western al-Andalus, the Garb al-Andalus, and to understand how Islamic social-cultural expansion, Islamic culture assimilation, people mobility, social inequalities, exchange of know-how, political propaganda, trades expansion, and raw material acceess and exploitation might have influenced this process.

In this framework, the application of a multidisciplinary approach to the study of Islamic glazed ceramics combining different disciplines (i.e. archaeology, history, archaeometry and ore geology) will permit the acquisition of a complete dataset to decipher different historical dynamics.

To this extent, starting from the production and diffusion of first glazed ceramic exemplars, it will be important to understand and evaluate the dissemination patterns between the heartland and the periphery, the social reasons behind the adoption of glaze ceramics, the diffusion of know-how in the following centuries, the multiplication of ceramic workshops, and the possible differentiation in raw materials procurement for glaze production in the periphery of the alAndalus if compared to the heartland of Islamic Iberia (i.e. Southern al-Andalus – Cordoba). These data will be used to evaluate the diffusion of Islamic glazed ceramics in the Garb alAndalus with a chronological, geographical, technological, and socio-cultural perspective.

The project hope to offer a new perspective of Medieval Iberia between the 9th to 13th century AD, tightly connected to the production, consumption, and promotion of glazed ceramics. The methodology employed will be innovative and it will include pXRF, OM, SEM-EDS, SEM-CL, lead isotopes and trace elements by LA-ICP-MS.

Acknowledgements: The research team wish to acknowledge the Portuguese Science and Technology Foundation (FCT) for the grant with number 2023.13937.PEX, https://doi.org/10.54499/2023.13937.PEX. The research team wish also to acknowledge the FCT for funding the Hercules Laboratory (UIDB/04449/2020 – UIPD/04449/2020).

<sup>[1]</sup> GC-CIGA, "Introdução e consumo de cerâmica vidrada no Garb al-Andalus", DOI https://doi.org/10.54499/2023.13937.PEX.

## A NOVEL APPROACH TO THIN SECTION PREPARATION FOR FTIR ANALYSIS OF WALL PAINTINGS

### <u>Victoria Beltran</u>,<sup>1,2</sup> Andrea Marchetti,<sup>1,3,4</sup> Ehab Al-Emam,<sup>1</sup> Mathilde Occelli,<sup>3</sup> Gihan Kamel,<sup>5,6</sup> Koen Janssens<sup>1,3</sup>

<sup>1</sup>AXIS Research Group, University of Antwerp, Belgium

<sup>2</sup>Royal Museum for Central Africa, Belgium

<sup>3</sup>ARCHES Research Group, University of Antwerp, Belgium

<sup>4</sup>European Decorative Arts Department, Royal Museums of Art and History, Belgium

<sup>5</sup>SESAME (Synchrotron-light for Experimental Science and Applications in the Middle East), Jordan

<sup>6</sup>Department of Physics, Helwan University, Egypt

victoria.beltran@uantwerpen.be

Thin sectioning is a common sample preparation method for multilayered materials, as it allows a clear observation of their stratigraphy. Additionally, it enables analysis by techniques that require thin samples, such as FTIR spectroscopy in transmission mode. This analysis mode produces the best possible-quality spectra (high strong signal-to-noise ratio, a straight baseline, and minimal spectral artifacts), compared to other FTIR modes like ATR or reflection.

However, preparing thin sections can be particularly challenging for fragile and porous materials. One notable example is wall paintings. Indeed, their porous and fragile nature hinders their analysis by FTIR in transmission mode, posing significant limitations on the detection of the organic materials used in their production and/or restoration. Wall painting fragments are particularly challenging to prepare in thin section because: 1) when embedded, the embedding medium can easily infiltrate, altering the obtained FTIR spectra; 2) unembedded fragments lack structural integrity, making them too brittle to section without crumbling.<sup>[1]</sup>

This study presents an innovative sample preparation method for obtaining complete thin sections from wall paintings. The method employs various consolidants that do not interfere with the FTIR spectra, allowing an accurate analysis using this technique. The results are compared with traditional approaches, [2] highlighting the strengths and limitations of each method.

**Acknowledgements:** The authors acknowledge the financial support of Belspo (funded project: Prf- $2021007\_EPITOX\#2$ ) and the funding received to perform the  $\mu$ SR-FTIR experiments at SESAME synchrotron (beamtime proposal 20230077).

<sup>[1]</sup> V. Beltran, N. Salvadó, S. Butí, G. Cinque, K. Wehbe & T. Pradell, *Analytical chemistry "Optimal sample preparation for the analysis of micrometric heterogeneous samples"* **2015**, 87(13), 6500-6504.

<sup>[2]</sup> E. Pouyet, A. Lluveras-Tenorio, A. Nevin, D. Saviello, F. Sette, & M. Cotte, *Analytica chimica acta "Preparation of thin sections of painting fragments: classical and innovative strategies"* **2014**, 822, 51-59.

# INTERPRETING THE MOLECULAR COMPLEXITY OF THE BASIC SYNTHETIC ORGANIC DYES PRESENT IN HISTORICAL PMTA PIGMENTS SAMPLES EXPLORED USING HPLC-PDA-HRMS

#### S. V. J. Berbers, 1,2 R. Pause, 1 I. D. van der Werf, 1 K. J. van den Berg, 1,3 M. R. van Bommel<sup>2,3</sup>

<sup>1</sup>Cultural Heritage Laboratory, Cultural Heritage Agency of the Netherlands, The Netherlands
<sup>2</sup>Analytical Chemistry Group, van 't Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands

<sup>3</sup>Conservation and Restoration of Cultural Heritage, Amsterdam School for Heritage, Memory and Material Culture, University of Amsterdam, The Netherlands

s.berbers@cultureelerfgoed.nl

PTMA pigments form a unique category of basic synthetic organic dyes precipitated with the heteropoly acids phosphotungstic acid (PTA) and phosphomolybdic acid (PMA). The first PTMA pigments were produced under the brand name Fanal® pigments by I.G. Farben between 1924 and 1932 as a novel way to precipitate basic synthetic dyes. PTMA pigments are still used today for a variety of printing and paint applications. This study employs high-resolution HPLCPDA-HRMS to analyse a set of 31 PTMA pigments, delving deep into the molecular makeup of these historical materials to understand their origins and stability.

Through our analysis, we discovered an intricate molecular compositions in each pigment—with mixtures of up to more than twenty synthetic organic dyes (SODs) and SOD precursors per sample. Using the HPLC-PDA-HRMS and MS/MS data, we mapped out the structures of these SODs, gaining critical insights into their potential roles within the pigment mixtures. This diversity suggests that these pigments were not merely single-color entities but rather complex chemical systems, perhaps optimized for stability, colour depth, or both. Our findings raise intriguing questions about these pigments that could reshape our understanding of early 20thcentury synthetic pigment and dye production: Were these diverse mixtures intentionally created to enhance pigment properties, or are they artifacts of degradation over time? Alternatively, might they represent byproducts of the synthesis or impure starting materials, with batch differences and changing synthesis procedures? By exploring these questions, our work contributes valuable molecular data that enhance not only our understanding of these historical PTMA pigments, but also our approach to interpreting complex pigment mixtures found in historical paint samples.

# FROM SPECIMEN TO DIGITAL TWIN: HIGH-THROUGHPUT PIPELINE FOR SYNCHROTRON IMAGING OF MUSEUM COLLECTIONS

<u>Camille Berruyer</u>, <sup>1</sup> Sofiane Terzi, <sup>1</sup> Awen Autret, <sup>1</sup> Duy Nguyen, <sup>1</sup> Limamou Gueye, <sup>1</sup> Barbara Fayard, <sup>1</sup> Jonathan Blettery, <sup>2</sup> Pauline Provini <sup>2</sup>

<sup>1</sup>NOVITOM, Grenoble, France <sup>2</sup>Museum National d'Histoire Naturelle (MNHN), Paris, France camille.berruyer@novitom.com

More and more museums and institutions are recognising the importance of digitising their collections and the immense scientific potential that lies in accessing the internal structures of objects housed within their walls. One of the main challenges associated with scanning vast volumes of data is ensuring that the resulting information is easily accessible to both researchers and the public. Thus, developing an effective methodology for data processing and management becomes central.

This study presents an innovative approach to digitising large series of specimens from museum collections. It leverages optimized specimen handling, state-of-the-art synchrotron imaging and a high-throughput processing pipeline developed by Novitom. The synchrotron provides unparalleled high-resolution, high-contrast 3D imaging capabilities that enable rapid acquisition of entire collections or series with exceptional quality. Our novel processing pipeline is designed to efficiently process large volumes of tomographic data. It integrates machine learning driven segmentation with advanced mesh generation techniques, allowing for adaptive mesh refinement tailored to specific requirements such as size, element count, and orientation. In addition, the platform automates metadata formatting in compliance with current nomenclature and cataloguing standards.

The result is a comprehensive digital twin of each specimen, preserving intricate morphological details while ensuring broader accessibility via dedicated web platforms. This digital archiving not only facilitates the dissemination and study of scanned artefacts but also opens opportunities for discovering previously inaccessible or hidden features.

This methodology has been applied to specimens from the arthropod collections at the National Museum of Natural History (MNHN) in Paris, as part of the e-COL+ project (ANR-21ESRE-0053). We envision applying this methodology to a wide range of samples, including those of biological, archaeological, and palaeontological origin. Ultimately, our approach offers a fresh perspective on managing museum collections by combining cutting-edge synchrotron imaging with versatile data processing tools to enhance both preservation and scientific inquiry.

### CHARACTERIZATION OF COMMERCIAL ANIMAL GLUES FOR RESTORATION

Elena Pulidori,<sup>1</sup> Chiara Pelosi,<sup>1</sup> Eleonora Micheli,<sup>1</sup> Celia Duce,<sup>1,2</sup> Emilia Bramanti,<sup>3</sup> Lidia Ciccone,<sup>2,4</sup> Brunella Cipolletta,<sup>5</sup> Gloria Tani,<sup>1</sup> Laura Dello Ioio,<sup>6</sup> Leila Birolo,<sup>5</sup> Ilaria Bonaduce<sup>1</sup>

<sup>1</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy <sup>2</sup>Center for Instrument Sharing of the University of Pisa (CISUP), University of Pisa, 56126 Pisa, Italy <sup>3</sup>Institute of Chemistry of Organometallic Compounds, National Research Council, Via G. Moruzzi 1, 56124 Pisa, Italy

<sup>4</sup>Department of Pharmacy, University of Pisa, via Bonanno 6, 56126, Pisa, Italy
<sup>5</sup>Department of Chemical Sciences, University of Naples Federico II, Complesso Universitario di Monte S.

Angelo, Via Cinthia 21, 80126, Naples, Italy

<sup>6</sup>Dello Ioio Restauri, Vico Equense, 80069, Naples, Italy

ilaria.bonaduce@unipi.it

Animal glues have been utilized since ancient times, but their popularity waned in the 20th century with the advent of synthetic adhesives.<sup>[1]</sup> Today, they are primarily employed in the restoration of artworks. These glues are obtained from animal tissues(e.g. bone, hide, cartilage, and connective tissues), from which collagen is partially hydrolyzed and solubilised.<sup>[2,3]</sup>

This study examines animal glue samples derived from bone and hide, specifically used for applications in veiling and carpentry. The samples were provided by the Museo Nacional del Prado in Madrid and the Restoration Workshop at the University Suor Orsola Benincasa in Naples. This study is part of the research project titled "Natural Materials Development from Collagen-Based Wastes," which aims to harness the collagen found in leather waste as a primary resource for designing and producing new sustainable collagen-based biomaterials. The aim of the research here presented is to thermally and structurally characterize collagen, gelatin, and animal glues, providing a foundation for understanding the properties of more complex systems like gelatins and glues derived from leather waste extracts.

Results from thermogravimetric, calorimetric, and structural analyses indicate that commercial animal glues are primarily composed of gelatin rather than collagen. Furthermore, the thermal and structural properties of these glues are significantly influenced by the type of animal tissue from which they are derived, the extraction method employed, and the conditions of drying and storage. Additionally, Fourier-transform infrared spectroscopy (FTIR) analysis reveals a relatively high presence of  $\beta$ -structures in all commercial glue samples, suggesting that these structures play a crucial for explaining the glue mechanical properties.

#### Acknowledgements:

This work is part of the MUR project PRIN 2022 PNRR ArtDECOW (project code P2022HWL7L). The project is financed by European Union-Next Generation EU, Mission 2, Component 1 (M2C1) CUP: I53D23005990001.



<sup>[1]</sup> N. C. Schellmann, Stud. Conserv. "Animal Glues: A Review of Their Key Properties Relevant to Conservation" **2007**, 52, 55–66.

<sup>[2]</sup> S. Ebnesajjad, "Characteristics of Adhesive Materials. In Handbook of Adhesives and Surface Preparation" **2011**, William Andrew Publishing, Oxford, 137–183.

<sup>[3]</sup> P. A. Fay, "A History of Adhesive Bonding. In Adhesive Bonding" 2021, 2nd ed., Woodhead Publishing, 3-40.

# ADVANCED INVESTIGATION OF THE BOOK OF THE DEAD OF KHA AT THE MUSEO EGIZIO OF TURIN: A MOLAB E-RIHS IN-SITU STUDY

Alessandra Botteon, Michela Botticelli, David Buti, Claudia Caliri, Laura Cartechini,

Annalaura Casanova Municchia,¹ Claudia Conti,¹ Valeria Di Tullio,¹ Enrico Ferraris,³ Margherita Giugni,¹,⁴ Loredana Luvidi,¹ Donata Magrini,¹ Letizia Monico,² Eva Luna Ravan,¹,⁴ Aldo Romani,⁵ Francesco Paolo Romano,¹ Francesca Rosi,² Gianluca Santagati,¹ Susanne Töpfer³

<sup>1</sup>Institute of Heritage Science (ISPC), National Research Council (CNR), IT
<sup>2</sup>Institute of Chemical Science and Technologies "Giulio Natta"(SCITEC), National Research Council (CNR), IT

<sup>3</sup>Fondazione Museo delle Antichità Egizie di Torino, IT
<sup>4</sup>Faculty of Literature, Department of Classics, Sapienza University of Rome, IT
<sup>5</sup>Department of Chemistry, Biology and Biotechnology, University of Perugia, IT
alessandra.botteon@cnr.it

In February 2024, a comprehensive MOLAB E-RIHS study was conducted at the Museo Egizio of Turin to investigate the painting materials, techniques, and conservation state of the *Book of the Dead of Kha*, a rare and remarkably well-preserved funerary papyrus from the 18th Dynasty. The study employed a multi-analytical approach, integrating advanced portable and non-invasive imaging and single-point techniques, including scanning Macro X-ray Fluorescence (MAXRF), UV-IR imaging, VIS-NIR hyperspectral imaging, high-resolution digital microscopy, mapping X-ray Diffraction (MAXRD), Raman spectroscopy, micro-SORS, and VIS-NIR and IR external reflection spectroscopy. The synergy of these techniques provided an in-depth characterization of the papyrus's pigments, binders, and overall conservation state. Imaging and scanning analytical methods allowed for a macro-scale depiction of the pigment palette and artistic techniques, highlighting key areas for further investigation using single-point methods. High-resolution microscopy offered valuable insights into surface morphology, painting texture and application, as well as the physical condition of the papyrus.

MAXRF revealed the elemental composition of various inorganic pigments, which were molecularly identified through vibrational and electronic spectroscopy, as well as MAXRD. Egyptian blue was found in both blue and black paints, while Egyptian green was used alongside a possible organic copper-based green. Different types of ochre paints, as well as arsenic-based yellow and red pigments, were detected. Huntite and carbon black were identified as white and black pigments, respectively. Micro-SORS enabled depth-profiling of arsenic-based pigments, providing insights into their alteration mechanisms. Meanwhile, FTIR spectroscopy facilitated the analysis of organic materials, including binders, restoration materials, and degradation products.



Figure 1: MOLAB E-RIHS study of the Book of the Dead of Kha (©Nicola Dell'Aquila, Museo Egizio)

## ILLUMINATING THE PAST: A TECHNICAL STUDY OF THE GENEALOGIA DO INFANTE D. FERNANDO

### <u>Silvia Bottura-Scardina</u>,<sup>1,2\*</sup> António Candeias,<sup>1</sup> Ana Teresa Caldeira,<sup>1</sup> Pedro Flor,<sup>3</sup> Susana Varela Flor,<sup>4</sup> Catarina Miguel<sup>1</sup>

<sup>1</sup>HERCULES Laboratory, University of Évora, Portugal <sup>2</sup>CNR-ISPC Catania, Italy

<sup>3</sup>Universidade Aberta e Instituto de História da Arte, Universidade Nova de Lisboa, Portugal <sup>4</sup>Instituto de História da Arte, Universidade Nova de Lisboa, Portugal

\*scardina@uevora.pt

The British Library (BL) hosts an item steeped in history: the Add Ms 12531 or Genealogia do Infante D. Fernando. This item was commissioned by the brother of King John III of Portugal, D. Fernando (1507-1534), who planned it as a sumptuous series of large-scale representations of the royal households of Portugal and Spain, celebrating his ancestors. The Genealogia was painted between 1530 and 1534 and was created through a collaboration between the Flemish Simon Bening of Bruges (1483-1561) and the Flemish-Portuguese António de Holanda (1480-1558). Unfortunately, the item was not completed, and its current form consists of only 13 parchment leaves. Moreover, an organisational shift occurred at a midway stage of its illumination. Some scholarship was conducted on the BL, Add Ms 12531, but it has primarily focused on the historical circumstances of its creation, with little attention given to the technical execution of this masterpiece. In light of this gap, this work aims to provide for the first time a systematic, technical characterisation of the BL, Add Ms 12531, adding the following pieces of information: (I) What is the artistic process behind the item? (II) Can material differences (such as pigments, binders and their distribution) be observed across the item? To address these questions, a multianalytical approach was adopted, characterising 7 leaves from the item using imaging (IRR), chemical imaging (MA-XRF scanning, Vis-NIR RSI), and spectroscopic techniques (h-EDXRF, UV-Vis-NIR-SWIR FORS) at the British Library. The analysis revealed material and technical differences across the item, corresponding to different illuminating approaches by Bening and Holanda.

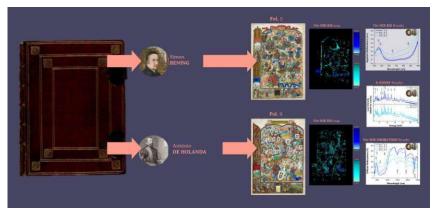


Figure 1: Graphical abstract

Acknowledgements: FCT financially supported the work through the ROADMAP project (PTDC/ARTHIS/0985/2021). The authors also thank the FCT financial support under the UIDP/04449/2020 and UIDB/04449/2020 projects and the Norma Transitória DL57/2016/CP1372/CT0012- a special thanks to the BL for making the Add Ms 12531 available for examination.

## RECONSTRUCTING MEDIEVAL MUSIC FROM MULTISPECTRAL IMAGES: A CASE STUDY

#### Anna Breger<sup>1</sup> and Wallace Peaslee<sup>1</sup>

<sup>1</sup>Department of Applied Mathematics and Theoretical Physics, University of Cambridge, United Kingdom <u>ab2864@cam.ac.uk</u>

Imaging modalities used for cultural heritage combined with machine learning methods have recently been applied to historical manuscripts with great success to enhance legibility. [1] Here, we study data obtained from multispectral imaging (MSI) of a degraded medieval music manuscript of historical importance. The manuscript contains several illegible passages with different degradations, also including deliberate erasure. As the manuscript could not be transported to an imaging laboratory, imaging was conducted with a portable imaging system, a multispectral camera with 8 bandpass filters (400-1000nm) with 5MP and 2456 x 2058 pixels. Images were taken with white/visible light as well as with broad UV light.

Even in this simple set up it was possible to greatly enhance the legibility through the multispectral information when employing suitable post-processing methods. In this presentation, we will compare and display results from several methods for the reconstruction of passages suffering from degradations. On one hand we apply commonly used methods such as principal component analysis (PCA) and the maximum noise fraction transform (MNF)<sup>[2]</sup> to receive visualizations of the multispectral data and compare it to visualizations obtained from other linear projections preserving different data characteristics, such as random orthogonal projections.<sup>[3]</sup> By using the linear projection methods, it was possible to recover meaningful notation that was previously illegible.

For parts that remained illegible, we employed a convolutional neural network, trained on lower frequency bands of well-preserved pages of the manuscript, where binarizations of clearly legible bands served as reference data. This approach allowed us to employ training data without manual annotations of the music notation, whilst operating in a supervised way. By applying the model to the strongly degraded notation, we were able to obtain additional information.

Lastly, we will discuss the potential biases introduced by the different methodologies, including the questions

- How can methods applied to a case study and introduced biases be balanced?
- Should a case study be completely unbiased in methodology?
- How should the output of a neural network be interpreted in digital restorations?

**Acknowledgements:** This research is funded by the Cambridge Centre for Data-Driven Discovery and Accelerate Programme for Scientific Discovery through the project "AI meets cultural heritage: Non-invasive imaging and machine learning techniques for the reconstruction of degraded historical sheet music".

<sup>[1]</sup> https://www.smithsonianmag.com/smart-news/three-students-decipher-first-passages-2000-year-old-scrollburned-vesuvius-eruption-180983738/. **2024.** 

<sup>[2]</sup> K. T. Knox, The Vatican Library Review "Hoku—A Multispectral Software Tool to Recover Erased Writing on Palimpsests" 2022.

<sup>[3]</sup> A. Breger, J. I. Orlando et al., Journal of Mathematical Imaging and Vision "On orthogonal projections for dimension reduction and applications in augmented target loss functions for learning problems" **2020.** 

## A STUDY OF CORROSION PRODUCTS IN AND ON TIN-ALLOY OBJECTS FROM DUTCH EAST INDIA COMPANY SHIPWRECKS

#### Inge de Bruin,<sup>1,2</sup> Fréderique Broers,<sup>1</sup> Tamar Davidowitz,<sup>1</sup> Luc Megens,<sup>3</sup> Florian Meirer<sup>2</sup>

<sup>1</sup>Conservation & Science, Rijksmuseum, Hobbemastraat 22, 1071ZC Amsterdam, The Netherlands
<sup>2</sup>Inorganic Chemistry & Catalysis, Institute for Sustainable and Circular Chemistry, Utrecht University,

Universiteitsweg 99, 3584 CG Utrecht, The Netherlands
<sup>3</sup>Rijkserfgoedlaboratorium, Rijksdienst voor het Cultureel Erfgoed, Hobbemastraat 22, 1071ZC Amsterdam, The

Netherlands

f.broers@rijksmuseum.nl

The Rijksmuseum collection contains thousands of metal objects from multiple Dutch East India Company shipwrecks. The objects were excavated in the 1970s and some were subsequently treated for conservation, although the (chemical) nature of this treatment remains unknown. [1] Most objects are heavily corroded (see fig. 1.A) and it is uncertain whether the formation of corrosion products is related to the treatment. Moreover, some of the corrosion products may be chemically unstable.

The aim of the presented research is to identify the chemical composition of the corrosion products that are found on the tin-alloy objects. This research has proven to be essential to the development of a Visual Identification Tool for Archaeological Tin (VITAL Sn). This tool allows conservators from the Rijksmuseum and other institutions to identify corrosion products based on visual characteristics. Previously, a VITAL Cu tool was developed from a study on copper-alloy objects in the collection.<sup>[2]</sup>

The corrosion products were studied with optical microscopy, SEM-EDX, Raman microscopy, and XRD. Measurements were performed on metallographic samples, isolated corrosion products and on the objects themselves. Tin- and lead-based corrosion products such as cotunnite (PbCl<sub>2</sub>) and cassiterite (SnO<sub>2</sub>) were found within the objects, see fig. 1.B. Unexpected corrosion products on the surface include copper-, iron-, and calcium-based materials, see figs. 1.C and D. An overview of the corrosion products found on representative tin artefacts from the collection will be given. These results will be used to design a VITAL Sn tool that can be used by conservators treating similar objects, without needing access to many analytical resources.

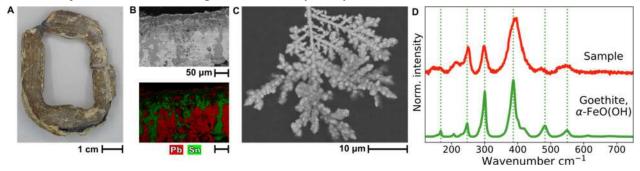


Figure 1: A) One of the corroded objects from the collection. B) SEM-EDX measurements on a metallographic sample. C) SEM image of one of the copper-based corrosion products. D) Raman spectra of a measurement on one of the metallographic samples and a reference spectrum of goethite (α-FeO(OH), RRUFF ID R120086).

<sup>[1]</sup> R. Cowan et al., The International Journal of Nautical Archaeology and Underwater Exploration 1975, 4.2, 267-300

<sup>[2]</sup> A. Hammond, An Investigation of Treated Cupreous Wreck Finds from the Hollandia Collection 2022, Amsterdam.

# HISTORICAL PRIMERS ON HERITAGE AIRCRAFT: ANALYSIS OF THE ZINC-CHROMATE ANTICORROSION PIGMENTS

## <u>Magali Brunet</u>, <sup>1</sup> Clément Holé, <sup>2</sup> Andrea Balbo, <sup>3</sup> Christophe Faulmann, <sup>1</sup> Letizia Monico, <sup>4</sup> Philippe Sciau<sup>1</sup>

<sup>1</sup>CEMES, CNRS, University of Toulouse, France

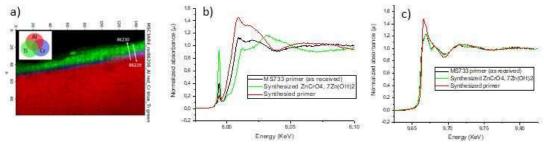
<sup>2</sup>ESRF, France

<sup>3</sup>University of Ferrara, Corrosion and Metallurgy Centre "A. Daccò" Ferrara, Italy

<sup>4</sup>SCITEC, CNR, Perugia, Italy

magali.brunet@cemes.fr

Although chromate-based pigments are known to be used in easel paintings as yellow pigments, they were also largely employed for their anti-corrosion properties in the protective layer (primer) of aeronautical metallic parts. In this work, two types of primers collected on heritage aircraft are studied. The first primer was sampled on a Dewoitine D.520 aircraft (1940) and contains zinc yellow (ZnCrO<sub>4</sub>.K<sub>2</sub>O.H<sub>2</sub>O) as an anti-corrosion pigment. The second is a wash primer developed after WWII,<sup>[1]</sup> sampled from a Morane Saulnier MS733 aircraft (1951). This primer, obtained by mixing a zinc tetraoxychromate (ZTO, a chromate with formula ZnCrO<sub>4</sub>, nZn(OH)<sub>2</sub>) with phosphoric acid in alcoholic solution and vinyl butyral polymer, was specifically developed to provide a higher protective efficiency than classical primers. The two primers were fully characterized with laboratory and synchrotron-based techniques (XRD at ID22 beamline and μXRF and μ-XANES at ID21 beamline of ESRF). In particular μ-XANES technique was used to probe the speciation of key elements (Cr and Zn) at the microscale in these layers and to provide information on the chemical reactions that took place between the zinc chromate and phosphoric acid at the interface with the aluminium alloy substrate. The incorporated pigments were compared with reference pigments, either commercial or synthesized from historical published articles. Although ZTO presents a high variability of stoichiometries depending on the ratios of ZnO/CrO<sub>3</sub> used as reagent, it is possible to reproduce a similar primer as the historical one. The XANES results highlight then that the ZTO pigment inside the MS733 primer has already been reduced during fabrication, i.e. the Cr(VI) content is lower than for the non-reacted synthesized pigment (see Figure 1). Historical primers, artificially aged by immersion 15 days in acidic rain (pH=4.3), were also studied to assess their protection efficiency. These results contribute in gaining knowledge on the fabrication of historical primers for aeronautical applications and on the longterm ageing of the chromate pigments with time and/or under severe weathering conditions.



*Figure 1*: a)  $\mu$ -XRF map (cross-section); b-c) XANES spectra at Cr K-edge and Zn-edge (ID21, ESRF) for the MS733 primer compared with synthesized ZTO pigment and synthesized primer (ZTO +  $H_3PO_4$  + PVB).

<sup>[1]</sup> L. R. Whiting, P. F. Wangner, U. S. Patent Office (Ed.) United States 1950, n° 2,525,107.

# SCIENTIFIC ANALYSIS OF V&A AND BEINECKE LIBRARY ILLUMINATIONS ATTRIBUTED TO ATTAVANTE DEGLI ATTAVANTI AND WORKSHOP

#### <u>Lucia Burgio</u>, <sup>1</sup> Valentina Risdonne, <sup>1,\*</sup> Richard Hark, <sup>2</sup> Marie-France Lemay, <sup>3</sup> Catherine Yvard <sup>1</sup> and

<sup>1</sup> Victoria and Albert Museum, London, United Kingdom
<sup>2</sup> Institute for the Preservation of Cultural Heritage, Yale University, West Haven, Connecticut, USA
<sup>3</sup> Yale University Library, New Haven, Connecticut, USA
\* now at the National Trust, Knole House, Sevenoaks, United Kingdom
valenting.risdonne@nationaltrust.org.uk

This study is the first step of a wider project exploring questions of authenticity, artistic intervention, restoration practices and 19th-century illumination through a comparative analysis of manuscript cuttings held at the Victoria and Albert Museum (V&A) and the Beinecke Rare Book & Manuscript Library at Yale University. The starting point is a leaf showing the Crucifixion surrounded by a full border in the style of Attavante degli Attavanti (1452-c.1525) now at the V&A (E.4588-1910). Exhibited as 'Florentine, c.1513-1521' and 'for a Missal executed for Pope Leo X' at the 1908 Burlington Fine Arts Club Exhibition of Illuminated Manuscripts (as no. 27), it was yet described in the acquisition register as 'copy of a leaf from a Missal' when it came to the V&A in 1910 as part of the Salting Bequest. Recent curatorial research at the V&A has been seeking to ask this question anew. As it is stylistically close to a fully illuminated leaf attributed to the same workshop now at the Beinecke Library (MS 712.129), from a gradual also at the Beinecke (Beinecke MS 42; Florence, late 15<sup>th</sup> century), scientific analysis methods, including digital microscopy, infrared reflectography, X-ray fluorescence mapping and Raman microscopy, were employed to compare the material composition and painting technique of the V&A and Beinecke leaves.

Through an interdisciplinary approach combining technical analysis with art historical research and connoisseurship, this project wishes to reassess the boundaries between original, restored and copied works, contributing to broader discussions on the perception of authenticity in illuminated manuscripts.



Figure 1: (a) The Crucifixion (V&A: E.4588-1910) and (b) Historiated initial depicting St. Felicitas (Beinecke: MS 712.129).

# ADVANCING MICRO-XRF IMAGING: A NOVEL FULL-FIELD APPROACH FOR HIGH-RESOLUTION ELEMENTAL MAPPING IN HERITAGE SCIENCE

#### Claudia Caliri, Gianluca Santagati and Francesco Paolo Romano 1

<sup>1</sup>Istituto di Scienze del Patrimonio Culturale, Consiglio Nazionale delle Ricerche (CNR-ISPC), Italy claudia.caliri@cnr.it

Analytical applications in Heritage Science often require noninvasive and simultaneous elemental mapping of samples with high spatial resolution and chemical sensitivity. Micro-X-ray fluorescence ( $\mu$ -XRF) is a well-established technique for mapping the lateral distribution of chemical elements and it is now routinely applied in the analysis of artworks when high resolution is necessary to obtain information on the elemental composition at the micrometric scale. Typically, elemental images are acquired by scanning samples with a primary X-ray beam focused to a spot size on the order of a few tens of microns. [1]

Recently, the XRAYLab at ISPC-CNR in Catania introduced a novel full-field XRF technique as an alternative to the conventional XRF scanning method. In this approach, a broad X-ray beam irradiates a large area of the sample (typically around 20 cm²), and the induced X-ray fluorescence is collected using a polycapillary optic positioned in front of a position- and energysensitive detector. This configuration enables rapid elemental imaging with a resolution of approximately 50µm, without the need for scanning operations. Moreover, the very large depth of focus (DoF) minimizes blurring effects on the acquired images, even when analyzing samples with complex three-dimensional morphology. The system employs a high-power X-ray tube (3 kW) for laboratory applications and a low-power tube (100 W) for in-situ measurements. A costeffective CCD detector, coupled with a 1:1 straight polycapillary, serves as the primary detection component and operates with a specialized photon counting technique that permits energy- and laterally resolved XRF spectroscopy. Compelling features of the device include its simple setup, compact dimensions, and user-friendly electronics—only a USB cable and an office PC are necessary to control the instrument—making it a valid alternative for micro-XRF imaging applications.

In this work, we introduce a novel extension to the system by incorporating a conical polycapillary, which enables high-resolution XRF imaging down to the micrometric scale. Furthermore, we explore the feasibility of performing in-depth three-dimensional mapping of stratigraphic samples. Results obtained on reference materials as well as real case studies using the new setup are presented and discussed.

Acknowledgements: PNRR project H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029, CUP B63C22000730005; E-RIHS European Infrastructure of Heritage Science (E-RIHS).

<sup>[1]</sup> H. C. Santos et al., Microchemical Journal 2016, 124, 241-246.

<sup>[2]</sup> F. P. Romano et al., Analytical chemistry 2016, 88(20), 9873-9880.

# IDENTIFICATION OF THE MANUFACTURING PROCESS OF SARDINIAN BRONZE STATUARY: A RESEARCH PROJECT THROUGH NEUTRON TECHNIQUES

<u>Francesco Cantini</u>,<sup>1,2</sup> Antonio Brunetti,<sup>3</sup> Anna Depalmas,<sup>3</sup> Anna Fedrigo,<sup>4</sup> Manuel Morgano,<sup>5</sup> Anders Kaestner,<sup>6</sup> Francesco Grazzi<sup>1,2</sup>

<sup>1</sup>Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata (CNR-IFAC), Sesto Fiorentino, Italy.

<sup>2</sup>Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Firenze, Sesto Fiorentino, Italy.

<sup>3</sup>Università di Sassari, Sassari, Italy.

<sup>4</sup>Institute Laue Langevin (ILL), Grenoble, France.
<sup>5</sup>Science and Technology Facility Council (STFC), ISIS Neutron and Muon Source, Chilton, UK.
<sup>6</sup>Paul Scherrer Institut (PSI), Villigen, Switzerland.

f.cantini@unifi.it

The production of "Nuragic" Bronze Figurines from Sardinia represents a rich historical archive that provides key information about the iconography, the metal production and casting techniques, and on the development of metallurgy in the Mediterranean basin. [1] Since the question about their manufacturing method still remains without definitive answer, the understanding of the Sardinian bronze metallurgy is essential to determine which manufacturing techniques were employed for the production of complex bronze artefacts. For example, complex bronze sculptures, made using lost wax technique, were rarely cast in a single solution: most of the parts of the wax model were moulded separately and then joined, as can be inferred also from a simple visual inspection.

This work is devoted to the identification of metallurgical procedures applied to the production of bronze artefacts of the "Nuragic" Period in Sardinia. We analysed a set of five artefacts, three anthropomorphic statues (a warrior, a priestess<sup>[2-3]</sup> and an offering figure), one miniature of a basket, one boat model;<sup>[4]</sup> all of them appear outstanding concerning the accuracy of their manufacture, the originality of the subjects and the descriptive details. The samples were made available by Museo Nazionale Preistorico "L. Pigorini" and by the Sassari Archaeological Survey Office. The analyses were performed using neutron tomography (NT) and Bragg Edge Neutron Transmission (BENT) at the Paul Scherrer Institut (PSI) and ISIS.

NT allowed the complete 3D volumetric reconstruction of the statues, thus obtaining important details on the casting procedures and on the connections between the different components, as well as revealing the presence of repairs, recasts. Furthermore, by exploiting the distribution of the pores it was also possible to hypothesize the position of the mould during the casting. BENT, on the other hand, provided the analysis of the composition of the Cu-Sn alloy and details on the microstructure. All the results obtained were obtained in a totally non-invasive way.

<sup>[1]</sup> A. Depalmas, "La scoperta della civiltà nuragica" 2018, Nautilus: Beinsaco (To), Italy, 46-65.

<sup>[2]</sup> A. Brunetti, *Materials* **2022**, *15*(12), 4174.

<sup>[3]</sup> F. Cantini et al., Journal of Archaeological Science: Reports 2024, 60, 104801.

<sup>[1]</sup> A. Depalmas, et al., Archaeological and Anthropological Sciences 2021, 13(6), 101.

# GOLD-COATING REMOVAL FROM HISTORIC/ARCHEOLOGICAL ARTIFACTS USING A THIOUREA-IODINE CHARGE-TRANSFER ADDUCT

Anna Caria,<sup>1</sup> Simone Murgia,<sup>1</sup> M. Carla Aragoni,<sup>1</sup> Alessandra Garau,<sup>1</sup> Vito Lippolis,<sup>1</sup> Enrico Podda,<sup>1,2</sup> Paola Meloni,<sup>3,4</sup> and Massimiliano Arca<sup>1</sup>

Scanning Electron Microscopy (SEM) of cultural heritage specimens often requires the application of a thin gold coating to the samples. This metallization reduces sample charging and enhances imaging of non-conductive samples, althought it renders them unsuitable for further analysis. Gold removal often relies on aggressive methods, such as cyanide-based solutions, which pose significant risks to both health and the environment. We present here a safe gold dissolution method carried out under mild conditions exploiting the 1:1 chargetransfer (CT) adduct between thiourea and diiodine in aqueous solution. The method is based on the oxidation of the gold coating, with chalcogen donor molecules coordinating the resulting metal cation,<sup>2</sup> according to previously adopted procedures for the recovery of noble metals such as palladium and gold from WEEE.<sup>3</sup> The gold dissolution method was tested on two samples: a gold coated vitrified ceramic fragment and a trachyte stone mock-up (Figure 1). The effect of the treatment was monitored by optical microscopy and colorimetry, while the amount of the gold leached was determined by means of ICP analysis of the solution and photogrammetric area determination of the samples. This immersion-based technique effectively dissolves the gold coating while fully preserving the integrity of the samples for further analysis, hence making this treatment particularly suitable for delicate cultural heritage and archaeological specimens.

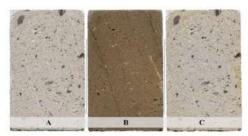


Figure 1: Plain light images of a trachyte mock-up: pristine (A), gold-coated (B), and after gold dissolution (C).

Acknowledgements: Ministero per l'Ambiente e la Sicurezza Energetica – Direzione generale Economia Circolare is kindly acknowledged for funding (RAEE– Edizione 2021).

<sup>&</sup>lt;sup>1</sup>Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554 bivio per Sestu, 09042 Monserrato, Italy

<sup>&</sup>lt;sup>2</sup>Centro Servizi di Ateneo per la Ricerca (CeSAR), Università degli Studi di Cagliari, S.S. 554 bivio per Sestu, 09042 Monserrato (Italy)

<sup>&</sup>lt;sup>3</sup>Dipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Università degli Studi di Cagliari, via Marengo 2, 09123, Cagliari, Italy

<sup>&</sup>lt;sup>4</sup>Laboratorio Colle di Bonaria, Università degli Studi di Cagliari, Via Ravenna snc, Cagliari, 09125, Italy. anna.caria@unica.it

<sup>[1]</sup> J. Sela, A. Boyde, J. Microsc. 1977, 111, 279.

<sup>[2]</sup> F. Isaia, M. C. Aragoni, M. Arca, C. Caltagirone, A. Garau, P. G. Jones, V. Lippolis, R. Montis, *Cryst. Eng. Comm.* **2014**, *16*, 3613.

<sup>[3]</sup> F. Isaia, M. C. Aragoni, M. Arca, C. Caltagirone, C. Castellano, F. Demartin, A. Garau, V. Lippolis, T. Pivetta, New J. Chem. 2020, 44, 2652.

# WHY LISTENING MATTERS: THE KEY ROLE OF ELICITATION STUDIES IN DEVELOPING NEW CLEANING TOOLS FOR ARTWORKS

#### Giulia Caroti, <sup>1</sup> Silvia Pizzimenti, <sup>1</sup> Nina Olsson, <sup>2</sup> Tomas Markevicius, <sup>3</sup> Ilaria Bonaduce <sup>1</sup>

<sup>1</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy

<sup>2</sup>ICOMOS Lietuva, Vilnius, Lithuania

<sup>3</sup>Faculty of Applied Physics, Ghent University, Ghent, Belgium

<u>giulia.caroti@phd.unipi.it</u>

The European project MOXY aims to revolutionize the cleaning and restoration of cultural heritage using atomic oxygen, a highly reactive species found in the Earth's upper atmosphere. The initiative focuses on developing user-friendly tool to produce atomic oxygen and validating its application for art conservation. This innovative approach provides a green alternative to traditional cleaning methods, eliminating the need for direct contact, solvents, or liquids, ensuring greater safety for both the artwork and conservators.

Elicitation studies have been central to the MOXY project's research from the beginning. This type of research follows a bottom-up approach to systematically gather insights from end users and stakeholders. Elicitation studies have been widely used for years across various disciplines, including psychology, management, anthropology, and computer science, to better understand perceptions, needs, and decision-making processes. In the context of the MOXY project, this method has been essential in identifying key requirements and expectations regarding the development of the novel tool based on atomic oxygen technology. And more, it has thus been possible to identify which are the most challenging substrates, type of dirt and in general conservation issues that could benefit from the use of this new cleaning tool.

By directly interacting with end users and stakeholders, we aim to understand their needs, the most valued technological features, and the factors that may help or hinder the adoption of this new solution. This process ensures that the technology being developed is not only scientifically and technically robust but also practical, user-friendly, and aligned with the real-world challenges faced by professionals in the field of cultural heritage conservation.

Semi-structured interviews were conducted with conservators and conservation scientists both from Europe and US affiliated to different institutions – museums, universities, research organizations, conservation institutions, private practitioners. These experts interviewed present different background: textiles, metals, paintings, paper, both ancient and modern materials.

These initial interviews have been very promising and have helped establish a crucial communication channel between scientists and conservators. This exchange has laid the foundation for further discussions and upcoming interviews, allowing us to gain deeper insights into the needs and expectations of all stakeholders who may eventually use the new tool.

## HALLOYSITE NANOTUBES' ENVIRONMENTALLY BENEFICIAL POTENTIAL AS GREEN CONSERVATION MATERIAL FOR LEATHER

#### Cristina Carsote, 1 Elena Badea, 2,3 Marianne Odlyha, 4 Chloe Pearce, 4 Genoveva Burca 5,6

<sup>1</sup>Center for Research and Physical-Chemical and Biological Investigations, National Museum of Romanian History, Bucharest, Romania

<sup>2</sup>Department of Chemistry, Faculty of Sciences, University of Craiova, Craiova, Romania

<sup>3</sup>The Research Institute of the University of Bucharest (ICUB), Bucharest, Romania

<sup>4</sup>Birkbeck College, University of London, London, United Kingdom

<sup>5</sup>Diamond Light Source Ltd, Didcot, United Kingdom

<sup>6</sup>STFC, Rutherford Appleton Laboratory, Didcot, United Kingdom

<u>criscarsote@gmail.com</u>

New nanoparticle conservation techniques have been employed to consolidate historical vegetable-tanned leathers and slow their deterioration. With their nanosized tubular shapes, high aspect ratio, and large surface area hallowsite nanotubes (HNTs) have been proved as compatible and chemically stable nano clays, suitable for use as reinforcing fillers. They may facilitate moisture levels within the leather, which is vital for preventing further chemical degradation and reducing risks of mold growth or drying out. The idea behind measuring leather's reaction to moisture is that leather artefacts, particularly in areas where the leather has deteriorated more, are known to be sensitive to environmental fluctuations in temperature and relative humidity. To simulate this situation in an experimental setting, leather samples were mounted in a custommade closed-cell and subjected to programmed cycles of RH at a controlled temperature while exposed to the neutron beam.<sup>[1]</sup> We report results for historical leather (a bookbinding from the first decade of 19th century) treated with a novel formulation based on HNTs functionalized with magnesium oxide nanoparticles dispersed in a mixture of collagen hydrolysate and glycerol. The neutron radiography results were compared with the changes in the hydrothermal stability of collagen fibres (shrinkage activity), collagen molecular structure (FTIR-ATR) and relaxometry parameters (<sup>1</sup>H NMR).<sup>[2]</sup> Using the same cyclic RH program, the Dynamic Mechanical Analysis (DMA) was used to measure changes in storage and loss moduli.<sup>[3]</sup> The collagen matrix's denaturation behavior was evaluated using micro-Differential Calorimetry (micro-DSC).<sup>[4]</sup> These outcomes were compared with those of leather bookbindings from the 17<sup>th</sup> and 18<sup>th</sup> century in order to better understand the impact of the protective treatment.

Acknowledgements: E. Badea and M. Odlyha are grateful for the UKRI Grant for Monitoring effects of RH fluctuations on leather based cultural heritage objects. Experiment RB2320345 (ISIS Neutron and Moun Source).

<sup>[1]</sup> A. Bridarolli, M. Odlyha, G. Burca, J. C. Duncan, F. A. Akeroyd, A. Church and L. Bozec, *ACS Applied Polymer Materials* **2021**, *3*(2), 777-788. DOI: 10.1021/acsapm.0c01073

<sup>[2]</sup> N. Proietti, V. Di Tullio, C. Carsote, E. Badea, Magn. Reson. Chem. 2020, 58, 840-859. DOI: 10.1002/mrc.5024

<sup>[3]</sup> M. Odlyha, "Handbook of Thermal Analysis and Calorimetry" 2003, M. E. Brown, P. K. Gallagher (eds.) Elsevier.

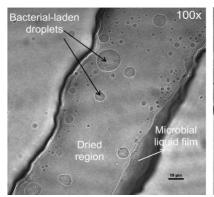
<sup>[4]</sup> C. Carsote and E. Badea, *Herit. Sci. "Micro differential scanning calorimetry and micro hot table method for quantifying deterioration of historical leather"* **2019**, 7, 48. DOI:10.1186/s40494-019-0292-8

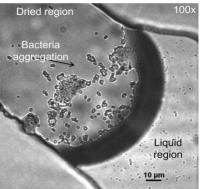
#### MICROFLUIDIC INVESTIGATION OF EVAPORATION SUPPRESSION AND SALT REDISTRIBUTION INDUCED BY *PARACOCCUS DENITRIFICANS* IN POROUS MEDIA

Jafar Qajar, <sup>1</sup> Selen Ezgi Celik, <sup>1</sup> Laurenz Schröer, <sup>2</sup> Amir Raoof <sup>1</sup> and Veerle Cnudde <sup>1,2</sup>

<sup>1</sup>Department of Earth Sciences, Utrecht University, The Netherlands
<sup>2</sup>Department of Geology, Ghent University, Belgium
s.e.celik@uu.nl

Preserving building stones and cultural heritage is challenging, particularly in materials with high salt content. Moisture and salt transport play critical roles in their deterioration and conservation. While chemical treatments exist, research explores bacteria's potential in stone conservation, raising key questions about their interaction with salt-laden pore networks. Evaporation-driven salt crystallization has been extensively studied, but the influence of microorganisms on drying dynamics remains poorly understood. Gaining insight into these interactions is crucial for developing sustainable, microbial-based preservation strategies. This study employs microfluidic tools to investigate the effects of *Paracoccus denitrificans* on isothermal drying dynamics and salt crystallization within porous structures. Experiments were conducted on brine-saturated control models and models containing a mixture of brine, growth medium and P. denitrificans to monitor liquid-gas interface evolution, microbial activity, and salt crystallization patterns. Drying experiments revealed that the brine-medium-bacteria significantly suppressed evaporation at the macroscale. Three pore scale key mechanisms were identified to explain this phenomenon: 1) bacteria-laden droplets formed in dried pore spaces, enhancing water retention; 2) biomass accumulation at the liquid-air interface distorted interface geometry, creating a physical barrier to evaporation; and 3) microbial treatment altered salt distribution, resulting in distinct crystallization patterns compared to control experiments (Fig. 1). These findings enhance our understanding of microbial interactions with drying processes in porous media, advancing microbial-based conservation and impacting geosciences, environmental engineering, and material science for sustainable construction and groundwater management.





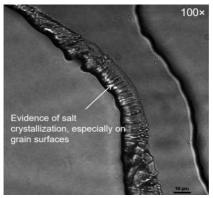


Figure 1: Pore-scale observations (obtained by confocal laser microscopy at 100x magnifications) of the postdrying micromodels initially saturated with a mixture of Na<sub>2</sub>SO<sub>4</sub> brine and P.denitrificans in a growth medium: (left) formation of bacterial-laden droplets in dried pore space, (middle) biomass aggregation at the liquid-gas interface, and (right) distinct salt precipitation pattern of the dried micromodel.

**Acknowledgements:** This project has received funding from the Dutch Research Council (NWO) through the BugControl project (project number VI.C.202.074) of the NWO Talent program.

# APPLICATION OF HYPERSPECTRAL IMAGING TECHNOLOGY FOR INFORMATION EXTRACTION FROM THANGKA PAINTINGS IN THE PALACE MUSEUM COLLECTIONS

Yao Chen, 1,2 Liang Qu, 1,2 Qian Wang, 1,2 Guanghua Li<sup>1,2</sup>

<sup>1</sup>The Palace Museum, China <sup>2</sup>China-Greece Belt and Road Joint Laboratory on Cultural Heritage Conservation Technology chenyao@dpm.org.cn

The Palace Museum houses an extensive collection of over 2,000 thangkas, with more than 600 displayed in their original condition. The majority of these thangkas originate from the Ming and Qing dynasties, periods that witnessed significant advancements in the art of thangka painting. However, prolonged exposure to unsuitable conditions within the palace has adversely affected the thangkas due to factors such as temperature, humidity, light, and gravitational stress. This has resulted in various forms of deterioration, including dust accumulation, staining, pigment fading, and flaking. To preserve and restore these invaluable thangka paintings, the Palace Museum employs various scientific analytical methods to investigate the deterioration and study the painting techniques used in their creation. Identifying pigments in stained and faded areas presents challenges, as destructive sampling and analysis are inappropriate due to the necessity of maintaining the integrity of the pigment layers. Hyperspectral imaging technology provides an efficient, non-destructive method for surface imaging that can identify affected pigments, map their distribution, and extract draft lines.<sup>[1]</sup> These findings are significant for the study of thangka painting techniques, as well as for their conservation and restoration. Research has been conducted on several thangka paintings. Taking the Portrait of Pelden Lhamo Buddha as an example, the distribution of pigments such as azurite and malachite was revealed. Furthermore, near-infrared imaging has uncovered draft lines that differ from the visible image, suggesting that the artist may have made alterations during the painting process.



Figure 1:Original Image of Pelden Lhamo Buddha

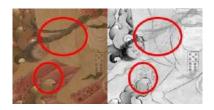
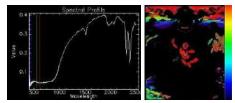


Figure 2: Comparison of local RGB image and nearinfrared image at the wavelength of 1805 nm of Portrait of Pelden Lhamo Buddha



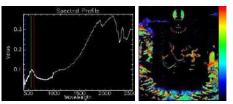


Figure 3: Reflectance spectrum and spatial distribution of azurite (left) and malachite (right)

<sup>[1]</sup> G. H. Li et al., Microchemical Journal "An automatic hyperspectral scanning system for the technical investigations of Chinese scroll paintings" 2020, 155.

# ANALYSIS OF GREEN COLORING MATERIALS IN THE *ILLUSTRATED*NATURAL HISTORY BOOKS OWNED BY TAKAMATSU MATSUDAIRA FAMILY USING HYPERSPECTRAL IMAGING

<u>Chih lien Chi</u>, <sup>1</sup> Junko Akiyama, <sup>1</sup> Kai Terashima, <sup>1</sup> Noriyoshi Nishida, <sup>1</sup> Tsuyoshi Chiba, <sup>1</sup> Masahide Inuzuka <sup>1</sup> and Keiko Takagi <sup>2</sup>

<sup>1</sup>Tokyo National Research Institute for Cultural Properties,13-43 Ueno Park, Taito-ku, Tokyo 110-8713, Japan 

<sup>2</sup>The Kagawa Museum, 5-5 Tamamocho, Takamatsu, Kagawa 760-0030, Japan 
<u>kishiren0922@gmail.com</u>

The Illustrated Natural History Books owned by Takamatsu Matsudaira family, a designated tangible cultural property of Kagawa Prefecture, are believed to have been produced in the midEdo period under the order of Matsudaira Yoritaka.<sup>[1]</sup> This 13volume collection comprises four categories: Shurinzu (Fish and other aquatic animal Illustrations), Shukin Gafu (Bird Illustrations), Shuho Gafu, and Shasei Gajo (both Plant Illustrations). These meticulously crafted illustrations provide valuable insights into Edoperiod natural history. Examining their coloring materials is crucial for art history research and the preservation of cultural property. Previous studies using infrared imaging have distinguished rokushō (malachite pigment) from green dyes based on indigo and yellow; however, accurately identifying mixed compositions has remained difficult. [2] In light of this issue, this study employed visible and near-infrared (VNIR) hyperspectral reflectance spectroscopy (400-1000 nm) using the hyperspectral camera NH-1S (Eba Japan) [3] to analyze green-colored areas in 35 artworks from Shuho Gafu and Shasei Gajo (Fig. 1).





Figure 1: One of the illustrations in Shuho Gafu and Shasei Gajo

Spectral data were acquired and analyzed using principal component analysis (PCA), with comparisons made to reference samples of known pigments and dyes for improved identification accuracy. Additionally, elemental analysis was conducted using X-ray fluorescence (XRF) with a portable Bruker Tracer 5i spectrometer (40 kV, 20 µA, 60-second exposure under atmospheric conditions) to validate the PCA-based interpretation. In the reflectance spectra, indigo showed absorption around 680 nm and high reflectance above 750 nm, enabling its identification. PCA of second-derivative spectra classified three groups: (1) areas primarily using *rokusho*, (2) areas primarily using indigo and yellow dyes, and (3) areas where both were combined. PCA scatter plots also indicated the potential for distinguishing variations in the mixing ratios of indigo with yellow or white colorants. However, areas where *rokusho* contained trace amounts of indigo, as well as in those where indigo was combined with black colorants, exhibited similar reflectance spectra, making differentiation difficult. By Integrating XRF analysis, clear identification was achieved by detecting copper, the primary component of *rokusho*.

Acknowledgments: This research was made possible with the cooperation of the Matsudaira Koueki-kai Foundation. This study was supported by JSPS KAKENHI (Grant Number JP24K04375).

<sup>[1]</sup> Takamatsu City Website: city.takamatsu.kagawa.jp.

<sup>[2]</sup> J. Akiyama, S. Ueno, R. Shikama, *Proceedings of the 36th Annual Meeting of the Japan Society for Scientific Studies on Cultural Properties* **2019**, 264–265.

<sup>[3]</sup> C. C. Lien, M. Inuzuka, Conservation Science 2022, 61, 93–107.

## COMPARISON OF THE RADON EXHALATION RATE IN BUILDING MATERIALS OF HISTORICAL AND ARTISTIC INTREST

<u>Daniele Chiriu</u>,<sup>2</sup> Francesco Caridi,<sup>1</sup> Stefania Da Pelo,<sup>3</sup> Giuliana Faggio,<sup>4</sup> Michele Guida,<sup>5</sup> Domenico Majolino,<sup>1</sup> Giacomo Messina,<sup>4</sup> Maurizio Ponte,<sup>6</sup> Silvestro Antonio Ruffolo,<sup>6</sup> Valentina Venuti<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, V.le F. Stagno D'Alcontres, 31-98166 Messina, Italy

<sup>2</sup>Dipartimento di Fisica, Università degli Studi di Cagliari, Cittadella Universitaria di Monserrato, Italy <sup>3</sup>Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.P. Monserrato-Sestu, km 0.700 - 09042 Monserrato, Italy

<sup>4</sup>Dipartimento di Ingegneria dell'Informazione, delle Infrastrutture e dell'Energia Sostenibile (DIIES), Università "Mediterranea", Loc. Feo di Vito, 89122 Reggio Calabria, Italy

<sup>5</sup>Dipartimento di Ingegneria dell'Informazione ed Elettrica e Matematica applicata (DIEM), Università degli Studi di Salerno, Via Giovanni Paolo II, 132 – Fisciano (SA), Italy

<sup>6</sup>Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Università della Calabria, Via Pietro Bucci, Arcavacata di Rende (CS), Italy

daniele.chiriu@dsf.unica.it

This study, conducted within the ATHENA project, focuses on radon (Rn-222) exhalation from building materials commonly found in historical structures. Radon, a radioactive gas produced by the decay of Ra-226, poses a significant health risk due to its ability to accumulate indoors, making it essential to understand and mitigate its sources.<sup>[1]</sup> The research aims to systematically compare radon exhalation rates across different lithotypes and evaluate the impact of environmental factors such as humidity, temperature, and laboratory treatments, including accelerated aging and consolidant applications.<sup>[2]</sup>

Experimental measurements were performed using the closed chamber method on samples collected from historical quarries. To ensure consistency, materials were dried to reduce moisture, cut into standardized shapes, and placed in a sealed steel chamber connected to a RAD7 detector. The detector measured radon concentrations by analyzing the 218Po peak, with equilibrium reached within approximately 15 minutes. Radon levels were monitored over a 10day period to assess emission behavior.

Results showed an initial exponential increase in radon concentration before stabilizing at equilibrium, demonstrating the influence of material properties such as composition and porosity on radon release.<sup>[3]</sup> These findings contribute to a better understanding of radon dynamics in built heritage, supporting the development of informed conservation strategies and mitigation measures to reduce indoor radon exposure. The study underscores the importance of continuous monitoring and regulatory efforts to enhance indoor air quality and public health.

<sup>[1]</sup> L. J. R. Nunes, A. F. Curado, S. E. I. Lopes, *Appl. Sci. "The Relationship between Radon and Geology: Sources, Transport and Indoor Accumulation"* **2023**, *13*. https://doi.org/10.3390/app13137460.

<sup>[2]</sup> A. P. D. Baltrocchi, L. Maggi, B. Dal Lago, V. Torretta, M. Szabó, M. Nasirov, E. Kabilov, E. C. Rada, *Sustain. "Mechanisms of Diffusion of Radon in Buildings and Mitigation Techniques"* **2024**, 16. https://doi.org/10.3390/su16010324.

<sup>[3]</sup> T. K. Abed, M. A. Fayad, A. A. Al-Amiery, H. A. Abdul Wahhab, J. K. Mohammed, H. S. Majdi, *Results Eng.* "Radon gas emission from home appliances: Understanding sources, implications, and mitigation strategies" **2024**, 22, 102133. https://doi.org/10.1016/j.rineng.2024.102133.

## IMMOBILIZED TRYPSIN – ENHANCED MALDI-IMAGING ANALYSIS OF SURFACES AND CROSS-SECTIONS OF WORKS OF ART

### <u>Brunella Cipolletta</u>, <sup>1</sup> Bertrand Thomas, <sup>2</sup> Georgia Ntasi, <sup>1</sup> Paola Cicatiello, <sup>1</sup> Paola Giardina, <sup>1</sup> Caroline Tokarski <sup>2</sup> and Leila Birolo <sup>1</sup>

<sup>1</sup>University of Naples "Federico II", Complesso Monte S. Angelo, Via Cintia 26, 80126, Napoli, Italy <sup>2</sup>Institute of Chemistry & Biology of Membranes & Nano-Objects, University of Bordeaux, UMR CNRS 5248, Proteome Platform, 146 rue Léo Saignat, Bordeaux 33000, France.

brunella.cipolletta@unina.it

Protein identification in works of art traditionally requires invasive micro-sampling, followed by protein digestion and analysis using bottom-up proteomics. While advanced MS techniques can now detect trace substances, these methods remain invasive. Recently, we developed a novel minimally invasive method for the analysis of proteinaceous materials in works of art. [1,2] This approach involves the use of a trypsin-functionalized cellulose acetate sheet, which digests proteins in situ on the surface of a work of art without any removal of material from the artifact. This method exploits the adhesion properties of fungal hydrophobins, which form a stable and homogeneous layer on the flexible sheet, allowing trypsin to be immobilized. After just 10 minutes (min) of contact at room temperature (RT), this bioactive film generates and extract sufficient peptides for unambiguous identification of the proteinaceous binder by proteomic analysis. Optical microscopy confirms that this procedure does not visibly alter the artwork or leave trypsin damaging residues.<sup>[1]</sup> A major advancement of this technique is its potential for spatially resolved imaging of surfaces or cross-sections of works of art. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry imaging (MSI) has emerged in very recent years as a powerful method to extract spatially resolved chemical information in complex materials. This study proposes the first use of MALDI-MSI on a trypsin-functionalized sheet, reflecting the protein content distribution of the work of art with which it has been in contact. In brief, a 1 cm<sup>2</sup> trypsin-functionalized sheet is placed in contact with the artwork at RT for 10 min, then adhered to a glass slide for direct MALDI-MSI analysis. The analysis is performed on an Atmospheric Pressure MALDI source (TransMIT, Germany) coupled to an Orbitrap Q-Exactive mass spectrometer (Thermo Fisher Scientific, Germany). The resulting MSI datasets is then processed using a home-built peptides database implemented on the Metaspace annotation platform. A series of experiments on artificially aged paint replicas will assess the method's feasibility, exploring factors such as MALDI matrix choice and deposition methods, trypsin amount and digestion conditions. Sensitivity limits in MSI acquisition related to surface heterogeneity and sample degradation/aging will also be addressed tuning instrumental parameters. The optimized method will be then applied to historical samples for validation. We aim to demonstrate that by "shaving" peptides from the surface or a crosssections of a work of art, accurate spatially resolved information about the protein content can be retrieved with minimal impact.

Acknowledgements: This work is financially supported by PNRR PE5 CHANGES (PE00000020). Artificially aged paint replicas are courtesy of Prof. I. Bonaduce and colleagues from the Dept. of Chemistry and Industrial Chemistry of the University of Pisa (Pisa, Italy).

<sup>[1]</sup> P. Cicatiello, Anal. Chem. 2018, 90, 17, 10128–10133.

<sup>[2]</sup> G. Ntasi, J. Proteomics. **2021**, 231, 104039.

# IMPLEMENTING A NON-INVASIVE ANALYTICAL PROTOCAL FOR IN-HOUSE IDENTIFICATION OF GEMSTONES PRESENT IN THE COLLECTIONS OF THE BIBLIOTHEQUE NATIONALE DE FRANCE

## Barbara Marjanovic,<sup>1</sup> <u>Lucy Cooper</u>,<sup>1</sup> Eleonora Pellizzi,<sup>1</sup> Maxence Hermant,<sup>1</sup> François Farges,<sup>2</sup> Anne Michelin<sup>3</sup>

<sup>1</sup>Bibliothèque nationale de France, Paris, FRANCE

<sup>2</sup>Institut de minéralogie, physique des matériaux et cosmochimie, Muséum national d'histoire naturelle, 75005 Paris, FRANCE

<sup>3</sup>Centre de Recherche sur la Conservation (CRC), Muséum national d'Histoire naturelle, CNRS, Ministère de la Culture, 75005 Paris, France

*lucy.cooper@bnf.fr* 

The collections at the Bibliothèque nationale de France include many objects decorated with precious gem stones. The identification of these minerals would allow in-depth studies on the materiality of these collections. However, currently, the institution relies upon analyses undertaken by experts from external laboratories. Whilst Raman spectroscopy is the most commonly used method for mineral identification, coupled with X-ray fluorescence (XRF) spectroscopy and UV fluorescence, the potential of Fibre Optic Reflectance Spectroscopy (FORS) is increasingly being explored. In order to evaluate the analytical capabilities of the equipment available at the BnF for the characterization of this type of collection, a collaboration was established in 2024 between the scientific laboratory and the BnF's Manuscripts Department, the Institute of Mineralogy, Materials Physics and Cosmochemistry (IMMPC) of the National Natural History Museum (MNHN) of Paris, and the Conservation Research Center (CRC).

This poster describes the on-going development of an analytical methodology for identifying gem stones, primarily using two portable devices already available at the BnF scientific laboratory: an XRF spectrometer XRF and a fibre optic spectrometer, measuring from ultraviolet to near infrared (225-2500 nm). The aim of this project is for XRF and FORS data collected on stones in the BnF collection to be compared to a database of gem stone references to determine whether this technique might be used to facilitate identification. A selection of un-mounted stones belonging to the French national gem collection were analysed on site at the MNHN mineralogy department using the portable BnF devices, and a portable Raman belonging to the CRC. The XRF, reflectance and fluorescence spectra will be compared to the Raman spectra to establish the contributions and complementarities of the three devices used for the identification of different typologies of gems. The portable XRF and fibre optic spectrometers used during the first phase will then be used insitu at the BnF Richelieu Museum to analyse gemstones found on a selection of rare manuscript bindings. Since this collection has been analysed by experts from the SPORANO team from the institut Lumière Matière (iLM) in Lyon, we will be able to verify the analytical methodology developed. It is then hoped that this in-house methodology can be used to facilitate the identification of other gem stones within the BnF collections.

Acknowledgements: This work benefited from State aid managed by the Agence Nationale de la Recherche (French National Research Agency) under the future investment program integrated into France 2030, bearing the reference ANR-17-EURE-0021 - Ecole Universitaire de Recherche Paris Seine—Foundation for cultural heritage sciences.

<sup>[1]</sup> A. G. Panczer et al., Gems & Gemology 2019, 55(1), 30-46.

<sup>[2]</sup> P. Ricciardi, Diffraction and Tomography in Art and Heritage Science 2021, 103-131.

<sup>[3]</sup> M. Aceto et al., Molecules 2022, 27, 4716.

### CYANOBACTERIA - BASED CONSOLIDATION TECHNOLOGY (CYA-TECH)

#### Luisa Corredor, <sup>1</sup> Federica Villa, <sup>1</sup> Francesca Capitelli <sup>1</sup>

<sup>1</sup>Department of Food, Environmental and Nutritional Science University of Milan, Milan, Italy luisa.corredor@unimi.it

CYA-TECH is a project funded by the Horizon Marie Skłodowska-Curie Actions (MSCA) Postdoctoral Fellowships Program (2024-2026). The aim of the project is to develop a novel cutting-edge, user- and environmental-friendly CYAnobacteria-based consolidation TECHnology that will restore and preserve monumental and ornamental calcareous stones in a sustainable way.

Photosynthetically active microorganisms, capable of producing calcium carbonate (CaCO<sub>3</sub>), have great potential for the development of sustainable biotechnologies. For the first time, the photosynthetic metabolism and the extracellular polymeric substances (EPS) of cyanobacteria will be exploited to precipitate calcium carbonate (biomineralization) and promote the restoration of the stone. Photosynthetic and biomineralization processes are directly related and light is the main driver of photosynthesis. Taking advantage of the cyanobacteria's responses to different wavelengths of light (physical switches) to promote the calcite precipitation, will allow the modulation of the microbial metabolism to enable on-demand and precision bioconsolidation, while sequestering anthropogenic CO<sub>2</sub> during photosynthesis. CYA-TECH is designed to maintain cell viability, efficient photosynthetic activity and to induce biomineralization associated with a delivery system innocuous to the monumental and ornamental calcareous stones.

The cyano-based consolidation technology, CYA-TECH, will be a novel solution overcoming the drawbacks of the chemical approaches and improving the performance and sustainability of the currently available biotechnologies.

## INVESTIGATING THE SOFTENING OF 20<sup>TH</sup> CENTURY OIL PAINTS: PRELIMINARY RESULTS ON JOAN MITCHELL AND GEORGES MATHIEU

<u>Chloë Coustet</u>,<sup>1</sup> Pauline Hélou-de La Grandière,<sup>2,3</sup> Victor Gonzalez,<sup>4</sup> Ayoub Traverson,<sup>4</sup> Letizia Monico,<sup>5</sup> Catarina Monteiro Pinto,<sup>5</sup> Ilaria Bonaduce,<sup>6</sup> Laurent Binet,<sup>7</sup> Mathieu Thoury<sup>1</sup>

<sup>1</sup>IPANEMA, CNRS, ministère de la Culture, UVSQ, MNHN, Université Paris-Saclay,

<sup>2</sup>Atelier La Grandière, conservation-restauration de peintures, Nîmes, France

<sup>3</sup>CY Cergy Paris Université, Cergy-Pontoise, France

<sup>4</sup>Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, France

<sup>5</sup>Centro SMAArt, University of Perugia, and CNR Heritage Institute, Italy

<sup>6</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Italy

<sup>7</sup>Chimie ParisTech, Université PSL, CNRS, Insitut de Recherche de Chimie Paris (IRCP), France

<u>chloe.coustet@cnrs.fr</u>

A number of oil paintings from the second half of the 20<sup>th</sup> century began to suffer from softening of paint layers and exudation of the binding medium less than 40 years after their completion. The kinetics of this process is a major challenge for their conservation and the triggering factors remain difficult to identify. The PhD project MODERN aims to provide a better understanding of the physico-chemical mechanisms involved and monitor the early stages of development of these changes in appearance by coupling techniques from the nano- and molecular-scale to the macroscale. The poster presented will provide a reflection around the terminology used to describe such alterations, and review the preliminary results obtained from recent analysis campaigns at les Abattoirs Museum (Toulouse) and Musée d'art moderne - Centre Georges Pompidou (Paris). In particular, both *in-situ* photoluminescence imaging and infrared spectroscopy have been used to probe markers of alteration and compare the state of the polymeric network between glossy and matt areas in a painting by Georges Mathieu and a quadriptych by Joan Mitchell.



Figure 1: Picture of an area of impasto with a surface turning glossy; under visible light (left) and UV illumination (right), showing the mobility and accumulation of oil binding medium. Detail from "A small garden" by Joan Mitchell (1980).

### APPLICATION OF PIXE ANALYSIS TO ROMAN BRASS IN THE MILAN AREA: A PROVENANCE STUDY

#### <u>Laura Cristina</u>,<sup>1</sup> Giulia Marcucci,<sup>1</sup> Maria Pia Riccardi,<sup>2</sup> Costanza Cucini,<sup>3</sup> Marco Tizzoni,<sup>3</sup> Quentin Lemasson,<sup>4</sup> Daniela Di Martino<sup>1</sup>

<sup>1</sup>Dipartimento di Fisica "G. Occhialini", Università di Milano-Bicocca and INFN, sezione di Milano-Bicocca, Milano, Italy

<sup>3</sup>IRAMAT, UMR 7065, CNRS, Université de Technologie Belfort Montbéliard, 90010 Belfort Cedex, France <sup>4</sup>Ministère de la Culture/Chimie ParisTech, 14 Quai François Mitterrand, 75001 Paris, France laura.cristina@unimib.it

Studying a population's metallurgical production can provide valuable insights into ancient technological advancements, trade routes and economic activities.<sup>[1]</sup> The present research focuses on the application of the Particle Induced X-ray Emission (PIXE) technique to investigate the elemental composition and provenance of Roman brass fragments from crucibles dating back to the 1st century BC. These fragments were found in the Roman city of Mediolanum.<sup>[2]</sup>

PIXE is a non-destructive analytical technique capable of enabling precise multi-elemental characterisation of metal artefacts<sup>[3]</sup> and has already been widely applied to the study of cultural heritage materials.<sup>[4]</sup> This technique is particularly well-suited to the analysis of trace elements in the investigated material, thus making it a valuable tool for provenance studies in the field of archaeometallurgy.<sup>[3]</sup> The presence of trace elements in Roman brasses suggests the potential use of these elements as diagnostic markers for the identification of zinc and copper ores. By exploiting the opportunities offered by this method of investigation, the aim is to study the production of brass during the Roman period in the Milan area, in order to determine the mineralogical origins, trading and technological advances in metallurgical activity.

This study involves the elemental analysis of some brass fragments found in Roman crucibles<sup>[2]</sup> and some minerals from the Bergamasque Alps. Indeed, literature suggests that these areas were exploited for metallurgical production in the past,<sup>[5]</sup> and the brass fragments found in Milan could provide crucial evidence to prove this. Particular attention will be given to the trace elements analysis, to clearly establish a connection between metallurgical artefacts and the mines of origin. Statistical methods of data comparison, such as the application of multivariate data analysis, will be proposed in order to improve the study of the data obtained. The information obtained will be essential to establish whether there was a workshop dedicated to working brass in the ancient city of Mediolanum and its role in processing and distributing metals. This research will demonstrate the effectiveness of PIXE analysis in provenance studies, providing an application case of considerable importance.

<sup>&</sup>lt;sup>2</sup>Dipartimento di Scienze della Terra e dell'Ambiente and Arvedi Laboratorio – sede di Pavia, Università degli Studi di Pavia, via Ferrata 9, 27100 Pavia, Italy

<sup>[1]</sup> R. Bugoi et al., Journal of Radioanalytical and Nuclear Chemistry 2003, 257(2), 375-383.

<sup>[2]</sup> G. Marcucci et al., The European Physical Journal Plus 2024, 139(6), 475.

<sup>[3]</sup> M. F. Guerra, X-Ray Spectrometry: An Int. Journal 1998, 27, 73-80.

<sup>[4]</sup> J. Salomon et al., Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2008, 266(10), 2273-2278.

<sup>[5]</sup> S. W. Merkel, Periodico di Mineralogia 2021, 90(2).

#### PRELIMINARY CHEMICAL CHARACTERIZATION OF CORE-FORMED GLASS VESSELS FROM OLBIA PONTICA (UKRAINE)

### <u>Kateryna D'Ayala</u>,¹ Anzhelika Kolesnychenko,² Patrizia Davit,¹ Annarosa Mangone,³ Nicola Mongelli,⁴ Monica Gulmini¹

<sup>1</sup>Department of Chemistry, University of Turin, Via Pietro Giuria, 7 – 10125 Torino (Italy)
<sup>2</sup>Science and Technology in Archaeology and Culture Research Centre, The Cyprus Institute, Konstantinou Kavafi Street, 20 – 2121, Aglantzia, Nicosia (Cyprus); Institute of Archaeology of the National Academy of Sciences of Ukraine, Volodymyr Ivasiuk avenue, 12 – 04210 Kyiv (Ukraine)

<sup>3</sup>Department of Chemistry and Laboratorio di Ricerca per la Diagnostica dei Beni Culturali, University of Bari "Aldo Moro", via Orabona, 4 – 70126 Bari (Italy)

kateryna.dayala@unito.it

This study analyses a collection of core-formed coloured glass vessels from the northern Pontic region, excavated in the Greek colony of Olbia Pontica and dating from the late 6<sup>th</sup> century BC to the early 1<sup>st</sup> century AD. The collection includes a variety of perfume and ointment containers, such as *amphoriskoi*, *oinochoai* and *alabastra*, with a predominance of blue hues. These artefacts are now preserved in the museum of the National Historical and Archaeological Reserve "Olbia" (Mykolaiv Oblast, southern Ukraine) and in the museum of the Institute of Archaeology of the National Academy of Sciences of Ukraine (Kyiv, Ukraine).

According to the archaeological classification based on typology, decorative style and periodization, the artefacts considered in this study are distributed across the three Mediterranean Groups (MGs). Based on typological and spatial analysis of MGs, researchers have suggested the existence of different centres for core-formed vessel production. Numerous studies have aimed to identify these centres and their related raw materials through a compositional approach. However, no data was available for core-formed vessels from sites on the Ukrainian Black Sea coast, and the first results are presented in this study.

To investigate their composition and production techniques, the samples were analysed using Optical Microscopy and SEM-EDS. The results confirmed a soda-lime-silica glass composition, with natron as the fluxing agent and sand as the silica source. Micromorphological and chemical characterization provided insights into manufacturing techniques, particularly about the bubble arrangement, and the deliberate use of colorants and opacifiers.

The analysis of the glass matrix based exclusively on elemental composition enabled a classification according to the system proposed by Lü et al..<sup>[1]</sup> This classification method applies to materials contemporary with those categorized within the Mediterranean Groups system, but offers more precise insights into the origin of raw materials and production centres. The analysis identified the majority of artefacts as Type II, indicating a Syro-Palestinian coastal origin for the silica raw material, while a smaller subset corresponds to Type III, characterized by higher Fe<sub>2</sub>O<sub>3</sub> levels, suggesting the use of Egyptian sands in their production. Further studies on trace elements will be necessary to provide a more detailed classification.

Acknowledgements: This research has been supported by funding of the "Ministero dell'Università e della Ricerca" (Italy) Bando Prin 2022 - Progetto CoMAR; the support of the Rakow Grant 2024; MSCA-101150345 is also acknowledged.

<sup>&</sup>lt;sup>4</sup>Department of Earth Science and Geoenviroment, University of Bari "Aldo Moro", via Orabona, 4 – 70126 Bari (Italy)

<sup>[1]</sup> Q. Lü et al., Scientific Reports 2021, 11.

### MULTI-ANALYTICAL APPROACH FOR THE CONSERVATION OF THE URBAN MURAL NIDO DI VESPE BY LUCAMALEONTE

### <u>Sara De Angelis</u>, <sup>1,2</sup> Rebecca Picca Orlandi, <sup>1,2</sup> Michela Renna, <sup>1</sup> Paola Mezzadri, <sup>1</sup> Giancarlo Sidoti <sup>1</sup>

<sup>1</sup>Istituto Centrale per il Restauro (ICR), Rome <sup>2</sup>Dipartment of Environmental Biology, University La Sapienza, Rome sara.deangelis-01@cultura.gov.it

In the last decades, contemporary muralism, particularly those related to *street* and *urban* art, has emerged as a form of artistic expression also with a strong socio-political denunciation value. An emblematic case is the mural painting *Nido di Vespe* (Fig.1), created in 2014 by Lucamaleonte in the Quadraro district of Rome (M.U.Ro – Museum of Urban Art of Rome). The artwork commemorates the anti-Nazi resistance of the neighborhood, which was known for its opposition to the German occupation during the Second World War and was consequently referred to as a "wasps' nest" by the Gestapo commander Kappler.

The durability and the conservation of these artworks are strongly compromised by environmental and anthropic factors to which they are constantly exposed. This vulnerability is exacerbated by the complexity of the constitutive materials (i.e. polymeric mixtures, pigments, fillers, and additives) that are particularly susceptible to the combined action of sunlight, air pollution, and thermo-hygrometric variations, accelerating degradation processes.

The urban mural shows widespread degradation morphologies, where the *fading* phenomenon is the most important one; the latter affects the yellow paint in the wasps' bodies, which has almost completely disappeared. Additionally, graphic vandalism with blue spray paint has compromised the artwork's overall visual perception introducing improper shapes and colour. A preliminary *in situ* diagnostic campaign was conducted to support the conservation process and to fully understand the original materials and techniques, as the degradation phenomena. A portable FTIR instrumentation was also used, followed by laboratory analyses through FTIR spectroscopy, PyGC/MS, and SEM-EDS, due to the size of the mural painting (90 m²). This multi-analytical approach contributed to the reconstruction of the stratigraphy of the urban mural, from the identification of the materials used both in the preparatory drawing and in the paint layers, to the characterization of the chemical composition of the binding media used in the graphic vandalism, thus assessing their impact on the original paint layer.

This contribution is part of broader research in the European PNRR project CHANGES, aimed at defining conservation protocols for public contemporary mural art based on eco-compatible cleaning materials and protective systems with self-cleaning and biocidal properties.



Figure 1: Overall view of the mural "Nido di Vespe", captured with Polycam software

Acknowledgements: David Diavù Vecchiato artist and curator of the project (M.U.Ro), the artist Lucamaleonte

## CHASING COLORS: RECONSTRUCTING ABRAHAM MIGNON'S DEGRADED YELLOW ROSE WITH HISTORICALLY APPROPRIATE PIGMENTS

Nouchka De Keyser, 1,2,3,4\* Katelyn Rovito, 5 Fréderique T. H. Broers, 1,2,4,6 Francesca Gabrieli, 1 Frederik Vanmeert, 1,2 Steven De Meyer, 1,7 Erma Hermens, 8 Geert Van der Snickt, 2,3 Koen Janssens, 1,2,3 Katrien Keune 1,4

<sup>1</sup>Rijksmuseum, Museumstraat 1, 1070 DN Amsterdam, The Netherlands
<sup>2</sup>University of Antwerp, Department of Physics, AXIS, Groenenborgerlaan 171, B-2010 Antwerp, Belgium
<sup>3</sup>University of Antwerp, Faculty of Design Sciences, ARCHES, Mutsaardstraat 31, B-2000 Antwerp, Belgium
<sup>4</sup>University of Amsterdam, van 't Hoff Institute for Molecular Sciences, 1090GD Amsterdam, The Netherlands
<sup>5</sup>Wintherthur/ University of Delaware, Program in Art Conservation, 5105 Kennett Pike, Wintherthur DE 19735
<sup>6</sup>Utrecht University, Inorganic Chemistry and Catalysis, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands
<sup>7</sup>Royal Institute for Cultural Heritage, Laboratories, Jubelpark 1, 1000 Brussels, Belgium
<sup>8</sup>Hamilton-Kerr Institute and Conservation and Science Division, Fitzwilliam Museum, University of Cambridge,
Trumpington Street, Cambridge, CB2 1RB, United Kingdom

n.de.keyser@rijksmuseum.nl

Abraham Mignon's *Still Life with Flowers and a Watch* (c.1660-1679), from the collection of the Rijksmuseum, features a yellow rose that has significantly degraded over time. The original light and shadow modeling are lost due to the degradation of natural orpiment and yellow lake, leaving the rose appearing flat compared to other flowers in the painting. This poster presentation will highlight the significance of an interdisciplinary approach—integrating reconstruction-based research with technical analysis and historical source research—to approximate the rose's original intended appearance.

In De Keyser et al.,<sup>[1]</sup> a multimodal combination of chemical and optical imaging techniques, including non-invasive macroscopic X-ray powder diffraction (MA-XRPD) and macroscopic Xray fluorescence imaging (MA-XRF), was used to understand the painting technique and the transformation of the original intended appearance of the rose into its current degraded state. MAXRPD detected lead arsenates (mimetite, schultenite) and arsenolite, secondary products of orpiment, which, along with the yellow lake's fading, altered the painting's original light-shadow modeling. MA-XRF element maps, nevertheless, still enabled to recapture the rose's once-visible, meticulously applied highlights and shadows. Based on the results from the technical analysis, an informed reconstruction using historically appropriate materials and techniques was undertaken, aiming to achieve a closer approximation of the rose's original intended appearance. The rose was reconstructed from the ground up to the top paint layers, and additional paint outs were made to assess the workability, grinding and optical properties of natural orpiment, when used alone or mixed with other pigments such as gypsum and quartz. Cross-section analysis and MA-XRF imaging were used to comparatively assess the reconstructions against the original painting, which

retrospectively proved useful to better understand the detection limits of the imaging techniques while also revealing additional complexities and challenges in pursuit of the ground truth.











Figure 1: (A) Abraham Mignon (1640-1679), Still life with Flowers and a Watch, c. 1660-1679, Oil on Canvas, 75x60 cm, inv. nr. SK-A-268, (B) detail and (C) corresponding arsenic distribution map (D) reconstruction, and (E) corresponding arsenic distribution map.

#### "CON QUESTA ROSETTA TOCCA I LABBRI E LE MELUZZE DELLE GOTE" VISUALIZING CENNINI'S RECOMMENDATIONS ON FLESH-TONE BUILD-UP THROUGH MA-XRF

#### Giulia Sara de Vivo<sup>1</sup>

<sup>1</sup>Rijksmuseum, The Netherlands G.de.Vivo@Rijksmuseum.nl

How flesh tones were built-up in Florentine XIV century tempera panel paintings is codified in Cennino Cennini's contemporary treatise Il Libro dell'arte. Above the extensive cool greenish underlayer he prescribes applying a warm pink partial underlayer to achieve blush on the cheeks: "con pennello di setole morbido ... va' sopra il tuo viso ... e con questa rosetta tocca i labbri e le meluzze delle gote". He even specifies which pigment should be used for this: "... e dove in muro fai le tue rosette di cinabrese ... in tavola vuole essere di cinabro".[1] Underlayers somehow shimmering through the myriad of overlayed and intermeshed thin brushstrokes typical of tempera technique, have an important role in achieving the final tone and volume desired. Not intended to be seen, these underlayers have long remained hidden, but new possibilities are offered by macro Xray fluorescence scanning (MA-XRF) that allows one to visualize the spatial distribution of elements on the (sub)surface of paintings. Within the work frame of the Italian paintings catalogue project in the Rijksmuseum, a group of XIV century Florentine paintings has been studied by means of MA-XRF. Elemental distribution maps for mercury (Hg-L), a marker for the pigment vermillion (cinabro), allowed to visualize the way in which Cennini's pink (rosetta) was laid-in; highlighting differences in application of this intermediate layer (i.e. round shapes, concentric circles of increasing intensity, or juxtaposed wide parallel brushstrokes: respectively fig. 1 a,b,c) so diverse as to suggest these might be indicative of different artists and workshop practices.

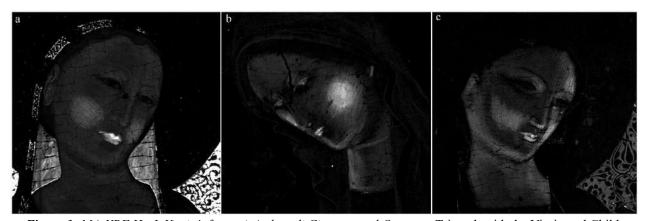


Figure 1: MA-XRF Hg-L Virgin's face; a) Andrea di Cione named Orcagna, Triptych with the Virgin and Child, Saints Mary Magdalene and Ansanus, 1350, SK-C-1608; b) Agnolo Gaddi (circle of) Madonna of Humility, c. 1390, SK-A-3031; c) Lorenzo Monaco (school of) Virgin and Child, 1381-1410, SK-A-4005.

<sup>[1] &</sup>quot;with a soft bristle brush ... go over your face ... and with this pink touch the lips and the little apples of the cheeks"; "... and whereas on the wall you make your pinks with cinabrese ... on panel they should be made with vermilion": C. Cennini, *Il libro dell'Arte (end of the XIV c.)* **1971**, F. Brunello ed., Vicenza; chapter LXVII (p.79) and chapter CXLVII (p.152) respectively (English translation in D.V. Thompson, *The Craftman's Handbook*, New York, **1960**, p.46 and p.94).

### HIGH RESOLUTION MULTIMODAL IMAGES REGISTRATION OF THÉO VAN RYSSELBERGHE'S *LA DAME EN BLANC* (1904)

#### Nathan de Vries,<sup>1</sup> Catherine Defeyt,<sup>1,2</sup> Edène Derzelle,<sup>1</sup> David Strivay<sup>1</sup>

<sup>1</sup>Université de Liège, Belgium <sup>2</sup>Royal Museum of Fine Arts of Belgium, 1000 Brussels, Belgium <u>ndevries@uliege.be</u>

Multimodal imaging techniques—ranging from high resolution photography under visible or UV light, infrared reflectography, X-ray radiography, hyperspectral imaging to macro XRF—are essential for unveiling key information about the material composition, hidden underdrawings, and conservation and restoration needs of paintings. Yet, comparing these multimodal images often present significant technical challenges. Often assembled from numerous local images, these images frequently suffer from resolution mismatches, capture or reconstruction-induced deformations, and the massive scale of gigapixel images.

To address these issues, a two-step image registration process has been employed based on mutual information—a robust metric for comparing multimodal images using the *Insight Segmentation* and *Registration Toolkit*.<sup>[1-3]</sup> Initially, an affine transformation establishes a coarse alignment, which is then refined using a B-spline transformation. In both steps, a pyramidal approach was implemented that progressively registers the images at multiple scales to enhance performance and accuracy. A LBFGSB optimizer is used to maximize mutual information, and all images are rescaled and aligned to a common reference—typically the high-resolution visible light photograph.

Once registered, the images are tiled using the Zoomable plugin from Photoshop and integrated into a custom viewer that allows smooth navigation and comparison between different modalities, even for gigapixel-scale images.

This method was applied to register multimodal images of the painting *La dame en blanc* (1904) by Théo Van Rysselberghe (1862–1926), a Belgian neo-impressionist painter. This artwork is part of the collection at the Museum of Fine Arts in Liège. The painting was studied as part of a corpus of nine paintings from Théo Van Rysselberghe in the context of the *Face to Face* project, focusing on the technical analysis of facial representation in European painting from the 15th to the 20th century.

<sup>[1]</sup> S. N. Wood, Y. Li, G. Shaddick, A. Augustin, Journal of Statistical Software 2018, 86, 1–39.

<sup>[2]</sup> Z. Yaniv, B. C. Lowekamp, H. J. Johnson, R. Beare, Journal of Digital Imaging 2018, 31, 290-303.

<sup>[3]</sup> B. C. Lowekamp, D. T. Chen, L. Ibáñez, D. Blezek, Frontiers in Neuroinformatics 2013, 7, 45.

#### LOOSING SALVADOR DALI'S ST ANTHONY?

### <u>Catherine Defeyt</u>,<sup>1,2</sup> Francisca Vandepitte,<sup>2,3</sup> Edène Derzelle,<sup>1</sup> Nathan de Vries,<sup>1</sup> Philippe Walter,<sup>4</sup> David Strivay<sup>1</sup>

<sup>1</sup>Centre Européen d'Archéométrie, University of Liège, Belgium

<sup>2</sup>Royal Museum of Fine Arts of Belgium, Belgium

<sup>3</sup>Vrije Universiteit Brussel, Belgium

<sup>4</sup>Laboratoire d'Archéologie Moléculaire et Structurale, Sorbonne Université - CNRS, France

catherine.defeyt@uliege.be

The temptation of St Anthony dated 1946, which is one of the most iconic paintings of the Catalan surrealist, currently displays worrying surface condition in specific areas, for instance the St Anthony character. The problematic paint layers typically exhibit uneven transparency and rugged surfacee. To characterize the degradation mechanisms that have taken place and to identify the involved materials, Dali's masterwork has been investigated in situ through a large panel of imaging and analytical techniques, including MA-XRF, Raman and FT-IR spectroscopies, Hyperspectral Imaging, XRD, IR Reflectography, Radiography and Highresolution photography. The obtained results were subsequently assessed against the material and technical information collected from Dali's 50 secrets magiques, [1] as well as against archive photographs showing The temptation of St Anthony. This in-depth study permitted to evidence the key role of amber based medium regarding the very unusual aspect of the degraded pictorial layers, due to the formation of amorphous chloride zinc salt resin acids.

<sup>[1]</sup> S. Dali, "50 secrets magiques" 1974, Edita/Denoël, Lausanne.

### OUT OF THE BLUE: RACHEL RUYSCH'S (1664 – 1750) USE OF BLUE GROUNDS

#### Kirsten Derks, 1 Erin Mysak, 2 Richard Newman<sup>3</sup>

<sup>1</sup>University of Antwerp, Belgium
<sup>2</sup>Harvard Library, United States of America
<sup>3</sup>Museum of Fine Arts, Boston, United States of America
kirsten.derks@uantwerpen.be

Rachel Ruysch was one of the most successful early modern flower painters, yet her paintings and her artistic practice have not been studied before. In the context of a technical research project into the artistic practice of Rachel Ruysch (1664 -1750), a number of paintings by the artist were thoroughly examined. This included the panel painting *A Still Life with Flowers in a Glass Vase on a Marble Table before a Niche* (1742), now part of the collection of the Museum of Fine Arts, Boston. The examinations showed that she used a blue ground to prepare this painting. A paint sample was extracted to study the materials and the layer build-up of the ground. The paint sample was examined using a variety of analytical techniques, including SEMEDS and Raman spectroscopy. The blue pigment in the ground layer was identified as Prussian blue, a pigment that had only been synthesized a few decades before Ruysch painted her *Still Life with Flowers*.

As far as we know today, this is the first time a blue ground was used in early modern oil painting. This paper deals with the results of the examinations of Ruysch's 1742 painting and her use of Prussian blue in the ground layers. We will explore how Ruysch used her materials and exploited the blue ground in creating optical effects. In other late paintings by Ruysch, also examined in the context of the same research project, it can be seen that the colour blue plays a prominent role. The blue ground can be seen as one of the many strategies employed by Ruysch to emphasize the colour blue. We will compare Ruysch's working methods with those of other specialized flower painters and the painting techniques identified in other paintings by Ruysch. Moreover, this paper delves into Ruysch's inspirations for this blue ground: there might be links with the use of blue paper in early modern drawings, as well as technical links with watercolour painting.

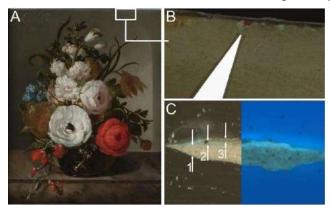


Figure: (A) Rachel Ruysch, A Still Life with Flowers in a Glass Vase on a Marble Table before a Niche, 1 742. Oil on panel, 24 x 19 cm. Museum of Fine Arts, Boston, inv.no. 2023.336. The white square indicates the area in B. (B) Area where the paint sample was extracted. (C) Paint sample 2023 336 S1, 20x in VIS and UV.

Acknowledgements: FWO, Flanders State-of-the-Art Fellowship, Fondation Custodia.

### IDENTIFYING THE BLOCKX PAINTS FINGERPRINT IN THÉO VAN RYSSELBERGHE'S PORTRAIT DE MADAME CHARLES MAUS (1890)

<u>Edène Derzelle</u>,<sup>1</sup> David Strivay,<sup>1</sup> Francisca Vandepitte,<sup>2,3</sup> Davy Depelchin<sup>2</sup> and Catherine Defeyt<sup>1,2</sup>

<sup>1</sup>CEA-Centre Européen d'Archéométrie, University of Liège, Belgium <sup>2</sup>Royal Museum of Fine arts of Belgium, Belgium <sup>3</sup>Vrij Universiteit Brussel, Belgium <u>ederzelle@uliege.be</u>

The Belgian paint manufacturer Blockx is at the heart of a project led by the European Centre for Archaeometry (CEA). As part of this initiative, both documentary and material archives, compiled since the company's founding in 1865, are being analyzed to gain a deeper insight into its history and the materials used in its products. These documents reveal paint orders placed by various artists, including Théo Van Rysselberghe (1862–1926), a key figure of Belgian NeoImpressionism. His works are also being studied as part of the *Face to Face* project, which focuses on the technical analysis of facial representation in European painting from the 15th to the 20th century.

As part of this study, a corpus of nine paintings by Théo Van Rysselberghe was analyzed in situ using imaging methods (high-resolution photography, infrared reflectography, X-ray radiography, digital microscopy) and non-invasive analytical techniques (MA-XRF, Raman spectroscopy, hyperspectral imaging). This presentation focuses on the painting *Portrait de Madame Charles Maus* (1890), belonging to the collection of the Royal Museums of Fine Arts of Belgium (RMFAB), as it marks a turning point in the artist's career, being one of his earliest pointillist works. Pointillism, typically executed with pure or minimally mixed colors and, in this case, without varnish. These elements facilitate the analysis and identification of the pigments used.

The objective of this study is to determine which specific paints from the Blockx range Van Rysselberghe used in his pictorial layer. To achieve this, data obtained from the painting are compared not only with a manufacturer's color chart dating back to 1909 but also with three paint boards belonging to Emile Claus (1849–1924), a prominent Belgian painter and a leading figure of Luminism. These boards, all dated to 1909, contain paint swatches from both Blockx and Lefranc Bourgeois, a French paint manufacturer established in 1720. By analyzing and comparing these references, this study aims to highlight the distinctive fingerprint of Blockx paints in *Portrait de Madame Charles Maus* (1890).

### STUDIES FOR CLEANING AND SPECTROSCOPIC CHARACTERIZATION OF STREET ART

#### G. Di Cara, S. Prati, M. Paolantoni, F. Rosi, A. Menichetti, F. Ramacciotti, G. Sciutto 1

<sup>1</sup>University of Bologna, Microchemical and Microscopy Art Diagnostic Laboratory, Ravenna, Italy 
<sup>2</sup> University of Bologna, Department of Chemistry G. Ciamician, Bologna, Italy 
<sup>3</sup>University of Perugia, Department of Chemistry, Biology and Biotechnology, Perugia, Italy 
<sup>4</sup>Institute of Chemical Sciences and Technologies "G. Natta"-CNR (CNR-SCITEC), Perugia, Italy 
giulia.dicara2@unibo.it

The growing recognition of street art as a valuable form of artistic and social expression has increased interest in its conservation. Originally associated with transgression, now urban artworks serve as a mean of collective cultural enrichment and contribute to the enhancement of public spaces. [1] In this context, even the interest of researchers and restorers is moving towards the conservation of street art objects, against natural detriment and human vandalism. As part of the Italian project "PRIN 2020 Superstar" (https://prin2020superstar.dcci.unipi.it/), we are optimizing innovative chemical cleaning systems for the selective removal of vandalic graffiti, preserving the underlying artwork. The proposed cleaning system, based on electrospun (ES) nonwovens as retentive medium of solvents, [2,3] is respectful for the operator, the artwork, and the environment. Firstly, a preliminary chemical-physical investigation of several green solvents, such as γ-valerolactone (GVL), water (W), dimethyl carbonate (DMC), ethanol (EL), cyrene (CY), and binary mixtures of them, has been carried out with the aim of explaining their macroscopic properties on molecular basis, facilitating the selection of effective cleaning solution. Specifically, exploring molecular interactions and chemical-physical behaviour of the system depending on the concentration, solubility parameters were investigated by Teas Chart and compared with UV-Vis, Raman and ATR-FTIR data. Next the cleaning system, based on pullulan nonwovens, GVL and DMC, has been applied both to artificially aged and unaged mockups of bilayer spray paint, revealing that the solubility of the upper paint layer to be removed changed depending on the state of preservation of the underlying paint. In order to understand the macroscopic behaviour in terms of solubility and to determine the microscopic molecular composition, according to the degree of ageing, pristine and aged standard samples were characterized with ATR-FTIR and Raman microscopy. It has been observed an enrichment of the apolar amide additive at the surface, upon induced ageing. Finally, ATR-FTIR data were analyzed using principal component analysis (PCA) to extract additional information. This approach contributes to the development of tailored conservation strategies for street art, respecting both artistic integrity and environmental sustainability.

Acknowledgements: Sustainable Preservation Strategies for Street Art (SuPerStAr) funded by MUR, PRIN.

<sup>[1]</sup> J. I. Ross, "Routledge handbook of graffiti and street art" 2016, ed. Routledge.

<sup>[2]</sup> F. Ramacciotti, G. Sciutto, L. Cazals, D. Biagini, S. Reale, I. Degano, M. L. Focarete, R. Mazzeo, M. Thoury, L. Bertrand, C. Gualandi, S. Prati, *Journal of Colloid and Interface Science "Microporous electrospun nonwovens combined with green solvents for the selective peel-off of thin coatings from painting surfaces"* **2024**, 663, 869 – 879.

<sup>[3]</sup> A. Menichetti, F. Ramacciotti, G. Sciutto, M. L. Focarete, M. Montalti, S. Prati, C. Gualandi, ACS Applied Materials & Interfaces "Nanofibrous Photothermal Materials from Natural Resources: A Green Approach for Artwork Restoration" 2024, 16(50), 69829-69838.

## SPECTROSCOPIC IMAGING AND ANALYSIS OF ISLAMIC-AFRICAN PAPER AMULET AND TALISMAN COLLECTION AT THE SLOVENE ETHNOGRAPHY MUSEUM

Abdelrazek Elnaggar,<sup>1</sup> Hend Mahgoub,<sup>1</sup> Laura Maestro-Guijarro,<sup>2</sup> Ana Crespo,<sup>3</sup> Paula María Carmona-Quiroga,<sup>2</sup> Santiago Sánchez-Cortés,<sup>3</sup> Žiga Rehar,<sup>4</sup> Gregor Kos,<sup>4</sup> Marko Frelih,<sup>4</sup> Matija Strlič,<sup>1</sup> Mohamed Oujja,<sup>2</sup> Marta Castillejo<sup>2</sup>

<sup>1</sup>Heritage Science Laboratory Ljubljana (HSLL), Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, 1000, Slovenia

<sup>2</sup>Instituto de Química Física Blas Cabrera, IQF-CSIC, Madrid, 28006, Spain

<sup>3</sup>Instituto de Estructura de la Materia, IEM-CSIC, Madrid, 28006, Spain

<sup>4</sup>The Slovene Ethnography Museum (SEM), Ljubljana, 1000, Slovenia

<u>abdelrazek.elnaggar@fkkt.uni-lj.si</u>

The technology of Islamic papermaking has not yet been comprehensively analysed historically or scientifically. Unlike European paper, knowledge of Islamic papermaking techniques and materials still requires in-depth research to deepen the understanding of Islamic material culture and improve conservation. In this study, we present a multi-analytical study of the 19th and 20th C Islamic-African amulet and talisman<sup>2</sup> paper collection of the Slovene Ethnography Museum in Slovenia (SEM), which originated in Mali, Chad and Niger. Following the Ethical Sampling Protocol,<sup>3</sup> a multi-analytical approach was followed using hyperspectral imaging (HSI), nearinfrared (NIR) and infrared spectroscopy (FTIR-ATR), as well as laser-induced breakdown spectroscopy (LIBS), laser-induced fluorescence (LIF) and Raman spectroscopies. We carried out examinations and analyses of selected objects to characterise the unique collection of inked and polychrome Islamic papers of the SEM thus providing key information for the understanding

of technological aspects, including the fibres furnish, sizing, inks, pigments, and dyes. The results show the use of verity of materials including the softwood fibres, iron-gall ink, Alizarin, and vermillion. The results will enable museum staff to make informed conservation decisions and allow curators to plan the exhibition of the collection to the public. The collection was analysed as part of the European H2020 IPERION HS (Integrated Platform for the European Research Infrastructure on Heritage Science) transnational access program in collaboration between the Heritage Science Lab at the University of Ljubljana (Slovenia), the Slovenian node of the European Research Infrastructure for Heritage Science (E-RIHS.si), and the Laser Laboratory for Heritage Science (LLHS) at IQF-CSIC, Madrid (Spain), representing E-RIHS.es, Spain.



Figure 1: An exa mple of inked and polychromed talisman from SEM

<sup>[1]</sup> H. Mahgoub, T. Bardon, D. Lichtblau, et al., Herit. Sci. "Material properties of Islamic paper" 2016, 4, 34.

<sup>[2]</sup> Y. Al-Saleh, *Heilbrunn Timeline of Art History "Amulets and Talismans from the Islamic World"* **2010**, New York: The Metropolitan Museum of Art. 2000.

<sup>[3]</sup> M. Strlič and Q. Anita, "Ethical Sampling - Icon Heritage Science Group survey report" 2017.

## NON-INVASIVE MA-XRPD AND MA-XRF ANALYSIS OF EGYPTIAN WOODEN FUNERARY STELAE FROM THE HELLENIC NATIONAL ARCHAEOLOGICAL MUSEUM

<u>Francesca Falcone</u>,<sup>1,2</sup> Nikoletta Kanella Kladouri,<sup>4,5</sup> Michela Botticelli,<sup>1,2</sup> Kalliopi Tsampa,<sup>4</sup> Eva Luna Ravan,<sup>1,3</sup> Gianluca Santagati,<sup>1,2</sup> Argyro Grigoraki,<sup>5</sup> Panagiotis Lazaris,<sup>5</sup> Ioannis Panagakos,<sup>5</sup> Kalliopi Tsakri,<sup>5</sup> Francesco Paolo Romano,<sup>1,2</sup> Costanza Miliani,<sup>1</sup> Andreas Germanos Karydas,<sup>4</sup> Claudia Caliri<sup>1,2</sup>

<sup>1</sup>Istituto di Scienze del Patrimonio Culturale, Consiglio Nazionale delle Ricerche (ISPC-CNR), Italy

<sup>2</sup>Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali del Sud (INFN-LNS), Italy

<sup>3</sup>Department of Science of Antiquities, University of Rome 'Sapienza', Italy

<sup>4</sup>Institute of Nuclear and Particle Physics, NCSR 'Demokritos', Greece

<sup>5</sup>Hellenic National Archaeological Museum, Greeece

francesca.falcone@cnr.it

Egyptian wooden funerary stelae were used from the Old Kingdom to the Third Intermediate Period, covering a period of about 1500 years, with their highest prevalence during the New Kingdom. [1] The stelae in the Egyptian Antiquities Collection of the Hellenic National Archaeological Museum (HNAM) in Athens, Greece, are part of a donation from Alexandros Rostovits, a Greek expatriate and antiquities collector from Cairo who donated his collection to the museum in 1904. Likely from the 25th Dynasty (712-664 BC), these funerary objects preserved the deceased's name and ensured divine protection through symbolic imagery and hieroglyphic inscriptions.

Advanced analytical techniques on artwork paint layers reveal production processes, evolution of colour palettes over time, and degradation patterns of these wooden artifacts. In this study, through non-invasive X-ray-based techniques available at the XRAYLab laboratory of ISPCCNR in Catania and INPP-NCSR "Demokritos" in Athens, seven Egyptian stelae from the collection of the HNAM were analyzed. The investigation, including MA-XRD and MA-XRF mapping, enabled the identification of chemical elements and mineralogical phases in the pigments and preparation materials. Results revealed significant Ca content, in some cases associated with sulfur, indicating variations in support preparation.<sup>[2]</sup> In red pigments two distinct types of compounds were identified, Fe and As based, while in the yellows there is only arsenic. Only one stela presents a different type of red, with a mixture of minium and hematite, and ochre for the yellow pigments; of this minimum is mostly associated with the Ptolemaic and Roman periods.<sup>[3]</sup> Traces of Pb and Sn were identified in Cu-based pigments, indicating that some samples may have been produced using an alternative method, where leaded bronze scraps were reused as copper source for the synthesis of Egyptian blue.<sup>[4]</sup> The data obtained suggests that pigment use may define different production classes, correlated with stylistic variations in the decorative representations of the artifacts, in line with the production period. The results of this study, integrated with archaeological research, significantly enhance the understanding of materials, sources, and production techniques of Egyptian funerary stelae, placing them within more defined historical periods.

Acknowledgements: PNRR projects: 1) CHANGES, "Science and Technologies for Sustainable Diagnostics of Cultural Heritage", PE0000020, CUP B53C22003890006; 2) H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029, CUP B63C22000730005; 2; E-RIHS European Infrastructure of Heritage Science (E-RIHS).

<sup>[1]</sup> M. Abdelrahiem. Studien Zur Altägyptischen Kultur 2011, 40, 1–8.

<sup>[2]</sup> M. F. Ali et al., Egyptian Journal of Archaeological and Restoration Studies 2022, 12, 187-196.

<sup>[3]</sup> D. A. Scott., Stud. Conserv. 2016, 61, 185-202.

<sup>[4]</sup> S. Schiegl, A.E. Goresy, Archaeometry 2006, 48, 707-709.

## ENHANCING INSIGHTS INTO IRON GALL INKS: AN IN-DEPTH STUDY OF INK REPRODUCTIONS IN PORTUGUESE HISTORICAL DOCUMENTS

Margarida Nunes,<sup>1</sup> Joana Costa Vieira,<sup>2</sup> Ana Paula Costa,<sup>2</sup> Maria Emília Amaral,<sup>2</sup> Bruno J. C. Vieira,<sup>3</sup> João Carlos Waerenborgh,<sup>3</sup> Helena I. S. Nogueira,<sup>4</sup> Scott G. Mitchell,<sup>5</sup> Ana Claro,<sup>6</sup> Teresa Ferreira<sup>1,7</sup>

<sup>1</sup>HERCULES Laboratory/IN2PAST, University of Évora, Évora, Portugal

<sup>2</sup>FibEnTech-UBI, University of Beira Interior, Covilhã, Portugal

<sup>3</sup>C<sup>2</sup>TN, DECN, University of Lisbon, Lisbon, Portugal

<sup>4</sup>CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal

<sup>5</sup>INMA, CSIC-Universidad de Zaragoza, Zaragoza, Spain

<sup>6</sup>CHAM, NOVA School of Social Sciences and Humanities, Lisboa, Portugal

<sup>7</sup>Chemistry and Biochemistry Department, ECT, University of Évora, Évora, Portugal

tasf@uevora.pt

Iron gall inks (IGIs) were the paramount writing medium in the Western world for centuries until the advent of synthetic inks in the late 19th century. [1,2] The severe decay of manuscripts associated with IGI poses a significant challenge to worldwide written heritage, much of which is already in dire condition. [2] The complexity of IGI-induced degradation in cellulosic supports underscore the need for further studies.

This work employed a two-fold methodology to study IGI reproductions based on 17th and 18thcentury recipes from historical Portuguese documents. We investigated both fresh and sixmonth naturally aged precipitates, along with the supernatant solutions (dried inks), and assessed the impact of IGIs on Whatman® paper during artificial ageing. Techniques such as FTIR, Raman and <sup>57</sup>Fe Mössbauer spectroscopies, and X-ray diffraction were utilised. Our findings revealed that iron (II) sulfates were the primary crystalline phase in the precipitates, while dried inks consisted of distinct Fe(III)-polyphenol (PPh) complexes. Over time, Mössbauer parameters indicated alterations in the complex structure, accompanied by the formation of Fe(II) sulfates. IGI-induced degradation in artificially aged brushed and written mockups was attested by the formation of Fe(II) oxalate, leading to the depletion of the Fe(III)-PPh fraction. The physical properties and XRD analysis also corroborated that the cellulose structure became increasingly degraded with ageing. Notably, the 18th-century ink, characterised by a higher weight ratio of Fe(II) sulfate to gallnuts (i.e. unbalanced composition), exhibited the most aggressive effects on the cellulosic support. Ink concentration per surface area emerged as a key factor influencing the cellulosic support weakness.

Acknowledgements: FCT supported this research through the Holy Bodies | An Atlas of the Corpi Santi in Portugal 10.54499/2022.01486.PTDC, 10.54499/UIDP/04449/2020, 10.54499/UIDB/04449/2020 & LA/P/0132/2020 (HERCULES Laboratory and IN2PAST); UIDB/Multi/04349/2019, UID/FIS/04559/2021 (C²TN); UIDB/00195/2020 (FibEnTech-UBI); UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020 (CICECO-Aveiro Institute of Materials); SFRH/BD/147528/2019 (PhD fellowship). The authors wish to acknowledge the professional support of the Interdisciplinary Thematic Platform from CSIC Open Heritage: Research and Society (PTI-PAIS) and the Laboratorio de Microscopias Avanzadas (LMA) at the University of Zaragoza for offering access to their instruments and expertise.

<sup>[1]</sup> C. James, in "Proceeding Iron Gall Ink Meet." "The evolution of Iron Gall Ink and its aesthetical consequences" **2000**, A. Brown, E. Jeand Eds., University of Northumbria, Newcastle, 13–22.

<sup>[2]</sup> M. Nunes, Micron "A holistic approach to understanding the iron-gall inks in the historical documents of the Portuguese Inquisition (1570-1790)" **2023**, 165, 103396.

## THE PITCH PROJECT: A LABORATORY-BASED PHASE CONTRAST X-RAY IMAGING SYSTEM FOR THE STUDY AND CHARACTERIZATION OF CULTURAL HERITAGE MATERIALS

A. Re,<sup>1,2</sup> E. Di Francia,<sup>1,2</sup> <u>C. Garagiola</u>,\*1,2 L. Guidorzi,<sup>1,2</sup> A. Lo Giudice,<sup>1,2</sup> R. Boano,<sup>3</sup> R. Giustetto,<sup>4</sup> G. Ricchiardi,<sup>5</sup> P. Cerello,<sup>2</sup> E. Fiorina,<sup>2</sup> M. Magalini,<sup>2</sup> M. Marabotto,<sup>2</sup> N. Mosco,<sup>2</sup> L. Ramello,<sup>6,2</sup> D. Trocino,<sup>2</sup> D. Di Martino,<sup>7</sup> G. Marcucci,<sup>7</sup> L. Vigorelli,<sup>7</sup> F. Pozzi,<sup>8</sup> C. Ricci<sup>8</sup>

<sup>1</sup>Dipartimento di Fisica, Università degli Studi di Torino, Torino, Italy

<sup>2</sup>INFN, sezione di Torino, Torino, Italy

<sup>3</sup>Dipartimento di Scienze della Vita e Biologia dei Sistemi, Università degli Studi di Torino, Torino, Italy

<sup>4</sup>Dipartimento di Scienze della Terra, Università degli Studi di Torino, Torino, Italy

<sup>5</sup>Dipartimento di Chimica, Università degli Studi di Torino, Torino, Italy

<sup>6</sup>Dipartimento per lo Sviluppo Sostenibile e la Transizione Ecologica, Università del Piemonte Orientale,

Vercelli, Italy

<sup>7</sup>Dipartimento di Fisica "G. Occhialini", Università di Milano-Bicocca e INFN, sezione di Milano-Bicocca, Milano, Italy

<sup>8</sup>Centro per la Conservazione ed il Restauro dei Beni Culturali "La Venaria Reale", Venaria Reale (Torino), Italy \*chiara.garagiola@unito.it

X-ray imaging is a standard tool for non-invasive inspection of the internal structure of materials. The conventional absorption contrast method is particularly beneficial for characterizing medium density samples or distinguishing materials with different attenuation powers but leads to poor image quality when the sample is weakly absorbing, typically in materials composed of light elements. On the contrary, Phase-Contrast (PC) X-ray imaging is an effective technique for detecting low contrast details in weakly absorbing samples, as it provides high-quality information on micro-structural features.<sup>[1]</sup> A coherent X-ray beam is the ideal tool to develop phase-sensitive X-ray imaging, and some techniques have already been implemented at synchrotron radiation facilities. [2] Among the PC methodologies, X-ray Grating Interferometry (GI), which provides differential phase and scattering (dark-field) images in addition to the standard absorption-based image, enables the realisation of systems that can be implemented in a laboratory setting. By using a liquid-metal-jet source, such a system will enable a major increase of the image acquisition speed with maintained resolution, thereby opening extremely interesting prospects in the cultural heritage (CH) field, such as conservation, archaeology, archaeometry, anthropology, paleopathology. The PITCH project (funded in the framework of PRIN2022) aims at designing, developing and characterising a laboratory GI-PC imaging setup based on a liquid-anode X-ray source, as well as at investigating and developing different data acquisition methods and algorithms for signal extraction and tomographic reconstruction. The system will be optimized for the analysis of CH materials. A selection of relevant materials, original fragments and possible mock-ups to use for preliminary tests has been made: pigment layers, metallic yarns, textile material, leather, gilding on paper, parchment, cartonnage, Barniz de Pasto, wood artifacts, shells and eggs from archaeological findings, pearls, mummified remains, animals preserved in formalin. Different samples' geometries will be tested as well. The analysis will be carried out to characterize the materials and to understand related issues. The preliminary characterization of mock-ups will lead to the study of real artifacts coming from museums and other cultural institutions.

<sup>[1]</sup> M. Endrizzi, Nuclear Instruments and Methods in Physics Research A "X-ray phase-contrast imaging" **2018**, 878, 88–98.

<sup>[2]</sup> A. Stevenson, Nuclear Instruments and Methods in Physics Research B "Phase-Contrast X-ray Imaging with Synchrotron Radiation for Materials Science Applications" 2003, 427-435.

### DEVELOPMENT OF A SMARTPHONE-BASED COLOR ANALYSIS METHOD FOR ILLUMINATED MANUSCRIPT STUDY

Marc Pedrol,<sup>1</sup> Diego A. Ahumada F.,<sup>1</sup> Georgios Magkanas,<sup>1</sup> Victor Arrés,<sup>1</sup> Neus Verger,<sup>2</sup> Anna Rosell,<sup>2</sup> Javier Saurina,<sup>1</sup> <u>José F. García</u><sup>1</sup>

<sup>1</sup>Department of Chemical Engineering and Analytical Chemistry, Faculty of Chemistry, Universitat de Barcelona, Spain

<sup>2</sup>Centro de Recursos para el Aprendizaje y la Investigación. Biblioteca de Fons Antic, Universitat de Barcelona, Spain.

jfgarcia@ub.edu

The study of illuminated manuscripts can include both the punctual analysis for identifying the pigments included in the decoration and the imaging analysis of the whole miniatures. In both cases, accurate colour recording is essential to progress on documenting, cataloging, and preserving these manuscripts.<sup>[1]</sup> Smartphones could become powerful analytical tools for cultural heritage documentation, providing an accessible and portable alternative to traditional colorimetric equipment<sup>[2]</sup> and extending their capabilities from punctual measurement to the capture of the entire image. However, the first step in this journey is obtaining reliable and reproducible color measurements with smartphones and this requires a systematic control of various factors that affect image acquisition and processing.<sup>[3]</sup>

This study presents a comprehensive methodology for objective color evaluation of illuminated manuscripts using smartphone-based colorimetry, complemented by portable XRF analysis for elemental validation. The approach combines response surface methodology for optimizing acquisition parameters (e.g., illumination distance, irradiation angles) with advanced image preprocessing techniques including sampling, noise reduction, and alignment. Different color identification strategies were evaluated, including partitional (k-means, k-medians), densitybased and probabilistic approaches. Color calibration involved multipoint RGB calibration and illuminance corrections using white references and color charts.

The methodology was applied to the analysis of two Books of Hours (Ms1841 from the 15<sup>th</sup> century and Castilian origin and Ms1856 from the 15<sup>th</sup>-16<sup>th</sup> century and Flemish origin). The smartphone-based approach successfully differentiated between red pigments, which were subsequently identified by p-XRF as vermillion (HgS) and minium (Pb<sub>3</sub>O<sub>4</sub>). Additionally, the methodology distinguished between two different gilding compositions, which are traditionally challenging to evaluate through image analysis. All the findings were confirmed by p-XRF, indicating that smartphone-based colorimetry can serve as a reliable, accessible, and non-invasive tool for preliminary pigment characterization in cultural heritage studies. This method offers possibilities for in-situ analysis and preliminary screening before using classical analytical techniques.

<sup>[1]</sup> C. Boust, Y. Arteaga, London Imaging Meeting 2023, 4, 45-50.

<sup>[2]</sup> A. Slavec, N. Sajinčič, V. Starman, Sustainability 2021, 13, 7312-7328.

<sup>[3]</sup> Y. Fan, J. Li, L. Zhang, X. Chen, Y. Hu, Measurement 2021, 171, 108829.

### POLYSACCHARIDES AND PROTEINS FROM MICROALGAE: A NOVEL MATERIAL FOR PAPER CONSERVATION AND RESTORATION

#### Giulia Gasperuzzo,<sup>1</sup> Maria Grazia Ortore,<sup>2</sup> Amina Antonacci<sup>3</sup>

<sup>1</sup>Department of Science of Antiquities, Sapienza University of Rome, Italy
<sup>2</sup>Departement of life and environmental science, Marche Polytechnic University, Italy
<sup>3</sup>Institute of Crystallography, National Research Council, Rome, Italy
giulia.gasperuzzo@uniroma1.it

Research in the field of cultural heritage conservation is increasingly focused on finding environmentally friendly and effective solutions. Using microbiology to address cultural heritage conservation has opened new possibilities for green materials and methods. Traditional cellulose derivatives are still used for paper-based artworks, but there is a growing interest in sustainable biomaterials. Specifically, polysaccharides extracted from microalgae are being explored due to their antioxidant and biodegradable properties, which make them suitable for protecting and restoring paper. Additionally, bio-based hydrogels, created by combining polysaccharides and proteins, offer versatile and environmentally responsible options. By incorporating these biomaterials into conservation practices, we can reduce our dependence on harsh chemicals and promote the long-term, sustainable preservation of cultural heritage. In this context, this research aims to characterise a mixture of polysaccharides and proteins extracted from microalgae culture with sustainable solvents and to explore its application as a consolidant and cleaning agent for paper-based artworks.

Freshwater strains of *Chlamydomonas reinhardtii* (CC125 and SAG 11-32b), as well as marine species of *Porphyridium purpureum sp.* and *Lyngbya sp.*, were selected as known sources of polysaccharides and bioactive compounds with antifungal and antibacterial properties. <sup>[2]</sup> Growth conditions were optimized to provide a satisfactory accumulation of polysaccharides and proteins in the extracts, which were investigated using FTIR and GC-MS. Moreover, colorimetric assays were carried out to quantify the antioxidant capacity and the content of carbohydrates, nucleic acids, and protein residues. The extracts were then applied on paper specimens aged and unaged as a consolidant by brush and as a cleaning agent. To assess the efficacy of the treatment, the paper samples were analysed through FTIR, contact angle, and pH measurements. <sup>[3]</sup> Microscopic examinations were also performed to observe the debris removal and evaluate potential damage to the paper fibers.

<sup>[1]</sup> M. R. Caruso, G. D'Agostino, S. Milioto, G. Cavallaro, G. Lazzara, J. Mater. Sci. 2023, 58, 12954–12975.

<sup>[2]</sup> A. Masi, F. Leonelli, D. Di Luca, L. Celio, G. Gasperuzzo, S. Lunardi, C. Rigon, M. Pitocco, M. Ioele, M. S. Storace, L. Medeghini, A. Antonacci, *Carbohydrate Polymer Technologies and Applications* **2025**, *9*.

<sup>[3]</sup> C. Mazzuca, L. Micheli, M. Carbone, F. Basoli, E. Cervelli, S. Iannuccelli, S. Sotgiu, A. Palleschi, *Journal of Colloid and Interface Science*, **2014**, *416*, 205-211.

### REVEALING THE PAST: NON-INVASIVE PRE-SCREENING METHODS FOR ANCIENT BONES

<u>Lucrezia Gatti</u>,\*1 Giorgia Sciutto,1 Stefano Benazzi,2 Emilio Catelli,1 Fabio Cavalli,3 Lea Legan,4,5 Francesca Seghi,2 Cristina Malegori,6 Paolo Oliveri,6 Sahra Talamo,7 Silvia Prati1

<sup>1</sup>Department of Chemistry "G. Ciamician", University of Bologna, Ravenna Campus, Via Guaccimanni, 42, 48121 Ravenna

<sup>2</sup>Department of Cultural Heritage, University of Bologna, Via degli Ariani 1, 48121 Ravenna
<sup>3</sup>Research Unit of Paleoradiology and Allied Sciences, Laboratorio di Telematica Sanitaria-Struttura Complessa Informatica e Telecomunicazioni, Azienda Sanitaria Universitaria Giuliana Isontina, 34149 Trieste, Italy
<sup>4</sup>Institute for the Protection of Cultural Heritage of Slovenia, Conservation Centre, Poljanska cesta 40, 1000
Ljubljana, Slovenia

<sup>5</sup>National Museum of Slovenia, Prešernova cesta 20, 1000 Ljubljana, Slovenia <sup>6</sup>Department of Pharmacy, University of Genova, Viale Cembrano 4, I-16148 Genova <sup>7</sup>Department of Chemistry G. Ciamician, Alma Mater Studiorum, University of Bologna, Via Selmi 2, 40126 Bologna lucrezia.gatti@unibo.it

The preservation of rare prehistoric bones is essential, as they are invaluable cultural and historical artifacts. Accurately assessing their state and determining their age while maintaining their integrity is a key challenge in archaeological research. However, detecting organic content and assessing crystallinity changes in bone apatite post-mortem is particularly complex when burial conditions are coupled with thermal degradation.

Within the framework of the PNRR CHANGES project (SPOKE 5), the University of Bologna (UNIBO) has developed advanced non-invasive pre-screening methods to detect collagen content in ancient bones. Near-infrared spectroscopy (NIR), combined with hyperspectral imaging (HSI), was employed to quantify and spatially map collagen distribution. <sup>[1]</sup> By integrating this noninvasive acquisition approach with a multivariate partial least squares (PLS) regression model, we generated chemical maps correlating collagen content with NIR absorptions at each pixel. This technique enables precise quantification and localization of collagen, optimizing sample selection for radiocarbon dating.

To provide an economical alternative, a portable FT-IR spectrometer (650–5500 cm<sup>-1</sup>) and a miniaturized near-infrared (MicroNIR) spectrometer (900–1700 nm) were also tested on burnt bones, and multivariate data analysis was applied to enhance spectral interpretation. Principal Component Analysis (PCA) revealed spectral variations that allowed differentiation among specimens based on their chemical alterations.

These results demonstrate that the integration of advanced spectroscopic and chemometric approaches in archaeological research paves the way for improved preservation strategies and more accurate assessments of ancient remains. The ability to rapidly and non-invasively screen bones enhance the efficiency of conservation and further investigation of our past.

Acknowledgements: We thank the project PE5 CHANGES: Cultural Heritage Active Innovation for Sustainable Society for founds, Soprintendenza Archeologia, Belle Arti e Paesaggio per la Città Metropolitana di Bologna e le province di Modena, Reggio Emilia e Ferrara, and Cinzia Cavallari for initiating the research project on the Funeral Rituals of Mutina. We thank Museo Civico di Modena, particularly Silvia Pellegrini, for permission to study and access the materials.

<sup>[1]</sup> C. Malegori et al., Commun. Chem. 2023, 6(1), 1-10.

### MONITORING MICROBIOLOGICAL COLONIZATION IN CULTURAL HERITAGE THROUGH NON-INVASIVE FTIR SPECTROSCOPY

### <u>Ludovico Geminiani</u>,<sup>1,2</sup> Cristina Corti,<sup>2,3</sup> Barbara Giussani,<sup>1</sup> Riccardo Marelli,<sup>1</sup> Laura Rampazzi,<sup>2,4,5</sup> Giancarlo Ranalli,<sup>6</sup> Elisabetta Zanardini<sup>1,2</sup>

<sup>1</sup>Department of Science and High Technology, Università degli Studi dell'Insubria, Como, Italy
<sup>2</sup>Centre for Science and Symbolic Studies of Cultural Heritage, Università degli Studi dell'Insubria, Como, Italy
<sup>3</sup>Centro di ricerca e trasferimento tecnologico, Università degli Studi dell'Insubria, Como, Italy
<sup>4</sup>Department of Human Sciences and of Innovation for the Territory, Università degli Studi dell'Insubria, Como, Italy

<sup>5</sup>Istituto per le Scienze del Patrimonio Culturale, Consiglio Nazionale delle Ricerche (ISPC-CNR), Milano, Italy <sup>6</sup>Department of Biosciences and Territory, Università degli Studi del Molise, Pesche, Italy lgeminiani@uninsubria.it; ludo.gemi@yahoo.it

Our cultural heritage (CH) is constantly threatened by degradation caused by wind, temperature fluctuations, rain, relative humidity, condensation, and air pollution.<sup>[1]</sup> In addition to these factors, microorganisms —including bacteria, archaea, fungi, and lichens—also contribute to deterioration, developing their growth and metabolism on various types of historical artworks, whether displayed indoor or outdoor.<sup>[2]</sup> Climate change is creating ideal conditions for microbial growth, accelerating the biodeterioration of CH. Rising temperatures and increasing humidity levels encourage the proliferation of fungi, bacteria, and insects that damage historic materials. Furthermore, flooding and extreme weather events—occurring with greater frequency due to climate change—exacerbate the problem by introducing moisture into historical buildings, archaeological sites, and museum storage areas. As these biological threats intensify, conservation strategies must evolve, necessitating more active monitoring and intervention. Our research explores the potential of external reflection (ER) FTIR spectroscopy—a proven, portable tool for investigating historic and artistic surfaces—to monitor microbiological colonization and degradation on stone materials. A series of experiments were conducted on marble specimens treated with different organic materials to evaluate the technique's performance over varying periods of microbial growth. To manage and interpret the large datasets generated, chemometric techniques such as Principal Component Analysis (PCA) and ANOVA-Simultaneous Component Analysis (ASCA) were applied. These methods help reduce data complexity and highlight variations, correlations, and trends that might otherwise go unnoticed. The results indicate that ER-FTIR technique is effective in detecting early stages of microbiological colonization on stone specimens and distinguishing between fungal and bacterial colonization. It also allows for the identification of degradation products associated with microbial metabolism, such as calcium oxalate and carboxylate. While further testing is necessary, this technique shows great promise as a non-invasive method for monitoring microbiological degradation on historic and artistic stone surfaces, while giving useful information about materials nature and other degradation phenomena taking place. Given the growing threat of climate change and the increasing risk of microbial colonization on CH, the insights from this research could contribute to the development of a standardized protocol for on-site assessment of microbial colonization type and severity. Such a protocol could also support conservation efforts by evaluating the effectiveness of biocide treatments over time, ultimately aiding in the preservation of our CH.

<sup>[1]</sup> G. Ranalli, "Biodeterioration - Including Cultural Heritage" 2009, Academic Press, 191-205.

<sup>[2]</sup> K. Sterflinger, Applied Microbiology and Biotechnology "Microbial deterioration of cultural heritage and works of art - Tilting at windmills?" **2013**, 97(22), 9637–9646.

### NEW APPROACHES FOR THE QUANTITATIVE ANALYSIS OF PESTICIDES

#### Mareike Gerken, 1 Roald Tagle, 1 Michele Gironda 1

<sup>1</sup>Bruker Nano Analytics, Am Studio 2D, 12489 Berlin mareike.gerken@bruker.com

X-ray fluorescence analysis (XRF) is a widely established technique for the analysis of heavy metal pesticides, e.g.. [1] Historically, these were metal salts containing As, Pb, Hg, or Br. Already by their nature of composition as well as application, pesticides can be ideally described as layered samples in units of mass deposition. While qualitative or semi-quantitative results are often capable of confirming the presence and nature of a heavy metal pesticide in general, quantitative results are occasionally necessary for a thorough assessment. While bulk quantification typically requires a homogeneous composition within the analytical volume, pesticide deposition on Cultural Heritage objects falls short of this criterion. Though often considered to be an obstructive factor, the finite thickness of multiple sample systems to X-rays doesn't preclude quantification. However, additional information and specific approaches are essential that consider the applying physical

principles of absorption and emission.

Our contribution aims to present approaches possible quantification, highlighting best acknowledging practices and limitations. We will be presenting an easy approach to describe pesticides in mass deposition, displayed on examples several of organic composition. This approach applicable to a large group of objects and instrumentation. The analytical technique rests on the principle of the standard-addition method, on the one side, and self-made nonpoisonous mock-ups, on the other side.

The latter open possibilities of validation taking into consideration the large variety of matrixes on which a pesticide may be deposited.

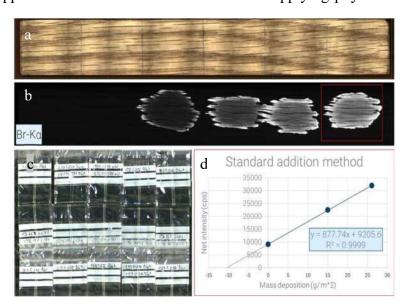


Figure 1: (a) KBr in different solutions deposited on oak wood specimen. (b) Mapping with the M4 TORNADO at 35 kV, 800 μA, displaying the Br-K distribution. (c) Set of self-made references with calculated mass deposition. (d) Results of the Standard addition method after calculating the amount of Br deposited in the uttermost right application of (b).

<sup>[1]</sup> A. Shugar, "Handheld XRF use in the identification of heavy metal pesticides in ethnographic collections" **2012**, A. Shugar, J. L. Mass, Leuven, 313–348.

#### CULINARY AND FOOD CONSUMPTION PRACTICES AT THE BRONZE AGE ERIMI-LAONIN TOU PORAKOU IN CYPRUS: ORGANIC RESIDUES ANALYSES OF COOKING POTS

#### Giulia Germinario, 1 Marialucia Amadio, 2 Luca Bombardieri<sup>2</sup>

<sup>1</sup>Institute of Heritage Sciences-National Council of Research (ISPC-CNR), Lecce, Italy <sup>2</sup>University of Siena, DFCLAM, Siena, Italy <u>giulia.germinario@.cnr.it</u>

This study focused on the analysis of organic residues (ORA) from cooking pots recovered at the Middle Bronze Age site of Erimi-Laonin tou Porakou in Cyprus (ca. 2000-1600 BC). The aim of the study is to highlight everyday consumption practices, in contrast to those interpreted as part of a 'communal ritual meal' (banquet). The selected ceramic vessels were recovered from a single primary, undisturbed domestic context, specifically Unit 6 in Area T2, which was excavated during the 2021 campaign.

ORA centers on the characterization of the lipid profile of pottery vessels, as this technique allows for the identification of various products, including animal fats (from both ruminant and nonruminant carcasses), marine and dairy products, plant oils, wine, beeswax, resins, and tars. Total lipids were extracted using a dichloromethane and methanol methodology<sup>[1]</sup> and analyzed via gas chromatography-high resolution mass spectrometry (GC-HRMS).

The data revealed high quantities of palmitic and stearic acids, along with saturated and branched C15:0 and C17:0 fatty acids, and multiple isomers of monounsaturated C18:1. These were found in combination with azelaic acid (the 9-carbon dicarboxylic acid product of its degradation), as well as mono- and di-acylglycerols, and cholesterol, together with its degradation products. These findings indicate the presence of ruminant fat, as these compounds are typically formed by microorganisms in the rumen.

Moreover, in some samples, the detection of a greater amount of palmitic acid compared to stearic acid, along with polyunsaturated fatty acids (eicosapentaenoic acid and docosahexaenoic acid), suggests the presence of marine fish fats. However, other constituents that would complete the characteristic pattern (such as isoprenoid acids and alkanoic acids) were absent. [2] Finally, traces of bitumen were identified through the presence of hopanes and steranes. Pine resin, commonly used after gentle heating, was recognized in most samples as well as in the soil of the stratigraphic unit. Therefore, its presence is not necessarily indicative of a deliberate addition to the cooking pots.

The findings of this study provide crucial insights into the food consumption practices of the prehistoric community of Erimi, shedding light on the culinary traditions that shaped daily life in Middle Bronze Age Cyprus. The data primarily indicate a diet centered on ruminant meat, with some possible evidence of fish consumption. Future research integrating a broader dataset and isotopic analysis will further refine our understanding of prehistoric foodways, technological choices, and their implications for social organization. Beyond subsistence, the detection of bitumen—likely obtained through long-distance exchange—suggests that the Erimi community was actively engaged in broader Mediterranean trade networks, challenging the notion of insularity often associated with prehistoric island societies.

<sup>[1]</sup> N. Garnier, S. M. Valamoti, Journal of Archaeological Science 2016, 74, 195-206.

<sup>[2]</sup> M. Regert, Mass spectrometry reviews 2011, 30(2), 177-220.

### RESIDUES ON ROMAN POTTERY: EXTRACTION OF BIOMARKERS VIA ATR-FTIR AND MACHINE LEARNING

#### Silvia Giampaolo, 1 Claudia Scatigno, 1 Luisa Migliorati, 2 Tiziana Sgrulloni, 3 Giulia Festa 1

<sup>1</sup>CREF-Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi, Via Panisperna 89a, c/o Piazza del Viminale 1, I-00189 Roma, Italia

<sup>2</sup>Unitelma University of Rome, Roma, Italia

<sup>3</sup>Independent PhD, Italy

silvia.giampaolo@cref.it

The analysis of residues on archaeological pottery focuses on detecting materials, typically in trace, that came into contact with vessels used for storing, preparing, or cooking food. As a result, the analysis of residual content within archaeological pottery can provide valuable insights such as diet, trade, food and beverage storage, as well as medical and ritualistic practices.

In this study, we present a collection of fragmented pottery found inside the *Forum Romanum* area of the archaeological site of *Peltuinum* in central Italy. The methodology employed involves the extraction of archaeological biomarkers using Attenuated Total Reflectance FourierTransform Infrared Spectroscopy (ATR-FTIR), combined with machine learning analysis. Preliminary results indicate the presence of lipids, such as terpenoids from various sources, which are distinguishable from inorganic residues, soil, silicates and carbonates. This work introduces a preliminary and systematic approach to the extraction of archaeological biomarkers through Machine Learning, without the need for chemical extraction, employing a nondestructive method that is suitable for ancient pottery.

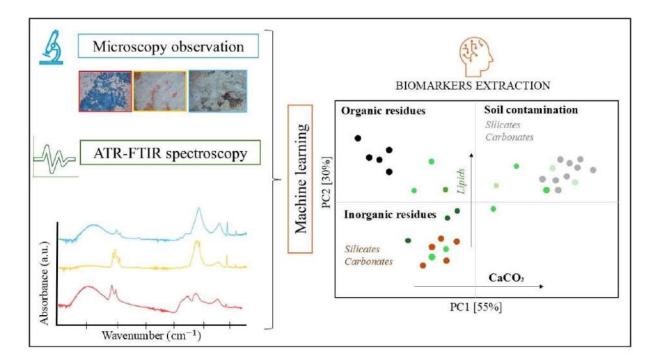


Figure 1: Illustrative scheme

## TRACE ELEMENTS ANALYSIS OF 16TH-CENTURY SILVER COINS MINTED IN NANTES - COUPLED HE-PIXE AND p-XRF MEASUREMENTS

A. Gillon, 1 C. Koumeir, 1,2 C. Pelé-Méziani, 3 G. Salaün, 3 F. Haddad, 1,2 G. Louarn 4

<sup>1</sup>GIP ARRONAX, 1 rue Aronnax, 44817 Saint-Herblain cedex, France
<sup>2</sup>Laboratoire SUBATECH, CNRS/IN2P3, 4 Rue Alfred Kastler, 44307 Nantes cedex 3, France
<sup>3</sup>Grand Patrimoine de Loire-Atlantique, Laboratoire Arc'Antique, Département de Loire-Atlantique, Nantes
<sup>4</sup>Institut des Matériaux Jean Rouxel (IMN), CNRS, Université de Nantes, Nantes
alexandre.gillon@univ-nantes.fr

This study focuses on a corpus of silver coins minted in Nantes in the second half of the 16th century, highlighting the historical and political context that has an impact on the supply of raw materials. Previous research<sup>[1]</sup> has traced the provenance of silver extracted from mines in South America (Mexico and Potosi) via trade between Spain and France around 1570-1575. A numismatic approach<sup>[2]</sup> on this corpus enables coins to be selected for chemical composition analysis, enabling trace elements such as gold, mercury, and indium to be quantified. The aim is to situate our measurements in relation to those presented in the literature data and bring a new, more local perspective to these results.

The preliminary results of experiments carried out at ARRONAX cyclotron and Arc'Antique laboratory have already been presented at TECHNART 2023. This new presentation will show the progress of this work and will focus particularly on high-energy PIXE to detect heavy elements (gold, mercury) and probe coins in depth with 68 MeV alphas and protons beams. Detection of gold and mercury by their L X-ray lines (surface analysis down to 30 µm) enables quantifying concentrations of a few hundred ppm. For in-depth HE-PIXE analysis, high-energy K X-ray lines (up to 500 µm for alphas and more than 1 mm thick for protons) were used. A weighted average value of a group of coins by year and by period was determined to compare our results with the measurements of other coins already analysed in the literature.

The proportions of gold and indium in Potosi silver are on average respectively 23±5 ppm and 6.9±2.6 ppm. Gold is much more abundant in Mexican and European silver (average of 1935±57 ppm) while indium is very low (around 0.1 ppm). As a result of gold concentration measurements, we identify two distinct coin groups, confirming the arrival of silver from Potosi in Nantes after 1575. The weighted standard deviation on the gold present in the coins minted in 1598 reflects difficulties in the supply of silver during this period corresponding to Nantes blockade. Concerning the indium, the HE-PIXE setup was optimized to improve the limit detection down to 10 ppm. We are able to detect indium in a few coins with high concentrations, but this small number is not sufficient to draw any conclusions. Furthermore, in the cases where mercury has been detected at the coin surface with the p-XRF, the HE-PIXE analysis reveals no mercury in the depth. It is therefore possible that the mercury, introduced in 1572 in Potosi for refining the ore, is a surface contaminant or that it migrated during the coin smelting process.

<sup>[1]</sup> E. Le Roy Ladurie, D. Richet, A. Gordus, J. Gordus et E. Le Roy Ladurie, *Annales. Histoire, Sciences Sociales* "Le Potosi et la Physique nucléaire" **1972**, 27, 6, 1235-1256.

<sup>[2] &</sup>quot;La Monnaie de Nantes et l'argent de l'Amérique espagnole - 1575-1625 (Recueil de textes de Gildas Salaün)" (online). Available at: https://www.cgb.fr/la-monnaie-de-nantes-et-largent-de-lameriqueespagnole-1575-1625-recueil-de-textes-de-gildas-salaun-gildas,lm329,a.html.

<sup>[3]</sup> A. Gillon et al., Eur. Phys. J. Plus "Elemental analysis by XRF and HE-PIXE on silver coins from the 16th-17th centuries and on a gilded crucifix from the 12th century" **2023**, 138, 10, 945. doi: 10.1140/epjp/s13360-023-04570-5.

<sup>[4]</sup> A. Gillon, *Journées de Rencontres Jeunes Chercheurs. Book of Proceedings* "High-energy ion beam analysis: the study of raw materials and manufacturing techniques for cultural heritage objects" 2024, (online). Available at: https://hal.science/hal-04609124.

### THE QUANTITATIVE ANALYSIS OF IRON GALL INKS: STANDARD FREE AND SUPPORTED QUANTIFICATION

#### Mareike Gerken, Roald Tagle, Michele Gironda

<sup>1</sup>Bruker Nano Analytics, Am Studio 2D, 12489 Berlin michele.gironda@bruker.com

Iron gall inks are among the most used historical inks for writing and drawing.<sup>[1]</sup> Analysing their metallic content—originating from the use of vitriols from various deposits—enables the differentiation of writing phases and the study of erased palimpsests, among other applications. The ratios of key sulphates relevant to X-ray fluorescence analysis (XRF), including FeSO<sub>4</sub>, ZnSO<sub>4</sub>, MnSO<sub>4</sub>, and CuSO<sub>4</sub>, can vary across regions and time periods, and have been extensively used in the past to separate inks of different origin.<sup>[1,3]</sup> While qualitative or semi-quantitative methods based on element ratios may address these concentration variations,<sup>[2,3]</sup> a full comparison between different instruments requires absolute numbers via a quantification. However, achieving accurate quantification is challenging, as it typically depends on a homogeneous composition within the analytical volume – a condition that ink applications on paper do not meet.<sup>[4]</sup> Despite this, the finite thickness of layered samples does not prevent quantification. Instead, additional information and specialized methodologies that account for the physical principles of absorption and emission are essential for an accurate quantification.

This study presents a quantitative approach for analysing historical iron gall inks using fundamental parameters-based coating thickness methods as well as the incorporation of reference samples for validation and calibration. By determining mass deposition, we explore the potential for describing iron gall inks in absolute units to facilitate comparison and origin differentiation. Method

development, optimisation, and validation will be discussed and applied to a collection of early 20<sup>th</sup> century postcards from La Habana, Cuba, with various iron gall ink writings. On these samples, we will be demonstrating best practices while addressing the limitations of the methodology.



**Figure 1:** Historical postcard from La Habana, Cuba, 20.06.1902. On the recto, a message is written in iron gall ink atop of a silver gelatine photography.

<sup>[1]</sup> C. Krekel, *International Journal of Forensic Document Examiners "The Chemistry of historical Iron Gall Inks"* **1999**, *5*, 54–58.

<sup>[2]</sup> O. Hahn, H.-E. Gorny, ZKK "Zerstörungsfreie Charakterisierung historischer Eisengallustinten mittels Röntgenfluoreszenzanalyse" **2000**, 14(2), 384–390.

<sup>[3]</sup> O. Hahn, W. Malzer, B. Kanngießer, B. Beckhoff, *X-Ray Spectrometry "Characterization of iron-gall inks in historical manuscripts and music compositions using x-ray fluorescence spectrometry"* **2004**, *33*(4), 234–239.

<sup>[4]</sup> T. Wolff, "Referenzprobenfreie quantitative Mikro-Röntgenfluoreszenzanalyse" **2009**, BAM-Dissertationsreihe, 50, Berlin.

# UNVEILING THE ARTISTIC PRACTICE OF COLANTONIO IN CONSEGNA DELLA REGOLA FRANCESCANA ALTARPIECE: A NON-INVASIVE, IN SITU APPROACH TO MATERIAL ANALYSIS IN CAPODIMONTE'S LABORATORY

Margherita Giugni,<sup>1,3</sup> Myriam Fiore,<sup>2</sup> Teresa Cacace,<sup>3</sup> Annalaura Casanova Municchia,<sup>4</sup> Maria Catrambone,<sup>4</sup> Cristiano Riminesi,<sup>5</sup> Donata Magrini,<sup>5</sup> Emanuela Grifoni,<sup>5</sup> Francesca Rosi,<sup>2</sup> Brenda Doherty,<sup>2</sup> Claudia Caliri,<sup>6</sup> Francesco Paolo Romano,<sup>6</sup> Angela Cerasuolo,<sup>3</sup> Costanza Miliani<sup>3</sup>

<sup>1</sup>Sapienza University of Rome, Faculty of Literature, Department of Classics, Piazzale Aldo Moro 5, 00185, Rome, Italy

#### margheritagiugni@cnr.it

The restoration of *Consegna della regola francescana* by Colantonio offered the opportunity to carry out a multi-modal investigation into the artist's materials and painting techniques in the newly established diagnostic lab at the Museo di Capodimonte. This 15th-century Neapolitan altarpiece—part of the SHARING project corpus—bears witness to the vibrant cross-cultural influences shaping local workshops during the transition from Gothic to Renaissance styles. Flemish and Iberian elements emerge in both material choices and technical solutions.<sup>[1]</sup>

Reflectance and fluorescence hyperspectral imaging (VNIR and SWIR), macro-XRF mapping (MA-XRF), external reflection FTIR (ER-FTIR), Raman spectroscopy, GC-MS, and highresolution 2D and 3D microscopy were employed to reconstruct the original stratigraphy and assess alterations. The analysis revealed a sophisticated gilding technique: gold leaf applied over a bole rich in iron oxides, complemented by gold-like details rendered with earth pigments and lead-tin yellow type I (confirmed by Raman). Organic residues identified by GC-MS pointed to a complex varnish composition including oils, resins, and wax.

Particular focus was placed on the depiction of the two angels, whose symmetrical appearance contrasts with notable material differences. The robe of the right angel showed a higher mercury content, while the left contained more copper. ER-FTIR analysis detected a lipidic binder in both draperies. Additionally, the left drapery exhibited traces of a resinous varnish—likely used as a binder for a red glaze—mapped as madder lake through fluorescence hyperspectral imaging.<sup>[2]</sup> Further spectral analysis revealed distinct alteration products: ER-FTIR identified lead soaps in the left angel's paint layers, while oxalates were observed on the right, likely resulting from differences in pigment layering and medium composition. <sup>[3]</sup>

<sup>&</sup>lt;sup>2</sup>Institute of Chemical Science and Technologies "G. Natta" (CNR-SCITEC), Via Elce di Sotto, 8, Perugia 06123, Italy

<sup>&</sup>lt;sup>3</sup>Institute of Heritage Science (CNR-ISPC), National Research Council of Italy, Via Cardinale Guglielmo Sanfelice 8, 80134, Napoli, Italy

<sup>&</sup>lt;sup>4</sup>Institute of Heritage Science (CNR-ISPC), National Research Council of Italy, Area della Ricerca di Roma 1, Montelibretti, Via Salaria Km 29,300, 00015 Rome, Italy

<sup>&</sup>lt;sup>5</sup>Institute of Heritage Science (CNR-ISPC), National Research Council of Italy, Via Madonna del Piano 10, 50019 SestoFiorentino, FI, Italy

<sup>&</sup>lt;sup>6</sup>Institute of Heritage Science (CNR-ISPC), National Research Council of Italy, Via Biblioteca 4, 95124 Catania, Italy

<sup>[1]</sup> Elvira Scialla et al., Heritage "Study of 'Cona degli Ordini' by Colantonio with IR and XRF Analyses" 2023, 6(2), 1785-1803.

<sup>[2]</sup> Catia Clementi et al., Applied Physics A "Vibrational and electronic properties of painting lakes" 2008, 92, 25-33.

<sup>[3]</sup> Letizia Monico et al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy "Non-invasive identification of metal-oxalate complexes on polychrome artwork surfaces by reflection mid-infrared spectroscopy" **2013**, 116, 270-280.

### FINE TUNING ARTIFICIAL AGING IN OIL PAINT MOCK-UPS BY COUPLING μ-MBI, ATR-FTIR AND GC-MS

Margherita Gnemmi, 1,2 Laura Fuster-Lopez, Miguel Ángel Herrero-Cortell, Elisabetta Zendri, Laura Falchi, Eleonora Balliana, Matteo Piccolo, Francesca Caterina Izzo Laura Falchi, Eleonora Balliana, Eleon

<sup>1</sup>Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Venice, Italy

<sup>2</sup>Sapienza University of Rome, National PhD in Heritage Science, Rome, Italy

<sup>3</sup>Universitat Politècnica de València, Instituto Universitario de Restauración del Patrimonio, Valencia, Spain

<sup>4</sup>Fondazione Musei Civici di Venezia, Galleria Internazionale d'Arte Moderna, Venice, Italy

margherita.gnemmi@uniromal.it

There are considerable doubts about the reliability of artificial ageing, often carried out to accelerate the chemo-physical processes in oil paintings to better understand the causes of failure phenomena. Knowingly, the reactions that take place under accelerated conditions are not the same as those that occur during the film formation processes of oil paints.<sup>[1]</sup>

The present study was carried out as part of a wider investigation aimed at demonstrating failure phenomena at the interface between acrylic grounds and oil paint films in painted structures. Since aged samples were required, it was necessary to fine-tune the artificial ageing process to produce mock-ups. Three sets of ad hoc mock-ups were produced, consisting of commercially primed canvas with various combinations of acrylic ground layers and an oil paint film. SET 1 was naturally aged while SETs 2 and 3 were artificially aged. The parameters of the artificial ageing were chosen based on the average seasonal relative humidity (RH%) and temperature (T) recorded at the Galleria Internazionale d'Arte Moderna of Venice (Italy), located in the historic Venetian building of Ca' Pesaro. [2] The first stage of this research was to define the suitable beginning of artificial ageing on SET2 and SET3. A multi-analytical approach consisting of percentage weight variation ( $\Delta W\%$ ) coupled with spectroscopic analysis was carried out on mock-ups every day after casting. The results showed that the greatest weight loss due to the decomposition of oxygen compounds such as hydroperoxides, resulting in the release of low molecular weight molecules such as aldehydes and ketones, occurred 21 days after casting. The ATR-FTIR analysis confirmed these findings, showing the disappearance of the peak related to the unsaturated C=C-H bond (at 3008 cm-1) and a broadening of the ester carbonyl stretching band, indicating the hydrolysis of triglycerides 21 days after casting. The second stage was carried out when SET 1 was naturally aged for 2 years and SETs 2 and 3 were artificially aged for 28 days. The aim was to evaluate the effectiveness of artificial ageing by comparing the failure mechanisms of the naturally aged specimens in their early drying stages and to check for correspondence with SET 2 and 3. The observation with μ-MBI revealed discrete wrinkles, protrusions and cracks in the naturally aged samples and more pronounced similar ones in the artificially aged samples. Moreover, ATR-FTIR and GC-MS analyses revealed similarities among the three SETs, indicating that this approach warrants further exploration to more accurately replicate the conditions and cycles of artificial accelerated aging.

Acknowledgements: The research is carried out as part of the National PhD in Heritage Science (PhD-HS.it). Multiband studies have been carried out in the framework of Grant PID2023-148300NB-I00 funded by MICIU/AEI/ 10.13039/501100011033, CIPROM/2023/9 and by "ERDF/EU". Ca' Foscari group thanks "Patto per Venezia".

<sup>[1]</sup> R. L. Feller, "Accelerated Aging: Photochemical and Thermal Aspects" 1994, Getty Conservation Institute, Los Angeles, 296.

<sup>[2]</sup> F. C. Izzo, E. Balliana, F. Pinton, E. Zendri, Conservation science in cultural heritage 2014, 14, 353-369.

#### NEUTRON IMAGING FOR ASSESSING VOLCANIC-BASED MORTARS AT ARCHAEOLOGICAL SITES

Jennifer Huidobro, <sup>1</sup> <u>Giulia Gorla</u>, <sup>1</sup> Idoia Etxebarria, <sup>1</sup> Sara Puente-Muñoz, <sup>1</sup> Iñaki Vázquezde la Fuente, <sup>1</sup> Ilaria Costantini, <sup>1</sup>, Marco Veneranda, <sup>2</sup> Nagore Prieto-Taboada, <sup>1</sup> Kepa Castro, <sup>1</sup> Cristina Macia-Castello, <sup>3</sup> Daniel Blanco-Lopez, <sup>3</sup> Mattia Gaboardi, <sup>3</sup> Cristina Marieta, <sup>4</sup> Tomonori Fukuchi, <sup>5</sup> Yasuo Wakabayashi, <sup>5</sup> Yoshie Otake, <sup>5</sup> Felix Fernández-Alonso, <sup>3</sup> Gorka Arana, <sup>1</sup> Juan Manuel Madariaga <sup>1</sup>

<sup>1</sup>IBeA research group, University of the Basque Country, UPV/EHU, Leioa, Spain

<sup>2</sup>ERICA research group, University of Valladolid, Valladolid, Spain

<sup>3</sup>Material Physics Center, CSIC-UPV/EHU, Donostia, Spain

<sup>4</sup>Department of Chemical and Environmental Engineering, Faculty of Engineering, Gipuzkoa, GIE-EIG, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain

<sup>5</sup>RIKEN Center for Advanced Photonics, RIKEN, Wako-shi, Japan

giulia.gorla@ehu.eus

The use of natural pozzolanic materials, such as lapilli, in mortar formulations offers a sustainable and historically appropriate solution for the conservation of archaeological sites in volcanic regions like Pompeii and Herculaneum. This approach reduces the environmental footprint while preserving the authenticity of ancient construction techniques. To ensure compliance with modern standards, both conventional mechanical tests and advanced techniques such as neutron imaging, were applied to assess the performance of different mortar formulations. Four mixtures were prepared: MIX 1 (100% Ordinary Portland Cement, OPC), MIX 2 (50% OPC, 50% Vesuvius lapilli, VL), MIX 3 (80% OPC, 20% VL), and MIX 4 (100% OPC-NIST standard). According to the European standard EN 206:2013+A2:2021<sup>[1]</sup> mortars used in road construction should achieve a compressive strength of 25-30 MPa at 28 days. Mechanical tests showed MIX 1, 3 and 4 met the standards, while MIX 2 was slightly below the required strength. Higher pozzolanic content required longer curing to reach the strength of cement-only specimens. To complement the mechanical tests, neutron images of the specimens were acquired after one month of curing. A high degree of mineralogical homogeneity was observed in MIX 1 and MIX 4, whereas MIX 2 and MIX 3 exhibited greater heterogeneity. This contrast in MIX 2 and 3 suggests that the volcanic material influences neutron absorption and emission, possibly due to its mineralogical composition. It should be noted that the samples were measured after one month of curing, meaning that the heterogeneity may be attributed to incomplete reaction of the material in MIX 2 and MIX 3. Additionally, neutron imaging has been shown to assist in identifying structural cracks in the samples, as evidenced by MIX 2, which fractured during transportation to RIKEN Laboratories (Japan). By integrating innovative analytical techniques with sustainabilitydriven material selection, more durable and environmentally responsible mortars can be developed for archaeological conservation. Future research should explore intermediate formulations, such as 70:30 cement-to-lapilli ratio, to refine the balance between strength and sustainability under local and international requirements.

Acknowledgements: This work was supported by SIDIRE project (PID2022-142490OB-C32) funded by the Spanish Agency for Research and the Diagnosis and Rehabilitation of Tangible Cultural Heritage – IKUR Strategic Framework (ILCIC3L4-D00171-2) funded by the Basque Government.

<sup>[1]</sup> CEN (European Committee for Standardization), EN 206:2013+A2:2021 2021.

## EXPLORING THE INKS OF THE CRETAN SCRIBE IOANNES RHOSOS IN MANUSCRIPTS PRODUCED FOR CARDINAL BESSARION THROUGH μ-XRF

#### <u>Katerina Grigoriadou</u>, <sup>1</sup> Olivier Bonnerot, <sup>1</sup> Grzegorz Nehring, <sup>1</sup> Silvia Pugliese, <sup>2</sup> Claudia Colini<sup>1,3</sup>

<sup>1</sup>Centre for the Study of Manuscript Cultures, University of Hamburg, Germany

<sup>2</sup>Biblioteca Nazionale Marciana, Italy

<sup>3</sup>Institut für Archäologie und Kulturgeschichte des antiken Mittelmeerraumes, University of Hamburg, Germany aikaterini.grigoriadou@uni-hamburg.de

Ioannes Rhosos was a prolific Greek scribe of the 15<sup>th</sup> century C.E, born in the island of Crete. Around the middle of the century, he emigrated to Italy together with other Byzantine figures, where he spent much of his career as a professional calligrapher. Commissioned by eminent patrons, with Cardinal Bessarion among them, he worked across Italian cities, such as Rome and Venice, copying and transmitting a broad range of texts from ancient Greek literature. Through his work, Rhosos made a significant contribution to the dissemination of Greek studies in Italy during the early Renaissance.<sup>[1]</sup>

As a professional calligrapher, he copied a vast number of manuscripts, both on parchment and paper. In many of these, he included a colophon, i.e. a note, usually at the end of the manuscript, that provided his name, the city where he copied the manuscript, the date and often the name of his commissioner. For other manuscripts, where he did not follow such a practice, attribution to his hand has been made based on his distinctive paleographical traits.

One of the aims of a broader research initiative is to explore potential correlations between specific ink types and Italian cities, using his colophons as provenance and time indicators. Within the context of the project, the black ink and red colorant of fifteen manuscripts copied by Rhosos were analyzed at the Biblioteca Nazionale Marciana in December 2024 with a range of spectroscopic techniques — UV-VIS-NIR microscopy, XRF, VIS, Raman and FTIR spectroscopy. [2] This paper presents a segment of this study, focusing mainly on the XRF analysis of the composition of the black inks employed by Rhosos in manuscripts that he produced for cardinal Bessarion in Rome during the second half of the 15<sup>th</sup> century.

Acknowledgements: The authors would like to thank the staff of the Biblioteca Nazionale Marciana for their invaluable help and support during the time of the analysis. The research for this paper was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2176 'Understanding Written Artefacts: Material, Interaction and Transmission in Manuscript Cultures', project no. 390893796. The research was conducted within the scope of the Centre for the Study of Manuscript Cultures (CSMC) at the University of Hamburg.

<sup>[1]</sup> D. Speranzi, "Omero, i cardinali e gli esuli. Copisti greci di un manoscritto di Stoccarda" 2016, Dykinson.

<sup>[2]</sup> C. Colini, I. Shevchuk, K. A. Huskin, I. Rabin & O. Hahn, *Exploring Written Artefacts "A new standard protocol for identification of writing media"* in J. B. Quenzer (Ed.), 161-182, De Gruyter. https://doi.org/10.1515/9783110753301-009

#### ISOLA BELLA AND COMPIÈGNE, THE PLACE TO BE FOR NAPOLEON'S GARDEN PARTIES. NON-INVASIVE MATERIALS STUDY OF TWO 19TH-CENTURY GOUPIL&CIE'S ENGRAVINGS (BORDEAUX AQUITAINE MUSEUM)

<u>Lou Groscol</u>, <sup>1</sup> Régine Bigorne, <sup>2</sup> Francesca Galluzzi, <sup>3</sup> Aurélie Mounier <sup>1</sup>

<sup>1</sup>Archéosciences Bordeaux (UMR CNRS 6034), University Bordeaux Montaigne, 33600 Pessac, France

<sup>2</sup>Museum of Aquitaine, 33000 Bordeaux, France

<sup>3</sup>Bordeaux Proteome Platform, University Bordeaux, 33076 Bordeaux, France

lou.groscol@u-bordeaux-montaigne.fr

Goupil & Cie was a French art dealership and publishing house active throughout the 19th century, dedicated to making art more accessible through the mass production of affordable reproductions. This approach catered to the emerging bourgeoisie, who eagerly acquired prints to decorate their interiors with depictions of country scenes, historical moments, and more. Today, a collection of 46,000 prints from the Maison Goupil is preserved at the Musée d'Aquitaine in Bordeaux, France. This study focuses on two late 19th-century engravings, *Isola Bella* and *Compiègne*, based on paintings by the French painter François Flameng. They depict scenes from the Napoleonic era in the early 1800s, illustrating festive garden parties with characters in colorful costumes. The locations, Isola Bella in northern Italy and Compiègne in northern France, were places where Napoleon and his wife Joséphine once travelled. A rare feature of these engravings is the addition of a hand-painted watercolor remarque by Flameng himself, which increased the value of the prints. Noteworthy, alongside the engravings, the museum also holds the original copper plate used for printing and a glass plate displaying the color palette employed for their colorization.

The analysis, carried out in the reserves of the museum, required non-invasive techniques to identify pigments, paper, inks, dyes and engraving processes. The following methods were used: portable digital microscopy, hyperspectral imaging (VIS-NIR), fiber optics reflectance spectroscopy (VIS-NIR), X-ray fluorescence, and Fourier-transform infrared spectroscopy.

The investigation with the portable microscope allowed us to identify the photoengraving process, including the printing of the different colors and the brush-applied patterns. For example, pigment analysis identified Prussian blue, mixed with yellow (orpiment, chrome yellow and yellow ochre) to create greens. The data also suggested the use of red ochre and vermilion used alone or mixed together to obtain specific red nuances. For white pigments, barium, zinc and lead indicated that lithopone or lead white were employed to create highlights and depth. Moreover, all the pigment seemed to have been mixed with these whites to widen the color shades.

The analyses showed that the same pigments have been used on the two prints and that *Compiègne*'s palette had a wider range of colors. The data showed that they adjusted the proportions of pigments in their mixture to vary the shades (for example, there are 9 red mixtures on *Compiègne*'s color palette). These findings demonstrate the complexity of characterization due to pigments mixtures, often two or three pigments for each color. Their identification was possible thanks to the complementarity of the methods used, the combination of diverse databases, and the presence of the color palette on glass in the collection.

### NON-INVASIVE INVESTIGATION OF LIGHT-INDUCED AGEING EFFECTS ON STREET ART PAINTS THROUGH MICRO-SORS

#### Nicolò Guarnieri, 1 Claudia Conti, 2 Kevin Ambrogioni, 3 Sara Goidanich 1 and Lucia Toniolo 1

<sup>1</sup>Dipartimento di Chimica, Materiali e ingegneria chimica "G. Natta", Politecnico di Milano, Italy.

<sup>2</sup>Institute of Heritage Science (ISPC), National Research Council (CNR), Italy.

<sup>3</sup>Dipartimento di Energia, Politecnico di Milano, Italy.

nicolo.guarnieri@polimi.it

Colour fading in contemporary murals represent a significant challenge for their conservation. Modern synthetic organic paints revealed to be instable in outdoor conditions, where factors such as UV radiation, humidity fluctuations, and rain contribute to the gradual deterioration of pigments and binding media, leading to loss of the message of the contemporary mural artworks. [1] This study focuses on the light-induced surface fading of acrylic-vinyl paint mockups, simulating the effects of natural aging under controlled conditions. The formation of a superficially faded layer of paint (thickness less than 10 µm) has been observed in real case studies through micro sampling characterization. This phenomenon involves the degradation of organic pigments (SOPs) and binder matrix, accompanied by a localized enrichment of white filler. [2] By employing micro-SORS, we aim to characterize compositional changes beneath the faded surface, offering a deeper understanding of colour fading mechanism. [3]

Two types of acrylic-vinyl paints were examined: a red paint containing PR112 pigment and a yellow paint containing PY3 pigment. Both formulations included calcite and kaolinite as fillers. The samples underwent artificial aging for 100 days in a custom-built chamber under high humidity conditions (around 85% RH in a saturated KNO<sub>3</sub> solution) and illuminated by seven 5500K compact fluorescent lamps (CFL) providing approximately 60-70 klux. After the aging process, a significant color difference (ΔE above 10 CIELab units for the red paint) was observed, demonstrating the effectiveness of the accelerated aging conditions.

Micro-SORS was employed to analyse non-invasively the depth distribution of chemical compounds within the aged paint layers, with the principal finding being a progressive decrease in the Raman peak ratio of calcite to the pigments as the offset increased. This indicated a reduction of calcite content relative to the pigment, going deep inside the paint layer. This finding aligns with the results reported in previous literature, suggesting a surface-localised faded layer.

The results obtained demonstrate the efficacy of micro-SORS in the non-invasive measurement of depth in contemporary paint layers, thereby facilitating a more profound comprehension of the distribution of pigments and white fillers of aged paints. This technique has the potential to be used also in situ with portable micro-SORS instruments to successfully identify the thin, faded superficial layers of paint.

<sup>[1]</sup> L. Pagnin et al., Coatings 2023, 13, 2044.

<sup>[2]</sup> N. Guarnieri et al., Dyes and Pigments **2025**, 239, 112733.

<sup>[3]</sup> A. Botteon et al., Journal of Raman Spectroscopy 2018, 49(10), 1652-1659.

## COLOURS OF THE WIND: INVESTIGATING THE USES AND MATERIALS OF A SELECTION OF FANS (18<sup>TH</sup>-19<sup>TH</sup> C.) USING MOBILE SPECTROSCOPIC TECHNIQUES (AQUITAINE MUSEUM, FRANCE)

#### Julie Guiraud, 1 Sarah Petitcolas, 1 Sophie Fontan, 2 Aurélie Mounier 1

<sup>1</sup>Archéosciences Bordeaux, UMR 6034 (CNRS, Bordeaux Montaigne University, University of Bordeaux, Ecole Pratique des Hautes Études, Esplanade des Antilles), Pessac, France

<sup>2</sup> Musée d'Aquitaine, 20 Cours Pasteur, Bordeaux, France julie.guiraud@etu-u-bordeaux-montaigne.fr

Fans are present in many museum collections across the world, yet only one study seems to have focused on their materiality (wood, nacre, ivory).<sup>[1]</sup> At first sight, fans may seem useful only for their refreshing effect, but throughout history, these precious objects have served a wide variety of purposes depending on their societal contexts. From being used by generals on battleground in Japan to their role among aristocratic women in European courts, and even as a means of spreading revolutionary ideas, fans have had a multitude of uses.

Our research focuses on nine hand-fans that were recently added to the collection of the Aquitaine Museum (Bordeaux, France) through a bequest from two collectors of 2000 fans (provenance of different countries & dated from 17<sup>th</sup> to 20<sup>th</sup> C). This selection of fans, date back to the 18th and 19th centuries, and were manufactured in France, China & Japan. Such diverse origins result in the use of a rich variety of materials (nacre, paper, parchment, pigments, textiles, wood...) and techniques (painting, carving, dyed textiles, collage...).

The combination of different materials on a relatively small non-flat surface presents various analytical challenges. The complexity of these fragile objects led us to adopt a non-invasive methodology, relying solely on portable devices (p-XRF, hyperspectral cameras, FORS, p-FTIR, LEDµSF, digital microscopes), allowing the measurements to be carried out in the museum reserves. This methodology developed in Archeosciences Bordeaux is particularly adapted when sampling is prohibited and when artworks are sensitive to light or to being handled. [2,3]

This study aims to shed a new light on the complex nature of fans. Digital microscope observation allowed, for example, to emphasize the complexity of some specimens: the support can be a paper sheet where textiles have been glued on to represent kimonos. The faces are cut out of ivory, glued on, and then decorated with traces of paint to position the eyes, lips, and noses...preliminary analyses enabled us to identify a diverse palette of pigments/dyes. The methods were able to detect the presence of both natural (azurite, ochres...) and synthetic (ultramarine blue, Prussian blue, orange II...) pigments and colourants, as well as both inorganic (vermilion...) and organic (indigo...) compounds. The identification was made possible, in part, thanks to a reference spectrum database produced within the laboratory.<sup>[4,5]</sup> This first study highlights the complexities of fans. Thus illustrating the importance of an adaptative methodology, using multiple analytical techniques to combine information to explore this so far poorly understood object.

<sup>[1]</sup> C. Paris, **2004**, Pierre et Marie Curie University, PhD.

<sup>[2]</sup> H. De La Codre et al., 2021, *The European Physical Journal Plus* **2021**, *136*, DOI: <u>10.1140/epjp/s13360-021-</u>02184-3.

<sup>[3]</sup> P. Claisse et al., *The European Physical Journal Plus* **2023**, *138*, DOI: 10.1140/epjp/s13360-023-04435-x.

<sup>[4]</sup> A. Mounier et al., Microchemical Journal 2018, 140, DOI: 10.1016/j.microc.2018.04.023.

<sup>[5]</sup> C. Biron et al., *Microchemical Journal* **2020**, *152*, DOI: <u>10.1016/j.microc.2019.104374</u>.

#### NEUTRON IMAGING FOR ASSESSING VOLCANIC-BASED MORTARS AT ARCHAEOLOGICAL SITES

<u>Jennifer Huidobro</u>,<sup>1</sup> Idoia Etxebarria,<sup>1</sup> Sara Puente-Muñoz,<sup>1</sup> Iñaki Vázquez-de la Fuente,<sup>1</sup> Ilaria Costantini,<sup>1</sup> Marco Veneranda,<sup>2</sup> Nagore Prieto-Taboada,<sup>1</sup> Kepa Castro,<sup>1</sup> Cristina Marieta,<sup>3</sup> Cristina Macia-Castello,<sup>4</sup> Daniel Blanco-Lopez,<sup>4</sup> Mattia Gaboardi,<sup>4</sup> Tomonori Fukuchi,<sup>5</sup> Yasuo Wakabayashi,<sup>5</sup> Yoshie Otake,<sup>5</sup> Felix Fernández-Alonso,<sup>4</sup> Gorka Arana,<sup>1</sup> Juan Manuel Madariaga<sup>1</sup>

<sup>1</sup>IBeA research group, University of the Basque Country, UPV/EHU, Leioa, Spain

<sup>2</sup>ERICA research group, University of Valladolid, Valladolid, Spain

<sup>3</sup>Department of Chemical and Environment Engineering, University of the Basque Country UPV/EHU, Donostia,

Spain

<sup>4</sup>Material Physics Center, CSIC-UPV/EHU, Donostia, Spain

<sup>5</sup>RIKEN Center for Advanced Photonics, RIKEN, Wako-shi, Japan

jennifer.huidobro@ehu.eus

The use of natural pozzolanic materials, such as lapilli, in mortar formulations offers a sustainable and historically appropriate solution for the conservation of archaeological sites in volcanic regions like Pompeii and Herculaneum. This approach reduces the environmental footprint while preserving the authenticity of ancient construction techniques. To ensure compliance with modern standards, both conventional mechanical tests and advanced techniques such as neutron imaging, were applied to assess the performance of different mortar formulations. Four mixtures were prepared: MIX 1 (100% ordinary Portland cement, OPC), MIX 2 (50% OPC, 50% Vesuvius lapilli, VL), MIX 3 (80% OPC, 20% VL), and MIX 4 (100% OPC-NIST standard). According to the European standard EN 206:2013+A2:2021 [1] mortars used in road construction should achieve a compressive strength of 25-30 MPa at 28 days. Mechanical tests showed MIX 1, 3 and 4 met the standards, while MIX 2 was slightly below the required strength. Higher pozzolanic content required longer curing to reach the strength of cement-only specimens.

To complement the mechanical tests, neutron images of the specimens were acquired after one month of curing. A high degree of mineralogical homogeneity was observed in MIX 1 and MIX 4, whereas MIX 2 and MIX 3 exhibited greater heterogeneity. This contrast in MIX 2 and 3 suggests that the volcanic material influences neutron absorption and emission, possibly due to its mineralogical composition. It should be noted that the samples were measured after one month of curing, meaning that the heterogeneity may be attributed to incomplete reaction of the material in MIX 2 and MIX 3. Additionally, neutron imaging is capable to identify structural cracks in the samples, as evidenced by MIX 2, which fractured during transportation to RIKEN Laboratories (Japan). By integrating innovative analytical techniques with sustainability-driven material selection, more durable and environmentally responsible mortars can be developed for cultural heritage conservation. Future research should explore intermediate formulations, such as 70:30 cement-to-lapilli ratio, to refine the balance between strength and sustainability under local and international requirements.

Acknowledgements: This work was supported by SIDIRE project (PID2022-142490OB-C32) funded by the Spanish Agency for Research and the Diagnosis and Rehabilitation of Tangible Cultural Heritage – IKUR Strategic Framework (ILCIC3L4-D00171-2) funded by the Basque Government.

<sup>[1]</sup> CEN (European Committee for Standardization), EN 206:2013+A2:2021 2021

#### PRESERVING PAPER ARTIFACTS: THE USE OF NANOCELLULOSE FOR JAPANESE WOODBLOCK PRINTS

Marcella Ioele, 1 Carolina Rigon, 1 Maria Vera Quattrini 1

<sup>1</sup>Istituto Centrale per il Restauro, Rome, Italy marcella.ioele@cultura.gov.it

In recent years is well-know that finding sustainable solutions as well as the use of eco-friendly products is a goal being pursued in multiple sectors and fields. In the area of Cultural Heritage, the trend of finding viable alternatives to promote solutions that are more sustainable is arising. Within the frame of the CHANGES project, we are testing different types of nanocellulose-based products to repair tears, splits, weakness and embrittlement on Japanese paper as an alternative to traditional adhesive products. Among natural-based innovative products, nanocellulose has recently proven to be a really encouraging material for cellulosic substrates treatment, mainly thanks to its chemical affinity but also for its biocompatibility and renewability properties. The aim of the research is to find a product that can be used on Japanese woodblock prints made from fibers of the paper mulberry, or kōzo (Broussonetia kajinoki). The main characteristics of this kind of artefacts is the paper transparency and the fact that the printed colour areas and black outlines can be observed from both sides (recto and verso) of paper sheets. This peculiar transparency feature should be preserved whenever restoring intervention is necessary, so the importance of using a material that do not produce visible film or glossing effects become essential. The Japanese woodblock prints were fully characterized by both non-invasive and invasive chemical investigations, so the early stages of the research involved the application of nano-products both on raw Japanese paper samples and on samples specifically realized by reproducing the artistic technique of the artefacts. Performances of nanocellulose-based compounds on Japanese paper have been monitored before and after artificial ageing, by colorimetric campaign to evaluate chromatic alteration and by scanning electron microscope to examine the interaction between nanocellulose and paper fibres.





Figure 1: detail of one of the Japanese woodblock prints and application of CNC on a paper specimen

Acknowledgements: This research was funded by the Project CHANGES "Cultural Heritage Active Innovation for Next-Gen Sustainable Society", National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 funded from Next-Generation-EU.

[1] M.V. Quattrini, *Restauro e conservazione delle stampe giapponesi*, in Conservazione dei materiali grafici e archivistici, a cura di M. Regni e P.G. Tordella, Umberto Allemandi & C. Editori, Torino 1999, pp.371-382.

## SCALING UP THE STUDY OF WALL PAINTINGS IN ROMAN GAUL: A MULTI-ANALYTICAL APPROACH TO UNDERSTAND PAINTING PRACTICES IN LIMONUM

#### Adriana Iuliano, 1 Isabelle Pianet, 1 Mathilde Carrive2

<sup>1</sup>Archéosciences Bordeaux - UMR 6034, CNRS, University Bordeaux Montaigne, University of Bordeaux, France <sup>2</sup>Hellénisation et romanisation dans le monde antique (HeRMA) – UR 15071, University of Poitiers, France adriana.iuliano@u-bordeaux-montaigne.fr

The expansion of Roman influence in Gaul from the 3rd century BC introduced new construction and decorative techniques, including wall painting. Initially following models from the Italian peninsula, Gallo-Roman decorative traditions progressively developed distinctive stylistic features from the second half of the 1st century AD. This raises questions about possible shifts in pigment choices and painting techniques employed by the craftsmen of the time. While the archaeological aspects of Gallo-Roman wall painting are well documented, physico-chemical studies have typically focused on individual sites or buildings, offering a fragmented view of painting practices. This research addresses the need for a broader perspective by investigating a large corpus of mural paintings from Gallia Aquitania, specifically from the ancient city of Limonum (Poitiers, France). The study examines seven collections from different excavation sites, displaying nine decorative schemes and dating from the 1st to the 3rd century AD. With approximately 15 boxes of painted plaster fragments, the implementation of a methodological strategy was crucial to handle the large dataset. A key feature of the approach is the use of hyperspectral imaging (HSI) for a preliminary screening, enabling the mapping of chemical information across large fragment assemblages and the selection of representative fragments for further analyses. The analytical protocol integrates non-invasive and micro-invasive techniques, including portable digital microscopy, HSI in the VNIR and SWIR ranges, x-ray fluorescence (XRF) spectroscopy, and x-ray diffraction (XRD), in a first step. These methods provided an initial characterisation of pigments such as red and yellow ochres, green earth (celadonite), Egyptian blue, cinnabar, and carbon black. In a second step, optical microscopy (OM) on microsamples and cross-sections, scanning electron microscopy coupled with energy-dispersive x-ray spectroscopy (SEM-EDS), micro-Raman spectroscopy, and Fouriertransform infrared (FTIR) spectroscopy were performed. Stratigraphic observations revealed the presence of pigment mixtures and complex paint layers, suggesting the use of a secco technique in some cases. Additionally, pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS), offered insights on the presence (or absence) of organic binders in the paintings. The analysis of multiple collections allows for a comparative study of painting practices across different sites, contexts and time periods, shedding light on the technical evolution of wall painting in Limonum. The focus on a Gallo-Roman city represents a significant contribution, as studies on provincial painting traditions are less frequent compared to the extensive research on Italian sites. This study highlights the benefits of a multi-analytical approach in tackling extensive archaeological collections. By integrating imaging techniques for rapid screening with targeted micro-chemical analyses, it provides a comprehensive understanding of the materials and techniques in GalloRoman wall paintings, contributing to broader discussions on technological transmission and adaptation in provincial artistic traditions.

## COMBINED REMOTE, MACRO- AND MICRO-LEVEL RIS USING A SINGLE VNIR CAMERA: CRITICAL COMPARISON TO MA-XRF AND MA-XRPD

<u>Koen Janssens</u>, <sup>1</sup> Nouchka De Keyser, <sup>2</sup> Francesca Gabrieli, <sup>2</sup> Arthur Gestels, <sup>1</sup> Matthias Alfeld, <sup>3</sup> Marta Ghirardello <sup>4</sup> and Fabrizio Preda <sup>4</sup>

<sup>1</sup>University of Antwerp, Belgium
<sup>2</sup>Rijksmuseum Amsterdam, The Netherlands
<sup>3</sup>Delft University of Technology, The Netherlands
<sup>4</sup>NIREOS, Milano, Italy
koen.janssens@uantwerpen.be

Reflectance Imaging Spectroscopy is an imaging method that allows to identify artists materials in works of art in a non-invasive manner. Different commercial systems are available on the market, operating from the visible into the infrared range. One of these systems, the HERA hyperspectral camera (manufactured by NIREOS, Milano, IT), allows the same camera to be used both for remote or macro-scale imaging of artworks as well as for micro-scale imaging of small subareas and of paint cross-sections. For the former, the hyperspectral camera is used as it is or equipped with a lens suitable for the envisaged spectral range. For the latter, the hyperspectral camera is mounted onto a regular optical microscope in the position of the observation camera.

To evaluate in practice the usefulness of the NIREOS HERA VNIR system (operating in the 4001000 nm wavelength range) for characterization of painted cultural heritage artefacts, RIS data sets from two quite different artworks were recorded: a 20<sup>th</sup> "fake" flower still life painting, executed in the style of 17<sup>th</sup> C. Dutch painters of the golden age (Fig. 1a) and a 16<sup>th</sup> C. illuminated manuscript folio (Fig. 1b). These artefacts were also characterized using a combination of Macroscopic X-ray fluorescence and Macroscopic X-ray powder diffraction scanning.

In this paper, maps of the principal pigments present in both works of art obtained by RIS, MAXRF and MA-XRPD will be critically intercompared while also the similarity/differences between the RIS data sets obtained in macro- and micro-mode will be discussed.





Figure 1: (a)  $20^{th}$  C. flower piece painting, executed in  $17^{th}$  C. Dutch style; (b)  $16^{th}$  C. illuminated manuscript folio.

# LASER CLEANING OF SILICEOUS BLACK CRUSTS FROM GRANITE COLLECTED AT CÔA VALLEY ARCHAEOLOGICAL PARK (PORTUGAL)

Gonzalo Buceta Brunetti,<sup>1</sup> Laura Andrés Herguedas,<sup>1</sup> Pablo Barreiro Castro,<sup>1</sup> Teresa Rivas Brea,<sup>1</sup> <u>Daniel Jose Jiménez Desmond</u>, Santiago Pozo Antonio<sup>1</sup>

<sup>1</sup>Universidade de Vigo, Spain danieljose.jimenez@uvigo.gal

One of the alteration forms affecting rock art is the formation of siliceous black crusts, which obscure engravings or paintings and threaten their preservation. These crusts can lead to material losses, such as scaling, flaking, cracking, etc.<sup>[1]</sup> compromising the artwork's readability and its transmission to future generations. Their formation is of natural origin derived from the precipitation, in an aqueous medium, of chemical elements dissolved in water, sometimes also accompanied by the deposition of micro fragments of rocks and minerals (detrital dust) in greater or lesser quantities. Depending on the environment, these crusts are usually composed of variable thickness layers rich on silica and at lesser extent phosphorus, aluminium, etc. and sometimes intermixed with other layers with calcium oxalates (whewellite-like), sulphates, carbonates, etc.<sup>[2]</sup> Therefore, the heterogeneity of these dense crusts and their firm adherence to the rock underneath make their cleaning both necessary and complex.

This study aims to analyse the suitability of the laser technology to remove these black crusts from granite samples collected at Côa Valley Archaeological Park (Portugal), a UNESCO World Heritage Site, which provides one of the best illustration of the iconography themes of Paleolithic rock art. For this purpose, a nanosecond pulsed Nd:YAG laser operating in Q-Switch mode at wavelengths of 1064 nm and 355 nm has been used. The results will be compared with a mechanical cleaning method employing a vibro-incisor under different working pressures (3 and 6 bars).

The side effects and the removal effectiveness of the treatments was evaluated using stereomicroscopy, colour spectrophotometry, Raman spectroscopy and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). Even though the extraction was not complete, the findings highlight the promising potential of laser cleaning, demonstrating superior effectiveness and substrate preservation compared to mechanical methods.

Acknowledgements: This study is part of the PID2021-123395OA-100 research project funded by MICIU/AEI/10.13039/501100011033 and, by "ERDF A way of making Europe". J.S. Pozo-Antonio was supported by the RYC2020-028902-I project funded by MICIU/AEI/10.13039/501100011033 and, by "ESF Investing in your future". For more information: <a href="https://laseringph.webs.uvigo.es/">https://laseringph.webs.uvigo.es/</a>

<sup>[1]</sup> Ewa Glos, "European Illustrated Glossary of Conservation Terms for Wall Paintings and Architectural Surfaces" edited by Angela Weyer, Pilar Roig Picazo, Daniel Pop, Joann Cassar, Aysun Özköse, Jean-marc Vallet, Ivan Srsa. ISBN: 978-3-7319-0260-7. 450p

<sup>[2]</sup> H. Green, A. Gleadow, D. Finch, J. Hergt, S. Ouzman, *Journal of Archaeological Science: Reports "A Mineral deposition systems at rock art sites, Kimberley, Northern Australia—Field observations"* **2017**, *14*, 340–352.

# REVEALING PRINTMAKING PRACTICES IN 16th-CENTURY FRANCE THROUGH INK CHARACTERISATION

Giovanna Vasco,<sup>1,2</sup> <u>Kilian Laclavetine</u>,<sup>2</sup> Caroline Vrand,<sup>3,4</sup> Eleonora Pellizzi,<sup>1</sup> Vanessa Selbach,<sup>3</sup> Eric Pagliano,<sup>2</sup> Lucy Cooper<sup>1</sup>

¹Département de la Conservation, Bibliothèque nationale de France (BnF), Paris, France
²Centre de recherche et de restauration des musées de France (C2RMF), Paris, France
³Département des Estampes et de la photographie, Bibliothèque nationale de France (BnF), Paris, France
⁴Département des Arts graphiques, Musée du Louvre, Paris, France
giovanna.vasco@bnf.fr

King Francis I commissioned an international group of artists from across Europe to decorate his residence at Fontainebleau. This group, known as The School of Fontainebleu, was a highly prolific artistic hub which became a cultural centrepiece of the French Renaissance and played a crucial role in the French printmaking practices during the 16<sup>th</sup> century. The group was initially under the direction of Rosso Fiorentino (1540) and then Francesco Primaticcio (1542), who had a key role in the Fontainebleau printshop. It is thought that Primaticcio, who had been active in Mantua in Giulio Romano's workshop, imported some of Mantegna's engraved copper plates to France, with consequent production of French copies after Mantegna, and diffusion of printmaking practices. Within the short period (1542-1547), an incredible number of woodcuts, engravings, and etchings were produced in Fontainebleau. However, frequent lack of signatures and dates, together with stylistic differences, means that many aspects remain to be clarified. Furthermore, the influence of the early printmaking practices of the Fontainebleau School on the engraving production of 16<sup>th</sup>-century Paris should be explored further.

In this study, a set of monochrome prints (brown, red, and black) was selected in order to examine the characteristics of the School of Fontainebleau, its differences with previous Mantegna's production in Italy, and its relationship with the early Parisian printmaking. A multianalytical approach allowed us to compare Mantegna's engravings, French copies after

Mantegna, Fontainebleau etchings, and Parisian prints, including both engravings and etchings. Applying Multispectral Imaging (MSI), the designs were compared using Infrared Reflectography (IRR) images, while the large-scale homogeneity of the inks was evaluated observing Infrared False Colour (IRFC) composite images. The microscopic characteristics were observed by using digital microscopes (Hirox in the VIS range, Dino-Lite in the UV-IR ranges). Complementary information was obtained using Raman Spectroscopy, Fiber Optics Reflectance Spectroscopy (FORS), X-Ray Fluorescence (XRF) Spectroscopy, and X-Ray Diffraction (XRD).

Differences, similarities and peculiarities were highlighted, better clarifying aspects of the Renaissance French printshops and, as far as we know, providing the first scientific evidence of the use of metal inks in printmaking practices.

# THE GARDENER OF THE GRAND DUKE: HISTORY AND ANALYSIS OF MS. 462 HORTUS PISANUS, ICONES VARIARUM PLANTARUM

Claudia Giostrella,<sup>1</sup> Giulia Lorenzetti,<sup>2</sup> Vincenzo Palleschi,<sup>2</sup> Luca Nodari,<sup>3</sup> Patrizia Tomasin,<sup>3</sup> <u>Stefano Legnaioli</u><sup>2</sup>

<sup>1</sup>Ministry of Culture SABAP Pisa-Livorno, Italy <sup>2</sup>ICCOM-CNR, Italy <sup>3</sup>ICMATE-CNR, Italy <u>stefano.legnaioli@cnr.it</u>

An herbal is a book, used since ancient times, that collects descriptions of plants and their pharmacological properties, often with names in different languages and information about their habitat. These books have evolved over time: illustrated herbals are painted herbals, also called horti picti, or herbaria before the Renaissance; they are different from the collections of dried plants, called horti sicci.<sup>[1,2]</sup>

Codex 462 of the Fondo Hortus Pisanus of the University Library of Pisa is a precious example of a 16th century illustrated herbal, Icones variarum plantarum, containing 35 tempera paintings by the German soldier Georg Dyckman, an amateur but highly talented artist. Between 1590 and 1591, the Flemish botanist Joseph Goedenhuize (who had Italianised his name to Giuseppe Casabona or Benincasa) went to the island of Crete, famous for its rich variety of plants and herbs with multiple virtues. He was in the service of the Medici court as prefect of the Giardino dei Semplici, and his aim was to study new spontaneous species to enrich the Tuscan garden. Dyckman's artistic skill depicted various spontaneous plants of the island.<sup>[3]</sup> The plates describe species collected by Casabona himself and then sent to the Grand Duke's court and show how botanical iconography had begun to favour images drawn from life. The work had a considerable impact on the scientific community of the time; among the spontaneous plants depicted are the Peonia Peregrina, the Euphorbia Spinosa and several specimens of Ranunculus asiatica, which only later spread to Italy. The manuscript was recently restored on the occasion of an international exhibition; the necessary preliminary studies for the restoration included a series of in-situ diagnostic studies using noninvasive techniques (digital Microscope, multispectral imaging, Raman, FTIR and XRF). These analyses proved useful in deepening the knowledge of the materials and the execution technique of this type of illustrated herbals and in choosing the most appropriate solutions during the restoration phase. In view of the growing interest in this type of historical evidence, which involves both art history and the history of science, this study offers an interesting new perspective on the subject, useful both from a technical point of view for future conservation and for analytical and historical artistic studies.

Acknowledgements: The authors thank the staff of the National Library of Pisa for their valuable collaboration.

<sup>[1]</sup> L. Tongiorgi Tomasi, "The Renaissance Herbal. The New York Botanical Garden" 2013, New York, The New York Botanical Garden.

<sup>[2]</sup> W. Blunt e S. Raphael, "The illustrated herbal" 1994, London, Frances Lincoln.

<sup>[3]</sup> L. Tongiorgi Tomasi, G. Hirchauer, "The flowering of Florence: Botanical Art for the Medici" 2002, Washington D.C., The National Gallery of Art.

### NATURAL MARINE WEATHERING FOR TESTING BRONZE SURFACES PROTECTIVE TREATMENTS

<u>P. Letardi</u>, <sup>1</sup> J. Vernet, <sup>1</sup> R. Stifanese, <sup>1</sup> P. Traverso, <sup>1</sup> S. Aronica, <sup>2</sup> I. Fontana, <sup>2</sup> G. Giacalone, <sup>2</sup> E. Catelli, <sup>3</sup> D. Spaleta, <sup>3</sup> G. Sciutto <sup>3</sup> and M. P. Casaletto <sup>4</sup>

<sup>1</sup>Institute of Anthropic Impacts and Sustainability in marine environment, CNR, Genova, Italy
<sup>2</sup>Institute of Anthropic Impacts and Sustainability in marine environment, CNR, Capo Granitola, Italy
<sup>3</sup>Department of Chemistry "G. Ciamician", University of Bologna, Ravenna Campus, Italy
<sup>4</sup>Institute for Nanostructured Materials, CNR, Palermo, Italy
paola.letardi@cnr.it

Over the years, scientific research has moved to an even deeper understating of the complex corrosion phenomena affecting outdoor bronze surfaces in changing environments. Nonetheless, the development of effective coating formulations to slow down the deterioration rate caused by atmospheric corrosion still remains an open issue, particularly in harmful environments such as the marine ones.<sup>[1]</sup> In this context, the MEDUSA project: "MarinE outDoor bronze sUrfaceS: a methodological Approach"[2] was intended to narrow the gap between scientific research and technological transfer of products and treatments to conservation professionals. Treatments based on a commercial microcrystalline wax (R21 Antares srl) are tested on quaternary bronze mockups patinated either with foundry "liver of sulfur" or "Messina green" patinas. Particular attention is given to effective protocols for the characterisation and monitoring of surface properties of the mock-ups upon treatment and weathering. Non-destructive techniques, such as profilometry, colorimetry, electrochemical impedance spectroscopy (EIS), Digital microscopy, µFT-IR, µRaman and VNIR hyperspectral imaging are used. Furthermore, the chemometric analysis is applied to handle the massive data acquired and integrate the analytical information. The performance of the wax added with benzotriazole (BTA) in a standard way - as reference treatment - are compared to the ones of the wax added with BTA nano-incapsulated in cyclodextrin.<sup>[2]</sup> Preliminary results related to natural weathering in urban (Genoa harbour) and rural (Capo Granitola) marine exposure sites (Figure 1) are presented. ISO STANDARDS for field exposure are adapted to heritage science test specimens, with standard monitoring of field parameters, such as meteo data and chloride deposition rate.<sup>[3]</sup>

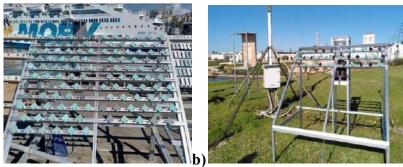


Figure 1: Marine natural exposure in: (a) Genoa (urban-industrial site) (b) Capo Granitola (rural site).

Acknowledgements: PRIN 2022KKKLX7 MEDUSA Project: "MarinE outDoor bronze sUrfaceS: a methodological Approach" is financially supported by European Union –NextGenerationEU.

<sup>[1]</sup> P. Letardi, Coatings 2021, 11, 131.

<sup>[2]</sup> M. P. Casaletto, "Proceedings of METAL2025" 2025, Cardiff (in press).

<sup>[3]</sup> T. Chang, A. Maltseva, P. Volovitch, I. O. Wallinder, C. Leygraf, Corros. Sci. 2020, 166, Article 108477.

# LARGE-SCALE MULTI-TECHNIQUE ANALYSIS OF GILT-LEATHER WALL COVERINGS: CHARACTERIZATION OF CONSTRUCTION AND RESTORATION MATERIALS

<u>Pablo Londero</u>,¹ Céline Bonnot-Diconne,² Valentina Pintus,¹ Fatema Khamis,¹ Noora AlZaabi,¹ Elsa Bourguignon,¹ Jerome Farigoule¹

<sup>1</sup>Scientific Research Unit, Louvre Abu Dhabi, United Arab Emirates

<sup>2</sup>Private practice, France

<u>plondero@louvreabudhabi.ae</u>

The manufacture of gilt-leather wall coverings reached the height of its popularity from approximately the mid-16<sup>th</sup> century until the middle of the 18<sup>th</sup> century. These painted golden panels were created by applying a layer of silver leaf to large sheets of leather that had been glued together, then coated with a translucent 'gold' varnish based on an oil-resin mixture to achieve a gold-like finish. It could then be embossed and/or painted, and sheets could be sewn into even larger panels.<sup>[1]</sup> *The Triumph of David*, acquired by the Louvre Abu Dhabi, consists of a set of 11 painted and gilded leather panels likely created by a Dutch workshop in the late 17th century. Notable for its scale and artistry, it decorated the interiors of Weißenstein Castle in Pommersfelden, built between 1711 and 1718 for Lothar Franz von Schönborn, Prince-Bishop of Bamberg and Elector of Mainz. As part of the restoration of the piece, we are performing an ongoing analysis to characterize its materials, construction, and past restorations.

A tiered analytical methodology was applied. Initial non-invasive methods included technical photography, 3-D structured light scanning, and Macro X-ray Fluorescence (MA-XRF) mapping. Cross-sectional analysis with Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM/EDS), Raman spectroscopy, Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), and optical microscopy characterized the panels' layers and pigment composition. Adhesives from prior treatments were characterized using Gas Chromatography-Mass Spectrometry (GC-MS), SEM/EDS, and FTIR.

Results to-date reveal a piece that is consistent with 17th-century Dutch practice, created using several novel methods and with some significant conservation and deterioration issues. The stratigraphy of the layered construction includes a preparatory adhesive, silver leaf, and ~100 mm varnish layer whose recipe will be a focus of future study. The exceptionally large silver leaf (12 cm across) is an interesting aspect of the workshop practice. Paint materials include a mixed Pb-and Zn-based white and shading using an as-of-yet unidentified iron-rich paint. Previous interventions also pose several issues. The removal protocol for a glue used to bond leather to a non-original textile backing had to be adjusted due to its paint-like formulation (calcite filler, umber pigmentation); a modern adhesive bonding a frame to the upper surface edge was found to contain polychloroprene, embedding chlorine into the paint.

Planned future studies include deeper analysis of the palette, resin recipe and embedded chlorine, further illuminating the construction and potential restoration issues of gilt-leather panels.<sup>[2]</sup>

**Acknowledgements:** We would like to thank Liaqut Ali and Muhammad Shiraz Ali, from the Spectrometry and Spectroscopy Core at New York University-Abu Dhabi, for the use of and assistance with their GC/MS system.

<sup>[1]</sup> R. Marie, Talanta 2020, 206, 120-191.

<sup>[2]</sup> R. Laurianne, Vibrational Spectroscopy 2020, 110, 103-133.

## THE DOORS OF THE BASILICA DI SAN MARCO: A SCIENTIFIC EXAMINATION THROUGH MA-XRF

S. Longo, R. Andolina, M. Botticelli, S. Bottura Scardina, F. Falcone, M. Fera, G. Ghiara, C. Miliani, E. L. Ravan, F. P. Romano, M. Mödlinger and C. Caliri

<sup>1</sup>Istituto di Scienze del Patrimonio Culturale del Consiglio Nazionale delle Ricerche (ISPC-CNR), Catania, Italy 
<sup>2</sup>Institut fur Urgeschichte und Historische Archaologie, Universitat Wien, Vienna, Austria 
<sup>3</sup>DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy 
<sup>4</sup>IMAREAL, Paris Lodron University Salzburg, Körnermarkt 13, 3500 Krems/Donau, Austria 
sveva.longo@cnr.it

This study focuses on the copper alloy doors of the Basilica di San Marco in Venice, renowned for their artistic and historical value, with particular attention to their chemical composition, production methods, and detailed inlays. Dating back to the 11th and 12th centuries, these doors exemplify a blend of Byzantine, Gothic, and Renaissance styles, featuring decorative motifs, biblical scenes, and depictions of saints, as well as the distinctive use of a variety of different inlays. Macro X-ray Fluorescence (MA-XRF) analysis, carried out during the GAPAMET MOLAB E-RHIS campaign, was employed to evaluate the elemental distribution and identify key materials present across the doors. For the first time, this advanced MA-XRF technology was utilized to reveal the elemental composition of the materials used as inlay on these historic bronze doors, providing new insights into their manufacture. The analysis uncovered a broad range of elements, including copper (Cu), silver (Ag), gold (Au), mercury (Hg), tin (Sn), lead (Pb), and zinc (Zn), with notable compositional differences between the Main Door (MD) and the San Clemente Door (SC). These variations imply that the doors were likely created in separate workshops or at different times, possibly utilizing different alloys. The ability to identify and map the distribution of these elements with high precision allows for a deeper understanding of the materials and techniques used by the craftsmen of the time, shedding light on the historical processes behind these iconic doors.



Figure 1: MA-XRF chemical elements maps of Saint Peter on San Clemente Door (SC-B5).

Acknowledgments: E-RIHS European Infrastructure of Heritage Science (E-RIHS); PNRR projects: 1) H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029, CUP B63C22000730005; 2) CHANGES, "Science and Technologies for Sustainable Diagnostics of Cultural Heritage", PE0000020, CUP B53C22003890006; 3) SAMOTHRACE, Sicilian Micronano Tech Research And Innovation Center, Ecosistema dell'Innovazione ECS00000022, CUP B63C22000620005

#### LIBS FOR BORON CHARACTERIZATION IN HISTORICAL ENAMELS

# <u>Laura Maestro-Guijarro</u>,<sup>1</sup> Mercedes Sedano,<sup>2</sup> Nadine Schibille,<sup>3</sup> Trinitat Pradell,<sup>4</sup> Mohamed Oujja,<sup>1</sup> Teresa Palomar<sup>2,5</sup>

¹Instituto de Quimica Fisica Blas Cabrera (IQF), CSIC, c/ Serrano, 119, 28006 Madrid (SPAIN)

²Instituto de Cerámica y Vidrio (ICV), CSIC. c/ Kelsen 5. Campus de Cantoblanco. 28049 Madrid (SPAIN)

³IRAMAT-Centre Ernest-Babelon, UMR 5060 CNRS, 3D rue de la Férollerie, 45071 Orléans cedex 2 (FRANCE)

⁴Physics Department and Barcelona Research Centre in Multiscale Science and Engineering, Universitat

Politècnica de Catalunya, Campus Diagonal Besòs, Av. Eduard Maristany, 10-14 08019 Barcelona (SPAIN)

⁵UI VICARTE − Vidro e Cerâmica para as Artes, NOVA School of Science and Technology, Universidade Nova de

Lisboa, Campus da Caparica 2829-516 Caparica (PORTUGAL)

lmaestro@iaf.csic.es

Stained-glass windows are commonly painted with grisailles and enamels. The latter are glassy materials with a low melting temperature fixed to the base glass by a firing regime. Lead and/or boron are commonly added to the painting material to decrease their melting temperature, so they can melt without deforming the glass support.

The chemical analyses of historical enamels is a complicated task. The most common portable techniques applied to cultural heritage objects, such as XRF, are unsuitable because they analyse chemical elements with atomic numbers (Z) higher than 13 (aluminum). In addition, they could not detect elements such as sodium (Z=11), one of the most common elements in historical glasses, or boron (Z=5), usual in glass surface paintings since the 17th cent.

In this work, we present laser-induced breakdown spectroscopy (LIBS) as a suitable in situ qualitative analytical technique to determine boron in historical enamels even in low quantities. To avoid the matrix effect, the boron intensity has been internally normalized with the intensity of lead and silica, common elements in historical enamels. Calibration curves were obtained from samples with well-known content on boron allowing to carry out quantitative analysis. The suitability of this approach has been proved with historical Spanish samples.

Acknowledgements: This research has been funded by the Fundação de Ciência e Tecnologia from Portugal (project ref. UIDB/EAT/00729/2020, UIDP/00729/2020, 2023.05135.RESTART, and researcher grant CEECIND/02249/2021), the Spanish State Research Agency (AEI) through the projects PID2022-1370170B100/AEI/1013039/501100011033 and PID2022-1377830B-100, the Regional Government of Madrid through the project TEC Heritage-CM (TEC-2024/TEC-39), the Generalitat de Catalunya through the Consolidated Group 2021 SGR 00343, and support from CSIC Platform 'Open Heritage: Research and Society' (PTI-PAIS) are acknowledged. Teresa Palomar thanks MICIU for Ramón y Cajal contract (RYC2023-045699-I).

# SAFE-AND-SUSTAINABLE-BY-DESIGN APPROACH FOR DEVELOPING GREENER MATERIALS FOR CULTURAL HERITAGE

### Olivia Gómez-Laserna,<sup>1</sup> Martina Romani,<sup>1</sup> Francesco Caruso,<sup>2</sup> Erlantz Lizundia,<sup>3,4</sup> Maite Maguregui<sup>2</sup>

<sup>1</sup>Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain

<sup>2</sup>Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain

<sup>3</sup>Department of Graphic Design and Engineering Projects, Faculty of Engineering in Bilbao, University of the Basque Country UPV/EHU, 48013 Bilbao, Spain

<sup>4</sup>BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Scientific Park, 48940 Leioa, Spain

maite.maguregui@ehu.eus

The Safe-and-Sustainable-by-Design (SSbD) concept, promoted by the European Union, aims to guide the development of new materials and chemicals to ensure safety for both human health and environment, while also being sustainable throughout their life cycle. The key principles of SSbD include: sustainability, life cycle thinking, functionality, and circular economy. The ENCLOSURE project (<a href="https://enclosure-project.eu">https://enclosure-project.eu</a>) aligns with the SSbD framework by developing novel nanocellulose-based materials for cultural heritage conservation. The nanostructured version of the biopolymer cellulose has been selected to promote its circular economy. Throughout the design and development of our nanocellulose-based materials, it was assessed that they do not pose risks to human health or ecosystems. Indeed, toxic substances, persistent pollutants, and bioaccumulative chemicals were not employed during their preparation and use.

This work presents an overview of our approach, illustrated by the production of a diverse range of nanocellulose-based materials. On the one hand, we have developed cryogels for desalination of wall paintings, and cleaning of varnishes/organic coatings from canvas paintings. This solution proposes a closed-loop recycling system to minimize waste generation by promoting the reuse. Besides, modified nanocellulose hydrogels have been introduced as an alternative to common solvents to remove soiling from canvas paintings and corrosion patinas from bronze heritage objects. The loading of fluids was also unnecessary, thus making their potential application simpler for conservators. Finally, nanocelluloses may be employed as effective stabilizers for Pickering Emulsions, integrating greener solvents capable of removing varnishes and organic coatings from canvas paintings.

For most of the new materials, Life Cycle Assessment metrics have been calculated to evaluate their environmental impact. However, further efforts are necessary to accurately reflect the entire life cycle of the new conservation solutions, encompassing raw materials extraction, production, use, and end-of-life disposal.

Non-invasive imaging methodologies (and the advanced treatment of their data by machine learning approaches) based on micro-ED-XRF, micro-Raman and hyperspectral imaging were instrumental to assess the efficacy and innocuousness of the new materials.

Acknowledgements: This work has been supported by grant TED2021-129299A-I00, funded by MCIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR. MR and OGL acknowledge funding from such a grant. FC acknowledges his Maria Zambrano fellowship from UPV/EHU, funded by MICIU and the European Union NextGenerationEU/PRTR.

# GHIRLANDAIO'S BLUE: A SEM STUDY OF SMALT IN THE TORNABUONI CHAPEL IN SANTA MARIA NOVELLA CHURCH, FLORENCE

#### Elisabeth Manship, 1 Alberto Felici, 2 Sofia Brizzi, 3 Laura Capozzoli, 4 Cristiano Riminesi 3

<sup>1</sup>Independent Researcher-Conservator, USA

<sup>2</sup>Soprintendenza Archeologia, Belle Artí e Paesaggio per la città metropolitana di Firenze e le province di Pistoia e Prato (SABAP), Italy

<sup>3</sup>National Research Council, Institute of Heritage Science (CNR –ISPC), Italy
<sup>4</sup>National Research Council, Institute of Chemistry of OrganoMetallic Compounds (CNR-ICCOM), Italy
<u>alberto.felici@cultura.gov.it</u>

In 1485, Domenico Bigordi (1448-1494) known as "Il Ghirlandaio", received the commission to paint a wall painting cycle in the Tornabuoni Chapel in the Church of Santa Maria Novella in Florence (IT). It has long been reported in the literature that in these paintings, Ghirlandaio used the blue cobalt-colored glass pigment smalt on the vast surfaces of the chapel walls. [1,2] However, the composition and physical characteristics such as the grain size of this blue pigment have not been able to be fully explored in the relevant scientific literature. [3] These aspects of manufactured glass pigments such as smalt are not standard due the use of different raw materials and recipes, [4-<sup>7]</sup> and can influence their color, covering power, stability, and durability over time.<sup>[8,9]</sup> This study was designed as a preliminary assessment that will be used to inform a broader study in the future about the use of smalt and its deterioration in these wall paintings. The objectives of this preliminary SEM study were: first, to assess the historical smalt present in microsamples from Ghirlandaio's painting for its elemental characterization by EDX, and the size, morphology and distribution of pigment grains in the samples; to gather information about the original painting technique; and to compare the smalt's compositional profile to that of other wall paintings from the same period as reported in the literature. The results of this study reveal that the composition of the blue cobalt pigment used by Ghirlandaio does not conform to a classical smalt profile proposed in literature, raising questions about its provenance and manufacture, and inspiring important questions about smalt deterioration in wall paintings and conservation strategies for the future.

<sup>[1]</sup> F. Cardinali (ed.), "Materiali e Tecniche nella pittura murale del quattrocento: Storia dell'arte, indagini diagnostiche e restauro verso una nuova prospettiva di ricerca, Vols. I-IV. Rome: Documentazione preliminare al Convegno Internazionale 20-22 Febbraio 2002", 2002.

<sup>[2]</sup> E. Manship, G. Cavallo, J. Gilardi, M. P. Riccardi, Studies in Conservation 2023, 68(1), 68-83.

<sup>[3]</sup> P. Bensi, *Studi di Storia dell'Arte* **1980**, *3*, 33-47.

<sup>[4]</sup> I. Borgia and C. Seccaroni, *OPD 17 Note di restauro "L'azzurro di smalto nella pittura e nelle fonti italiane del XV e XVI secolo"* **2007**, 152–164.

<sup>[5]</sup> I. Borgia, B. Brunetti, P. Moioli, C. Seccaroni, A. Sgamellotti, "Raphael in Perugia: The Fresco of San Severo, the Baglioni Altarpiece and the Gonfalone of Citta' di Castello" 2007, in A. Roy, M. Spring (eds.) "Raphael's Painting Technique: Working Practices Before Rome", National Gallery conference, 35-43.

<sup>[6]</sup> S. Cagno, K. Janssens, and M. Mendera, Analytical and Bioanalytical 2008, 391, 1389–1395.

<sup>[7]</sup> C. Salerno, C. and S. Ferroni, Rivista della Stazione Sperimentale del Vetro 1999, 6, 293-302.

<sup>[8]</sup> P. Santopadre, M. Verità, Studies in Conservation 2006, 51(1), 29-40.

<sup>[9]</sup> D. Ajò, U. Casellato, E. Fiorin and P. A. Vigato, Journal of Cultural Heritage 2004, 5, 333-348.

# PATINAS ON SILVERWORK: AN ANALYTICAL APPROACH FOR DISTINGUISHING INTENTIONALLY AND NATURALLY CORRODED SURFACES

Daniela Landeiro, Maria Alexandra Barreiros, Marta Manso 1-3

<sup>1</sup>Faculty of Fine-Arts, University of Lisbon, Portugal <sup>2</sup>LNEG, Portugal <sup>3</sup>LIBPhys-UNL, NOVA University of Lisbon, Portugal <sup>2</sup>VICARTE, NOVA University of Lisbon, Portugal marta.manso@fct.unl.pt

The patination of silverwork to modify surface color and finish became increasingly popular in Europe during the 19th century. This decorative technique is often achieved using sulfur-based solutions, leading to the formation of silver sulfide patinas. The chemical composition of these patinas closely resembles that of naturally formed corrosion layers, making it challenging to distinguish patinated surfaces from naturally corroded ones during conservation cleaning actions. However, patinated silver surfaces may exhibit a characteristic glossy finish, in contrast to the matt appearance typically associated with natural environmental degradation. Considering this, we aimed to differentiate the optical properties of patinated silver from those of naturally corroded patinated silver. Our approach involved measuring CIE L\*a\*b\* color parameters and the reflectance in the visible spectrum of sterling silver samples patinated in a sulfur-based solution and subsequently subjected to corrosion by immersion in a sulfide-containing solution. While reflectance in the visible spectrum yielded similar results for both surface types, the CIE a\*b\* color parameters provided a clear distinction between them. These findings were further supported by scanning electron microscopy observations, which show distinct surface morphologies.

Our results demonstrate that colorimetry is a viable tool for distinguishing patinated silver from naturally corroded patinated silver, providing valuable insights for conservation and restoration practices.

Acknowledgements: This work was funded by Fundação para a Ciência e a Tecnologia, under de projects referenced by DOI:10.54499/UIDB/04559/2020; DOI:10.54499/UIDP/04559/2020; DOI:10.54499/CEECINST/00102/2018/CP1567/CT0038).

<sup>[1]</sup> J. Rudoe, "Metal Plating and Patination: Cultural, Technical and Historical Developments" 1993, S. La Niece & P. Craddock, Oxford, 161–170.

<sup>[2]</sup> I. Tissot, O. C. Monteiro, M. A. Barreiros, M. F. Guerra, Corros. Prot. Mater. "Atmospheric corrosion of patinated silverwork: a conservation Challenge" 2016, 35, 15-19.

### A NON-INVASIVE MULTI-ANALYTICAL STUDY ON THE GLASS-GEMS COLLECTION OF THE NATIONAL ARCHAEOLOGICAL MUSEUM OF AQUILEIA

<u>Giulia Marcucci</u>,<sup>1</sup> Elisabetta Gagetti,<sup>2</sup> Maria Pia Riccardi,<sup>3,4</sup> Quentin Lemasson,<sup>5</sup> Claudia Caliri,<sup>6</sup> Gianluca Santagati,<sup>6</sup> Francesco Paolo Romano,<sup>6</sup> Francesca Rosi,<sup>7</sup> Francesca Sabatini,<sup>7,8</sup> David Buti,<sup>9</sup> Maya Musa,<sup>3</sup> Marta Novello,<sup>10</sup> Annalisa De Franzoni,<sup>10</sup> Daniela Di Martino<sup>1</sup>

<sup>1</sup>Dipartimento di Fisica "G. Occhialini", Università degli Studi di Milano-Bicocca and INFN Sezione di MilanoBicocca, Milan, Italy

<sup>2</sup>Università degli Studi di Milano "La Statale", Milan, Italy.

<sup>3</sup>Dipartimento di Scienze della Terra e dell'Ambiente (DSTA), Università degli Studi di Pavia, via Ferrata 9, 27100 Pavia, Italy

<sup>4</sup>Arvedi Laboratorio – sede di Pavia, via Ferrata 9, Università degli Studi di Pavia, 27100 Pavia, Italy <sup>5</sup> Centre de Recherche et de Restauration des Musées de France, C2RMF, 75001 Paris, and Lab-BC (UAR3506 CNRS/Ministère de la Culture/ENSCP-PSL University), France

<sup>6</sup>CNR-ISPC, Via Biblioteca 4, 95124 Catania, Italy

<sup>7</sup>CNR-SCITEC, via Elce di Sotto, 8 Perugia, Italy

<sup>8</sup>Department of Earth and Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126 Milan, Italy

<sup>9</sup>CNR-ISPC via Madonna del Piano 10, Firenze, Italy

<sup>10</sup>Ministero della Cultura Museo Storico e il Parco del Castello di Miramare – Direzione regionale musei nazionali Friuli Venezia Giulia -Museo Archeologico Nazionale di Aquileia, via Roma 1, 33081 Aquileia (Udine), Italy giulia.marcucci@unimib.it

Since antiquity, glass has been used to imitate natural gemstones, leading to the development of advanced recipes for producing opaque and coloured glass-gems. Roman glassmakers mastered the art of glass production, controlling both opacity and colour through specific firing technologies and the incorporation of chromophore elements, such as transition metals, and opacifier agents. These sophisticated techniques contributed to the widespread diffusion of glassmaking workshops across the Roman Empire, leaving a significant archaeological legacy in museum collections. The National Archaeological Museum of Aquileia (Italy) houses an outstanding collection of over 6000 gems, including approximately 1300 glass-gems, dating from the 2nd century BCE to the 3rd century CE. Despite their historical significance, these artefacts remain largely unexplored from a material and technological view.

In this perspective, we present a fully non-invasive investigation of a subset of glass-gems to shed light on their composition. This study is part of the ongoing research project "Glass-gems Exploration by Multidisciplinary Methods, Analyses and Experiments" (GEMMAE).<sup>[1]</sup> A multitechnique analytical approach has been applied in situ using portable instrumentation provided by the MOLAB platform of ERIHS.it. Elemental and spatial distribution analyses were carried out through X-Ray Fluorescence imaging and Particle-Induced X-Ray/Gamma Emission, while micro-Raman spectroscopy was employed to identify crystalline phases responsible for opacity. The integration of these techniques enabled a comprehensive and fully non-invasive characterization of the glass-gems. This multi-technique approach aims to establish a noninvasive protocol which exploits the advantages of each method to overcome their intrinsic limitations, enabling a deeper characterization of the glass-gems composition in relation to their unique and stunning features.

# THE HIDDEN CRAFT: INVESTIGATING INK ERASURE TECHNIQUES IN MEDIEVAL ARABIC SCRIBAL PRACTICES

### Giuseppe Marotta, <sup>1</sup> Claudia Colini, <sup>1,2</sup> Sowmeya Sathiyamani, <sup>1</sup> Katerina Grigoriadou <sup>1</sup>

<sup>1</sup>Centre for the Study of Manuscript Cultures, Universität Hamburg, Germany
<sup>2</sup>Institut für Archäologie und Kulturgeschichte des antiken Mittelmeerraumes, Universität Hamburg, Germany giuseppe.marotta@uni-hamburg.de

The act of writing inherently includes its opposite, the act of erasing. Several methods have been employed during the course of time with the purpose of erasing writing, and, in some cases, they have been transmitted in technical handbooks, treatises and other sources. In the Arabic world, recipes recording such methods can be found in several treatises on the arts of the book. [1,2] The present contribution investigates eleven methods to erase writing, selected among the preparations recorded in four significant Arabic treatises dating 9<sup>th</sup>-13<sup>th</sup> c. CE and compiled in different regions of the Islamic lands. We systematically tested and replicated the procedures described by the authors on mock-ups of carbon and iron-gall inks applied on papyrus, parchment, and paper supports. The study aims at assessing: a) the practicality and effectiveness of these methods; b) the detectability of treatments through non-destructive analytical techniques. In order to answer the question concerning the feasibility of the erasing methods, we considered three parameters related to their preparation and application: time needed and ease of preparation, effectiveness in ink removal, and damage induced to the support. The assessment of each parameter was based on the testing experience and on the visual observation of the erased samples. The material analysis was conducted adopting a multi-analytical approach, including digital microscopy, micro XRF fluorescence, ATR and ER-FTIR, and UV-Vis-NIR spectroscopy. The replication phase highlighted how different erasing strategies might have been preferred according to the intended purpose, thus supporting the understanding of the context of a correction or reuse. Having identified some markers of the erasing methods through material analysis, we plan, in a second stage, to repeat the analysis on the same mock-ups to assess possible changes after their artificial ageing. Additionally, the findings contributed to the compilation of a database that can facilitate the identification of erasing methods employed in historical samples.

Acknowledgements: We would like to thank: Dr. Grzegorz Nehring, for his help and suggestions during the analytical examination; Sara Fani, who helped in the identification of ingredients and interpretation of difficult passages of the recipes; Michele Cammarosano for having inspired this research with his work; Valentina Yañez Langner, Annie Muller, and Chen Yu for their contribution during the recipes' testing. The research for this study was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2176 'Understanding Written Artefacts: Material, Interaction and Transmission in Manuscript Cultures', project no. 390893796. The research was conducted within the scope of the Centre for the Study of Manuscript Cultures (CSMC) at Universität Hamburg.

<sup>[1]</sup> S. Fani, "Prendi, aggiungi, mescola e scrivi. Ricettari arabi sulla preparazione di inchiostri" 2023, Milano.

<sup>[2]</sup> M. Levey, Transactions of the American Philosophical Society "Mediaeval Arabic Bookmaking and Its Relation to Early Chemistry and Pharmacology" **1962**, 52(4), 1–79.

# ENHANCING MULTIMODAL HYPERSPECTRAL IMAGING ANALYSIS THROUGH TARGETED DIMENSIONALITY REDUCTION AND DATA FUSION

Alessia Di Benedetto,<sup>1</sup> Elisabetta Martinelli,<sup>1</sup> Alessia Candeo,<sup>1</sup> Gianluca Valentini,<sup>1</sup> Matthias Alfeld<sup>2</sup> and Daniela Comelli<sup>1</sup>

<sup>1</sup>Department of Physics, Politecnico di Milano, Piazza Leonardo da Vinci 32, Milano, Italy
<sup>2</sup>Delft University of Technology, Department of Material Science and Engineering, Mekelweg 2, 2628 CD Delft

<u>elisabetta.martinelli@polimi.it</u>

The scientific investigation of cultural heritage (CH) materials is essential to characterize their composition and assess their conservation status. Hyperspectral imaging (HSI) has emerged as a powerful non-invasive technique, enabling the acquisition of detailed spectral information across an object's surface. CH artifacts often exhibit complex and heterogeneous material distribution and to accurately assess their condition, multi-analytical strategies that emphasize non-destructive methodologies are commonly employed.<sup>[1]</sup>

Recent progress in multimodal imaging systems has facilitated the acquisition of aligned data from different imaging techniques within a single setup, enabling for the collection of different optical responses of materials while maintaining spatial correspondence through the datasets.<sup>[2–3]</sup> Conventionally, these datasets are analysed separately, with comparisons made only after dataset reduction. However, early-stage integration of complementary imaging modalities can enhance the interpretation of material composition and interactions.<sup>[4]</sup> Despite these advantages, the high dimensionality of hyperspectral data, especially when combining multiple modalities, poses significant computational challenges, demanding more efficient processing strategies.

In this study, we present recent advancements in the development of experimental setups and data acquisition protocols for multimodal imaging. Our approach integrates hyperspectral reflectance and photoluminescence (PL) imaging, time-gated PL and lifetime imaging, as well as Raman and PL microimaging. To manage the high dimensionality of these datasets, we implement a computational strategy based on spatial and spectral selection techniques, reducing data complexity while preserving essential information. By identifying the most relevant wavelengths and focusing on key regions of interest, we significantly decrease computational demands without compromising analytical accuracy. The optimized datasets from different imaging modalities are then fused at the spectral level and analyzed using multivariate and clustering methods. This workflow enables efficient multimodal data integration, leveraging spatial alignment and complementary spectral characteristics to enhance analytical potential while overcoming computational constraints.

<sup>[1]</sup> J. K. Delaney et al., Sci. Rep. 2017, 7.

<sup>[2]</sup> B. Ardini et al., J. Phys. Photonics 2024, 6, 035013.

<sup>[3]</sup> R. Moreau et al., *X-ray spectrometry* **2023**.

<sup>[4]</sup> M. Alfeld et al., C R Phys 2018, 19, 625-635.

<sup>[5]</sup> A. Paul et al., Evol. Intell. 2021, 14, 1793-802.

### CONDITION ASSESSMENT SCANNER (CAS): A FAST, HIGH PRECISION SCANNER TO ASSESS AND MONITOR THE TOPOGRAPHY OF PAINTINGS

Ana Martins,<sup>1</sup> Andre Derksen,<sup>2</sup> Dick van Lankvelt,<sup>2</sup> Christiaan ten Hove,<sup>2</sup> Sander Broers,<sup>2</sup> Lars Maxfield,<sup>2</sup> Anup Vasu Padaki,<sup>2</sup> Harm Belt,<sup>2</sup> Johan Reinink,<sup>2</sup> Kathrin Pilz,<sup>1</sup> Maranthe Lamers,<sup>1</sup> Saskia van Oudheusden,<sup>1</sup> Ruth Hoppe<sup>1</sup>

<sup>1</sup>Van Gogh Museum, Museumplein 6, 1071 DJ Amsterdam, The Netherlands <sup>2</sup>ASML, De Run 6501 · 5504 DR, Veldhoven, The Netherlands a.martins@vangoghmuseum.nl

The assessment and monitoring of paintings' appearance and condition is paramount to their care and preservation, whether in advance or return from loan, in preparation for an exhibition or conservation treatment, or in the scope of a collection survey. This assessment is generally carried out by conservators and is a painstaking activity that would benefit from a more quantitative and automated approach. In 2019, The Van Gogh Museum partnered with ASML, a Dutch multinational specialized in the development and manufacturing of photolithography machines, to develop a Condition Assessment Scanner (CAS) able to register, evaluate, and monitor the topography and colour of paintings and to fulfil the conservators' requirements for speed, accuracy, precision and operability.

The CAS prototype currently includes a fast and high-accuracy 3D imaging Keyence probe that uses pattern projection lighting complemented with 2D colour inspection. Post-processing algorithms were developed to correct the individual height and RGB images for vignetting and tilting and to create overall 2D and 3D mosaics that can be visualized and annotated in a browserbased platform. The platform also allows the comparison of images acquired at different points in time and the visualization of changes that may have occurred on the surface of a painting, for example before and after a loan. These gigapixel datasets also require smart data management to store and easily retrieve relevant information.

The CAS will soon be implemented and tested in the museum environment, while ASML proceeds with the development of a second probe for the measurement of colour and colour change.

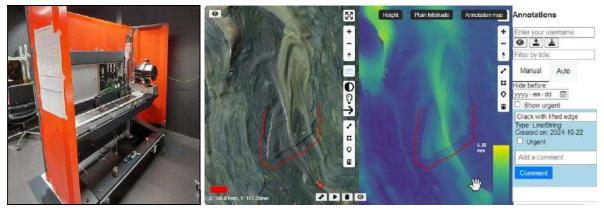


Figure 1: Condition Assessment Scanner (CAS) and CAS data visualization platform

### QUANTITATIVE MONITORING OF PHOTO-OXIDATIVE DEGRADATION OF CADMIUM YELLOW OIL PAINTINGS USING SPECTROSCOPIC TECHNIQUES AND MATHEMATICAL MODELING

<u>Sara Mattana</u>, <sup>1</sup> Francesca Rosi, <sup>1</sup> Aldo Romani, <sup>2</sup> Maurizio Ceseri, <sup>3</sup> Mario Pezzella, <sup>4</sup> Roberto Natalini, <sup>3</sup> Marine Cotte <sup>5</sup> and Letizia Monico <sup>1,2</sup>

<sup>1</sup>CNR - Institute of Chemical Science and Technologies "G. Natta", Via Elce di Sotto 8, I-06123 Perugia, Italy; <sup>2</sup>SMAArt Centre, Department of Chemistry, Biology, and Biotechnology, University of Perugia, Via Elce di Sotto 8, I-06123 Perugia, Italy

<sup>3</sup>CNR - Institute for Applied Mathematics "M. Picone", Via dei Taurini, 19 - 00185 Rome, Italy <sup>4</sup>CNR - Institute for Applied Mathematics "M. Picone", Via P. Castellino, 111 - 80131 Naples, Italy <sup>5</sup>European Synchrotron Radiation Facility, Grenoble, France

sara.mattana@cnr.it

Cadmium yellows, a class of semi-conductor pigments based on cadmium sulphide (CdS), were widespreadly used by modern and contemporary artists during the late 19th and early 20th centuries. Colour changes due to the oxidation of CdS to cadmium sulphate (CdSO<sub>4</sub>) has been found in paintings by Edvard Munch and Henri Matisse.<sup>[1, 2]</sup> This effect has been also induced in oil-based paint mock-ups for the investigation of degradation factors.<sup>[3,4]</sup>

The aim of this work consists in the acquisition of quantitative experimental parameters required for the development of a new mathematical model that simulates and predicts the formation of the CdSO<sub>4</sub> oxidation products. <sup>[5]</sup> In particular, we analysed thin sections obtained from linseed oilbased painting mock-ups, made with hexagonal CdS and aged artificially under controlled conditions of light and moisture (RH≥95%), with spectroscopic techniques at the microscale level. The concentration of CdSO<sub>4</sub> formed on the surface, confined to thin layers with a thickness of less than 20 μm, was evaluated through μ-XANES imaging and then compared and integrated with data obtained from μ-FT-IR images. These evidences were correlated to measurements performed with a range of non-invasive and non-destructive spectroscopic techniques, including VIS-NIR reflectance, Raman and FT-IR, which are able to assess the formation of CdSO<sub>4</sub> from CdS and the modifications induced in the oil binder. Moreover, a kinetics was derived by monitoring the FT-IR bands associated to the newly formed sulphate, and the intensities of three specific bands show a significant increment after delivering 1.4•10<sup>7</sup> lux•h, followed by a linear increase for values above this threshold. Finally, these findings will be added to open-access databases for the Heritage Science community, as part of the collaboration between PNRR Changes and H2IOSC projects. <sup>[6,7]</sup>

Acknowledgements: This research is financed by PNRR CHANGES and H2IOSC projects.

<sup>[1]</sup> L. Monico et al., Sci. Adv. 2020, 15, 6(20). doi: 10.1126/sciadv.aay3514.

<sup>[2]</sup> J. L. Mass et al., Applied Physics A 2012, 111(1), 3421–3428. doi.org/10.1007/s00339-012-7418-0

<sup>[3]</sup> L. Monico et al., Chemistry—A European Journal 2018. doi: 10.1002/chem.201801503.

<sup>[4]</sup> Assunta Pisu F. et al., Materials (Basel) 2022. doi: 10.3390/ma15165533.

<sup>[5]</sup> M. Ceseri, R. Natalini, M. Pezzella, Preprint. DOI: 10.48550/arXiv.2411.06997

<sup>[6] (</sup>https://www.fondazionechanges.org/en/)

<sup>[7] (</sup>https://www.h2iosc.cnr.it/).

## MULTIANALYTICAL CHARACTERISATION OF MATERIALS USED BY CONSTANT PERMEKE IN THE *RECHTSTAAND FIGUUR* SCULPTURE

### Amandine Colignon, Inneke Schwickert, Jana Sanyova and Francisco Mederos-Henry 1,4

<sup>1</sup>Materials Science for Conservation Research (MatCoRe) unit, Laboratories department, Royal Institute for Cultural Heritage (KIK-IRPA), Brussels, Belgium

<sup>2</sup>Permekemuseum/Mu.ZEE, Ostend, Belgium

<sup>3</sup>Polychromed Artifacts Laboratory, Laboratories department, Royal Institute for Cultural Heritage (KIK-IRPA), Brussels, Belgium

<sup>4</sup>Research Centre in Archaeology and Heritage (CReA-Patrimoine), Université Libre de Bruxelles (ULB), Brussels, Belgium

amandine.colignon@kikirpa.be

Constant Permeke, a major 20th-century Belgian artist primarily known for his Expressionist paintings, also created a significant body of sculptures at a later stage in his career. A research project carried out between Mu.ZEE and KIK-IRPA focused on a series of sculptures belonging to the Permekemuseum/Mu.ZEE's collections, aiming to characterize the employed constitutive materials and gain a deeper understanding of the artist's sculpting techniques. Among the thirteen sculptures analysed, dating between 1937 and 1949, the *Rechtstaand Figuur* (1937, #K000208) depicting a standing nude woman, revealed an uncommon choice of materials applied using a distinct manufacture technique.

The analysis of this artwork was conducted using a combination of analytical techniques, including optical microscopy under polarized and ultraviolet light (OM-POL/UV), Fourier transform infrared microspectroscopy ( $\mu FTIR$ ) chemical imaging, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), Raman microspectroscopy ( $\mu MRS$ ), and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS).

These analyses allowed for the precise identification of the materials used in the sculpture. The body of the *Rechstaand Figuur* was determined to be modelled from an unfired clay mass, whereas the other analysed sculptures – part of the artist's principal oeuvre – were made of gypsum. On top of the sculpture body, a complex buildup of five layers was found. The first four layers were composed of different types of organic binding or isolating materials, including siccative oil, shellac or mixtures of both of these materials. Thin metal brass foils were also found to be included in certain oil-based layers, showing signs of degradation attested by the formation of different types of metal carboxylates. Finally, a topmost brown coloured layer was found to be composed of earth pigments bound with an acrylic resin.

Such a unique choice and utilization of materials underscore Constant Permeke's early experimental approaches to sculpting and highlight the *Rechstaand Figuur's* exceptionality, not only within the sculptural *corpus* of the artist but also in regard to other contemporary Belgian modern artists.

#### Acknowledgements:

The present research was funded by the Flemish Government's Cultural Heritage degree initiative.

# NON-INVASIVE ANALYSIS OF AN ILLUMINATED MANUSCRIPT FROM SHIRAZ – REVEALING TECHINQUES AND MATERIALS

### Lucia Noor Melita, 1 Giulia Cardin, 1 Ursula Sims-Williams 1

<sup>1</sup>The British Library, 96 Euston Rd., London NW1 2DB, United Kingdom lucia.melita@bl.uk

This study presents a non-invasive analysis of the *Shahnameh* (Book of Kings) manuscript, one of the most renowned Persian illustrated epic poems, detailing the ancient kings of Iran. Composed by the poet Firdawsi in the 11th century, the poem consists of approximately 55,000 verses. The manuscript (IO Islamic 741), which is divided into two volumes, originates from Shiraz, Iran, and is believed to have been copied by the scribe Hidāyat Allāh Shirāzī in the late 16th century. Scholars suggest that the paintings within the manuscript were executed by two distinct artists, with evidence of later retouching on some of the folios.

Recently, volume one of the manuscript underwent conservation treatment to address structural issues caused by the historical binding, which had created tension in the folios. Additionally, the pigments were consolidated to stabilise the paintings before the manuscript was rebound in a more supportive text block.

The recent upgrade of the scientific laboratory facilities in the British Library Centre for Conservation provided a unique opportunity to conduct scientific analysis on the paintings, to identify the colour palette and gain insight into the production techniques of the late 16<sup>th</sup> century Shiraz artists. Ten paintings were analysed using X-Ray Fluorescence (XRF), Fibre Optic Reflectance Spectroscopy (FORS), Narrow Band Multispectral Imaging (MSI), and digital microscopy. These analyses revealed detailed information about the pigments, dyes, and materials used, highlighting the diverse artistic techniques employed in the manuscript. They also uncovered evidence of pigment discolouration and tarnishing of silver details. The findings offer a deeper understanding of the manuscript's historical significance and the craftsmanship of the artists involved.



Figure 1: IO Islamic 741, vol 1, folio 94v - XRF analysis

# LEATHER BLOOM: A MULTI-ANALYTICAL INVESTIGATION OF ITS ORIGINS AND IMPLICATIONS FOR CONSERVATION

#### Jaynisha Mistry, 1 Lucia Noor Melita1

<sup>1</sup>Conservation Department, British Library, 96 Euston Rd., London NW1 2DB, UK jaynisha.mistry@bl.uk

Leather materials, commonly encountered in historical collections, are susceptible to a variety of deterioration phenomena over time, such as mould, salt efflorescence, soap deposits and spew formations.<sup>[1-3]</sup> An unknown white substance, or 'bloom', was observed on the spines of select leather-bound volumes in the British Library collection, prompting an in-depth investigation due to its potential impact on preservation and conservation practices, as well as on public access to this active collection. The complex composition of leather shaped by tanning processes, <sup>[3,4]</sup> biological variation in the animal skin, leather dressings, and possible conservation treatments, poses a challenge in determining the exact origin of such blooms.

A multi-analytical approach was employed, utilising imaging techniques such as digital microscopy and SEM-EDX, along with Fourier-transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-MS). Preliminary results suggest that the bloom is not mould but is fatty in origin; potentially linked to natural fats from the animal hide, fats and oils used in leather manufacturing, previous conservation treatments, or a combination of these sources. However, further analysis is required to fully characterise its chemical composition and understand the environmental factors – such as temperature and relative humidity – that contribute to its formation.

Understanding the origins of this bloom is crucial for developing effective conservation strategies, widening the acceptable range of environmental parameters to reduce energy consumption, and sharing these insights with the field. This research is particularly significant as cultural heritage institutions aim to adopt more sustainable practices, minimise their carbon footprints, and address the challenges of climate change, while maintaining the integrity of their collections.

<sup>[1]</sup> W. McLean, Skin Deep "Leather 'Bloom'- Causes and Remedies" 1996, 2, 19-20.

<sup>[2]</sup> B. Pemberton, AICCM Bulletin "Identification of a white substance on 20th century leather bindings" **2008**, 31(1), 28-35.

<sup>[3]</sup> Various authors from Koninklijke Bibliotheek (KB) and the Central Research Laboratory for Objects of Art and Science, "Guidelines for the conservation of leather and parchment book bindings" 1997 (This publication is a translated and revised edition of the "Richtlijnen voor de conservering van leren en perkamenten boekbanden" issued in 1995.)

<sup>[4]</sup> P.Garside and E.Richardson, "Conservation Science: Heritage Materials" 2<sup>nd</sup> edition **2021**, The Royal Society of Chemistry, 129-160.

# PERSPECTIVE: A PROJECT DEDICATED TO THE DEVELOPMENT OF INNOVATIVE ANALYTICAL STRATEGIES FOR THE KNOWLEDGE AND PREVENTIVE CONSERVATION OF PLASTIC HERITAGE

F. Modugno, <sup>1</sup> F. Rosi, <sup>2</sup> I. Bargagli, <sup>2</sup> L. Cartechini, <sup>2</sup> C. Costantino, <sup>2</sup> A. C. Boccia, <sup>2</sup> I. Degano, <sup>1</sup> J. La Nasa, <sup>1</sup> A. Ferretti, <sup>1</sup> D. Comelli, <sup>3</sup> S. Samela, <sup>3</sup> M. A. Cardinali, <sup>3,4</sup> L. Andena, <sup>5</sup> G. de Cesare, <sup>6</sup> A. Botteon, <sup>7</sup> V. di Tullio, <sup>7</sup> D. Buti, <sup>7</sup> L. Barchi, <sup>7</sup> C. Miliani, <sup>7</sup> J. Striova, <sup>8</sup> V. Righetti Comezi <sup>9</sup>

<sup>1</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa

<sup>2</sup>CNR-SCITEC

<sup>3</sup>Dipartimento di Fisica, Politecnico di Milano

<sup>4</sup>Dipartimento di Chimica Biologia e Biotecnologie, Università di Perugia

<sup>5</sup>Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano

<sup>6</sup>Accademia delle Belle Arti dell'Aquila

<sup>7</sup>CNR-ISPC

<sup>8</sup>CNR-INO

<sup>9</sup>CNR-IOM

francesca.modugno@unipi.it

The introduction of plastics in the 19<sup>th</sup> century marked the beginning of a revolutionary era, characterized by the widespread adoption of semi-synthetic and synthetic polymers. Initially used for everyday objects, these materials quickly expanded into the domains of art and design. Today, plastic artworks and design objects constitute a significant portion of modern and contemporary museum collections. However, the short-term stability of these artifacts poses significant challenges to conservators and curators, primarily due to their heterogeneous and complex composition. The conservation of plastics is further complicated by the limited and often imprecise information available in museum catalogues.

The development of non-invasive methods, a priority in Heritage Science, becomes even more crucial for plastic artworks due to their peculiar vulnerability, heterogeneity, and material complexity. These factors hinder the standardization of effective and repeatable conservation and restoration procedures.

This poster presents the activities of the PRIN2022 interdisciplinary project PERSPECTIVE—PolymEr Research Studies for PreventivE Conservation Through non invasIVe analytical strategiEs (https://perspective.cnr.it), aimed to develop multimodal analytical approaches for the knowledge, monitoring, and preservation of plastic heritage. These approaches will deepen our understanding of ageing phenomena by combining non-invasive, in situ investigations with laboratory-based analytical techniques, eventually applicable to optimize conservation strategies for plastic artworks and design objects. In collaboration with a network of contemporary art museums across Italy and Europe, the project integrates innovative non-invasive and microdestructive traditional methods through the contextual interpretation of results obtained from the analysis of model and reference materials, conservation materials, and case studies. By correlating compositional data with mechanical properties, the project will advance our understanding of plastic heritage in art and design museums and deepen our knowledge of the degradation processes affecting these materials.

# DECIPHERING PIGMENTS AND BINDERS IN COMPLEX MIXTURES: IDENTIFICATION AND QUANTIFICATION OF SWIR SPECTRUM USING FITTING STRATEGIES

Raphael Moreau,<sup>1</sup> Lucile Brunel-Duverger,<sup>1</sup> Paola Buscaglia,<sup>2,3</sup> Tiziana Cavaleri,<sup>2,4</sup> and Laurence de Viguerie<sup>1</sup>

<sup>1</sup>Laboratoire d'Archéologie Moléculaire et Structurale - UMR 8220 - Sorbonne Université, Tour 23-33, 4 place
Jussieu, 75005 Paris cedex, France

<sup>2</sup>Fondazione Centro Conservazione e Restauro "La Venaria Reale", Italy

<sup>3</sup>Department of Applied Science and Technology, Politecnico of Turin, Italy

<sup>4</sup>Department of Economics, Engineering, Society and Business Organization, University of Tuscia, Italy

\*\*r.moreau@cyi.ac.cy\*\*

Painted works of art are unique and invaluable cultural heritage objects. They are typically complex, heterogeneous structures, composed of multiple layers and diverse materials, either pure or mixed, applied on various types of supports. Over the past two centuries, the heritage science community has focus on the extensive technical analysis of paintings, for conservation and restoration purposes, as well as for a deeper understanding of artistic techniques and authentication. Among non-destructive analytical methods, Short Wave Infrared (SWIR, 10002500 nm) spectroscopy has drawn the attention of scholars for the past ten years as a promising technique for the rapid in-situ identification of organic materials in paintings, such as binders, varnishes and pigments. However, the full potential of this method is still underexploited, as the identification of such materials based solely on SWIR spectra is challenging due to the intrinsic complexity of the signal with multiple overlapping contributions from the present materials. This study aims to assess the potential of fitting strategies to decompose the SWIR signatures of paint systems. To this end, mockups with known pigment and binder compositions were prepared as models of complex mixtures. The selected pigments—azurite, which exhibits strong absorption bands in the SWIR range, and vermilion, which lacks SWIR absorption features—were combined with linseed oil and egg yolk, two historically significant binders. These binders exhibit overlapping SWIR absorption bands, further complicated by the presence of azurite. For each mockup, our objective was to extract the contribution of each material by applying different fitting strategies, modeling the SWIR signature as a linear combination of pure material spectra, and reporting the resulting coefficients. The results demonstrated promising potential for material identification, with a degree of correlation between material quantity and fitting coefficients. A similar approach was applied to hyperspectral imaging (HSI) datacubes of mockups created at the Centro per la Conservazione e Restauro dei Beni Culturali "La Venaria Reale," successfully identifying materials through spectral fitting. These findings highlight the potential of SWIR spectroscopy combined with advanced fitting strategies for the identification—and possibly quantification—of painting materials. Future research could extend this approach by incorporating a broader spectral database of materials and refining modeling techniques for improved accuracy and reliability.

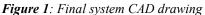
## DEVELOPMENT OF AN X-RAY SPECTRAL CT IMAGING SYSTEM FOR CULTURAL HERITAGE

Maria Pia Morigi,<sup>1</sup> Matteo Bettuzzi,<sup>1</sup> Cecilia Riccardizi,<sup>1</sup> Nayyab Amjad,<sup>1</sup> Mirco Andreotti,<sup>2</sup> Nicolò Biesuz,<sup>2</sup> Riccardo Bolzonella,<sup>2,3</sup> Rosa Brancaccio,<sup>2,3</sup> Viola Cavallini,<sup>2,3</sup> Alessandro Saputi,<sup>2</sup> Angelo Taibi,<sup>2,3</sup> Eleonora Luppi<sup>2,3</sup> and Massimiliano Fiorini<sup>2,3</sup>

<sup>1</sup>Department of Physics and Astronomy "Augusto Righi", University of Bologna, Italy <sup>2</sup>National Institute for Nuclear Physics (INFN), Ferrara Division, Italy <sup>3</sup>Department of Physics and Earth Sciences, University of Ferrara, Italy mariapia.morigi@unibo.it

A novel prototype X-ray imaging system has been designed to fulfil the growing demand for noninvasive and increasingly advanced analysis in the field of Cultural Heritage. Within the international Medipix4 Collaboration, a hybrid-pixel photon counting detector based on the Timepix4 Application-Specific Integrated Circuit (ASIC) has been developed, [1] aiming at realizing a system (fig.1) with photon counting and energy resolving capabilities, suitable for energy-resolved radiography and multi-energy computed tomography (MECT). Compared to the well-known energy-integrating detectors, these detection systems represent a cutting-edge advancement in spectral imaging. They can detect individual X-ray photons, determine their position with high spatial and temporal resolution, and most importantly measure their energy. Notably, they enable material characterization through selective energy thresholding, allowing the identification of element distribution throughout the object volume using a polychromatic Xray tube. The Timepix4 chip features a 448×512 matrix bump-bonded to semiconductor pixelated sensors (55 µm pitch) of various materials and thicknesses, providing tailored applications. Initial calibration and characterization tests have been performed on an assembly equipped with a 100 µm Si sensor.<sup>[2]</sup> Additionally, a preliminary radiographic result (fig.2) was successfully obtained using a Gallium Arsenide (GaAs) sensor, demonstrating its imaging potential. The project also involves the use of a Cadmium Telluride (CdTe) sensor to exploit its higher detection efficiency, which can lead to better results in terms of image quality and material differentiation. These advancements can mark a significant step forward in non-invasive, highresolution imaging for Cultural Heritage.





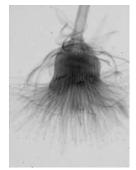


Figure 2: Radiography of a dandelion flower

*Acknowledgements*: Progetto PRIN2022, 2022ATYHZ2\_002, CUP [J53D23001740006], PNRR Missione 4 Componente 2 Investimento 1.1, finanziato dall'Unione europea – NextGenerationEU

<sup>[1]</sup> X. Llopart et al., Journal of Instrumentation 2022, 17, C01044.

<sup>[2]</sup> R. Bolzonella et al., Journal of Instrumentation 2024, 19, P07021.

## A MULTISPECTRAL APPROACH TO THE CHARACTERIZATION OF ARTWORKS BY BRAZILIAN MODERNIST PAINTER DJANIRA

#### Raysa Nardes, 1 Andre Pimenta, 1 Valter Felix, 1 Renato Freitas 1

<sup>1</sup>Instrumentation and Computer Simulation Laboratory, Federal Institute of Rio de Janeiro (IFRJ), Brazil <u>rc.nardes@gmail.com</u>

This study combines spectral imaging results to investigate the painting techniques and materials used by the artist Djanira da Motta e Silva (1914 – 1979), an important painter of the Brazilian modernist movement who emerged in the mid-1940s.<sup>[1]</sup>

A total of five authentic paintings by Djanira and one questioned painting, attributed to her, were analyzed by infrared reflectography (IRR), handheld X-ray fluorescence (XRF), and macro X-ray fluorescence scanning (MA-XRF). The authentic paintings date from 1944, 1951, 1966, 1975, and 1979, spanning four decades of the artist's production. The analyzed paintings are part of collection at the National Museum of Fine Arts (MNBA) Rio de Janeiro, Brazil.

The research aimed to develop a comprehensive repository of analytical data of the authenticated paintings, providing a scientific basis to assist in the conservation, restoration, and forensic examination of questioned paintings through direct comparisons of the materials and techniques used. Through comparative analysis, it is possible to identify inconsistencies in the color palette, material application techniques, and stratigraphic layers of the painting. [2]

The preliminary results of the analyses performed on authentic paintings revealed crucial details of the artist's creative process, such as *pentimenti*, materials used (pigments, fillers, ground or *imprimatura*), underdrawing, techniques employed, and state of conservation.

The application of advanced statistical treatment, including correlation tests between elemental maps obtained by MA-XRF and the differential attenuation of the characteristic X-rays, which is based on the calculation of the  $K\alpha/K\beta$  and  $L\alpha/L\beta$  ratios, allowed inferences about pigment mixing and the sequence of pigment layers. Furthermore, the non-invasive techniques employed highlighted the uniqueness of the artist's pictorial style, demonstrating that her works are the result of meticulous elaboration to reach the final solution.

The IRR analysis on the questioned painting revealed the presence of a hidden signature, which placed the painting two years later than originally supposed. MA-XRF analyses showed that the pigment used in the visible signature of the questioned painting is inconsistent with the palette of pigments used by the artist, indicating an addition that is likely not by the artist.

Thus, the present research represents the first examinations of scientific investigations of artworks by the painter Djanira of uncertain origin and authenticity, contributing to the preservation of her legacy and, consequently, of the Brazilian artistic heritage.

<sup>[1]</sup> F. Scovino, Artforum International 2019, 58, 23.

<sup>[2]</sup> S. Saverwyns et al., Microchemical Journal 2018, 137, 139–147.

# THIS ISN'T A MONKEY BUSINESS: MATERIALS AND TECHNIQUES IN FRANCIS BACON "STUDY FOR CHIMPANZEE"

<u>Luca Nodari</u>,<sup>1</sup> Patrizia Tomasin,<sup>1</sup> Stefano Legnaioli,<sup>2</sup> Giulia Lorenzetti,<sup>2</sup> Jacopo La Nasa,<sup>3</sup> Anna Piccolo,<sup>5</sup> Alfonso Zoleo,<sup>5</sup> Luciano Pensabene Buemi<sup>5</sup>

<sup>1</sup>CNR-ICMATE, Corso Stati Uniti 4, 35127 Padua, Italy
<sup>2</sup>ICCOM -CNR, Via G. Monuzzi 1, 56124 Pisa, Italy
<sup>3</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124, Pisa, Italy
<sup>4</sup>Department of Chemical Science, University of Padova, Via Marzolo 1, 35127 Padua, Italy
<sup>5</sup>Peggy Guggenheim Collection, Palazzo Venier dei Leoni, Dorsoduro 701, 30123, Venice, Italy

<u>luca.nodari@cnr.it</u>

Study for Chimpanzee is a vibrant artwork by Francis Bacon, belonging to the Peggy Guggenheim Collection in Venice, in which a bright magenta background provides a strong contrast with the image on the front, a Chimpanzee sitting on a trunk. The canvas was painted in the late '50 (1957, according to the Guggenheim catalogue) and it is defined as oil and pastel on canvas. This communication shows the preliminary results obtained by a multi-analytical approach combining in situ non-invasive analyses and laboratory microinvasive ones. The research aims to provide insights into the nature of pigments and binders, as well as to determine whether various materials and techniques were employed to achieve the strong contrast that defines the chimpanzee profile. Moreover, the presence of alteration products was investigated. Non-invasive in situ investigations were performed by means of Vis-NIR multi-spectral imaging, optical microscopy, FORS and ER-FTIR. While the former investigations reveal important information about the painting methods, such as the presence of lines that could be associated with a "pentimento" or represent construction lines of the painting itself (figure 1), the latter highlights the presence of different binders, depending on the selected areas. For instance, Bacon has preferred the use of a lipid-based binder in brownish areas, while the magenta one exhibits complex non easily interpretable spectra. To elucidate the information coming from the noninvasive campaign, several micro-fragments were collected and studied by Py-GC-MS, microRaman and micro-ATR spectroscopy, SEM-EDS. For instance, Py-GC-MS, performed on a magenta fragment, shows the presence of different organic moieties, as well as polyvinyl acetate, bee-wax and sugar.

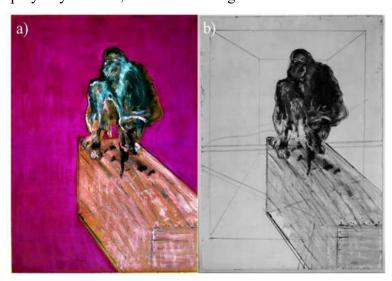


Figure 1: VIS-NIR multispectral imaging of Study for Chimpanzee: (a) RGB, (b) IR (1050)

### UNRAVELLING THE LINK BETWEEN THE SIMULACRA OF ST CLEMENTE OF PALÁCIO NACIONAL DE QUELUZ AND ST FORTUNATO & ST SEMUC OF SANTA CASA DA MISERICÓRDIA DE ALMADA

Teresa Ferreira,<sup>1,2</sup> Paula Monteiro,<sup>3</sup> Ricardo Falé,<sup>1</sup> <u>Margarida Nunes,</u><sup>1</sup> Joana Palmeirão,<sup>1,4</sup> Ana Curto,<sup>1</sup> Ana Manhita,<sup>1</sup> Luís Piorro<sup>3</sup>

<sup>1</sup>HERCULES Laboratory/IN2PAST, University of Évora, Évora, Portugal <sup>2</sup>Chemistry and Biochemistry Department, ECT, University of Évora, Évora, Portugal <sup>3</sup>Laboratório José de Figueiredo, Museus e Monumentos de Portugal, Lisboa, Portugal <sup>4</sup>CITAR, School of Arts, Universidade Católica Portuguesa, Porto, Portugal mrmpn@uevora.pt

Martyr's simulacra is a distinctive category of reliquaries that became popular from the late 17th century to the late 19th century. These complex artefacts featured the bones of early martyrs exhumed from the Roman catacombs. The devotion to these individuals, who died for their faith during the Roman Empire's persecutions, intensified after the catacombs' rediscovery in 1578.<sup>[1]</sup> Reflecting the Baroque style in both the textiles and urns, the bones were meticulously arranged with anatomical precision within metallic frameworks, artfully portraying the body as if it were reclined on a mattress and pillows, facing the viewer. These reliquaries were sent across Christendom under the Church's authority, overseeing the entire process from exhumation to arrival in the countries. One key figure during this period was Nicola Landini, Bishop of Porphyreon (1764-1782), who authenticated several relics, including St Clemente from Palácio Nacional de Queluz. Its urn bears a red wax seal confirming Bishop Landini's coat of arms, marking its arrival in Portugal in the late 18th century. Further examination of the textiles and garments associated with these three simulacra, as well as related items like flower crowns, martyrdom palms, and helmets, along with the position of the bodies and the materials used in the simulacra production, will contribute to supporting the existence of a dedicated workshop in Rome for their creation. In-situ digital radiography and endoscopy were employed to investigate the internal structure and characteristics of the bones, while digital microscopy focused on examining the textiles. Radiocarbon dating offered information about the age of the bone fragments. Chromatographic techniques such as HPLC-DAD-MS and Py-GC-MS were applied to identify natural dyes in the textiles and binding agents used in the face assemblage. Infrared spectroscopy was an essential preliminary technique for Py-GC-MS in analysing pastes, resins, adhesives, and other organic substances. Raman microscopy and SEM-EDS provided additional insights into the martyrdom palm.

Acknowledgements: The authors extend their gratitude to Dr Paula Costa and the Social Bodies of Santa Casa da Misericórdia de Almada for granting access to the simulacra of St Fortunato and Saint Semuc during in-situ campaigns and for their invaluable support in facilitating the research. We also sincerely thank Doutor António Nunes Pereira, Director of Palácio Nacional de Queluz, and Dr Joana Loureiro from Parques de Sintra – Monte da Lua, S.A., for providing access to St Clemente during the in-situ campaigns. Finally, we acknowledge FCT for its financial support through the "Holy Bodies" Project (10.54499/2022.01486.PTDC) (J. Palmeirão fellowship) and Strategic Projects 10.54499/UIDP/04449/2020, 10.54499/UIDB/04449/2020 (HERCULES Laboratory), 10.54499/LA/P/0132/2020 (IN2PAST).

<sup>[1]</sup> J. Osborne, "The Roman Catacombs in the Middle Ages. Papers of the British School at Rome" **1985**, *53*, 278-328, doi:10.1017/S0068246200011569

# HYPERSPECTRAL IMAGING FOR MONITORING LITHOBIONTIC COMMUNITIES IN THE ARCHAEOLOGICAL PARK OF POMPEII

### <u>Dmytro Nykonenko</u>, <sup>1</sup> Marta Cicardi, <sup>2</sup> Sergio E. Favero Longo, <sup>2</sup> Diego Elia, <sup>3</sup> Monica Gulmini <sup>1</sup>

<sup>1</sup>Dipartimento di Chimica, Università di Torino, Italy <sup>2</sup>Dipartimento di Scienze della Vita e Biologia dei Sistemi, Università di Torino, Italy <sup>3</sup>Dipartimento di Studi Storici, Università di Torino, Italy dmytro.nykonenko@unito.it

Hyperspectral imaging has emerged as a promising tool for characterizing a wide range of materials in various applications, including cultural heritage preservation.<sup>[1]</sup> In this study, we explore the application of hyperspectral imaging for detecting lithobiontic communities and following their dynamics in the Archaeological Park of Pompeii (UNESCO 829bis-001), a unique open-air archaeological site that faces extensive biological deterioration. The study was conducted as part of an interdisciplinary research initiative which bases in the House of the Ancient Hunt (VII.4.48).<sup>[2]</sup> A key objective of our research was to test and establish a hyperspectral imaging-based approach for tracking and documenting the expansion or regression of lithobiontic communities, by exploiting the possibility to obtain images at specific wavelength, tailored to enhance the selectivity of the imaging for the detection of the different lithobionts. The Muses 9 HS camera from Spectricon, operating within the spectral range of 365 to 1000 nm, was utilized for hyperspectral data acquisition. The surveys have been carried out in October 2024 with the aim of setting up the best conditions for data acquisition, which has been then employed in October 2025 in the same areas of the colonized walls. In addition, the camera has been used on areas previously treated with biocides and mechanically cleaned to follow the recolonization, if any. Specific spectral images extracted from the hyperspectral cube were processed using an automated computational approach based on a custom-developed Python script, which enables comparative analysis of grayscale images by quantifying brightness variations and calculating the percentage of surface coverage by the lithobionts. Additionally, it facilitates the comparison of images, allowing for the assessment of colonization dynamics over time.

The procedure indicates that hyperspectral imaging has potential to markedly improve the detection and quantitative assessment of communities in comparison to conventional RGB photography. In addition, the comparison with other image elaboration approaches is also discussed.<sup>[3]</sup>

**Acknowledgements:** The PNRR - Partenariato Esteso 5 project "CHANGES" - Spoke 6: history, conservation and restoration of Cultural Heritage is acknowledged for financial support.

<sup>[1]</sup> M. Picollo, C. Cucci, A. Casini, L. Stefani, Sensors "Hyper-Spectral Imaging Technique in the Cultural Heritage Field: New Possible Scenarios" **2020**, 20, 1-13.

<sup>[2]</sup> D. Elia, S. Guion, V. Meirano, M. Serino, S. E. Favero-Longo, M. Cicardi, C. Tonon, M. Morando, E. Matteucci, M. Gulmini, D. Nykonenko, D. Castelli, L. Guidorzi, A. Re, A. L. Giudice, F. Brigadeci, M. Cardinali, M. C. Canepa, A. Scarcella, *Scavi di Pompei "La Casa della Caccia Antica (VII 4,48): nuove ricerche interdisciplinari e studi sulla colonizzazione lichenica"* **2024**, *22*, 2-16.

<sup>[3]</sup> C. Gazzano, S. E. Favero-longo, E. Matteucci, R. Piervittori, *The Lichenologist "Image analysis for measuring lichen colonization on and within stonework"* **2009**, *41*(3), 299–313.

## WATERPROOF TEXTILES IN THE HIPPOMOBILE HERITAGE COLLECTION OF KMKG-MRAH

<u>Mathilde Occelli</u>, <sup>1,2</sup> Henri Cosemans, <sup>1</sup> Ferenc Borondics, <sup>3</sup> Emile Van Binnebeke, <sup>4</sup> Koen Janssens, <sup>1,2</sup> Andrea Marchetti <sup>1,2,4</sup>

<sup>1</sup>ARCHES research group, University of Antwerp, Antwerp (BE)

<sup>2</sup>AXIS research group, University of Antwerp, Antwerp (BE)

<sup>3</sup>SMIS beamline, SOLEIL synchrotron, Gif-Sur-Yvette (FR)

<sup>4</sup>Royal museums of Art and History (KMKG-MRAH), Brussels (BE)

mathilde.occelli@uantwerpen.be

Historical horse-drawn vehicles such as carriages or sledges were constantly exposed to outdoor environmental conditions which included direct contact with rain, snow or high humidity. Thus, specific materials including waterproof coated textiles were needed to protect the water-sensitive components of the vehicles. The abundance of such waterproof fabrics in various locations on historical vehicles clearly shows the crucial protective purpose they served. Despite this key role, waterproof coated textiles have never been the subject of thorough research. Their composition, context of use and technology remain, therefore, still an open question.

This study aims to shed light on such materials through the investigation of waterproof coated textiles found in the hippomobile heritage collection of the Royal Museums of Art and History (KMKG-MRAH) in Brussels. This collection includes over 100 vehicles representing a complete cross-section of European society from late 17<sup>th</sup> until early 20<sup>th</sup> century. Several analytical techniques (OM, SEM-EDX, µATR-FTIR and SR-µFTIR in transmission) were performed in order to gain information on the textile fibers and coating materials involved as well as the context of their use. This allowed the identification of four preliminary classes of coated textiles, that presented significant differences not only in terms of macroscopic appearance and functional purposes, but also in terms of chemical composition and stratigraphy.

These results constitute the first systematic study of such materials, representing a first step towards a better understanding of the chemistry and historical technology of waterproof fabrics. This information will be relevant for the preservation of all collections containing waterproof coated textiles, as well as to better understand the historical context of these unique materials.



**Figure 1:** Examples of waterproof coated textiles in the collection of KMKG-MRAH: a) decorated oilcloth in a gala berline (1856), b) early linoleum in a gala berline (first half of 19<sup>th</sup> c.), c) curtain made of oilcloth in a travel carriage (approx. 1860).

### ELEMENTAL FEATURES EXTRACTION IN X-RAY FLUORESCENCE SPECTROSCOPY THROUGH MACHINE LEARNING FOR HISTORICAL PIGMENTS

### <u>Ivan Oliverio</u>, <sup>1,2</sup> Claudia Scatigno, <sup>2</sup> Giulia Festa<sup>2</sup>

<sup>1</sup>Dipartimento di Fisica, Università La Sapienza di Roma, 00185, Roma, Italy
<sup>2</sup>CREF – Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi, Via Panisperna 89a c/o P.za del
Viminale 1, 00184 Roma, Italy
ivan.oliverio@uniroma1.it

The authenticity, production methods, and conservation status of oil paintings are key questions that can be addressed through the application of material characterization techniques. Among these methods, X-ray fluorescence (XRF) stands out as a powerful tool for elemental analysis of pigments in paintings. In the literature, two primary methodological approaches have been developed to classify pigments with different compositions using machine learning algorithms: a semi-quantitative approach, which employs normalized peak areas, and a more qualitative approach that utilizes the entire spectrum. In the semi-quantitative approach, background signal intensity is removed, which can lead to the omission of organic information. Conversely, the qualitative approach, which uses the entire spectrum, is influenced by the significant difference in count rates between the sample's major lines. Proper normalization could mitigate these issues and facilitate the extraction of additional features.

Here we present a novel methodology that combines X-ray fluorescence and machine learning, using the entire spectrum normalized with respect to its maximum intensity. The methodology is tested on a heterogeneous dataset of historical pigments from the INFRA-ART database, an opensource spectral library. The results are in agreement with traditional methods, while also showing an improvement in classification effectiveness through the new method. This study is expected to significantly impact the field of art authentication, contributing to the development of a robust procedure for the attribution of oil paintings and art prints.

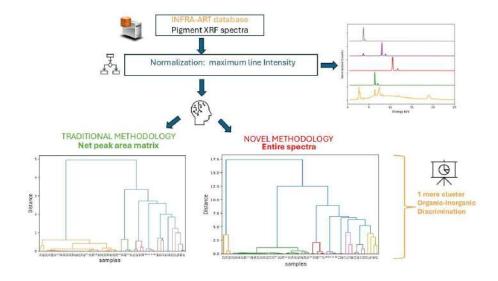


Figure 1: Schematic Abstract.

# TEY AND FY COMPLEMENTARY APPLICATION FOR THE ANALYSIS OF LAYERED SAMPLES WITH XAS IN CULTURAL HERITAGE SAMPLES

### Jacopo Orsilli, 1,2 Anna Galli, 1 Simone Caglio, 1 Francesco d'Acapito 2

<sup>1</sup>Department of Materials Science, University of Milano-Bicocca, U5, Via Roberto Cozzi, 55, Milano 20126, Italy <sup>2</sup>CNR - Istituto Officina dei Materiali (IOM), c/o ESRF LISA CRG, Avenue des Martyrs 71, Grenoble 38000, France <u>jacopo.orsilli@unimib.it</u>

XAS analysis is a great tool for investigating the local environment of an atomic species; however, like many X-ray techniques (e.g. XRF), the information collected is always an average of the whole volume investigated. Besides, the investigated volume size depends on various factors: i.e. source energy, sample density and composition, and collection mode. For example, in transmission, the whole irradiated volume is investigated, in fluorescence the volume depends on the geometry of acquisition and the fluorescence line energy, while in total electron yield, it depends on the Auger electron energy.

The definition and quantification of the volume investigated may not be necessary if the sample is homogeneous. Still, it becomes crucial if we work with layered samples, as it often occurs in fields like electrochemistry (electrodes may be subjected to changes on the surface during their working cycles) or cultural heritage (where photochemical alteration processes are mostly observed on the sample's surface).<sup>[1]</sup>

In this presentation, we will talk about the advantages and issues in the analysis of layered samples in fluorescence and Total Electron Yield (TEY) mode, showing the complementarity of these two techniques in the cultural heritage samples analysis, both for punctual analyses and for mapping purposes, showing their application for the study of ceramics Luster samples.<sup>[2-4]</sup> Indeed, these samples present a complex layered structure, with various elements in different oxidation states in their layers, and can be easily employed as benchmark samples.

<sup>[1]</sup> L. Monico, F. d'Acapito, M. Cotte, K. Janssens, A. Romani, G. Ricci, C. Miliani, L. Cartechini, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2023**, *539*, 141–147. doi:10.1016/j.nimb.2023.03.040.

<sup>[2]</sup> S. Padovani, I. Borgia, B. Brunetti, A. Sgamellotti, A. Giulivi, F. D'Acapito, P. Mazzoldi, C. Sada, G. Battaglin, *Appl. Phys. A* **2004**, *79*, 229–233. doi:10.1007/s00339-004-2516-2.

<sup>[3]</sup> S. Padovani, C. Sada, P. Mazzoldi, B. Brunetti, I. Borgia, A. Sgamellotti, A. Giulivi, F. D'Acapito, G. Battaglin, *Journal of Applied Physics* **2003**, *93*, 10058–10063. doi:10.1063/1.1571965.

<sup>[4]</sup> S. Padovani, D. Puzzovio, C. Sada, P. Mazzoldi, I. Borgia, A. Sgamellotti, B. G. Brunetti, L. Cartechini, F. D'Acapito, C. Maurizio, et al. *Appl. Phys. A "XAFS Study of Copper and Silver Nanoparticles in Glazes of Medieval Middle-East Lustreware (10th–13th Century)"* **2006**, *83*, 521–528. doi:10.1007/s00339-006-3558-4.

### SURFACE AND IN-DEPTH PHYSICAL AND STRUCTURAL CHANGES ON DAMMAR AND ACRYLIC VARNISHES UPON ARTIFICIAL AGING

Mohamed Oujja, <sup>1</sup> Laura Maestro-Guijarro, <sup>1</sup> Marta Castillejo, <sup>1</sup> Paula María Carmona-Quiroga, <sup>2</sup> Alice Dal Fovo, <sup>3</sup> Raffaella Fontana, <sup>3</sup> Francesca Rosi, <sup>4</sup> Martina Alunni Cardinali, <sup>5</sup> Aldo Romani, <sup>5</sup> Lucia Comez, <sup>6</sup> Cristiano Riminesi, <sup>7</sup> Magdalena Iwanicka, <sup>8</sup> Piotr Targowski, <sup>9</sup> Magdalena Kowalska, <sup>9</sup> Aggelos Philippidis <sup>10</sup> and Paraskevi Pouli <sup>10</sup>

<sup>1</sup>Instituto de Química Física Blas Cabrera (IQF), CSIC, Madrid, Spain

<sup>2</sup>Instituto de Ciencias de la Construcción Eduardo Torroja (IETcc), CSIC, Madrid, Spain

<sup>3</sup>Consiglio Nazionale delle Ricerche-Istituto Nazionale di Ottica (CNR-INO), Florence, Italy

<sup>4</sup>Consiglio Nazionale delle Ricerche-Istituto di Scienze e Tecnologie Chimiche (CNR-SCITEC), Perugia, Italy

<sup>5</sup>Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia, Italy

<sup>6</sup>Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali (CNR-IOM), Perugia, Italy

<sup>7</sup>Consiglio Nazionale delle Ricerche-Istituto di Scienza del Patrimonio (CNR-ISPC), Sesto Fiorentino, Italy

<sup>8</sup>Faculty of Fine Arts, Nicolaus Copernicus University in Toruń, Toruń, Poland

<sup>9</sup>Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Toruń, Poland

<sup>10</sup>Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology-Hellas (FORTH),

Heraklion, Crefe, Greece

m.oujja@iqf.csic.es

Varnishes are used in painted artworks for protection from atmospheric pollution and oxidation and for improving the aesthetic appearance of paintings by providing an even and brilliant surface finish. Varnishes are sensitive to environmental conditions (light, temperature, humidity, etc.) and therefore are prone to physical and chemical modifications over time. Detailed studies have been undertaken to investigate the possible induced degradation effects and offer safe procedures to improve and complement painting conservation and restoration practices. In the present study, a multi-analytical approach has been tested to assess the surface and in-depth physical and chemical changes induced on dammar and acrylic varnishes upon artificial aging (photo and thermohygrometric aging). The adopted approach is based on the use of different photonic spectroscopies and microscopies such as Reflectance Imaging Spectroscopy (RIS) in the Visible, Optical Coherence Tomography (OCT), Laser Scanning micro-Profilometry, Non-linear Optical Microscopy in the modality of Multiphoton Excitation Fluorescence (NLOM-MPEF), Brillouin Spectroscopy (BLS), external Reflection FTIR Spectroscopy and Laser Induced Fluorescence (LIF). The obtained results signpost the correlations between the varnish nature, aging conditions, and the presence of the underlying painting material on the varnish degradation. While, as expected, dammar shows serious damage effects upon photo-aging, the acrylic varnish reveals better stability and resistance. Chemical/compositional variations due to light-ageing have been correlated with morphological, optical and visco-elastic changes. NLOM-MPEF has allowed in a non-invasive way the determination of in-depth photo-degradation gradients for dammar varnish. Finally, the proposed multi-analytical approach could be used as a non-invasive tool for monitoring the varnish conditions and its possible influence on the underlying paint.

#### Acknowledgments:

This work is partially funded by the IPERION HS project of the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement n. 871034. Funding from projects PID2022-137017OB-I00 (of MCIN/AEI/10.13039/501100011033/FEDER, UE) and TEC Heritage-CM (TEC-2024/TEC-39 of Regional Government of Madrid) and support from the CSIC Interdisciplinary Platform "Open Heritage: Research and Society" (PTI-PAIS) are acknowledged.

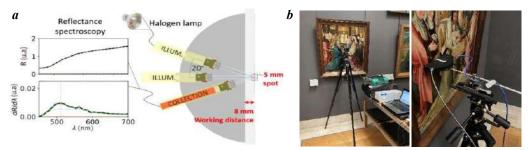
#### OPTICAL ANALYSIS OF GOLD AS A PAINTING MATERIAL

### <u>Laura Paggi</u>, Aurélie Tournié, Lionel Simonot, Maëlle Vilbert, Anne Pillonnet, Romain Thomas and Christine Andraud

<sup>1</sup>Centre de Recherche sur la Conservation (CRC), Muséum national d'Histoire naturelle, CNRS, Ministère de la Culture, 75005 Paris, FRANCE

<sup>2</sup>Institut Pprime, Université de Poitiers, 86 360 Chasseneuil-du-Poitou, FRANCE <sup>3</sup>Institut Lumière Matière, Université Claude-Bernard-Lyon-I, 69 100 Villeurbanne, FRANCE <sup>4</sup>Institut National d'Histoire de l'Art, 75 002 Paris, France laura.paggi@mnhn.fr

The use of gold as a painting material in Western Europe after the Middle Ages was long considered abandoned by art historians. However, while its prevalence has indeed declined, gold has never completely disappeared from easel paintings. AORUM is an interdisciplinary project bringing together history, techniques and optics around an original corpus dating from the 16<sup>th</sup> and 17<sup>th</sup> centuries.<sup>[1]</sup> The intrinsic properties of metals give them a very unique reflectance distribution in space as well as inducing their highly specific colours.<sup>[2]</sup> Spectral and colorimetric analysis of specular and diffuse reflectance components of a painted surface is a staple for retrieving its appearance attributes. However, understanding these spectral and colour data is a complex task, as the probed areas are composed of textured stacked layers of varying materials. In addition, measurements can be challenging due to fragility, limited accessibility and preciousness of art works.



**Figure**: a. Operating principle of 3D printed fibre spectrometer head allowing for both specular and diffuse reflectance measurements. b. In situ measurements of easel painting gildings

In this paper, we present as part of the AORUM project optical section, the analysis of gold samples and gilding mock-ups using derivative reflectance spectroscopy, in order to identify gold purity as well as surface condition effects on their reflectance profile. Experimental results are backed up with optical simulations. Finally, we report the development of a contactless measurement tool and protocol for *in situ* characterization of easel paintings, presented in the above figure.

Acknowledgements: AORUM is funded by the French National Research Agency (ANR-22-CE27-0010), and received financial support from the Fondation des Sciences du Patrimoine (ANR-17-EURE-0021), the Université Paris Lumières, the Université Paris Nanterre, the Musée du Louvre, and the IPERION-HS/ARCHLAB network (EU). Since December 2023, AORUM is a research programme of Institut national d'histoire de l'art.

<sup>[1]</sup> R. Thomas, E. Adam, AORUM – Le Projet 2022, Hypotheses. https://aorum.hypotheses.org.

<sup>[2]</sup> A. Bartecki, J. Burgess, *The Colour of Metal Compounds* **2000**, Gordon and Breach Science Publishers, Amsterdam, 37-111.

## SCIENTIFIC RECONSTRUCTION OF THE SMELL OF A HISTORIC PERFUME THROUGH GC-MS-O AND SENSORY ANALYSIS

### Emma Paolin, <sup>1</sup> Fabiana Di Gianvincenzo, <sup>1,2</sup> Matija Strlič<sup>1</sup>

<sup>1</sup>Heritage Science Laboratory Ljubljana, Faculty of Chemistry and Chemical Technology, University of Ljubljana,
Slovenia

<sup>2</sup>Rijksmuseum, Netherlands
emma.paolin@fkkt.uni-lj.si

The volatile organic compounds (VOCs) emitted by heritage objects give not only information on their material composition and state of preservation but also represent their distinctive smells. Recently, the study of heritage smells has gained significant interest, highlighting their role in communicating history and learning about the past.<sup>[1]</sup>

Characterisation of the olfactory profile of materials requires chemical and olfactory information that can be obtained through gas-chromatography coupled with mass spectrometry and olfactory detection (GC-MS-O) combined with sensory analysis by a panel of trained assessors.<sup>[2]</sup> Our current research focusses on the reconstruction of heritage smells based on such data, exploring two approaches to reconstruction:

- 1. Concentration-based approach: This considers compounds found in the highest concentrations using GC-MS. Their olfactory impact is assessed by calculating the odour activity value (OAV), i.e. the ratio of compound concentration to its odour detection threshold (ODT), ensuring that only compounds relevant for the smell are included in the reconstruction.
- 2. **Perception-based approach:** The compounds perceived as strong odorants during olfactory analysis with GC-O are taken into account. Once the odorants are identified by matching with the corresponding chromatographic peaks, their respective OAVs are used to develop the reconstructed mixture.

A case study involving a historic perfume from the 1940s is presented. Its headspace was analysed using GC-MS-O. The reconstruction process begins with a minimal set of five key compounds and is incrementally expanded to a maximum of 15 compounds. GC-MS-O analysis identified 15 principal odorants in the heritage perfume, including linalool, linalool oxide, pcymene, eucalyptol, and camphor, which contribute to floral and fresh notes. Each reconstructed mixture is validated by a trained sensory panel and is analysed with GC-MS to ensure consistency with the original chemical composition.

This optimised reconstruction method would enable the preservation of historic smells and smells of heritage objects while also offering museums the possibility to exhibit such smells for a more immersive experience.

Acknowledgements: Slovenian Research and Innovation Agency (projects N1-0228, P1-0447, and P1-0153).

<sup>[1]</sup> C. Bembibre, S. Barrat, L. Vera, M. Strlič, ICOM-CC18th Trienn. Conf. Copenhagen 2017, 4–8.

<sup>[2]</sup> E. Paolin, C. Bembibre, F. Di Gianvincenzo, J. C. Torres-Elguera, R. Deraz, I. Kraševec, A. Abdellah, A. Ahmed, I. Kralj Cigić, A. Elnaggar, A. Abdelhalim, T. Sawoszczuk, M. Strlič, *Journal of the American Chemical Society* **2025**.

# PHYSICO-CHEMICAL STUDY OF PIGMENTS AND INKS USED IN MANUSCRIPTS FROM *LA GRANDE CHARTREUSE*

### <u>Hélène Pasco</u>, <sup>1</sup> Victor Poline, <sup>1</sup> Sophie Rochut, <sup>2</sup> Laurence Rivière Ciavaldini, <sup>3</sup> Nils Blanc, <sup>1</sup> Pierre Bordet, <sup>1</sup> Pauline Martinetto <sup>1</sup>

<sup>1</sup>Université Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, France
<sup>2</sup>Laboratoire d'Archéologie Moléculaire et Structurale, Sorbonne Université, France
<sup>3</sup>Laboratoire Universitaire Histoire Cultures Italie Europe, Université Grenoble Alpes, France

<u>helene.pasco@neel.cnrs.fr</u>

This study focuses on the physico-chemical analysis of manuscripts from *la Grande Chartreuse* monastery. They were kept at the monastery until the end of the 18<sup>th</sup> century and are now stored at the *Bibliothèque d'Etude et du Patrimoine* in Grenoble (France). The aim of this work was to explore the material composition of pigments and inks used in these manuscripts through noninvasive methods developed in our laboratory,<sup>[1]</sup> combining X-ray Fluorescence (XRF) and X-ray Powder Diffraction (XRPD), which have already proved their value for the study of heritage objects and medieval manuscripts in particular.<sup>[2]</sup> The analyses were performed on two medieval manuscripts: the first (out of four) volume of the *Grosse Bible de Chartreuse* (ms.2) and its associated *Homiliaire* (ms.22), dated from the second half of the 12<sup>th</sup> century.

The analyses revealed a variety of pigments used in the illuminations, including lead white, minium, cinnabar, lapis lazuli, azurite and orpiment, predominantly in mixtures. Iron gal ink has been identified in the original text throughout the whole manuscripts, while copper- and zinc-rich inks were used for later additions in the text. These first results differ significantly from those obtained during the previous study on another Bible, the so-called *Notre-Dame de Casalibus* (mss.1,8,3),<sup>[2]</sup> written in the same monastery and dating from the beginning of the 12th century. Only a few decades separate these manuscripts, but the palette and the way in which the colors were used by the decorators and copyists indicate a break in the techniques and materials used. Additionally, comparison across the different folios allowed for the distinction between the different decorators and copyists, corroborating earlier codicological studies.<sup>[3]</sup> Moreover, the cracks networks in the illuminated initials have been examined to obtain information about the binders used by the decorators. Finally, these results have provided insights into the origin of raw materials (local *vs.* imported), and suggested the possible existence of shared or evolving recipes and craftsmanship practices within the monastic community over time.

These findings enhance our understanding of historical and cultural exchanges within medieval monasticism and contribute to the broader field of manuscript studies and conservation science.

**Acknowledgements:** The authors are grateful to I. Westeel, E. Spagnol and F. Wanecq from the Bibliothèque d'Etude et Du Patrimoine (Grenoble, France) for giving access to the manuscripts. This work was supported by the fundings of labex PATRIMALP (IDEX UGA).

<sup>[1]</sup> V. Poline, P. Bordet, O. Leynaud, A. Prat, R. Bruyère, N. Blanc, F. Lelong & P. Martinetto, *The European Physical Journal Plus* **2023**, *138*(3), 239.

<sup>[2]</sup> V. Poline, «Développements méthodologiques pour l'analyse par rayons X d'œuvres du patrimoine culturel: instrumentation mobile et intelligence artificielle appliquée au traitement de quantités massives de données» 2024, (PhD thesis, Université Grenoble Alpes).

<sup>[3]</sup> D. Mielle de Becdelièvre, «Prêcher en silence : enquête codicologique sur les manuscrits du XIIe siècle provenant de la Grande Chartreuse » **2004**, 17, PU Saint-Etienne, 590p.

## MULTI-CLASS NORMALIZED POTENTIAL CONTRAST AND APPLICATIONS TO MULTISPECTRAL IMAGES OF MANUSCRIPTS

### Wallace Peaslee, <sup>1</sup> Anna Breger, <sup>1</sup> Carola-Bibiane Schönlieb <sup>1</sup>

<sup>1</sup>Department of Applied Mathematics and Theoretical Physics, University of Cambridge, United Kingdom wep25@cam.ac.uk

Determining which bands in a multispectral (or hyperspectral) image contain the most relevant information for a given task can be challenging. Potential contrast (PC) is a useful tool for identifying such bands, e.g. those which show degraded notation most clearly. PC was introduced as an image quality measure in the context of multispectral images of ostraca.<sup>[1]</sup> It quantifies the maximal contrast possible between samples from two classes of pixels following an arbitrary grayscale transformation, generating a binarized image. The measure requires labelling a few pixels relevant to a given task and aims to capture the underlying information content inherent in an image rather than its perceived visual quality. We generalized PC to multiple classes and introduced a normalized version that is consistent across imaging formats.<sup>[2]</sup>

Here, we illustrate the utility of multi-class normalized PC when applied to multispectral images, primarily as a method to evaluate which bands have useful information but also as a preprocessing or image segmentation tool. The examples we use are drawn from historic music manuscripts that contain common features and challenges like the presence of multiple pigments, ink bleeding through manuscript pages, and various degradations. Below, Figure 1 shows an example where two different inks are used in a 15<sup>th</sup>-century manuscript at the Gonville & Caius College Library (number 810). There are three classes (two inks and the background), so binary PC cannot be applied directly. A multispectral band (centred around 425nm) gives a multi-class normalized PC value of 0.9964. A second band (centred around 570nm) has a value of 0.8506. So, when choosing a band for distinguishing between the two inks, we can select the one with the highest multi-class normalized PC value (i.e. the band centred around 425nm); for this band we also provide the segmentation produced by multi-class normalized PC. Through similar examples, we will illustrate how multi-class normalized PC can be applied in range of contexts.



Figure 1: From left to right. 1) A multispectral band centred around 425 nm with labels showing two inks (in red and green) and background (in blue). 2) A band centred around 570nm with the same labels. 3) A multi-class PC segmentation showing the classes corresponding to the two inks and background in black, grey, and white respectively. Image use by kind permission of the Master and Fellows of Gonville and Caius College, Cambridge.

Acknowledgements: WP is supported by an EPSRC Doctoral Training Partnership grant EP/W524633/1.

<sup>[1]</sup> S. Faigenbaum et al., *Journal of Archaeological Science "Multispectral images of ostraca: acquisition and analysis"* **2012**, *39.12*, 3581-3590.

<sup>[2]</sup> W. Peaslee, A. Breger, and C. B. Schönlieb, "Potential Contrast: Properties, Equivalences, and Generalization to Multiple Classes" 2025, submitted.

### A NOVEL BASED APPROACH FOR WAX-RESIN LINING ADHESIVE REMOVAL

### <u>Ilaria Pecorelli</u>,<sup>1</sup> Theofania Xantouli,<sup>2</sup> Sofia Carletti,<sup>3</sup> Kristalia Melessanaki,<sup>2</sup> Grazia De Cesare,<sup>3</sup> Paraskevi Pouli<sup>2</sup>

<sup>1</sup>University of Rome Tor Vergata, Department of History, Cultural Heritage, Education and Society, Via Columbia 1, 00133 Rome, Italy

<sup>2</sup>Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology-Hellas (FORTH), 100 N. Plastira str, Vassilika Vouton, GR 71300, Heraklion, Crete, Greece

<sup>3</sup>Academy of Fine Arts of Macerata, Restoration and Conservation Institute of the Marches (I.R.M.), Piazza Vittorio Veneto 5, 62100 Macerata, Italy

ilaria.pecorelli97@gmail.com

Lining is a practice long employed in painting conservation involving the attachment of a second canvas using an adhesive to reinforce the weakened original. Among the adhesives historically used, wax-resin lining was introduced by the Dutch conservator Nicoolas Hopman in the 19th century. This lining method was considered to be effective for paintings in humid climates, leading to its wider adoption across Europe and beyond. However, following the Greenwich Conference – hosted in 1974 and regarded as the main conference regarding lining practice - and the subsequent observation of the adhesive's ageing, several risks and degradation issues emerged<sup>[1-2]</sup> leading to its gradual abandonment.

A current challenge in conservation is the removal of the wax-resin adhesive. As the structural support provided by the lining diminishes over time, its removal and replacement is necessary. The effectiveness of a new lining, which employs alternative adhesives, depends on the thorough elimination of the wax-resin. [2] Traditionally this removal has been performed mechanically using scalpels, a method that damages the fibres of the original canvas support, along with solvents, which can produce folds and wavings in the painting along with unwanted penetration into the paint layer. [2]

In this study, we investigate various laser systems and a novel approach to removing the waxresin adhesive. We developed mock-ups replicating a real case study, a wax-resin lined oil canvas entitled *Portrait of Matilde Monori Puini* by Gualtiero Baynes in 1905. Near infrared (NIR) and visible (VIS) systems employing Nd:YAG lasers at respectively 1064 nm and 532 nm, as well as Excimer KrF and ArF (UV) lasers emitting at 248 nm and 193 nm were used to clean the verso of the mock-ups. Our systematic study demonstrates that the KrF excimer laser at 248 nm can achieve controlled and effective cleaning without damaging the canvas fibers, unlike the traditional methods. This research extends the current state of the art by establishing optimal cleaning parameters, which were assessed using optical and scanning electron microscopy (SEM).

<sup>[1]</sup> G. A. Berger, H. I. Zeliger, *Preprints:ICOM Committee for Conservation 4<sup>th</sup> triennial meeting Venice 13-18 October 1975* **1975**.

<sup>[2]</sup> P. Ackroyd, Conserving canvas 2023, C. Shwarz, I. McClure, J. Coddington, 60-66.

# DECODING THE PAST: MOLECULAR AND MICROBIAL SIGNATURES OF HISTORICAL PARCHMENTS

### Maria João Penetra, António Candeias, 1,2,3 Catarina Miguel, Ana Teresa Caldeira Cal

<sup>1</sup>HERCULES Laboratory -Cultural heritage, Studies and Safeguarding & IN2PAST – Associate Laboratory for Research and Innovation in Heritage, Arts, Sustainability and Territory, Évora University, Palácio do Vimioso, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal

<sup>2</sup>Chemistry Department, School of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671 Évora, Portugal

<sup>3</sup>City University of Macau Chair in Sustainable Heritage & Sino-Portugal Joint Laboratory of Cultural Heritage Conservation Science, University of Évora, Casa Cordovil, 7000-651 Évora, Portugal

d53086@alunos.uevora.pt

Parchment, a writing material crafted from processed animal skins, has been central to the transmission of knowledge for centuries. Derived from sheep, calves, and goats, identifying the precise animal source is sometimes challenging due to the extensive processing methods and environmental factors these materials undergo, affecting their long-term preservation and the degradation of biomolecular signatures over time.<sup>[1–5]</sup>

This study applies a multidisciplinary methodology to characterize historical parchment samples at both the molecular and microbial levels. Mitochondrial DNA analysis combined with 16S rRNA metabarcoding was utilized to determine parchment animal origin and to investigate the microbial communities associated with the material. To complement these findings, non-invasive spectroscopic techniques, including Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR) and Raman Spectroscopy, were applied to assess the chemical composition and structural integrity of the samples.

By integrating genetic, microbial and spectroscopic data, this research enhances our ability to identify the biological origins of parchment and sheds light on the impact of historical production and preservation processes. The findings will contribute to the refinement of conservation strategies for historical documents and broaden our understanding of ancient manuscript materials.

Acknowledgements: The authors wish to acknowledge the financial support of FCT – Foundation for Science and Technology, I.P.-within the scope of UI/BD/154922/2023 (Penetra, M. J. PhD Grant), the project "ROADMAP - Research On Antonio De Holanda Miniatures Artistic Production" (PTDC/ART-HIS/0985/2021), the HERCULES Lab (DOI:10.54499/UIDB/04449/2020) and City U Macau Chair in Sustainable Heritage & Sino-Portugal Joint Laboratory of Cultural, and IN2PAST (DOI:10.54499/LA/P/0132/2020).

<sup>[1]</sup> D. Pangallo, K. Chovanova, A. Makova, *J. Archaeol. Sci. "Identification of Animal Skin of Historical Parchments by Polymerase Chain Reaction (PCR)-Based Methods*" **2010**, 37, 1202–1206, doi:10.1016/j.jas.2009.12.018.

<sup>[2]</sup> G. Piñar, H. Tafer, M. Schreiner, H. Miklas, K. Sterflinger, Environ. Microbiol. "Decoding the Biological Information Contained in Two Ancient Slavonic Parchment Codices: An Added Historical Value" 2020, 22, 3218–3233, doi:10.1111/1462-2920.15064.

<sup>[3]</sup> F. Cappa, G. Piñar, S. Brenner, B. Frühmann, W. Wetter, M. Schreiner, P. Engel, H. Miklas, K. Sterflinger, *Int. Biodeterior. Biodegradation "The Kiev Folia: An Interdisciplinary Approach to Unravelling the Past of an Ancient Slavonic Manuscript"* **2022**, *167*, 105342, doi:10.1016/j.ibiod.2021.105342.

<sup>[4]</sup> E. Malea, S. C. Boyatzis, D. Karlis, D. Palles, S. Boghosian, S. Zervos, *Journal of Raman Spectroscopy "The Complementary Use of Raman, ATR-FTIR Spectroscopy, and Chemometrics for Investigating the Deterioration of Artificially Aged Parchment"* **2024**, *55*, 1266–1280, doi:10.1002/jrs.6755.

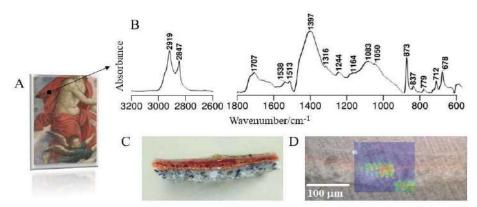
<sup>[5]</sup> A. Malissa, F. Cappa, M. Schreiner, M. Marchetti-Deschmann, *Molecules "Spectral Features Differentiate Aging-Induced Changes in Parchment—A Combined Approach of UV/VIS, μ-ATR/FTIR and μ-Raman Spectroscopy with Multivariate Data Analysis"* **2023**, *28*, doi:10.3390/molecules28124584.

### ATR-FTIR MAPPING OF PIGMENTS, BINDERS, AND DEGRADATION PRODUCTS IN A 17TH-CENTURY ARTWORK

### <u>Ewa Pieta</u>, <sup>1</sup>Justyna Olszewska-Świetlik, <sup>2</sup> Aleksandra Zając, <sup>2</sup> Wojciech M. Kwiatek, <sup>1</sup> Katarzyna Pogoda <sup>1</sup>

<sup>1</sup>Institute of Nuclear Physics Polish Academy of Sciences, PL-31342 Krakow, Poland
<sup>2</sup>Department of Painting Technologies and Techniques, Institute for the Study, Conservation and Restoration of Cultural Heritage, Nicolaus Copernicus University in Torun, Sienkiewicza 30/32, PL-87100 Torun, Poland
<a href="mailto:ewa.pieta@ifj.edu.pl">ewa.pieta@ifj.edu.pl</a>

This study applied Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (ATRFTIR) and optical microscopy to investigate the composition of pigments, binders, fillers, and degradation products in the 17th-century painting *The Coronation and Assumption of the Blessed Virgin Mary*, housed in the Convent of the Sisters of St. Catherine in Orneta, Poland. The nondestructive nature of ATR-FTIR, coupled with the spatial resolution of about 5 microns, enabled the analysis of micro-samples from different areas of the painting (Figure 1).<sup>[1]</sup>



*Figure 1*: Selected part of the painting – Christ's robe (A), ATR-FTIR spectrum (B), optical microscopy image of the micro-sample cross-section (C), ATR-FTIR map distribution of chalk (surface map for the 874 cm<sup>-1</sup> band) (D).

The results revealed a diverse range of materials, including white, blue, red, and black pigments, and identified binding media such as proteins, triglycerides, fatty acids, and resin acids. Degradation products like whewellite, moolooite, and lead soaps were also detected. The painting's multilayer structure was confirmed through optical microscopy, and ATR-FTIR mapping provided detailed chemical distributions. Notably, lead white, smalt, azurite, cinnabar, and red ochre were identified, reflecting techniques commonly used at the turn of the 16th century. The findings suggest that the painting was influenced by Northern European (most probably Dutch) artistic traditions, particularly in using grey underpainting and combining pigments such as lead white and chalk. This suggests the use of a white known as ceruse, a mixture of lead white and chalk in a 1:1 ratio. Among others, ceruse was mentioned by Théodore Turquet de Mayerne (1573-1655). These insights contribute to understanding the painting techniques of the Polish North School and offer valuable data for its future conservation.

<sup>[1]</sup> E. Pięta, J. Olszewska-Świetlik, C. Paluszkiewicz, A. Zając, Wojciech M. Kwiatek, *Vibrational Spectroscopy* **2019**, *103*, 102928.

### INSIGHTS INTO GILT LEATHER GOLD VARNISH BY MULTIANALYTICAL PY-GC/MS ANALYSES

### <u>Valentina Pintus</u>, <sup>1</sup> Celine Bonnot-Diconne, <sup>2</sup> Pablo Londero, <sup>1</sup> Elsa Bourguignon, <sup>1</sup> Jerome Farigoule <sup>1</sup>

<sup>1</sup>Louvre Abu Dhabi (LAD), United Arab Emirates (UAE) <sup>2</sup>Private practice, France vpintus@louvreabudhabi.ae

This work focuses on the elucidation of the main organic constituents used for the gold varnish in a gilt leather panel – *The Triumph of David* (17<sup>th</sup> century) - as part of a more extensive research, which includes conservation treatments and an in-depth multi-analytical approach aiming to understand the materiality, state of conservation, and different materials used in past restorations (see poster *P. Londero et al.*). The term gold varnish does not imply the use of gold in the varnish but instead it refers to the application of an oil/resin-based varnish on to silver leaf glued on a leather-type of support with a final gold-like appearance. Recipes adopted for such varnishes generally contained different ingredients depending on the geographical area, period, and workshops. Mainly due to their process of production, ageing conditions, and conservation treatments, it is generally considered highly challenging to identify and characterize the main gold varnish constituents, especially those occurring as only minor amounts such as amber, saffron, and asphalt. The detection of such minor constituents in addition to the main ones may be used as markers for discriminating the recipes, and therefore their detection would provide important and valuable historical information.

For this purpose, an advanced multifunctional Pyrolysis – Gas Chromatography / Mass Spectrometry (Py-GC/MS) approach as well traditional GC/MS analyses were performed to investigate semi-quantitatively the lipidic, resinous, waxy, and proteinaceous contents on selected gold varnish-based samples. The data obtained on such samples were then compared to those obtained on specific gilt leather gold varnish models previously prepared and reported elsewhere. [1] More precisely, different Py-GC/MS-based techniques such as reactive Single-Shot (SS) PyGC/MS, partially reactive Double-Shot (DS) Py-GC/MS, Evolved Gas Analysis (EGA)-MS, Heart-Cut EGA-GC/MS, as well as the recently developed SS Py-GC/MS with FunctionalSplitless injection for high-sensitivity analysis of trace samples, were applied and newly compared, demonstrating their respective advantages and limitations in identifying gold varnish minor and major constituents.

The results obtained within this work provided valuable information about the main and minor constituents used for the gilt leather gold varnish, thus assisting with attribution to a specific type of historical gold varnish, and therefore perhaps specific workshops. Additionally, it also offers a useful guidance for selecting the optimal Py-GC/MS-based method for gold varnish analysis in the cultural heritage field to gain the most information with minimal sample amount.

Acknowledgements: We would like to thank Laurianne Robine, Marie Radepont, Sylvie Heu-Thao (Centre de Recherche sur la Conservation (CRC), Muséum national d'Histoire naturelle, Ministère de la Culture, CNRS, Paris, France) for providing us the gilt leather gold varnish models and for sharing their valuable knowledge.

<sup>[1]</sup> L. Robinet, S. Heu-Thao, M. Radepont, C. Bonnot-Diconne, Vibrational Spectroscopy 2020, 110, 103133.

# ANALYSIS OF ALLOYS AND CORROSION STRUCTURES IN ANCIENT BRONZES USING THE COMBINED PROTOCOL OF X-RAY FLUORESCENCE AND MONTE CARLO SIMULATION (XRF-MCS)

Marta Porcaro, <sup>1</sup> Caterina Canovaro, <sup>2</sup> Gilberto Artioli, <sup>2</sup> Anna Depalmas, <sup>3</sup> Carlo Casi, <sup>4</sup> Barbara Barbaro, <sup>5</sup> Rosario Maria Anzalone, <sup>6</sup> Caterina De Vito, <sup>1</sup> Antonio Brunetti <sup>7</sup>

<sup>1</sup>Department of Earth Sciences, Sapienza University of Rome, Rome, Italy

<sup>2</sup>Department of Geosciences, University of Padova, Italy

<sup>3</sup>DUMAS department, University of Sassari, Sassari, Italy

<sup>4</sup>Fondazione Vulci, Montalto di Castro, Italy

<sup>5</sup>Soprintendenza Archeologia Belle Arti e Paesaggio per la provincia di Viterbo e per l'Etruria meridionale, Italy

<sup>6</sup>Musei Reali di Torino, Torino, Italy

<sup>7</sup>Biomedical Sciences Department, University of Sassari, Sassari, Italy

marta.porcaro@uniromal.it

One of the key aspects to consider when dealing with a cultural asset is its uniqueness, which necessitates its preservation. Therefore, the development and application of nondestructive techniques is indispensable in the field of diagnostics. Among these, X-ray fluorescence (XRF) is one of the most widely used methods for investigating the elemental composition of archaeological objects, such as metal artifacts. However, qualitative elemental analysis alone is often insufficient to fully understand the composition of an alloy and, consequently, the metallurgical knowledge of the society that produced it. Although bronze is a relatively simple alloy, it has a complex microstructure due to the natural corrosion processes that have been formed by the interaction between the surface and the environment. These processes generate heterogeneous multilayer patinas, which can also produce phenomena such as selective enrichments or depletions of specific elements within the alloy. Such alterations pose significant challenges to the accurate characterization of ancient bronze artifacts. To overcome these challenges, an advanced analytical protocol was developed that integrates X-ray fluorescence (XRF) with Monte Carlo simulation (MCS).<sup>[1]</sup> MCS is a probabilistic algorithm used, in this case, to simulate a real XRF measurement. This approach enables modeling of multilayer corrosion structures, allowing for a more precise quantification of the elemental composition and a deeper understanding of the original alloy's characteristics. By applying this methodology, we can identify the original alloys of an artifact and variations in composition, due to rework or restoration of the object or alteration processes through characterization of corrosive structures.<sup>[2]</sup> In addition, a portable XRF instrument was used in these studies, so the analyses were performed directly in situ, without the need to move the artifact. This technique has been successfully applied to many bronze artifacts, including Sardinian-made navicelle and tools, as well as Etruscan fibulas and statuettes. The data obtained using the XRF-MCS protocol were also compared with those acquired using destructive techniques, obtaining very similar results, underscoring the method's reliability and potential for applications in the field of cultural heritage conservation and archaeometallurgical studies. [3]

<sup>[1]</sup> A. Brunetti, B. Golosio, Spectrochimica Acta Part B: Atomic Spectroscopy 2014, 94–95, 58.

<sup>[2]</sup> M. Porcaro, S. Lins, A. Depalmas, R. M. Anzalone, R. Iannaccone, A. Brunetti, *Materials* 2023, 16.

<sup>[3]</sup> M. Porcaro, B. Barbaro, C. Canovaro, G. Artioli, C. Lucarelli, F. Lugli, A. Depalmas, A. Brunetti, *Journal of Archaeological Science: Reports* **2023**, *51*, 104230.

#### A SYNERGY BETWEEN PICTORIAL SKILLS AND MACROSCOPIC X-RAY FLUORESCENCE IMAGING TO PRODUCE HIGH TECH MOCK-UPS

#### Simone Porcinai, <sup>1</sup> Giulia Ciabattini, <sup>1</sup> Lucrezia Sepiacci <sup>1</sup> and Monica Galeotti <sup>1</sup>

<sup>1</sup>Opificio delle Pietre Dure, Ministero della Cultura, Italy simone.porcinai@cultura.gov.it

Representative mock-ups of ancient artefacts are essential in conservation studies to investigate degradation mechanisms and compare the performance of conservation approaches, but they are even more important as a testing ground for new analytical strategies. Polychrome surfaces are typically characterized by layered systems and resolving their complexity through a non-invasive approach is the greatest challenge of the last years in the field of heritage science. Both to evaluate the ability of mono- or multi-technique approaches to provide the correct distribution of materials in paintings<sup>[1,2]</sup> and to train algorithms for automatized processing and interpretation systems,<sup>[3]</sup> it is key to create mock-ups that reproduce the complexity of real paintings and that have not only defined composition and sequence, but also known thickness of the layers. In this work, we started from an extensive survey of the scientific literature on microscopic analyses of samples taken from Renaissance paintings to get to produce and characterize mock-up coupons with structural and compositional features similar to those of real polychrome objects. The coupons were made by an experienced conservator following the typical Italian egg-tempera technique, that is, by applying layers of various pure pigments or mixtures of them with egg yolk on a plaster base, with and without an imprimitura layer made of white lead. The addition of an amount of strontium to the gypsum and glue plaster and the application of macroscopic X-Ray Fluorescence (MA-XRF) imaging enabled us to achieve a pixels wise characterization of the thickness of painting layers. To do this, we mapped the  $K\alpha/K\beta$  ratio of the strontium in the ground layer and we built up calibration curves for the XRF data<sup>[4,5]</sup> by preparing crosssections of samples taken from the mock-ups and measuring the thickness of the individual layers with a scanning electron microscope.

In this way, we were able to connect the *a priori* known composition and sequence to information on the thickness of the individual layers and to set up a protocol for the production of high-tech pictorial mock-ups.

<sup>[1]</sup> E. Kechaoglou, K. A. Agrafioti, G. P. Mastrotheodoros, D. F. Anagnostopoulos, C. Kosmidis, *J. Anal. At. Spectrom.* **2024**, *39*, 854.

<sup>[2]</sup> L. M. de Almeida Nieto, F. Gabrieli, A. van Loon, V. Gonzalez, J. Dik, R. Van de Plas, M. Alfeld, *X-Ray Spectrometry* **2024**, *53*, 438-452.

<sup>[3]</sup> Z. Preisler, R. Andolina, A. Busacca, C. Caliri, C. Miliani, F. P. Romano, Science Advances 2024, 10, eadp6234.

<sup>[4]</sup> S. Porcinai, A. Heginbotham, Spectrochimica Acta Part B: Atomic Spectroscopy 2021, 180, 106158.

<sup>[5]</sup> R. Zito, L. Bonizzoni, N. Ludwig, Sustainibility 2024, 16, 2467.

# ADVANCED REMOTE SENSING FOR CULTURAL HERITAGE: RAMAN SPECTROSCOPY, FLUORESCENCE ANALYSIS AND LIBS FOR NON INVASIVE DIAGNOSTICS

#### Stefania Porcu<sup>1</sup> and Daniele Chiriu<sup>1</sup>

<sup>1</sup>Department of Physics, University of Cagliari, SP8, 09042 Monserrato CA, Italy stefania.porcu@dsf.unica.it

Remote sensing technologies play a crucial role in the conservation of cultural heritage, offering non-invasive and highly precise analysis of both artworks and architectural structures. Advanced spectroscopic techniques such as Raman spectroscopy, fluorescence analysis, and Laser-Induced Breakdown Spectroscopy (LIBS) enable the detailed characterization of material composition, degradation processes, and past restorations.<sup>[1–3]</sup> These methods allow conservators to detect hidden alterations and environmental effects that may compromise the integrity of heritage assets. Raman spectroscopy provides molecular identification of pigments, binders, and degradation products, aiding in the authentication and conservation of paintings, sculptures, and historical artifacts. Fluorescence analysis helps reveal varnish layers, organic compounds, and previous restoration treatments, while LIBS enables elemental composition analysis, crucial for identifying materials used in different historical periods. Together, these techniques facilitate a deeper understanding of material aging and degradation, supporting the development of more effective and minimally invasive conservation strategies.

By integrating remote sensing tools, conservation professionals can adopt a proactive approach to heritage preservation, minimizing physical interventions while enhancing diagnostic capabilities. The continuous advancement of these technologies strengthens sustainable conservation efforts, ensuring the long-term protection of invaluable cultural artifacts and architectural heritage.

<sup>[1]</sup> B. Yogurtcu, N. Cebi, A. T. Koçer, A. Erarslan, *Molecules "A Review of Non-Destructive Raman Spectroscopy and Chemometric Techniques in the Analysis of Cultural Heritage"* **2024**, *29*, doi:10.3390/molecules29225324.
[2] V. Lazic, R. Fantoni, "Applicazioni della Laser Induced Breakdown Spectroscopy (LIBS) per i beni culturali" **2020**, Contenute

<sup>[3]</sup> F. A. Pisu, C. M. Carbonaro, P. C. Ricci, S. Porcu, D. Chiriu, Heritage "Cadmium Yellow Pigments in Oil Paintings: Optical Degradation Studies Utilizing 3D Fluorescence Mapping Supported by Raman Spectroscopy and Colorimetry" **2024**, 7, 2426–2443, doi:10.3390/heritage7050115.

# ILLEGIBLE WRITINGS RECOVERED IN CARBONIZED FIREDAMAGED MANUSCRIPTS WITH HIGH LATERAL RESOLUTION AND HIGH CHEMICAL SENSITIVITY μ-XRF SCANNING: THE CASE OF THE *TORINO*, *BNU*, *L.II.14*.

Eva Luna Ravan, 1,2 Silvia Bottura-Scardina, 1 Rosario Andolina, 1 Irene Barba Castagnaro, 3 Michela Botticelli, 1 Sveva Longo, 1 Marco Maulu, 4 Costanza Miliani, 1 Gianluca Santagati, 1 Francesco Paolo Romano, 1 Claudia Caliri 1

<sup>1</sup>CNR-ISPC Catania, Italy

<sup>2</sup>Department of Classics, Sapienza University of Rome, Italy

<sup>3</sup>Department of Physics, University of Calabria, Cosenza, Italy

<sup>4</sup>Department of History, Human Sciences, and Education Italy, University of Sassari, Italy

evaluna.ravan@uniromal.it

The legibility of ancient fire-damaged manuscripts remains a significant challenge, even after substantial restoration work. Direct or indirect contact with fire causes a series of extreme, complex, and irreversible material and structural changes, including uneven thermal contraction of the support and denaturation of the parchment, resulting in the shrinkage of the textual parts. Moreover, such damage may add to previous degradation phenomena occurring in medieval manuscripts, such as oxidation and the migration of inorganic compounds in the writing inks across the support. Even after restoration, ancient fire-damaged manuscripts may show an unrecoverable loss of optical contrast between the writing and the support, particularly in highly carbonised pages, making it impossible to access their literary content. Optical methodologies, such as UVfluorescence photography, either alone or in combination with contrast enhancement techniques, have been tested in the past<sup>[1]</sup> but can be insufficient for severely damaged items. Mobile μ-XRF scanning techniques offer a promising alternative, as they can generate 2-D elemental distribution maps of the materials used in ink in a completely non-invasive and contact-free manner. Considering the above, this paper presents the work towards the development of an analytical methodology for writing recovery in severely fire-damaged parchment manuscripts using a mobile μ-XRF scanning system with real-time imaging capabilities developed by CNR-ISPC (Catania) and featuring an innovative hodoscopic detection system based on 4-SDDs, enabling high chemical sensitivity. The methodology has been applied to the French-Picard manuscript L.II.14 (dating back to 1311) of the Biblioteca Nazionale Universitaria (BNU), Turin. A fire that broke out in 1904 affected the BNU and damaged Ms L.II.14, along with a large part of the entire manuscript collection, posing significant challenges for legibility and conservation.<sup>[2]</sup> The results of μ-XRF imaging of the manuscript conducted at various lateral resolutions to accommodate the morphological irregularities of individual folios and combined with advanced data post-processing techniques, enabled the recovery of textual portions that were previously completely inaccessible to the naked eye.

Acknowledgements: 1) PNRR projects: PRIN PNRR 2022 "AFAF: All Fire, all Flames", M4C2, CUP B53D2302879001; 2) E-RIHS European Infrastructure of Heritage Science (E-RIHS). 3) CHANGES, Spoke 5 PNRR PROJECT PE0000020; 4) H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029.

<sup>[1]</sup> F. Pottier, A. Michelin, L. Robinet, Journal of Cultural Heritage 2019, 36, 183-190.

<sup>[2]</sup> V. Cachia, *Scrineum Rivista* **2020**, *17*, 193-210; see also <a href="https://bnuto.cultura.gov.it/biblioteca-digitale/la-cultura-deldono/incendio-1904/">https://bnuto.cultura.gov.it/biblioteca-digitale/la-cultura-deldono/incendio-1904/</a> (last accessed 20 March 2025).

### VIBRATIONAL SPECTROSCOPY INVESTIGATIONS IN IPERION HS IDELA, KHIPUS, AND PEPI PROJECTS

<u>Klara Retko</u>,<sup>1,2</sup> Lea Legan,<sup>1,3</sup> An Jacqemain,<sup>4</sup> Lucrezia Milillo,<sup>5</sup> Marei Hacke,<sup>6</sup> Aurore Mathys,<sup>7,8</sup> Polonca Ropret<sup>1,2</sup>

<sup>1</sup>Research Institute, Institute for the Protection of Cultural Heritage of Slovenia, Research Institute, Slovenia

<sup>2</sup>Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

<sup>3</sup>National Museum of Slovenia, Slovenia

<sup>4</sup>Museum M, Belgium

<sup>5</sup>University of St Andrews, Scotland

<sup>6</sup>Swedish National Heritage Board, Sweden

<sup>7</sup>Royal Museum for Central Africa, Belgium

<sup>8</sup>University of Liège, Belgium

klara.retko@zvkds.si

The results from vibrational spectroscopy conducted across three selected IPERION HS transnational access—IDeLA, KHIPUS, and PePI—as part of the FIXLAB platform are presented, aiding interpretation of museum objects and their historical contexts by providing materialtechnical insights. The workflow, challenges, and outcomes are discussed. Project IDeLA focused on identifying historical decorative laminates (catalogue and museum samples). Raman spectroscopy revealed colouring agents such as zinc sulphide, titanium dioxide, and organic red and green pigments (PR112, PG8).<sup>[1]</sup> Additionally, FTIR spectroscopy in mapping mode allowed for the identification and distribution of materials like melamine-formaldehyde, ureaformaldehyde, cellulose, and lignin, providing insights into the versatile, multi-layered composition of the laminates.<sup>[1]</sup> In the KHIPUS project, vibrational spectroscopy played a role in the material analysis of khipus—colourful knotted cords used as a writing system in the Andes. Conventional Raman spectroscopy detected mercury sulphide (cinnabar) on one sample, while Surface-Enhanced Raman Spectroscopy (SERS) identified purpurin in another, indicating the use of a purpurin-rich madder dye. The PePI project focused on identifying the pigments used on a selection of Pende masks at the Royal Museum for Central Africa. Over 20 samples of different masks, all painted with red pigments but varying in shade, were analysed. Due to the strong fluorescence, conventional Raman spectroscopy was limited, so SERS were also employed. These techniques revealed the presence of iron oxide (hematite) and lead oxide. Additionally, the vibrational spectra (FT-Raman, SERS, and FTIR) suggested the presence of compounds associated with the species of *Pterocarpus* genus, most likely santalins, showing the possibility of the use of the red pigment tukula/n'gula.



Figure 1: a) Cross-section of a historical decorative laminate sample, examples of b) khipu and c) Pende masks.

Acknowledgements: IPERION HS (Grant Agreement n. 871034.)

<sup>[1]</sup> A. Jacquemain, K. Retko, L. Legan, P. Ropret, F. Waentig, V. Cattersel, Heritage Science 2023, 11, 98.

#### UNVEILING ANCIENT MARITIME SECRETS TROUGH X-RAY COMPUTED TOMOGRAPHY (CT): IRON-BASED FINDS FROM THE ARCHAIC SHIPWRECK OF GIGLIO-CAMPESE

<u>Cecilia Riccardizi</u>,¹ Matteo Bettuzzi,¹ Maria Pia Morigi,¹ Nayyab Amjad,¹ Anna Mazzinghi,² Lucilla Fabrizi,³,⁴ Rosarosa Manca,³ Alessandro Naso,⁵ Marco Benvenuti³,6

<sup>1</sup>Department of Physics and Astronomy "Augusto Righi", University of Bologna, Italy

<sup>2</sup>Department of Physics and Astronomy, University of Florence, Italy

<sup>3</sup>Department of Earth Sciences, University of Florence, Italy

<sup>4</sup>Museo "La Specola"- University Museums System, University of Florence, Italy

<sup>5</sup>Department of Humanistic Studies, University of Naples Federico II, Italy

<sup>6</sup>Institute of Geosciences and Earth Resources, National Research Council, Italy

cecilia.riccardizi@unibo.it

In the 1980's, the Island of Giglio (Tuscany, Italy) became the site of an extraordinary discovery: a shipwreck in the Bay of Campese, dating back to the early 6th century BC. Initially located by professional divers (about two decades earlier), it was through the meticulous excavation led by Mensun Bound, who would later become a prominent figure in underwater archaeology, that both the ship's cargo and its structural remains were brought to light. Thanks to the extremely heterogeneous composition of the load of international scope, this archaeological find represents a break-through in understanding archaic trade networks across the Tyrrhenian Sea. As part of a wide-ranging multidisciplinary collaboration involving various institutions and experts, our team employed X-ray computed tomography (CT) to explore the mysterious history of the ship and, in turn, of our own past. Among the numerous remarkable samples, some highly corroded and splintered iron-based materials were analysed with a custom-designed CT system, suitable for both on-site and laboratory scanning. These fragments are characterized by degradation phenomena and a thick layer of concretions, making the original shape illegible and, therefore, also their function. Hence, two measurement campaigns were organised with the aim of reconstructing their original morphology and thus identifying the type of artifacts. The analyses were carried out in our X-ray imaging laboratory in Ravenna (Emilia-Romagna, Italy). The setup was equipped with a 200 kVp X-ray tube and a flat-panel detector with an area of approximately 19×24 cm<sup>2</sup>, with 127 µm pixel size. The objects were held and slowly rotated by means of a solid rotation platform, featuring a precision high-load rotary stage. In this configuration, more than 20 tomographic scans were performed with a voxel size of about 100 µm, resulting in a massive amount of data. While calcareous incrustations can be virtually removed, it has not yet been possible to define with certainty the type and function of the investigated artefacts. Some hypotheses have been proposed based on the profiles, mostly of quadrangular section, originally occupied by the metal, now entirely or almost entirely consumed by corrosion, leaving only a layer of mineralized concretion containing little to no metallic core. To support our investigation, complementary X-ray fluorescence analyses (XRF) were performed on specific points of the finds allowing us to determine also their elemental composition. Although what remains of these objects found in the depth of the Tyrrhenian Sea is just a "ghost" of the original ones, our CT examination, together with visual inspection and XRF results, contributed to throw light on ship's cargo composition of Greek and Etruscan origin and on its route's stages.

*Acknowledgements*: Progetto PE 0000020 CHANGES, CUP [J33C22002850006], PNRR Missione 4 Componente 2 Investimento 1.3, finanziato dall'Unione europea – NextGenerationEU.

### INSIGHTS ON THE COMPOSITION OF POMPEIAN PIGMENTS INTO THE WALL PAINTINGS OF THE *DOMUS DI ARIANNA* IN POMPEII

### S. Brizzi, M. M. N. Franceschini, 1,2 S. Vettori, I. Osticioli, B. Salvadori, L. Chiarantini, D. Magrini, C. Riminesi

<sup>1</sup>National Research Council, Institute of Heritage Science (CNR-ISPC), Via Madonna del Piano 10, Sesto Fiorentino (FI), Italy

The domus di Arianna (Regio VII, Insula 4) is one of the largest houses in Pompeii and it resulted from the union of two independent houses: a Samnite house in Doric style, which in the 2nd century BC was added to a peristyle in the Ionic style and a Tuscanic atrium.<sup>[1]</sup> The domus had various uses over the centuries, including wool production and the creation of aesthetic products such as perfumes and unguents. [2,3] The polychrome wall paintings inside the domus offer a varied representation of Roman painting techniques, particularly remarkable for their stylistic diversity and the completeness of their material and chromatic variety. This research aims to identify the pigments used in Roman wall paintings, focusing specifically on the red pigments. The characterization was carried out using molecular and elemental techniques in a multi-scale and multi-resolution approach on wall paintings samples pre-selected by in-situ investigation through non-invasive techniques (p-XRF, ER-FTIR and FORS). A combination of techniques, SEM-EDS, synchrotron radiation-based X-ray techniques (μ-XRPD) and vibrational spectroscopy methods (μ-Raman and u-FTIR with FPA chemical imaging) were used to identify the compositional pigments in the stratigraphy. The red pigments show the presence of cinnabar and red ochres, which, in IV Style decoration, are combined with different lead compounds, such as cerussite (PbCO<sub>3</sub>), laurionite (PbCl(OH)) and traces of wulfenite (PbMoO<sub>4</sub>). The results of the comparative analysis of the different wall paintings found in the domus reveal similarities and differences in the ground layers, pigment palettes, and periodic artistic techniques, which are critically discussed in relation to the literature. [4-6]

Acknowledgements: The research activity was conducted within the ARIANNA Project (PRIN2022, NEXT GENERATION EU – CUP B53D23022390006). Authors warmly thank the Archeological Park of Pompeii in Naples, in particular the Eng. V. Calvanese for support in organizing the campaigns. Some analysis were performed at ESRF at ID13 in the framework of the proposal HG-237 under GA 870313, Streamline).

<sup>&</sup>lt;sup>2</sup>Department of Science of Antiquities, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy <sup>3</sup>National Research Council, Institute of Applied Physics (CNR-IFAC), Via Madonna del Piano 10, Sesto Fiorentino (FI), Italy

<sup>&</sup>lt;sup>4</sup>Center of Electronic Microscopy and Microanalysis (MEMA), University of Florence, Via G. Capponi 3r, (FI), Italy cristiano.riminesi@cnr.it

<sup>[1]</sup> V. Bruni, "Case a peristilio di Pompei: funzioni e forma" 2023, Quasar, Roma.

<sup>[2]</sup> M. Bustamante Álvarez, E. Huguet Enguita, A. Ribera i Lacomba, "Studi e ricerche del Parco archeologico di Pompei" **2020**, 40, 267-280. DOI: 10.1400/276441

<sup>[3]</sup> M. Bustamante-Álvarez, A. R. i Lacomba, "Approaches to the Analysis of Production Activity at Archaeological Sites" 2020, 25.

<sup>[4]</sup> M. Cotte, E. Checroun, J. Susini, P. Dumas, P. Tchoreloff, M. Besnard, P. Walter, *Talanta* **2006**, *70(5)*, 1136-1142. DOI: 10.1016/j.talanta.2006.03.007

<sup>[5]</sup> C. Cucci, M. Picollo, L. Chiarantini, G. Uda, L. Fiori, B. De Nigris, M. Osanna, *Microchemical Journal* **2020**, *158*, 105082. DOI: 10.1016/j.microc.2020.105082

<sup>[6]</sup> P. Walter, P. Martinetto, G. Tsoucaris, R. Brniaux, M. A. Lefebvre, G. Richard, E. Dooryhée, *Nature* 1999, 397(6719), 483-484. DOI: 10.1038/17240

#### DEVELOPING A NATIONAL TRUST PAINT SAMPLE ARCHIVE

#### Valentina Risdonne, 1 Christiane Offner, 1 Emma Schmuecker, 1 Rebecca Hellen 1

<sup>1</sup>Royal Oak Foundation Conservation Studio (ROFCS), Knole House, Kent, United Kingdom valentina.risdonne@nationaltrust.org.uk

The National Trust (NT) is embarking on a transformative project to establish a Paint Sample Archive that will centralise, catalogue, and facilitate access to thousands of historic paint samples. This initiative aims to enhance interdisciplinary research, support conservation efforts, and foster collaboration among heritage professionals. In addition, the archive also has a role in supporting the development of public-facing information that provides an engaging and more authentic experience for NT visitors. The investigations centered around the pigment archive provide opportunities to inform and engage visitors through under the bonnet insights into conservation processes, and previously unknown stories relating to the collection and interiors.

NT oversees the UK's largest collection of paintings, wall paintings, and painted interiors across 200 historic buildings, spanning from Roman-era sites to 20th-century vernacular architecture. Paint samples, collected through conservation projects, hold critical information on decorative schemes, material history, and degradation mechanisms. However, these resources remain largely unpublished, inconsistently documented, and physically dispersed across NT properties and external institutions.

This project seeks to address these challenges by establishing an accessible Paint Sample Archive based at the Royal Oak Foundation Conservation Studio (ROFCS) at Knole, Kent. The archive will serve as an active collection, integrating past and future sampling with standardised documentation and innovative research methodologies. The initiative aligns with NT's strategic research goals and UK Research and Innovation (UKRI) infrastructure ambitions, enhancing internal scientific capabilities and positioning NT as a leader in paint research.

By engaging with the conservation and heritage science community, we aim to ensure the Paint Sample Archive becomes a valuable resource for both NT properties and the wider sector. At the conference, we will invite attendees to provide feedback on the project's framework and share insights on best practices for structuring and utilising such an archive. The work frame and suggested methodology will be outlined and a survey will be available to gather perspectives on access needs, research applications, and potential collaborations. Join us in shaping the future of paint research at the National Trust.

Acknowledgements: This research is supported by funding from RiCHES (Research Infrastructure for Conservation and Heritage Science), part of UK Research and Innovation (UKRI). We gratefully acknowledge their support in advancing heritage science research and facilitating collaboration across institutions. Grant ID AH/Z506060/, Reference APP20065.

# NEW INSIGHTS ABOUT GIORGIO DE CHIRICO'S PAINTING TECHNIQUE: THE AUTOMATIC MATERIALS RECOGNITION OF THE ARTWORK MOBILI NELLA STANZA (1927), BY MACHINE LEARNING AND CHEMOMETRIC APPROACH BASED ON SPECTROSCOPIC DATA

Martina Romani, <sup>1</sup> Lucilla Pronti, <sup>1</sup> Giuseppe Capobianco, <sup>2</sup> E. Gorga, <sup>2</sup> Isaure Landèche, <sup>2</sup> B. Valenti, <sup>1</sup> Antonella Balerna, <sup>1</sup> Gianluca Verona Rinati, <sup>3</sup> Giuseppe Bonifazi, <sup>2</sup> Marcella Ioele, <sup>4</sup> Barbara Lavorini, <sup>4</sup> Marco Angelucci, <sup>1</sup> Giacomo Viviani, <sup>1</sup> Vittorio Sciarra, <sup>1</sup> Silvia Serranti <sup>2</sup> and Mariangela Cestelli Guidi <sup>1</sup>

<sup>1</sup>INFN – Laboratori Nazionali di Frascati, via Enrico Fermi 54, 00044, Frascati, Italy <sup>2</sup>Dipartimento Ingegneria chimica materiali ambiente, Università di Roma "Sapienza", via Eudossiana 18, 00184, Roma, Italy

martina.romani@lnf.infn.it

Spectroscopic analyses acquired in situ and in reflection mode from the visible through the midinfrared (IR) range (400 nm to 28 µm) provide fundamental information about organic and inorganic materials used by the artists in paintings. Starting from multi-analytical approaches <sup>12</sup>, multi-sensor strategies have been developed in recent years leading to optimization and integration of the results obtained from different diagnostic techniques. In this work we combined hyperspectral data obtained from reflectance spectroscopy and external reflection FTIR data to identify the pictorial technique and the chemical composition of the materials used in the painting "Mobili nella Stanza", realized in 1927 by Giorgio De Chirico and now conserved at the Carlo Bilotti Museum Aranciera di Villa Borghese in Rome. Complementary and nondestructive techniques (i.e. X-ray fluorescence, UV Fluorescence and Raman spectroscopy) were used to validate the achieved results and to add other information concerning the pictorial layers. Moreover, the automatic characterization of the painting's materials, was performed by using machine learning methods and chemometric approach based on spectroscopic data. <sup>[6]</sup>

**Founding:** ARTEMISIA Project: Det. G07413, dated 16.06.2021, published in BURL No. 61 on 22.06.2021, Commitment Act of 18.10.2021, Public Notice by LAZIO INNOVA, an in-house company of the Lazio Region, Framework Program Agreement "Research, Technological Innovation, Telematic Networks" (APQ6) — Section "Implementation of programmatic interventions and new initiatives related to the Technological District for new technologies applied to cultural heritage and activities." Intervention TE1 — Invitation to the Center of Excellence to submit projects for the second phase — RSI Projects.

**Acknowledgement:** The authors acknowledge the technical support of INFN-DA $\Phi$ NE-L technical Staff. The authors acknowledge all the staff of the Muesum Carlo Bilotti Aranciera di Villa Borghese in Rome.

<sup>&</sup>lt;sup>3</sup>INFN-Dipartimento di Ingegneria Industriale, Università degli Studi di Roma Tor Vergata, via del politecnico 1, 00133 Roma, Italy

<sup>&</sup>lt;sup>4</sup>ISCR – Istituto Superiore per la Conservazione ed Centrale per il Restauro, via di San Michele 25 - 00153 Roma (RM)

<sup>[1]</sup> F. Gabrieli et al., Science Advances **2019**, *5*, 1-10.

<sup>[2]</sup> L. Pronti et.al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2018, 200, 10-19.

<sup>[3]</sup> M. Romani et.al., Microchemical Journal 2020, 156, 104920.

<sup>[4]</sup> G. Bonifazi et.al., *Journal of Imaging* **2019**, *5*(*1*), 8.

<sup>[5]</sup> M. González-Cabrera et.al., Scientific Reports 2022, 12, 1-14.

<sup>[6]</sup> G. Capobianco et.al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2024, 304, 123412.

### A ROBOTIC MULTIMODAL XRF-IR SPECTROMETER FOR NONINVASIVE IN SITU ANALYSIS OF 3D HERITAGE OBJECTS

<u>Francesco Paolo Romano</u>, <sup>1</sup> Francesca Rosi, <sup>2</sup> Rosario Andolina, <sup>1</sup> Tecla Arcidiacono, <sup>1</sup> Michela Botticelli, <sup>1</sup> Claudia Caliri, <sup>1</sup> Francesca Falcone, <sup>1</sup> Costanza Miliani, <sup>1</sup> Letizia Monico, <sup>2</sup> Zdenek Preisler, <sup>1</sup> Aldo Romani, <sup>3</sup> Gianluca Santagati <sup>1</sup>

<sup>1</sup>Istituto di Scienze del Patrimonio Culturale, CNR, Catania, Italy
<sup>2</sup>SCITEC, CNR, Catania, Italy
<sup>3</sup>Centro SMAART, Università di Perugia, Italy
francescopaolo.romano@cnr.it

The integration of advanced analytical technologies, robotics and artificial intelligence represents a new frontier in the study of tangible cultural heritage, enabling a deeper understanding of compositional materials and their degradation processes. A multimodal spectrometer that integrates two of the most informative analytical techniques in Heritage Science - XRF and IR spectroscopy - into a single system is under development within the activity of the project CHANGES.

From an analytical perspective, this spectrometer is unique in its ability to merge elemental XRF data with IR molecular spectroscopy. The IR component is based on a novel customized configuration implemented on a compact platform that features a global SiC source, a permanently aligned interferometer, and a TE-MCT detector. This setup enables acquisition across the broad IR spectrum, including the mid and SWIR ranges (5000-800 cm<sup>-1</sup>), at a speed two to three times faster than the state of the art.<sup>[1-3]</sup>

Meanwhile, the XRF device utilizes a compact, low-power X-ray source coupled with an SDD detector, achieving optimal geometric compactness and facilitating seamless integration with the IR module.

From a technological standpoint, its main innovation consists in the use of high-performing mechatronics implemented on a collaborative anthropomorphic robotic arm extended with an ancillary linear stage. The system is designed for high versatility, allowing the analysis of complex three-dimensional objects (e.g., statues and sculptures) as well as large surfaces (e.g., paintings spanning up to 3 meters in one direction) within a single measurement session.

The measurement process incorporates artificial intelligence, which performs real-time data processing. The immediate data makes it possible to manage large volumes of analytical information, automating the data processing and facilitating their interpretation. The system is still on a development step. Technical aspects and reference pilot studies on historical objects are illustrated and discussed.

Acknowledgements: PNRR projects: 1) H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029, CUP B63C22000730005; 2) CHANGES, "Science and Technologies for Sustainable Diagnostics of Cultural Heritage", PE0000020, CUP B53C22003890006. E-RIHS European Infrastructure of Heritage Science (ERIHS)

<sup>[1]</sup> F. Gabrieli et al., Science Advances 2019, 5(8), 10.1126/sciadv.aaw7794.

<sup>[2]</sup> G. Sciutto et al., Talanta 2020, 1(209), 120575.

<sup>[3]</sup> S. Legrand et al., Analyst 2014,139, 2489-2498.

# REFINING CONSERVATION STRATEGIES FOR WATERLOGGED WOODEN HULLS: A CASE USTUDY USING X-RAY TOMOGRAPHY AND SR-µXRD ON XVII-CENTURY SHIPS FOM PLAÇA DELS CARROS

#### <u>Nati Salvadó</u>, <sup>1</sup> Francesc Albert-Tortosa, <sup>1,2</sup> Patricio Guerrero, <sup>3</sup> Victòria Beltran, <sup>4,5</sup> Oriol LópezBultó, <sup>6</sup> Rut Geli, <sup>7</sup> Trinitat Pradell, <sup>8</sup> Núria Jiménez<sup>1</sup>

<sup>1</sup>Departament d'Enginyeria Química, Universitat Politècnica de Catalunya-Barcelona Tech (UPC), Spain

<sup>2</sup>A-PECS Research Group, University of Antwerp, Belgium

<sup>3</sup>Dept. of Mechanical Engineering, KU Leuven, Celestijnenlaan 300, Leuven, Belgium

<sup>4</sup>AXIS Research Group, University of Antwerp, Belgium

<sup>5</sup>Royal Museum for Central Africa, Tervuren, Belgium

<sup>6</sup>Archaeological Museum of Catalonia - Barcelona (MAC)

<sup>7</sup>Centre for Underwater Archaeology of Catalonia, Archaeological Museum of Catalonia (CASC-MAC)

<sup>8</sup>Departament de Física, Centre de Recerca en Ciència i Enginyeria Multiescala de Barcelona, Universitat

Politècnica de Catalunya-Barcelona Tech (UPC), Spain

nativitat.salvado@upc.edu

Historical ships, like Vasa and Mary Rose, highlight the importance of understanding degradation processes of waterlogged wood. [1-3] These hulls face conservation challenges, partly related to the accumulation of iron and sulfur compounds, even after polyethyleneglycol treatment. Restorers and conservators face the challenge of stabilizing wooden ship hulls before exhibition by determining the extent of degradation particularly around iron nails. Identifying the affected area is crucial, as insuficient removal may leave reactive compounds that could continue to deteriorate the wood, while excessive removal risks causing unnecessary damage to the historical structure. To address this issue, this study examines wood fragments from the XVII-century ships of Plaça dels Carros (Tarragona) using industrial X-ray computed microtomography and synchrotron radiation micro-X-ray diffraction (SR-µXRD). µXCT enables non-destructive method visualization of internal structures and degradation patterns in three dimensions, offering valuable insights into the spatial distribution of light and heavy species (notably made of sulfur and iron) species. Combined with SR-µXRD, it allows for a detailed assessment of the extent of chemical alteration in which pyrite, iron oxides and iron-containing sulfates play a role, along with polyethylene glycol. The findings will help refine conservation strategies by defining the optimal volume of material to be removed, ensuring the ship's preservation while minimizing unnecessary loss of original material and contribute to developing more effective conservation methodologies for underwater cultural heritage.

Acknowledgements: This work was financially supported by the MCIN/AEI/FSE grant PRE2020-092363, PID2022137783OB-I00, and MCIN/AEI/FEDER, CEX2023-001300-M (10.13039/501100011033), as well as the Generalitat de Catalunya (2021 SGR 00343). The BAG project was supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No. 870313 (Streamline), DOI: 10.15151/ESRF-ES-1371497379.

<sup>[1]</sup> Y. Fors, M. Sandström. Chem. Soc. Rev. 2006, 35, 399.

<sup>[2]</sup> S. Norbakhsh et al., *Holzforschung* **2014**, *68*, 649

<sup>[3]</sup> J. Preston et al., *PLOS one* **2014**, *9*, e84169.

### UNVEILING HISTORIC MORTARS: HIGH-RESOLUTION SR-μXRPD AND FPA-FTIR INSIGHTS INTO BINDER COMPOSITION

#### Sara Calandra, <sup>1</sup> Emma Cantisani, <sup>2</sup> <u>Barbara Salvadori</u> <sup>2</sup>

<sup>1</sup>Department of Earth Sciences, University of Florence, Florence, Italy
<sup>2</sup>Institute of Heritage Science, National Research Council of Italy, Sesto Fiorentino (Florence), Italy barbara.salvadori@cnr.it

The binder of ancient natural hydraulic mortars derives from firing marly or siliceous limestone rich in clay minerals or silica. Its composition and setting process vary with raw materials, environment, and age. Micro-X-ray powder Diffraction (SR- $\mu$ XRPD) and high-resolution 2D imaging Fourier Transform Infrared microscopy (FTIR) with Focal Plane Array detector (FPA) were applied to investigate the composition of binders in samples from religious and historic buildings in Tuscany (Italy), including Giotto's Bell Tower, the Medici Riccardi Palace and the Trebbio Castle. Polished thin sections were prepared with a thickness of 50  $\mu$ m, on a polycarbonate support. This type of preparation allows the same area to be studied with both techniques and demonstrates the complementarity of these high-resolution imaging techniques.

SR-μXRPD mapping was performed at the SR-μXRPD branch of the ID13 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble) thanks to the BAG Historical Materials (proposal HG-172).<sup>[1]</sup> Chemical imaging was performed using a Bruker LUMOS II FTIR microscope (Bruker Optics GmbH, Ettlingen, Germany) equipped with a liquid-N<sub>2</sub> cooled 32x32 element FPA detector, in external reflection mode.

Preliminary characterization of these mortars using conventional techniques, such as OM, SEMEDS, TGA, XRPD, ATR FTIR revealed that they consist of a natural hydraulic lime binder mixed with silicate and carbonate sand. [2,3] The weak hydraulic properties are due to the development of calcium silicate phases (i.e. CASH and CAS) in combination with calcium carbonate polymorphs such as calcite, aragonite and vaterite. Calcite, aragonite, vaterite, portlandite, CAS and CASH crystalline phases were detected and mapped through SR-μXRPD. Calcite, aragonite and the amorphous and crystalline silicate phases were characterized and mapped using FPA-FTIR. The relative abundance and distribution in the analyzed samples suggest that the presence of amorphous silicates may hinder the carbonation process, leading to the coexistence of metastable calcium carbonate polymorphs such as aragonite and vaterite alongside calcite.

These results provide answers to the controversial aspects of the stability of calcium carbonate polymorphs and of crystalline and amorphous calcium silicate in the binder of ancient mortars. They also provide valuable insights into historical production techniques and the chemical transformations responsible for the hydraulic properties and long-term durability of these materials.

<sup>[1]</sup> M. Cotte et al., Molecules 2022, 27(6), 1997.

<sup>[2]</sup> S. Calandra et al., Scientific Reports 2024, 14, 19979.

<sup>[3]</sup> E. Cantisani et al., Construction and Building Materials 2021, 267, 120801.

### LAB-BASED XAS SPECTROSCOPY IN THE STUDY OF PIGMENT MATERIALS SERVING THE FIXLAB PLATFORM OF E-RIHS

<u>Gianluca Santagati</u>,<sup>1,2</sup> Tecla Arcidiacono,<sup>1,2</sup> Michela Botticelli,<sup>1,2</sup> Claudia Caliri,<sup>1,2</sup> Francesca Falcone,<sup>1,2</sup> Costanza Miliani,<sup>1</sup> Eva Luna Ravan<sup>1,3</sup> and Francesco Paolo Romano<sup>1,2</sup>

<sup>1</sup>Istituto di Scienze del Patrimonio Culturale, Consiglio Nazionale delle Ricerche (CNR-ISPC), Italy 
<sup>2</sup>Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali del Sud (INFN-LNS), Italy 
<sup>3</sup>Department of Science of Antiquities, University of Rome 'Sapienza', Italy 
gianluca.santagati@cnr.it

X-ray Absorption Spectroscopy (XAS) is a well-established technique for chemical speciation, widely applied at synchrotron facilities for pigment analysis. Being highly sensitive to the local atomic structure, it provides unique insights into oxidation states, bond types, bond lengths, and coordination environments, even in amorphous or poorly crystalline phases.<sup>[1]</sup> In particular, the XANES (X-ray Absorption Near Edge Structure) region is especially sensitive to local coordination and oxidation states in transition metal ions.<sup>[2]</sup> The EXAFS (Extended X-ray Absorption Fine Structure) region, extending beyond the absorption edge, reveals interatomic distances, coordination numbers, and structural disorder. [2] When used together in painting investigation, XANES and EXAFS provide a comprehensive view of both the electronic and geometric factors influencing the pigment stability or its degradation due to aging, environmental factors or pigment-binder interaction. Recent improvements in X-ray sources and detectors now enable XAS measurements in laboratory environments, reducing reliance on large-scale facilities. In this work we present a novel lab-based XAS system recently installed at XRAYLab of ISPCCNR in Catania, accessible through the FIXLAB platform of E-RIHS. We demonstrate the feasibility of using this instrument to characterize ancient and modern pigments, both in the form of compressed pellets or thin paint fragments, typically obtained from the sampling often performed during the restoration procedures of real artworks. Specifically, we have developed a dedicated protocol for the instrument to analyze real samples, incorporating guidelines for sample preparation that include the minimum quantity of pigment required and the minimum detection time needed for obtaining reliable spectra.

Preliminary results showcase the ability of lab-based XAS system to 1) reproduce XAS spectra obtained at synchrotron facilities for reference standards and specific pigment materials; 2) detect subtle spectral shifts and features indicative of phase transformations in pictorial pigments.

Acknowledgements: PNRR projects: 1) H2IOSC "Humanities and Cultural Heritage Italian Open Science Cloud", IR0000029, CUP B63C22000730005; 2) CHANGES, "Science and Technologies for Sustainable Diagnostics of Cultural Heritage", PE0000020, CUP B53C22003890006; 3) SAMOTHRACE, "Sicilian MicronanoTech Research And Innovation Center", ECS00000022, CUP B63C22000620005. E-RIHS European Infrastructure of Heritage Science (E-RIHS)

<sup>[1]</sup> S. Mangold et al., J. Anal. At. Spectrom. 2003, 18, 723-729.

<sup>[2]</sup> D. C. Koningsberger, R. Prins," X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES" 1988, Wiley, New York, 692.

#### UNDERSTANDING ARABIC PAPYRUS PROTOCOLS THROUGH MATERIAL ANALYSIS

#### Sowmeya Sathiyamani, Grzegorz Nehring, Olivier Bonnerot, Giuseppe Marotta, Alba Fedeli, Claudia Colini<sup>1,2</sup>

<sup>1</sup>Centre for the Study of Manuscript Cultures, Universität Hamburg, Hamburg, Germany
<sup>2</sup>Institut für Archäologie und Kulturgeschichte des antiken Mittelmeerraumes, Universität Hamburg, Hamburg, Germany

sowmeya.sathiyamani@uni-hamburg.de

Papyrus protocols are documentary texts written on the outermost sheet of the papyrus roll, featuring information relevant to its manufacture. Adopted from Byzantine traditions, these documents in Islamic Egypt served as markers certifying the production of papyrus rolls in statecontrolled mills. The text often included religious phrases, such as verses from the Qur'an, names of the current caliph, governor of Egypt, and other high-ranking officials, as well as the production location of the papyrus roll. [1,2] The papyrus sheet used for this purpose was traditionally thicker and coarser than other sheets, and the protocol text typically appears to have been executed with a brush rather than a reed pen, with broad strokes, using a brown-black ink. Occasionally, traces of red and sometimes green inks can be observed in these documents, interspersed between the lines written in black ink. In several cases, both the black and colored inks exhibit signs of deterioration and fading, making them difficult to read. To better understand the material aspects of these objects, an analytical campaign was undertaken with the aim to characterize the inks and pigments used in the production of papyrus protocols in early Islamic Egypt.

In this work, we present the results of our analytical examination of a selection of Arabic papyrus protocols dated between the 8<sup>th</sup> and10<sup>th</sup> centuries CE, preserved at the Austrian National Library in Vienna. The fragments were analyzed on site at the library using a non-destructive analytical methodology.<sup>[3]</sup> The results indicate a significant level of coherence in the type of ink used for writing the protocols, suggesting a degree of standardization in the materials used for their production. Additionally, for some protocol fragments, elemental maps obtained using scanning micro X-ray fluorescence (XRF) spectroscopy revealed another layer of text accompanying the protocol text, written in what appears to be the remnants of an originally red ink. These results offer insights into the production of papyrus protocols, particularly in understanding the causes of deterioration and fading of the red ink, and potential strategies for digitally recovering and preserving these texts and fragments.

**Acknowledgements:** We would like to thank the director of the Vienna Papyri collection and staff at the Austrian National Library, Vienna particularly Guus Van Loon and Elena Kersten for their help and support.

The research was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2176 'Understanding Written Artefacts: Material, Interaction and Transmission in Manuscript Cultures', project no. 390893796. The research was conducted within the scope of the Centre for the Study of Manuscript Cultures (CSMC) at Universität Hamburg.

<sup>[1]</sup> G. Khan, "Arabic Papyri. In The Codicology of Arabic Manuscripts" 1995, ed. Yasin Dutton, London: al-Furqān Islamic Heritage Foundation, 1-16.

<sup>[2]</sup> W. M. Malczycki, Journal of the Economic and Social History "The Papyrus Industry in the early Islamic era" **2011**, 54(2),185-202.

<sup>[3]</sup> C. Colini, I. Shevchuk, K. A. Huskin, I. Rabin and O. Hahn, "A new standard protocol for identification of writing media. Exploring Written Artefacts. Objects, Methods, and Concepts, Studies in Manuscript Cultures" 2021, 25, 161-182.

### MODELLING THE DEGRADATION OF COLORS IN PAINTINGS: YELLOW, RED AND PRUSSIAN BLUE

Alessandra Satta, 1 Claudia Caddeo, 1 Simona Fantacci, 2 Genís Lleopart Motis 1

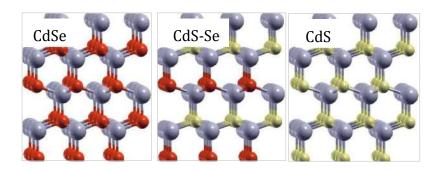
<sup>1</sup>CNR-IOM Cagliari, Italy <sup>2</sup>CNR-SCITEC Perugia, Italy alessandra.satta@cnr.it

Several historical colored pigments found in paintings from the late 1800s and early 1900s are undergoing an irreversible degradation process. In the specific case of cadmium pigments, which derive their yellow/red coloration from cadmium sulfide (CdS) and cadmium sulfoselenide (CdS<sub>1-x</sub>Se<sub>x</sub>), research is being conducted to understand the relationship between their electronic structure and degradation mechanisms. Our findings highlight the role of structural defects, aiming to connect the material's history to the reactivity of the pigment surface.

Regarding Prussian Blue—discovered in the 18th century—a ferric ferrocyanide known for its intense blue hue, its magnetic properties and their role in oxidation mechanisms are being investigated. Its potential relevance in advanced materials for energy applications are also investigated.

Unlike research on novel materials, in the field of Cultural Heritage—where pigments already have a long history—experimental analysis takes precedence over theoretical methods. However, theory remains an excellent complementary tool, aiding in the interpretation of complex mechanisms that are not easily accessible through experiments.

This study is conducted using a fully theoretical approach based on density functional theory.



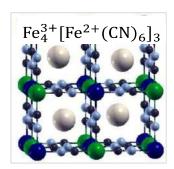


Figure 1: Ball&Sticks representation of cadmium red, yellow and Prussian Blue

Acknowledgements: C.C. acknowledges Project MUR-PRIN 2022 IMPACT (B53D23015220006) and HADES (B53D23028700001) funded by European Union - Next Generation EU - PNRR, Missione 4 Componente 2 Investimento 1.1. We acknowledge CINECA for computational support through the ISCRA initiative.

A.S. acknowledges ICSC-Centro Nazionale di Ricerca in High Performance Computing, Big Data and Quantum Computing, funded by European Union-Next Generation EU-PNRR, Missione 4 Componente 2 Investimento 1.4 (B93C22000620006), and Project MUR-PRIN2022 NEWATOMISTS (B53D23004630006) and Project MUR-PRIN 2022 PNRR ORIENTING (B53D23025530001) funded by European Union-NextGeneration EU-PNRR, Missione 4 Componente 2 Investimento 1.1.

#### UNRAVELING ANTEDATING IN BELGIAN ABSTRACT MODERNISM

<u>Steven Saverwyns</u>, Brynn Sundberg, Chiara Bianchi, Sergio Servellón, Teresa Scovacricchi, Koen Janssens, Frederic Lynen and Christina Currie

<sup>1</sup>Royal Institute for Cultural Heritage (KIK-IRPA), Belgium

<sup>2</sup>FeliXart & Eco museum, Belgium

<sup>3</sup>University of Antwerp, AXES Research Group, Belgium

<sup>4</sup>Ghent University, Separation Science Group, Belgium

<u>steven.saverwyns@kikirpa.be</u>

Belgian abstract modernism presents significant challenges in art historical research due to the widespread practice of *antedating*, where artists intentionally misdated paintings to earlier decades. This phenomenon, particularly prevalent in the 1960s, complicates the reconstruction of the movement's chronology. Some artists reworked older paintings, while others created entirely new compositions that were then assigned false early dates. This study employs advanced analytical techniques to distinguish between genuinely historical works and later reworked or misattributed paintings.

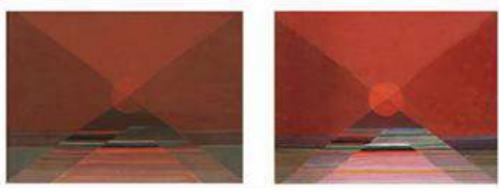


Figure 1: Belgian Abstract Modernist paintings by Felix De Boeck. Left: Paysage Abstrait, 1923, Musée L (Belgium); right: Compositie, 1960, collective Vlaamse Gemeenschap, FeliXart Museum

A multi-technique approach, with an emphasis on non-invasive methods such as macro-X-ray fluorescence (MA-XRF) and micro-Raman spectroscopy (MRS), was applied to a large corpus of Belgian abstract modernist paintings. While synthetic organic pigments (SOPs), such as phthalocyanine green (PG7) and phthalocyanine blue (PB15), serve as key markers for dating—given their commercial availability only after 1935—other pigments, including titanium white (rutile, post-1945), also provide critical chronological indicators. The identification of these materials has allowed for the detection of anachronistic features in paintings attributed to the 1920s, raising questions about their true dates of production.

However, interpretation is complicated by the fact that many paintings could have been reworked later by the artists themselves. This introduces mixed material profiles, where both early and later pigments may coexist within the same composition.

While this research is still in progress, the methodological framework has been developed and applied to a series of paintings by Felix De Boeck, upon which first conclusions can be drawn. Future work will expand this approach to other artists within Belgian abstract modernism, broadening the scope of comparative analysis and refining dating strategies.

#### UNVEILING CASORATI'S COLORS AND STUDIO PRACTICE: A MULTI-ANALYTICAL STUDY OF A TEMPERA MASTERPIECE

Tiziana Cavaleri,<sup>1</sup> Elena Magnabosco,<sup>2</sup> Alessandra Bassi,<sup>1</sup> John R Gilchrist,<sup>4</sup> Jon Danskin,<sup>4</sup> Federica Pozzi,<sup>1</sup> <u>Dominique Scalarone</u><sup>2,3</sup>

<sup>1</sup>Centro per la Conservazione ed il Restauro dei Beni Culturali "La Venaria Reale", Venaria Reale (Turin), Italy

<sup>2</sup>SUSCOR, University of Turin, Venaria Reale (Turin), Italy

<sup>3</sup>Department of Chemistry, University of Turin, Turin, Italy

<sup>4</sup>Clyde HyperSpectral Imaging and Technology Ltd., UK

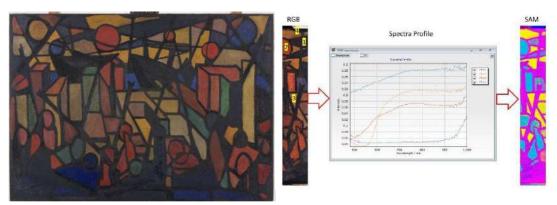
dominique.scalarone@unito.it

A tempera painting on canvas by Francesco Casorati, from a private collection in Turin, Italy, was investigated at the Centro per la Conservazione ed il Restauro dei Beni Culturali (CCR) "La Venaria Reale" as part of a Master's Degree thesis in Conservation and Restoration of Cultural Heritage at the University of Turin.

The artwork exhibited significant conservation issues, including the detachment of the paint film from the underlying layers and the presence of substantial dirt deposits. To address these concerns, a tailored analytical plan was developed and implemented to gather technical and scientific data on the materials used in the painting and their interactions—key information for designing an appropriate conservation treatment.

Notably, preliminary cleaning of the dirt deposits helped restore the subtle color variations within areas delineated by black outlines (Figure 1). Differences observed through visible photography and multiband imaging (UVL, IRR, IRFC) enabled the initial identification of 27 distinct color paints, consisting of 8 yellow, 6 red, 2 green, 2 purple, 2 black, and 7 blue hues—each a mixture of different pigments and binders. The palette composition was further analyzed using XRF and FORS spot spectroscopies, while the combination of HSI with PCA/SAM data processing provided a more comprehensive and precise mapping of the color paints.

Additionally, GC/MS analysis revealed an unusual aspect of the artist's technique, namely the presence of rubber latex mixed with glue as a binder for the paint mixtures. This discovery suggests a possible link between the binder's composition and the observed paint detachment, offering new insights into both the painting's material history and its conservation challenges.



**Figure 1.** Francesco Casorati, Senza Titolo, tempera on canvas. At right: comparison of spectral responses of different regions of the painting in VNIR range, and SAM result based on identified endmembers.

Acknowledgments: The authors would like to express their gratitude to Luca Avataneo (CCR "La Venaria Reale") and Fabio Belloni (University of Turin) for their valuable contributions as members of the thesis group. Special thanks are extended to the Casorati family for making this research possible.

#### LOOSING SALVADOR DALI'S ST ANTHONY?

### <u>Catherine Defeyt</u>,<sup>1,2</sup> Francisca Vandepitte,<sup>2,3</sup> Edène Derzelle,<sup>1</sup> Nathan de Vries,<sup>1</sup> Philippe Walter,<sup>4</sup> David Strivay<sup>1</sup>

<sup>1</sup>Centre Européen d'Archéométrie, University of Liège, Belgium

<sup>2</sup>Royal Museum of Fine Arts of Belgium, Belgium

<sup>3</sup>Vrije Universiteit Brussel, Belgium

<sup>4</sup>Laboratoire d'Archéologie Moléculaire et Structurale, Sorbonne Université - CNRS, France

<u>catherine.defeyt@uliege.be</u>

The temptation of St Anthony dated 1946, which is one of the most iconic paintings of the Catalan surrealist, currently displays worrying surface condition in specific areas, for instance the St Anthony character. The problematic paint layers typically exhibit uneven transparency and rugged surfacee. To characterize the degradation mechanisms that have taken place and to identify the involved materials, Dali's masterwork has been investigated in situ through a large panel of imaging and analytical techniques, including MA-XRF, Raman and FT-IR spectroscopies, Hyperspectral Imaging, XRD, IR Reflectography, Radiography and Highresolution photography. The obtained results were subsequently assessed against the material and technical information collected from Dali's 50 secrets magiques, [1] as well as against archive photographs showing The temptation of St Anthony. This in-depth study permitted to evidence the key role of amber based medium regarding the very unusual aspect of the degraded pictorial layers, due to the formation of amorphous chloride zinc salt resin acids.

<sup>[1]</sup> S. Dali, "50 secrets magiques" 1974, Edita/Denoël, Lausanne.

### NEW MATERIAL AND TECHNOLOGICAL ASPECTS OF RED-FIGURE POTTERY FROM SOUTH ITALY

#### Vojtěch Šupita,<sup>1,2,3</sup> Silvie Švarcová,<sup>2</sup> Petr Bezdička,<sup>2</sup> Marek Verčík,<sup>3</sup> Dominika Zákutná<sup>1</sup>

<sup>1</sup>Department of Inorganic Chemistry, Faculty of Science, Charles University, Czech Republic

<sup>2</sup>ALMA Laboratory, Institute of Inorganic Chemistry, Czech Academy of Science, Czech Republic

<sup>3</sup>Classical Archaeology, Faculty of Arts, Charles University, Czech Republic

supitav@natur.cuni.cz

Red-figure is one of the main types of pottery decoration used by ancient Greeks. This technique was introduced in ancient Athens around 530 BCE and was exported to other parts of the Greek world, such as Southern Italy, in the following century. Within this contribution, I will present painting techniques of three South Italian schools based on the comprehensive non-invasive study of more than ten objects using X-ray fluorescence, X-ray powder diffraction (XRPD), infrared and Raman spectroscopy and optical microscopy. In addition, scanning electron microscopy and other micro-analytical techniques were used for investigation of fragmentary pieces. Emphasis will be given to 11 Lucanian, Apulian, and Campanian vases, dated to the second half of the 4<sup>th</sup> century BCE according to the stylistic analysis (the middle and late phases of respective schools).



Figure 1: Apulian Peliké 20.3 analysed by XRPD (photo by Vojtěch Šupita)

Based on the presence of low-temperature phases such as kaolinite (detected by XRPD, see fig. 1) in the coating layer, I will discuss the maximum temperature reached during the firing process, as well as other consequences, such as the possible coloring agent of the black gloss. Other interesting findings include the identification of cinnabar and lead white. The former was probably used instead of the traditional red wash, indicating the high value of the vase, while the latter was used for executing details in added white. The presence of lead white raises questions about the authenticity of these details.

In the end, I will put these findings into the context of potential technological transfer between late red-figure pottery and early Hellenistic polychrome pottery, primarily produced in Canosa.

<sup>[1]</sup> A. D. Trendall, "Red Figure Vases of South Italy and Sicily: Handbook" 1989, London, 288.

# IN-DEPTH SPECTROSCOPIC ANALYSIS OF CW NIR LASER IRRADIATION OF PLATTNERITE TO THERMALLY RECOVER DARKENED RED LEAD WALL PAINTINGS

<u>Amelia Suzuki</u>,<sup>1,2</sup> Iacopo Osticioli,<sup>3</sup> Francesco di Benedetto,<sup>4</sup> Werner Oberhauser,<sup>5</sup> Haida Liang,<sup>2</sup> Francesco d'Acapito,<sup>6</sup> Cristiano Riminesi<sup>1</sup>

Institute of Heritage Science – National Research Council ISPC-CNR, Italy

Imaging and Sensing for Archaeology, Art history and Conservation ISAAC team, Nottingham Trent University, UK

Institute of Applied Physics "Nello Carrara" - National Research Council IFAC-CNR, Italy.

Department of Physics and Earth Science, University of Ferrara, Italy.

Institute of Chemistry of OrganoMetallic Compounds - National Research Council ICCOM-CNR, Italy.

CNR-IOM Sez. Grenoble c/o ESRF-LISA, France.

mariaameliasuzuki@cnr.it

The main discolouration affecting the bright red lead pigment (Pb<sub>3</sub>O<sub>4</sub>) in wall paintings is a darkening phenomenon generally ascribed to the transformation of the primary pigment into the black-brown plattnerite (β-PbO<sub>2</sub>). Up to now, no restoration methods to effectively recover the darkened red lead in wall paintings have been established yet and their development is crucial to safeguard the integrity and enhance the readability of artworks. Only in the last two decades, a method based on Continuous Wave (CW) laser irradiation has been tested on mock-ups and in one real wall painting.<sup>[1,2]</sup> Although very promising, the method still needs to be fully characterized (penetration depth, stability, by-products etc.). Understanding the main mechanisms is crucial for the improvement of the method and to identifying the potential risks.

In this work a multi-spectroscopic method based on VIS-NIR and short wave infrared (SWIR) hyperspectral imaging (400-2000 nm),  $\mu$ -Raman spectroscopy, synchrotron based (SR) micro Xray powder diffraction mapping ( $\mu$ -XRPD) and Near-edge X-ray absorption spectroscopy (XANES) at the Pb LIII edge, has been used to characterize the laser-induced products and their distribution in the paint layer of a plattnerite wall painting mock-up treated with a CW 1064 nm laser. The combination of these analytical techniques enabled to experimentally demonstrate the predominant thermal effect of the laser reconversion of darkened red lead, thanks to the identification of non-stoichiometric lead oxides.

<sup>[1]</sup> S. Aze, J.-M. Vallet, O. Grauby, V. Detalle, P. Delaporte, *Techniques de l'Ingénieur "Restauration des peintures au plomb par irradiation laser"* **2013**, *RE 224*, 1-11.

<sup>[2]</sup> T. de Seauve, V. Detalle, A. Semerok, S. Aze, O. Grauby, S. Bosonnet, K. Ginestar, J. M. Vallet, *Appl. Phys. B* "Continuous wave laser thermal restoration of oxidized lead-based pigments in mural paintings" **2021**, 127.

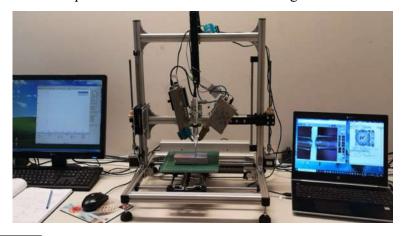
# CONFOCAL MACRO-XRF SPECTROMETER AND FPM MODEL FOR QUANTITATIVE ANALYSIS OF CULTURAL HERITAGE, BIOLOGICAL AND NUCLEAR OBJECTS

#### <u>Imre Szalóki</u>, <sup>1</sup> Emese Csipa, <sup>1</sup> Péter Kirchknopf, <sup>1</sup> Éva Széles, <sup>1</sup> Gergely Dósa, <sup>1</sup> Péter Völgyesi, <sup>1</sup> Anita Gerényi<sup>2</sup>

<sup>1</sup>Nuclear Security Department, HUN-REN Centre for Energy Research, Budapest, Hungary <sup>2</sup>Institute of Nuclear Techniques, Budapest University of Technology and Economics, Budapest, Hungary

A new confocal macro X-ray spectrometer (CM-XRF) and some its possible applications will be presented. The frame of the analytical instrument was built using the mechanical structure of a commercial 3D printer (Velleman K-8200) having one vertically (z) and two horizontally (x,y) movable units. The ED-XRF spectrometer consists of an SD detector and an air-cooled X-ray tube with a maximum power of 4 W, those units are mounted on a vertically movable consol. The sample to be analysed can be fixed on a horizontally movable (x-y) flat plate.<sup>[1]</sup> The sample to be analysed can be scanned horizontally with the x-y stage, in both 2D perpendicular directions, within a total length of 20 cm. The spatial accuracies of the mechanical positioning of the movable parts are 5 µm for each direction (x-y-z) and the minimum step size of 100 µm. The collimators of the X-ray tube and the SD detector can be exchanged for different diameters and lengths. This feature allows the diameter of the focal point irradiated by the confocal instrument on the sample surface to be varied in the range 0,5-5 mm. The intersection of the axes of the irradiating Xray beam and the collimator of the detector must be on the sample surface, which can be achieved by changing the vertical position of the spectrometer, which can be accurately positioned using a small digital microscope or two mini laser units.

An FPM model was developed<sup>[2]</sup> to determine the quantitative composition of solid and liquid samples i.e. to calculate the concentrations of chemical elements in the material under study. To demonstrate the analytical synergy that can be achieved by combination of CMXRF spectrometer and FPM code, analytical examples for the quantitative determination of the composition of archaeological and biological materials<sup>[3]</sup> will be presented. The combination of the CM-XRF and gamma spectrometry for purpose of safeguard analysis will be presented in order to determine the quantities chemical elements with high atomic number.



<sup>[1]</sup> I. Szalóki, A. Gerényi, G. Radócz, X-Ray Spectrom. "Confocal macro X-ray fluorescence spectrometer on commercial 3D printer" 2017, 46, 497.

<sup>[2]</sup> I. Szalóki, T. Pintér, I. Szalóki, jnr., G. Radócz, A. Gerényi, J. Anal. At. Spectrom. "A novel confocal XRF-Raman spectrometer and FPM model for analysis of solid objects and liquid substances" 2019, 34, 1652.
[3] A. Gerényi, V. Czech, F. Fodor, L. Vincze, I. Szalóki, X-Ray Spectrom. "In vivo XANES measuring technique

for studying the arsenic uptake in cucumber plants" **2017**, 46, 143-150.

# SCIENTIFIC INVESTIGATION SUPPORTING THE CONSERVATION OF A CONTEMPORARY MURAL IN LOS ANGELES: CHALLENGES AND OPPORTUNITIES

Camilla Tartaglia,<sup>1</sup> Teal Patterson,<sup>1</sup> Kiernan Graves,<sup>2</sup> Laleña Vellanoweth,<sup>3</sup> Davide Gulotta<sup>1</sup>

<sup>1</sup>Getty Conservation Institute, Science Department, Los Angeles, California

<sup>2</sup>Site&Studio Conservation, LLC, Los Angeles, California

<sup>3</sup>LA County Department of Arts and Culture, Los Angeles, California

CTartaglia@getty.edu

Besides providing critical insights to inform the design and implementation of conservation projects, scientific investigations offer a unique opportunity for training emerging professionals and exposing practitioners from adjacent professional fields to the multidisciplinary nature of heritage preservation. Here, we discuss how such an approach was pursued in the collaborative project for the conservation of an iconic contemporary mural in Los Angeles County. *Inner Resources* is a large mural (25x11m) painted in 2000 by artist Paul Botello. It was created as a community-based project: the artist engaged the community during the mural design process, incorporated their feedback into the iconography of the work, and was assisted by people from the neighborhood throughout its production.

The original protective coating applied on the mural has been progressively deteriorating over the years, showing weathering patterns like cracking, detachment, and loss of transparency. This characteristic deterioration has also been affecting other murals exposed to similar challenging outdoor conditions throughout the Los Angeles County area, i.e., daily cycles of intense sunlight depending on the orientation, exposure of extensive painted areas to direct rain and rain run-off due to the absence of sheltering elements. Given the severity of the deterioration phenomena, the Los Angeles County Department of Arts and Culture called for an intervention on the mural: similar to its original inception, the conservation project was conceptualized and implemented as a collaborative work, where the intervention itself, and the scientific investigation supporting it, integrated training opportunities for emerging conservation professionals and emerging artists who have a connection to the local community. The scientific component was structured in four steps to address specific characterization and treatment issues and to provide training sessions:

- 1. A preliminary characterization was carried out to assess the state of conservation of the mural, conducting in situ condition assessment and analyzing micro-samples of representative deterioration patterns in the lab (optical microscopy, FTIR, SEM-EDS).
- 2. A sustainable and simple field-based methodology was designed to answer treatment questions within the timeline of the intervention, based on non-invasive or minimally invasive methods (colorimetry, gloss measurements, water contact angle measurements).
- 3. A post-treatment monitoring protocol to assess the performance and durability of the new acrylic protective coating was designed and is still ongoing. This protocol and the related outcomes will provide valuable information to inform future strategies for treatment selection and, possibly, for long-term monitoring of similar contemporary outdoor murals in the Los Angeles area.
- 4. Dedicated training sessions were incorporated into the schedule of the scientific work to expose the trainees to the potential of portable methods to address weathering and treatment questions in situ, and the integration of laboratory methods to complement field-based data.

### ACCELERATED METHODS FOR REPRODUCING ARCHAEOLOGICAL BRONZE *PATINA*:

### STRATIGRAPHIC COMPARISON AND IMPLICATIONS FOR CONSERVATION AND AUTHENTICATION

Edoardo Tartaglia,<sup>1,2</sup> Francesco Abate,<sup>1,2</sup> Monica Galeotti,<sup>3</sup> Andrea Cagnini,<sup>3</sup> Simone Porcinai,<sup>3</sup> Enrico Verlato,<sup>4</sup> Maria Antonietta Baldo,<sup>2</sup> Chiara Zanardi,<sup>2</sup> Arianna Traviglia<sup>1</sup>

<sup>1</sup>Center for Cultural Heritage Technology (CCHT), Istituto Italiano di Tecnologia (IIT), Via Torino 155, Venezia, Italy

<sup>2</sup>Department of Molecular Sciences and Nanosystems (DSMN), Ca' Foscari University of Venice, Via Torino 155, Venezia, Italy

<sup>3</sup>Opificio delle Pietre Dure (OPD), Viale F. Strozzi 1, 50129 Florence, Italy
<sup>4</sup>Institute of Condensed Matter Chemistry and Technologies for Energy (CMATE-CNR), Corso Stati Uniti 4, 35127 Padova, Italy

edoardo.tartaglia@iit.it

The development of advanced methods for replicating archaeological bronze patinas is of paramount importance in conservation and restoration, facilitating the testing of new products<sup>[1]</sup> and deepening our understanding of the complex corrosion processes at play. [2] Most existing methods available in the literature focus on patinas formed in outdoor environment, [1,2] however they produce replica mock-ups whose corrosion layers exhibit significant compositional and stratigraphic differences from patinas of objects aged in a burial context. The few protocols available for the replication of archaeological *patinas* usually require extended burial periods, [3] posing major operational challenges. This study introduces two rapid protocols for archaeological patina replication: an electrochemical method requiring just 24 hours, and a burial-involving approach based on a counterfeiter's method, monitored through 150 days of aging. The research compares the compositional and stratigraphic properties of patinas produced by both methods with those observed on genuine archaeological artifacts. Superficial analysis using ER-FTIR and stratigraphic examination via optical microscopy, SEM-EDX and microRaman spectroscopy (Fig.1) revealed both similarities and discrepancies in composition and stratigraphy between the replica samples and authentic objects. Additionally, this study monitors burial-induced aging and patina formation over time to understand the corrosion mechanisms involved and highlight diagnostic features that can support future authentication studies.

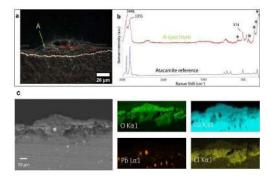


Figure 1. Raman spectroscopy and SEM EDX analysis of a mock-up sample after electrochemical aging

<sup>[1]</sup> B. Salvadori et alii, Journal of Applied Polymer Science 2017, 123-46011.

<sup>[2]</sup> M. B. Rosales et alii, Corrosion Science 2010, 52, 10, 3212-3234.

<sup>[3]</sup> F. Boccaccini et alii, *Heliyon* **2023**, *9*, e19626.

### STUDY OF ROMAN WALL PAINTING MORTARS BY X-RAY COMPUTED TOMOGRAPHY AND COMPLEMENTARY TECHNIQUES

#### <u>Francesc Albert-Tortosa</u>,<sup>1,2</sup> Patricio Guerrero,<sup>3</sup> Victòria Beltran,<sup>4,5</sup> Salvador Butí,<sup>1</sup> Núria Jiménez,<sup>1</sup> Lídia Font,<sup>6</sup> Trinitat Pradell,<sup>7</sup> Nati Salvadó<sup>1</sup>

<sup>1</sup>Departament d'Enginyeria Química, Universitat Politècnica de Catalunya-Barcelona Tech (UPC), Spain

<sup>2</sup>A-PECS Research Group, University of Antwerp, Belgium

<sup>3</sup>Dept. of Mechanical Engineering, KU Leuven, Celestijnenlaan 300, Leuven, Belgium

<sup>4</sup>AXIS Research Group, University of Antwerp, Belgium

<sup>5</sup>Royal Museum for Central Africa, Tervuren, Belgium

<sup>6</sup>Museu d'Història de Barcelona MUHBA, Institut de Cultura – Ajuntament de Barcelona, Spain

<sup>7</sup>Departament de Física, Centre de Recerca en Ciència i Enginyeria Multiescala de Barcelona, Universitat Politècnica de Catalunya-Barcelona Tech (UPC), Spain

francesc.albert.tortosa@upc.edu

Wall paintings are one of the most remarkable legacies from the Roman period. These paintings were structured in a multilayered disposition, and the mortar played an important role in the stability and visual and structural integrity of the artworks. [1] In wall painting fragments from the *Domus Avinyó* and *La Sagrera* archaeological sites (Barcelona, Spain), relevant differences in density were observed between mortars belonging to different parts of the painting. Additionally, fragments with a stucco or polychrome layers showed an elevated number of cracks and crevices in the surface, which could be related to structural changes in the mortar. Therefore, the composition of the mortar based on its application as an underlying layer to the paintings has been assessed.

To this end, wall painting fragments from both sites have been studied by X-ray computed tomography (XCT) to determine the particle size and morphology, porosity, and pore size. A range of complementary analytical techniques has been used to complete the characterization of the materials: optical microscopy (OM), scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX), synchrotron radiation-based micro-X-ray diffraction ( $\mu$ SR-XRD), Fourier-transform micro-infrared spectroscopy ( $\mu$ FTIR) and micro-Raman spectroscopy. The study allowed to assess how different mortars had been prepared according to their application in the context of Roman wall painting.

Acknowledgements: This work was financially supported by the MCIN/AEI/FSE grant PRE2020-092363, PID2022137783OB-I00, and MCIN/AEI/FEDER, CEX2023-001300-M (10.13039/501100011033), as well as the Generalitat de Catalunya (2021 SGR 00343). µSR-XRD experiments were performed at BL13-XALOC beamline at ALBA Synchrotron facility (grant 2020094552).

<sup>[1]</sup> M. Lanzón, M. J. Madrid-Balanza, I. Martínez-Peris, V. E. García-Vera, D. Navarro-Moreno, *Construction and Building Materials* **2023**, *408*.

### MULTISPECTRAL IMAGING GIVES NEW INSIGHTS ON A OLD CONTROVERSY ON THE AUTHENTICITY OF A RAPHAEL PAINTING

L. Baratin, A. Cantarini, F. Bottacin, B. Fazi, P. Triolo, S. Legnaioli, V. Palleschi L. Baratin, A. Cantarini, F. Bottacin, B. Fazi, B. Fazi, P. Triolo, S. Legnaioli, V. Palleschi

<sup>1</sup>DiSPeA, University of Urbino, Italy <sup>2</sup>DISCUI, University of Urbino, Italy <sup>3</sup>DIRAAS, University of Genoa, Italy <sup>4</sup>ICCOM-CNR, Italy paolo.triolo@uniurb.it

The debate on the authenticity of the "Madonna della Palma" (Madonna of the palm tree), an oil of panel attributed to Raphael, whose attribution has been the subject of several discussion in recent decades, has been based not only on stylistic and historical considerations, but also on the botanical nature of the tree depicted by the artist in his painting.

The completely non-invasive investigations carried out by researchers from the University of Urbino and the National Research Council of Pisa are the first analytical studies in over fifty years since the restoration carried out by the Central Institute for Restoration in Rome.

Traditional IR-VIS-UV multispectral imaging techniques have been used; the acquired images have been processed with experimental techniques based on derivative chromatic imaging (CHROMADI) in blind separation mode or computational applications for the study of surface morphology (Reflectance Transformation Imaging).

The results obtained have allowed us to identify peculiar aspects of the execution technique (spolvero and pentimenti), while at the same time highlighting the significant changes made during the restoration interventions. Comparison with the archive documentation (conservation report, archive photographs in visible light, infrared and X-rays, studies by famous art historians who studied the subject in the 1970s and 1980s) has allowed to formulate new ideas on the subject, resolve the controversies and place this important 16th century painting in its rightful place in time, giving a plausible reconstruction of the origins of the panel.



Figure 1: "Madonna della Palma" comparison between the VIS and CHROMADI image

### THE VAN GOYEN PROJECT: ON THE TECHNICAL EVOLUTION OF A 17TH-CENTURY DUTCH ARTIST

<u>Sara Valadas</u>,<sup>1,2,3</sup> Alexandra Lauw,<sup>4</sup> Maria Mayer,<sup>5</sup> Dóris Santos,<sup>2,6,7</sup> Patrícia Telles,<sup>2,8,9</sup> Antonio Candeias,<sup>1,2,3</sup> Vanessa Antunes,<sup>10,11</sup>

<sup>1</sup>HERCULES Laboratory, Évora University, Portugal

<sup>2</sup>Associated Laboratory IN2PAST, Portugal

<sup>3</sup>Cátedra CityUMacau in Sustainable Heritage, Évora University, Portugal

<sup>4</sup>Instituto Superior de Agronomia - CEF, Lisbon University, Portugal

<sup>5</sup>Museu Medeiros e Almeida, Portugal

<sup>6</sup>IHA NOVA-FCSH, Portugal

<sup>7</sup>Museu Nacional do Traje, Lisbon, Portugal

<sup>8</sup>CHAIA – Évora University, Portugal

<sup>9</sup>Museus e Monumentos de Portugal E.P.E., Lisbon, Portugal

<sup>10</sup>Centro de Investigação e Estudos e Belas-Artes (CIEBA), Lisbon University, Portugal

<sup>11</sup>Laboratório José de Figueiredo, Museus e Monumentos e.p.e., Lisbon, Portugal

svaladas@uevora.pt

The project "The Materials and Techniques of Jan van Goyen: A Technical Study of Eight Small Paintings" investigates the material composition and artistic techniques of eight paintings attributed to Jan van Goyen (1596–1656), housed in the Medeiros e Almeida Museum (Lisbon).

Spanning different phases of the artist's career (1620s-early 1650s), this research examines his evolving pictorial methods through X-ray-based techniques (MA-XRF, EDXRF) and complemented by multi-modal imaging (RIV, FIV, VIS, UV) and microanalytical techniques (OM, SEM-EDS). This interdisciplinary study, conducted in collaboration with HERCULES Laboratory, CHAIA, and IHA—research units of the IN2PAST Associated Laboratory—aims to reconstruct Van Goyen's material choices and their implications for workshop practice, pigment degradation, and conservation strategies. The integration of dendrochronological analysis provides terminus post quem dating for the wooden supports, allowing a comparative perspective on the correlation between painting execution timelines and wood sourcing practices. This study also contributes to expanding Portugal's dendrochronological database, reinforcing methodologies for dating European panel paintings. Beyond its technical contributions, the Van Goven Project is committed to public dissemination, producing a scientific video within the IN2PAST framework. This will integrate high-resolution analytical data with visual reconstructions, providing an accessible yet detailed exploration of the artist's technical evolution over 36 years of production. By employing cutting-edge analytical techniques, this research advances understanding of Dutch 17th-century painting materials and fosters new conservation approaches for cultural heritage collections.

Acknowledgements: The author's want to thank to IN2PAST for the financial support (Ref. EXPL/In2Past/2023/11), to Medeiros e Almeida Museum (Portugal), Faculty of Veterinary Medicine of Lisbon (Portugal) and Oslo Nasjonalmuseet (Norway).

<sup>[1]</sup> P. W. T. Klein, "Dendrochronological Analyses of Paintings of Gdansk Painters of the 15th to the 17th Century" 1991

<sup>[2]</sup> Jan van Goyen, Drawing album, sketch-book by Jan van Goyen 1627, British Museum.

<sup>[3]</sup> P. Noble, A. van Loon, J. J. Boon, Proceedings of Paintings Group Interim Meeting ICOM Committee for Conservation 31 May-1 June 2007 in London "Selective darkening of ground and paint layers associated with the wood structure in the seventeenth-century panel paintings, Preparation for Painting: The Artists Choice and Its Consequences" 2008, 68–78.

#### PRELIMINARY RESULTS ON DIAGNOSTIC ASSESSMENTS OF HIGH-PRESSURE WATER MICRONEBULISER CLEANING EFFECTS ON STONE SURFACES

Emma Vannini,<sup>1,2</sup> Daniela Porcu,<sup>1</sup> Alice Dal Fovo,<sup>1</sup> Raffaella Fontana,<sup>1</sup> Filippo Edoardo Capasso,<sup>3,4</sup> Giuliana Codato,<sup>3</sup> Federica Antonelli,<sup>5</sup> Marco Bartolini,<sup>6</sup> Eleonora Gioventù<sup>3</sup>

<sup>1</sup>National Research Council—National Institute of Optics (CNR-INO), Largo E. Fermi 6, 50125 Firenze, Italy

<sup>2</sup>Department of Physics and Astronomy, University of Florence, Via Sansone 1, 50019 Sesto Fiorentino, FI, Italy

<sup>3</sup>Stone Materials Laboratory, Istituto Centrale per il Restauro, Via di San Michele 25, 00153, Roma, Italy

<sup>4</sup>Department of Environmental Biology, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy

<sup>5</sup>Bio.Co.Ré. Lab., Via Reatina 10, Scurcola Marsicana, Italy

<sup>6</sup>Biology Laboratory, Istituto Centrale per il Restauro, via di San Michele 25, 00153, Rome, Italy

<u>emma.vannini@ino.cnr.it</u> <u>emma.vannini@unifi.it</u>

Advancements in diagnostic techniques for assessing the condition of stone surfaces have played a crucial role in the development of sustainable restoration methods. High-resolution imaging technologies, such as Optical Coherence Tomography (OCT) and laser scanning microprofilometry, enable precise evaluation of surface roughness, structural integrity, and material composition before and after treatment. These diagnostic tools are essential for understanding the impact of cleaning methods on cultural heritage materials.

Among the emerging eco-friendly restoration techniques, high-pressure water micronebulisation has gained attention for its ability to clean stone surfaces affected by biological colonization. While research has demonstrated its effectiveness, it is equally critical to assess whether this method alters the physical and aesthetic characteristics of the treated materials. Potential changes in color, modifications in water absorption and permeability, and shifts in surface roughness, all of which influence the bioreceptivity of the substrate, could occur after the treatment.

This study presents a comparative evaluation of laboratory tests conducted on three natural lithotypes (Carrara marble, Travertine, and Peperino) commonly found in Roman archaeological contexts. By analyzing aesthetic, physical, and chemical parameters through techniques such as stereo-microscope and colorimetric analysis, contact angle measurements, and surface roughness assessments using OCT and laser scanning micro-profilometry, this research aims to determine the extent to which high-pressure water micronebulisation interacts with these materials. Understanding these effects is essential for ensuring that restoration methods maintain both the structural integrity and visual authenticity of cultural heritage assets.

#### Acknowledgements:

This work is the result of a collaboration between Spoke 5 (Science and Technologies for Sustainable Diagnostics of Cultural Heritage) and Spoke 7 (Protection and Conservation of Cultural Heritage against Climate Changes, Natural and Anthropic Risks) within the PNRR CHANGES (Cultural Heritage Active Innovation for Sustainable Society) project, funded by the European Union – Next Generation EU.

The research was partially funded by PNRR H2IOSC (Humanities and Cultural Heritage Italian Open Science Cloud) Project (IR0000029), CUP B63C22000730005, funded by Next Generation EU.

[1] F. E. Capasso, F. Antonelli, M. Bartolini, M. Lavorgna, E. Spinelli, S. Licoccia, E. Gioventù, "Coping with stone biodeterioration using low environmental impact materials and methods" in "Methodologies and Strategies for Cultural Heritage Protection and Conservation Against Climate Changes, Natural and Anthropic Risks" 2025, edit by F. Di Ciaccio, L. Fiorini, G. Tucci, Springer, Berlin, 338-343.

### EXPLORATION OF THE PAPER LANGWEIL MODEL OF PRAGUE UTILIZING X-RAY COMPUTED TOMOGRAPHY

#### Daniel Vavrik, Lucie Zivna<sup>2</sup>

<sup>1</sup>Institute of Theoretical and Applied Mechanics, Czech Academy of Sciences, Czech Republic

<sup>2</sup>Museum of Prague, Czech Republic

<u>vavrik@itam.cas.cz</u>

The work presents the possibility of non-invasive survey of a paper model of Prague using X-ray computed tomography. The model, created by Antonín Langweil between 1826 and 1837, is a unique historical document that, on an area of almost 19 square meters consisting of 52 parts, provides testimony to the appearance of Prague in the 19th century. The whole model is part of the collections of the Museum of Prague. Due to its extraordinary level of detail, it has become an invaluable resource for researchers studying the development of urban architecture and urbanism. The aim of the tomographic survey was to visualize the internal structure of the Langweil model, which allowed us to explore how the individual buildings of the model were constructed. It is obvious that computed tomography can help to identify the materials used, detect possible damages and map the distribution of higher density materials. For the initial validation of the computed tomography capabilities, two parts were selected from the Prague model. In addition, one other building made by Langweil that is not part of the Prage model was also scanned. The results show that CT examination is a useful tool for better assessing the condition of the collection item and capable of uncovering entirely new facts about its creation.

Since computed tomography has proved to be very beneficial, it is planned to gradually perform CT scans of all parts of the Prague model. It should be noted that the total volume of data will be enormous and it will require specialized procedures for manipulation and exploratation.

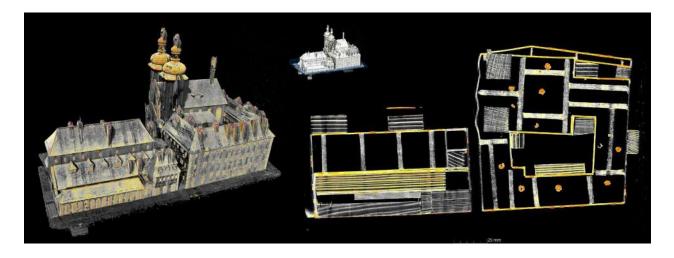


Figure 1: Tomographic reconstruction of part 6. Its external three-dimensional shape with highlighted high-Z materials is shown on the left. The horizontal section on the right shows different types of wood and paper, in addition, a peppercorn was found on the floor of each room with a typical cavity in the middle, these are highlighted in orange.

### MULTI-DIAGNOSTIC ANALYSIS FOR RESTORATION OF THE $15^{TH}$ CENTURY MAP OF ITALY FROM THE CORRER MUSEUM OF VENICE

#### <u>Lisa Vergelli</u>, <sup>1</sup> Marcella Ioele, <sup>1</sup> Maria Speranza Storace<sup>1</sup>

<sup>1</sup>Istituto Centrale per il Restauro, Rome, Italy lisa.vergelli@uniroma1.it

The Map of Italy is a parchment painting dated 1449, housed at the Correr Museum in Venice. It has been attributed to the Venetian cartographer Giovanni Leardo, based on stylistic similarities with the world map of the Civic Library of Verona, created by Leardo in 1442 [1-2]. These similarities are particularly evident in the handwriting of inscriptions and letters, as well as in the design of urban centres, notably the almost identical representation of the city of Venice in both maps. In September 2024, the Map of Italy was transferred to the laboratory of conservation of paper and parchment at the Istituto Centrale per il Restauro in Rome for a comprehensive scientific investigation, aimed at designing an appropriate conservation strategy. The current artifact's state of preservation is severely compromised due to previous restoration interventions, which have contributed to its deterioration. The parchment support exhibits deformation and abnormal tension due to stitched tears and gap reintegration. Additionally, partial backing on the verso has compressed the support, leading to noticeable wrinkles. This compromises the readability of the image, as does the deposit of superficial overlaid organic materials. The study aimed to characterize the original materials and any subsequent integration, identifying support, inks, pigments, binding media and adhesives, while assessing the overall conservation state. Since any sampling on parchment is inherently invasive, we chose non-invasive techniques, conducted in situ. Digital microscopy in visible and UV (375 nm) light, X-ray fluorescence (XRF) for spot analysis and elemental mapping (Fig. 1), and portable FTIR spectroscopy, integrated by micro-FTIR analysis on extracts from solvent swabs, provided crucial insights on original materials and past conservation treatments. The analyses guided the development of a conservation procedure compatible with the historical and artistic significance of the artefact.

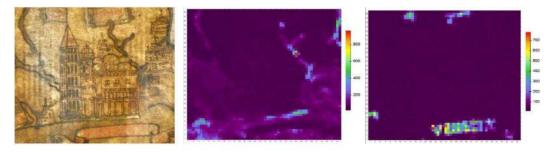


Figure 1: The city of Venice (left), one of the portions investigated through XRF-mapping: Cu (middle), Hg (right).

Acknowledgements: Authors thank the Correr Museum of Venice for the permission. This research was funded by the Project CHANGES "Cultural Heritage Active Innovation for Next-Gen Sustainable Society", National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 funded from Next-Generation-EU.

<sup>[1]</sup> M. Rossi, *Humanistica: an international journal of early Renaissance studies "Cosmografia e cartografia nell'Umanesimo veneto (sec. XIV-XV)"* **2021**, *XVI*, *1/2*, edited by F. Serra, 101-138.

<sup>[2]</sup> M. Milanesi, *Il territorio nella Società dell'informazione*. *Dalla cartografia ai sistemi digitali "Monumenta Italiae Cartografica (sec. XV)"* **2004**, curated by A. Cantile, edited by Istituto Geografico Militare, 30-34.

### UNVEILING MICROBIAL SPECTRAL FINGERPRINTS IN PAPER ARTIFACTS THROUGH HYPERSPECTRAL IMAGING (HSI)

#### M. Vieri de Mitri Fernández, 1,2 O. A. Cuzman, 1 R. Giorgi, 3 C. Riminesi 1

<sup>1</sup>National Research Council, Institute of Heritage Science, Via Madonna del Piano 10, Sesto Fiorentino (FI), Italy <sup>2</sup>Department of Science of Antiquities, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy <sup>3</sup>Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, Sesto Fiorentino (FI) <u>marina.vieridemitri@uniroma1.it</u>

Biological deterioration represents one of the most critical threats to paper-based heritage artifacts, leading to the degradation of invaluable historical, cultural, and scientific records. The activity of fungi and bacteria that induce enzymatic hydrolysis and the production of acid metabolic byproducts manifest as a structural weakening and discoloration phenomena, often in the form of pigmented stains or the characteristic brown speckling known as foxing. [1] Addressing such damage requires an accurate and early diagnosis to identify the responsible microorganism and select an appropriate conservation strategy. However, this process is often time-consuming, costly, and destructive, especially when DNA-based analyses and paper sampling are required. This challenge becomes more pronounced in cases of extensive microbial deterioration, where assessing the effectiveness of cleaning treatment is crucial, highlighting the need to develop more efficient diagnostic methodologies. This study proposes hyperspectral imaging (HSI) as a non-invasive diagnostic tool to assess microbial deterioration in historical paper artifacts and control the treatment's efficacy. [2,3] Several 19th-century documents exhibiting varying degrees of biodeterioration were analyzed using a hyperspectral imaging system operating across the Visible and Near-InfraRed (VNIR, 400-1000 nm) and ShortWave InfraRed (SWIR, 1500-2500 nm) spectral ranges. The acquired spectral data were processed using chemometric algorithms to detect microbial growth patterns, distinguish spectral fingerprints of different fungal and bacterial species, and assess the extent of the damage (size of the colonized area). The imaging results were validated through microbiological sampling, establishing correlations between spectral features and the spatial distribution of microbial communities. The findings demonstrate that hyperspectral imaging emerges as a valuable tool, providing conservators with real-time, spatially detailed insights into microbial activity through extensive mapping. Adopting HSI represents a significant advancement in aligning paper-based artifact conservation with state-of-the-art analytical methodologies.

<sup>[1]</sup> D. Melo, S. O. Sequeira, J. A. Lopes, M. F. Macedo, *Journal of Cultural Heritage "Stains versus colorants produced by fungi colonizing paper cultural heritage: A review"* **2019**, *35*. DOI: 10.1016/j.culher.2018.05.013 [2] A. Jochemsen, G. Alfredsen, I. Burud, *International Biodeterioration and Biodegradation "Hyperspectral imaging as a tool for profiling basidiomycete decay of Pinus sylvestris L."* **2022**, 174. DOI: 10.1016/j.ibiod.2022.105464

<sup>[3]</sup> E. Matoušková, K. Kovářová, M. Cihla, J. Hodač, European Journal of Remote Sensing "Monitoring biological degradation of historical stone using hyperspectral imaging" **2023**. DOI: 10.1080/22797254.2023.2220565

#### RACEMIZATION OF ANIMAL GLUES IN PAINTINGS

#### Vojtěch Vilím, 1,2 Jakub Hraníček, 2 David Hradil, 1 Silvie Švarcová 1

<sup>1</sup>Institutite of Inorganic Chemistry of the Czech Academy of Sciences
<sup>2</sup>Department of Analytical Chemistry, Faculty of Science, Charles University
vilim@iic.cas.cz

Material research on paintings is valuable, as it is one of the most reliable sources of information. There are well-established techniques which provide us with information about materials used and the composition of individual layers, but there is only a handful of dating techniques. The radiocarbon method is applicable to date materials of substrates (wooden panels, canvas), frames, or lead white as recently reported.<sup>[1]</sup> However, required sample size and inability to date artefacts from some periods, due to the fluctuations in calibration curve, represent substantial limitations of the method.

Amino acid racemization (AAR) is a chemical method for dating materials of biological origin used in forensic and quaternary science as well as archaeology. Despite the wide use of proteinaceous binders (eggs, animal glues, casein) in painting, to our best knowledge this method has never been used for dating paintings, however, we believe it has a great potential to complement existing methods. AAR is based on racemization, a reaction converting one enantiomer of a chiral compound (an amino acid from protein) into another one until equilibrium is reached. Most living organisms throughout their life maintain *L*-amino acids homochirality, although it is energy-intense process as racemization naturally occurs, however, defective proteins are usually repaired or replaced. Thus, at the moment of death, there are none or negligible *D*-amino acids and racemization starts to proceed unimpeded. That is the starting point to which age estimation is linked and if the reaction rate is known, and a racemization ratio is determined, the age of sample can be estimated.

$$R = \frac{1}{1} OH$$
 $R = \frac{1}{1} OH$ 
 $R = \frac{1}{1$ 

Figure 1: Mechanism of amino acid racemization<sup>[2,3]</sup>

Herein we present preliminary results of animal glue extraction from mock-ups of grounds, composed of different mixtures of animal glue, carbonates and oils. Subsequently extracted animal glue was hydrolyzed and racemization of amino acid determined. These experiments create a base for upcoming research in this area and development of AAR method for dating of painted artworks.

**Acknowledgements:** The research is supported by the Czech Academy of Sciences within the frame of the research programme Strategy AV21 no. 36 The power of objects: Materiality between past and future.

<sup>[1]</sup> L. Hendriks, *Radiocarbon* **2019**, *61*(2), 473–493.

<sup>[2]</sup> O. Takahashi, Chemistry & Biodiversity 2010, 7(6), 1625–1629.

<sup>[3]</sup> T. Hua, New Journal of Chemistry 2019, 43, 12340-12350.

# 3D DOCUMENTATION OF TINY METALLIC OBJECTS: A COMPARATIVE STUDY ON A WAX SEAL RING OF PETER VOK OF ROSENBERG

Michal Vopálenský, 1 Jakub Novotný, 1 Martina Pechová, 2 Markéta Hrdličková 2

<sup>1</sup>Czech Academy of Sciences, Institute of Theoretical and Applied Mechanics, Czech Republic

<sup>2</sup>State Regional Archive in Trebon, Czech Republic

vopalensky@itam.cas.cz

Recent developments in imaging and manufacturing technologies have lowered their prices, significantly broadened their use, and made them much more affordable for end users. Particularly in the field of art and cultural heritage, they are a real game-changer in investigation and documentation methods. Depending on its complexity, the surface scanning of an object may be sufficient for creating its digital 3D model. Such scanning can be performed with visible light by capturing a set of images from different directions and calculating the 3D representation. Specific devices are available for this purpose, but nowadays even a smartphone can yield surprisingly good results. For better accuracy, laser-based devices are used. However, simple optical surface scanning is limited in the case of more complex objects where some sections are hardly visible from any angle. Here, X-ray computed tomography is a popular solution. It not only visualizes all the details on the surface but also reveals the internal structure of the object. Both optical scanning and X-ray tomography are non-invasive methods.

3D manufacturing allows for the creation of a physical, material body based on the virtual 3D model obtained from the scanning. Obviously, this new object can represent an exact copy of the original piece, but it can also be deliberately scaled or modified in various ways (e.g., virtual removal of corroded parts). The available materials today range from polymers and ceramics to metals.

However, there are serious complications for tiny metallic objects, such as jewelry: the scanning must be done with relatively high resolution to conserve the details; the reflective or transparent surface makes it difficult to acquire a quality dataset optically; and the behavior of metals under X-ray (scattering, reflections, and beam hardening) deteriorates the achievable resolution of the tomographic reconstruction. Finally, creating a high-quality 3D manufactured object requires a corresponding resolution in the additive manufacturing process. Consequently, making a highquality copy of a tiny precious object using modern scanning and manufacturing technologies can be surprisingly difficult.

In this study, the wax seal ring of an important Bohemian Renaissance nobleman, Peter Vok of Rosenberg, was scanned both optically and by X-ray microtomography. Negative and positive models of the ring were manufactured. The study demonstrated the possibilities and limitations of all the methods used.

### RESEARCH ON THE MANUFACTURING TECHNOLOGY OF IRON SWORD UNEARTHED FROM A HAN TOMB IN YANGZHOU

Xiangjun Wei,1\* Shuyu Sun,2 Zhen Liu,1 Yong Lei,3 Ziyao Wang4

<sup>1</sup>Shanghai Synchrotron Radiation Facility, Shanghai 201204, China <sup>2</sup>Henan Normal University, Henan 453007, China <sup>3</sup>The Palace Museum, Beijing 100009, China <sup>4</sup>Yangzhou Museum, Yangzhou 225002, China weixj@sari.ac.cn

Using a variety of scientific methods, the manufacturing technology of iron sword unearthed from a Han tomb in Yangzhou was studied through the analysis of metallographic structure, microstructure, element composition and crystal structure.

### ANALYSIS OF PAINTING TECHNOLOGY CHANGES IN TADEUSZ MAKOWSKI'S WORKS BY SPECTROSCOPIC METHODS

#### Magdalena Wróbel-Szypula, <sup>1</sup> Tomasz Jeziorowski <sup>2</sup>

<sup>1</sup>Laboratory of Research and Protection of Museum Collections, National Museum in Warsaw, Poland <sup>2</sup>Collection of Temporary Art, National Museum in Warsaw, Poland mwrobel@mnw.art.pl

Tadeusz Makowski (1882 – 1932) was a Polish painter born in Oświęcim. He studied firstly in Kraków, which he left at the age of 25. The rest of his life he spent in France, where his style underwent significant evolution mainly thanks to the group of Cubists.

The chemical composition of four paintings from different decades was analysed by X-ray fluorescence (XRF) and Fourier-transform infrared (FTIR) spectrometers. A variety of inorganic pigments as well as typical organic binders and varnishes were detected.

The earliest investigated masterpiece is *Woman in a Kraków folk costume* from 1906. The pigments used to paint the main character wearing colourful dress consisted mostly of chrome and cadmium yellows, cinnabar in all red parts, and viridian green. The background is painted using ochres and other iron red pigments. Further analysed works are already from French period. In opposition to the earlier painting, *Study of a nude* from 1912 has very limited palette. Apart from cinnabar in the part of lips, the rest of the painting is built of the earth pigments mixed with lead white surrounded by black outline of the woman. The painting *Bucolic* from

1920 illustrates Makowski's latest favourite subject, namely portraits of children. Apart from paints used in earlier paintings, namely: red cinnabar, chrome yellow and iron compounds, though a new green pigment was introduced, precisely emerald green, which contains toxic copper (II)-acetoarsenite. It was also possible to detect several synthetic blue paints, popular at that time: ultramarine, cobalt blue and possibly Prussian blue. The last investigated painting, *Bath*, from 1930 perfectly shows evolution of style, where children on the portraits have sharp geometric forms, though Makowski mostly continued his earlier workshop using cinnabar, iron reds, ochres, chrome yellow, emerald green, Prussian blue and ultramarine. Additionally in opposition to the earlier painting zinc white and yellow were detected.

Signals from lead, calcium and barium in nearly all of the measured points proved the presence of the lead white, calcium carbonate and barium sulphate in the background. Also in all four paintings infrared spectra showed the presence of oil binder and different types of natural resins. These results are the base for broader study of Tadeusz Makowski's workshop which will have the potential to be compared to works of other Polish and European painters living at the same time and of finding correlation between date, place and composition of paints used by the artist.

### VIBRATIONAL SPECTROSCOPY ON MARTIROS SARIAN'S $20^{TH}$ -CENTURY PAINTINGS

Tzu-Yi Yang,1 Sergei G. Kazarian1

<sup>1</sup>Department of Chemical Engineering, Imperial College London, United Kingdom v.yang23@imperial.ac.uk

Pigment identification provides material information, aiding the understanding of artworks and giving reference to future conservation. Martiros Sarian, an Armenian artist born in the late 19th century, created his paintings mainly in the second half of the 20th century. During the early and mid-20th century, both newly invented modern and traditionally used pigments were utilized. This work aimed to characterize diverse pigments from the paintings of this Armenian artist by employing Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopic imaging and Raman spectroscopy. [1] The compositional information from these two vibrational spectroscopies was interpreted with elemental data from Scanning Electron Microscopy (SEM) and energy dispersive X-ray Spectroscopy (EDS).

The study focused on red, blue, yellow, and green colours from nine of Sarian's paintings between 1911 and 1957. In red colours, sulphide salts, vermilion and cadmium red were observed. Cobalt-based pigments, such as cobalt blue and cerulean blue, were found in blue colour. Cadmium yellow and strontium yellow were detected in yellow samples. The green colour was achieved using chromium green. The analysis revealed the presence of different types of metallic pigments, including mineral, metal glass, and metallic salt. White pigments and fillings, such as lead white, zinc white and chalk, were commonly used in these paintings. Additionally, degradation products, including metal carboxylates and gypsum were observed by ATR-FTIR spectroscopic images. While ATR-FTIR and Raman spectroscopy proved useful for pigment identification, some pigments were difficult to identify due to spectra range and substrate fluorescence. In such cases, SEM-EDS provided an alternative method of characterizing artistic material in paintings.

**Acknowledgements:** The authors thank Prof. Ambrose Taylor from the Department of Mechanical Engineering at Imperial College London for supporting SEM-EDS analysis and the Sarian House Museum for providing samples.

<sup>[1]</sup> G. L. Liu and S. G. Kazarian, Heritage 2023, 6, 6777–6799.

#### UNVEILING COLANTONIO'S ARTISTIC PRACTICE IN SAN FRANCESCO CONSEGNA LA REGOLA: A NON-INVASIVE, IN SITU APPROACH TO DRAWING AND PAINTING PROCEDURES THROUGH IR AND X-RAYS IN CAPODIMONTE'S LABORATORY

#### Paola Improda, 1 Stella Zenga, 2 Orazio Lovino 1

<sup>1</sup>Researcher at the Department of Letters and Cultural Heritage, Università degli Studi della Campania 'L. Vanvitelli' – Santa Maria Capua Vetere, Italy

<sup>2</sup>PhD student of Heritage Science (39th cycle) – University of Rome "La Sapienza"

stella.zenga@uniroma1.it

The experimental laboratory, established in the conservation laboratories of the *Museo e Real Bosco di Capodimonte* thanks to an agreement (September 2022) among the *Università della Campania "Luigi Vanvitelli"*, the *Istituto di Scienze del Patrimonio Culturale* (ISPC-CNR) and the Museum, is currently researching the painting technique introduced at the end of 15th century in Naples by the masters of the so-called Southern Renaissance.

From what historical sources report and from what the scholars have acknowledged so far, Colantonio was the main Neapolitan painter of the fifteenth century and the protagonist of the Southern Renaissance, who was capable of developing an original painting style and technique by interpreting Flemish and Spanish models.<sup>[1,2]</sup>

Multidisciplinary analysis and scientific investigation hold a crucial role both as a key for the knowledge of the artist's painting technique and as a support for the reconstruction of past restorations and the planning of future conservation. [3,4] In order to better define the figure, style and catalogue of the painter, technical research and multispectral analysis with DiLBeC instrumentation has been undertaken since 2021 on paintings attributed to Colantonio and preserved in the *Museo e Real Bosco di Capodimonte*, including the *San Francesco consegna la Regola*, currently under restoration (Project "*Restituzioni*" 2024-2025 promoted by Intesa San Paolo). [5]

IR Reflectography (IRR) performed with the Opus Instruments Apollo camera made it possible to detect the presence of the underdrawing, to study the method of execution of the drawing and to identify the changes made during the painting process, allowing a better understanding of the painter's modus operandi. [5,6,7] The radiographic study, further than an aid to detect the changes in composition (i.e. the position of Saint Francis' hands and the profiles of the books), is providing useful information for the study of the painting's support by detecting the nails for the fixing of the crossbeams and the joint lines of the boards.

- [1] "Il polittico di Colantonio a San Lorenzo" **2001**, catalogo della mostra, a cura di Ferdinando Bologna, Napoli, 1-47.
- [2] P. Leone De Castris, Confronto: studi e ricerche di storia dell'arte europea "La riscoperta di Colantonio" **2019**, 2, 42-65.
- [3] M. Cardinali, M. B. De Ruggieri, C. Falcucci, "Diagnostica artistica. Tracce materiali per la storia dell'arte e per la conservazione" 2007, Roma, 120-135.
- [4] M. Cardinali, "Dalla Diagnostica Artistica alla Technical Art History. Nascita di una metodologia di studio della storia dell'arte (1874-1938)" 2020, Torino, 57-88.
- [5] P. Improda, "Technical Art History, indagini multispettrali, beni culturali e musei. I documenti e le immagini di una nuova storia dell'arte per il Museo di Capodimonte" 2023-2024, tesi di dottorato (XXXVI ciclo), I-II, Università della Campania Luigi Vanvitelli, I:80-220.
- [6] P. Improda, "La pala d'altare di Colantonio nella chiesa di San Lorenzo Maggiore a Napoli. Aggiornamenti sulle due tavole a Capodimonte" in "Svelare l'invisibile. Tracce nascoste di storie, opere e contesti" **2023**, atti del Convegno Internazionale, Padova 17-18 novembre 2022, Padova, 35-46.
- [7] E. Scialla, P. Improda et al., Heritage "Study of 'Cona degli Ordini' by Colantonio with IR and XRF Analyses" **2023**, 6.2, 1785-1803.

## PERIODIC CORROSION PHENOMENON AND LIESEGANG PATTERN -CROCSS-SECTION ANALYSIS ON TWO ANCIENT BRONZE SAMPLES

Zou Feichi, 1 Chen Weidong, 2 Wang Chong, 2 Guo Jianbo, 2 Xie Zhenbin, 2 Chen Kunlong, 3 Liu Jianyu, 1 Qu Liang 1

<sup>1</sup>Conservation Standards Department, Palace Museum, Beijing 100009, China;

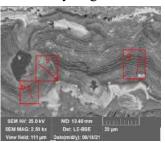
<sup>2</sup>Sichuan Archaeology Research Institute, Chengdu 610041, China;

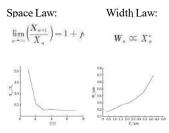
<sup>3</sup>Institute for Cultural Heritage and History of Science & Technology, University of Science and Technology, Beijing 100083, China;

zoufeichi@dpm.org.cn

The phenomenon of alternating layered structures of two types of corrosion products is called "periodic corrosion phenomenon", which occasionally found in archaeological excavations of bronze, but there is still no theoretical explanation for this phenomenon yet. Two bronze artifacts (CB-1 and LJB-38) unearthed in Sichuan, China were taken as an example to study the "periodic corrosion phenomenon", metallographic microscopy, SEM-EDS analysis, and Raman spectroscopy analysis techniques were applied to analyse the cross-section of these two samples. It was found that the bands in the corrosion of CB-1 sample were alternating layers of low crystallinity tin corrosion products and high crystallinity cuprite. This pattern of oscillatory bands might be attributed to the Liesegang crystallization cycle of cuprite in gel, which consists of uniform amorphous tin corrosion products. The bands in the corrosion of LJB-38 sample were alternating layers of tin corrosion products (including malachite) and cuprite, but did not present any ordered pattern, this might be due to the occurrence of "decupurification", which led to the rapid outward migration of copper, besides, the pseudomorphic structure of  $(\alpha+\delta)$  eutectoid in casting bronze corrosion destroyed the uniformity of gel fluid.

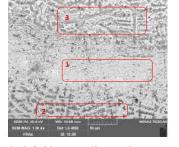






**Figure 1**: periodic corrosion phenomena (a: dark field in metallurgical microscope of CB-1; b: Liesegang bands in SEM; c: empirical rules of Liesegang pattern)





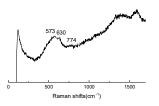


Figure 2: cross-section analysis of LJB-38(a: dark field in metallurgical microscope; b: pseudomorphic structure of  $(\alpha+\delta)$  eutectoid in SEM; c: Raman spectrum of tin corrosion products)

<sup>[1]</sup> D. A. Scott, Studies in Conservation "Periodic corrosion phenomena in bronze antiquities[J]" **1985**, 30(2), 49-57.

### FROM LEFTOVER TO CLASSIC: THE CHANGES OF PAINTING HISTORY OF POSTBOXES AND TELEPHONE BOOTHS

#### Yanki Wong,1 Cheryl Ho1

<sup>1</sup>Conservation Office, Leisure and Cultural Services Department, HKSAR vykwong@lcsd.gov.hk

In post-war Hong Kong, communication technology was not as advanced as it is today. Tools such as postboxes and telephone booths played crucial roles during that era, not only as channels for conveying information but also as vital bridges connecting people. Letters sent through postboxes carried heartfelt messages, while telephone booths allowed real-time conversations with loved ones. Pillar postboxes first appeared in Hong Kong in 1892, and while the slow process of letter delivery was gradually replaced by telecommunication, public telephone booths—first introduced in 1954—became particularly popular in the 1990s. However, with technological advancements providing global network coverage, the use of postboxes and telephone booths has significantly declined, leading to their removal from many parts of the city. Studying the painting history of these objects during their peak usage offers valuable insights into Hong Kong's past and cultural identity.

This project examines a mid-20th-century telephone booth collected by the Hong Kong Museum of History and postboxes that remain in use today. By analyzing paint film samples through cross-section analysis and material identification using multi-analytical techniques such as EDS, FTIR, and Raman spectroscopy, the study not only sheds light on Hong Kong's painting industry but also provides essential information for conservation planning and material selection for treatment. Interestingly, analysis revealed that the selected telephone booth contained only a few green-tone paint layers (Fig. 1), whereas the postboxes exhibited multiple red layers interspersed with yellow/orange anti-rusting lead primers beneath the green layers (Fig. 2). Although both public communication tools were introduced from Britain in the mid-20th century, their differing painting practices reflect varying governmental choices. One theory suggests that the red paint adhered to British standards, while another posits that green was used due to post-war material shortages, prompting the government to repurpose available wartime supplies. However, further research is needed to verify these claims.

The postboxes remain in good condition with regularly maintenance, requiring no additional treatment. In contrast, the oversized telephone booth, now obsolete and stored outdoors due to its weight and size, exhibits peeling paint, rust formation, and a cracked door window. As the booth is set to be displayed in the upcoming permanent exhibition at the Hong Kong Museum of History, selecting and implementing an appropriate conservation treatment is crucial to ensure visitor safety and prevent further deterioration of paint layer. This study will discuss the selection and formulation of suitable conservation treatments, the challenges of relocating the booth from remote storage, and the secure methodologies employed. Additionally, it explores strategies for revitalization of its historical significance in mid-20th-century Hong Kong.

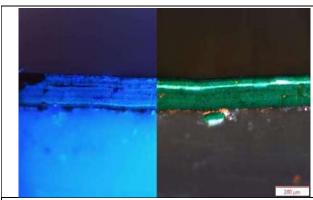


Figure 1: Paint film from telephone booth showing several layers of green tone paint (L:UV fluorescence, R: visible)



Figure 2: Paint film from postbox showing numerous red layers interspersed with orange primer (R:UV fluorescence, L: visible)

### MAY IT BE LIGHT AGAIN: FIRST APPLICATION OF ATOMIC OXYGEN TO REVERSE LEAD WHITE DARKENING

<u>Tomas Markevicius</u>,<sup>1,2</sup> Gianluca Pastorelli,<sup>3</sup> Sofie Wikkelsø Jensen,<sup>3</sup> Nan Yang,<sup>2,4</sup> Marta Cremonesi,<sup>4</sup> Yijia Song,<sup>2</sup> Anton Nikiforov,<sup>2</sup> Rino Morent,<sup>2</sup> Koen Janssens,<sup>4</sup> Geert Van der Snickt,<sup>4</sup> Klaas Jan van den Berg,<sup>1</sup> Alison Norton,<sup>5</sup> Nina Olsson,<sup>6</sup> and Ilaria Bonaduce<sup>7</sup>

<sup>1</sup>University of Amsterdam, Amsterdam, Netherlands, <sup>2</sup>Ghent University, Ghent, Belgium, <sup>3</sup>National Gallery of Denmark / Statens Museum for Kunst (SMK), Copenhagen, Denmark <sup>4</sup>University of Antwerp, Antwerp, Belgium, <sup>5</sup>Moderna Museet, Stockholm, Sweden <sup>6</sup>ICOMOS Lietuva National Committee, Vilnius, Lithuania <sup>7</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy

#### tmarkevicius@fulbrightmail.org

The lead white pigment has been extensively used from antiquity until the 19th century and is present in numerous works of art. However, exposure to environmental pollutants can cause severe darkening due to lead sulfide (PbS) formation, especially in water-based paints, leading to the visual deterioration of drawings, prints, and other works on paper [1]. This phenomenon has been recognized since the 17<sup>th</sup> century, yet effective treatments have remained limited in number. The commonly used hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) presents known adverse effects and risks [2]. Recently, atomic oxygen (AO), naturally occurring at altitudes of 80–1000 km, has emerged as a promising alternative [3]. Generated under atmospheric conditions by means of a 13.56 MHz radiofrequency (RF) non-equilibrium helium plasma, AO represents a novel non-contact approach, which can be tailored for diverse materials is currently under development by the authors. The ground-state O (3P) species exhibits a high oxidation potential (2.4 eV) and, within a plasma environment, can reverse the discoloration by converting PbS into white lead sulfate (PbSO<sub>4</sub>) at relatively low energy and temperature (~36-45°C). This study reports the first successful application of AO for treating darkened lead white using short-lived (milliseconds) AO species that do not persist in the substrate. The primary interaction mechanism is mild surface oxidation, which is less invasive than the wet H<sub>2</sub>O<sub>2</sub> treatment that involves radicalinduced oxidation, hydrolysis, acid formation, and potential cellulose degradation. The study investigates the effects of AO on mock-ups of artificially darkened lead white in gelatin and gum Arabic, applied on unsized 100% cotton paper. Treatments were conducted under varying AO conditions, benchmarked against 3% H<sub>2</sub>O<sub>2</sub> treatment. Preliminary findings indicate that tailoring AO parameters is critical: insufficient AO density results in incomplete PbS conversion, while elevated temperatures or low humidity promotes the formation of lead oxides. To evaluate AO used XRD mapping, colorimetry, SEM-EDX, HIROX microprofilometry, wettability and pH assessment, micro-ATR-FTIR, XPS and GC-MS. Optimal treatment conditions and AO generation were investigated using optical emission spectroscopy (OES), time-resolved FTIR, laser spectroscopy (TALIF) and temperature measurements. Plasma parameters were investigated using a multi-frequency in-line RF voltage, current, and phase measurement probe. The study demonstrates the feasibility of AO for effectively reversing lead white darkening. It serves as an initial step, and further research is required to refine treatment parameters, conduct the treatment trials, and clarify long-term treatment effects to accelerate its integration into the bench practice.

<sup>[1]</sup> G. Pastorelli et at. Darkening of lead white in Old Master Drawings and Prints, Microchemical journal 199, 2024

<sup>[2]</sup> S. M. Lussier, G.D. Smith A review of lead white darkening, Studies in Conservation, 52:sup1, 41-53, 2007

<sup>[3]</sup> T. Markevicius et al. Nascent Oxygen Innovation in Art Conservation, ICOM-CC Valencia, 2023

#### UNVEILING ALMEIDA JÚNIOR'S ARTISTIC STYLE: A MULTI-TECHNIQUE STUDY OF HIS LATE MASTERPIECES

Júlia Schenatto, <sup>1</sup> Marcia A. Rizzutto, <sup>1</sup> Vitória D. de Sousa, <sup>1</sup> Gabriel L. Osés, <sup>1</sup> Yuri F. Quevedo, <sup>2</sup> Mariana N. Agostinho <sup>2</sup> and Alexandre F. Xavier <sup>2</sup>

<sup>1</sup>Laboratório de Arqueometria e Ciência Aplicada ao Patrimônio Cultural (LACAPC), Institute of Physics,
University of São Paulo (USP), São Paulo, Brazil

<sup>2</sup>Pinacoteca do Estado de São Paulo, São Paulo, Brazil

rizzutto@if.usp.br

José Ferraz de Almeida Júnior (1850–1899) is a renowned Brazilian painters of the late 19th century, often considered the father of the Regionalism movement in Brazil. His works blend the academic style of Realism with a uniquely representation of everyday provincial life, contributing to the consolidation of a national identity in Brazilian art. Although extensive historical research has been conducted on his artistic style and iconography, [1-2] no analytical studies have been carried out to characterize his paintings. To meet this demand, researchers from the Archaeometry Laboratory LACAPC at the University of São Paulo, in collaboration with the Pinacoteca of São Paulo, conducted an in-depth scientific analysis of two paintings from Almeida

Júnior's late artistic period: Caipira Picando Fumo – study and final version (1893) – Amolação Interrompida – study (1893) and final version (1894). This research was part of a broader project led by the Pinacoteca, resulting in a book publication about his artworks and an exhibition. [3] This work presents a detailed in situ multi-technical analysis of Almeida Júnior's paintings. Imaging techniques included technical photography, infrared reflectography (IRR), and radiography. Spectroscopic methods comprised energy-dispersive X-ray fluorescence (ED-XRF) and Raman spectroscopy. The results revealed aspects of Almeida Júnior's color palette, pigment application techniques, and underlying compositional structures. Spectroscopic analysis identified periodcharacteristic pigments such as calcium, barium, zinc and lead white pigments, present in different layers of the painting. It was identified chromium based yellow and green pigments, vermilion red, cobalt blue, and iron based pigments. Imaging techniques provided insights into the artist's brushwork, decision-making process, and construction of pictorial layers. They also unveiled hidden sketches and compositional adjustments, revealing distinct functions for carbon lines found in different layers of the paintings. While the chemical composition of pigments remained consistent between the study and final versions, imaging analysis revealed significant changes in artistic decisions, with variations in the scene and the preparatory sketches.

This study highlights the critical role of integrating physical and historical methods in cultural heritage analysis. The collaboration between physics and museum studies has shed new light on key aspects of the artist's creative process, enriching our understanding of his technique and providing fresh perspectives for art historians and heritage scientists.

Acknowledgements: Thanks to the Pinacoteca team for all the support provided. MAR thanks FAPESP (2017/07366-1), CNPq (302823/2021-2), and GLO FAPESP (2022/06485-5) for financial support.

<sup>[1]</sup> F. M. Pitta, "Um povo pacato e bucólico: costume, história e imaginário na pintura de Almeida Júnior" 2013, Thesis (PhD Degree in Art History) – Escola de Comunicações e Artes da Universidade de São Paulo, São Paulo.

<sup>[2]</sup> A. M. Szlachta Junior and S. L. Menezes, Tempo, Espaço e Linguagem "Almeida Junior, o caipira construtor de imaginários" **2019**, 10(1), 195-213.

<sup>[3]</sup> J. Volz, Y. F. Quevedo, F. Pitta, A. Montenegro and E. Dias, "Os caipiras: das derrubadas à saudade" 2024, Pinacoteca de São Paulo.

# CHNART 20

International Conference on Analytical Techniques for Heritage Studies and Conservation Perugia, 6<sup>th</sup> - 9<sup>th</sup> May, 2025

### WITH THE SPONSORSHIP AND SUPPORT OF











CULTURAL HERITAGE ACTIVE INNOVATION FOR NEXT GEN SUSTAINABLE SOCIETY

















