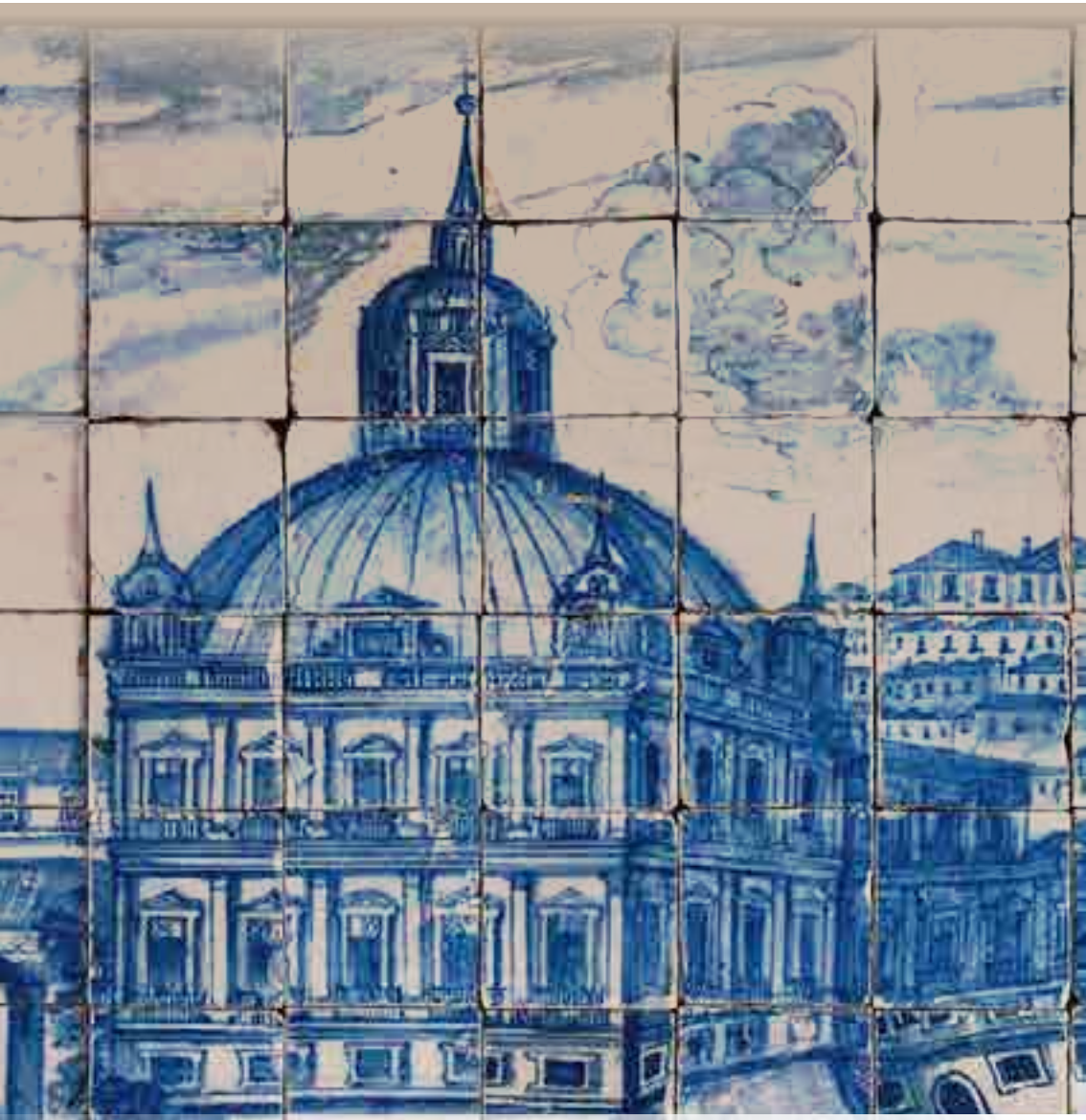
Aiding the conservation of two wooden Buddhist sculptures with 3D imaging and spectroscopic techniques

TECHNART 2023
LISBOA

International conference
on analytical techniques
in art and cultural heritage

LISBON | 07›12 MAY



BOOK OF ABSTRACTS

TECHNICAL INFORMATION

TECHNART2023 BOOK OF ABSTRACTS

TITLE
TECHNART2023
Non-destructive and Microanalytical Techniques in Art and Cultural Heritage. Book of Abstracts

EDITORS
Marta Manso, Vanessa Antunes, Maria Luísa Carvalho

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NOTE
Authors are responsible for the text included in the abstracts, for the reliability and truthfulness of the information and for the rights to publish any material included in the text

FOREWORD

The first **TECHNART** conference was held in Lisbon in 2007 by the initiative of the Atomic Physics Center from the University of Lisbon, current Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics (LIBPhys). The conference aimed to provide a cultural heritage science forum where the use of analytical techniques in art and cultural heritage were presented and discussed.

After five editions held in different European cities and a hiatus of four years due to COVID, it is a privilege to welcome in 2023, once more in Lisbon, the **TECHNART** conference.

The conference topics covers the application of a large range of analytical methods to art and cultural heritage investigations, namely X-ray analysis, confocal X-ray microscopy, synchrotron, ion beam and neutron-based techniques, FT-IR and Raman spectroscopy and microscopy, UV-Vis and NIR absorption/reflectance and fluorescence, laser-based analytical methods, magnetic resonance techniques, chromatography and mass spectrometry, optical and coherent imaging techniques, remote sensing and hyperspectral imaging.

The **TECHNART2023** program is organized in thematic sessions on analytical methods and their application to art and cultural heritage. Eight invited speakers will open thematic sessions on analytical methodologies, textiles, pigments and dyes, varnishes and resins, and metals. For four days, **TECHNART2023** brings in over 180 oral communications in three parallel sessions and more than 260 posters distributed in four sessions. The abstracts from oral and poster communications are collected in this book.

The conference accounts circa 400 participants representing around 50 countries from all over the world, offering an outstanding opportunity for exchanging knowledge and establishing new networks with other cultural heritage science researchers.

TECHNART2023 results from the straight collaboration between LIBPhys and the other organizing institutions (NOVA School of Science and Technology, Faculdade de Ciências da Universidade de Lisboa, Universidade de Coimbra, Associação para o Desenvolvimento do Departamento de Física da Universidade de Coimbra) with the support from the TECHNART International Scientific Committee. It was equally important the partnership with Centro HERCULES, Museu Nacional do Azulejo, Microchemical Journal, and Journal of Cultural Heritage, as well as the participation of the commercial companies (HIROX Europe, OPUS instruments, NIREOS, BRUKER, FORENSCOPE) and the sponsoring of Heritage journal, Xpecam commercial company and the European X-ray Spectrometry Association (EXSA).

Marta Manso and Maria Luísa Carvalho, May 2023 (Chairs)

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09h20		Invited speaker				
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11h00		Coffee break	Coffee break	Coffee break	Coffee break	
11h30 12h30		OP	OP	OP	OP	
13h00 13h30		Lunch break	Lunch break	Lunch break	Lunch break	
14h00	Registration					
14h30		Invited speaker	Invited speaker	Invited speaker	Invited speaker	
15h00 16h00		OP	OP & CS	OP	OP	
16h30		Coffee break	Coffee break	Coffee break	Coffee break	
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20h00				Conference dinner		

OP Oral Presentations
CS Commercial session

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15h30	5578	Arthur Gestels, Thomas De Kerf, Frederik Vanmeert, Francesca Gabrieli, Koen Janssens, Gunther Steenackers and Steve Vanlanduit ***Calibration of reflectance imaging spectroscopy using MA-XRPD for 16th century illuminated manuscript***
15h45	5757	Barbara Wagner, Jakub Karasiński, Ludwik Halicz, Piotr Targowski, Dorota Jutrzenka-Supryn, Ewa Chlebus, Paulin Pludra-Żuk, Monika Opalińska and Zofia Stos-Gale ***Pb isotope-based studies of manuscripts' origin: non-invasive tracing of parchment fragments to the 11th century***
16h00	6022	Natércia Teixeira, Hugo Cruz, André Neto E Silva, Luís Cunha-Silva, Paula Nabais, Fernando Pina, Victor de Freitas and Maria João Melo***Medieval writing: the chemistry behind iron gall inks***
16h15	6086	Grzegorz Nehring, Oliver Hahn and Ira Rabin ***Exotic writing inks and how to identify them***
16h30		Coffee break
17h00 **18h30**		Poster Session 2

TUESDAY 9TH | BUILDING C3 - AUDITORIUM 3.2.13

SESSION C - GLASS AND RELATED MATERIALS | CHAIRED BY SOPHIE WOLF

09h30	2651	Emma Paolin, Fabiana Di Gianvincenzo, Irena Kralj Cigić and Matija Strlič ***Chemical and sensory analysis of a perfume flask with gas chromatography-olfactometry***
09h45	1743	Victoria Corregidor, Luís C. Alves, Inês I. Mendes da Silva, Ana L. Rodrigues, António P. Gonçalves, Luís Ferreira, Miguel Reis, Cristina Chaves, Dulce Russo and Rosa Marques ***Non-destructive characterization of colored mineral glazed beads***
10h00	2284	Grégoire Chêne, Bernard Gratuze, Patrick Degryse, David Strivay and Line Vanwersch ***Early medieval age glass production techniques studies : an Inter-laboratory and multi-analytical techniques intercomparison campaign***
10h15	5939	Francesca Gherardi, Marine Cotte, Ewan Campbell, Rachel Tyson and Sarah Paynter ***Investigating the role of iron and manganese oxides in colouring late antique glass by XANES and micro-XRF spectroscopies***
10h30	5718	Carla Machado, Mohamed Oujja, Marina Martínez-Weinbaum, Laura Maestro-Guijarro, Marta Castillejo, Márcia Vilarigues and Teresa Palomar ***Laser-based techniques for the characterization of historically accurate grisaille paint reproductions***

10h45	6015	Hon Wen Chen and Chin Ssu Cheng ***Nondestructive XRD (X-ray Diffraction) crystallization and XRF (X-ray fluorescence) analysis of Taiwan indigenous glass beads***
11h00		Coffee break
SESSION C + A - GLASS AND RELATED MATERIALS + ANALYTICAL METHODS | CHAIRED BY ANDREAS KARYDAS		
11h30	6341	Sophie Wolf, Alessandra Vichi and Francesco Caruso ***Unveiling the secrets of 'verre églomisé' paintings: potential and limits of a non-destructive analysis***
11h45	8160	Oleh Yatsuk, Sabrina Molinaro, Patrizia Davit, Anzhelika Kolesnychenko, Stanislav Zadnikov, Iryna Shramko, Lorena Carla Giannossa, Annarosa Mangone, Giulia Berruto, Roberto Giustetto and Monica Gulmini ***Analysis of vitreous beads from the Iron Age site of Bilsk hillfort (Ukraine): an insight into glass-making technology and trade networks.***
12h00	9426	Stefania Martiniello, Claudia Sciuto, Antonella Capitanio, Giulia Lorenzetti, Stefano Legnaioli, Filippo Sala, Paolo Torriti and Simona Raneri ***Portable XRF and Raman spectroscopies to outline the story of Medieval precious objects***
12h15	1573	Alexandra Rodrigues, Mario Bandiera, Paul van Laar, Erma Hermens and Márcia Vilarigues ***Blue enamels. A preliminary non-invasive study of the blue enamels in objects from the Fitzwilliam Museum***
12h30	4474	Joana Palmeirão, Margarida Nunes, Ana Manhita, Maria Coutinho, Eduarda Vieira and Teresa Ferreira ***The ceroplastic simulacra of Vitoria, Eleonora and Martian***
13h00		Lunch break (Building C7)
COMERCIAL SESSION | CHAIRED BY MAURO GUERRA		
15h00		Emilien Leonhardt, Hirox ***100 billion pixel 3D color scan of Vermeer's Girl with a Pearl Earring using the Hirox digital microscope***
15h15		Marta Ghirardello, NIREOS **HERA: a novel hyperspectral camera for cultural heritage analysis**
15h30		Michele Gironda, Bruker Nano Analytics ***Bruker Nano Analytics, Iconic Instruments for Art***
15h45		Hannah Conway-Laws, Opus Instruments ***An Introduction to Opus Instruments: Leaders in Art & Analysis***
16h00		Jani Santos, XpectraCAM ***Optimization of Art Analysis methods based on the XpeCAM Solution***
16h30		Coffee break
17h00 **18h30**		Poster Session 2
WEDSNESDAY 10TH | BUILDING C3 - AUDITORIUM 3.2.14		
SESSION J - PIGMENTS AND DYES | CHAIRED BY KOSTAS HATZIGIANNAKIS		
09h00		Victor Gonzalez ***Investigating the synthesis, use and alteration of historical pigments at the multi-scale***
09h30	4352	Sanne Berbers, Rika Pause, Inez van der Werf, Klaas Jan van den Berg and Maarten van Bommel ***Fanal® pigments in the spotlight***
09h45	4366	Silvia Garrappa, Valentina Pintus, Anthony J. Baragona, David Hradil, Ferenc Szabo and Katja Sterflinger ***Different shades of cadmium soaps in mock-up oil paints: first multi-analytical investigation***
10h00	6025	Nina Deleu, Steven De Meyer, Frederik Vanmeert, Geert Van der Snickt, Jana Sanyova and Koen Janssens ***Combined in situ MA-XRPD and cross-section SR-μ-XRPD imaging for the study of copper sulfates: an overlooked group of green copper pigments in Flemish Renaissance art***
10h15	6174	Paula Nabais, Mara Santo, Natércia Teixeira, Mila Crippa and Dominique Cardon ***Molecular fluorescence: disclosing the dyeing formulations of weld yellows from 18th-century recipe books***
10h30	7057	Cyrielle Messager, Lucile Beck, Dominique Blamart, Patricia Richard, Katarina Batur, Victor Gonzalez and Eddy Foy ***Carbon isotopes in lead white: absolute dating and manufacturing process identification of the pigment***
10h45	8529	Camilla Tartaglia, Maria Pia Riccardi, Gianlorenzo Bussetti and Alberto Grimoldi ***Micromorphological observations as a potential method to study indigo blues***
11h00		Coffee break

SESSION J - PIGMENTS AND DYES | CHAIRED BY VICTOR GONZALEZ

11h30	1349	Giovanni Cavallo, Mariapia Riccardi and Roberto Zorzin ***A mineralogical and geochemical database of Fe-bearing mineral pigments from North-Eastern Italy***
11h45	1820	Marta Magalini, Alessandro Lo Giudice, Alessandro Re, Laura Guidorzi, Alessandro Borghi, Massimo Vidale, Dennys Frenez, Toshi Nozaka, Leonardo La Torre, Laurent Pichon, Quentin Lemasson, Brice Moignard and Claire Pacheco ***New light on the provenance of lapis lazuli found in Shahr-i Sokhta site using Ion Beam Analysis.***
12h00	5131	Corentin Cou, Hortense de la Codre, Xavier Granier and Aurélie Mounier ***Pearson correlation-based method on hyperspectral images for the study of similarity of pigments and dyes***
12h15	6901	Lucia Burgio ***The Renaissance of Indigenous American Lacquer - a Review of Current Research***
12h30	7462	Ekaterina Morozova, Irina Kadikova and Svetlana Pisareva **Titanium dioxide-based paints produced in the USSR: a study of archival materials and reference samples**
12h45	8288	Jorien Duivenvoorden, Federico Caporaletti, Sander Woutersen, Katrien Keune and Joen Hermans ***DSC and cryo-FTIR indicate presence of water clusters in zinc-white oil paint***
13h00		Lunch break (Building C7)

SESSION K - VARNISHES AND RESINS | CHAIRED BY EMELINE POUYET

14h30		Stamatis C. Boyatzis ***Non-invasive infrared spectroscopy of varnishes on artworks***
15h00	2243	Victoria Beltran, Andrea Marchetti, Patricio Guerrero, Ferenc Borondics, Christophe Sandt, Mario Scheel, Wim Dewulf, Ligia Maria Moretto and Karolien De Wael ***The interaction between geranium lake particles and drying oil assessed by SR-µFTIR and SR-XCT***
15h15	3633	Chiara Chillè, Charis Theodorakopoulos and Marianne Odlyha ***Further studies on the breakdown of selected natural and synthetic artists' varnishes upon Er:YAG laser irradiation***
15h30	8131	Valentina Pintus, Carlotta Cozzani, Silvia Miklin, Paula Gassmann and Katja Sterflinger ***Mind the cracks! Chemical and physical changes of blended Thitsiol/Urushiol Asian lacquers elucidated through a novel multi-analytical study***
15h45	5207	Elisabet Serrat, Javier Becerra, Anna Vila and Aleix Barberà ***Use of 3D Scanning to the study of craquelures on Joan Miró's "Pintura"***
16h30		Coffee break
17h00		Poster session 3
20h00		Dinner at *Casa do Alentejo*

WEDNESDAY 10TH | BUILDING C3 - AUDITORIUM 3.2.15

SESSION L - MURAL PAINTINGS | CHAIRED BY MAITE MAGUREGUI

09h30	2586	Alice Dal Fovo, Jana Striova, Enrico Pampaloni, Irene Lunghi, Marco Raffaelli and Raffaella Fontana ***Revealing unseen evidence of the hand of Masolino, Masaccio and Lippi in the Brancacci Chapel frescoes***
09h45	2623	Ilaria Costantini, Idoia Etxebarria, Iñaki Vázquez de la Fuente, Julene Aramendia, Gorka Arana, Irantzu Martinez-Arkarazo, Juan Manuel Madariaga, Macarena Sanz, Lucía Pérez, Ángel Yedra, Beatriz Yécora and Tamara Oroz ***Multi-technical approach for the study of the conservation state of mural paintings of Navalcarnero (Spain)***
10h00	2885	Tiziana Lombardo, Marta Caroselli, Camilla Martinucci, Erwin Hildbrand, Patrizia Moretti and Patrick Cassitti ***Investigation of the Carolingian and Romanesque wall paintings detached from the church of St. Johann in Müstair***
10h15	9809	Valeria Di Tullio, Noemi Proietti, David Buti, Sveva Longo, Alberto Felici, Donata Magrini and Cristiano Riminesi ***Water profile distribution inside wall paintings by NMR-MOUSE in combination with evanescent-field dielectrometry technique and near-IR reflectance spectroscopy***
10h30	719	Sihan Zhao, Zhibo Zhou, Lin Zhang and Hui Zhang- ***Identification of Fake Gold Gilding Material in the Ancient Wall Paintings by Mass Spectrometry Imaging***
11h00		Coffee break

SESSION L - MURAL PAINTINGS | CHAIRED BY MILENE GIL

11h30	3854	Giasemi Frantzi, Harikleia Brekoulaki, Andreas Germanos Karydas, Georgios P. Mastrotheodoros, Stamatios Boyatzis and Panayiotis Theoulakis ***Investigating colour on Archaic architecture: A case study on the Peisistrateion Telesterion at Eleusis***
11h45	3863	Francesca Sabatini, David Buti, Fauzia Albertin, Brenda Doherty, Letizia Monico, Aldo Romani, Francesca Rosi, Maria Sileo, Nicodemo Abate, Antonio M. Amodio, Nicola Masini, Antonio Pecci and Laura Cartechini ***Urban art in Milan: non-invasive analytical strategies for the study of street art murals***

12h00	4468	Maite Maguregui, Francesco Caruso, Francesco Giannici, Alessandra Vichi, Claudio Ventura Bordenca, Olivier Mathon and Marine Cotte ***Metallic mercury, at last! Synchrotron radiation-based study on Pompeian cinnabar wall paintings***
12h15	7854	Ermanno Avranovich Clerici, Steven De Meyer, Frederik Vanmeert, Letizia Monico, Costanza Miliani and Koen Janssens ***Cumengeite in wall paintings, intentional application or secondary product?***
13h00		Lunch break (Building C7)
SESSION I - GRAPHIC DOCUMENTS | CHAIRED BY VICTORIA CORREGIDOR		
15h00	6148	Michela Perino, Edoardo Colonna, Anna Candida Felici, Vittoria Bruni, Domenico Vitulano and Michela Rosellini ***New insight into the palimpsests of Ars Prisciani***
15h15	6315	Sara Mazzocato, Dafne Cimino and Claudia Daffara ***Integrated microprofilometry and multispectral imaging for full-field analysis of ancient manuscripts***
15h30	6494	Heinz-Eberhard Mahnke, Tzulia Angos, Tobias Arlt, Klaus Lips, Joseph E. McPeak and Verena Lepper ***A New Approach for Accessing Hidden Text on Papyri Written with Carbon Ink****
15h45	7594	Lucía Pereira-Pardo, Paul Dryburgh, Marc Vermeulen, Elizabeth Biggs, Peter Crooks, Adam Gibson, Molly Fort, Constantina Vlachou-Mogire, Moira Bertasa, John R Gilchrist and Jon Danskin ***Reading the Unreadable. Advanced Imaging to Recover Illegible Text in Historic Documents***
16h00	7948	Juliana Bittencourt, Márcia Rizzutto, Wanda Engel, Maria Aparecida Borrego, Phablo Fachin, Regina Hauy, Jean Souza, Igor Cassemiro, Maria Luiza Lamardo and Mariza Koga ***Material investigation on Italian and Portuguese papers from the Republican Museum Convention of Itu, Brazil***
16h15	8493	Andrej Kazanskii, Jitka Neoralová, Rita Lyons Kindlerová, Dana Novotná, Petra Vávrová, Daniel Vavřík, Ivana Kumpová, Michal Vopálenský and Tomáš Kyncl ***The use of X-ray computed tomography and X-ray fluorescence in the research of historical printing from the 17th century***
16h30		Coffee break
17h00		Poster Session 3
20h00		Dinner at *Casa do Alentejo*
WEDNESDAY 10TH |AUDITORIUM 3.2.13		
SESSION M + A - POLYMERS + ANALYTICAL METHODS | CHAIRED BY EVA MARISOLE		
09h30	148	Eva Mariasole Angelin, Anna Micheluz and Marisa Pamplona ***Investigation of the discoloration of polyurethane elastomeric plastics in computer heritage: have we met an analytical challenge?***
09h45	288	Tjaša Rijavec, Matija Strlič and Irena Kralj Cigić ***Predicting the yellowing of PVC objects in heritage collections***
10h00	635	Jacek Bagniuk, Monika A. Koperska, Dominika Pawcenis and Joanna Profic-Paczkowska ***A systematic approach to study natural polymer ageing and condition. Analysis contra model***
10h15	1262	Irene Bargagli, Laura Cartechini, Brenda Doherty, Francesca Sabatini, Martina Alunni Cardinali, Lucia Comez, Marco Paolantoni, Valeria Di Tullio, Noemi Proietti, Costanza Miliani, Daniele Fioretto, Elisa Storace, Sara Russo, Rafaela Trevisan and Francesca Rosi - ***Mechano-chemical monitoring of plastic degradation: surface and sub-surface modification of artificially aged ABS***
10h30	5972	Ioanna Mantouvalou, Leona Bauer, Oleksandra Marushchenko, Ioannis Siouris, Maram Naes and Birgit Kanngießer ***SyncLab for cultural heritage - joint X-ray imaging and spectroscopy measurements at the synchrotron and in the laboratory***
10h45	5852	Wolfgang Kautek, Valentina Ljubic Tobisch, Klaudia Hradil, Karin Whitmore, Christina Streli and Peter Wobrauschek ***Surface Characterization of Austrian Daguerreotypes***
11h00		Coffee break
SESSION N - SCIENTIFIC AND TECHNOLOGICAL HERITAGE | CHAIRED BY ISABEL TISSOT		
11h30	902	Aurore Malmert, Clarisse Chavanne, Alain Brunelle and Emeline Pouyet ***Non-invasive analyses of E. Chevreul's chromatic circles***
11h45	3785	Jacopo La Nasa, Catharina Blaensdorf, Eleonora Dolcher, Riccardo Ducoli, Serena Del Seppia, Jeannette J. Lucejko, Antonella Mannariti, Anna Micheluz, Francesca Modugno, Neva Capra, Lucia Giovannini, Maria Luisa Tomasi, Marisa Pamplona, Maria Perla Colombini, Ilaria Degano and Ilaria Bonaduce - ***Aerospace technology as part of our heritage: characterization of aircraft materials and study of their degradation processes by analytical pyrolysis***
12h00	4606	Lorna Brundrett, Rebecca Ploeger, Aaron Shugar, Jiuan Jiuan Chen, Emily Hamilton and Theresa J. Smith ***19th-Century Medical Saddlebag: An Analysis of the Medicinal Contents***

12h15	2101	Miriam Pressato, Teresa Lança Ruivo, Catarina Miguel, António Candeias and Sara Valadas ***Study of 18th century Chinese wallpapers from the National Museum of Ancient Art (Lisbon): a multi-analytical approach***
12h30	4288	Taren Ginter, Megan Gallagher, Shaelyn Horvath, Josephine La Macchia, Sonia Marotta and Fiona E. McNeill ***The Beautifying Properties of Historical White Lead Makeup***
12h45	5051	Jens Gold, Francesco Caruso, Noëlle Lynn Wenger Streeton and Maite Maguregui ***Discovering Lippmann interferential colour photography at the Preus Museum through a non-invasive multianalytical approach***
13h00		Lunch break (Building C7)
SESSION O - MODERN MATERIALS AND CONTEMPORARY ART | CHAIRED BY CLAUDIA CALIRI		
15h00	8390	Tea Ghigo, Kelly Domoney, Daniel Bone and Andrew Beeby ***Archival research and material analyses to explore artists' attitudes towards pigments' durability: John Ruskin and the 19th-century Colour Revolution***
15h15	8043	Francesca Galluzzi, Rémy Chapoulie, Floréal Daniel, Regine Bigorne, Laurent Vedrine and Aurélie Mounier ***Goupil & Cie and the democratisation of art in the 19th century: A non-invasive investigation of mechanical reproductions of artworks***
15h30	8343	Fauzia Albertin, Aldo Romani, Claudio Costantino, David Buti, Letizia Monico, Francesca Sabatini, Donata Magrini, Claudia Caliri, Claudia G. Fatuzzo, Zdenek Preisler, Francesco Paolo Romano, Costanza Miliani, Aurélie Tournie, Christine Andraud, Irina Crina Anca Sandu, Jin Strand Ferrer, Giorgio Luciano, Laura Cartechini and Francesca Rosi - ***Multi-source data fusion of modern complex paintings***
15h45	9962	Pierre Taugeron, Sullivan Bricaud, Cindie Kehlet and Jens Dittmer ***New techniques for NMR depth profiles with enhanced resolution and sensitivity and the study of mobile phases in paint layers, applied to a white Nevelson sculpture***
16h00	297	Stefano Legnaioli, Giulia Lorenzetti, Luca Nodari, Rosa Costantini, Patrizia Tomasin and Luciano Pensabene Buemi ***"Ce n'est pas la colle qui fait le collage": the analytical challenge of Ernst's multi-material artworks***
16h30		Coffee break
17h00		Poster Session 3
20h00		Dinner at *Casa do Alentejo*

THURSDAY 11TH | BUILDING C3 - AUDITORIUM 3.2.14		
SESSION P - METALS | CHAIRED BY ROBERT VAN LANGH		
09h00		Isabel Tissot - ***Through a metal darkly: How analytical techniques brighten the conservation of cultural heritage metallic objects***
09h30	603	Stephen Merkel, Paolo D'Imporanzo, Rory Naismith, Gareth Davies and Jane Kershaw ***New application of portable laser sampling for Pb isotope analysis of silver***
09h45	2594	Isabel Rute Fontinha, Maria João Correia and Elsa Eustáquio ***Electrochemical techniques for patinas and coatings assessment in conservation studies***
10h00	2762	Alexandre Gillon, Charbel Koumeir, Charlène Pelé-Méziani, Gildas Salaün, Ferid Haddad and Guy Louarn ***Investigation of the new world silver provenance and trade in Europe during the 16th and 17th centuries: HE-PIXE and p-XRF spectroscopic analysis***
10h15	4056	Javier Moreno-Soto, Miguel A. Respaldiza, Simona Scrivano, Ruth Pliego, Blanca Gómez-Tubío, Enrique García-Vargas and Francisca Chaves-Tristan ***An approach to the metallic composition of the Carthage mint coins from the tetrarchic hoard of Tomares***
11h00		Coffee break
SESSION A+ Q - ANALYTICAL METHODS + PAINTS |CHAIRED BY STAMATIS BOYATZIS		
11h30	6957	Pedro Alexandre Caetano Alves and Francesca Caterina Izzo ***The Molecular Clock of Ageing Oils***
11h45	2880	Ophélie Ranquet, Giulia Caroti, Rafaella Georgiou, Patrick Dietemann, Norbert Willenbacher, Celia Duce and Ilaria Bonaduce ***Mass spectrometry and thermoanalytical techniques to understand the transition from egg tempera to oil paint in Italian Reinassance***
12h00	4783	Ida Fazlic, Marine Cotte, Victor Gonzalez, Frederik Vanmeert, Arthur Gestels, Steven De Meyer, Fréderique Broers, Joen Hermans, Annelies van Loon, Ermanno Avranovich Clerici, Koen Janssens, Petria Noble, Jitte Flapper, Bas De Bruin and Katrien Keune ***Lead(II) Formate: from Historical to Model Paints***
12h15	3533	Lucie Laporte, Guylaine Ducouret, Sophie Rochut, Frédéric Gobeaux and Laurence de Viguerie ***Influence of lead driers on oil paint properties***

12h30	3713	Lucilla Pronti, Martina Romani, Marcella Ioele, Ilaria Sinceri, Elena Cianca, Eleonora Gorga, Gloria Tranquilli, Francesca Fumelli and Mariangela Cestelli Guidi ***Micro and Macro FT-IR spectroscopic imaging and mapping as a tool for the detection of degradation products and for monitoring the cleaning processes of painted surfaces***
12h45	7043	Alba Alvarez Martin, Teresa Scovacricchi, Jusal Quanico, Ermanno Avranovich Clerici, Geert Baggerman, Frederik Vanmeert, Arthur Gestels and Koen Janssens ***Tracking secondary products in aged paint cross-sections by MALDI-MS Imaging***
13h00		Lunch break (Building C7)
SESSION P - METALS | CHAIRED BY DAVID BUTI		
14h30		Francesco Grazzi ***Non-invasive analysis of historical and archaeological metal artefacts through neutron imaging and neutron diffraction: highlights and case studio***
15h00	790	Giulia Festa, Claudia Caliri, Giulia Privitera, Claudia G. Fatuzzo, Danilo P. Pavone, Claudia Scatigno, Enrico Ferraris, Johannes Auenmüller, Costanza Miliani and Francesco Paolo Romano ***Studying Ancient Egyptian metal vessels by X-ray diffraction and Machine Learning.***
15h15	955	Yueer Li, Lambert van Eijck, Francesco Cantini, Oriol Sans Planell, Marta Magalini, Johannes Auenmüller, Sara Aicardi, Valentina Turina, Luisa Vigorelli, Lorenzo Dotto, Alessandro Re, Alessandro Lo Giudice, Leila Es Sebar, Miriana Marabotto, Sabrina Grassini, Nícla Gelli and Francesco Grazzi ***New insights into ancient Egyptian bronze votive coffins for animal mummies through Neutron Imaging and Neutron Activation Analysis***
15h30	8437	Francesco Abate, Michela De Bernardin, Maria Stratigaki, Giulia Franceschin, Fauzia Albertin, Matteo Bettuzzi, Rosa Brancaccio, Anita Bressan, Maria Pia Morigi, Salvatore Daniele and Arianna Traviglia ***Renewing archaeological practice with modern technology: µXCT for the facile screening of excavated copper coins***
15h45	8566	Francesco Armetta and Maria Luisa Saladino ***Methodological approaches for underwater archeological metals investigation***
16h30		Coffee break
17h00 **18h30**		Poster session 4

THURSDAY 11TH | BUILDING C3 - AUDITORIUM 3.2.15		
SESSION D - SUSTAINABLE CONSERVATION | CHAIRED BY KATRIEN KEUNE		
09h30	276	Maduka Lankani Weththimuni, Chaehoon Lee, Chiara Milanese, Barbara Vigani, Marco Malagodi, Silvia Rossi and Maurizio Licchelli - ***A Comparative study of "green" and synthetic gels as tools for the cleaning of artifacts***
09h45	2796	Lucrezia Barchi, Gabriele Cencetti, Massimiliano Frattoni, Marco Michelozzi, Cristiano Riminesi, Aldo Romani, Francesca Rosi, Diego Sali, Francesca Vichi and Costanza Miliani ***New strategies for VOCs control in museums showcases***
10h00	3363	António Carrapiço, Maria Rosário Martins, Ana Teresa Caldeira, Ana Cardoso, Elisabete Carreiro, José Mirão and Luís Dias ***AgNPs applied to Cultural Heritage: Exploring its antimicrobial potential using "Green" approaches***
10h15	6250	Chaehoon Lee, Maduka L. Weththimuni, Francesca Di Turo, Barbara Vigani, Fabio Beltram, Pasqualantonio Pingue, Silvia Rossi, Maurizio Licchelli, Marco Malagodi, Haejin Park, Yongjae Chung, Francesca Volpi and Giacomo Fiocco ***Not Just for Eating! Alginate-based Gels and Their Application Studies***
10h30	7074	Chiara Genova, Marzia Beccaccioli, Alessandro Lazzara, Alessandro Ciccola, Simona Sennato, Gabriele Favero and Alessia Masi ***Development of environmentally-friendly biocidal systems based on chitosan-nanoparticles loaded with R-(+)-pulegone to protect wood from fungal attack***
10h45	1612	Francesca Ramacciotti, Laure Cazals, Giorgia Sciutto, Rocco Mazzeo, Silvia Prati, Loïc Bertrand and Mathieu Thoury - ***Photoluminescence MA-imaging for the assessment and study of new cleaning systems***
11h00		Coffee break
SESSION E + R - ARCHAEOLOGICAL MATERIALS AND SITES + STONE | CHAIRED BY FRANCESCO CARUSO		
11h30	3698	Iñaki Vázquez de la Fuente, Idoia Etxebarria, Ilaria Costantini, Marco Veneranda, Nagore Prieto Taboada, Giuseppe Di Girolami, Angela Di Lillo, Marina Caso, Mario Notomista, Rossella Di Lauro, Kepa Castro, Gorka Arana and Juan Manuel Madariaga - ***Degradation of tuff buildings at the Archaeological park of Herculaneum (Italy): preliminary multianalytical study***
11h45	4798	Ewa Bulska, Mariusz Ziółkowski - ***Analytical scenario for the investigation of Machu Picchu cultural heritage in Peru***

12h00	9285	Jorge Sanjurjo Sánchez, Rebeca Blanco-Rotea, Rosa Benavides, David Freire Lista, Jose Carlos Sánchez-Pardo, Isabel Prudêncio, Isabel Dias and Chris Burbidge ***Absolute dating of building materials from the Santalla de Bóveda Monument (Lugo, NW Spain)***
12h15	7999	Rana Nur Karataş, Amine Seyhun Alkan Reis, Mahmud Çavur, Murat Güvenç, Yonca Erkan, Sude Erkmen and Füsun Alioğlu ***Remote Sensing for Land Use and Land Cover Change: Interpretation of Iznik's Rural Heritage***
12h30	7243	Fernanda Carvalho, Maria Margarida Lima and João Pedro Veiga ***Mineralogical identification of historical mortars from built heritage using Raman spectroscopy***
13h00		Lunch break (Building C7)

SESSION R - STONE | CHAIRED BY PATRIZIA TOMASIN

15h00	783	Sara Calandra, Claudia Conti, Irene Centauro and Emma Cantisani - ***Micro-Raman spectroscopy for identification of calcite types in historical mortars: applications in archaeometry***
15h15	3043	Milena Anfosso, Doria Costa, Laura Gaggero, Silvia Vicini, Francesca Piqué, Mauro Matteini and Angelita Mairani - ***A new consolidation protocol with Di-ammonium phosphate for Italian Stones***
15h30	4670	Paulina Guzman Garcia Lascurain, Sara Goidanich, Irene de Giuli, Carlos Rodríguez-Navarro and Lucia Toniolo ***Study of the influence of micro- & nano-cellulose on the growth and carbonation kinetics of portlandite particles***
15h45	6147	Andrea Campostrini, Sabrina Manente, Alessandro Di Michele, Elena Ghedini, Michela Signoretto and Federica Menegazzo ***High-tech multifunctional marmorino plaster with antimicrobial and self-cleaning properties***
16h00	6297	Luís Almeida, António Santos Silva, Rosário Veiga and José Mirão ***Combined application of petrography and SEM-EDS: outputs for accurate identification of binders in hydraulic mortars***
16h30		Coffee break
17h00 **18h30**		Poster session 4

THURSDAY 11TH |BUILDING C3 - AUDITORIUM 3.2.13

SESSION A + R - ANALYTICAL METHODS + ROCK ART | CHAIRED BY MÁRCIA VILARIGUES

09h30	2221	Clarissa Dominici, Chiaramaria Stani, Giovanni Birarda, Francesco Boschin, Lisa Vaccari and Adriana Moroni - ***Monitoring changes in human activities across the Upper Palaeolithic: a statistical approach for the critical assessment of ancient organic residues through SR-FTIR microscopy***
09h45	5178	Daniela Puzio, Alessia Andreotti, Luca Bachechi, Giulia Lorenzetti, Stefano Legnaioli, Simona Raneri and Vincenzo Palleschi - ***Discovering the rock paintings of the Ethiopian plateau: the Goda Daga Barru and Enda Aba Shillemun shelters***
10h00	5751	Laura Rabbachin, Guadalupe Piñar, Irit Nir, Ariel Kushmaro, Mariela Pavan, Elisabeth Eitenberger, Monika Waldherr, Alexandra Graf and Katja Sterflinger - ***From the desert to the Alps: a study to unveil biodeterioration patterns of historical petroglyphs integrating metagenomics with analytical techniques***
10h15	5839	José Tapia, Myriam Eveno, Pablo Arias, Thomas Calligaro, Laurent Pichon, Sebastian Schöder, Katharina Müller and Ina Reiche - ***Confocal XRF depth profiling combined with XRF mapping to non-destructively understand the stratigraphy of prehistoric cave art***
10h30	5922	Victory Jaques and Katarína Holcová -***Calcareous nannofossils assemblage in paintings chalk ground for provenance analysis: 3 original paintings compared to European source materials***
10h45	5145	Pablo Pérez-Vasallo, David Juanes and Eusebio Solórzano ***WideXcan: An automated high resolution X-ray radiography system for large artwork pieces***
11h00		Coffee break

SESSION E + A - ARCHAEOLOGICAL MATERIALS + ANALYTICAL METHODS | CHAIRED BY MIGUEL ANGEL RESPALDIZA

11h30	1729	Dorothy Parungao, António Candeias, Joao Lopes and Catarina Miguel ***Are Infrared and Chemometrics up to the Tusk? On the Use of In-situ Infrared Spectroscopic Techniques for the Study of the Provenance of Historic Ivories***
11h45	8045	Laurent Tranchant, Pierre Gueriau, Sebastian Schöder, Serge Cohen, Loïc Bertrand and Mathieu Thoury ***Detecting visual and chemical modifications induced by the high-flux synchrotron X-ray analysis of ancient teeth***
12h00	7832	Enrico Greco, Andrea Maria Gennaro, Daniela Costanzo, Dario Piombino-Mascali, Simona Accardo, Sabina Licen, Pierluigi Barbieri, Sara Signoretti, Caterina Gabriele and Marco Gaspari ***Dental proteomic analyses reveal the sex of human remains from the Greek cemetery of San Giorgio Extra, Reggio Calabria (Italy)***
12h15	4916	Leila Birolo, Georgia Ntasi, Andrea Carpentieri, Manuela Rossi, Schisano Chiara, Chiara Melchiorre, Miriam Alberico, Brunella Cipolletta, Giovanna Scarano and Alessandro Vergara ***Ancient proteins: from identification to characterization. A review and the case of the funeral equipment in a Hellenistic young woman tomb from Battipaglia***
13h00		Lunch break (Building C7)

SESSION S + A - WOOD + ANALYTICAL METHODS | CHAIRED BY DIEGO TAMBURINI		
15h00	3189	Costanza Cucci, Juri Agresti, Giovanni Bartolozzi, Francesco Grazzi, Marcello Picollo, Lorenzo Stefani, Teresa Brancolini, Giulia Basilissi and Anna Consonni - ***Technical studies in Egyptology. Multi-modal imaging and multi-range spectroscopies shed light on a rare wooden polychrome chest***
15h15	4882	Sveva Longo, Enza Fazio and Silvia Capuani ***Non-destructive identification of wood from XVII Century panel painting using clinical X-ray computed tomography Hounsfield Units scale***
15h30	8880	Chiara Ricci, Paola Buscaglia, Debora Angelici, Anna Piccirillo, Federica Pozzi, Paola Manchinu, Leila Es Sebar, Luca Lombardo, Sabrina Grassini, Federico Di Iorio, Sara Croci, Laura Vigo and Davide Quadrio ***Aiding the conservation of two wooden Buddhist sculptures with 3D imaging and spectroscopic techniques***
15h45	9209	Eva Hartlieb, Pascal Ziegler, Andreas Baumann, Peter Schöler and Peter Eberhard ***Newly developed transportation frame for a fragile wooden panel painting***
16h00	1910	Chiaramaria Stani, Claudia Invernizzi, Giovanni Birarda, Patrizia Davit, Lisa Vaccari, Marco Malagodi, Monica Gulmini and Giacomo Fiocco ***Revealing new secrets behind the Stradivari's craftsmanship: an infrared investigation at the nanoscale.***
16h30		Coffee break
17h00		Poster session 4
18h30		Closing session
FRIDAY 12TH | AZULEJO NATIONAL MUSEUM		
10H00 **13H00**		VISIT TO MNAZ

POSTER SESSIONS

MONDAY 8TH | SESSION 1

N.	Authors	Title	ID
1	Silvia Macedo-Arantes, M. Rosário Martins, António Candeias and A. Teresa Caldeira	***Essential Oils/Cyclodextrin Inclusion Complexes as eco friendly antimicrobials for Cultural Heritage: an approach with essential oils of Mentha pulegium and Mentha spicata and Calamintha nepeta from Alentejo (Portugal)***	252
2	Alberto Viani, Dita Machová and Petra Mácová	***The assessment of state of conservation of bone material in the UNESCO World Heritage site of Sedlec, Czechia.***	302
3	Máté Szarka, Ákos Csepregi, Boglárka Döncző, Zsófia Kertész, Anikó Angyal and Zita Szikszai	***Considerations for improved monitoring in ion beam analysis of organic heritage materials***	464
4	Forough Armal, Luis Dias, José Mirão, Vera Pires, Fábio Sitzia, Sérgio Martins, Mafalda Costa and Pedro Barrulas	***Multi-analytical study and assessment of commercial coating hydrophobic effectiveness and durability in carbonate stones - a case study of built heritage protection and preservation***	516
5	Simone Murgia, M. Carla Aragoni, Gianfranco Carcangiu, Veronica Caria, Paola Meloni, Anna Pintus, Enrico Podda and Massimiliano Arca	***Protection of carbonate stone samples via treatment with ammonium N-2-picolyloxamate***	550
6	Inês Silva, Cátia Salvador, Ana Miller, António Candeias and A. Teresa Caldeira	***Microbial induced stone discoloration in Alcobaça Monastery: a comprehensive study***	595
7	Luisa Vigorelli, Francesca Tansella, Alessandro Re, Laura Guidorzi, Miriana Marabotto, Sabrina Grassini, Gabriele Ricchiardi and Alessandro Lo Giudice	***Use of X-Ray imaging techniques for analysis in the Cultural Heritage field***	975
8	Anna Fialová, Jan Válek, Petr Kozlovcev, Olga Skružná, Jana Maříková-Kubková, Iva Herichová, Dita Frankeová, Alberto Viani	***Characterization of mortars from Romanesque floors excavated in St. Bartholomew's church at Prague Castle***	1334
9	Anderson de Paula, Alessandra Machado, Olga Maria Araújo, Ricardo Lopes, Davi Oliveira	***Portable CT characterization for in situ analysis***	1382
10	Aneta Gójska, Ewelina Miśta-Jakubowska, Łukasz Kruszewski, Michał Przeździecki, Michał Paczkowski, Leszek Marynowski, Magdalena Wilczopolska, Ryszard Diduszko, K Pyżewicz, Tymoteusz Kosiński, Michał Szubski and Krystian Trela	***Thermal transformation of chalcedonite artefacts from the Magdalenian site of Ćmielów 95 "Mały Gawroniec" (Poland)***	1407
11	Águeda Sáenz-Martínez, Marta Pérez-Estébanez, Mónica Álvarez de Buergo, Margarita San Andrés	***Testing acid products thickened with xanthan gum for the removal of calcareous deposits on ceramics***	1493
12	Jose. F. Garcia, Raul Cabeza-Navarro, Pere Castanyer, Marc Bouzas, Josep Burch, Sònia Sentellas	***Identification of wine markers in ancient pottery using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS)***	1764
13	Monica Dinu, Lucian Cristian Ratoiu, Camelia Calin, Gerard Calin	***Statistical classification of LIBS and hyperspectral data for mapping the interventions on a historical building***	2034
15	Clarisse Chavanne, Laurence de Viguerie, Romain Berraud-Pache, Christelle Souprayen, Sophie Rochut, Brunelle Alain, Philippe Walter, Maguy Jaber, Emeline Pouyet	***Operando monitoring of photo-ageing in hybrid material using a Cultural Heritage dedicated platform***	2129
16	Idoia Etxebarria, Marco Veneranda, Ilaria Costantini, Nagore Prieto-Taboada, Aitor Larrañaga, Cristina Marieta, Bruno De Nigris, Alberta Martellone, Valeria Amoretti, Gorka Arana, Juan Manuel Madariaga and Kepa Castro	***Searching for a new pozzolanic component for the formulation of compatible preservation mortars***	2280
17	Graciela Ponce-Antón, Maria Cruz Zuluaga, Giuseppe Cultrone, Luis Ángel Ortega, Ricardo Gómez-Val	***Multi-analytical characterization of 19-century bricks and plaster from the Church of Sant Rafael (Barcelona, Spain)***	2420
18	Giuseppe Capobianco, Daniela Isola, Luca Lanteri, Claudia Pelosi, Silvia Serranti, Oriana Trotta, Giuseppe Bonifazi	***Multi-technique approach to evaluate the effect and durability of biocides treatments on Peperino stone in the "Basilica San Francesco alla Rocca" (Viterbo, Italy)***	2940
19	Laure Cazals, Lauren Dalecky, Simo Huotari, Alessandro Mirone, Emmanuelle de Clermont-Gallerande, Christoph Sahle, Agnès Desolneux and Loïc Bertrand	***Spectral Denoising and Image Segmentation methods for the Processing of Inelastic X-ray Scattering and X-ray Raman Data***	3251

20	Patrícia Carvalho, Flávia Leite, Lara Carramate, Sofia Pessanha, Maria Luísa Carvalho, José Paulo Santos, João Veloso and Ana Luísa Silva	***Analysis of large area Portuguese Ceramic Samples using a Full-Field EDXRF Imaging System with MPGDs***	3470
21	Luis Alves and Victoria Corregidor	***Combing Ion Beam Analytical techniques for the characterization of cultural heritage materials***	3492
22	Valeria Godoy, Isabel Amaya-Torres, Francisca Márquez and Carmen Royo-Fraguas	***Conservation science to rescue the collective memory of the conflict. The case of General Baquedano's public monument at the 18-O Chilean Social Outburst***	3541
23	Mustafa Kansiz	***Non-contact Submicron O-PTIR and Simultaneous Raman microscopy with Fluorescence imaging - Review of Cultural Heritage Applications***	3671
24	Ioana Cortea, Alecsandru Chiroșca and Laurențiu Angheluță	***INFRA-ART Spectral Library: A New Open Access Infrastructure for Heritage Science***	3952
25	Jorge Sanjurjo Sánchez, Victor Barrientos and Juan Luis Montero Fenollós	***Characterisation of Iron Age pottery from the archaeological site of Tell el-Fara (Palestine)***	3979
26	Clarimma Sessa, Eva M. Angelin, Nadia Thalguter, Simon Mindermann, Randa Deraz, Rebecca Tehrani, Katja Lorenz, Hany Helal, Hector Bagán, Jose F. García, Markus Santner, Christoph Herm, Christoph Krekel, Marcello Picollo, Costanza Cucci, Christian Grosse, Marisa Pamplona, Heike Stege and Thomas Danzl	***insiTUMlab: the new analytical infrastructure for non-destructive in-situ studies of Cultural Heritage***	4011
27	Dâmia Carina Dias Do Carmo, Pérside Omena Ribeiro, Selma Otília Gonçalves da Rocha, Alessandra Rosado and Luiz Antônio Cruz Souza	***Well preserved rare red glazes in Brazilian Baroque Polychrome Sculptures: Characterization and Conservation***	4071
28	Ainhoa Ainhoa Alonso-Olazabal, Iosu Etxezarraga Ortuondo, Luis Angel Ortega, Maria Cruz Zuluaga and Ana Martínez Salcedo	***New insights of manufacturing tradition of roof tiles from Basque Country, north of Iberian Peninsula***	4083
29	Bilyana Kostova, Boyan Dumanov and Katerina Mihaylova	***Archaeological bricks and tiles from Southeast Bulgaria - determination of production technology by methods of archaeological chemistry***	4146
30	Marcus Vinicius Oliveira Andrade, Dâmia Carina Dias Do Carmo, Alessandra Rosado and Luiz Antônio Cruz Souza	***GOIA Project - An initiative between the Federal Police and Universities in Brazil against Crimes envolving Cultural Property and Works of Art***	4375
31	Raysa Nardes, Francis Sanches, Ramon Santos, Hamilton Gama Filho, Eliane Zanatta, Renato Freitas, Roberta Leitão, Catarine Leitão, Davi Oliveira, Ricardo Lopes, Joaquim Assis and Marcelino Anjos	***Pigment identification in a 19th century carriage by non-destructive analytical techniques***	4549
32	Vera Hubert, Charlotte van de Walle, Erwin Hildbrand, Tiziana Lombardo and Katharina Schmidt-Ott	***Evaluation of handheld XRF for the assessment of biocide contamination in cultural heritage objects***	4587
33	Suset Barroso-Solares, Elvira Rodríguez-Gutiérrez, Carlos Sanz-Minguez, Javier Pinto and Eusebio Solórzano	***X-ray microtomography: unveiling hidden information from historical and cultural heritage***	4600
34	Ewa Bulska	***Analytical scenario for the investigation of Machu Picchu cultural heritage in Peru***	4798
35	Federica Nardella, Alessio Giannaccini, Marco Mattonai, Jacopo La Nasa, Gloriana Pace, Andrea Camilli and Erika Ribechini	***Development and optimization of organic residue analysis methods in potsherds from "Cantiere delle Navi Antiche di Pisa"***	5018
36	Idoia Etxebarria, Marco Veneranda, Iñaki Vazque de la Fuente, Ilaria Costantini, Nagore Prieto-Taboada, Giuseppe Di Girolami, Angela Di Lillo, Marina Caso, Rossella Di Lauro, Mario Notomista, Gorka Arana, Juan Manuel Madariaga and Kepa Castro	***Selecting a tuff from the Italian active quarries for future restoration works at the Archaeological Park of Herculaneum***	5236
37	Dzemila Sero, Frans Pegt, Bodill Lamain, Bieke van der Mark, Isabelle Garachon, Erma Hermens and Kees Joost Batenburg	***Analyzing epidermal ridge impressions and tool marks on Rijksmuseum terracotta sculptures***	5405
38	Pattra Lertsarawut, Weerawat Pornroongruengchok, Sarinrat Wonglee, Sakchai Laksee, Thitirat Rattanawongwiboon, Kasinee Hemvichian	***Characterization and consolidation of wooden artifacts by radiation-assisted curing of HPMA for wood preservation***	5594

39	Silvia Pizzimenti, Tomas Markevicius, Alessia Andreotti, Anton Nikiforov, Nina Olsson, Agnieszka Suliga, Gianluca Pastorelli, Nan Yang, Geert Van der Snickt, Klaas Jan van den Berg, Dieuwertje Schrijvers, Jurate Markeviciene, Ilaria Bonaduce	***MOXY project: preliminary investigation of a non-contact cleaning of some typical art materials using atomic oxygen***	5672
40	Simon Brenner, Hans Clausen, Gerlinde Schneider, Ivana Dobcheva, Wilfried Vetter, Manfred Schreiner, Robert Sablatnig	***A Repository for Storage, Linking and Dissemination of Multidisciplinary Manuscript Research Data***	5684
41	Federica Nardella, Jacopo La Nasa, Ilaria Degano, Francesca Modugno, Ana-Maria Gruia, Ioana Cova, Andrea Beatrix Magó, Márta Guttmann, Erika Ribechini	***A multi-analytical approach to disclose the composition of 18th century ointments from the "History of Pharmacy Collection" in Cluj***	5803
42	Luminita Ghervase, Monica Dinu, Victoria Atanassova, Ioana Gomoiu	***Monitoring the outcome of new biocleaning methods with the help of spectroscopic techniques***	5835
43	Gael Latour, Giulia Galante, Maëlle Vilbert, Céline Bonnot-Diconne, Laurianne Robinet and Marie-Claire Schanne-Klein	***In situ non-invasive measurement of varnish thickness on historical artefacts by line-field confocal OCT***	5991
44	Mihaela-Doina Niculescu, Lucretia Miu, Emanuel Vacalie and Cristina Carsote	***Multi-analytical Evaluation of Glues Obtained from Various Types of Hides and Skins***	6130
45	Anastasios Asvestas, Emmanuel Kechaoglou, Dimosthenis Chatzipanteliadis, Theofanis Gerodimos, Georgios P. Mastrotheodoros, Konstantina Athanasia Agrafioti, Anastasia Tzima, Mareike Gerken, Roald Tagle, Aristidis Likas, Konstantinos Kosmidis and Dimitrios Anagnostopoulos	***MA-XRF AND LIBS INVESTIGATION OF GREEK RELIGIOUS ICONS***	6132
46	Maria Cruz Zuluaga, Céline Rémazeilles, Abdelali Oudriss, Egle Conforto, Haizea Portillo, Luis Angel Ortega, Ainhoa Alonso-Olazabal and Juan José Cepeda-Ocampo	***A metallurgical study to the understand the manufacturing process of iron nails from the archaeological site of Loiola (Vizcaya, Northern Spain)***	6245
47	Vaclav Krupicka, Julie Arslanoglu and Caroline Tokarski	***Top-Down MS: the next frontier in MS proteomic analysis of cultural heritage samples?***	6275
48	Weronika Machowicz-Musiał, Elżbieta Szmit-Naud, Wojciech Kujawski and Joanna Kujawa	***Attempts to use head space gaschromatography to determine solvent retention in easel painting paint layers subjected to conservation treatments***	6601
49	Sarinrat Wonglee, Weerawat Pornroongruengchok, Pattra Lertsarawut, Sutasinee Kotayee and Piyanud Thongjerm	***Preliminary study of irradiation effect on polymer-impregnated wood for cultural heritage preservation using neutron imaging***	6803
50	Alberto Viani, Dita Machová, Petra Mácová	***Quantitative approach to the conservation of bone collections by means of solid state NMR spectroscopy.***	7065
51	Victor Gonzalez, Marine Cotte, Frederik Vanmeert, Letizia Monico, Catherine Dejoie, Manfred Burghammer, Wout de Nolf, Loïc Huder, Ida Fazlic	***The Heritage "BAG" at the European Synchrotron Radiation Facility: a new collaborative access modality for the structural analysis of historical materials***	7198
52	Ana Cristina Hernández Santomé, Jorge Sanjurjo Sánchez, Carlos Alves	***Use of hand-held gamma-ray spectrometry to assess decay of granite buildings of a coastal area of NW Spain (Barbanza, Galicia)***	7214
53	Luminita Ghervase, Ioana Maria Cortea, Lucian Cristian Ratoiu	***New ways of assessing biodeteriogens in cultural heritage***	7968
54	Alessandro Re, Miriana Marabotto, Luisa Vigorelli, Andrea Alessio, Laura Guidorzi, Chiara Donazzolo, Alessandro Lo Giudice, Federico Picollo, Marco Truccato	***A multi-technique setup based on a liquid anode X-ray source for the non-invasive characterization of materials***	7998
56	Jolanda van Iperen, Isabelle Garachon, Margot van Schinkel, Annelies van Hoesel, Neha Verma, Femke Diercks and Katrien Keune	***The White Glaze of Delft Blue. Variations in composition in its glory period, from 1625 to 1800.***	8237
57	Sveva Longo, Federica Egizi, Valeria Stagno, Maria Giovanna Di Trani, Gianni Marchelletta, Tommaso Gili, Enza Fazio, Gabriele Favero and Silvia Capuani	***Magnetic Resonance Imaging clinical scanner for archaeological waterlogged wood investigations***	8304
58	Victoria Corregidor, Norberto Catarino, Carlos Cruz, João Cruz and Luís C. Alves	***Reflective Transformation Imaging technique with visible, infrared and ultraviolet light***	8675
59	Silvia Vettori, Emma Cantisani, Francesca Giannetti, Riccardo Avanzinelli, Eleonora Braschi, Marta Casalini, Antonio Langone, Carlo Virili, Alessandro M. Jaia and Alessandro Zanini	***Multi-methodological approach from non-invasive to micro-destructive techniques for the characterization of Final Bronze Age vitreous materials: Paduli site (Colli sul Velino, Rieti) in central Italy***	8688

60	David M. Freire-Lista, Ana J. López Díaz, Alberto Ramil, Said Jalali and Eunice Salavessa	***Construction Phases, Characterisation of Granite Ashlars and Frescoes Pigments of St. Leocadia Church (Chaves, Galicia-North of Portugal Euroregion)***	8704
61	Ákos Török and Szilárd Papp	***Characterization and provenance analysis of Gothic stone sculptures, the use of petrography in the reassembling of fragmented stone sculptures***	8866
62	Victory A. J. Jaques, Jan Petřík, Karel Slaviček, Katarína Holcová, Kateřina Vaňatková, Marta Kerkhoff, Tomáš Zikmund and Jozef Kaiser	***X-Ray Computed Tomography For Natural And Cultural Heritage Objects: A matter of size and contrast***	9124
63	Lucretia Miu, Emanuel Vacalie, Mihaela Niculescu, Roxana Constantinescu and Nicolae Catrina	***Study on Behaviour of Gilded Wood to Artificially Ageing***	9303
64	Maja Gajic Kvascev, Velibor Andrić and Aleksandar Bulatović	***The newest metal findings from the Early Eneolitic house in South-eastern Serbia***	9480
65	Hernán Fernández García, Koen Janssens and Piet Van Espen	***ATLAS, a versatile MA-XRF imaging spectrometer and its applications***	9680
66	Oğuz Emre Kayser, Merve Mina Çetintürk and Osman Eşki	***Use of Mobile All in One Multispectral Devices in the Analysis of Artworks***	9841
67	Yaowen Zhu, Yonghao Zhou, Zhenkai Chen, Wenjing Zhou and Yingjie Yu	***Digital Speckle interferometry coupled with photoacoustic for detecting defects under different depth***	3901
68	Zhenkai Chen, Wenjing Zhou, Hongbo Zhang, Liang Qu, Guanghua Li and Yingjie Yu	***Identification of Mural Damages with Laser Holographic Speckle Interferometry with Acoustic Excitation***	4249
69	Frederik Vanmeert, Alba Alvarez Martin, Julien Volper, Koen Janssens and Siska Genbrugge	***Multi-analytical characterization of Woyo masks***	9891
70	Tiziana Cavaleri, Chiara Ricci, Claudia Pelosi, Stefano Laureti, Rocco Zito, Federico Di Iorio, Alessandro Re, Federica Pozzi and Marco Ricci	***A new model for radiographic image processing in painting investigation***	3964
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2	Weronika Patrycja Polańska, Lavinia de Ferri, Calin Constantin Steindal and Knut Ivar Austvoll	***Preliminary investigation of the production technology of Norwegian Bronze Age ceramics***	129
3	Benedetta Vitale, Eliano Diana, Angelo Agostino, Marco Guglielminotti Trivel and Carolina Orsini	***Scientific investigations of Tang Dynasty pottery figurines***	605
4	Davi Oliveira, Francis Sanches, Ramon Santos, Alessandra Machado, Roberta Leitão, Olga Maria Araujo, Catarine Leitão, Marcelino Anjos, Joaquim Assis and Ricardo Lopes	***Characterization of a terracotta Indian sculpture through microCT and XRF techniques***	706
5	Giulia Franceschin, Roberta Zanini, Francesco Abate, Gianluca Iori, Elena Longo, Luisa Vigorelli, Lara Chiaberge, Luisa Guidorzi, Alessandro Re, Alessandro Lo Giudice and Arianna Traviglia	***Laboratory and synchrotron x-ray computed microtomography to investigate corroded Roman glass***	1186
6	Madoka Murakushi, Yoshinari Abe, Chisato Kato, Makiko Fukushima, Izumi Nakai	***Non-destructive and on-site X-ray fluorescence analysis of national treasure glass beads from Okinoshima Island, Japan***	2610
7	Josef Hormes, Lisa Langlois, Wantana Klysubun, Sveva Gai, Norbert Börste, Markus Kleine	***Ancient glass samples from the Cathedral in Paderborn: an investigation using synchrotron radiation based techniques***	2878
8	Mitra Almasian, Erma Hermens, Nathan Daly, Paul van Laar and Marcia Vilarigues	***An interdisciplinary approach to the making of enamels: multimodal imaging of historical processes and materials***	3304
9	Silvia Vettori, Davide Romoli, Teresa Salvatici, Valentina Rimondi, Elena Pecchioni, Sandro Moretti, Marco Benvenuti, Pilario Costagliola, Beatrice Agostini and Francesco Di Benedetto	***Non-Invasive SWIR Monitoring of White Marble Surface of the Cathedral of Santa Maria del Fiore (Florence, Italy)***	3493
10	Elena Platania, Silvia Garrappa and Christina Spaarschuh	***Characterization of secondary products in a late-medieval alabaster relief from the church of Lade (Norway)***	4732
11	Ana Saraiva, Mathilda Coutinho, Joaquina Soares, Carlos Tavares da Silva and João Pedro Veiga	***Preliminary results of archaeometric analysis of Chalcolithic ceramic from Charneca de Fratel (Vila Velha de Ródão, Portugal)***	6193
12	Bilyana Kostova, Boyan Dumanov, Zhivko Uzunov and Katerina Mihaylova	***Chemical, phase, and thermal characterization of Roman and Late Antique clay wall plasters***	6447

13	Valentina Lončarić, Pedro Barrulas, Ana Margarida Arruda, Esther Rodríguez González, Sebastián Celestino Pérez and Mafalda Costa	***Glass in the Southwestern Iberian Peninsula during the Iron Age - the case study of Casas del Turuñuelo (Guareña, Badajoz, Spain)***	6466
14	Amelia Suzuki, Emma Cantisani, Marilena Ricci and Silvia Vettori	***Combined use of Synchrotron based X-ray techniques and micro-Raman spectroscopy for Pb compounds mapping of red stains in heritage marbles***	3735
15	Yoshinari Abe, Madoka Murakushi, Hiroshi Shiino, Hiroki Nagai, Yoshihide Nakajima	***Introduction of a new silicon drift detector equipped with graphene window to a portable X-ray fluorescence spectrometer and application on nondestructive and onsite analysis of historical glass artifacts***	7206
16	Marta Magalini, Laura Guidorzi, Luisa Vigorelli, Riccardo Quaranta, Erika Fissore, Toshi Nozaka, Akira Seike, Joseph Ryan, Jun Mitsumoto, Naoko Matsumoto, Monica Gulmini, Alessandro Lo Giudice, Alessandro Re	***Micro-Computed Tomography applied to the study of Japanese pottery***	7332
17	Nikolaos Zacharias	***A Technological and Provenance Study of LBA Glass from Thessaly, Greece: The Profitis Elias Kompotades Cemetary***	7646
18	Massimo Beltrame, Ginevra Coradeschi, Ana Manhita, Sergio Martins, Cristina Barrocas Dias, Simona Rafanelli, JosÉ MirÃo	***What was stored inside the big ceramic containers of the Domus dei Dolia at Vetulonia (Italy)***	7816
19	Elena Platania, Calin Steindal, Tone Olstad	***Multi-analytical investigation of the glass-based pigment of the Kinn altarpiece (Norway)***	7939
20	Mareike Gerken, Christian Hirschle, Andrew Menzies, Falk Reinhardt, Kathrin Schneider, Roald Tagle	***Ceramics quantification: Exploring potentials of XRF for a fast and reliable workflow***	7973
21	Roberta Zanini, Valentina Risdonne, Francesco Abate, Lucia Noor Melita, Reino Liefkes, Lucia Burgio and Arianna Traviglia	***Portable XRF to assess glass alteration in museum settings: advantages and limitations***	1807
22	Mareike Gerken, Christian Hirschle, Andrew Menzies, Falk Reinhardt, Kathrin Schneider, Roald Tagle	***Quantification of Cultural Heritage objects: From glasses to metals***	2717
23	Malgorzata Walczak and Edyta Bernady	***Non-invasive study of baroque Silesian glasses from museum collections in Poland.***	9129
24	Catarina Reis Santos, Andreia Ruivo and Inês Coutinho	***The study of the Portuguese glass arcana with the tools of the future***	9298
25	Elena Badea, Cristina Carsote, Ilaria Quaratesi, Irina Petroviciu, Lucretia Miu, Noemi Proietti and Valeria di Tullio	***STUDY OF A COLLECTION OF CHANCELERY PARCHMENT DOCUMENTS OF 600-YEAR-OLD***	101
26	Mareike Gerken, Michele Gironda, Christian Hirschle, Andrew Menzies, Falk Reinhardt, Kathrin Schneider and Roald Tagle	***Colored journals: An insight to 19th century printing materials by means of micro-XRF***	244
27	Efstathia Tsioufi, Vasiliki Kokla, Anna-Arietta Revithi and Athanasios Karampotsos	***Studying color engravings of 19th century. Case study: engravings of the book "Histoire Naturelle des Perroquets" belongs to the Library of the Greek Parliament***	306
28	Alessia Coccato, Germana Barone, Paolo Mazzoleni and Jonathan Prag	***First insights on the rubrication of Sicilian inscriptions:***	350
29	Francesca Assunta Pisu, Tullia Carla David, Stefania Porcu, Pier Carlo Ricci, Carlo Maria Carbonaro, Jarmila Kodric and Daniele Chiriu	***Preliminary study on the effects of salinity on ancient paper by optical techniques***	381
30	Sophie Vullings, Marco Roling and Ana Martins	***Identifying, Organizing and Managing Scientific Research Assets at the Van Gogh Museum***	4013
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32	Elena Gonzalez, Consuelo Imaz, Ana Albar and Maria Antonia Garcia	***CHARACTERIZATION OF MATERIALS CONSTITUTING METAL ACID INKS BY GAS-MASS CHROMATOGRAPHY AND SCANNING ELECTRON MICROSCOPY***	5396
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3	Alessandra Botteon, Claudia Conti, Chiara Colombo, Maria Catrambone, Marco Realini, Sotiria Kogou, Chi Shing Cheung, Haida Liang and Antonio Sansonetti	***Non-invasive advanced investigation of Leonardo's mural painting in Sala delle Asse***	196
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5	Meropi Katsantoni and Theodore Ganetsos	***Study of the wall paintings with spectroscopic techniques for the determination of their decaying products on the hermitage Holy Cross on Olympus, Greece***	291
6	Cristina Carsote, Elena Badea, Dumitrita Daniela Filip and Nicoleta Cioatera	***Comparative study of two sets of icons from Museikon Museum (Romania) for identifying evidences of Russian Religious Art Transfer in Transylvania***	292

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31	Alice Dal Fovo, Jana Strova, Silvia Innocenti, Lucrezia Sepiacci and Raffaella Fontana	***Study of an early 20th century artist's forgery of a Botticelli portrait painted in tempera on tile***	4175
32	Flávia Lima, Alexandre Pais, Marta Manso	***Unveiling the colours of José António Jorge Pinto tilework***	1877
33	Giovanni Cavallo, Patrizia Moretti, Francesca Piqué, Ana Isabel Giraldo Ocampo, Maurizio Aceto, Luca Villa and Patrick Cassitti	***The non-invasive study of a group of Early Medieval wall paintings in the Raetia Curiensis region***	4177
34	Maria Pia Riccardi, Maya Musa, Alessandro Croce, Maddalena Patrini, Pietro Galinetto, Benedetta Albini, Serena Chiara Tarantino, Mario Lazzari and Sandro Baroni	***The relationship between science and art in Taramelli's watercolors***	4179
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38	Eva Luna Ravan, Francesco Paolo Romano, Claudia Caliri, Costanza Miliani, David Buti, Donata Magrini, Claudia Conti, Alessandra Botteon, Marco Realini, Elena Davanzo, Enrico Ferraris, Valentina Turina and Francesca Rosi	***Multimodal noninvasive approach revealing the ancient Egyptian palette***	4770
39	Domagoj Mudronja, Anja Mioković, Iva Božičević Mihalić and Stjepko Fazinić	***Investigation of paint layer cross sections using micro analysis and imaging techniques with focused MeV ions***	4779
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41	Elena Castagnotto, Federico Locardi, Tom Sandström, Paolo Oliveri and Maurizio Ferretti	***CdZnS paint films degradation: effect of pigment's properties and environmental conditions***	4885
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44	Daniel José Jiménez Desmond, José Santiago Pozo Antonio and Anna Arizzi	***Evaluation of the physical compatibility of nano-silica-based reintegrations on frescoes***	5244
45	Sara Mazzocato and Claudia Daffara	***From artistic archive to climate archive: can an artwork surface be a source of information on climatic changes?***	5377
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49	Milene Gil, Mafalda Costa, Sara Valadas, Inês Cardoso, Ana Cardoso, Ana Manhita, Alberto Barontini	***Mapping and identification of decay on the modern mural paintings sets by Almada Negreiros at the Maritime stations of Alcântara, Lisbon: type, origin, and consequences***	697
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51	Penka Girginova and Milene Gil	***Microscopic studies of red ochre fresco paint layers replicas treated with nanolime***	6400

52	Svetlana Pisareva and Irina Kadikova	***Two Palettes by Henri Matisse from the Collection of the Pushkin State Museum of Fine Arts***	6547
53	Giulia Procopio, Martina Massarelli, Fabio Aramini, Lucia Conti, Ludovica Ruggiero, Giancarlo Sidoti and Carla Giovannone	***Dry pastel: from the artistic technique on Gaulli's frescoes to material for the wall paintings reintegration***	6570
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55	Roberta Iannaccone, Sara Lenzi, Gabriella Gasperetti, Stefano Giuliani and Antonio Brunetti	***The characterization of roman wall painting fragments. An insight into pigments and materials in roman Sardinia (Italy)***	1848
56	Lamprini Malletzidou, Triantafillia Zorba, Dimitrios Karfaridis, Konstantinos Chrissafis, Georgios Vourlias and Konstantinos M. Paraskevopoulos	***Consumed by flames: Investigating the markers of wall-paintings effected by fire***	4422
57	King Wai Chiu, Dickson Tik San Sin and May Chui In Long	***Palette to palette - an integrated of spectroscopic study analysis and UMAP on Wu Guanzhong's paint palette and his painting***	5530
58	Francis Sanches, Raysa Nardes, Fernando Gonçalves, Ramon Santos, Hamilton Gama Filho, Roberta Leitão, Catarine Leitão, Davi Oliveira, Ricardo Lopes, Joaquim Assis and Marcelino Anjos	***Analysis of paintings using X-ray macro fluorescence and Compton scattering imaging***	6773
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63	Carolina Rodrigues Ferreira, F. A. Baptista Pereira, Mercês Lorena , Lília Estêves, Luís Piorro, Sara Valadas, Ana Cardoso, António Candeias	***Study of the wooden supports of Madeira Island Primitive Flemish paintings: knowing to preserve***	6905
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2	Andrea Marchetti, Natalia Ortega Saez, Victoria Beltran, Vincent Cattersel, Gert Nuyts, Henri Cosemans, Karolien De Wael, Geert Van der Snickt and Emile Van Binnebeke	***Shedding light on the 19th c. waterproofing technology of historical carriages, a multi-analytical approach***	5473
3	Sofia Serrano, Ana Filipa Machado, Rui J.C. Silva, Elin Figueiredo	***Proto-historic plain gold rings from western Iberia: a detailed study by multifocus OM, pXRF, micro-XRF and SEM-EDS***	5768
4	Victoria Corregidor, Luís C. Alves, Pedro Valério, João Cruz, Manuel C. Pereira and Samantha Coleman	***Material characterization of Queen Catarina of Braganza and King Charles II of England medallions***	6115
5	Florica Matau, Iva Matolínová, Mitica Pintilei, Ovidiu Chiscan and Alexandru Stancu	***A multi-analytical approach for the archaeometric identification of the Cucuteni pottery firing technology***	6889
6	Radek Ševčík, Jana Machotová, Lucie Zárybnická, Petra Mácová and Alberto Viani	***Aqueous polyacrylate latex nanodispersions used as consolidation agents to improve mechanical and water transport properties of treated Prague sandstone***	3419
7	Josef Hormes, Lisa Langlois, Wantana Klysubun and Alexey Maximenko	***X-ray absorption near edge structure (XANES) spectra: A thermometer for the firing temperature of ceramics?***	3827
8	Sarah Richiero, Vincent Detalle, Nicolas Wilkie-Chancellier	***Advantages and limitations of Laser Induced Breakdown Spectroscopy (LIBS) to detect light elements in different ferrous cultural heritage objects***	6919

9	Ilaria Costantini, Simon Alexander Schröder, Juan Manuel Madariaga, Gorka Arana	***Study of the influence of marine and industrial environment in the formation of salt efflorescence and metal runoff***	7092
10	Catarina Pinheiro, Mathilda Larsson, Carlo Bottaini, Marius Araujo, Bárbara Maia, Joana Madureira, Filipa Pereira	***Eusébio da Silva Ferreira, the "Black Panther": Analytical techniques applied to metal statues***	7386
11	Xueshi Bai, Sarah Richiero, Florian Téreygeol, Yvan Coquinot, Vincent Detalle	***Laser-induced breakdown spectroscopy (LIBS) in 3D lightweight element analysis on heterogenous materials of cultural heritage***	7836
12	Neva Maria Elisabetta Stucchi, Giulia Franceschin, Chiara Coletti, Andrea Vavasori, Claudio Mazzoli, Arianna Traviglia	***Minero-petrographic characterisation of roman mosaic tiles from Aquileia***	2341
13	Krystian Trela, Aneta Gójska, Ewelina Miśta-Jakubowska and Adam Kędzierski	***Elemental Analysis of Extraordinary Silver Coins Discovered on Polish Territories***	8150
14	Dominique Scalarone, Giulia Pellis, Barbara Salvadori, Antonio Sansonetti, Paola Letardi, Paola Rizzi and Barbara Giussani	***Looking for a substitute for Incralac: formulations, application approaches and stability over time of acrylic coatings for the protection of bronze artworks.***	218
15	Letizia Ciarlo, Elena Castagnotto, Alessandro Zucchiatti and Elias Sidera-Haddad	***Multivariate analysis of XRF data: a non-invasive method for gold foil thickness determination***	363
16	Nagmeldeeneen Hamza, Fatema Almarzooqi	***Limited technology and unlimited results: an integrated approach about study and conservation of daggers from Ras Al-Khaimah national museum***	1618
17	Valentina Ljubic Tobisch, Albina Selimovic, Wolfgang Kautek	***Metalworking influence on the corrosion behaviour of Ag and Ag-coated Cu***	2264
18	Valeria Comite, Cristina Della Pina, Paula Carmona-Quiroga, Laura Maestro-Guijarro, Mohamed Oujja, Ana Crespo, Andrea Bergomi, Chiara Andrea Lombardi, Mattia Borelli, Marta Castillejo, Paola Fermo	***Stratigraphy of metals in heritage pollution crusts by LIBS***	2698
19	Sofia Serrano, Ana Filipa Machado, Elin Figueiredo	***Gold and silver Iron Age lunulae from western Iberia: a study by multifocus OM, pXRF and digital imaging processing***	2812
20	Roberta Iannaccone, Sara Lenzi, Gabriella Gasperetti, Stefano Giuliani, Antonio Brunetti	***The case of tabella immunitatis discovered in Porto Torres (Italy): characterization of the metal composition***	2894
21	Jiakun Wang, Qian Zhang, Jing Yang, Hui Jiang, Min Hu, Hui Zhang	***Non-destructive Analysis of Corrosion Products of Bronzes by Terahertz Time-domain Spectroscopy and Imaging***	2909
22	Darina Trojkova and Tomas Trojek	***Uncertainty of quantitative X-ray fluorescence micro-analysis of metallic artefacts caused by their curved shapes***	3102
23	Giulia Privitera, Claudia Caliri, Francesco Paolo Romano, Costanza Miliani and Paola Letardi	***In-situ XRD measurements on outdoor bronze artwork as a tool to deepen the knowledge on patinas***	4430
24	João Cruz, Elin Figueiredo and Luís Alves	***Bullion coins circulating in Portugal in the 12th-13th centuries: an analytical approach***	1748
25	Giulia Pellis, Alessia Calabrese and Dominique Scalarone	***Double shot pyrolisis GC/MS characterization of modified Paraloid coatings for the protection of outdoor bronzes***	4744
26	Susana Gomes, Ana Arruda, Pedro Valério, António Soares, Carlos Pereira, Elisa Sousa and Fátima Araújo	***Minor and trace elements in Roman lead from Monte Molião archaeological site (Portugal)***	4871
27	Pedro Valério, Salomé Sequeira, Vanessa Dias, Gisela Encarnação and M. Fátima Araújo	***The composition of Roman metals from Moinho do Castelinho and Quinta da Bolacha (Amadora, Portugal)***	4964
28	*Imre Szalóki* and Anita Gerenyi	***Quantitative analysis of cultural heritage and safeguards objects by in-house developed confocal macro XRF spectrometer***	5274
29	Silvia Pérez-Diez, Luis Javier Fernández-Menéndez, Matthieu Boccas, Cheyenne Bernier, Christophe Pécheyran, Nerea Bordel, Christof Vockenhuber, Max Döbeli and Maite Maguregui	***Development of in situ LIBS and EDXRF methods validated by ion beam techniques to quantify halides in Pompeian pyroclasts and c***	3075

30	Paolo Antonino Maria Triolo	***Implementation of the diagnostic capabilities of the CMOS sensor in the NIR environment, using 1070nm interference filter and a conventional band-pass filters set***	5103
31	Patrícia Gatinho, Cátia Salvador, Silvia Macedo Arantes, M. Rosário Martins, Amélia M. Silva, Ana Z. Miller and A. Teresa Caldeira	***Prospection of bioactive compounds produced by bacterial isolates from pristine environments***	5368
32	Marta Porcaro, Antonio Brunetti, Anna Depalmas, Carlo Casi, Rosario Maria Anzalone and Caterina De Vito	***Use of X-ray fluorescence combined with Monte Carlo simulation for determination of bronze alloys***	799
33	N.K. Kladouri, S. Skaltsa, Th. Gerodimos, K. Pezouvani and A.G. Karydas	***Compositional μ-XRF analyses of copper-based coins from Rhodes, Greece, 4th c. BCE to 2nd c. CE***	9750
34	Isabel Amaya-Torres, Constanza Acuña, Valeria Godoy, Karla Leiva, Rosalía Astorga	***Climate data analysis for sustainable conservation of cultural heritage***	2004
35	Ada Sáez, Mónica Álvarez de Buergo, Natalia Pérez-Ema	***Portable non-destructive techniques applied to the study of the deterioration pattern of partially submerged heritage in reservoirs***	2576
36	Maria Kylafi	***The Pylos Geoarchaeological Program: Fusion of Images towards understanding Ancient Landscape***	8955
37	Maria Zdończyk, Barbara Łydżba-Kopczyńska, Joanna Cybińska	***Luminescent coatings for the anti-theft protection of cultural heritage glass and metal objects***	2026
38	Vanessa Antunes, Jorge Machado, Marluci Menezes, Carla Tomás, José Cruz, Gunnar Liestol, João Serra	***Collaborative Efforts in Preserving Cultural Heritage: The "Forte das Memórias" Project***	6365
39	Cátia Salvador, Silvia Macedo Arantes, M. Rosário Martins, António Candeias, Cesareo Saiz-Jimenez and A. Teresa Caldeira	***Microbial communities of underwater caves from Algarve coast: Biological activities prospection***	686
40	Jorge Sanjurjo Sánchez, Carlos Arce Chamorro, Adolfo Fernández Fernández, Alves Carlos, Jose Carlos Sánchez-Pardo and Rebeca Blanco-Rotea	***Geophysical survey using gamma ray spectrometry (GRS) on the archaeological site of Cidadela (Galicia, NW Spain)***	4901
41	Iñaki Vázquez de la Fuente, Inés Barbier, Sara Puente Muñoz, Nagore Prieto Taboada, Gorka Arana and Juan Manuel Madariaga	***Natural materials for cleaning metallic leachates (based on iron and copper) on marble surfaces as alternative of traditional gels***	5521
42	Tomas Trojek, Pavel Novotny, Martin Hlozek and Darina Trojkova	***X-ray fluorescence imaging with benchtop devices for scanning and full field techniques***	9984
43	Martina Romani, Erlantz Lizundia and Maite Maguregui	***μ-EDXRF imaging to evaluate desalination ability of cellulose foams and sponges applied on wall paintings***	8794
44	Nouchka De Keyser, Fréderique Broers, Annelies van Loon, Francesca Gabrieli, Frederik Vanmeert, Steven De Meyer, Arthur Gestels, Victor Gonzalez, Petria Noble, Koen Janssens and Katrien Keune	***Pararealgar and semi-amorphous arsenic sulfides discovered in Rembrandt's Night Watch***	3922
45	Joanna Zwinczak, Krzysztof Kruczała and Marek Bucki	***Retouches of the paint layer: Research into physical and chemical changes of the materials used in conservation studios in the National Museum in Kraków***	3956
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ABSTRACTS
PLENARY LECTURES

Non-invasive and imaging techniques for the study and conservation of cultural heritage - the HERCULES Lab experience

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The range of analytical instrumentation currently available for heritage research and conservation is broad and encompasses both in-situ non-invasive techniques and micro-analytical and high resolution laboratory techniques. Since each technique gives its own type of information and has its own suitability strengths and weaknesses, a previous assessment is essential to avoid a disorientated and useless examination. One of the problems is the use of a limited analytical methodology or tendency to focus on specific research details that result in incomplete information that can be problematic for carrying out conservation interventions or historical studies. Furthermore, in most cases, no single analytical technique can determine the full composition and/or structure of an object and provide valuable conclusions. In most cases a compliance of the results from several complementary techniques must be employed. Sampling is often carried out to allow the analysis of art/heritage objects but recent advances in imaging and non-invasive point and mapping techniques are changing this situation and allowing the development of comprehensive non-invasive studies and integrated conservation projects. In this talk we will explore new non-invasive and imaging techniques and their introduction and application in conservation and heritage science projects at HERCULES Laboratory

Integrated Multi-modal approaches for Imaging of Cultural Heritage Objects

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Today a wide range of instruments is available for the investigation of cultural heritage objects. Many of them are not limited to the investigation of individual spots on the surface of objects but allow for the acquisition of images that show the distribution of elements or chemical compounds.

The two most relevant methods are currently scanning X-Ray Fluorescence (XRF) imaging and Reflectance Imaging Spectroscopy (RIS) in the Visible and Near InfraRed (VNIR, 400-1000 nm) and Short Wave InfraRed (SWIR, 1000-2500 nm) ranges. These methods have their own capabilities and limitations. XRF allows for clear elemental distribution images containing information of sub-surface layers but has only limited depth information. RIS provides chemical information, but is less straight forward to interpret and is in the shorter wavelength regime only sensitive to surface layers.

It is obvious that a combination of XRF and RIS would provide much deeper insight into the chemical composition of objects and their stratigraphy. However, one challenge is the proper weighting of data sets during the analysis, resp. extracting features on which the focus should be. While for selected cases it could be shown that a joint factorization of fused XRF and RIS data is feasible, a general solution to this problem is missing [1].

In this contribution we will show how XRF can be enhanced by using it in combination with other methods to illustrate the possibilities and provide a perspective for future developments. We will show how a combination of a factorized VNIR RIS data set with a XRF data set of an illuminated manuscript can be used to separate the contributions of recto and verso side of the manuscript [2]. Further, it will be shown how the combination of the spatial information encoded in a photograph can be used to denoise an XRF data set acquired on the same object. This has the potential to accelerate data acquisition and thus enhance the resolution of XRF maps or the number of objects investigated [3]. Finally, the possibilities of fitting peaks of known features in the SWIR range can be used for mapping certain pigments in historical paintings and how this approach compares to XRF [4].

[1] Alfeld, M., Pedetti, S., Martinez, P., & Walter, P. (2018). Joint data treatment for Vis–NIR reflectance imaging spectroscopy and XRF imaging acquired in the Theban Necropolis in Egypt by data fusion and t-SNE. *Comptes Rendus Physique*, *19*(7), 625–635. DOI: 10.1016/j.crhy.2018.08.004

[2] Fiske, L. D., Katsaggelos, A. K., Aalders, M. C. G., Alfeld, M., Walton, M., & Cossairt, O. (2021). A Data Fusion Method For The Delayering Of X-Ray Fluorescence Images Of Painted Works Of Art. *2021 IEEE International Conference on Image Processing (ICIP)*, 3458–3462. DOI: 10.1109/ICIP42928.2021.9506300

[3] Chopp, H., McGeachy, A., Alfeld, M., Cossairt, O., Walton, M., & Katsaggelos, A. (2022). Denoising Fast X-Ray Fluorescence Raster Scans of Paintings. arXiv preprint arXiv:2206.01740

[4] L.M. de Almeida Nieto, F. Gabrieli, A. van Loon, V. Gonzalez, J. Dik, R. Van de Plas, M. Alfeld, Comparison of Macro X-ray Fluorescence and Reflectance Imaging Spectroscopy for the Semi-Quantitative Analysis of Pigments in Easel Paintings, *under revision.*

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From Europe to Asia: on the introduction of early synthetic dyes in traditional dyeing practices

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The invention of early synthetic dyes in 1856 marks a pivotal point in economic, societal and art history. The development and spread of these new commercial products were so fast that in a few decades the European textile-making industry was completely revolutionised, and these new colours were exported from Europe to every corner of the world. However, the driving forces that guided the import/export and the introduction of these materials into millenary traditional dyeing practices are complex and require cross-disciplinary expertise to explore them.

With a focus on 19th century Central Asian and Southeast Asian textiles from the British Museum and other museums' collections, the challenges related to the identification of early synthetic dyes in historic objects are discussed from an analytical point of view with particular attention to the difficulties of finding reliable reference materials, overcoming nomenclature challenges, and building molecular databases using high pressure liquid chromatography mass spectrometry. Synthetic dyes ultimately provide information to refine the dating and enhance our knowledge of museums' textile collections and represent a window on the changes in dyeing and textile-making practices that occurred in the 19th century.

Keywords: dye analysis; liquid chromatography; mass spectrometry; Asian textiles; synthetic dyes

"Strengthening the MOLAB platform of E-RIHS through advanced hyperspectral chemical imaging at the macro-scale"

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The identification of chemical compositions whilst fully respecting the object's integrity are all intrinsic and well consolidated aspects of the state-of-the-art Heritage Science. If the available single point analytical investigations can lead to powerful diagnostic results, the most comprehensive answer to the complex and challenging questions of heritage professionals requires acquisition of a knowledge which generally goes beyond the chemical composition of the localized area/point. To give comprehensive answers to heritage professionals questions, it is essential to integrate the chemical identification of materials with their macro-scale semi-quantitative spatial distribution associating molecular information to colors, hues, brushstrokes and more generally to what is visible to the naked eye. In other word, analytical chemistry must provide the image of the distribution of the chemical composition, information that can be more easily interpreted and more profitably discussed/ evaluated by experts of the CH field.

Driven by this, in the last years Heritage Science efforts have been directed through the development and application of analytical hyperspectral imaging/scanning techniques experiencing a wide diffusion as new powerful tools. In the same way, the European Research Infrastructure for Heritage Science (E-RIHS-http://www.e-rihs.eu/) considered key the strengthening of the analytical hyperspectral imaging/scanning facilities of the mobile laboratory hy-MOLAB through the development and application of advanced technologies able to inform about the chemical composition and distribution at the macro-scale.

More traditional and consolidated imaging techniques as well as new imaging possibilities offered by E-RIHS probing different chemical properties, probing unexplored spectral ranges, and based on multimodal/integrated systems will be presented. Developments and tests on laboratory mock-ups as well as in situ case studies will be discussed. Hints on data processing and chemical images reconstruction will be also done.

Investigating the synthesis, use and alteration of historical pigments at the multi-scale

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Omnipresent in paintings since the Antiquity, inorganic pigments are key materials of art history. Collecting accurate chemical information on them is essential to achieve a better understanding of ancient pictorial practices, as well as to develop new conservation strategies. However, this objective faces several scientific challenges. First, pigments were obtained in the past following complex chemical syntheses, whose parameters are not always known to us [1]. Secondly, painters were combining these materials in variable formulations, and applied these formulations with their own unique artistic techniques, resulting in a strong heterogeneity of the hybrid [pigment(s) + binder] paint systems [2]. Finally, paintings are dynamic objects: chemical interactions within paint layers can result in the *in situ* formation of non-original organo-metallic and/or inorganic compounds [3]. The presence of these neo-formed materials can threaten the optical and/or physical integrity of artworks.

This communication will present recent research aimed at deciphering the past synthesis, formulation by artists, and potential alteration mechanisms of historical pigments. A special focus will be put on the advantages of multi-scale chemical analysis to tackle the chemical complexity of the composite paint systems. At the micro-scale, the analytical power of synchrotron radiation, notably using structural analysis via X-ray Powder Diffraction (XRPD), enables to discriminate between the multiple inorganic compounds present in paint layers, but also to provide detailed information on their composition and microstructure. At the macro-scale, the development of chemical imaging prototypes, based on X-ray or photoluminescence, enables the charting of crystalline species on the entire surface of historical paintings. The communication will illustrate the complementarity of structural and molecular data collected at the multi-scale on carefully design model samples, historical paint fragments and entire artworks. The case of lead and cobalt-based pigments and their associated alteration products will be specifically discussed.

[1] A. Gambardella, M. Cotte, W. De Nolf, K. Schnetz, R. Erdmann, R. Van Elsas, V. Gonzalez, A. Wallert, P. Iedema, M. Eveno, K. Keune, Science Advances 6(18), 2020, aay8782
[2] L. de Viguerie, M. Jaber, H. Pasco, J. Lalevée, F. Morlet-Savary, G. Ducouret, G. Rigaud, T. Pouget, C. Sanchez, P. Walter, Angewandte Chemie International Edition 56(6), 2017, 1819.
[3] F. Vanmeert, N. de Keyser, A. van Loon, L. Klaasen, P. Noble, K. Janssens, Analytical Chemistry (2019) 91(11): 7153

Non-invasive infrared spectra of varnishes on artworks

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Non-invasive identification of natural resins used in traditional varnishes of artworks has been made a routine task by applying reflection infrared spectroscopy [1–3]. Varnish formulations, developed by mixing various resins, and occasionally, heated siccative oils, induce molecular changes depending on composition, heating conditions, and often on the underlying layers that hamper the certainty of identification. Additionally, various physical phenomena, such as irregularly reflected infrared beams on uneven surfaces, add to the complexity of reflection spectra. An extra difficulty may be added to the understanding of spectra due to derivative-shaped bands caused by Fresnel reflection, which generally can be dealt with the Kramers-Kronig transformation [4,5]. Also, in surface films containing pigment or other particles, peak inversion due to the *reststrahlen* effect may also occur [6,7]. In all, applying reflection techniques, widely available through technological advancement, demands a reevaluation of infrared spectra [8–10].

Latest results from the research in our lab will be presented, where the strengths and limitations of external reflection infrared spectroscopy applied on varnished surfaces will be discussed. Comparisons with spectra from standard sampling techniques, such as powder samples and solvent-extracted organics by using cotton tabs directly from the varnish layers shed light on the chemical and physical complexity of coated surfaces and its influence on the final spectra.

[1] J. Kattner, H. Hoffmann, External Reflection Spectroscopy of Thin Films on Dielectric Substrates, in: J.M. Chalmers, P.R. Griffiths (Eds.), Handb. Vib. Spectrosc. Vol. 2, John Wiley and Sons, Hoboken, NJ, 2002: pp. 1003–1015.

[2] T. Ford, A. Rizzo, E. Hendriks, T. Frøysaker, F. Caruso, A non-invasive screening study of varnishes applied to three paintings by Edvard Munch using portable diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Herit. Sci. 7 (2019) 1–13.

[3] S.C. Boyatzis, Materials in Art and Archaeology through Their Infrared Spectra, Nova Science Publishers, New York, 2022.

[4] S. Boyatzis, A.M. Douvas, V. Argyropoulos, A. Siatou, M. Vlachopoulou, Characterization of a water-dispersible metal protective coating with Fourier Transform Infrared Spectroscopy, modulated differential scanning calorimetry, and ellipsometry, Appl. Spectrosc. 66 (2012) 580–59.

[5] P.R. Griffiths, J.A. de Haseth, Fourier Transform Infrared Spectrometry, Second Edition, 2nd ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 2007.

[6] J.E. Bertie, Optical Constants, in: P.R. Griffiths (Ed.), Handb. Vib. Spectrosc., John Wiley & Sons, Ltd, Chichester, UK, 200.

[7] V.G. Gregoriou, S.E. Rodman, Vibrational Spectroscopy of Thin Organic Films, in: P.R. Griffiths (Ed.), Handb. Vib. Spectrosc., John Wiley & Sons, Ltd, Chichester, UK, 2006.

[8] C. Invernizzi, T. Rovetta, M. Licchelli, M. Malagodi, Mid and near-infrared reflection spectral database of natural organic materials in the cultural heritage field, Int. J. Anal. Chem. 2018 (2018).

[9] A.B.D. Nandiyanto, R. Oktiani, R. Ragadhita, How to read and interpret ftir spectroscope of organic material, Indones. J. Sci. Technol. 4 (2019) 97–11.

[10] T. Poli, E. Alice, O. Chiantore, Surface Finishes and Materials: Fiber-Optic Reflectance Spectroscopy (FORS) Problems in Cultural Heritage Diagnostics, E-Preserv. Sci. 6 (2009) 174–179.

Through a metal darkly: How analytical techniques brighten the conservation of metallic heritage objects

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Analytical techniques are used in conservation studies of cultural heritage metallic objects to deepen our knowledge of corrosion processes, highlight marks of use, assess treatments, and define conservation strategies.

In a model of continuous iteration, as new conservation challenges arise, new analytical strategies are developed, and as new technological developments emerge, it is possible to detail the conservation questions that still remain. To illustrate this iteration two research subjects are presented: the conservation of gold objects and that of industrial machinery.

The atmospheric corrosion of gold has long been a subject of research. However, specific conservation strategies for gold objects are scant and mainly based on those defined for silver alloys. The analytical techniques used for gold alloy objects studies focus on corrosion products' identification. Based on objects of distinct chronologies (*e.g.* Egyptian goldwork, Bronze Age goldwork, Art Noveau jewellery) from different museum collections, and by using an analytical protocol including SEM-EDS, XRD, UV-Vis spectroscopy and ellipsometry, it was for the first time demonstrated that at the surface of tarnished gold alloys a corrosion film develops as a layer-by-layer structure in a two-step corrosion mechanism with a thickness estimated in the order of 100 nm [1]. The enlightenment on the corrosion mechanism of gold alloys raises a new conservation challenge concerning the removal of nanometric layers.

Unlike the conservation of gold objects, that of industrial machinery with functioning mechanisms is a recent topic with many open questions. One of the main issues is how to assess the dynamic systems behaviour of these objects. This question is fundamental to determine appropriate conservation plans and decide if an object can be preserved in operational condition. Currently, this assessment is made empirically based on the experience of those responsible for machinery maintenance. Analytical techniques can contribute to this issue, but their application is yet to be explored. A first approach to the definition of an analytical protocol using magnetoscopy, thermography and vibrational analysis enabled to evaluate the potentiality of these techniques to characterise the movement (*i.e.* operating speed), the wear and monitoring in real-time and in the long-term the movement and its alterations [2].

The two cases demonstrate how, in one long-studied and another emerging theme, analytical techniques are a powerful tool for metallic heritage conservation and how they can answer open questions and be the basis for new conservation challenges.

[1] I. Tissot, J. Correira, O.C. Monteiro, M.A. Barreiros, M.F. Guerra. J. Anal. At. Spectrom., 34, 2019, 1216.
[2] I. Tissot, B. Ottone Alves, F. Nogueira, T. Silva, In full swing: material characterisation and condition monitoring of a 20th-century steam engine, 2023, submitted.

Non invasive analysis of historical and archaeological metal artefacts through neutron imaging and neutron diffraction: highlights and case studio

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In recent years, neutron imaging and neutron diffraction affirmed as reliable and powerful methods of investigation for non-invasive characterization of metal artefacts. Several important questions related to manufacturing technology of historical and archaeological metal artefacts were solved thanks to these techniques.
Neutron imaging and diffraction provide morphological, phase composition and microstructural details which allow to infer important details about production technology as manufacturing strategy, alloy composition, application of thermal and mechanical treatments, and, in general, optimization of the technological process.
In this presentation, a brief overview of the method with advantages and drawbacks will be shown, together with specific examples of steel and copper alloy artefacts analysis and achieved results.

ABSTRACTS
ORAL COMMUNICATIONS AND POSTER SESSIONS

Revealing layers of the past in Old Goa Vice-Roy Portraits Gallery (India): a new approach by macro-XRF scanner

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The recent development of macro-XRF Scanning systems has enabled a scientific breakthrough in the study of artistic and cultural heritage. These systems are increasingly faster and more efficient and allow for totally non-invasive elemental distribution analysis over large areas.

In January 2023, a CRONO XRF system (BRUKER AXS) travelled between Portugal and Goa (India) under a collaborative research project funded by the Fundação para a Ciência e Tecnologia, the Old Goa Revelations project (2022.10305.PTDC), for a field mission comprising several non-invasive analytical instrumentation at the Old Goa Museum of the Archaeological Survey of India. The approach combines imaging techniques (standard, racking light and UV fluorescence photography, infrared reflectography and X-Ray radiography) with chemical analysis by handled EDXRF, macro-EDXRF and Raman spectrometry to study the Vice-Roys portrait Gallery. This collection comprises portraits from the 16th century until mid 20th century making it one of the most important and time lasting portrait collections in the world. These paintings have been subjected to several repaints over the centuries covering the original paint layers with more modern repaints and often leading to misinterpretation of these artworks unique values and raising further questions in art history and conservation.

The analytical approach proposed aims to investigate on the materiality of these paintings and the discrimination between original compositions and later interventions. In this communication we intend to show the power of combining 2D chemical elemental mapping with the historical layered build-up of these paintings to reveal the underneath layers and discover hidden decoration armors, coat of arms, golden decorations and even the different identity of the portrayed, as exemplified in the figure.

STUDY OF A COLLECTION OF CHANCELERY PARCHMENT DOCUMENTS OF 600-YEAR-OLD

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A collection of parchment documents (33 documents, 13 of which have single or multiple pendant seals) issued by the Royal Chancellery of Stephen the Great, Prince of Moldavia (1457-1504), currently owned by the Romanian Academy Library, was studied using portable instruments and micro-analytical methods. Parchment support, inks, dyes, wax seals and their silk cords were analysed using appropriate techniques, from optical microscopy to scanning electron microscopy, from elemental (XRF) to structural techniques (ATR-FTIR, NMR MOUSE), including identification techniques (HPLC-DAD-MS) [1-2].
The results obtained provided significant information about the manufacturing of materials and their deterioration, offering a wealth of information for better understanding and interpreting their provenance (including commercial routes and local production). Besides, the deterioration patterns of parchment revealed by the NMR MOUSE technique combined with ATR-FTIR and thermal microscopy shed new light into the ability of collagen to retain structural water and moisture, which is essential for its integrity [3-4], enabling us to group the documents depending on the mechanism of collagen deterioration. The overall conservation condition of documents was interpreted to define their preventive conservation: accessibility (consultation, digitization, and exhibition), microclimate and air quality (knowing that the NO_x level was above the limits allowed for library materials). The innovative part of this study stands on investigating whether it is possible to obtain new information from the parchment documents using non-destructive methods.

[1] E. Badea, C. Carsote, The secrets of the parchment containing Marco Polo's will. In "*Ego Marcus Paulo volo et ordino. I segreti del Testamento di Marco Polo*", Ed. T. Plebani, Scrinium, Venice, Italy. 2017, p. 246-271.
[2] I. Petroviciu, F. Albu, I. Cretu, M. Virgolici, A. Medvedovici, J. Cult. Her., 28, 2017, 164-171.
[3] F. Cappa, I Paganoni, C Carsote, M. Schreiner, E. Badea, Polym. Degrad. Stab., 182, 2020, 109375.
[4] C. Sendrea, E. Badea, A. Adams, Rev. Chim., 68(8), 2017, 1780-1785.

Preliminary investigation of the production technology of Norwegian Bronze Age ceramics

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Archaeological ceramics are among the most studied artifact categories since they can refer to both social and economic traditions of past communities. Investigations usually point at determining the production technology and special attention has been given to the firing conditions. This poster presents the intricate knowledge system of pottery production occurring in Norway in the Bronze Age (1300–900 BCE). To this aim, aliquots of clays sampled in Norway, Germany and Poland were fired in an electric furnace at 500, 550, 600, 700, 800 and 900°C and successively analyzed by colorimetry, XRD and FTIR-ATR to determine modifications in term of structure and mineralogical composition. Temperatures were chosen based on pre-existing knowledge of ceramic technology in the geographical region of interest in that period [1].

Results were compared with those obtained on a set of ten ceramic fragments dated to the Bronze Age at the site of Hunn in Eastern Norway. The aim was to estimate the temperature used in the production of these prehistoric ceramics exhibiting typological similarities with contemporary finds from Southern and Central Sweden as well as Northern Poland [2].

Due to the abundance of the thermally stable grain minerals such as quartz and feldspar, the study of the clayish fraction through XRD resulted particularly hostile, while FTIR-ATR confirmed its usefulness in investigating ceramics and ceramic-related materials. A progressive modification of the color of the fired material, turning towards a reddish hue, was due to the gradual formation of iron oxide (Fe_2O_3), starting from 700 °C. In parallel, carbonates decompose and weak features due to CaO appeared. In addition, small amounts of chlorite, a phase decomposing at 600–650 °C, were found through the petrographic analysis of some archaeological sherds highlighted, . However, its structural similarity with other clay minerals and the abundence of silicate phases, made the identification of chlorite by XRD and FTIR not possible in the fired clays.

Despite this, the experiment helped to strengthen the hypothesis about the technological correspondence of similar ceramics in Eastern Norway and Western Pomerania in the Bronze Age, as the results seem to indicate that the Bronze Age ceramics were fired at a temperature not higher than 700 °C, more probably ranging between 600 and 650 °C.

[1] H.M. Hop Wendelbo, Keramikk fra norske bronsealdergraver: En studie av morfologi, kronologi, forbindelser og deponeringspraksiser i tidsrommet 1700-500 f. Kr., 2020

[2] T. Eriksson, Kärl och social gestik: keramik i Mälardalen 1500 BC-400 AD, Uppsala universitet/ Riksantikvarieämbetet, 2000

Jean-Auguste-Dominique Ingres' pictorial praxis by a mutli-analytical approach

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Jean-Auguste-Dominique Ingres (1780-1867) was a French painter and draftsman who was a leading figure in the Neoclassical movement. He is recognized for his highly detailed portraits and for Renaissance inspired historical and mythological scenes. He studied at the École des Beaux-Arts in Paris, and was a student of Jacques-Louis David, the leading French painter of the time. Although Ingres's early work was strongly influenced by David, he developed his own style. Ingres's work was highly regarded during his lifetime, and he received numerous commissions from the French government. Despite his success, Ingres was a controversial figure within the art world, and his work was often criticized for its conservatism and lack of innovation. Nevertheless, he remains one of the most important figures in the history of French art.

We will present here the results of our research on three of his paintings, namely *Bonaparte, First Consul* (1804, Liège Museums), *Augustus Listening to the Reading of the Aeneid* (1814, Royal Museums of Fine Arts of Belgium, Brussels) and *Selfportait* (1864, Royal Museum of Fine Arts of Antwerp). Data and images have entirely been acquired on museum sites thanks to the portable instrumentation of the CEA. The set of analytical and imaging methods includes hyperspectral imaging (HSI), X-ray fluorescence spectroscopy in mapping mode (MA-XRF), Fourier-Transform Infra-Red spectroscopy (FTIR), Raman spectroscopy (RS), high-resolution photography (UV, Vis, raking), digital microscopy, infrared reflectography (IRR) and X-ray radiography (XRR). We will show the evolution of his technique and the used pigments.

Investigation of the discoloration of polyurethane elastomeric plastics in computer heritage: have we met an analytical challenge?

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* Both authors intend to attend the conference and present the contribution together

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Laptops iBook G3 Clamshell produced by the technology company Apple Inc. between 1999 and 2000 are part of numerous private and museum collections as they represent milestones in computer science, information technology and iconic design objects. Moreover, many technical features and design ideas first adopted in the iBooks G3 are nowadays standard in laptop computers as the multiple color options for the shell [1]. Two iBook models, "Graphite" and "Indigo" from the Deutsches Museum show a dramatic color change of the soft-colored plastic on the laptops' upper side (Figure 1), most likely due to light exposure, as verified by colorimetry [2]. As their color appearance is an integral part of the aesthetic, historical and material authenticity of these heritage laptops, the investigation of their discoloration is relevant. This work investigated the chemical composition and the molecular decay of the soft-colored plastic by considering the triad "polymer-colorants-additives" within a multi-analytical approach [3]. The aim was to understand the susceptibility of each component towards photodegradation and their individual contribution to the plastic discoloration. ATR-FTIR and Raman in situ analysis identified both plastics as ether-based PUR elastomer and the same polymer composition (methylene diphenyl diisocyanate, poly(tetrahydrofuran) soft segments and 1,4-butanediol chain extender) was corroborated by Py-GC/MS analysis. TD-GC/MS was the most suitable method for characterizing additives, which include several phthalate esters as plasticizers, and Tinuvin 328 as UV-absorber. The lack of elements associable to inorganic pigments by XRF suggested the presence of organic or organometallic colorants, which can be hypothetically attributed to indanthrone derivatives [4]. Moreover, ATR-FTIR suggested the formation of photo-oxidation functions on the upper sides, corroborated by EGA-MS showing a shift to higher decomposition temperatures of both isocyanate and polyol of the PUR, when compared to the undersides (Figure 1). The knowledge gathered in this study lays the basis for a future research proposal aiming to systematically research the PUR elastomer's color stability.

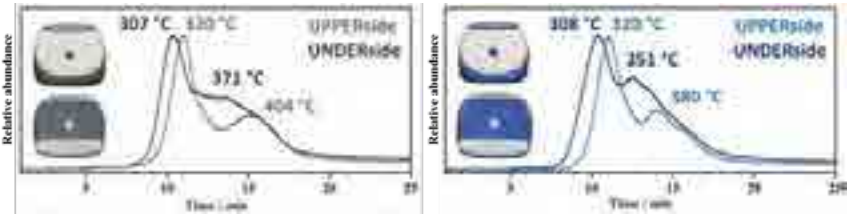

Fig. 1 – EGA-thermograms of the "Graphite" (left) and "Indigo" (right).

[1] L. Kahney L. Jony Ive - The Genius Behind the Apple´s Greatest Products, NY: Penguin; 2013.
[2] E.M. Angelin, M. Pamplona. In: Siniscalco A, editor. Colour and Colorimetry Multidisciplinary Contributions. Milano: Gruppo del Colore - Associazione Italiana Colore Vol XVII A; 2022. p. 137-142.
[3] A. Micheluz, E.M. Angelin, J. Almeida Lopes, M.J. Melo, M. Pamplona. Polymers 13, 2021, 2278.
[4] Webber TG, editor. Coloring of plastics. New York: John Wiley & Sons Inc.; 1979.

An Egyptian mummy of the Roman period with a painted shroud: a multi-analytical study of its technical features

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This contribution focuses on the technical study of a rare Egyptian mummy with a painted shroud belonging to the Museo Civico Archeologico of Bologna (MCABo EG 1974). Long stored in its warehouses, this artifact was recently rediscovered thanks to an interdisciplinary project promoted by the museum and the Institute for Mummy Studies of Eurac Research. The painted shroud was notably preserved in its original location around the mummy, to which is secured with textile straps and resin. Dating to the Roman period (1st–2nd century A.D.), confirmed by ^{14}C analysis, it displays a series of technical features that are quite complex and unique. In this context, scientific analysis aimed to deepen our current understanding of the artistic practices of the Roman period through an in-depth study of the painting technique, context of production, and possible provenance of the Egyptian mummy and its shroud, while promoting an improved, science-informed preservation of the mummified human remains.

This research has relied on an integrated analytical protocol based on imaging techniques, non-invasive spot analysis and mapping, and micro-invasive investigation of samples, carried out at different partnering institutions. Computed tomography highlighted, among other things, varying radio-densities for some of the flesh tones and red decorations. Visible diffuse and raking light photography, infrared reflectography and false color processing, ultraviolet-induced visible fluorescence, and visible-induced infrared luminescence provided preliminary information on the nature and distribution of various materials on the surface. FORS, XRF, and Raman contributed to the characterization of the color palette employed for the painted shroud, offering insight into the use of mineral pigments and dyes derived from plants or insects. A combination of transmission FTIR and chromatographic techniques was used to identify the paint binders' molecular class and any additional organic substances involved in embalming practices and ritual traditions. Through access to MOLAB equipment and expertise, XRF imaging, 1D confocal XRF, as well as XRD spot analysis and mapping integrated the study by providing a conclusive identification of the inorganic pigments. Finally, mineralogical data on surface deposits and soil residues found on the mummy allowed the team to put forward hypotheses on its provenance, previously unknown.

Non-invasive advanced investigation of Leonardo's mural painting in Sala delle Asse

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Sala delle Asse is a renowned hall in the Falconiera Tower in Castello Sforzesco commissioned by Ludovico il Moro, who entrusted its decoration to Leonardo da Vinci. The walls and the ceiling of the room were decorated at the end of the 15th century with mural paintings representing interlaced trees. The decoration was whitewashed and forgot for centuries but, during the 19th and 20th centuries, the painting was rediscovered and restored twice, uncovering the remnants of original layers. Starting from 2013, new conservation works were planned by *Ministry of Culture,* aiming at restoring a correct legibility of the decorations.

To develop the conservation best practice, an in-depth study of the materials applied on the room surfaces is in progress. Recently, an advanced non-invasive approach was used, combining micro-XRF mapping, Raman spectroscopy and remote hyperspectral imaging systems (400-2500nm), which allowed investigating also the inaccessible parts of the panting such as the ceiling (Figure 1a). The selected areas under analysis included both cleaned and uncleaned portions in order to identify the pigments used for the original painting and the subsequent restorations. Moreover, pigments distribution was visualized *via* chemical images, permitting a preliminary reconstruction of layers superimposition (Figure 1b and 1c). The results obtained on this prestigious case study enrich the knowledge about Leonardo's technique used on Milanese wall paintings.

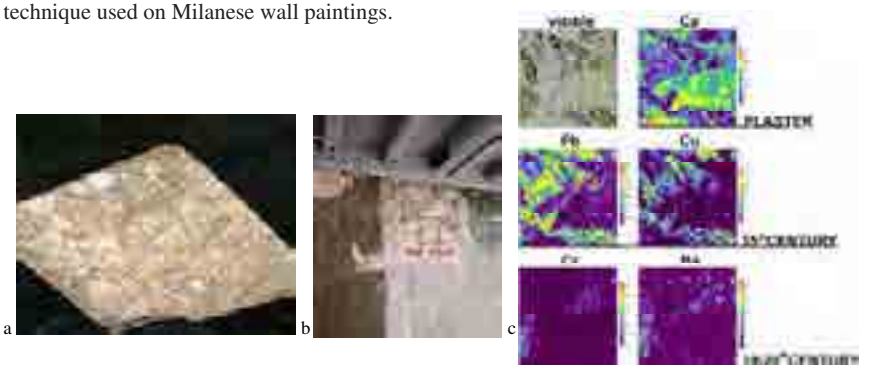

Figure 1. Area of the ceiling analysed remotely by hyperspectral imaging (a). Mural painting detail (b), and micro-XRF elemental distribution (min and max counts for each element) with interpretation of the layers sequence on a tree and sky of the mural painting (c).

Looking for a substitute for Incralac: formulations, application approaches and stability over time of acrylic coatings for the protection of bronze artworks

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Conservation of metal artistic objects must deal with many challenges, especially for those placed outdoors, as they must face exposure to weathering and reactive compounds present in the atmosphere that can interact with the surfaces of the artworks. In the case of bronzes, even a slight difference in their composition, influences the type of corrosion products. Moreover, bronze is one of the few metal alloys we are used to perceive covered by corrosion products. Over time they become part of the history of the object and, in some cases, conserve important information about the original shape, decoration or manufacturing techniques. So, there is the need to choose the right conservation method in order not to alter the aesthetic of these precious objects. The most widely used common practice for the protection of metals is the application of a coating on the surface [1]. In general, coatings for conservation are applied aiming at avoiding the contact of the metal-patina layer with the actively corroding agents present in the environment. Moreover, an ideal protective coating should prevent the object from degradation without modifying its appearance. Eventually, the properties of these treatments should assure a total compatibility with the surfaces involved, a good protective performance, reversibility, long-term durability and a low-cost maintenance.
The most frequently applied coating for bronze protection is Incralac®, an acrylic resin containing the inhibitor benzotriazole (BTA) that have the role to slow down the corrosion processes, but also exhibits some drawbacks related to lack of stability, poor stay on the surface and suspected toxicity. Due to these limitations, the search for alternative products to Incralac is of great interest [2]. In particular, we have focussed our research on Paraloid® B44 coatings combined with low-toxicity corrosion inhibitors and light stabilisers. The goal was studying the effect of different combinations of these additives on the photostability, solubility, glass transition temperature and transparency of the coating. Furthermore, the persistency of the inhibitor in the all-in-one coating was compared with the protective treatment consisting in the application of the inhibitor first, followed by the acrylic coating.

[1] P. Letardi, Coatings 2021, 11, 131.
[2] B. Salvadori, A. Cagnini, M. Galeotti, S. Porcinai, S. Goidanich, A. Vicenzo, C. Celi, P. Frediani, L. Rosi, M. Frediani, G. Giuntoli, L. Brambilla, R. Beltrami, S. Trasatti, J. Appl. Polym. Sci. 2018, 135, 46011.

Blockx oil paintings: archives and historical materials

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Founded in 1865, Blockx has established itself over time as a high-end artist paint brand that can cite among its customers big names such as Salvador Dalí or Edvard Munch. Installed near Liège, it has preserved an exceptional collection of archives made up of several tens of thousands of pages carefully accumulated during its 160 years of existence. No large-scale study had been undertaken until then to analyze this promising fund.

A project was recently initiated in order to collect, digitize and analyze the Blockx archive collection. The first stage of the study consisted of an inventory of the various documents and materials stored in the factory in order to establish a draft inventory. A wide variety of documents is available, ranging from color charts sometimes dating from the beginnings of the brand to copies of letters listing all the orders placed at a given time and to the recipe notebooks.

A complete digitization of the archive collection has been undertaken. It will allow constant and lasting access to all the documentation contained in the collection, thus avoiding excessive handling of papers sometimes in poor condition.

The range of products offered by Blockx over time, ranging from raw pigments to paints, including dissolved amber whose recipe only Blockx seems to know, will be presented.

Analysis of the historical Blockx color charts has been performed by MA-XRF, Raman and FT-IR spectrometries. Results will be compared with a color chart made with Blockx products in 1909 by the Belgian artist Emile Claus.

Colored journals: An insight to 19th century printing materials by means of micro-XRF

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Just like today, the newspaper in the 19th century was a medium for rapid news exchange drawing the reader's attention not only by catchy headlines but also by colorful images. Although considered a short-lived medium, colored publications played an important role in the printing press. However, back then, the visual depiction of an event was a more complex task. *Le Petit Journal* was a daily Parisian newspaper founded in 1863 by journalist, entrepreneur and banker Moïse Polydore Millaud and published until 1944. In 1895, it was the world's largest newspaper with a circulation of two million copies [1]. Early colored prints were created by inter alia French engraver and writer Fortuné Méaulle (1844-1916) [2] or caricaturist and illustrator Henri Meyer (1841-1899). An overview study was now applied on 22 colored prints of 12 issues of the journal dated 1895,1899, 1909, 1919 and 1920, aiming to gain knowledge on technology and preservative state. The analytical approach was based on micro-X-ray fluorescence scanning (µ-XRF) with a M6 JETSTREAM, focusing on a general identification of the pigments used for printing. Results clearly show a reduced palette based on red, yellow, blue, and black, sophisticatedly applied to cut costs. The price of the pigments as well as their integration into the printing process played a major role in the choice of materials, thus giving an insight into 19th century French pigment market and printing techniques. Pigments detected are comparable to those used in other countries such as USA [3]. Moreover, the outcomes of this study link to recent studies on printing techniques in the first half of the 19th century [4], giving new insights into the subsequent development of the technique. With this, the examination of a variety of journal editions originating from late 19th century to 1920 allows not only to study the economization of the general production process of a journal with decreasing readership since the beginning 20th century but also to retrace the change of inorganic pigments in printed mass media in a period when the pigment market quickly adopted the use of synthetic-organic pigments. Additionally, XRF techniques are well known to be capable of determining the amount of material deposited on a given surface. The study gives an easy approach to calculate the amount of vermilion used for color prints, thus enabling to display the economization process over the period studied. Potentials and limits of this approach for further non-invasive determination of inorganic components in printing media will be highlighted.

[1] Ivan Chupin, Nicolas Hubé and Nicolas Kaciaf, Histoire politique et économique des médias en France, La Découverte, 2009.
[2] Rémi Blachon, La gravure sur bois au XIXe siècle: l'âge du bois debout, Éditions de l'Amateur, 2001.
[3] Silvia A. Centeno, Virginia Llado Buisan and Polonca Ropret, Raman study of synthetic organic pigments and dyes in early lithographic inks (1890–1920). Journal of Raman Spectroscopy 37, 2006 1111-1118.
[4] Elizabeth Savage, Linda Stiber Morenus, Pre-Industrial Western Printing Inks, c. 1450-1850. In Abigail Bainbridge (ed.), Conservation of Books, Routledge, 2023, p. 331-344.

Essential Oils/Cyclodextrin Inclusion Complexes as eco-friendly antimicrobials for Cultural Heritage: an approach with essential oils of *Mentha pulegium* and *Mentha spicata* and *Calamintha nepeta* from Alentejo (Portugal)

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Cultural Heritage (CH) is an invaluable and irreplaceable asset for humanity and its conservation is a challenge. Deterioration for CH, including microbial biodeterioration, represents significant financial losses for this sector [1], causing serious aesthetic and structural damage to building materials and other artefacts [2]. Many of the commercial pesticides used to prevent or mitigate biodeterioration are potentially hazardous, to people and to the environment, and studies have reported their ineffectiveness over the long term and either the development of antimicrobial resistances to this biocides [3]. Essential oils (EOs) are an eco-friendly alternative to the chemically synthesized products, due to their antibacterial properties and low toxicity [4]. Additionally, the effectiveness of EOs as antimicrobial agents in heritage artworks hasn't been fully explored, and due to their volatility, they may not be effective when applied directly [5]. Therefore, it is crucial to develop new formulations concerned with their applications in several cultural heritage conditions, as well as to reduce the component degradation and volatilization of EOs.

For this study, it was selected essential oils from three flavoring plants of Alentejo (Portugal), *C. nepeta*, *M. pulegium* and *M. spicata* in order to evaluate the antimicrobial potential of free EOs and their EO/β-cyclodextrin (β-CD) inclusion complexes against to biodeteriogenic microbial strains, previously isolated from cultural artworks.

EOs were obtained by hydrodistillation and charcterized by GC-FID/GC-MS. EOs/β-CD inclusion complexes were prepared by co-precipitation method [6], with the EOs/β-CD different ratios to evaluate the impact of the ratio on the inclusion efficiency of β-CD for EOs encapsulation. Antimicrobial activity was assessed both by solid wells-diffusion and the

minimum inhibitory concentration methods and evaluated against filamentous fungi (*A. niger*, *F. oxysporum* and *Penicillium* sp.), yeast strains (*Exophiala* sp. and *Rhodotorula* sp.) and a bacterial strain (*Bacillus* sp.), previously isolated from heritage assets.

Selected EOs are rich in oxygenated monoterpenes (>70 %) and *C. nepeta* EO exhibited the isomenthone/pulegone/menthol chemotype, *M. pulegium* EO the pulegone/menthol chemotype, and the *M. spicata* EO the carvone chemotype. Free EOs show a wide range of antimicrobial potential with high antimicrobial activity against the studied biodeteriogenic microorganisms. EOs/β-CD inclusion complexes of three EOs show very high antimicrobial activity against *Bacillus* sp. and EOs/β-CD inclusion complexes of *M. pulegium* EO show high antimicrobial activity against *Rhodotorula* sp..

Results highlight the antimicrobial potential of these EOs and due to low toxicity, they may be used as environmentally friendly alternative to commercial antimicrobials, to reduce CH biodeterioration without negative environmental or human further consequences. Moreover, the inclusion EO/β-CD nanoparticles can be an alternative to the free EOs, when their application is not possible, reducing the volatility of the EO and minimizing interactions between free EO and the matrix of historical assets.

Keywords: Cultural Heritage; Biodeteriogenic microorganisms; Essential Oils; Cyclodextrin inclusion complexes

References:

[1] F. Cappitelli, C. Catto, F. Villa. Microorganisms, 8(10), 2020.
[2] M.A. Kakakhel, F.S. Wu, J.D. Gu, H.Y. Feng, K. Shan, W.F. Wang. International Biodeterioration & Biodegradation, 143(2019, 104721.
[3] K. Sterflinger. Fungal Biology Reviews, 24(1-2), 2010, 47-55.
[4] M.A. Ashraf, S. Ullah, I. Ahmad, A.K. Qureshi, K.S. Balkhair, M. Abdur Rehman. J Sci Food Agric, 94(3), 2014, 388-403.
[5] F. Palla, M. Bruno, F. Mercurio, A. Tantillo, V. Rotolo. Molecules, 25(3), 2020.
[6] R.L. Abarca, F.J. Rodriguez, A. Guarda, M.J. Galotto, J.E. Bruna. Food Chem, 196(2016), 2016, 968-975.

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A Comparative study of "green" and synthetic gels as tools for the cleaning of artifacts

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Prior to conservation interventions, cleaning of any undesired matter (aged coatings, degraded materials, deposits of pollutants, graffiti, dust and dirt) from the surfaces of artifacts is essential and needs a delicate approach. The challenge is to remove foreign matter without affecting the original properties of artifacts. Different kinds of gels have been used as suitable tools (transporting medium of solvents or emulsions) for cleaning purpose over the last decades. Among the gel materials used in this field, both physical (e.g. xanthan gum, gellan gum, agar, and chitosan) and chemical gels (e.g. acrylamide and bisacrylamide hydrogels), the ones made with synthetic polymers have shown better performance than the others [1-2]. However, there is a strong necessity to elaborate new cleaning systems for water sensitive artifacts with eco-friendly gel materials. For this purpose, a new bio-degradable gel material was prepared by combining the natural polymer (konjac glucomannan) with two different synthetic polymers (Polyvinyl alcohol, PVA, and Polyvinylpyrrolidone, PVP). The performances of the investigated gel were compared with the traditional materials, i.e konjac glucomannan (reacted with borax) and hydrogel obtained from HEMA-MBA (2-hydroxyethyl methacrylate/N,N-methylenebisacrylamide) copolymer and PVP.

All the considered gel materials were characterized using different techniques in order to comparatively assess their properties that are relevant for cleaning purpose: gel content, equilibrium water content, retention capability, morphology, tensile strength, hardness, and durability. Gels were loaded with appropriate amounts of nano-structured emulsions containing different concentrations of cleaning agent (eco-friendly surfactant and/or organic solvents) and their performances tested after application on the surface of laboratory biocalcarenite (e.g. Lecce stone) specimens. In particular, a comparative study of the nanoemulsion-loaded gels was carried out in order to evaluate their ability to remove old acrylic polymer coatings (e.g. Paraloid B-72), graffiti, soil, and organic pollutant from the stone surface. Different analytical techniques were used to investigate the performances: chromatic variations and contact angle measurements, optical microscopy, iodine vapour staining test, SEM-EDS, FTIR and micro-FTIR (in ATR mode).

The newly synthesized gel material showed better performances than the considered traditional gels in cleaning approach of soiled stone surface. Moreover, it is mainly based on a natural polymer and is more affordable compared to completely synthetic hydrogel's. Therefore, it can be considered as a promising tool for cleaning procedures applied to artifacts.

[1] J. A. L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Langmuir 29, 2013, 2746-2755.
[2] C. Lee, F. Volpi, G. Fiocco, M. L. Weththimuni, M. Licchelli, M. Malagodi, Materials 15(3), 2022, 1100.

Predicting the yellowing of PVC objects in heritage collections

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Poly(vinyl chloride) is a modern material, widely used in our daily lives – from domestic items, furniture, costumes, medical devices, and construction to the production of artworks [1]. Many of these have become heritage items. As a result, museums have increasingly large collections of objects from PVC in various degradation states with no specific guidelines for preventive care [2]. Chemical degradation of PVC proceeds as dehydrochlorination, which is an autocatalytic reaction that leads to formation of polyene sequences. This results in yellowing of the material. The guaranteed lifetime of an object, from an industrial point of view, can range from a few years to a few decades, but PVC objects can become part of heritage collections long after that. Unfortunately, predictions of PVC degradation during long-term storage have not been assessed yet [3].

The purpose of this work was to model the rate of degradation of PVC at room conditions by exposing a set of sacrificial samples to accelerated degradation at moderate conditions (50 °C and 70 °C at 30% and 80% relative humidity) and including 25-35 years old naturally aged samples (18 °C, 50% RH), to enable lifetime prediction of heritage collections. Degradation was monitored as yellowing measured with a reflection spectrophotometer, while the samples were characterized with gas chromatography and size-exclusion chromatography. The effect of material and environmental variables on the yellowing was assessed using multiple linear regression (Figure 1). The '1-°C-equivalent' concept was introduced to enable variable prioritisation from a heritage management aspect.

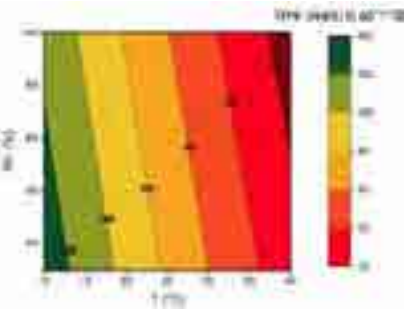

***Figure 1**: The predicted lifetimes of PVC objects demonstrating the effect of temperature and relative humidity. The isochrone plot was created for an object with an average plasticizer content (14%) and an average MW 120000 g/mol.*

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[1] S. Patrick, (2005), Practical Guide to Polyvinyl Chloride; 1st ed.; Rapra Technology: Shawbury.
[2] T. Rijavec, M. Strlič, I. Kralj Cigić, (2020), Plastics in Heritage Collections: Poly(vinyl chloride) Degradation and Characterization. *Acta Chim. Slov.*, 67, 993–1013.
[3] A. Royaux, I. Fabre-Francke, N. Balcar, G. Barabant, C. Bollard, B. Lavédrine, S. Cantin, (2017), Aging of plasticized polyvinyl chloride in heritage collections: The impact of conditioning and cleaning treatments. *Polym. Degrad. Stab.* , 137, 109–121.

Study of the wall paintings with spectroscopic techniques for the determination of their decaying products on the hermitage Holy Cross on Olympus, Greece

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Pythion with an altitude of 650m is located in the western foothills of Olympus. The ancient city of Pythion is located in the same place, with the city Dolichi and Azoro forming the Perrheabian Tripoli. It extended to the area north of Elassona and was bordered to the north by the mountains Olympus, Titarus and Kamvounia. It flowed by the river Titaresius and communicated with Macedonia through the straits of Petra and Sarantaporos. The city in the Byzantine era was moved to a new fortified place on the hill "Kastri". On the top of the hill is preserved a fortification of the citadel and building remains are preserved, indicative of the continuous habitation of Pythion during the Byzantine Period. The hermits found refuge on the hill "Kastri" in the 14th century. The well-preserved hermitage of the Holy Cross is located on the southern slope of the hill.

The hermitage of the Holy Cross extends into a small cave and it consists of three rooms: the chapel in the cave, the narthex and the hermit's cell on the platform. The last two rooms were covered by a wooden roof. The hermitage maintains remarkable wall paintings. Hierarchs and saints are depicted at the bottom of the temple and scenes from the life of Christ in the upper part of the temple. According to the founding inscription located at the entrance of the sanctuary, the foundation and hagiography date back to 1339 [1].

This project presents the results from the measurements of portable spectroscopic techniques Raman and XRF on wall paintings in the Hermitage Holy Cross in Pythion, Olympus. The research work focused on the deterioration products that exist on the surface of the wall paintings and are caused by environmental factors such as humidity and the remains of insects [2].

[1] Gialouri A., Plastara Aik., Mitsatsikas M., The Church of the Panaghia at Pythion in the Municipality of Elassona, 7th Ephorate of Byzantine Antiquities, 2014, 7-8
[2] Pitarch A, Ruiz J.F, De Vallejuelo S.F, Hernanz A., Maguregui M., Madariaga J.M., In Situ Characterization by Raman and X-ray fluorescence Spectroscopy of post- Palaeolithic blackish pictographs exposed to the open air in Los Chaparros shelter (Albalate del Arzobispo, Teruel, Spain), The Royal Society of Chemistry, 2014, 6, 6641-6650

Comparative study of two sets of icons from Museikon Museum (Romania) for identifying evidences of Russian Religious Art Transfer in Transylvania

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This study aims at studying 12 icons owned by Museikon Icon Museum (Alba Iulia, Romania) attributed to various schools of Russian icon painters, and comparing them with a set of 13 Transylvanian icons from the same period and museum with the purpose of identifying evidences of Russian religious art transfer in Transylvania in the XVIIIth and XIXth centuries. The study was performed within the ERC project RICOTRANS, *Visual Culture, Piety and Propaganda: Transfer and Reception of Russian Religious Art in the Balkans and the Eastern Mediterranean (16th – early 20th century).* The challenges that arose during the project were impossible to overcome without an in-depth study of the material aspects of the icons, from the panel preparation to the pigments, binders and varnishes, and painting technique, including specific mechanical and chemical deterioration pathways [1-2].

Multi-technique *in situ* and *ex situ* analysis intended to identify and study the materials used for icon manufacturing, assess their deterioration, evaluate the overall conservation condition of icons and support the restoration decisions were performed in 2021 and 2022. *In situ* analysis approach included optical microscopy, elemental X-Ray Fluorescence spectroscopy, Raman microscopy, while a number of micro-samples were analysed in laboratory through FTIR spectroscopy, in both ATR (Attenuated Total Reflection) and transmition mode, Raman spectroscopy, X-ray diffraction analysis (XRD) and SEM-EDX.

With a few exceptions, all the characteristics of the icons attributed to the Russian school, from the way of preparing the wooden panel and the ground, to that of obtaining the varnish and up to the preference for certain pigments, all these elements have converted to a common characteristic, namely Russian icon mass production. On July 28, 1785, the Aulic Chancellery of the Habsburg Empire recommended a ban on trade with Russian icons in Transylvania [3]. Even though, our study demonstrates that 18th and 19th century Russian mass production icons continue to be identified in the Transylvanian museum collections and as a result of field research.

Keywords: *icons, XRF, XRD, FTIR, Raman, SEM-EDX*

[1] D. D. Filip, C. Carsote, E. Badea, E. Hadimbu, I. M.Caniola, S. M. Paunescu, Museikon - A Journal of Religious Art and Culture/Revue d'art et de culture religieuse 5, 2021, 347-352.
[2] D. D. Filip, E. Badea, C. Carsote, I. M. Caniola, E. Hadîmbu, S. M. Paunescu, Acta Musei Apulensis - Apulum, 59 (2), 2022, 331-349.
[3] A. Dumitran, V. Dane, V. Rus, V. Wollmann, Annales Universitatis Apulensis Series Historica 25 (I), 2021, 145-187.

"*Ce n'est pas la colle qui fait le collage*": the analytical challenge of Ernst's multi-material artworks

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Despite the significance of the collage technique in 20th-century art history, scientific investigations on this type of artworks are very scarce. The term "collage" comes from the French word *coller*, or "to glue", and it indicates a picture composed of cut-up scraps pasted together: the multi-materiality of these objects represents a real challenge for analytical studies.

In the frame of a project aimed at disclosing the techniques and the materials used by the German painter Max Ernst in his *ouvres* belonging to the Peggy Guggenheim Collection in Venice [1,2], three collages were investigated by non-invasive in situ analysis (Vis-NIR multi-spectral imaging, X-ray fluorescence, external reflection FTIR and Raman spectroscopy): **Little Machine Constructed by Minimax Dadamax in Person** (*Von minimax dadamax selbst konstruirtes maschinchen,* 1919-20), **Sea, Sun, Earthquake** (*La Mer, le soleil le tremblement de terre*, 1931) and **The Postman Cheval** (*Le Facteur Cheval*, 1932).

Ernst loved to experiment with different techniques (frottage, grattage, oscillation, dripping and decalcomania) always reinventing them; so, he developed also his own collage technique which the Surrealist considered a way to express the unconscious and to free the mind [3]. This complex mix of pictorial methods and materials gave rise to unusual works, as also testified by Ernst's statement "*Si sont le plumes qui font le plumage, ce n'est pas la colle qui fait le collage*" [4]. Regardless their complexity, the present paper discusses how collage artworks could be analysed with non-invasive techniques. The results not only provided new insights in Ernst's high skilled work but demonstrated that, despite the limits of non-invasive methods, even multi-material artworks can be analysed and studied.

[1] Zuena, M. *et al.* An Integrated Diagnostic Approach to Max Ernst' s Painting Materials in His Attirement of the Bride. *J. Cult. Herit.* (2019)
[2] *Zuena, M. et al* Portrait of an Artist at Work: Exploring Max Ernst's Surrealist Techniques, *Herit Sci* **10**, 139 (2022). https://doi.org/10.1186/s40494-022-00777-4
[3] Bischoff, U. *Max Ernst, 1891-1976: Beyond Painting*, Taschen, 1994
[4] *Max Ernst : retrospective* ,W. Spies and J. Drost Eds. ; Albertina & Fondation Beyeler, Vienna 2013

The assessment of state of conservation of bone material in the UNESCO World Heritage site of Sedlec, Czechia.

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The Sedlec Ossuary, a UNESCO site located in Kutná Hora (Czechia), is one of the most famous examples of skeletal collections in the world, with more than 380 000 visitors per year. Bones from people died during the plague epidemics in the 14th century and the Hussite wars of the 15th century, starting from the 16th century were positioned in forms of skeletal decorations (Fig. 1). Their arrangement and the microclimatic conditions are posing a threat to the integrity of the osteological material.

Human remains are a common heritage whose conservation is considered an ethical imperative; therefore, to gain knowledge on their state of conservation is essential for the preservation of their integrity for further studies. To this aim, in this work ^{1}H, ^{31}P and ^{13}C magic-angle-spinning nuclear magnetic resonance spectroscopy has been adopted in support of more traditional analytical techniques, such as histological analysis, Fourier transform infrared spectroscopy and X-ray diffraction quantitative phase analysis.

The quantitative description of the component of the ^{31}P signal attributed to the external amorphous hydrated layer of the apatite platelets in the bone mineral compartment (Fig. 1) was found a sensitive index of the bone integrity. Differences in proton and phosphorus resonances were related to deterioration effects, allowing for the identification of local conditions posing a threat to bone preservation [1].

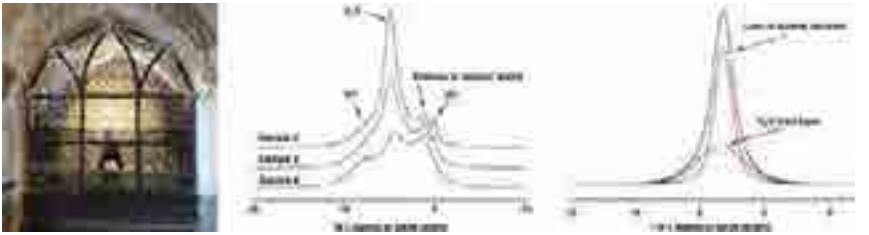

Figure 1. Detail of the ossuary (right), components in ^{1}H (center) and ^{31}P NMR spectra (right)

[1] A. Viani, P. Mácová, D. Machová, T. Čendak, Archaeometry 61 (5), 2019, 1144.

Studying color engravings of 19th century. Case study: engravings of the book "Histoire Naturelle des Perroquets" belongs to the Library of the Greek Parliament

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Introduction

Bird engravings were popular from the 18th century and throughout the 19th century. Initially, they were made only with black ink, while in the following years colored inks were also used. Each engraving was created as a single work of art. Several times, a number of engravings with a similar illustration were collected, thus creating a book.

The aim of this paper is to study the fabrication of the engravings found in the book "Histoire Naturelle des Perroquets" belonging to the Library of the Greek Parliament, applying historical research and analysis techniques such as multispectral imaging and SEM/EDS. analysis.

Experimental

The historical researches were based on the historical bibliography of the time when the engravings were made. Multispectral imaging was implemented, macroscopically and microscopically, in different bands between 380 nm and 1000 nm using a FujiFilm XT-10 full-frame camera and dino-lite microscopes.

Element analysis was performed using the JEOL JSM-6510LV scanning electron microscope (SEM) coupled to energy dispersive X-ray spectrometer of the Oxford X-act system.

Results

Various historical information was collected on the illustration of the respective books, on the engravers who created such engravings, on the engraving techniques used, and on the publishers, who issued such books [1, 2].

The engraving techniques applied can be recognized using multispectral techniques as well as the features of the colored inks used. The chemical elements of the materials used (color inks and paper) can be determined using SEM/EDS analysis [3].

Figure 1. Engraving PL 18 in visible, infrared and ultraviolet band (from left to right).

Conclusion

The applied methodology yielded significant results in terms of the features and chemical elements that make up the materials of the engravings, as well as their preservation conditions (Figure 1).

The chemical composition of at least ten different colored inks and the additives used to make the paper can be recognized.

References

1. Levaillant, F., *Histoire naturelle des perroquets, par Francois Levaillant*. Tome premier, a Paris, chez Levrault, freres, libraires, quai Malaquai. Strasbourg, de l'imprimerie de Levrault, 1801 & 1805.
2. Orna, M.V.; Fontani, M. The Modernity of Ancient Pigments: A Historical Approach. *Colorants*, **1**, 2022, 307–346. https://doi.org/10.3390/ colorants1030019
3. Townsend H. J., Carlyle L., Khanderkar N., Woodcock S., Later nineteenth century pigments: Evidence for additions and substitutions, *The Conservator*, 1995, 65-78.

In-situ non-invasive characterization of Sephardic Torahs from Ponta Delgada, Azores

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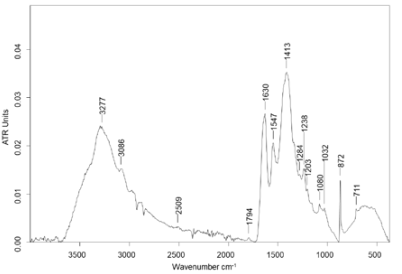
Writing a Torah scroll (*Sefer Torah*) is a religious act, involving strict criteria regarding size, lettering style, layout, and materials to be used in its production: parchments must be made from the skin of a *kosher* animal and inks shall be produced according to specific rules.
This work presents the first Portuguese comparative study of a set of five Torahs scrolls from Ponta Delgada-Azores (four Torahs scrolls belonging to the Museological Nucleus of the Old Synagogue of Ponta Delgada, and one, belonging to the Municipal Library of the same city), based on the material characterization of parchments, and writing inks used for its production. For this, in-situ non-invasive techniques: technical photography, digital microscopy, elemental (h-EDXRF) and molecular (ER-FTIR and UV-Vis-NIR FORS) spectroscopies were used, to provide answers regarding the composition of the materials used to produce these five Torah scrolls, as well as to give insights regarding the geographical origin of the scrolls as well as date them, as it is thought to know that these scrolls were brought to the Azores in the 19th century by Sephardic Jews from North Africa, although this information is not confirmed.
Results show that the parchment treatment was not the same for all Torah and different inks were used.
This study was carried out under the Portuguese Platform for European Research Infrastructure in Heritage Sciences (E-RIHS.PT).

Detail of one of the studied Torahs.



ER-FTIR spectrum reveals the presence of calcium carbonate in the parchment.

Molecular characterization of the Mesoamerican traditional dye extracted from the *Justicia spicigera* plant

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Due to their complex composition and their instability over time, the identification of organic natural dyes in historical artefacts is a challenging task. Chromatographic methods hyphenated to UV-Vis absorption, fluorescence detection or mass spectrometry are particularly adapted for the characterisation of complex natural products; however, these techniques face limitations in their application in the cultural heritage field due to the sampling possibilities. The identification relies thus mainly on the use of non-invasive spectroscopic techniques giving global spectral fingerprint of the studied coloured material. This approach requires a preliminary in-depth knowledge of the chemical composition of the dyes to link the recorded spectral features to compounds from the natural extracts.

This work focused on the characterisation of a natural dye used in the *Codex Borbonicus*, a 16th century Aztec manuscript. The dye extracted from *Justicia spicigera* leaves, a tinctorial plant from Central America, was tentatively identified in the paint layers of the manuscript by comparison of the recorded Raman and UV-Vis fluorescence emission signals with published data. However, this dye is poorly characterised and the lack of knowledge about its chemical composition make it impossible to ensure that the compounds responsible for the spectral features are specific to this plant species. Besides, to the author's knowledge, this is the unique identification of the use of this traditional textile dyestuff in a Mesoamerican codex and no historical sources describe its preparation to produce paint layers.

The main objective of the project is to broaden the knowledge regarding the natural dye from the *Justicia spicigera* leaves through the structural elucidation of the compounds responsible for its colour and the characterisation of paint layers mock-ups, some of them being artificially aged. In particular, this will allow to confirm its identification in the *Codex Borbonicus*.

First, a preparative liquid chromatographic method was developed for the purification of the main coloured compounds from the *Justicia spicigera* extract. Then, a multi techniques approach involving high-resolution mass spectrometry, nuclear magnetic resonance, vibrational (infrared absorption and Raman) and electronic (ultraviolet-visible absorption and fluorescence) spectroscopies was carried out to propose a molecular structure of the purified compounds. In addition, model paint layers were produced from *Justicica spicigera* leaves and were artificially aged under light exposition to evaluate whether the protocol for the preparation or the degradation state of the dye could prevent its identification.

The molecular and spectral characterisations gathered in this work provide a solid base of knowledge for the identification of the *Justicia spicigera* dye in other Mesoamerican artefacts.

First insights on the rubrication of Sicilian inscriptions:

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Although the polychromy of ancient statuary has become a regular topic in archaeological discussions also thanks to archaeometrical analyses [1, 2], it appears that little attention has been given to such aspects in the field of epigraphy [3, 4]. The interdisciplinary ERC-funded "Crossreads" project dedicates a whole work-package to the study of the materiality of ancient inscriptions of Sicily (VIII c. bC – VIII c. AD). Here we focus on stone inscriptions with visible traces of pigments.

In parallel to the characterization of the stone supports by means of a multi-scale approach (*in situ* digital imaging and portable X-rays fluorescence analyses (pXRF), sampling for minero-petrographic and geochemical investigations) attention is given to the traces of rubrication. As the name suggests, this is the practice of applying red paint to the letters, to improve readability of the text [5]. As is well known, inorganic red pigments based on haematite (α-Fe_2O_3), minium (Pb_3O_4), and cinnabar (HgS) have been used since antiquity, all of which have been identified on inscriptions [6-9]. Synthetic analogues have also been reported for all three, with vermillion having been likely used as well in modern restoration practices [7].

The results presented here confirm that all three pigments were used on inscriptions, as shown by pXRF spectra acquired directly inside museum premises. In addition, microsamples are subjected to micro-Raman spectroscopy to clarify the actual mineralogical composition of pigments. For the first time, systematic analytical data are available on Sicilian inscriptions, which enable us to avoid the use of generic terms, such as rubrication, and to assess the exact nature of pigments, overcoming long-standing misinterpretations of the ancient literature (e.g. *minium* [10]). More interestingly, the identification of pigments of such different price ranges, alone or in mixtures, implies conscious choice of materials in private and public contexts. In general, the precise identification of the materials employed, including the provenance of the support (both at a regional level and across the Mediterranean, as in the case of crystalline marbles) and the pigments will support a deeper understanding of the exploitation of natural resources, power and wealth, trade routes, manufacturing processes, and the symbolic use of materials, both in the public and private sphere.

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[1] J.S. Ostergaard, Proceedings of the Danish Institute at Athens 8, 2017, 149.
[2] M.B. Abbe, T. Şare Ağtürk, Technè 48, 2019, 100.
[3] R. Rebuffat, Revue archéologique de Picardie, 10(1), 1995, 23.
[4] J.R.W: Prag, Zeitschrift für Papyrologie und Epigraphik, 2017, 119.
[5] Pliny the Elder, Naturalis Historia, 40.
[6] J. Powers, N. Dimitrova, et al, Zeitschrift für Papyrologie und Epigraphik, 2005, 221.
[7] C. Richards, Teaching History, 51(1), 2017, 7.
[8] N. Rovella, A. Arcudi, et al, The European Physical Journal Plus, 133(12), 2018, 539.
[9] F. Caridi, B. Testagrossa et al, SCIRE-IT Scientific Research and Information Technology, 10(2), 2020, 81.
[10] H. G. Edwards, D. W. Farwell et al, Analyst 124(9), 1999, 1323.

Multivariate analysis of XRF data: a non-invasive method for gold foil thickness determination

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To determine the thickness of metallic coatings in the case of art and historical objects, such as gilded surfaces, minimal interaction with the sample is required [1,2]. The aim of this work is to develop a fast and reliable non-invasive method to determine gold foil thickness based on the multivariate analysis elaboration of X-ray Fluorescence (XRF) data. A series of gold foils of nominal thickness and different carats (24K, 23 ¾K, 22K) were hand-produced by a certified artisanal goldbeater still active today in Venice, and applied with two different preparations: *bolo* and *mordente*. The samples were analysed at the Florence's National Institute of Nuclear Physics (INFN) facilities by means of Particle-Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS). RBS with 3MeV protons has measured the real reference foils thickness and its uniformity over the foil surface; the linearity between the PIXE gold yield and the foil thickness has been investigated, demonstrating that the energy loss of the 3 MeV protons in gold is in the keV range and therefore the samples can be considered *thin samples*. The gold leaves have been then analyzed with a portable XRF instrument, comparing the results: the instrument has been calibrated and linearity of the peak-yield/leaf-thickness relation has been verified. XRF spectra have subsequently been used to create a dataset and perform Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). This allowed us to differentiate between groups of leaves belonging to different thicknesses and to identify substrate types, which contribution does not interfere with clustering and classification. The joint XRF-multivariate analysis method has finally been applied to original historical samples from *Galleria Nazionale di Palazzo Spinola*, previously analyzed with PIXE and RBS: all samples were correctly classified and assigned to right thickness class.

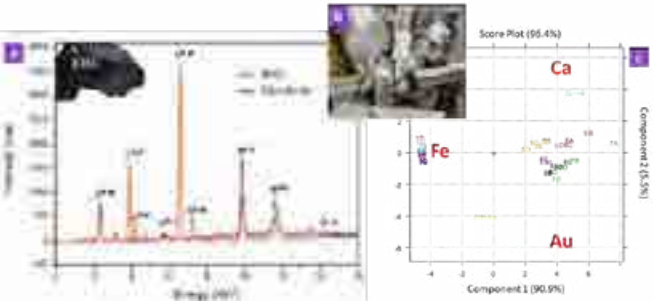

Figure. (a) XRF spectra highlighting differences in gold foil substrates; (b) RBS-PIXE instrument head; (c) PCA Biplot of XRF spectra showing clustering.

Acknowledgments: the authors would like to thank the RADIATE program that granted access to the LABEC 3meV Tandem Accelerator (RADIATE programme proposal 21002424-ST).

[1] Q. Wu et al. J. Cult. Herit. 49, 211–221 (2021)
[2] C. Fiorini et al. X-Ray Spectrom. 31, 92–99 (2002)

Preliminary study on the effects of salinity on ancient paper by optical techniques

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Nowadays most of the books and documents preserved in the archives present numerous critical issues. The causes of risk of archival assets can be due to chemical, physical and biological phenomena, but also to human factors such as the lack of preventive measures of conservation-restoration as well as their protection. In recent decades, the number of extreme natural events (torrential rains, flash floods, floods, etc.) has also increased due to climate change which, unfortunately, does not exclude the recurrence of such adverse situations.

In this work, we studied the effects produced by direct contact (in immersion) with different water solutions for various types of paper and how this can influence their degradation. Various saline solutions are made to reproduce different degrees of salinity associated with the most common hydrogeological phenomena listed above. In particular, we wanted to study the effects of salt on the crystalline structure of the paper. Normally, archival items subjected to hydrogeological phenomena undergo some processes to remove the salt. Thus, our ultimate goal is to establish whether such washing processes are really necessary and if the sample can be prevented from being subjected to further stress.

The study was carried out using optical techniques such as luminescence, reflectivity, and Raman spectroscopy. These techniques, as well as being non-destructive, can be portable so they are suitable for carrying out in situ measurements, making them easy to apply and very useful in the field of cultural heritage

This work focuses only on paper, a future goal will be to evaluate the effects of salt considering also the presence of inks and pigments.

Machine learning and NIR spectroscopy for dating of books

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Dating is often a controversial issue of significant importance for historical, conservational, and scientific reasons. Methods combining near-infrared (NIR) spectroscopy and machine learning have been proposed for material characterization of several heritage materials, including for dating of paper [1-2], parchment [3], and photographs [4]. The resulted models inevitably exhibit uncertainty, often significant and so far not systematically investigated.

Figure 1. Schematic overview of dating models combining NIR spectroscopic data and machine learning.

Here, we present a study to predict the publication dates of books using NIR spectroscopic data and supervised machine learning (Figure 1), exploring the possible sources of uncertainty of the dating models. To this end, 100 books dated between 1851 and 2000 from the collection of the National and University Library of Slovenia (Ljubljana, SI) were selected according to a stratified random strategy to have a representative sample set. Different pages and points in a page were measured to address the inherent inhomogeneity of real books due to paper variability (pages of the same book block from different batches), and degradation (margins generally more degraded than the centre of a page as exposed to pollutants and light). Spectral preprocessing strategies, variable selection methods, and three supervised machine learning techniques were evaluated. The accuracy obtained using partial least squares, i.e. 12 years, is in line with those already reported in literature for comparable time periods [1,2]. However, the two non-parametric methods employed provide much more accurate predictions, i.e., 6 to 2 years. Moreover, degradation does not meaningfully influence the prediction accuracy. Interestingly, common spectral features, typical of cellulose and protein structures, are of importance for all three supervised machine learning methods.

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[1] T. Trafela, M. Strlič, J. Kolar, D. Lichtblau, M. Anders, D. Pucko Mencigar, B. Pihlar, Analytical Chemistry 79(16), 2007, 6319-6323.
[2] N. Brown, D. Lichtblau, T. Fearn, M. Strlič, Heritage Science 5(47), 2017, 1-14.
[3] A. Možir, M. Strlič, T. Trafela, I. Kralj Cigić, J. Kolar, V. Deselnicu, G. de Bruin, Applied Physics A 104(1), 2011, 211-217.
[4] A. Martins, L.A. Daffner, A. Fenech, C. McGlinchey, M. Strlič, Analytical and Bioanalytical Chemistry 402(4), 2012, 1459-1469.

ROADMAP – Research On António De holanda Miniatures Artistic Production

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More than 450 years after the death of the great Renaissance artist António de Holanda (c. 1480-1557), a transnational multi-institutional research consortium – the ROADMAP project - is, for the first time, developing an integrated and interdisciplinary study of his illuminated masterpieces spread by several Libraries across Europe. From the eight manuscripts selected for this chronological study are the “Atlas Miller” (Bibliothèque Nationale de France, GE DD-683-5 RES, dating from 1519), the “Chronicle of D. João I” (DGLAB/TT - Crónicas n.o8, dating from 1515), the "Genealogy of Infante D. Fernando” (British Library, Add MS 12531, no7, dating from 1530), and the “Chronicle of D. Afonso Henriques by Duarte Galvão” (Museu dos Condes Castro Guimarães, PT-MC-MCCG-Inv14, attributed to 1534), already analysed by the team members of the ROADMAP project. In this sense, a deep study of the iconographic references present in the codices (such as the depictions of the city of Lisbon), the drawings as well as the painting and material techniques were profusely analysed and compared, for the establishment of a chronological perspective of the artwork of António de Holanda. For this, in-situ non-invasive analyses were performed, including elemental (h-EDXRF), molecular (UV-Vis-NIR-FORS) and chemical imaging (MA-EDXRF, hyperspectral imaging and IR reflectography) aiming at providing data to better understand the creative process of the painter and of his workshop. Special attention was given to the analyses of the use of a possible binding media formulations transversal to the four illuminated manuscripts, based on the analysis of UV-Vis-NIR spectra following a chemometric approach based on Principal Component Analysis, and to the evaluation of a special *modus opperandi* of creating illuminations and paints by the António de Holanda in the context of the art of illuminating manuscripts during the Renaissance period.

First results from the PUMA synchrotron beamline, dedicated to heritage studies

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The PUMA beamline (French for "Photons used for ancient materials") at the SOLEIL synchrotron near Paris has been created to perform experiments on heritage samples and objects. It is a hard X-ray beamline offering the possibility to perform X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) experiments with a lateral spatial resolution of 5 to 10 µm.

The majority of the available beamtime is reserved for experiments in the heritage field. Since the beamline opened its doors to users in 2019, a large number of experimental teams have carried out their experiments at the beamline, studying systems as diverse as paint constituents, materials from archaeological ceramic artefact, natural history fossils or historical papers [1-7].

Our presentation will present the current status of the beamline, including its technical and scientific specifications and to discuss its possible evolution in the context of the next major upgrade of the SOLEIL synchrotron facility. We will base our presentation on some of the results obtained by the first groups of users who have used the beamline.

Figure, left: Aerial image of the SOLEIL synchrotron site close to Paris. Figure, right: Photo of the experimental endstation at the PUMA beamline.

[1] Moutsiou, T. et al. Heritage 14 (2022).
[2] Godet, M. et al. J. Anal. At. Spectrom. 37, 1265-1272 (2022)
[3] Gimat, A., Schöder, S., Thoury, M. & Dupont, A.-L. Cellulose 29, 4347–4364 (2022).
[4] Gianoncelli, A. et al. Applied Sciences 11, 8052 (2021).
[5] Eveno, M. & Ravaud, E. Eur. Phys. J. Plus 136, 685 (2021).
[6] Gimat, A. et al. Biomacromolecules 21, 2795–2807 (2020).
[7] Gianoncelli, A. et al. Microchemical Journal 154, 104629 (2020).

Considerations for improved monitoring in ion beam analysis of organic heritage materials

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For the non-destructive scientific characterization of art and archaeological objects, ion beam analysis (IBA) is a well-accepted method in the global community. Nevertheless, extreme care should be exercised to avoid adverse effects when samples are submitted to IBA, especially for those containing organic matter.

In this work, a non-destructive, comprehensive, and systematic analytical approach was introduced to investigate the exposure of model parchment and silk mockups to an in-air extracted proton beam with the goal of identifying possible radiolytic processes within the material. During the experiments a wide range of radiation doses were delivered to the organic compound containing model materials, expressed as deposited charge per unit area. The dose-range also encompassed the standard fluences used during IBA.

Before and after irradiation, attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR) was used at the same measurement spot to evaluate the changes compared to the sample's own reference state in cases where the proton beam incident was perpendicular to the sample surface. Since accelerated particles deposit the majority of their energy below the surface, scanning electron microscopy (SEM) and Raman microscopy were employed on samples arranged in a multi-sheet, "sandwich" manner. Sandwich samples were positioned in front of the in-air extracted proton beam to achieve a particle incidence that was tangential to the sample surface. This allowed the tracking of the so called Bragg peak along the surface of the model material. Ionizing radiation has been shown in the literature to cause color changes in a variety of materials. To further investigate the dynamics of this phenomenon, digital video capturing and processing was also carried out during in-air extracted proton beam irradiations of parchment and silk model subjects.

Our findings suggest that monitoring organic heritage items like silk or parchment in a particular configuration during or after ion beam irradiation can reveal changes inside the material that are easily missed by direct inspection.

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Aging of paints used in urban art murals: an approach in the identification of pigments and their influence in the fading of the artworks

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Contemporary murals are one of the artistic expressions in public spaces [1]. The artistic value of these outdoor artworks could be compromised due to the deterioration processes affecting the paints and derived from the action of the environment factors [2-6]. For this reason, the preservation and conservation of these urban artworks has become one of the most discussed topics in the field of conservation of Cultural Heritage [7-9].

Decolouration (fading) is one of the most common deterioration forms of painted murals, being generally attributed to the degradation of organic compounds, either pigments or binders [3, 4, 6, 10]. Based on a study in which the color change of a real contemporary mural was monitored for one year, the paints suffering the highest color change have been selected. These paints were characterized by Fourier transform infrared spectroscopy (FTIR) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) with tetramethylammonium hydroxide in double-shot mode to: (1) perform the chemical characterization before aging and (2) identify the chemical changes produced after a year of exposure. Moreover, laboratory mock-ups made by applying the paints to concrete slabs were exposed to an outdoor exposure in a marine setting for 12 months and to an ultraviolet radiation exposure test during 4620 h. Before and after the aging tests, mockups have also been analyzed by FTIR and Py-GC/MS.

This research aims to delve into the usefulness of FITR and Py-GC/MS techniques to characterize the pigments of paints used in the contemporary muralism and to identify the degradation processes that they suffer and that cause fading.

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[1] E. Gayo, Ge-Conserv. 10, 2017, 26-28.
[2] M. Veneranda, J. Aramendia, L. Bellot-Gurlet, P. Colomban, K. Castro, Corros. Sci. 133, 2018, 68-77.
[3] E.M. Alonso-Villar, T. Rivas, J.S. Pozo-Antonio, Prog. Org. Coat. 154, 2021, 106180.
[4] D. Cimino, R. Lamuraglia, I. Saccani, M. Berzioli, F.C. Izzo, Heritage, 5, 2022, 581-609.

[5] G. Pellis, M. Bertasa, C. Ricci, A. Scarcella, P. Croveri, T. Poli, D. Scalarone, 165, 2022, 105576.
[6] T. Rivas, E. M. Alonso-Villar, J.S. Pozo-Antonio, Eur. Phys. J. Plus 137, 2022, 1257.
[7] W. Shank, D.H. Norris, Stud. Conserv. 53, 2008, 12-16.
[8] M. Chatzidakis, Stud. Conserv. 61, 2016, 17-23.
[9] D. Scalarone, M. Bertasa, P. Croveri, M. Cardinali, S. Stoisa, C. Ricci, I. Saccani, G. Cavanna, R. Bestetti, D. Riggiardi, A. Tibiletti, in Proccedings of the VIII Congresso internazionale Colore e Conservazione, Venezia Mestre, Italy, 23-24 November 2018, Il Prato: Saonara, Italy, 2020; ISBN 978-88-6336-494-1.
[10] A. Bosi, A. Ciccola, I. Serafini, M. Guiso, F. Ripanti, P. Postorino, R. Curini, A. Biano, Spectrochim. Acta A Mol. Biomol. Spectrosc. 225, 2020, 117474.

Multi-analytical study and assessment of commercial coating hydrophobic effectiveness and durability in carbonate stones – a case study of built heritage protection and preservation

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Stone decay is becoming an increasingly worldwide concern in the field of conservation of built heritage. Among the known causes of stone decay, water has been identified a key factor in the alteration of the original stone's properties and aesthetics, directly impacting its sociocultural and socioeconomical value. Here, a multi-analytical approach was employed to study the correlation between the effectivity, compatibility, and durability of three different commercial hydrophobic coatings, and the physical, chemical, and mineralogical features of carbonate stones.
Stone sample mock-ups were observed under digital microscopy and analyzed by colorimetry, XRF and XRD prior to the application of the commercial hydrophobic coatings. Following the application, the mock-ups were once again subjected to an assessment using digital microscopy and colorimetry, and an optical tensiometer was employed to evaluate the hydrophobic effectiveness. This methodology was repeated after accelerating ageing in climatic chambers to also assess the coating's durability. The results obtained demonstrate the coating composed of silane/siloxane with modified fluorinated additives, is the most effective, compatible, and durable hydrophobic coating among those tested. These results obtained in this study will be used as steppingstones for the development of new eco-friendly and cost-effective coatings.

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Protection of carbonate stone samples via treatment with ammonium N-2-picolyloxamate

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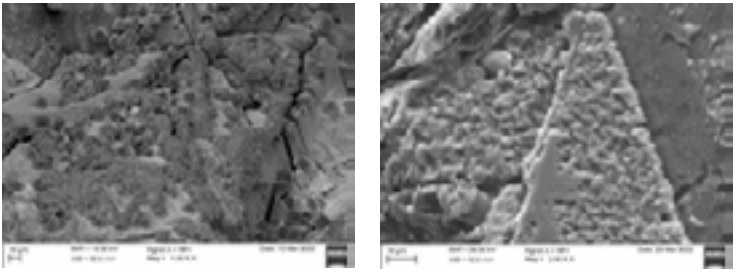
During the past years, monoester and monoamide derivatives of ammonium oxalate have proved to be useful conservation agents for carbonate stones, such as marble and calcarenites [1,2]. Accordingly, new synthetic methodologies have been developed for the synthesis of *N*-alkyl and *N*-aryl oxamic acid derivatives [1–3].

In this work, the ammonium *N*-2-picolyloxamate has been synthetised, fully characterized by microchemical and spectroscopic means and tested by the immersion method on different carbonate substrates: calcium carbonate powder, white Carrara marble, and biomicritic limestone. The characterization of the treated stone samples through diffractometric techniques and microscopy, colorimetric, and porosimetry measurements demonstrated that these compounds react on the stone surface to give a passivating layer of ammonium oxalate while preserving the mechanical and chromatic properties of the treated samples.



SEM images of the stone surface in Carrara marble mock-ups treated with a 5% (left) and 12% w/w solution (right) of ammonium N-2-picolyloxamate, showing the newly-formed phase

[1] L. Maiore, M. C. Aragoni, G. Carcangiu, O. Cocco, F. Isaia, V. Lippolis, P. Meloni, A. Murru, E. Tuveri, M. Arca, J. Colloid Interface Sci. 448, 2015, 320–330.

[2] A. Pintus, M. C. Aragoni, G. Carcangiu, L. Giacopetti, F. Isaia, V. Lippolis, L. Maiore, P. Meloni, M. Arca, New J. Chem 42, 2018, 11593–11600.

[3] M. Matteini, Sci. Cult. Herit. 8, 2008, 13–27.

Microbial induced stone discoloration in Alcobaça Monastery: a comprehensive study

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The Alcobaça Monastery (Portugal), a UNESCO World Heritage Site, currently exhibits a high degree of surface alterations of the stone architectural elements inside the church, including an extensive pink coloration in the walls and columns (Fig. 1 A-B), bacteria biofilms, and salt efflorescences (Fig. 1C). The main goal was to identify the microbiota that colonizes the walls and columns of this monument, to help custodians and conservators-restorers in the selection of the correct cleaning procedure to be adopted for the conservation of the monument.

Regarding the observed pink discoloration, and considering previous studies, we hypothesized that it is caused by biofilms formed by bacteria or other microrganisms that produce pigments of the same color, particularly carotenoids. Curiously, a distinct phenomenon was noticed (Fig. 1A): the pink discoloration always seems to appear at a very similar height in most of the columns and walls, starting at 40 cm to the floor and associated with the presence of salts on the walls. Using high-throughput sequencing approaches, we were able to characterize the microbial community present. We identified several bacteria that are producers of pink pigments and halotolerant such as *Bacillus aryabhattai*, *Rubrobacter radiotolerans* and *Halalkalicoccus* sp. and thus develop in areas of high salinity [1-4].

Figure 1: (A) distinct phenomenon observed at the altar of the monastery church; (B) pink colored biofilms on the walls; (C) evidence of the presence of salts on the walls.

[1] Paz, A., Carballo, J., Pérez, M. J., & Domínguez, J. M.. World Journal of Microbiology and Biotechnology, 2016, 32(10).
[2] Yoo, S. J., Weon, H. Y., Song, J., & Sang, M. K.. Journal of Microbiology and Biotechnology, *29*(7), 2019, 1124–1136.
[3] Imperi, F., Caneva, G., Cancellieri, L., Ricci, M. A., Sodo, A., & Visca, P.. Environmental Microbiology, 9(11), 2007, 2894–2902.
[4] Egas, C., Barroso, C., Froufe, H. J. C., Pacheco, J., Albuquerque, L., & da Costa, M. S.. Standards in Genomic Sciences, *9*(3), 2015, 1062–1075.

The authors acknowledg to FCT – Foundation for Science and Technology, I.P., within the scope of the projects: UIDB/04449/2020, MICROCENO (PTDC/CTA-AMB/0608/2020), ART3mis (2022.07303.PTDC) and I. Silva PhD Grant (UI/BD/153582/2022); and Directorate-General for Cultural Heritage (DGPC).

New application of portable laser sampling for Pb isotope analysis of silver

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After thorough method development and testing [1], this is the first full-scale study applying portable laser ablation sampling for high-precision Pb isotope analysis of silver artefacts in a museum collection. Fifty of the earliest medieval silver Anglo-Saxon and Frisian pennies and Merovingian and Carolingian silver deniers housed at the Fitzwilliam Museum in Cambridge were investigated.

First, the coins were analysed by *in situ* laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) at the Department of Earth Sciences at the University of Cambridge to capture elemental concentrations. Each coin was ablated three times with a spot size of 80µm. In addition to the highly sensitive measurement of minor and trace elements, the analysis produced time-resolved spectra that permitted the identification of elemental surface enrichment and a historical and modern forgery.

Second, the coins were sampled at the Fitzwilliam Museum using a portable Nd:YAG 532 nm wavelength laser. Based on the lead content of the silver, 2 to 10 spots were ablated and collected on pre-cleaned Teflon filters, which were processed under clean laboratory conditions for Pb isotope analysis using multicollector (MC-)ICPMS. The coins analysed were of variable condition, which was found to play no role in the analytical results. This method has numerous advantages compared to traditional sampling methods and *in situ* laser ablation for Pb isotope analysis: the sample sizes are not visible to the unaided eye and the quality of the analytical results are comparable to destructive sampling and are superior to *in situ* nano-second LA-MC-ICPMS.

The results of the analysis shed light on a major turning point in the development of the European economy. After the fall of Rome, the supply of gold for coinage in the West gradually dwindled over centuries, giving rise to the flourishing use of silver, which dominated European currency into the modern age. The switch to silver in the 7th century AD was thought to have been driven by new mining of silver in the West [2], representing a move of economic independence from the advanced Byzantine East, but the analyses overturn this theory, and, only with Charlemagne, a century later, did the last traces of eastern silver disappear.

[1] S. Merkel, et al., J. Anal. At. Spectrom. 37, 2022, 148-156.
[2] C. Loveluck, et al., Antiquity 92(366), 2018, 1571-1585.

Scientific investigations of Tang Dynasty pottery figurines

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Among the ancient East Asian art production, funerary statuettes called *mingqi* ("spirit objects") played a relevant role in bearing witness to the belief systems of early China. In particular, *mingqi* pottery figurines became extremely popular in the Tang Dynasty (618-907 CE). They vividly depicted vibrantly painted horses, Bactrian camels, and exotic musicians, reflecting the high level of cosmopolitanism of the golden age of imperial China. [1] Then, starting from about the 1910s, *mingqi* statuettes strongly attracted Western collectors. Therefore, modern reproductions of these statuettes proliferated in the art market. [2, 3]

The present research study is based on the archaeometric investigation of a group of *mingqi* terracotta figurines stored at the Museum of Cultures (Mudec) of Milan. The examined finds were stylistically attributable to the Tang period. However, very little *provenance* information is available, and the authenticity is not quite certain.

Here, the scientific survey aims at shedding light on the material composition and realization technique of the museum figurines. First, the visual examination and portable micro-Raman spectroscopy were performed to identify the relevant sampling zones. Then, a multi-technique and multi-scale approach was employed. All the collected micro-samples were deeply characterized by a combination of laboratory microscopies and synchrotron-based micro-analysis. More specifically, micro-Raman and micro-FTIR spectroscopies were carried out on the raw fragments. Next, thin cross-sections were analyzed by SEM-EDS, synchrotron-based µXRF/µXRD mapping, and Fe K-edge µXANES. [4]

The employed methodological approach allowed for maximizing the analysis performed on the same sample and obtaining complementary outcomes from the different techniques. Together with the iconographic analysis, the results of scientific examinations led to getting insight into the manufacturing process and looking closer at the historical context of the finds.

Thus, the present research represents the early attempts to perform scientific investigations of Tang *mingqi* figurines of uncertain *provenance* and authenticity, which nowadays can be widely found in Western museums and private collections.

[1] S. Rastelli, Ceramica cinese. *Evoluzione tecnologica dal Neolitico alle Cinque Dinastie*, Libreria Editrice Cafoscarina, Venezia, 2004, 118-122.

[2] D. K. Strahan, A. Boulton, *Studies in Conservation* 33 (1), 1988, 149-154.

[3] C. Hentze, W. P. Yetts, *Chinese Tomb Figures. A Study in the Beliefs and Folklore of Ancient China*, ed. E. Goldston, London,1928.

[4] M. Cotte, V. Gonzalez, F. Vanmeert, L. Monico, C. Dejoie, M. Burghammer, L. Huder, W. De Nolf, S. Fisher, I. Fazlic, C. Chauffeton, G. Wallez, N. Jiménez, F. Albert-Tortosa, N. Salvadó, E. Possenti, C. Colombo, M. Ghirardello, D. Comelli, E. A. Clerici, R. Vivani, A. Romani, C. Costantino, K. Janssens, Y. Taniguchi, J. McCarthy, H. Reichert, J. Susini, *Molecules* 27 (6), 2022, 1997.

A systematic approach to study natural polymer ageing and condition. Analysis contra model

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Natural polymers, including cellulose, fibroin and keratin, constitute most of the materials found in cultural heritage objects, such as paintings on paper, wood or canvas and textiles. The survey of the mechanism of their degradation seems crucial not only for their preservation at optimum safe conditions but also for the rational, facts-based decisions on their conservation or restoration that utilize the modern achievements in science and technology.

This presentation is a result of our more than 20-year experience in the study of paper, silk and wool degradation to help rescue books in libraries, paintings and drawings, banners and arrases of the collection of Polish and foreign museums, the examples of which can be found in [1-4]. Within these studies, we have devised a universal approach to ascertain the arartifact's conditions by studying their degradation mechanism understood in terms of chemistry. Our methodology consists of several stages that start with the thorough physical-chemical analysis of aged model samples using complementary methods to recognise different structural features of the material. They include both in situ and "in vivo" spectroscopic and diffractional tests of their degradation progress at artificial conditions and ex-situ analysis of the model samples artificially aged at different conditions, which are selected in such a way as to distinguish single degradation pathways. The second step involves proposing and verifying the degradation mechanism that combines bonds cleavage due to depolymerisation or hydrolysis, functional groups formation due to oxidation and the changes in the sample's crystallinity. Indeed, all the reaction pathways are tangled together in real objects, and thus a part of the effort in the first stage is to recognize the conditions at which one single path dominates. The core of analytical tools that investigate natural polymers are in situ infrared, Raman and UV-Vis spectroscopic methods and X-ray diffractional techniques and size exclusion chromatography, aided by additional techniques that answer specific structural questions [3,4].

Thus what the survey of the natural polymers has in common is i) the approach to study them based on selected complementary analytical techniques and ii) the general mechanism of degradation that is shared by all of them. The similarities in these two issues will be discussed in this article using cultural heritage objects based on paper, silk and wool as examples.

[1] T. Łojewski, K. Zięba, A. Knapik, J. Bagniuk, A. Lubańska, J. Łojewska, Appl. Physics A: Materials 100 (2010) 809-821.
[2] M. A. Koperska, D. Pawcenis, J.M. Milczarek, A. Blachecki, T. Łojewski, J. Łojewska, Polym Deg. Stab. 120 (2015) 357-367 (IF2015=3.163) 35
[3] J. Łojewska, I. Rabin, D. Pawcenis, J. Bagniuk, M. A. Aksamit- Koperska, M. Sitarz, M. Missori, M. Krutzsch, Scientific Reports (Group of Nature) 7, 2017
[4] A. Mosca Conte, O. Pulci, M. C. Misiti, J. Lojewska, L. Teodonio, M. Missouri, Applied Physics Letters 104, 22 (2014) art. 224101 (IF2015=3.352) 40

Microbial communities of underwater caves from Algarve coast: Biological activities prospection

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Microorganisms are known to be an important source of bioactive compounds. Lately, the microbiota of hypogenic environments, such as underwater caves, has been explored, since they constitute complex ecosystems, which bring unique conditions for the development of organism's niches with unknown biodiversity. These microorganisms may have interesting characteristics regarding the high potential to produce new bioactive compounds with antitumoral, antioxidant, antimicrobial and pesticide properties, with potential application in Cultural Heritage safeguarding [1-2].

This study under the PROBIOMA project aims to search for new bioactive compounds produced by bacterial cultures, isolated from marine caves. Samples were collected in two underwater caves on the Algarve coast and microbial biodiversity was assessed by High-throughput sequencing and cultivable microorganisms were isolated on marine agar medium 2216 [3].

Metagenomics showed mostly bacteria from the *Proteobacteria*, *Bacteroidetes* and *Firmicutes* phyla. DNA of 269 selected bacterial isolates was extracted and the identification was performed by sequencing 16SrDNA. Antimicrobial spectra of metabolites produced by selected isolates (*Brevibacterium* sp., *Pseudoalteromonas* sp., *Vibrio* sp., *Cobetia* sp., *Cellulophaga* sp., *Tenacibaculum* sp., *Bacillus* sp., *Mesonia* sp., *Rhodobacteraceae* sp., *Agarivorans* sp. and *Sulfitobacter* sp.) was evaluated in solid and liquid media against bacterial strains of *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Escherichia coli* and *Pseudomonas aeruginosa*, and in solid medium against biodeteriogenic fungi *Mucor* sp., *Aspergillus niger*, *Fusarium oxysporum*, *Cladosporium* sp., and two *Penicillium* sp.. On the other hand, supernatants of cultures from selected isolated bacterial strains were screened for evaluation of antitumor potential against breast cancer epithelial cell line MDA-MB-231[4]. Direct supernatants (without prior concentration) did not show significant antifungal action against the selected fungal strains. However substantial antibacterial activity was observed in direct supernatants of *Brevibacterium* sp., *Pseudoalteromonas* sp., *Vibrio* sp. and *Sulfitobacter* sp.. Aditionally several supernatants of selected strains showed high antiproliferative activity against this breast tumour cell line, namely *Sulfitobacter*, *Cobetia* and *Pseudoalteromonas*.

Overall, there were some very promising results concerning the prospection of new biocompounds with biological properties obtained from microbial communities of underwater caves from Algarve coast, constituting new potential for green-safe and sustainable solutions and representing an opportunity for the valorization of these Natural, Genetics and Cultural Heritage.

Keywords: Natural, Genetics and Cultural Heritage; Underwater caves; hypogenic environments; Microbiota; Biological compounds; Green-safe and sustainable solutions

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References:

[1] J.L. Gonzalez-Pimentel, T. Martin-Pozas, V. Jurado, A.Z. Miller, A.T. Caldeira, O. Fernandez-Lorenzo, S. Sanchez-Moral, C. Saiz-Jimenez. PeerJ, 9, 2021, e11386.
[2] T. Rosado, M. Silva, L. Dias, A. Candeias, M. Gil, J. Mirao, J. Pestana, A.T. Caldeira. J King Saud Univ Sci, 29(4), 2017, 478-486.
[3] A. T. Caldeira, N. Schiavon, G. Mauran,C. Salvador,T. Rosado, J. Mirão, A. Candeias. Coatings of MDPI 11(2),2021;1–17.
[4] S.M. Arantes, A. Piçarra, M. Guerreiro, C. Salvador, F. Candeias, A.T. Caldeira, M. R. Martins. Food Chem Toxicol, 133, 2019, 110747.

Towards IBA characterisation of gilding on european paintings

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The use of gilding in European paintings fell from fashion in the 16th and 17th centuries, and although some gilded elements persisted in this period, the use of gilding here has been largely overlooked in modern art history. In this work, we develop external IBA analytical methods at AGLAE, applicable to gilded artworks without sampling, destined to contribute to a database of physico-chemical properties, alongside optical properties and historical elements. This new information will help enrich the art historical knowledge of the period and reveal clues about the gilding techniques in this special period.

As a first step, we have investigated the elemental composition of modern burnished, unburnished, and gold powder gilding mockups for which, in contrast to real artworks, destructive and sampling analytical methods may also be applied.

Judicious choice of ion beam, and detectors with different foils and angles for in-air IBA allows determination of elements from Na up to Au (Fig. 1). First, the concentration of gold and other elements was calculated using PIXE with one detector optimised for low energy x-rays for matrix composition and three detectors optimized for high energy x-rays for trace element determination. Simultaneously, proton EBS spectra were acquired from detectors at two different angles, giving elemental depth concentrations from the backing. The thickness of the gold layer was determined utilizing of 3 MeV RBS by alpha beam. Our in-air composition results are consistent with those obtained under vacuum with the SEM-EDX method, showing that the in-air IBA characterization is a promising approach to populating a database of the elemental compositions of these gilded artworks.

Further work is planned, aiming at consolidating the metrological aspects of the IBA methodology – reproducibility, detailed uncertainty budget and so on, and optimization of the IBA methodology with respect to minimization of potential evolution of the analysed samples under the beam.

(A)

(B)

Figure 1: A) Experimental set-ups, B) Schema for the description of experimental set-ups

Mapping and identification of decay on the modern mural paintings sets by Almada Negreiros at the Maritime stations of Alcântara, Lisbon: type, origin, and consequences

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This paper provides an overview of the decay affecting the mural painting sets made by Almada Negreiros in 1945, and 1949, at the two maritime stations of Alcântara, Lisbon (Alcântara and Rocha do Conde de Óbidos). In both cases, the paintings show different states of conservation, with some chromatic layers more affected than others. Mapping and identifying the underlying degradation phenomena for future conservation works was the main goal of a multidisciplinary research carried onsite and in the laboratory between 2020 and 2023.

The research activities encompassed the identification and characterization of the main deterioration features attaining the paint layers by visual inspection, technical photography in the Vis, Vis-Rak and UV; h-OM and h-EDXRF, complemented by OM, XRD and SEM-EDS of microsamples. Moreover, the identification of structural anomalies, as well as the validation of the existing documentation regarding geometry and structural elements was also carried out. To this end, a wide-spread sample measurements were taken and a detailed photogrammetric survey of the most deteriorated parts of the building at Rocha do Conde de Óbidos was conducted. Non-destructive evaluation strategies were applied to support the research (i.e., thermographic inspection, ultrasonic pulse velocity test and rebound hammer test).

Results show that the mean deterioration features found in both painting sets are flaking and powdering of paint layers. Some paint layers are also suspected to have undergone chromatic alteration. The colours more affected are light greens, yellows, browns, and blacks made with natural and different types of synthetic pigments (eg. Green earths, Fe, Cr and Cd-based pigments and PG's). The occurrence and activity of gypsum, and other sulphates, found on the paint surface and underneath mortars can be highlighted as the main decay phenomenon. The poor condition of the structural elements, the original building materials, and the past building repairs, combined with a particularly aggressive external environment (e.g., air traffic pollution, sea spray) are the likely source of the water infiltrations and of the sulphates present on the paint structure.

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Characterization of a terracotta Indian sculpture through microCT and XRF techniques

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In this work, a polychrome terracotta statuette was analyzed by means of X-Ray computed microtomography (microCT) and X-ray fluorescence (XRF). The sculpture represents Krishna, one of the major deities in Hinduism, and it is said to have been manufactured in the city of Vrindavan, India. It is a city of a wide-encompassing historic heritage as it has for long been one of the most sacred places for the Vaishnavism tradition, given that well-known religious texts claim that Krishna spent most of his childhood days there. Given that there are no official records or documents on the statue's origin, the objective of this paper was to evaluate its structural characteristics and the elemental composition of the pigments employed in an attempt to track down the period of time when the statue was crafted, as well as the manufacturing techniques employed while sculpting it. The projection images were acquired using the VTomex (BHGE) microCT system. Two scans were performed with an effective pixel size of 104 µm. The data was subsequently reconstructed using the Datos X reconstruction (BHGE) software. At a later moment, the scans were merged together in order to generate the full volume of the statue. Thanks to the resulting images, it was possible to visualize details related to the construction of the sculpture, its conservation state, and also quantitatively analyze the porosity and inclusions of the terracotta matrix. The XRF analyses were carried out using a portable XRF device (ARTAX 200 - Bruker). Several spectra were acquired in different regions of the statue in order to obtain the elemental composition of each color and gain access to their corresponding pigments. Also, the spectra of the terracotta matrix and the preparatory layer were achieved. The system detected the presence of elements such as Ca, Ti, Cr, Mn, Fe, Cu, Zn, Sr, Ba, and Pb, thus indicating the presence of the pigments Chrome Yellow, Lead Red , White Lead, Han Blue, and Burnt Siena. The analysis of the preparatory layer indicates the presence of the pigment Lithopone. The combined characterization using both techniques revealed important information about the statue, and it is expected that the acquired data will be helpful to understand the manufacturing techniques employed in that specific region and period of time.

Identification of Fake Gold Gilding Material in the Ancient Wall Paintings by Mass Spectrometry Imaging

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Keywords: fake gold, gilding material, tin leaves, wall paintings, DESI-MS

Tiny pieces of metallic foils (gold, silver or tin) were often used for decoration in ancient architecture, sculpture and paintings. Our previous study has shown that both tin and gold leaves were used as the gilding foils in Cave 171 of Kizil Grottoes (5th-7th Century A.D.), China [1]. Several gilding leaf samples from the wall paintings of Simsum Grottoes (China, 4th-8th Century A.D.) and Kizil Grottoes were determined as tin foil by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS), but showed yellow color just as gold leaf, which is known as "fake gold", a phenomenon also appeared in medieval paintings in Europe [2,3]. To further investigate the fake gold gilding material, desorption electrospray ionization-mass spectrometry (DESI-MS) imaging method was applied on the both sides of tin leaf samples. Amur-cork tree (*Phellodendron amurense Rupr.*), a natural plant dye, was identified on the yellow tin leaves. This result was further confirmed by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) analysis. This is the first report about the exact composition of fake gold gilding material in ancient wall paintings along the Silk Road. The use of Amur-cork tree for fake gold is also quite different from the ancient Chinese archive such as *T'ien-kung k'ai-wu*, in which safflower oil was mentioned to be used as fake gold for silver gilding. Our results also demonstrate that DESI-MS imaging is capable of identifying and locating organic dyes on the surface of the artwork samples, which has great potential for the non-destrutive analysis of organic materials in precious heritage objects, addressing a number of questions of interest to artists, scientists, and conservators.

[1] A. Zhou Z, B. Ling S, C. Chen L, et al. Microchemical Journal 154, 2020, 104548.
[2] A. Mounier A, B. Daniel F, C. Bechtel F. Proceedings of the 37th International Symposium on Archaeometry, 2008, 273–278.
[3] A. Sandu I, B. MHD Sá, C. Pereira M C. Surface and Interface Analysis 43(8), 2011, 1134-1151.

Micro-Raman spectroscopy for identification of calcite types in historical mortars: applications in archaeometry

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Radiocarbon dating of mortars may present many issues in its application. The datable component is represented by anthropogenic calcite, namely lime binder of mortar, which is the carbon fraction to be isolated for dating [1]. Anthropogenic calcite is typically mixed with aggregates of several different compositions, even carbonaceous, and under-burnt rock fragments used for production of lime; may be present may alter the original carbon content.
A complete characterization of the mortar before radiocarbon dating is mandatory to identify the type of mortar and to develop an efficient analytical approach that allows to select the most suitable component of mortar for absolute dating. A further analysis on selected portions of sample is necessary, thus non-destructive techniques need to be found to identify the type of calcite in the sample [2]. This would allow to completely characterize the material truly used for dating, avoiding its contamination by other carbon sources. Given the widespread use of infrared spectroscopy to distinguish between calcites formed by different processes, from order/disorder in the calcite crystal structure [3-5], we extended this approach to Raman spectroscopy. A wide range of different carbonate rock (geogenic calcite) and lime binder of mortar (anthropogenic calcite), obtained, respectively, by different geological and archaeological/historical contexts were selected.
A high-resolution micro-Raman spectrometer was used to explore the possibility to differentiate the calcite originated by anthropogenic or geological sources. Frequency, intensity (height) and peak area of the normal vibrations of carbonate groups were considered; Key Influence Factor analysis (KIF) and Principal component analysis (PCA) were used, respectively, for visual inspection and reducing dimensionality of dataset from different calcite types. Some parameters collected successfully classified calcite from different domains, opening new perspectives in Raman spectroscopy and heritage science.

[1] R. Hayen, M. Van Strydonck, L. Fontaine, M. Boudin, A. Lindroos, J. Heinemeier,... & M. Caroselli, Radiocarbon 59(6), 2017, 1859–1871.
[2] S. Calandra, E. Cantisani, B. Salvadori, S. Barone, L. Liccioli, M. Fedi, C. A. Garzonio, JPCS 2204(1), 2022, 012048.
[3] V. Chu, L. Regev, S. Weiner, E. J. Boaretto, Archaeol. Sci. 35, 2008, 905.
[4] L. Regev, K. M. Poduska, L. Addadi, S. Weiner, E. J. Boaretto, Archaeol. Sci. 37, 2010, 3022.
[5] B. Xu, M. B. Toffolo, L. Regev, E. Boaretto, K. M. Poduska, Anal. Methods 7, 2015, 9304.

Studying Ancient Egyptian metal vessels by X-ray diffraction and Machine Learning

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Metalworking and the techniques employed in creating objects in metal played a key role in many ancient cultures [1-4]. A collection of 12 Egyptian bronze vessels and stands belonging to the set of grave goods of Kha and Merit [5,6], preserved at the *Museo Egizio* in Turin and dating back to the mid-18th Dynasty of the New Kingdom (ca. 1425–1352 BC), is studied to extract information regarding the metalworking methods. These objects have a high archaeological and culture-historical significance because they are daily use vessels, stem from the same burial context and have been preserved in the same conditions and are, as the whole assemblage, considered a *unicum*.

Non-destructive and non-invasive X-ray powder diffraction coupled with machine learning is applied to carry out a comparative analysis of the 12 bronze artefacts, underlining similarities and differences between those objects and between different parts of the same object to extract valuable information which helps in both understanding and interpreting the ancient Egyptian working methods.

[1] R. F. Tylecote A History of Metallurgy, 2nd Edition, Boca Raton: CRC Press, 1992.
[2] R. J. Forbes, Studies in Ancient Technology: Metallurgy in Antiquity, volume 9, Leiden: Brill 1972.
[3] J. Ogden. Metals, in Ancient Egyptian Materials and Technology, ed. Paul T. Nicholson and Ian Shaw, Cambridge: Cambridge University Press 2009, 148–76.
[4] M. Fitzenreiter. Technology and Culture in Pharaonic Egypt: Actor Network Theory and the Archaeology of Things and People (Elements in Ancient Egypt in Context). Cambridge: Cambridge University Press, 2023.
[5] E. Schiaparelli, La tomba intatta dell'architetto Kha nella Necropoli di Tebe, Turin: Casa Editrice Giovanni Chiantore 1927.
[6] E. Ferraris, La tomba di Kha e Merit, Modena: Franco Cosimo Panini 2018.

Non-invasive investigation of three paintings attributed to Cavalier d'Arpino by means of ED-XRF, FORS and Multispectral Imaging

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The aim of this work was to characterize the palette and painting technique used for the realization of three late sixteenth century paintings from "Galleria dell'Accademia Nazionale di San Luca" in Rome attributed to Cavalier d'Arpino (Giuseppe Cesari), namely "Cattura di Cristo" (Inv. 158), "Autoritratto" (Inv. 546) and "Perseo e Andromeda" (Inv. 221).

This study presents a diagnostic campaign that was carried out with non-invasive and portable techniques such as Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometry, Fiber Optics Reflectance Spectroscopy (FORS) and Multispectral (MS) Imaging.
This work was part of a project founded by Regione Lazio and MUR ("IMAGO - Multispectral Imaging for Art, Gamification and hOlografic reality" project).

FORS and ED-XRF analyses allowed the preliminary characterization of the pictorial materials in a reliable non-invasive way.
In particular, it was possible to identify most of the pigments used for the production of the paintings attributed to Cavalier d'Arpino.

The MS images were acquired between the ultraviolet and the near-infrared regions of the electromagnetic spectrum (UV-Vis-NIR) by using different illumination sources and a cooled CCD camera equipped with interferential filters.
It was possible to observe significant differences between the visible and the NIR images with some details of the paintings which resulted transparent in the infrared region.

Furthermore, MS images were investigated in-depth by the application of data clustering algorithms to obtain semantic segmentation. This methodology exploits the information reported in MS images to generate a pixel classification based on statistical methods together with image analysis techniques. The result provides both an extrapolation of salient parts of the work as well as a better perception of some details.

The combined results of this work allowed to investigate in-depth the production of one of the main painters from Italian mannerism.

Use of X-ray fluorescence combined with Monte Carlo simulation for determination of bronze alloys and corrosive layers

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One of the elements to consider when dealing with a cultural asset is its uniqueness, which implies the need to ensure its preservation. Therefore, the use and development of nondestructive techniques, are essential to perform diagnostic studies. X-ray fluorescence (XRF) is certainly among the most exploited techniques, due to its non-destructive approach to investigating the elemental composition of archaeological objects, such as metals. It should be considered, however, that qualitative-level knowledge alone of the chemical elements present in an alloy does not guarantee a complete understanding of its composition or the productive knowledge possessed by a population. Among ancient alloys, bronze was certainly one of the most widely used. Therefore, characterizing it means characterizing the composition and structure, which, despite the simplicity of the alloy, is very complex. This is due to the action of corrosion that produces multilayered, irregular structures on the surface (*patina*), and also possible selective enrichment/depletion of certain elements within the alloy. To overcome this problem, an analytical protocol has been developed that combines X-ray Fluorescence (XRF) with Monte Carlo (MC) simulation that allows multilayer structures to be simulated. This approach makes it possible to characterize and quantify the chemical elements present in alloys and to define the structures of even very complex artifacts [1]. In this paper, we highlight how the XRF-MC method can be exploited to identify the original alloying of an artifact and changes in composition, due to remanufacturing of the object or alteration processes, by characterizing corrosive structures such as surface enrichments in tin, caused, for example, by decuprification processes [2]. All this without the need to sample or remove the most superficial layers. This methodology has been successfully exploited on many bronze artifacts, such as Sardinia-made *Navicelle* and tools, and Etruscan-made fibulas and weapons. The data obtained using the XRF-MC protocol were also compared with those acquired using destructive techniques, obtaining very similar results, which highlighted the method's effectiveness and potential in the field of Cultural Heritage.

[1] A. Brunetti, M. Porcaro, A. Bustamante, G. Stegel, R. Cesareo. Combining X-ray Fluorescence and Monte Carlo Simulation Methods to Differentiate between Tumbaga and Gold-Alloy or Gildings. *Materials* 2022, *15*, 4452

[2] M. Porcaro, A. Depalmas, S. Lins, C. Bulla, M. Pischedda, A. Brunetti. Nuragic Working Tools Characterization with Corrosion Layer Determinations. *Materials* 2022, *15*, 3879

The Deposition by Raffaello Sanzio, analytical insights on cross sections for the characterization of pictorial palette

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In 2020, the year celebrating the 500th anniversary of Raphael's death, the Deposition, the altarpiece also known as the "Pala Baglioni", dated 1507 and located at the Borghese Gallery of Roma, has been submitted to a restoration intervention, and in-depth diagnostic campaigns through non-invasive techniques. The study of Raffaello painting techniques was also performed through the study of old cross sections, prepared between 1966 and 1972, during the past restoration intervention conducted by the Istituto Centrale per il Restauro and preserved in ICR laboratory of chemistry and testing materials archive. The stratigraphic sections from the 1960s are an interesting and useful document for reconstructing the precious painting conservation history, as they "photograph" the situation of the original pictorial film and restoration repaintings before intervention of 1966-1972.

In this contribution we present the results of analytical insights on Raphael's pictorial palette carried out by the analysis of the old ICR stratigraphic sections, through the use of SEM-EDS, micro-Raman (633 nm), while Surface Enhanced Raman Scattering analysis through colloidal paste was tested for the identification of organic lakes present in low concentration. This combined diagnostic approach has made it possible to recognize the pigments employed in the different pictorial layers, including those in traces and those based on organic materials, highlighting further aspects of the illustrious master refined painting technique, especially in terms of selected materials, completing and integrating the studies conducted so far [1].

Figure 1. The Deposition, before restoration intervention of 2020

[1] L. Ferrara, Storia e restauro della Deposizione di Raffaello, Catalogo della mostra Museo e Galleria Borghese Roma 1972-1973, Istituto Grafico Tiberino (1973); K.H. Fiore, La Deposizione in Galleria Borghese. Il restauro e studi storico-artistici, F. Motta Ed. (2010) ISBN 9788871795812; R. Alberti, T. Frizzi, M. Gironda, M. Occhipinti, T. Parsani, C. Seccaroni, A.Tatì From noise to information. Analysing macro-XRF mapping of strontium impurities in Raphael's Baglioni Entombment in the Galleria Borghese, Rome. Journal of Cultural Heritage Vol. 58, 2022, p 130-136, ISSN 1296-2074; Restauro e lo Studio della Deposizione di Raffaello, presso la Galleria Borghese di Roma, Silvana Ed in press. 2023

Multi-sensor imaging coupled with chemometric techniques for the characterization of pictorial materials

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Multi-sensor imaging in different spectral ranges is gaining an increasing interest as a diagnostic tool in the field of cultural heritage and it has been largely utilized in the last decades thanks to its ability to obtain both spatial and spectral information from analyzed sample [1-2]. In order to evaluate the potential of a multi-sensor approach for the characterization of pictorial materials, several imaging techniques have been applied, i.e. hyperspectral imaging in visible and short-wave infrared ranges (VIS-SWIR HSI), macroscopic X-ray fluorescence (MA-XRF) and macroscopic Fourier transform infrared scanning in reflection mode (MA-rFTIR), to an oil painting attributed to Giacomo Favretto [3]. A multi-sensor methodological approach is proposed to combine the advantages of each spectroscopic technique for the optimal identification and correlation of the elemental and molecular composition of the different investigated pictorial materials (i.e., pigments, dyes, varnishes and binders) [3]. The main purpose of this study is the development of a chemometric approach extracting the most relevant information from huge spectral data to recognize the specific spectral features of a material, even in mixtures. This work is part of the ARTEMISIA project (ARTificial intelligence Extended-Multispectral Imaging Scanner for In-situ Artwork analysis) [4] funded by Lazio Region (Italy) in the contest of DTC Excellence Centre for Cultural Heritage.

[1] Bonifazi, G., Capobianco, G., Serranti, S., & Calvini, R. (2020, September). Image data fusion applied to pictorial layers recognition. In 2020 Italian Conference on Optics and Photonics (ICOP) (pp. 1-4). IEEE.
[2] Catelli, E., Li, Z., Sciutto, G., Oliveri, P., Prati, S., Occhipinti, M., Tocchio, A., Alberti, R., Frizzi, T., Malegori, C. & Mazzeo, R. (2023). Towards the non-destructive analysis of multilayered samples: A novel XRF-VNIR-SWIR hyperspectral imaging system combined with multiblock data processing. Analytica Chimica Acta, 1239, 340710.
[3]https://www.aboutartonline.com/ldea-il-bozzetto-e-poi-lopera-un-bozzetto-inedito-spiega-la-tecnica-pittorica-di-giacomo-favretto/
[4] https://artemisia.lnf.infn.it

Non-invasive analyses of E. Chevreul's chromatic circles

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During the early 19th century colour's theories flourished together with the contemporaneous development of spectrophotometry and dedicated apparatus [1]. In this context Eugène Chevreul (1786-1889), recently appointed as the head of the Gobelin's manufacture, developed a three-dimensional hemispherical colour space that is still used as a reference nowadays to identify and classify colours. It is composed of a dozen of chromatic circles (whose colours are folded down by a linear increasing proportion of black) designed for craftsmen to: 1) define colours, 2) visualize the mixing of two different colours, and 3) visualize the colours simultaneous effect of contrast [2]; this former point is the concrete application of his law of contrast.

In order to characterize the materials and techniques used to realize the chromatic circle, non-invasive macro X-ray fluorescence, visible hyperspectral imaging, and reflectance Fourier Transform InfraRed spectroscopies have been combined. It allowed the characterization of both inorganic and organic pigments applied during the intaglio printing on copper (also known as chromocalcography) (Fig.1) and provided additional information regarding their degradation level. Additionally, the results obtained were compared to the colorimetric measurements of a later edition of 1864, performed by F. Viénot *et al.* in 2001 [3], to further investigate the variability of the two published versions.

Chevreul's chromatic circles played a central role for numerous artists from the turn of the 19th century, most notably neo-impressionists, and among them Paul Signac (1863-1935). The painters used and replicated these chromatic systems and laws in their paintings [1]. As such, the characterization and understanding of Chevreul's colours classification system represent a unique opportunity to better understand their creative process.

Figure 1 : 1st chromatic circle of E. Chevreul containing the bold colors, "Cercles chromatiques de M.E. Chevreul reproduits au moyen de la chromocalcographie par R.H. Digeon", 1855- BNF [2]

[1] J. Gage, « 9. Colour under Control: The Reign of Newton », in *Colour and culture-Practice and meaning from Antiquity to Abstraction*, Thames & Hudson, 1993, p. page 153-176.

[2] « Cercles chromatiques de M. E. Chevreul, reproduits au moyen de la chromocalcographie, gravure et impression en taille douce combinées par R.-H. Digeon », 1855.

[3] F. Viénot et A. Chiron, « Michel–Eugène Chevreul and his colour classification system », *Color Res. Appl.*, vol. 26, nº S1, p. S20-S24, 2001.

New insights into ancient Egyptian bronze votive coffins for animal mummies through Neutron Imaging and Neutron Activation Analysis

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A comprehensive study of eight so-called "bronze votive coffins for animal mummies" is being undertaken by a multidisciplinary team of scientists from Italy and The Netherlands in cooperation with Museo Egizio of Torino (Italy), in the framework of the INFN CHNet_NICHE project. The aims of the study still in progress are a) to determine the faunal remains inside the coffins and b) to obtain detailed data about the manufacturing method – the so-called "lost-wax technique" – by means of a non-invasive methodology. Neutron CT scans revealed both the 3D structure of the coffins and the mummy packages, enabling the gain of direct insights into technological choices and craftsmanship in the context of the Egyptian Late Period and Graeco-Roman bronze casting and animal mummy manufacture. As will be shown, the results obtained on the bronze figure of a cat (Cat. 887) allow for the characterization of the microstructure and porosity of the alloy and the identification of the core pins necessary for casting hollow objects, next to other technological elements. Furthermore, the faunal remains and textile wrappings can be discerned in detail. Besides X-ray and Neutron CT scans, X-ray fluorescence (XRF) and Neutron Activation Analysis (NAA) are used to non-invasively determine elemental composition and concentrations in the bronze alloy beyond the external corroded surface. These results suggest, for example, that gold was not only used on the exterior of the coffin but also in some items inside. In this study we demonstrate the effectiveness of the scientific techniques mentioned above also for the totally non-invasive study of faunal remains inside the bronze votive coffins. The present study answers key analytical and conservation questions and provides unique and never-seen-before morphological data and microstructural information that allow for further insights into the sophisticated manufacturing method of those bronzes.

Keywords: tomography; elemental composition; bronze sculpture; animal mummy; neutron; non-invasive analysis.

Fig. 1 (left) Neutron Computed Tomography (CT) reconstruction of the cat bronze statuette Cat. 887 of the Museo Egizio, Torino. (right) distribution of gold from the NAA experiments.

Use of X-Ray imaging techniques for analysis in the Cultural Heritage field

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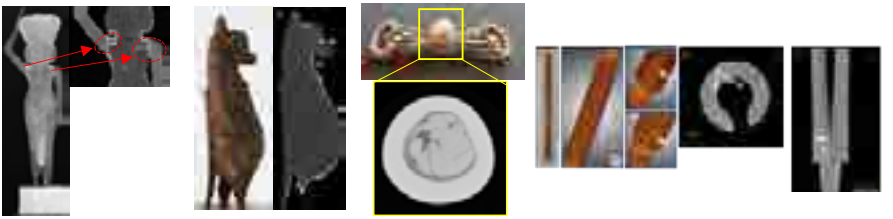
The study and development of different types of instruments based on X-ray emission has had a great boost over the decades. In particular, computed tomography (CT) used mainly for analysis in the medical field, is now widely applied in many other areas, including Cultural Heritage: thanks to the non-invasiveness and the high penetrating power of X-rays, CT applied to objects of artistic and cultural interest is very widespread [1, 2]. In particular, it allows the visualization and study of the internal structure, thus obtaining information on the composition, manufacturing techniques and state of conservation. Due to the high heterogeneity of the constituent materials, the shapes and sizes of these type of objects, specific experimental set-ups have been developed over time, optimized for the different needs.

In this work, different applications of CT analysis on different kind of artifacts are shown: the analysis allowed to distinguish some features otherwise visible only with invasive techniques requiring the cut of the samples. Some interesting results obtained will be presented, highlighting the versatility in analysing objects ranging from centimetres to half a metre such us pearls, ceramics, wooden statuettes. For example, on wooden statuettes from Ancient Egypt valuable information about the techniques of assembly, execution, gilding and previous interventions were provided [3, 4]. Moreover, micro-CT was able to distinguish natural from cultured pearls [5]. Furthermore, CT analysis was applied also to historical woodwind musical instruments (18th century) [6] with the aim to finally get playable replicas realized with additive manufacturing technique and replicate their ancient sound, since, for conservation reasons, is not possible to directly play the originals.



[1] Morigi, M.P. et al., 2010, *Applied Physics* A, 100, pp. 653-661.
[2] Re, A. et al., 2014, Heritage Science, 2:19
[3] Vigorelli, L. et al., 2021, *J. Imaging*, 7, 229
[4] Vigorelli, L. et al., 2022, *ACTA IMEKO* (2022) Volume 11, Issue 1, March 2022, pp 1-10
[5] Vigorelli, L. et al., 2021, *Condens. Matter*, 6, 51.
[6] Tansella, F. et al., 2022, *J. Imaging*, 8, 260.

Non-invasive characterization of the first papers produced in Rio de Janeiro (Brazil) in 1809

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On November 22nd 1809, one year after the Portuguese royal family moved to South America, Friar José Marianno da Conceição Vellozo (1742-1811) sent a letter to Count of Linhares (Dom Rodrigo de Sousa Coutinho, 1745-1812), Secretary of State for Foreign Affairs and War, attaching "The First paper, made in Rio de Janeiro on November 16th 1809". It also announced that a bleached example would follow. With these successful experiments, Vellozo wrote, Portugal would soon have its first paper factory in Brazil.

Produced from native plant fibres instead of linen, cotton or rags, these two examples are the only known survivors of earliest papers produced in Brazil. They preceded later XIXth century papermaking initiatives using Brazilian native plants as raw material.

In situ characterization with portable equipment and non-invasive organoleptic and spectroscopic analytical techniques of EDXRF and FTIR revealed an unusual composition. In addition to comparative results of the elements and chemical compounds identified in these examples principal component analyses (PCA) were applied, making clear the differences between Brazilian and European papers, suggesting innovations in the papermaking process.

Figures: Image reproduction of Friar José Marianno da Conceição Vellozo's papers.
On the left, *O Primeiro papel, que se fez no Rio de Janeiro a 16 de Novembro de 1809* (*The First paper, made in Rio de Janeiro on November 16th 1809*). Ink on paper, 31,0 x 22,0 cm.
On the right: the second paper. Collection Museu Imperial (Petrópolis, RJ).

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Optimization of the methodology for the FT-IR spectroscopic characterization of archaeological human long bone samples

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In this work we discuss an optimized methodology for the spectroscopic characterization of archaeological human long bone samples. Long bone fragments from a prehistoric archaeological site in Cyprus were analyzed by FT-IR imaging and spectroscopy at the DAFNE-Light Synchrotron Radiation Facility[1]; each sample was prepared for reflection analysis by incorporating a fragment of approximately 1 cm in resin and polishing it. Simultaneously, a small amount of bone dust from the cortical region was collected. Attenuated total reflection (ATR), external reflection (ER) FT-IR spectroscopy and FPA imaging analysis were used to analyze them.

The aim of this work is to understand which IR spectroscopy modalities are best suited to answer different archaeologically relevant questions, such as bone composition, calculation of diagenetic indicators, collagen distribution within the bone and more. Archaeological human remains and their contexts provide direct data on populations living in the Eastern Mediterranean, considered a key region for understanding key developments in human history. Furthermore, the obtained result are useful in optimizing future sample preparation protocols and assist in targeted sample selection for future research applications such as DNA & isotope analysis.

Keywords: FT-IR spectroscopy, Attenuated total reflection (ATR), External reflection (ER) FT-IR, FPA Imaging analyses, archaeological human long bone.

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Registration of multimodal images of artworks: an approach based on mutual information

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An essential but challenging step in the interpretation and presentation of multimodal technical imaging of artworks is image registration. Typical feature-based registration algorithms may struggle to provide successful registration results as the individual images in the multimodal set may have dissimilar levels of brightness and different features may be apparent in each of the various modalities. Thus, a new automated approach for the registration of multimodal technical images based on incremental maximisation of mutual information is proposed. The approach makes use of metrics that rely on the overall pictorial composition of the working images and is based on methods utilised in the medical imaging sector [1]. The method was developed for the registration of stacks of element distribution maps resulting from macro X-Ray Fluorescence (MA-XRF) scanning of works of art to a target visible image but can be used for a range of image types including infrared reflectograms, X-radiographs and raking light and UV-induced luminescence images. The results obtained with a selection of Tudor and Stuart period portrait miniatures included in the 'Unlocking the English Portrait Miniature' web resource developed at the Fitzwilliam Museum in Cambridge [https://unlocking-miniatures.fitzmuseum.cam.ac.uk] will be presented.

The stack of XRF element maps is treated as the moving image and, in a consecutive manner, the slices of this stack are individually registered to the target visible image (Fig. 1). All transformations within a prescribed range of parameters are evaluated for each slice of the stack. The transformation that provides the highest average mutual information across all slices is then kept to serve as the starting point for the next stage. This allows the best transformations with consensus among all element slices to be identified. The result is a unique, optimised transformation that can be applied to each XRF map within the image stack. The registration results obtained will be presented. The potential benefits to the final registration of augmenting the stack by including an additional composite, made by merging two or more element maps specifically selected for a given artwork, will also be discussed.

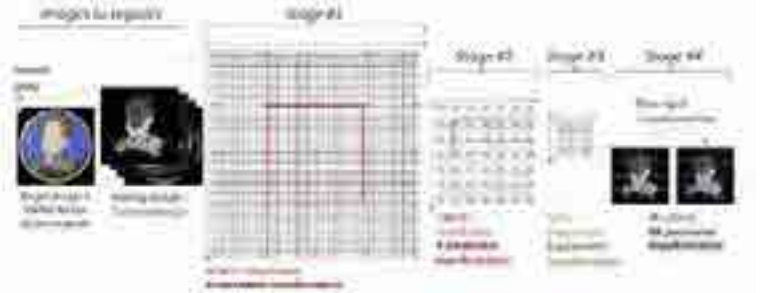

Fig. 1 - Stack of element maps [2] for individual registration in consecutive stages. The resulting transformation can be applied to the moving image to obtain the best alignment between the two images when overlapped.

[1] K. Marstal, F. Berendsen, M. Staring and S. Klein, "SimpleElastix: A user-friendly, multi-lingual library for medical image registration," International Workshop on Biomedical Image Registration (WBIR), IEEE Conference on Computer Vision and Pattern Recognition Workshops, pp. 574 - 582, July 2016.
[2] The Thomson Collection at the Art Gallery of Ontario: Images of the miniature portrait of Jane Boughton.

Laboratory and synchrotron x-ray computed microtomography to investigate corroded Roman glass

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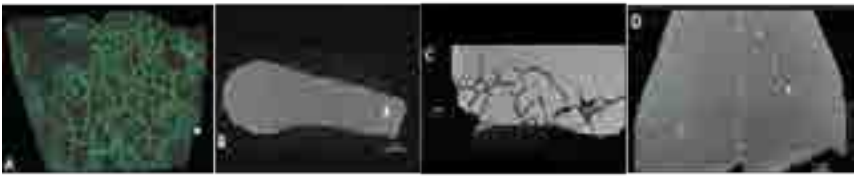
Computed tomography (CT) is a non-destructive diagnostic technique ideal to obtain structural and compositional information from cultural heritage objects [1,2]. This work explores, in a non-destructive manner, the 3D inner structure of ancient glass fragments using both laboratory X-ray micro-computed tomography (µCT) and phase contrast synchrotron X-ray computed microtomography (SXµCT). For this purpose, three degraded glass samples affected by diffused 3D cracking were characterized combining medium resolution scans obtained with the UniTO-INFN laboratory CT instrument (in the framework of the OpenAIAr project [3]) and high-resolution synchrotron radiation microtomography at Elettra Sincrotrone (Proposal n. 20222195). The µCT scan allowed to visualize the cracks in the reconstructed volume and to appreciate their internal structure and size (voxel size between 7µm and 11 µm). Several cracks totally filled with mineralized material, possibly coming from the soil in which the object was buried for centuries, extend into the bulk below the glass surface as visible in the slices reported in the figure below. The scans collected from SXµCT enable 3D reconstruction with higher spatial resolution (up to ~ 2 µm), and so to observe in detail the distribution of the material filling the fractures. The grains of the soil are clearly distinguishable as well as the areas into the cracks where air is present. Compared to µCT, the SXµCT scans highlight the welding effect of the material inside the cracks that seems to act as cement between the single glass fragments. This result turns high-resolution µCT analysis to be a valuable technique to aid restoration interventions on glass objects, when cleaning actions are required to remove adventitious soil from the cracks, and the loss of cohesion between the fragments of unaltered glass must be avoided.



[1] L. Vigorelli, A. Re, P. Buscaglia, N. Manfredda, M. Nervo, T. Cavaleri, P. Del Vesco, M. Borla, S. Grassini, L. Guidorzi, A. Lo Giudice, Journal of Archaeological Science: Reports 44 (2022) 103518.
[2] F. Albertin, M. Bettuzzi, R. Brancaccio, M.P. Morigi, F. Casali, Heritage. 2 (2019) 2028–2038.
[3] https://www.associazioneaiar.com/wp/openaiar/

To be or not to be - On the use of biosignatures approaches for the analysis of parchment origin

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Produced from sheep, goat, or calf skins, parchment is an important reservoir of historical, cultural, and biological information [1, 2]. Determining the origin of the animals used to produce the parchments of illuminated manuscripts is an important task for the characterization of manuscripts, scriptoria, and ateliers, as well as for the conservation of the documents [1, 3–5]. Traditionally, parchment animals' origin is identified based on the analysis of the follicular pattern, however, some of them are very similar or may have undergone morphological changes during the production of the manuscript, that difficult the identification of the animal [5]. Over the last few years, molecular analysis has been used for the identification of parchment animal origins, reducing the amount of samples required for the analysis, and improving the accuracy of the identification of the animal origin [1, 6]. Other studies have focused on microbiome analysis of parchments by Next-generation sequencing (NGS), either for the identification of its colonizers, for establishing a relation between some microorganisms with their damage potential, or for conservation matters [1, 4, 7].

In this work, several DNA extraction methods and PCR-based assays were optimized for the specific identification of mostly animals used in parchment production. After that both invasive and non-invasive techniques were tested in parchment samples and compared to establish a viable method to identify the parchment origin, that could minimize the amount of sample, conserving and preserving as much as possible the ancient documents. The optimized methodology was further applied in some case studies. Furthermore, a microbiome analysis was performed by High-throughput sequencing (HTS), as a way of identifying microbial communities that colonize the surface of those parchment manuscripts and trying to perceive if there is a microbiome pattern associated with a specific type of parchment.

Overall, it was possible to establish a method that could characterize several parchment manuscripts, by identifying their animal origin and their microbiome with very low invasiveness.

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[1] S. Fiddyment, M. D. Teasdale, J. Vnouček, É. Lévêque, A. Binois, and M. J. Collins, "So you want to do biocodicology? A field guide to the biological analysis of parchment," *Herit. Sci.*, vol. 7, no. 1, pp. 1–10, 2019.
[2] M. G. Campana *et al.*, "A flock of sheep, goats and cattle: Ancient DNA analysis reveals complexities of historical parchment manufacture," *J. Archaeol. Sci.*, vol. 37, no. 6, pp. 1317–1325, 2010.
[3] N. Poulakakis, A. Tselikas, I. Bitsakis, M. Mylonas, and P. Lymberakis, "Ancient DNA and the genetic signature of ancient Greek manuscripts," *J. Archaeol. Sci.*, vol. 34, no. 5, pp. 675–680, 2007.
[4] G. Piñar, F. Cappa, W. Vetter, M. Schreiner, H. Miklas, and K. Sterflinger, "Complementary Strategies for Deciphering the Information Contained in Ancient Parchment Documentary Materials," *Appl. Sci.*, vol. 12, no. 20, 2022.
[5] D. Pangallo, K. Chovanova, and A. Makova, "Identification of animal skin of historical parchments by polymerase chain reaction (PCR)-based methods," *J. Archaeol. Sci.*, vol. 37, no. 6, pp. 1202–1206, 2010.
[6] S. Fiddyment *et al.*, "Animal origin of 13th-century uterine vellum revealed using noninvasive peptide fingerprinting," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 112, no. 49, pp. 15066–15071, 2015.
[7] G. Piñar, H. Tafer, M. Schreiner, H. Miklas, and K. Sterflinger, "Decoding the biological information contained in two ancient Slavonic parchment codices: an added historical value," *Environ. Microbiol.*, vol. 22, no. 8, pp. 3218–3233, 2020.

Multi-analytical approach to assess the Protective Coatings for the safeguard of Street Art Cultural Heritage

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Street Art has assumed a social, political, and ethical value worldwide only in the latest years, leading to its recognition as a Cultural Heritage to be protected [1]. This awareness introduced new evaluations to be developed both in the field of conservation practices, still limited to interventions on more traditional artworks, and in the diagnostic field, for the knowledge of painting techniques, the characterization of manufactured paint materials, their interaction with the outdoor environment, and their degradation and chemical-physical stability [2].

For this reason, studying protective coatings has become a necessity to preserve the integrity of these works of art. Their main characteristics include transparency, reversibility, surface compatibility, long-term durability, low-cost maintenance, and non-toxicity. They allow to confer to the painted surface the following properties: water and oil repellency, chemical and photochemical stability, heat and mechanical resistance, resistance to vandalism and biodeteriogen actions. The classes of materials generally used are silanes and siloxanes, acrylic resins, fluorinated polymers, and anti-graffiti systems, mainly waxes. Considering that their application for the protection of Street Art is still limited [3], this research project has the main objective of testing the compatibility, efficacy, and ageing stability (by temperature excursion, UV irradiation, and rain washout) of purposely selected commercial protective coatings both on mock-ups and on real artworks.

Compatibility with the substrate and the paint materials, effectiveness, as water repellents and their stability in different exposure conditions, will be tested using non-invasive and micro-invasive techniques. Colourimetry, glossmetry, and Fiber Optic Reflectance spectroscopy (FORS) will be used to verify aesthetic compatibility. The interaction between water and the paint layer with and without the protective coating, will be studied by measuring the changes in contact angle and water absorption by capillarity [4]. Also important will be the adhesion of the layers which will be evaluated by microscopic observations and surface mechanical testing (micro-scratch test). Finally, for the evaluation of the coating stability before and after artificial ageing, ATR-FTIR will be performed [5].

This work presents the planned experimental campaign of the research project and the preliminary results, together with the scientific considerations that have emerged. Within the framework of the SuperStar project [6] coordinated by prof. F. Modugno (University of Pisa), it aims to strengthen the collaboration among the various partners in the diagnostic, scientific, and conservation sectors, supporting the institutions engaged in the conservation of urban muralism and developing new conservation guidelines.

[1] A. Cadetti, Conservare la street art. Le problematiche del muralismo contemporaneo in Italia, Italy, 2020.
[2] P. Mezzadri, Heritage 4, 2021, 2515–25.
[3] J. La Nasa, et al, Journal of Cultural Heritage, 48, 2021; 129–40.
[4] A. Macchia, et al, Journal of Cultural Heritage, 41, 2020, 232–7.
[5] L. Pagnin, E. Zendri, F.C. Izzo, Polymers, 14, 2022, 1831.
[6] PRIN SUPERSTAR - Progetto di Ricerca di rilevante interesse Nazionale Bando 2020 - Prot. 2020MNZ579. https://Prin2020superstarDcciUnipiIt/ 2021.

Mechano-chemical monitoring of plastic degradation: surface and sub-surface modification of artificially aged ABS

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The 1960s saw the definitive affirmation of plastic as an indispensable part of everyday life and thanks to its versatility it has also conquered the vast fields from toys, car parts, food packaging to design and art. Understanding the physical and chemical properties of these complex systems is crucial for defining their degradation tendency, monitoring their conservation state, and developing appropriate preservation strategies. In this work, a new mechanochemical approach is presented to reveal the combined compositional and structural properties of plastic materials at both surface and sub-surface levels informing about the conservation state and monitoring the degradation. Acrylonitrile-Butadiene-Styrene (ABS) is chosen as a case study widely used in art and design objects. It is a copolymer made of acrylonitrile–styrene continuous phase (SAN) and partially grafted polybutadiene (PB, as a dispersed phase) acting as an impact modifier and giving excellent mechanical properties to the material. Photochemically aged ABS has been studied by combing conventional spectroscopic methods (external reflection FT-IR spectroscopy in the mid and near-IR ranges) and Brillouin and Raman micro-spectroscopy (BRaMS), an innovative method only recently applied in the field of heritage science [1]. BRaMS enabled combined measurements of Brillouin light scattering (BLS) and Raman spectroscopy in a micro-spectroscopic setup providing for the simultaneous monitoring of chemical and mechanical changes occurring during ageing, mainly at the sample surface [2]. The simultaneous probing of the chemical and mechanical properties enabled us to associate the compositional change responsible for the photochemical degradation with the corresponding variation in sample stiffness and rigidity. Modifications of the mechanical properties were also assessed by Unilateral NMR spectroscopy, which allowed to perform non-invasive bulk measurements of relaxation times and profilometry directly related to the molecular mobility of the material [3]. The knowledge acquired on model samples has been finally applied to monitor the conservation state of design plastic objects made of ABS and non-invasively investigated through the MOLAB platform of the European Research Infrastructure of Heritage Science-ERIHS.

[1] M. Alunni Cardinali, et al., Sci. Adv., 8(26), 2022
[2] F. Scarponi, et al., Phys. Rev. X, 7(3), 2017, 031015
[3] B. Blümich, et al., Acc. Chem. Res., 43(6), 2010, 761-770

HVPD-hydrogel as a smart cleaning solution for removal of corrosion patinas and aged resins on carbonate stone materials

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Carbonate stone materials have been widely used since ancient times for the realization of artistic and architectural works of inestimable value. However, due to their chemical and structural nature, they are subjected to multiple forms of degradation. Important problems in the field of cultural heritage are formation of corrosion products of metallic materials, that could be present in the stone as impurities or as metallic artefacts [2, 3] and acrylic and vinyl resins, that over time have undergone photochemical and thermal reactions, resulting difficult to remove [3]. Classic methods of intervention could present the risks of irreversibility and pollution, so the demand for high performing systems is growing [3]. The aim of this research is to develop and test an eco-friendly and versatile method, able to make the cleaning process safe both for artifacts and users, through the use of a High Viscosity Polymer Dispersion [2]. This method involves the use of a soft matter that avoids dispersion and permanence of products in porous matrices or evaporations of solvents during the application, since it consists of a High Viscosity Polymeric Dispersion Hydrogel (HVPD-hydrogel). The product has been tested on samples of Travertine, Lecce Stone, and Carrara Marble and was obtained from the cross-linking reaction between PVA and borax; it was enriched with chelating agents to remove bronze corrosion patinas, artificially induced on the specimens and will be tested in the case of aged acrylic and vinyl resins. Two types of HVPDs with different concentrations of borax have been synthesized, to evaluate the difference in mechanical properties; the best formulation was enriched with two different types of chelants: EDTA and TSC. On all specimens of HPVDs-hydrogel Flow Sweep experiments were conducted, to evaluate the dynamic viscosity, and Frequency Sweep experiments, to evaluate mechanical properties. Structural and chemical investigations were conducted on HVPDs-hydrogel using Scanning Electron Microscope, high field Nuclear Magnetic Resonance spectroscopy and relaxometry. Cleaning tests on stones samples were validated by SEM, unilateral low-field NMR and FT-IR ATR.

[1] Stagno, V.; Ciccola, A.; Curini, R.; Postorino, P.; Favero, G.; Capuani, S. Non-Invasive Assessment of Pva-Borax Hydrogel Effectiveness in Removing Metal Corrosion Products on Stones by Portable Nmr. *Gels*, **2021**, *7* (4). https://doi.org/10.3390/gels7040265.

[2] Angelova, L. V.; Matarrese, C.; Fratini, E.; Weiss, R. G.; Dei, L.; Carretti, E. Chelating Agents in Aqueous, Partially-Hydrolyzed, Poly(Vinyl Acetate) Dispersions Crosslinked with Borax. Physicochemical Characterization and an Application. *Colloids Surfaces A Physicochem Eng Asp*, **2018**, *556*, 61–71. https://doi.org/10.1016/j.colsurfa.2018.07.044.

[3] Chelazzi, D.; Fratini, E.; Giorgi, R.; Mastrangelo, R.; Rossi, M.; Baglioni, P. Gels for the Cleaning of Works of Art. *ACS Symp Ser*, **2018**, *1296*, 291–314. https://doi.org/10.1021/bk-2018-1296.ch015.

Analytical investigation into cellulosic materials from traditional Japanese samurai armours

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The presentation aims to show limits and possibilities of ATR-FTIR spectroscopy applied to the study of cellulosic textiles collections. The work discusses some common issues and offers some hints for the interpretation of ATR-FTIR spectra from cellulosic textiles collections.

The spectral differences derived from the plant composition were reviewed and discussed in light of new experimental data, to propose diagnostic bands able to discriminate fibres coming from different plants. Similarly, the influence of the environmental humidity uptake was studied through water absorption tests and peak fitting analysis [1,2]. The contribution of ageing [3] was also considered and replicated through accelerated ageing tests, demonstrating that sometimes aged fibres cannot be reliably recognized. Thus, the visual inspection through SEM, which is relatively non-invasive, is still often decisive in recognizing natural fibres. The proposed protocol was tested on microsamples of various materials coming from traditional Japanese samurai armours dating back from 16th to 20th century (Morigi Collection, Museo delle Culture, Lugano, Switzerland). A part of the work was devoted to the study of metallic threads, a complex and unique multimaterial with specific characteristics in Japanese tradition (*kinran*) which has been characterized for the first time.

The results permitted to get a complete characterization of the materials and demonstrated that the protocol can be useful for the study of a wide variety of cellulosic materials, including fibres, and paper. It was found that it is possible to discriminate natural and regenerated cellulosic fibres, thanks to the OH stretching region, which is the most diagnostic. The method is micro-invasive, quick and simple to use during an analytical campaign on a textile collection and it permits to identify both ancient natural and recent regenerated fibres. The information is of a great help to find out past restoration materials and to reconstruct the history of the work of art. As modified cellulose fibres appeared in 20th century, the recognition of chemical modifications operated on the fibre gives a certain *terminus post quem* for dating or a clear sign of a recent restoration. Eventually, the knowledge could help to find out the best conditions to display objects and to stabilise them for long-term storage.

[1] Olsson AM, Salmén L. The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy, "Carbohydr Res.", 339, 2004, pp. 813–8.
[2] Fengel D. Influence of Water on the OH Valency Range in Deconvoluted FTIR Spectra of Cellulose, "Holzforschung", 47, 1993, pp. 103–8.
[3] Małachowska E, Dubowik M, Boruszewski P, Przybysz P. Accelerated ageing of paper: effect of lignin content and humidity on tensile properties, "Herit Sci.", 9, 2021, pp. 1–8.

Characterization of ancient paper degradation state – micro- and noninvasive multimethod approach

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Paper is the most important information carrier throughout human history and a material holding immense amount of cultural heritage. Paper sheets consist of randomly entwined cellulose fibers with a multilevel, partially crystalline and partially amorphous structure. There is a distinct difference in the durability of paper depending on papermaking technology. The least durable papers are made between 1850 and 1990 due to its high acidity and use of wood as primary fiber source. For this type of paper, acidic hydrolysis of glycosidic bonds can be assigned as the dominant degradation pathway [1]. Thus just measurement of the degree of polymerization (DP) using size exclusion chromatography (SEC) or viscometry can be used to assess its degradation state. Hydrolysis is much slower in the case of ancient papers – their original pH was neutral or mildly basic – and other degradation pathways play a more significant role, i.e. cellulose oxidation and hornification.

Oxidation of cellulose leads to the formation of carbonyl groups, which affect the hydrogen-bond network, increase the brittleness and cause yellowing of paper. Hydrolysis and oxidation proceed predominantly in amorphous regions partially consuming them and partially allowing the growth of crystalline regions. Both processes may lead to the shortening of cellulose macromolecules. Hornification is a result of water adsorption-desorption cycles without chemical changes in macromolecules. It also leads to increased brittleness and is caused by expanding and collapsing pores within fiber structure until they form stiff links, increasing cellulose crystallinity [2]. Finally, all mentioned processes depend on presence of water within fiber's structure and simultaneously affect water adsorption capacity. These processes take place simultaneously affecting each other at all levels of fiber organization. Their relative rates depend both on internal and external factors.

The proposed method involves measurement of DP by SEC, oxidation indexes derived from FT-IR and UV-VIS [3] (later aided with TD/DFT calculations) spectra and various crystallinity indexes obtain by FT-IR and XRD techniques to track progress of hydrolysis, oxidation and hornification in ancient paper samples. All of the techniques can be used micro- or noninvasively and they allow more comprehensive assessment of degradation state, which better insight in degradation process and is essential for informed decision-making on appropriate conservation treatments.

[1] A. Barański, J.M. Łagan, T. Łojewski, e-Preservation Science 3, 2006, 1.
[2] K.L. Kato, R.E. Cameron, (1999) Cellulose 6(1), 1999, 23.
[3] J. Bagniuk, D. Pawcenis, A.M. Conte, O. Pulci, M. Aksamit-Koperska, M. Missori, J. Łojewska, Polymer Degradation and Stability 168, 2019, art. no. 108951.

Characterization of mortars from Romanesque floors excavated in St. Bartholomew's church at Prague Castle

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St. Bartholomew's church is a part of archaeological excavations located at the Prague Castle, Czech Republic. This church stood in the center of the present Third Courtyard in the 12th – 13th centuries. Nowadays, its remains are covered with a reinforced concrete structure below the paving of the Third Courtyard and are not accessible to the public. The last archaeological survey carried out in the church area revealed two Romanesque floors placed above each other. Both of the floors consist of several layers similar to the layers of the Roman floor structures [1]. Mortar samples were collected from each layer of both floors and characterized by means of different analytical techniques. A thin section of each mortar sample was prepared for optical microscopy (OP), scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS). A part of each sample was gently crushed and sieved to obtain a particle fraction under 63 μm. This fraction is supposed to contain almost pure binder particles and was used for thermal analysis (TA) and X-ray diffraction analysis (XRD). During the sample crushing, lime lumps present in mortars were separated and analyzed by means of TA separately. Last parts of mortar samples were dissolved in the hydrochloric acid in order to obtain pure aggregate fraction on which particle size distribution was determined.

According to the results, all mortar samples were made from feebly to moderately hydraulic lime, the degree of hydraulicity of the younger floor mortars was slightly higher. Few lime lumps corresponding to the pure aerial lime were found in all samples and their composition indicates the use of raw materials from different sites. On the other hand, there were no under-burnt lime particles which are usually common in the medieval lime mortars. This could be due to the careful selection of the lime which was intended for the construction of a great importance. A sedimentary limestone from the Prague basin was determined as a raw material used for mortar preparation. Mineralogical composition of aggregates was similar for all mortar samples, individual samples differed slightly in maximal grain size and representation of the size fractions. Quartz was the main mineralogical component, minor components were muscovite, feldspars and clays. Fragments of calcareous marls were also presented. It is supposed that all used aggregates come from the same or analogous source. Differences in the size of the aggregates were probably technologically intended, not the result of the different sources.

This research was funded by the Technology Agency of the Czech Republic, grant number TL03000603, program ETA, project title: "Archaeological areas of Prague Castle as part of the architecture and the national cultural identity in the post-war periods".

[1] Vitruvius, The Ten Books on Architecture, Book VII, Chapter I.

A mineralogical and geochemical database of Fe-bearing mineral pigments from North-Eastern Italy

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The provenance of mineral pigments, especially Fe-oxides and Fe-oxi-hydroxide, is a well consolidated research topic in Prehistoric archaeology [1-3]. This is consequence of the large use of such natural materials for several utilitarian and symbolic applications in many contexts all over the world [4-6]. The most relevant aspect is the possibility to trace gatherers-hunters mobility and possible interactions of different human groups [7].

The provenance of Fe-bearing pigments used in wall paintings, also including Fe-rich silicates such as celadonite and glauconitic minerals, has not been explored in a systematic way as the main interest is related to their characterization, pivotal for planning adequate conservation strategies. However, the knowledge of the provenance may provide important information concerning the routes of the raw materials during historical periods [8], explain the absence of basic pigments in specific sites, establish correlation for sites belonging to the same chronological phase. The source of the mineral pigments may act as a spatial and temporal marker for a more in-depth comprehension of the historical processes behind a heritage site.

The Western part of the Lessini Mountains in North-Eastern Italy represents an ideal setting for studying such materials as they were exploited for long time until at least the middle of the last century [9-10]. The mineralogical analysis carried out through X-ray Powder Diffraction (XRPD) and the geochemical characterization (major, minor and trace elements) through Inductively Coupled Plasma Mass Spectrometry (ICP-MS) allowed for the creation of a database of the raw materials. In particular, the mineralogical and geochemical database allowed for a clear distinction of hematite and goethite based mineral pigments associated to Mesozoic, Cenozoic carbonated rocks and to Palaeogenic volcanoclastic terrains having specific mineral assemblages and/or specific mineral phases. In addition, celadonite from Monte Baldo is clearly marked by the presence of opal-CT; geochemical signatures will also be presented.

[1] Attard Montalto M., Shortland A., Rogers K. Journal of Archaeological Science, 39, (2012), 1094-1102.
[2] Bonneau A., Pearce D.G., Pollard A.M. Journal of Archaeological Science, 39, (2012), 287-294.
[3] Dayet L., Texier P.-J., Daniel F., Porraz G. Journal of Archaeological Science, 40, (2013), 3492-3505.
[4] Velo J. Current Anthropology, (1984), 25(5), 674.
[5] Schmandt-Besserat D. The Coming of the Age of Iron, Yale University Press, (1980), 127-150.
[6] d'Errico F., Moreno R. G., Rifkin R. F. Journal of Archaeological Science, 39, (2012), 942-952.
[7] Pradeau, J.-V., Binder, D., Vérati, C., Lardeaux, J.-M., Dubernet, S., Lefrais, Y., Regert, M. Journal of Archaeological Science, 71, (2016), 10-23.
[8] Secco, M., Rainer, L., Graves, K., Heginbotham, A., Artioli, G., Piqué, F., Angelini, I. Minerals (2021), 11, 67, 1-35.
[9] Cavallo G., Fontana F., Gonzato F., Peresani M., Riccardi M. P., Zorzin R. Geoarchaeology, (2017a) 32, 437-455.
[10] Cavallo G., Fontana F., Gonzato F., Guerreschi A., Riccardi M.P., Sardelli G., Zorzin Journal of Archaeological and Anthropological Sciences, (2017b), 9(5), 763-775.

New findings on the Rijksmuseum *Holy Family* attributed to Giovanni Larciani. The role of complementary non-invasive analytical techniques such as MA-XRF and RIS.

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The Florentine panel painting from the beginning of the XVI century depicting the *Holy Family with the Infant John the Baptist*, formerly attributed to Fra Bartolommeo's circle, and now to Giovanni Larciani and others, was studied as part of the Italian paintings catalogue project in the Rijksmuseum. The close examination of the paint surface was aided by a series of traditional and novel complementary non-invasive analytical techniques. Among these, macro X-ray fluorescence scanning (MA-XRF), reflectance imaging spectroscopy (RIS, both SWIR and VNIR) and fiber optics reflectance spectroscopy (FORS). A small number of micro samples were also studied with light microscopy and scanning electron microscopy with energy dispersed X-ray analysis (SEM-EDX) to answer specific questions.

New technical findings revealed an unexpected complex genesis for this workshop piece. They showed many changes in composition, both in the underdrawing and in the painting phases, with major parts, such as the gestures of the main Virgin and Child group, and the architectural background, reworked various times. The combination of elemental information from MA-XRF, coupled with molecular information coming from the spectroscopies, aided by statistical approaches such as MNF, allowed to distinguish at least four types of underdrawing media. This, coupled with at least two ways of paint handling and build-up, suggests the presence of various hands. The analytical approach also allowed for the interpretation of the sequence in which the changes evolved; and helped to understand the origin of the element zinc that was discovered in the original layers of the painting.

Figure 1. Giovanni Larciani and others, *The Holy Family with the Infant John the Baptist*, 1505-15 circa, Rijksmuseum, SK-A-3376; (a) overall; two previous versions of the architecture at top right can be seen in the MA-XRF Zn-K (b) and combined MA-XRF Hg-L and Cu-K, shown respectively in red and green, in (c); four 5x5cm details --areas indicated by the squares in (a)—of the RIS-SWIR false-colour (1050, 1300, 1700 nm) are shown in (d-e-f-g), different kinds of underdrawing can be seen.

Portable CT characterization for in situ analysis

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The development of portable CT solutions for in situ analysis of cultural heritage artifacts has become increasingly popular among research institutes and museums. The challenge is to create a device capable of inspecting objects of high cultural value in a non-destructive manner, generating high-resolution data. Another requirement is the low interference in the conservational activities occurring simultaneously to the inspection work. The analysis equipment must be characterized, and its settings, optimized. For the purpose of this research work, a portable CT system was developed and image quality tests were conducted. The CT system is composed of a portable Tungsten target X-Ray tube, an a-Si flat panel detector, and a rotary table controlled by arduino. Quantitative tests for the measurement of the focal spot size, modulation transfer function (MTF), and spatial resolution were performed for different exposure and acquisition settings. The quality of the X-Ray incident spectrum was also evaluated, as well as the isodose curve. Once the quality tests were successfully performed, the system was deployed to analyze statues, carved wooden panels, and paintings on wooden boards. A procedure to merge multiple scans for objects larger than the field of view was also developed. The results depicted the importance of the characterization tests in order to establish the detection limits of the system, with optimized acquisition settings and lower radiation exposure to field analysis conditions. The merging of multiple scans proved to be efficient for evaluating large objects, as the resulting images displayed sufficient spatial resolution and contrast sensitivity. Additionally, the details of the analyzed pieces could be clearly visualized and quantified.

A novel MA-XRD/MA-XRF scanner for pigment-specific mapping of paintings

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Pigments often present a polycrystalline nature and X-ray powder diffraction (XRPD) can be used for their direct identification even in the case of complex mixtures.
This work presents a novel MA-XRD/MA-XRF system developed at the XRAYLab of ISPC-CNR in Catania. The main component of the device is a measurement-head consisting of a microfocus Cu-anode source coupled to a slightly focusing polycapillary and two X-ray detectors for recording both XRD patterns and XRF spectra simultaneously on the same irradiated spot. A mechatronic device moves the measurement-head in 1mm steps along the XY directions. A total area of 50x50cm2 can be covered in one scan. A laser distance sensor controls an ancillary Z axis to keep the focus position pixel-by-pixel during the scanning allowing us to measure paintings even with an irregular morphology. The device operates XRD measurements in a parafocusing geometry. Diffraction patterns are collected in one-shot with a 1D microstrip single-photon-counting detector covering an angular range of 16-44deg (2θ). Angular resolution in the diffraction patterns is about 0.25deg and typical dwell-time per pixel is about 3s. In parallel, a SDD detector collects the fluorescence spectra on the same irradiated spot allowing to combine XRF and XRD distribution maps during the analysis.
For one scanning session several tens of thousands of XRD patterns are recorded. Given the number of patterns, a manual analysis of the full dataset is not feasible. Hence, we have modeled the measurement geometry and we have developed a custom-built minimization routine for the automatic pixel-per-pixel analysis including theta-shift correction, XRD pattern calibration and crystalline phase identification. MA-XRF data are used to inform the analysis during the search-match procedure of the crystalline phases. Finally, we have extended the analytical methodology to determine the crystalline phases distribution even for stratigraphic samples, as in the case of paintings. Some results on compelling application in painting analysis are presented and discussed.

The formation of metal soaps in oil paintings under variable relative humidity followed by ATR-FTIR

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The deterioration of oil paintings due to the formation of metal soaps is an extended phenomenon which affects some of the most significant paintings by artists of relevance of different periods [1]. Metal soaps are formed by the reaction of the free fatty acids of a drying oil with some metal ions contained in the pigment such as lead or zinc. Their formation mechanism includes the generation of metal carboxylates in a first step, developing an ionomeric-like structure which will subsequently lead to the crystallization of metal soaps [2]. The effect of the different environmental conditions on this mechanism is a field of study that has yet to be deepened. Although some studies have shown that certain conditions of relative humidity and temperature favor the formation of metal soaps, in most of the works carried out to date, extreme conditions of accelerated aging have been adopted, far away from what usually occurs in reality. Besides, fixed values of temperature or relative humidity are generally tested [3].

The main objective of this research is to study the influence of the variability of the relative humidity on the formation rate of metal carboxylates during the first stage of curation. To this aim, models of oil paints were prepared using different pigments containing lead or zinc and two types of siccative oils: cold-pressed linseed and nuts oils. Dried painting models were then cured under different relative humidity (RH) conditions: 30, 50 and 70 % RH and 8 hours cycles of variable RH between 30-50 and 50-70%. Temperature was set to 21ºC in all cases and the maximum curing time was 16 weeks.

Formation of metal carboxylates was recorded by ATR-FTIR analysis at different curing times on both the external and internal surfaces of the painting. The area of the metal carboxylate bands around 1500 cm^{-1} and the free fatty acid around 1700 cm^{-1} were normalized to the ester band (~1730 cm^{-1}) and plotted versus curing time. In some cases, metal carboxylates start forming during the drying process and the intensity of the bands increases very fast in the first weeks and slows down afterwards. Pigment degradation with time was followed by XRPD. This methodology allows to investigate the effect of the relative humidity, fixed of variable, on the first stages of formation of metal carboxylates in oil paintings.

[1] P. Noble, A. Van Loon, J.J. Boon, Chemical changes in old master paintings II: darkening due to increased transparency as a result of metal soap formation processes. In: 14th triennial meeting, The Hague, 12-16 September 2005: ICOM Committee for Conservation: preprints Verger, James & James, 2005, vil.1, pp 496-503.
[2] J. J. Hermans, Metal soaps in oil paint: Structure, mechanisms and dynamics. Amsterdam: Ph.D. Dissertation, Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, 2017
[3] F. Casadio, K. Keune, P. Noble, A. Van Loon, E. Hendriks, S. A. Centeno, G. Osmond, G.in: Metal Soaps in Art. Conservation and Research. Ed. Springer, New York (2019).

Thermal transformation of chalcedonite artefacts from the Magdalenian site of Ćmielów 95 ”Mały Gawroniec” (Poland)

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Two chalcedonite artefacts from the Magdalenian (15000-8000 BC) site of Ćmielów 95 (Poland), with macroscopic features suggestive of thermal treatment, were subjected to a multi-instrumental analysis (fig.1): computed tomography (CT), Raman spectroscopy (RS), electron X-ray microanalysis (EPMA) and X-ray diffraction (PXRD). The red upper layer of the objects consists of ”protohematite”, implying temperature-driven goethite-to-hematite transition. The red layer shows traces of carbonized matter with saccharides and levoglucosan (from burning wood) as well as fatty acids. PXRD data suggest a source of higher temperatures (up to ~800 ^{o}C) within the bottom layer, with ~200-300 ^{o}C range ascribed to the red layer. On the basis of the collected data the artefacts are proposed to be relics of cooking stones.
The structure of the hearths in which the chalcedonite slabs functioned as “frying-pans” covering the combustion zone from the top. The manner of thermal treatment without a direct contact with flames/open fire. It appears that such a procedure, which combined frying with smoking or drying, not only improved the taste of the food, but was also a way of food preservation. The type of fuel – deciduous tree wood, most likely birch or willow.

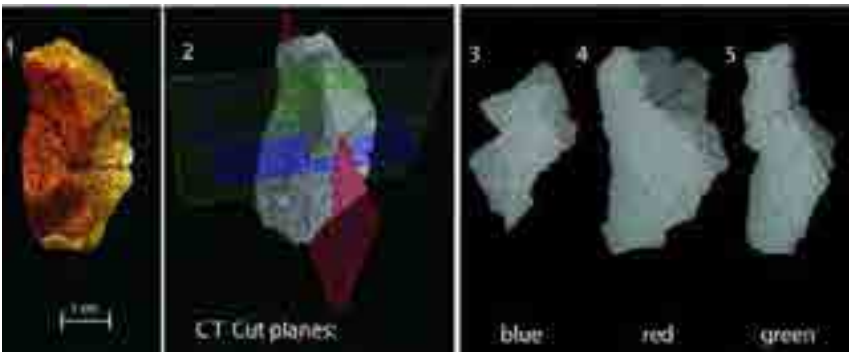

Fig. 1. Structure of the analysed artefacts. CT images.

Cutting-edge techniques for the investigation of ancient flax textiles

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Textiles are common materials in the fields of art and archaeology, but they are often overlooked by archaeologists and researchers in favour of metals, stones, ceramics, glass and pigmented layers. Thus, although textiles can be useful for understanding the structure of human societies and the cultural exchanges between ancient populations, the literature on the degradation mechanisms of plant fibres as well as the fibre processing or the interaction between plant fibre cells and foreign materials is scarce. However, this situation has gradually changed in recent years thanks to an increasing interest in textiles [1,2].

For the work presented here, several flax yarns were sampled from a palette of different objects from ancient Egypt kept at the Louvre Museum (Paris, France). This work aimed at combining cutting-edge characterization techniques, like atomic force microscopy or X-ray micro- and nanotomography, to better understand the flax fibres' degradation mechanisms found in different archaeological contexts. Both synchrotron and laboratory facilities were used to obtain information on mechanical properties, biochemistry and fibre ultrastructure.

One example is a single thread of a funerary fabric dated 2140-1976 BC and kept at the Louvre Museum. Figure 1.a shows the detail of an elementary flax fibre observed by scanning electron microscopy (SEM); big defects were detected. Although the defects appeared undamaged, they proved to be deeply fractured under second harmonic generation microscopy (SHG) (Figure 1.b). In complement, when examined by atomic force microscopy (Figure 1.c), the fibres from the yarn did not show signs of mineralization and had a homogenous stiffness.

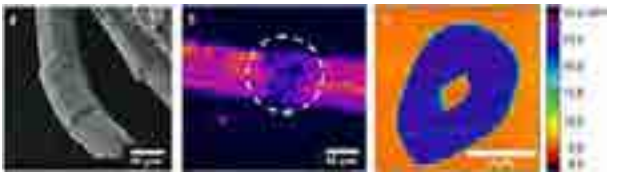

Figure 1. a) SEM image of a yarn from an archaeological mortuary fabric with defects along the fibres. b) An example of fissured defect highlighted by second harmonic generation imaging (white circle) and c) AFM in peak-force mode to estimate the fibre stiffness. The stiffness is homogeneous and no mineralization is visible

[1] C. Reynaud, M. Thoury et al., PNAS 117(33), 2020, 19670-19676.
[2] A. Melelli, D. Shah et al., Nature Plants 7(9), 2021, 1200-1206.

Characterization of original organic binding media and restoration products in Pompeian wall paintings

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Identification of binders in archaeological artworks is a challenging task, due to the degradation of the organic compounds, the small sample quantity (if ever available), the possible contamination from biological agents and/or conservation materials [1].

Wall paintings in Pompeii were mainly executed with the *fresco* technique. However, careful observation of the painting layers suggests the application of a *secco* technique. In this work, for the first time, fragments from Pompeian wall painting that never underwent conservation treatment (recovered during the 2000s excavations of the House of Marcus Lucretius, Regio IX 3, 5/24) were preliminarily investigated by Optical Microscopy (OM), Reflectance Transformation Imaging (RTI), and micro Energy Dispersive X-Ray fluorescence spectrometry (μ-EDXRF) to unveil the presence of overlying painting layers. This first non-destructive strategy served as a guide for microsampling for subsequent analyses by micro infrared in transmittance mode (FTIR) and Direct Temperature Mass Spectrometry (DTMS).

Restored wall painting fragments were also studied and the employed organic restoration materials were identified. The latter were obtained from the same House of Marcus Lucretius, the House of Ariadne (Regio VII 4, 31/51) and the House of the Golden Cupids (Regio VI 16, 7).

The analyses conducted on the non-restored samples by μ-FTIR revealed the presence of a proteinaceous material. By DTMS, fragment ions likely related with protein and cholesterol were detected, confirming a protein-based medium, probably egg, used to execute these *secco* layers (see Figure 1). Besides, wax was ubiquitous in samples taken from restored mural paintings, thus highlighting the importance of selecting appropriate candidates for the study of original organic binders.

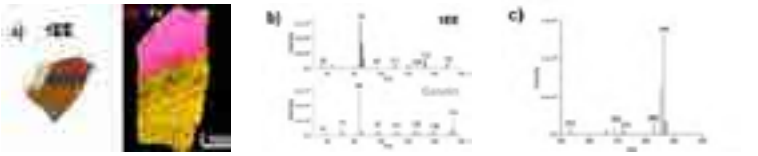

Figure 1. Photograph and μ–EDXRF map (a), DTMS spectrum showing peaks associated to the proteinaceous material (b) and the assignation of the molecular ion of cholesterol (m/z 386) (c) of 1EE non-restored sample.

[1] J. Cuní, Heritage Science 4, 2016, 44.

Testing acid products thickened with xanthan gum for the removal of calcareous deposits on ceramics

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Calcareous deposits are one of the most common alterations found in archaeological ceramics. If their removal is not mandatory (i.e. conservation reasons, exhibitions), current tendencies prefer to leave them under controlled ambient conditions, and instead, using non-invasive techniques for the ceramics study [1]. However, sometimes this alternative becomes difficult for most archaeological projects and small museums, due to a lack of funding. For this reason, traditional mixed cleaning treatments are still in use. These treatments include a first step based on a chemical product to soften the deposits, followed by a mechanical removal of the deposits residues, which constitute the second step [2,3]. Nevertheless, some studies proved the alteration of ceramic archaeological objects after cleaning treatments based on acid products, with changes in their composition as well as surface damages [4,5].

The main objective of this research was to determine the viability of indirect application methods of acid products by using thickening materials. With this purpose, cleaning tests based on acetic and nitric acid solutions at low concentrations (1 % v/v) thickened with xanthan gum (Vanzan® NF-C) were pursued on ceramic specimens (fired between 650-1100 ºC) covered with artificial calcareous deposits generated on their surfaces [6]. The efficacy and safety of these treatments, as well as the possible remain of residues, were determined from a multi-analytical perspective by X-Ray Fluorescence (XRF), Powder X-ray diffraction (XRPD), Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) and Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) analysis.

The results allowed to identify soluble salts in ceramic specimens treated with the thickened mixture with acetic acid, after the cleaning treatments and their neutralization. For these reason, the rinsing method would not be useful in this particular case, following the methodology performed [7]. Nevertheless, significant changes or residues remains were not detected in general, meaning that the designed treatments were effective and safe for the ceramic materials.

[1] C. Caple, Conservation skills : judgement, method and decision making, 2000.
[2] C. Fernández Ibáñez, Monte Buciero 9, 2003, 303–325.
[3] G. M. Crisci, *et al*, Appl. Phys. A Mater. Sci. Process. 100, 2010, 855–863.
[4] J.S. Johnson, *et al*., MRS Proc. 352, 1995, 831–837.
[5] J. S. Johnson, Conserv. O Gram 6, 1999, 1–3.
[6] Á. Sáenz-Martínez, *et al*., Mediterr. Archaeol. Archaeom.2019, 107–117.
[7] Á. Sáenz-Martínez, *et al*., Eur. Phys. J. Plus 136 (798), 2021, 1-16.

Enlightening the darkness: Sevillian influence in Óbidos workshop studied by analytical techniques

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Francisco de Zurbarán had large influence not only in Spanish art but also in South America and European art in the 17th century. One of the Portuguese painting workshops that highlight greatly Zurbarán artistic influences is the Óbidos workshop, the most important partnership of the 17th century Portuguese painting.

The two most important masters of Óbidos workshop are Baltazar Gomes Figueira (Óbidos, Portugal, 1604-1674) and his daughter and follower Josefa d'Óbidos (Seville, Spain 1630-Óbidos, Portugal, 1684).

One of the paintings that reflects most the plastic and chromatic values of this artist and Zurbarán's influence is the "Genealogy of the Virgin" (c.1650, Lourinhã Convent, Portugal). Josefa, the most important Portuguese female painter, never left Portugal after coming in her childhood from Seville. Although, she developed during her apprenticeship, the Spanish influences that mostly characterized the painting of her father, evidencing Zurbarán artistic style and ideology.

A multianalytical methodology incorporating micro-X-ray Diffraction (μ-XRD), Energy Dispersive X-ray, Fluorescence spectrometry (EDXRF), scanning electron microscopy - energy dispersive spectroscopy, (SEM-EDS), micro-Raman spectroscopy (μ-Raman) and micro-Fourier Transform Infrared spectroscopy (μ-FTIR) were used to characterize the paintings materials and techniques of Zurbarán Spanish influence in Óbidos painting workshop, Portugal.

Conclusions for conservation resolutions and lightening effects were drawn from data observation on materials and technique. The characterization of the palette and ground layers and the study of the overlapping of pigment layers unveiled materials and techniques of Óbidos paintings and highlighted the importance of the materials chosen for the final lightening effect. The choice of the ground layer colors has produced a great effect when putting in evidence the Zurbarán Sevillian influence in Óbidos painting workshop Portugal.

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Multi-analytical approach for investigation of the hidden layers in a post-byzantine icon

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The icon depicting the Holy Great Martyr Theodore the Tyron is part of a set of eight double-faced high artistic value panel painted icons delimiting the narthex of The Episcopal Church from Curtea de Argeş - built by Neagoe Basarab in 1517 [1]. The icons are representative for the proficiency of the Romanian 15-16th century post-Byzantine Wallachian iconography, and now they are part of the collection of the Cozia Monastery. The one under study is severely deteriorated and presents lacks of the pictorial composition on more than 25% of its surface. The remaining artistic composition, as well as the support, were subjected to a multi-analytical investigation using Hyperspectral Imaging (HSI), UV Fluorescence Imaging, X-Ray radiography (XRR), X-Ray Fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy and Laser Induced Breakdown Spectroscopy (LIBS) in order to characterize the constituent materials and the state of conservation [2-5]. Based on the imagistic techniques results (HSI and XRR) it is clear that the icon was fully repainted, some of the original motifs and decorations being lost underway. The spectroscopic analyses helped identify the materials (traces of gold leaf, lead pigments, earth pigments, cinnabar, traces of copper-based pigments and several blue pigments, protein binder, varnish, natural resin, as well as degradation products on the pictorial layer: lead-based carboxylates and calcium oxalates. LIBS was performed on several interest areas, using 20 pulses stratigraphy, and correlated to HSI helped differentiate the painting layers attributed to different historical and stylistic representations.

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[1] Efremov, A. - *Icoane Romanesti*, Meridiane Publishing House, Bucharest, 2002
[2] Ghervase, L., Cortea, I.M., Radvan, R., Ratoiu, L., Chelmus, A. - *Complementary investigations of two Lipovan-style icons*. Microchemical journal. 2018, 138. Pp. 509-518, https://doi.org/10.1016/j.microc.2018.01.047
[3] Udrea, I., Marutoiu, C., Nemes, O.F., Bratu, I., Nemes, D., Toader, D. - *Spectroscopic Analysis of the Romanian Icon "The Entry of the Lord into Jerusalem" by Grigore Ranite*, Analytical Letters. 2023, 56(2), pp. 312-330, https://doi.org/10.1080/00032719.2022.2067169
[4] I.M. Cortea, L. Ratoiu, A. Chelmuş, T. Mureşan - *Unveiling the original layers and color palette of 18th century overpainted Transylvanian icons by combined X-ray radiography, hyperspectral imaging and spectroscopic spot analysis*, in X-Ray Spectrometry, 2022, 51(1), pp. 26-42, https://doi.org/10.1002/xrs.3249.
[5] Gaudiuso, R. - *Laser-induced breakdown spectroscopy in cultural heritage science*, 2021, 10.1016/B978-0-12-818860-6.00002-7.

Blue enamels. A preliminary non-invasive study of the blue enamels in objects from the Fitzwilliam Museum

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It is well known that the dark blue colour in enamels, either applied on metal supports, or on glass, in stained glass, as well as in ceramic glazes, is mostly associated with the presence of cobalt (see for instance [1-4]). However, the need for a greater understanding of historic cobalt sources and their relation to blue enamel recipes, as well as ore processing, through time and space, has been pointed out by several authors [1,2].

For this paper, blue enamels on a selection of exquisite enamels from the collection of the Fitzwilliam Museum, in Cambridge, were examined. The 21 metallic enamelled objects, dated from the 13th-to the 19th century, with polychrome decorations, were analysed using a multi-analytical and non-invasive approach – Energy Dispersive X-Ray Fluorescence (EDXRF), UV-Visible Fiber Optics Reflectance Spectroscopy (UV-Vis FORS) and Optical Microscopy were applied to obtain information on the chemical composition and colouring agent(s) of the blue enamels. For comparison, turquoise blue and green enamels are also considered, in order to discuss pigment materials and colorising elements.

Chemical qualitative analyses performed using EDXRF, allowed the identification of the elements present as well as the identification of the composition of the different blue enamels. UV-VIS FORS spectroscopy was used to identify cobalt as the main colouring agent, highlighting some differences likely due to the use of various cobalt-ores or to different chemical composition of the glass matrix.

A statistical approach using Principal Component Analysis (PCA) was used to preliminarily identify elements associated with cobalt, which are related to its mineral sources. The statistical data can be mined to retrieve some initial information about the elements associated to the glass matrix and to the main colouring agents. Furthermore, this approach was also useful to assess the possible correlations with historical recipes.

Finally, based on the new analytical results and the comparison with existing data from the literature, the relationship between the composition and the historical questions on the origin and date of the production of these materials, will be used to inform a more global historical overview. The final goal will be to gain more insights into the cobalt-ore used to colour the enamels, its processing and which type of glass matrix was used, as well as assess if these features continued through the centuries.

[1] Ph. Colomban, B. Kırmızı, and G. Simsek Franci, Minerals 2021, 11(6), p. 633.
[2] I. Biron, M. Verità, Journal of Archaeological Science 2012, 39 (8), p. 2706-2713.
[3] A. Machado, M. Vilarigues, Glass Technology - European Journal of Glass Science and Technology Part A 2016, 57(4), p. 131-140(10)
[4] R. Giannini, I. Freestone, A. J.Shortland, Journal of Archaeological Science 2017, 80, p. 27-36.

Development and characterization of a modular MA-XRF spectrometer for Cultural Heritage applications

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Macroscopic X-Ray Fluorescence Spectrometry (MA-XRF) is nowadays a widely established technique in Cultural Heritage (CH) applications, since it provides elemental distribution images, well perceived by non-expert curators, archaeologists, and art-historians. The MA-XRF images allow a firmly and enhanced characterization of raw materials and provide useful insights into the production process of ancient materials and historical artworks [1,2].

In this work, we present the development and characterization of a modular portable MA-XRF spectrometer. The system consists of a transmission 12W Rh tube, a silicon drift detector (SSD) of a 150mm^2 active area and a laser proximity sensor integrated on a three-axis motorized platform (75cm x 50cm x 25cm). The proximity sensor allows reproducible alignment of the spectrometer head and control of the measurement geometry. The setup is controlled by an in-house developed LabView program. Modular optics, including a polycapillary X-ray lens and diaphragms of variable diameters provide a tunable sized exciting beam from ~0.1mm to several mm's, optimized for different applications. Moreover, the possibility to precisely adjust the position of the tube and optics versus the analyzed surface allows to keep a constant and reproducible detection geometry.

Monte Carlo simulations using the PenRed [3] code, an extensible and parallel Monte-Carlo framework for radiation transport based on PENELOPE, XMI-MSIM [4] and X-ray tracing code [5] were applied to characterize the excitation spectrum in terms of energy distribution, spatial resolution, and divergence in various optic-to-sample distances. The theoretical estimations are compared with the experimental results and the overall performance and applicability of the MA-XRF spectrometer in CH applications is discussed.

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[1] Romano F.P., Caliri C., Nicotra P., Di Martino S., Pappalardo L., Rizzo F., Santos H., Journal of Analytical Atomic Spectrometry, 32(4), 2017, 773-781
[2] C. Caliri, M. Bicchieri, P. Biocca, F.P. Romano, X-Ray Spectrometry, 50 (4), 2021, 332-340
[3] V. Giménez-Alventosa, V. Giménez Gómez, S. Oliver, Computer Physics Communications, 267, 2021
[4] T. Schoonjans, L. Vincze, V. A. Solé, M. Sanchez del Rio, P. Brondeel, G. Silversmit, K. Appel & C. Ferrero, 2014. XMI-MSIM 5.0. Zenodo
[5] P. Tack, T. Schoonjans, S. Bauters, L. Vincze, Spectrochimica Acta Part B: Atomic Spectroscopy 137, 2020, 105974.

To be or not to be – what can material analysis say about the *so-called* Infante D. Henrique in the Crónica Geral da Guiné?

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Most probably the most debated and controversial iconographies in Portuguese Art History, the one of Infante D. Henrique (1394-1460), is a depiction of *a man wearing a chaperon*. Known as the great entrepreneur of 15th-century Portuguese maritime discoveries, the Infante was the fifth son of King D. João I (1357-1433) and D. Filipa de Lencastre (1360-1415). His most iconic representation can be found in one painting (called the *Panel of the Infante*), which belongs to a set dedicated to Saint Vincent, exhibited nowadays at the Museu Nacional de Arte Antiga, but once held at the Lisbon Cathedral. Being a work of highly symbolic importance in Portuguese Art History and among one of the most extraordinary painted group portraits in the European early Renaissance context, it is likewise one of the most contentious paintings of Portuguese historiography, not only for the matters related to its authorship but also for the identification of *the man wearing a chaperon* as the Infante D. Henrique. The association was based on a similar depiction of a man with the same sort of hat and features present in the frontispiece of the 15th-century illuminated *Crónica dos feitos da Guiné* (MS Portugais 41 Réserver) by Gomes Eanes de Zurara, held by the Bibliothèque nationale de France. Nevertheless, the right identity of this portrait is also controversial, as the attribution made based on the motto flaunted (*talent de bien faire*), which indeed belongs to the Infante D. Henrique, has been deeply questioned by some authors in the past, who believe that the illumination represents not the Infante but one of his brothers –King D. Duarte (1391-1438)- [1] and that the folio does not even belong to the original version of the *Crónica* [2]. Within this context, the outstanding illuminated *Crónica dos feitos da Guiné* presents itself as a central piece for better understanding the identity of *the man wearing a chaperon* depicted in the panel of the old Saint Vincent altarpiece.

This work presents the first analytical study of the illuminated frontispiece present in *Crónica dos feitos da Guiné*, with a deep focus on the representation of *the man wearing a chaperon* and its link to the similar representation present in the *Painéis de São Vicente* altarpiece held by the Museu Nacional de Arte Antiga. Aiming at contributing to the clarification of the state

of the art of such outstanding representation in the Portuguese Art history context, in-situ non-invasive analyses of the illuminations present in the frontispiece of the *Crónica dos feitos da Guiné* were performed, including elemental (h-EDXRF), molecular (UV-Vis-NIR-FORS) and chemical imaging (MA-EDXRF, hyperspectral imaging and IR reflectography) analysis. The results presented for the first time at this conference will bring important answers to this controversial subject of Portuguese historiography, contributing to a better understanding of the history of *the man wearing a chaperon* present in the *Crónica dos feitos da Guiné* (MS Portugais 41 Réserver) and its relation with the representation at the Painéis de São Vicente (Museu Nacional de Arte Antiga).

Fig. 1. MA-XRF analysis of the *Crónica dos feitos da Guiné* (MS Portugais 41 Réserver).
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[1] A. Bélard da Fonseca, “Dom Henrique? Dom Duarte? Dom Pedro?”. Lisboa: Livraria Bertrand, S/d [1960].

[2] D. Markl, “O Retábulo de S. Vicente da Sé de Lisboa dos Documentos”. Lisboa: Editorial Caminho, 1988.

Photoluminescence MA-imaging for the assessment and study of new cleaning systems

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The evaluation of cleaning procedures in terms of effectiveness and minimal invasiveness to artworks is a cornerstone of current conservation research. New systems proposed for use in restoration should be evaluated to understand their physicochemical mechanism of action [1,2]. The majority of restorers do not have easy access to advanced scientific techniques. It is therefore important to develop analytical protocols that strike a balance between cost, practicality, and reliable interpretation of results [3]. One technique that stands out from this point of view is photoluminescence (PL) imaging, a surface analysis that exploits the photochemical response of materials to form images [4,5].

Recently, *Focarete et al.* have patented a new cleaning method based on electrospun tissues as a carrier of dimethyl carbonate, a volatile green organic solvent. The tissues ensure a one-step procedure as they act as retentive media for solvents and as adsorbers toward the partially solubilized varnish [6].

Here, we report on a protocol based on PL macro-imaging to monitor this cleaning procedure on paint mock-ups. We characterise the capillary rise of the dammar varnish within the fabric, providing a better insight into the action of the cleaning system. Coupled with microfluidic studies, this approach will allow further optimisation and upscaling of cleaning processes. This method was used to characterise mock-ups after treatment. Statistical image processing was used to quantify varnish residues and assess the cleaning efficiency. These initial results form the basis for optimising the set-up in terms of collection conditions and data processing towards the development of a restorer-friendly setup. Crucial aspects are the reduction of the radiation dose [7] and the maximisation of the information that can be obtained with respect to possible instrumental and environmental stray light noise.

This project was supported by the European Commission in the framework of the GoGreen project (GA no. 101060768).

[1] L. Baij, C. Liu, J. Buijs, A. Alvarez Martin, D. Westert, L. Raven, N. Geels, P. Noble, J. Sprakel and K. Keune, Herit. Sci., 2021, 9, 155

[2] M. Raudino, N. Giamblanco, C. Montis, D. Berti, G. Marletta and P. Baglioni, Langmuir, 2017, 33, 5675–5684.

[3] M. Iwanicka, P. Moretti, S. van Oudheusden, M. Sylwestrzak, L. Cartechini, K. J. van den Berg, P. Targowski and C. Miliani, Microchem. J., 2018, 138, 7–18.

[4] A. Nevin, J.-P. Echard, M. Thoury, D. Comelli, G. Valentini and R. Cubeddu, Talanta, 2009, 80, 286–293.

[5] M. Thoury, J. P. Echard, M. Réfrégiers, B. Berrie, A. Nevin, F. Jamme and L. Bertrand, Anal. Chem., 2011, 83, 1737–1745.

[6] Maria Letizia Focarete, Chiara Gualandi, Giorgia Sciutto, Francesca Ramacciotti, Silvia Prati, Rocco Mazzeo, Italian Patent n. 102021000020426, 2022

[7] Bertrand, S. Schöeder, D. Anglos, M. B. H. Breese, K. Janssens, M. Moini and A. Simon, TrAC Trends Anal. Chem., 2015, 66, 128.

Limited technology and unlimited results: an integrated approach about study and conservation of daggers from Ras Al-Khaimah national museum.

Abstract

The importance and quality of Archaeological research come from the process of extracting information from materials which are completely have no information. although the Traditional and limited technology used in culture heritage methods (imaging, drawings), might not give a complete image about the story of collection. but if this traditional and limited technology used in a right manner It might be sufficient to obtain the required information from the collection.

The research focuses and discuses two case study known as Khanjar خنجر in the form of Jambiya جَنْبِيَّة from National Museum of Ras Al Khaimah collection. The objects registered under the museum number *RAK 430* and *RAK 11584* and were kept in the museum storage and presented to receive the investigation, restoration, and conservation treatment in preparation for future display in the museum gallery for the first time.

According to the availability of traditional and limited technology in examination of the two objects prior to treatment indicated a significant important for the history, materials and technology of this special type of dagger. The results obtain information that may represent the historical context, materials technology, and the local community environment in which these pieces were produced.

Are Infrared and Chemometrics up to the Tusk?

On the Use of In-situ Infrared Spectroscopic Techniques for the Study of the Provenance of Historic Ivories

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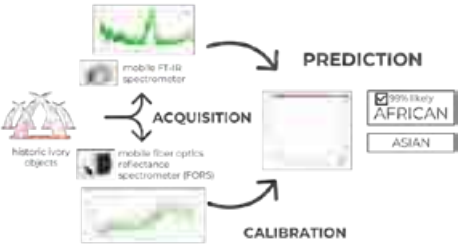
Ivory trafficking is a multifaceted problem that has long endangered the fate of African and Asian elephants. In field investigations, it is important to conduct ivory inspections in a non-destructive manner to prevent the inclusion of non-compliant materials. In this research, a practical approach to identify Asian and African elephants' ivories was developed using an integrated methodology of art history, vibrational spectroscopy, and chemometrics. Spectra were acquired by a FT-IR spectrometer and a fiber optics reflectance spectrometer (FORS) in the UV-Vis-NIR region. The discriminant methods were calibrated with spectra acquired from Asian and African elephant ivory tusks and applied to historic ivory objects (n = 78) of uncertain origin. Models based on the chemometric methods principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA), were able to successfully classify ivory objects into Asian and African ivory, with an estimated true prediction rate (TPR) of 99% both for African and Asian ivory samples. This study demonstrated the potential of FT-IR spectroscopy and FORS, as suitable tools for ivory investigations, aiding to the existing set of ivory trafficking prevention methods.



Non-destructive characterization of colored mineral glazed beads

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During an archaeological work on Av. 24 de Julho, ancient riverside contexts were identified, including numerous pieces of vessels in levels corresponding to the old Boavista beach, including a very significant part of a medium-sized vessel. This archaeological context was chronologically framed between the 3rd quarter of the 17th century and the beginning of the 18th, according to the material culture in association. Within the material that was in association with that vessel, it was found a significant set of glazed beads that, in a preliminary analysis, could be originally from some Asian country. However, in a preliminary approach, evidence indicates that the vessel Boa Vista 5 has mostly oceanic characteristics, which brings out some questions about the routes that this ship navigated.

Five representative pieces of these beads, with similar shapes and sizes and different colors (from pale orange to dark blue/black) were selected for preliminary chemical and mineralogical characterization by means of non-destructive techniques: particle induced X-ray emission (PIXE), ionoluminescence, X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR) and high energy particle induced X-ray emission (HE-PIXE).

The aim of this study is to contribute for the establishment of the beads provenance, and provide clues about the route traced by the vessel.

Preliminary results show that quartz is the main mineral phase and traces of different elements such as Cr, Pb and Zr can be identified, depending on the bead (see figure 1). A complete discussion of the results will be presented in this work

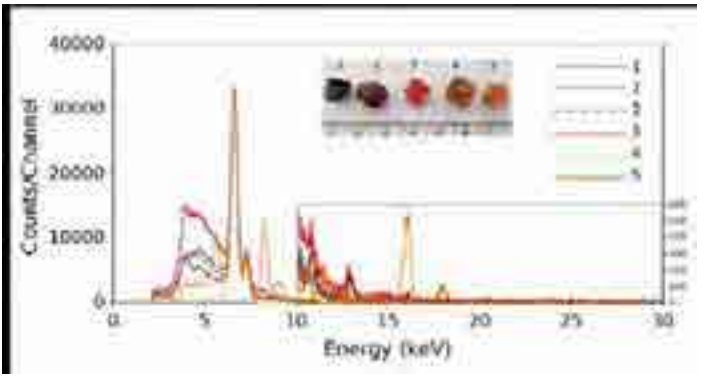

Figure 1. HE-PIXE normalized spectra of the selected glazed beads (inset) using a 3.0 MeV proton beam and a CdTe detector.

Bullion coins circulating in Portugal in the 12th-13th centuries: an analytical approach

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With the collapse of silver production in the Central Asian mines and the resultant decline in the flow of Islamic silver, a "silver famine" ravaged Europe from ca. 930 to 1130. This white metal shortage only ended after the discovery of the rich ore fields in northern England [1]. Chronologically, it coincides with the formation of the kingdom of Portugal – 1139.

The most common coin minted during the first Portuguese dynasty (1139-1383) was the *dinheiro*, a bullion coin which along its 250-year-old existence saw a decrease in its silver content from ca. 23 wt.% to only traces.

This work presents the analysis results of several *dinheiros* from the first two Portuguese kings, D. Afonso I (1139-1185) and D. Sancho I (1185-1211), using the IBA techniques PIXE (Particle Induced X-ray Emission) and EBS (Elastic Backscattering Spectrometry) at the nuclear microbrope installed at the CTN-IST Van de Graaff 2.5 MV accelerator. This allowed to determine the silver content of these bullion coins and the quantification of minor and trace elements that are related with the metals provenance and flow which supplied the Portuguese mints. Also, detailed observations were made on the surface of the coins and at a cross-section by multifocus Optical Microscopy to evaluate surface corrosion and alloy heterogeneities. These results helped the evaluation/interpretation of elemental mappings that show material heterogeneities, being able to distinguish among metal phases and corrosion products.

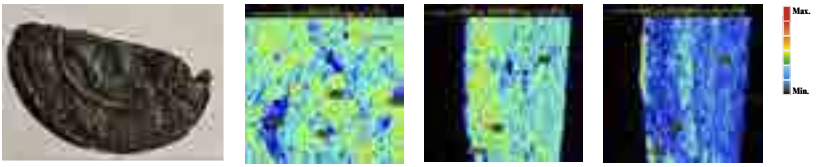

Figure. Photograph of D. Afonso I dinheiro (anverse) and PIXE elemental surface maps (2640×2640 μm^2) for Ag Lα and Cu Kα, obtained with a 1975 keV proton microbeam (3×4 μm^2).

[1] I. Blanchard, Mining, Metallurgy and Minting in the Middle Ages, Vol. 2, 2001.

Identification of wine markers in ancient pottery using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS)

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Between the third BC and fifth AD centuries, the Roman empire spread throughout the Mediterranean area influencing the lives of all its people. Today much of this legacy can be found buried in archaeological sites and offers a great opportunity to study the lifestyle of these nations. Indeed, the characterization of the organic residues that ancient pottery contains will be of great help to ascertain the type of food they contained and, as a result, to understand those societies.

Wine was very appreciated in the Roman empire, thus it was produced in many regions and became a key product in the Mediterranean trade. Pottery that contained this beverage is often found in the Roman villas, however, as these kinds of vessels may not differ from others storage containers, reliable methods for its content confirmation are needed in order to broaden the knowledge of these villas.

In this work, a liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) method was established for the determination of organic acids, mainly tartaric acid, and other compounds, which are known to be important components of wine, in fragments of dolia from Roman sites. However, tartaric acid, as well as other wine components, can be extensively found in the plant rhenium, and thus the presence of these compounds in the studied pottery fragments cannot be considered unequivocal evidence of their use. Appropriate blank samples, exposed to the same environmental factors, are then required to be able of drawing the correct conclusions. The strategy proposed here deals with using the outside part of the studied fragments for comparison purposes.

The optimized approach was then used for analyzing fragments of dolia from the Roman sites of Empúries, Collet de Calonge i Sant Antoni, Olivet d'en Pujol and Vila de casa del Racó in the province of Girona. The analysis of the samples studied has shown that the fragments of dolia from Empúries, Olivet d'en Pujol and Vila de casa del Racó contain tartaric and malic acid in a significantly higher concentration on the interior side than on the exterior side, suggesting that they may have contained wine in the past. On the contrary, in the fragments of Collet de Calonge these indicators have not been found, so the possibility that they contained wine can be ruled out.

Portable XRF to assess glass alteration in museum settings: advantages and limitations

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The complex interaction between the intrinsic physical and chemical properties of the vitreous objects (i.e. composition, impurities) and the extrinsic factors acting on them (i.e. temperature, humidity, pollutants) determine their state of preservation. Small variations in the concentration of the glass network components (silica, alkali, alkaline earth) can determine strong differences in the objects' durability [1].

In order to enact a suitable preventive conservation strategy, it is essential to be able to identify the glass compositions that are chemically more stable than others, thereby discriminating between stable and unstable glass within museum collections. This work aims to explore the ability of handheld X-ray fluorescent (XRF) spectrometer to discriminate between different types of glass compositions in a completely non-invasive way. This pilot study explores the advantages and the limitations of the in-situ glass characterization using a handheld XRF, tthrough the analysis of 40 objects belonging to the Victoria and Albert Museum.

The analyses were performed with a Bruker Titan S1 XRF spectrometer. The GeoExploration method was selected, as recommended by the manufacturer, in order to monitor lighter elements (manganese, aluminium and silicon) [2]. Glass samples from the Corning Museum of Glass were used as standards to validate the method.

The results show that the GeoExploration method has limited applicability if the concentration of heavy elements, such as lead, is relatively high. This limits our ability to quantify major and minor elements, and therefore precludes the correlation between the degree of glass alteration and the chemical composition (and therefore period and place of production) and the chemical stability of glass object.

Nevertheless, the results allow to evaluate qualitatively the relationship between glass fragility and chemical composition, enabling museums and collections to identify objects that are more prone to corrosion processes when exposed to high levels of humidity and temperature. This study represents the first step in the evaluation of other portable XRF inbuilt instrumental methods that will allow non-destructive, non-invasive analysis of museum objects, and will help in categorising the latter as stable or unstable glass. This will provide the opportunity to rethink how glass objects are displayed and stored, according to their chemical stability.

[1] R.B. Heimann, Int. J. Appl. Glass Sci. 9 (2018) 29–41.
[2] http://www.bruker.com/s1titan, S1-TITAN_Mining_brochure.pdf

New light on the provenance of lapis lazuli found in Shahr-i Sokhta site using Ion Beam Analysis.

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The Shahr-i Sokhta site, located in eastern Iran and dated back to the 3rd millennium BCE, was an important hub for the trade routes crossing the Iranian plateau during the Bronze Age, and, in particular, a consumer of high-quality lapis lazuli material [1]. In the context of a join collaboration with archaeologists from the University of Padua, 25 lapis lazuli working fragments discovered at Shahr-i Sokhta have been analyzed with Ion Beam Analysis (IBA) techniques at the in-vacuum microbeam line of the INFN-LNL laboratory (Legnaro, Italy) and the external microbeam line at NewAGLAE accelerator (C2RMF, Paris) with the ultimate goal to deepen the knowledge on the suppliers for this site of lapis lazuli raw materials from easternmost regions.

Although the historical source for lapis lazuli used in antiquity is commonly known to be the Badakhshan Province (Afghanistan), other hypotheses have been suggested and their confirmation on a scientific basis could be of uttermost importance for the knowledge of ancient trade routes. In the past years, our group have developed and successfully applied to lapis lazuli objects a protocol to identify the provenance of the raw material by means of a non-invasive methodology based on IBA [2]. The use of μ-PIXE (Proton Induced X-ray Emission) and μ-IBIL (Ion Beam Induced Luminescence) has proved effective in finding physicochemical markers within reference geological rocks able to distinguish among five provenances: Afghanistan, Tajikistan, Siberia, Chile and Myanmar [3]. Due to the lapis lazuli heterogeneity, these markers are searched inside single mineral phases (e.g. diopside and pyrite) by exploiting proton microprobes.

The multi-technique approach adopted in the investigation of the Shahr-i Sokhta samples will be presented together with the results on the provenance of these semi-precious blue stones obtained through the application of the protocol. In addition to the description of the current methodology adopted, a comparison among two techniques, innovative for the lapis lazuli provenance study, will be briefly presented: μ-PIXE (routinely adopted in our protocol but limited by the access to accelerators in national laboratories) and Scanning Electron Microscope with Wavelength Dispersive X-ray Spectrometry (SEM-WDX) adopted for the quantification of trace elements in diopside.

[1] M. Vidale, Lapis Lazuli Bead Making at Shahr-i Sokhta. Antilia, Rome, 2017.

[2] A. Lo Giudice et al., Archaeological and Anthropological Sciences 9, 2017, 637-651.

[3] L. Guidorzi et al., European Physical Journal - Plus (EPJ Plus), accepted.

The characterization of roman wall painting fragments. An insight into pigments and materials in roman Sardinia (Italy).

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The ancient Roman town of Turris Libisonis was a Roman colony since the 1st century BCE and become one of the richest towns in Sardinia during the 2nd century CE.

Among the archaeological findings, the fragments of wall paintings are interesting in order to characterize and compare the materials used in this colony with other case studies in different regions and provinces of the empire itself and to shed light on pigments and the use of colour in Roman Sardinia, a relatively undeveloped field of research, with a few published case of studies, besides the city of Nora [1].

The thirty-one fragments, dating mostly between the 1st and 3rd century CE, are exhibited in the Antiquarium Turritano in the modern city of Porto Torres, built on the ancient roman city, in the northwest of Sardinia. They were analyzed through a well-established protocol [2] that includes non-invasive and portable techniques, such as Multiband Imaging techniques (MBI), X-ray fluorescence spectroscopy (XRF), Total Reflection Fourier Transform Infrared Spectroscopy (TR -FTIR), Raman spectroscopy and Optical Microscope documentation.

The analyses were carried out directly in the museum preventing any excessive handling of the pieces and the sampling, allowing the preservation of the fragments with the aim of maximum protection of these unique artefacts. The results obtained can form a first dataset of information about the wall painting in Turris Libisonis and become useful support for the archaeologists in the study of the wall painting in Roman Sardinia.

[1] F. Donati, *Lineamenti per una sintesi sulla pittura murale romana nell'Italia centrale e insulare (Sardegna)*, in Y. Dubois, U. Niffeler (eds.), Pictores per provincias II – *status quaestionis. Actes du 13e Colloque de l'Association Internationale pour la Peinture Murale Antique (AIPMA), Université de Lausanne, 12 – 16 septembre 2016*, Basel 2018, pp. 537-552.
[2] Iannaccone R., Bracci S., Cantisani E., Mazzei B., Applied Physics A: Materials Science and Processing, 2015, 121(3), pp. 1235–1242.

Non-destructive vibrational spectroscopy study of Edvard Munch's monumental Aula Paintings

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The 11 monumental oil paintings by Edvard Munch that adorn the Aula (i.e., the auditorium) of the University of Oslo have undergone different major conservation treatments since their completion and display (1916), with the first one having been carried out in 1925.

In the framework of the Munch Aula Paintings project (MAP, ongoing since 2005) [1], support materials, painting techniques, original appearances, conservation history and challenges relating to condition and cleaning/conservation have been examined. To improve the care and preservation of the paintings and understand the degradation phenomena, extensive scientific characterization of the materials used in the paintings has been carried out since 2007-2008 [2–4]. The largest instrumental non-destructive campaign (348 measurements) was carried out between 2018 and 2021 by portable Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and portable Raman spectroscopy on 7 of the 11 paintings.

In this paper, results from these campaigns, giving information about binding media, pigments, fillers, grounds, and material changes occurring will be presented. The interpretation of the results has been supported by classical spectral evaluation (nth derivatives, smoothing, …) and by data science methods (hierarchical clustering, principal component analyses, and so on).

[1] University of Oslo, The Munch Aula Paintings project (MAP) - Department of Archaeology, Conservation and History, (2022). https://www.hf.uio.no/iakh/english/research/projects/aula-project/index.html (accessed February 3, 2023).
[2] T. Frøysaker, C. Miliani, M. Liu, Non-invasive Evaluation of Cleaning Tests Performed on "Chemistry" (1909-1916) - A Large Unvarnished Oil Painting on Canvas by Edvard Munch, Restauro. 4 (2011) 53–63.
[3] L.P. Stoveland, M. Stols-Witlox, B. Ormsby, F. Caruso, T. Frøysaker, Edvard Munch's monumental Aula paintings: a review of soiling and surface cleaning issues and the search for new solutions, in: Interact. Water Paint., Archetype Publications, London, 2019.
[4] J.D. Cutajar, A. Babini, H. Deborah, J.Y. Hardeberg, E. Joseph, T. Frøysaker, Hyperspectral Imaging Analyses of Cleaning Tests on Edvard Munch's Monumental Aula Paintings, Stud. Conserv. 67 (2022) 59–68. https://doi.org/10.1080/00393630.2022.2054617.

Unveiling the colours of José António Jorge Pinto tilework

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José António Jorge Pinto (1875-1945) was one of Lisbon's leading painters of Art Nouveau tilework. Despite that, the materials, and the technology of production of his tilework is yet to be explored. In this work we present the first analytical results on the coloured glazes from two of his tile panels, *The foundry* (1906) and *La Pastourelle* (1920's) belonging to the Museum of Lisbon. The tile panels were studied *in-situ* using a don-destructive analytical methodology that combined digital microscopy, colourimetry, and X-ray fluorescence spectrometry (XRF) for an elemental composition characterisation of the coloured glazes. XRF evaluation shows that all glazes have silicon as the glass-forming element, lead as flux and a tin-based opacifier. Concerning the colouring agents, antimony-based yellows were used either alone or with iron to obtain orange hues. Blues are cobalt based and greens were obtained by mixing the yellows and the blues. Purples are manganese based or mixed with iron to make them as darker as the black colour. Chromium, tin and calcium have also been identified in pink shades, possibly resulting from the use of chromium-doped tin-based sphene (malayte) pink pigment [1].

[1] X. Faurel, A. Vanderperre, P. Colomban, J. Raman Spectrosc. (34) 2003, 290.

Acknowledgments
The authors wish to express their gratitude to Dr Joana Monteiro, Director of the Museum of Lisbon for providing access to the collections and making possible the analytical study of the artworks, to Dr Aida Nunes, coordinator of the Conservation and Restoration Department for the logistic organisation and to the conservators Arminda Brito, Helena Leitão and Joaquim Jorge, for the assistance during the analytical campaigns.

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Innovative method for provenance study: a new algorithm based on observables from high-resolution Raman spectra

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Red ochre generally comes from iron oxides and hematite and, in prehistoric times, has been used for a range of different applications, including cave paintings, symbolic use in burials etc. [1] Many different techniques have been applied to characterize the physic-chemical composition and structure of ochre, among which Raman micro spectroscopy, Infrared spectroscopy, Transmission Electron Microscopy and X-ray powder diffraction, which permitted the identification of different "recipes" employed in its production. This has allowed scholars to utilize pigment sourcing as a significant proxy to investigate patterns of population mobility, exchange networks and human-environment interaction. The importance to discover new methods for provenance determination, based on non-destructive portable techniques, constitutes a new challenge in the field of diagnostics of cultural heritage [2].

In this work, we present the data coming from the analysis of several non-flaked tools and ochre-stained bones, showing evidence of ochre processing at the Mesolithic site of S'omu e S'Orku in Sardinia (Italy).

With the intention to perform a provenance study of the ochre (hematite phase) found on the massive stone belonging directly to the site and the one used for covering the bones, we propose three different approaches derived from the high-resolution Raman spectra of ochres by identifying the maximum number of observables that can be reconducted to unicity criteria. The approaches are based on correspondence criteria, principal component analysis (PCA) clustering and the curve crystallinity versus purity ratio of hematite [3]. As reference samples for our provenance study, we analyzed different minerals as possible ochre sources extracted in the proximity of the excavation and from several caves in the entire Sardinia.

The reliability of this method allows us to develop an automatic algorithm of Artificial Intelligence able to recognize the provenance of raw materials used for the realization of a relic.

In addition, with this study we shed light on one of the earliest and unique Mesolithic burials found in Sardinia so far, providing important information about the peopling of the island and the symbolic behavior of the human groups occupying the island during the Holocene.

[1] Rosso D. E., Martí A. P., d'Errico F. 2016. Middle Stone Age Ochre Processing and Behavioural Complexity in the Horn of Africa: Evidence from Porc-Epic Cave, Dire Dawa, Ethiopia PLoS One. 2016; 11(11): e0164793.
[2] Chiriu, D.; Pisu, F.A.; Ricci, P.C.; Carbonaro, C.M. Application of Raman Spectroscopy to Ancient Materials: Models and Results from Archaeometric Analyses. Materials 2020, 13, 2456.
[3] Gialanella, S. Belli, R:, Dal Meri, G., Lonardelli, I., Mattarellli, M.,Montagna, M., Toniutti, L. Artificial or natural origin of hematie based red pigments in archaeological contexts; the case of Riparo Dal Meri (Trento – Italy), 2011, Archaeometry 53, 5 (2011) 950–962

In-situ multimodal study of 18th c. pastels

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The characterisation of fragile artworks on paper, in particular pastel paintings, requires adapted analytical methodologies. The risks involved when handling such works of art make their access difficult and their complex and composite nature explains challenges encountered in the field [1, 2]. Exceptionally, taking advantage of an ongoing restoration campaign, three pastels by M. Q. de La Tour (1704-1788), housed at the Musée A. Lécuyer, FR, have been investigated unframed (Fig. 1) [3]. Multiple *in-situ* analytical techniques were combined to non-destructively identify, locate and unmix the signatures of the different components of pastels.

The methodology developed provides an efficient and synergetic use of X-ray and reflectance spectroscopies. More specifically, a contactless spectroscopic continuum going from the visible to the mid-infrared region 25000 to 400 cm^{-1} is achieved by combining i) reflectance imaging spectroscopy in the visible and near infrared range (RIS VNIR; 400-1000 nm; 25000-10000 cm^{-1}), ii) fibre optic reflectance spectroscopy (FORS) in the short wave infrared (SWIR; 1000-2500 nm; 10000-4000 cm^{-1}), and iii) Fourier-Transform mid-infrared spectroscopy (midFT-IR; 7000-400 cm^{-1}) in reflectance mode. Those data are combined to single point elemental analysis by X-ray fluorescence spectroscopy (XRF). The methodology provides new insights into the nature and state of conservation of the paper support, as well as the composition and application of the pastel materials (colouring materials, fillers and binders). Bridging technical art history, conservation science and analytical chemistry, this research offers a unique insight into the choice of materials and artistic techniques developed by the famous pastellist, and sheds new light on an artistic technique poorly studied until now.

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Figure 1: Pastel on paper, M.Q. de la Tour a) Abbot Jean-Jacques-Clément Huber reading, 1742; b) King Louis XV, 1748; c) opera singer Marie Fel, around 1757.

[1] C. Gombaud, « Analysis and Conservation of Maurice Quentin de La Tour's Portrait of the Princesse de Rohan », vol. 22, 2015.
[2] L. Sauvage et C. Gombaud, « Liotard's pastels: techniques of an 18th-century pastellist », 2015.
[3] Jeffares, N., "Maurice Quentin de La Tour : life and work", Essay, published online http://www.pastellists.com/Articles/LaTour.pdf, 2022-1.

Revealing new secrets behind the Stradivari's craftsmanship: an infrared investigation at the nanoscale.

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Thanks to their incredible sound, the Stradivari's violins are probably the most famous bowed string instruments in the world. It is well known that the manufacturing technique influences their aesthetic and acoustic features [1]. Several scientific studies have been conducted in the last years focusing the attention on the complex coating system employed by Stradivari for the finishing treatments of his masterpieces. Even though great efforts have been directed to the characterization of the vanish layers [2], the spreading at the interface between the wood and the varnish of a preparation layer, possibly made by proteinaceous materials with the function to fill the outer pores of the wood, is still a debated question among the experts of Stradivari's instruments [3-5]. In this work we studied the cross-sections of two precious Stradivari's violins, the Toscano 1690 and the San Lorenzo 1718 by probing the capabilities of Synchrotron Radiation FTIR microscopy and Infrared scattering-type Scanning Near Field Optical Microscopy (IR s-SNOM) [6].

Despite the advantages offered by the high brilliance of the synchrotron radiation, the far-field FTIR microscopy was not sufficient for a clear identification of the materials composing the preparation layer, probably too diluted in the wooden matrix to be detected at the microscale. For this reason, the application of an approach that enhances the spatial resolution (down to few tens of nanometers) and the chemical sensitivity was mandatory for maximizing the level of attainable details. The s-SNOM punctual analyses clearly highlighted the spreading of a thin proteinaceous layer between the wood and the varnish in both the investigated violins, adding new details on its sub-optimal preservation degree [6].

The obtained results encourage the further application of this cutting-edge technique for detailed investigations of very small and complex samples in the field of Cultural Heritage.

[1] Lämmlein, S. L. et al., Influence of Varnishing on the Vibro-Mechanical Properties of Wood Used for Violins. J. Mater. Sci. 2019, 54 (11), 8063–8095.
[2] Echard, J.-P. et al., Insights into the Varnishes of Historical Musical Instruments Using Synchrotron Micro-Analytical Methods. Appl. Phys. A 2008, 92 (1), 77–81
[3] Echard, J. P. et al., The Nature of the Extraordinary Finish of Stradivari's Instruments. Angew. Chemie - Int. Ed. 2010, 49 (1), 197–201.
[4] Brandmair, B., Greiner, S. P. Stradivari Varnish, Eigenverlag: London and Munich, 2010.
[5] Invernizzi, C. et al., Non-invasive mobile technology to study the stratigraphy of ancient Cremonese violins OCT NMR-MOUSE XRF and reflection FT-IR spectroscopy. Microchem. J. 2020, 155, 104754.
[6] Stani C. et al., A Nanofocused Light on Stradivari Violins: Infrared s-SNOM Reveals New Clues Behind Craftsmanship Mastery, Anal. Chem. 2022, 94, 43, 14815–14819

Time-resolved hyperspectral imaging to detect faint luminescent pigments in paintings

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Photoluminescence (PL) hyperspectral imaging is currently employed during scientific investigation of works of art to characterize, identify and map luminescent compounds distributed on the artwork surface through their peculiar emission spectrum.

The main drawback of the method is the poor specificity of the emission that hampers the interpretation and correct attribution of the collected PL spectra. In fact, many and different luminescent materials are simultaneously present on the surface of a work of art, which often display similar spectral features. When using a continuous detection scheme, only those materials emitting with the highest intensity can be effectively identified (or at least mapped), while the emission from faint luminescent materials cannot be resolved.

The use of a time-gated detection approach strongly improves the possibility of discriminating between compounds having different emission lifetimes. In the recent past, we demonstrated the effectiveness of this approach by coupling a time-gated camera with a hyperspectral interferometer, an approach that has allowed us to identify and map the presence of modern luminescent paints, as cadmium yellows and reds, zinc white and titanium white, even in presence of other highly luminescent compounds, as protective varnishes and paint binders [1].

Here, we extend this approach by proposing the combined application of PL lifetime imaging and PL time-gated hyperspectral imaging to estimate the lifetime of the emitters and reconstruct their spectral emission at the different timescales. The paper will focus on demonstrating how the approach is particularly effective for the identification and mapping of weak luminescent pigments, as lead white and ultramarine blue, thanks to their long-living emission (with lifetime of hundreds of microseconds), despite the presence of other strongly fluorescent materials. For the purpose illustrative examples on different artworks, as paintings and preparatory cartoons, and paint stratigraphies, will be discussed putting light on advantages and drawback of the approach.

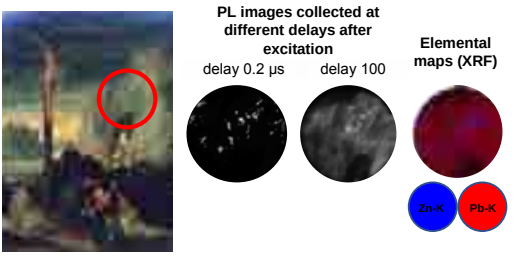

Figure 1: Time-gated PL imaging of a part of the painting "Christ en croix et Saintes Femmes" by Albrecht Altdorfer through allows the mapping of zinc white and lead white paints.

[1] M. Ghirardello *et al.*, "A novel photoluminescence hyperspectral camera for the study of artworks," *EPJPlus* 136: 10 (2021), doi: 10.1140/epjp/s13360-021-02028-0.

SWIR spectral contributions in varnished paintings

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The last decade saw a tremendous rise of hyperspectral reflectance imaging spectroscopy (HSI) in the Cultural Heritage domain (CH), particularly in the visible range (400-900 nm) which is now a well-established method to map the distribution of colouring materials. HSI in the short-wave infrared range (SWIR, 1000-2500 nm) progessively follows a similar trend, yet the complexity of interpretation, and the absence of dedicated data treatment procedure for CH materials limits its systematization.

While identification and referencing of pure materials have already been conducted [1, 2], the questions regarding the spectral contributions of individual components in complex multilayered and/ or mixed systems is still understudied [3]. With the objective to address this issue, our study primarily focused on the characterization of both natural and synthetic varnish coatings on painted surfaces. With characteristic signature in the SWIR range when applied as a single layer material [1], its identification by SWIR in historical paintings remains challenging. Different factors that may hinder its spectral contribution are considered: the varnish coating composition, thickness as well as the reflectance response of the underlying painting surfaces. In order to specifically understand their relative effects on the varnish signal, replicas of natural (mastic, colophony and dammar) and synthetic (PVA) varnishes were applied alone or on top of paint layers with various compositions. The different results will be presented, as well as the mathematical manipulation to establish the best procedure to extract both major and minor information from those complex multi-layered systems.

[1] M. Vagnini, C. Miliani, L. Cartechini, P. Rocchi, B. G. Brunetti, and A. Sgamellotti, « FT-NIR spectroscopy for non-invasive identification of natural polymers and resins in easel paintings », *Anal Bioanal Chem*, vol. 395, nº 7, p. 2107-2118, déc. 2009, doi: 10.1007/s00216-009-3145-6.

[2] J. Brocchieri, L. Viguerie, C. Sabbarese, and M. Boyer, « Combination of noninvasive imaging techniques to characterize pigments in Buddhist thangka paintings », *X-Ray Spectrom*, vol. 50, nº 4, p. 320-331, août 2021, doi: 10.1002/xrs.3189.

[3] M. Longoni, B. Genova, A. Marzanni, D. Melfi, C. Beccaria, and S. Bruni, « FT-NIR Spectroscopy for the Non-Invasive Study of Binders and Multi-Layered Structures in Ancient Paintings: Artworks of the Lombard Renaissance as Case Studies », *Sensors*, vol. 22, nº 5, p. 2052, mars 2022, doi: 10.3390/s22052052.

Climate data analysis for sustainable conservation of cultural heritage

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Climate control of humidity and temperature is necessary to reduce risk in the heritage collections' conservation; however, there is growing concern about the climate crisis and sustainable alternatives for heating, ventilation, and air conditioning systems (HVAC).

On the other hand, most Chilean museums need more resources for the optimal conservation of their collections [1], so is common to detect shortcomings in climate control and biodeterioration problems in the institutions. In this context, data science could contribute to a sustainable solution to conservation problems.

Using the existing seasonal data, an exploratory study was carried out on four museums in the country's central zone using the R programming environment. The study made it possible to simplify the visualization of the data (figure 1) and to characterize the general behavior of temperature and relative humidity in each museum in terms of set points and permissible fluctuations. These results will enable the delivery of specific recommendations to each institution about climate-related risks.

In addition, the study allowed us to understand the existing data, especially to identify deficiencies and problems to be solved. Based on these challenges and opportunities, future studies that include more institutions and depth in the analysis could be performed. Moreover, it allows testing of the feasibility and usefulness of the data science approach in the context of cultural heritage conservation.

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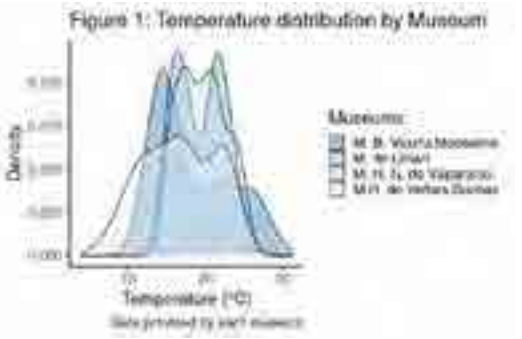

[1] Área de Estudios, SNM (2021). Santiago de Chile: Subdirección Nacional de Museos, Ministerio de las Culturas, las Artes y el Patrimonio.[En línea] https://www.registromuseoschile.cl/663/w3-article-115281.html

Evaluation by FTIR-ATR of the efficacy of mucilages hydrogels in removal a natural adhesive (*gacha*) from the reverse side of a canvas

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In the field of conservation of cultural heritage, the use of gels in removal natural glues from cultural objects is becoming increasingly common, as they allow the application of controlled humidity on surfaces sensitive to it [1]. In most cases, these gels are made with algae or even clays, such as agar- agar or Laponite® RD, respectively.

One of these glues is *gacha*, an adhesive commonly used in the Mediterranean in lining processes of painted canvases and composed basically of flour and animal glue. Sometimes during conservation processes it is necessary to eliminate the canvas used to reinforce the original one because of different reasons (fungus, loss of adhesiveness, etc.). In this case, it is frecuently also necessary to eliminate the remaining adhesive before continuing the restoration of the canvas.

In this work, the authors evaluate the use of vegetal mucilages for the elimination of *gacha* from the reverse side of a canvas. Different mucilages has been tested: some extracted from the seeds in the laboratory (chia, flax and psyllium), others yet commercially available (guar, konjac and locust bean mucilage) and a reference material, agar-agar. Mucilages are heterogeneous polysaccharides from higher plants. They are macromolecules, consisting of monosaccharides such as galactose, mannose, glucose and other glucid derivatives linked by glycosidic bonds. Mucilages are, thus, biodegradable materials whose processing does not imply a significant carbon footprint. They can be found in different plant organs (bulbs, roots, stems, leaves and flowers) and in seeds, especially in the outer tegument [2]. Their ability to retain water gives them a high thickening capacity, forming highly viscous solutions at low concentrations, due to the presence of branched structures containing hydroxyl groups that can form hydrogen bonds with water [3].

The efficacy of such mucilages as hydrogels to remove the remains of *gacha* present on a lined canvas has been tested on a mock-up. The mucilage-based hydrogels were applied for different times up to 30 minutes and two application methods were studied: direct application and indirect by interposing Japanese paper as a barrier material. Finally, the degree of cleanliness, as well as the mucilage residues, were determined by FTIR-ATR analysis. To do so, it has been assumed that a greater cleaning effectiveness will mean more intense bands corresponding to the linen canvas, while less cleaning means more intense bands corresponding to the materials used in the elaboration of *gacha.*

This methodology has made it possible to evaluate the efficacy of hydrogels, made using mucilages as thickening materials, in the elimination of *gacha* and opens the door to be applied for the elimination of other adhesives.

[1] E. Various authors, Gels in the Conservation of Art, Archetype Publications Ltd, London, 2017.
[2] E. Castillo García, I. Martínez Solís, Manual de fitoterapia. Ed. Elseiver, Barcelona, 2021.
[3] M. Tosif, A. Najda, A. Bains, R. Kaushik, S. Bala Dhull, P. Chawla, M. Walasek-Janusz, A Comprehensive Review on Plant-Derived Mucilage: Characterization, Functional Properties, Applications, and Its Utilization for Nanocarrier Fabrication in Polymers 13, 2021, 1066.

Luminescent coatings for the anti-theft protection of cultural heritage glass and metal objects

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Currently, the challenge is to develop a reversible method of applying anti-theft marking to cultural heritage objects using organic dyes and lanthanide-compounds. Placing visible indication marks (e.g. inventory numbers) directly on the objects is hardly used due to potential damage and making the surface unreadable. For this reason, our research aim is to propose a method of applying identification markings directly to the surface objects such as coins, ceramics or jewelry. Designed marks are difficult to observe in visible light, and since that identification is possible under strictly defined conditions e.g. UV or NIR radiation (applying appropriate dyes with specific optical characteristics). Importantly, the protection itself is reversible, also in a way that it will not affect the state of the preservation of the object.

We tested two ways of obtaining appropriate markings - one using commercially known organic dyes which undergo simple pH modification [1]. The distinguishing factors in the synthesis of our materials are relatively simple reactions to change the optical properties of organic dyes (e.g., pH dependence). Second one, using luminescent compounds of lanthanides synthesized *in situ* in the sol-gel material.

In preliminary study, coins and the coating itself were tested using nondestructive spectroscopic methods (absorption, luminescence spectroscopy and Raman spectroscopy. Analysis of the object's properties before and after removal of the protection is going to be carried out to determine the potential impact of the coating on the cultural heritage object. Similar tests will also be carried out for other objects, e.g. ceramic samples.

Figure. The process of preparing appropriate coatings using the sol-gel method.

[1] M.Zdończyk, B. Potaniec, M. Skoreński, J.Cybińska, Materials, 15(1), 2022, 203.

Statistical classification of LIBS and hyperspectral data for mapping the interventions on a historical building

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The Golești Manor Ensemble consists in architectural monuments dating back to the 17th, 18th and 19th centuries and can be classified as "maison de pleisance" with ephemeral architecture roots from Phanariot times, but also some pre- Brancovan influences. The Turkish steam bath is placed in the northeast of the enclosure and it is thought to have been built by Stroe Leurdeanu, based on the specific bricks pattern and ornaments. The bricks are connected by thick layers of lime mortar and sand mixed with crushed bricks that gives the building a reddish color [1]. Although there are still original fragments of the old plaster that have been preserved, it has undergone several restorations during the time, some of them poorly documented. Statistical classification methods (PCA, LSU, and SAM) were used on LIBS data combined with HIS, in order to map the original elements and trace the undocumented interventions previously made [2-4]. Using FCIR mode, RGB channels were assigned to different combinations of wavelengths ranging from 954 to 2250 nm in order to track similarities and differences in material behavior and a total of seven areas were selected for end-members' attribution. LIBS stratigraphy was performed based on the HSI results. The main chemical elements identified using LIBS can be traced to oxides commonly found in clay bricks, and the PCA helped distinguish 2 main types of bricks and mortars. LIBS PCA results were correlated and, further on, processed in ENVI, using SAM and LSU applied complementary in order to validate the accuracy of the classification and mapping, as seven endmembers were extracted for three brick areas (#1, #2, and #3), three mortar areas (#1, #2 and #3) and one material considered to be impregnated in the surface. Using PCA, SAM, and LSU, a distribution map of the area was obtained where previous interventions were identified [5].

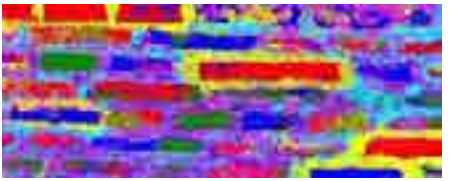

Fig. 1. Distribution map of the studied area [5]

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[1] F. Pally, Ansamblul memorial Goleşti, Asociaţia Română pentru Educaţie Individual Adaptată Publishing (2012)
[2] E. Adamopoulos, Learning-based classification of multispectral images for deterioration mapping of historic structures, J. of Building Pathology and Rehabilitation, 6:41 (2021)
[3] P. Pořízka, J. Klus et al., On the Utilization of Principal Component Analysis in Laser-Induced Breakdown Spectroscopy Data Analysis, a Review. Spectrochim. Acta, Part B, 148, pp. 65–82, (2018)
[4] G Vítková, L. Prokeš et al., Comparative study on fast classification of brick samples by combination of principal component analysis and linear discriminant analysis using stand-off and table-top Laser-Induced Breakdown Spectroscopy, Spectrochimica Acta Part B: Atomic Spectroscopy, 101, pp. 191-199 (2014)
[5] M. Dinu, L.C. Ratoiu, C. Călin, G. Călin, Multi-analytical investigations of the Medieval Turkish Bath from Golești Open Air Museum, Buildings 2022, 12.

Study of 18th century Chinese wallpapers from the National Museum of Ancient Art (Lisbon): a multi-analytical approach

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In 1949 a set of six hand-painted wallpaper panels – which were probably previously hanging in a Portuguese palace – was donated to The National Museum of Ancient Art (MNAA) of Lisbon. Since then, the panels became part of the oriental collection of the Museum, but they have never been displayed to the public. The use of Chinese wallpapers as decorating elements in wealthy houses and palaces in Europe was very popular during the second half of the 18th century [1]. Despite the large interest raised around these artifacts in the past few decades, though, few technical studies have been published to date [2].

In this framework, a multi-analytical approach was adopted for the investigation of the wallpapers belonging to the MNAA. More specifically, non-invasive techniques – such as FORS, EDXRF, Hyperspectral imaging, technical photography – were combined with micro-destructive techniques – such as SEM-EDS, FTIR, XRD. The results allowed to identify the painting technique, the use of pigments and binders, to explore the structure and composition of the paper sheets and some of the issues related with the degradation processes. The outcomes of this study will give new insights on the production and the characterization of the constituent materials of these artifacts, and – at the same time – will provide useful data for the conservation treatment, in view of the exhibition of the panels in the Museum.

[1] I. Lambert, C. Laroque, Studies in Conservation, 47(sup3), 2002, 122–128.
[2] S. Pessanha, A. Guilherme, M.L. Carvalho, M.I. Cabaço, K. Bittencourt, J.L. Bruneel, M. Besnard, Spectrochimica Acta Part B, 64(6), 2009, 582–586.

Multi-analytical survey of the Norwegian Sea Trade Archive collection of manuscripts with iron-gall ink

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The Norwegian Sea Trade Archive from the University of Bergen Library, Norway, is part of the UNESCO documentary heritage and contains unique documentation of the activity of companies that traded in stock fish in Norway and Europe (16th-20th century). The archive consists primarily of bound paper manuscripts written in iron-gall ink. Due to the commercial context in which these books were used, they currently show different levels of soiling and colonisation by microorganisms, which in some cases prevent access to the collection. In the present work we surveyed the material composition and the condition of this collection focusing on the paper carrier and iron-gall ink and using a multi-analytical approach. The survey was performed on overall 6% sample randomly selected (n=133).

The characterisation of paper was based upon the measurement of its thickness, water absorbency and surface pH. As an additional tool, SurveNIR [1] analysis was performed on a quarter of all tested materials, providing information regarding paper pulp type (rag, groundwood or chemical pulp), lignin, protein, and rosin content, degree of polymerization and mechanical properties [2].

The manuscripts' inks were examined visually by incident light and in UV light according to the condition rating of iron-gall ink [3]. The presence of Fe^{2+} and copper ions was determined via bathophenanthroline and copper tests, respectively [4]. A small selection of objects (6% of all samples) was measured with XRF to verify the presence of other transition metals such as Cu, Zn, Co, and Ni that might influence the condition of ink and paper [5]. The level of biodeterioration caused by microorganisms was determined visually under incident and UV light.

General tendencies of paper and ink degradation based on differences in paper making were observed. Surface pH measurement, SurveNIR pH, rosin and protein concentration data and comparison of the SurveNIR results of this collection with that of the Ravenna library [2] showed that most rag papers were of middle to low quality, generally from 4.1 to 6.0 surface pH and low protein content [6]. A high rosin size concentration correlated to very low pH (2.9-5.0) in documents dated after 1800. Inks before 1800, generally contained Fe, Zn and Cu, while in the 19th c. the main ingredient of iron-gall inks was Fe. Objects heavily affected by mould were mostly gelatin sized rag papers from the first half of the 19th c., and 'copy papers' – thin papers of pure cellulose with almost no sizing.

Decisions regarding storage and treatment of large collections require a holistic approach. Although each object follows a unique path of degradation, there are certain typical features, and grouping objects by specific period and type is an important approach to help in a decision-making process.

Key words: iron-gall ink, biological deterioration, SurveNIR, XRF, condition survey

[1] Official SurveNIR website: https://lichtblau-germany.com/SurveNIR_System.html /- accessed 6.01.2023

[2] Brown, Natalie, et al. "Non-Destructive Collection Survey of the Historical Classense Library. Part I: Paper Characterisation." Heritage science 8.1 (2020): 1-11.

[3] Birgit Reissland. 1999. Condition Rating for Iron-gall Ink. ICN-information. Nr.1 Institut Collectie Nederland. https://www.cultureelerfgoed.nl/binaries/cultureelerfgoed/documenten/publicaties/2001/01/01/condition-rating-for-paper-object-with-iron-gall-ink/informatieblad_01_condition_rating_eng.pdf

[4] Cuprotesmo, paper test for detection of copper ions (I and II) on surfaces, sensitivity 0,05 g. Macherey-Nagel. https://www.mn-net.com/qualitative-test-paper-cuprotesmo-for-copper-0.05-mg-cu-on-surfaces-90601?number=90601 - Accessed 20.01.2023

[5] Strlič, M., et al. "A Comparative Study of Several Transition Metals in Fenton-Like Reaction Systems at Circum-Neutral pH." Acta Chimica Slovenica2003. 619-32. Vol. 50.

[6] Barrett, Timothy, Mark Ormsby, and Joseph B. Lang. "Non-Destructive Analysis of 14th–19th Century European Handmade Papers." Restaurator 37.2 (2016): 93-135.

Detection and monitoring of defects in the Brancacci Chapel wall paintings via Holographic Interferometry and Microwave Reflectometry

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The assessment of the state of conservation is a mandatory prerequisite for planning the subsequent restoration work also for wall paintings. In common practice, restorers make the preliminary evaluation by visual and tactile inspection, without the use of any special scientific instrumentation. Cracks, cavities, lack of material, detachments, out-of-plumb and deformation of (non-)structural elements are reported in a damage map to document the state of decay at a given point in time [1]. In particular, the detachments are recognized by the finger knocking test, but it is a discretionary method and highly subjective. Thus, there is a strong demand for the development of a non-invasive, in-situ and instrumental approach that refines this preliminary survey. Many analyses can be conducted for this purpose, such as magnetometric, sonic, endoscopic, ultrasonic, or thermographic, but all these techniques are not able to determine the effective stability of the detachments. So, a properly combination between DHSPI (Digital Holographic Speckle Pattern Interferometry [2])-based on the comparison of interferograms acquired after a small thermal excitation is applied to the system to be analyzed- and a MWR (Microwave Reflectometry [3]) was setup. The proposed approach was validated on mock-ups mimic the real condition of a detachments in wall painting, then a in situ experimentation has been performed on the wall paintings of the Brancacci Chapel in the church of Santa Maria del Carmine in Florence (painted by Masolino, Masaccio and Filippino Lippi in 1422-75). The combination of these two techniques served to locate the depth of the discontinuity inside the wall and to objectify the overall legend made by the restorers during the preliminary survey, in which the detachments were indicated as *"stable"*, *"not very stable"* and *"unstable"*, i.e., close to falling. The integrated use of the two techniques, which have different operating principles, proved to be very suitable in establishing risk prioritization to consequently guide restoration strategy. In particular, DHSPI, as a completely non destructive, non contact, repeatable technique, is confirmed to be a powerful physical tool with high diagnostic potential in locating and measuring invisible and hidden defects with submicrometer accuracy [2].

[1] P. Mora, L. Mora, P. Phlippot, Conservation of Wall Paintings, Sevenoaks: Butterworths, 1984.
[2] V. Tornari, Light: Advanced Manufacturing, 2022, 3(18).
[3] M. Riggio, et al., Structural Control and Health Monitoring, 2016, 24(7).

Stratigraphy of metals in heritage pollution crusts by LIBS

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Atmospheric pollution interacts with stone materials and generates various decay typologies. The formation of black crusts is one of the most harmful phenomena for architectural heritage. These are formed mainly by gypsum, carbonaceous substances, elemental carbon, and heavy metals. Previous studies have revealed the necessity to deepen our knowledge on the in-depth distribution of metals in order to better understand the crust formation processes. In our study the LIBS technique [1] was used to shed light on the processes and mechanisms involved in the formation of such degradation processes. For this purpose, mock-up marble samples covered with known amounts of pollutants (heavy metals and elemental carbon) were subjected to accelerated ageing in climatic chambers. Additionally, real samples of black crusts taken from monuments of the Monumental Cemetery of Milan (Italy) were analyzed. These samples were characterized in previous studies with different analytical techniques [2-3]. The analyses carried out on the mock-up marble samples showed that the heavy metals tend to migrate towards the inner layer of the substrate. In real black crusts, instead, different trends on the in-depth distribution of heavy metals have been observed and could attributed to different periods of accumulation or exposure to pollutants.

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References

[1] Martínez-Hernández A et al. Journal of Cultural Heritage 32 (2018) 1-8.
[2] Comite V et al. 2020 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, 2020, Pages. 435–439.
[3] Comite V et al. International Conference on Metrology for Archaeology and Cultural Heritage, 2022 (in press).

Quantification of Cultural Heritage objects:

From glasses to metals

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X-ray fluorescence (XRF) has played a key role in the analysis of objects in the field of Cultural Heritage research. The multi-elemental sensitivity and non-invasive nature of the technique make it an ideal investigative tool. A significant part of the work is qualitative or semi-quantitative analysis. Main obstacle in the quantification of Cultural Heritage objects is the requirement of working non-destructive. This has hampered the quantification as many materials do not have a defined composition within the analytical volume of the technique, for example, paintings, polychrome sculptures and art on paper or parchment. In contrast, objects made of glass or metals, do have a more-or-less defined analytical compositional volume. Accordingly, quantitative results may contribute or directly help to answer research questions.

However, the quantification of such samples usually encounters two main sources of error: firstly, aspects related to the samples themselves, and secondly, to the quantification algorithm or instrument used for the analysis. Both these topics will be discussed using specific examples and highlighting benefits and potential pitfalls. The first case study will focus on the quantification of glasses, as this is affected by the low light-element sensitivity of XRF measurements at air, as well as, by the degradation of the material itself, resulting in a non-representative analysis of the sample surface. The second case study will show the quantification of metal alloys, which is also influenced by surface effects. Specifically, corrosion or patina formation may result in enrichment or depletion of certain elements, for example, in silver samples or archaeological objects including Cu- and Au-alloys. In addition, the analysis of metals might be encountering the effects of material heterogeneity at both millimeter and sub-millimeter scale. Furthermore, the analysis of metal alloys suffers from strong matrix effects, peak overlap, and diffraction peaks as important analytical artifacts. Despite these complexities, the analysis of metals is usually quite forgiving, and metals can still be considered an ideal material, suited for precise quantification. Nevertheless, these analytical challenges require a well-thought approach to ensure meaningful results.
The main intention of this overview on quantification is, thus, to illustrate the capabilities of the non-invasive technique and principal possibilities for the large variety of materials in Cultural Heritage science by using existing analytical instruments and routines.

NMR spectroscopy and micro-analytical techniques for studying the *corami* (gilt and painted leather) wall coverings from Chigi Palace, Italy

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Italian leather with a gilded or silvered background, tooled and painted in bright, transparent colors is called “corami” (from the Latin *corium*), "cuoi d'oro" or "cuoridoro" (gilt leather). When it comes from Spain, it is called cordovan leather. In fact, the first gilded/silvered and painted leathers were manufactured in Muslim Spain, Cordoba being the center with the most flourishing production. This type of leather then spread in Europe thanks to imports from Spain and Middle East. In Italy, the manufacturing of the so-called *corami* reached its peak in the XVIth and throughout the XVIIth century. The most important production centers were Naples, Rome, Venice, Bologna, Ferrara and Modena. *Corami* were preferred for wall covering or to decorate the front part of the altars. It is known that gilt leather rarely survives in its original state due to the inherent problems of leather as a support for the richly decorated surface. The specific layering of materials in this type of leathers (leather support, animal glue, silver leaf, oil paints, glazes and varnishes) makes their conservation and restoration a challenge.

For this reason, one of the most spectacular example of *corami* wall coverings from the XVIth century, conserved in Palazzo Chigi, located in Ariccia, near Rome, was the subject of comprehensive *in situ* and *ex situ* analysis campaigns intended to study the materials used for manufacturing, assess their deterioration and evaluate the overall conservation condition of the wall panels. The NMR MOUSE measurements conducted *in situ* provided the thickness of leather and its stratigraphy. A number of micro samples were analyzed by Fourier transform infrared (FTIR) spectroscopy, Raman microscopy, optical microscopy, SEM-EDX, micro-differential scanning calorimetry (micro-DSC) and ^{13}C CPMAS NMR spectroscopy.

The results obtained revealed the type(s) of leather (very thin goatskin), tannins (sumac and alum), pigments (verdigris, iron oxide), varnish (pine resin) and media (gelatin) used in this rare type of *corami*, as well as their deterioration forms (presence of both copper and calcium oxalates, collagen conversion to gelatin and further to amorphous form). The *corami* also exhibited physical and mechanical deterioration forms (dust and soiling matters, cracks and brittleness, shrinkage, erosion and losses of painted surfaces).

The novelty in this case study stands in the combination of NMR spectroscopy and micro-analytical techniques, which allowed us to obtain significant results on such a sophisticated and fragile material and highlight potentials, limitations and future developments of NMR techniques for investigating gilt and painted leather.

Untitled (no. 74/90) an Acrylic Paint on Lead on Wood by Günther Förg: Diagnosis and Conservation

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Untitled (no. 74/90) is a large format painting (280,5 x 160,5 cm) by Günther Förg (1952-2013) a prolific German artist in the abstract painting sphere. The whole painting is composed by a sole lead sheet glued on a dovetail solid wood support. The lead surface is partly covered by an orange acrylic paint layer.

Since its acquisition in 1995 the painting was kept in pristine conditions on the storage facilities until 2018 when some blisters where observed on the four lead edges of the artwork. The painting was on an itinerancy exhibition between 2018 and 2019 when the blisters became more pronounced. Between 2019 and 2020 some cracks and tears appeared around some of the brittle blisters. Even though the painting was stored and exhibited in controlled environment condition, the edges were weakening and some of the blisters exploded showing a white powder coming from the inner part of the lead sheet. The air pockets where localized only on the edges. The orange paint layer showed good conservation conditions however the lead surface was showing a subtle whitish patina, which it was also observed in some areas of the edges and on certain Förg lead paintings from other collections. Until now, it is out of our knowledge the presence of blisters in other Förg artworks.

The white corrosion powder, the wood from the support and the glue around the edges were analyzed by infrared spectroscopy (FTIR) and pyrolysis gas chromatography mass spectrometry (py-GCMS). Results indicated that the powder is mainly composed of lead carbonate $(PbCO_3)_2 \cdot Pb(OH)_2$ (hydrocerussite). Some phenolic-based compounds were present in the white powder as well. The same phenolic-based compounds were detected in the wood sample, while an epoxy resin was used as a glue, according to py-GCMS analysis.
As reported in literature, lead is often affected by the presence of acids. Lead corrosion can be linked to the presence of volatile organic compounds emitted by wood and glues. The organic compounds, specially the acetic acid can corrode the surface of the lead sheet and convert it to lead carbonate. Why the deterioration was only being developed in the edges?

The conservation treatment permitted to observe and analyze that the upper and lower surface of the wood panel was sealed with the transparent-milky epoxy resin without being glued to the lead sheet and the lead was not corroded, while the wood edges were not sealed but glued to the lead with the epoxy resin.

Based on the artwork observation and analysis, a decision was taken with the approval and guidance of the Gunther Forg Estate. The damaged lead edges were gently removed as well as the epoxy resin used to glue the lead edges to the wood. The wood edges were sealed with a new acid free adhesive and the new lead sheet bands were also glued to the edges with the acid free adhesive. The new lead bands were adapted and integrated to the painting giving back to the artwork its solid effect. The cloudy whitish patina from the lead surface was cleaned and removed to return the object its original appearance.

Investigation of the new world silver provenance and trade in Europe during the 16th and 17th centuries: HE-PIXE and p-XRF spectroscopic analysis

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The European economy of the second half of the 16th century was driven by trade and the supply of silver from the New World. The mine of Potosi discovered in 1545 has been exploited since 1548 by the Spanish Crown. Silver quickly became a crucial resource for the manufacture of coins. The silver route reached the Atlantic coast in France where Spanish coins were converted into French currency. The analysis of the provenance of silver in coins minted in Nantes between 1551 and 1625 potentially shows the impact of the Wars of religion and political decisions on the silver supply between Spain and France.

The silver from the "Cero Rico" mine is characterized by the element indium, which is specific to this ore and makes it a good marker [1]. Gold is also present in silver but it is not specific to silver ore from Potosi, high gold proportion rather characterizes Mexican and European supply. With regard to the concentrations of indium and gold in the Nantes coins, it is hoped to be able to distinguish transitory periods of supply of American silver. Mercury could also be an interesting element to examine because of the amalgamation process introduced in the Potosi mine in 1572.

More than forty coins were irradiated by High Energy Particle Induced X-Ray Emission technique (HE-PIXE) [2] and X-Ray Fluorescence was performed with a handheld XRF spectrometer. The indium and gold X-ray lines are detected in the spectrum and can be used to evaluate the concentration of these two elements in relation to the silver content.

The detection limits of gold in a silver matrix are on the order of a few hundred ppm, which is sufficient for our case study. However, indium requires a long irradiation time (more than an hour) to be detected by HE-PIXE, which limits the beam time to a few samples. An indium content of 10 ppm cannot be achieved by our XRF device [3]. Nevertheless, this method offers a good complementary approach to HE-PIXE to quickly identify rich gold coins and explore indium content only on previously selected samples.

Based on the results of the coins' spectroscopic analysis, the numismatist can interpret the variations of the gold and indium content in different copies corresponding to years of interest. A global representation of the composition of the coins between 1561 and 1575 and between 1597 and 1600 can help to clarify the reorganization of the trade from Nantes to Seville from 1565 and to show the isolation of Nantes during the Wars of Religion until 1598.

[1] M. F. Guerra, A. Gondonneau, et J.-N. Barrandon, « South American precious metals and the European economy: A scientific adventure in the Discoveries time », *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.*, vol. 136-138, p. 875-879, mars 1998, doi: 10.1016/S0168-583X(97)00754-4.

[2] S. Santra *et al.*, « Analysis of some coins by energy dispersive X-ray fluorescence (EDXRF) and high energy particle induced X-ray emission (PIXE) techniques », *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.*, vol. 229, nº 3-4, p. 465-470, avr. 2005, doi: 10.1016/j.nimb.2004.12.125.

[3] M. Guerra, M. Manso, S. Longelin, S. Pessanha, et M. L. Carvalho, « Performance of three different Si X-ray detectors for portable XRF spectrometers in cultural heritage applications », *J. Instrum.*, vol. 7, nº 10, p. C10004, oct. 2012, doi: 10.1088/1748-0221/7/10/C10004.

New strategies for VOCs control in museums showcases

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A common practice to limit the problem of volatile organic compounds (VOCs) in museum showcases is to test the emission of raw materials used to build the display cases through the Oddy test [1,2]. However, it lacks of reproducibility, of an objective interpretation of the results and none identification and quantification of the emitted species are achievable.

In this study some alternative strategies for facing off the conservation problem caused by VOCs in museum showcases are presented. Goppion company, an internationally recognized manufacture of display cases, provided the display cases materials that were studied and tested through different approaches. A sort of emission chamber was specifically adapted to a first identification and quantification of the mainly emitted compounds. The use of the SPME-GC-MS method was also tested as an alternative fast qualitative characterization of the materials emissions and the identification of further possible dangerous compounds. Finally, as a relatively robust method for gas sensing in other application fields, FT-IR spectroscopy was also tested to identify the emitted species of the materials by using a heated gas IR cell. Early experiments were conducted on standard compounds and on some typical display cases materials, showing promising results.

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[1] E. Canosa, A. Wiman, S. Norrehed, M. Hacke, Riksantikvarieämbetet, 2019, 67.
[2] O. Chiantore, T. Poli, Atmosphere, 12 (3), 2021, 364.

Gold and silver Iron Age lunulae from western Iberia: a study by multifocus OM, pXRF and digital imaging processing

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During Proto-history diverse decorative objects were manufactured in gold and silver. In the Iberian Peninsula, during Bronze Age, mainly gold was used to produce artefacts that were usually simple massive objects, decorated with geometric motifs, and made of an alloy containing 5 to 25 wt. % Ag and <1 wt. % Cu. During Iron Age, more complex shapes began to be produced and new materials and technologies were introduced. Despite this, some shapes and aesthetics persisted with only a few changes in technological or material tradition. In the present work we will present a multifocus Optical Microscopy (multifocus OM) and portable X-ray fluorescence spectrometry (pXRF) analyses to 5 Iron Age lunulae from western Iberia. All are presently part of the of the National Museum of Archaeology (MNA, Lisbon, Portugal) collection, with four of them from Pragança archaeological site and one of them from the Viseu region (Portugal). Usually, lunulae are objects that refer to Chalcolithic or Early Bronze Age, and emblematic examples are known from Ireland, besides some other Atlantic regions. These early examples normally consist of flat and thin gold necklaces shaped like a crescent moon, decorated with geometric repousse [1]. In the present study, we will present a unique Iron Age lunulae collection, that despite having some resemblances to the earlier ones, show a distinct shape, narrower and thicker, distinct decoration techniques, which include punches, and that materialize the use of a larger variety of alloy compositions, namely silver alloys. Extended depth of field images generated by multifocus OM of the decorated surfaces will be presented, as well as the elemental composition obtained by pXRF, considering different areas of analysis as well as possible compositional heterogeneities along surface depth. Also, 3D modelling will be used to reconstruct missing parts of the object's bodies and to enhance the visualization of the detailed decorated surfaces, of special importance in the silver lunulae, which suffer from severe tarnishing.

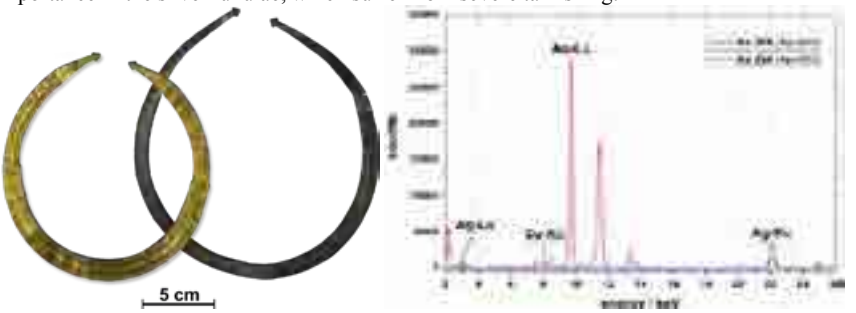

Figure 1. Photographs of a gold lunula (Au 294 from Viseu) and a silver lunula (Au 208 from Pragança) (left half) and two pXRF spectra of one gold and one silver lunulae, with some characteristic Ag, Au and Cu X-ray lines depicted (right half).

[1] J. Taylor, "Lunulae Reconsidered" in *Proceedings of the Prehistoric Society*, 36, 1970, pp. 38-81, doi:10.1017/S0079497X00013086.

Analytical investigation into silk from traditional Japanese samurai armours

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In order to correctly manage collections of historical silks, it is a good practice to gain an insight into conditions and nature of the yarns. This paper presents the results of a wide work of characterisation of silk fabrics coming from a collection of traditional Japanese samurai armours which date back from 15th to 20th century (Museo delle Culture, Lugano, Switzerland). An analytical protocol based on microinvasive ATR-FTIR spectroscopy and non-invasive External Reflection FTIR (ER-FTIR) spectroscopy was employed. The ER-FTIR technique is rapid, portable, and widely employed in the cultural heritage field, but rarely applied to the study of textiles. The ER-FTIR band assignment for silk was discussed for the first time. The obtained data are a part of a challenging work of characterisation of the majority of ancient materials in armours, which is a never made before project. Data have been interpreted with the help of peak fitting analysis and chemometric elaboration with PCA.

ATR-FTIR spectroscopy permitted to give clear indications about the decay condition of silks, thus giving the opportunity to discriminate original and restoration materials. In particular, the region of amide I and II bands was studied in order to obtain conformational information about silk proteins, which could be related to different decay stages. An indication of the decay status of the silk yarn was hypothesized by observing the shift of the amide I peak.

Another issue of interest was the detection of degumming. This process is generally applied to eliminate sericin from the fibroin core; the obtained fibre is named soft silk, in contrast with hard silk which is unprocessed. The distinction between hard and soft silk could give both historical information and useful indication for informed conservation. ER-FTIR spectra, evaluated in the OH stretching region, allowed a reliable distinction between hard and soft silk, allowing to overcome the difficulties in detecting hard silk which are typical of ATR-FTIR spectroscopy.

[1] Maguregui, M. A non-invasive in situ methodology to characterise the lacquers and metals from the Edo period Japanese armour, Microchemical Journal, 2018, vol. 137, pp. 160–167
[2] Dalewicz-Kitto, S. Japanese armour and the conservation of a Sakakibara family armour at the Royal Armouries, Journal of the Institute of Conservation, 2013, vol. 36 (1), pp. 35–52
[3] Badillo-Sanchez, D. Characterization of the secondary structure of degummed Bombyx mori silk in modern and historical samples, Polymer Degradation and Stability, 2018, vol. 157, pp. 53–62
[4] Peets, P. Reflectance FT-IR spectroscopy as a viable option for textile fiber identification, Heritage Science, 2019, vol. 7 (1), pp. 93

Metal thread lace: Scientific identification methods as a source of information on manufacturing techniques of historical haberdashery

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Historic textiles decorated with different types of metal threads are often regarded as pieces of high artistic, cultural, and historical value. An example of this is lace, which developed from the embroidery technique of cutwork and became popular in Europe during the sixteenth century [1]. Lace was typically made from linen, but silk was later introduced. In many cases the textile grounds were also decorated with metal threads or lace could have been made entirely from metallic threads. The physico-chemical investigation of metallic threads found in textile-based objects most likely started in the late 19th century [2]. The material composition and techniques employed to create these objects are useful pieces of information for art historians and textile conservators. The National Museum in Krakow houses in its textile collection a large assemblage of lace objects dating from the seventeenth to the nineteenth century. These objects were produced using the bobbin technique, which involves the complex interweaving of many threads, which are bound on bobbins that traditionally were made of wood or bone. These objects have different shapes and many of them consist of bands of various widths, offering the possibility of achieving interesting aesthetic effects. This presentation summarizes the results obtained after analyzing 575 samples taken from 192 lace objects. Examination of the objects started with optical microscopy (OM) and scanning electron microscopy with energy dispersive X-ray microanalysis (SEM-EDS) in order to enhance the knowledge about their fabrication techniques, morphology, and to contextualize the results in light of previously published results. This was followed by analytical work, which required the use of X-ray fluorescence spectroscopy (XRF) and Fourier-transform infrared spectroscopy (FTIR). OM allowed to characterize the metal threads in terms of metallic color, direction of the braids, and degree of degradation of the metals. Furthermore, XRF and SEM-EDS analysis allowed to classify the objects into 4 groups based on the composition of metal threads and their stratigraphic layers: Ag/Cu alloy plated with Au, Cu/Zn alloy, Ag plated with Au, and Ag/Cu alloy. In addition, FTIR spectroscopy allowed to identify the textile substrates of either linen or silk.

[1] M. Watt, Textile Production in Europe: Lace 1600-1800", In: Heilbrunn Timeline of Art History, The Metropolitan Museum of Art, New York, 2002.
[2] M. Jaró, A. Toth, Endeavour 15(4), 1991, 175-184.

The Portrait of Leo X by Raffaello: characterisation of the painting materials and techniques by means of MA-XRF

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In the occasion of the 500th anniversary of the death of Raffaello (2020), there has been a large exhibition at the Scuderie del Quirinale in Rome, occasion that acted as a springboard for the study, and for conservation interventions when needed, of a number of many paintings and drawings by the Old Master. One of these paintings is the object of this study, the portrait of Leo X with two cardinals belonging to the collection of the Uffizi galleries in Florence. Prior to the exhibition, the painting underwent conservation treatments at the Opificio delle Pietre Dure [1] where a deep study of the painting materials and technique was supported by a comprehensive diagnostic campaign. In this work, the results of macro-X-ray fluorescence (MA-XRF) analysis, carried out exploiting the instrument developed by INFN-CHNet, are shown [2].
As consistent with other paintings by Raffaello and with the materials available to artists during the Renaissance period, lead white, vermilion, earth/ochres, Cu-based compounds, and lead–tin yellow were masterfully used by the artist to paint different fabrics and flesh tones. Mn most likely indicates the use of glass powder in red lakes [3], while Bi suggest the use of a rare “bismuth black”, also attested in other paintings by Raffaello [4], employed to give the metallic appearance of objects such as the silver handbell, but also the grey tone of the cassocks and of the architectural background. Of interest, the distribution of the Cu map in the architecture attests that the painting was meant as a triple portrait since the beginning and not as an individual portrait of the pope as hypothesised by scholars.

As demonstrated also in this study, MA-XRF allows the non-invasive mapping of the elemental distribution of the materials, making the technique a powerful tool for a preliminary non-invasive and non-destructive analytical method.

[1] R. Bellucci; C. Frosinini, Un caso complesso di pianificazione dell’immagine in Raffaello: Il triplice ritratto di Leone X, Giulio de’ Medici e Luigi de’ Rossi. In Raffaello e il Ritorno del Papa Medici: Restauri e Scoperte sul Ritratto di Leone X con i Due Cardinali; Ciatti, M., Schmidt, E.D., Eds.; EdiFir Edizioni Firenze: Firenze, Italy, 2020; pp. 119–142
[2] A. Mazzinghi et al., Heritage, 5, 2022, 3993-4005
[3] M. Spring, Colourless Powdered Glass as an Additive in Fifteenth- and Sixteenth-Century European Paintings; Technical Bulletin, Volume 33; National Gallery: London, UK, 2012; pp. 4–26
[4] M. Spring et al. ‘Black Earths’: A Study of Unusual Black and Dark Grey Pigments used by Artists in the Sixteenth Century. Nat. Gal. Tech. Bull. 2003, 24, 103–105

Ancient glass samples from the Cathedral in Paderborn: an investigation using synchrotron radiation based techniques

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Within this project ancient glass samples were investigated that were collected during the archaeological excavations in the Paderborn cathedral between 1978 and 1980 [1]. Archaeologists assume that the oldest glasses were "locally" fabricated at one of the two glass factories located less than 20 km from Paderborn and just about 10 km apart. Thus it was the central goal of this investigation to find out if it is possible to assign glasses to one of those places, for example by comparing elemental distributions of the glasses found at the cathedral with those of glasses found at the glass factories. A second goal was finding out whether by a "chemical analysis" it is possible to learn details about the fabrication techniques (reducing of melting temperature, additives for coloration.

The element distribution of the glasses was determined by X-ray fluorescence spectroscopy (XRF). The "chemical analysis" was carried out by measuring X-ray absorption fine structure (XAFS) spectra, specifically X-ray absorption near edge structure (XANES) spectra, of some elements of interest (e.g. Cu and Fe). XANES spectra "start" ~ 50 eV below the corresponding "edge" of the element of interest and reach up to ~ 100 eV above the edge. The "edge" is the jump of the absorption coefficient when the energy of the incoming X-rays is high enough for exciting the corresponding inner shell electron into the continuum or into an empty orbital. XANES spectra contain quite detailed information about the electronic structure and the local geometric vicinity of the absorbing atomic species. Both types of experiments (XRF, XANES) were carried out using synchrotron radiation at either the Center for Advanced Microstructure and Devices (CAMD) of Louisiana State University in Baton Rouge or at the SIAM Photon Lab of the Synchrotron Light Research Institute in Nakhon Ratchasima (Thailand).

Based on the results of the XRF experiments, mainly the concentrations of Pb, Cu and Ca, glasses from the cathedral can be clearly assigned into 3 groups. Differences in the concentration of trace elements indicate that the glasses of one of the three groups were fabricated using different starting material and thus perhaps a different glass factory. Also glasses from one of the glass factories could be assigned to 2 groups and both of these groups showed significant differences compared to the glasses from the second glass factory allowing a preliminary assignment of the glasses from the cathedral to one of the glass factories. The XANES spectra, e.g. from the Cu-K-edge but also the Fe-K-edge, show strong differences between not just between samples from different groups but also between samples belonging to the same group. A more detailed analysis of the spectra provides some information about additives and melting conditions, e.g. the atmosphere in the melting furnace.

[1] U. Lobbedey: Die Ausgrabungen im Dom zu Paderborn 1978/80 und 1983, Teilbände 1-4, Denkmalpflege und Forschung in Westfalen, Bonn 1986

Mass spectrometry and thermoanalytical techniques to understand the transition from egg tempera to oil paint in Italian Reinassance

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Italian Renaissance Old Masters, such as Sandro Botticelli, Domenico Ghirlandaio and Leonardo Da Vinci, used paints based on mixtures of oils and proteins (Figure 1) [1], but "how" and "why" this was done is still not understood today.

Figure 1. Sandro Botticelli, the Lamentation of Christ, Detail. St. John's feet show the typical egg tempera layer build-up and paint application by hatching. In contrast, the grass foreground (including the dark green (almost black) paint layer) shows typical properties of oil paints. Both egg and oil are detected in the paint layers. Pictures: © Wibke Neugebauer, Munich.

Egg and drying oil can be combined in the paint in many different ways resulting in varying microstructures with substantially different behaviors of the wet paint but also affecting drying and curing reactions. In this work we prepared paint formulations based on combinations of egg yolk and linseed oil and systematically investigated chemical and rheological properties of the paints obtained. Egg (yolk and egg glair) can be used to control the flow behavior of an oil paint, its wrinkling and drying kinetics [2]. On the other hand, oil can be used to modify the microstructure of an egg tempera paint, affecting its brushability and hardening.

A combination of mass spectrometry and thermoanalytical techniques were used to understand the chemistry and kinetics of the oil curing as well as the molecular features of the paint films produced. The final aim is to contribute to elucidate the complex consequences of Old Masters combining egg and drying oils in their paints, bringing new insights into the technical artistic revolution that took place during the Renaissance period.

[1] J. Dunkerton, in Early Italian Paintings: Techniques and Analysis (eds. R.Hoppenbrouwers, H. Dubois, T. Bakkenist, T.) (1997) 29–34
[2] O. Ranquet, C. Duce, E. Bramanti, P. Dietemann, I. Bonaduce, N. Willenbacher Nat Commun 14, 1534 (2023). https://doi.org/10.1038/s41467-023-36859-5

Investigation of the Carolingian and Romanesque wall paintings detached from the church of St. Johann in Müstair

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The Benedictine monastery of St. Johann in Müstair is UNESCO World Heritage Site, hosting an extraordinary cycle of Carolingian wall paintings of the late 8th/early 9th century in the main church. This cycle, which originally covered the walls of the entire building, was partially repainted with Romanesque paintings around 1200, then further concealed by successive decorations and lime wash, and finally forgotten in the following centuries.

In 1908-1909, 26 large fragments of wall paintings from the upper register of the Carolingian and Romanesque cycles, which due to the construction of vaults in late-Gothic period had been left uncovered in the attic of the church, were detached. First the Romanesque paintings were removed by the *stacco* technique (transferred to a rigid support made of gypsum), then the Carolingian paintings were detached by the *strappo* technique (transferred to a textile support and mounted onto wooden strainers) [1]. The latter intervention was not fully successful, and traces of the original paintings (so-called imprints) are still visible in the attic of the church. The detached painting fragments are now part of the collection of the Swiss National Museum (SNM), but their heterogeneous aspect and their state of conservation have limited their potential for exhibition and valorisation.

Since some of the paintings were assessed in a critical condition, a project was initiated [1]. The paintings in the SNM and the imprints left in Müstair were analysed using multispectral imaging, portable XRF and FTIR. Targeted samples were also collected and analysed by Raman spectroscopy, SEM-EDS and FTIR. The study of historical documents supplemented the analytical information. The results, on the one side, confirmed the data obtained from previous investigations [2] [3], and, on the other side, opened up interesting new findings about the painting materials and techniques of these unique artworks.

[1] N. Ellwanger, T. Lombardo, P. Cassitti, C. Martinucci, A. Felici, M. Caroselli, M. Leuthard, R. Emmenegger, Zeitschrift für Schweizerische Archäologie und Kunstgeschichte, 79(1), 2022, 5-22.
[2] G. Cavallo, M. Aceto, R. Emmenegger, A.K.Keller, R. Lenz, L. Villa, S. Wörz, and P. Cassitti, Archaeological and Anthropological Sciences, 12(73), 2020, https://doi.org/10.1007/s12520-020-01024-2.
[3] J. Goll, R. Emmenegger, P. Cassitti, Zeitschrift für Schweizerische Archäologie und Kunstgeschichte, 78(4), 2021, 169-294.

The case of *tabella immunitatis* discovered in Porto Torres (Italy): characterization of the metal composition.

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Between the 19th and the beginning of the 20th century, the city of Porto Torres, in the northwest of Sardinia (Italy) was improved with new infrastructures. The ruins of the Roman buildings of the ancient town of Turris Libisonis and thousands of ancient objects were re-used to fill the underwater foundations of the pier of the lighthouse.
During the recent works for the extension of the harbour (2006 - 2007), thousands of artefacts were rediscovered and among them, there was a *tabella immunitatis* dating back to the mid-3rd century CE. As the inscription suggests, this was originally nailed to a ship whose owner was Flavia Publicia, a well-known priestess (Vestale Maxima) in Rome. Her portrait is carved in the central part of the *tabella.* The inscription says that the ship should not pay taxes in the harbours [1, 2, 3].

This exceptional artefact, linked to one of the most famous *Vestales* of the mid-3rd century Rome, was analyzed through Energy dispersive X-ray fluorescence spectrometry (EDXRF), integrated by Monte Carlo simulation (MC) [4,5]. The results were integrated by Multiband Imaging techniques (MBI), Total Reflection Fourier Transform Infrared Spectroscopy (TR-FTIR), Raman spectroscopy and Optical Microscope documentation.

All the analyses were carried out directly in the museum with non-invasive and portable techniques with the aim of maximum protection of this unique artefact. The results obtained provide helpful information to the archaeologists for the study of the piece itself and the comparison with other known *tabellae* belonging to the Roman period.

[1] G. Gasperetti, *Una* tabella immunitatis *dal porto di* Turris Libisonis, in A. Mastino, P.G. Spanu, R. Zucca (eds.), Naves plenis velis euntes, Roma 2009, pp. 266-277.
[2] G. Gasperetti, *Reperti dal porto commerciale di Porto Torres*, in L. Usai (eds.), *Memorie dal sottosuolo. Scoperte archeologiche nella Sardegna centro – settentrionale*, Cagliari 2013, pp. 267-272.
[3] P. Gianfrotta, *Sulla* tabella immunitatis *della Vestale Massima Flavia Publicia a Porto Torres*, in *Archeologia Classica* 2018, 69, pp. 793-802.
[4] Brunetti A., Golosio B., Schoonjans T., Oliva P., Spectrochim. Acta - Part B, 2015, 108, pp. 15-20.
[5] Cesareo R., Brunetti A., D'Oriano R., Canu A., Demontis G.M., Celauro A., Appl. Phys. A Mater. Sci. Process., 2013, 113, pp. 905-910.

Non-destructive Analysis of Corrosion Products of Bronzes by Terahertz Time-domain Spectroscopy and Imaging

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Different corrosion products can be produced on the bronze artefacts during their long-term exposure to various aggressive environment. Those corrosion products containing Cl^-, such as $Cu(OH)_3Cl$, may cause severe damage to the bronzeware. Therefore, the accurate understanding of the composition of these corrosion products and their distribution on the bronze surface, is of great importance for the restoration and preservation of bronze artefacts. However, it is still challenging to simultaneously obtain the composition and distribution of the corrosion products in a non-destructive way.

In our work, Terahertz time-domain spectroscopy (TDS) is proposed for the in-situ analysis and imaging of the corrosion products of bronzeware. The THz spectral database of standard corrosion products of bronzeware, including their featured adsorption bands and refractive indices, was established by combining the TDS measurement and density functional theory (DFT). Simulated corroded copper samples were prepared using HCl solution and further analyzed by TDS scanning non-destructively. The distribution of corrosion products on the surface layer can be obtained according to the spectral database. Since the terahertz wave can totally reflect on the metal surface, the thickness of the corrosion layer can be achieved using the time-of-flight delay of the terahertz signal and the refractive indices of detected corrosion products. Therefore, both the chemical image and thickness distribution map of the corrosion layer can be obtained simultaneously. Then this technique was successfully applied on the corrosion analysis of the 3000 years old bronzeware excavated from Sanxingdui Ruins in Sichuan Province, China. In addition, the polymorphs of basic copper chloride (atacamite, paratacamite, clinoatacamite and botallackite), a harmful corrosion product of bronze, can be distinguished by TDS. These results, combined with the TDS measurements on the corroded copper samples, can also provide valuable insight into the corrosion mechanism of bronze artefacts.

Multi-scale and multi-technical survey of Van Gogh's *Small Pear Tree in Blossom* to create a digital twin

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In 2019, the Van Gogh Museum (VGM) and ASML entered a Partnership in Science to promote and conduct research dedicated to the preservation of Van Gogh's legacy. Several projects are ongoing in collaboration with the Cultural Heritage Agency of the Netherlands (RCE), the University of Amsterdam (UvA), Eindhoven University of Technology (TU/e), and The Rijksmuseum (RMA). One of these projects seeks to create a digital framework for hosting and showcasing digital twins of paintings, acting as a repository for the knowledge and data on paintings as well as an interactive platform for visually exploring that information. The digital twin framework will also provide means to simulate change in paintings including colour change and evolution of cracks.

A crucial step in this endeavour is to gather, create, and organize as much documentation and data on the painting to be twinned. Van Gogh's *Small Pear Tree in Blossom* was selected as a test case for the development of the digital twin framework and data visualization tools. To this end, a multiscale and multi-technical research was conducted that included non-invasive and micro invasive techniques — namely, technical photography, chemical mapping using MA-XRF and RIS, in situ spot analysis with Raman, XRF, and R-FTIR, and sample examination and analysis with optical microscopy, SEM-EDX, and HPLC. Combined with technical examination and the study of historical sources and conservation documentation, new insights in the painting's palette, artist process, and changes in *Small Pear Tree in Blossom*'s conditions have emerged. Highlights of these findings will be presented using visualization tools being developed for the digital twin framework, including a desktop viewer for comparing and integrating multi-mode images and a browser-based explorer for MA-XRF data and distribution maps.

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Multi-technique approach to evaluate the effect and durability of biocides treatments on Peperino stone in the "Basilica San Francesco alla Rocca" (Viterbo, Italy)

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Consolidation and biopatinas control represent two main concerns in outdoor stone cultural heritage conservation. The work was developed in the framework of the COLLINE project (https://www.enea.it/it/fusione-e-sicurezza-nucleare/progetto-colline) whose aim is to develop, test and evaluate in real conditions and on the monuments being restored, a recovery protocol for degraded stone surfaces thanks to the synergistic use of innovative materials for conservative restoration, modern and innovative diagnostics and techniques and sensors and computerization of data,, updated in real time, for remote monitoring and management. Three low-impact products for biopatinas removal have been applied on Peperino stone, an Italian volcanic tuff, used for the construction of several architectural and sculpture elements in Viterbo and Central Italy. The hexagonal pulpit of the "*Basilica San Francesco alla Rocca*" was selected to perform the investigations. This study aimed to investigate and test the efficiency and stability of the treatment with DMSO-based gel, essential oils (BioTersus) and enzymes (Nasier) in removing the biological patinas. Color measurements, VIS-NIR-SWIR reflectance spectra (400-2500 nm) and hypercolorimetric multispectral imaging data were acquired before and after the cleaning process to characterize the distribution and concentration of the biological patina on the designed areas and to develop a monitoring model that simultaneously detects the biological activity and the efficiency of the considered low-impact products. In this study, the results show that combining different analytical approaches with chemometric modelling can lead to develop a fast, reliable and robust quality control approach that can be used to characterize and monitor *in situ* coating products in a non-destructive method.

Paint cross-section layer composition identification and prediction using MALDI-MSI

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The accurate identification of the various components of paints and their current degradation states in cultural heritage (CH) objects is essential for our understanding of artists' techniques, as well as for well-informed conservation efforts. A variety of spectroscopic techniques have been employed to answer such questions. One technique that is yet to be applied widely, and that offers high chemical specificity, requires no tags, and has significant multi-modal potential, is mass spectrometry imaging (MSI). Unlike, for example, electron microscopy with energy dispersive spectroscopy and vibrational spectroscopies (Raman scattering and Fourier transform infra-red spectroscopy) which provide information on elemental and chemical bond composition, MSI can directly map molecular distributions with a high chemical specificity based on the mass-to-charge ratio (*m/z*). MSI allows for label-free chemical imaging of proteins, lipids, metabolites, and pigments (organic and inorganic) directly on the sample.

Here we describe the first application of matrix-assisted desorption ionization (MALDI) MSI on painting cross-sections. An optimized sample preparation workflow was developed for the preparation of thin cross-sections of paintings using a common stationery adhesive tape. Painting cross sections were then imaged using an Atmospheric Pressure MALDI (TransMIT, Germany) source able to reach a pixel size of 5 µm, and coupled to an Orbitrap Q-Exactive mass spectrometer (Thermo Fisher Scientific, Germany) at a mass resolution of 70,000. The resulting MSI datasets were then processed using a home-built pigment database implemented on the Metaspace annotation platform. Due to the limitations and lack of available curated databases, a supervised machine learning approach was used to develop a least absolute shrinkage and selection operator (LASSO) model to identify and predict binder and pigment compositions of paint layers. The model was trained using a set of layered paint models with known compositions prepared at the Pratt Institute (New York) in 2008. The developed model can identify a variety of binders such as collagen glue, linseed oil, whole egg tempera, and casein. Furthermore, it can assign these binders for a variety of pigments (ochre, sienna, ultramarine…) with high specificity (>95%). This is of particular interest as we will show that MALDI-MSI can discriminate different binders within consecutive paint layers made with identical pigments.

The presentation will include a discussion of the advantages of MALDI-MSI for the analysis of the composition of CH objects as well as the challenges of data interpretation in the absence of curated databases dedicated to CH samples. We will highlight the potential of MALDI-MSI to give complementary information to more commonly used LC-MS/MS methods when employed in the study of historic samples. Furthermore, we will demonstrate the potential of machine learning techniques in building universal models for the analysis of large MSI datasets.

A new consolidation protocol with Di-ammonium phosphate for Italian Stones

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The consolidation of stone materials is a burning issue in conservation science. Several sensitive artworks require a consolidation procedure to reduce the loss of material especially when that are exposed outside. Over the years different products have been studied to counter these phenomena and in the last years the research has focused on Di-ammonium phosphate (DAP)[1]. It is an inorganic product thus very compatible with stone materials and it is specifically used to carbonate substrates; DAP reacts with calcium carbonate, partially transforming the original mineral into new formed phases (different phases of calcium phosphates) less soluble than calcium carbonate. The effectiveness of DAP has been demonstrated in different studies[2], however there are still many unresolved issues. The method of application or the concentration of product can significantly change the expected results, in particular depending of the nature of the stone[3]. This research presents a new application protocol called “two-steps procedure” and test different DAP concentrations. The two-steps procedure involves the consecutive use of two solutions of increasing concentration to allow deeper and more homogenous penetration into the substrate[4,5]. The two-steps procedure was compared with the single procedure, moreover different concentrations of DAP were tested for each protocol of testing. The following concentrations were tested: 0.5%-4% (two-steps) versus 4.5% (one step) and 1%-8% versus 9%. Starting from synthetic samples of calcium carbonate to consider different lithotypes frequently used in Italian cultural heritage. The multi-analytical approach proved to be the most adequate to verify the efficacy of the treatment. FTIR were initially used on the carbonate tablets, followed by the use of other techniques such as XRD and SEM on the lithotypes and finally, different physical-mechanical tests were carried out to verify the consolidation effectiveness.

[1] M. Matteini *et al.*, “Ammonium phosphates to consolidate carbonatic stone materials: an inorganic-mineral treatment greatly promising,” Built Herit. 2013 Monit. Conserv. Manag., pp. 1278–1286, 2013.
[2] E. Possenti *et al.*, “Consolidation of building materials with a phosphate-based treatment: Effects on the microstructure and on the 3D pore network,” Mater. Charact., 154, pp. 315–324, 2019.
[3] E. Possenti *et al.*, “Synchrotron radiation μ X-ray diffraction in transmission geometry for investigating the penetration depth of conservation treatments on cultural heritage stone materials,” Anal. Methods, 12, pp. 1587–1594, 2020.
[4] M. Anfosso *et al.*, “Eco-innovation in the conservation of built heritage: Two-steps protocol of Di-ammonium phosphate application,” Mater. Lett., 333, 133618, 2023.
[5] A. Bordi *et al.*, “2-step DAP consolidation of marble busts on the facade of Lugano’s Cathedral” in S. Siegesmund, B. Middendorf, Monument Future. Decay and Conservation of Stone, Proc. 14th Int. Congress on the Deterioration and Conservation of Stone, Göttingen, 2020.

Ink Analysis in Carolingian Manuscripts: A Study in black and red

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Black writing materials of different types and compositions have varied in use over time and different geographical regions. In this presentation, we would like to contribute to their study by the archaeometric analyses of the black and red inks used in the manuscripts from monastic production dated to the period 8th -10th centuries. Although up until to now, studies of inks have focused on the comparison of different ratios of contaminants in the ink to iron, we noticed the existence of non-vitriolic iron-gall inks, i.e., inks containing no other metallic element than iron [1]. Curiously enough, no explanation was put forward before 2020 though such inks have been already observed a decade before [2]. We propose here to measure the amplitude of this phenomenon by varying the types of texts studied (Bibles, hagiographies, formulae, i.e., sample letters and charters…), the places of copying, and the period studied. We propose to study the same phenomenon with red, in order to verify whether several types of red coexisted, and whether we can explain the reasons for these differences in preparation within the same geographical space, scriptorium, or manuscript. The results will be compared with several other archaeometric studies of contemporary manuscripts as well.
To this aim, sixty-four manuscripts have been analysed within the framework of two projects: the 'C08 – East Frankish Manuscripts Containing Collections of Formulae" project and the Coenotur project, both based at the Manuskriptkulturen in Asien, Afrika und Europa (University of Hamburg) in close collaboration with the Bundesanstalt für Materialforschung und -prüfung, Berlin (BAM). In this regard, we adopted a non-invasive protocol that included near-infrared imaging and X-ray fluorescence analysis for on-site measurements supported by historical and palaeographic analysis.
In present study that equally involved humanities and natural sciences, we aim to provide new insights as to how the scholars of the early Medieval Ages prepared manuscripts and writing materials.

[1] O. Hahn, Oliver, G. Nehring, R. Freisitzer, I. Rabin. 'A Study on Early European Inks from St Paul in Lavanttal'. Gazette Du Livre Médiéval 65, no. 1 (2021): 58–81. https://doi.org/10.3406/galim.2019.2150
[2] B. Frühmann, F. Cappa, W. Vetter, M. Schreiner, F. Petrus. 'Multianalytical Approach for the Analysis of the Codices Millenarius Maior and Millenarius Minor in Kremsmuenster Abbey, Upper Austria'. Heritage Science 6, no. 1 (December 2018): 10. https://doi.org/10.1186/s40494-018-0176-3. P. Roger, A. Bosc. 'Étude Sur Les Couleurs Employées Dans Des Manuscrits Datés Du VIIIe Au XIIe Siècle Provenant de l'abbaye de Fleury'. In Abbon, Un Abbé de l'an Mil, edited by A. Dufour, G. Labory, 415–36. Bibliothèque d'histoire Culturelle Du Moyen Âge 6. Turnhout: Brepols, 2008. https://doi.org/10.1484/M.BHCMA-EB.3.199.

Development of in-situ LIBS and EDXRF methods validated by ion beam techniques to quantify halides in Pompeian pyroclasts and cinnabar-containing frescoes

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The pyroclastic materials ejected in the eruption of Mount Vesuvius in 79 AD sealed Pompeii, protecting the ancient Roman city against external deterioration sources, alas annihilating life. However, these pyroclasts represent a threat for the conservation of the exquisite Pompeian mural paintings, due to their high fluoride and chloride contents, among other ions that can be leached by rain- or groundwater [1,2]. More concretely, chlorides take part in the degradation of cinnabar pigment in the wall paintings of Pompeii [2]. It becomes then crucial to estimate the concentration of these halides in accretions of pyroclastic materials and in cinnabar-decorated paintings to predict the minimum content of halides that assists the transformation of this pigment. Hence, the aim of this work was to develop non-destructive methodologies to quantify Cl and F using portable Laser Induced Breakdown spectroscopy (LIBS) and handheld Energy Dispersive X-ray fluorescence spectrometry (HH-EDXRF). These methods have been validated by Nuclear Reaction Analysis (NRA) and Particle Induced X-ray Emission (PIXE) experiments, carried out at the Laboratory of Ion Beam Physics of ETH Zurich in the framework of the EU-funded RADIATE initiative.

Three sets of calibration materials were prepared: i) solutions of the mentioned halides spiked on fresco cinnabar mock-ups; ii) powdered halides added to synthetic cinnabar and calcite pressed pellets; iii) powdered halides on pressed pellets of Pompeian pyroclasts. The ultimate halides content was determined by NRA and PIXE analyses. The high accuracy of these measurements allowed the building and fine-tuning of the calibration curve obtained by p-LIBS and HH-EDXRF. Successful calibration methods were obtained in all the cases with the notable exception of p-LIBS with the pyroclast matrix, due to a lack of correlation of its results with the ones from NRA/PIXE.

[1] S. Pérez-Diez et al., Angew. Chem. Int. Ed. 60 (2021) 3028–3036.
[2] S. Pérez-Diez et al., Anal. Chim. Acta. 1168 (2021) 338565.

Uncertainty of quantitative X-ray fluorescence micro-analysis of metallic artefacts caused by their curved shapes

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The effects of an irregular shape on the result of a quantitative X-ray fluorescence (XRF) micro-analysis are summarized. These effects become relevant when the XRF analysis is performed directly on an investigated material. A typical example is the XRF analysis of valuable and historical objects whose measurements should be performed non-destructively and non-invasively, without taking a sample.

Lot of measurements and computer simulations were performed for selected metallic materials and shapes to evaluate the accuracy and precision of the XRF. Experiments and theoretical calculations are related to a tabletop device for XRF micro-analysis designed and used to analyze various historical artefacts at the Czech Technical University in Prague. This XRF system consists of an SDD detector, an air-cooled X-ray tube with a Mo anode and a maximum power of 50 W (50 kV, 1 mA), and a positioning system for XRF scanning. The X-ray tube has a fixed polycapillary focusing optics with a 15 μm focal spot (FWHM for 17.4 keV) at a working distance of 4 mm from the output end of the optics. The X-ray spectrum of the X-ray tube is modified by the optics.

The Monte Carlo method is a suitable numerical calculation method for math problems that are difficult to be solved analytically. It is based on generating random or rather pseudo-random numbers and simulating radiation transport in matter. Common tasks of quantitative XRF analysis can be solved analytically using equations coming from Sherman's equation. If the studied problem is more complicated and it considers irregular shapes, for instance, the application of the Monte Carlo method is recommended. The Monte Carlo code MCNP running on a normal PC was used for recent calculations [1]. The computing time was several minutes for an individual task.

The surface effects in X-ray fluorescence micro-analysis of metallic artefacts were quantified by applying the Monte Carlo calculation method. Its main advantage is quite short computing time for XRF experiments and the possibility to simulate almost arbitrary geometric arrangement and any composition of materials. The attention was paid especially to historical metallic materials requiring non-destructive and non-invasive XRF micro-analysis. The presented results refer mainly to copper, silver, and gold alloys. The results of Monte Carlo simulations show the relative uncertainty of 5-10% or more in quantitative analysis of minor elements due to an irregular shape of a surface.

[1] T. Trojek, T. Cechak, Nuclear Instruments and Methods in Physics Research B 263, 2007, 72–75

Relative humidity, light, and extenders: defining different roles on the ageing of oil paints

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In the past few decades, increasing attention has been paid to oil-based modern (from the 20th century onwards) binding media and their complex conservation issues [1]. Indeed, as repeatedly shown by case studies with unexpected degradation problems, predicting the behavior of modern oil paint films is not trivial. This can be linked to the complexity of tubes' formulation, the pigment(s) present, and the various environmental parameters interacting, both separately and combined, with the paint layers [2]. When designing accelerated ageing tests to study degradation mechanisms, balancing all these variables is challenging and hence approaches are not standardized, and results are not always easily comparable. This can be observed also in the case of lightfast pigments, such as Prussian blue [3].

The present work aims to systematically define how different variables may affect the stability of Prussian blue oil paint films containing two types of extenders, calcite, $CaCO_3$, and hydromagnesite, $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$. To discriminate the influence of visible light from that of relative humidity (RH%), paint samples were aged at 50%, 70%, and 90% RH both in the dark and exposed to an irradiance of 60 W/m^2. Chemical changes at the surface of the paint layers were tracked through attenuated total reflectance infrared spectroscopy (ATR-FTIR), which allowed to assess variations in polymeric network related to hydrolysis and oxidation reactions. The possible formation of metal soaps and oxalates was also monitored through the spectroscopic technique, and confirmed through scanning electron microscopy.

The results indicate that the presence of hydromagnesite in the paint can be crucial for the formation of the oxalates, which were only revealed in Prussian blue samples displayed at 90% RH. Through the comparison of the outcomes from the ageing in the dark and under visible light, it is shown how the effects of RH are barely noticeable in the irradiated mock-ups. This underlines how the light ageing conditions used, commonly employed to study modern oil paint, may not realistically portray the competing processes affecting the binding medium.

1. Izzo, F.C.; Kratter, M.; Nevin, A.; Zendri, E. A Critical Review on the Analysis of Metal Soaps in Oil Paintings. *ChemistryOpen* **2021**, *10*, 904-921, doi:https://doi.org/10.1002/open.202100166.
2. Modugno, F.; Di Gianvincenzo, F.; Degano, I.; van der Werf, I.D.; Bonaduce, I.; Van Den Berg, K.J. On the influence of relative humidity on the oxidation and hydrolysis of fresh and aged oil paints. *Scientific Reports* **2019**, *9*, 1-16, doi:https://doi.org/10.1038/s41598-019-41893-9.
3. Samain, L.; Silversmit, G.; Sanyova, J.; Vekemans, B.; Salomon, H.; Gilbert, B.; Grandjean, F.; Long, G.J.; Hermann, R.P.; Vincze, L. Fading of modern Prussian blue pigments in linseed oil medium. *Journal of analytical atomic spectrometry* **2011**, *26*, 930-941, doi:https://doi.org/10.1039/C0JA00234H.

Technical studies in Egyptology. Multi-modal imaging and multi-range spectroscopies shed light on a rare wooden polychrome chest

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In the last decades Egyptological studies have undergone a profound methodological transformation, thanks to the integration of scientific analysis in the traditional approach to the documental and archaeological research. The remarkable gamma of analytical techniques has enabled the acquisition of significant additional data on materials and objects, shedding new lights on several aspects of the ancient Egyptian civilization (materials, manufacturing processes, technological capabilities and socio-economic aspects). However, the Egyptian collections still include several puzzling items and artefacts, whose interpretation remains unsolved. Only the extensive systematization of multi-analytical investigations would provide the data needed to fill some of current lacks of knowledge. To respond to this need, experimental protocols sustainable for museums - that is highly informative yet non-invasive, operable in-situ and in different conditions - are required. This pilot study aims at proposing a suite of last-generation portable techniques, singled out in order to support investigations on wooden polychrome Egyptian artefacts. Keeping in mind this point of view, the Egyptian section of the National Archaeological Museum in Florence and the CNR-IFAC has selected as case-study a rare wooden polychrome chest, whose function and provenance are still essentially unknown, although supposed linked to the falcon cult. Among the few existing exemplars, two of them are kept in Florence. From an archeological point of view, these objects are considered as highly significant [1]. To gain as much information as possible without sampling this rare artefact, a suite of portable techniques has been implemented aimed at providing mapping and identification of materials. The sequence included both multimodal imaging techniques and multi-range spot spectroscopic techniques, and it was implemented in-situ. The multimodal imaging included portable HyperSpectral Imaging (HSI) in the Visible-Near Infrared (400-1000nm) range implemented in both reflectance and fluorescence modes; this was combined with high-spatial resolution photographic techniques: photographic Infrared reflectography (photographic IRR), UV-induced luminescence (UVL) and Visible Induced Luminescence (VIL). Subsequently, multi-range spot analysis was implemented with the following techniques: portable XRF, Vis-NIR-SWIR Fiber Optics Reflectance Spectroscopy (FORS), total reflectance FT-IR, Micro-Raman and Optical Microscopy. Along with the almost complete identification of pigments, the investigations provided valuable tips on the executive and artistic process, giving clues for comparative analysis with the other example of chest belonging to the collection. The defined suite of techniques proved to be a replicable, effective experimental protocol for the comparative analysis of several similar artefacts in the collection.

[1] A. Tillier, 'Portable chests for the falcon cults of Akhmim, MDAIK 72 (2016), 239-51.

Spectral Denoising and Image Segmentation methods for the Processing of Inelastic X-ray Scattering and X-ray Raman Data

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Inelastic X-ray scattering and X-ray Raman have been shown to provide a valuable contrast mechanism for non-invasive 3D probing of heritage materials composed of light elements, without significant prior preparation [1–3]. It has therefore been used for the chemical and spatial characterisation of carbonaceous fossils and archaeological materials which are relatively radiation-resistant [2,4,5].

Here, we report results from the study of more radiation-sensitive samples of the major post-war artist, Simon Hantaï (1922–2008). The "fresh" organic nature of these materials makes them susceptible to various degradation mechanisms, in particular related to heating and the formation of radical species that diffuse throughout the material via liquid water, and can lead to mechanical damage or initiate chemical reactions [6]. Irradiation must therefore be reduced by several orders of magnitude compared to more resistant systems.

In the framework of a long-term project at ID20 (ESRF, Grenoble, France), we have developed methodologies to reduce the X-ray dose to which the sample is exposed.

We have generated 3D images of a painted canvas sample made by the painter. We collected data at a small number of energy points per pixel with a short acquisition time in order to minimise alteration, which complicates the spectral interpretation. However, by taking advantage of the large number of pixels combined with the density distribution of the sample, we will show that statistical analysis can provide a noise-robust understanding of the spatial-spectral information. This is a first step towards several methodological strategies to attempt combining experimental strategies and statistical approaches in order to compensate for the low signal-to-noise ratios.

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[1] S. Huotari, T. Pylkkänen, R. Verbeni, G. Monaco, and K. Hämäläinen. Nature Materials, 2011, 10.7, pp. 489–493.
[2] Gueriau, P., Rueff, J.-P., Bernard, S., Kaddissy, J. A., Goler, S., Sahle, C. J., Sokaras, D., Wogelius, R. A., Manning, P. L., Bergmann, U., & Bertrand, L., Analytical Chemistry 89(20), 2017, 10819–10826.
[3] R. Georgiou, C. Sahle, D. Sokaras, S. Bernard, U. Bergmann, J.-P. Rueff, and L. Bertrand. X-ray Raman scattering: A hard X-ray probe of complex organic systems. Chem. Rev., 122(15):12977–13005, 2022.
[4] Georgiou, R., Gueriau, P., Sahle, C. J., Bernard, S., Mirone, A., Garrouste, R., Bergmann, U., Rueff, J.-P., & Bertrand, L., Science Advances 5(8), 2019, eaaw5019.
[5] R. Georgiou, R. S. Popelka-Filcoff, D. Sokaras, V. Beltran, I. Bonaduce, J. Spangler, S. X. Cohen, R. Lehmann, S. Bernard, J.-P. Rueff, U. Bergmann, and L. Bertrand. Proc. Natl Acad. Sci. USA, 119(22):e2116021119, 2022.
[6] L. Bertrand, S. Schöder, D. Anglos, M. B. H. Breese, K. Janssens, M. Moini, and A. Simon. Trac-Trends Anal. Chem., 66:128–145, 3 2015.

Elemental analyses of heritage building wall paint using X-ray fluorescence (XRF) for conservation works: Malaysian case studies

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Building conservation works require that the original design and materials of a building be restored. Conservators need to identify the chemical elements in parent materials before commencing with the reparation works. This is particularly challenging when there are no surviving records on the original materials and the construction methods. Therefore, X-ray fluorescence (XRF) is a valuble tool in finding the missing information needed. The aim of this study is to conduct an elemental analysis on the wall paint samples taken from a historical royal palace and an office building that has been categorised as a heritage building. The royal palace is located in Terengganu, a state on the east coast of Malay Peninsula, and was completed in 1903. The office building located in Pulau Pinang, an island state in the northern part of the peninsula, is more than 100 years old.

The samples were obtained to identify the composition of elements in the original material (parent material) before conservation and repair works commence. Eight (8) numbers of samples used for the XRF test, for which six (6) numbers of tests were conducted for each sample. The full area testing covering the entire surface area of the sample conducted once, while the multi-point test consists of selecting five (5) points on the surface of the sample. A single point is considered as a single test. The tests were conducted according to the ASTM E1621-21 Standard Guide for Elemental Analysis By Wavelength Dispersive X-ray Fluorescence Spectrometry.

The full area testing analyses on the samples from the royal palace have shown that Titanium (Ti) is the most dominant element with 61.2% by weight. However, the samples from the office building showed almost equal amount of presence of Titanium and Calcium (Ca) (47.1% and 45%, respectively). Calcium is not commonly found in its elemental form naturally, but is found in sedimentary rocks such as limestone, gypsum and fluorite, materials that are often used in construction. The presence of titanium suggests the use of titanium oxide (TiO_2) as a component in white pigment and coating. The results demonstrated that the conventional materials such as limestone, gypsum, and titanium oxide were and are still used in the construction industry.

An interdisciplinary approach to the making of enamels: multimodal imaging of historical processes and materials

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Research question: This study concerns the multimodal imaging of the layer build-up and composition of a selection of 16th and 17th-century Limoges enamels, and the interpretation of phenomena imaged by both OCT and MA-XRF [1,2].
Methods: Our aim is to understand the making of enamels through non-invasive multimodal imaging, in combination with analysis of the raw materials and study of historic recipes. Our approach is to interpret the obtained data through interdisciplinary collaboration, combining the methodologies of (technical) art history, scientific analyses, and artisan expertise, in order to arrive at an integrated understanding of the objects.
Objects and materials: We studied four 16th-17th-C enamels using OCT and MA-XRF. Additionally, the elemental compositions of eight 17th-C coloured glass cakes fragments, from the Rijksmuseum, were determined by pXRF for comparison. Results were set against historical recipes.[3]
Multimodal imaging: We used OCT to visualize the structural build-up of the enamel application, and MA-XRF to reveal the chemical composition. Cross-sectional images were collected using a Thorlabs OCT system at 1300 nm with an axial resolution of 5.5 µm in air and a lateral resolution of 13 µm. A Bruker M6 Jetstream MA-XRF scanner (30 W Rh anode tube run at 50 kV and 600 µA, dual 60 mm^2 SDD detectors with a 275 kcps threshold) with polycapillary optics was used to scan the objects using a spot size as small as 40 µm.
Results: OCT clearly visualizes structural build-up, metal decorations, metal leaf and variation in transparency of the enamel layers, and the variety of internal patterns in the background layers, seemingly caused by differences in making processes. MA-XRF shows elemental compositions and distribution of enamel and surface metal decorations, and visualises the use of metal leaf. Taken together, these imaging techniques provide novel complementary information on the production methods of Limoges enamels, and combined with analysis of the glass cakes, are key to a better understanding of the historical recipes and instructions, and vice versa.

[1] M. Read et al. Proc . SPIE O3A VII, 2019. doi: 10.1117/12.2527092.
[2] K. Seibel and M. Gerken. Opulenz und Reduktion. Jahrestagung des Fachausschusses V der DGG, 2020.
[3]See for example: Haudiquer de Blancourt, *The Art of Glass*. Printed for Dan Brown London 1699, Paris 1697.

MA-XRF aiding the conservation of the Virgin with Child by Mantegna

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The Madonna with Child by Andrea Mantegna owned by the Museo Poldi Pezzoli in Milan is a work of art painted on canvas with an unusual distemper technique, in which pigments are bound with animal glue or gum, instead of the more traditional egg tempera. Paints were applied directly on the unprepared thin canvas, which underwent just a simple priming treatment. Distemper paintings were meant to be left unvarnished [1]. During the 1853-1865 the painting was restored by Giuseppe Molteni, a painter-conservator of those times who surely, at the least, lined and varnished the painting [2]. The identification of potential retouchings by Molteni, possibly covering part of the original layer, where the object of this work.
To carefully study this hypothesis, the painting went to the Opificio delle Pietre Dure (a public conservation institute in Florence, Italy) for a comprehensive diagnostic campaign. By X-ray radiography, carried out at the OPD, it was initially hypothesized that Molteni's intervention was indeed extensive, particularly on the mantle of the Virgin, and that potentially covered most of the original Mantegna's paint layer.
To better evaluate the extension both of Molteni's intervention and original Mantegna's layer, the MA-XRF spectrometer developed by CHNet -INFN (Cultural Heritage Network - National Institute of Nuclear Physic) [3] gave important information.
MA-XRF allowed the discrimination of the two paint layers, identifying the materials and the extension of both "artists". Indeed, the elemental maps showed that Molteni's work entirely covered the mantle of the Virgin, even changing the fold of the draperies and enriching the red robe with highlights painted with shell gold, giving a different appearance to the painting. Moreover, MA-XRF also revealed that, underlying Molteni's layer, the original Mantegna was still mostly intact: a decisive guide for the conservation works [4].

These results were indeed the basis for the technical decision of removing the varnish and Molteni's version, unveiling the original Mantegna. A second MA-XRF campaign was then carried out to fully characterize the materials of this unusual painting technique.

[1] A. Rothe, Mantegna's painting in distemper, in Andrea Mantegna, ed. J. Martineau, Milan, 1992, pp 80-88
[2] F. Mazzocca et al., Giuseppe Molteni (1800-1867) e il ritratto nella Milano romantica - Pittura, collezionismo, restauro, tutela. Milano, 2000
[3] F. Taccetti et al., Rend. Lincei Sci. Fis. Nat. 30, 2019, 307–322
[4] L.M. Bresci, OPD Restauro n. 32, 2020, 288-296

An FTIR and GC/MS study on the formation of zinc soaps in aged oil paint models

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Zinc salts of fatty acids (zinc soaps) are degradation products formed by reaction of an oil binder and zinc oxide used as pigment or ground in paintings. Their presence is associated with changes in the appearance and structural stability of oil paintings, such as surface efflorescence, delamination and paint transparency. During polymerization and oxidation of drying oils, two different phases of zinc soaps are formed: amorphous ionomers and crystalline polymorphs of saturated mono and diacids. The presence of these species can be characterized by infrared spectroscopy [1].

This study focuses on the reactivity of zinc oxide with four drying oils used in modern oil paints: linseed oil, walnut oil, sunflower oil and safflower oil. Mock-ups were prepared by mixing artist grade zinc oxide (Cornelissen) with oil in a 1:1 w/w ratio and application on glass slides. The paint mock-ups were aged in two conditions: at room temperature and exposed to UV light with a maximum at 370 nm (1627 $\mu W/cm^2$, 22 °C and 42 % RH). Samples were removed periodically from the mock-ups and analized by ATR-FTIR spectroscopy. Zinc soaps obtained by saponification of the four oils, acidification and reaction with zinc acetate were used as references. Linseed oil revealed the formation of ionomeric zinc soaps after 15 days of exposure at room temperature, while walnut oil formed crystalline soaps as indicated by the presence of two bands at 1527 and 1545 cm^{-1} in the IR spectrum [1]. Sunflower and safflower oil mock-ups did not show significant changes up to 2 months of exposure. UV ageing of the mock-ups revealed a similar trend as for natural ageing with sunflower and safflower oils being less reactive than linseed oil and walnut oil. After 40 hs UV ageing, sunflower and safflower oils showed very weak bands at 1559 and 1506 cm^{-1} that shifted to a broad peak centered at 1571-1574 cm^{-1} after 100 hs ageing, which is characteristic of a zinc soap ionomeric phase. This band remained unchanged after 4000 hs UV ageing. Walnut oil showed a broad band with two overlapped peaks at 1530 and 1553 cm^{-1} after 40 hs ageing, which shifted to a band at 1580 cm^{-1} after 100 hs ageing. Linseed oil showed a broad band with a peak at 1562 cm^{-1} after 40 hs of ageing that shifted to a ionomer phase band at 1580 cm^{-1} after 100 hs ageing and remained unchanged after 4000 hs.

Samples extracted from the mock-ups after 4000 hs UV ageing were analyzed by GC-MS applying a three step procedure using two different silylating reagents to identify free fatty acids and zinc soaps [2] as well as trimethylsulfonium hydroxide (TMSH) to characterize fatty acids from remaining triacylglycerides in the aged samples.

[1] M. Beerse, K. Keune, P. Iedema, S. Woutersen, J. Hermans, Applied Polymer Materials 2, 2020, 5674.
[2] J. La Nasa, A. Lluveras-Tenorio, F. Modugno, I. Bonaduce, Heritage Science 2018, 6:57.

MA-XRF imaging of paintings: comparative studies by using classical analysis and artificial intelligence

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The current advancements of noninvasive imaging methods applied for the study and conservation of cultural heritage have driven a rapid development of novel computational methods. Macro x-ray fluorescence (MA-XRF) is well-established and used for the investigation of paintings. However, MA-XRF generates large datasets that can be challenging to analyze. In the following, we employ machine learning approaches for the analysis as they allow for identification of non-trivial dependencies and classification across the high dimensional data, hence promising a comprehensive interrogation. We have built a novel deep learning algorithm trained on a synthetic dataset that allows for fast and accurate analysis of the XRF spectra in MA-XRF datasets circumventing typical drawbacks of the classical deconvolutional approach.
The synthetic XRF spectra are generated using Monte Carlo simulations based on a Fundamental Parameters approach and tuned for our MA-XRF setup. The simulations assume a four-layer stratigraphy model of a painting with a large number of possible historical and modern pigments. The presented approach yields high-quality results in terms of analysis of MA-XRF scans. In particular, we recover the absolute intensities of elemental lines, and we show the improvements of our approach in comparison with the output of the classical analysis. Here, on top of using the above stratigraphy model, we use a mixture of targeted multi-layered models tailored to describe selected paintings with complex stratigraphies. The neural network is modified to also infer the parameters of these models, such as layers thickness, suggesting in some cases a possible extension of our methodology beyond what is normally possible with a traditional deconvolution analysis. We discuss the results of this methodology applied to the analysis of both historical and modern paintings.

AgNPs applied to Cultural Heritage: Exploring its antimicrobial potential using "Green" approaches

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Cultural Heritage (CH) deterioration by microorganisms (MOs) is a major problem and available techniques for microbial suppress may themselves contribute for an imbalance in microbial communities [1]. Additionally, some of the products applied are environmentally concerning [1]. Metal-based nanoparticles have been studied as an alternative due to their promising antimicrobial properties [2]. However, given that their conventional synthesis may produce harmful products [3,4], it is important to develop "greener" methods such as the use of MOs or plant extracts [4,5]. In this work, we aimed to produce silver nanoparticles (AgNPs) using supernatants of several microbial cultures. Initially, AgNPs synthesis was confirmed by UV-Vis. After isolation, the AgNPs were analyzed using diverse characterization techniques including electron microscopy and spectroscopic-based equipments. Additionally, the antimicrobial activity of AgNPs was tested against MOs isolated from CH materials. Our results note that AgNPs synthesis can be accomplished by supernatants from microbial cultures. Results obtained through several characterization techniques showed the presence of AgNPs (< 100 nm) whose morphology and elemental composition seems to be conditioned not only by the isolate used for microbial culture but also by the nature of the culture media. The presence of different organic molecules (*e.g.* proteins) that seem to contribute to the stabilization of the nanoparticles was also detected. Antimicrobial potential of AgNPs was observed in liquid and solid media. In future research, synthesis optimization and antimicrobial studies on specimens made from materials typically used in CH (*e.g.* stone) will be made.

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[1] Cappitelli, F.; Cattò, C.; Villa, F. *Microorganisms* **2020**, *8*, 1542
[2] Wang, L.; Hu, C.; Shao, L. *Int. J. Nanomedicine* **2017**, *Volume 12*, 1227–1249
[3] Khandel, P.; Yadaw, R.K.; Soni, D.K.; Kanwar, L.; Shahi, S.K. *J. Nanostructure Chem.* **2018**, *8*, 217–254
[4] Ijaz, I.; Gilani, E.; Nazir, A.; Bukhari, A. *Green Chem. Lett. Rev.* **2020**, *13*, 223–245
[5] Singh, J.; Dutta, T.; Kim, K.-H.; Rawat, M.; Samddar, P.; Kumar, P. *J. Nanobiotechnology* **2018**, *16*, 84

Inelastic X-ray Scattering: A new probe to identify and image artists' materials

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In recent years, synchrotron-based inelastic X-ray scattering (IXS) and X-ray Raman scattering (XRS) have been developed as a spectroscopic and spectral imaging method to study the composition of heritage materials for art, history, archaeology [1–3]. In particular, the use of hard X-rays (6–15 keV) at the carbon K-edge (280–320 eV) and oxygen O K-edge (530–550 eV) has allowed the bulk speciation of organic materials in-situ with little or no sample preparation, which is crucial in the study of heritage systems [4]. Here, we explore the application of these techniques to the 3D imaging of multiscale heterogeneous organics in paint stratigraphies and kinetics studies of contemporary paint materials. This involves long-term methodological developments to minimize X-ray doses on sensitive samples and to quantitatively the kinetics of irradiation effects [5]. Based on significant methodological development at synchrotron facilities in the framework of two long-term projects (at ID-20, ESRF, Grenoble, France and 15-2, SSRL, Stanford, US) and an in-house collaboration with GALAXIES, synchrotron SOLEIL, we have performed iterative experimentation in spectroscopy and chemical imaging, coupling data collection with statistical analysis. We will show the first results of this long-term international initiative showing the promises of IXS as a novel spectroscopic technique for the discrimination and in-depth chemical characterization of pigment compositions, including the discrimination of crystal polymorphs in paints. We will show in particular that the contrast among spectral signatures can be exploited for unforeseen 2D and 3D spectral imaging, opening the way towards further exploration of the potential of IXS in the years to come.

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[1] Georgiou, R., Gueriau, P., Sahle, C. J., Bernard, S., Mirone, A., Garrouste, R., Bergmann, U., Rueff, J.-P., & Bertrand, L., Science Advances 5(8), 2019, eaaw5019.
[2] Gueriau, P., Rueff, J.-P., Bernard, S., Kaddissy, J. A., Goler, S., Sahle, C. J., Sokaras, D., Wogelius, R. A., Manning, P. L., Bergmann, U., & Bertrand, L., Analytical Chemistry 89(20), 2017, 10819–10826.
[3] R. Georgiou, R. S. Popelka-Filcoff, D. Sokaras, V. Beltran, I. Bonaduce, J. Spangler, S. X. Cohen, R. Lehmann, S. Bernard, J.-P. Rueff, U. Bergmann, and L. Bertrand. Disentangling the Chemistry of Australian Plant Exudates from a Unique Historical Collection. Proc. Natl Acad. Sci. USA, 119(22):e2116021119, 2022.
[4] Georgiou, R., Sahle, C., Sokaras, D., Bernard, S., Bergmann, U., Rueff, J.-P., & Bertrand, L., Chemical Reviews, 122(15), 2022, 12977–13005.
[5] L. Bertrand et al. Mitigation strategies for radiation damage in the analysis of ancient materials. TrAC-Trends Anal. Chem., 66:128–145, 3 2015.

Object-tailored CT scans for cultural heritage objects

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Computed tomography (CT) has proven itself to be a powerful non-invasive tool to analyze cultural heritage objects by allowing museum professionals to obtain 3D information about their interior. These insights may help with the conservation or restoration of the objects, as well as provide contextual information on the objects' history or making process. [1]

Cultural heritage objects exist in a wide variety and have characteristics which present challenges for CT scanning: multi-scale internal features, different sizes and shapes of objects and multi-material objects. Because X-ray absorption is related to the density and thickness of the material, the challenge is greater when the object consists of multiple different materials with varying densities, especially when one of the materials is a metal.

Thus, the multi-material nature of cultural heritage objects presents a challenge for CT imaging [2]. Acquiring CT scans of these objects in an uninformed and untailored way can lead to reduced image quality and heavy visual errors in the perception or representation of information called image artifacts. However, a tailored acquisition, which we illustrate in this work, can reduce these artifacts and leads to a higher information gain (see Fig 1).

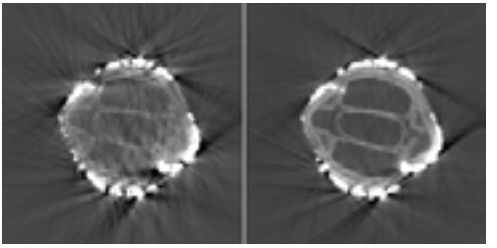

Fig 1: Cross-section of an early-17th century velvet knife sheath elaborately decorated with gold and silver embroidery, and freshwater seed pearls. Left: untailored CT scan with heavy metal/beam-hardening artifacts; Right: object-tailored CT scan

To make this work accessible to a broad audience including museum professionals as well as X-ray imaging specialists, it is split into four parts. Firstly, we describe the technique of CT, address common errors encountered when scanning cultural heritage objects and describe basic strategies to prevent these errors. Secondly, we discuss the use of filters to optimize the emitted X-ray beam for improved image quality for multi-material objects. We showcase that this can be done also with limited resources in a low-cost and DIY fashion with thin filter-sheets of metal, 3D-printed filter frames and a filter holder. Thirdly, a step-by-step guideline is presented to determine an object-tailored acquisition protocol for cultural heritage objects in a straightforward and reproducible way. Finally, we illustrate the application of this guideline with two case study objects from the cultural heritage sector.

[1] P. Wilson, M. Smith, J. Hay, J. Warnett, A. Attridge, M. Williams, Heritage Science 6:58, 2018.
[2] F. G. Bossema, S. B. Coban, A. Kostenko, P. van Duin, J. Dorscheid, I. Garachon, E. Hermens, R. van Liere, K. J. Batenburg, Journal of Cultural Heritage 49, 2021, p38-47.

The formation of oxalates in natural resins

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Oxalates are found in historical objects, specifically in the interfaces between materials and/or in crusts formed on their surface, altering not only their chemical composition but also their physical appearance. [1]

These compounds are formed when oxalic acid reacts with a metallic ion. Metallic ions may come from the original materials used to elaborate the object or from an external source, such as the dust deposited on the materials' surface. On the other hand, the presence of oxalic acid has been related to different processes, one of them is the degradation reactions of certain organic materials.

Previous studies reported the formation of oxalates linked to the degradation of gums, sugars and materials containing a high proportion of lipids such as drying oil, egg or human skin.[2,3] Nevertheless, there are still open questions regarding the precise mechanism that leads to the formation of oxalates, which organic materials produce oxalates or which molecular structures allow their formation.

This work is focused in the formation of oxalates in raw natural resins during 10 years of natural ageing by FTIR spectroscopy. Results show that the formation of oxalates is accelerated by the light and that, under the same conditions, diterpenic resins based on abietane structures do not form oxalates or they are formed in a much slower way than other materials such as drying oils or other resins. Additionally, the comparison among the molecular structures found in each material allowed to tag the chemical features that lead to the formation of oxalates.

These results provide new information on the formation mechanism of oxalates and allow to foresee in which materials oxalates aggregates may be formed, helping to plan the suitable preservation/restoration strategies.

[1] L. Rampazzi. J. Cult. Herit. 40, 2019, 195–214.
[2] F. Cariati, L. Rampazzi, L. Toniolo, A. Pozzi. Stud. Conserv. 45, 2000, 180–188.
[3] M. Cotte, P. Walter, G. Tsoucaris, P. Dumas. Vib. Spectrosc., 2005, 159–167.

Aqueous polyacrylate latex nanodispersions used as consolidation agents to improve mechanical and water transport properties of treated Prague sandstone

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The use of polyacrylate latex nanodispersions as potential consolidation agents for weak stone materials has been investigated. Four different dispersions have been prepared at the scope. The effect of polymer fluorination and chemical crosslinking was tested on the Prague sandstone, an example of natural stone exhibiting high susceptibility to weathering and employed in the past as construction material and to realize monuments. The treatments have been employed using two concentration levels of nanodispersions (around 30 and 3 wt. %) and then tested for physical-mechanical properties and microstructural modifications. Significant improvement in water transport properties and mechanical properties has been obtained as a consequence of the consolidation treatment. Positive effects were observed even with highly diluted nanodispersions. The consolidation agent revealed good filling and bridging capacity within the matrix (Fig. 1). Taking advantage of the possibility of acting on the polymer structure – by tuning crosslinking capability, polymer fluorination and gel content, allowed for optimizing the obtained properties of the consolidated material in the function of the specific characteristics of the stone and the type of decay. Therefore, the flexibility of their chemistry offers new opportunities for the preservation of objects of cultural heritage.

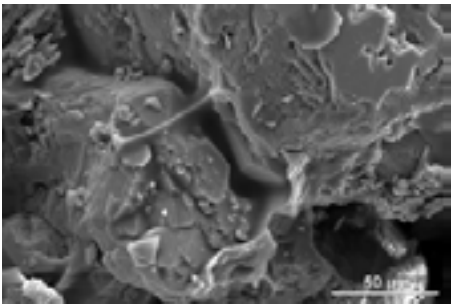

Fig. 1: An example of the polymer`s good adhesion and bridging capacity of grains within the structure of consolidated Prague sandstone.

An investigation into the materials of Vermeer's *The Art of Painting* using MA-XRF and MA-XRPD

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The Art of Painting (1668, Kunsthistorisches Museum, Vienna) is one of the largest and most complex paintings created by Johannes Vermeer (1632 - 1675). Within *The Art of Painting* Vermeer invites the viewer to slip into the role of visitor of a brightly illuminated artist's studio in which a painter is in the process of capturing a young woman posing as Clio, the muse of history. Here, Vermeer does not depict a studio scene in the usual sense but an allegory of painting. It is generally accepted that Vermeer created *The Art of Painting* as a demonstration piece, illustrating his mastery as an artist to visitors and potential clients.

About ten years ago, an investigation of a series of paint micro samples from *The Art of Painting* revealed among others that (1) Vermeer used a final layer of lead white with extremely fine particle size, (2) a bright green underpaint of verdigris was present beneath a dark blue drapery and (3) a previously unknown degradation product, palmierite $K_2Pb(SO_4)$, had formed within the paint layers [1]. In order to extrapolate these results to the entire painting, *The Art of Painting* was recently examined using state-of-the-art non-invasive imaging techniques, such as macroscopic X-ray fluorescence (MA-XRF) and macroscopic X-ray powder diffraction (MA-XRPD).

From these imaging investigations we found (a) at least four different types of the pigment lead white, a synthetic pigment consisting of basic and neutral lead carbonate, resp. hydrocerussite $2PbCO_3.Pb(OH)_2$ (HC) and cerussite $PbCO_3$ (C), ranging from nearly pure HC to a mixture containing 65/35 HC/C; (b) ultramarine abundantly used not only in blue areas, such as Clio's mantle, but also in the black clothing of the painter; (c) possible indications for a discoloration from green to blue in e.g. the laurel crown and (d) the presence of anglesite ($PbSO_4$) and gypsum ($CaSO_4.2H_2O$) next to palmierite throughout the surface of the painting. These findings will be linked to the other works by Vermeer within the collection of the Rijksmuseum (Amsterdam) and the Mauritshuis (the Hague) that have recently been investigated.

Keywords: X-ray diffraction, Vermeer, imaging, alteration, pigments

[1] Boon, J. J.; Oberthaler, E., In Vermeer, Die Malkunst – Spurensicherung an einem Meisterwerk, Haag, S.; Oberthaler, E.; Pénot, S., Eds. Residenz Verlag, 2010, 328-335.

Non-Invasive SWIR Monitoring of White Marble Surface of the Cathedral of Santa Maria del Fiore (Florence, Italy)

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The monitoring of stone alteration represents a key factor in the knowledge and prediction of the status of conservation of building stones in the urban framework. A continuous monitoring requires a non-destructive analytical approach and, possibly, a simple, low-cost and effective tool to study the decay processes. Previous studies demonstrated the capability of the SWIR hyperspectral technique to gain information on the degree of sulfation of carbonate stone surfaces [1-2]. In this study we aim at setting up a protocol to investigate on-site the sulfation degree of the white marble cladding surfaces of the worldwide-famous Santa Maria del Fiore Cathedral in Florence (Italy). The proposed protocol couples information by SWIR hyperspectral and colorimetric techniques. The on-site monitoring was performed using: a portable spectrophotometer to obtain the colorimetric coordinates and a field portable high-resolution spectroradiometer to collect reflectance measurements. The latte is equipped with a contact reflectance probe with an internal light source, enabling the investigation of a spot area of about 1.5 cm^2.

We have proved that, in selected areas investigated at a distance of nine years, the colour and the mineralogical changes (i.e., sulfation) are significantly greater than the relative uncertainties of the two methods. Moreover, the proposed protocol results rapid, repeatable and fully not invasive.

[1] A. Suzuki, S. Vettori, S. Giorgi, E. Carretti, F. Di Benedetto, L. Dei, M. Benvenuti, S. Moretti, E. Pecchioni, P. Costagliola. Laboratory study of the sulfation of carbonate stones through SWIR hyperspectral investigation, Journal of Cultural Heritage 32, 2018, 30–37.

[2] S. Vettori, M. Verrucchi, F. Di Benedetto, E. Gioventù, M. Benvenuti, E. Pecchioni, P. Costagliola, A. Cagnini, S. Porcinai, V. Rimondi, S. Moretti. Hyperspectral sensor: A handy tool to evaluate the efficacy of cleaning procedures, Journal of Cultural Heritage 49, 2021, 79–84.

Non-invasive quantitative assessment of collagen degradation in parchments by polarization-resolved SHG microscopy

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Non-invasive and quantitative investigation techniques are highly sought-after to establish the degradation state of cultural heritage artefacts and assess the relevance of conservation conditions or restoration processes. This is crucial for ancient parchments that are a precious testimony of the past and a key source of information for historians, since they were the main writing support material in the Middle Ages in Western Europe. However, up to now, the degradation state of parchments is assessed when possible by thermal techniques which are destructives. Nonlinear Optical (NLO) microscopy enables three-dimensional (3D) imaging with micrometer-scale resolution based on an intrinsic optical sectioning and multimodal capability. Two-photon excited fluorescence (2PEF) signals are emitted by a wide range of materials (fluorophores) in historical artifacts with specific absorption and emission fluorescence spectra [1]. Second harmonic generation (SHG) signals are specific for dense and well aligned structures such as fibrillar collagen, and vanish for centrosymmetric materials such a gelatin, which is the ultimate degradation state of collagen. Accordingly, SHG microscopy provides structural information about the 3D organization of the fibrillar collagen within parchments and other skin-based artefacts (Fig. 1(a)) [2,3].

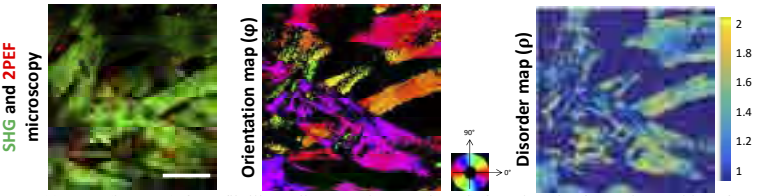

Fig. 1 (a) SHG (in green) from fibrillar collagen and 2PEF (in red) from keratin, fat or dust residues from a contemporary parchment, scale bar: 50 µm. Quantitative information extracted from P-SHG measurements: (b) orientation mapping of fibrillar collagen and (c) anisotropy parameter mapping.

In this study, we implement advanced NLO microscopy imaging for quantitative *in situ* mapping of parchment degradation by introducing two parameters: the ratio of 2PEF to SHG signals (I_{2PEF}/I_{SHG}), which probes the loss of the non-centrosymmetric organization of fibrillar collagen, and the anisotropy parameter extracted from polarization-resolved SHG (P-SHG) measurements, which is sensitive to the sub-micrometer scale disorder (Fig. 1(c)) [4]. We first rigorously validate this method on artificially aged model samples by comparing NLO to hydrothermal measurements. We show that thermal analysis as well as the P-SHG anisotropy parameter probe the first steps of degradation corresponding to a slight disorder of the collagen fibrils, while the further steps, when the hierarchical organization of the fibrillar

collagen is lost, are revealed by an increase of the I_{2PEF}/I_{SHG} parameter. We then analyze and map the conservation state of Middle Age historical parchments from the Chartres' library (France), which suffered from fire (and water) as a result of bombing at the end of the 2nd World War [4].

[1] G. Latour, J.-P. Echard, M. Didier, M.-C. Schanne-Klein, Optic. Express 20, 2012, 24623-24635
[2] G. Latour, L. Robinet, A. Dazzi, F. Portier, A. Deniset-Besseau, M.-C. Schanne-Klein, Scientific Reports 6, 2016, 26344
[3] L. Robinet, S. Thao, M;-C. Schanne-Klein, G. Latour, ICOM-CC 18th Triennial Conference Preprints, 2017, art. 1609
[4] M. Schmeltz, L. Robinet, S. Heu-Thao, J.-M. Sintès, C. Teulon, G. Ducourthial, P. Mahou, M.-C. Schanne-Klein, G. Latour, Science Advances 7, 2021, eabg1090

Influence of lead driers on oil paint properties

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Lead compounds have been used since the Renaissance period to fasten the drying process of siccative oils. Lead (II) oxide PbO was the most frequently used, according to the numerous historical recipes mentioning this practice [1, 2]. The drier was ground, added to the oil and the mixture was heated, possibly with water. Such treatments modify the physicochemical properties of the system as well as its chemical composition - the triglycerides of the oil are partially saponified and lead soaps are formed.

In order to characterize these modifications, treated oils were prepared and investigated along drying, at the macroscopic, mesoscopic and molecular scales. The combination of SAXS (Small Angle X-ray Scattering) with optical and electronic microscopies (TEM after cryofracture and optical microscopies) allowed to unravel the multi-scale structuring of the saponified oil samples, in the liquid state and after application as thin films. As an example, at high lead content (50 mol% PbO, see figure) the presence of lamellar domains dispersed in an unorganized matrix could be assessed and linked to the observed modifications of their rheological properties: from Newtonian without lead, to viscoelastic systems with shear-thinning behavior. Moreover, measurements carried out after the application of the films, i.e. during the drying and ageing of lead-treated oils, indicate the appearance of a new lamellar order.
This multi-scale investigation allows a better understanding of the pictorial practices in use from the 15th century and shed new light on the organization of historical paint films, their evolution and possible alterations.

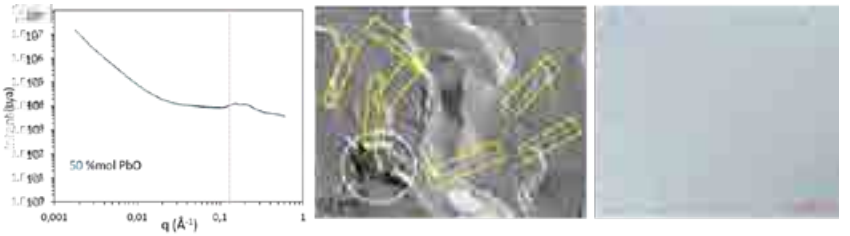

Figure: Results obtained on oil heated with 50 %mol PbO. SAXS profile (left, the dotted line indicates the signal of the lamellar organization of lead soaps), transmission electron microscopy after cryofracture (middle) and differential interference contrast optical microscopy (right).

[1] M. Faidutti, C. Versini, Le Manuscript de Turquet de Mayerne présenté par M. Faidutti et C. Versini, Pictoria Sculptoria et quae subalternarum artium -1620, Audin Imprimeurs, Lyon, 1967.
[2] L. de Viguerie, P.A. Payard, E. Portero, Ph. Walter, M. Cotte, Progress in Organic Coatings 93, 2016, 46-60.

Conservation science to rescue the collective memory of the conflict. The case of General Baquedano's public monument at the 18-O Chilean Social Outburst

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The public monument to Baquedano General is an equestrian sculpture representing a 19th-century military politician, which has been historically given name to the Plaza Baquedano (Baquedano Square), the main urban reunion space of the Chilean capital city.

On October 18, 2019 (18-O), an unprecedented protest started in what is now recognized as the most significant social movement in Chile's history**.** Part of many massive street demonstrations in South America, the outburst was accompanied by several iconoclastic and demonumentalisation actions. However, the Chilean movement was characterized by a high engagement of street artists and performers who appropriated the public space and curated social demands. Thus providing a powerful voice and a visual mark that accompanied the social discourse and that later was amplified by social networks.

Understanding that the social transformation processes that affect the monuments located in the public space are materialized narratives that directly influence the perception and valuation of the monumental heritage, through traditional conservation science analysis, we intend to characterize the material history of the transformations over the Baquedano sculpture, as a means to contribute to the valuation of non-official heritage expressions, and more recently to the recuperation of the memory erased after the removal of the monument from the iconic square.

The scientific approach involved a micro-scale stratigraphic study of the painting and other transformations added to the monument to establish the layering of memories of its recent history, followed by a deeper stratigraphic morphological cross-analysis that includes the number and color of layers attributed to the authorized or social discourse.

The main findings revealed the intensive dialogue between the official authority narrative and the counter-narrative from the social movement represented in the stratigraphic sequences of the samples. Results also showed the color palette's change and confirmed the velocity of the transformation actions over the sculpture. The analytic approximation will be later complemented with an anthropological study that contextualizes the results with the photographic record and recent historical milestones.

Moreover, this case represents a unique opportunity to establish a precedent about the significance of the participation of conservation science discipline in discussing the public space's relationship with heritage and collective memory.

Acknowledgments: This work was supported by Project FAIP-N-47 2022 and CNCR-A-25-TEC. The authors thank the Department of Imagenology from the CNCR and the *Consejo de Monumentos Nacionales*.

Long-lasting flavor compounds of myrtle and helichrysum from ancient Egyptian tombs: a study by multi-shot analytical pyrolysis

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Myrtle and helichrysum are evergreen shrubs typical of the Mediterranean area with known aromatic and medicinal properties and high content of essential oil in their leaves, flowers and fruits. They have many applications in cosmetic, food and pharmaceutical industries [1,2].
Both plants have been used in funerary production in the Roman period as ornamental garlands and wreaths which are preserved in several European museums [3,4]. These plant-remains are in a good state of preservation and still retain their flavor. Numerous volatile molecules are responsible for the characteristic scent of these plants and their characterization is typically performed through the analysis of the headspace composition by solid phase microextraction (SPME) followed by statistical processing of the data. This can also be used to perform speciation [2].

In this study, the classical SPME method was compared to an innovative approach employing evolved gas analysis-mass spectrometry (EGA-MS) and double-shot analytical pyrolysis-gas chromatography-mass spectrometry (DSPy-GC/MS). Both methods provide the same advantages, such as small sample amount which does not require any pretreatment. Nevertheless, the use of analytical pyrolysis increases the range of the detectable products by performing not only thermal desorption of the volatile compounds but also the pyrolysis of the polymeric fraction.
The methods were used to study the degradation of myrtle and helichrysum samples provided by the Berlin Ägyptisches Museum. Qualitative and semi-quantitative information on both the volatile and non-volatile fractions were used to characterize these samples and to establish their species by comparison with samples collected from different Italian herbaria.

The thermal desorption profiles for helichrysum samples were characterized by the signals of phenolic compounds while myrtle samples mainly showed the peaks of mono- and sesquiterpenes. On the contrary, the pyrograms obtained for the different species were similar, showing a high amount of aromatic compounds and carbohydrates.
Finally, the data from DSPy-GC/MS were processed with principal component analysis (PCA) to highlight the compositional differences among the herbarium and archaeological samples.

[1] M. Fadil, A. Farah, B. Ihssane, T. Haloui, S. Lebrazi, S. Rachiq, J. Appl. Res. Med. Aromat. Plants. 7 (2017) 35–40.

[2] A. Maggio, M. Bruno, R. Guarino, F. Senatore, V. Ilardi, Chem. Biodivers. 13 (2016) 151–159.

[3] J. Edmondson, P. Bierkowski, W. V Davies, R. Walker, Biol. Anthropol. Study Anc. Egypt. (1993) 169–174.

[4] M. Boi, Archaeometry. 59 (2017) 316–330.

Combined study for the identification of an original varnish on a Flemish panel painting

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This work focuses on the identification and study of an original protective layer of a Flemish votive panel painting from the XV century located in the parish-church of Zumaia in Gipuzkoa (Spain). This study is part of an integral restoration project carried out by a multidisciplinary team formed by technicians from the Provincial Council of Gipuzkoa, The Royal Institute for Cultural Heritage, KIK-IRPA (Brusels), and independent professionals. This project lead to the attribution of the Flemish origin of the work commissioned by the sailor Juan Martínez de Mendaro to commemorate the victory in the Battle of Gibraltar (1475).

Varnish is a film-forming substance applied to the surface of an object, providing it with a protective film, being and essential part of the pictorical technique, however it is difficult and sometimes impossible to study this stratum since, in most cases, it is not preserved today. Since it is the layer most exposed to external agents, the varnish easily suffers alterations and abrasions and accumulates deposits of dust and dirt. This leads to the need of removing the layer of altered varnish, with total or partial cleaning, [1] sometimes just reducing the varnish layer or even leaving encrusted remains. On this irregularly cleaned surface, new layers of protective varnish were usually added [1], sometimes with materials related to the previous varnish, or with another type of film-forming substance. This usual practice has resulted in very heterogeneous layers, turning even more difficult the identification of a possible underlying original varnish stratum.

This work focuses on the description of the original varnish layer of the Flemish painting, as well as on its identification on different stratums of the pictorical layer. To do that, it was applied a methodology based on combined studies, taking into a count that a simple chemical identification of the varnish layer is not enough to ensure its originality. Therefore, advanced imaging techniques were carried out by means of macro photography in visible light and under ultraviolet light. The optical study was completed with chemical analysis and sampling using Gas chromatography-mass spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR-ATR) and FTIR-ATR Mapping [2].
Finally, this work draws the conclusions reached by combining the information provided by the different study methods and the documentary references, confirming that the combined study is a necessary methodology to identify an original varnish.

[1] J. Dunkerton, R. White, The Discovery and Identification of an Original Varnish on a Panel by Carlo Crivelli, National Gallery Technical Bulletin 21, 2000, 70

[2] Chemical analysis reports from Artelab Laboratory (Madrid) by Andres Sanchez Ledesma and from the KIK-IRPA Laboratory by Jana Sanyova

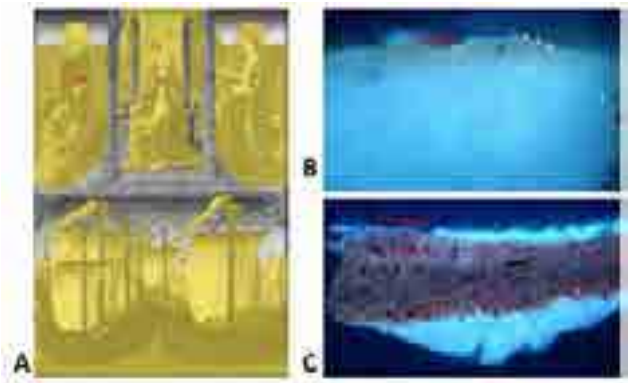

Figure 1. (A) In yellow, areas were the original varnish was applied. Identification of the varnish layer marked with the red raw on the cross-section of a sample from the gilding of the nimbus of the Virgin (B) and from the mantle of Saint Peter (C)

"Stories of the Life of Saint George" by Barbelli: Study of painting materials and techniques

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Gian Giacomo Inchiocchio (1604-1656), better known as Barbelli, was one of the main exponents of the cremasque painting of the XVII century, to whom an extensive production of drawing, mural and oil paintings is ascribed. [1] Despite his broad contribution, there are still open questions regarding his technique and the materials he used for his famous mural paintings.

In this poster, an in-depth study of the cycle Stories of Saint George's life that originally decorated the presbytery of the parish church of Casaletto Vaprio (Cremona, Italy) was performed. [2] These frescoes, detached in the 20th century, are currently subjected to conservation treatments and relocation. Firstly, non-invasive Visible Reflectance spectroscopy has been applied in situ to verify the consistency of the chromatic areas and reveal the possible presence of modern retouching, helping to select the regions where representative sample can be extracted. Afterwards, the microsamples have been analysed via optical microscopy (OM), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy to determine the main components of the mural paintings.

Results provided new insights into the palette and technique of Barbelli, helping to determine the best restoration and preservation conditions for his paintings.

[1] G. Colombo, M. Marubbi, M. Annunziata, *Gian Giacomo Barbelli. L'opera Completa*, Bolis, Bergamo, (2011).
[2] S. Zenone, *Gian Giacomo Barbelli. Ritorno a Casaletto Vaprio*, Scripta, Venice (2022).

Further studies on the breakdown of selected natural and synthetic artists' varnishes upon Er:YAG laser irradiation

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Keywords: Er:YAG laser, Dammar, Ketone N, MS2A, Paraloid B67, ATR/FT-IR, SEM, Thermogravimetry and kinetics

Over the past decades, free-running Er:YAG lasers (2940 nm) have been considered suitable for cleaning art objects. The strong absorption of 2940 nm photons from the hydroxyl groups in varnishes, pigments and binders leads to diverse photo-thermal and mechanical effects on the surface of artworks [1–4]. As a result, it is common practice to pre-wet the area to be irradiated with water and aqueous solutions to maximise laser absorption on the surface.

This work aimed to investigate the potential of Er:YAG lasers (2940 nm) for the treatment of varnished surfaces, exploring and deepening knowledge of the laser's thermal and breakdown effects on different commercial varnishes. Dammar, Ketone Resin N (poly(cyclohexanone)), MS2A (poly(cyclohexanol)) and Paraloid B67 (poly(isobutyl methacrylate polymer)). Resins were chosen due to their wide use in fine art. Prior to making of varnish films, thermogravimetric analysis (TGA) was performed to determine the order of thermal stability of the resins as received by the manufacturer. Measurements were made at six different heating rates and the respective kinetic activation energies (E_a) were determined by the Kissinger and the Flynn-Wall-Ozawa methods [5]. Kinetic studies are in progress. Varnishes of those resins were cast as films and were subjected to accelerated ageing [light (170.6 klux.h) and hydrothermal (40°C and 40% RH)]. The aged varnishes were employed for the laser studies. A pulsed Er:YAG laser was employed in Very Short Pulse (VSP - pulse duration ≅ 100 µs) and Short Pulse (SP ≅ 300 µs) modes. The 2940 nm laser beam was set at 4 mm diameter and delivered to the substrates by an R11 handpiece at a working distance of 20 cm.

Single laser pulses with fluences ranging between 0.5 and 2.7 J/cm^2 were fired onto dry and pre-wetted varnishes. A pre-wetting solution of 1% (v/v) non-ionic polysorbate-based surfactant (Tween®20) in deionised water was applied on the substrate at the beginning of each laser test.

Transmission studies were conducted on the aged varnishes in real-time upon laser irradiation, showing that the energy transmitted upon a single laser pulse in VSP and SP modes increased almost linearly with fluence, apart from the B67 resin, where no significant modification was recorded.

Chemical changes in the laser-irradiated aged varnishes were monitored with Attenuated Total Reflection/Fourier Transform Infrared (ATR/FT-IR) spectroscopy, registering a reduction of hydroxyl groups and carbon-hydrogen bonding as a function of fluence for dammar and Ketone N films, and almost no change for the dry and pre-wetted MS2A film. Low vacuum Scanning Electron Microscopy (SEM) in the Backscattered Electron (BSE) mode revealed that the laser spots were less marked in the pre-wetted varnishes compared to the dry-irradiated films.

1. De Cruz, A.; Wolbarsht, M.L.; Hauger, S.A. Laser removal of contaminants from painted surfaces. *J. Cult. Herit.* **2000**, *1*, S173–S180, doi:10.1016/S1296-2074(00)00182-5.
2. Chillè, C.; Sala, F.; Wu, Q.; Theodorakopoulos, C. A study on the heat distribution and oxidative modification of aged dammar films upon Er:YAG laser irradiation. *J. Inst. Conserv.* **2020**, *43*, 1–20, doi:10.1080/19455224.2019.1707699.
3. Chillè, C.; Agresti, J.; Ciofini, D.; Mencaglia, A.; Osticioli, I.; Siano, S. Measurement of temperature gradients during Er:YAG laser irradiation of poly(vinyl alcohol). *J. Phys. Conf. Ser.* **2022**, *2204*, 012071, doi:10.1088/1742-6596/2204/1/012071.
4. Pereira-Pardo, L.; Korenberg, C. The use of erbium lasers for the conservation of cultural heritage. A review. *J. Cult. Herit.* **2018**, *31*, 236–247, doi:10.1016/j.culher.2017.10.007.
5. Al-Salem, S.M.; Behbehani, M.H.; Karam, H.J.; Al-Rowaih, S.F.; Asiri, F.M. On the Kinetics of Degradation Reaction Determined Post Accelerated Weathering of Polyolefin Plastic Waste Blends. *Int. J. Environ. Res. Public Heal. 2019, Vol. 16, Page 395* **2019**, *16*, 395, doi:10.3390/IJERPH16030395.

Characterization of black deposits inside the ornate Palaeolithic Ebbou cave, Ardèche, France.

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Prehistoric caves containing artworks present many challenges; among them, understating the processes occurring on the walls and their evolution with time, is a major issue, being the support of parietal art. The walls are affected by different physico-chemical processes, as a result, the presence of coatings is commonly observed. The extensive study of these coatings is important and a methodology to record this variety of walls states including their characterization is more and more implemented in decorated caves, to achieve a global understanding. An application case is presented here with the characterization of the blackish-greyish coatings extensively present in the Ebbou cave, which contains Paleolithic engravings and is located in the Ardèche region, close to the famous Chauvet cave. Three main areas of the cave present black coatings both on the walls and soils: the entrance gallery, the ornate area and the Great Room (figure 1a and 1b).

The analytical strategy put in place started first with in-situ observations and portable X-ray Fluorescence (XRF) measurements, and these results further led to a sampling campaign (figure 1c-f). Collected samples were then analysed using laboratory equipment with Raman spectroscopy and XRF and observed under scanning electron microscopy (SEM). In this work, attention will be focused on the results achieved in the Great Room and in the ornate area. Obtained results for the elemental composition, which showed the presence of phosphorus, iron and manganese, together with the Raman spectroscopy analyses looking for some carbon signatures, allow us to discuss the different assumptions regarding the origin of the coatings for each area [1]. Considering these results in a bigger picture with the history of the cave, make this data essential in the development of interdisciplinary studies of the rock art panels.

Figure 1. Black coatings in the Ebbou cave. a) view of a wall in the ornate area; b) view of the soil in the Great Room; c) portable XRF measurements in the Great Room; d)-f) typical samples collected in the Ebbou cave.

[1] Audra P., De Waele J., Bntaleb I., Chroňáková A., Krištůfek V., D'Angeli I. M., Sanz-arranz, A. Guano-related phosphate-rich minerals in European caves. International Journal of Speleology, 48(1), 2019, 75-105.

Non-contact Submicron O-PTIR and Simultaneous Raman microscopy with Fluorescence imaging – Review of Cultural Heritage Applications

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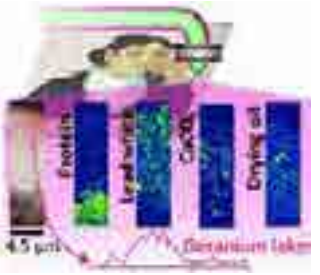
The recent advent of Optical Photothermal IR (O-PTIR) spectroscopy, has enabled for the first time, true submicron spatial resolution (20x better than FTIR) infrared microscopy in far-field reflection mode, generating "FTIR transmission-like" spectral quality, without spectral artefacts and distortions such as Mie Scattering associated with traditional FTIR or other emerging QCL based IR microscopy systems. Furthermore, it is now possible to combine O-PTIR with Raman and widefield fluorescence for trimodal correlative microscopy.

Photothermal spectroscopy is not new and has been exploited for decades with techniques such as PhotoAcoustic Spectroscopy (PAS) and AFM-IR (nano-IR). Where O-PTIR differs to is that it uses an optical (green laser) probe for detection, being analogous to the microphone in PAS and the AFM tip in AFM-IR. The use of this optical probe is the key enabling breakthrough in O-PTIR allowing for non-contact measurements, providing for advantages in capabilities relative to traditional FTIR/QCL microscopy but also in instrument architecture, thus enabling the first combined (correlative) IR and Raman (IR+Raman) platform that provides for simultaneous IR and Raman spectral information at the same time, from the same spot with the same submicron spatial resolution. When combined with fluorescence imaging, image contrast not visible in the brightfield image can be used to guide the O-PTIR measurements, without any image registration issues as the same sample, same platform and same objective is used for IR, Raman and fluorescence measurements.

These unique and exciting synergistic capabilities are now spawning interest in cultural applications [1-4]. A broad range of cultural heritage applications will be presented from the identification of a previously difficult to identify paint layer in a Van Gogh painting [1], to the analysis of zinc soap heterogeneity [2] and the non-invasive characterization of heritage glass-metal objects [3].



Beltran, et. al., *Angewandte Chemie*, **2021**, *60 (42), 22753-22760*

Figure 1. O-PTIR hyperspectral imaging of various components from extremely small fragment from Van Gogh's painting L'Arlésienne (portrait of Madame Ginoux). The striking results obtained, including the detection of geranium lake pigments as well as the complete analysis of the stratigraphy, failed with other state-of-the-art techniques, highlight the potential of this method [1]

[1.] Ma X., et. al., *Analytical Chemistry,* **2022**, *94 (7)*, 3103-3110
[2.] Marchetti A., et. al., *Science Advances*, **2022**, *8 (9)*
[3.] Calligaro T., et. al., *Forensic Science International*, **2022**, *336*, 111327

pXRF screening of damaged silks in museum collections

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Treating silk fabric with metal salts to increase its weight as well as its drapeability was a common practice in Europe in the 19th and 20th century [1]. Today, this so called weighting is believed to accelerate and aggravate the deterioration of historical silk textiles [2]. Although this is currently considered as one of the most pressing issues in costume conservation, relatively little research has been done on estimating the prevalence of weighted and degraded silks in museum collections.

Within the framework of the Safesilk research project [3], a first screening in the collections of the Antwerp Fashion Museum (MoMu) and the National Museum of Slovenia was initiated with the aim to assess (a) the proportion of weighted silk objects, (b) to identify the weighting salts employed and (c) to probe for a link with their state of conservation.

First, objects were categorized by time of creation, colour, weave pattern and physical condition. Next, a handheld XRF instrument was employed to identify metals salts, as portable X-ray fluorescence spectrometry (pXRF) allows for quick, non-invasive and in-situ analysis, and is sensitive towards most of the anticipated elements. Although XRF analysis is usually applied to dense inorganic materials, previous authors reported successful applications of pXRF for the elemental analysis of historical textiles as well [4-6]. Nevertheless, to verify the obtained data, single threads were extracted from the fabrics and examined by SEM-EDS.

Based on the presence of certain metals in silk objects identified by pXRF, the percentage of metal-weighted silks in the collections was determined. The obtained data was combined with a review of historical sources, including patents, to gain an insight on which weighting practices were most used and their evolution over time.

The next step of the Safesilk project, devoted to shedding light on the deterioration of weighted silk, will be based on these findings. Revealing the link between the weighting method and the condition of the textile will allow to choose the most appropriate technique for creating mock-ups of weighted silk fabric, which will then be aged and used for unravelling the salt-induced degradation pathways. In-depth understanding of such process is anticipated to be crucial for improving the storage conditions of collections and preventive conservation measures.

[1] N. Luxford, PhD Thesis, University of Southampton, 2009, 2.
[2] M. Hacke, Studies in Conservation 53(sup2), 2008, 3.
[3] The Research Foundation – Flanders (FWO) project G060422N
[4] N. Luxford, D. Thickett, P. Wyeth, ICOM-CC: 16th Triennial Conference in Lisbon, Portugal 1(2), 2011, 47.
[5] S. Krug, O. Hahn, Studies in Conservation, 59(6), 355.
[6] J. R. Anderson, N. Odegaard, M. Dawley, D. J. Farley, W. Zimmt, Objects Specialty Group Postprints, 21, 2014, 181.

Degradation of tuff buildings at the Archaeological park of Herculaneum (Italy): preliminary multianalytical study.

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Herculaneum (Italy) is one of the most important archaeological parks in the world. Since the site was uncovered, it has shown a constant and extremely aggressive degradation of the tuff used by the Romans for the construction of the buildings. Aiming at palliating this conservation issue, the Archaeological Park of Herculaneum recently signed a collaboration agreement with the University of the Basque Country (UPV/EHU) to study the degradation products, and understand the chemical/physical mechanisms behind their origin.

In the framework of this collaboration, researchers from the IBeA group have carried out in situ analysis with multiple portable and non-destructive analytical techniques, including a thermographic camera and Raman, FTIR, VisNIR and EDXRF spectrometers. Focusing on the study of the *Casa degli Augustali*, the formation of salt efflorescence was visible on the internal walls of the house. According to thermographic surveys, the crystallization of these salts could be traced back to the capillary rise of humidity from the ground (Figure 1). Concerning their molecular composition, FTIR analysis detected the presence of sulfates, with thenardite (Na_2SO_4) being the main alteration product.

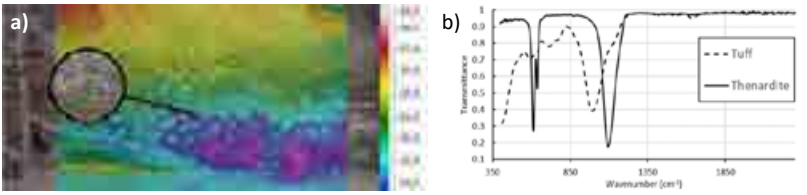

Figure 1. a) Thermographic image of a tuff brick wall from Casa Augustali; b) FTIR spectra, one of the weathered tuff without efflorescence and another of the efflorescence.

Agreeing with FTIR results, complementary spectroscopic analysis confirmed the systematic detection of several types of sulfates with a minor presence of nitrates. Guided by the in-situ results, the researchers collected samples to perform additional laboratory analysis (XRD and ion chromatography). As a whole, the combination of in-situ and laboratory investigations will help to understand the chemical reactions occurring between the soluble salts and the tuff, thus revealing the mechanisms of alteration. The final goal is to provide the conservators of the *Herculaneum Conservation Project* (HCP) [1] with the necessary information to identify the ideal conservation treatments to mitigate the detected alteration process.

[1] The Herculaneum Conservation Project is a joint initiative of the Packard Humanities Institute (also through the Istituto Packard per i Beni Culturali) and the Parco Archeologico di Ercolano. In the over 20 years that it has been underway many other partners have also been involved. For further information on HCP please see annual contributions to the Rivista di Studi Pompeiani and the broader selection of publications accessible under Herculaneum Conservation Project on academia.edu.

Characterization of portable X-Ray Fluorescence instruments for non-invasive analyses in archaeometry

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X-Ray Fluorescence (XRF) spectroscopy is employed for the elemental analysis of a wide range of materials. As XRF can make use of a non-invasive approach for the analyses, it is especially appreciated in archaeometry, where the preservation of the remains of ancient materials is mandatory.

In any instrumental analytical procedure, it is important to know the potential and the limits of the available instruments, in order to set the overall performances of the equipment and, as a consequence, the quality of the analytical outcome. Within INFN-CHNet, the network of the Italian National Institute of Nuclear Physics (INFN) devoted to Cultural Heritage, a new bench-top MA-XRF scanner, based on a previously designed one [1], is being developed and a full characterization of its performances is still missing. The new instrument is designed to perform different X-ray based techniques (namely: XRF, X-Ray Luminescence (XRL) and Radiography (RX)) for applications to cultural heritage objects using one tunable X-ray source. In this work, the characterization of energy resolution, dimension of the beam spot and limits of detection of the XRF setup is presented. The same procedure is carried out also on the portable unit Bruker Tracer 5i and the results are compared.

A flat-panel detector with a pixel size of 49.5 μm is used in order to establish the dimension and the shape of the spot in collimated and uncollimated (if possible) conditions. To determine the detection limits of the instruments, a set of reference glasses provided by the Corning Museum of Glass [2], by the Society of Glass Technology and the CRM soda-lime flat glass 620 by the National Institute of Standards and Technology are employed. The choice of using different type of glasses derives from the fact that RMs offered on the market contain a wide selection of elements, but the resemblance with materials of cultural heritage interest is poor. To establish the energy resolution of the instruments a Rhodochrosite ($MnCO_3$) mineral is used. The possible correlation between the results and the experimental parameters such as voltage, current and acquisition time is also investigated.

[1] F. Taccetti, L. Castelli, C. Czelusniak et al. . A multipurpose X-ray fluorescence scanner developed for in situ analysis. Rendiconti Lincei, Scienze Fisiche e Naturali, 2019, 30: 307-322.
[2] B. Wagner, A. Nowak, E. Bulska, K. Hametner, D. Gunther. Critical assessment of the elemental composition of Corning archaeological reference glasses by LA-ICP-MS. Anal Bioanal Chem, 2012, 1667-1677.

Characterising the degradation of green colourants on early printed and hand-coloured works on paper

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A comprehensive characterisation of the materials is crucial to developing successful preservation strategies for the heritage collections. Despite the technical developments in recent years in non-destructive identification of artists' materials in easel paintings, the technical analysis of paper-based art remains under-developed, partially due to the challenges of low concentration of analytes and high delicacy of the substrates.

This poster presents an in-progress research project that was born to gain an in-depth understanding of the degradation of the green colourants, its effect on the paper substrates, and the preservation needs for the collections of early printed and hand-coloured works on paper. Eight valuable objects from 16th – 17th century are selected from the collections in the Maurits Sabbe Library KU Leuven as case studies. In the first stage of the research, narrowband UV-VIS-NIR multispectral imaging (NBMI) and fibre optics reflectance spectroscopy (FORS) are used as the main non-destructive techniques for data collection. On the one hand, reference samples are prepared using historical recipes for comparison with the data collected from the historic objects. On the other hand, statistical methods, such as principle component analysis (PCA) and multivariate regression, are used to extract the chemical information from the images and the spectra to obtain evidence that is related to the material composition and the degradation state of the objects.

The initial results from the first stage of this research will be discussed in the poster presentation. This presentation will not only show the new findings on the use of green colourants in early books and maps, but also demonstrate the potential of NBMI and FORS on the investigation of the degradation of colourants on paper.

Micro and Macro FT-IR spectroscopic imaging and mapping as a tool for the detection of degradation products and for monitoring the cleaning processes of painted surfaces

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The study of the degradation products in paintings plays an important role in the choice of cleaning treatments since, for restauration purposes, it is necessary to carry out selective actions avoiding damages. To this end, the use of analytical techniques makes it possible to evaluate the state of conservation o as well as the effectiveness of the chosen restoration treatments [1].

Macro-FTIR spectroscopic mapping allows to obtain information on the distribution of specific degradation products (such as calcium oxalates, carboxylates, gypsum, etc.) or on the nature of finishing treatments (applied by the artists or previous restorers) [2]. This technique is performed without any sampling and is complementary to other non-invasive imaging techniques (i.e., Macro-XRF, hyperspectral imaging, multispectral imaging, etc.).

However, although the molecular composition reached by Macro-FTIR spectroscopic mapping is related to "macro" areas (of the order of square centimeters), it comes from superficial layers (2-3 microns), therefore this technique does not allow to investigate the nature of the inner layers. To overcome this disadvantage, micro-FTIR spectroscopic imaging can be performed on micro-samplings obtaining the stratigraphic structure [3].

In this work, we present a monitoring of the cleaning processes performed on a 13th century wooden painted crucifix conserved at San Gaggio (Florence) by using Micro and Macro FT-IR spectroscopic imaging and mapping.

[1] M. Romani, L. Pronti, C. Ruberto, L. Severini, C. Mazzuca, G. Viviani, A. Mazzinghi, M. Chiari, L. Castelli, F. Taccetti, A. Damiani, C. Gorga, M. Angelucci and M. Cestelli-Guidi, European Physical Journal Plus, 2022, 1–12.

[2] S. Legrand, M. Alfeld, F. Vanmeert, W. De Nolf and K. Janssens, Analyst, 2014, 2489–2498.

[3] L. Pronti, M. Romani, G. Viviani, C. Stani, P. Gioia and M. Cestelli - Guidi, Rendiconti Lincei, 2020, 485–493.

Combined use of Synchrotron based X-ray techniques and micro-Raman spectroscopy for Pb compounds mapping of red stains in heritage marbles

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Heritage marbles are frequently affected by different alteration phenomena. Among them, the presence of chromatic discolouration, such as the red stains, is one of the most widespread on Cultural Heritage buildings. Previous multi-analytical studies demonstrated that the red stains in some heritage marbles are mainly due to the presence of minium (lead tetraoxide) concentrated prevalently in the calcite crystal boundaries [1]. In order to reveal the presence and distribution of other Pb compounds at the micro-scale level, small fragments of several red stains originated in different environmental contexts and marble types were analysed. The samples under study come from Florentine historical buildings (San Giovanni Baptistery and Santa Maria del Fiore Cathedral) and monumental fountains. The investigation combines structural information from 2D high lateral resolution X-Ray Powder Diffraction (XRPD performed at ID13 ESRF synchrotron facility) [2] and micro-Raman spectroscopy, with the elemental distribution performed with micro-X-Ray Fluorescence mapping (μ-XRF performed at ID21, ESRF) and EDX-SEM.

Both structural and elemental information, a part from minium, highlight the presence of cerussite and hydrocerussite distributed in different ways depending on the sample and co-present in some cases with light elements like P and S. All these information suggest the conditions of the solution from which these compounds precipitated [3] and help us to shed light on the environmental factors that affect the formation of the red stains.

[1] E. Cantisani et al., Analyst, 2019, 144, 2375–2386.
[2] M. Cotte, et al., Molecules, 2022, 27, 1997.
[3] D. A. Lytle and M.R. Schock, Journal AWWA, 2005, 97:11, 102-114.

How are they aging? Tracking past treatment materials in modern mural painting sets by Almada Negreiros in the two maritimes stations of Alcântara, Lisbon

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Over the last six decades, the mural paintings of the Maritime stations of Alcântara and Rocha do Conde de Óbidos, executed by Almada Negreiros between 1943-49, were the subject of past interventions and monitoring by conservator-restorers of the now designated José de Figueiredo Laboratory (LJF). The documental survey carried out in 2022 in the IJF archive enabled to track, and identified various inpection processes and repports from work brigades, in which there are references to the painting conditions and treatments performed. Particularly important are the data from the first intervention carried out in 1971 at both maritimes stations, which repports the use of Mowiol, and of tests made with gelvatol and paraloid B72, with the aim of fixing paint layers with lack of adhesion and cohesion. As part of ALMADA project, these paint layers were revisited from 2020 to 2022, and it was ascertain the aging and effectiveness of the treatments after 52 years. This paper repports the preliminary results of the methodology used on-site based on technical photography in Vis, Vis-Rak and UVF, h-Optical Microscopy, complemented with the analysis of micrsamples by OM-Vis, SEM-EDS, μ-FTIR and Py-GC-MS.

Acknowledgements
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Moisture detection under leather panels using THz imaging

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In recent years the field of diagnostics applied to cultural heritage has seen a significant use of techniques operating in the Terahertz spectral band. This was possible by exploiting the characteristics of this type of radiation such as its longer wavelength compared to infrared radiation and the sensitivity towards polar liquids such as water, which absorb and reflect this radiation [1]. Unlike infrared, visible and UV radiation, the photons in the THz frequency range, thanks to its low energy available (longer wavelength) has a greater penetration into dielectric materials. This greater capacity of penetration was used to detect hidden works of art [2, 3, 4] and the presence of both structural detachments and air bags that can be created below the plaster layers during freeze-thaw cycles. Recently, at the laboratories of the ENEA center of Frascati (Rome) was developed a THz imaging system operating in reflection mode able of acquiring in real time images of the sub superficial layers [5]. This system has been thought to measure the phase-shift of the reflected radiation, therefore, through this phenomenon is possible to get information on the optical properties of the sample. In Fig.1 is shown the device during a scan of a leather sample coming from ancient 'Palazzo Chigi' in Ariccia. The purpose of this study is to simulate and at the same time detect the presence of water infiltrations under the leather panels once used to cover the walls of ancient noble palaces.

Fig. 1:THz setup operating at 97 GHz in reflection mode. On the right a leather sample and his corresponding reconstructed THz image

[1] Jackson, J. B., Bowen, J., Walker, G., Labaune, J., Mourou, G., Menu, M., & Fukunaga, K. (2011). A survey of terahertz applications in cultural heritage conservation science. IEEE Transactions on Terahertz Science and Technology, 1(1), 220-231. doi:10.1109/TTHZ.2011.2159538.

[2] Doria, A., Gallerano, G. P., Giovenale, E., Greco, M., & Picollo, M. (2017). THz detection of water: Applications on mural paintings and mosaics. Paper presented at the International Conference on Infrared, Millimeter, and Terahertz Waves, IRMMW-THz, doi:10.1109/IRMMW-THz.2017.8067164.
[3] Gallerano, G. P., Doria, A., Germini, M., Giovenale, E., Messina, G., & Spassovsky, I. P. (2009). Phase-sensitive reflective imaging device in the mm-wave and terahertz regions. Journal of Infrared, Millimeter, and Terahertz Waves, 30(12), 1351-1361. doi:10.1007/s10762-009-9560-0.
[4] Walker, G. C., Bowen, J. W., Jackson, J. B., Matthews, W., Labaune, J., Mourou, G., . . . Hodder, I. (2012). Sub-surface terahertz imaging through uneven surfaces: Visualizing neolithic wall paintings in çatalhöyük. Paper presented at the 2012 Conference on Lasers and Electro-Optics, CLEO 2012.
[5] Doria, A., Gallerano, G. P., Giovenale, E., Senni, L., Greco, M., Picollo, M., Cucci, C., Fukunaga, K. and More, A. C., "An alternative phase-sensitive THz imaging technique for art conservation: history and new developments at the ENEA center of frascati," Applied Sciences 10(21), 7661 (2020).

Aerospace technology as part of our heritage: characterization of aircraft materials and study of their degradation processes by analytical pyrolysis

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Historical airplanes have entered museum collections to show the development of aviation and are part of our technical heritage. The period between the beginning of the aviation history and World War II is characterized by giant progressions in the chemical industry. During these years a wide increase in the production of new materials and coatings was observed, that replaced the natural materials used in the aircraft industries due to their improved properties. The study deals with the characterization of the materials used in the paint layers of three airplanes, an Ansaldo A.1 (Comune di Casale Monferrato, complete plane, 1918) and two Messerschmitt Bf 109 (Private owner, original cabin roof, 1937; Deutsches Museum, complete plane, 1938-repainted until 1975) [1], including overpainting layers from later use and museum presentations. The study is aimed at understanding the materials chosen in aviation technology, also in relation to the developing chemical industry, and to understand if and how the paint composition can be related to the conservation condition of the paint layers and of the aircrafts. In this study we applied for the first time analytical pyrolysis coupled with gas chromatography and mass spectrometry for the characterization of the painted layers. The analyses were carried out directly on the paint fragments, in some cases also with the use of hexamethyldisilazane as derivatizing agent. A selection of samples was also analyzed by infrared spectroscopy. The paint samples were characterized by a very complex stratigraphy, with extremely thin paint layers well-adhering to each other, and thus impossible to be mechanically separated. A careful sampling campaign allowed us to obtain information on the sample build up and the history of the planes. For the plane from the First World War the analyses allowed us to characterize the constituting materials and to highlight the ongoing degradation processes. The study carried out on samples from the two Messerschmitt planes allowed us to characterize the original materials used to produce the planes and to study those used in the different restoration campaigns which have been carried out until 1974. The use of analytical pyrolysis was crucial to characterize a wide range of natural and synthetic materials, allowing to resolve complex mixtures. Data show an interesting evolution of the painting materials used in the two

different historical periods, which include natural materials, as a drying oil and Pinaceae resin, but also several synthetic materials, including cellulose acetate, alkyd resin, nitrocellulose, phenol formaldehyde resin as original materials, and more than other six different synthetic polymers used during the restoration campaigns.

[1] Jacopo La Nasa, Catharina Blaensdorf, Eleonora Dolcher, Serena Del Seppia, Anna Micheluz, Francesca Modugno, Marisa Pamplona, Ilaria Bonaduce, "Historical aircraft paints: analytical pyrolysis for the identification of paint binders used on two Messerschmitt Bf 109 planes", Journal of Analytical and Applied Pyrolysis, 2022, Vol. 163, article number 105468

Application of spectroscopic and imaging techniques for the study of historical natural dyes.

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The Michelangelo Guggenheim's textile collection has been studied using a multi analytical approach. Specifically, False color imaging, Fiber Optics reflectance spectroscopy (VIS range) and Surface Enhanced Raman Scattering (SERS) spectroscopy were used to identify the dyestuff in the perspective of checking their compatibility with both declared historical period and the origin. Most of them are dated to the XVI century, while the stylistic analysis together with the technical characteristics traced them back to an Italian manufacture.
The cross checking of spectroscopic data allowed to confirm most of the results acquired in a previous non-invasive investigation. However, new data obtained in micro-invasive mode resulted fundamental to understand the complexity characterizing some of the sampled threads. In many cases colors were obtained by mixing several dyes: all the presented methodologies have well known limitations but they often compensate each other allowing for the identification of different components co-existing in the same sample. In particular, in FORS, absorption bands of natural dyes are often broad, tend to overlap or to generate new structures; in parallel, SERS if often blind to some dyes, especially when mixtures involve components with very different cross sections. Finally, in FCI colours deriving from the contemporary presence of several compounds can interfere creating new shades difficult to interpret.
Raman spectra of the Guggenheim collection mainly showed cochineal in red-based artefacts and indigo in blue ones. Additionally, other interesting dyes such as orcein or annatto were identified in many samples. At the same way, VISRS spectral profiles were affected by indigotin on green textile fragments, on which SERS gave information about the yellow dye. However, yellow dyes are particularly challenging and despite the application of a multi-technique approach, in some of the fragments it was not possible to recognize any specific compound.
In some cases, equivalent results were obtained for the three tested techniques, while in others more complex situations emerged, showing the utilization of mixture instead of single dyes as previously assumed based on pure non-invasive results. This highlights the importance of utilizing a set of complementary analytical techniques when approaching historical textiles.
FCI can also be a very interesting technique to obtain preliminary non-invasive data, but the study highlighted the need for the creation of a complete database of historical dyes employed with different dyeing procedures, substrates, mordants, and as mixtures with different proportions.

X-ray absorption near edge structure (XANES) spectra: A thermometer for the firing temperature of ceramics?

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X-ray absorption fine structure (XAFS) spectra are measured by using tunable monochromatic X-rays (in most cases synchrotron radiation) for measuring the energy dependence of the photoabsorption coefficient in a narrow region around an inner shell absorption edge of the element of interest. The "edge" is the jump of the absorption coefficient when the energy of the incoming X-rays is high enough for exciting the corresponding inner shell electron into the continuum or into an empty orbital. The X-ray absorption near edge structure (XANES) used in this project starts ~ 50 eV before the edge and reaches up to ~ 100 eV above the edge. XANES contains detailed information about the electronic structure and the local vicinity of the absorbing atomic species.

In a previous publication [1] we could show that a detailed quantitative analysis of the spectral features of Ca-K-XANES can be used for determining the firing temperature of ceramic objects. Test samples fabricated similar to Poverty Point objects using silty loam from the UNESCO World Heritage Site Poverty Point in Louisiana were fired in a defined way to 300^0C, 500^0C, and 800^0C in an oxidizing atmosphere. The Ca-K-XANES spectra of these samples and of the non-heated one were analyzed and the results used for determining a calibration cure for finally determining the firing temperature of two "real" Poverty Point objects. This preliminary publication left several important questions open, for example, if the firing parameters e.g. the atmosphere or the storage conditions of a sample (humidity in the soil) will change the XANES spectra and thus the calibration curve and thus also the determined firing temperature. Unclear was also if it will be possible to establish a "universal calibration curve" for all ceramic objects.

In this contribution results from an expanded set of experiments are presented. Measurements of Ca-K-XANES spectra at Poverty Point test objects in a reducing atmosphere show that the calibration curve does not depend on the atmosphere, i.e. the observed changes in the spectra are not the result of a chemical reaction with oxygen but most likely a modification of the "crystallographic structure" around the Ca atoms. XANES measurements at other edges of these test samples (e.g. Si-K, Fe-K) show that also Fe-K-XANES spectra can be used for a quantitative analysis leading to a calibration curve . Additional measurements have been carried out with "modern clays" with strongly varying elemental composition Also for these clays calibration curves can be derived from the Ca-K-XANES spectra supporting the hope for a "universal calibration curve" for all ceramic objects independent from the chemical/ crystallographic composition of the clay used as starting material.

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[1] J. Hormes, L. Bovenkamp-Langlois, W. Klysubun, O. Kizilkaya, Microchemical Journal, 154, 2020, 104571

A comprehensive methodology for the characterisation of 18th-century tapestry dyeing materials: between point analyses and hyperspectral imaging

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In the 18th century, royal regulations imposed a list of limited materials to manufacture tapestries. Among these materials, 15 natural organic dyes are authorised to dye the shades necessary for weaving the works. The molecular structures of some of these dyes are similar, especially the reds and yellows, which makes it difficult to identify them. The characterisation of those dyes, therefore, requires the implementation of a specific analysis methodology.

This study proposes to present the non-invasive methodology set up to characterise materials used in 18th-century tapestries thanks to recreated model samples. The reference sample database comprises more than 600 samples dyed according to the recipes of 18th-century treaties. The analytical methodology was initially developed around point methods (UV fluorimetry, portable XRF or optical fibre reflectance spectroscopy) to characterise each dye's specific markers. Principal component analyses based on these data led to the discrimination of several dyes, such as cochineal and kermes or to detect the presence of tannins in mixtures. Then, in a second step, false colour imaging, especially in the SWIR range, allowed us to highlight differences in the absorption of samples, especially in the presence of tannin or iron mordant.

The complementarity of point methods and hyperspectral imaging has thus been applied to map and characterise the materials of the *Grande Verdure with the coat of arms of the Count of Brühl* from the Aubusson manufactures dating from the 18th century.

Urban art in Milan: non-invasive analytical strategies for the study of street art murals

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The findings highlighted by the present diagnostic campaign are settled within the project PRIN-2020 *SUPERSTAR Sustainable Preservation Strategies for Street Art* (coordinator Prof. Modugno, University of Pisa) [1] which aims at developing integrated protocols, optimizing innovative cleaning procedures and protective coatings for the preventive conservation and long-term monitoring of street art murals.
In recent years, the perception of street art has radically changed, rendering outdoor murals highly appreciated and valuable artworks. Street art murals are directly exposed to environmental agents and vandalism, thus developing effective conservation strategies for preserving these artworks from degradation is fundamental. The knowledge of the used painting materials results to be the first step to finetune the best conservation approach [2].
In this study, a combination of punctual techniques, as External Reflectance Fourier Transform Infrared spectroscopy (FT-IR), Raman spectroscopy, UV-Vis-NIR Reflectance spectroscopy and X-Ray Fluorescence spectroscopy (XRF), and hyperspectral mapping/imaging techniques in the X-ray (MAXRF), Vis-NIR and SWIR range has been used to develop a multi-technique non-invasive approach for in situ investigations of street art murals [3]. The methodology has been implemented with the support of laboratory spectroscopic studies on sample mock-ups. The analytical approach was applied to elucidate the composition of the constituting materials and the state of conservation of two iconic mural paintings of the city of Milan (Italy). The diagnostic campaign was performed in collaboration with Politecnico di Milano (Prof. Lucia Toniolo) and with the support of *Comune di Milano* (*Area Museo delle Culture, Progetti Interculturali e Arte nello Spazio Pubblico*, Dr. Marina Pugliese and Dr. Alice Cosmai). The first is "Necesse" by Smoe (2021), one of the largest painted walls in Italy (1300 m^2), dedicated to those who worked intensively to safeguard the community during the COVID. The latter, "Or.Me" by Orticanoodles (2017), partially faded and altered, belongs to the urban pictorial art project involving the entire Ortica neighborhood. The data collected on the murals allowed us to characterize the colorful "palette" of spray paints as regards the inorganic/organic pigments and fillers, and to give indications about the binder and the protective possibly applied. The in-situ analyses were integrated with the multispectral and thermal mapping of the overall surface obtained by Unmanned Aircraft Systems (UAS) combined with the relative virtual reconstruction by laser scanner.

[1] https://prin2020superstar.dcci.unipi.it
[2] A. Bosi et al, Street art graffiti: Discovering their composition and alteration by FTIR and micro-Raman spectroscopy. *Spectrochim Acta A Mol Biomol Spectrosc*. 225, 117474, 2020.
[3] B. Brunetti et al, Non-invasive investigations of paintings by portable instrumentation: the MOLAB experience, Analytical Chemistry for Cultural Heritage, 41-75, 2017.

Reflecting on Local Choices: The Hunt for Indian Yellow

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During the late eighteenth century, the British East India Company's expanding colonial control in India influenced the subject matters, materials, and techniques used by British, Indian, and Chinese artists working within the Company's orbit. The cross-use of European and Indian materials by these artists is of interest to scholars as it may reflect the cultural exchange of application techniques. In preparation for an upcoming exhibition on British East India "Company" Paintings organized by the Yale Center for British Art, two works of watercolor on paper were analyzed to identify the pigments present. These works were used as case studies to expand the understanding of these artists' choices on material selections and application. The works of art were selected based on the characteristic fluorescence of the yellow and orange pigments under UVA lamps which indicate the presence of Indian yellow. Indian yellow is a historic pigment that is no longer produced using the traditional route and is unique to India, and therefore, it reflects on the artists' choice to incorporate indigenous materials into their compositions.

To characterize and visualize the pigment palette with a focus on the yellow, orange, and red colorants, only *in-situ* spectroscopic measurements were considered in a multi-analytical approach. Indian yellow was verified in both watercolors along other pigments such as red lead, lead white, realgar, and vermilion using micro-Raman spectroscopy. The distribution of the former was visualized using UV-induced visible fluorescence imaging, while the latter was visualized with large area scanning X-ray fluorescence (XRF) spectroscopy. Further characterization using reflectance spectroscopy, both in imaging mode (RIS) and point mode (as fiber optics reflectance spectroscopy, FORS), and reflectance Fourier-transform infrared (FTIR) spectroscopy was undertaken to document the pigment palette and application technique. This study provided an opportunity to evaluate UV-induced fluorescence imaging, reflectance imaging spectroscopy, and reflectance FTIR spectroscopy for identifying Indian yellow in both mixtures and layered with several other pigments identified in this study.

Digital Speckle Interferometry coupled with photoacoustic for detecting defects under different depth

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A digital speckle interferometry coupled with photoacoustic system and method for non-destructive detection of defects under different depth is introduced and tested. Ultrasound wave was induced by pulsed laser based on photoacoustic effect, thus propagating from the rear surface of the object to the front. In order to acquire information about surface deformation, the front surface was illuminated by continues wave laser and imaged onto the camera. The different pattern interferometry fringes indicated the presence and location of the defects in the inner parts qualitatively. In this study, the method is validated by detecting medium density fiberboard with simulated cracks. The interferometry fringe of areas with or without defects was compared and discussed. The system and method to distinguish depth of defects was proposed and validated.

Keywords: Digital speckle interferometry; Photoacoustic effect; Defects inspection; Qualitatively depth analysis; Cultural heritage

Pararealgar and semi-amorphous arsenic sulfides discovered in Rembrandt's *Night Watch*

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In July 2019, the Rijksmuseum embarked on a large-scale research and conservation project called *Operation Night Watch* to meticulously study Rembrandt's *Night Watch* (1642). The project goal is twofold and aims to (1) assess the current condition of the painting to determine its preservation for the future as well as (2) to gain a deeper insight into Rembrandt's *modus operandi*. During the research phase, which included multimodal non-invasive chemical imaging and micro-sample analysis, an unexpected type of arsenic sulfide compound was identified.

Arsenic sulfide pigments are not commonly associated with Rembrandt's pigment palette and until now were found only in two paintings from his late period: *The Jewish Bride*, dated c. 1665 (Rijksmuseum, Amsterdam), and *The Man in a Red Cap* dated c. 1660 (Museum Boijmans van Beuningen, Rotterdam). In both cases, Van Loon et al. discovered the presence of small yellow spherical particles, a purified form of artificial orpiment glass obtained from the dry process method [1].

For *The Night Watch*, MA-XRF and MA-XRPD mapping, allowed us to discriminate between an arsenic pigment and its associated degradation products, present in the embroidered buff coat of Willem van Ruytenburch, one of the central figures. Two targeted paint cross-sections were taken from areas identified with MA-XRF as being rich in arsenic and were analyzed with light microscopy, scanning electron microscopy, Raman spectroscopy, and synchrotron radiation-based X-ray powder diffraction imaging. Compared to the small spherical particles in the two other Rembrandt paintings, large angular yellow, and orange-red tabular particles were found in the paint cross-sections from *The Night Watch*, which were identified by Raman spectroscopy as pararealgar (As_4S_4), and a semi-amorphous arsenic sulfide. This finding is unique as this type of arsenic sulfide pigment rarely has been found in other old master paintings, and is a new addition to Rembrandt's pigment palette. This presentation will illustrate the analysis conducted and elaborate on the hypotheses for the production process/origin of the pigments and the implication of the identified degradation products for the original appearance of the costume.

Figure 1: (A) Rembrandt van Rijn (1606-1669), *The Night Watch*, 1642, oil on canvas, 379.5cm × 453.5cm, (B) MA-XRF distribution map of arsenic (As-K), (C) light microscopic image of paint cross-section SK-C-5_017 from Van Ruytenburch's buff coat, (D) Raman spectra of large angular yellow particle (A) and an orange-red (B) particle.

[1] A. van Loon, P. Noble, A. Krekeler, G. Van der Snickt, K. Janssens, Y. Abe, I. Nakai, J. Dik. Heritage Science. 5, 26, 2017.

Advancing the Analysis of Historical Manuscripts by Combining Machine Learning with Reflectance Imaging Spectroscopy

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The Leiden Riddle (Leiden, Bibliotheek der Rijksuniversiteit, Vossius Lat. 4° 106, 25v) is a 9th or 10th century manuscript (iron gall ink on parchment) and one of very few surviving examples of the Old Northumbrian dialect of Old English [1]. This makes the thorough comprehension of this text key to understanding the evolution of the English language during the medieval period. However, after a millennium of wear and 19th-century attempts at making the text more legible by chemical reagents, certain locations of the text have become challenging to read.

To increase legibility, we focus on technically advancing our ability to discern Old Northumbrian text from other types of writing, noise, and damage present in the parchment. To accomplish this, we used reflectance imaging spectroscopy (RIS) in the visible and near-infrared range (VNIR, 400-1000 nm) and subsequently analyzed this highly multivariate imaging dataset first with standard RIS data processing methods (e.g. spectral angle mapping, SAM), after which we progressed to more advanced machine learning approaches. We employed unsupervised machine learning methods, such as non-negative matrix factorization (NMF) and uniform manifold approximation and projection (UMAP), for open-ended exploration of the data structure. Finally, we implemented a supervised machine learning approach, namely a tree-based model, an XGBoost classifier, able to successfully discern Old Northumbrian text from other writing, different stain types, and the parchment background. Overall, the combination of multivariate machine learning approaches with the data-rich RIS measurements holds particular promise for advancing our understanding of faded text in historical manuscripts.

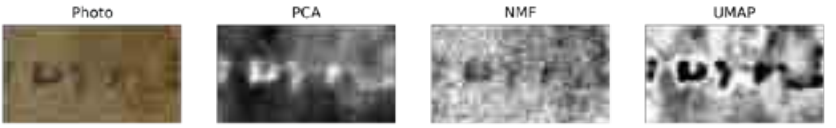

Figure 1: Selected results of unsupervised machine learning methods.

[1] M. B. Parkes, "*The Manuscript of the Leiden Riddle*", Anglo-Saxon England Vol. 1, 1972, pp. 207-212.

INFRA-ART Spectral Library: A New Open Access Infrastructure for Heritage Science

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Web-based open-access spectral databases relevant to conservation are nowadays a real necessity for heritage scientists and other heritage-related professionals that work with spectroscopic techniques. Fast and easy access to reliable high-quality databases is amplified by the fact that portable analytical techniques are becoming increasingly more used for in situ investigation of objects of art and archaeology. Among the wide range of modern analytical instrumentation, Raman, and Fourier transform infrared (FTIR) spectroscopy, along with handheld XRF, stand among the conventional analytical methods available to most heritage scientists today. These easily accessible spectroscopic techniques are probably the most frequently used analytical tools in conservation and heritage science as they offer a series of advantages such as relatively low-cost, non- or minimal-invasiveness, and complementary information (on both organic and inorganic compounds).

Quite often in the process of characterizing and identifying cultural heritage-related materials, there is a need for reference data. For vibrational spectra, typically, fingerprinting is used, meaning that the spectrum of an unknown sample is compared against a database with reference spectra. Thus, the availability of databases with high-quality reference spectra is a key aspect to the use of these analytical techniques. Despite a large number of available commercial spectral libraries, dedicated databases for the cultural heritage field are scarce or, as in the case of the freely available spectral databases on the web, the range of artists' materials is limited. To address this need, within the frame of the postdoctoral project INFRA-ART, an open-access spectral library exclusively dedicated to art and cultural heritage materials has been developed [1]. The INFRA-ART Spectral Library is an ongoing compilation of spectra, freely accessible online [2], that now contains over 1300 ATR-FTIR, Raman, and XRF spectra linked to over 680 known reference materials. The implementation of a bottom-up architecture allows further extensions of the database with other types of analysis, Laser Induced Fluorescence (LIF) and hyperspectral data, registered on well know historical pigments as well as on paint mockups, being among the new uploads planned to be carried out by the end of this year.

To support universal access and the reuse of scientific data, the INFRA-ART database follows the European Commission's recommendation on access to scientific information as well as the FAIR Guiding Principles on research data that result from publicly funded research. The INFRA-ART Spectral Library was registered as a resource within the European Open Science Cloud (EOSC) Portal and is currently part of the services offered by the Romanian hub within E-RIHS (The European Research Infrastructure for Heritage Science) Digilab.

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[1] I.M. Cortea et al. (2023). INFRA-ART: An open access spectral library of art-related materials as a digital support tool for cultural heritage science, in *Journal on Computing and Cultural Heritage*, 16(2). - *in press*
[2] INFRA-ART Spectral Library. https://infraart.inoe.ro/

Retouches of the paint layer: Research into physical and chemical changes of the materials used in conservation studios in the National Museum in Kraków

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Ageing of the materials is a process that has an unquestionable effect on the condition of artworks. To maintain or reestablish the original appearance of an object with respect to its history and the transformations it has gone through, conservation or restoration works are conducted. In order to understand its structure, symbolism and history one has to consider each artwork individually and choose the right tools and materials. However, these materials themselves also undergo the ageing process, sometimes in a different way and pace than the original ones. The changes in the conservation materials may be visual, changing well-matched fills, such as retouches into ill-fitting but also structural, affecting their reversibility.

These two aspects of ageing have to be taken into consideration to avoid applying unstable materials the removal of which could pose a risk to the original substance. A list of retouching materials used in the ateliers of the museum has been created based on the interviews with the conservators and observation of the restored paintings in the galleries of the National Museum in Kraków, whereas collaboration with the museum's laboratory and the Faculty of Chemistry of the Jagiellonian University lead to formulating a research programme. In Figure 1 a picture of chosen materials is given. The paints contain ultramarine and cadmium yellow as pigments and can be divided into two classes of watercolours brands: Leningrad (1), Schmincke (2) and four oil and resin-based paints: RestaurArte (3) (ketone resin), Rembrandt (4) (oil paints with the addition of cyclohexanone varnish), Gamblin (5) (urea aldehyde resin Laropal A81) and Kremer (6) (urea aldehyde resin Laropal A81)

Figure 1. Retouching paints: Leningrad (**1**), Schmincke (**2**) RestaurArte (**3**) Rembrandt (**4**), Gamblin (**5**) and Kremer (**6**) with ultramarine (**a**) and cadmium yellow (**b**) pigments.

The analysis included measurements of three types of specimens: freshly dried, naturally and artificially aged samples of paints. The artificial ageing entailed thermal ageing at 120°C (binder loss) and exposition to UV irradiation with a xenon lamp (oxidation – increase signal C=O groups), while the natural ageing process took four years and was held in darkness. The chemical changes were investigated by ATR FTIR spectroscopy, colour change ΔE_{00} by spectrophotometry, and surface polarity by measurements of contact angle. The changes in solubility were determined with Wolbers test (ethanol and white spirit in various proportions). Thermal ageing leads mostly to the loss of the binder, whereas UV irradiation causes the oxidation of the organic part (formation of C=O groups) and an increase in the surface polarity. The results of the research clarified the knowledge of the ageing process of the retouching materials and helped to select a palette of the materials most suitable for the restoration of paintings.

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A new model for radiographic image processing in painting investigation

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A multi-technique approach is key to the scientific investigation of cultural heritage as it allows researchers to combine complementary results from different analyses for an improved and evermore comprehensive knowledge of the artwork under study. Considering the great material complexity of most museum artifacts and the usefulness of data integration, it is highly desirable, when conducting technical studies, to carry out spot analysis with different techniques on the same select locations of the object's surface (e.g. XRF, FORS, Raman spectroscopy, etc.). Moreover, the acquisition of multi-source/multi-modal images plays a crucial role in the field of technical art history, albeit spatial resolution may vary depending on the type of instrumentation employed. However, direct image comparison often poses a challenge due to alignment difficulties and deformation effects related to the specifics of the equipment used. In an effort to address this issue, this contribution presents a multi-institutional endeavor to develop methodologies for the co-registration of images and maps from different techniques, with the final goal to facilitate data comparison and fusion [1].

While the problem of image deformation of both photographic techniques and multispectral imaging can be solved through photogrammetry and orthorectification [2], for other methods such as radiography, MA-XRF, and thermography, manual post-processing of the images is commonly performed. The X-ray apparatus at the CCR "La Venaria Reale" (Torino, Italy) enables the acquisition of digital radiographs of large artworks, i.e. up to 2x3 m^2, using a linear detector that is fine-moved along the horizontal axis [3]. However, due to the geometry and type of cone beam used, a certain deformation is induced at the radiograph edges, affecting the overall quality of the final mosaic, especially in the case of large-format paintings. To tackle this issue, we acquired several radiographs of a regularly-spaced metallic grid that covered the whole field of view to reconstruct the deformation map of the imaging system by evaluating the geometrical shrinkage/elongation of the grid on the images. The geometric correction model developed as a result of this study, similar to the lens correction function in Adobe Photoshop, will be applied here onwards to all X-ray images acquired with this equipment.

[1] F. Gabrieli et al., Reflectance Imaging Spectroscopy for Operation Night Watch: Challenges and Achievements of Imaging Rembrandt's Masterpiece in the Glass Chamber at the Rijksmuseum, Sensors, 21, 6855, 2021.
[2] A. Pamart et al., A robust and versatile pipeline for automatic photogrammetric-based registration of multimodal cultural heritage documentation. Remote Sensing, 12(12), 2051, 2020.
[3] A. Lo Giudice et al., A new digital radiography system for paintings on canvas and on wooden panels of large dimensions, 2017 IEEE International Instrumentation and Measurement Technology Conference (I2MTC), Turin, Italy, 1-6, 2017.

GUADAMECI ALTARPIECE : A CASE OF STUDY EMPLOYING DIFFERENT ANALYTICAL METHODOLOGIES

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The case of study is a Guadameci Altarpiece belonging to Museo Nacional De Artes Decorativas.Stylistically is a priceless cultural good since it is a clear sample of the firm Renaissance introduction in Spain.It is made in leather using the relevant and complex guadamecí technique : tanned leather with silver leaves and a varnish given as "douradura" [1].As an intervetion for restoration and preservation is needeed it is essential the caracterization of all the constituent materials and a deep knowledge of the technique used.As there are no many examples of gilt leathers this case is a great opportunity for a in- depth research which will allow a better undestanding of guadamecíes.

The main objective of this work is the analysis of the Alterpiece by different analitycal techniques.An exhaustive study has been carried out using gas chromatography with mass spectrometry (GC/MS),liquid chromatography with DAD and mass espectometry (HPLC-DAD-QTOF), Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and Attenuated Total Reflection-Fourier transformed infrared spectroscopy (ATR-FTIR). The outcome data obtained by the combination of all these techniques have been a valuable contribution for the guadameci caracterization.

Proteomic analysis of the leather by HPLC-QTOF allowed to determinate the animal specie: Ovis aries[2] .The use of zumac for tanning as well as the natural dyes present in the guadameci were also analyzed by HPLC-DAD-QTOF[3]. Binders and coatings were determined by GC/MS and FTIR[4]. The identification of all the inorganic pigments used were achieved by SEM-EDX technique.

[1] DAVILLER, CH. (1879): *Notas sobre los cueros de Córdoba*. Gerona. Imprenta del Hospicio Provincial.
[2] VINCIGUERRA, R., DE CHIARO, A. et al.(2016):" Proteomic strategies for cultural heritage: from bones to painting".*Microchemical Journal,*126, pp.341-348
[3] ABU-REIDAH, I.M. et al. (2015): "HPLC-DAD-ESI-MS/MS screening of bioactive componets from Rhus coriaria L. (Sumac) fruits". *Food Chemestry* 166 (2015) 179-191.
[4]MILLS, J.S., WHITE, R. (1987): *The organic chemistry of Museum Objects*. London: Butterworth.

Characterisation of Iron Age pottery from the archaeological site of Tell el-Fara (Palestine)

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The archaeological site of Tell el-Fara in Palestine is located 10 km northeast of the West Bank city of Nablus and 25 km west of the Jordan River. The site was excavated by Roland de vaux, between 1946 and 1960 [1,2], and identified as a reference site for the study of the Bronze and Iron Ages in the intersection between the north and south of the Levant. Leading biblical scholars interpreted Tell el-Fara as the site of the biblical city of Tirzah, capital of the kingdom of North, founded around 925 BC by King Jeroboam according to the Hebrew Bible. This possible identification remains valid today [1]. From 2017, an international archaeological project, led by the Universidade da Coruña, in cooperation with the Ministry of Tourism and Antiquities of Palestine and the Universidade Nova de Lisboa was launched for recovering and studying the site.

Eighty-two pottery fragments corresponding to the Iron II levels have been identified and characterized. They correspond to different kinds of ware attributed to regional and non-regional origin [4,5]. The characterization has been performed to identify any possible group of samples that could correspond to imported pottery, as well as identifying possible imitations of so-called "Assyrian Palace Ware". Petrological analyses, mineral analyses by X-Ray Diffraction, and elemental analyses by X-Ray fluorescence, and Inductively coupled to plasma Mass Spectrometry have been used with this purpose.

[1] R. De Vaux, et al. The new encyclopedia of archaeological excavations in the Holy Land, vol.2, 1993, 433-440.
[2] A. Chambon, Tell el-Far'ah 1. L'Âge du Fer, 1984.
[3] W. Albright, JPOS 11, 1931, 241-250.
[4] J.L. Montero Fenollós, F. Caramelo, J. Yasen, S. Deis, J. Sanjurjo, Aula Orientalis, 38, 2020. 335-349.
[5] J.L. Montero Fenollós, F. Caramelo, J. Yasen, S. Deis, J. Sanjurjo, I. Bejarano, Res Antiquitatis 2, 2020,104-131.

insiTUMlab: the new analytical infrastructure for non-destructive in-situ studies of Cultural Heritage

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The insiTUMlab is a newborn analytical infrastructure for non-destructive in-situ studies of Cultural Heritage, part of the Chair of Conservation-Restoration, Art Technology and Conservation Science of the Technical University Munich (TUM). It is funded by the German Research Foundation (DFG) for the next five years and afterwards, it will be supported by the TUM. The new facility aims to build knowledge on complex queries about cultural heritage. It offers a set of cutting-edge non-destructive, complementary, and portable analytical tools able to support studies on site of architectural surfaces and artworks for their understanding and preservation. The equipment consists of a two sensors Hyperspectral system (spectral range 400-1000/960-2500 nm), a Macro X-Ray-fluorescence scanner, complemented by handheld Raman and Infrared spectrometers. Access to advanced laboratory analytical tools is possible thanks to the partners and TUM facilities. The interdisciplinary research group includes three heritage scientists and a conservator. A Ph.D. thesis focused on Hyperspectral imaging applications in collaboration with the Doerner Institut and the IFAC-CNR is planned. Official external partners are the Doerner Institut; the Deutsches Museum, the Staatliche Akademie der Bildenden Künste Stuttgart and the University of Barcelona. In this contribution the results of some case studies will be presented: Wall paintings of the Magdalen Chapel, S. Emmeram, Regensburg; Roman wall paintings fragments from the Municipium Claudium Virunum, Austria in collaboration with the Hochschule für Bildende Künste Dresden; First German Daguerreotypes by C. A. von Steinheil in collaboration with the Deutsches Museum; Soluble salts formations in the Khufu Pyramid in collaboration with the Cairo University and the TUM Chair of non-destructive testing; Application of Hyperspectral imaging for the investigation of selected W. Baumeister paintings in collaboration with the Akademie der Bildenden Künste Stuttgart as well as Venetian paintings of the Bavarian State Painting Collections in collaboration with the Doerner Institut.

Identifying, Organizing and Managing Scientific Research Assets at the Van Gogh Museum

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The Van Gogh Museum (VGM) is a leading centre for knowledge on Vincent van Gogh and his contemporaries. An integral part of its mission is to promote research and support collaboration with institutions all over the world. In the 50 years since the VGM was founded, scientific research has played an increasingly salient role in the study of the museum's collection. This has created a legacy of scientific research assets including data, reports, paint samples and other reference materials that is steadily increasing, even more so now that the museum has embarked on a *Partnership in Science* with ASML dedicated to the preservation of Van Gogh's legacy. In addition, the majority of this research is being generated in collaborative projects and some of the generated assets are dispersed amongst several institutional and international partners.

The museum is currently examining how it can best fulfil its mission of promoting scientific research, while also preserving and sharing its output with the field and the wider public. On the one hand, the museum acknowledges the need to implement a research data management (RDM) plan and ensure that the scientific data generated on its collection is following FAIR principles (Findable, Accessible, Interoperable and Reusable) and supports open and reproducible science. On the other hand, the museum recognizes the inestimable value of the paint samples and cross sections taken over the years from the art objects in its collection for the purpose of scientific research. When properly preserved and catalogued, these samples can be re-examined in different contexts and newly developed techniques, to extract further knowledge on the artistic process, painting materials and degradation.

The museum conservation scientists and data steward recently teamed up to take on these two projects: implement a research data management plan and create a database for its historical samples. The very first step, for both projects, was to conduct a survey of the research assets hosted at the museum and at the partnering institutions in order to assess the current and anticipated volume, existing licensing agreements, associated risks and vulnerabilities. For both RDM and sample database, cost of implementation, expertise required to set up and maintain commercial versus open source solutions and integration with existing museum systems are being evaluated against a list of wishes and requirements collected in interviews with the creators and current custodians of those research assets. Highlights of the survey, interviews and search for RDM and database solutions will be presented to illustrate the effort and progress of the museum to identify, organize and manage its scientific research assets.

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An approach to the metallic composition of the Carthage mint coins from the tetrarchic hoard of Tomares

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The Tomares hoard, discovered in Tomares (Seville, Spain) on 27 April 2016, consists of approximately 53.000 *nummi* of Tetrarchic period. This period is characterized by great political instability, so the study of the hoard supposes an opportunity to better understand the monetary circulation in the Hispanic provinces. In addition, the hoard can offer information concerning the recurrent decreases in silver content and coin weight because of scarcity in the supply of precious metal and economic difficulties. For this purpose, a group of 533 *nummi* have been analysed with the non-destructive XRF technique to characterize the metallic composition. The chosen coins belong to the mint of Carthage between AD 297 and 307. The reason for selecting this mint is as a consequence of the few studies that exist on the same with a lower number of pieces than in this work. Therefore, this study increases our understanding of the mint of Carthage in both material and historical terms. The coins did not present great differences in its composition, so we could conclude that the same alloy was used in the four active mint's *officinae*. However, coins minted early in the first Tetrarchy were found to feature higher concentrations of silver than in later periods, reflecting the economic problems that arose in those periods. This work is the first step in the study of the metallic composition of the Tomares hoard. When other mints and monetary series are similarly analysed shall we be able to contribute significantly to ongoing debates around this turbulent historical period.

Well preserved rare red glazes in Brazilian Baroque Polychrome Sculptures: Characterization and Conservation

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Translucent and colored layers (glazes) are often found in polychrome baroque sculptures, mainly due to their property of providing aesthetically pleasing optical effects and varied shades to the metallic surfaces on which they are applied. They are composed of terpenic resins and lakes, making it possible their transparency.

Souza (1996) highlights the red glaze applied over the gilding on two altars at the Main Church of Our Lady of Conception, in Catas Altas do Mato Dentro – Minas Gerais, Brazil: Altar of Santo Antônio (1745) and Altar of Nossa Senhora da Assunção (1745). This glaze has madder as a red dye, and has drawn our attention because of its beautiful transparent red color effect and also due to the use of starch on its formulation [1]. More recently, during the painted ceiling restoration process of the Church of Our Lady of Conception of the Military, in Recife – Pernambuco, Brazil, completed in 2021, samples were collected for characterization through physical-chemical analysis at the Conservation Science Laboratory (LACICOR) from the Federal University of Minas Gerais. The fragments have shown to have the same color, aspect and microscopical characteristics as the ones collected previously in Minas Gerais.

The characterization of the samples involved the observation of fragments in a Stereo Microscope, as well as their stratigraphic section by Optical Microscopy, Scanning Electron Microscopy, Fourier-Transform Infrared Spectroscopy and Raman Spectroscopy.

The use of starch as a component in the production of lacquers is described in the Bologna manuscript (15th century), of unknown authorship, as a proposal for an producing the red glazes [2]. However, it was in Luiz Souza's Ph.D. thesis (1996), that this finding was described for the first time in Brazil. This glaze is worth to be described and well understood in terms of its composition and making, due to its originality and the optical qualities it gives to the finished gilded surface. In terms of conservation, it is also important to reiterate its occurrence due to problems that may arise if the cleaning is not performed properly.

As a future perspective of this work, it is intended to reproduce the original lacquer recipe, found in the Bologna manuscript, at the LACICOR - UFMG.

[1] SOUZA, Luiz Antonio Cruz. **Evolution of Polychrome Technology in Sculptures in Minas Gerais in the 18th Century: The unfinished interior of the Main Church of Nossa Senhora da Conceição, in Catas Altas do Mato Dentro**, an exemplary monument. Advisor: Dr. Dusan Stulik. 1996. Thesis (Doctor of Science - Chemistry) - Chemistry Department of the Exact Sciences Institute of the Federal University of Minas Gerais, Belo Horizonte, 1996.
[2] MERRIFIELD, W.P., **Original Treatises dating from the XIIth to XVIII centuries on the arts of painting in oil miniature mosaic and on glass of gilding dyeing and the preparation of colours and artificial gems**, London, v.2, 1849.

New insights of manufacturing tradition of roof tiles from Basque Country, north of Iberian Peninsula.

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The archaeological roof tiles from Basque Country located at the north of Spain evidence a specific manufacturing technique. Recent roof studies have provided significant new data of manufacturing practices using waste from the ore smelting process. From Roman times, the Basque Country was an important smelting center until the 19th and 20th centuries. Moreover, the Middle Ages represent a crucial period in the evolution of iron production in this region.

Roof tiles from several sites of Basque Country were analysed to determine the manufacturing process. Multianalytical approaches have been used to mineralogical and microstructure characterization: optical microscopy, scanning electron microscopy (SEM), X- ray diffraction (XRD) and Raman microspectroscopy. Chemical composition of roof tiles was assessed for the raw material characterization.

The paste of the tiles is commonly fine-grained where aplastic inclusions are not abundant. The iron processing wastes often occurs as blackish inclusions and were intentionally added. The microstructure and mineralogical characterization indicate that tiles were manufactured with local clays and fired at high temperatures. Roof tiles with similar characteristics from different sites suggest a specific similar manufacturing tradition. This study sheds new light on the technology of archaeological tile making.

Investigation of the influence of lead white on the alteration mechanism of smalt in paintings by SR µXRD and µXANES

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The blue pigment smalt, a synthetic potash glass tinted with cobalt, was widely used in paintings between the 16th and the 18th centuries. It is known for its tendency to weather in oil paintings going from a blue to a yellowish hue and the alteration mechanism has been well studied [1][2]. However, an overview of the alteration state of smalt in painting, which have been studied at the C2RMF has shown that the weathering mechanism isn't a time depending process and that the depth of the smalt containing paint layer in paint stratigraphies doesn't seem to play a role in the weathering of the pigment [3]. We were therefore interested in the influence of the other components of smalt containing paint layers, in particular, the type of lead white, which is mixed with smalt. In a previous study, it was observed that hydrocerussite (HC) seems to accelerate the weathering of smalt [4].

Eight historical samples were analyzed by SEM-EDS, 2D-µXRD [5] and µ-XANES at the Co K-edge at the SOLEIL and the ESRF synchrotron facilities to determine their composition, the type of the lead white present and the smalt preservation state. Historical samples, where smalt is altered, show a predominance of HC over cerussite (C) in smalt containing paint layers (figure 1)[4].

To verify this hypothesis, mock-up samples were created by mixing smalt with pure C or pure HC and aged artificially. These twenty samples underwent comparable analyses as the historical ones.

Results obtained on historical and mock-up samples will be synthetized in order to explain the interactions between smalt and the other components in the paint layers during the alteration process.

Figure 1: a: optical image of a historical cross-section. b: overlay of SR 2D-µXRD maps of C and HC. c: diffractogram of cross-section, characteristic peaks are indicated. Arrows indicate peaks used to extract maps.

[1] M. Spring, C. Higgitt, et D. Saunders, « Investigation of Pigment-Medium Interaction Processes in Oil Paint containing Degraded Smalt », *Nat. Gallery Tech. Bull.*, vol. 26, 2005.

[2] L. Robinet, M. Spring, S. Pagès-Camagna, D. Vantelon, et N. Trcera, « Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge », *Anal. Chem.*, vol. 83, nº 13, p. 5145–5152, juill. 2011, doi: 10.1021/ac200184f.

[3] I. Reiche, C. de Mecquenem, et M. Eveno, « L'utilisation du smalt et son altération dans les peintures des collections françaises. », in *Les bleus et les verts : couleurs et lumières*, Hermann., 2022.
[4] C. de Mecquenem *et al.*, « A multimodal study of smalt preservation and degradtaion on the painting "Woman doing a Libation or Artemisia" from an anonymous painter of the Fontainebleau school », *EPJ+* submitted
[5] M. Cotte *et al.*, « The "Historical Materials BAG": A New Facilitated Access to Synchrotron X-ray Diffraction Analyses for Cultural Heritage Materials at the European Synchrotron Radiation Facility », *Molecules*, vol. 27, nº 6, p. 1997, mars 2022, doi: 10.3390/molecules27061997.

Archaeological bricks and tiles from Southeast Bulgaria - determination of production technology by methods of archaeological chemistry

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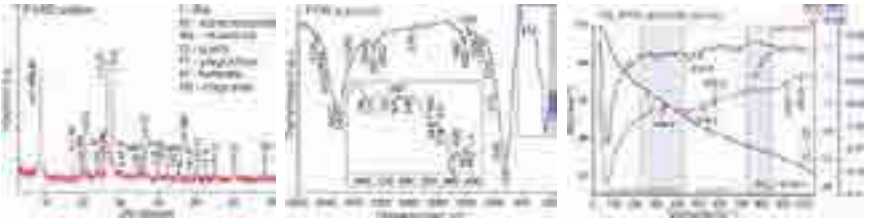
Keyword: archaeological ceramic; thermal analysis; phase and structural analyses

This work deals with sixteen Roman and Late Antique bricks and roof tiles from eight archaeological sites in Southeast Bulgaria. The samples studied were through X-ray fluorescence, powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR), and thermal analysis (TG/DTG-DSC) [1]. The results indicate the successful combination of the experimental methods to determine with great accuracy the characteristics of the raw clay (given that there are no clay deposits in the geographical area to make comparisons with), the firing technology, and some findings of high ceramic quality and durability over time.



Sample No.12 - floor brick - site No. 17 Gorno Novo Selo village, fortified settlement

The results evidence the use of identical ceramic manufacturing technology in the entire geographical area during the Roman and Late Antique periods, and a clear perspective for future investigation. They also complement the known archaeological background by interpreting people's knowledge continuity from the Roman age to Late Antiquity and on economic and cultural life, based on ceramic investigations by methods of archaeological chemistry [2].

[1] P. Cardiano, S. Ioppolo, Co. De Stefano, A. Pettignano, S. Sergi, P. Piraino, Analytica Chimica Acta 519, 2004, 103–111.
[2] K. Elert, G. Cultrone, C.R. Navarro, E. S. Pardo, Journal of Cultural Heritage 4, 2003, 91–99.

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Study of an early 20th century artist's forgery of a Botticelli portrait painted in tempera on tile

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In this work, a tempera painting of uncertain attribution from the Uffizi Galleries was studied. The painting, which portraits a man with apparently Botticellian features, was probably created by one of the most skillful forgers of the early 20th century, Umberto Giunti, better known as Il Falsario in calcinaccio. He used a flat tile (embrice) as a support, covered with preparatory layers emulating a wall painting. Given the uniqueness of the case study, it was crucial to investigate the execution technique, the state of conservation and the composing materials. To this end, non-invasive spectroscopic and imaging optical techniques were applied. Specifically, VIS-NIR multispectral reflectography was used to reveal the presence of overpaintings, *pentimenti* or a possible preparatory drawing. Raman and Fiber Optics Reflectance Spectroscopies allowed identifying the pigments used by the artist. Finally, color variations due to different cleaning methods were monitored in order to choose the most suitable procedure.

The non-invasive study of a group of Early Medieval wall paintings in the *Raetia Curiensis* region

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In Europe, most of surviving Early Medieval wall paintings are found in the ancient region of Raetia Curiensis, which includes the current Swiss Canton of Grisons, parts of today's Northern Italy [1], and Austria. Although these paintings are among the best preserved of the period, they have never been studied systematically and compared with an archaeological and scientific approach. To fill this gap, a 4-year multi-disciplinary research project (2022-2026) entitled "Forgotten colors - Rediscovering the original polychromy of Early Medieval wall paintings in the *Raetia Curiensis* region" is ongoing and includes historical and archaeological research, integrated with scientific investigations[1]. The wall paintings selected for the study are located in the following sites: St. Johann's church and Heiligkreuzkapelle (Holy Cross chapel) at Müstair, St. Martin in Disentis, St. Stephan in Chur and St. Peter in Mistail (Grison Canton, Switzerland), St. Benedikt in Mals/Malles, St. Prokulus in Naturns/Naturno, St. Peter above Gratsch (South Tyrol, Italy). The project aims to characterize the painting materials and the mode of application, determine the provenance of the raw materials, and the technology of production of artificial pigments.
This contribution presents the results of the non-invasive scientific campaigns carried out on the wall paintings in-situ and/or on painted fragments recovered during past archaeological excavations. The investigations began with non-invasive mapping techniques, such as technical photography in visible, infrared and ultraviolet ranges, followed by portable spectroscopic point analyses, namely X-Ray Fluorescence (XRF), Fiber Optics Reflectance Spectroscopy (FORS), and Reflection FT-IR Spectroscopy (FTIR). The findings revealed the composition of most pigments such as iron-bearing pigments (yellow and red ochre, green earth), lead-based pigments (i.e., lead white and red lead), and natural ultramarine blue. In addition, Visible Induced IR Luminescence (VIL) images combined with point analyses allowed the identification of Egyptian blue. Overall, these pigments seem to be mostly lime-bound, but the occasional presence of oxalates suggests degraded organic materials to be further investigated. The non-invasive results will allow planning a sampling strategy aimed at determining stratigraphy and composition of the paint components on each layer.
This study provides a valuable example of the potential of a completely non-invasive multi-technical approach to understand materials and techniques used in these Early Medieval sites.

[1] G. Cavallo, M. Aceto, R. Emmenegger, A.T. Keller, R. Lenz, L. Villa, S. Wörz, P. Cassitti, Journal of Archaeological and Anthropological Sciences 12, 2020, 1-20.

[1]Project funded by the Swiss National Science Foundation (SNSF) https://data.snf.ch/grants/grant/201055

The relationship between science and art in Taramelli's watercolors

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Consequently to the 100th anniversary of the scientist's passing away, the year 2022 has been dedicated to Prof. Torquato Taramelli, one of the most important Italian geologists, cartographers, passionate naturalists, and amateur painters. As a result of this special occasion, the University of Pavia, Taramelli's historical affiliation, together with the Soprintendenza Archeologia Belle Arti e Paesaggio per le province di Monza-Brianza e Pavia, have organized many scientific and didactic initiatives [1]. Those included the restoration and the exhibition of Taramelli's watercolors collection, given by the author to the University of Pavia and kept at the Department of Earth and Environmental Sciences. The collection consists of a set of thirty-three views; all painted between about the half and the end of the XIX century [2]. The restoration also represented a privileged opportunity to carry out a characterization study, performed by a multidisciplinary approach and focused on the pigments identification, conservation state of the artworks, and techniques used by the author. Indeed, selected watercolors have been studied by combining portable X-Ray Fluorescence, micro-Raman Spectroscopy, and multispectral imaging techniques, facing stratigraphy issues during the analysis process. Then, the identification of the pigments has supported the hypotheses about the interpretation of the techniques and the author's scopes. In fact, as a scientist, Taramelli applied a sort of "scientific painting" with an educational aim.

[1] M.G. Piccaluga. La Provincia Pavese, 04 Gennaio 2022 (https://laprovinciapavese.gelocal.it)
[2] C. Lupi, Guaschi P., Guioli S. exhibition "Terra Nascosta", Museo Kosmos, piazza Botta 9, Pavia (Italy), 5th March-12th June 2022.

Identification of Mural Damages with Laser Holographic Speckle Interferometry with Acoustic Excitation

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Identification of mural damages is important for culture preservation. Application of optical non-destructive for damage identification has been rapidly developed [1-3]. For identification of the mural damages, we propose a novel laser holographic speckle interferometry with acoustic. Based on the speckle pattern on the surface of the tested object, before and after acoustic excitation by using a speaker, the fringe patterns could be obtained by applying the Fourier space carrier method. Results show that the laser holographic speckle interferometry is able to accurately and effectively discover the main disease conditions of the murals. The schematic diagram of optical system of laser holographic speckle interferometry is shown in Figure 1(a), which uses a green laser with a wavelength of 532 nm to form two diffuse point light sources after a fiber beam splitter. The field of view of optical system is 8cm × 8cm, and the detected minimum deformation is 5μm. The system is able to identify surface cracks, sub-surface voids and other diseases of ancient mural in the Palace Museum of China, as shown in Figure 1(b).

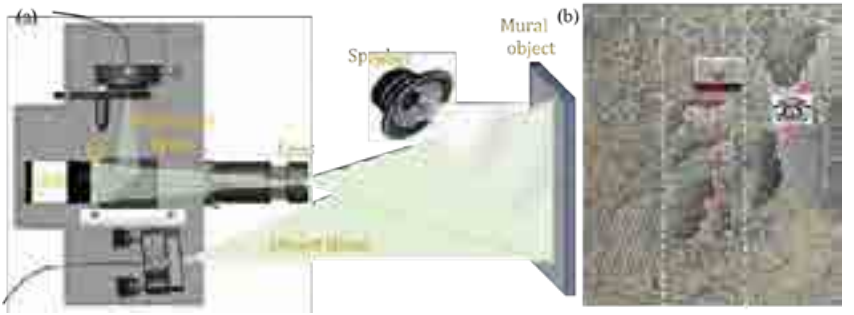

Figure 1 (a) Schematic diagram of optical system of laser holographic speckle interferometry with acoustic; (b) Deformation fringe patterns with acoustic excitation on ancient murals.

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[1] W. Osten, W. Jueptner, U. Mieth, Proceedings of SPIE, Interferometry VI. San Diego, USA, 1994, 256-268.
[2] W. Zhou, Y. Liu, Z. Chen, Y. Chen, H. Zhang, Y. Yu, V. Tornari, Applied Sciences 12(15), 2022, 7799.
[3] V. Tornari, Light: Advanced Manufacturing 3(1), 2022, 1.

The beautifying properties of historical white lead makeup

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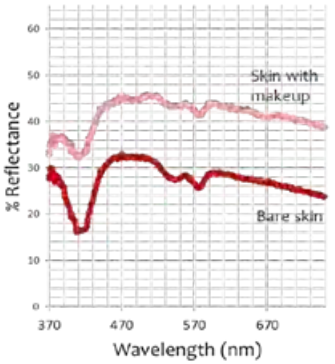
Many museums hold white lead cosmetics, or their containers, in their collections. These objects date from antiquity up to the early 20th century[1]. White lead cosmetics have been popular for millennia, and although formulae have changed over time, there must have been a reason why white lead remained popular. People evidently had strong motivation to wear it. 'Skin Whitening' has been cited as a goal[2], but there is no modern data on the appearance of these makeups when worn on the skin. Due to the toxic properties of lead, we cannot today paint white lead cosmetics on living people to see what they looked like.

We have therefore developed an experimental methodology to not only see what recreated white lead cosmetics look like to the eye, but to quantify the beautifying properties they may have brought to skin.



Using diffuse reflectance spectroscopy[3], we measure the spectra from pigskin before and after painting white lead makeup. The spectral changes are shown in the figure. We have identified that white lead makeup changes the measured spectra in terms of hemoglobin and melanin absorption. There are also shifts in the overall colour of the skin following application of white lead cosmetics. We have established multiple regression models to predict colour changes that depend on the starting skin colour in 3-D colour space, and on the level of makeup applied. By measuring the total diffuse and specular reflection, we can show that these white lead makeups had optical properties similar to modern blurring compounds that are considered to beautify skin in modern north American culture.

We will present the methodology we used, and share data on recreated historical cosmetics. We have found that many white lead makeups look remarkably natural and could have had significant beautifying properties. The data we will share could help to explain why women would choose to wear a cosmetic even if they knew it could be toxic.

[1] Walter P, Martinetto P, Tsoucaris G, Brniaux R, Lefebvre MA, Richard G, Talabot J, Dooryhée E. Making make-up in Ancient Egypt. Nature. 1999 Feb 11;397(6719):483-4.
[2] Peiss K. Hope in a jar: The making of America's beauty culture. Macmillan; 1999 May 15.
[3] Zonios G, Bykowski J, Kollias N. Skin melanin, hemoglobin, and light scattering properties can be quantitatively assessed in vivo using diffuse reflectance spectroscopy. Journal of Investigative Dermatology. 2001 Dec 1;117(6):1452-7.

Fanal® pigments in the spotlight

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With the discovery of precipitating early triphenylmethane dyes with complex phosphorus-tungsten and molybdenum salts, I.G. Farbenindustrie started to launch the Fanal® pigments in the beginning of the 1920s. Famous for their bright colours, their relatively low lightfastness inspired developments in their precipitation methodology, resulting in new improved brands which were introduced at specific dates until the early 1930s. The organic colourants were originally designed as dyes for the paper and textile industry, when converted into the Fanal® pigments, the light and solvent sensitivity was not compatible with the purposes of fine artist materials.[1] However, recent research in the archives of I.G. Farben and Dutch paint manufacturer Talens has shown that these synthetic organic pigments (SOPs) were used in fine artist paints in the 1930s and beginning 1940s.[1] They were eventually replaced in Talens' production by more lightfast SOPs like phthalocyanines.

Knowledge on the type of Fanal® pigment present in artworks can provide crucial information for heritage professionals when developing conservation strategies, including the choice of solvents, and determining exhibition lighting requirements. However, the constant changes in the production process had a significant impact on the characteristics of the specific Fanal® brand used. This study concerns the possibilities and limitations to analytically distinguish the different historic Fanal® brands.

A unique collection of thirty historic Fanal® pigments, including red, pink, violet, blue, yellow and green tints originating from the TU Dresden was studied. It covers the period 1920-1930 when these pigments underwent drastic technological developments. The reference samples were examined with a wide range of analytical techniques that are typically part of the conservation scientists tool box when studying an object suspected of containing SOP's: XRF and micro Raman spectroscopy, SEM-EDX and HPLC-PDA-HRMS.[2]
Analytical results were combined with detailed art technological source research of patents and original production recipes for the historic Fanal® pigments. To demonstrate the feasibility of the different techniques applied, we included an oil painting from Dutch artist J.M.J. Wijnsouw, 'Still life with palette' made in 1940. This provided important insights into the limitations when studying the characteristics of SOPS present in modern artworks.

[1] Pause, R. de Keijzer, M. van den Berg, K. Studies in Conservation 67 (8) 2022, 569-583
[2] Sundberg, B. N., Pause, R., van der Werf, I. D., Astefanei, A., van den Berg, K. J., & van Bommel, M. R. Microchemical Journal, 170 (106708) 2021

Identification of pigments and binders in paintings of Serbian romantism and realism

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Restoration of an old, historical painting is a very valuable and responsible task in the preservation and protection of sensitive cultural heritage. Historical paintings matrix is usually extremely complex, with numerous chemical compounds originating not only from pigments, but also from binders, ground layers, varnishes, fillers etc. Therefore, it is very useful for conservators to have information revealed from the material characterisation of paintings, so pigments and binders are identified. It is an imperative to have as few interventions on paintings as possible, hence non-invasive analytical methods are likely to be used.

The subject of this study is the investigation on paintings of two prominent Serbian painters, Georgije (Đura) Jakšić and Uroš Predić, the first one representing the romantism from late 19th century and the later representing realism from beginning of the 20th century. The investigated paintings are all from the fund of Gallery of Matica srpska, one of the oldest national museums in Serbia. Pigments and binders identifications were made using non-invasive analytical techniques: X-Ray Fluorescence spectroscopy (XRF), Fourier Transform Infra-Red spectroscopy (FTIR) and mobile microscopy with various lights (UV/Vis/IR). The obtained results are good basis for future restoration and conservation efforts.

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Different shades of cadmium soaps in mock-up oil paints: first multi-analytical investigation

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Metal carboxylates formation is a well-known issue in oil paintings, and it is certainly one of the most recurrent topics in the conservation science research of the last 20 years [1,2]. In this work the formation of cadmium soaps in light-aged modern oil mock-up paints made of a mixture of linseed oil and cadmium red PR108 (CdS, xCdSe) and cadmium yellow PY37 (CdS, ZnS) has been investigated for the first time by using a multi-analytical approach. Light Emitting Diode (LED)-based lighting and a halogen lamp were used for the sample exposure thereby reproducing indoor museum conditions.

For this purpose, Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) - Energy Dispersive spectroscopy (SEM-EDS) were used for visualizing and documenting the formation of cadmium soaps and their different shapes and distribution in the considered samples both on the paint surface and in cross-section. A micro-Fourier Transform Infrared Spectroscope (μ-FTIR) in Attenuated Total Reflection (ATR) mode equipped with both Mercury-Cadmium-Telluride (MCT) and Focal Plane Array (FPA) detectors was employed for the chemical mapping of the cadmium carboxylates possibly formed. Protrusions formed on the surface of mock-ups were then collected and analyzed by μ-FTIR in transmission mode by using a diamond cell. Furthermore, X-Ray Powder Diffraction (XRPD) analysis allowed the detection of crystallized phases complementing the spectroscopic data.

The results obtained within this research highlighted the appearance of cadmium soaps together with the formation of possible cadmium oxalates. Furthermore, yellow and red mixtures aged under LED light showed a larger averaged distribution and protrusions comparing to those aged under halogen lamp and natural light.

[1] F. C. Izzo, M. Kratter, A. Nevin, E. Zendri. ChemistryOpen, (9), 2021, pp. 904–21.

[2] M. Cotte, E. Checroun, W. De Nolf et al. Studies in Conservation (62), 2017, pp. 1–22.

GOIA Project – An initiative between the Federal Police and Universities in Brazil against Crimes envolving Cultural Property and Works of Art

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The annual global trade in art and antiquities in 2018 was estimated at around USD 70 billion, of which around USD 1.6 billion is due to illegal transactions related to theft, counterfeiting, smuggling and organized crime. In Brazil, between 2014 and 2018, the Brazilian Federal Police seized 842 pieces of art and historical and cultural heritage. All of the pieces were related to investigations involving money laundering in cases of active and passive corruption.

The refinement of forgery and adulteration techniques does require a multidisciplinary and technological approach to the process of authenticity, attribution and valuation, which is inevitably based on a triangle formed by three disciplines: art history, heritage science and material sciences.

The GOIA Project (Guard, Observation, Investigation and Analysis of Cultural Assets and Works of Art) is an innovative initiative of the Brazilian Federal Police in partnership with renowned research institutions in the area of Conservation and Restoration, such as the Center for Conservation and Restoration of Cultural Heritage at the Federal University of Minas Gerais (CECOR/UFMG) in Brazil, with possibilities for enlarging the partnership with other centers around the country.

In about three years, the project enabled the high-level training of forensic professionals through their enrollment and exchanges with well stablished research groups and graduate courses. Currently, the academic and forensic partnership enables the use and study of complex techniques such as Determination of Isotopic Ratio for studies of origin and dating of materials, mapping and determinations by X-Ray Fluorescence and Gas and Liquid Chromatography using detectors such as Mass, UV-VIS, TOF-SIMS, among others. The creation of a wide collaboration network between the advanced analytical park of the National Institute of Criminalistics and the Universities involved, mainly UFMG, also provided initiatives for the development and expansion of databases such as stolen works, at risk, analytical data, studio artist's materials, and collections of sample archives, in addition to integrated scientific events, increasing the scope and performance of conservation professionals in the field of Forensic Sciences.

[1] US DEPARTMENT OF TREASURY**. Study of the Facilitation of Money Laundering and Terror Finance Through the Trade in Works of Art**. Washington: [s.n.]. Disponível em: <https://home.treasury.gov/system/files/136/Treasury_Study_WoA.pdf>. Acesso em: 24 abr. 2022.

[2] Polícia Federal, **"Operação Lava Jato."** www.pf.gov.br/imprensa/lava-jato.

[3] J. Ragai, **The Scientist and The Forger - Probing a turbulent art world**, 2nd ed., vol. 1. New Jersey: World Scientific Publishing Europe Ltd, 2018.

[4] P. Schossler, J. C. D. A. de Figueiredo Júnior, I. Fortes, and L. A. Cruz Souza, **"Scientific analysis and historical aspects as tools in the legal investigation of paintings: A case study in Brazil**," Science and Justice, vol. 54, no. 6, pp. 465–469, 2014, doi: 10.1016/j.scijus.2014.06.013.

Consumed by flames: Investigating the markers of wall-paintings effected by fire

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The effects of a fire on artifacts vary and depend on the time of exposure to the event, but also on the temperatures developed during it. In the case of wall paintings, these effects range from the deposition of surface pollutants, to their total destruction due to the collapse of the substrate or masonry. The main purpose of this study is to examine the possibility of detecting organic binders as a function of the maximum developed temperature. This is important in the case of wall paintings, as the presence or absence of organics is one of the criteria for the determination of the applied painting technique. Thus, the study of the characterization of a wall painting that has undergone such an incident may lead to erroneous conclusions about the presence or the absence of organic binders.

In the framework of this study, traditional recipes were applied for the preparation of wall painting mock-ups. Thus, using yellow ochre, the painting layer was applied on freshly prepared Ca(OH)2 ground using water (fresco technique), and on dried ground using egg yolk, linseed oil, gum arabic, and casein as the binder (secco technique). After undergoing a fire protocol representative of temperatures/duration for compartment fires, the mock-ups were studied by Fourier transform infrared spectroscopy (FTIR), micro-FTIR imaging, DRIFT spectroscopy using a climatic chamber, X-rays diffraction (XRD), Thermogravimetry (TGA), UV-Vis Spectrophotometry, X-rays photoelectron spectroscopy (XPS) and optical microscopy. The results showed that there are strong indications that a wall painting which has survived after a fire incident can carry information regarding the applied binder.

In-situ XRD measurements on outdoor bronze artwork as a tool to deepen the knowledge on patinas

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The challenge for more effective conservation treatments for outdoor bronze artworks is manifold because of the need to consider the quite complex system bronze+patina/coating/environment [1]. Several properties need to be characterised to deepen the knowledge of the complex interface of outdoor bronze artworks with the exposure environment [2-5]. The lack of such a knowledge prevent to transfer research on more effective conservation treatments to conservation-restoration practice. Based on previous experience both on *in situ* measurements on outdoor bronzes and preliminary tests on bronze artworks at Staglieno Cemetery, the Astorri's Angel (AA) was selected for portable XRD measurements. The main research interest was the characterisation of the surface corrosion layer, with a special interest in identification of Nantokite, as XRD is more effective in this task with respect to other spectroscopies [6]; moreover, it was a good testing framework for *in-situ* XRD application to non-destructively identify corrosion products in selected areas (i.e., without removing them from surface). This is of utmost interest to test effectiveness of treatments against cyclic corrosion on copper alloys artworks [6]. Quaternary bronze coupons with marine natural patina enriched with Nantokite from previous projects [6] was also used to check and calibrate measurement setups. Different types of patinas were considered, and a well-defined measurement grid was defined to compare multi-analytical NDT results. Measured data widen the knowledge on the variability of outdoor bronze surface properties and enlighten the possible applications of XDR *in-situ* measurements.

[1] P. Letardi, Coatings 11(2), 2021, 131.
[2] C. Chiavari, K. Rahmouni, H. Takenouti, S. Joiret, P. Vermaut, L. Robbiola, Electrochimica Acta 52, 2007, 7760-7769.
[3] E. Bernardi, C. Chiavari, B. Lenza, C. Martini, L. Morselli, F. Ospitali, L. Robbiola, Corrosion Science 51, 2009, 159-170.
[4] T., Chang, A. Maltseva, P. Volovitch, I. Odnevall Wallinder, C. Leygraf, Corrosion Science 166, 2020, 108477.
[5] C. Petiti, L. Toniolo, D. Gulotta, B. Mariani, S. Goidanich, Environ Sci Pollut Res 27, 2020, 13081–13094.
[6] G. Monari, M. Galeotti, M. Matteini, B. Salvadori, R. Stifanese, P. Traverso, S. Vettori, P. Letardi, Environ Sci Pollut Res, 2022.

A pigmented lime plaster consolidation with an ethyl silicate and calcium hydroxide based consolidant: an experimental approach

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Lime mortars are commonly extended materials in historical building constructions. Nevertheless, ancient porous calcareous materials are susceptible to decay leading structures to a significant decrease in their cohesion and mechanical properties. Consolidants are usually applied to recover the strength of degraded materials as well as to decrease the deterioration rate of the substrate.

This study aims to investigate the consolidation treatment effectiveness on archaeological pigmented lime plaster from the 16th-century cistern of Amaiur Castle (Navarre, Spain). Applied treatment consisted of an experimental mixture of ethyl silicate and calcium hydroxide-based consolidants (i.e., ESTEL 1000 and Calosil® E25, respectively). In order to assess the consolidation effectiveness polarized light microscopy (PLM), X-ray diffraction (XRD), scanning electron microscopy with X-ray microanalysis (SEM-EDX), X-ray microtomography (Micro-CT), colourimeter, Equotip Leeb hardness Tester (HDL) and mercury intrusion porosimetry (MIP) analyses were performed. Hygric properties were also tested by measuring differences in water vapour permeability (WVP), static contact angle and capillary water absorption (WAC). Furthermore, the reactivity of the consolidation mixture and formation of C-S-H during the curing process was also investigated.

Preliminary results show a significant increase in the mechanical properties and a reduction in the capillary water absorption rate while also preserving the water transmission rate and aesthetic properties.

Metallic mercury, at last! Synchrotron radiation-based study on Pompeian cinnabar wall paintings

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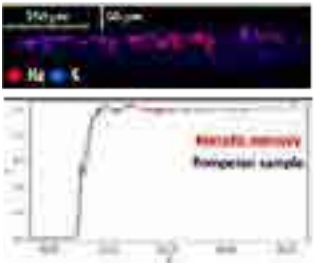
Since their discovery in 18th century, the worldwide famous wall paintings at the archaeological site of Pompeii have received the attention from scientists with different backgrounds, due to the wide range of questions that have arisen during their study and conservation. One of the most challenging problems has been about the darkening/blackening of the precious Roman cinnabar, widely used in the composition of the above-mentioned wall paintings.



Following the hints given by our former in situ and laboratory investigations [1,2], we present the results from a large experiment carried out at ID21, BM23 (HG-184 experiment), and ID13 (HG-172 experiment in the context of the Historical Material BAG initiative) beamlines of the European Synchrotron Radiation Facility in Grenoble (France). The aim of this work was to elucidate many of the aspects of the chemical reactivity leading to the degradation of cinnabar on Roman fresco paintings by µXRF and µXANES at S and Cl edges, µHERFD-XANES at Hg edge and µXRD. Experiments were conducted on archaeological samples that were exposed to the 79 AD volcanic eruption. In these samples, cinnabar was a minor component of a mixture with other ochre pigments, having an allegedly protective role. However, corderoite ($Hg_3S_2Cl_2$), calomel, metacinnabar (β-HgS), and metallic mercury were clearly identified for the first time in historical samples of this type (see Figure). Furthermore, the massive sulfation and chlorination of calcite was also detected. On the other hand, in samples protected from the eruption, it was not possible to clearly identify such degradation products in the cinnabar-containing pictorial layers.

Our results highlight the key role of the 79 AD volcanic eruption in the transformation process of this mineral pigment and offer precious new insight in the understanding of its chemistry.

[1] S. Pérez-Diez, A. Pitarch Martí, A. Giakoumaki, N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, A. Martellone, B. De Nigris, M. Osanna, J.M. Madariaga, M. Maguregui, Anal. Chem. 93, 2021, 15870.
[2] S. Pérez-Diez, L.J. Fernández-Menéndez, M. Veneranda, H. Morillas, N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, N. Bordel, A. Martellone, B. De Nigris, M. Osanna, J.M. Madariaga, M. Maguregui, Anal. Chim. Acta., 2021, 338565.

The ceroplastic simulacra of Vitoria, Eleonora and Martian

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On May 31, 1578, excavations accidentally revealed the entrance to a perfectly preserved ancient Christian hypogeum on a vineyard along the via Salaria Nova [1]. It marked the "rediscovery" of the catacombs of Rome during the modern period. Burial in the catacombs allied to the blood vessel was an undoubtful indicator of martyrdom and frequently sufficient to declare the bones' authenticity. Encouraged by the recent Council of Trent, together with an infinite source of martyrs' bones available in the catacombs, the following three centuries converted into a period of faith, pilgrimage, and massive migration of the holy bones to the four corners of Christendom [2]. Martyrs' simulacra are a particular type of reliquaries used from the late 17th to the mid-19th century. The sacred bones (*corpi santi*) were positioned inside a simulated body representing the martyr, shaped with gauze, papier-mâché, wax and other materials, and supported by a metallic structure. The simulacra were then ceremonially dressed in Baroque clothes as Roman legionaries or virgins and exhibited the signs of martyrdom [3].
Portugal followed the same trend as the rest of Europe. Saint Martian in the parish Church of saint Sebastian (Óbidos) and saints Victory and Eleonora in the Palace of Marquis of Pombal (Oeiras) are good examples of ceroplastic simulacra received in the country during the 18th century. Here we present part of Portugal's first scientific study on simulacra made of wax. The aim was to establish the materials and the manufacturing techniques adopted and to unveil their complexity from the material, technical and decorative points of view. For that, a combined multi-analytical approach was used, which included imaging (radiography, OM and SEM), spectroscopic (EDS & ATR-FT-IR) and chromatographic (LC/DAD/MS & Py-GC/MS) techniques. Comparison with other simulacra in the north and centre of Portugal strongly suggests that a national production replaced the original Roman output.

[1] P. Boutry. Les saints des Catacombes. Itinéraires français d'une piété ultramontaine (1800-1881). Mélanges de l'Ecole Française de Rome. Moyen-Age, Temps Modernes, 91(2), 1979, 875–930.
[2] S. Baciocchi, P. Boutry, C. Duhamelle, P.-A. Fabre, & D. Julia. La distribution des corps saints des catacombes à l'époque moderne: de Rome aux nations. (J.-P. Zúñiga, Ed.), Pratiques du transnational. Terrains, preuves, limites. Paris: Centre de recherches historiques, 2011.
[3] J.L. Bouza Álvarez. Religiosidad contrarreformista y cultura simbólica del barroco. Madrid: Consejo Superior de Investigaciones Científicas, 1990.

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Archaeometry of 16th to 18th c. tiles produced in the Lisbon area

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Following previous compositional studies of pottery ceramic pastes, clay raw materials, and firing experiments [1-4], an enlarged and detailed archaeometric study of selected tiles produced in the region of Lisbon, North and South of Tagus River, dated from the early 16th to the late 18th century, has been made. The information provided by the XRD, XRF and SM techniques were used to characterize the ceramic bodies of the tiles produced in the Lisbon region. Despite of the enormous diversity and number of tiles produced in the Lisbon region during that period, we could simply sort its ceramic pastes into four types.

A parallel and similar study was performed for *cuerda seca* and *arista* tiles belonging to museum collections or found in Lisbon archaeological contexts, and usually reported as Seville (Triana) productions (15th and 16th centuries).

Moreover, for the Lisbon and Seville tiles, biplots of the Potassium (K) *versus* Calcium (Ca) contents, normalized to the silicon content of each ceramic paste, allowed us to exhibit manifest differences between the two production centres.

Confirming the traditional attributions, the compared results with those obtained on the Oratory of Garcia de Resende tiles (Évora) identified a Seville production.

Santo António da Charneca's tiles 16th c., 1st half | Acanto leaves's tile 17th c., 1st quarter | Camellia's tile 17th c., 3rd quarter | Barroque tile, 18th c., 2nd quarter

[1]Vieira Ferreira LF, Conceição DS, Ferreira DP, Santos LF, Casimiro TM, Ferreira Machado I (2014). Portuguese 16th century tiles from Santo António da Charneca's kiln: a spectroscopic characterization of pigments, glazes and pastes. J Raman Spectrosc., 45, 2014, 838-847. http://dx.doi.org/10.1002/jrs.4551

[2]Vieira Ferreira LF, Ferreira Machado I, Pereira MFC, Casimiro TM, Portuguese Blue-on-Blue 16th-17th c. Pottery. Archaeometry, 60, 2018, 695-712. http://dx.doi.org/10.1111/arcm.12336

[3]Vieira Ferreira LF, Ferreira Machado IL, Gonzalez A, Pereira MCC, Casimiro TM. Portuguese 16th to Early 18th Century Tin Glazed Ceramics Found at the Tagus Estuary Saltpans, Glob J Arch & Anthropol, 11, 2021, 156-168. https://doi.org/10.19080/GJAA.2021.11.555823.

[4]Vieira Ferreira LF, Gonzalez A, Pereira MFC, Santos LF, Casimiro TM, Ferreira DP, Conceição DS, Ferreira Machado I. Spectroscopy of 16th century Portuguese tin-glazed earthenware produced in the region of Lisbon. Ceram Intern. 41, 2015, 13433–13446. http://dx.doi.org/10.1016/j.ceramint.2015.07.132.

A multi-analytical study of lead white darkening in old master drawings at the National Gallery of Denmark

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Old master drawings are precious artworks that are treasured for their aesthetic value and historical significance. They often feature white highlights, which are typically created using lead white, one of the most used historical white pigments. However, many of these highlights have discoloured over time, becoming dark brown or black due to unclear degradation processes. This phenomenon not only misrepresents the original artworks, but also detracts from their beauty, diminishes their longevity and threatens their suitability for public display.

To ensure their preservation, it is essential to determine why some lead white highlights in these artworks retain their light tones while others are prone to darkening. The LeadMad project coordinated by the National Gallery of Denmark aims at advancing preventive conservation of old master drawings by identifying the relationships between the composition, provenance, and production methods of lead white pigments as well as the environmental factors that contribute to their discoloration on drawings, lithographs and early photographs. To gain a deeper understanding of the problem and develop possible solutions, selected samples and objects were examined using a variety of analytical techniques such as X-ray fluorescence spectroscopy (XRF), X-ray powder diffraction (XRPD), Raman spectroscopy, and isotope geochemical investigations. These methods allowed us to inspect the darkening of lead white at an elemental, molecular, and micro-structural level. XRF analyses confirmed the presence of lead as the main element in the majority of the highlights, while XRPD measurements identified both cerussite and hydrocerussite in the white highlights. Moreover, galena, a black crystalline compound, and anglesite were associated with the darkened highlights. Raman spectroscopy assisted in the identification of white and dark compounds, while isotope analyses identified three main groups of raw materials.

Through these measurements, the lead white pigments were classified according to their physicochemical properties in relation to the raw materials used, the fillers and binders added, and the geographical/temporal origin. Additionally, monitoring of storage conditions, which play a crucial role in the darkening process, identified relative humidity and concentrations of airborne pollutants as key factors. The research conducted thus far has provided a deeper understanding of the degradation process of lead white pigments and has helped formulate hypotheses for upcoming experiments that will aid in advancing preventive conservation efforts for these precious artworks. These findings will be of great value to museums, conservators, and other stakeholders in the field of art conservation.

Pigment identification in a 19th century carriage by non-destructive analytical techniques

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Pigment identification is key for understanding the history of cultural heritage or archeological material, providing useful information, such as technical knowledge of a culture, and the solution of problems related to conservation, restoration, dating, and artist attribution [1]. However, characterizing the pigment is not always easy because most of the historical paints are mainly constituted by inorganic pigments, pure or mixed, spread on the surfaces using different binding agents. The knowledge of different constituents of the paint, as well as of the mixing and pictorial techniques, is crucial for a careful program of conservation of polychrome works [2]. Consequently, the analysis requires the combination of analytical techniques with high spatial resolution and multielementar sensitivity. A multitechnique approach performs an important and unique role: that of providing a scientific basis for the development of art history, archeology, museology, and related areas. In the present study, the decorative painting pigments of the Imperial Horse-drawn carriage of Emperor D. Pedro II were analyzed by non-destructive techniques (UV light fluorescence, X-Ray Fluorescence, Macro-X-Ray Fluorescence Scanning, Electron Microscopy of Scanning coupled to the Energy Dispersion System and Raman spectroscopy). The imperial carriage, also known as D. Pedro II's Berlin Device, was specially commissioned for the coronation ceremony of D. Pedro II, in 1841. Belonging to the Imperial Museum, located in Petrópolis, RJ, Brazil, it is a museological object with very important historical implications for Brazilian culture. Altogether, seven colors (green, red, yellow, blue, black, brown, and white) and gold leaf gilding were characterized. According to the key elements detected, it was possible to suggest the pigments Verdigris, Green Earth, Vermilion, Naples yellow, Chrome Yellow, Ocher pigments, Lead white, Cobalt and Oil gilding technique. The results found are in agreement with those described in the literature.

1. A. Lluveras-Tenorio, A. et al., J Therm Anal Calorim 138 (2019) 3287–3299.
2. D. Fontana, et al., J. Cult. 15 (2014) 266-274.

Study of the 'Adoration of the Magi' by Artemisia Gentileschi with multispectral imaging and XRF analysis

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The present work concerns the diagnostic analysis of the painting depicting the Adoration of the Magi by Artemisia Gentileschi [1], one of the three works she created to decorate the choir of the cathedral of San Procolo in Pozzuoli (Naples, Italy). After her arrival in Naples in 1630, the painter was in fact involved in the grandiose decorative project conceived in the second quarter of the 17th century by Bishop Martín de León y Cárdenas [2]. In Naples there was an evolution in the artist's pictorial lexicon as well as her style influenced Neapolitan painters, such as Paolo Finoglio and Francesco Guarino, in a constant osmosis between the artist and the historical context in which she he entered.

The painting is currently in the Museum of the Cathedral of Pozzuoli and its proper conservation and study are part of the Puteoli Sacra cultural social inclusion project launched by the Regina Pacis Foundation.

Non-invasive X-Ray Fluorescence (XRF) diagnostic investigations and multispectral images were carried out to collect data which, combined and compared with what can be inferred from the artistic literature on the Artemisia activity prior to 1630, can lead to new acquisitions in on the executive technique of the painting and the palette and provide information on the materials used in the previous restoration interventions. The goal is also to draw, from the data analysis, useful information to understand how much her palette has been influenced by the relationship with the painters active in Naples in that period.

XRF analysis [3] was used to determine the elemental composition of the painting, enabling the identification of the pigments and materials used in the paint and in the preparatory layers. Point XRF measurements were performed using ELIO Bruker XGLab portable spectrometer. Of some regions of particular interest, like the fingers of Gasparre's hand, a mapping (MA-XRF) was also carried out.

Multispectral imaging investigations [4] were carried out by inspecting the work with different wavelengths (VIS, IR and UV) to differentiate pictorial materials such as pigments, varnishes and dyes; the images were acquired with a Samsung NX500 digital camera 28 MPX with BSI sensor and appropriate filters and light sources. The images are processed with graphics programs.

The contribution will provide the results obtained and their discussion to obtain the maximum information on this important painting and its author.

[1] N. Righi, R. Della Rocca. Artemisia Gentileschi, L'Adorazione dei Magi. Silvana Editoriale, 2019.
[2] M. Merolle, I tesori della cattedrale di Pozzuoli: Artemisia Gentileschi a Napoli tra naturalismo e classicismo. In Proculus 95, 2020, 7-45.
[3] M. S. Shackley. An introduction to X-ray fluorescence (XRF) analysis in archaeology. In X-ray fluorescence spectrometry (XRF) in geoarchaeology, Springer, 2011, 7-44.
[4] A. Macchia, et al. Combined use of non-invasive and micro-invasive analytical investigations to understand the state of conservation and the causes of degradation of I tesori del mare (1901) by Plinio Nomellini. Methods and Protocols, 5(3), 2022,52.

Evaluation of handheld XRF for the assessment of biocide contamination in cultural heritage objects

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Although biocides are no longer in use in most cultural heritage institutions including the Swiss National Museum, they were massively used in the past to prevent damage caused by insects or fungi on organic cultural heritage objects. Nowadays, their use is regulated by the law and due to their toxicity they are a potential health hazard for staff and visitors. Their assessment in cultural heritage artefacts (in museums and heritage sites) is therefore of high importance.

Handheld X-ray fluorescence spectrometry (h-XRF) is a versatile and fast method to be used for the determination of possible biocide contamination and has been already used in the past [1, 2, 3]. However, the reliability of the method has been seldom evaluated [4, 5].

In this study, a Bruker Tracer 5g h-XRF was used for the determination of different marker elements (Cl, As, Hg, Pb) present in organic and inorganic biocides. Analyses have been performed on model samples of different materials representative for museum collections (paper, wool, felt, leather, softwood, walnut, and oak). Four different concentrations of single contaminants and mixtures were applied on the model samples which were then analysed by h-XRF and atomic absorption spectrometry (AAS) after digestion.

The results of this investigation state the reliability of h-XRF measurements to assess the presence of biocides in heritage objects and can be used to estimate their concentrations.

[1] N. Odegaard, D.R. Smith, L.V. Boyer, and J. Anderson. Collection Forum; 20(1–2), 2006, 42–48.
[2] N. Odegaard, L.V. Boyer, et al. AIC Objects Specialty Group Postprints, Volume Ten, 2003, 33-42.
[3] J. Bartoll, A. Unger, K. Püschner, and H. Stege. Studies in Conservation 48, 2003, 195–202.
[4] Ö.G. Üstün, ICOM-CC Ethnographic Conservation Newsletter, Number 30, 2009, pp. 5-8.
[5] S. Krug, O. Hahn, Studies in Conservation, 59:6, 2014, 355-366.

Characterization of architectural plasters and pigments from the Neolithic site of Çatalhöyük by micro-Raman spectroscopy

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The Neolithic settlement of Çatalhöyük (7100 – 5900 cal BC) has long been recognized for its architecturally standardized mud-brick houses, the large majority of which display a high degree of conformity in the construction, arrangement and use of their interior spaces. Recent excavations of a small-sized building at this site, a type of structure insufficiently studied in the past, have revealed its high degree of architectural and symbolic elaboration, which include wall paintings [1]. Raman spectroscopy, a non-destructive technique, was applied to these remains in order to identify and characterize the inorganic materials of both artistic and archeological interest.

In this study, three samples of painted plaster (figure 1) and two control samples, obtained from the walls and floors of Building 114, were analyzed by micro-Raman spectroscopy.

Hematite and lead white were identified, respectively, as the red and white pigments in the painted plasters. Calcite, dolomite, α-quartz, gypsum and anatase were also found in these samples. The observation of the anatase band reveals the possible presence of kaolin clay in the plasters [2]. Raman analysis of the control samples shows bands of the aforementioned minerals together with carbon black, which is related to organic residues. This is in accordance to the soil materials employed in the site constructions with the exception of gypsum, which occurs as post-depositional crystallitic formations, as observed by thin-section analysis, and it currently constitutes a mayor conservation challenge at his site.

Figure 1. Photo of painted wall plasters in Building 114, Çatalhöyük, Turkey

[1] M.Z. Barański, A. García Suárez, C. Kabukcu, *et al.* Continuity and change in architectural traditions at Late Neolithic Çatalhöyük, in I. Hodder and C. Tsoraki (eds.) Communities at Work: The Making of Çatalhöyük. 2022.
[2] E. Murad, American Mineralogist, 12, 1997, 203.

X-ray microtomography: unveiling hidden information from historical and cultural heritage

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X-Ray microtomography (µCT) is a versatile technique [1] and its use is being extended from the industrial field to other fields. Thus, the unique capabilities and non-destructive character of X-Ray µCT are remarkable suited for the study of historical and cultural heritage [2].

Recently, X-Ray µCT have proved to be a matchless resource for the study of ancient glass beads, providing valuable information about the production routes employed more than two thousand years ago [3]. This work aims to take advantage of this technique for the study of singular polychrome glass beads of great complexity found at the necropolis of "Las Ruedas" (archaeological site of "Pintia", Padilla de Duero, Valladolid, Spain). This archaeological site, declared BIC in 1993, has been studied in the last 40 years, being the primary source of knowledge about the Vaccaei, a pre-Roman culture that inhabited the sedimentary plains of the Duero valley (IV-I BC). Among the vastness of the findings recovered in Pintia, a collection of about one thousand pre-Roman glass beads stands out, promoting Pintia as a key location to understand the presence of these imported goods in the Iberian Peninsula. In particular, six of the most sophisticated glass beads from this collection, one of them an extraordinary glass core pendant, were studied by X-ray µCT at the facilities of CENIEH (Burgos, Spain) (Figure 1.a), providing detailed information about the inner distribution of the diverse glass phases present on each one of them (Figure 1.b). From the three-dimensional reconstruction of each phase (Figures 1.c), it was possible to trace back their fabrication procedure, modifying in some cases the previous conceptions about their manufacture.

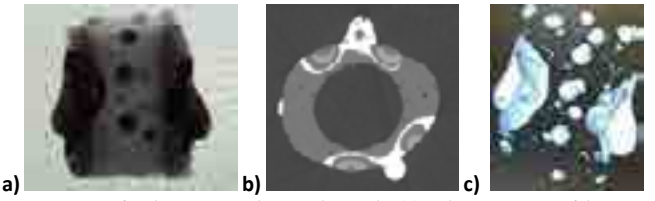

Figure 1. X-Ray µCT of a glass core pendant. Radiography (a) and cross-section of the tomographic reconstruction (b) evidencing the presence of different glass phases). 3D reconstruction of only white and orange phases (c).

References:

[1] Solórzano, E., Pinto, J., Pardo, S., Garcia-Moreno, F., & Rodriguez-Perez, M. A. (2013). Application of a microfocus X-ray imaging apparatus to the study of cellular polymers. Polymer Testing, 32(2), 321–329. https://doi.org/10.1016/j.polymertesting.2012.11.016
[2] Lehmann, E., & Mannes, D. (2021). Neutron and X-ray tomography in cultural heritage studies. In Spectroscopy, Diffraction and Tomography in Art and Heritage Science. Elsevier Inc. https://doi.org/10.1016/b978-0-12-818860-6.00009-x
[3] Zhang, X., Lei, Y., Cheng, Q., & Zhou, G. (2020). Application of Computed Tomography in the analysis of the manufacture of eye beads technique. Microchemical Journal, 156(August 2019). https://doi.org/10.1016/j.microc.2020.104798

19th-Century Medical Saddlebag: An Analysis of the Medicinal Contents

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Dr. Levy H. Warner practiced medicine from 1825-1864 in the Elba, NY area. Of his possessions, a leather saddlebag was incorporated into the Buffalo History Museum's collection in 1913. This bag would have straddled the back of a horse, enabling Dr. Warner to transport medicines to the homes of his patients. Unidentified medicinal substances found within the mid-1800's saddlebag were investigated using radiography and multi-modal imaging techniques including UVA induced visible fluorescence and reflected near infrared. The substances were identified further using micro-transmission Fourier Transform Infrared Spectroscopy, pyrolysis Gas Chromatography Mass Spectrometry, X-Ray Fluorescence Spectroscopy, Raman Spectroscopy and the reference collection of the SUNY Buffalo State Eckert Herbarium. Housed within glass vials and paper packets, the medicinal samples from seventeen different containers were analyzed using one or more of these methods. Medicines with probable identification were found to be of both mineral and botanic origins: mercurous chloride, lead acetate, magnesium carbonate, iron oxides, gum arabic, ground croton seeds, benzoin resin and *Fabaceae senna* and *Arctostaphylos uva-ursi* leaves.

Learning about the medicines that Dr. Warner procured and applied provides insight into the ailments suffered by his patients and the accepted medical theories of the time. This investigation revealed that some of these historical medicines are health hazards and would place the caretakers of this saddlebag at risk. The results of this study led to a safe handling/display solution and illuminated the historic pharmaceutical practices of a Western New York doctor.

Keywords: radiography, UVA, IR, *trans*-FTIR, *py*-GCMS, XRF, Raman, calomel, health hazards, history of medicine

Analysis of Eleonore Koch's artwork and powdered pigments from MAC-USP and Pinacoteca of São Paulo collections

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Eleonore Koch (1926-2018) is a german-born brazilian modernist painter who painted many artworks under the influence of several international and brazilian artists, mainly Alfredo Volpi (1896-1988). The aim of the present work is to study the painting *Sem Título, 1963* by Eleonore Koch, through different analysis methodologies, including spectroscopy and imaging techniques. Energy Dispersive X-Ray Fluorescence (ED-XRF), Raman and Fourier-Transformed Infrared (FTIR) Spectroscopy were the techniques chosen to perform the systematization of the elemental and molecular composition of the materials present in the work. Multi-band technical imaging is applied as a good method to provide more information for this artwork examination. The diverse techniques applied such as Radiography, Ultraviolet, Infrared photography and visible light (also grazing and transmitted) employed have their own specific importance and results. The artist's personal collection of powdered pigments, that were donated to Pinacoteca do Estado de São Paulo, is used as reference material to relate these powdered pigments with those used in the canvas painting aiming to better support the claims made about the material composition of the painting and also support future conservations and restoration process.

All techniques applied in the study use portable instrumentation, which allowed the painting study in situ, in the MAC-USP museum itself. The infrared reflectography analysis, used to visualize underlying paint traces, showed no carbon-based traces present in this artwork. The painting presents a very thin pictorial layer and through transmitted light it was possible to observe and discriminate painting areas by white spaces, instead of by a separation line. The artist's pigments found in the canvas are quite consistent with the powdered pigments results [1]. The characterization of the green powdered pigments in the artist's collection showed the presence of many chromium-based (Chrome Oxide or Viridian Green) and cobalt-based (Cobalt Green, Cobalt Chromite/Titanate Green) pigments. When it came to the identification of the green pigment in the painting, the XRF analysis showed that chromium and calcium are the majority elements, highly suggesting that Eleonore Koch used the Chrome Oxide or Viridian Green in her work. The assumption has been confirmed by Raman analysis, as the green pigments spectra show the characteristic peaks of Chrome Oxide Green. Moreover the Raman spectra also revealed the presence of chalk mixed with the Green Oxide pigment, confirming the XRF suggestion. In this way, the color palette suggestion used by Eleonore Koch in the painting are Titanium and Chalk as white pigments, Cobalt Yellow (sometimes mixed with the white pigments), a mixture of Marsred, Massicot and Litharge as brown pigment, Chrome Oxide Green (mixed with chalk), Phthalocyanine Blue and Bone Black.

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[1] Vitória D. Sousa and M. Rizzutto. Caracterização de pigmentos com Fluorescência de Raios X In *Resumos de Comunicações Livres 72ª Reunião Anual da SBPC* – ISSN: 2176-1221, online event, 2020.

Identification of photographs' constitutive materials as a contribution to their historical study

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The knowledge of materials and production technologies can be related to historical and aesthetic aspects of photographs, contributing to the interdisciplinary study of these objects. Energy Dispersive X-ray Fluorescence (ED-XRF) and Fourier Transformed Infrared (FT-IR) spectroscopies were used to identify the constitutive materials of photographs from the Carlos Eugênio de Moura collection of the Museu Paulista, Universidade de São Paulo, Brazil. The analysis was carried on as a complement tool to methodologies of process identification based on observation and visual inspection with magnification [1]. This work intends to contribute to a better understanding of historical photography materials present in photographs that circulated in Brazil.

The correct identification of photographic and photomechanical processes is essential to interpret the state of conservation of these objects and plan the conditions for their preservation and access, in addition to contributing to the understanding of the historical context of their production. Analisis with ED-XRF [2] has been used to characterize elements related to the image-forming substance, as well as to other layers of its stratigraphy, like the primary or the secondary support. FT-IR spectroscopy, in turn, is applied in the identification of organic compounds, present both in the binder or in the primary support of photographs as well as on major components from coating materials that may have been applied on the surface.

The results of these systematic analyses demonstrated that differences in their constitutive materials can be related to their state of conservation and help to distinct procedures adopted for processing photographs produced by the same photographic studio. ED-XRF analysis showed the presence of elements associated with imaging toning materials [3], such as gold and platinum, that ensured a greater preservation of the same, when compared to untoned photographs from the collection. FTIR analysis allowed the identification of binders and coatings that also interfered with the preservation of the photographs.

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[1] J. M. Reilly. Care and identification of 19th century photographic prints. Rochester: Eastman Kodak Company, 1986.

[2] D. Stulik; A. Kaplan. Application of a handheld XRF spectrometer in research and identification of photographs. In: Shugar, Aaron N, and Jennifer L. Mass. Handheld XRF for Art and Archaeology. Leuven, Belgium: Leuven University Press, 2012.

[3] W. E. Lee. Toning: its invention and role in photography. In: E. Ostroff (Ed.). Pioneers of Photography: their achievements in science and technology. Springfield: The Society for Imaging Science and Technology, 1987.

Study of the influence of micro- & nano-cellulose on the growth and carbonation kinetics of portlandite particles

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The construction sector is one of the main global contributors to green-house gas emissions and waste production [1,2]. In consequence, alternative solutions to reduce the environmental impact of this sector have become fundamental, particularly in the case of built heritage conservation. The latter, in turn, contributing to the preservation of the history and identity of our cities. A critical aspect of restoration and renovation works is the use of compatible and durable mortars. In this regard, lime-based mortars are nowadays preferred by specialists since they generally show a higher compatibility with historic masonries, in terms of physico-chemical, mechanical, and mineralogical aspects, as compared with cement [3,4]. However, their slow setting and hardening (via carbonation), and poor durability prevent their full acceptance and their widespread use. One course of action to solve these issues is to act on the improvement of the quality of the binder through the use of natural-organic additives. According to previous research [5], the usage of additives during the lime slaking phase may have a higher impact than their regular inclusion in the mortar's mix design.
In the present work the analysis of the growth of $Ca(OH)_2$ particles in presence of 10, 100 and 1000 ppm of micro- and nano-cellulose is studied via titration of $CaCl_2$ in an aqueous solution of NaOH. Moreover, the carbonation kinetics of dry powder samples of $Ca(OH)_2$ additivated with micro- and nano-cellulose is followed for 20 days using FTIR spectroscopy on days 0, 1, 5, 12, 15, and 20; X-Ray Diffractometry was used on day 20 to analyze $CaCO_3$ polymorph formation. Results showed that the addition of micro- and nano-cellulose retarded the nucleation of $Ca(OH)_2$ particles and increased the reactivity of calcium hydroxide, leading to a faster carbonation. Moreover, the nano-cellulose addition also had an influence on the polymorph of $CaCO_3$ formed. The control samples showed that, after 20 days of carbonation, metastable vaterite was more prevalent than stable calcite. In contrast, the samples additivated with micro- and nano-cellulose contained a higher amount of calcite. These results show that the use of micro- and nano-cellulose as an additive during the slaking of lime has profound effects both on the reactivity of calcium hydroxide and the phase evolution during carbonation, which in turn will positively affect the physical-mechanical properties of the set binder.

[1] Ortiz O, Castells F, Sonnemann G. Sustainability in the construction industry: A review of recent developments based on LCA. Constr Build Mater. 2009;23:28–39.
[2] Arıoğlu Akan MÖ, Dhavale DG, Sarkis J. Greenhouse gas emissions in the construction industry: An analysis and evaluation of a concrete supply chain. J Clean Prod. 2017;167:1195–1207.
[3] Isebaert A, Van Parys L, Cnudde V. Composition and compatibility requirements of mineral repair mortars for stone – A review. Constr Build Mater. 2014;59:39–50.
[4] Santos AR, do Rosário Veiga M, Matias L, et al. Durability and Compatibility of Lime-Based Mortars: The Effect of Aggregates. Infrastructures 2018, Vol 3, Page 34. 2018;3:34.
[5] Rodriguez-Navarro C, Ruiz-Agudo E, Burgos-Cara A, et al. Crystallization and Colloidal Stabilization of Ca(OH)2 in the Presence of Nopal Juice (Opuntia ficus indica): Implications in Architectural Heritage Conservation. Langmuir [Internet]. 2017 [cited 2021 Dec 12];33:10936–10950. Available from: https://pubs.acs.org/doi/abs/10.1021/acs.langmuir.7b02423.

Study of Foxing on Watercolor Paper

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In Singapore's hot and humid climate, watercolor papers are highly susceptible to foxing. Foxing is the chromatic alteration of paper, which can be classified as biotic (fungal growth) and abiotic (metal oxidation) [1]. In this multi-analytical study, the nature and causes of foxing based on their cellulose matrix, were analyzed. The two groups of samples were from 1990s.

For each type of paper, the old samples with and without foxing, as well as the fresh samples, were characterized using laser confocal scanning microscopy (LCSM), optical microscopy (OM), field emission scanning electron microscopy with energy dispersive X-Ray spectroscopy (FESEM-EDX), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The morphologies of fibers and fungi, the elemental distributions in papers, the structural evolutions of cellulose, and the degrees of paper degradation were studied. According to the findings, biotic foxing is the dominant source. Moreover, this type of foxing is less common in papers made from pure cotton, which are mostly composed of cellulose with high structural integrity, than in papers made from a mixture of wood pulp and cotton. The outcomes provide end-users with guidelines on the watercolor paper selection. It further assists research in the development of protection strategies.

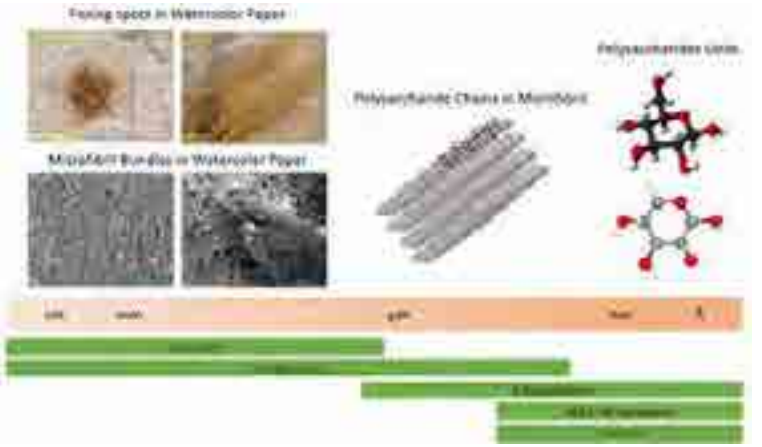

Figure 1. Multi-analytical methods used under various length scales.

Acknowledgements: The authors gratefully acknowledge support from the Nanyang Technological University for funding the project and providing chemical and biological lab access.

[1] Melo, D., et al. (2019). "Stains versus colourants produced by fungi colonising paper cultural heritage: A review." Journal of Cultural Heritage 35: 161-182.

Characterization of secondary products in a late-medieval alabaster relief from the church of Lade (Norway)

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Norway is one of the countries in Europe to preserve two splendid examples of late-medieval English alabaster reliefs. One is conserved at the Church of Værøy in northern Norway, while the other is conserved at the Church of Lade in Trondheim (Fig.1). The polychromy of these objects is so far undocumented and the alabaster reliefs from the church of Lade have been only recently investigated through scientific methodologies.[1]

Specifically, scientific analyses carried out on a green paint cross-section taken from the Lade alabaster reliefs, showed presence of the copper-based green pigment verdigris bound in oil. Interestingly, EDS elemental maps of the paint cross-section showed a quite homogeneous distribution of the element chlorine in the paint-layer. This analytical evidence suggested the possibility of detecting copper chlorides as alteration products in the paint-layer.

However, investigations of the paint-layers through micro-Raman and micro-ATR-FTIR spectroscopy did not detect such compounds, but rather showed evidence of another class of alteration products, namely calcium oxalates.[2]

In order to assess the role played by the chlorine ions in the paint-layer, X-Ray diffraction spectroscopy (XRD) was adopted for a further analysis of the paint cross-section.

Figure 1. One of the "predella" of the alabaster relief depicting the burial of Jesus

[1] C. Spaarschuh, E. Platania, *"History and polychromy of the English alabaster reliefs in the church of Lade, Norway" in "Alabaster as a material for medieval and renaissance sculpture". 8th Annual Ards Conference. Postprints.* Under publication process.
[2] J. T. Kloprogge, Encyclopedia of spectroscopy and spectrometry 2017, 267-281.

Double shot pyrolysis GC/MS characterization of modified Paraloid coatings for the protection of outdoor bronzes

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When treating outdoor bronzes, one of the most used conservation methods is the application of polymer-based coatings: the main aim is protecting the artwork from weathering and reactive compounds present in the atmosphere. This is defined as a passive approach to prevent degradation; it can be converted in an active one by adding corrosion inhibitors, which are able to slow down or prevent further corrosion.[1] The most used inhibitor is benzotriazole. However, it is suspected of being cancerogenic, therefore further studies are currently being performed in order to find safer solutions. The widest employed compound class of corrosion inhibitors are the heterocyclic compounds since the presence of heteroatoms such as nitrogen, sulphur and phosphorous in the organic molecule improves their copper corrosion inhibiting action. [2] In spite of that, a critical limitation of this class is their light sensitivity that can be overcome including light stabilizers in the formulation. [3] Another problem is the loss of inhibitors which leave the coating over time and are released into the environment. In this work, Paraloid ® B44 based coatings in solution with a combination of a corrosion inhibitor and a UV absorber were prepared. The corrosion inhibitors employed were 5-mercapto-1-pheniltetrazole (MPT) and 2-amino-5-ethyl-1,3,4-thiadiazole (AEDTA) while the UV stabilizers were Tinuvin® 312, N-(2-ethoxyphenil)-N'-(2-ethylphenil) and Tinuvin® 5050, a mixture of 2-(2-hydroxyphenyl) benzotriazole and a HALS-Hindered Amine Light Stabilizer (the structure is unknown) in 1-methoxy-2-propanol, a green solvent. The aim of this research was to determine the stability over time of the corrosion inhibitors inside the formulated coatings towards UV exposure. The obtained solutions were applied on microscope slides and aged for 1000 hours inside a UV chamber with irradiance of 0.68 W/m^2 at 340nm at 50°C. They were analysed at time zero and after 1000 hours by means of Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS). Thermogravimetric analysis was employed as well, in order to obtain information concerning the operating temperatures for multi-shot Py-GC/MS and to shed light on thermal stability of the investigated corrosion inhibitors compared to benzotriazole. Py-GC/MS was performed in double-shot mode that is subjecting the sample to a first heat treatment at low temperature (250 °C) and a subsequent pyrolysis step at higher temperature (500°C). The double shot mode favoured a selective study of low molecular weight additives (UV stabilizers and corrosion inhibitors), that are analysed in the first shot, and a better understanding of their stability and persistence in the coating, whose polymer fraction is analysed in the second shot of the analysis. This allowed to achieve a precise chemical characterization of the single compounds before and after the aging process and to investigate the aging effects due to UV exposure.

[1] C. Chemello, L. Brambilla, and E. Joseph, "A Sustainable Approach to the Conservation of Bronze Artworks by Smart Nanostructured Coatings," *Proc. Interim Meet. Icom-Cc Met. Work. Gr.*, 2016, no. September.
[2] M. M. Antonijevic and M. B. Petrovic Mihajlovic, "Copper Corrosion Inhibitors. A Review," *Int. J. Electrochem. Sci.*, vol. 10, no. 2, 2015, pp. 1027–1053.
[3] M. S. De Luna *et al.*, "Long-Lasting Efficacy of Coatings for Bronze Artwork Conservation : The Key Role of Layered Double Hydroxide Nanocarriers in Protecting Corrosion Inhibitors from Photodegradation," 2018, pp. 7380–7384.

A holistic in-situ non-destructive approach for supporting the conservation on archaeological sites. The case of conservation of mosaics from ancient Plotinopoli, Didymoteicho, Greece.

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In the field of conservation, especially on archaeological sites, it is essential a holisitc approach of non-destructive techniques for supporting the conservation projects. A number of combined techniques, such as thermal imaging from 3-5 μm, diffuse reflectance spectroscopy - colorimetry, molecular (μRaman and FTIR in reflectance mode) and elemental spectroscopy (portable XRF) and acoustic-ultrasonic tomography can provide a significant amount of data and can drastically assist the decisions about the conservation progress.

Furthermore, the processing of data simultaneously with the conservation contributes to ensure that the treatment tasks are targeted at areas that show pathology more intense than that detected during macroscopic observation.

In this context, a number of non-destructive techniques were implemented before, during and after the conservation of mosaics on ancient Plotinopolis' archaeological site.

Plotinopoli, a rocky, fortified hill on the southeast side of Didymoteicho in the Regional Unit of Evros in North Greece has been identified since quite a while ago with Plotinopolis, which was founded by the Roman emperor Trajan (98-117 AD) in honor of his wife Plotina.

The excavational research from 1977 up until today have yielded significant findings, demonstrating that the site had been inhabited from the Neolithic period (5th millennium BC) to the 6th century AD. Building complexes (Figure1) dating to Roman times (2nd century AD) with frescoes and mosaic floors (Figure 2) of exceptional interest, decorated with birds, floral motifs, geometric designs and pictorial representations, were revealed.

The conservation of the mosaics of Plotinopolis was carried out in the Summer of 2022 in the context of an action incorporated in the NSRF Operational Program "Eastern Macedonia - Thrace 2014-2020" implemented by the Ephorate of Antiquities of Evros.

During the conservation project, acoustic-utrasonic tomography from μm to m level of resolution and imaging (from 32KHz-250MHz), μRaman spectroscopy with 1064nm laser source, FTIR in reflectance mode and portable XRF spectroscopy and colorimetry, were implemented. The use of acoustic-ultrasonic tomography, revealed the depth of the cracks on

the surface and the structure of the mosaics making the consolidation progress more targeted. In addition, the use of colorimetry, in selected tesserae, confirmed the quality of the conservation progress, after the cleaning. Moreover, through elemental and molecular spectroscopy it was able to identify the construction materials of the tesserae and verify the pathology of the mosaics, while the results of the conservation were documented.

The use of Diagnosis Mutlisystems' and Ormylia's Foundation mobile laboratory equipment for the conservation of the mosaics on Plotinopolis' archaeological site it was essential, and revealed the necessity of a holistic approach of the conservation on the archaeological sites.

Figure 1 Underfloor pipe system

Figure 2 Excavation of 2022

A Technical Study of James McNeill Whistler's Pastels

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Throughout his career, James McNeill Whistler (1834-1903) employed pastel as a drawing medium to make preparatory drawings for his oil paintings, for instance the study *Four women on a terrace by the sea* (1870-1872), and later to create stand-alone works, such as *Salute, Sundown* (1880). His pastels are often small, and the bright coloured crayons have been scumbled across the surface, only covering part of the paper carefully selected by the artist. Even though all areas of Whistler's oeuvre have been subject to extensive art historical analysis [1], only limited technical analysis has been conducted [2]. In particular, his pastels have not been subject to comprehensive technical analysis.

Figure 1 James McNeill Whistler, Salute - Sundown, 1880, The Hunterian, Glasgow

The current 'Whistler pastels project' aims to address this gap by creating a better understanding of the role of pastels in Whistler's artistic practice, identifying and understanding the materials used to make these works, and assessing the light sensitivity of these works. Additionally, Whistler's use of pastel and his materials is being compared with those of his contemporaries, such as Edgar Degas. To achieve this, a selection of pastels from the Hunterian's collection - containing works from the early 1870s until 1902 offering a unique opportunity to study the development of Whistler's pastel technique and potential change in materials across his career - is being examined using a combination of non-invasive techniques: visible and ultraviolet light imaging including raking light and transmitted light, infrared reflectography (IRR), stereomicroscopy, portable X-ray Fluorescence (pXRF), reflectance transformation imaging (RTI), micro-fading testing (MFT), imaging-Fourier Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy. This paper will show the approach taken and the results of the analysis conducted at the Hunterian. A comparative study of Whistler's pastels at Colby College Museum of Art, Maine, USA, will be conducted to test the conclusions from our work on the Hunterian collection.

Figure 2 RTI analysis of a pastel mock-up

[1] M. F. MacDonald, G. Petri, James McNeill Whistler: The paintings, a catalogue raisonné, University of Glasgow, 2020, website at http://whistlerpaintings.gla.ac.uk.; M. F. MacDonald, G. Petri, M. Hausberg, and J. Meacock, *James McNeill Whistler: The Etchings, a catalogue raisonné,* University of Glasgow, 2012, on-line website at http://etchings.arts.gla.ac.uk; M. F. MacDonald, *James McNeill Whistler: Drawings, Pastels, and Watercolours: A Catalogue Raisonné*, Yale University Press, 1995.

[2] L. Glazer, E. Jacobson, B.E. McCarthy, K. Roeder, J.M. Whistler, and Freer Gallery of Art. *Whistler in Watercolor: Lovely Little Games*. Washington, District of Columbia: Freer Gallery of Art, Smithsonian, 2019; H. K. Stratis, M. Tedeschi, N.R. Spink, K.J. Lochnan, N.B. Smale, T.R. Way, & J.M. Whistler (1998). *The lithographs of James McNeill Whistler*. Art Institute of Chicago in association with the Arie and Ida Crown Memorial.; J.H. Townsend (1994). 'Whistler's oil painting materials.' Burlington Magazine, 136(1099), 690-695.; West FitzHugh, E., Leona, M., & Shibayama, N. (2011). Pigments in a paint box belonging to whistler in the library of congress.' Studies in Conservation, 56(2), 115-124.

Multimodal noninvasive approach revealing the ancient Egyptian palette

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A non-invasive multi-modal approach aimed at detailing materials and artistic techniques was used to investigate six painted boxes belonging to the intact grave goods of the Tomb of Kha and Merit (late 18th dynasty, ~1350 BC), found in the theban necropolis in 1906 by the Missione Archeologica Italiana [1-2] and now conserved at the Egyptian Museum in Turin. The six boxes, although attributed to the same period show evident stylistic differences: three being decorated with geometrical elements and the other three showing figurative/symbolic representation of Egyptian tradition. Attributing these differences to objects belonging to distinct dead persons (Merit or Kha) or to the so-called "temporary workshop", a flexible and unstructured workshop organization of the craftsmen, is still unknown and a topic of debate. To give new insights into this subject, a scientific study of materials and techniques was carried out by the portable non invasive techniques of the Italian national hub of the European infrastructure for heritage science (www.ERIHS.it). Non-invasiveness of the approach enabled extensive investigation of the objects acquiring several compositional data depicting a huge variability in the selection of painting materials and techniques. Multimodality of the methodology enabled to overcome intrinsic limitation of single investigation/technique providing for a detailed picture of both inorganic and organic materials, original, retouching and degradation products. Elemental imaging through MAXRF has been integrated with single point molecular spectroscopies (reflection Vis-NIR, Raman & SORS, external reflection mid&near FT-IR) and Macro X-ray diffraction (MA-XRD) by a synergistic and dynamic analytical approach aimed at maximizing the compositional information.
Along with the widespread use of Egyptian blue, found not only on the blue areas, but also for green and dark/black paints, a variety of green (Egyptian green, copper oxalates and carboxylates), black (pyrolusite & manganite, C-based), red (ochre, realgar) and orange (ochre, orpiment) pigments has been assessed. Arsenic-based degradation compounds have also been identified (pararealgar and arsenolite). The non-invasive study was able to inform also about inorganic accessory compounds in mixture with the pigments as well as about the organic binder identified as gum in most of the boxes with some exceptions including fat-based binders, protein and waxes.

[1] E. Schiaparelli, La tomba intatta dell'architetto Kha nella Necropoli di Tebe, Turin: Casa Editrice Giovanni Chiantore 1927.
[2] E. Ferraris, La tomba di Kha e Merit, Modena: Franco Cosimo Panini 2018

Investigation of paint layer cross sections using micro analysis and imaging techniques with focused MeV ions

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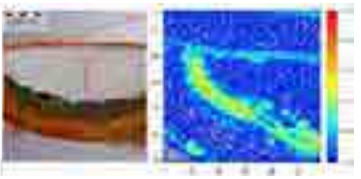
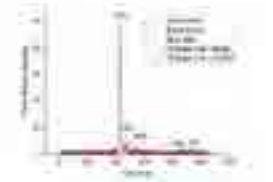
The RBI Tandem Accelerator Facility is equipped with the ion microprobe [1] often used in archaeometry [2,3]. Commonly used techniques are PIXE (Particle Induced X-Ray Emission) and RBS (Rutherford Backscattering Spectrometry). PIXE is usually used with the energy dispersive detectors (EDX). In some cases overlaps of X-ray lines may presend an obstacle for analysis. We have recently developed Wavelength Dispersive PIXE spectrometer (WDX-PIXE), enabling simultaneous EDX and WDX PIXE measurements together with RBS.

Here we demonstrate the capabilities of the upgraded ion microprobe for the analysis of paint layer pigments. Analysis was done on a paint layer cross sections with multiple elements that have very close X-ray energies (like PbM + SKα, BaL + Ti Kα). Paint layers are from a wooden inventory of a 14-century church of saint Mary in small village of Beram, in Istria, Croatia. The wooden inventory was probably repainted in late 19th to beginning of 20th century, which gave as a good pigment/elemental combination for this research. Investigation showed that simultaneous use of WDX and EDX micro-PIXE can add significant contribution to the analysis, resolving issues related to overlapping of Pb (M-lines) with S (K-lines), or Ba (L-lines) with Ti (K-lines) or Ba (L-lines) with Cr (K-lines)



Paint layer cross section (left) with 2D PIXE map (right)

Paint layer cross section with selected PIXE line and point scans



'WDX PIXE spectra of Pb M and S K X-ray region from selected points

[1] M. Jakšić et al., Nucl. Instrum. Meth. B 260(1), 2007, 114-118.
[2] D. Mudronja et al., Journal of Archaeological Science **37** (2010) 1396.
[3] I. Božičević Mihalić et al., Journal of Analytical Atomic Spectrometry **36** (2021) 654-667

Lead(II) Formate: from Historical to Model Paints

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Within the project *Operation Night Watch*, mobile macro-scale x-ray powder diffraction (XRPD) mapping of Rembrandt's *Night Watch* (1642, Rijksmuseum) was carried out on selected areas and complemented with synchrotron radiation micro-scale XRPD (SR-µ-XRPD) on paint samples. The analyses unexpectedly revealed the presence of lead(II) formate, $Pb(HCOO)_2$ (LF), a compound never reported before in historical oil paintings.

To elucidate the origin of LF in *The Night Watch*, model paints were prepared based on historical recipes. These paints were then analyzed with different analytical probes: optical, molecular (µ-FTIR in transmission and ATR-FTIR) and structural (SR-µ-XRPD) [1]. The objectives of the analyses were to follow the early formation, long-term stability and 2D spatial distribution of LF within oil paint films.

Investigation of the model paints demonstrated crystallization of LF within a few hours. After 3 years of natural ageing, LF crystals can still be detected in the model samples and with a heterogeneous distribution inside the paint films [2].

Comparison of the results on model paints to those obtained on historical micro-fragments offered new clues on possible origins of LF in *The Night Watch*, yielded valuable insight into the complex chemistry of historical oil paintings and revealed further implications for their preservation.

Key words: Rembrandt, lead formate, synchrotron/x-ray diffraction, lead drier, oil painting

[1] M. Cotte et al., (2022). The "Historical Materials BAG": A New Facilitated Access to Synchrotron X-ray Diffraction Analyses for Cultural Heritage Materials at the European Synchrotron Radiation Facility. *Molecules*, *27*(6). https://doi.org/10.3390/molecules27061997

[2] V. Gonzalez et al., (2023). Lead(II) Formate in Rembrandt's Night Watch: Detection and Distribution from the Macro- to the Micro-scale. *Angew Chem Int Ed Engl*. https://doi.org/10.1002/anie.202216478

Rediscovering *tempera grassa*: physico-chemical properties of emulsion-based paints

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Painting technique in Europe went through a major shift in the 15th century, thanks to the newly-developed control of the drying of oil. The use of egg as a binder in *tempera* paintings was gradually replaced by oil paint. This transitional period probably saw the occasional use of mixed techniques, in which both types of binders, egg and oil, are present in a painting, sometimes even mixed together in a single layer of paint, a technique called *tempera grassa* [1]. This practice was later rediscovered in the 19th and 20th century by artists influenced by the recipes of Max Doerner for instance [2].

These emulsion-based paints remain barely studied from a physico-chemical point of view. The description of their macroscopic properties (flow, aspect, drying), strongly connected to their colloidal organization, is essential to precise and understand artistic practices.

Without pigment, stable direct emulsions can be formed with egg yolk and oil over a wide range of oil fractions, allowing straightforward tuning of the flow of the binder. The drying mechanism of these mixed systems was explored by NMR relaxometry and FTIR spectroscopy. Features of the drying of both tempera and oil paints were highlighted. When pigments are added, numerous colloidal systems may be formed depending on the relative fractions, characteristic sizes and affinities of each phase [3,4]. Paints based on modern recipes, with pigments such as Sienna or lead white were characterized, revealing a strong influence of the formulation on the rheological and drying properties of the system, which can be linked to its structure at a colloidal scale.

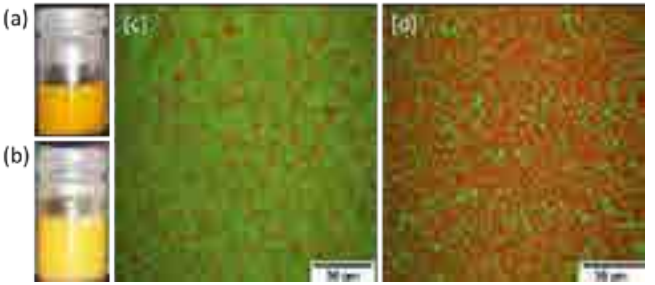

Figure: Oil-in-water emulsions prepared with (a)10wt% and (b) 40wt% linseed oil dispersed in egg yolk. (c) and (d): confocal microscopy images of emulsions (a) and (b) respectively. Oil droplets (in red) are dispersed in a continuous egg yolk phase (in green).

[1] J. Dunkerton, *Modifications to traditional egg tempera techniques in fifteenth-century Italy*, in *Early Italian Paintings: Techniques and Analysis*, Symposium, Maastricht 1996
[2] M. Doerner, *The Materials of the Artist and Their Use in Painting,* trans E. Neuhaus*,* 1934
[3] P. Dieteman, *e-Preservation Science*, 11, 2014, 29
[4] E. Koos, *Current opinion in Colloid & Interface Science*, 19 (6), 2014, 575

Analytical scenario for the investigation of Machu Picchu cultural heritage in Peru

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The biodegradation of the rocks in Machu Picchu facility has been of concern to those responsible for protection of this cultural heritage in the National Archeological Park [1]. Therefore the analytical approaches, enabling to identify the elemental signature as well as the types of biodeteriogens.

Due to the historical heritage it was of great importance to identify, what and how biodeteriogens, like lichens, could affect the structures of stones at the archaeological sites. Worth to highlighted, that the understanding of the on-going processes can support designing the adequate conservation methods, which in the best case could allow the successful removal, cleaning and thus preventing of re-growing of the unwanted organisms. Various techniques were used towards collecting of the complementary information on the objects of interest, moreover the analytical scenario was designed as to fulfils the requirements being a fit-for-purpose [2].

The microscopy and molecular methods (e.g. DNA barcoding) were used for the identification of the morphotype of lichens, funded on carefully selected places. In order to collect the information on the elemental signature, X-ray fluorescence (XRF) as well as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used. The Laser Ablation ICP-MS was used for the evaluation of the distribution of selected elements over the surface as well as sub-surface domains of the sample [3]. The low-molecular weight compounds were identified by HPLC-ICP-MS, this enabling to follows selected metabolites of the lichens.

All results were undergoing the data treatment using Principal Component Analysis (PCA) which allows to discover potential correlation between the state of the investigated samples and the date obtained from various techniques.

[1] Machu Picchu in Context, eds. M. Ziółkowski et al., Springer Nature AG (2022)
[2] Wagner B., Nowak A., Bulska E., Kunicki-Goldfinger J., Schalm O., Janssens K., "Complemenatary analysis of historical glass by SEM/EDS and LAICPMS", *Microchim. Acta*, **162** (3-4), 405-424 (2008)
[3] Wagner B., Bulska E., "On the use of laser ablation inductively coupled plasma mass spectrometry for the investigation of written heritage", *J. of Anal. At. Spectrom.,* **19**, 1325-1329 (2004)

Minor and trace elements in Roman lead from Monte Molião archaeological site (Portugal)

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Evidence of metallurgical practices resulting from Roman presence are widely spread over the Portuguese territory. Among them, the archaeological site of Monte Molião (Lagos), located in southern Portugal at the left bank of the Bensafrim river, testimonies the importance of the Roman archaeology in the Algarve region. Archaeological excavations carried out at the site assembled a wide variety of materials including table wares, coarse wares and amphorae, as well as metallic artefacts and metallurgical remains [1, 2]. A metallurgic workshop for the production of copper-based artefacts assigned to the Roman Republican period (late 2nd – 1st century BC) constitutes an important example of these Roman metallurgical activities in southern Portugal [1, 3]. However, no archaeometallurgical studies have been carried out concerning the lead findings.

The present work focused on the elemental characterisation of 31 lead artefacts consisting of a ponderal, three ingots and 27 metallurgical remains assigned to the late $2^{nd}/1^{st}$ century BC - 2nd century AD. Analytical procedure required ~50 mg of sample using a drill bit (HSS DIN 338, 2 mm ϕ), after removing the corrosion layer. Samples were dissolved with 20 % HNO_3 solution in an ultrasonic bath (35 ºC; 1 h) following suitable dilution. Ni, Cu, As, Ag, Sn, Sb and Bi analysis were carried out in a clean room, class 5, using an ICP-MS with a Quadrupole mass filter, ELAN DRC-e (Axial Field Technology) from PerkinElmer Sciex.

Overall, Cu and Ag are present in all lead samples varying between 54-1143 mg/kg and 44-407 mg/kg, respectively. Sn content is more variable ranging from not detected up to 3407 mg/kg. On the contrary, Sb and Bi contents are more homogeneous, except in a few samples where they can reach higher values up to 1554 mg/kg and 11361 mg/kg, respectively. Ni and As are nearly always present at rather low levels (<17 mg/kg and <41 mg/kg, respectively), but the sample with higher Sb content also shows a higher As content (630 mg/kg). The variable composition points out to different raw materials and metallurgical techniques on lead production, such as the reduction of litharge or the smelting of non-argentiferous galena.

[1] A.M. Arruda, C. Pereira, XELB 10, 2010, 695.
[2] A.M. Arruda, C. Pereira, E. Sousa, D. Varandas, SAGVNTUM 52, 2020, 117.
[3] P. Valério, E. Voráčová, R.J.C. Silva, M.F. Araújo, A.M.M. Soares, A.M. Arruda, C. Pereira, Applied Physics A, 121, 2015, 115.

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Non-destructive identification of wood from XVII Century panel painting using clinical X-ray computed tomography Hounsfield Units scale

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X-ray Computed Tomography (CT) is a well-established non-destructive imaging technique mainly used to investigate structures and materials of complex objects that can be useful for conservation purposes [1]. In this study, a novel methodology for cultural heritage materials identification directly on computed tomography (CT) images is shown. The approach consists of the adoption of the Hounsfield Units (HU) scale, generally used in medical radiology, which corresponds to the linear attenuation coefficient (μ) and is related to the density of the material expressed in Kg/m^3 [2]. Clinical instrumentation and software were employed to analyse different types of wood material that constitute the support of a seventeenth-century panel painting from the collection of the National Academy of San Luca Gallery in Rome. These data were compared with reference samples elaborated with the same methodology and three-dimensional Volume Render Techniques (VRT) CT filters, calibrated on human body tissues, were selected, and classified as the most suitable for non-destructive heritage material identification in order to develop a protocol optimized for art radiology.

[1] M. P. Morigi, F. Casali, M. Bettuzzi, R. Brancaccio, and V. D'Errico, Application of X-Ray Computed Tomography to Cultural Heritage Diagnostics, Applied Physics 2010, 100 (3) 653–661.
[2] S. Longo, C. Corsaro, F. Granata, E. Fazio, Clinical CT densitometry for wooden cultural heritage analysis validated by FTIR and Raman spectroscopies, Radiation Physics and Chemistry 2022, 119, 110376.

CdZnS paint films degradation: effect of pigment's properties and environmental conditions

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$Cd_xZn_{1-x}S$ solid solutions have been employed as pigments since the 1920's, thanks to their bright shades from yellow to orange. Cd/Zn sulphurs present a strong catalytic activity, and variations in morphology, stoichiometry, and micro crystal structure can influence the action that these pigments exercise over the organic binder in which they are dispersed, leading to a rather fast paint degradation [1,2]. In this work, a series of $Cd_xZn_{1-x}S$ nanocrystal solid solutions (NCSSs) (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1) have been synthesized and characterized with the aim of studying their catalytic activity in relation to the degradation of linseed oil. Initially, the influence of temperature, time, and starting reagents was investigated by a Design of Experiment (DoE) model to optimize a synthesis method and obtain compounds with controlled characteristics in terms of properties such as stoichiometry, crystal phase (cubic, hexagonal, amorphous or mixtures), and particle size. Powders have been characterized by means of X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and UV-Vis Reflectance Spectroscopy. The powders have been used to reproduce paint samples that were exposed to artificial ageing, in two different environmental settings: a) simulated sunlight, ~ 30°C, low humidity, and b) dark, 30°C, 65% RH. Principal Component Analysis (PCA) was applied to the spectroscopic and colorimetric data, while the study of the effects of the various properties, especially structure, on the degradation of oil was carried out with a DoE model, using values extrapolated from Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflectance (ATR-FTIR) spectra as a Response.

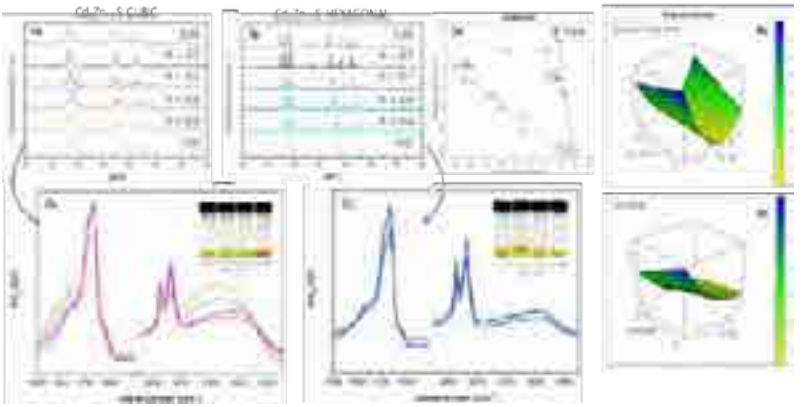

Figure. XRD plots of $Cd_xZn_{1-x}S$ NCSSs with (1a) cubic or (1b) hexagonal main phase, and respective (2a, 2b) FTIR-ATR spectra; (3a) PCA Score plot of FTIR-ATR data highlighting the ageing trends of the two cub/hex groups, and DoE Response Surfaces of samples aged under SOL lamp (4a) and in the dark (4b).

[1] Ghirardello, M. et al., Anal. Chem. 90, 10771–10779 (2018).
[2] Huang, H. B. et al., J. Mater. Chem. A 8, 3882–3891 (2020).

Geophysical survey using gamma ray spectrometry (GRS) on the archaeological site of Cidadela (Galicia, NW Spain)

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Geophysical exploration methods allow the detection of archaeological features before any excavation. In situ Gamma-Ray Spectrometry (GRS) is a technique commonly used for geological exploration and mapping [1], although scarcely used in archaeology [1]. In situ GRS is a non-destructive method that allows direct assessment of the activity concentration of uranium-238 (^{238}U) and thorium-232 (^{232}Th) from daughter radionuclides of their decay chains, as well as potassium-40 (^{40}K), on soils and rock outcrops. The technique allows the estimation of the concentration of these isotopes in the upper 25-30 cm of the topsoil being useful to detect archaeological structures such as buried remains of walls or foundations. It must be assumed that the surveyed archaeological objects must contain a different concentration of radionuclides than the surrounding sediment or soil. This is the case of tocks, bricks and other materials, in contrast to the soil or sediment. Although this tool has been scarcely used in archaeology, we have tested GRS to detect buried walls in the archaeological site of Cidadela (Galicia, NW Spain), being later excavated the surveyed area. The results indicate that this technique is very useful to detect buried structures using the U/Th, Th/K and U/K ratios obtained from measurements [3,4].

[1] L. Rybach, G. Schwarz. Ground gamma radiation maps: Processing of airborne, laboratory, and in situ spectrometry data. First Break, IAEA, 1995, 13, 97–104.
[2] M. Moussa, M. Journal of Applied Geophysics, 48, 2001, 137-142.
[3] A. Ruffell, J.M.., Mckinley, C.D., Lloyd, C., Graham, C. Journal of Environmental and Engineering Geophysics, 11, 2006, 53-61.
[4] J. Sanjurjo-Sánchez, C. Arce Chamorro, C. Alves, J.C. Sánchez-Pardo, R. Blanco-Rotea, L.M. Costa-García. Journal of Cultural Heritage, 34, 2018, 247-254.

Ancient proteins: from identification to characterization. A review and the case of the funeral equipment in a Hellenistic young woman tomb from Battipaglia

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Lessons from the past. Materials used in the past in artworks and crafts have been the subject of numerous investigations. The recent technical advances in analytical chemistry and mass spectrometry (MS) allowed the emergence of new methods adapted to the study of ancient biomolecules constitutive of works and objects of cultural heritage, and specifically proteins are central to several paleoproteomic projects aimed to develop knowledge as well as to provide molecular details useful for conscious restoring interventions.
While, in the early of this century, the big question was whether it was possible to identify proteins in degraded and complex environments such as those of artistic objects and archaeological finds, the biggest challenges we are facing today in relation to proteins in cultural heritage materials, relate to the characterization of their modifications and degradation profile, their networks and interaction with other components (organic and inorganic material). See for instance [1].
On the other side, methodology development is now in the direction of facing the compelling request for less invasive and more sensitive analyses that can meet the needs of the world of cultural heritage. See for instance [2]
The case of the funeral equipment (oil container *bombilyos* T2.2 and two bowls *skyphos* T2.5 and T2.6) from a Hellenistic tomb in Battipaglia will be presented. We identified chemical components compatible with a makeup kit for the young woman corpse. The red, yellow, black, and blue pigments were identified as hematite, a tin-based pigment, amorphous carbon, and indigo, respectively. Sugars, lipids, and proteins of milk were identified, strongly indicating milk as a ligand for the paste production in the bowls. We suggest that the content in T2.6 was produced by mixing the milky orange paste of T2.5 with some volcanic ashes containing basaltic reflecting silica glasses. Ultimately, we suggest that the T2.5 skyphos contains a paste used as a sort of blush for face (based on milky cream and hematite), whereas T2.6 could contain an eyeshadow (with shimmering effect due to basaltic glasses). The *bombilyos* T2.2 was likely used for anointing the corpse, where the multiple pigments (hematite, tin-based yellow, carbon and indigo) would provide multiple body shades.

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[1] G., Ntasi. I., Rodriguez Palomo, G., Marino, F., Dal Piaz, E., Cappellini, L. Birolo, and P., Petrone P. Sci. Rep. 12, 2022, 8401.
[2] G., Ntasi, D.P., Kirby, I., Stanzione, A., Carpentieri, P., Somma, P., Cicatiello, G., Marino, P., Giardina, L., Birolo. J Proteomics 231, 2021, 104039

New understanding of the 16th and 17th century murals in Enebakk Church in Norway: An interdisciplinary and multi-analytical approach

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Enebakk Church in Middle Norway is a Medieval stone church with remains of 16th and 17th century murals. In the Norwegian art tradition, murals on lime-based supports are often defined as "*kalkmalerier*" [1], implying that they are painted with lime as binder. However, the painting techniques of these murals are not well studied. Especially those from the after-reformation period have never been analyzed before.

In this work we analyze for the first time the murals from the church of Enebakk. One of the main research questions posed by this study was the identification of the binding medium, with the aim to assess if the paint technology adopted in such murals points actually towards "*kalkmalerier*" or rather towards alternative paint techniques, such as distemper paint.

Scientific investigations were carried out with portable X-Ray fluorescence (pXRF), optical microscopy (OM), micro-Raman spectroscopy and Gas Chromatography Mass Spectrometry (GC/MS). Micro-Raman spectroscopy allowed the identification of the pigments present in the paint-layer, whereas GC/MS allowed the identification of the binding medium. The results of this study constitute the first analytical evidence of the investigation of Norwegian "kalkmalerier" from 16th an 17th century and provide preliminary information on the paint materials adopted in these mural paintings.

Figure 1. Detail from the 17th century murals in the north nave wall of Enebakk Church.

[1] S. Kaun, NIKU rapport 111, 2021, 1-26.
[2] Sigrid M. Christie og Håkon Christie. 1969. «Enebakk kirke», Norges kirker, Bd. 2 Akershus, s. 116-130 og https://norgeskirker.no/wiki/Enebakk_kirke, sett 21.1.2023

The composition of Roman metals from Moinho do Castelinho and Quinta da Bolacha (Amadora, Portugal)

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Recent archaeological excavations conducted by Museu Municipal de Arqueologia (CM Amadora) at the site of Moinho do Castelinho (Amadora) identified a domestic area occupied from the 1st century BC to the 1st century AD, which was later reused as necropolis by the inhabitants of the nearby Roman *villa* of Quinta da Bolacha (Amadora) between the mid-3rd and the 5th century AD [1].

The work involves the compositional study by micro energy dispersive X-ray fluorescence spectrometry of metal artefacts recovered at Moinho do Castelinho and Quinta da Bolacha to identify the metals and alloys commonly used by those Roman dwellers. The selected set of 9 artefacts comprised small ornaments, tools and implements of different type (*fibula* pin and spring, shroud pin, punches, *spatula* and nail), in addition to fragments of unknown functionality such as a handle with a ring and a small bar. The results identified a diversified metallurgy with the presence of copper (Cu), binary bronzes (Cu-Sn) and leaded bronze alloys (Cu-Sn-Pb) with arsenic, nickel, antimony and iron as minor or trace elements. Moreover, despite the small number of studied items there seems to be some selection of metal/alloy according to the type and/or function of the artefact, as evidenced for instance by a bronze handle with a ring showing a high lead content (5.4 % Pb) to improve the alloy castability.

Finally, the obtained results were compared with other studies on roman artefacts from *Lusitania* [2-4] to identify the characteristic features of the copper-based metallurgy in this Roman province, which enabled an initial assessment of the technological development and level of integration of this region into the Roman World.

[1] G. Encarnação, V. Dias, in Arqueologia em Portugal 2020 – Estado da Questão, Associação dos Arqueólogos Portugueses, Lisboa, 2020, 1361.
[2] M.F. Araújo, T. Pinheiro, P. Valério, A. Barreiros, A. Simionovici, S. Bohic, A. Melo, Journal de Physique IV 2003, 104, 523.
[3] P. Valério, E. Voráčová, R.J.C. Silva, M.F. Araújo, A.M.M. Soares, A.M. Arruda, C. Pereira, Applied Physics A 2015, 121, 115.
[4] F. Lopes, R.J.C. Silva, M.F. Araújo, V.H. Correia, Materials and Manufacturing Processes 2017, 32/7-8, 827.

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Development and optimization of organic residue analysis methods in potsherds from "Cantiere delle Navi Antiche di Pisa"

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This work describes the research carried out within ARCANA (Archaeometry investigations at the Cantiere delle Navi Antiche di Pisa) project funded by the Tuscany region and aimed at the development and optimization of analytical methods mainly based on chromatography and mass spectrometry to study organic residues in archaeological ceramic. The archaeological site of "Cantiere delle Navi Antiche di Pisa" located in Pisa, was the ancient commercial harbor which disclosed a series of ship wreckages and their loads of commercial items in an excellent state of preservation. Among these, ceramic artifacts were the more numerous. Ceramic has been one of the most common materials used for preparation, storage, cooking and transport of numerous products since ancient times. Potsherds can preserve organic substances over time and the organic residue analysis can provide several information on ancient population [1,2]. The characterization and the consequent identification of the uses of the ceramic remains is very complex because of the compositional modification incurred by the original material at molecular level.

For these reasons, within ARCANA project, the use of advanced analytical techniques to extract and analyze the samples will improve the recovery of the analytes of interests maximizing the information achievable from a micro-sample. As preliminary approach, the research was focused on food residue with particular attention to lipids. Experimental design strategies were employed starting from the study of reference samples. The mockups, prepared by spiking virgin ceramic with standard solutions of triacylglicerides and oils, were subjected to artificial aging with the attempt of recreating the reactions occurred in the original material. The optimized methods will be adopted to investigate the archaeological findings collected from the site. The obtained analytical data will be combined with the other characteristics of the samples such as origin and morphology and correlated with the archaeological background.

[1] C. Heron, R.P. Evershed, Archaeol. Method Theory. 5 (1993) 247–284.

[2] L. Blanco-Zubiaguirre, E. Ribechini, I. Degano, J. La Nasa, J.A. Carrero, J. Iñañez, M. Olivares, K. Castro, Microchem. J. 137 (2018) 190–203.

Discovering Lippmann interferential colour photography at the Preus Museum through a non-invasive multianalytical approach

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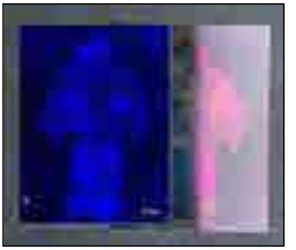
Keywords: Lippmann colour, early colour photography, photography conservation, micro-XRF, micro-Raman spectroscopy.

Lippmann interferential colour photography is one of the most fascinating examples of early colour photography. Unlike most other colour techniques, Lippmann photography does not use dyes or pigments. Today, only a few institutions and collectors worldwide have original examples of these rare images. Little research has been done concerning the conservation, preservation, and materiality of the Lippmann colour process. [1,2] Preus Museum has a large collection of 12 unique Lippmann colour plates made by Richard Neuhauss and Hans Lehmann. The 4-years research project of the conservation department at Preus Museum aims to investigate such photographic objects in terms of their materiality, preservation, and conservation challenges. This work presents the application of a multianalytical non-invasive methodology based on the use of micro-X-Ray Fluorescence imaging and micro-Raman spectroscopy, among other techniques, to characterize the materials used and to elucidate their possible degradation pathways. Interferential colour plates made by Richard Neuhauss and newly produced facsimile plates have been investigated. First results on the identification of used photographic binder materials, evidence for existing deterioration, processing chemicals, as well as the composition of the photographic objects, will be presented.



Richard Gustav Neuhauss (1855-1915). "Bromsilber-Gelatine" Still life. Interferential colour photography. 11.8 cm x 9 cm. 1898. Preus Museum and corresponding sulfur distribution map.

[1] H. Hannouch (Ed.), Gabriel Lippmann's Colour Photography – Science, Media, Museums, Amsterdam University Press, 2022.

[2] J. Gold, Materiality, Identification, and Conservation of Lippmann Plates - in Hanin Hannouch (Ed.) Gabriel Lippmann's Colour Photography: Science, Media, Museums; Amsterdam University Press, Florence 2022, Chapter 9, pp. 213-250.

Design and Study of Cost-effective Method for the Conservation of Watercolor Paper

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Current approaches for the preservation of watercolor artworks in museums, institutions, and private collections are sophisticated and costly. These methods not feasible for the large pool of artists or less not-so-wealthy collectors to adopt. Moreover, any introduction of foreign preservative materials that interact with the art materials may affect the original visual result of artworks. Therefore, watercolor art collection has become less attractive to collectors as compared to oil paintings done on canvases. This work aims to provide an alternative, simple, and cost-effective method for the conservation of watercolor artwork painted on artistic grade watercolor paper. Artist grade watercolor paper is the most common paper consumed by regular watercolorists and hence that is the most appropriate source for this study. This further avoids additional contaminants that complicates the study.

The protective method makes use of commercially available acrylic gesso and coat it onto the new sheet of the watercolor paper. This coated sheet of watercolor paper will be used as backing for framing and display of the original watercolor artwork. No foreign preservative materials are added to the original artwork. The effectiveness of the protection method was assessed by comparing the foxing behaviors of protected and unprotected paper artworks stored for 20 years. These samples were also characterized by optical microscopy (OM), field emission scanning electron microscopy with energy dispersive X-Ray spectroscopy (FESEM-EDX), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Compared with the uncoated samples, seldom foxing spots were observed on any treated sample, and both the oxidation and degradation of cellulose fibers were reduced. Results also showed the acrylic gesso composed of inorganic calcium carbonate ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), rutile (TiO_2), and organic acrylic. The carbonates provided a mildly alkaline environment to neutralize the acid in the papers. The titanium dioxides were biocidal and fungicidal effective due to their photo-catalytic properties. The acrylic bonded and dispersed the inorganic components, and the coating provided an impermeable barrier to prevent the infiltration of moisture and foreign substances. Besides the marked enhancement of the papers' resistance to foxing, the methods presented in this study are very cost-effective, readily available to artists or all collectors while no preservative materials will be added to the original artworks.

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[1] A. Author, B. Author, . Author, Journal of Journals 1(2), year, page.

Implementation of the diagnostic capabilities of the CMOS sensor in the NIR environment, using 1070nm interference filter and a conventional band-pass filters set.

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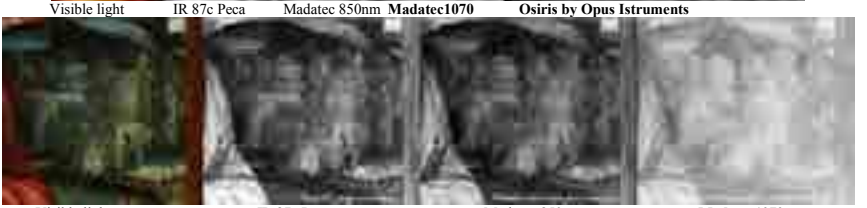
NIR reflectography with silicon sensors (CMOS) is commonly conducted with 780nm band-pass filters that allow the acquisition of clear images and low shutter speeds, while maintaining a low instrumentation cost. In this way, however, acquisition between 1000nm and 1150nm where the silicon sensor is still formally infrared sensitive is in fact always overhelmed by the higher amount of sensor detection capacity in the infrared spectrum portion between 780 and 980nm. With the use of a Madatec 1070nm (+/10nm) interferencial filter coupled to an 850nm band pass filter acquisitions in this portion of the NIR spectrum were carried out, witnessing a outstanding increase in visibility of underdrawings and repentances. A comparative test of the effectiveness of the filter system mounted on the Nikon D800 IRUV and on the Samsung NX3300 Full Spectrum by Madatec was made comparing the results with those obtained through the Osiris InGaAs detector by Opus Instruments. The verification was performed on the "*Deposition*" (oil on panel) by Antonio Semino (1485-1555) in the collection of the Accademia Ligustica of Genoa, highlighting a significant qualitative proximity between the results obtained with the interference system and those with InGaAs detector, compared to the conventional acquisition with bandpass filter. In addition, the 1070nm interference filter system alternated with a series of IR band-pass filters (780, 850, 950nm) was used to increase the recognition capability of blue pigments both in reflectography and in VIL (visible induced luminescence), in particular studying the variation of the spectrum of azurite. This procedure increase the possibilities of first-impact diagnostics by means of low-cost and easily commercially available imaging systems.

Visible light IR 87c Peca Madatec 850nm **Madatec1070** **Osiris by Opus Istruments**



Visible light IR 87c Peca Madatec 850nm **Madatec1070**

Material Characterization of 19/20th century manuscripts from Northern Thailand

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In the northern part of present-day's Thailand, the so-called "Tai Lan Na" manuscript culture has flourished at least from the fifteenth century with its dominating Tham (Pali: Dhamma) Lan Na script used for writing both Buddhist scriptures and secular literature. In the Lan Na region, the common writing supports in use were palm-leaf manuscripts, mulberry-paper leporello manuscripts, and industrial paper manuscripts. It is often noticeable that different inks, and sometimes also pigments, were found in different types of writing support. Even though the study of Tai Lan Na manuscript culture has advanced during the past few decades, the literature available on the identification and characterization of materials used in Thai manuscripts are relatively limited, particularly ones involving the study of inks and material supports [1]–[3]. The aim of our work is to carry out comprehensive analytical investigations on four manuscripts from Northern Thailand and determine a link, if any, between the nature and provenance of the manuscripts, choice of the writing supports and inks used, and the composition of the pigments employed to decorate them.

The four manuscripts at the focus of our study belong to the 19/20th century, and were written in the Tham Lan Na script. Two of these are palm-leaf manuscripts: one of which includes a pair of wooden covers decorated with red and gold pigments. The leaves of the other look a little darker, probably due to age and poor storage which does not include a wooden cover like in the previous case. The other two manuscripts were written on paper. Black ink was used in all the four cases. In the cases of palm-leaf manuscripts, the text was incised on the surface with a stylus, before black ink, traditionally made of soot and resin oil, was applied. After the surface was cleaned, the ink remained stuck in the inscribed traces, letting the texts appear. The two paper manuscripts were instead simply written with inked pens or quills. These four manuscripts provide an interesting case study for determining the relationship between the choice of ink and changes in material support.

We used a combination of non-destructive techniques including digital microscopy (with visible, infrared, and ultraviolet light), X-ray fluorescence spectroscopy (XRF), and Raman spectroscopy, to characterize the inks and pigments present in the manuscripts. The results will help increase our understanding of Thai writing practices.

[1] L. Burgio, R. J. H. Clark, and P. J. Gibbs, 'Pigment identification studiesin situ of Javanese, Thai, Korean, Chinese and Uighur manuscripts by Raman microscopy', *J. Raman Spectrosc.*, vol. 30, no. 3, pp. 181–184, Mar. 1999, doi: 10.1002/(SICI)1097-4555(199903)30:3<181::AID-JRS356>3.0.CO;2-8.

[2] K. Eremin *et al.*, 'Examination of pigments on Thai manuscripts: the first identification of copper citrate', *J. Raman Spectrosc.*, vol. 39, no. 8, pp. 1057–1065, Aug. 2008, doi: 10.1002/jrs.1985.

[3] A. Helman-Ważny, V. Grabowsky, D. Injan, and K. Boulyaphonh, 'The Techniques and Materials Used in Making Lao and Tai Paper Manuscripts', in *Manuscript cultures*, vol. 15, Special Issue: Natural Sciences, Technology and Informatics in Manuscript Analysis, 2020, pp. 133–162.

Portable and non-invasive analytical techniques applied to the investigation of an easel painting by the Brazilian painter Oscar Pereira da Silva

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The interdisciplinary study of artworks from museum and private collections has become increasingly common. Besides comprehending more about an artwork, the partnership between physicist, chemist, historian and conservator contributes to a better knowledge of an artist's materials and techniques and provide the basis for an appropriate conservation and restoration treatments. Due to their fragility, historical and economic values, these objects require caution when handled and often can't have samples removed. In that sense, analyzes should be carried out with non-invasive techniques.

The artwork investigated in this work, "Desembarque de Pedro Álvares Cabral em Porto Seguro 1500", was painted by the Brazilian artist Oscar Pereira da Silva in 1900 and belongs to the Museu Paulista collection of the University of São Paulo. To its characterization it was used visible light (VIS) and ultraviolet-induced visible fluorescence (UVF-Vis) photography, Infrared reflectography (IRR), Energy Dispersive X-ray Fluorescence (ED-XRF) and Raman spectroscopies. To the application of these methodologies, analyses were performed *in situ* with portable equipment.

The images obtained allowed us to verify stages of the artist's creative process that had already been identified in previous research [1]. With the IRR method, it was possible to observe screen squaring of the canvas for the proper reconstruction of the scenery, preparatory sketches with graphite and corrections of these sketches..

ED-XRF and Raman methods determine that the artist's palette is composed by brown pigments based on iron and manganese, green pigments based on chrome, copper and arsenic, yellows on strontium and cadmium, reds on mercury and sulfur and a variety of white pigments based on lead, calcium, barium, and zinc. With the Pigment image database under UV [2] and with the UVF-Vis image, it was possible to identify very outstanding uses of different white pigments on the beach sands and on the rock formation that can be seen in the background of the scenery. Also, the red, purple, and pink tones regions were composed of vermilion pigments mixed with white ones. Moreover, with the ED-XRF method, the preparation base painting was identified, which is composed of lead white pigment, a common technique in the 19th and 20th century. Finally, the results obtained in this research, allow to determine the palette and the creative process of the artist Oscar Pereira da Silva, contributing to a greater knowledge of the materials used as well as his style of work. In addition, these studies help to increase knowledge of Brazilian cultural heritage objects.

Acknowledgements: Thanks to CNPq (National Council for Scientific and Technological Development) for the financial support (302823/2021-2 and 131907/2021-2). Also thanks to Paulista Museum collaborators for allowing the analytical studies of this artworks.

[1] P.H.O.V. Campos, E.A.M. Kajiya, M.A. Rizzutto, A.C. Neiva, H.P.F. Pinto, and P.A.D. Almeida, "X-ray fluorescence and imaging analyses of paintings by the Brazilian artist Oscar Pereira da Silva", Radiation Phys. and Chem., 95, 2014.

[2] A Cosentino, "Identification of pigments by multispectral imaging: A flowchart method", Heritage Science, 2014.

Pearson correlation-based method on hyperspectral images for the study of similarity of pigments and dyes

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The emergence of hyperspectral cameras (NIR-VIS) has made it possible to acquire millions of spectra on samples. This has generated a need to use data processing and visualization methods because manual observation is no longer possible. However, when the data becomes complex with variations in recipes, intensity or mixture within the same dye or pigment, common methods of segmentation no longer work very well (classification according to the intensity and not the shifts visible on the spectra for example). Pearson correlation-based data treatment is developed and discussed in this paper.

We find the use of reflectance spectra to answer questions in many cases. For example, the study of 18th century Aubusson tapestries dyes by crossing hyperspectral imaging and other non-invasive analyses methods is carried out for dye identification purposes [1]. Another illustration is the use of hyperspectral imaging on Iznik ceramics tiles inside the Saint-Maurice Residence (Cairo). Patterns similar to those of the residence exist dotted around Cairo [2]. Their study allows for traceability in the context of reuse. But in both cases, problems arise due to huge amounts of data for variations of the same pigments and dyes [3], and therefore we needed to develop a new method to reduce them.

This study proposes a method to enhance the robustness of hyperspectral images processing and reduce the amount of data by generating tools for a similarity study between studied spectra and a database. The first step is the creation of a database of key spectra used for correlations. Then, some pre-processing are applied to the studied hyperspectral imaging (like spatial filtering for denoising). The main point of our method is that we compute a Pearson correlation coefficient between the studied spectra and each of the key spectra from the database. These new values obtained can be used for common methods of segmentation and visualisation.

Our processes have been applied to different cases. After testing it on simple dyes colour charts with an internal database for validation, we applied it to the tapestry with an external dyes colour chart to obtain a PCA in which the clusters are much sharper than a classic PCA on raw data. It therefore allowed a finer identification of the dyes. As an illustration, we identify the red dyes on a tapestry as madder over cochineal dye. Finally, the method was applied to groups of pigments on the Iznik ceramic tiles and made it possible to drastically reduce the amount of data by keeping only the relevant information. Visualizations help to show similarities or dissimilarities across tile patterns. These cases illustrate the improvement in robustness while reducing the amount of data in relevant criteria for the similarity of dyes or pigments.

[1] De La Codre, 2021, *The European Physical Journal Plus*, https://doi.org/10.1140/epjp/s13360-021-02184-3
[2] Avcıoğlu, N., 2017, *John Wiley & Sons, Inc*, https://doi.org/10.1002/9781119069218.ch43
[3] Sciuto, C., 2022, *Journal of Field Archaeology*, https://doi.org/10.1080/00934690.2022.2135066

WideXcan: An automated high resolution X-ray radiography system for large artwork pieces

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Radiography is one of the most extended techniques to study artwork pieces. Many different types of objects can be examined by this technique. Among others we can cite paintings (both wood painting and woven textiles), wooden or yeast sculptures, metallic objects, musical instruments, ceramics, etc.

Film radiography is still the most used technique in museums across Europe since it provides the best imaging resolution. This is crucial, particularly, in the case of paintings. Digital compositions based on film radiography can be achieved via film scanning. This process is generally carried out at 50 µm nominal resolution which reduces the original resolution of the film. A digital composition of the complete artwork is later generated based on the scanned films images using software for digital imaging processing. This is a manual and tedious process since it is necessary to correct different mismatches and other features. As a summary this process comprises these steps: film preparation in a wall, X-ray exposure, film removal, film processing in liquids, film digitalization and final composition. For a 1200x800mm canvas this process may take, in total, a minimum of 20 working hours until the final X-ray digital composition is ready.

Different solutions based on digital image has been attempted in the different years. Nevertheless, both computed radiography (CR) or digital radiography (DR) offer different inconveniences that will be discussed in our paper. Particularly in case of DR technology the limited resolution of traditional flat panel detectors (200-100 microns pixel size) is one of the main reasons for not using this technology. Last generation of flat panels present a pixel size of 75-50 microns which offers new possibilities for this field.

We have created an automated digital X-ray system with capabilities for inspecting parts up to 3000x3000mm at resolutions of 50microns. The system named WideXcan provides an automated radiographic composition based on individual images of approximately 220x280mm. The tiling process is not supported by stitching algorithm thanks to the high precision of the axis system (linear encoder with 1µm nominal resolution) and precise system calibration. In combination with an adequate X-ray tube it is possible to generate high quality (resolution & contrast) images. Typical scanning times for a 1200x800mm canvas is less than 8 minutes. A final radiographic composition with a perfect pixel matching and impressive quality is achieved. Bottom image shows one of the results obtained.

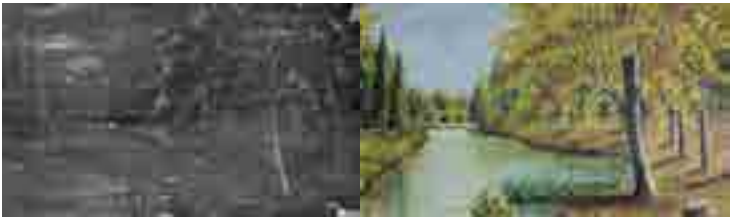

Figure 1 X-Ray radiography obtained with WideXcan and a photography of the drawing compared over the same surface.

Discovering the rock paintings of the Ethiopian plateau: the Goda Daga Barru and Enda Aba Shillemun shelters.

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The aim of this work is the study of prehistoric cave paintings from two shelters located in the northern and southern area of Ethiopia. The artistic expression attributed to Ethiopian prehistory can be dated mainly between the 3rd and 1st millennium BC and are part of the World Heritage Site at high risk of extinction. These are in fact subject to progressive degradation, due to climate change. Most of the paintings are in open environments, under rock shelters, and the significant increase in annual rainfall has led to the acceleration of the degradation process of the rock paintings with a total or partial detachment from the rock supports. Sadly, natural factors are only one of the many threats to which the paintings are subject: vandalism, socio-political reasons, and art illegal trade contribute exponentially to the partial or total destruction of an ever-increasing number of archaeological sites.
To avoid the total loss of this part of human history, however, some innovative tools are nowadays available, such as the use of photogrammetry to obtain a three-dimensional virtual reconstruction of the sites, even with the use of a common digital camera. This is of paramount important, because the painted shelters are often in remote places, difficult to reach and where it is not possible to transport more sophisticated equipment.
During the last experimental campaign, some pigment samples fallen for natural detachment from the walls of the shelters were collected and analyzed with spectroscopic techniques (Raman, Gas chromatography–mass spectrometry, Pyrolysis). The main results are here reported, highlighting mainly the use of hydroxide and oxide iron compounds as pigments, and egg yolk and tree vegetable gum as binders.
The data emerging from this research confirms those of previous studies carried out over the years on samples from other paintings coming from the Horn of Africa and attributable to the same large period.

Use of 3D Scanning to the study of craquelures on Joan Miró's "Pintura"

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Laser scanning is a non-invasive technique whose use in historical heritage is often associated with the digitization of works. In this study, this technique has been employed to study the state of conservation of the work *Pintura* (1925) by Joan Miró. This easel painting is characterized by the presence of cracks that could condition its conservation. The methodology most widely employed to date to study these alteration indicators involved the use of photographic techniques such as visible light photography, raking light, infrared imaging and so on. However, as these are visual techniques, there is an element of subjectivity to them that will depend on the observer and on the circumstances in which the observation is conducted. Laser technologies and three-dimensional (3D) scanning have been used to overcome these limitations. Very few studies have been published on the use of this technique to specifically study cracks in pictorial works [1].

For the study of cracks, a FARO® 7-axis Design ScanArm 2.5C with the PRIZM™ full colour Laser Line Probe 3D scanner was used for data capture. The 3D model made it possible to obtain a high-resolution scan that reveals the exact state of conservation of the work at that time, allowing us to determine not just its state of deterioration with micrometric precision, but also to identify and quantify any three-dimensional variation that the work may be suffering. Measurements can be made, both for pictorial motifs and brushstrokes, their thicknesses or the dimensions of cracks and other degradations.

The use of 3D software (Faro RevEng™ 2020.0) allowed us, among other functions, to rotate the image, to alter the angle of incidence of the light to emphasize any irregularities in the surface, and to change the rendering of the surface relief. Thus, the use of this scanning technique has made it possible to analyse the patterns of the cracks in two and three dimensional views. This study was complemented by an in-depth analysis using traditional imaging techniques and micro-invasive analytical techniques.

The results obtained show that the different crack patterns are linked to the presence of an underneath previous work and the materials that make up that underlying painting. The main advantages of this non-invasive technique include the ability to attain high resolutions that make it possible to analyse the various types of cracks, distinguishing primary from secondary ones, drawing maps of alterations on which it is possible to measure the network of cracks and the surface reliefs in sections. Environmental conditions such as relative humidity, light and temperature in which the work has been exhibited since its creation and at presence are part of the aim of this research as part of the evaluation plan of the sustainable museum condition standards.

[1] W. S. Elkhuizen *et al.*, "Comparison of three 3D scanning techniques for paintings, as applied to Vermeer's 'Girl with a Pearl Earring,'" *Herit. Sci.*, vol. 7, no. 1, pp. 1–22, 2019.

Selecting a tuff from the Italian active quarries for future restoration works at the Archaeological Park of Herculaneum

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The city of Herculaneum, buried by the eruption of Vesuvius in 79 A.D., is entirely built with Neapolitan Yellow Tuff (NYT) [1]. As strong alteration processes are currently undermining the conservation of original NYT masonry, the Archaeological Park of Herculaneum is looking for a compatible tuff, with an enhanced resistance to weathering, to be used for future restorations. Collaborating on this project, the IBeA research group sampled tuff blocks from the main Italian quarries (located in the provinces of Rome, Viterbo and Grosseto) to perform a reliable comparison of their mineralogical and geochemical characteristics, as well as their mechanical and weathering resistance properties.

Focusing on XRD semiquantitative results (see Figure 1), tuffs from Roman quarries mainly differs from the NYT (Erc O) sampled at the Archaeological Park of Herculaneum by the high content of calcite. Similarly, red (R) tuffs from Tufitalia and Etrusco differ by the presence of quartz. Looking at the main phases of the NYT [2], the ratio between zeolite minerals (phillipsite, chabazite and analcime) and sanidine is similar to the tuffs extracted from Ecoblock (yellow, Y) and Etrusco (gray, G) quarries.

After comparing their mineralogical, geochemical and structural properties, accelerated weathering test will be performed to identify the material that better responds to the weathering agents that are currently threatening the preservation of Herculaneum buildings.

%		Rome				Viterbo							Grosseto	Naples
		Ecoblock		Cave Riunite		Tufitalia		Foffi	Etrusco				Pianedirena	Herculaneum (NYT)
		Y	G	Y	G	R	G	R	Br	Y	R	G	Y	O
Zeolite	Offretite	3	3	3	3	0	0	3	3	3	2	2	3	0
	Phillipsite-Na	24	26	12	17	12	22	21	27	52	13	22	41	36
	Analcime	8	7	2	6	5	12	9	12	2	25	8	2	2
	Chabazite	29	25	11	24	28	40	46	35	7	22	33	4	26
TOT zeolite		**64**	**61**	**28**	**50**	**45**	**74**	**79**	**77**	**64**	**62**	**65**	**50**	**64**
Feldspar	Sanidine	29	32	58	36	15	23	21	23	33	13	25	50	23
Carbonate	Calcite	6	7	14	13	0	3	0	0	3	0	10	0	0
Quartz		0	0	0	0	30	0	0	0	0	24	0	0	0

Figure 1: XRD semiquiantitative results. Y-Yellow; G-Gray; R-Red; B-Brown; O-Original.

[1] R. Ling, Journal of Roman Archaeology 5, 1992, 331-337.
[2] A. Colella et al., Construction and Building Materials 136, 2017, 361-373.

Preliminary evaluation of nano-silica-based chromatic reintegrations on frescoes

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In outdoor exposed wall paintings, material loss (in the form of lacuna) is one of the main deterioration forms [1] and, with it, the intervention of conservator-restorers through the application of reintegration treatments is required. Nowadays, the most recommended binder for chromatic reintegration related to outdoor wall paintings is silica-based paint, that is a mixture of pigments with a mineral binder. The most common methods those based on potassium, sodium, or ethyl silicate [2-4]. It is known that potassium and sodium silicates can lead to the formation of salts. While the behaviour of ethyl silicate as a consolidant of stone substrates has been extensively studied, its behaviour when is used for chromatic reintegration has been vaguely studied.

Therefore, a study has been carried out aiming to analyse the physical compatibility between fresco paintings and their nano-silica-based chromatic reintegrations. For this, fresco paint mock-ups were prepared following the old master's recipes, and chromatic reintegrations were carried out with a silica-based nano-consolidant (Nano Estel). The pigment selection criterium was based on colour (blue, green and red pigments) and historic period of use (ancient times, Middle Age and modern times -19th century onwards-).

This compatibility has been studied form the physical point of view by stereomicroscopy, colour spectrophotometry, measurements of gloss, reflectance, roughness, and hydrophobicity and peeling test. Samples were also characterized by means of X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). Moreover, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was used to study microtexture and elemental composition.

REFERECES

[1] EwaGlos, European Ilustrated Glossary of Conservation Terms for Wall Paintings and Architetcural Surfaces (2016). 450 p.

[2] Canosa, G., Alfieri, P. V., & Giudice, C. A. (2013). Pinturas acuosas basadas en dispersiones poliméricas modificadas para la protección de fachadas del patrimonio cultural. Jornada de Técnicas de Reparación y Conservación del Patrimonio, 11.

[3] Juan Baldó, J. M. (2016). Reintegración de pinturas murales exteriores: estudio y valoración de sistemas y materiales. Dissertation, Universitat Politècnica de València.

[4] Pons, M. S., & Bigagli, D. S. (2021). Los silicatos como aglutinantes pictóricos de pinturas murales en los siglos XX y XXI: caracterización de las principales tipologías. *Ge-conservacion*, (20), 318-336.

Assessment of synchrotron X-ray alteration on paintings with time and spatially resolved VIS-NIR Hyperspectral imaging

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When analysing historical materials the main duty of an investigator must be to obtain as much reliable information as possible with minimum risk of alteration. Unfortunately the photons and particles used in probing the material properties can potentially change the materials even in analytical techniques commonly considered to be non-invasive. The importance of assessing the safe limits of irradiation has been recognized with more efforts devoted to such research, especially for X-Ray synchrotron radiations, which are orders of magnitude more intense and brighter than conventional laboratory sources [1,2]**.** Still, little is known regarding the characteristics and reversibility of alterations induced by intense radiation sources (synchrotron radiations, ion-beams and lasers), which is essential for the development of mitigation strategies and necessary for the improvement of the techniques used for the analysis of cultural heritage artifacts. The most common way to assess the occurrence of an alteration/damage is the visual inspection, however, damages can appear instantaneously or over time, can be transient or permanent and not always clearly visible by eye. Another common way to assess damage by synchrotron-based X-ray techniques is to monitor the changes during the measurement using the technique itself, but in some cases this method fails, as the damage induced is detectable only by other complementary techniques [3]. VIS-NIR hyperspectral imaging has been demonstrated to be extremely useful for monitoring a broad variety of damages induced on paintings by lasers commonly exploited for Raman spectroscopy that were not possible to see by eye, nor from Raman spectra itself [4]. Hyperspectral imaging allows the monitoring of the extent in space and the reversibility in time of the alteration. In the case of Raman spectroscopy, fast reversible changes (in the order of seconds) were detected prior to the occurrence of permanent damage when increasing the exposure energy dose [5,6]. This reversible change appears to be extremely useful as a marker for the prediction of damage and can be used to define safety thresholds.

Based on this experience, we propose the use of VIS-NIR Hyperspectral imaging for the monitoring over time and space of possible damages induced by Synchrotron X-Rays on paintings. The potentialities of the method will be shown and the preliminary results of long-term monitoring (up to 11 days) on painting mock-ups after synchrotron-based X-ray irradiation will be discussed.

[1] L. Bertrand et al., TrAC Trends in Analytical Chemistry, 2015, Volume 66, 128-145.
[2] M. Cotte et al., Molecules, 2022, 27, 1997.
[3] C. Gervais et al., Applied Physics A, 2015, volume 121, 949–955.
[4] A. Suzuki et al., SPIE, Optics for Arts, Architecture, and Archaeology (O3A) VIII, June 2021.
[5] Y. Li et al., European Physical Journal Plus, 2022, 137, 1102
[6] A. Suzuki et al., 13th International Conference on Lasers in the Conservation of Artworks (LACONA), September 2022.

Quantitative analysis of cultural heritage and safeguards objects by in-house developed confocal macro XRF spectrometer

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A confocal macro XRF spectrometer was designed and built for analysis of elementary composition of near surface layers on solid objects having non-regular spatial shape. Mechanical frame of a commercial 3D printer was applied as a carrier structure moving in vertical directions (z) for the CM-XRF spectrometer consisted of which the main elements an SD detector and a low-power (4W) air-cooled X-ray tube were [1]. The investigated object can be fixed on a horizontal linear scanning stage within a total length of 20 cm for both 2D perpendicular directions (x,y). The spatial precision of the positioning step of each mechanical parts (x-y-z) of the 3D frame is 5 µm the step-size is 100 µm. The diameter of the irradiated focal spot of the confocal measuring geometry can be set (d > 480 µm) using a variable collimator system. Positioning the analysed spot that is the cross of axis of the irradiation beam and the axis of detector collimator on the sample surface is applied a mini digital microscope and two laser beam.

For determination of the quantitative compositions of the samples an FPM model was developed [2] for analysis of solid and liquid samples. To illustrate the analytical performance of this in-house developed FPM model and CM-XRF spectrometer analytical examples of quantification of archaeological and safeguard samples will be presented.

[1] I. Szaloki, A. Gerenyi, G. Radocz, Confocal macro X-ray fluorescence spectrometer on commercial 3D printer, *X-Ray Spectrom*., 46, 497–506, 2017, 10.1002/xrs.2781

[2] I. Szalóki, T. Pintér, I. Szalóki, jnr., G. Radócz, A. Gerényi, A novel confocal XRF-Raman spectrometer and FPM model for analysis of solid objects and liquid substances, J. Anal. At. Spectrom., 2019, 34, 1652, 10.1039/C9JA00044E

Chromatographic analysis of natural dyes used in Islamic paper manufacture

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A rich variety of manuscripts was produced in the Islamic cultural realm, extending from the eastern borders of China to Islamic Spain from the 8th century AD to the 17th century AD [1]. These papers were dyed with various natural dyes, which are difficult to detect in modern times due to low concentration and degradation.

Following the historical recipes (10th to 17th century) to dye Islamic paper in yellow and red using natural dyes, we produced a set of reference papers using henna, shellac, madder, weld, turmeric, saffron, and safflower. Based on the recorded protocols to extract and analyse dyes in textiles [2], these reference papers were used to develop an analytical method based on high-performance liquid chromatography coupled with diode array detection (HPLC-DAD). We then applied the method to investigate 40 historical paper samples, produced from the 15th to the 19th century in the Islamic world and selected from the collections of the Heritage Science Laboratory at the University of Ljubljana (Slovenia) and Ain Shams University (Egypt). The samples were selected based on a visual assessment by an expert paper historian and conservator, who estimated that the natural dyes mentioned above may have been used to achieve the colour of these samples.

The HPLC-DAD analysis is based on the identification of marker compounds for each dyestuff. Five of the seven dyes considered here were identified in the historical paper samples. Interestingly, two or more different dyes have been identified in many of the studied samples. The use of different dyes together is reported in historical recipes, and our results reflect this practice, which was common across the geographical contexts investigated in this study. Shellac lac in particular seems to have been frequently used together with other dyestuffs in the collections studied.

Future studies will focus on the patterns of dyestuff use and their connections to the cultural and historical context in which the manuscripts were produced.

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[1] J. M. Bloom. *Paper Before Print; the History and Impact of Paper in the Islamic World*. London: Yale University Press, 2001.
[2] J.J. Łucejko, M. Vedeler, I. Degano, *Textile Dyes from Gokstad Viking Ship's Grave*. Heritage (4), 2021, 2278-2286.

Prospection of bioactive compounds produced by bacterial isolates from pristine environments

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Pristine environments can be defined as places with limited or no connections to anthropogenic activities [1], for example, karstic and marine caves, important landmarks of Natural and Cultural Heritage. Usually, these environments are exposed to extreme factors such as temperature, salinity, osmolarity, UV radiation, pressure, or pH, with values close to the limit of life. In these extreme environments, living organisms biosynthesize secondary metabolites with potential bioactivities giving them unique survival skills to grow in hostile conditions [2]. This study aims to search for new bioactive compounds produced by Actinobacteria, Firmicutes, Bacteroidetes and Proteobacteria stains isolated from pristine environments such as Selvagens Islands (Madeira, Portugal) and the Paleolithic Escoural Cave (Montemor-o-Novo, Portugal) [3]. The antioxidant activity and antimicrobial action spectra against *Gram*-negative and *Gram*-positive bacteria were evaluated. Additionally, supernatants of bacterial strains cultures were screened for antitumor potential using a breast cancer epithelial cell line MDA-MB-231. The results obtained suggest that selected bacteria isolates produce biologically active compounds with potential application in biotechnology and biomedicine. Bioprospection and discovery of new compounds represent an opportunity for the study and valorization of these Natural and Cultural Heritage habitats, allowing new products obtained by fast and low-cost biotechnological processes to be implemented as novel green-safe and sustainable solutions.

[1] S. Atashgahi, MM. Häggblom, H. Smidt. Environmental Microbiology 20(3), 2018, 934–48. https://doi.org/10.1111/1462-2920.14016.
[2] D. Giordano, Marine drugs of MDPI 19(11), 2020; 1–7. https://doi.org/10.3390/md19110642.
[3] A. T. Caldeira, N. Schiavon,G. Mauran,C Salvador,T. Rosado,J. Mirão, A. Candeias. Coatings of MDPI 11(2),2021;1–17. https://doi.org/10.3390/coatings11020209.

Acknowledgements: The authors acknowledge to FCT – Foundation for Science and Technology, I.P., within the scope of the projects UIDB/04449/2020, MICROCENO (PTDC/CTA-AMB/0608/2020), ART3*mis* (2022.07303.PTDC) and C. Salvador (DL 57/2016/CP1372/CT0019) to individual support.

From artistic archive to climate archive: can an artwork surface be a source of information on climatic changes?

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This research starts from a question: can surfaces be interpreted as archives of information, especially when subjected to different spatio-temporal processes, i.e., after interaction with environmental or anthropic factors?

To investigate the issue, we employed the optical scanner microprofilometer to acquire in a contactless way different surfaces of artistic interest subjected to climatic alterations, performing a multiscale analysis [1]. In fact, a surface is a complex structure that includes several length scales (i.e., spatial wavelengths) of superimposed stochastic signals (roughness), which are then reproduced in the digitized surface according to the properties of the instrument, with the shortest spatial structure set by the effective sampling resolution and the longest one by the sampling length.

Here, the focus is on a small-scale surface (order of centimeter sampled at the micrometer scale) analyzed in a multiscale approach using the surface metrology workflow, namely, the surface topography is analyzed by quantitative descriptors from ISO standard (amplitude, spatial, and hybrid parameters), beyond the simple, holistic inspection of surface morphology. The surface signals are divided in components of different bandwidth along the scan length, i.e., the texture is separated from the form and then the roughness (irregularities at smaller scales) and the waviness (more widely spaced variations) are studied. The inspection of the variation of the texture features with the scale is performed with two different kinds of multiscale analysis: scales inspection and signals separation. The first part aims to deeply study the variation of the roughness in subregions, evaluating the roughness behavior with the variation of the evaluation length. In the second part the separation of roughness is performed on the whole sample by Gaussian filtering with different cutoff values: this procedure allows to study the roughness parameters in the scale-limited surface components.

The key aspect is to understand the scales of interest of the various processes, i.e., the scale-limited features that are most informative of the surface response, by studying the length scale characterizing the in-band roughness signals. Statistical descriptors, such as power spectrum density function, are also used for the analysis.

[1] Daffara C., Mazzocato S., Marchioro G. Multiscale roughness analysis by microprofilometry based on conoscopic holography: a new tool for treatment monitoring in highly reflective metal artworks. Eur. Phys. J. Plus 137 (4), 2022

CHARACTERIZATION OF MATERIALS CONSTITUTING METAL ACID INKS BY GAS-MASS CHROMATOGRAPHY AND SCANNING ELECTRON MICROSCOPY

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The Institute of Cultural Heritage of Spain has been the beneficiary of a grant for the hiring of Technical Support Personnel from the State Research Agency (AEI) for the project: "Study of constitutive materials in metalloacid inks". The project has the participation of the General Archive of Simancas (AGS), the National Library of Spain (BNE) and the support of the State Program for the Promotion of Talent and its Employability in I+D+i of the Ministry of Science and Innovation.

Metal acid inks are the most common medium for writing in western culture from the middle ages to the 20th century. They are aqueous solutions formed from metallic salts that, together with gallic acid form a dark-colored metallic organic complex which is bound with some natural gum (generally gum arabic). In its composition there are metallic elements that interact with the scriptural support, causing alterations and degradation of it [1]. Ink corrosion is a very common alteration in the world of archival landscape. Nowadays there is no a clear and defined analytical methodology that encompasses organoleptic tests and analytical procedures for the early detection of alterations in acid metal inks in their deterioration process.

The main objective of this research is the development of an effective methodology and a protocol to provide an early detection and action, avoiding the advance in the deterioration of books and documents produced by the existence of metal acid inks. It has been structured in two phases, the first delves into the study of the manufacture of inks, the reproduction of recipes, as well as the optimization of qualitative tests [2] and sampling. In the second phase, compositional analysis by gas-mass chromatography (CG-MS) and scanning electron microscopy (SEM-EDX) will be carried out. All the assays were realized both with models done in phase one and real samples (manuscripts).

This poster presents the results obtained in the second phase of this project. The literature indicates that ellagic acid from tannins increases during aging, and may contribute to ink color [2]. The analytical techniques such as CG-MS are very useful for the determination of this compound. In addition, the formation of other sugars produced during the ink preparation process can be monitored and characterize these calligraphic inks. The SEM-EDX technique provides results about the metallic elements [4] they contain and that validate the qualitative tests carried out in the first phase.

[1] Ruggiero, D. Gli inchiostri ferrogallici negli archive e nelle biblioteche, - Laboratorio di fisica dell' Istituto per il Restauro e la Conservazione del Patrimonio Archivistico e Librario 2004.

[2] Neevel, J., Reissland, B. Bathophenanthroline Indicator Paper: Development of a New Test for Iron Ions. PapierRestaurierung. 2005, Vol. 6, no. 1, pp. 28–36

[3] Kolar J, Strlič, M. Iron gall inks on manufacture, characterisation, degradation, and stabilisation. National and University Library, 2006, pp 173.

[4] I. Espadaler, M.C. Sistach, M. Cortina, E. Eljarrat, R. Alcaraz, J. Cabanas, J. Rivera. Organic and inorganic components of manuscript inks. Anales De Quimica,Springer-Verlag Iberica, c1996-c1997, Barcelona, Spain, 1995, pp. 359–364.

Chemical characterisation of a peculiar necklace of the Bronzetti Sardi tomb (Early Iron Age Etruria)

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The, so-called, Sardinian Bronzes tomb (it. *Tomba dei Bronzetti Sardi*) was a wealthy burial of a woman and a child that has been unearthed more than 60 years ago near the archaeological site of Vulci (Lazio, Italy). The peculiarity of the tomb is not only in its configuration but also in the goods that were found inside. Apart from three Nuragic bronze figurines that gave the tomb its name, several dozens of beads of various types and, apparently, materials were found [1]. Given the importance of the burial and typological parallels of several types of glass beads in the Final Bronze Age (FBA), the necklace was included in the INGOT-EL PhD research project (INvestigation of Glass Origin and Technology in Etruscan Lands) and analysed using non-invasive methods and portable equipment (Optical Microscope (OM), portable X-Ray Fluorescence spectrometer (p-XRF) and Fibre Optics Reflection Spectroscopy setup (FORS)). One glass bead from this necklace was analysed in the laboratory using Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry (SEM-EDS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

The first chemical examination of beads of the Final Bronze Age typology from an Early Iron Age context has proven their correspondence to the Low Magnesium High Potassium or LMHK glass finds. Glasses of similar composition were, probably, produced in Frattesina or surroundings (North Italy) during FBA [2]. In addition, the hypothesis for the material employed in non-glassy beads on the necklace emerged from the compositional analyses.

[1] Arancio ML, Moretti Sgubini AM, Pellegrini E. Corredi funerari femminili di rango a Vulci nella prima età del Ferro: il caso della tomba dei bronzetti sardi. Preistoria e Protostoria in Etruria. L'alba dell'Etruria. Fenomeni di continuità e trasformazione nei secoli XII-VIII aC Ricerche e scavi. Atti del IX Incontro di studi (Valentano-Pitigliano, 12-14 settembre 2008), Negroni Catacchio, N.[ed.], Milano: Centro di Studi di Preistoria e Archeologia. 2010:169-213.
[2] Koch LC. Glas und glasartiges Material in Italien zur Bronze-und Früheisenzeit–Forschungsstand und Perspektiven. In: Klimscha F. Karlsen HJ. Hansen S. Renn L. Eds. Vom künstlichen Stein zum durchsichtigen Massenprodukt. Innovationen in der Glastechnik und ihre sozialen Folgen zwischen Bronzezeit. Berliner Studien zur Antiken Welt Berlin 2021: 67–103.

Analyzing epidermal ridge impressions and tool marks on Rijksmuseum terracotta sculptures

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In archaeology, the study of fingerprints found on pottery from ancient cultures is a minor but active research topic which aims at a more nuanced understanding of the organization of past societies [1]. Fingerprints, or other epidermal ridge impressions, as well as tool traces, are often found on the visible surface of terracotta sculptures held in private or museum collections. However, there is presently no standardized work-flow for acquiring, storing, and processing images of these marks.

We designed a forensic-like, reproducible, and standardized protocol to acquire epidermal ridge impressions and tool marks found on terracotta sculptures. We separate the inspection, detection, and labeling of potentially interesting visible marks in two stages. The first phase aims at recording and tagging the location of any visible marks on the sculpture by using a smartphone with high-resolution cameras (both primary and macro camera settings are used), professional torch, tripod, and metric bar. Regarding epidermal ridge impressions, these can be labeled as fingerprints only after careful evaluation of the patterns found on the image; such an assessment is heavily dependent on the image resolution and lighting conditions at the capture time. During the second stage of our evaluation, we proceed with an in-depth inspection of the most interesting marks by using camera-equipped stereo microscopes (Ceramics, Glass and Stone Conservation department at the Rijksmuseum), (three-dimensional) 3D Micro Computed Tomography (Centrum Wiskunde & Informatica), 3D photogrammetry from different devices and Reflectance Transformation Imaging (RTI) (fotostudio at the CollectieCentrum Nederland – Rijksmuseum). We will discuss the advantages and challenges of each imaging instrument and acquisition configuration implemented. Because epidermal ridge impressions and tool marks are frequently detected on the surface of terracotta sculptures, our methods provide a novel pipeline for conservators, restorers, and scientists to record marks in a standardized and consistent manner, potentially easing data and knowledge exchange on the topic. Given the advances achieved using forensic methods on fingerprint-based analysis in archaeology, our methodology provides motivation to investigate completely unexplored research areas in fine arts.

[1] D. Sero, I. Garachon, E. Hermens, R. V. Liere, and K. J. Batenburg, “The Study of Three-Dimensional Fingerprint Recognition in Cultural Heritage: Trends and Challenges,” *J. Comput. Cult. Herit.*, vol. 14, no. 4, 2021, pp. 1–20

Comparative study of objects from the Hungarian Conquest period of Hajdú-Bihar County, Hungary

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In recent years, the evaluation of finds of the Hungarian Conquest period in the Carpathian Basin has increasingly involved the use of material composition analysis techniques. As a result, composition data for approximately 300 items is now available. However, these investigations were primarily aimed at examining a single grave, cemetery, or site.

The possibility of summarizing the available results in a database and supplementing them with additional measurements arose during the preparation of a summary volume presenting the finds of the Hungarian Conquest period in Hajdú-Bihar County. In order to have representative results from the entire area included in the volume, we selected various sorts of artifacts from a group of interests covering numerous micro-regions and different types of sites. Images of the samples were recorded by a Keyence VHX-6000 digital 3D microscope to investigate the surface, and then elemental composition analysis was carried out using a Bruker M4 TORNADO micro-XRF instrument.

The examined objects can be divided into two main groups: silver and copper alloys (Fig.1). The relics show heterogeneity within the same grave, they cannot be classified by chronology, however, the elemental composition correlates with the function of the object.

Figure 1a: gold platted silver object with the measured area; 1b: bronze object with the measured area. Both measurement areas are marked with red rectangles, insets depict higher magnification images of the measured zones, 10x and 100x respectively.

In the present work, we aim to draw conclusions regarding the general composition of the materials and to define material groups, subject groups, and regional groups based on the previously determined material composition of the finds.

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Shedding light on the 19th c. waterproofing technology of historical carriages, a multi-analytical approach

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Despite carriages and sledges occupying a central role in society for several hundred years and being present nowadays in a great number of museum collections all over the world, hippomobile heritage remains a heavily understudied field in Conservation Science. Throughout history, horse-drawn vehicles represented not only functional objects and a popular mean of transport, but were also a fashion statement and a symbol of social status. As such, the materials, technology and overall expertise employed in the production of these objects, faithfully reflect technological, scientific and societal developments. Due to a lack of research, this knowledge potential remains mostly untapped.

The Belcaire (BELgian CArriage Interior REsearch) project, a collaboration between the Antwerp Cultural Heritage Science (ARCHES) group and the Royal Museum of Art and History (KMKG) of Brussels, aims at shedding light for the first time on this unique type of cultural heritage. In particular, research of historical sources and state-of-the-art analytical techniques are combined to study the unique collection of historical carriages and sledges of KMKG. This include outstanding pieces such as the "Rapide" (1830-1840), travel carriage of Belgian king Leopold I, a one-of-a-kind vehicle combining luxurious materials and state-of-the-art technology (Figure 1). The analyses allowed to identify a broad number of materials in complex combination, including lacquer, waterproofed leather, composite materials such as oilcloth and linoleum, textiles, early synthetic materials, exotic wood, ivory and many more.

Figure 1. The "Rapide", travel carriage of king Leopold I (1830-1840): a) the carriage; b), c) cross-section of microsamples of lacquered wood and waterproofed leather, both showing a complex layered structure.

In this work, we present the first results obtained from the multi-analytical investigation (handheld XRF and FTIR-ATR spectroscopies, MA-XRF, SEM-EDX, µRaman) of a selection of top pieces of the collection, including the "Rapide". The focus is put on the characterization of paint, lacquer and other waterproof finishes used to protect the exterior of the carriages against outdoor environmental conditions (Figure 1 b,c). These results enable a first discussion on how provenance, time period, manufacturer and social status are reflected in the materials and techniques employed, while supplying first insights into the evolution of historical waterproofing technology.

Natural materials for cleaning metallic leachates (based on iron and copper) on marble surfaces as alternative of traditional gels.

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The cleaning of leachates appeared in the marbles close to metallic sculptures is an important goal to be solved in the field of cultural heritage conservation. The most common sculptures which generates this kind of problems are made with bronze and iron, thus, the leachates are based on copper (green color) and iron (reddish color). The use of aggressive reactants to clean them could damage the materials and this point must be addressed carefully. Up to now, Agar gels have been among the best options to put the reactant in contact with the material, controlling its application. However, the appearance of fungi can be promoted since Agar gels are a good substrate for them. Moreover, the most used reactant in this works is EDTA, but its application is becoming more and more controversial due to its environmental impact and the damage that could generate in the marble. In this sense, new natural alternatives have appeared, such as Kudzu starch, which has antimicrobiological activity, improving the classical applications. Analogously, Konjac gel also shows good qualities as alternative.

To evaluate the usefulness of these new materials, as alternative of Agar gels different test were carried out. To increase the cleaning potential to the gels, the addition of different chelants has been studied in order to see which combination of gelling agent plus chelator achieves greater cleaning of the metallic leached material without damaging the marble.

First of all, the new materials were studied to obtain gels similar to Agar, selecting the best protocols for their preparation, regarding the concentration of gel, temperature required to obtain the gels, and the possibility of mix with other reactants. Then, gels were applied with different chelants (gluconic acid, sodium oxalate, EDTA and sodium citrate), times of applications (Periods of 8 hours or 2 days, which is the time necessary for the gels to dry), and concentrations in artificially generated patinas of iron and cooper in marble mock-ups. To evaluate the cleaning efficiency, different non-destructive image analytical techniques were used, such as colorimetry and Raman and EDXRF spectroscopies. Moreover, ICP-MS was also used for the quantitative study of the elements extracted by the gels.

Taking all of these into account, the cleaning potential of citrate has been highlighted with any of the three gelling agents. EDTA achieved similar cleaning values but a quick look at the amount of calcium extracted in the gels indicated the great damage that the use of this chelant does on marble surfaces. Thus, citrate seems to be a good alternative for these kind of cleaning works without the problems that EDTA presents.

Finally, regarding the gelling agents, Konjac achieved very good cleaning results even without chelates, being a real alternative to Agar. It is worth noting the ease of preparation that Konjac presents. This gel does not require temperature for its preparation and, if desired, can be applied to a specific surface within seconds of preparation (while still maintaining a viscous consistency) which aids in cleaning complex surfaces where a rigid agar gel would not arrive.

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IAEA fosters the development and applications of accelerator-based analytical techniques for Heritage Science.

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The IAEA Physics Section is pursuing efforts on utilizing accelerator-based nuclear analytical techniques to support fundamental and applied research, as well as provide education and training world-wide.

Characterization of cultural and natural heritage for their conservation is among the key priority areas of accelerator applications. Relevant accelerator-based analytical techniques include ion beam analysis, accelerator mass spectrometry and synchrotron-based techniques.

There are various tools and mechanisms to foster accelerator science and technology for characterization, dating, authentication, and provenance of cultural and natural heritage such as knowledge transfer and knowledge sharing with the scientific community, heritage science stakeholders and the public. Optimization of the analytical conditions and developing mitigation strategies towards safe analysis have outmost importance in our activities [1]. Through the IAEA Technical Cooperation projects, we are also assisting developing Member States in creating new installations and upgrading/advancing accelerator-based and nuclear analytical techniques to strengthen their role for heritage science.

A specific workspace on the IAEA Accelerator Knowledge Portal designed to serve the scientific and industrial community highlights the use of accelerator-based techniques and the dedication to pursuing safe analysis of heritage objects and materials [2].

The presentation will give an insight of the IAEA activities on the characterization and conservation of cultural heritage with special emphasis on how to enhance the involvement and collaborations with the IAEA.

[1] L. Bertrand et al., Mitigation strategies for radiation damage in the analysis of ancient materials, Trends in Analytical Chemistry 66 (2015) 128-145.

[2] IAEA workspace Accelerators for Heritage on the IAEA Accelerator Knowledge Portal: https://nucleus.iaea.org/sites/accelerators/Pages/Accelerators4Heritage.aspx.

Palette to palette - an integrated study of spectroscopic analysis and UMAP on Wu Guanzhong's paint palette and his painting

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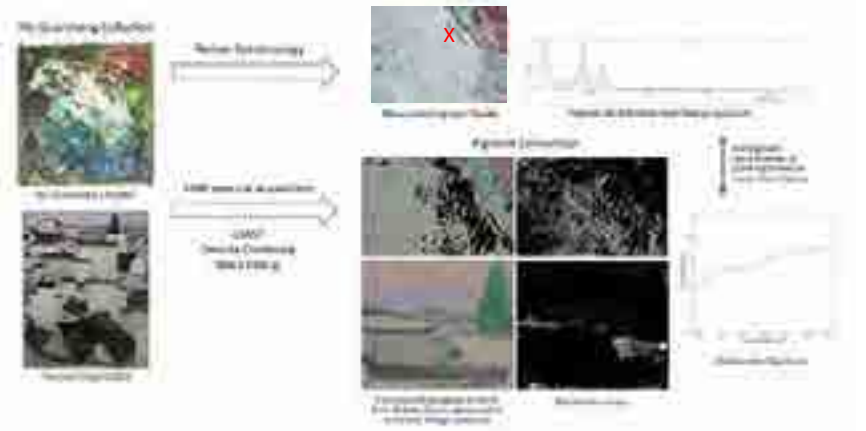
The twentieth century Chinese master painter Wu Guanzhong (1919-2010) was considered one of the finding fathers of Chinese modern art. Through the generous donations of the artist and his family, the Hong Kong Museum of Art is home to over 450 items of the artist, from paintings, personal memorabilia to manuscripts, a retrospective collection that showcases the historic and artistic journey of Wu spanning over half a century. A paint palette of the artist was studied with the non-invasive techniques hyperspectral (HSI) and macro-X-ray fluorescence (MA-XRF), though the period of the palette is unknown, technical investigation reveals the pigments are typical of that from the late twentieth century. Micro-samples were collected from selected pigments on the palette which were analyzed with micro-Raman spectroscopy. The HSI data of the palette was then compared with a non-invasive study on Wu's oil painting 'Xidi Village' (2001), the data sets were processed within one Uniform Manifold Approximation and Projection (UMAP) model, in an attempt to establish connection and identify the pigment on the painting from the learnt result from the artist's palette. This study has shown the potential by means of an integrated technological investigation on the artist's palette, where sampling is less invasive to the visual integrity of the work, the results could generate a paint reference library to support further studies of the artist's paintings via non-invasive technologies and machine learning models.



[1] Vermeulen, M., Smith, K., Eremin, K., Rayner, G. and Walton, M., Application of Uniform Manifold Approximation and Projection (UMAP) in spectral imaging of artworks. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 252, 2021, 119547. https://doi.org/10.1016/j.saa.2021.119547.
[2] Rosi, F., Grazia, C., Fontana, R. et al., Disclosing Jackson Pollock's palette in Alchemy (1947) by non-invasive spectroscopies. Heritage Science 4 (18), 2016. https://doi.org/10.1186/s40494-016-0089-y
[3] Lutzenberger, K. and Stege, H., From Beckmann to Baselitz – Towards and improved micro-identification of organic pigments in paintings of 20th century art, e-Preservation Science, 6, 2009, 89-100.
[4] Lomax, S. Q. and Learner, T., A review of the classes, structures, and method of analysis of synthetic organic pigments, Journal of the American Institute for Conservation, 45(2), 2006, 107-125.

Combining PIXE with BS provides more information on paint layers

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Up to now, Ion beam analysis (IBA) has been used occasionally for analyzing paintings. The restricted number of studies is due to two main issues: quantitative PIXE analysis is sometimes difficult to interpret due to the layered structure, the presence of varnish and organic binder and, in some cases, a discoloration of the pigments can be observed due to the interaction of the ion beam with the compounds.

In order to improve the characterization of paintings, it was proposed ten years ago to combine backscattering spectrometry (BS) and PIXE simultaneously, to collect complementary information such as layer thickness and quantification of the organic part (binder). Simultaneous PIXE and BS experiments also have the advantage of analyzing the same area in one experiment. This combination, implemented with the AGLAE external beam, was successfully applied on paintings [1-2] and on painting cross-sections for the study of Italian Renaissance masterpieces [3].

However, M. Mayer and T. F. Silva (2017) recently pointed out that the BS spectra depend also on the pigment size and distribution [4]. We present here results obtained on paint layers containing pigment particles of various sizes (from 13 to 64 µm mean diameter) mixed with linseed oil. The results show that the combination of the IBA techniques provides complete information on both the pigments and the binder.

[1] L. Beck, C. Jeynes and N.P. Barradas, Nucl. Instr. and Meth. B 266, 2008, 1871-1874
[2] L. Beck et al., Nuclear Instruments and Methods in Physics Research. B 268, 2010, 2086-2091
[3] L. de Viguerie et al., Analytical Chemistry 81, 2009, 7960-7966
[4] M. Mayer et T. F. Silva, Computer simulation of backscattering spectra from paint, Nuclear Instruments and Methods in Physics Research B 406, 2017, 75–81

Calibration of reflectance imaging spectroscopy using MA-XRPD for 16th century illuminated manuscript

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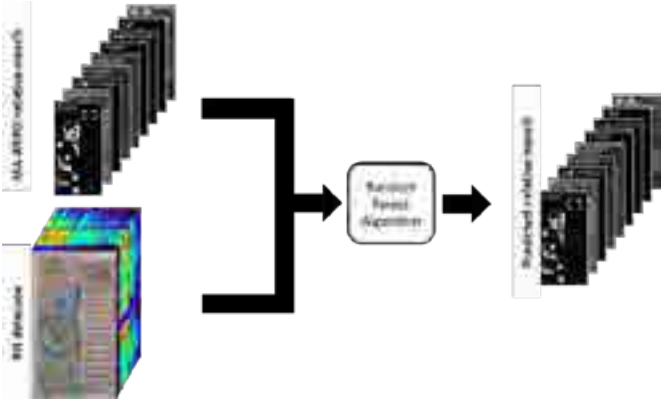
Abstract:

This study presents a method for predicting the relative abundance of the artistic pigments used on illuminated manuscripts by using reflectance imaging spectroscopy (RIS) from visible to short-wave infrared range (400-2500 nm), calibrated using X-ray diffraction data. A folio of an illuminated manuscript, likely from the 16th c., was analysed using multiple hyperspectral cameras (RIS) and a macroscopic X-ray powder diffraction scanner (MA-XRPD). From the MA-XRPD analysis, we were able to identify a number of common pigments found in historical manuscripts such as: azurite ($Cu_3(CO_3)_2(OH)_2$), malachite ($Cu_2CO_3(OH)_2$), lead white (hydrocerrusite, $Pb_3(CO_3)_2(OH)_2$), vermillion (cinnabar, HgS), calcite ($CaCO_3$), gypsum ($CaSO_4{\cdot}2H_2O$) and lead tin yellow (Pb_2SnO_4). Also the less commonly found pigment, posnjakite ($Cu_4SO_4(OH)_6$), was found to be present, which allows to date the manuscript to the 16th c. The MA-XRPD data was used to calculate a relative mass percentage of the identified pigments in each pixel. Although the MA-XRPD measurements result in detailed information, the acquisition time is long when compared to RIS measurements. The disadvantage of the RIS measurements is that they are difficult to interpret. Thus the MA-XRPD-based relative concentrations were used as baseline data for training machine learning algorithms to interpret the RIS dataset of the same manuscript folio. Using the trained models, it is possible to derive concentration maps of some of the pigments based on the RIS images alone, such as azurite and malachite. Suggesting the possibility to predict the concentration maps in other non MA-XRPD scanned areas of the same (or other) manuscript(s).

Keywords: Reflectance imaging spectroscopy, XRPD, Machine Learning, Random Forest Regression



Abundance of colors: pigments and wall painting techniques at the frontiers of the Roman Empire

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Due to their aesthetic beauty, Roman wall paintings have been a source of fascination among scholars and the general public alike. Despite being extensively studied over time, Roman mural paintings continue to attract interest and stimulate new research. At the moment there is a large corpus of data on wall painting supports and pigments coming from Rome and Pompeii. Wall painting fragments discovered in other parts of the empire, such as Northern Italy, Spain, France, Great Britain, Greece, and Slovenia, have also been studied. However, in the provinces located at the frontiers of the Roman Empire, such as Dacia, there is a lack of scientific investigations concerning Roman wall paintings. To this date, there are only two scientific publications that investigate the materials and painting techniques of several 2nd c. wall painting fragments discovered in two important archaeological sites.

In this study, we report the results of our most recent investigations carried out on new wall painting fragments excavated in what is probably the most important Roman archaeological site in Dacia - *Ulpia Traiana Sarmizegetusa*, the first city established by the Romans in the Northern part of the Danube. The employed methodology included non- and minimally-invasive techniques such as Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Fluorescence (XRF), Scanning Electron Microscopy–Energy-Dispersive X-ray Spectrometry (SEM–EDS), and X-ray diffraction (XRD). The aim of the study was to gain further insights into the materials and wall painting production methods used by the ancient artisans in this part of the Roman Empire. The results of the study are discussed and compared with our previous findings, in order to outline the artistic practice within the region.

Up until now, our research studies revealed a rich color palette, that included common earth pigments (*colores austeri*), but also, in some particular situations, expensive pigments (*colores floridi*) as well. Pigments such as minium, orpiment, or azurite could be identified in trace amounts on several wall painting fragments investigated, inferring the idea that the original wall decorations were once brightly colored compared to what we see today. In terms of painting technique, the presence of a protein binder could be inferred in some of the investigated fragments, testifying the high technical skills and esthetic awareness of the Roman artisans. We believe that the findings add an important contribution to the existing literature, notably the identification of organic binders, more so as until recently Roman wall paintings were regarded within the region exclusively as frescoes.

Acknowledgment
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[1] F. Pique, and G. Verri (2015). Organic materials in wall paintings: Project report. Los Angeles: Getty Conservation Institute.
[2] I.M. Cortea et al. (2020). First analytical study on second-century wall paintings from Ulpia Traiana Sarmizegetusa: insights on the materials and painting technique, in *International Journal of Architectural Heritage*, 14(5):751-761.
[3] I.M. Cortea et al. (2021). Investigation of ancient wall painting fragments discovered in the Roman Baths from Alburnus Maior by complementary non-destructive techniques, in *Applied Sciences*, 11(21):10049.

Characterization and consolidation of wooden artifacts by radiation-assisted curing of HPMA for wood preservation

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As one of the oldest materials, wood has been used in various applications from musical instrument to tool and from shelter to furniture. Wood is generally prone to biodeterioration which can be caused by a number of factors such as sunlight, moisture, temperature and microbial. These factors can alter both chemical and physical properties of wood. This research focused on consolidation of wooden artifacts using radiation-induced curing of hydroxypropyl methacrylate (HPMA). After consolidation, properties of impregnated wood were investigated using FTIR, SEM, contact angel and universal testing machine (UTM). For this study, pine wood was chosen and used as an example for a wooden heritage. Results showed that gamma radiation was able to induce curing of HPMA onto wood. Optimum degree of impregnation was approximately 66% at 5 kGy. Results also showed that wood consolidation improved mechanical properties and wettability. Results from this preliminary study proved that wood consolidation is an effective method that can be used to preserve wooden artifacts, in terms of their physical and chemical stability, while simultaneously preventing them from further biodeterioration.

MOXY project: preliminary investigation of a non-contact cleaning of some typical art materials using atomic oxygen

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Today, contact-based "wet" and "dry" cleaning methods, using organic solvents/water/gels, are broadly used. However, contact approaches can be limited when treating fragile and porous materials or sensitive artworks and non-contact cleaning technologies are highly desirable. The ongoing EU-funded MOXY project [1] has embarked on a mission to develop a non-contact cleaning methodology, based on atomic oxygen (AO), generated by non-thermal plasma at ambient pressure to remove carbon-based contaminants in a non-contact way.

In this study, 39 mock-ups were produced using a range of materials commonly found in cultural heritage such as plaster, limestone, canvas, paper, acrylic and oil paint, and pastel. These mock-ups were exposed to AO using the low Earth orbit oxygen environment simulator LEOX at the European Space Agency. The samples were intentionally soiled with typical problematic contaminants such as soot, spray paint, ballpoint pen, markers, and lipstick. During the LEOX experiment, half of each sample was masked with aluminum foil and exposed to the AO flux for varying lengths of time.

Samples were examined visually and by spectro-colorimetry at first. In many cases, the colour differences between the pristine and AO-treated areas were around and below the perceivable threshold, indicating that AO efficiently cleaned the surface of the substrate [2,3]. Investigation with other analytical methods is currently taking place, and includes optical microscopy (OM), 3D Hirox scanning microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR–ATR), confocal laser microscopy (CLM), gloss measurements, and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS). Directed to the mock-up's surface, AO removes carbon-based contaminants by converting them mainly into CO, CO_2 and H_2O vapours [4]. To evaluate the efficiency in removing contaminants, it is possible to rely on some approaches also employed for contact-based methods. However, a new methodology is needed for the AO approach. In contact and solvent/gel-based methods, it is often necessary to evaluate the presence of residues on the artwork surface, or the degree of diffusion of solvents used for cleaning. Differently from the contact methods, for the AO-cleaning, this is not necessary, but the possible effects of atomic oxygen on the artwork itself need to be investigated in depth. This calls for tailored mock-ups and new testing approaches and protocols for cleaning assessment to be used in combination with the traditional assessment methods. The poster presents the preliminary results obtained and discusses the new challenges faced.

[1] Green Atmospheric Plasma Generated Monoatomic OXYgen Technology for Restoration of the Works of Art –Art – MOXY - 2022-2026. Grant agreement ID: 101061336. https://cordis.europa.eu/project/id/101061336.
[2] Sharma, G., Bala, R. 2003. Color fundamentals for Digital Imaging. In Digital Color Imaging Handbook (1st ed.). CRC Press: 31.
[3] Miller, N.J. Druzik, J.R. 2012. Demonstration Assessment of Light-Emitting Diode (LED) Retrofit Lamps at an Exhibit of 19th Century Photography at the Getty Museum (No. PNNL-21225). In Technical Report, Pacific Northwest National Lab.(Lab. (PNNL), Richland, WA (United States).
[4] Banks, B., Rutledge, S., Karla, M., Norris, M., Real, W., Haytas, C. 1999. Use of an Atmospheric Atomic Oxygen Beam for Restoration of Defaced Paintings, in Proceedings of the 12th Triennial ICOM-CC Meeting, 1999, NASA/TM-1999-20941.

Submission: https://technart2023.com/

Unravelling The Fading Pink Dye In Peranakan Textiles using SERS and LC-MS

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Pink, deemed an auspicious colour, is favoured in early 20th century Peranakan[a] textiles for important ceremonies such as weddings. Also termed the "*Peranakan Red*", this pink shade manifested in cotton linings of several Peranakan textiles is particularly susceptible to light damage and is a concern to exhibition display. A Peranakan bed hanging with different shades of fading pink is selected to determine the fading pink dye composition for preservation. Tiny pink threads sampled from faded and unfaded areas were analysed with Surface Enhanced Raman Spectroscopy (SERS) [1] and Triple Quadruple Liquid Chromatography Mass Spectrometry (LC-MS). With LC-MS, two types of extraction methods were tested: direct dissolution in methanol and multi-step acid extraction [2]. Results of the same thread samples show distinct differences using the three method variations, demonstrating the challenges of dye analysis and the importance on the choice of analytical method. Finally, the dye composition of "*Peranakan Red"* is characterised as synthetic dyes from the xanthene group (notably eosin with lower levels of rhodamine B; phloxine and rhodamine 6G may be present in the dye recipe). Eosin as a red lake pigment has been well-characterised in easel paintings [3], but its characterisation on a cotton-dyed textile work of art is probably the first revealed to our understanding. These data can be used as a reference point for the characterisation of xanthene dyes in textile collections of the Southeast Asia region.

Footnote

[a] Peranakans here refer to a mixed ethnicity group formed by local descendants of Chinese who immigrated from Southern China to the Straits Settlements until the end of the 19th century.

References

[1] Cesaratto, Anna, Marco Leona, and Federica Pozzi. "Recent advances on the analysis of polychrome works of art: SERS of synthetic colorants and their mixtures with natural dyes." *Frontiers in Chemistry* 7 (2019): 105.

[2] Smith, Gregory D., et al. "Forensic dye analysis in cultural heritage: unraveling the authenticity of the earliest Persian knotted-pile silk carpet." *Forensic Science International: Synergy* 3 (2021): 100130.

[3] Fieberg JE, Knutås P, Hostettler K, Smith GD. "Paintings Fade Like Flowers": Pigment Analysis and Digital Reconstruction of a Faded Pink Lake Pigment in Vincent van Gogh's Undergrowth with Two Figures. Appl Spectroscopy, 71(5), 2017, 794-808

A Repository for Storage, Linking and Dissemination of Multidisciplinary Manuscript Research Data

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Research on historical manuscripts is increasingly supported by technical disciplines: Multi- and Hyperspectral Imaging support the recovery of degraded or deliberately removed contents [1] and spectroscopic analysis methods are used for the identification and characterization of inks, pigments and substrates, which in turn provides evidence for reconstructing the origin and history of a manuscript [2].

Each line of investigation produces specific digital artifacts such as scientific imagery, spectroscopic measurements, or high-level analysis results. If the various investigations are carried out by different institutions and at different times, the artifacts produced mostly exist independently from each other and lack a common frame of reference. Thus, the potential for re-use in interdisciplinary research is limited and their effective life cycle often ends with the research projects in which they are acquired.

We present a repository for the archiving and dissemination of manuscript research data in the form of Multi-Modal Manuscript Representations, in which the various digital artifacts are spatially and logically related. With respect to long-term preservation and linked open data, special emphasis is put on the use of established and open standards for data and metadata. The resulting virtual objects are disseminated via technical interfaces but also via an interactive web viewer (see Figure 1). Thus, the data available in the repository is made long-term accessible not only for natural sciences and technology, but also for research and education in the humanities.

Figure 1: Browsing measurements in the web viewer.

[1] A. Tonazzini, E. Salerno, Z. A. Abdel-Salam, M. Abdel Harith, L. Marras, A. Botto, B. Campanella, S. Legnaioli, S. Pagnotta, F. Poggialini, V. Palleschi. Analytical and mathematical methods for revealing hidden details in ancient manuscripts and paintings: A review. Journal of Advanced Research 17, 2019, 31–42.
[2] K. Nesměrák, I. Němcová. Dating of Historical Manuscripts Using Spectrometric Methods: A Mini-Review. Analytical Letters 45(4), 2012, 330–344.

Laser-based techniques for the characterization of historically accurate grisaille paint reproductions

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Grisaille is a glass-based paint used in stained glass windows from the 12th century until today. It was the first paint to be applied on stained-glass panels, and it is composed of a mixture of metal oxides (iron and copper) with high lead-silica-based glass. Studies focused on the reproduction of this paint based on historical written sources have been made in the last years, with the aim of understanding the technological evolution of grisailles paint production throughout time. In this work, three grisailles were reproduced based on three different recipes from three different sources: the 14th-century recipe book of Antonio da Pisa "*Secreti per lavorar li vetri secondo la dottrina de Maestro Antonio da Pisa*"; the 17th-century (1635) treatise of Pierre Lebrun "*Recueil des essaies des merveilles de la peinture* (Brussels Manuscript)"; and 19th-century treatise of Georges Bontemps "*Guide du verrier"*.
The reproduced samples were characterized by laser-induced breakdown spectroscopy (LIBS), laser-induced fluorescence (LIF), non-linear optical microscopy (NLOM) in the modality of multiphoton excitation fluorescence (MPEF) and perfilometry. The combined use of these techniques aims to test and disseminate an innovative multi-analytical approach for the study of grisaille paint layers in a non/micro invasive way. LIBS and LIF analysis determined the composition of the different grisaille paint layers, including minor and trace elements. This, together with the raw materials characterization results, allowed the understanding of possible changes in the composition throughout the grisaille production and firing. With NLOM-MPEF and perfilometry, the thickness and morphology of the painted layers were also characterized, providing an understanding of the influence of different raw materials and production methodologies on the final paint layer morphology.
The results obtained from this study were also compared with historical stained-glass window samples from the same chronology as the recipes reproduced, advancing the understanding and knowledge of the technological evolution of grisaille paint layers production. This research has also demonstrated and proved a new non/micro-invasive methodology for the characterization of grisaille paint layers.

Acknowledgments

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From the desert to the Alps: a study to unveil biodeterioration patterns of historical petroglyphs integrating metagenomics with analytical techniques

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Rock art, as petroglyphs and pictograms, is considered to be one of the most interesting types of remains to study past civilizations, since it gives a glimpse into the everyday life of our ancestors throughout time [1]. Rock art can be found worldwide in very different environments, and its weathering processes (physical, chemical and biological) are highly dependent on the environmental settings to which it belongs. Biological colonization especially, can be a common problematic for outdoor stone artefacts and can give rise not only to an aesthetical impairment but also induce severe physical and/or chemical damages to the stone (biodeterioration) [2]. The ecology and biodeteriorative potential of the biological colonization is highly dependent on the age and status of the stone artefact, its bioreceptivity and the environmental conditions [3], which also influence the dominant species.

In our study two different petroglyph sites were considered: one in the Negev desert of Israel and one in the east alpine region of Austria (Dachstein area), two very different places, but sharing extreme conditions. The main objective of the study was to explore and compare the possible biodeterioration effects of the microbial communities that colonize the petroglyphs, analyzing their composition and interaction with the lithic substrate.

Through the use of molecular methods (metagenomics), we characterized the microbiomes of the samples which revealed complex communities with mostly bacterial taxa in the desert, and that included Bacteria, Archaea, and Eukaryotes in the samples from the Alps. By means of XRD, XRF and Raman spectroscopy, we defined the composition of the stone (limestone) and of the black crust coating the desert samples, unveiling also the presence of biological pigments, such as carotenoids. Thin sections of the samples were observed with optical microscopy and further analysed by SEM-EDX. SEM observations were employed to check the penetration and spread of the biological colonization in the stone, revealing the presence of filamentous microorganism and moss´s rhizoids boring through the substrate of the Alps samples. SEM-EDX mappings highlighted instead deterioration patterns (e.g. leaching of calcium carbonate) in the desert samples, possibly connected to the action of biodeteriorative microorganisms. A final evaluation and comparison of the effects of the lithobionts on the studied petroglyph sites were done, keeping in mind that in environments with high levels of abiotic stress biofilms can also have a bioprotective effect [3][4].

[1] T. Dowson, "UNESCO World Heritage Convention," 2006. https://whc.unesco.org/en/activities/733/.
[2] A. A. Gorbushina and W. E. Krumbein, *Microorg. Soils Roles Genes. Funct.*, vol. 3, pp. 59–84, 2005, doi: 10.1007/3-540-26609-7_3.
[3] X. Liu, Y. Qian, F. Wu, Y. Wang, W. Wang, and J. D. Gu, *Trends Microbiol.*, vol. 30, no. 9, pp. 816–819, 2022, doi: 10.1016/j.tim.2022.05.012.
[4] S. E. Favero-Longo and H. A. Viles, *World J. Microbiol. Biotechnol.*, vol. 36, no. 7, pp. 1–18, 2020, doi: 10.1007/s11274-020-02878-3.

Multi-sensor points cloud Data Fusion for metrological analysis and monitoring of a Renaissance panel paintings

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This paper reports the workflow designed for the 3D survey of a panel painting using image- and range-based remote sensing techniques such as close-range photogrammetry, conoscopic microprofilometry, and structured light scanning.

The painting presented herein is the central panel of a polyptych composed of three panels by a late Gothic painter active in central Italy in the late 15th century.

The multi-sensor points cloud data fusion provided a quantitative information that increases the potential of the results obtained from the above techniques used individually. In fact, it made it possible to: *i)* create an accurate three-dimensional documentation of the artwork, with a multiple level of detail (LoD); *ii)* quantitatively assess the damage through advanced metrological analysis of the surface morphology and the support thickness, using mathematical and morphological algorithms (in particular, quantifying the macro-deviation of the wooden support from theoretical flatness, calculating the deformation arrow before and after restoration) [1]; *iii)* monitoring the state of conservation of the pictorial surfaces and the wooden support through multi-temporal comparison between the 3D models from acquisitions made at different times (Cloud-to-Cloud distance calculation) [2]; *iv)* making a multi-resolution and multi-scale 3D model for topographic characterization and roughness analysis of the pictorial surfaces. The hyper-dense profilometric point cloud dataset improves the readability of micrometric details in the pictorial layer, such as compass etching of haloes, punch marks, *graffiti* decorations, and craquelure pattern.

The metrological issues derived from this multi-sensor approach enabled an appropriate planning of the restoration and long-term conservation interventions to be conducted on the panel painting.

[1] L. Cocchi, B. Marcon, P. Mazzanti, L. Uzielli, C. Castelli, A. Santacesaria, Verifica del funzionamento di una traversatura elastica applicata su un dipinto su tavola: la Deposizione dalla Croce di Anonimo abruzzese, XVI secolo, OPD Restauro, No. 26 (2014), pp. 83-94.
[2] D. Lague, N. Brodu, J. Leroux, Accurate 3D comparison of complex topography with terrestrial laser scanner: Application to the Rangitikei canyon (N-Z), ISPRS Journal of Photogrammetry and Remote Sensing 82, 2013, pp. 10-26.

Pb isotope-based studies of manuscripts' origin: non-invasive tracing of parchment fragments to the 11th century

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Varying Pb isotope ratios can be taken as a marker for different ores used as pigment raw materials and accurate information on all of them is required for comparative studies. Radiogenic ^{208}Pb, ^{207}Pb and ^{206}Pb are formed at the end of the U and Th decay chain, while ^{204}Pb is a non-radiogenic isotope. In the case of valuable artefacts, there is no question of obtaining permission to take even the smallest sample of historic material, which, in turn, limits the possibilities of cooperation. Manuscripts can be taken here as the crowning example of the limitations in question. Therefore, the new method applying transfer of Pb with other metals to indicator papers soaked in BPhen (4,7-diphenyl-1,10-phenanthroline, $C_{24}H_{16}N_2$) and indirect measurements of the Pb isotopic ratios was proposed as an alternative in such investigations. Model studies showed that no fractionation occurred during the application of the indicator papers. Furthermore, Pb from historical lead pigments immobilised in the paper indicators showed the same isotopic composition as the original item. This clearly demonstrates that such non-invasive isotopic studies may be used as an alternative to classical analyses.

The method is exemplified by unique objects: parchment fragments discovered in a book binding of a Hebrew grammar published in 1600. In the book-binding process, additional protective guards of parchment often taken from old manuscripts, were sawn into the book block. Today, they are a valuable source of information for codicologists and historians. Two parchment fragments were attached to the cover. They were identified as re-used fragments of a Latin psalter with a continuous gloss in Old English. Comparative analyses enabled us to date them to the 11th c. in England [1].

The results of multi-instrumental investigations, including direct macro-XRF and OCT examinations, preceded indirect elemental screening of indicator papers by LA-ICP-MS, and MC-ICP-MS isotopic ratio measurements. Most relevant to supporting the hypothesis of the 11th c. origin of the fragments were the results of lead isotope analyses, which reflected the composition of red lead pigment from the script. The obtained Pb isotopic ratios indicated with high probability that the pigment may have come from a lead mine in the East of England in Derbyshire (South Pennines, Peak District) which was first worked by the Romans and subsequently by the Saxons.

[1] M. Opalińska, P. Pludra-Żuk, E. Chlebus, The Eleventh-Century 'N' Psalter from England: New Pieces of the Puzzle, The Review of English Studies, 2022; hgac081, https://doi.org/10.1093/res/hgac081

Proto-historic plain gold rings from western Iberia: a detailed study by multifocus OM, pXRF, micro-XRF and SEM-EDS

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During Pre- and Proto-history gold was mainly used to produce artefacts with decorative and aesthetical functions, many of those to be worn on the body, such as bracelets, necklaces and earrings. By Late Bronze Age, gold artefacts were frequently massive objects decorated with geometric motifs. In Western Iberia, gold alloys typically incorporated 5 to 25 wt.% Ag and <1 wt.% Cu. In this presentation, 4 pairs of plain gold rings from LBA Western Iberia will be presented (a total of 8 rings), namely one pair from a recent excavation at São Julião (Aveiro, Portugal) and 3 pairs belonging to the National Museum of Archaeology (Lisbon, Portugal) collection, which were recovered in Lisbon and Leiria districts, Portugal. All rings present similar characteristics and dimensions, with a solid body of circular section with a crescent shape with short and thin terminals and can be interpreted as pairs of earrings. Characterization by Multifocus Optical Microscopy (multifocus OM), portable X-ray fluorescence spectrometry (pXRF), micro-XRF and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) was performed. The study allowed the generation of extended depth of field (EDOF) images of the surfaces of the rings, the evaluation of the alloy composition of each ring, the comparison between rings belonging to the same pair as well as a comparison between pairs. It was revealed that the surface of the rings presents many irregularities (Figure 1), as well as small decorative motifs in some of them. By comparing XRF quantitative results using silver K-lines or L-lines it was found that the objects show compositional differences along depth. Generally, a loss in silver was found towards the surface, possibly due to the dissolution of anodic constituents at the surface of the objects. These differences are more pronounced than compositional differences found among different areas of the same object, and thus of significance for the interpretation of the original alloy composition of the artefacts.

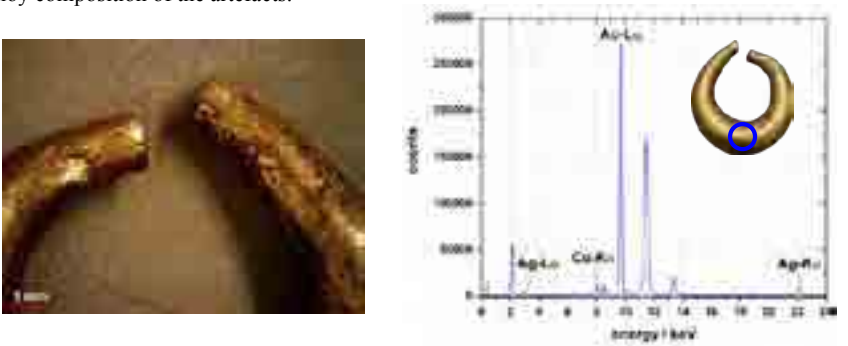

Figure 1. At left detailed image (multifocus OM) of the terminals of a ring (2017.5136). At right a pXRF spectrum of the ring, with indication of some characteristic Ag, Au and Cu X-ray lines.

SWIR hyperspectral imaging to unveil the numerous restorations of the Lady and the Unicorn tapestry (15th C, Musée de Cluny)

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The Lady and the Unicorn wall-hangings are one of the great masterpieces of the world. It was supposedly made at the end of the 15th century and was acquired by the Musée de Cluny in 1882. Since their discovery, the six tapestries have undergone more than a dozen restoration campaigns. Some of these have been quite invasive, leaving visible traces and contributing to considerable degradation. Furthermore, the incomplete documentation of these campaigns hinders their understanding.

The study will be focused on the "Mon seul désir" and "le Toucher" tapestries. During two analysis campaigns, several contactless spectroscopic techniques were used to identify materials (dyes, mordants, fibres) in both medieval and restoration zones. This paper aims to show how the treatment of hyperspectral data in the short-wave infrared range can highlight restored areas that are otherwise invisible, as well as enabling the selection of more precise areas for punctual analysis. Other non-invasive and portable methods, such as optical microscopy, hyperspectral imagery in the visible range, X-Ray Fluorescence and fluorimetry, have been performed in those specific areas revealed by false colour imagery. The combination of these spectroscopic techniques allowed the identification of natural dyes in medieval parts, such as indigo and madder. It gave many clues to explain the advanced degradation of the restored areas carried out in 1889. For example, the *chiné* weaving technique, the use of *waste wool*, and different mordants (alum, iron, copper…) or dyes mixtures (weld + madder + cochineal) were found, explaining partly why the restorations are visible today as faded colours.

The confrontation of hyperspectral images and punctual data with the recent restoration surveys provides a solid basis for a better understanding of the history of restoration techniques used on the Lady and the Unicorn tapestry, furthering our knowledge of those precious tapestries.

Keywords: hyperspectral imaging; the Lady and the Unicorn; dyes; tapestry; p-XRF; fluorimetry; restoration; degradation

A multi-analytical approach to disclose the composition of 18th century ointments from the "History of Pharmacy Collection" in Cluj

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The investigation of historical pharmaceutical preparations provides interesting information about human activities and technical knowledge of natural resources through time [1,2,3]. Historical remedial ointments were mainly composed of mixtures of natural substances and active compounds extracted from natural sources. The final formulations result in quite complex mixtures, not only due to the multiple ingredients employed during preparation, but also for the chemical modifications induced by the interactions among the materials and the ageing processes [4]. Thus, from an analytical point of view, the characterization of ointments is challenging due to the variation of the formulations used over the centuries.

In present work, a multi-analytical approach was used to investigate the organic residues collected from fourteen historical containers from the 18th century from "The History of Pharmacy Collection" in the National Museum of Transylvanian History (Cluj-Napoca), within the activities of the research project "Pharmatrans – Farmaciile secolelor XVI-XX din Transilvania. Colecția de Istorie a Farmaciei din Cluj-Napoca".

The array of analytical techniques used comprises gas chromatography-mass spectrometry (GC/MS) to identify the main ingredients of the formulations and to define specific analysis to further characterize each constituent. Solid phase microextraction- gas chromatography-mass spectrometry (SPME-GC/MS) was employed to characterize the volatile fraction of the samples. Finally, the characterization of lipids and waxes along with dyes components was performed by high-performance liquid chromatography coupled with high resolution mass spectrometry (HPLC-ESI-Q-ToF) to determine their botanical/animal origin.

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1562, within PNCDI III and lead to a broad overview of the composition of Romanian historical ointments in the 18th century.

[1] Ribechini, E., Modugno, F., Pérez-Arantegui, J., Colombini, M.P., Anal. Bioanal. Chem. 401 (2011) 1727–1738.

[2] F. Saliu, I. Degano, M.P. Colombini, J. Chromatogr. A. 1346 (2014) 78–87.

[3] C. Riedo, D. Scalarone, O. Chiantore, Anal. Bioanal. Chem. 401 (2011) 1761–1769.

[4] F. Saliu, F. Modugno, M. Orlandi, M.P. Colombini, Anal. Bioanal. Chem. 401 (2011) 1785–1800.

Unveiling the colours of the 17th-18th century azulejos using a multi-analytical non-invasive approach

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This work contributes to the knowledge of the colouring material of 22 Portuguese glazed tiles (*azulejos*) stored in the National Tile Museum, in Lisbon, Portugal. The tiles are dated from the 17th to 18th century and represent different colour combinations used throughout several decades.

Building on a previous study where the basic chemical composition of the 17th-century colour palette was identified [1], we used a non-invasive methodology to further identify compositional differences among identical colours within a wider timeframe.

The colours (blue, white, yellow, orange, purple, green and brown) were analysed by EDXRF to obtain qualitative and (in some samples) quantitative information on their chemical composition. UV-VIS FORS and μ-Raman spectroscopy were used to identify the main colouring agents. Finally, colorimetric measurements of the different hues of each colour were performed to address the relation between colour and chemical composition. All analyses were performed on the surface of the tiles.

The analytical results showed that green colour could be obtained through copper base pigment or a mixture of a lead-antimonate-based pigment and a cobalt-blue pigment. Although cobalt is the colouring agent of the blue pigments, the compositional differences detected through the analyses suggest using different raw materials or adding other elements to modify the hue. On the other hand, different yellow hues (from lemon-yellow to orange) were manufactured by mixing lead-antimonate base pigment with zinc, tin, or iron oxide. A manganese ore was used to make the purple pigment.

Detail of a tile showing a variety of colours

[1] Coentro, S., Mimoso, J., Lima, A., Silva, A., Pais, A., & Muralha, V. (2012). Multi-analytical identification of pigments and pigment mixtures used in 17th century Portuguese azulejos. Journal of the European Ceramic Society 32, 37-48

Monitoring the outcome of new biocleaning methods with the help of spectroscopic techniques

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A large part of the worldwide painted patrimony includes mural paintings. Depending on their location and on various intrinsic and extrinsic factors, these might require restoration or conservation works during their lifetime. When dealing with historical interventions, some of the materials used might need to be removed later in time. Within the frame of the national project "*Biocleaning of mural paintings with new ecological products based on microbial metabolites*" new ecological and user-friendly ways of cleaning mural paintings were tested and, along with those, various ways to rapidly and accurately evaluate the results of these cleaning procedures [1-2]. While the first option used was based on the complementary use of microscopy, SEM (scanning electron microscopy), colorimetry and FTIR (Fourier transform infrared spectroscopy), some other methods were also tested, including hyperspectral imaging. In this paper, the focus was on testing Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS), with and without statistical analysis methods, and on exploring the usefulness of these methods as compared to the golden standard of using FTIR. Raman spectroscopy was chosen due to its non-destructive and non-contact character, along with the wide range of materials it can detect [3] and the fact that it offers higher *in-situ* operability as compared to FTIR. Despite not being entirely non-destructive, LIBS was also selected because of its ability to stratigraphically detect the chemical composition [4] of both organic and inorganic materials.

[1] I. Gomoiu, R. Cojoc, R. Ruginescu, S. Neagu, M. Enache, M. Dumbravician, I. Olteanu, R. Radvan, L. Ghervase, Applied Sciences, 12, 2022, 7229.
[2] I. Gomoiu, R. Cojoc, R. Ruginescu, S. Neagu, M. Enache, G. Maria, M. Dumbravician, I. Olteanu, R. Radvan, L.C. Ratoiu, V. Atanassova, L. Ghervase, Fermentation, 8(9), 2022, 462.
[3] J. Jehlička, A. Culka, Analytica Chimica Acta, 1209, 2022, 339027.
[4] V. Detalle, X. Bai, Spectrochimica Acta Part B: Atomic Spectroscopy, 191, 2022, 106407.

Confocal XRF depth profiling combined with XRF mapping to non-destructively understand the stratigraphy of prehistoric cave art

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(5) Fédération de Recherche 3506 CNRS New AGLAE– MC

Paleolithic cave representations are one of the oldest forms of art from modern humans, and as such it is important to understand the coloring matters used. An analytical procedure has already been developed for the *in situ* analysis of blacks based on manganese oxides. Reds on the other hand are more complicated, as the trace elements of the matter and the composition of the cave wall present a similar chemical composition [1-5].

That is why two sampled stalagmites presenting red coloring matter from prehistoric caves (La Garma and El Otero, from Northern Spain) have been studied with complementary techniques. A micro-X-ray fluorescence (µXRF) chemical cartography was obtained at the PUMA beamline of the SOLEIL synchrotron, followed by a non-destructive depth-resolved confocal XRF scan using our LouX^{3D} device. This CXRF depth scan allows us to precisely determine the chemical composition layer by layer, with a spatial resolution of ten µm.

The combination of these two techniques, supported by others, made it possible to find differentiation criteria distinguishing the cave wall and the prehistoric coloring matter, as well as to obtain reliable information on the creation of the prehistoric figures.

Results of this combined study highlight the advantages of CXRF analysis for the non-invasive technical study of the wall-coloring matter composition, allowing to learn information about the stratigraphy and helping us to improve *in situ* analyses.

Figure 1. Location of one of the sampled prehistoric painted stalactite at La Garma cave, Northern Spain © CNRS-C2RMF/ José Tapia

[1] Trosseau A, Maigret A, Coquinot Y, Reiche I. J Anal At Spectrom. 2021;36(11):2449–59.

[2] Gay M, Alfeld M, Menu M, Laval E, Arias P, Ontañón R, et al. J Anal At Spectrom. 2015;30(3):767–76.

[3] Gay M, Müller K, Plassard F, Cleyet-Merle JJ, Arias P, Ontañón R, et al. J Archaeol Sci Rep. 2016 Dec;10:878–86.

[4] Gay M, Plassard F, Müller K, Reiche I. J Archaeol Sci Rep. 2020 Feb;29:102006.

[5] Submitted Reiche et al, proceedings GMPCA 2022

Surface Characterization of Austrian Daguerreotypes

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In 1839 Louis Jacques Mandé Daguerre published the first photographic process [1]. Due to the insufficient sensitivity of the silver-plated substrates, the process could not be used to produce images of moving scenes. Decisive steps in further development, increasing the sensitivity of daguerreotype plates, and developing the first mathematically calculated portrait lens with a specially designed camera were already taken in Vienna around 1840 [2]–[4]. Collections throughout Austria and abroad are contacted and a selection of daguerreotypes are examined for their special surface properties. A far-reaching determination of techniques and production processes, based on the presence or absence of certain characteristic elements, but also of possible process variants, is the aim of a current interdisciplinary study of historical daguerreotypes in Austria [5]. The surface morphology and surface chemistry of daguerreotypes are the most important sources of information related to their production methods and the corrosion and aging processes affecting their long-term preservation [6], [7]. Three non-destructive and non-contact examination methods were identified to be the standard for analyzing the daguerreotypes in this project: digital optical microscopy, scanning electron microscopy, and micro-X-ray fluorescence. Thus, corrosion states, surface features due to various production steps, possible conservation interventions and storage conditions, have been observed.

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[1] L. J. M. Daquerre, *Historique et Description des Procedes du Daguerreotype et du Diormama.* Paris: Delloye Libraire, 1839.
[2] M. Gröning and M. Faber, *Inkunabeln einer neuen Zeit : Pioniere der Daguerreotypie in Österreich 1839-1850*. Wien: Christian Brandstätter Verlag, Albertina, 2006.
[3] M. Ponstingl, Ed., *Die Explosion der Bilderwelt. Die photographische Gesellschaft in Wien 1861-1945*, vol. 6. Wien: Christian Brandstätter Verlag, 2011.
[4] M. Faber and T. Starl, "'Wäre die Zeit Null', Daguerreotypie in Wien 1839 bis 1841," *Fotogeschichte*, vol. 22, no. 83, pp. 3–20, 2002.
[5] V. Ljubic Tobisch, A. Artaker, and W. Kautek, "PHELETYPIA," *Project PHELETYPIA "The impact of early photography and electrotyping media on the creation of images and contemporary art" (Heritage 2020-060 PHELETYPIA) by the Heritage Science Austria grant program of the Austrian Academy of Sciences*. 2023.
[6] V. Ljubić Tobisch and W. Kautek, "Die Daguerreotypie zu Beginn der 1840er-Jahre in Wien: eine Rekonstruktion von neu entwickelten Verfahren am Beispiel einer geätzten

Daguerreotypieplatte aus dem Technischen Museum Wien," *Pap. Conserv.*, vol. 37, pp. 147–161, 2020.

[7] V. Ljubić Tobisch and W. Kautek, "Highly Photosensitive Daguerreotypes and their Reproduction: Physico-chemical Elucidation of Innovative Processes in Photography Developed around 1840 in Vienna," *Chempluschem*, vol. 84, no. 11, pp. 1730–1738, Nov. 2019.

Calcareous nannofossils assemblage in paintings chalk ground for provenance analysis: 3 original paintings compared to European source materials

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In Europe, chalk was used as priming from the Gothic period [1] to the 18th Century for painted objects. Economically speaking, chalk was not advantageous to transport, as this material can be easily found all around Europe. Principally before the 19th century, even though the first written source concerning the sale of Champagne chalk dates back to the 15th Century [2]. Four geological chalk basins are determined in Europe: Paris-London, North Sea, Westphalia - Low Saxe and North Germany - Poland [3]. These relatively northern areas can be referred to as a boreal domain. The deposition took place in relatively shallow marine (50 - 200 m depth) warm (20° - 25° C) waters [3].

In biogeography, the possibility of using calcareous nannoplankton was first robustly demonstrated by McIntyre and Bé (1967) [4]. They studied coccolithophoridae assemblages of the Atlantic Ocean and distinguished 5 climatic groups, namely, tropical, subtropical, transitional, subarctic, and subantarctic (based on the temperature range for each calcareous nannoplankton species). Comparable paleobiogeographical differences could also be expected from Cretaceous nannoplankton. They can be easily analysed in art primings, being the main component of chalk (up to 98 %) [5].

In our work, we used the high abundance of nannoplankton in micro-sample artworks and their known biogeography variability (localisation) to determine the provenance of chalk material used in artworks.

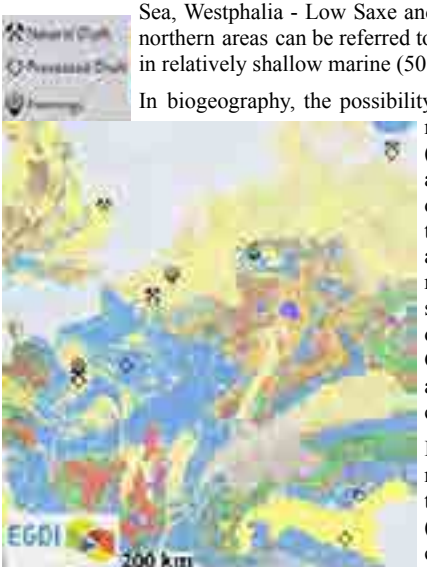

Figure 1 Geological map of part of Europe with the reference material analysed and the artwork's provenance.

Calcareous nannoplankton assemblages from five historical chalk-mining areas (Ruegen/D; Champagne/F; Bologna/I; Belgium; England; Fig. 1) were compared to assemblages from three original paintings. Based on multidimensional statistics, the chalk painting nannoplankton assemblages showed affinities to Champagne chalk in France.

[1] L. Švábenická, *Vestn. Cesk. Geol. Ust*, 69 (3), 1994, 47–51
[2] J. Rohleder, F. W. Tegethoff, Ed. Basel: Birkhäuser Basel, 2001, 55–68.
[3] F. Robaszynski, *Barb.*, 12 (7), 2001, 271–279
[4] A. McIntyre and A. W. H. Bé, *Deep Sea Research and Oceanographic Abstracts*, 14 (5), 1967, 561–597
[5] M. Kędzierski and M. P. Kruk, *Journal of Cultural Heritage*, 34, 2018, 13–22

New insights into the dyes of 19th-century Central Asian ikat textiles

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Central Asian ikat textiles are characterised by their bold and large abstract patterns, made up of vibrant colours and carrying the characteristic "blurriness" or "feather-like" effect, which makes them some of the most famous and recognisable fabrics worldwide.

In the framework of a collaborative study, ten ikats from the Guido Goldman collection at the National Museum of Asian Art (Washington, DC, USA) and six ikats from the collection of the British Museum (London, UK) were investigated with the aim to identify the dyes and expand on recent research carried out on Central Asian ikats [1]. The ikats selected were produced between the first half of the 19th century and the early 20th century, thus possibly containing both natural and synthetic dyes. The dye identification was obtained by applying high pressure liquid chromatography coupled to diode array detector and tandem mass spectrometry (HPLC-DAD-MS/MS) to small samples taken from all the colours.

Some of the textiles from the two collections show the same decorative patterns and the results were interpreted to explore possible connections. The palette of natural dyes is confirmed to be relatively limited and restricted to American cochineal (*Dactylopius coccus*) for red, larkspur (*Delphinum semibarbatum*) for yellow, and indigo for blue as main dye sources. Madder (*Rubia tinctorum*) for red and pagoda tree (*Sophora japonica*) for yellow were also detected as minor components in some cases. However, new synthetic dyes, such as scarlet red (C.I. 16150 and 16155), rose bengale (C.I. 45440), eosin A (C.I. 45380), auramine (C.I. 41000) and diamond green G (C.I. 42040), were added to the more common synthetic dyes, such as fuchsin (C.I. 42510), crystal violet (C.I. 42555) and diamond green B (C.I. 42000) already found on similar textiles [1, 2]. These results provided significant additional information about the changes in ikat production that occurred in the 19th century with specific attention to the introduction of synthetic dyes into traditional practices.

Keywords: dye analysis; liquid chromatography; mass spectrometry; ikat textiles; Central Asia

REFERENCES

1. Tamburini, D., et al., *Exploring the transition from natural to synthetic dyes in the production of 19th-century Central Asian ikat textiles.* Heritage Science, 2020. **8**(1): p. 114.
2. Chen, V.J., et al., *Chemical analysis of dyes on an Uzbek ceremonial coat: Objective evidence for artifact dating and the chemistry of early synthetic dyes.* Dyes and Pigments, 2016. **131**: p. 320-332.

Investigating the role of iron and manganese oxides in colouring late antique glass by XANES and micro-XRF spectroscopies

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This research aims to study colouring technologies in 5/6th century glass imported to Atlantic Britain by correlating the iron (Fe) and manganese (Mn) ratios and oxidation states with glass colour. Despite having a similar matrix chemical composition and concentrations of Fe and Mn oxides, these glass vessels display different colours (from green to yellow, sometimes with purple streaks) [1,2]. Colour changes in this type of glass can be induced by controlling the reduction-oxidation reactions that occur during glass production, which are influenced by the raw materials, furnace and melt atmosphere, and recycling. To evaluate these parameters, reference glasses were prepared, following the composition of late antique archaeological glass recovered from Tintagel (UK) and Whithorn (UK). A corpus of archaeological and experimental glass samples was analysed using bulk Fe and Mn K-edge X-ray absorption Near Edge Structure (XANES) spectroscopy, micro-XANES and micro X-ray fluorescence (µ-XRF) at beamline ID21, at the European Synchrotron Radiation Facility (ESRF).

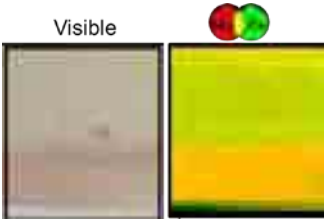

Figure 1. Micro-XRF Fe and Mn maps of a yellow glass sample with purple stripes

Fe and Mn XANES spectra of the archaeological glass samples indicate that Fe and Mn are in a similar oxidation state in all the yellow samples, while iron is reduced in the green samples. No detectable difference in Mn and Fe oxidation state occurs in the purple stripes compared to the yellow glass bulk. Micro-XRF maps of the distribution of Fe and Mn in the samples demonstrated that Mn concentrates in the purple stripes of the samples (Figure 1). Accordingly, in this case, it is concluded that the colour change is mainly due to Mn/Fe ratio.

Many archaeological fragments display dichroism, as they appear pale green in transmitted light but honey-coloured in reflected light. Using a focused beam, XANES spectra were collected from the surface of the archaeological and experimental samples (within 20 µm) to evaluate any changes in Fe and Mn oxidation states of the surface compared to the bulk. Results suggest the post-burial formation of a surface layer where Mn is more oxidised, which is believed to scatter transmitted and reflected light differently and might be responsible for the dichroism.

[1] A. Bidegaray, S. Godet, M. Bogaerts, P. Cosyns, K. Nys, H. Terryn and A. Ceglia, Journal of Archaeological Science: Reports 27, 2019.
[2] L. De Ferri, R. Arletti, G. Ponterini and S. Quartieri, European Journal of Mineralogy, 23, 969-980.

Balkan triptych of The Mother of God, "The Unfading Rose"

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This paper presents the investigation and restoration of a Byzantine triptych from a private collection. It is initially characterized as a work of the Russian school of iconography, the image analyses in general, but also those of structure, especially those of pigments - photo analysis, macro-photographs, radiographs and pXRF and Raman spectral analyzes - located in the Balkans, in the first half of the 18th century. An activity stretched over ten years, from consolidating the pictorial layer to the final varnishing.

A triptych with flanked by Saints Nicholas and Haralambis, in a carved and gilded wooden frame Greek, 17th century, rendered traditionally, the features with dark colours, the bright garments with gilded details, the central panel in the form of an ogee arch supported by columns with Corinthian capitals, the spandrels carved with flower-buds and leaves, with extended dimension: 13¾ x 18¼ in. (34.9 x 46.4 cm).

SyncLab for cultural heritage – joint X-ray imaging and spectroscopy measurements at the synchrotron and in the laboratory

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X-ray imaging, diffraction and spectroscopy can reveal compositional, structural and chemical information of heterogeneous objects. In most cases, minimal sample preparation is necessary and non-destructive experiments can be realized, if radiation damage is monitored. This leads to the fact, that such techniques are widely used in the field of art and archaeometry.
While routine investigations on many objects can be performed with laboratory equipment with techniques such as XRF or XRD, more specialized investigations are sometimes only possible at synchrotron radiation facilities, due to the higher brilliance or other characteristics of the X-radiation. The combination of using laboratory and synchrotron instruments can be beneficial to both communities – the cultural heritage experts as well as the scientists responsible for the instruments.
In the framework of the joint research group SyncLab between the Helmholtz-Zentrum Berlin and the TU Berlin, experiments are performed both at the BLiX – the Berlin laboratory for innovative X-ray technologies – and at BESSY II. External users have the possibility when applying for beamtime at BESSY II to additionally use laboratory equipment offered by BLiX before or after the beamtime.
We present showcases of the synergy effects offered by the combination of synchrotron and laboratory experiments leading to optimized analytical results.

In situ non-invasive measurement of varnish thickness on historical artefacts by line-field confocal OCT

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Optical Coherence Tomography (OCT) is today a well-established technique based on white-light interferometry. This technique provides information on the various layers (interfaces between two adjacent layers) and on the presence of particles (scattering particles). The collected signals are based on the reflection or scattering of light, i.e. spatial variation of the refractive index [1-3]. As standard non-destructive and non-invasive three-dimensional (3D) imaging technique, OCT can be brought on site for the study of cultural heritage artefacts. However, the most common OCT devices usually provide a lateral resolution between few to 10 µm that impedes accurate measurements of micrometric structures as thin varnish layers or small particles.

Line-field Confocal OCT (LC-OCT) is a new 3D imaging technique that combines OCT with confocal microscopy, in order to provide improved spatial resolution (here, isotropic resolution of about 1 µm) and imaging speed, while still providing a similar penetration depth as in usual OCT setups [4]. LC-OCT images of 18th century gilt leathers from wall-hangings showed two interfaces: air-varnish and varnish-silver leaf. In colored areas, the more complex stratigraphy can be elucidated [5]. LC-OCT has also been used to characterize varnish removal during a restoration. Finally, beyond OCT imaging, one of the challenges is to automatically determine and map the varnish thickness on the studied area. An interface detection from a 3D mapping program was adapted to automatically determine the varnish thickness from our LC-OCT images.

[1] P. Targowski, M. Iwanicka, B. J. Rouba, C. Frosinini, in Optical Coherence Tomography (Springer International Publishing), 2015, 2473-2495
[2] C. S. Cheung, M. Spring, H. Liang, Optics Express 23, 2015, 10145
[3] G. Latour, J.-P. Echard, B. Soulier, I. Emond, S. Vaiedelich, M. Elias, Applied Optics 48, 2009, 6485
[4] A. Dubois, O. Levecq, H. Azimani, D. Siret, A. Barut, M. Suppa, V. Del Marmol, J. Malvehy, E. Cinotti, P. Rubegni, J.-L. Perrot, Journal of Biomedical Optics 23, 2018, 1-9
[5] G. Galante, M. Vilbert, M.-C. Schanne-Klein, G. Latour, Leather and Related Materails Working Group ICOM-CC, 2022 (in press)

Non-invasive identification of coloring materials based on terahertz continuous-waves (THz-CW) spectroscopy

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Techniques based on terahertz (THz) radiation allow non-destructive and non-invasive analysis, making them highly interesting technologies in the Cultural Heritage field [1]. Moreover, THz radiation has a low photon energy (~4.2 meV at 1 THz) which assures no molecular ionization and therefore, it cannot cause any damage to the materials under investigation nor issue to the operators [1,2].

For these reasons, this study aimed to obtain the spectral response for pigments and dyes with terahertz continuous wave spectroscopy (THz-CW) in the spectral range 0.1-3 THz with a compact and portable experimental set-up with high-frequency resolution (in the order of 100 MHz) in transmission mode. The results demonstrated that THz-CW spectroscopy can be considered a complementary methodology for Cultural Heritage related materials' characterization since it allowed the extraction of the optical parameters (absorption coefficient and refractive index) in the spectral range of interest for the compounds.

Furthermore, a preliminary characterization of compounds of interest was performed following a multi-analytical approach, based on ED-XRF and FORS spectroscopies.

Moreover, since mixtures were often used to achieve desired hues, add shading, darken the mineral pigment, or correct the faded dye [3], some mixtures were investigated. The resulting experimental spectra obtained with THz-CW spectroscopy were then theoretically calculated as the weighted linear combination of the absorbance of each pure component [4,5]. The results showed that it is possible to differentiate single components in mixtures, proving that THz-CW is a reliable methodological high-resolution approach in the Cultural Heritage field.

[1] K. Fukunaga, THz Technology Applied to Cultural Heritage in Practice, Springer Nature, 2016.
[2] M. Naftaly, Terahertz Metrology, Artech House Publishers, 2015.
[3] I. Nastova, O. Grupce, B. Minceva-Šukarova, M. Kostadinovska, M. Ozcatal, Vibrational Spectroscopy (78), 2015, 39-48.
[4] A. D'Arco, D. Rocco, F. Piamonte Magboo, C. Moffa, G. Della Ventura, A. Marcelli, L. Palumbo, L. Mattiello, S. Lupi, and M. Petrarca, Optics Express (30), 2022, 19005-19016.
[5] E. M. Kleist, C. L. Koch Dandolo, J. Guillet, P. Mounaix, T. M. Korter, Journal of Physical Chemistry A (123), 2019, 1225-1232.

Nondestructive XRD (X-ray Diffraction) crystallization and XRF (X-ray fluorescence) analysis of Taiwan indigenous glass beads

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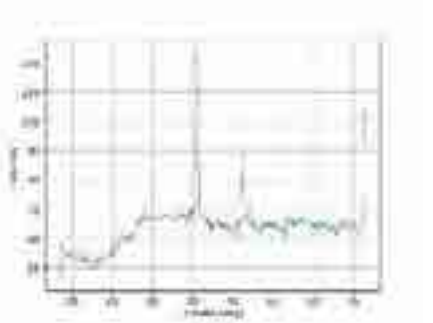
ABSTRACT

In this study, XRF and XRD scientific analyzes were carried out on aboriginal glass beads from different sources in Taiwan, and the application of non-destructive and destructive XRD were compared.
To achieve this, the sample was examined by non-destructive XRD. This method prevents the damage issue of traditional XRD that needs to grind the sample for detection, as well as the issue of confusing analysis of materials with pattern heterogeneity with glass beads. Since there is no need to grind the sample, the crystal structure analysis can be carried out at a single point within 3 mm of the sample that do not cause damage. In addition, to further study XRD and beans origins, the light element analysis part of the flux is processed by small area XRF helium blowing mode XRF.
The research result shows that glass beads have the highest content of amorphous phase components, and that there are localized quartz in different regions, and differences in the crystallization of other mineral particles. According to the XRD pattern of the crystalline components in these glass beads, it can be inferred that there are two sources of crystallization: 1. Raw materials being the micron-sized (Micro size) mineral grains remaining after high-temperature melting. 2. The crystal grains could be secondary nano-size structures after high-temperature melting.
For future study, more samples of ancient glass beads for further non-destructive systematic research can be done to increase the database for regional and temporal classification of sources.



Keywords: indigenous glass beads, Nondestructive XRD, helium blowing, XRF

Medieval writing: the chemistry behind iron gall inks

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Until the beginning of the 20th century, a significant part of our cultural heritage was recorded using iron gall inks [1]. Unfortunately, many historical documents are at risk of total loss due to degradation of the writing support caused by the corrosion of these inks [2].

Our knowledge on the molecular structures of the chemical compounds present in these inks is very limited and this gap prevents us to devise informed strategies for preserving the world written heritage.

The goal of this work is to characterize iron-polyphenol complexes present in iron gall inks. The tannins present in the gall extract were characterized by HPLC-DAD-ESI-MS, showing that the main compounds are pentagalloylglucose, hexagalloylglucose and gallic acid [3-5].

We were able to find out more about the ability and the favorable conditions for the iron-complexes to be formed. Gallotannins from *Quercus infectoria* galls were isolated by preparative HPLC-DAD and iron-complexes were prepared and analyzed through UV-VIS spectroscopy and electrochemical studies. Experiments were conducted with and without inert atmospheres. pH and Fe(II)/Fe(III) titrations were carried out alongside kinetic studies in 2-5 pH range. There are strong evidences that the bi-exponential kinetic starts with a faster step due to the formation of a complex with Fe(II), while the ink is only formed during the slower kinetic step.

MALDI-MS and ESI-MS were used to study the nature of the iron-complexes in aqueous solution. Structural characterization was further complemented with SEM, FTIR, Raman microscopy and X-ray analysis.

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[1] Kolar, J., et al., Analytica Chimica Acta, 555(1), 2006, 167-174.
[2] Neevel, H., Kolar, Jana and M. Strlic, Iron gall inks: on manufacture characterisation, degradation and stabilisation, Ljubljana: National and University Library, 2006.
[3] Díaz Hidalgo, R.J., et al., New insights into iron-gall inks through the use of historically accurate reconstructions, Heritage Science, 6(1), 2018, 63.
[4] Teixeira, N., et al., In-depth phenolic characterization of iron gall inks by deconstructing representative Iberian recipes, Scientific Reports, 11(1), 2021, 8811.
[5] Díaz Hidalgo, R.J., et al., The making of black inks in an Arabic treatise by al-Qalalūsī dated from the 13th c.: reproduction and characterisation of iron-gall ink recipes, Heritage Science, 11(7), 2023.

Combined in situ MA-XRPD and cross-section SR-µ-XRPD imaging for the study of copper sulfates: an overlooked group of green copper pigments in Flemish Renaissance art

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This contribution deals with the detection and localisation of a range of copper sulfate pigments, such as posnjakite ($Cu_4(SO_4)(OH)_6 \cdot H_2O$), in 16th c. Flemish paintings. The occurrence of this class of green pigments in Renaissance easel paintings, and its prevalence in works originating mostly from the County of Flanders and the Duchy of Brabant, was first reported by Spring (1). Technical examination, via analysis of paint samples, in works of the National Gallery (London) revealed the presence of copper sulfates in sixteen 16th c. Netherlandish paintings (SEM-EDX, µ-RS and µ-FTIR).

By means of macroscopic x-ray powder diffraction imaging (MA-XRPD), copper sulfate pigments (CSP) can now also be identified in a non-invasive manner; in-situ mapping measurements can be directly performed on the paintings. In this way, the distribution of posnjakite was first visualised by MA-XRPD on areas of mid-16th c. overpaint on the 15th c. Ghent Altarpiece (2, 3). This finding prompted us to do additional and more systematic research into the use of copper sulfates in 16th c. Flemish paintings. As such, MA-XRPD analyses on easel paintings from, e.g. Quinten Massijs and Joachim Patinir, allowed to visualise the CSP distribution and link it to the brushwork and to different green hues of the composition. Complementary analysis of paint micro samples by synchrotron-based micro-XRPD (SR-µ-XRPD) yielded more information on the way the CSPs were incorporated in the paint stratigraphy.

A literature survey listing all positive identifications of CSP confirms that copper sulfates are mainly found in paintings created by Flemish artists during the first half of the 16th c. This coincides with Antwerp's golden age when it was Europe's largest harbour city and trading hub. With the developing interest for natural and botanical sciences in the 16th c., initiating the dawning of landscape and still life painting, it is not unthinkable that Flemish artists were keen on expanding their limited range of green hues to enhance their realistic representation of nature and experimented with new pigments.

In this contribution, the insights derived from the literature survey will be discussed, supplemented with results of a first series of *in-situ* MA-XRPD measurements on historical paintings combined with chemical characterisation by SR-µ-XRPD of corresponding paint cross-sections.

1. Spring M. New insights into the materials of fifteenth- and sixteenth-century Netherlandish paintings in the National Gallery, London. Heritage Science. 2017;5(1):40.
2. Dubois H. The turbulent Material History of the Ghent Altarpiece. An Analysis Integrating Technical Examination and Historical Sources (1432-1894). University of Ghent; 2022.
3. Sanyova J, Van der Snickt G, Mederos-Henry F. The Ghent Altarpiece: the Challenges of a Complex Stratigraphy from a Chemical Point of View. In: Steyaert G, Postec M, Sanyova J, Dubois H, editors. The Ghent Altarpiece: research and Conservation of the Interior: the Lower Register. Contributions to the Study of the Flemish Primitives. Brussels: Brepols; 2021. p. 111-45.

Exotic writing inks and how to identify them

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The focus of our group at the BAM is to reconstruct the history of writing materials through the analysis of historic samples and comparison with written evidence and research conducted on lab-made mockups. The black writing inks of antiquity are generally associated with carbon-based ones that consist of carbon particles suspended in a water-soluble binder. We also know that medieval scribes in Europe and in the Middle East used iron-gall inks that are result from a chemical reaction between iron (II) ions and tannins in an aqueous binder solution. Curiously, the first proper recipe for an iron gall ink comes only from the 12th century, hundreds of years after the first inks of this type were introduced, as suggested by scientific analysis [1]. It seems that the transition from one predominant ink type to another one was a gradual process, that was accompanied by the use of the exotic inks. For example, late-ancient scribes sometimes used carbon inks containing metals [2], [3], or tannins [4].
As recently discovered, iron-gall inks could be produced using various sources of iron [5]. In this presentation, we will focus on the development of new archaeometric, non-destructive protocols that allowed us identifying and distinguishing among different black writing inks. This work includes our discovery of the oldest metal-bearing inks in a case study of two Greek documents from the collection of the Egyptian Museum and Papyrus Collection in Berlin, as well as non-vitriolic inks from the codices in the collection of the Benedictine monastery St. Paul in Lavanttal. Finally, we will discuss a medieval Torah scroll from a private collection that was inscribed and corrected with seemingly identical iron-gall inks.

[1] Ghigo, T., Rabin I., Buzi, I., Archaeological and Anthropological Sciences 70, 2020.
[2] Nehring, G., Bonnerot, O., Krutzsch, M., Gerhardt, M., Rabin I., Archaeological and Anthropological Sciences 13, 71, 2021.
[3] Christiansen, T., Bulletin of the American Society of Papyrologists 54, 2017, 167–195.
[4] Cohen, Z., Composition Analysis of Writing Materials in Cairo Genizah Documents, Brill 2021.
[5] Hahn O., Nehring G., Freisitzer, R., Rabin I., Gazette du Livre Médiéval 2021.

Material characterization of Queen Catarina of Braganza and King Charles II of England medallions

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The Museu Medeiros e Almeida, in Lisbon, has in its collection a pair of medallions portraying D. Catarina de Braganza (as Queen of England) and her husband, Charles II of England (see figure 1).

Referred to in documentation as “ebony portraits”, “charcoal sculptures” or “Stuart carvings”, these medallions were, until recently, listed in the museum's inventory as jet medallions, of an unknown author, dating from c. 1662. However, new research has now attributed the pair of carvings to Robert Town, active in the mid-18th century and author of several royal portraits in cannel coal in other European museums and collections.

In order to identify the material, in-situ X-ray fluorescence measurements on these medallions were done. The identification of some trace elements, such as Fe, Zn or Sr will help to identify the carbon based raw material. Also, well-known jet pieces from Museu Décio Thadeu at IST were analyzed for comparison.

Figure 1. Medallions portraying D. Catarina de Braganza (left) and Charles II of England (right).

Multi-analytical Evaluation of Glues Obtained from Various Types of Hides and Skins

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Collagen extracted from skin, tendons, cartilage, animal and fish bones, is a product that has been used over time as an adhesive, binder and consolidant for various organic and inorganic materials in museums, libraries, archives, etc. [1, 2]. The special requirements for the reversibility of treatments stipulated in specific norms, require the use of these types of collagen-based adhesives, glues or gelatins in the restoration activity due to their properties (reversibility, non toxicity for humans and environment, glues a wide variety of materials on any dry or wet surface, high validity in normal dry glue storage conditions, etc.) [3, 4, 5, 6].
For this purpose, the technology of water extraction of gelatins from the skins of various animals was studied, in 3 steps, at a pH lower than the isoelectric point: at 70°C with the collection of the first gelatin fraction with a homogeneous appearance, at 85°C with the collection of the second homogenous gelatin fraction and at 95°C with collection of the last gelatin fraction. Gelatins were characterized in terms of physico-chemical properties (ash, total nitrogen, amino nitrogen, dermal substance, pH of analytical solution). The strength of the gelatins was determined by the Bloom test, and the consistency, elasticity and adhesion force were evaluated by the CRT test. Through FTIR spectroscopy, comparative structural properties were highlighted, depending on the type of skin used.
The experiments included adhesion tests on collagen supports (leather and parchment, newly made especially for the restoration activity, samples of historical parchment, pieces of parchment detached from the backside of a heritage object, wood), followed by the characterization of the physical-mechanical properties (shear resistance and peel resistance).
All the tests were carried out in comparison with rabbit glue as a control, this being a commonly used adhesive in the restoration/conservation of art objects. In general, the bonds made with experimental gelatins are more compact and uniform than those made with rabbit glue. The results of the specific analyses in terms of the strength of the glued parts demonstrate that their effectiveness is similar to that of the control, and in particular, the gelatin extracted from goat skin confers superior peel resistance to the control.
In conclusion, the gelatins made in this study meet the conditions to be included in the category of glues for the restoration/conservation of objects with historical value, but also for industrial applications and agricultural crops.

Acknowledgement
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References
[1] Cennino Cenini, Tratatul de pictură, Editura Meridiane, București, 1977, pg 102.
[2] Cesare Brandi , Teoria restaurării, Editura Meridiane, Bucuresti, 1996.
[3] Schellmann, N. C., Reviews in Conservation, 8, 2007, 55-66.
[4] Ken Kroeger, 2010, https://postpressmag.com/articles/2010/adhesives-in-the-bindery-an-overview/
[5] Baglioni P., Berti D., Bonini M., Carretti E., Dei L., Fratini E., Giorg R., Advances in Colloid and Interface Science, 205, 2014, 361–371.
[6] Melià-Angulo, A., Fuster-López L., Vicente- Escuder A., 2017, https://doi.org/10.4000/ceroart.5152

MA-XRF AND LIBS INVESTIGATION OF GREEK RELIGIOUS ICONS

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The oil painting technique on canvas prevailed in post-medieval Europe and largely replaced traditional panel painting. However, post-15th century Greek painters kept manufacturing icons (i.e., religious panel paintings) by employing and adapting medieval panel painting techniques. The activity of these very painters' accounts for the thousands of icons nowadays demonstrated in public as well as private collections, and also serving as items of worship in churches, convents, and privately.

In this work, we will present the results of ongoing research focused on examining Greek icons using scanning macro-X-ray fluorescence (MA-XRF) [1,2]. We apply macroscopic X-ray fluorescence scanning spectroscopy, using different experimental set-ups, extending from the state-of-the-art M6 JetStream to an in-house built scanning spectrometer using the handheld spectrometer Tracer 5i. By interpreting the data, we unveil information about the identity of pigments and other additive materials, visualize hidden layers such as underdrawings, reveal technical details, determine the state of preservation/conservation history, and identify previous restoration interventions.

The multi-layered structure characterizing the paintings imposes difficulties in the XRF data interpretation, as the penetration depth of X-rays in pigments incorporated in binders is of the order of tens of microns. The complementarity of applying Laser Induced Breakdown Spectroscopy (LIBS) [3] has thus been examined. In this framework, a series of mock-up samples were manufactured following traditional byzantine painting techniques. These samples were analyzed by LIBS and XRF, and the corresponding experimental results were evaluated to resolve possible depth dependence of the LIBS and XRF signals.

Artificial intelligence (AI) methods, like clustering and neural networks, have been applied for data analysis. The methods benefit inexperienced users as they can analyze the big data sets without exhaustive knowledge of the involved underlying physics.

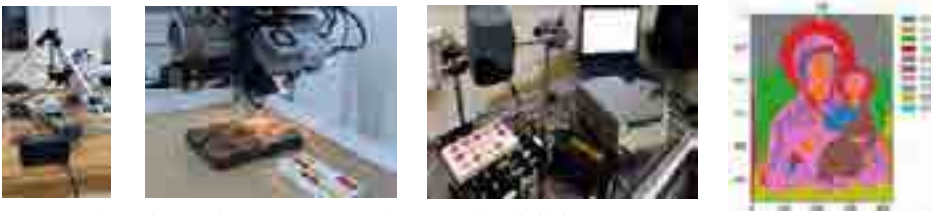

Figure: a) In-house developed XRF scanner using the Tracer 5i handheld, b) M6-Jetstream MA-XRF scanner, c) LIBS set-up, d) Cluster analysis for MA-XRF big data.

[1] M. Alfeld , J. V. Petroso , M. van Eikema Hommes , G. Van der Snickt , G. Tauber , J. Blaas , M. Haschke , K. Erler , D. Joris, K. Janssens , A mobile instrument for in situ scanning macro-XRF (MA-XRF) investigation of historical paintings, J. Anal. At. Spectrom., (2013), 28 , 760 —767

[2] T. Gerodimos, A. Asvestas, G. P. Mastrotheodoros, G. Chantas, I. Liougos, A. Likas, D. F. Anagnostopoulos, Scanning X-ray Fluorescence Data Analysis for the Identification of Byzantine Icons' Materials, Techniques, and State of Preservation: A Case Study. Journal of Imaging, (2022).,8(5), 147.

[3] Botto A., Campanella B., Legnaioli S., Lezzerini M., Lorenzetti G., Pagnotta S., Poggialini F., Palleschi V., Applications of laser-induced breakdown spectroscopy in cultural heritage and archaeology: A critical review, Journal of Analytical Atomic Spectrometry, (2019), 34(1), 81–103

High-tech multifunctional *marmorino* plaster with antimicrobial and self-cleaning properties

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Venetian *marmorino* is a traditional plaster used, since the XV century, in several palaces in Venice and ancient villas spread around the Veneto region. This material has great resistance, nevertheless, it could still undergo various surface degradations processes [1]. These can negatively affect its aesthetic properties, leading to the formation of stain deposits of different origins (*i.e.*, pollution, bio-deterioration, vandalism), which can eventually change the color of this material, and even trigger other severer degradation phenomena.

An appealing way to avoid these events is the use of photocatalytic self-bleaching coatings, by which these deposits are chemically removed as soon as they start to form, using just oxygen from the atmosphere and light as energy source [2]. Through photocatalysis, these materials can degrade the main organic and inorganic environmental pollutants (VOC, NOx), confer self-cleaning properties, and reduce bacterial attacks or fungal growth [3]. In this work, some oxide-based photocatalysts, namely titania (TiO_2) and zinc oxide (ZnO), were added to the *marmorino*, both as top coating and within the mortar itself.

Through X-ray diffraction (XRD), N_2 physisorption, and electron microscopy (SEM), it was evaluated how the photocatalysts influenced the properties of the plaster. The self-bleaching activity was evaluated by irradiation with visible light at room temperature, both using methylene blue, as model stain compound, and real case stain products. Colorimetric analyses were performed to evaluate the photocatalytic self-cleaning properties of the materials. The biocidal properties of the materials were verified by optic microscopic observations of fungal colonies growth on the *marmorino* mock-ups with different compositions or *finitura* layers. Hence, a more detailed analysis by electron microscopy (SEM) was made to confirm the biocidal properties. In particular, the two Fungi *Penicillium* s.p. and *Cladosporium* s.p. were chosen as reference microorganisms attacking wall materials in Venice.

The results obtained in this study show that it was developed a high-tech multifunctional *marmorino*, not only able to reduce the pollutants present in the environment, but also capable to prevent surface degradation and inhibit fungal growth, along with the consequent biodegradation, resulting in a slowdown in the ability to take root and lack of spore's development.

[1] F. Doglioni, L. Scappin, A. Squassina, F. Trovò, Conoscenza e Restauro degli intonaci e delle superfici murarie esterne di Venezia, *Campionature, Esemplificazioni, Indirizzi di Intervento*, 2017.
[2] S.A. Ruffolo and M. F. La Russa, *Frontiers in Materials* (6), 2019, 147.
[3] A. Markowska-Szczupak, W. Kunlei Wang, P. Rokicka , M. Endo, Z. Wei, B. Ohtani, A.W. Morawski, E. Kowalska, *Journal of Photochemistry and Photobiology B: Biology* (151), 2015, 54-62.

New insight into the palimpsests of *Ars Prisciani*

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Written at the beginning of the 6th century AD, in 18 books, the *Ars Prisciani* is the last and greatest Latin grammar handbook of Antiquity [1]. In 2019, the European Research Council (ERC) funded the Advanced Grant PAGES, which aims to digitally restore the palimpsest manuscripts of the *Ars*. The word "palimpsest" comes from the Greek "παλίμψηστος" which means "a manuscript scraped clear for reuse". Nowadays, invisible traces of scraped-off writings can be recovered with imaging technologies [2,3].

The aim of this work is to combine imaging technologies (e.g., multispectral imaging) with advanced image processing techniques, including Artificial Intelligence methods of Deep Learning and Computer Vision [4]. We will show preparatory work in which we train a number of Neural Networks with encoder-decoder architectures (including a U-net) to carry out Semantic Segmentation over a synthetic dataset and robustly model overwritten letters. We will discuss caveats and future prospects of our Machine Learning approach.

The results contribute to the new critical edition of the Ars providing up-to-date knowledge of Priscian's work.

[1] https://web.uniroma1.it/pages/home
[2] M. Perino, Reading the medieval palimpsests, (CARMEN Working Papers 2022), forthcoming.
[3] L. Pronti, M. Perino et al., Journal of Spectroscopy 2018, 2081548.
[4] A. Starynska, D. Messinger et al., JDAR 24 (3), 2021, 181–195.

Molecular fluorescence: disclosing the dyeing formulations of weld yellows from 18th-century recipe books

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Organic dyes have been used for artworks such as textiles, for millennia, and have great artistic and historic value. They may provide clues to the understanding of the technology behind an artwork's production. The characterization of natural organic colorants in artworks is still a challenge to this day, and of the natural dyes used in cultural heritage, yellows are some of the most difficult to identify. In fact, many of the techniques used still require sampling, which might not be possible in many cases. Molecular fluorescence in the UV-VIS offers high sensitivity, selectivity, fast data acquisition, good spatial resolution, and the possibility of in-depth profiling without the need to sample [1,2]. The technique, allied with a chemometric approach, can provide insight well beyond the identification of the single fluorophore. It can disclose important information on recipes' specificities, leading to chronological and location particularities, enabling a better understanding of the making of the artists' materials [1,2].

To test this approach on yellow dyes, we have reproduced yellow-dyed textiles made with weld (*Reseda luteola* L.) using recipes from French master dyers of the 18th century, Antoine Janot and Paul Gout [3-6]. They wrote treatises similarly entitled *Mémoires de Teinture* (Memoirs on Dyeing), illustrated with dozens of dyed textile samples. To understand the fluorescence signals of these historical reconstructions, the references of the standard chromophore molecules present in weld were also analyzed. The contribution of the main flavonoids in the fluorescence spectra was accessed. This characterization was complemented by HPLC-DAD analysis, where the percentage of the main chromophores was linked to the formulations. Moreover, we will also disclose our first approach to portable fluorescence measurements, comparing the data with the bench-top equipment.

In this study, we will present how molecular fluorescence has allowed us to assess the influence of the ingredients, as well as the distinct dyeing methods for both masters. This will provide key knowledge on the technological processes for dyeing with weld from these 18th c. French masters, while delivering proof-of-concept of the use of fluorescence for the analysis of artworks.

[1] P. Nabais, M.J. Melo, J.A. Lopes, T. Vitorino, A. Neves, R. Castro, Heritage Science 6(13), 2018.
[2] P. Nabais, M.J. Melo, J.A. Lopes, M. Vieira, R. Castro, A. Romani, Heritage Science 9(32), 2021.
[3] D. Cardon, The Dyer's Handbook – Memoirs of an 18th century Master Colourist. Oxford and Philadelphia: Oxbow Books, 2016.
[4] D. Cardon, Des Couleurs pour les Lumières - Antoine Janot, teinturier Occitan (1700-1778), CNRS Editions, 2019.
[5] D. Cardon & I. Brémaud, Le Cahier de Couleurs d'Antoine Janot / Workbook, Antoine Janot's Colours, CNRS Editions, 2020.
[6] D. Cardon & I. Brémaud, Les 157 Couleurs de Paul Gout / Paul Gout's 157 Colours, La Geneytouse: Éditions Lucien Souny, 2022.

Preliminary results of archaeometric analysis of Chalcolithic ceramic from Charneca de Fratel (Vila Velha de Ródão, Portugal)

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The archaeological site of Charneca de Fratel, in Vila Velha de Ródão, Portugal, is a fortification that had been radiocarbon dated from the 3rd millennium cal BC. The archaeological fieldwork of 1987 revealed the first Chalcolithic settlement on the northern bank of the Portuguese Tagus River. Its architectonic concept is similar to that observed in southern Portugal, proving new insights in the study of the process of chalcolitization [1] of the western Iberia. Its location in proximity with the Tagus River, near fertile soils, fishing and hunting areas and close to raw materials sources, probably used for the production of stone tools and pottery indicates a self-sustained society in the frame of an accentuated tendency to sedentarization [2].

In the present study, 20 samples of ceramic fragments were analyzed by means of Optical Microscopy, Wavelength Dispersive X-Ray Spectrometry and X-Ray Diffraction, to obtain their chemical and mineralogical constitution. The preliminary results show a strong coherence among the materials used in the manufacture of the pottery, indicating a probably common and regional/local source of raw materials.

Acknowledgments

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[1] J. Soares (Ed.), *Social complexity in a long term perspective* (Setúbal Arqueológica, 16). Setúbal: Museu de Arqueologia e Etnografia do Distrito de Setúbal/Associação de Municípios da Região de Setúbal/ UISPP, 170 pp., 2016.

[2] J. Soares, «O Povoado da Charneca do Fratel e o Neolítico Final/Calcolítico da Região Ródão-Nisa - Notícia Preliminar», *Alto Tejo*, Vila Velha de Ródão, pp. 3–6, 1988.

A metallurgical study to the understand the manufacturing process of iron nails from the archaeological site of Loiola (Vizcaya, Northern Spain).

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The archaeological site of Loiola (La Arboleda, Biscay, North Spain) provides evidences allowing tracing the manufacturing process of iron objects from the obtainment of the raw material to the finalized objects. Microstructural characterization of archaeological iron nails was performed in order to address Roman manufacturing technique since hand-forged nails show distinctive metallurgical structures.

To achieve elemental composition and structural characterization of mineral phases, EDS (Energy Dispersive Spectroscopy) coupled to ESEM (Environmental Scanning Electron Microscopy) and micro-Raman spectroscopy were used. Then, metallurgical properties and crystallographic texture were studied by combining microscopic methods such as optical microscopy (OM) and EBSD (Electron BackScatter Diffraction realized in environmental mode). Local Vickers' microhardness measurements were also performed to characterize the microstructures of nails according to the hardness values and the Iron-Carbon diagram.

All nails show a significant loss of material due to a very advanced corrosion, which products are mainly goethite (α-FeOOH) and magnetite (Fe_3O_4). The non-metallic inclusions are distributed along the deformation flow and are composed of iron silicates such as fayalite (Fe_2SiO_4) and iron-containing glassy phases, suggesting a strong hammering of the metal during the forging process. The metallic composition of nails consists in ferrite and pearlite. The microstructure presents different patterns with large-sized grains zones and small sized-grain zones clearly delimited in a same nail. Microstructure of ferrite grains outlining prior-austenite grain boundaries were also observed. Both are the result of heating the steel to an extremely high temperature and a subsequent quick cooling by immersing the artifact in water.

Not Just for Eating! Alginate-based Gels and Their Application Studies

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In artwork preservation, cleaning is necessary for the maintenance of the object and to prevent damage from various environmental factors, including physical, chemical, and biological attacks. Thanks to the simple preparation, physically-bonded rigid Agar gel is widely used for cleaning paper, painting, frescos, etc. [1]. However, due to its rigidity, it appeared to be fragile when handled with the risk to leave gel residues on the surface. Also, the weak bonding of Agar network might not prevent the excessive spreading of the loaded solvent on sensitive substrates (e.g. water-sensitive paper, wood, and paintings) [2].
For this reason, the authors proposed an alternative natural polysaccharide, alginate, as a novel bio-compatible cleaning system [3, 4]. Alginate gel physically bonded with calcium cations was systematically characterized using different analytical techniques to assess the mechanical properties, equilibrium water content, and retention capability, in comparison with Agar. To further strengthen the network of the gel, we also introduced alginate chemically crosslinked with 3-glycidyloxypropyltrimethodxysilane (GPTMS). The cleaning performance of the new formulations was tested on water-sensitive substrates (e.g. removing dust, sweat, or animal glue from wooden reproduction of ancient musical instruments). Before and after the removal of the organic and inorganic contaminants, non-invasive analyses were performed with reflection Fourier Transform Infrared Spectroscopy (FTIR), X-ray Fluorescence (XRF), colourimetry, and microprofilometry in comparison with Agar.
The results demonstrated that the alginate-based gels may offer an affordable solution for a controlled and safe cleaning of sensitive artworks, offering a retentive substrate for loading water solvent solutions.
This work was supported in part by the Italian Ministry of Foreign Affairs and International Cooperation, grant number PGR10141.

[1] A. Sansonetti, M. Bertasa, C. Canevali, A. Rabbolini, M. Anzani, D. Scalarone, Journal of Cultural Heritage. 2020(44), 285–296.
[2] C.L. Scott, AIC Objects Spec. Gr. Postprints. 2012(19), 71–83.
[3] C. Lee, F. Volpi, G. Fiocco, M. L. Weththimuni, M. Licchelli, M. Malagodi, Materials. 15(3), 2022, 1100.
[4] C. Lee, F. Di Turo, B. Vigani, M.L. Weththimuni, S. Rossi, F. Beltram, P. Pingue, M. Licchelli, M. Malagodi, G. Fiocco, F. Volpi, Polymers. 15(1), 2023, 36.

Top-Down MS: the next frontier in MS proteomic analysis of cultural heritage samples?

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Deciphering the identification and degradation of proteins in cultural heritage is key to revealing new historical insights or aiding in the preservation of precious objects. Bottom-up proteomics is becoming a mainstream method to identify the primary sequence of ancient proteins, as well as their biological origins and chemical modifications. But bottom-up proteomics has some limitations, in particular, the identification of protein breakdown or truncations and the loss of combinatorial posttranslational modification (PTMs) patterns which are conserved in top-down proteomics. Here we describe a top-down proteomic method to analyze ancient proteins from limited paint samples of a few micrograms, well below levels considered for robust top-down experiments. We were particularly interested in studying tempera paints due to their prevalence throughout the history of art. Egg binder analysis in particular is challenging, as most of the proteins present in egg are highly heterogeneous due to various PTMs such as glycosylation and phosphorylation. This presentation will describe our analytical workflow showing how top-down proteomics is a valuable resource to the study of ancient proteins revealing sample heterogeneity through the "bird's eye" view offered.

Focusing on lysozyme (14 kDa) and ovalbumin (45 kDa without PTMs) protein standards first, and then from egg binder and egg tempera paint models, the intact spectra at femtomolar concentrations were acquired. Both nanoLC separation and MS settings for MS and MS/MS were optimized for improved separation and identification of intact proteins and their breakdown products. The combination of CAD, EThcD and UVPD fragmentation modes allowed protein coverage over 50% for lysozyme to be achieved from sub-µg of model paint samples. The successful deconvolution and assignment of the spectra allowed the identification of various chemical modifications and isoforms. For example, highly heterogeneous patterns such as those observed for ovalbumin due to its extensive N-linked glycosylation (N292) and phosphorylation were acquired allowing confident protein identification despite several overlapping patterns. The occurrence of high molecular weight degradation forms of the targeted proteins was also screened in paint models sampled during drying and aging to demonstrate the capability of the method.

The presentation will describe the full method from sample preparation to protein analysis and data processing. It will discuss the challenges of ancient protein analysis considering the additional protein heterogeneity provided by deamination and protein *in situ* cleavages. The first applications to historic samples will be used to illustrate how a top-down approach can increase our knowledge of the degradation state of the art material.

Tracing the roots of Jan van Goyen's paintings: a dendrochronological analysis of materials and techniques

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This research project focuses on the application of dendrochronology in the analysis of eight paintings attributed to Jan van Goyen (1596-1656), a prominent Dutch landscape painter of the 17th century. By dendrochronology, the project aims to identify the wooden panels used by Van Goyen and to date them with accuracy, providing insight into the artist's working methods and the historical context of his art. The project also conducts technical analysis of the painting, including pigment, layer, and preparation analysis, to further enhance our understanding of Van Goyen's materials and techniques. The interdisciplinary approach of the project, which combines art history, materials science, and dendrochronology, will contribute to the ongoing development of the field of technical art history. The project will provide a unique perspective on the relationship between materials and artistic intent in Van Goyen's work, offering valuable insights into the broader cultural and historical context of Dutch painting of the period.

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Evolution of Raman Spectroscopy for Cultural Heritage: advanced prototypes

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The technological evolution of Raman Spectroscopy for increasingly effective applications in Cultural Heritage field is the topic of the research carried out over the last few years at ISPC Raman Laboratory in collaboration with the Rutherford Appleton Laboratory and the University of Cincinnati [1, 2]. Significant modifications to a commercial micro-Raman instrument led to the development of a benchtop prototype with high lateral and spectral resolution coupled with depth sensitivity and 3D mapping capabilities. Three micro-SORS variants (defocusing, internal beam-steered and point-like) are integrated in the prototype enabling the system to be easily adapted to fit specific applications efficiently. The coupling of micro-SORS with different imaging/mapping modalities (conventional, StreamLine and StreamHR) is paving the way for studies of high-resolution molecular distribution of compounds within volumes in art objects. Moreover, an external horizontal probe permits the non-invasive investigation of large objects too.

The in-house portable prototype is designed for a rugged, effective detection of Raman signals both in conventional and spatially offset geometries with high spectral and spatial resolution. This feature is achieved by using a linear fiber bundle to conserve the offset information on the detector, permitting simultaneous acquisition of Raman photons emerging from the surface and subsurface in separate spectra.

Different designs and applications to case studies in Cultural Heritage will be presented and discussed.

a) b)

Fig.1: Benchtop (a) and portable (b) Raman prototypes at ISPC Raman Lab

[1] S Mosca, C Conti, N Stone, P Matousek, Nature Reviews Methods Primers 1 (1), 2021, 1-16.
[2] A. Botteon, C. Colombo, M. Realini, C. Castiglioni, A. Piccirillo, P. Matousek, C. Conti, Journal of Raman Spectroscopy, 51 (10), 2020, 2016-2021

"Hearts of gold" (Cuori d'oro): the leather corams of Palazzo Chigi in Ariccia

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Keywords: Collagen based materials; Leather wallpaper; Ion Beam Analysis (IBA); Macro Area X-Ray Fluorescence (MA-XRF); Scanning Electron Microscopy-Energy Dispersive X-ray Analysis;

Abstract: Collagen based materials are frequently employed in the manufacturing of cultural heritage artefact. Derived from animal skin like goat, sheep, cattle and others, the leather, the parchment or the alum-tawed skin have been used through the centuries to produce artefacts for the everyday use, such as clothes, but also to produce works of arts, writing supports and book covers. The peculiar fibrillary structure of the collagen molecule in animal skin, its orientation in fibrils and bundles of fibrils to compose the fibre, gives to the collagen products their peculiar physical properties. Differently from the others materials, for leather is the tanning step, part of the manufacturing process, that converts the raw skin into a stable and imputrescent material. The stabilization of the collagen protein obtained thorough the tanning process makes the leather suitable for a number of applications giving to the material peculiar feature such as the flexibility, mechanical strength and the durability [1].
A very peculiar employ of leather is its use as wallpaper to enrich stately buildings. This application can be dated back to ancient times and still employed at least until the eighteenth century, when its use began a slow decline, being replaced by fabrics and then printed papers. This is the case of the rooms of *Palazzo Chigi of Ariccia* (Rome), an ancient princely residence in the countryside of Rome. The rooms of the building were enriched with decorated corams of the seventeenth-century, still covering the walls of many rooms of the building. Numerous fragmented and incomplete wallpapers are, instead, preserved in the archives of the palace and they can be traced back to different types of use such as table covers, dresser beds, chair covers, valances, hat covers, etc. [2].

Thanks to the Excellence's Center of the Technological District for Culture (DTC) of Regione Lazio, within the ADAMO project, it has been possible to perform different characterizations of these interesting artefacts. Recent studies regard the finding of alternative treatment for the biodegradation removal with respect to the conventional mechanical or chemical systems [3]. In this work we present the results obtained in order to perform the characterization of the chromatic richness, the employed materials and the iconographic elements of different fragments of the leather corams of the building. Different microscopic and spectroscopic analysis were performed by means of ~~the~~ Ion Beam Analysis (IBA) and Macro Area X-Ray Fluorescence (MA-XRF) techniques available at the INFN LABEC ion beam laboratory in Florence [4] and the Scanning Electron Microscopy-Energy Dispersive X-ray Analysis of the Research Center for Nanotechnology applied to Engineering (CNIS) of Sapienza University of Rome.

[1] Kite M. et al., Conservation of leather and related materials, (Elsevier, Oxford) 2006.
[2] Contadini A., in Arte veneziana e arte islamica: atti del Primo simposio internazionale sull'arte veneziana e l'arte islamica, edited by Grube E.J., (Edizioni l'Altra Riva, Venice) 1989.
[3] Vadrucci M. et al. Frontiers in Materials, 7 (2020).
[4] Chiari M. et al. Eur. Phys. J. Plus, 136 (2021) 472.

Combined application of petrography and SEM-EDS: outputs for accurate identification of binders in hydraulic mortars

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Identifying the binders in mortars, especially when designing a plan for the conservation and restoration of the built heritage, is crucial for a correct intervention. The characterisation of building materials has therefore been part of the solution in the context of proper rehabilitation.

Among other techniques used in the characterisation of binders, the importance of those related to microscopy (both optical and electronic) are particularly relevant. Microscopy and its combined techniques can be indeed the keys to such identification [1-3], as the classical approaches to mineralogical identification are not sufficiently conclusive in the investigation of the types of hydraulic binders in mortars. Since more than one binder can be applied simultaneously it is unproductive to investigate them without the use of microscopy techniques.

The present work aims to contribute to the systematisation of an analysis procedure that allows the unambiguous identification of binders in hydraulic mortars, considering the combined use of petrography and SEM-EDS. This work analyses mortar specimens with known characteristics, which served as a reference for the analysis of coating mortars from buildings built in 20th century that were awarded the Valmor architecture prize. The results showed that the proposed methodology allowed (1) the identification of the type of binder, (2) determine binder clusters according to the chemical composition of the paste, and (3) the influence that aggregate/binder ratio and the mineralogy of the aggregates can have on the investigation of binders in hydraulic mortars.

[1] J. Walsh. 2007. Petrography: Distinguishing Natural Cement from Other Binders in Historical Masonry Construction Using Forensic Microscopy Techniques. Journal of ASTM International 4(1), 2007.

[2] J. Weber, A. Baragon, F. Pintér, C. Gosselin. Hydraulicity in ancient mortars: its origin and alteration phenomena under the microscope. 15th Euroseminar on Microscopy Applied to Building Materials, 17-19 June 2015, Delft, The Netherlands.

[3] I. Vidovszky, F. Pintér. An Investigation of the Application and Material Characteristics of Early 20th-Century Portland Cement-Based Structures from the Historical Campus of the Budapest University of Technology and Economics. International Journal of Architectural Heritage 14, 2018, 358-375.

Integrated microprofilometry and multispectral imaging for full-field analysis of ancient manuscripts

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In this research we propose a novel workflow to combine the use of two powerful techniques in the study of ancient manuscripts: optical microprofilometry and multispectral imaging.
Multispectral imaging in the optical range is routinely used and has proven to be effective in the study of these special fragile objects [1]. In-band analysis allows to examine each individual *folium* as a superposition of layers that give different responses in the UV VIS NIR bands. 2D spectral imaging enables the analysis of the condition of an object, the mapping of previous restorations or the detection of writings no longer visible. The downside of this technique is the lack of quantitative data on surface morphology.
On the other hand, surface microprofilometry on book heritage is unexplored; furthermore, the technique requires advanced instrumentation and metrology skills. The optical scanning microprofilometer used in this work employs single-point, interferometric depth-sensors based on conoscopic holography that enable to measure the surface topography of the manuscript (deformation and roughness) at micrometer scale. The instrument achieves high resolution and accuracy both in depth (down to 1 µm) and in lateral (down to 5 µm) directions as well as being able to scan the manuscript in full-field (areas of tens of centimeters) [2].
The crucial task of the spatial referencing of surface topography at micrometer scale with respect to the manuscript visible features is performed with a novel procedure that solves the problem of the lack of reference points in the microprofilometer height data. We explore the use of the raw intensity signal (Total) collected by the sensor to register interferometric measurements with the multispectral image stack in the UV VIS NIR range. The key-step is that the Total dataset is intrinsically registered with the height dataset allowing the mapping of the in-band imaging information on the surface topography. The joint exploration of the quantitative microsurface knowledge and the in-band imaging responses enables a more comprehensive exploration of the artifact, improving the study of the various features, from the different supports to the different inks. The potential of this new workflow is proved with exemplary case studies presenting different substrates (parchment, paper), inks, pigments, and conservation states (integer, stains, abrasion).

[1] Easton, R. L.; Christens-Barry, W. A.; Knox, K. T., Spectral image processing and analysis of the Archimedes Palimpsest, in: 2011 19th European Signal Processing Conference, Barcelona, Spain, 2011, 1440-1444

[2] Daffara, C.; Mazzocato, S. Surface Metrology Based on Scanning Conoscopic Holography for In Situ and In-Process Monitoring of Microtexture in Paintings. *Sensors,* 22, 2022, 6637.

Analytical pyrolysis for the characterization of mural paintings in street art

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In the last decade, works of street art, located outdoors in urban contexts, have received increasing attention from the public and art history due to their social and cultural relevance [1], but also from conservation science. The ephemeral character, free access, and exposure to the environment and anthropic actions, make indeed public paintings vulnerable to neglect, removal, vandalism, and degradation. Beyond that, the strategies aimed at their preservation and fruition are rather unclear or lacking. The Italian project PRIN 2020 "*SUPERSTAR: Sustainable Preservation Strategies for Street Art"* sets as a goal the definition of innovative guidelines for the preservation strategy of street art, aimed at safeguarding its powerful social and cultural message in the urban context [2]. The availability of effective analytical tools for the identification of artworks materials is thus crucial to support defining the best preservation practices. The cooperative consortium for the Project SUPERSTAR is composed of University of Pisa (project coordinator Prof. Francesca Modugno); University of Bologna (Prof. Silvia Prati), Politecnico di Milano (Prof. Lucia Toniolo), University of Turin (Prof. Dominique Scalarone) and CNR -Perugia (Dr. Laura Cartechini). Superstar project case studies include two prominent public mural paintings located in Milan, selected with the support of Comune di Milano (Area Museo delle Culture, Progetti Interculturali e Arte nello Spazio Pubblico, Dr. Marina Pugliese and Dr. Alice Cosmai): Or.Me by Orticanoodles in Via S. Faustino (2017) and Necesse by SMOE in via Ludovico di Breme (2021).

The two mural paintings have been the object of study of an extensive in-situ non-invasive campaign of measurements carried out by CNR-Perugia [3]. Within this analysis campaign, it was possible to collect some samples from damaged and altered areas in the mural paintings.

The poster describes the results obtained in the analysis of the paint samples by analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS), applied to characterise paint binders and organic additives in the paint formulations [4]. The analyses allowed for the identification of paint binders in the two murals and were interpreted contextually with the results of non-invasive External Reflectance Fourier Transform Infrared spectroscopy (FT-IR). In particular, polyvinyl acetate plasticised with Veova and styrene-acrylic resins were detected in Or.Me, while a nBA/MMA acrylic resin was the binder in Necesse.

[1] J. I. Ross, P. Bengtsen, J. F. Lennon, S. Phillips, J. Z. Wilson, In search of academic legitimacy: The current state of scholarship on graffiti and street art, The Social Science Journal 54, 2017, 411.

[2] https://prin2020superstar.dcci.unipi.it/

[3] B. Brunetti, C. Miliani, F. Rosi, B. Doherty, L. Monico, A. Romani, A. Sgamellotti, Non-invasive investigations of paintings by portable instrumentation: the MOLAB experience. Analytical Chemistry for Cultural Heritage, 2017, 41.

[4] I. Degano, F. Modugno, I. Bonaduce, E. Ribechini, M.P. Colombini, Recent advances in analytical pyrolysis to investigate organic materials in heritage science. Angewandte Chemie International Edition, 57, 2018, 7313.

Unveiling the secrets of 'verre églomisé' paintings: potential and limits of a non-destructive analysis

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As part of a research project on the recipe book of the 18th-century reverse glass painter Ulrich Daniel Metzger [1], we examined two paintings by the artist and one by his close friend and master Gerhard Janssen. The three artworks were executed in the *verre églomisé* technique, a special kind of reverse glass painting that involves the application of leaf metal to the painted side of the glass panel [2]. The layer of leaf metal prevents direct access to the painted glass surface, occasionally leaving only small areas uncovered (Fig. 1). Non-destructive analysis of *verre églomisé* paintings is therefore very challenging. In our case, the analysis was further complicated by the fact that the artworks are very fragile and have altered over time and that they have been restored in the past. To tackle these problems, we have used a combination of non-destructive and non-invasive methods that include visual analysis, analytical photography, reflectance transformation imaging (RTI), micro-XRF and micro-FTIR spectroscopy in external reflection mode. The aim of our work is thus twofold: firstly, to match historical paint recipes, including the ones noted in Metzger's manuscript, with the materials present in the reverse glass paintings; secondly, to discuss the pros and cons of the various methods we used. The combination of the different techniques proved to be a powerful tool for the characterisation of pigments, binders, leaf metals and other painting materials used in *verre églomisé* paintings, but it also revealed the difficulties encountered when analysing complexly structured and fragile artworks that have deteriorated and been restored. This study thus not only provides new information on the materials and techniques used by 18th-century reverse glass painters. It also shows the potential and limits of our multi-analytical approach and sheds light on the challenges and practicalities of analytical methods frequently used in cultural heritage analysis and conservation science.

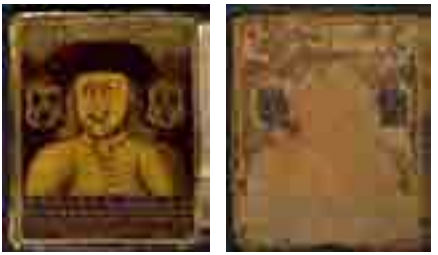

Fig. 1. Ulrich Daniel Metzger, recto and verso of the portrait of Gerhard Janssen, 1725, 150 mm × 122 mm × 3.8 mm, Vitromusée Romont, PSV_824, photos (VIS, RTI) by Martin Stollenwerk, SIK-ISEA.

[1] U. Bergmann, S. Wolf, M. Gartenmeister, E. Ambrosio, U.D. Metzger – Handschrift eines Hinterglasmalers. Digitale Edition, Kommentar und Werkverzeichnis, Romont, 2022. https://ulrichdanielmetzger.digital (last access 11/01/2023).
[2] E. Ambrosio, S. Wolf, «Bleÿgelb, Umbra únd Silbergledt». Les recettes de couleurs du peintre-verrier et peintre sous verre Ulrich Daniel Metzger, NIKE-Bulletin 1, 2019, 48–51.

Collaborative Efforts in Preserving Cultural Heritage: The "Forte das Memórias" Project

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The project is the "Forte das Memórias," funded by the European EEA Grants program, seeks to revitalize tangible and intangible heritage through the safeguarding of the Fort of Nossa Senhora dos Anjos de Paimogo, Lourinhã (Portugal). By recovering traditional technological knowledge and the history of the site, the project aims to foster the local community culture. The ongoing research is grounded in a dynamic interaction with the community, which will facilitate the understanding and integration of the spirit of the place in an exhibition space within the Fort.

The "Forte das Memórias" project involves various aspects, including research on the history and culture associated with the Fort of Paimogo, interviews with local residents, documentary research, analysis of historical images, and rehabilitation of the Fort. The rehabilitation process will respect the original architecture and materials, and a permanent exhibition will be installed to narrate the history of the Fort and its connection with the local community. The exhibition will include photographs, audiovisuals, and other materials gathered during the research.

The project also plans to develop a website and virtual platform for the local community to access and interact with the information collected during the research process, as well as to expand the dissemination of the project's results and activities.

The "Forte das Memórias" project exemplifies the importance of interdisciplinary collaboration between art history, conservation, education, and science in preserving cultural heritage. By engaging with the local community and utilizing research and technology, the project aims to promote an understanding and appreciation of the Fort's history and cultural significance. Ultimately, the project seeks to preserve local heritage, foster a sense of identity, and encourage continued learning and interaction within the community.

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Microscopic studies of red ochre fresco paint layers replicas treated with nanolime

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Wall paintings are subject of constant aging and deterioration as increasingly threatened by natural and human impacts, deserving particular attention in terms of conservation. This implies an urgent need of innovative non-toxic sustainable materials, compatible with the original artwork, with long-term efficiency, easy for application. Nanomaterials have been seen for the last decade as a good alternative to traditional materials for long term preservation of cultural heritage. They exhibit distinct properties when compared to their bulk analogues and their main advantages are high surface area and increased chemical reactivity. Alcohol nanoparticles dispersions of alkali earth metals hydroxides ($M(OH)_2$, where M = Ca (nanolime), Mg, Sr) have been seen as suitable alternative of traditional materials for consolidation of lime mortar, stone, paper, wood and earthen constructions [1]. Some of their beneficial characteristics are enhanced stability, good penetration capacity inside decayed substrates, high potential for long-term durability and efficiency. However, there are still factors related to their application that have to be fully understood; for example, the carbonatation mechanism after the application and how the aesthetical changes of the treated substrates (for example, the common white veil/haze formation) may be avoided.

In this regard we have developed innovative nano- and sub-micro innovative consolidants for different substrates. In the course of our studies on the effectiveness of laboratory synthesized nanoparticles of $Ca(OH)_2$ and $Mg(OH)_2$ as consolidants for wall paintings we have focused our research to widen the understanding of the effect of treatment with alcohol dispersions of $Ca(OH)_2$ on lime frescoes and *buon* frescoes paint layers with lack of cohesion [2]. This is of particular interest given that paint layers have important role for the support preservation despite their aesthetical significance [3]. For this purpose, replicas of paint layers with lack of cohesion were prepared and treated with concentrated dispersions of laboratory synthesized nanolime ($Ca(OH)_2$ dispersed in 2-propanol, 25 g/L). The preliminary results [2] have shown that the laboratory nanolime carbonatates incompletely and also red ochre paint layers were most affected with aesthetical change through a white haze formation in comparison to yellow ochre and smalt. In this communication we report the microscopy analysis of the effect of treatment with nanolimes on red ochre paint layers prepared by *buon* and lime fresco techniques. With this research we intend to contribute towards better understanding of the effect of the nanolimes on lime frescoes and *buon* frescoes ochre paint layers that would be beneficial for conservator-restorers.

[1] J. Zhu, P. Zhang, J. Ding, Y. Dong, Y. Cao, W. Dong, X. Zhao, X. Li, M. Camaiti, Journal of Cultural Heritage 50, 2021, 25.
[2] B. Baiza, M. Gil, C. Galacho, A. Candeias, P. I. Girginova, Heritage 4, 2021, 3288.
[3] M. Gil, Conservar Patrimonio 39, 2022, 45.

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Lead Isotope Analysis of Delftware via Portable Laser Ablation

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Delftware is a type of earthenware pottery that originated in Delft (NL) in the 17th century, characterized by its blue and white decoration applied to a white glaze. Lead-tin glazes are rich in lead, ideal for lead isotope analysis, a technique that provides information on the provenance of the raw materials, the method and time of production of these objects. This study investigates the application of portable laser ablation and MC-ICPMS (multi-collector inductively coupled plasma mass spectrometry) to analyse the lead isotope ratios (LIR) of seventeen 17-18th century Delftware earthenware objects. A method was developed to minimize invasiveness while obtaining enough material for accurate analysis. The results will be used to gather more information about the total variation, in time and space, of LIR between of Delftware produced in The Netherlands. All objects were analysed in triplicates to establish the heterogeneity of LIR within the glaze and to assess the amount of ablation needed for future sampling campaigns.

The proposed sampling method was successful, allowing to sample, on average, 400 ng of lead, leaving a microscopic hole invisible to the naked eye. The triplicate analyses demonstrated that the LIR were homogeneous within the glaze, suggesting that a single ablation per object is sufficient. The comparison of the LIR of the 17 Delftwares indicated a main "Dutch" cluster, with a common provenance of lead (British) used to in the lead-tin glaze. Within this cluster, small LIR variations were observed, possibly due to minor changes in the lead source in time. The study also found that lead used for post-production glaze retouching had significantly different lead isotope ratios, showing that the use of a different materials is easily detectable using lead isotopes.

In conclusion portable laser ablation combined with lead isotope analysis has great potential for further application in the study of lead-tin glaze earthenware. The data can be used to build a dedicated LIR database for Delftware. This database, once fully implemented, can provide useful information on the provenance of the raw materials used to produce Delftware, and used by museums and other institutions to test the authenticity of lead-tin glaze objects. Future isotopic studies will focus on distinguishing Delftware according to the time of production and factory of origin. This could provide valuable new insights into Delftware production, establishing a more detailed understanding of the history of Delftware and its place in the cultural and economic context of the 17-18th century Netherlands.

Chemical, phase, and thermal characterization of Roman and Late Antique clay wall plasters

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Keyword: Late Antique and Roman plasters; thermal analysis, phase and structural analyses

This work investigates the chemical and phase compositions as well as the thermal behavior of eight clay wall plasters from six Bulgarian archaeological sites (three from the Roman age and three from Antiquity). For this purpose, a suitable complex of analytical methods was used - X-ray fluorescence, powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR), and thermal analysis (TG/DTG-DSC) [1].

The results prove the application of low-temperature treatment to the plasters (~300°C up to 400°C). During the fieldwork, no evidence of fire was found in the archaeological sites. This is an indication of a purposeful implementation of a thermal process during the plasters' preparation. Such thermal treatment, with approximately the same temperature, indicates the same approach in plaster preparation during both epochs.

The analyses detect the mineral composition and the types of raw clay - non-calcareous and calcareous, which also determines the different colors of the thermally treated wall plasters [2, 3]. The specified plasters' phase composition coincides with the possible weathering products of the rocks' outcrop on the earth's surface at the archaeological sites, which suggests the use of local raw materials with high probability (5 of the sites are without clays nearby). The use of local clay can also be accepted for the sixth site, where clays exist.

The obtained results are fundamental, showing good knowledge of the environment during both periods, skill in using various raw materials, and continuity in technology, which is a decisive prerequisite for achieving sustainable results. The characterization of wall plasters also has practical value, such as creating wall plasters compatible with the old ones in order to restore and conserve archaeological sites.

[1] P. Cardiano, S. Ioppolo, Co. De Stefano, A. Pettignano, S. Sergi, P. Piraino, Analytica Chimica Acta 519, 2004, 103–111.
[2] Z. Goffer Archaeological chemistry. John Wiley & Sons, Inc., Hoboken, New Jersey 2007p 623.
[3] A.V. Kornilov, Reasons for the different effects of calcareous clays on strength properties of ceramics. Glass and Ceramics. 62, 2005, 391–393.

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Advances in neutron resonance absorption imaging for material characterisation

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We present recent advances in the implementation of a non-destructive radiographic technique, named Neutron Resonance Transmission Imaging (NRTI), performed at the INES [1] beamline of the ISIS spallation neutron source [2].
High epithermal neutron fluxes are made available by neutron spallation sources, enabling the isotopic and elemental characterisation of materials thanks to the presence of intense resonance structures in the neutron-induced reaction cross-sections [3]. The NRTI technique is based on the resonant absorption of the incident epithermal neutrons, resulting in a transmitted neutron beam containing characteristic dips univocally related to the material's elemental composition.
A time and spatial-resolved detector is employed for NRTI measurements, allowing the visualisation of radiographs of the object bulk. In contrast with standard neutron radiography, through NRTI is possible to localize the distribution of elements and isotopes by selecting a resonance of interest, enhancing the contrast between elements with similar neutron attenuation coefficients.
The striking features of NRTI make it suitable for the characterization of inhomogeneous samples [4,5], in particular for Cultural Heritage studies. Reference NRTI measurements have been performed on different certified samples to test the elemental and isotopic sensitivity of the imaging set-up. Potential applications of NRTI will be presented with special examples of characterization of archaeological samples.

[1] A. Pietropaolo *et al.*, Applied Spectroscopy, 64(9), 2010, 1068–1071.
[2] https://www.isis.stfc.ac.uk/
[3] H. Postma, P. Schillebeeckx, Encyclopedia of Analytical Chemistry (ed John Wiley & Sons Ltd), 2009.
[3] F. W. K. Firk 1979 Nucl. Instr. Meth. 162:539-563
[4] A. Fedrigo *et al.*, J. Anal. At. Spectrom. 34, 2019, 2420-2427.
[5] G. Festa *et al.*, J. Anal. At. Spectrom. 30, 2015, 745-750.

Glass in the Southwestern Iberian Peninsula during the Iron Age – the case study of Casas del Turuñuelo (Guareña, Badajoz, Spain)

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The archaeological site of Casas del Turuñuelo, located in the municipality of Guareña (Badajoz, Spain) in the vicinity of the Guadiana River, is a monumental earthen building. Dated from the 6th to 5th centuries B.C., this extremely well-preserved protohistoric building being excavated since 2014, is a testament of the Tartesian civilization settled on the Guadalquivir basin but with an area of influence that included the whole Southwestern Iberian Peninsula [1,2].

Excavations campaigns carried out in Casas del Turuñuelo in 2016, 2017 and 2022 uncovered a set of five glass beads, four glassworking by-products and a granule of Egyptian blue frit. Preliminary analysis using a non-destructive methodology including handheld X-ray fluorescence (h-XRF), variable pressure scanning electron microscope coupled with energy dispersive X-ray spectrometry (VP-SEM-EDS) and micro-X-ray diffraction (µ-XRD) indicate that the glass samples from Casas del Turuñuelo bear witness of an, as of yet, underrepresented Iron Age glassmaking tradition which relies on using plant ashes (wood ash and/or a mix of wood and halophytic plant ashes) as the fluxing agent, as opposed to the dominant contemporary tradition of using mineral soda (natron) fluxing agent [3]. The addition of trace element analysis, using the minimally invasive laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), will provide more information regarding the raw materials used in the production of the glass found in Casas del Turuñuelo and shed light on the location of the primary production center where the glass was manufactured. This study will bring forth new information regarding the complexity of glass production and exchange in Mediterranean and Iberian world in the Iron Age.

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[1] E. Rodríguez González, S. Celestino Pérez. CuPAUAM 45, 2019, 179-202.
[2] E. Rodríguez González, J.R. Casals, S. Celestino Pérez. Virtual Archaeology Review 14(28), 2023, 38-53.
[3] J. Henderson. Ancient glass. An interdisciplinary exploration, 2013. New York: Cambridge University Press.

A New Approach for Accessing Hidden Text on Papyri Written with Carbon Ink*

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In the Papyrus Collection of the Egyptian Museum in Berlin (as well as in magazines worldwide) a multitude of papyri is stored, fragments of different sizes, some rolled, some folded, some quite irregular bundles. To get access to this source of profound knowledge we have to reveal the texts hidden in these delicate and precious objects and make them publicly available in open access databases. In particular, the inter- and multi-disciplinary research (humanities, imaging technologies, image processing and data visualization) has reached a high quality in recent years allowing to address this challenging task. Conventional X-ray or synchrotron radiation tomography was recently quite successful in getting access to the text when higher Z element containing admixtures were used in the inks.

In the case of carbon black - the majority of ancient papyri is written with carbon ink; however, the contrast between ink and papyrus is not sufficient, and other means of contrast are mandatory to distinguish writing from base material. Here we present preliminary results of a different, very promising approach using electron paramagnetic resonance (EPR) spectroscopy. As summarized in the EPR spectral library of pigments [1], carbon black shows a single-line, well-pronounced signal from the unpaired electron within the pigment. Fragments from the papyrus collection of the Egyptian Museum in Berlin written with carbon black ink and mockups prepared with carbon black showed an EPR signal of high intensity as compared to fragments without ink. These results and recent progress in largely improved sensitivity in EPR may comprise a promising step forward in the development of an imaging tool for papyri written with carbon ink.

[1] O.R. Kuzio, J.P. Hornak, Heritage 5 (2022) 545-566.

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Two Palettes by Henri Matisse from the Collection of the Pushkin State Museum of Fine Arts

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Many works by Henri Matisse from the collection of the State Museum of Fine Arts were donated by Lydia Nikolaevna Delektorskaya, Matisse's secretary. Among her gifts there are two of the artist's palettes of 1937 and 1939, the unique objects that allow us to discover what colors Matisse preferred to use and how he mixed them (Figure 1).

Fig. 1. Photos of Henri Matisse's 1937 palette. On the back side there is a donation inscription *Mme Lydia Delectorskaya Henri Matisse 37* and a label stating that the palette was exhibited in the Galerie Rene Breteau, Rue Bonaparte 70, Paris, in 1944.

The technological study of the palettes is caried out in the laboratory of the State Research Institute for Restoration. To identify the chemical composition of art materials, microsamples of paints were examined by means of analytical methods, such as polarizing microscopy (PLM), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), μ-FTIR spectroscopy, and μ-Raman spectroscopy.

The study showed that while working on the palette (Figure 1) the artist used a variety of paints. The following pigments were identified: lead and zinc whites, French ultramarine (mixed with lead white), viridian (mixed with lead white), yellow ochre with kaolinite, strontium yellow (mixed with zinc white), cadmium yellow, cadmium orange (mixed with zinc white; an atypical spherical shape of cadmium orange crystals is observed in the sample), two types of cadmium red with varying selenium content, synthetic alizarin (mixed with lead white and kaolinite), brown ochre (with kaolinite, gypsum and barium sulfate), and two types of cobalt violet (cobalt phosphate and cobalt magnesium arsenate). Oil, natural resin, and in some cases protein were identified as components of the paints binder.

Direct inlet pyrolysis GC-QToF-MS for the study of organic materials in cultural heritage

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Analytical pyrolysis has long been recognized as an extremely useful technique for the study of cultural heritage material, especially for polymeric organic compounds [1]. Various types of pyrolyzers exist, but all are generally characterized by an almost instantaneous heating rate and temperatures between 400-1000 °C. Another thermal decomposition method can be obtained by using the Thermal Separation Probe, or TSP, which allows direct inlet pyrolysis-GC-MS, or DIP-GC-MS. The TSP sits in a multimode inlet (MMI), which is able to heat up to a temperature of 450 °C. Although this temperature is lower than traditional flash pyrolysis, it is high enough to thermally decompose many compounds. DIP-GC-MS has already been shown to afford a method of analysis comparable to Py-GC-MS for many organic cultural heritage materials, such as synthetic resins [2] and amber [3].

This paper will illustrate how direct inlet pyrolysis-gas chromatography-quadrupole-time of flight-mass spectrometry (DIP-GC-QToF-MS), may be utilized to analyse a variety of natural organic cultural heritage materials, including indigo and lake pigments, through comparison with more traditional Py-GC-MS. The TSP is highly versatile, able to analyse liquid or solid samples with a variety of derivatization agents, with similar inlet conditions to either GC-MS or Py-GC-MS. A series of examples will be used to illustrate how the combination of extremely small sample requirements of a GC-QToF instrument, together with the possibility of undertaking tandem mass spectrometry (MS^2) for structural studies, makes this a powerful tool for the investigation of paintings and archaeological artefacts.

[1] I. Degano, F. Modugno, I. Bonaduce, E. Ribechini, MP. Colombini, Angewandte Chemie International Edition 57, 2018, 7313–23.
[2] J. Poulin, M. Kearney, M-A. Veall, Journal of Analytical and Applied Pyrolysis 164, 2022, 105506.
[3] J. Poulin, K. Helwig, Organic Geochemistry 86, 2015, 94–106.

Dry pastel: from the artistic technique on Gaulli's frescoes to material for the wall paintings reintegration

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Keywords: Gaulli's frescoes, reintegration, handcrafted dry pastels, reversibility, UV fluorescence, zinc white marker.

On the frescoes by Giovan Battista Gaulli (1639-1709) and his pupils in the deconsecrated church of Santa Marta al Collegio Romano (1671-1672) in Rome, the diagnostic investigations (XRD, FT-IR, Raman Spectroscopy, SEM-EDS) revealed the use of dry pastel. Starting from these unexpected results, this work aims to test the validity of handcrafted and self-produced dry pastels as uncommon reintegration method on mural painting in comparison with the materials typically used in the reintegration of stains and abrasions, such as lime painting, varnish colours [1, 2].
As a first step, we have produced a wide range of handcrafted dry pastels, mixing three different concentrations of gum tragacanth with the pigments used on Santa Marta paintings: Ochre and Brown earth, Cinnabar, Malachite, Smalt, White Lead (Figure 1). Then, we have applied on different specimens of frescoes the handcrafted pastels and we have tested the UV stability, the adhesion and reversibility properties (i.e. scotch tape test) in comparison with two commercial brands of dry pastels (Schmincke and Rembrandt soft pastels). The effects of UV radiation exposure, in the climatic chamber with UV (340 nm, 1W/m^2), T = 50 °C, have been monitored for 40 days by spectrocolorimetry. These measurements have shown that the handcrafted pastels have good UV stability and better reversibility than commercial pastels, with high potential for wall paintings reintegration approach.
Finally, we have tested Zinc White (ZnO) as a marker of reintegration, adding two different concentration into the formulations of handcrafted pastels (Figure 2). This pigment has been useful to give an intense fluorescence to the handcrafted pastels: this promising approach ensures the easy recognition of the dry pastels over the reinstated wall paintings.

Figure 1, Handcrafted dry pastels based on Gaulli's palette

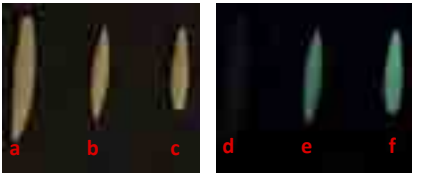

Figure 2, Handcrafted dry pastels; left: under VIS light (a=0% ZnO, b=1% ZnO, c=3% ZnO); right: under UV light (d=0% ZnO, e=1% ZnO, f=3% ZnO)

[1] C. Gombaud, L. Sauvage, Sources on Art Technology. Back to Basics= Proceedings of the Sixth Symposium of the ICOM-CC Working Group for Art Technologie Source Research, held at the Rijksmuseum, 2016, pp. 115-23.
[2] J. H. Townsend, The Paper Conservator, 22 (1), 1998, pp. 21-28.

Curing of ultramarine blue oil paints: the effect of different characteristics of the pigment

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Ultramarine blue is a deep blue inorganic pigment. It's a sodium aluminium sulfosilicate with approximate formula $Na_{6-8}Al_6Si_6O_{24}S_{2-4}$, where the proportions of Al, Si and O are fixed, while those of Na and S are variable [1]. Originally, this color was made by grinding lapis lazuli, a precious stone known since the Egyptians, and purifying it with a complex process. Starting from the 19th century, ultramarine blue has been artificially produced by heating kaolin, soda, sulfur and coal at high temperatures (800°C) [2]. The chemical composition of artificial ultramarine blue is variable and depends on the ratio between the raw materials and on the experimental conditions of the preparation.

A previous study [3] demonstrated that synthetic ultramarine blue in an oil paint has the tendency to favor the oxidative degradation of the organic binder over cross-linking. This may have consequences on the stability of the paint layers produced, as they can be quite polar and poorly cross-linked. The aim of this study is to understand how the origin and the characteristics of different ultramarine blue pigments influence the effect exerted by the pigment in the curing of an oil paint layer.

To this aim, we selected different artificial ultramarine blue pigments and a sample of natural ultramarine blue from lapis lazuli. The pigments differ for particle size distribution, types of additives and the presence of superficial coatings. The pigments were characterized by SEM and XRD to investigate the particle characteristics and mineralogical composition. Model paints were prepared with linseed oil, and were analyzed using ThermoGravimetric Analysis (TGA), Rheological Analysis, Solid Phase Micro Extraction – Gas Chromatography – Mass Spectrometry (SPME-GC-MS) and Evolved Gas Analysis – Mass Spectrometry (EGA-MS). This approach enabled the systematic comparison of the rheological properties, curing kinetics, oxidative behavior of the paints, and the molecular characteristics of the paint films.

[1] J. Plesters, Studies in Conservation 11.2, 1966, 62-75
[2] R. Mayer, The Artists' Handbook of Materials and Techniques, 1991.
[3] S. Pizzimenti, L. Bernazzani, M. R. Tinè, V. Treil, C. Duce, I. Bonaduce, ACS Applied Polymer Materials 3.4, 2021, 1912-1922
[4] L. Vannoni, S. Pizzimenti, G. Caroti, J. La Nasa, C. Duce, I. Bonaduce, Microchemical Journal 173, 2022, 107012

Attempts to use head space gaschromatography to determine solvent retention in easel painting paint layers subjected to conservation treatments

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Conservation treatments often consist of removal of aged varnishes or overpaintings. During these actions, the original paint layers may be exposed to the harmful side-effects resulting from the retention of used solvents which penetrated into the structure of the painting layer [1], [2], [3].

The scale of this side-effects may vary, depending on the application method and solvents used [4]. However, in terms of the effectiveness of the conservation procedure itself, the side-effects are only intuitively assessed during the solvent selection.

This work presents preliminary studies on the correlation between the type of solvent carrier used, extent of the solvent residues and their retention in the painting layer. The studies were carried out using gas chromatograph, equipped with FID as a detector and a headspace to analyze qualitatively the solvents retained in the painting layer.

For this research, four different carriers were selected, each of which possessed different nature and composition and an exemplary two-component solvent mixture that might be used to remove the secondary layer (such as the aged varnish or the overpainting).

The tests were conducted on mockups of identical paint layers, prepared with a hand-made paint containing oil binding medium, imitating an old paint layer. Four-time intervals for collecting data, i.e., amount of individual solvent present in the oil paint layer were selected [5].

The results of this study will allow to determine the possibility of using the elaborated procedure to predict the consequences of solvents application by different methods during overpaintings removal in easel paintings, which is planned in the next stage of research.

[1] A. Phenix, K. Suterland, The cleaning of paintings:effects of organic solvents on oil paint films, Studies in Conservation, 46 (2001), 47-60.

[2] S. Zumbühl, E. S. B. Ferreira, N. C. Scherrer, V. Schaible, The Nonideal Action of BinarySolventMixtures on Oil and Alkyd Paint: Influence of SelectiveSolvation and Cavitation Energy, Conference: Cleaning 2010. New Insights into the Cleaning of Paintings Volume: SmithsonianContributions to Museum Conservation. Number 3, p. 102.

[3] L. Baij, J. Hermans, B. Ormsby*et al.* A review of solvent action on oil paint. Herit. Sci. 8, 43 (2020)

[4] D. Stulik, D. Miller, H. Khanjian, N. Khandekar, R. Wolbers, J. Carlson, W. C. Petersen, Solvent Gels for the Cleaning of Works of Art: The Residue Question, Getty Publications, 2004

[5] L. Masschelein-Kleiner, Les solvants, vol. 2 from Cours de conservation, Institut royal du patrimoine artistique, 1994, p. 35-38

Vermeer under different wavelengths

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In the last decades hyperspectral reflectance imaging spectroscopy (RIS) has gained a firm foothold in the non-invasive examination of paintings [1]. RIS in the visible to near infrared spectral range (VNIR, 400 to 1000nm), is more sensitive to the surface composition and is a useful tool for the identification and mapping of artist's pigments. RIS in the short wavelength infrared (SWIR, 900 to 2500nm) has a higher penetration depth and it is used to create IR false color images, which provide information about underlayers, revealing under-modelling and compositional changes, as well as mapping specific pigments. The combination of RIS-VNIR and -SWIR can be used to investigate the order of paint reconstructing a sort of non-invasive paint stratigraphy. The combination of molecular information provided by RIS with the complementary elemental information, obtained by macro scale X-Ray fluorescence (MAXRF) imaging, provides a unique tool for the non-invasive characterization of materials as well as the investigation into painting technique and artistic choices.

In the run-up to the most extensive Johannes Vermeer exhibition held in 2023 at the Rijksmuseum (Amsterdam), this imaging toolbox, has been used to analyze an extraordinary series of Vermeer's paintings dating from around 1655 to 1669, spanning from early to late in his career. Exclusive insights were gained into Vermeer's unique painting technique, and trends and developments were discovered. The new research expanded on the previous project of the *Girl in the Spotlight* [2]. In this paper, Vermeer's masterpiece *The Milkmaid* (1660), from the collection of the Rijksmuseum, serves as a center case study to navigate into Vermeer's unique creative process throughout time and production. Focus will be given to the use of RIS-SWIR false color images to unveil changes in composition and understand how Vermeer defined light and shadow in the underpaint. The combination of the chemical information gained in different spectral ranges, will highlight Vermeer's unique implementation of glazes on top of or underneath a more opaquely pigmented layer to achieve a specific tonality.

Figure 1: a) Visible image of The Milkmaid, Vermeer (1660), b) False color RIS-SWIR (1000,1500,2250nm),c)RIS-VNIR map of Ultramarine obtained using Spectral mapper algorithm (SAM).

[1] Striova, J., Dal Fovo, A. and Fontana, R., 2020. La Rivista del Nuovo Cimento, 43(10), pp.515-566
[2] Collection of 10 articles in Heritage Science (2019, 2020): https://www.springeropen.com/collections/gits

Analysis of paintings using X-ray macro fluorescence and Compton scattering imaging

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Macro X-ray Fluorescence Imaging (MA-XRF) is a well-established method for non-invasive investigation of painting surfaces, producing elemental maps. Elemental distribution images acquired by this method can reveal hidden sub-surface layers including modifications made by the artist, provide information about the artist's creative process and his paint palette, also restorations or conservation history of painting. Transmission techniques are well-known methods for inspecting the internal structure of artworks. This method focuses on studying the changes in the intensity of the beam that was transmitted by the sample. These changes are caused by differences in the internal composition of the sample. During a MA-XRF analysis, when we place a scattering material behind the painting, it will be possible to obtain, simultaneously, an elemental mapping of the object and a mapping of the transmission of the scattered radiation. Since the scattering material will increase the contribution of Compton scattering, which will be attenuated in the sample, thus providing a transmission mapping, with information about the structure of the analyzed sample. In this work two paintings were analyzed by MA-XRF technique using a lucite plate as a scatter material in the painting's background. A painting on wood and a painting on canvas were analyzed. The painting on wood is dated 1949 and has dimensions of 37.6 x 46.2 cm. The canvas painting has an unknown execution date and dimensions of 27 x 19 cm. The measurements were carried out using an automated, portable MA-XRF system developed in our laboratory which consists of a low power X-ray tube with a silver target and a SDD detector (Silicon Drift Detector) with energy resolution of 142 eV at 5.9 keV. MA-XRF system moves in the XYZ axes, and it is controlled by a microcomputer. Measurements were performed in the XY plane, the Z axis was for focal adjustment. The scattering material used behind the painting for Compton scattering transmission analysis was a 2 mm thick lucite plate. Through the results obtained by the MA-XRF analysis in the paintings, it was possible to obtain the elemental maps distribution of the following elements: Al, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba and Pb. The Compton scattering transmission analysis obtained better results in the analysis of painting on wood, showing the structural conditions of the artwork, such as cracks in the wood. The combination of the Compton scattering transmission study with the MA-XRF imaging technique in the paintings analysis can be a very useful research tool, enabling, simultaneously, the creation of elemental distribution and transmission maps. This proved to be a very useful technique for a prior analysis of paintings before performing a radiography.

A multi-analytical approach for the archaeometric identification of the Cucuteni pottery firing technology

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Keywords: pottery, Chalcolithic, firing techniques, SEM-EDX, XRD, magnetic measurements

The Cucuteni-Trypillia civilization is considered one of the most intriguing subjects when analyzing South-Eastern European prehistory (5th -4th millennia BC). The ceramic repertoire consists of anthropomorphic and zoomorphic figurines and sophisticated polychrome pottery which has significantly improved our knowledge of daily life and manufacturing skill of Old European civilizations.

This study aims to examine the degree of standardization registered in various sequences of the ceramic *chaîne opératoire*. To identify the technological characteristics of the ceramic production, we have applied a multi-analytical methodological approach to the analysis of thirty-nine pottery samples selected from the eponymous site of the Cucuteni civilization and of ceramic replicates prepared in the laboratory. The compositional and microstructural features of the ceramic paste were determined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), while the firing parameters were identified by X-ray diffraction (XRD) and magnetic measurements.

The estimation of the firing parameters for the majority of the investigated pottery samples suggests the use of a controlled atmosphere and temperature throughout the firing process. This may be caused by a possible transformation in the social and economic strategy related to pottery manufacturing.

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Study of the wooden supports of Madeira Island Primitive Flemish paintings: knowing to preserve.

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The current case study is part of a larger research project on Primitive Flemish paintings from the Sacred Art Museum of Funchal (Madeira Island), with the goal of contributing to the conservation of the wooden supports.

Eleven paintings attributed to the major Flemish workshops from the late 15th century to the first half of the 16th century [1], were chosen for this research. The aim of this study was to identify and characterize the original support, as well as the restorations of the painting's support and preparation layers, while comparing technical solutions and materials.

The technical and material characterization included:

a) the manufacture of the original wooden supports;
b) the restoration of the wooden supports, especially the intervention in the former *Institute of Examination and Restoration of Works of Art* in Lisbon between 1949 and 1955, which was overseen by Fernando Mardel (1884-1960), a 20th century painter-restorer in charge of restoring paintings in Portugal (between 1934 and 1960) [2].

The majority of the paintings are made of Baltic oak wood, according to the research, and the dendrochronology examination allowed the *terminus post quem* production period to be established [3].

It was possible to identify and map the areas intervened on the wooden supports using radiography, as well as characterize the constituent and assemblage elements.

The intervention materials were identified using laboratory chemical analyses, specifically Micro-Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy coupled with Energy Dispersive X-Ray spectrometry, Pyrolysis Gas Chromatography Mass Spectrometry.

This study was conducted as part of the first author's PhD project in Fine Arts - Art Sciences at the Faculty of Fine Arts - Lisbon University, which was funded by ARDITI (Regional Agency for the Development of Research Technology and Innovation of the Autonomous Region of Madeira) through the HERITAS doctoral program.

[1] L. Clode, F. A. B. Pereira. Arte Flamenga: Museu de Arte Sacra do Funchal, Funchal: Edicarte, 1997.

[2] C. Ferreira, F. A. B. Pereira, A. Candeias, M. Lorena. O estudo das intervenções de Fernando Mardel nas pinturas do MASF flamengas do MASF. Contributos para a sua conservação. *MASF Journal, 1*, 72-90.

[3] A Lauw, E. Jansma, H. Pereira. The art trade between Flandres and Madeira Island in the 15th and 16th centuries - The contribution of dendrochronology to the history of portuguese heritage. *Journal of Archaeological Science*, (2022), 42.

Advantages and limitations of Laser Induced Breakdown Spectroscopy (LIBS) to detect light elements in different ferrous cultural heritage objects

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Laser Induced Breakdown Spectroscopy (LIBS) is an optical spectroscopy technique used in many domains that enables multi-elemental mapping and stratigraphic information and detection of light elements in qualitative and quantitative way. LIBS can also perform direct analysis on the objects at ambient conditions.
In order to study archaeological ferrous metals, we used LIBS for the quantification of light element distribution, such as carbon and phosphorus. It remains a challenge for identifying these elements' concentration in ferrous matrices because the iron element has a very large number of emission lines.
We will present in this study the quantification of light elements in archaeological steels with two types of instrumentation: LIBS bulk analysis as in situ and µLIBS mapping. The analysis was carried on the corpus representing the various types of objects encountered in the heritage, such as a semi-finished steel from an archaeological site (several centimeters), a sample of armor from a museum collection (a few mm) and a nail from a historical monument without sample preparation.

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

X. Bai, T. Calligaro, L. Pichon, B. Moignard, Q. Lemasson, M. Gosselin, S. Richiero, P. Dillmann, F. Téreygeol, J. Auber-Le Saux, N. Wilkie-Chancellier, V. Detalle, *Comparative study on quantitative carbon content maping in archaeological ferrous metals with laser-induced plasma spectroscopy (LIBS) and nuclear reaction analysis (NRA) for 3D representation by LIBS*, Spectrochim. Acta B At. Spectrosc., 194 (2022). 106454.

The Molecular Clock of Ageing Oils

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Abstract

The context of this presentation is to give insight into how the process of ageing of different standard Oils connects the actual back traceability to the identification and "date" samples (when available) from paintings or a know palette or oil paint tubes as in this case Aleksander Rodchenko's ones.

The importance of this study, besides attributing a time scale of degradation or *Molecular Drying* of the cold pressed oils, of traceable origin, was to assume this could also be applied to an actual dating/attribution of paint tubes by a inbetween wars timeline, where knowingly there was a shortage of more drying Oils.

The Periodic sampling was undertook during a 6 year PhD project employing both natural and accelerated ageing. These results can contribute to a wider Database of the MaSC user's Group, reportedly to characterise biomarkers, primarily used to diagnose the effect of ageing; secondly the uncertain siccative nature of each oil and its mixtures and admixtures with pigments. Given the variable nature of pigments' electronegativity - more oxidative or reducing. Thirdly, the molecular aided prooxidative effect of metals synergistically combined with heating to different temperatures and/or fourthly washing treatments to remove mucilage.

The standard oils [#]were extracted at Tate Britain in 2009 (according to HART project[]) and aged over a period of 5 years, artificially aged (Xenon arc Solar box) in Lisbon and are still in the process of natural ageing, whom those where regularly sampled.

All samples of the oil paint tubes from the Rodchenko palette (kindly allowed sampling by Maria Kokkori) were analysed in 2010 (Netherlands Royal Heritage Center) within the context of putting these findings in practice (with assistance of Francesca Izzo), 9 tube's samples were analysed by GC-MS with TMAH derivatization, which can be recognizable with their FA profile (whole sample / extracted / residue) and was able to find the traceability back to their components "as Formulated by their " branded companies.

Tracking secondary products in aged paint cross-sections by MALDI-MS Imaging

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In the last two decades, the field of Conservation Science has gained considerable attention in museums and cultural institutions with the aim to better preserve our cultural heritage for future generations. Until recently, the perception of the discoloration of works of art has been based on the empirical observation and experience of artists and conservators. However, over the last 10 years, major advances in non-invasive spectroscopic methods and imaging techniques have made it possible to investigate in great detail the chemical mechanisms involved in (mainly inorganic) pigment deterioration. On the other hand, traditional mass spectrometry (MS) techniques coupled to liquid or gas chromatography are used to identify organic pigments, but the sample preparation required for chromatographic separation implies the destruction of the spatial arrangement within the sample. This makes it difficult to properly track down original organic pigments and their degradation products.

Recently, the AXIS research group started a new research line centered on spatially resolved 2D distribution organic pigment analysis by Matrix Assisted Laser Desorption Ionization - Mass Spectrometry Imaging (MALDI-MSI). Here, we show for first time the potential of MALDI-MSI to investigate the correlation between spatially resolved molecular information with the discoloration process of oil paintings. We will discuss a protocol for the analysis of paint cross-sections achieving a lateral resolution of 10 µm and without losing ionization efficiency due to topography effects. The efficacy of this method was investigated on oil paint samples containing a mixture of organic and inorganic pigments, such as geranium lake and lead white.

The data generated with MALDI-MSI reveals that the pattern of secondary products is significantly different at the light-exposed paint surface than in the bulk and it evolves over time. Furthermore, with this technique we show (1) that it is possible to detect the formation of aggregates between the oil and the metallic ions present in the sample and (2) that their migration throughout the paint during the aging can be monitored. Finally we will discuss the possibilities of combining these results with SR-µ-XRPD data on the crystalline components of the paint samples.

Carbon isotopes in lead white: absolute dating and manufacturing process identification of the pigment

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Lead white has been used for artistic and cosmetic purposes since Antiquity. The recipes for the manufacture of this pigment are recounted in many treatises on painting [1]. Depending on the period considered, cerussite and hydrocerussite were synthetized by corrosion of lead or by industrial processes.

In all cases, a carbon input, mainly in the form of carbon dioxide, was necessary to form lead carbonates [2]. In early times, CO_2 came from microbial activity or fermentation of organic matter, but from the 19th century on, CO_2 was derived mainly from fossil materials. Thus, lead white carried a ^{14}C and ^{13}C isotopic signature that reflects, to the nearest isotopic fractionation, the nature of the reactants [3].

In this presentation, the isotopic signatures of a large corpus of synthetic lead carbonates were measured by Accelerator Mass Spectrometry (AMS) and Isotopic Ratio Mass Spectrometry (IRMS). Results show that ^{14}C discriminates the manufacturing processes of lead white according to the organic or fossil nature of the CO_2 source, and provides absolute dates for pigment produced by the corrosion of metallic lead in a natural fermentation medium. ^{13}C identifies the origin of the CO_2 source more precisely by distinguishing organic, mineral and gas sources.

In conclusion, carbon isotopes identify and date lead white productions [4-7].

[1] Stols-Witlox, MJN. Historical recipes for preparatory layers for oil paintings in manuals, manuscripts and handbooks in North West Europe, 1550-1900: analysis and reconstructions. Chapter 13: Lead white: the implications of the use of different qualities of lead white, 2014. pages 298-319
[2] Gonzalez V et al., Corrosion Science 146, 2019. 10-17
[3] Messager C et al., Journal of Archaeological Science: Reports 46, 2022, 103685
[4] Beck L et al., Communications Chemistry 1, 2018, 34
[5] Hendriks L et al., Radiocarbon 61, 2019, 473-493
[6] Beck L et al., Scientific Reports 10, 2020, 9582
[7] Hendriks L et al., Anal. Chem. 92, 2020, 7674-7682

Quantitative approach to the conservation of bone collections by means of solid state NMR spectroscopy.

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The identification of markers of the modifications occurring in human bones after death in order to assess their state of preservation is of interest for several scientific disciplines and in museums for conservation purposes. To this aim, two indices, obtained from the spectral deconvolution of the ^{31}P and ^{1}H MAS NMR spectra of bones, expressing the relative amount of external amorphous hydrated layer in the apatite platelets of the bone mineral compartment and relating the number of organic protons to the amount of hydrogen nuclei in the OH-groups of bioapatite, respectively, are proposed (Fig. 1). They have been applied to describe the state of preservation of osteological material from three different sites, including one skeletal collection open to the public and bone material hosted in the National Museum in Prague (Czech Republic). The latter index was found to correlate positively with the P/A index obtained from infrared spectroscopy (Fig. 1), and considered an indicator of changes in collagen content relative to the changes in the mineral fraction, as a consequence of alteration of the bone signature at the time of death.

Their sensitivity to changes in the physical and chemical characteristics of bone allowed to identify conditions posing a threat to the preservation of the bones and to recognize distinct diagenetic pathways specific to each group and linked to the burial conditions [1,2,3,4].

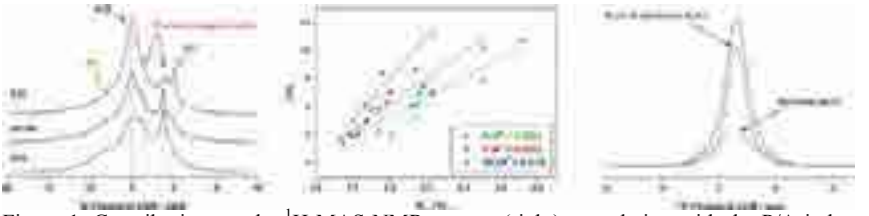

Figure 1. Contributions to the ^{1}H MAS NMR spectra (right), correlation with the P/A index derived from infrared spectroscopy (center) and components in the ^{31}P NMR spectrum (right)

[1] A. Viani, P. Mácová, D. Machová, G. Mali, Forensic Science International 323, 2021, 110783.
[2] A. Viani, P. Mácová, D. Machová, T. Čendak, Archaeometry 61 (5), 2019, 1144.
[3] D. Machová, P. Mácová, G. Mali, P. Velemínský, A. Viani, Arch. Anthropol. Sci. 12, 2020, 257.
[4] A. Viani, D. Machová, P. Mácová, G. Mali, P. Velemínský, Arch. Anthropol. Sci. 13 (3), 2021, 39.

Development of environmentally-friendly biocidal systems based on chitosan-nanoparticles loaded with R-(+)-pulegone to protect wood from fungal attack

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As society is increasingly aware to environmental issues, research into new sustainable strategies is becoming a central topic in the field of Cultural Heritage conservation. This study is aimed to develop a novel biocidal system for the conservation of wooden artworks, by employing reagents, products and synthesis procedures consistent with Green Chemistry principles. To this aim, R-(+)-pulegone (Pu), which is a natural derivative having assessed biocidal properties against several microorganisms [1], also responsible of biodegradation of wood, was selected to be loaded in chitosan nanoparticles (ChNPs) and applied on wooden sample artificially aged and colonized with *Aspergillus niger*, causing soft-rot on wooden artefacts. Nanoencapsulation was performed with a simple and harmless synthesis method, based on ionic gelation of chitosan, which is a versatile polysaccharide derived from chitin and is attracting attention for its non-toxicity, biocompatibility, biodegradability, biocidal properties as well as its consolidant action, recently studied for the conservation of archeological and waterlogged wood [2]. The inhibition properties and the concentrations of pure chitosan and pulegone against *A. niger* were established *in vitro* through a *Multiwell Assay* (MA) and chitosan nanoparticles loaded with pulegone (ChNPs-Pu) at different Ch:Pu ratios (1:0; 1:0.25; 1:0.5; 1:1) were obtained following experimental procedures described in other studies [3], with some modifications to obtain ChNPs-Pu having suitable characteristics for the application on wooden samples. The morphological characteristics of the NPs and their stability on time were considered and characterized through different analytical methods, included dynamic and dielectrophoretic light scattering (DLS), UV-Visible spectrophotometry, Fourier Transformed Infra-Red (FTIR) spectroscopy and SEM analysis. The biocidal and inhibitory potentials of ChNPs at different R-(+)-pulegone concentrations were evaluated against *A. niger* at different experimental conditions. After the successful results obtained with MA, we are experimenting the spray application of the ChNPs-Pu on wooden samples with variable degree and type of biological colonization. Antimicrobial effect of ChNPs will be evaluated by several methodologies, such as colorimetric assays, measurements *A. niger* colonization and relative vitality.
The valuable achievements obtained suggest that adopting natural compounds represent a promising strategy to preserve the Cultural Heritage from biocolonization.

[1] M. Božović, R. Ragno, Molecules, 22(2), 2017, 290.
[2] M. Christensen, E. Larnøy *et al.*, J. Am. Inst. Conserv., 54(1), 2015, 3-13.
[3] X. Wang, Y. Hu *et al.*, JCH, 53, 2022, 206-2011.

Pigments, Dyes, Inks and Binders in a medieval illuminated Psalter: a non-invasive characterization

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The aim of the present work is the non-invasive study of the painting techniques of a magnificent medieval illuminated Psalter kept at the *Biblioteca Antica del Seminario Vescovile* of Padua (MS 353). This parchment manuscript was made in Paris at the end of the 13th century for a prestigious client and represents a superb yet little-known example of Parisian Gothic art [1]. It consists of a wonderful collection of full-page illuminations and historiated initials, a colorful calendar made with refined inks, several decorated initials and decorative elements along the text.

The Psalter has already been the subject of in-depth historic and artistic studies [2] but no analytical investigations have been carried out to date. The combined use of non-invasive analytical methods in portable configuration (Optical microscopy, UV-Vis Fiber Optics Reflectance spectroscopy (FORS), micro-Raman, External reflection infrared spectroscopy (ER-FTIR) and Multispectral Imaging) allowed the comprehensive characterization of painting palette and techniques.

The results highlighted the sophistication of the details and shown the extensive use of precious materials. A very wide micro-Raman (with laser line 785 nm) and FORS investigation was carried out on the pigments, dyes, and inks of the Psalter miniatures. Brown, green, red, orange, pale blue, blue, gray, black, white areas were present. Among the most notable findings, crossing ER-FTIR and Raman it was possible to assess that lapis lazuli was used not only in the blue ink and in the deep blue of holy figures' garments, but in any blue area, as well as on the gray robes and gray backgrounds: gray was a combination of lapis lazuli and carbon black. Pale blue areas were realized mixing San Giovanni white and lapis lazuli. FORS supported the main Raman/ER-IR assignments and allowed the identification of brown areas as due to an organic dye, likely a Kermes-type lake, and green areas as verdigris. ER-FTIR has shown the use of proteinaceous binders, probably egg-white [3], on all the analyzed areas. Finally, Multispectral Imaging using a Full Range Nikon D-800 camera and IR Reflectography using an Opus Osiris camera, with specific passband filters and modified lights, supported the analysis of the technique, underdrawings and particular details related to the use of a different mix of materials confirming the high level and value of this manuscript.

[1] S. Zonno, S., Art de l'Enluminure: Hors-série de arts & métieurs du livre 44,2013, 2-31
[2] S. Zonno, S., Art de l'Enluminure: Hors-série de arts & métieurs du livre 44,2013, 32-57
[3] L. Nodari, P. Ricciardi, Heritage Science 7 (7), 2019, 1-13.

Study of the influence of marine and industrial environment in the formation of salt efflorescence and metal runoff

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This work investigates the influence of marine and urban-industrial environment on the deterioration of a funerary monument located in Getxo (Basque Country, Spain). By means of *in situ* analysis with portable instruments, Raman and X-ray fluorescence spectroscopy, the building materials of the monument, limestone and bronze, and their corrosion products (metal runoff and salt efflorescences) were studied. In addition, some selected sample were taken and they were analysed by means µ-EDXRF and Raman spectroscopy in the laboratory. The results showed that the composition of decay products was strongly influenced by the dry and wet deposition of marine aerosols, acid gases and particulate matter of the atmosphere. In particular, it could be shown, by spectroscopic mapping and point-by-point analysis, that the elemental and molecular distribution in the degradation products was dependent on their sheltering conditions. In addition to the ED-XRF data showing high concentrations of sulfur in the samples, the presence of posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$), brochantite ($Cu_4SO_4(OH)_6$) and antlerite ($Cu_3SO_4(OH)_4$) indicated a high SO_4^{2-} concentration in the environment. Furthermore, a trend we observed was that with the increasing growth of the crust, the formation of malachite was preferred, indicating a decrease of the atmospheric SO_4^{2-} concentration in recent years. The samples collected at an unsheltered position exhibited a layered structure where L1 is a deeper layer and L4 the surface of runoff (Figure 1). Malachite was present in L1, L2, and L3, while copper sulfates were present in L2 and L3. In contrast, the outer layer L4 contains defective Cu2O, sharply separated from the other copper compounds, exactly till the interface of L3. The presence of chlorine compounds such as atacamite ($Cu_2Cl(OH)_3$) and thenardite (Na_2SO_4) could be attributed to secondary marine aerosols, which cannot easily be washed off at this position due to protection from the rain. In addition, the presence of moolooite ($Cu(C_2O_4) \cdot nH_2O$) in the lowest layer of the crust indicated biological activity and an acidic milieu with a high concentration of chlorine beneath the crust.

Figure 1. Image of a sample taken in an unsheltered area and Raman image with copper compounds distribution, where yellow map indicates malachite, blue map copper sulfates and green map defective Cu_2O.

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A novel mobile MA-XRF scanner based on a hodoscopic multi-detector system for application in the cultural heritage field

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Macro X-Ray Fluorescence (MA-XRF) allows us the non-invasive characterization of artworks providing relevant information about original materials and how they have been combined through the peculiar technological or artistic processes. In the last years several technological developments for MA-XRF have been introduced by different research groups working on the field. In this work, we present a novel MA-XRF scanner based on a new 3D multi-detector array composed of 6 SDDs operated in parallel in a fast-mapping mode and arranged in a compact hodoscopic geometry. The total active area of the hodoscope is 240mm^2. The new 6-detector configuration (instead of a single detector with the same active area working with a single detection angle) allows us to increase the overall chemical sensitivity maximizing the output count rate vs. the input count rate while minimizing the dead-time and to investigate objects with a complex topography. The mechatronics of the scanner integrates a three-axes travel system (XYZ) and a real-time processing unit (CPU) with high-computing capabilities. A surface of 120x90cm^2 can be covered in a single scan. The maximum scanning speed is 150mm/sec with a minimal sampling time of 7ms (i.e., corresponding to 1mm pixel-size). However, the scanning can be performed at a maximum lateral resolution of 50µm enabling micro-XRF measurements even in macroscopic contexts. The novel technological aspects of the MA-XRF scanner and some compelling applications are presented and discussed.

The toxicity of historical white lead makeup

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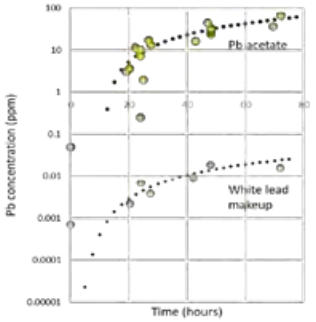
Nowadays, it seems evident that the white lead cosmetics worn by women (and men) for millennia must have been toxic. Museum curators have speculated on the dangers of the practice[1]. However, the toxicokinetics of white lead in makeup is potentially complex. For many makeups[2], people would need to ingest a tablespoonful to be fatally poisoned[3]. We were interested in discovering whether these cosmetics were as dangerous as expected. Being less harmful may have been a reason women continued to wear them until the early 20th century.

One way in which these cosmetics could be extremely poisonous is if lead in makeup was absorbed through skin. Only organic lead is generally believed to be absorbed through skin[4], but we discovered there is little experimental evidence and no published data for white lead[5].

We therefore developed an experimental system to assess the absorption of lead from historical makeup recipes through skin. We use Franz cells, a standard drug testing methodology, to measure the diffusion of lead in recreated historic recipes through pigskin. We will discuss the challenges of measurement of lead absorption through skin.



We will share our data and the mathematical models we use to explain the diffusion of lead through skin from various makeups. For example, this figure shows measurements of the lead levels in saline after diffusion through skin for lead acetate and a white lead makeup. The diffusion depends on several factors, including the important question, 'what exactly is the white lead in our recipes?'.

We shall discuss x-ray diffraction and transmission electron microscopy results that helped us understand the composition of the white lead used in our recipes and the factors that could affect absorption into skin. Our diffusion results map onto simple diffusion models, but. lead is ubiquitous and contamination can make data noisy. Better models may explain the diffusion. We will discuss whether synchrotron μ-XRF lead distribution measurements through pigskin may help explain the toxic properties of white lead makeup.

[1] https://www.sciencemuseumgroup.org.uk/blog/dangerous-beauty-hazardous-chemicals-and-poisons-in-historic-cosmetics/ (Retrieved February 2, 2023)
[2]Chandler CF. REPORT OF PROF. CF CHANDLER TO THE METROPOLITAN BOARD OF HEALTH. American Journal of Pharmacy (1835-1907). 1870 Jul 1:362.
[3] Lech T. Exhumation examination to confirm suspicion of fatal lead poisoning. Forensic science international. 2006 May 10;158(2-3):219-23.
[4] Kehoe RA. Pharmacology and toxicology of heavy metals: lead. Pharmacology & Therapeutics. Part A: Chemotherapy, Toxicology and Metabolic Inhibitors. 1976 Jan 1;1(2):161-88.
[5] Toxicological Profile for Lead, ATSDR, Department of Health and Human Services, USA August 20

Seeing the invisible: unveiling degraded World War 1 diary of the writer C. E. Gadda through an innovative approach

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Carlo Emilio Gadda was an important Italian writer and poet born in 1893 and died in 1973. He joined Great War as a lieutenant of the Alpini corps and in October 1917 he was taken prisoner with his squad during the famous battle of Caporetto. In this period, he wrote a detailed series of diaries of his life as a soldier and prisoner, in the way that a writer is able to do it. One of this original war diary was conserved in the National Library and damaged by the flooding of the Arno river in 1966 together with more than one million books, periodicals and journal. After a period of waterlogging, the diary was rescued, each page was separated, washed, dried and then consolidated using Japanese paper applied on each page of the diary. The combined effect of ink dilution by water and the covering with Japanese paper, made most of the pages of the diary illegible. The multidisciplinary approach of ink characterization combined to multiband imaging allowed a specific approach to the issue of hard legible text in the document. A preliminary analysis on the ink and the paper support using XRF and FTIR spectroscopies have made it possible to specifically apply multiband imaging investigations. UV, infrared, and visible range were used in combination to maximize the contrast between ink residue and the paper [1], with the fundamental role of the post-processing where ad-hoc algorithms were written to solve all the specific issues affecting the pages such as stains, decay and the presence of very little ink traces. With this approach, most of the 92 pages were made legible and were returned to the scholars, allowing the examination of landmark documents written by an important writer during World War 1.

[1] Gargano, M., Bertani, D., Greco, M., Cupitt, J., Gadia, D., & Rizzi, A. (2015). A perceptual approach to the fusion of visible and NIR images in the examination of ancient documents. Journal of Cultural Heritage, 16(4), 518-525.

The Heritage "BAG" at the European Synchrotron Radiation Facility: a new collaborative access modality for the structural analysis of historical materials

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In 2020, the ESRF was upgraded to become the ESRF-EBS (Extremely Brilliant Source), resulting in an increased brightness and coherence of the synchrotron beam, paving the way to cutting-edge analytical capacities [1]. Within the upgrade, continuous developments of beamline instrumentations boosted their speed. This motivated the development of new access modalities, one of which is the new block allocation group (BAG) for structural investigations of historical materials, which combines many short (< 1shift) proposals from different groups into a single proposal [1]. Within the Heritage BAG, different projects are grouped together under the requirement that they all need structural information obtainable by X-ray powder diffraction (XRD) at the ESRF, either through high-angular resolution XRD at ID22 [2] or high-lateral resolution 2D µXRD mapping at ID13 [3]. Through the BAG, regular access to ID22 and ID13 (once every 6 months) is provided for a 3-year period (2021 - 2024) to all the partners. As of today, 11 research groups from 6 European countries are collaborating in the Heritage BAG [4]. While they all work on different projects and materials, they all share the same need for state-of-the-art structural information. The BAG allows the synergy between "expert" synchrotron user groups and new groups to be increased, thus creating a new scientific network structured around the ESRF, fostering new European collaborations, and finally resulting in an important scientific output.

This poster will present the BAG in detail, by providing specifications on the analytical configurations accessible and introducing research case studies already tackled within the BAG. The objective is to highlight how this new access mode provides an easier and efficient access to synchrotron capacities to our community and to encourage new groups to join this collaborative venture.

Keywords: synchrotron, X-ray diffraction, BAG, new access modes

[1] M. Cotte et al., Molecules (2022) 27(6):1997
[1] https://www.esrf.fr/about/upgrade
[2] V. Gonzalez et al., Anal. Chem. (2017) 89(24): 13203
[3] V. Gonzalez et al., Angew. Chem. (2019) 58(17): 5619
[4] https://www.esrf.fr/BAG/HG172

The "Historical Materials" Block Allocation Group: A New Shared Access

Introduction of a new silicon drift detector equipped with graphene window to a portable X-ray fluorescence spectrometer and application on nondestructive and onsite analysis of historical glass artifacts

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Graphene is a material composed of a monolayer of carbon atoms. Because of a superior transmittance for low-energy X-rays and a light-shielding property, graphene has been focused as a new material for an entrance window of a silicon drift detector (SDD), one of the most important components of X-ray analytical devices, including portable equipment suitable for onsite analysis. In this study, a new SDD equipped with the window made by graphene was introduced to a portable X-ray fluorescence spectrometer (P-XRF) with the aim of applying it to nondestructive and onsite analysis of cultural heritage and arts.

P-XRF used in this study is a custom model of 100FA (Ourstex Co., Ltd.), which was originally designed to enable the efficient detection of both Na and Mg by utilizing a sample chamber connected to a small vacuum pump and a SDD equipped with a thin polymer window [1]. After the successful introduction of a new SDD module (VITUS H30, KETEK GmbH) with the graphene window (~900 nm thickness) into the measurement head of this equipment, we analyzed certified standard glass samples in a laboratory to verify its analytical performance, especially a sensitivity for light elements such as Na and Mg. As the result, it was verified that our spectrometer with the new graphene window SDD has a good sensitivity for both Na and Mg at the similar level as the previous model with the polymer window SDD under the vacuum condition. In addition, we also demonstrated the spectrometer enabled us to detect small amount of Na and Mg without making physical contact between the sample surface and the equipment under normal atmospheric pressure.

As practical applications for the onsite investigation of cultural heritage, we brought the spectrometer into museums and research facilities in Japan and used it for chemical composition analysis of historical glass artifacts in the nondestructive and non-contact manner. Because the abundance of light elements including Na and Mg is a significant indicator in distinguishing types of raw materials used for historical glass artifacts, their accurate quantification is necessary. For example, we analyzed some pieces of ancient glass vessels stored at Okayama Orient Museum and revealed that they all are made of soda-lime glass but composed by several compositional types associated to different primary production regions, i.e., Mediterranean region, West Asia, and Central Asia. By applying this approach to other cultural heritage and arts that are difficult to destroy or move to investigate, we will gain a new scientific understanding of them in the nondestructive and onsite manner.

[1] Y. Abe, R. Shikaku, I. Nakai, *Journal of Archaeological Science: Reports* **17**, 2018, 212-219.

Use of hand-held gamma-ray spectrometry to assess decay of granite buildings of a coastal area of NW Spain (Barbanza, Galicia)

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Non-destructive methods are widely demanded in research on Cultural Heritage. In the last years, several techniques have been proposed, attempted and even routinely tried on research on assessing the deterioration of stone of Cultural Heritage buildings and monuments. We test here the use of hand-held gamma-ray spectrometry (GRS) to assess the decay of stone in Heritage buildings. GRS is a non-destructive technique widely used in mineral exploration [1]. It provides an estimate of the environmental gamma radiation dose but also of the content of some radioisotopes of uranium, thorium and potassium in rocks and minerals. Such radioisotopes are present in very variable contents depending on the rock type. They have a different behavior when a stone overcome weathering processes, being usually the K and U leaching, while Th tends to be considered as an immobile element [2,3,4].

We have tested GRS on three granite rock buildings of the Peninsula of Barbanza (Galicia, NW, Spain): Santiago de Lampón, San Cristobal de Abaqueiro and San Martiño de Noia. In the only previous similar study, GRS provided promising results [5]. Measurements were compared with adjacent outcrops of fresh granite to assess the correlation between the exposure time on the façades and decay in the built environment. The studied buildings are located very close to the sea (<1km), a factor involved in the degree of deterioration of these monuments. The values obtained from the rock mass are similar to the usual range of granodiorites and granites *sensu stricto*. However, the values of K in the monuments are above those estimated in the rock mass, while the values of U are lower. This is because U is a very mobile element and is commonly leached during weathering processes. In the case of Th, although it is considered not mobile, strong differences are observed between façades.

[1] L. Rybach, G. Schwarz. Ground gamma radiation maps: Processing of airborne, laboratory, and in situ spectrometry data. First Break, IAEA, 1995, 13, 97–104.
[2] R.W. Boyle, Geochemical prospecting for thorium and uranium deposits. .
[3] M. Gascoyne, Uranium-series disequilibrium: applications to Earth, marine and Environmental sciences, 1992, 35-61.
[4] M. Lima, C. Alves, J. Sanjurjo-Sánchez. Advances in Materials Science Research, vol. 20, 77-93.
[5] J. Sanjurjo-Sánchez, C. Arce Chamorro, M. Couto, C. Alves. Conserving Cultural Heritage, 2018, 107-109.

Mineralogical identification of historical mortars from built heritage using Raman spectroscopy

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The study of historical mortars may present some challenges from the point of view of the adopted analytical approach. They correspond to a carbonated material, with years or centuries of use, often subjected to very different environmental and conservation conditions. Furthermore, since the monuments are usually of historical relevance, the sampling is usually limited to the minimum necessary in terms of quantity, to cause the least possible impact on the sampled area. Another important factor to be considered when defining the study methodology, although not directly related to the characterization of the samples themselves, is the sampling campaigns. They require access permits and field campaigns, that condition the study and make the preservation of samples fundamental for the development of future work. Historical samples are unique study opportunities that often require a multi-analytical approach and methodology adaptations [1]. Regarding the characterization of historical mortars, many studies include the identification of the type of binder and mineralogy of aggregates through invasive or even destructive techniques, such as acid or mechanical separation of the binder and aggregates or the preparation of thin sections, requiring large sample quantities, not always available. In this work an alternative multi-analytical approach is proposed, adapted to the cases of low quantity mortar samples, in which the identification of the constituent minerals of the binder and aggregates is made using a spot analysis approach by μ-Raman. Complementing with optical microscopy it is also possible to identify other characteristics of the mortars concerning the colour, shape, size, and distribution of grains in the binder. This methodology allows for a set of responses that are very close to those obtained by traditional methods, focusing on the preservation of the samples and requiring a simpler sample preparation process. Although the main constituent minerals of mortars, such as calcite and quartz present spectra with excellent signals and clearly identifiable, some minerals from the clay and cement groups can result in Raman spectra with weaker signals, or present a greater impact of background and fluorescence, which makes the interpretation of the results difficult.

[1] A. Arizzi, G. Cultrone, Archaeological and Anthropological Sciences 13 (2021), 1-22.

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We thank FEDER funds through the COMPETE 2020 Programme and National Funds through the Fundação para a Ciência e a Tecnologia under the project ref. UIDB/50025/2020-2023 and, SFRH/BD/145308/2019 (F. Carvalho). Funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under Horizon 2020, the EU Framework Programme for Research and Innovation, through the RM@Schools4.0 Project (PA 20069) and AMIR-LIH (PA 20114), is acknowledged.

Analytical study of the powdered pigments collection from the Brazilian artist Gilda Neuberger (1911-2011)

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This paper reports the first analytical approach performed on 16 powdered pigments found in Gilda Gelmini Neuberger's (1911-2011) studio that she probably used in her latest works. The Brazilian artist was a student of Candido Portinari and Edson Motta in Brazil and Bruno Saetti in Italy [1]. With more than 60 years of experience, Gilda painted her oeuvres using different painting techniques, such as oil, gouache, watercolour, and fresco. She was one of the rarest fresco artists in Brazil in the 20th century and probably the only one to use the fresco technique in unconventional supports. Gilda created her largest wall fresco entitled "Tribute to the workers" in the Ciferal factory in Rio de Janeiro to pay tribute to the factory working class, recognised as a local Cultural Heritage by the cultural agency of the state of Rio de Janeiro in 1994 [2]. She also made more than 200 frescoes on unconventional supports.

The pigments belonged to her daughter after her death in 2011 and were left unlabelled. The work presented here aims to characterise the pigments found in her studio and to try to match them with the materials used by Gilda in her fresco palette and in other pictorial techniques. The analytical setup comprises ATR-FTIR, XRD, SEM-EDS, and PLM techniques to characterise the materials' colours in terms of chemical, mineralogical, morphological composition, and optical properties.

Preliminary results have shown that samples seem to constitute traditional pigments to the fresco palette, e.g. ochres, and modern pigments such as titanium dioxide and alizarin. In addition, pigments historically not recommended for frescoes works were also identified, such as Prussian blue and lead yellow. The results will be used as a reference for future comparative research with the artworks of Gilda Neuberger.

References

[1] Available at http://gildagelminineuberger.com.br/index.php/biografia. Accessed on 17 Jan. 2023.
[2] Decreto n° 13.057
http://www.rio.rj.gov.br/dlstatic/10112/4722991/4121891/097DECRETO13057PainelAfrescodeGildaGeminiNeuberger.pdf. Accessed on 17 Jan. 2023

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ARTEMISIA: artificial intelligence to support diagnostic technologies for Cultural Heritage. An integrated multi-modal approach for assessing the state of conservation of pictorial works.

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Reflectance spectroscopy in the IR range is a widely used technique for the non-invasive analysis of paintings. Depending on the spectral range used, it is possible to identify different materials: VIS-NIR is mainly indicated to identify inorganic pigments, through the absorption bands in the range 400-1000 nm [1-2]; organic materials (dyes, varnishes, binders) can be identified by FT-IR spectroscopy in the range 7000-350 cm-1 (1428 nm-28 micron) [3, 4].

In this work we present the possibility of combining the two spectral ranges in the same device, obtaining the so-called "Broad Spectrum Reflectance Spectroscopy", applied to a real work of art. The aim of the project is to increase the ability to simultaneously identify all the constituent materials of the pictorial layer, which is generally composed of mixtures of inorganic and organic materials. To enhance the capabilities of the technique, machine learning algorithms were applied to generate a virtual image of the painting from the fused dataset, resulting in a comprehensive tool for expert and non-expert users to extract information about painting components and their status of conservation. A user-friendly graphical interface allows you to obtain information on the work of art at different levels, deepening your knowledge of the various aspects related to diagnostics, conservation, restoration or even knowledge of the artist's executive technique.

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[1] G. Bonifazi, G. Capobianco, C. Pelosi, S. Serranti, Journal of Imaging 5(1):8 (2019), 19.
[2] L. Pronti, A. C. Felici, M. Ménager, C. Vieillescazes, M. Piacentini, Applied Spectroscopy 71 (12) (2017), 2616-2625.
[3] L. Pronti, M. Romani, G. Viviani, C. Stani, Rendiconti Lincei. Scienze Fisiche e Naturali 31(11) (2020), 1-9
[4] C. Miliani, F. Rosi, A. Daveri, B. Brunetti, Applied Physics A 106 (2012), 295–307.
[5] A. Biancolillo, R. Bucci, A. L. Magrì, A. D. Magrì, F. Marini, Analytica chimica acta, 820, (2014) 23-31.
[6] M. Romani M., Almaviva S., Colao F., M. Marinelli, A. Pasqualucci, A. Puiu, G. Verona-Rinati, Journal of Applied Spectroscopy, 86, 360–368 (2019).

Micro-Computed Tomography applied to the study of Japanese pottery

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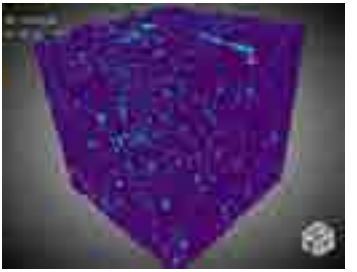

In the framework of the BeArchaeo European project, X-ray imaging has been applied to characterise pottery fragments from several Japanese archaeological sites: radiography for a first screening and Computed Tomography (CT) for a complete volume reconstruction, 3D rendering and segmentation. CT revealed to be useful to distinguish and visualize different characteristics of the sample, such as internal porosity (voids size and their directionality) and principal mineral components, that can give valuable information on manufacturing and execution techniques of the artifact. Usually, these results are obtained with a high spatial resolution in an invasive way by means of a Scanning Electron Microscope (SEM), while using CT similar results can be obtained non-invasively, even if with a lower resolution. For this purpose, tomographic acquisition of the central part of every sample was performed (Local Tomography) to reach the maximum possible resolution in the final CT reconstruction. A methodology for data processing has also been developed and tested, with a particular focus on the correction of the artifacts that could afflict CT analysis, the so called "ring artifacts". In the reconstructed volume, the various ceramics components are clearly visible with different grey levels according to the material density and composition. The grey level variations are in fact due to the different X-ray attenuation coefficient of the present elements and their atomic packing, giving an indication of the chemical composition. Higher density areas, composed of more heavy chemical elements, are visible as brighter areas, while dark areas indicate the presence of voids and porosity that extends over the entire investigated volume. Areas with an intermediate grey level represent medium density material, such as other types of minerals or inclusions and the ceramic matrix. The 3D visualization of the CT images is usually performed to qualitatively characterise the microstructure of the sample. In this case, threshold-based method for segmentation was used: grey levels correspondent to the different materials are separated and different colours are virtually assigned to each of them. Linking this information with the one obtained by the invasive techniques (petrographic examination, SEM-EDS, XRF, XRD etc..), it is possible to propose some correlations with different inclusions inside the fragments.

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Eusébio da Silva Ferreira, the "Black Panther": Analytical techniques applied to metal statues

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The iconic Eusébio da Silva Ferreira statue attracts a lot of attention of Benfica Football fans and fans worldwide. The public is eager to show its affection and respect for the football player, what it represents, and they do so by touching and posing with the statue, a proximity that the sports Club promotes and encourages. Created in 1992, the statue is in a good state of conservation. Nevertheless, some issues were to be expected, such as the wore-off patina in the areas where most people touch the statue and localized signs of possible corrosion – visible green and white stains that were detected and in need of further evaluation. Despite being a relatively modern statue and being catalogued as a bronze, its exact composition was unknown. In order to evaluate its conservation conditions and to design proper conservation strategies, a multi-analytical approach combining portable equipment (handheld X-ray fluorescence (h-XRF) and 3D scanner) with laboratory techniques (X-ray diffraction (XRD) and variable pressure scanning electron microscopy (VP-SEM-EDS)) was applied.

To determine the composition of the bulk metal alloy, the patina and the weld, a total of 12 points were analysed by h-XRF. The elemental analysis showed the presence of major (Cu, Zn, Sn and Pb) and minor (Fe, Ni, Sb and As) elements. Based on the concentration of the major elements, the statue is predominantly comprised of a Cu-Zn alloy while displaying also variable levels of Sn. These differences can be explained by the manufacturing technique used, which involved the separate production of different parts of the statue and their subsequent joining. The mineralogical composition revealed by XRD of the concretion samples, confirmed the presence of calcite and gypsum for most samples, particularly where white hues were noticed. In one of the samples $ZnSO_4$ was identified but no copper compounds were present. However, VP-SEM-EDS analysis revealed the presence of Cu and Cl in some of the concretions confirming that these areas are corrosion products of the metal alloy. Additionally, Pb was also identified in one of the VP-SEM-EDS samples, collected from a joint between two sections of the statue, which might indicate the use of lead in the welding.

These techniques, together with the 3D scan imaging with an Artec Eva 3d Scanner for larger areas, and an Artec Spider for sharper detail acquisition in smaller areas, allow for a proper mapping, monitorization and future planning of the conservation strategies for such an iconic and important statue.

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Retrieving images from badly tarnished daguerreotypes using tunable X-rays: recent observations

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The retrieval of fine images from 19th century daguerreotypes tarnished beyond recognition using X-ray fluorescence imaging with a tunable X-ray beam has opened immense opportunities in the studies of the very first commercial photographs of human history. [1] This technique will have impact from conservation to preservation as well as materiality and esthetic experience. [2] It will offer great promise in retrieving tarnish daguerreotype of historical significance and beyond. [3]

This presentation reports a series of systematic studies of tarnished daguerreotypes from the collection of National Gallery of Canada, George Eastman Museum as well as private collection using a tunable X-ray microbeam with energies varying from 3 keV to 15 keV. Variable excitation energy tunes the elemental sensitivity as well as probing depth. For example, S, Cl, K, Ag and Hg maps have been obtained with energies tuned to the vicinity of the corresponding absorption edges. These maps in turn allows for the analysis of spots of interest resulting from surface corrosion. The applicability of this technique to the general area of cultural heritage materials and art and archaeology will be noted.

[1] M. S. Kozachuk, T.-K. Sham, R. R. Martin, A.J. Nelson, I. Coulthard and J. P. McElhone, **Scientific Reports** 8, 2018, Article number: 9565.
[2] A. Stark, F. Filice, J. Noël, R. M. Martin, T.-K. Sham, Y. Zou Finfrock and S. M. Heald, **Heritage,** 4(3), 2021, 1605-1615.
[3] Averie Reinhardt, Renfei Feng, Qunfeng Xiao, Yongfeng Hu, Tsun-Kong Sham, **Heritage,** 3(3), 2021, 1035-1045.

Beyond the youth smile: investigating techniques and materials in Caroto's paintings

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Giovanni Francesco Caroto (ca 1480-1555) with his restless and strange vision was an eclectic artist active at the court of the Gonzaga in the late Renaissance in Northern Italy. Caroto, who was born and died in Verona, moved from Veneto to Lombardy and Piedmont to improve his skills under the guide of masters such as Andrea Mantegna, Bramantino and Bernardo Luini [1]. His masterpieces "Red-headed youth holding a drawing", in figure, represents one of the symbols of the civic art collection of the city of Verona and curiously inspired Dr Harry Angelman in the description of a medical rare condition lately called Angelman syndrome [2]. Nevertheless, his rich production has never been investigated in terms of palette, art technique and changes in style during the four decades of production.

This work introduces the characterisation study carried out with a non-invasive approach on twenty Caroto's paintings, from public and private collections, that were collected in 2022 within the exhibition "Caroto and the arts, from Mantegna to Veronese". In particular, the diagnostic protocol included imaging techniques in the VIS and NIR spectral ranges and IR reflectography up to 1700 nm, that were performed in full-field to guide the use of the pointwise spectroscopy techniques such as fiber optics reflectance spectrometry and X-ray fluorescence spectrometry. The huge amount of imaging and spectral data unlocked the painting technique and the materials of Caroto artist and allowed us to trace the history of these paintings from artistic and conservation points of view. It was highlighted a different use of the colour palette, also depending on the place or the period. Of particular interest, a curious and non-continuous use of smalt pigment, not only in blue (or gray, when degraded) areas, but also in pink ones, revealing a potential awareness of the painter of the fastness of this pigment.

G.F: Caroto, Red-headed youth holding a drawing, 1523

[1] F. Rossi, G. Peretti, E. Rossetti, Monografie d'arte, Silvana Editoriale, 2020, pp.240
[2] A. Battaglia, J.C. Carey, American Journal of Medical Genetics Part C: Seminars in Medical Genetics, 187, 2, 2021, 144-147

Titanium dioxide-based paints produced in the USSR: a study of archival materials and reference samples

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The report presents the results of the study of archival materials and technical literature on the production of the paints based on titanium dioxide (TiO_2) in the USSR. In addition, the reference paint samples produced by the Leningrad Factory of Artistic Paints, the main Soviet manufacturer of art materials, were investigated by a complex of analytical methods including polarizing microscopy (PLM), SEM-EDS, μ-FTIR spectroscopy, μ-Raman spectroscopy and GC-MS.

While artistic paints containing TiO_2 appeared on the European market as early as the mid-1920s [1, 2], the production of white paint in the Soviet Union started only in the 1960s (as polyvinylacetate tempera) [3]. The first artistic oil paint was developed at the Leningrad Factory in 1972, and, according to the technical specifications, contained about 20% wt. of zinc white, with pentaerythritol ester of drying oil fatty acids as a binder (Figure 1).

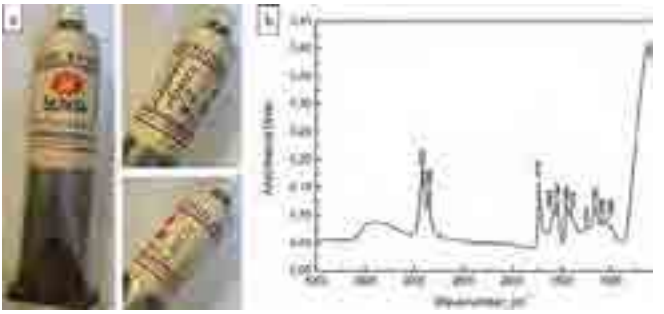

Fig. 1. (a) Photos of «Titanium White» artistic oil paint tube from the pilot batch produced by the Leningrad Factory of Artistic Paints in 1972; (b) FTIR spectrum of the reference sample shown at (a): a number of low intensity absorbance bands in spectral interval of 1060-1018 cm^{-1} can be assigned to C-O-H vibrations in pentaerythritol fatty acid ester [3].

The comparison of the chemical composition of titanium dioxide whites produced in the USSR with the formulas of some foreign artists' colourmen (Lefranc, Royal Talens and F. Weber & Co.) [4] revealed a number of technological features that allow to differentiate paints of Soviet and foreign manufacture.

[1] M. Laver, Artists' Pigments. A Handbook of their History and Characteristics, Vol. 3, 1993, 295-355.
[2] E. Morozova, I. Kadikova, S. Pisareva, International Journal of Conservation Science 13(1), 2022, 1553-1566.
[3] Y. Grenberg, S. Pisareva, Oil paints of the 20th century and the expertise of painting. Composition, discovery, commercial production and examination of paints, 2010, p. 194.
[4] A. Phenix, A. Soldano, K.J. van den Berg, B. van Driel, ICOM-CC 18th Triennial Conference Preprints, 2017.

Ten years of practical advances towards safer analysis of heritage samples and objects

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In 2013, a group of scientists met under the auspices of the International Atomic Energy Agency (IAEA) in Vienna to initiate a program to ensure safer conditions for the examination of heritage objects. The results of this meeting were presented at the Technart 2013 conference in Amsterdam. At that time, they had identified only a handful of works in the field dedicated to the impact or to the scientific study of potential radiation damage to art, archaeological, palaeontological or palaeoenvironmental samples or objects. They assumed that the growing use of ionising sources and their increasing brightness required awareness and new research projects [1]. Since then, we are aware of more than 30 research projects that have developed on the topic, and have identified more than 80 articles addressing different aspects of the prevention of radiation side effects to heritage samples or objects. European Commission projects, instrumentation projects and surveys in facilities, scientific dissemination material, and a range of other initiatives have grown out, including two dedicated IAEA technical meetings (Paris, 2015; Amsterdam, 2017). Among the main trends regarding X-ray, UV and ion beam experiments, we have seen detailed reports in supplementary material [2,3], and characterisations performed as part of the main data analysis and interpretation [4]. Several research articles entirely focused on the description of induced side effects, their mechanisms and/or methodologies to mitigate them [5, 6, 7]. We observed the development of analytical strategies and new dedicated instruments to better detect and limit the effects of irradiation in real experiments on ancient samples and objects (e.g., for portable instruments, at the SSRL, SOLEIL or SIRIUS synchrotron facilities or at the AGLAE ion beam facility). Emerging trends include detailed mechanistic studies on more specific systems, the development of statistical methods to reduce the doses required to study samples [8], and the development of integrated early warning systems capable of feeding back into the experiment while an acquisition is in progress. This work also leads us to consider with caution the binary distinction between destructiveness and non-destructiveness, whereas the possible alterations are part of a continuum inherent in the history of objects.

[1] L. Bertrand et al., Trac–Trends Anal. Chem. 66, 2015, 128.
[2] A.A. Gambardella et al., Microchem. J. 125, 2016, 299.
[3] S.R. Stock et al. J. R. Soc. Interface, 17, 2020, 20200686.
[4] M. Ganio et al., Pure Appl. Chem. 90, 2018, 463.
[5] L. Monico et al., Eur. Phys. J. Plus 137, 2022, 311.
[6] L. Beck et al., Nuclear Instrum. Meth. Phys. Res. B 409, 2017, 96.
[7] M. Godet et al., J. Anal. At. Spectrom. 37, 2022, 1265.
[8] S.X. Cohen et al., J. Synchrotron Rad. 27, 2020, 1049.

Reading the Unreadable. Advanced Imaging to Recover Illegible Text in Historic Documents

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From fires to floods, from invisible inks to redactions, information has been accidentally or intentionally obscured on countless documents, maps and photographs, in archives, libraries, and museums across the world. Removed from catalogues and reading rooms and therefore inaccessible to researchers and the general public, what new and fascinating stories would these obscured documents reveal, if we were able to read them?

This paper demonstrates that current imaging technologies can be used to unlock this 'lost' archive. In this study, we imaged a selection of medieval documents relevant to the 'Virtual Record Treasury of Ireland', a digital reconstruction of archives destroyed in 1922 at the Public Record Office of Ireland at the outset of the Irish Civil War [1]. We used Multiband Imaging, Hyperspectral Imaging and X-Ray Fluorescence (XRF) scanning to reveal illegible letter-forms and whole words written in iron gall ink on parchment.

While both UV luminescence and UV reflected imaging were very effective at improving the readability of faded iron gall ink and enhanced the contrast of the text and the parchment in areas with old damp stains and ingrained dirt, the "galled" documents[1] required more advanced imaging techniques. The iron distribution maps obtained by XRF scanning helped to recover text from the galled areas, but it posed several challenges, such as minimising movement of the parchment during overnight scans and separating the data corresponding to iron on the front which was combined with the signal from the back. Through subtraction of other elemental maps during post-processing, we managed to tackle the latter issue. Hyperspectral imaging also proved helpful to read galled documents, particularly after applying PCA image processing. However, care has to be taken with instrument configurations where the light source is relatively close to the object, as surface heating can occur quickly and cause the parchment to distort.

These combined imaging techniques enabled records experts to identify individual characters and whole words, thereby recovering the meaning of texts that were previously indecipherable [2]. Further research will adapt the methodology to the broad range of causes of information loss, as well as the variety of document media and temporalities, which require an extensive and multi-faceted approach of advanced imaging and post-processing techniques, in balance with the preservation needs of these fragile and invaluable historic materials.

[1] https://virtualtreasury.ie (consulted on 19/01/2023)
[2] Biggs E, Dryburgh P (forthcoming, 2023), 'Report into the State of the Exchequer c. 1284: TNA E 101/234/19', *Analecta Hibernica*

[1] "Galling" was an extended practice of 18th, 19th and early 20th century scholars, which consisted in applying chemicals (such as gallic acid or cyanide-based compounds) to temporarily enhance faded iron gall ink. However, this subsequently left the parchment permanently stained and, once again, unreadable.

A Technological and Provenance Study of LBA Glass from Thessaly, Greece: The Profitis Elias Kompotades Cemetary

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In 2009, a systematic excavation at Profitis Elias, Kompotades (Phiotis) revealed an ancient cemetery of diachronic use, spanning from Mycenaean to Hellenistic times. The present archaeometric study is towards the technological and provenance of a set of 22 glass artefacts from two undisturbed tombs of the cemetery [1].

Recently, an increase in archaeometry research of Late Bronze Age glass from Greece has allowed for a deeper understanding of the technological and chemical fingerprinting of this material and the possible identification of production zones and thus trade routes [2, 3, 4].

While these studies have added to the discussion of how this prestige good traveled across the eastern Mediterranean, questions still remain about the types of vitreous materials found especially in areas where there is lack of documented Mycenaean palatial centers. One such area is Thessaly, central Greece, where Mycenaean sites were revealed during resque and systematic excavations providing evidence of activites and importance of the area as part of the Bronze Age world.

The study included SEM/EDS for the technological examination and the base glass characterization; ICP-MS on selected artefacts provided the complete minor and trace element chemical pattern of the analysed material.

Samples were polished with a soft Dremel prior to analysis by SEM/EDS at the University of the Peloponnese. The glass is typical of LBA Eastern Mediterranean High Magnesium glass, having 65.39±2.22 wt% SiO_2, 16.37±1.21 wt% Na_2O, and 3.95±0.55 wt% MgO. Of likely interest is the difference in CaO between relief beads (7.67±1.41) and simple beads (9.86±0.63), potentially suggesting preferential use of raw glass dependant on its final form, as first suggested due to variation of alumina between beads and relief plaques found in the Argolid [4].

LA-ICP-MS is in progress at the British Geological Survey, Nottingham on samples taken from a selection of the beads. This will provide vital evidence for the provenance of the glass and help to build a picture of the wider trade of international trade networks in the Aegean.

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[1] (Karantzali E., 2013, The diachronic use of the cemetery at Profitis Elias, Kompotades Fthiotis: A first approach based on the findings of Tomb IV, in Proceedings of the 5th Symposium on the History of Fthiotis 2010, 51-94 (in Greek).
[2] Henderson, J., Evans, J. and Nikita, J., Isotopic evidence for the primary production, provenance and trade of Late Bronze Age glass in the Mediterranean, *Journal of Mediterranean Archaeology and Archaeometry* 10, 1, 1-24 (highlighted in *Science*).
[3] Kaparou M. and Oikonomou A., 2022. Mycenaean through Hellenistic glass in Greece: where have we got to? Archaeological and Anthropological Sciences 14, 92.
[4] Zacharias N., Kaparou M., Oikonomou A., Kasztovszky Z., 2018. Mycenaean glass from the Argolid Peloponnese, Greece: a technological and provenance study. Microchemical Journal 141, 404-417.

Massimo Campigli, an Italian painter, studied with non-invasive and portable analytical techniques

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The Museum of Contemporary Art of the University of São Paulo (MAC-USP/BR) holds one of the most important collections of modern Italian painting of the first half of the 20th century outside Italy. Particularly, this research presents a study of the painting "Os Noivos" (Engaged Couple - 1929) by the artist Massimo Campigli (1895-1971), belonging to this Italian collection. The analysis performed aimed to understand and characterize the artist's creative process, as well as determine his palette. The artist's creative process interest is related to previous artwork studies that suggest an archaic and ancient visual with voluminous way and a mixture of techniques, which conveys an idea of a fresco [1].

To investigate this canvas painting, a set of portable analytical techniques with non-invasive methods and multi-band technical imaging were used. The various imaging techniques used (Visible, Transmitted and Tangential light, Infrared Reflectography, Radiography and Ultraviolet fluorescence) provide typical and independent information. However, when compared they provide much more information if they were studied separately (figure 1).

The analytical techniques ED-XRF, FTIR, and Raman spectroscopies used showed that the artist's palette consists of pigments with earthy tones based on iron, such as ocher, Mars red, and iron oxide, black pigments, such as bone black and charcoal, cobalt blue and a variety of whites based on lead, calcium, barium, zinc and titanium. In particular, the combination of these analyzes allowed to determine that Campigli used a preparation base with calcite and then deposited a white layer of lithopone, mostly over the white regions. The artist also mixed calcite and lead white in the regions with a thick grayish white around the bodies of the painted man and woman and lead white to produce the lighter tones of their faces.

Correlating the UVF-Vis image and spectroscopy results, it was possible to suggest that the artist deposited a layer of titanium white over the painting non-homogeneously outlining the elements of the painting, due to its known purple visible fluorescence [2]. This detail is exemplified in figure 1, at the woman's necklace under the UVF-Vis technique. This image suggests that Campigli decided to redo the white region with this pigment after the finalization of the painting. Finally, with the FTIR analysis, it was verified that the pigments are made with a temper-oil binder, which is a different process present in his artwork.

Figure 1: Partial Image: VIS (left) and UVF-Vis (right) of the woman's necklace with the purple visible fluorescence of the titanium white pigment outlining it.
Credit: LACAPC/IFUSP

Acknowledgments: Financial support from FAPESP (Project no. 2017/07366-1 and 2019/16810-8) and CNPq (302823/2021-2)

[1] Raffaele Carrieri, Con un ritratto dell'artista, in Franco Russoli, Campigli, Artisti Italiani Contemporanei, Ed. Del Milione, Milão 1965, p. 06.
[2] A Cosentino, "Identification of pigments by multispectral imaging: A flowchart method", *Heritage Science*, 2-8, 2014, http:/www.heritagesciencejournal.com/content/pdf/2050-7445-2-8.pdf

The Red Vineyards near Arles by Vincent van Gogh: The Results of Technological Examination

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The Red Vineyards near Arles is one of the central paintings of the van Gogh's oeuvre and is considered to be the only documented work sold during the master's lifetime. The provenance of the painting is well-known. It was executed in November 1888, two years later it was exhibited at the annual exhibition of *Les XX* in Brussels, where it was sold to the Belgian artist and collector Anna Boch. In 1906, the masterpiece was purchased by Russian industrialist and art collector Ivan Morozov, who systematically and purposefully collected contemporary French paintings. After nationalization, the painting was passed to the Moscow Pushkin State Museum of Fine Arts and since then has never left its walls. In 2021, the Museum, supported by LG SIGNATURE, launched an extensive project dedicated to the research and conservation of Vincent Van Gogh's masterpiece [1].

The scientific part of the project aimed to investigate various aspects of the artist's work, however, in the present report we focus on the technological study of art materials, which was carried out in the laboratory of the State Research Institute for Restoration. To identify the chemical composition of art materials, microsamples of the primer and paint layer were examined by means of analytical methods, such as polarizing microscopy (PLM), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), μ-FTIR spectroscopy, and μ-Raman spectroscopy. Also, cross-sections were prepared for the investigation of the paint layer structure.

Today, researchers already know a lot about the paints that van Gogh preferred to use in his work. This is not only because of the detailed investigation of numerous paintings [2], but also through the artist's letters to his brother Theo, in which van Gogh often asked him to send over certain paint tubes and canvases or speculated about his paintings [3]. All these data allow considering our results in the light of available scientific knowledge. The study showed that in working on *The Red Vineyards near Arles*, the artist used a characteristic for this period set of pigments, including lead and zinc whites, French ultramarine, Prussian blue, emerald green, viridian, vermilion, eosin, and chrome yellow [2]. Moreover, some atypical features were revealed. For example the fact, that the artist primed the canvas himself with a mixture of natural baryte with small amount of calcite. Such composition of the primer is not common to his work, on the contrary, the artist preferred commercially primed canvases [2].

[1] https://www.museumconservation.ru/data/specprojects/van-gogh-red-vineyard/index-eng.html
[2] Van Gogh's Studio Practice / M. Vellekoop, L. Jansen, M. Geldof, E. Hendriks and A. de Tagle (eds.). – Mercatorfonds, 2013. – 464 pp.
[3] https://vangoghletters.org/vg/

Integrated investigations to study degradation issues on the urban mural painting *Ama il tuo sogno* by Jorit Agoch

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Abstract

The urban mural painting *Ama il tuo sogno*, designed by the contemporary artist Jorit Agoch in Matera (Italy), was built on a masonry wall set against a filler ground. A few months after its creation (2019), it started to be affected by several degradation forms, where salt damage seems to be the main conservation issue. In view of conservation works, a diagnostic study was performed through chemical-mineralogical analyses and in situ Infrared thermography. The chemical composition of the pictorial film was investigated by means of Fourier transformed – infrared spectroscopy (FT-IR) and pyrolysis/ gas chromatography- high resolution mass spectrometry (Py/GC-HRMS) with and without tetramethyl ammonium hydroxide (TMAH). The stratigraphy of the pictorial layers was examined on polished cross sections by means of polarized light microscopy (PLM) under UV and VIS light, as well as through scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS). The mineralogical-petrographic composition of the two mortars employed in the pictorial support was investigated on thin sections with PLM under transmitted light combined with SEM-EDS. Moreover, to know the mechanism underlying the degradation, some infrared thermographic images were acquired to highlight the water paths, and the humidity distribution in the mural painting. In addition, ion chromatography (IC) and X-ray diffractometry (XRD) were used to detect and quantify soluble salt ions and their mineralogical phases, respectively, and to identify their source. The analyses were performed on whitish patinas and efflorescences formed on the pictorial film, as well as on the mortars from the support. These latter were also performed on the raw mortar materials used for the plaster layers and on some samples from the stone wall in the area around the painted panel. The results show a stratigraphy with one or two painting layers made with spray paints based on an alkyd resin, as shown by the FTIR spectrum [1]. The pyrograms obtained after derivatization with TMAH allow us to establish that the alkyd resin was obtained from polycondensation of orthophthalic acid, with pentaerythritol [2], while the profile of the fatty acids follows that of *L. breviflorus* seed oil [3]. IC results show that salts affecting the painted panel mainly consist of phosphates and sulphates, according to the presence of magnesium phosphate and gypsum, which were detected by XRD. The overall results of CI and XRD analyses performed on the mural painting seem to indicate that the main source of the salts are the mortars layers and the ground back to the underlying wall.

[1] Learner, T. *Analysis of modern paints*; The Getty Conservation Institute: Los Angeles, 2004
[2] Ploeger, R.; Scalarone, D.; Chiantore, O. The characterization of commercial artists' alkyd paints. *Journal of Cultural Heritage* 2008, *9*, 412–419, doi:10.1016/j.culher.2008.01.007
[3] Saviour A. Umoren, Emmanuel E. Essien, Edidiong E. Effiong, The utilization of Lagenaria breviflorusseed oil in the synthesis of alkyd resins, *J. Mater. Environ. Sci. 7,* 2016*, 6, 1846-1855*

Analytical SEM-EDS and μ-Raman study of iron gall ink mockups degradation reproduced by historic Greek recipes

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Due to their corrosive nature, historic iron gall inks can lead to a total substrate loss caused by soluble compounds of iron and the production of sulfate ions that accelerate the catalytic acidic hydrolysis.

From the conservation science perspective and for preservation purposes, understanding the chemical composition, mechanism of corrosion and degradation of iron gall inks is essential for the selection and implementation of a successful conservation treatment [1]. The analytical investigation of corrosion products present in the iron gall inks may provide useful insights into the mechanisms of degradation processes.

Aim of the present study was the reproduction of iron gall inks through Greek historical recipes, with natural ingredients and pure compounds. The reproduced inks were applied on different substrates, such as parchment and paper, which were submitted to thermal accelerated aging. The iron-gall inks were examined before and after the thermal accelerating aging with SEM-EDS, whereas the possibility of the bond weakening between the inks molecules was examined using μ-Raman Spectroscopy [2], [3].

After artificial aging SEM-EDS revealed different formation of crystal deposits in the cellulosic fibers compared to those in the parchment, whereas the increased percentages of sulfur indicates the effect of catalytic acid hydrolysis accelerated by the presence of sulfate ions. Furthermore, the examination with μ-Raman suggested the slight broadening of main bands and documented an increase of fluorescence after accelerating aging that was attributed to degradation and excess amount of added organic compounds.

[1] Melo J. M. et al., 2022. Iron gall inks: a review of their degradation mechanisms and conservation treatments. Heritage Science, pp. 1-11.

[2] Hidalgo R. et al., 2018. New insights into iron gall inks through the use of historically accurate reconstructions. Heritage Science, pp. 1-15.

[3] Daher C. et al., 2010. A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes. Journal of Raman Spectroscopy, pp. 1494-1499.

Shikonin: a photochemical study in solution and in the solid state of a dye of the Nara period (8th century)

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"L'uso del colore nell'arte è stato determinato dai materiali a disposizione dell'artista almeno quanto lo è dalle sue inclinazioni personali e dal contesto culturale in cui opera."[1]

In the Nara period (Japan, 710 – 794 ac), only the royal family and the highest ranking officials were allowed to use a purple dye in silk dresses. This dye was extracted from the roots of *Lithospermum erythrorhizon*, and the major dyeing component was *Shikonin* (**Shk**). Despite the relevance of this dye, it remained forgotten in the context of historic dyes. Structurally, **Shk** (see inset in Fig. 1) is a natural phenolic compound belonging to the naphthoquinone family with a known low solubility in water and poor lightfastness.[2]

The photophysics of **Shk** is found complex and was the subject of a recent experimental and theoretical investigation where it was shown that the basic dihydroxy-naphtoquinone core drives its decay pathways.[3]

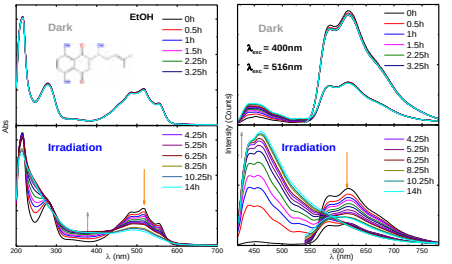

Figure 1. (*Left*) Absorption and (*Right*) fluorescence emission spectra, at different irradiation times @ λ_{exc} = 400 and 516 nm, and in dark conditions for Shk in ethanol.

The present work constitutes a step forward in the study of **Shk**, namely its stability towards light (Figure 1), where polychromatic wide band and monochromatic light were used to irradiate this molecule (and model hydroxynaphthoquinone dyes) in solution and in the solid state. Low ϕ_R values ($<10^{-4}$) were obtained in solution, thus providing quantitative evidence for the stability, towards light, of this molecule. The irradiated solutions were also studied by chromatographic and mass spectrometric methods to identify possible degradation products. In order to mimic the degradation process in textiles, **Shk** was extracted from *Alkanna tinctoria* (the European source of **Shk**, also rich in its stereoisomer alkannin) and used to dye silk, cotton, linen and wool textiles that were then irradiated with polychromatic light and further characterized by electronic spectroscopies.

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References

1. Ball, P., *Colore. Una Biografia. Tra Arte Storia E Chimica, La Bellezza E I Misteri Del Mondo Del Colore*; Rizzoli, 2017.
2. Cardon, D., *Natural Dyes: Sources, Tradition, Technology and Science*; Archetype, 2007.
3. Pinto, C. M.; Pina, J.; Delgado-Pinar, E.; Seixas de Melo, J. S., Excited State Deactivation Mechanisms in Shikonin Rationalized from Its Naphthoquinone Parent Structures. *Physical Chemistry Chemical Physics* **2022**, *24*, 20348-20356.

New materials for painting at the outset of modern age

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It is well known that from the second half of the 15th century till the early 17th century, numerous changes in European painting technique have appeared (e.g., spreading of oil painting on canvas, colouring of originally white grounds, etc.). A number of changes were triggered by the availability of materials. As we have previously published [1-2], for example, the cheap availability of pottery clays led to the application of clay grounds instead of *gesso* first in Italy at the turn of the 16th and 17th centuries [1]. In Central Europe, some pigments were newly emerging (e.g., Co-rich smalt), some, on the contrary, gradually disappeared (e.g., Pb-Sn yellow), while others were exclusively occurring just in this period of time (e.g., fluorite). Although the impact of rapidly developing key mining areas of Central Europe (especially the Ore Mountains and the Upper Hungary/Slovakia) is being generally assumed, these links have never been precisely verified and researched.

In this contribution, we will show how differences in materials composition can be investigated on micro-samples using a multi-analytical approach and how they can contribute to dating and determination of regional provenance of paintings in this period. An example would be smalt whose minor accompanying elements are related to the source ore (before the 16th century it was silver, later cobalt ore) or azurites, which, according to minor/trace elements can be divided between Hungarian and French. Azurites from French deposit in Chessy were available only from the 15th century, while the Hungarian ones were already used since earlier period. Another interesting example is the composition of Late Gothic poliments, which contain Al-rich bauxite-type material [2] instead of a red bole and therefore had to be colored. The possible source of this material will also be discussed. The research was supported by the Czech Science Foundation, project no. 22-17966S.

[1] D. Hradil, J. Hradilová, K. Holcová, P. Bezdička, Applied Clay Science 165, 2018, 135.
[2] D. Hradil, J. Hradilová, P. Bezdička, C. Serendan, Applied Clay Science 135, 2017, 271.

Imaging and material characterisation of the incunabula *Liber Chronicarum* from the University of São Paulo: an multi-analytical approach

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This study focuses on the application of a multi-analytical approach combining image and material characterisation techniques of an incunabula from the Institute of Brazilian Studies, a specialized research unit of the University of São Paulo (USP), in Brazil. The Nuremberg Chronicle from 1493, or Liber Chronicarum, is the oldest document from the USP and one of the most important works of the 15th century printed by Anton Koberger (1440-1513), a recognized goldsmith, printer and publisher. Incunabula are objects of immense historical value. They are the fruit of the early history of printing and this exemplar is illustrated with woodcuts produced by Michael Wohlgemuth and Wilhelm Pleydenwurff (both masters of Albrecht Dürer) and represent historical events related to the Bible, the papacy, natural phenomena, as well as illustrating views of numerous cities such as Nuremberg, Vienna and Basel [1].

During the conservation process of this important book, realized in partnership with De Vera Artes atelier, some folios present brittleness and damage resulting from the degradation of paper cellulose. The study goal identifies and characterizes its material composition by means of a multi-analytical approach consisting of imaging, elemental and compositional spectroscopic techniques. The great historical, artistic and documental value that each incunabula has requires that the methods used for its study respect its physical integrity and its chemical nature, which is why EDXRF and FTIR, both portable equipment, are ideal techniques for the study of inks and paper supports. The applied imaging methodology allowed to register six different watermarks with transmitted light, diagnose the state of conservation of some folios with UVA-induced visible fluorescence photography, as it highlights stains, and verify the potential of NIR image to reconstruct degraded areas in one of the folios. The material analysis through EDXRF and FTIR indicated the use of copper in the blue and green pigments that suggest the use of azurite mineral (2CuCO3.Cu(OH)2) in the blue and malachite (CuCO3-Cu(OH)2) in the green pigments. Mercury was also identified in the red, suggesting vermilion, as well as lead, indicating lead red. Iron was characteristic of the ochres pigments. Similar pigments were observed by Scardina et al. [2]. Paper degradation was associated with copper ion migration from pigments containing copper.

Acknowledgements: MAR thanks to CNPq (National Council for Scientific and Technological Development) for the financial support (302823/2021-2).

[1] R. Horch, M. Rosetto, M. I. Conte, E. C. Ribeiro. Bibliotheca universitatis: acervo bibliográfico da Universidade de São Paulo, séculos XV e XVI. EDUSP/Imprensa Oficial, 2002, 45-52.
[2] S. Bottura Scardina, F. Themudo Barata, A. Nogueira Alves, y C. Miguel, «Image processing methods integrated to imaging and material characterisation for the study of incunabula illustrations: an innovative multi-analytical approach on a case-study», Ge-conservacion, 2020, 362-374.

Using negative muons for the characterization of thin layers in cultural heritage science

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Corrosion crusts, patinas and gilding are as important as the artefacts that they are covering. The identification of these layers, in terms of composition or thickness, can give information about the material, its conservation status, the manufacturing process or the evidence of debasement. Information that can be crucial, especially during restoration processes or for sample characterization. However, sometimes it is useful to pass through these layers to have information from the bulk of the sample. And with most common techniques it is difficult to get both. Yet, a new approach to this type of analysis is represented by large-scale facility techniques and, in particular, by Muonic atom X-ray Emission Spectroscopy (μ-XES). μ-XES is a rather novel method in heritage science that uses negative muons to investigate matter [1,2]. When a muon is captured in matter, it forms the so-called "muonic atom", in which the muon travels quickly through the muonic orbitals up to the nucleus. This process produces radiative X-ray emissions that are highly energetic and characteristic of the emitting atoms. In addition, by varying the muon beam energy, the muon stops at different sites inside the sample (up to several microns, depending on the material density), thus providing information both from the surface and from the bulk. Hence, μ-XES is a multi-elemental and depth-selective technique, that can provide material characterization along with depth profile studies in a non-destructive way. In the case of layered structures, a new approach to the assessment of the thickness is provided by the coupling of data analysis with Monte Carlo simulation methods, like SRIM-TRIM or Geant4 [3,4]. In this work, we report the results of the analysis of a set of gilded samples that were measured at the ISIS Neutron and Muon Source. For each sample, an energy scan with increasing muon beam energy was performed. Data analysis consisted of peak identification and peak fitting of the acquired X-ray spectra. From that, a profile describing the variation of gold peak intensities along with muon energy was retrieved. Then, the samples were modelled in the Monte Carlo software and the interaction with the negative muon beam was simulated; as before, a depth profile for gold was retrieved from the simulation output. Finally, the results of both the experiment and the simulations were compared and a good agreement was reached, defining a gold layer of several microns for each of the investigated areas.

[1] A.D. Hillier, D. Paul, K. Ishida, Microchem. J. 2015,125, 203–207.
[2] K. Ninomiya, M.K. Kubo et al., Anal. Chem 2015, 87 4597-4600
[3] S. Agostinelli, J. Allison et al., Nucl. Instrum. Methods Phys. Res. Sect. A, 2003, 506, 250–303
[4] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, Nucl. Instrum. Methods B 2010, 268, 1818-1823

What was stored inside the big ceramic containers of the *Domus dei Dolia* at *Vetulonia* (Italy)

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Destroyed because of a fire, the ruins of the *Domus dei Dolia* remained hidden until an archaeological campaign started, in 2009. The Domus dei Dolia is located in the Hellenistic quarter of the old town of *Vetulonia*, nowadays Poggio Renzetti. Based on the archaeological data, the Domus, and probably the whole city, was destroyed around the first century BC due to the reprisals of *Lucio Cornelio Silla* after the victory over *Gaio Mario*. This happened because Etruscan cities took party in favor of the latter during the Roman civil war.

This Domus represents an exceptional discovery for the archaeological area of *Vetulonia* and for Etruscan archaeology, as well-preserved dwellings with high rises (over 1.60 m and about 6 cm in thickness) have rarely been found. Moreover, because of the fire, the roof collapsed, sealing and preserving an old context with a wide variety of materials. The building is divided into 12 rooms (the excavation is still underway), and from the excavation data (ongoing study) it seems to have had three different construction phases.

In the context of the collaboration between the HERCULES Laboratory, the Isidoro Falchi Archaeological Museum in Vetulonia, and the Town Hall of Castiglione della Pescaia, several ceramic container samples from two different divisions of the *Domus* (division A – storage room; division B – product processing area) were selected for an archaeometric study. This includes the bottom part of 3 different Dolia from division A, and one sample each of a tub and a big vase from division B.

The main goals were to determine the provenance of the ceramic containers and eventually their content. The data acquisition techniques consisted of optical microscopy (OM), X-ray diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy coupled to X-Ray Dispersive Energy Detector (SEM-EDS), and Gas Chromatography coupled to Mass Spectrometry (GC/MS).

Results evidenced that 4 out of 5 ceramic containers were not locally produced, and the raw material employed is compatible with the ophiolitic outcrops of la *Bartolina*, roughly located 15 km from the town. Just the vase from division B was probably produced using locally available raw materials. Regarding their content, on ceramic containers from division A biomarker analysis points to the presence of vegetable oils, and in some samples erucic acid was detected. This unsaturated fatty acid is a known marker for the presence of *Brassicaceae* oils, which have been mentioned, for example, in Roman classical texts as illuminants for oil lamps (Pliny, Natural History XV:7). In the case of ceramic container from division B no conclusive results were obtained regarding their content.

Acknowledgements

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Dental proteomic analyses reveal the sex of human remains from the Greek cemetery of San Giorgio Extra, Reggio Calabria (Italy)

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Sex estimation is one of the most fundamental steps in mortuary studies and bioarchaeology, and it is essential for a deeper understanding of ancient societies, with wide applications in gender archaeology. The aim of this paper is to create a new and reliable protocol for sex determination of the deceased, matching proteomic analyses, archaeological evidence, and anthropological data from a Greek cemetery located in Reggio Calabria (or the ancient *Rhegion*). There, excavations carried out in the San Giorgio Extra district, headed by the Superintendence for the archaeological heritage of Calabria during the years 2004 and 2007, led to the discovery of the most significant Hellenistic cemetery in the city. Specifically, archaeological campaigns brought to light thirty Greek inhumation burials and their related funerary objects. Through proteomic analyses, we monitored a total of eight characteristic peptides for the amelogenin isoform variants AMELX and AMELY from the dental enamel of twelve selected individuals. The presence or absence of the AMELY variant (exclusively present in male subjects, being encoded by the Y gene) allowed us to determine the sex of the analyzed individuals with high accuracy. AMELX variant peptides were monitored as positive controls in order to confirm successful protein extraction from the enamel. These analyses were performed on approximately 10 mg of dental enamel for each individual through acid digestion, purification [1], and injection through a nanoLC column in an EasyLC 1200 chromatograph coupled to a Q-Exactive "classic" Orbitrap Mass Spectrometer. At the same time, archaeological studies based on artifacts discovered inside the graves and double-blind bio-anthropological sex estimation of the twelve subjects were performed in order to compare these evaluations with data from the proteomic analyses. Comparison between these different approaches produced totally congruent results. However, proteomic analysis additionally allowed to establish the sex of four poorly preserved subjects for whom sex estimation was somewhat doubtful, as well as for one indetermined individual. Finally, proteomic results were produced with a protocol faster than those found in the literature [2], and potentially down-scalable to much lower sample amounts.

[1] D. Taverna et al, J. Mass Spectrom. 56, 2021.
[2] F. Lugli et al, Scientific Reports 9:1, 2019.

Laser-induced breakdown spectroscopy (LIBS) in 3D lightweight element analysis on heterogenous materials of cultural heritage

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Laser-induced breakdown spectroscopy (LIBS) has proven in our previous work to be capable of identifying whether the residual organic fraction is sufficient for radiocarbon dating which has become a standard tool for archaeologists since the late 1940s. LIBS can measure the carbon (% C) and nitrogen (% N) concentration indicating the residual amount of collagen resulting from the diagenesis (or degradation) of the bone and also the possible carbon pollution[1]. The main advantage of LIBS analytical technique is to be implemented in situ, providing a rapid and micro-destructive approach directly on the sample.

This presentation will pay particular attention to the quantification of light elements, such as carbon and nitrogen, in the heterogeneous archaeological materials, especially the bones with different mass densities, representing biological issues, shown in Figure 1. This work focuses on the improvement of analytical protocols in 3D mapping, stratigraphic examination and attempts to find criteria to assess matrix homogeneity. These criteria can then be applied to LIBS analysis of heterogeneous materials in other areas as well as in cultural heritage.

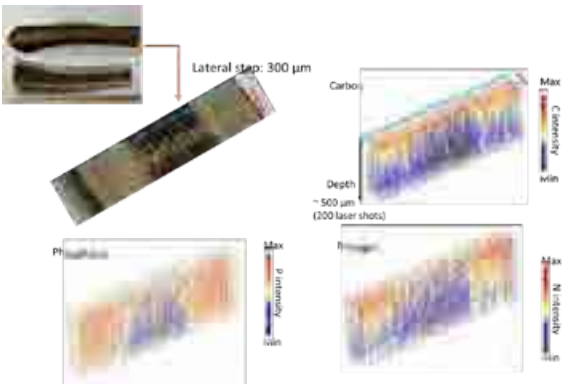

Figure 1. 3D intensity of C I at 247 nm, P I at 206 nm, and N I 744.2 nm of deer antler section by LIBS with a ns laser of 266 nm.

[1] X. Bai; A. Pin; J. Lin; M. Lopez; C.K. Dandolo; P. Richardin; V. Detalle. *Spectrochim. Acta Part B* **2019**, *158*, 105606.

Combining *in situ* Elemental and Molecular Analysis: the Vice-Roys Portraits in Old Goa, India

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The Vice-Roy's Portraits Gallery hosted at the Old Goa Museum of the Archaeological Survey of India in Goa, India, is a unique panel painting collection, spanning from the 16th till the 18th centuries, and representing the Portuguese Viceroys and Governors who administrated the Portuguese provinces in the coastal region of the Indian Ocean. During the Old Goa Revelations project (a collaborative inter-institutional consortium between Evora University HERCULES Lab, Lisbon University Fine Arts Faculty, Archaeological Survey of India and Ghent University), this important collection of panel paintings was examined *in-situ* using a non-invasive approach with mobile analytical instrumentation. Next to a series of imaging techniques, point analysis has been performed, using both, elemental and molecular spectroscopic methods. On the one hand, handheld X-ray fluorescence analysis was used to obtain the elemental composition, while on the other hand, mobile Raman spectroscopy was implemented to obtain molecular information. During the analysis the handheld XRF instrument (Bruker Tracer) and the probe head of the TSI-Enwave Raman spectrometer were manually positioned and kept in contact with the panels' surface. Both non-destructive techniques were used to determine the composition of the paint layers and to study the different treatments (e.g. overpaintings, changes in compositions, etc.) that the artworks have witnessed since their creation.

Cumengeite in wall paintings, intentional application or secondary product?

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In a medieval painted fragment from the Upper Basilica of Saint Francis of Assisi the atypical mineral *cumengeite* ($21PbCl_2 \cdot 20Cu(OH)_2 \cdot 6H_2O$), a mixed (Pb,Cu) basic chloride salt, rarely found in paintings, was identified by synchrotron radiation-based X-ray powder diffraction at the micro-scale (SR-µ-XRPD) (Fig 1).

In the field of heritage science, *cumengeite* has been identified previously in historical bronzes and Roman coins as degradation patina. Regarding painted surfaces, this compound was only detected instead in a series of wall paintings by Hradil et al., where it was interpreted as an intentionally applied blue pigment. In this specific case, a lack of lead-containing compounds was found in the vicinity of *cumengeite*, thus excluding the possibility of its *in situ* formation as result of paint degradation processes. Nevertheless, because of its rare occurrence in nature, a historical recipe for the preparation of this blue pigment has been proposed to explain its presence in mural paintings [1].

The data collected from the fragment from the Upper Basilica of Saint Francis of Assisi, does not allow to distinguish between the intentional application of *cumengeite* due to the large abundance of traditional pigments containing lead and copper identified in the same location and therefore suggesting the plausible *in situ* formation of cumengeite. In this work by accelerated ageing of several model samples, we were able to observe *in vitro* the formation of *cumengeite* when Pb and Cu carbonates are exposed to chlorine under alkaline conditions, thus suggesting a pathway for its formation as a secondary product in the Assisi Basilica. In addition, using crystalline compound specific distribution maps the consumption of the starting pigments in favor of the formation of this complex compound was highlighted.

[1] Švarcová, S.; Hradil, D.; Hradilová, J. et al., Anal. Bioanal. Chem. 395, **2009**, 2037-2050.

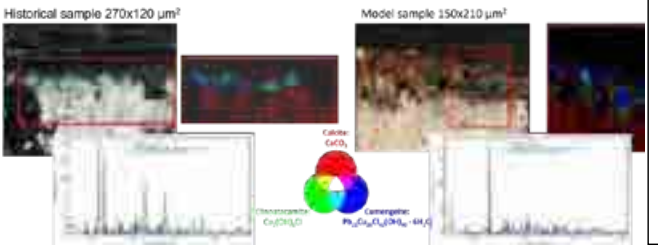

Fig 1: Microphotograph, XRPD distribution maps and 1D XRD patterns collected from an historical sample(left) and a mockup(right) showing the presence and distribution of cumengeite, clinoatacamite and calcite

Etruscan wall paintings from Domus dei Dolia (Vetulónia, Italy): render mortar and pigments characterization

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Destroyed as a result of a fire, the ruins of the Domus dei Dolia remained hidden until 2009, the year of the beginning of the archaeological work. The Domus dei Dolia is located in the Hellenistic quarter of the old town of Vetulonia, now Poggio Renzetti. Basing on the classification of the archaeological materials recovered the Domus, and the whole city, was probably destroyed around the 1st century BC, due to the reprisals made by Lucio Cornelio Silla after the victory over Gaio Mario in the bitter dispute that saw the Etrurian cities take party in favour of the latter during the Roman civil war.

In the context of the collaboration between the HERCULES laboratory, the Isidoro Falchi de Vetulónia Museum and the Town Hall of Castiglione della Pescaia, several render mortar samples were collected for their compositional and textural characterization. All the samples come from different division of the house, and display red, blue, yellow and black mural painting. Most of the samples exhibit a clear stratigraphy: a chromatic layer over a white/grey mortar render, which in turn rests on a beige/yellowish mortar. The data acquisition techniques consisted of X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy coupled to X-ray dispersive energy detector (SEM-EDS) and thin-section optical microscopy.

The integration of the various techniques indicates that render mortars consist of a preparatory layer (*intonaco*) with calcitic aggregates displaying very angular contours which suggest the use of in situ brittled recrystallized limestone/marble. Quartz aggregates are rare and very small in size. The binder is an aerial calcite lime. For the *intonaco* mass loss (39.9 – 42.7 %) in the range 500-900°C was determined using TGA, corresponding to a calcite amount of 91 to 97% attributed to the binder.

The underlying beige/yellowish mortar (*arriccio*) is clearly contrasting from the compositional and textural point of view. The aggregates are mainly silicates prevailing the quartz over the feldspars, lithics (sandstones, slates, cherts), clay pellets being still observed nodules of lime. The shape of the aggregates is rolled to well rolled suggesting a significant transport, probably corresponding to a river sand. The binder is identical to the intonaco that is an aerial lime of calcitic composition. For the *arricio* the mass loss (8.6 – 10.9%) determined by TGA was lower, corresponding to a calcite amount of 20 to 25% attributed to the binder.

The results obtained for the different samples show a strong coherence with each other. On the other hand, they reveal clear criteria in the choice of the raw materials as well as the specific techniques of application for each layer.

Regarding pigment application red ochre, yellow ochre, and charcoals were utilized to obtain red, yellow and black wall piantings, while the blue pigment is still under study.

Acknowledgements

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Something new, something blue: Investigating the compositional conundrums of a mixed-media artwork using FTIR and SEM-EDS

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Contemporary art has seen a massive explosion in variety of materials and techniques incorporated by artists. Furthermore, the instant accessibility of commercial products, usually containing a mixture of several materials, offer the artists ample area for experimentation in order to realize their creative pursuits. It is not uncommon to find amongst the artists' materials certain products whose intended use and longevity may contradict that of artworks as museum objects. The questionable stability of these materials is further complicated by the result of their often unconventional application method and combined use. This signals the importance of thorough investigation and evaluation of the understanding of a mixed-media artwork in order to offer solutions to foreseeable future issues and enrich the knowledge of the materials comprising it, as well as the interaction between them.

This research described has been conducted as part of the University of Amsterdam's Advanced Professional Program in Contemporary Art Conservation, partnered with the University of West Attica and the National Museum of Contemporary Art, Athens. The case-study that prompted this research is the mixed-media artwork "Heinrich Did It" (2016) by Maria Tsagkari, whose upper-top layers of Alkyd-based primer and Polyurethane-based pigmented lacquer were analysed with the use of FTIR spectroscopy and SEM-EDS. The coupling of these techniques helped in identifying the pigments and the various stages of polymerization of the materials. It also provided indications where future degradation could occur due to the specific stratigraphy of this artwork and the manufacturing process followed during its creation. Given that these analytical tools are becoming increasingly present in research labs that analyse artwork materials, their synergy in obtaining useful results is highlighted.

The opportunity to compare different natural ageing stages of the materials was facilitated by the artist's donation of objects for analysis, which contained the same material composition and stratigraphy as the original but were kept in different environmental conditions. Freshly produced mock-ups were also prepared and analysed. The comparison between the infrared spectra of the different samples using the different FTIR modes, namely reflectance, transmittance, and ATR, as well as the comparison between two different pieces of equipment, namely Bruker's Alpha II and Agilent's 4300, will be a key focal point of this presentation. The shortcomings of the different methods will be elaborated in an attempt to help other researchers in choosing the most suitable equipment to analyse similar materials.

Multi-analytical investigation of the glass-based pigment of the Kinn altarpiece (Norway)

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The Kinn altarpiece is a XVIIth century altarpiece conserved in the church of Kinn in western Norway. According to the Kinn church accounts, the polychrome altarpiece was made around 1644 by Peiter Bilthugger and painted around 1703.

Interestingly, the blue painted areas of the altarpiece wings, are characterized by a glass-based pigment. In addition, particles of glass are added on the paint surface, likely to produce an extra glossy effect [1, 2].

Glass-based pigments were produced since ancient times. The study of these compounds offers interesting insights in terms of archaeometrical research. The production of this class of pigments required in fact a high knowledge in terms of metallurgy and pyrotechnology. In addition, different types of materials and products would help to shed light on different technological and manufacturing processes [3].

This work presents a multi-analytical approach based on the application of optical microscopy (OM), scanning electron microscopy coupled with energy dispersive X-ray Spectroscopy (SEM-ED) (Fig. 1), micro-infrared spectroscopy (μ-FTIR) and X-ray diffraction analysis (XRD) for the characterization of the blue glass-based pigment present in the wings of the Kinn altarpiece. Composition, stability, manufacturing and technology questions concerning the analyzed pigment are discussed in the present work.

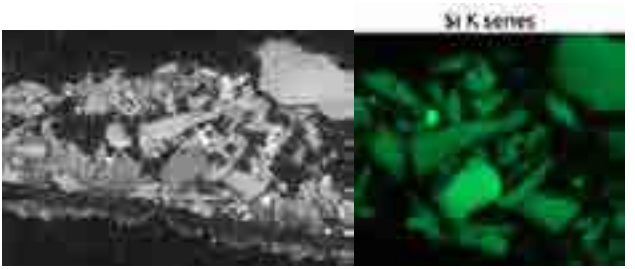

Figure 1. BSE image and EDS map of a paint cross-section.

[1] C. Spaarschuh, T. Olstad, T. Ragazzon, NIKU oppdragsrapport 89, 2022, 1-23.
[2] J. Solstad, NIKU Rapport kunst og inventar 12, 2006, 1-15.
[3] G. Cavallo, M. P. Riccardi, Archaeological and Anthropological Sciences, 13:199, 2021, 1-13.

Material investigation on Italian and Portuguese papers from the Republican Museum Convention of Itu, Brazil

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The Republican Museum Convention of Itu from the University of São Paulo, Brazil, specializes in Brazilian history from the 19th and early 20th century. Documents from this period are currently preserved in its archive. Such documents are written on European papers, especially Italian and Portuguese. Analyses performed on inventories produced between 1850 and 1900 allow the identification of the papers' materials and their watermarks. The studies were carried out through an interdisciplinary approach by historians, physicists, chemists, biologists, conservators and philologists, who consider paper an artifact as well as a support for writing.

Based on the comparison between the two regions of Pescia, in Italy, and Tomar, in Portugal, we intend to evaluate the paper production processes in the second half of the 19th century and discuss paper importation in Brazil [1]. The analysis of the writing was also considered inseparable from the culture and social functioning in which it is inserted, as much as the content.

The material constitution of the papers (composition and fibers) was analyzed by elemental and compositional spectroscopic techniques and by microscopy. The analyses conducted with X-Ray Fluorescence [2] and FT-IR techniques allowed grouping the papers and understanding differences in their constitutive materials. The microscopy techniques allowed the identification of cotton fibers in the majority of the samples and the presence of other fibers different from cotton in a few of them.

The watermarks were documented with transmitted light and helped determine the origin of the different types of paper. The composition of the inks was also studied with FT-IR spectroscopy. Additionally, the ultraviolet-induced visible fluorescence photography aided in the diagnosis of the state of conservation of the inks on these documents.

All the techniques applied demonstrated the potential of this approach for a greater understanding of the materiality and the history of paper production and circulation in Brazil during the second half of the 19th century.

Acknowledgements: Thanks to CNPq (National Council for Scientific and Technological Development) for the financial support (302823/2021-2) and Republican Museum Convention of Itu employees, especially Anicleide Zequini, for the support offered.

[1] M.A.M. Borrego, M. A. Rizzutto, P.R.M. Fachin, R. Hauy, W.G.P. Engel, J.G. Souza, J. B. Bovolenta, I.A.S. Cassemiro. Italian and Portuguese papers in the hinterland of Brazil (1850-1900). In: Claude Laroque et Maryse Pierrard (dir.), 2021 Les papiers filigranés de la période 1830-1950 (Actes de la journée d'étude du 8 octobre 2021), Paris, sites de l'HiCSA et de l'ENS, mis en ligne en novembre 2022.
[2] M. Manso; M. Costa; M. L. Carvalho. X-ray fluorescence spectrometry on paper characterization: A case study on XVIII and XIX century documents. Spectrochimica Acta Part B: Atomic Spectroscopy, v. 63, n. 11, p. 1320-1323, nov. 2008.

New ways of assessing biodeteriogens in cultural heritage

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Outdoor monuments are prone to degradation through a variety of external pathways. Besides the natural environmental conditions, which include day/night and seasonal variations of the relative humidity, temperature, light, wind and rainfall, monuments are also subjected to the action of pollutants. These degradation sources include the atmospheric [1], water [2], and even biological [3] pollution. The main body of literature available regarding biodeteriorating organisms is focused either on the direct detection of biodeteriogens, or on the indirect detection of photoautotrophic biodeteriogens, based on the detection of the chlorophyll signal, mainly using the LIDAR (LIght Detection and Ranging) technique. This paper tries to explore another viable alternative for the detection of chlorophyll and biodeteriogens, the hyperspectral imaging (HSI). This method has the potential of characterizing a wide range of cultural heritage-related materials, including pigments, binders, adhesives, leather, papyrus, paper, mortars [4-7]. The obtained results were compared against those obtained using FTIR (Fourier-transform infrared spectroscopy) and have demonstrated that HSI has the potential of highlighting biocontamination.

[1] V. Comite, A. Miani, M. Ricca, M. La Russa, M. Pulimeno, P. Fermo. Environmental Research, 201, 2021, 111565.
[2] M. Ricciardi, C. Pironti, O. Motta, R. Fiorillo, F. Camin, A. Faggiano, A. Proto. Environmental Science and Pollution Research, 29, 2022, 29409.
[3] L. Bruno, F. Vila, C. Urzí, P. Di Martino. International Biodeterioration & Biodegradation, 175, 2022, 105509.
[4] L. de Viguerie, N. Oriols Pladevall, H. Lotz, V. Freni, N. Fauquet, M. Mestre, P. Walter, M. Verdaguer. Microchemical Journal, 155, 2020, 104674.
[5] S. Sugawara, S. Sugizaki, Y. Nakayama, H. Taniguchi, I. Ishimaru. Infrared Physics & Technology, 117, 2021, 103809.
[6] M. Dinu, L.C. Ratoiu, C. Călin, G. Călin, Buildings, 12.2022.
[7] R. Qurechi, M. Uzair, K. Khurshid, H. Yan. Pattern Recognition, 90, 2019, 12.

Ceramics Quantification: Exploring potentials of XRF for a fast and reliable workflow

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Ceramics have been a steady companion of humans for several thousand years. For many reasons, including the abundance and easy preservation, they are among the most common remains of human activity ranging from daily utensils for cooking, transport and storage to even writing substrates. Ceramics record the human process of travelling and cultural exchange like no other material. One of the main research fields of ceramics are provenance studies. Provenance or ceramic characterization has often been done geochemically as well as petrographically/mineralogically. These studies are mainly invasive and time-consuming. Despite the distinction potentials, these approaches are in themselves limiting not only the number but also the choice of samples that can be analyzed, as unique Cultural Heritage objects are often not available for invasive analysis. However, XRF-based analysis offers a non-invasive way of elemental analysis. Here we will discuss some points of consideration.

Ceramics are made of clay with more or less sophisticated processes of preparation. The raw material can usually be obtained at numerous locations and are the end product of erosion. Their composition is strongly related to the nature of the rocks from which they originate. The main chemical components, besides oxygen, are Na, Mg, Al, Si, K, Ca and Fe (order not related to abundance). Even though these elements' concentrations might vary between clays of different origin and quantification is possible to even relative low concentration levels, there is a major problem that is often not considered. This limitation is the relatively low information depth of less than 50 µm for these rather light elements. This results in a sample-related analytical uncertainty, as the surface of the material might "show" a composition not representative for the sample itself. Typical coating processes or contamination during use and subsequent ground deposition can strongly affect analytical outcomes. The information depth depends strongly on the energy of the fluorescence line used for quantification. Focusing on elements with fluorescence in a higher energy range, such as Rb, Sr Y, Zr and Nb, information depths of several hundred micrometers can be utilized. The presented results will include quantification of ceramics, focusing on the determination of the lower limit of quantitation across different analytical instruments (Bruker's TRACER, ELIO, M4 TORNADO), as well as discussing the best practice for "real-life" work. Moreover, the potential effects of contamination and requirements for sample preparation will be addressed.

Atomic Force Microscopy Nanoindentation as nanoinvasive method for characterizing mechanical properties of art and archeological paintings

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This contribution presents the first results obtained in a study aimed at exploring the capability of atomic force microscopy-nanoindentation (AFM-NI) for evaluating the change in the mechanical properties of the different painting techniques and the changes in the mechanical behavior of the paintings on aging. The study has been based on a prior work in which AFM-NI was successful in evaluating consolidation treatments of polychromed wooden architecture [1]. Several mock-up specimens of panel and canvas paintings prepared two and twenty years ago have been compared to discriminate their mechanical behavior. A second series of mock-up specimens were prepared using the same binding medium and different pigments. A specific method of preparation of samples for AFM-NI analysis has been developed that overcomes the interferences associated with the dust and mineral deposits on the surface of the painting. Mock-up specimens have been compared with real samples of a 13th-century altarpiece from the Valencian Community (Spain). The elastic modulus values indicate that the developed AFM-NI method can discriminate among different techniques and ages (figure 1 and table 1). Acknowledgments: MCIN/ AEI/10.13039/501100011033, grant number PID2020-113022GB-I00, and it also benefited of a Margarita Salas grant from the Requalification program of the Spanish University System of the Ministry of Universities financed by the European Union-NextGenerationEU. (* corresponding author).

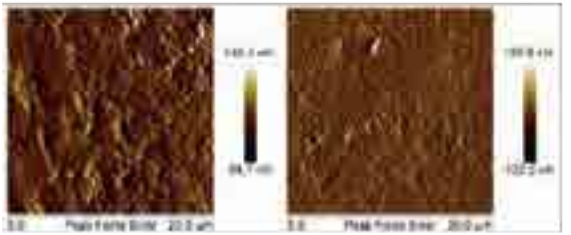

Figure 1.-Topological graph of varnish dated back to: a) 13th century ; b) 21th century

Table 1

	Elastic Modulus (Mpa)	
Age	**Diterpenoid varnish**	**Proteinaceous binder**
21th century	1997±10	1327±5
13th century	4121±700	862±4
Pigment	**Linseed oil**	
Zinc white	1088±10	
Ultramarine blue	736±5	
Binding media	**Zinc White**	
Linseed oil	1088±10	
Porcine gelatin	1327±10	

[1] Y. Lee, S. Martín-Rey, L. Osete-Cortina, I. Martín-Sánchez, F. Bolívar-Galiano, M.T. Doménech-Carbó, Journal of Adhesion Science and Technology, 32(21), 2018, 2320–2349.

A multi-technique setup based on a liquid anode X-ray source for the non-invasive characterization of materials

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In the last decades, a novel technology for X-ray sources based on the use of a liquid anode has been developed, in order to increase the maximum achievable brilliance by at least one order of magnitude compared to conventional microfocus sources [1].

With this innovative equipment, a High-Brilliance X-ray laboratory (HiBriX Lab) is presently under development at the University of Turin, hosted at the NIS inter-departmental Centre. It was designed by integrating different detectors and focusing optics to represent a unique laboratory in Italy and with a handful of comparable examples in the world. The aim is to cover several applications such as:
- material characterization via µXRD and µXRF maps;
- investigation of detector performances in terms of charge collection efficiency or as a function of damage effects;
- single cell level radiobiology;
- X-ray imaging (2D radiography and 3D computed tomography - CT) of objects having a wide size range.

Procurement of the different components has been almost completed and their integration is underway, also by means of the development of specifically dedicated software for system control. To date, concerning the microfocused branch of the lab, a minimum spot size of about 25 microns has been achieved by means of a set of twin paraboloidal mirrors, and a maximum flux density of 2.7×10^{10} ph s^{-1} mm^{-2} has been obtained with a polycapillary optics system specifically delivered by INFN X-lab in Frascati. On the other side, where a 30° cone beam is available, a versatile X-ray imaging setup is installed, which allows the acquisition of radiographs and tomographic scans of very different kinds of samples: objects of dimensions in the sub-mm to few tenths of cm range, with wide variability in atomic number and density values, such as the samples of interest in the field of cultural heritage.

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[1] O. Hemberg et al., Liquid-metal-jet anode electron-impact x-ray source, Appl. Phys. Lett. 83, 1483 (2003)

Remote Sensing for Land Use and Land Cover Change: Interpretation of Iznik's Rural Heritage

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This study focuses on analyzing the changes in the rural landscape of Iznik/Turkey between 1985-2022. Iznik is an important historical city on the UNESCO World Heritage Site Tentative List and has gained and preserved its identity as a rural landscape from the past to the present. The city has a strong connection with the rural landscape and surroundings since the town has been in interaction with its rural surrounding hinterland since prehistoric times [1]. Analyzing the change and transformation of the rural landscape in the region over time using remote sensing data will guide further studies for its preservation. It will show how the development in the built environment changed and impacted the rural heritage.

In this study, land use and land cover (LULC) maps for the years 1985 and 2022 were obtained using remote sensing and geographical information systems, and they are compared with each other. A series of Landsat scenes from these years were processed through a pixel-oriented method. It is used in the following step, which involves obtaining classified maps by labeling the 30×30 pixels of the composited Landsat scenes according to the seven classification classes; water, built-up areas, agricultural lands such as arable and permanent lands, forests, reeds, and open spaces with no vegetation created in the ArcGIS Pro software. In the next step, an accuracy assessment is applied. As a result, the average classification accuracy for these years is 84%. This proves that the LULC maps of 1985 and 2022 obtained by using SVM on the Landsat scenes, which have high and close classification accuracy, are reliable outputs that can be compared in a healthy way for the analysis of land cover change [2]. In the last step, change detection analysis is performed to establish the differences between 37 years. This analysis revealed 49 different classes of change. The most striking changes were observed within agricultural lands and between agricultural lands and the built environment.

The methodology in the study followed for creating Land Use Land Cover (LULC) maps using Landsat scene data provide information about the changes affecting rural heritage areas in different ways. In 1985, there were 428,76 hectares of built-up areas, increasing to 894,96 hectares in 2022. More than 50% of this change has occurred on agricultural lands. On the other hand, it has been determined that there is a transformation from 996,57 hectares of arable land to permanent agricultural sites. In addition to these major changes, other changes affecting rural land and lifestyle have been detected on the bases of lakes and water reserves, and forest landscapes.

The result of this study indicates that there have been dramatic changes in the rural heritage site over the last 37 years. Furthermore, this can encourage conservation decisions in the hinterland to be made at a larger scale since changes in land use have permanent effects on the rural landscape and the conservation efforts for the historical city of Iznik itself.

Key words: Change detection, Image classification, Rural landscape changes, Land cover changes, Iznik, Conservation of rural landscape.

[1] Alioğlu, F., & Kösebay Erkan, Y., A Walled City: Nicea in the History. The Reuse of Ancient Fortified Settlements from Middle Ages to Early Modern Time, Scientific Bulletin Vol.65, Europa Nostra, 2012.
[2] Zhou, Z.-H., Ensemble Methods: Foundations and Algorithms, CRC Press, 2012.

Goupil & Cie and the democratisation of art in the 19th century: A non-invasive investigation of mechanical reproductions of artworks

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Keywords: non-invasive analytical study, VIS-NIR-SWIR imaging, coloured print reproductions, engraving techniques, Goupil collection

In the 19th century, advances in printing technology and mechanical reproduction created unprecedented access to art for the general public. Goupil & Cie, leading print publishers and dealers of that time, was one of the principal actors of this "revolution" in artistic production. Established in Paris in 1829 and active until 1921, this company applied and patented many printmaking and photographic techniques, including etching, engraving, aquatint, lithography and photogravure, to reproduce copies of artworks. The prints were then enhanced with colours and sold. Through its national and international distribution, Goupil popularised the painters of its time and the masters of the past, participating in the dissemination of taste, acting as a source of inspiration for many artists and above all, exerting a decisive influence on the globalisation of the art market.

Twenty artworks, hitherto unstudied, have been selected from the extensive collection of the Goupil Museum (including 46 000 prints), hosted by the Museum of Aquitaine in Bordeaux (France), to get a deeper understanding of their printmaking techniques and their state of conservation. A multi-analytical approach based on non-invasive, contactless and portable techniques, including portable optical microscope, VIS-NIR-SWIR Imaging, FORS, and XRF, was implemented to characterise colouring materials (dyes, pigments and inks) and binders. The complementarity of these analyses allowed the revealing of distinctive features of the printmaking techniques. For example, the application of gum arabic to enhance some details of the picture has been observed in a few former reproductions, such as in the lithograph "*Ce n'est pas ma faute*" (1834), which is one of the oldest works in the collection. The study also identified the pigments used by Goupil (synthetic and natural, like viridian, ultramarine, cerulean, minium, molybdenum orange, etc.) and elucidated the evolution from hand-colouring with watercolours when the production was modest to printing inks once the company had assumed industrial dimensions. The access to an extensive set of historical reference pigment charts from the Goupil Museum permitted the creation of a comprehensive analytical database that facilitated the identification of the prints'compounds and provided information on their alterations.
The investigation of some reproductions of the same subject with different analytical techniques allowed us to observe differences in their materials and properties as well as in their state of conservation, as in the case of the two prints "*Enfin… seuls!*" (both from 1883), where the burin engraving displayed higher degradation than the photoengraving. Finally, some elements of paper degradation were highlighted, including support yellowing and foxing. The paper will detail how the observed degradation products might suggest a potential correlation between mass reproduction at lower cost and the loss of material quality.

Detecting visual and chemical modifications induced by the high-flux synchrotron X-ray analysis of ancient teeth

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Synchrotron-based X-ray methods provide unique information about the 2D and 3D anatomy and chemistry of fossils. The asset of using the high-brilliance synchrotron beam may, however, induce chemical modifications of the materials that can be either apparent to the naked eye (e.g. teeth darkening [1]) or non-visible (e.g. degradation of ancient DNA [2], photo-reduction or oxidation of redox-sensitive elements such as rare earths [3]). Little is known about the chemical origin and kinetics of such side-effects, and very few monitoring and mitigation strategies have been implemented to visualize and/or prevent these effects [4].

In this contribution, we will present the first results of a study investigating the behavior of a corpus of ancient teeth (ranging from 20,000 up to 70 million years in age) under micro-focused beam irradiation. We developed an original approach aiming at detecting, localizing and monitoring color changes using full-field multispectral X-ray excited optical luminescence (XEOL) microscopy combined with the assessment of speciation changes using X-ray absorption spectroscopy (µXAS). Among results, we observed interesting decay patterns of XEOL by performing irradiation sequences in the minute time-scale (Fig. 1). Post-irradiation UV illumination is commonly used to "reverse" tooth darkening. We therefore collected XEOL measurements with and without concomitant UV illumination and under different excitation energies. While the excitation energy appears to have a limited impact on the kinetics of XEOL decay, UV illumination allowed for a faster and more complete recovery of the XEOL signal after high-flux X-ray irradiation.

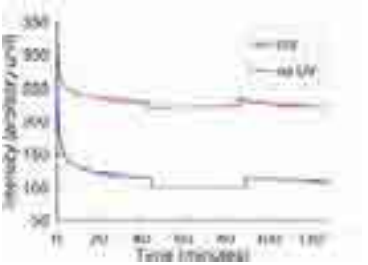

Figure 1: Evolution of the XEOL signal intensity for a 32-million-year-old *Mesohippus* enamel irradiated by a 12 keV X-ray beam with and without concomitant illumination by a UV source at 385 nm. The beam was cut between minutes 45 and 90.

[1] G.D. Richards *et al*., American Journal of Physical Anthropology 149, 2012, 172-180.
[2] A. Immel *et al*., Scientific Reports 6, 2016, 32969.
[3] P. Gueriau *et al*., Analytical Chemistry 87, 2015, 8827-8836.
[4] L. Bertrand *et al*., TrAC-Trends in Analytical Chemistry 66, 2015, 128–145.

Painting layers of gothic stone sculptures of Buda Castle, compositional analysis and colour reconstruction

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This research study focuses on the painting techniques and materials of 15th-century Gothic sculptures from Buda Castle, Hungary[1]. These sculptures are unique because they came from a destroyed, buried medieval atelier that was excavated in 1974. It means the original painting layers were never overpainted or treated over the centuries.

Although the painted surfaces were damaged when those were buried, the intense sampling and the detailed optical (PLM) and scanning electron microscopic (SEM-EDX) examination of the cross sections of the painted layers revealed novel relationships between the painting techniques, material, and workshops.

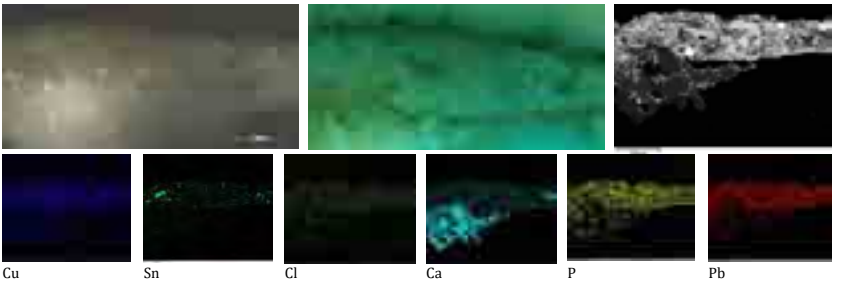
A strong connection between the surface treatment of the stone material with a special tooth chisel and the priming technique was found. Distinctive and conscious application of the ground was detected, and three different groups of statues were identified: 1) statues with ground, 2) without ground, and 3) and statues where ground was applied below certain colours. Scratched surfaces showing toolmarks were observed only at the grounded surface (type 1).

The same sophisticated solutions, pigments, and painting techniques were identified on the sculptures belonging to the same group. This grouping helps us find relationships between artists, sculptors and painters working in the same atelier.

We have found evidence supporting the French artistic influences and connections representing the artistic style of the court of Sigismund of Luxemburg (r. 1387–1437). These include the special stone surface finish, the use of the lead-tin yellow type I in the first part of the 15th century, the mixed green colour from blue azurite and yellow pigments instead of copper greens (malachite), and the usage of lead and the calcium-phosphate in paints.

It was possible to digitally reconstruct the original colour of several statues based on this research.

This detailed database of the samples provides further opportunities to compare medieval painted stone sculptures of different countries and workshops. The samples have the potential for further instrumental analysis to discover the locations and origins of materials and obtain additional information on painting techniques and materials.



Green layer without ground. Cross section / VIS / BV luminescence/ SEM-BSE
The green colour from a mixture of azurite and lead-tin yellow I. The azurite is transformed by soluble salts to copper-chloride The lead, calcium and phosphorus containing isolation layer are clearly visible under the green layer over the stone.

[1] This research was financed by National Research, Development and Innovation Fund project: "Sigismund Period Sculpture Finds from Buda Castle" OTKA K1[illegible] Principle investigator: Szilárd Papp, art historian. Statues are in the collection of Budapest History Museum.

Mind the cracks! Chemical and physical changes of blended Thitsiol/Urushiol Asian lacquers elucidated through a novel multi-analytical study

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A blend of Thitsiol with Urushiol Asian lacquers was a mixture often used for lacquerware exported to Europe from Japan in the XVII century [1]; it is also used to produce new lacquer by the coating industry [2]. Despite the importance of East Asian lacquer's use in the west and some of their degradation issues such as micro-cracks formation, which are of great concern in indoor museum collections, there is a lack of scientific studies for understanding their curing, aging, degradation, and photo-ageing processes.

In this work, blend-models of Thitsiol with Urushiol in different percentage concentrations were prepared and for the first time their curing process, as well as ageing, degradation, and photo-ageing processes, were studied by a multi-analytical approach. Pyrolysis in thermally assisted hydrolysis and methylation mode, coupled with gas chromatography and mass spectrometry (THM-GC/MS), μ-Fourier transform infrared (μ-FTIR) spectroscopy in transmission and attenuated total reflection (ATR) mode were used for this research in addition to digital microscopy, optical coherence tomography (OCT), and colour measurements. For the curing, the specimens were dried at 20 °C and 80 % rH% and then aged in dark-environmental conditions for two years. The light-aging was then carried out for a maximum of one-month in a daylight chamber, which uses radiation with wavelengths from 320 nm.

The data obtained within this research highlights specific micro-cracks formations at the surface level and oxidation markers for the Thitsiol-Urushiol blends, and their mechanism of reactions are proposed according to the results obtained with the different techniques used.

[1] Chasen J., Heginbotham A., Schilling M., The Analysis of East Asian and European Lacquer Surfaces on Rococo Furniture, in Wilson G., Heginbotham A. (Eds.): French Rococo Ébénisterie in the J. Paul Getty Museum, J. PAUL GETTY MUSEUM, LOS ANGELES, Getty Publications, Los Angeles, U.S.A., 2021, pp. 9-16

[2] Honda T., Ma X., Lu R., Kanamori D., Miyakoshi T. Preparation and characterization of a new lacquer based on blending urushiol with thitsiol, J. Ana. Appl. Sci. 121 (2011) 2734-2742.

Elemental Analysis of Extraordinary Silver Coins Discovered on Polish Territories

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SEM-EDX (Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy) measurements and ED-XRF (Energy-Dispersive X-ray Fluorescence) and μ-PIXE (Proton Induced X-ray Emission) were made in order to discuss the performance of these methods and their applicability in archaeometry. The early medieval Polish coins called cross dinars (*denary krzyżowe*, *krzyżówki*) were chosen as an object of study. Elemental composition of surface and core of the coins were measured with EDS. Thanks to the identification of corrosion pits on the surface we were able to carry out a detained analysis of cross dinars. One of these are composed of an Ag-Cu alloy while the others were manufactured by means of plating a Cu-Zn based core with a silver sheet. So far, it was believed that such coins had been homogeneous Ag-Cu alloys. Optical microscopy examinations demonstrate a layered structure and a presence of the core inside coin. Between the core and silver overlays there is an empty space, which indicates that these coins were made by hammering (plating) of silver sheets forming an overlays onto the central part i.e. core. Presented method revealed a significant difference in chemical composition of surface comparing to core. We observe mayor difference in Ag and Cu. Obtained results present the strong argument in application of EDS and XRF in archaeometry of coins. The application of mentioned techniques on micrometer scale allowed us the identification of Cu-Zn cores in early medieval silver Polish coins [1].

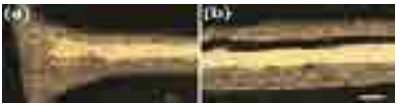

Fig. 1. Microscopic photo of Coin A (cross-section).

Fig. 2 SEM – BSE image of Coin A (cross-section).

[1] Ewelina Miśta-Jakubowska, Microanalysis of early medieval archaeological objects made of silver alloy, Wiadomości Numizmatyczne, R. LXVI, 2022, z. 210

A New Look into NASA's Pioneering Atomic Oxygen Treatment Removing Lipstick Defacement from Andy Warhol's "Bathtub"

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"I never understand how the lipstick business goes on because lipstick lasts forever" Andy Warhol told Paloma Picasso in a 1980 conversation published in Interview [1]. After an event for a cosmetics company was held in the galleries at the Andy Warhol Museum in 1997, and a vandal kissed Warhol's *Bathtub* (1961) with red lipstick, the prospects of the damage "lasting forever" seemed fateful, as the red smudge could not be removed using the available means. Conservators at the museum turned to NASA, where B. Banks and S. Miller pioneered an atomic oxygen (AO) method to remove the lipstick without physically touching the surface [2] but the AO effects were not investigated. AO is an emerging green non-contact mean and has unique potential for otherwise problematic porous and fragile surfaces that cannot tolerate mechanical "wet" or "dry" cleaning. In the context of Horizon Europe MOXY (2022-2026) and FWO PLASMART (2022-2026) projects and in collaboration with the European Space Agency ESA, the researchers experimented with AO on typical cultural heritage materials and contaminants, using the low Earth orbit oxygen environment simulator LEOX. The samples also included a lipstick, which in the past has been time and again used for art vandalism [3]. The poster focuses on the interim results, characterization and reconstruction of NASA's lipstick treatment. In this study AO was produced using laser detonation method and the fluence was calculated using the mass loss calculation of the Kapton HN witnesses. Surface morphology was investigated using high-definition 3D microscopy (HIROX) and SEM, chemical surface changes were investigated using FTIR-ATR and XPS. The lipstick composition contained red iron oxides, which are not affected by AO. However, the AO role was essential, as it converted organic compounds in the lipstick into harmless volatile byproducts (CO, CO_2, H_2O), which enabled minimally invasive dry-removal of the powdery residuum in a second step, repeating NASA's methodology in their treatment of Warhol's *Bathtub*. The findings indicate that AO reacts incrementally with diverse organic compounds on the surface, but at differing rates, which allows formulation of targeted and innovative non-contact treatments, which do not require organic solvents and liquids. The reconstruction of the two-phase cleaning approach was confirmed by inventor B. Banks and the mechanism behind was explained by the new findings, using imaging and analytical tools were not available back in 1997 when the treatment of *Bathtub* took place.

A. Warhol "Bathtub" treatment

Samples exposed to AO at LEOX

1997 lipstick cleaning (left), 2022 reconstruction cleaning tests

[1] https://www.interviewmagazine.com/culture/paloma-picasso-the-diamond-dove-andy-warhol
[2] Banks, B., Rutledge, S., Karla, M., Norris, M., Real, W., Haytas, C. 1999. Use of an Atmospheric Atomic Oxygen Beam for Restoration of Defaced Paintings, in Proceedings of the 12th ICOM-CC Meeting, 1999, NASA/TM-1999-20941
[3] Banks B., Markevičius T., Olsson, N. 2017. Monoatomic oxygen system for non-contact nanoscale cleaning of vandalized 20th c. modern and contemporary artworks, CeRoArt pp.1-10.

Analysis of vitreous beads from the Iron Age site of Bilsk hillfort (Ukraine): an insight into glass-making technology and trade networks.

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Vitreous materials were known and appreciated by the population of the areas north of the Black Sea region during Scythian time [1]. Bilsk settlement was one of the most important regional centres of craftsmanship and trade in that period [2]. Glass finds underline the role that Bilsk played as a center connecting the Barbarian hinterland and the coastal Greek colonies. The comprehensive chemical characterisation of 28 glass and faience objects from this site was performed in this study by Optical Microscopy, Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry, micro-Raman spectroscopy, Laser Ablation Inductively Coupled Plasma Mass Spectrometry and micro-X-Ray Diffraction. Selected methodology provided compositional (SEM-EDS, LA-ICP-MS) and structural (OM, SEM-EDS, μ-Raman, μ-XRD) information with the possibility of cross checking of the obtained results.

Based on the compositional data, information on the sources of silica was obtained by comparing the trace elements concentrations with the compositions of coeval vitreous materials found in the area, and the question of local/regional production emerged. The focus was then set on colouring agents, and the technology of glass colouring was revealed for each object. Chemical data suggest that the Bilsk settlement was connected to the main glass-making regions of the time through a far-reaching trade network.

[1] I. Shramko, M. Tarasenko. Egyptian Imports of 6th Century BC in the Materials of Forest-Steppe Scythia. Shodoznavstvo, (2022), 89, pp. 139–180.
[2] I. Shramko, Bilsk (Belsk) City-Site. Ancient West & East, (2021), 20, pp. 171-218.

Assessing the existence of a late-medieval royal scriptorium in Lisbon: A multi-analytical characterisation of 15th-century Portuguese illuminated court manuscripts

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Fifteenth-century chronicles and political, philosophical, and moral treatises make a unique instance of the social implications of late-mediaeval art patronage among the Portuguese royal court. Realised across the entire century, these manuscripts express the way in which artists attended to the political inclinations and need for social promotion of certain individuals [1]. So intimate was the connection between the members of the Portuguese elite and the artists they contracted, that the hypothesis of the involvement of a dedicated royal scriptorium was set forth [2].

The existence of such a scriptorium has found some art-historical support [3]; however, scientific evidence has not been explored thoroughly to support the hypothesis. Considering this fact, this work proposes a technical inspection of three case studies to cover the entire century of activity of this royal scriptorium. For the purpose, three manuscripts produced across the entire period have been selected as case studies: the Livro da Virtuosa Benfeitoria in the municipal library of Viseu (ca. 1430); the Crónica Geral de Espanha de 1344 in the Academia das Ciências, Lisbon (ca. 1430) and the Crónica de D. Duarte de Meneses in the Arquivo Torre do Tombo, Lisbon (ca. 1470).

More specifically, this work aims at verifying the existence of material consistencies within this manuscript production or its technical trends through a multi-analytical approach. With imaging, elemental and molecular analytical techniques (DM, IRR, p-EDXRF, MA-XRF and ER-FTIR, UV-Vis-NIR FORS), a selection of miniatures was analysed at their conservation site with portable instruments to characterise the materials of the illuminations (binders and extenders). Technical clusters are drawn by assessing the artistic process adopted across the case studies (technical and stylistic features), and the material uniformity of the binding media is drawn with chemometric analysis coupled to UV-Vis-NIR FORS. For the calibration of the chemometric models, the blue paints from the case studies are compared to laboratory mock-ups prepared at several formulations (type of carrier, pigment concentration, thickness of the pictorial layer, type of extender used) and different naturally aging rates.

[1] M. Ventura, A corte de D. Duarte: política, cultura e afectos, 2013.
[2] C. Tibúrcio, O fascínio do gótico: um tributo a José Custódio Vieira da Silva, 2016, 87-105.
[3] C.Tibúrcio, S.Valadas, A.Cardoso, A.Candeias, C.Barreira C.Miguel, Microchemical Journal 153, 2020, 104455.

The White Glaze of Delft Blue

Variations in composition in its glory period, from 1625 to 1800

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Delft Blue (Delftware) is earthenware with a white lead glaze to which tin has been added, applied to both the front and back of the earthenware and usually provided with a bright blue fine decoration. The Rijksmuseum (Amsterdam, The Netherlands) holds one of the world's largest collection high quality Delftware from the 17th and 18th centuries. In 2016, a comprehensive technical study started using energy dispersive micro-X-ray fluorescence spectroscopy (EDµXRF) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) to study differences in composition of the white glaze from the rise to the fall of Delftware.

Throughout the entire period, from 1625 to 1800, when up to 33 factories were active in the city of Delft, potters constantly strived to produce high quality earthenware. They did this to compete with the highly demanded thin and glossy Chinese porcelain and with the cheaper English creamware later. As only a limited number of recipes have been found in written manuscripts, it is believed that recipes were shared through oral tradition from generation to generation and between families and factories, suggesting that only minor differences in composition are to be expected within Delftware [1, 2]. This hypothesis is supported in this study by principal component analysis (PCA) of the white glaze EDµXRF data of 250 marked earthenware pieces. It shows a cluster of Delftware measurement points separated from measurement points of earthenware produced elsewhere (Portugal, Friesland or later ceramic additions). This indicates that PCA on EDµXRF data can be used as an aid to questions of geographic origin and authenticity.

Secondly, after excluding data from the fronts - thus avoiding artifacts of overglaze and decorations – the EDµXRF white glaze data from the backs of 170 marked Delftware pieces demonstrated minor but clear variations in elemental composition over time. Based on 30 elements, a partial least squares regression model (PLS) has been made. This model predicts the age of undated pieces on average within +/- 40 years. Thirdly, hierarchical clustering was used on the EDµXRF dataset to investigate whether anonymous pieces can be attributed to a specific factory in Delft based on composition. The application has proved limited, but is potentially promising when including the dating. Lastly, the presence of strontium in the white glaze appeared to be related with the ingredient soda from kelp (seaweed). The first appearance of strontium in the white glaze of Delftware overlaps with the introduction of kelp soda from the UK to the Netherlands around 1670.

Detail of plate with blue flower decoration, BK-1963-29, De Grieksche A, 1690-1705

[1] J. van Dam, Mededelingenblad Nederlandse Vereniging van vrienden van Ceramiek en Glas 3-4, 1999, 1-98.
[2] M. van Aken-Fehmers, L. Schledorn, T. Eliëns, Geschiedenis van een nationaal product Deel II, 2001, 1-359.

Assessing attribution and artist materials and methods of botanical drawings using non-invasive technical analysis

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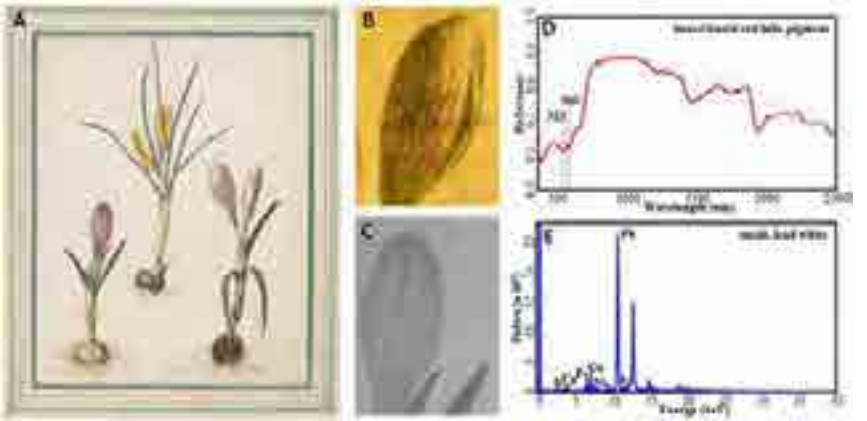
The botanist and art collector Agnes Block (1629–1704) commissioned numerous artists to paint the plants in her garden at her country estate, Vijverhof, near Utrecht in the Netherlands. While some of these botanical drawings have survived in a bound album (now in the collection of the Rijksmuseum), others have been dispersed across many museum collections. So far, more than a dozen such drawings have been tentatively identified within the Fitzwilliam Museum's collection, most of which have been previously attributed to the artist Alida Withoos (c.1661/2–1730). However, as many drawings are unsigned and have varying styles of execution, it is suspected that other artists were also involved in their creation, with some drawings appearing to involve collaboration between multiple hands.

In this research project a suite of non-invasive imaging and spectroscopic methods have been employed to discover Block-commissioned drawings within the collection of the Fitzwilliam Museum and to learn more about the number and identity of artists' hands in these works. Methods used in this study include transmitted light imaging, near infrared imaging, X-ray fluorescence (XRF) spectroscopy, fibre optic reflectance spectroscopy (in the ultraviolet, visible and near-infrared range) (FORS), and Raman microspectroscopy. Taken together, this analysis revealed variation in the presence and quality of underdrawing, which was coupled with a systematic assessment of the palette used on each drawing to create groupings of works by the same hand. This systematic, multimodal research approach has solidified a methodology to aid attribution of drawings as associated with Agnes Block and has revealed the collaborative nature of her commissioning process.



Willem de Heer, *Three different kinds of crocus* (PD.925-1963). **A** visible image, **B** transmitted light image detail showing inscription with the artist's name verso, **C** 925 nm NIR image detail of purple flower, **D** FORS spectrum of purple flower, **E** XRF spectrum of purple flower.

DSC and cryo-FTIR indicate presence of water clusters in zinc-white oil paint

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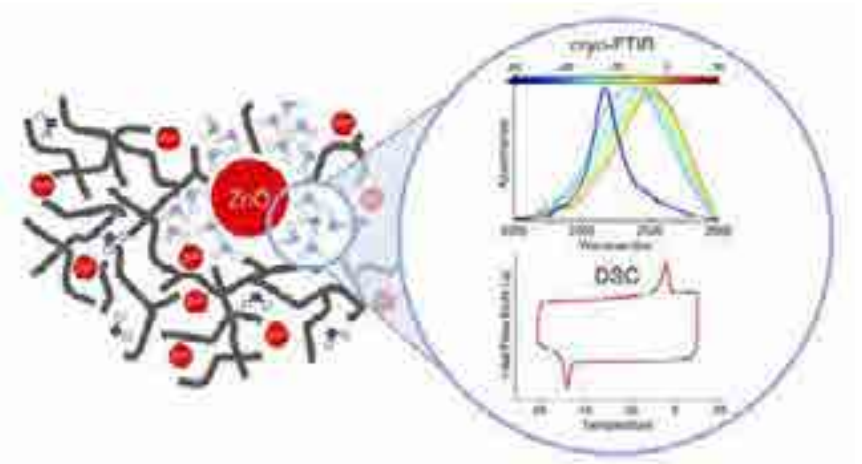
A growing body of oil paint research suggests that there is considerable heterogeneity in the chemical conditions within oil paint layers. This variation in local conditions has a large influence on the scope of chemical reactions and transport mechanisms that take place. Here, we investigate how water is distributed in oil paint at a molecular scale. Liquid-like water clusters, as opposed to molecularly distributed water, can play a crucial role in the dissolution and transport of ions and small molecules. Therefore, understanding the environmental factors or paint compositions that favour the presence of clustered water in oil paint is hugely relevant for elucidating chemical degradation pathways and developing preventive conservation strategies.

We focus on zinc-white oil paint, a type of oil paint particularly prone to water-related degradation phenomena [1]. By measuring water freezing and melting transitions in water-saturated zinc-white paint films, differential scanning calorimetry (DSC) can distinguish between freezable water and non-freezable water, corresponding to clustered and molecularly distributed water, respectively. Isotope-diluted cryo-Fourier-transform infrared spectroscopy (cryo-FTIR) confirmed the existence of both types of water, while the O-D vibration bands also gave insight in the chemical environment of water in the paint. In addition, a comparison to titanium-white paint films and zinc-ionomer model systems gave rise to the hypothesis that clustered water in water-saturated zinc-white paint is located near the pigment-polymer interface. Furthermore, the remarkably low freezing point of water in these paint systems allows an estimate of the approximate size of the water clusters.

[1] M. Beerse, K. Keune, P. Iedema, S. Woutersen, J. Hermans. ACS Applied Polymer Materials, 2(12), 2020, 5674-5685.



Magnetic Resonance Imaging clinical scanner for archaeological waterlogged wood investigations

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Moisture is the main factor that causes deterioration in cultural heritage objects made of porous materials. At the same time, it is essential to choose non-destructive and non-invasive approaches for more sustainable investigations and make them safe for the environment and the sample. The question addressed in the work concerns the possibility and the opportunity to investigate waterlogged wood by Nuclear Magnetic Resonance Imaging (MRI) made with clinical scanners to carry out non-destructive volumetric diagnostics. In this study, MRI, the most important non-invasive medical imaging technique for human tissue analysis, was applied to study archaeological waterlogged wood samples. This type of archaeological material has a very high moisture content (400%–800%), thus proving to be an ideal investigative subject for MRI which detects water molecules inside matter [1]. By this methodology, it is possible to obtain information about water content and conservation status through T_1, T_2, and T_2* weighted image analysis, without any sampling or handling, and samples are directly scanned in the water where they are stored [2]. Furthermore, it permits processing 3D reconstruction that could be an innovative tool for marine archaeological collections digitalization. In this study, an MRI protocol analysis is shown using a clinical NMR scanner operating at 3T. Results were compared with X-Ray Computed Tomography (CT) images and useful information about moisture content and conservation status in an all-in-one methodology were obtained.

[1] Dvinskikh S. V., Henriksson M., Berglund L. A., Furò I, A multinuclear magnetic resonance imaging (MRI) study of wood with adsorbed water: estimating bound water concentration and local wood density, Holzforschung, Vol. 65, Issue 1 (2011) pp 103-107

[2] Capuani S., Stagno V., Missori M., Sadori L., Longo S. High-resolution multiparametric MRI of contemporary and waterlogged archaeological wood, Magnetic Resonance in Chemistry, Vol. 58, Issue 9 (2020) pp 860-869

Art-Technical Analysis of an 14th century illuminated Napolitan Bible with a diverse toolbox of analytical and imaging tools. Documentation and discoveries

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The multimodal art technical research project on the 14th century illuminated Bible of Anjou made clear that its material characteristics could be documented and studied in an innovative way. They shed new light on the production process and long provenance of the Bible (Naples, 1340, illuminated manuscript on velum, kept at Maurits Sabbe Library, KU Leuven, Mss 1). High quality, well documented and consistently produced digital images of the Bible have proven to be crucial assets for the study and conservation of the manuscript, including condition reporting, study of the codicology, textual scholarship, and more in depth, the identification of the used materials by the illuminators (inks and pigments).

An initial research period ran between 2007 and 2009 (published in 2010 and 2011)[1][2], building on that a new research campaign started in 2021-2022. It applies research infrastructure which was unavailable in 2009 and led to new unexpected insights for non-invasive research on medieval illuminations. This lecture will present the new applied methods and equipment, illustrated with research questions concerning the Bible of Anjou. A selection of illuminations and specific passages were captured with the White Light Microdome, a Multi-Light Reflectance imaging tool, followed with captures by the Multi-Spectral Microdome. This same corpus of illuminations was examined with a new generation of research and imaging devices by KIK-IRPA (Brussels) and VIEW (KU Leuven) by means of MA-XRF scanning, Fiber Optics Reflectance Spectroscopy (FORS), Raman spectroscopy and Narrow Band Multi-Spectral Imaging (NBMSI).

The new findings and visual documentation are focusing on a selection of five topics in the Bible of Anjou: the use of pigments and inks, the topography of the pictorial layers, the erased ex-libris, the skillful repairs on the marginal borders and the overpainted original coat of arms. Especially the case of the identification of indigo, gold and silver in the underlying erased coat of arms of the first owner of the Bible shed new surprising light on the patronage of this unique Angevin manuscript.

[1] Watteeuw, L., Van Bos, M. (2010). Illuminating with Pen and Bruch. The Techniques of a Fourteenth-Century Neapolitan Illuminator Explored. In: L. Watteeuw, J. Van der Stock (Eds.), *The Anjou Bible. Naples 1340. A Royal Manuscript Revealed. Corpus of Illuminated Manuscripts, vol. 18*, (147-170). Paris - Leuven - Warlpole: Peeters
[2] Van Bos, M., Watteeuw, L. (2011). Analysis of the Anjou Bible. In: M.A. Miranda, M.J. Melo, M. Clarke (Eds.), *Medieval Colours, Between Beaty and Meaning*, (194-204). Lisbon: Instituto de História da Arte.

Step by step: Modelling as a first key to introduce an indirect method of studying heritage inks

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Manuscripts written in inks which are a combination of soluble compounds of transition metals with plant tannins are a large part of collections in archives, libraries and museum throughout the world. It has been noticed that, despite a generally consistent concept of their production, the inks are characterized by a wide variety of chemical compositions, mostly as a result of randomness in the proportions and addition of unusual compounds, such as wine or honey. Lack of reproducibility and significant changeability of inks' compositions often results in their instability, leading to the degradation of paper or parchment substrate.

In 2005 Neevel proposed a use of colorimetric reaction of iron (II) ions with a 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) ligand for the evaluation of ink corrosion risk in manuscripts [1,2]. During the use of an indicator paper soaked with the ligand, ions present in the ink migrate to its surface. Presence of iron (II) ions is manifested by a strong colorimetric effect, while others can be detected with advanced measurements, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [3]. It seems that the study of indicator papers could enable indirect and non-invasive measurements of inks' elemental composition. However, it requires a knowledge of particular individuals' effectiveness in migrating into the indicator papers [4].

Figure 1. Model inks and gall nuts - a natural source of tannins (photo by B. Wagner)

The aim of the ALINA project is to engage machine learning methods in encoding the chemical information hidden in the indicator papers used by the conservators during the examination of the manuscripts. The baseline for the project requires creation of a database containing diverse model metal-tannin inks and corresponding indicator papers. Therefore, a large group of inks with compositions based on the literature and their variations was produced. The inks were manufactured by mixing a gall nut extract with gum arabic and salts of iron or other metals, e.g. copper, zinc, lead, tin or cobalt. 102 mock-ups of the paper inscribed with the obtained inks were aged in the conditions of increased temperature and alternating humidity. The actual composition of the obtained inks and migration of their compounds to the indicator papers will be studied with the use of the spectral methods, including LA-ICP-MS and X-Ray fluorescence (XRF).

[1] J.G Neevel, B.Reissland, Bathophenanthroline indicator paper, Papier Restaurierung (2005) 6: 28–36;
[2] J.G.Neevel, Application Issues of the Bathophenanthroline Test for Iron(II) Ions, Restaurator (2009) 30:3-15;
[3] B.Wagner, E.Bulska, On the use of laser ablation inductively coupled plasma mass spectrometry for the investigation of written heritage, J. Anal. At. Spectrom. (2004) 19:1325-1329;
[4] B.Wagner, A.Czajka, Non-invasive approximation of elemental composition of historic inks by LA-ICP-MS measurements of bathophenanthroline indicators, Talanta (2021) 222:121520

Multi-source data fusion of modern complex paintings

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In recent decades, hyperspectral imaging techniques devoted to works of art investigations have incredibly grown in technical advancements. This provides scientists and conservators with unprecedented depictions of the artworks, in terms of material and technique identification along with their spatial distribution. Nowadays, in situ Macro X-ray Fluorescence (MA-XRF), HyperSpectral Imaging in the Visible, Near and shortWave IR (HSI VNIR and SWIR), and - more recently - Macro X-ray diffractions (MA-XRD) analyses are available for the study of paintings. Nevertheless, the definition of an effective and robust data-processing, able to manage this impressive amount of multimodal spectral data spanning from elemental to molecular information, is still in the early stages. The implementation and exploitation of a multi-source data fusion approach could surpass these limitations. This would enable pixel-by-pixel correlation between techniques and elemental and molecular information.

Here will be presented the data-fusion approach implemented for the imaging analysis of a selection of Edvard Munch paintings (from Warnemunde period, 1907-1908), from the Munch Museum's collection (Oslo, Norway). As for the artist corpus, the artworks are characterized by a complex mixture of paints with variable thickness, mixing, layering and the darkening of some colored areas. The aim was to get a better understanding of the artist's technique, painting materials and to shed light on the complexity of early industrial painting materials used. These have been investigated through the imaging facilities offered by the MOLAB platform of the ERIHS infrastructure, and the study included the exploration of the wide spectral range spanning from X-ray (for the elemental composition and distribution-MAXRF, and crystalline phases identification MA-XRD-mapping) to SWIR, comprehending the Vis and NIR, for the molecular characterization of both organic and inorganic materials.

Low-level data-fusion of HSI, SWIR and MA-XRF have been performed using the imaging of the entire paintings. For selected areas, also MA-XRD data were added. Different statistical data-treatments to the fused data cube have been applied, such as Principal Component Analysis (PCA) and Non-negative Matrix Factorization (NMF). Moreover, the results have been compared with more common data-treatment on individual cubes, such as elemental mapping for XRF and Spectral Angle Mapping for HSI.

Correlative X-ray Fluorescence and Ptychography Tomography at the Nanoscale Elucidate Different Smalt Mixtures used in *The Night Watch*

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In 2019, *Operation Night Watch* started at the Rijksmuseum in Amsterdam. A wide range of macro-, micro-, and nanoscale techniques were used to study this masterpiece by Rembrandt van Rijn. One of the common pigments used in *The Night Watch* (1642) is smalt, a ground blue potash glass colored by cobalt (Co) ions.[1] In this synchrotron radiation-based study, we used a combination of nanoscale X-ray fluorescence (XRF) imaging and ptychography, both in tomographic mode[2], to visualize and assess samples from different paint mixtures containing smalt. The experiments were conducted at beamline P06, Petra III, DESY(Hamburg, Germany).

Three samples were studied, taken from Co-containing areas in the painting that have different tonalities and pigment composition (Figure 1a). Due to the irregular shape and size of the smalt particles, it is difficult to assess the amount of smalt in the paint samples based on 2D techniques such as light microscopy or SEM-EDX. The 3D investigation of the samples at high spatial resolution enabled us to count the smalt particles, as well as to study their shape and volume. The analysis of the spatial correlation of cobalt with other elements present in smalt (As, Ni, and Bi) provided information about the smalt production, which in turn allowed determining whether Rembrandt had used different types of smalt. Figure 1c shows the 3D distribution of Pb, Fe, Ca, Co, Cu, Ti, and K in one of the samples used to provide semi-quantitative information on the composition of the paint mixtures and the differences between the three smalt-containing samples. Ptychographic reconstruction enabled us to visualize the whole paint sample, including the organic fraction and components containing only elements lighter than sulfur, such as glass (SiO_2).

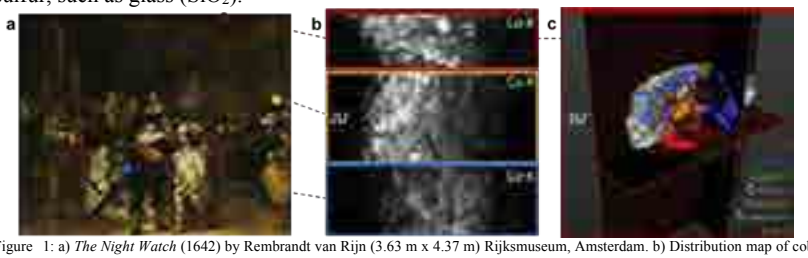

Figure 1: a) *The Night Watch* (1642) by Rembrandt van Rijn (3.63 m x 4.37 m) Rijksmuseum, Amsterdam. b) Distribution map of cobalt of three paint samples containing smalt. c) 3D rendering of the distribution of elements in the paint sample from a smalt-rich area in the background (indicated with red outline in b).

[1] L. Robinet, M. Spring, S. Pagès-Camagna, D. Vantelon, and N. Trcera, Anal. Chem. 83, 2011, 5145–5152.
[2] K.W. Bossers, et al., J. Am. Chem. Soc. 142, 2020, 3691−3695

Archival research and material analyses to explore artists' attitudes towards pigments' durability: John Ruskin and the 19th-century Colour Revolution

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The 19th-century Industrial Revolution left a mark that spread well beyond the fields of science and technology and came to influence significantly ideas around colour stability and permanence across art and literature. While pigment manufacturing was increasingly industrialised, artists slowly lost control over their painting materials [1–3]. William Perkin's discovery of Mauveine, the first coal-tar dye, in 1856 further fueled the mass production of new synthetic colourants that continued throughout the 19th century and beyond [4–6].

John Ruskin ─the influential English artist, social critic and leading cultural commentator of his age─ while referring to the recent introduction of the dye Magenta, which immediately followed Mauveine, severely stated: "We moderns, who have preferred to rule over coal-mines instead of the sea […], have actually got our purple out of coal […]! And […] have completed the shadow, and the fear of it, by giving it a name from battle, ─Magenta." [7].

Ruskin's contempt towards coal-tar dyes, and more in general towards industrialisation, which he considered the ill of a modern, materialistic society [8], contributed to spreading the idea that he categorically excluded from his palette any form of synthetic pigment. This contribution challenges state-of-the-art by presenting the investigation carried out on Ruskin's watercolours at the Ashmolean Museum. The combination of archival research and material analysis carried out with XRF, XRD and FORS showed that Ruskin intentionally used newly-introduced synthetic pigments such as Prussian blue, cadmium yellow and emerald green. Rather than dismissing all products of industrialisation, Ruskin seems to have chosen his pigments depending on their stability to light, thus mirroring concerns around colour stability that were very common at the time and resulted in early perspectives on preventive conservation.

[1] Hunt W Holman. The present system of obtaining materials in use by artist painters, as compared with that of the old masters. J Soc Arts. 1880;28(1431):485–99.
[2] Carlyle L. Authenticity and adulteration: What materials were 19th century artists really using? The conservator. 1993;17(1):56–60.
[3] Townsend JH, Carlyle L, Khandekar N, Woodcock S. Later nineteenth century pigments: evidence for additions and substitutions. The Conservator. 1995;19(1):65–78.
[4] Garfield S. Mauve: how one man invented a color that changed the world. WW Norton & Company; 2002.
[5] Zollinger H. Color chemistry. John Wiley & Sons; 2003.
[6] The Great Exhibition; about dyes and beauty and coal-tar mauve and magenta how made extraordinary specimen of aniline art and new colours. New York Times. 1862 Jul 28;2.
[7] Ruskin J. The Complete Works of John Ruskin in 39 volumes. The Library Edition. Cook ET, Wedderburn A, editors. George Allen and Unwin; 1903, Vol. 19, pp 379-80.
[8] Ribeyrol C. Religion and ritual. In: Loske A, editor. A cultural history of color in the age of industry. London: Bloomsbury Publishing Plc; 2021. p. 89–109.

Renewing archaeological practice with modern technology: µXCT for the facile screening of excavated copper coins

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Copper-based coinage represents a class of metal artefacts with extraordinary historical value. Although copper coins are frequently retrieved at excavation sites, they are typically found in a poor conservation state and are hardly identifiable. While the usual archaeological practice involves an approximate on-site cleaning process, this procedure remains rather controversial in view of its low efficacy and the risk of information loss [1]. Off-site cleaning is occasionally performed; however, the large number of recovered copper coins makes their study unsustainable in terms of time and human resources. This leads to entire coin collections being left unstudied [2].

Here, we highlight the use of lab-based X-Ray Computed Microtomography (µXCT) to address the above-mentioned limitations and demonstrate the feasibility of integrating this technique into the archaeological workflow. µXCT analysis has been performed on a group of Roman copper-based coins in their current state, as found during an archaeological survey. The reconstructed volumes have been elaborated to extract the key features required by numismatists for coins identification through database crosscheck. The same coins further underwent a physical cleaning performed by a professional restorer, to directly compare the traditional and the proposed methodology. The results prove the capability of µXCT in providing enough details to identify Roman copper coins. The comparison between the two methodologies shows that the XCT-based protocol outperforms the current practice on the coins reading (Fig.1), the mitigation of information-loss risk and time-consumption, setting a new paradigm for the study of large-scale collections of copper coins.

In conclusion, we demonstrate that the integration of XCT into the archaeological practice is nowadays feasible and can significantly advance the work of archaeologists, numismatists, conservators and restorers.

Figure 1 Compared results of physical cleaning and µXCT virtual cleaning on one coin.

[1] C. Sease, A Conservation Manual for the Field Archaeologist. Cotsen Institute of Archaeology Press, 1994.
[2] A. Stella, Too big to study?, EUT Edizioni Università di Trieste, 2019.

The use of X-ray computed tomography and X-ray fluorescence in the research of historical printing from the 17th century

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This work presents the use of X-ray computed tomography and X-ray fluorescence in analyzes and expert surveys of historical manuscripts and early prints. Historic early prints and manuscripts retain much information about their origins, owners, and creators, or various defects hidden in the bookbinding or hidden between layers of material. The Department of Research Laboratories of the National Library of the Czech Republic has long been involved in non-invasive methods of making visible and documenting information that is not available during normal historical or restoration research.

The book that was selected for the survey was a 17th-century historical print of the collection of the Slavonic Library originally from Kiev, with the full title Eukhologīon albo Molitoslov, ili Trebnik. The survey's main purpose was to confirm whether the book binding is original or whether it is a rebinding, and whether there are no fragments of older texts in the book binding. Radiography was unable to provide sufficient quality documents confirming or refuting the binding or the presence of layers in the bookbinding carrying the text. Computed tomography made it possible to display the detailed structure of bookbinding materials, including wooden boards. No fragments or layers with older texts were found in the structure of the bookbinding therefore, there is no need for invasive intervention. All bookbinding elements were visible and no internal defects in materials and stitching were detected. The possibility of reading text in a closed book based on X-ray computed tomography will be presented, as this option may be advantageous for massively damaged manuscripts. Thanks to a detailed representation of the wood structure using tomography, it was possible to carry out a dendrochronological survey without invasive intervention. The dendrochronological analysis confirmed the original bookbinding materials corresponding to the age of early printing. As part of the survey, elemental analysis of the font was also carried out using an X-ray fluorescence spectrometer. The letters in the CT reconstruction have significantly different contrasts. The different elemental composition of the printing inks was verified using XRF analysis.

Micromorphological observations as a potential method to study indigo blues

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Indigo is an organic colouring substance used since ancient times in dyeing and painting, and it can be derived from different vegetal sources [1]. The plants *Indigofera tinctoria* and *Isatis tinctoria* (woad) range among the most important sources of this colour in European history. The issue of how to distinguish the different sources of indigo by analytical means on ancient artifacts is long-standing, as the main marker of all types of indigo is indigotin. Until now, the attempts have mainly encompassed analyses of minor components through spectroscopic and chromatographic techniques, sometimes leading to good results, but the detection on aged artifacts is not always easy and the matter still appears problematic [2,3,4].

In this study, a multi-analytical characterization of painting layers of a 15th-century wooden ceiling located in Cremona (Italy) was carried out, using mainly confocal μ-Raman spectroscopy (633, 532 and 473 nm excitation wavelengths) and SEM observations combined with EDS elemental analyses. Raman spectroscopy led to identifying indigotin in blue painting layers. Under SEM-EDS observation, these same indigotin-based layers displayed a distinctive micromorphology, revealing the presence of fibre-like or porous regular framework ascribable to plant tissues. In some cases, these pores are elongated and show a morphological axiality along their length that recalls the structure of a vegetal fibre; in other points, traces of the "honeycomb" microstructure typical of plant leaves is highlighted, and some of the characteristic hollow hexagonal cells are visible.
The combined spectroscopic and microscopic results clearly indicate the presence of an indigo blue. The productive and geographical context in which the painted ceiling was created led to attributing the indigotin-based layers to the woad plant: indeed, historical studies tell us that woad was easily available in Cremona at the time, being extensively used in local textile-dyeing manufactories. This is therefore one of the few findings of plant residuals in ancient painting layers that have been traced back specifically to woad [5].

Micromorphological observations are usually not enumerated among the methods for studying indigo blues. The detection of an indigotin-based pigment attributable to woad, that displays characteristic microtextural features, sets the basis for a discussion on whether micromorphology studies could become a new method for identifying woad blue in opposition to other kinds of indigo. The discussion is not only based on microstructural characteristics, but can also encompass the manufacturing procedures of the different kinds of indigo blue and how these might influence the morphology of the final obtained pigment.

[1] Cardon, D., *Paris: Éditions Belin*, 2003.
[2] Degano, I., Ribechini, E., et al., *Applied Spectroscopy Reviews, 44*(5), 2009, 363- 410.
[3] Nyström, I., *Studies in Conservation, 60*(6), 2015, 353-367.
[4] Humphrey, P. I., *McNair Scholars Research Journal, 10*(1), 2017, 73-87.
[5] Montana, G., Giarrusso, R., et al., *Archaeological and anthropological sciences, 14*(9), 2022, 1-16.

Verdigris alteration: influence of medium and conservation conditions

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Verdigris is a green copper organometallic pigment widely used in the XVI and XVII century and then slowly discarded due to its proclivity to darken and brown with ageing [1]. However, alterations are not systematic as demonstrated by the coexistence of altered and unaltered areas on the same painting. Several hypotheses have been formulated to address the colour changes, but the mechanism of degradation has not been fully yet elucidated [2]. The aim of this work is to better understand the reactivity of Verdigris in relation to the different environmental factors and, thus, propose a model that could help to evaluate the alteration's evolution in the pictorial layers.

Various samples of $Cu(CH_3COO)_x \cdot xH_2O$ have been synthesized exposing copper thin sheets to acetic acid at different concentrations, obtaining pigments in anhydrous phase or with different hydration degree. Copper acetate monohydrate has been selected to be artificially aged. Its behaviour has been examined when mixed with oils having a progressive increase of fatty acids, i.e. walnut, linseed, and poppyseed [3]. Artificial ageing conditions have been devised through a Design of Experiment (DoE) model, investigating the influence and interaction of light, humidity, and oil/pigment ratio. Pigment powders have been characterized by means of Light Optical Microscopy (LOM), X-Ray Diffraction (XRD), UV-Vis spectroscopy and Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflectance (FTIR -ATR); Verdigris paint films deterioration has been monitored through IR spectroscopic and colorimetric analysis. Moreover, the wide dataset obtained has been elaborated with Principal Component Analysis (PCA).

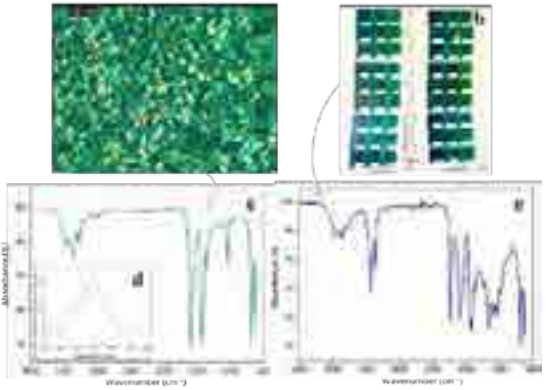

Figure. Verdigris pigment (a) LOM image, (c) FTIR-ATR spectra, and (d) UV-Vis reflectance spectra; Verdigris/Linseed oil paint films (b) picture and (e) FTIR-ATR spectra.

[1] M. San Andrés, J. M. De la Roja, V. G. Baonza, N. Sancho, Journal of Raman Spectroscopy, 41, 1468-1476 (2010).
[2]R.Wouhuysen-Keller, Historical Painting Techniques, Materials and Studio Practice, 26–29 June 1995, 65–69
[3]M.Gunn, G.Chottard, E.Rivière, J.-J.Girerd, J.-C Chottard, Studies in Conservation, 47, 1, 12-23 (2002).

A multi-instrumental approach for studying the writing ink of a 17th-century Portuguese Codex

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Iron gall inks (IGIs) played a crucial role in our written cultural heritage. This medium was produced by mixing oak galls extract (solutions of tannin-rich plants) and vitriol (ferrous sulphate and sometimes salts of other metals like copper and zinc) in solvents, such as water or wine [1,2]. Due to its acidic nature, IGI-induced degradation poses a persistent problem for the safekeeping of IGI items. It triggers a host of damages on the writing supports, including colour alteration and progressive brittleness resulting in cracks and material loss [2]. The conservation state of IGI items is often ambiguous; in a single document, it is possible to find well-preserved parts contrasting with severely degraded ones [3]. That is precisely the case of an overlooked 17th-century Portuguese Codex held by the Public Library of Évora, which stands out for its rich calligraphy and ornamentation. Written by a Portuguese Jesuit father and dedicated to D. Teodósio (Prince of Brazil), it comprises three pedagogical treatises: *Orthographia, Arithmetica and Sciencias*. While most of the Codex is well preserved, a set of folios with fine calligraphy presents dramatic degradation patterns.

Here we present a multi-analytical study using 3D digital microscopy, SEM/EDS, PIXE and RBS, EDXRF, XPS and Mössbauer spectroscopy to explore the writing ink, attempting to relate the composition and the conservation state. Results showed that copper, lead, and zinc were detected in addition to iron and sulphur, providing direct evidence that different IGI formulations may have been used. Furthermore, the oxidation state of iron seems to have an essential role in the degradation processes. Mössbauer results showed that not all Fe(II) ions from the vitriol underwent oxidation to Fe(III). This study sheds new light on the writing inks used in this Codex, and provides fundamental insight into new approaches for preserving written IGI heritage.

[1] Y. Liu, I. Cigic, M. Strlic. Polymer Degradation and Stability. 142, 2017, 1-19.
[2] V. Corregidor, R. Viegas, L. M. Ferreira, L. C. Alves, Heritage, 2, 2019, 2691-2703.
[3] M. Nunes, F. Olival, S.G. Mitchell, A. Claro, T. Ferreira, Micron, 165, 2023, 1-10.

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Reducing Raman Spectroscopic Interferences when Analyzing Weak Scatterers: the Case of Parchment

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During the last decades, Raman spectroscopy has grown to a well-appreciated analytical approach in cultural heritage research because it allows non-destructive analysis of a broad range of materials. In painting analysis, Raman microscopes allow to identify particles of few µm of diameter, while in micro-Raman mapping setups Raman spectrometers yield detailed information about the pigment distribution at high lateral and axial resolution, in cross sections or in a section of paint. Along with these established approaches, mobile Raman instruments have similarly grown to valid tools in cultural heritage research: for instance, they can reveal reliable information about the chemical nature of pigments and their degradation products *in situ*, avoiding the need to remove the artefact from its place, or the need of artifact sampling.

Inspecting certain artistic materials with Raman spectrometers requires special care. In fact, the Raman effect is relatively weak and prone to interferences, such as ambient light or fluorescence. To avoid fluorescence, implementing an infrared excitation laser is a common strategy, yet at the expense of spectral quality: since the Raman effect is proportional to the 4th power of the excitation frequency, the resulting Raman spectrum is of low intensity. Moreover, typically, multichannel detectors are less sensitive in the infrared region, compared to the visible range.

When analyzing weak Raman scatterers, sensitivity can be improved by enhancing the laser power. However, this may result in damage to the sample or artefact. Otherwise, measuring over a longer time may sometimes result in a better signal-to-noise ratio, but often measurement time is limited. Altogether, these effects are significant, especially for materials with a tendency to manifest broadband fluorescence emission and reducing possible interferences originating from the spectrometer is imperative.

In this work, we address exactly the last point. We demonstrate here the effect of spectral corrections that can be applied to avoid spectral interferences caused by the components in a mobile Raman spectrometer, as well as to deal with non-uniform quantum efficiency of the different detector-elements. This is particularly interesting when studying low intensity Raman bands of weak scatterers, such as organic molecules. The approach is demonstrated by examining Raman spectra of contemporaneous parchment samples of different animal origin.

Preliminary investigation of the painting technique of Thalia Flora-Karavia: The 'Paris' case study.

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In the present work, a preliminary study of the painting technique of the Greek painter Thalia Flora-Karavia is presented, through the non-invasive analysis of her painting 'Paris'. Thalia Flora-Karavia (1871-1960) was one of the most important female painters, with a significant contribution in the artistic life of Greece in the late 19th and early 20th century [1]. Having established herself on the art scene, she was an influential figure for her contemporaries and especially for other women painters. She began her studies in private schools in Munich with very important teachers, such as Gyzis, Vokos, Iakovidis, Nauen, Azbe, and Thor, following the academic painting style. She then continued her studies at the Grand Chaumiere (Académie de la Grande Chaumière) private painting school in Paris, adopting many elements of the new artistic movements.

The painting under study, hosted at the Gallery of Contemporary Greek Art in Kalamata (Greece), represents a view of the Seine in Paris. In it, the painter seems not to be limited by contours, emphasizing light and color. The research protocol, which focused on the use of non-destructive testing coupled with non-invasive analytical techniques, included the application of hyperspectral and false color imaging techniques to investigate the internal paint layers structure, the eventual existence of an underpainting and the imaging of the chemical distribution of pigments, as well as the use of portable X-ray fluorescence (p-XRF) spectroscopy and portable Raman (p-Raman) spectroscopy to identify the painter's palette.

The analysis of the results showed that 'Paris' was painted directly on the cardboard substrate, while the existence of an underdrawing was not observed. Through infrared false color imaging, the chemical distribution of pigments in the painting was documented, giving useful information about the painter's technique (e.g. selective application of paint in specific areas). Finally, through spectroscopic analyses, the pigments used in the painting were identified, showing a limited palette. It was observed that the painter made heavy use of modern synthetic organic pigments, such as phthalocyanine green and Hansa red, as well as more traditional pigments such as chrome yellow and barium white [2].

The analysis of the painting 'Paris' by Thalia Flora-Karavia added significant information about the painting technique and palette used by a very important Greek painter. The present work, which stands as the first effort to examine one of her paintings, sheds light on the artistic life of Greece in the late 19th and early 20th century.

Acknowledgement

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[1] M. Papanikolaou, Greek Art of the 20th century - Painting - Sculpture, Banias, 2006 (in Greek).
[2] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, The Pigment Compendium A Dictionary of Historical Pigments, Elsevier, 2004

Reflective Transformation Imaging technique with visible, infrared and ultraviolet light

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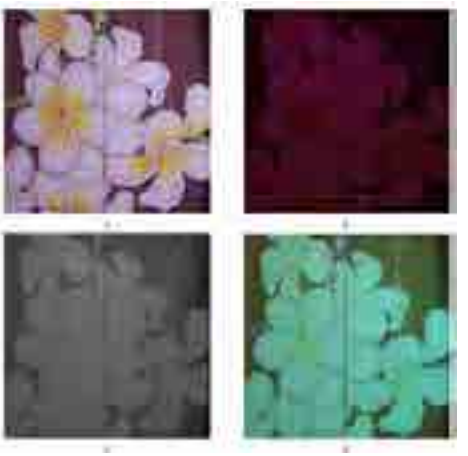
Reflection Transformation Imaging (RTI) technique allows the visualization of the relief and texture of the surface of an object allowing a better representation than standard images. After image processing and by moving the virtual light it is possible to enhance details of the surface and identify, for example, morphological changes, craquelure, or canvas weave. This work reports the upgrade of the low-cost and portable RTI set-up developed by the team [1] with the addition of infrared and ultraviolet LEDs to the existing visible light LED and using a Mirrorless Canon EOS R6 Full Spectrum Camera. Different objects such as manuscripts, pigments, paintings and ceramics were photographed with this set-up. The figure shows the images obtained in a paint on wood support.



Hand made painting on wood support. Illumination from the top. Visible light (a), UV light (b), IR light (c) and false colour (d).

The team acknowledges the support from H.Luz (Canon-Portugal).

[1] V. Corregidor, R. Dias, N. Catarino, N. et al. Arduino-controlled Reflectance Transformation Imaging to the study of cultural heritage objects. SN Appl. Sci. 2, 1586 (2020). https://doi.org/10.1007/s42452-020-03343-4.

Multi-methodological approach from non-invasive to micro-destructive techniques for the characterization of Final Bronze Age vitreous materials: Paduli site (Colli sul Velino, Rieti) in central Italy

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Here we present a two-step analytical protocol for the study of vitreous materials from the Middle Bronze Age to the Early Iron Age of the lakeshore settlement of Paduli (Colli sul Velino, RI) in central Italy. The first step was based on non-invasive techniques and, once acquired and evaluated the data, a second step was planned based on the collection of micro-fragments, from those objects considered representative to be analysed with micro-destructive techniques. In the first step, portable X-Ray Fluorescence (p-XRF), Fibre Optic Reflectance Spectroscopy (FORS) and X-Ray Diffraction (XRD) for acquiring information about elemental composition, chromophoric elements and crystalline phases in the glass matrix, were employed. The results of the first step allowed to address the sampling to the more significant and representative objects, also reducing the size and number of samples. So, five samples (starting from about 20 objects) were selected and analysed (i.e. 2 blue beads, a "star" bead with light and dark blue bands, a vessel fragment bichrome blue and white and a blue barrel bead with white spiral decoration) to obtain microstructure information, chemical composition, colorants and Sr-Nd-Pb isotopes information not otherwise obtainable. All samples were analysed by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) for morphological and chromophoric investigation. Major and minor elements were analysed by Electron Probe Microanalysis (EPMA), whilst trace elements concentrations were obtained through Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Isotopic fingerprints of Sr, Nd and Pb were determined via Thermal Ionization Mass Spectrometry (TIMS). The data collected by this multidisciplinary approach, carried out for the first time on such materials of this period in central Italy, allowed us to identify the provenance of raw materials and the production technology, confirming the importance of the site into the network of international traffic.

Construction Phases, Characterisation of Granite Ashlars and Frescoes Pigments of St. Leocadia Church (Chaves, Galicia-North of Portugal Euroregion)

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Several analytical techniques have been carried out for the study of granite ashlars and frescoes pigments of the Romanesque St. Leocadia Church (Chaves, Galicia-North Portugal Euroregion). The aims of this work are to determine the church construction phases, to characterize the main building granite and the frescoes pigments.

Ashlars petrography and surface roughness, mason's marks glyptography, and walls stratigraphy were used to determine the church construction phases. The façades have been surveyed using automated digital photogrammetry and by petrographic evaluation of the granite ashlars. The roughness has been measured with a laser scanner in original Romanesque ashlars and in ashlars used in successive construction phases. The roughness has been measured with a laser profilometer in original Romanesque ashlars and in ashlars used in successive construction phases. The area roughness parameters (ISO 25178), Sa (Arithmetical mean height) and Sq (Root mean square height) were used to express the texture. Frescoes samples have been analyzed with polarized optical microscopy (POM), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), Raman spectroscopy, and X-ray fluorescence (XRF).

Analysis of the mason's marks indicates that at least six stonemasons have built the original Romanesque church. The church has had several reforms and extensions throughout its history. The apse is the part of the church that has suffered the fewest interventions, although it has been raised. The nave has been enlarged, and the original ashlars are mixed with more recent ashlars. Different building granites have been used in the construction phases. The granite used in the Romanesque ashlars is finer crystal-size than that used in successive construction phases. The original ashlars have lower values of Sa and Sq than the most recent ashlars. The frescoes are from the 15th and 16th century. Their main colours are ocher and reddish tones, with oxides of Fe, Mg and Ti. The black and grayish pigments come from vegetal carbon and manganese. This data is useful for future restorations of Galicia-North Portugal Euroregion churches.

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Evaluation of the combined application of elemental and imaging spectroscopies for the non-invasive analytical characterization of 19th century paintings

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The comprehensive non-invasive analytical characterization of painting artworks requires the combined application of diverse spectroscopic techniques with compatible spatially resolved capabilities. The comparative evaluation and interpretation of the acquired maps, across different regions of the electromagnetic spectrum, can provide cohesive information on the construction techniques and materials of the investigated painting artworks. Within a National funded project (PROTEAS), aimed to develop an integrated platform of physical and digital means for the analysis and conservation of large-sized paintings which will operate in an open-lab fashion, Macro X-ray Fluorescence (MA-XRF), Hyper-Spectral, Fluorescence and Infra-Red Imaging set-ups/devices/apparatuses and methodologies were developed.

To evaluate the analytical performance of PROTEAS spectroscopic tools, a mock-up easel painting was created as a benchmark. Its design was driven by the need to assess the analytical merits of each apparatus in identifying 19th century compatible paint layers and pigments with optimum spectral and spatial resolution. Traditional materials and a few early modern pigments were used in the mock-up. Each chosen pigment was applied by following a given/specific stratification regarding the number of paint layers, whereas distinct geometrical patterns of organic and inorganic based pigments were applied above the preparation and individual paint layers, respectively. The obtained multi-modal data were post-processed and cross-correlated and the performance of the PROTEAS instruments was evaluated and discussed in terms of spectral response, throughput, analytical sensitivity, and spatial resolution.

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μ-EDXRF imaging to evaluate desalination ability of cellulose foams and sponges applied on wall paintings

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Most of the analytical methodologies used to evaluate the efficiency of desalination (salt removal) strategies on wall paintings are based on destructive approaches. In the last years, Energy Dispersive X-ray fluorescence spectrometry (EDXRF) imaging through macro scanners or other portable alternatives have been used to study canvas and mural paintings.

In this work, we present an analytical methodology based on μ-EDXRF imaging to evaluate, in a fast and direct way (no sample preparation), the efficiency of desalination of cellulose foams and sponges. The main case study is focused on chlorides removal from cinnabar (α-HgS) decorated wall paintings preserved in museums and storage rooms. This precious Roman pigment tends to dark in presence of UV radiation, humidity and chlorides [1]. Therefore, the removal of these salts becomes essential for its preservation. In addition, the ability to remove other salts (e.g., sulfates) will be also discussed. Decorated fresco mock-ups enriched with salts were prepared to verify the adsorption capacity of the foams. Different alternatives to infiltrate salts (e.g., vacuum impregnation) were tested by using mock-ups to mimic in a realistic way wall paintings affected by salts. Before and after desalination, both mock-ups and foams/sponges were subjected to μ-EDXRF imaging. The efficacy of these new materials was compared with that of conventional cellulose poultices (Arbocel). Thanks to that, a semi-quantitative evaluation of the salts removed was obtained (Fig. 1). The methodology here presented could be totally transferable to an in situ application through the use of XRF macro scanners or at least instrument that allow to conduct in situ imaging, giving the possibility of making on site quick decisions about the effectiveness of the applied desalination protocol.

Fig. 1: Cl distribution acquired by μ-EDXRF before (a) and 30 minutes after (b) cellulose foam application.

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[1] Marie Radepont, Yvan Coquinot, Koen Janssens, Jean-Jacques Ezrati, Wout de Nolf, and Marine Cotte, "Thermodynamic and experimental study of the degradation of the red pigment mercury sulfide", Journal of Analytical Atomic Spectrometry, vol.30, 2015, pp. 599-612, doi: 10.1039/C4JA00372A

A two-step GC-MS procedure for the characterization of alkyd paint media

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Alkyd resins are oil-modified polyesters manufactured from polyols, aromatic polyacids and drying oils (or a source of fatty acids). They have been introduced as commercial binders for paints in the 1940s. Their painting performance, very close to traditional oil paints, and their higher speed of drying prompted their use in contemporary art. GC-MS procedures using different derivatization reactions have been developed for the characterization of alkyd paint components. GC-MS with thermally assisted hydrolysis and methylation with tetramethylammonium hydroxide (TMAH) [1] or (*m*-trifluoromethylphenyl)-trimethylammonium hydroxide [2] proved effective for methylating polybasic and fatty acids, but polyols rendered mixtures of methylating products and adducts with the reagents.

In this work, we developed a two-step GC-MS procedure for the analysis of alkyd components from a single paint sample. The alkyd paint sample was dissolved in chloroform, treated with a solution of tetramethylsulfonium hydroxide (TMSH) in methanol at room temperature [3] and analyzed by GC-MS. Dibasic and fatty acids were characterized as their methyl esters while polyols did not react with TMSH. Then, the mixture was evaporated under nitrogen and a solution of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was added and heated at 70ºC. Further analysis by GC-MS allowed the identification of silylated polyols. The optimized methodology was applied to the analysis of an unpigmented alkyd medium for artists (Flow´n dry, Sennelier), a titanium white Alba alkyd house painting and three Griffin paints (W & N) containing Prussian blue, titanium white and permanent rose as pigments.

The four paint formulations revealed the presence of phthalic acid, glycerol and pentaerythritol, together with palmitic (16:0), stearic (18:0), oleic (18:1) and linoleic (18:2) acids. The two-step methodology was rapid and with minimal sample handing.

[1] R. Ploeger, D. Scalarone, O. Chiantore, Journal of Cultural Heritage 9, 2008, 412.
[2] M.R. Schilling, J. Keeney, T. Learner, Studies in Conservation 49, 2004, 197.
[3] J. Dron, R. Linke, E. Rosenberg, M. Schreiner, Journal of Chromatography A 1047, 2004, 111.

Application of analytical techniques in the assessment of cleanliness in modern pictorial surfaces with eco-sustainable formulations

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This paper presents a practical case on the elimination of a terpenic varnish in a modern pictorial finish by applying different gel formulations with non-toxic and eco-sustainable solvents.

There is a need to limit the use of volatile organic solvents in the task of cleaning pictorial surfaces, which present a certain degree of danger to human health and the environment, without compromising the effectiveness of the treatment. From the beginning of the 21th century, the use of aqueous methods began as an alternative to traditional cleaning systems with organic solvents, and only more recently have studies on the applicability of eco-sustainable gelled systems and organic solvents begun.

In recent years, the market offers more and more non-toxic and sustainable products that may have a potential application in cleaning pictorial surfaces and that need to be investigated in terms of applicability, efficacy and risk.

Before this situation, we have studied the applicability of different less toxic and eco-sustainable cleaning systems to replace those that are traditionally used. In this work we have also covered the study to reduce the risk of cleaning modern pictorial surfaces of the 20th century, where due to the type of pictorial technique or pigments used (such as the case of titanium white), it is possible that we find ourselves with an extremely delicate pictorial film where any treatment to remove organic coatings can compromise the morphological and mechanical integrity of the painted surface.

The purpose of the study is to compare different cleaning solvents that reduce the mechanical action of the swab for varnish removal, thus reducing the risk of pigment loss.

The removal of the varnish was carried out with different emulsified aqueous gel systems with only 1% solvents. The evaluation of the applicability of the gel with the solvent, the effectiveness of cleaning and the permanence of residues on the pictorial surface have been carried out using different microscopic techniques (ME, MO vis-UV, SEM), spectroscopic (EDX, FTIR-ATR) and chromatographic (GC-MS).

Characterization and provenance analysis of Gothic stone sculptures, the use of petrography in the reassembling of fragmented stone sculptures

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A stone atelier was set up in Buda Castle when Sigismund of Luxembourg, the Holy Roman Emperor, established and refurbished his residence in Hungary's capital Buda in the early 15th century. Broken sculptures were found in the 1970'ies when excavations unburied this medieval sculpturist atelier. The study focuses on identifying stone types, textural characterization and provenance analysis. The main aim was to reassemble the broken pieces, outline the differences in the stone material used by different artists, and provide evidence of the provenance of stone resources. More than 60 sculptures depicting saints and royal family members have been analyzed. Small samples were taken and tested using polarizing microscopy and scanning electron microscopy. Non-destructive tests such as a portable moisture meter and surface hardness tester were also applied to detect the physical properties of the sculptures and their broken and dismantled parts, such as arms, legs, heads, etc. Our analyses have revealed that Miocene porous limestone is the principal stone material of the sculptures, representing six different lithotypes. These include fine-grained ooidal limestone, fine-grained ooidal limestone with abundant bioclasts, fine to medium-grained ooidal limestone, very fine-grained limestone with well-sorted ooids and fine micritic limestone. The artistic style suggests that the sculpturists were French. The lithotypes resemble French porous limestones such as Tuffeau, but our detailed petrographic analyses proved that the stone material was extracted from Medieval quarries of the Buda Mountains rather than transported to Buda from France. The detailed petrographic studies also helped reconstruct broken pieces, and smaller fragments of hands, arms, and legs were reassembled using geometric matching and textural similarities.

Gothic stone sculpture from the atelier of the palace of Sigismund of Luxembourg (Buda, Hungary)

Improving the identification of red lake pigments on historical hand-painted magic lantern glass slides

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Magic lantern was the earliest form of image projection used from the 17th to the 20th century, which played a determinant role in social and visual culture worldwide. The first images projected were hand-painted on glass slides producing the most astonishing transparent colours. The FCT-funded project MAGICA, is carrying out the first systematic study of the materiality of hand-painted magic lantern glass slides. We have found experimental evidence on historical magic lantern slides of the materials mentioned in the written historical sources on the production of the hand-painted slides [1]. However, identifying these historical materials in complex matrices, particularly the red lake pigments, is a known challenge [2].

This work focuses on analysing the red colours of 50 hand-painted magic lantern glass slides belonging to the Cinema Museum – Portuguese Cinematheque, dated from the 19th century, covering different production techniques, places and manufacturers. To support this investigation, we will build a set of paint reproductions of cochineal, madder and geranium lake pigments prepared following historical recipes, including from the 19th-century archive database of Winsor & Newton, a leading artists' colourman of that time that particularly supplied these materials for colouring magic lantern slides [3-5]. First, all red colours will be analysed by UV-VIS Spectroscopy. Then, a microspectrofluorimeter and a portable spectrofluorimeter will be used in selected areas. Chemometrics models will be tested using the spectral data from the paint reconstructions in order to improve the in situ identification of red colourants in the historical magic lantern slides. Micro-samples will be further characterised by micro-Fourier Transform Infrared Spectroscopy and High-Performance Liquid Chromatography-Diode Array Detector to strengthen the in situ analytical methodology.

Applying these highly selective and sensitive techniques will allow us to discriminate specificities of the pigment formulations, which is key to attributing production periods, places and manufacturers. Moreover, creating this database will enable us to work at heritage institutions, eliminating the need to take these fragile objects to the laboratory and contributing to their safeguarding.

[1] https://www.magica-project.com/
[2] M. J. Melo, P. Nabais, M. Vieira, R. Araújo, V. Otero, J. Lopes, L. Martín, Dyes and Pigments 208, 2022, 110815.
[3] V. Otero, T. Veiga, Â. Santos, M. Vilarigues, Proceedings of the 9th Interim Meeting of the Art Technological Source Research ICOM-CC Working Group, *to be published*.
[4] T. Vitorino, V. Otero, L. Carlyle, M. J. Melo, A. J. Parola, M. Picollo, Proceedings of the ICOM-CC 18th Triennial Conference, Copenhagen, 2017, art. 0107.
[5] J. Kirby, Proceedings of the 1st Symposium of the Art Technological Source Research ICOM-CC Working Group, 2007, 69-77.

Aiding the conservation of two wooden Buddhist sculptures with 3D imaging and spectroscopic techniques

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The conservation of Buddhist sculptures that were transferred to Europe at some point during their lifetime raises numerous questions: while these objects historically served a religious, devotional purpose, many of them currently belong to museums or private collections, where they are detached from their original context and often adapted to western taste.

This contribution focuses on a heterogeneous group of seven wooden polychrome sculptures from the Museo d'Arte Orientale (MAO) in Torino, Italy, which has recently undergone an in-depth study and conservation treatment at CCR "La Venaria Reale". The information contained in museum entries for these objects, never exhibited before, is generally rather scarce: they are all of Chinese provenance and likely dated from the 16th to the 18th century. Within this multidisciplinary project, special attention was paid to the study of two of the sculptures, which portrayed two Bodhisattvas and looked very similar to one another except for the symmetrical gesture of their hands. A scientific study was carried out to address questions from MAO curators in terms of whether these artifacts might be forgeries or replicas, and how they may have transformed over time. Several analytical techniques were used for materials identification and to study the production technique, ultimately aiming to discriminate the original materials from those added within later interventions. The analytical methodology involved non-invasive techniques, followed by sampling and micro-invasive investigations: in particular, XRF and FTIR analyses were performed to characterize pigments and binders, while optical microscopy and SEM/EDX were used to investigate the painting stratigraphy and to assess the possible occurrence of biodeterioration phenomena. In addition, one micro-sample was removed for wood identification.

Tridimensional imaging proved particularly useful to complement data from point analysis. X-ray computed tomography of one of the two Bodhisattva revealed precious details of its inner structure, based on the assembly of several wooden blocks. In an effort to fully document the object as well as the distribution of materials on the surface and outmost layers, a multispectral imaging campaign was then carried out for the creation of a multispectral 3D model within an ongoing partnership with the Politecnico di Torino. The approach used is based on the integration of photogrammetry and multispectral imaging, enabling the correlation of geometrical, morphological, and radiometric data in a single 3D model, which combines information that could support the design of suitable conservation treatments. The two sculptures are currently displayed within the MAO exhibition "Buddha^{10}. A Fragmented Display on Buddhist Visual Evolution" (October 2022 - September 2023) [1].

[1] https://www.maotorino.it/en/eventi-e-mostre/exhibition-buddha10

The Pylos Geoarchaeological Program: Fusion of Images towards understanding Ancient Landscape

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The coastal zone in the area of Pylos, Messenia, constitutes a landscape of incomparable beauty and of particularly great historical, archaeological and environmental importance, while also providing for great tourist development, which includes the bay of Navarino, the Yialova lagoon , the Voidokoilia bay together with the land masses to the west, the island of Sphakteria, the Koryphasio peninsula and opposite it, Voidokoilia beach, as well as the hills of Prophitis Ilias and Koukouras [1].

The five-year research program of "Pylos Geoarchaeological Program – GEAPP" is in operation since 2021. Among the goals of the Program that stand out are landscape reconstruction, the use of new technological tools for archaeological and environmental research, commitment to informing local bodies about the rich cultural heritage and the special ecosystem, while contributing to the balanced and sustainable development of the area [2].

The endeavour of the present study is an attempt to fuse data and images [3] from a series of approaches, namely geophysical survey using magnetometry [4], aerial photography with the use of UAS ([5] and past excavation (since 1963) photos, implemented during the survey season of July 2021 covering an area of ca. 6,000m^2 North-East of the Profitis Elias hill.

The co-evaluation of the geophysical data, remote sensing methods and surface research are targeting in maximizing the obtained information and increasing the reliability of the interpretation in the detection of archaeological targets. The results of the study provided a case depended methodology aiming to a better resolution and accuracy of the spotted antiquities and therefore towards a successful management of the area, safeguarding and promoting buried antiquities.

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[1] Korres et al., Κορρές, Γ., Π. Καλογεράκου, Ελ. Κουντούρη, Αφρ. Χασιακού, «Ανασκαφές Πύλου» και Πρόγραμμα «Πυθαγόρας», Ανακοίνωση στη Διημερίδα Τομέα Αρχαιολογίας ΕΚΠΑ, Αθήνα, Απρίλιος 2005 (in Greek).
[2] S.E. Alcock, Andrea M. Berlin, Ann B. Harrison, Sebastian Heath, Nigel Spencer , David L. Stone, Pylos Regional Archaeological Rroject, Part VII: Historical Messenia, Geometric through Late Roman, Hesperia 74 (2005)
[3] Karamitrou A., Bogiatzis P. and Tsokas G. N. (2019) Fusion between Geophysical and Satellite images for the study of Archaeological sites. Archaeological Prospection, DOI: 10.1002/arp.1766.

[4] Tsokas, G. N., Tsourlos, P. and Papadopoulos, N., (2009) Electrical resistivity tomography: a flexible technique in solving problems of archaeological research. In Seeing the Unseen. Geophysics and Landscape Archaeology, edited by S. Campana and S. Piro.
[5] Panagiotidis V. V. & Zacharias N., (2022). Digital Mystras: An approach towards understanding the use of an archaeological space, 2nd International Conference on Global Issues of Environment & Culture, Scientific Culture Vol. 8 No. 3, pp 85 99.

New insight into lac dye reds: optimization of portable molecular fluorescence for the characterization of dyed textiles

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Extracted from a resin-like secretion produced by scale insects, lac dye is a red-purple organic colourant valued since Antiquity [1]. Historical evidence of the use of lac dye as a dyestuff and a lake pigment can be found in medieval treatises and artworks, including manuscript illuminations and textiles [1,2]. Lac-producing insects belong to the genus *Kerria* which includes twenty-nine species found in India and Southeast Asia, among which *Kerria lacca* is the most exploited one [3]. Although several other *Kerria* species have been used for centuries for their colouring potential, specificities (species markers and colours) haven't been fully explored yet. In this work, we have addressed this knowledge gap through systematic research into the dye composition of different lac species while developing a multi-analytical approach for the unequivocal identification of lac dye in cultural heritage objects.

Currently, the most efficient method for the characterisation of dyes and their degradation products is HPLC-DAD-MS, but it requires sampling, which might not be always possible. This has been overcome by the team at DCR FCT NOVA which has successfully developed confocal microspectrofluorimetry and exploited its high sensitivity and selectivity, good spatial resolution and in-depth profiling for *in-situ* characterisation of organic colourants [2]. This technique is a powerful method used nowadays to pinpoint the recipes' specificities and shed new light on the artworks' dating and place of production [4]. Nevertheless, not being transportable nor portable, only a restricted number of artworks can access a laboratory and benefit from the results offered by the bench-top fluorimeter, hence the development of new portable equipment is desirable to reach out to museums' collections.

This work presents the first proof of concept for the use of a portable fluorimeter optimized for the characterisation of raw materials from various lac species, dyeing formulation and lac-dyed textiles. We will discuss the challenges inherent to the portable equipment, including the most suitable light sources (LEDs) for the analysis of red colours, fiber-optic setup, spatial resolution, spectral features and data correction. In addition, the preliminary results acquired with the portable device will be compared and validated with the database of reference spectra obtained with the bench-top spectrofluorimeter. This work provides a first insight into the new possibilities offered by a portable fluorimeter, specifically its usefulness and validity for disclosing colours' identities and formulations as well as its accessibility allowing for the analysis to be performed where the artwork is normally conserved, thereby reducing the chances of damage due to transportation.

[1] D. Cardon, Le monde des teintures naturelles. Belin, 2014, 633-642, ISBN: 978-2701126784.
[2] MJ. Melo, A. Claro, Accounts of Chemical Research 43(6), 2010, 857-866.
[3] ScaleNet: http://scalenet.info/catalogue/Kerria/. Last access 17/01/2023.
[4] P. Nabais, MJ. Melo, JÁ. Lopes, M. Vieira, R. Castro, A. Romani, Heritage Science 9(32), 2021, 1-18.

Direct gel-supported liquid extraction from paint layers: a new invisible procedure for SERS and HPLC-HRMS identification of dyes in complex matrices

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The study of dyes employed in artworks is of big interest for history and conservation research, but the most critical aspect in such matter is the necessity of sampling. Dyes are easy to fade and usually low in concentration compared to inorganic components, thus, their signals in mixtures can be easily covered during non-invasive analyses.

With the rise of SERS supports for minimally invasive analyses of dyes, more and more attention has been given to hydrogels. Hydrogels are substances able to hold more than 90% of water (v/v) in their three-dimensional network, showing a solid-fluid dualism [1]. This property makes them able to absorb aqueous solutions and release them in a controlled way. Besides their employment in surface cleaning [2], during the last decades it became clear hydrogels loaded with appropriate solutions could be used for direct dyes microextraction from cultural heritage, for SERS identification [3, 4].

The presented work, based on previous research [5], was aimed at challenging the gel-supported liquid extraction to multi-technique dyes identification. The procedure was designed to extract three different dye classes from paint layers obtained using three different binders. Madder, indigo and brazilwood were employed to prepare pigments to mix with Arabic gum, egg yolk and linseed oil. The paint mock-ups were aged using T and RH cycles and a Xenon lamp. Agar-gel (3% w/v Agar in water) was loaded with mild water-based extraction solutions [6, 7] and applied on the paint layers. After removal, dyes were re-extracted from the gels and identified by means of SERS and HPLC-HRMS. The procedure perceptivity was carefully measured by means of colorimetry and analysis of images.

[1] N. Ichinose, H. Ura, Sci Rep., 10(1), 2020, 2620
[2] A. Sansonetti, M. Bertasa, C. Canevali, A. Rabbolini, M. Anzani, D. Scalarone, Journal of Cultural Heritage, 44, 2020, 285-296
[3] M. Becucci, M. Ricci, C. Lofrumento, E. Castellucci, Optical and Quantum Electronics, 48(9), 2016
[4] M. Ricci, C. Lofrumento, E. Castellucci, M. Becucci, Journal of Spectroscopy, 3, 2016
[5] G. Germinario, A. Ciccola, I. Serafini, L. Ruggiero, M. Sbroscia, F. Vincenti, C. Fasolato, R. Curini, M. Ioele, P. Postorino, A. Sodo, Microchemical Journal, 155, 2020, 104780
[6] L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, A. Bianco, Microchemical Journal, 126, 2015, 373-380
[7] K. Lech, E. Fornal, Molecules, 25, 2020, 3223

The Materials and Methods of the Glasgow Boy artist

D.Y. Cameron

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This research offers the first known technical examination of the materials and methods of the Scottish artist David Young Cameron (1865-1945); integrating the findings with contextual evidence. Cameron was an associate of the group of avant-garde artists active in and around Glasgow in the late nineteenth century - the Glasgow Boys. In comparison to better known artists of the nineteenth century, such as Whistler, Turner, and the Impressionists, who have received significant attention regarding their working methods and materials [1], the Glasgow Boys have been largely overlooked.

In recent years, interest in the Glasgow Boys has been renewed as evidenced by exhibitions in both the UK and in The Netherlands [2]. However, despite this interest in the Boys as a group, only one technical study has been published to date [3]. Additionally, Cameron has been overlooked in recent writing on the Glasgow Boys despite having been considered part of the group by contemporary art critics during his lifetime. This research aims to bring D.Y. Cameron, back to the forefront and provide greater insight into the materials and techniques of the Glasgow Boys. Six oil paintings by Cameron have been examined using non-destructive techniques - visible, ultraviolet, infrared light and X-radiography imaging, optical microscopy, and portable X-ray Fluorescence (pXRF) - as well as Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Scanning Electron Microscopy – Energy Dispersive X-ray (SEM-EDX) both of which require microsamples. These techniques help in the identification of the pigments and media used, the working process and present condition of the works. Additionally, a paintbox owned by Cameron was sampled and examined to better understand the materials available to him. The research discusses who influenced D.Y. Cameron, aspects of innovation in his materials, for instance the use of traditional and modern pigments, and techniques such as the rubbing in or scraping back of paint layers to create different surface textures.

Figure 1 pXRF analysis of Morning in Lorne, D.Y. Cameron, The Hunterian, Glasgow

[1] Bomford, D. *et al.* (1990) *Art in the making: Impressionism*. Edited by David Bomford. London; New Haven, Conn; National Gallery.; Hermens, E. *et al.* (2017) "Matthijs Maris at work." Amsterdam: Rijksmuseum.; Townsend, J.H. (1994) "Whistler's Oil Painting Materials," *The Burlington Magazine*, 136(1099), pp. 690–695.; Townsend, J. H. (1993). The Materials of J.M.W. Turner: Pigments. *Studies in Conservation*, *38*(4), 231–254.
[2] Fine Art Society London, 2004; Kelvingrove Art Gallery, Glasgow, and RA, London, 2010-2011; Drents Museum, Assen, 2015 - 2016; Fleming Collection, Berwick-Upon-Tweed, 2020; plus, exhibitions in private and local Scottish and English galleries, 2013-2021.
[3] McConkey, K., Hellen, R., & Chardon-Marchetto, E. (2007). 'Neither Shakespeare's Audrey nor Nature's Grass; Audrey and her Goats by Arthur Melville (1855-1904)'. *The British Art Journal*, *XVIII* (3), 19–27.

X-RAY COMPUTED TOMOGRAPHY FOR NATURAL AND CULTURAL HERITAGE OBJECTS:

A matter of size and contrast

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Computed tomography (CT) for Natural and Cultural Heritage is becoming more and more used for whole objects, showing incredible images of the surface and the internal morphology of artefacts. CT systems use the density of the materials to create 2D images made of grey values. These images are reconstructed together to create a 3D volume of the object scanned. Though, CT has a richer variety of results than pure images. Indeed, X-ray computed tomography can be used for measurements (2D, 3D), features morphology, topology of (sub)surfaces, layer correlation, particles shape and distribution, component determination, porosity, cracks detection, past restoration, and the list is continuously improving and increasing. Correlation with acknowledged methods, such as optical and scanning electron microscope, is also strongly developing to verify some information, or enhance the interpretation. CT results observation and quantification are bound to the resolution and contrast of the data. These are related to the sample to be scanned (size, components), to the parameters of the device (detector-sample-X-ray distance), and finally to the volume reconstruction and filtering options (blur, alignment). Phase-contrast retrieval is one CT technique that enhances the contrast between the materials. It can be crucial for the visualisation of a painting canvas (organic fibres) and the painted layers (principally inorganic particles), for example. Generally, the larger the sample, the lower the resolution. Which is why the analysis of micro-samples can give other information than a whole object. The easier access to laboratory CT with resolution comparable to second generation synchrotron makes them also appealing. We would like to present studies of original paintings, archaeological ceramic and microfossils, showing the CT achievable results according to the type of sample correlated to the question related to each object. Paintings are mostly about layering, particles distribution and canvas, while archaeological ceramics temper and shaping methods. Finally, microfossils are about morphology, shape, bioerosion and comparison between specimens.

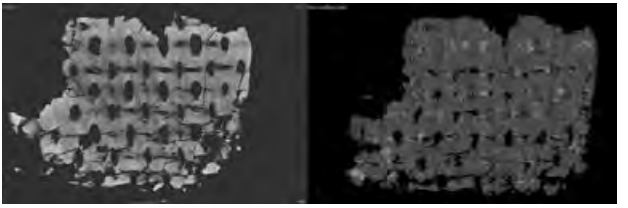

Figure 1 *Original painting [length 7.58mm]: (a) micro-CT fibres pattern and cracks in the painted layer.*

Keywords: Computed tomography, Non-destructive, Submicron, 3D, Cultural Heritage, Natural Heritage, Painting, Archaeological Ceramic, Microfossils

Non-invasive study of baroque Silesian glasses from museum collections in Poland.

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During the 17th and 18th centuries, glass manufacturing reached a very high level in the Silesia region. The Preussler family founded glasshouses Weissbach and Weiberberge in Szklarska Poręba, and Schwarzbach in Czeniawa. The state of art decorations was created in Cieplice and Sobieszów.

In Poland's museum collections, at least 400 examples of Baroque Silesia glasses could be found. The most important set of glasses is owned by National Museums in Warszawa and in Wrocław. In a recent project, interdisciplinary research was undertaken to determine the exact origin of these glasses by characterizing their chemical composition and recognizing different decoration styles [1].

The history and provenance of about 250 objects were investigated. Analytical and imaging techniques such as a high-resolution 3D optical microscope, X-ray fluorescence (XRF) (handheld XRF spectrometer with a *historical glass* calibration and macro XRF scanner) and optical coherence tomography (OCT) were applied.

Obtained results confirmed a potassium-lime glass composition type, determining the high transparency and durability. Glass decorations were performed using different engraving techniques, for example, Hochschnitt and Tiefschnitt, also, sometimes by painting. An additional outcome of the research facilitated the comparison between Silesia and Bohemia Baroque glass vessels.

This research was founded by the Polish Ministry of Science and Higher Education under the programme: National Programme for the Development of Humanities, grant no. 0332/NPRH7/H11/86/2018.

[1] E. Gajewska- Prorok, A. Kasprzak, *Engraved and cutting decorations techniques of baroque Silesian Glass.*, in: Dziedzictwo rzemiosła artystycznego – tradycyjne techniki oraz nowoczesna konserwacja i restauracja. Tom 1, P. Niemcewicz, M. Chylińska (eds.), 2020, pages 179- 205.

New insights on Titian's Ecce Homo materiality by coupled MA-XRF, RIS and LIS scanning

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Scanning macro X-ray fluorescence (MA-XRF) has proven over the past two decades its added value to XRF point analysis. By imaging pigment distribution within large areas of paintworks based on their elemental signature, new insights were gained regarding materiality, techniques and even artwork history such as restoration or underlying composition. Reflection imaging spectroscopy (RIS) and luminescence imaging spectroscopy (LIS) are non-invasive techniques that usefully complement MA-XRF analysis by mapping and identifying pigments over the studied area, thus corroborating MA-XRF results or revealing organic materials, non-detectable by MA-XRF only.

We present here the study of an *Ecce Homo* easel painting by Titian (private ownership, Cyprus) in which previous X-Ray Radiography (XRR) and point XRF analyses revealed the presence of an underlying unidentified man portrait [1]. New insights were gathered by applying MAXRF-RIS-LIS scanning of the composition in a single-pass. The instrument used for this operation is a multi-sensor scanner recently developed in collaboration with the STARC allowing the simultaneous acquisition of MA-XRF, RIS and LIS mappings. Data interpretation is facilitated by the natural alignment of all datasets, thus providing a combined XRF, Reflectance and Luminescence signature for each point of the scanned area.

The results obtained from this operation brought confirmation to the conclusion drawn from the previous single point upper layer materials analysis and stratigraphy observations. A better visualization of the underlying composition was obtained, owing to the intrinsic characteristics of the XRF methods and a complementary scan from the back of the canvas, revealing details of the face of the man depicted in the underlying composition. Moreover, the XRF elemental maps also allowed highlighting specific details, unseen by point analysis alone. New clues regarding the pigment composition of the painting were also brought through this study, revealing a different palette of pigments for the front and the hidden compositions. Differences between the flesh tones composition of both figures, i.e. Christ and unknown man, are clearly displayed, as the underneath composition present a higher amount of vermillion. Differences could also be noted for some background elements, such as the use of smalt and copper pigments for decorative items i.e. table and curtains of the underlying portrait, not observed on the upper layer. RIS maps shows the use of ultramarine at different locations in the upper composition, and the LIS map allows the visualization of the different varnish qualities, corresponding to ancient and restoration varnishes. All the elements shed to light after this large scope analysis brought numerous information, questioning once again the history of this impressive composition.

[1] Gasanova S, Bakirtzis N and Hermon S 2017 Non-invasive sub-surface analysis of the male portrait underlying the Titian's Studio Ecce Homo *Herit Sci* **5** 33

Newly developed transportation frame for a fragile wooden panel painting

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The transport of cultural heritage is one of the common tasks of conservators. As more and more artworks are moved from one museum to another, conservators are increasingly concerned about the behavior of the painting in response to shock and vibration during transport. Especially the transport of wooden panel paintings is generally considered as being critical. The painting considered in this contribution is a cradled medieval panel painting of high fragility from the collection of the Bavarian National Museum in Munich. Because of its enormous size and the extremely thinned substance of the panel, regular transport is impossible. Therefore, an appropriate strategy is needed to be acquired to transport this cradled painting. Furthermore, since a complete isolation of vibration is impossible, a customized packaging system has been developed to handle the painting and enable it to be transported.

Dynamic investigations of the painting were carried out to find and avoid the excitation of the critical eigenfrequencies by using the finite element (FE) method. With the FE model, different boundary conditions were investigated, which led to the development of the specially built transportation frame. An almost rigid aluminum transportation frame was then designed that facilitated transportation while maintaining the current deformation state of the panel painting. This transportation frame allows more efficient vibration isolation by clamping the batten of the cradle without stressing the wooden panel and paint layers.

This contribution captures the complete development process from assessing the most dangerous exposures on the painting using the FEM. Using FEM, a transportation frame was designed and used for transport. Evaluation of the damage after transport showed that the painting was successfully transported maintaining its current mechanical state without material damage or loss.

Linking historical recipes and ageing mechanisms: the issue of iron gall inks

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Iron gall inks have been among the most important inks of our society historical and artistic heritage. Due to their wide popularity and use, several iron gall ink's recipes are described in ancient treatises, which mention the use of polyphenols extracted from oak galls in combination with ferrous sulphate and gum Arabic. Owing to the development of synthetic chemistry, iron gall ink recipes were improved with new materials and procedures in the late 19th and early 20th century [1]. Notably, many conservation issues arise from the interaction between iron gall inks and the paper support of manuscripts and drawings [2]. To date, most research has been aimed at paper preservation, and was performed by non-destructive analytical methods, which provide only limited information on degradation process trends and minor components that can be representative of iron gall ink's recipes [3]. Therefore, analytical investigation in heritage science requires new approaches for the analysis of writing inks and the determination of ageing mechanisms.

In the present work, different 19th-20th century historical recipes of iron gall inks were characterized. The *Reid* and *modern gall inks* are traditional formulations, which differ for the air exposure time and the relative percentage of oak galls, while *alizarine ink* is an iron gall ink in which oxidation is delayed thanks to the use of metallic iron and acetic acid as additives. The molecular markers of iron gall inks, such as *gallic acid*, *ellagic acid*, *poly-galloyl glucose* and *poly-galloyl gallate* were detected by an optimized protocol [4] based on high performance liquid chromatography coupled to high resolution mass spectrometry (HPLC-ESI-Q-ToF). Furthermore, by performing ageing tests on reference materials in different conditions (natural and artificial ageing), two degradation mechanisms were observed: hydrolysis of poly-galloyl glucose and auto-oxidation of gallic acid. Moreover, the analytical procedure allowed us to reveal different chemical profiles and to highlight different effects of ageing in relation to the ink's recipes.

Our studies devised a methodology that enables the identification of the molecular markers of the organic components in inks, thus introducing ultra-sensitive chromatographic and mass spectrometric methods in the array of analytical tools available in this field.

[1] C. A. Mitchell, Inks: their composition and manufacture, **1904**.
[2] J. Kolar, S M. Strlič, Iron Gall Inks: On Manufacture, Characterisation, Degradation and Stabilisation, **2006**.
[3] M. Aceto, E. Calà, Analytical evidence of the use of iron-gall ink as a pigment on miniature paintings. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2017**, pp. 1–8.
[4] A. Ferretti, F. Sabatini, I. Degano, A Model Iron Gall Ink: An In-Depth Study of Ageing Processes Involving Gallic Acid. *Molec* **2022**.

Predictions by pXRF raw spectra: classification of medieval enamels by machine learning

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Classification models are increasingly used in material science [1] and cultural heritage [2] as valuable way of speeding up analytical procedures and data processing. This study aims to compare the predictive ability of decision tree, random forest and support vector machine models in classification of different enamels manufacturing processes by using a dataset comprising measurements performed by portable X-ray Fluorescence spectrometry (XRF). While dating procedures based on machine learning approaches have relied heavily on quantitative XRF analysis [3], the method proposed here uses unprocessed raw spectra directly, avoiding the need for time-consuming processing and simplifying the prediction process.

Several analytical protocols were adopted until now for investigating compositional features of medieval limousin enamels and later-period artefacts [4], but these diagnostic techniques usually require sampling at relatively high time and cost. Although UV-visible-NIR diffuse reflectance spectrophotometry with fiber optics (FORS) turned out to be a good technique for obtaining preliminary results able to distinguish medieval and XIX-XX century artefacts by analysing the ubiquitous blue enamels [5], the need to investigate other colours or other enamels sub-groups prompted the adoption of other techniques and procedures.

Therefore, this work shows another method to provide a fast and non-invasive approach for authentication and dating different colours and manufacturing processes of enamelled artefacts, based on classification models trained by a dataset made of XRF spectra collected on artefacts with known period of production. The models trained on this dataset, consisting of nearly one hundred XRF measurements of 58 enamelled objects from different European collections, are able to distinguish different manufacturing processes with a good accuracy.

[1] J. Wei, X. Chu, X. Sun, K. Xu, H. Deng, J. Chen, Z. Wei, M. Lei, InfoMat 1(3), 2019, 338-358.
[2] M. Fiorucci, M. Khoroshiltseva, M. Pontil, A. Traviglia, A. Del Bue, S. James, Pattern Recognition Letters 133, 2020, 102-108.
[3] A. Heginbotham, R. Erdmann, L.C. Hayek, Journal of the American Institute for Conservation 57(4), 2018, 149-168.
[4] P. Dandridge, M.T. Wypyski, MRS Online Proceedings Library 267, 1992, 817-826.
[5] M. Aceto, G. Fenoglio, M. Labate, M. Picollo, M. Bacci, A. Agostino, Journal of Cultural Heritage 45, 2020, 33-40.

Absolute dating of building materials from the Santalla de Bóveda Monument (Lugo, NW Spain)

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The Santalla de Bóveda Monument (Lugo, NW Spain) is a small semi-buried building, under the Bóveda Parish Church, built in the 18th century, with an apsidal quadrangular floor plan, which was divided into three naves, a small vaulted apse and a rectangular floor plan vaulted, where paintings depicting birds and plant elements have been well preserved. The monument has aroused great interest since its discovery, but its chronology and functionality has always been the subject of controversy. Several hypotheses have suggested that the monument were built in the Roman Period and some others around the 9th century AD [1]. However, any direct evidence or absolute age has been provided until today. The stratigraphic analysis of the building suggests five constructive phases for the building [2]. Taking such analyses we have taken brick and mortars samples of all phases to perform absolute dating techniques to get a precise and accurate chronology. Radiocarbon dating of mortars and luminescence dating of mortars and bricks has been used to this purpose. A total of 21 samples were taken, being 20 Optically Stimulated Luinescence (OSL) and 15 ^{14}C ages obtained for mortars, on the quartz aggregate and carbonate lime or charcoal fragments, respectively. 5 brick samples were also dated by Thermoluminescence (TL). The obtained ages have allowed, for the first time, stablishing an accurate and precise chronology being the first phase assigned to the second half of the 4th century AD. Alterations of the building and the vault paintings were performed in the late 6th and early 7th centuries, while the construction of the second floor and occasional repairs were performed during the 10th-12th centuries. Later, occasional alterations and clogging of the monument was done in the 18th century.

[1] R. Benavides R, Blanco-Rotea, Santa Eulalia de Bóveda, 2008. 43-82.
[2] R. Blanco-Rotea R, Benavides García J, Sanjurjo Sánchez D, Fernández Mosquera Arqueología de la Arquitectura, 6, 2009 149-198.

The study of the Portuguese glass arcana with the tools of the future

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This research focuses on the study of Portuguese glass arcana, or glass batch books, dating from the period between the 18th and the 20th centuries. The period under consideration, of a great length and with significant differences between the considered centuries, has been of increasing interest to researchers since little is known on glass making in the above period, which nevertheless includes various key points for understanding the beginning and the evolution of the glass industrial age.

One of the consequences of glassmakers leaving Murano and spreading throughout Europe in the late 17th century was the proliferation of a variety of glass compositions [1]. Because of the great amount of new compositions entailed the need to write down the new recipes in these personal notebooks, some including the results of experiments and tips for the future [2]. However, not all these new recipes worked or had the desired characteristics for the type of object they wanted to produce. These failed attempts were also noted down in the arcana, possibly with the aim of knowing what has or has not been tested and what works. Since the arcanum is an object of personal use and usually only the author should be able to understand it, what we verify is that sometimes these failed recipes are not marked, or with a note of what failed in their production.

In order to ascertain the arcana and their importance as historical object, the methodology followed in this research includes the reproduction of a selection of recipes in laboratory-scale quantities, followed by the elemental, thermal and mechanical characterization of the resulting glass samples. In this presentation, the results of differential scanning calorimetry (DSC), dilatometry, and Vickers hardness test will be presented, since they are techniques that enable us to test if the compositions in question are good, workable, and fit for the creation of which type of objects (DSC and Dilatometry); finally, the Vickers test gives us information about the suitability of the glass for cutting and engraving, decorative techniques that were very appreciated in the period in question [3].

In this way, we can understand if we are reproducing the glasses in a historically accurate way and if the compositions under study can be included in a database of compositions, which can be used as a tool in the attribution of authorship for the historical objects displayed in Portuguese museums, as well as in performing aging tests or create new restoration methodologies.

[1] Tait, H. (2012). Europe from the Middle Ages to the Industrial Revolution. In 5000 Years of Glass (pp. 156–178). London: British Museum.

[2] Reis Santos C, Vilarigues M, Dabas P, Coutinho I, Palomar T. Reproducing crystal glass from three 18th-20th centuries Portuguese glass arcana. Int J Appl Glass Sci. 2020;00:1–13. https:// doi.org/10.1111/ijag.15611

[3] Shelby JE. Introduction to Glass Science and Technology. London: The Royal Society of Chemistry; 1997.

Study on Behaviour of Gilded Wood to Artificially Ageing

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This paper presents the initial results of a larger study on the behavior of some gilded wooden surfaces to artificially aging, in order to assess adhesives used in the restoration of some altars of Orthodox churches (16th-19th centuries). For this case study, a fir wood rod conditioned for ten years was chosen, which was gilded using a traditional technique (application of layers: adhesive, primer – multiple layers, bolus, with intermediate sanding, then application of 22kt gold leaf with final polishing using agate stone). From the beginning, this stratigraphic structure consisting of materials and layers with different physical and chemical properties has a predisposition to splitting – the separation of two perfectly overlapping layers – to peeling, cracking and grinding.

The surface morphology of the samples was evaluated mainly by non-invasive analytical techniques specific to the diagnosis and scientific studies of cultural heritage goods. Optical microscopy, SEM, colorimetry (CIE L*a*b* system) were mainly used to evaluate the behavior of the gilded surfaces and the interference between the metal surface and the other layers specific to the manufacture of gilded wood. The adhesives used were based on rabbit glue and bovine hide glue, the latter made as part of a research project. The gilded wood samples were artificially aged in a special Binder-type aging chamber at 60°C for 7 days, followed by conditioning in an incubator at 70% R.H., at 25°C for 2 days, in several cycles. The artificially aging process determined the appearance of dimensional and chemical changes at the substrate level, as well as in the wood [1-3], but also in the gilding layers [4]. Results from this study indicate, depending on accelerated ageing cycles, changes/damage in the surface morphology, both for the gold leaf and the fir wood substrate, as well as significant changes in colour (particularly parameters L* and a*).

The use of these techniques to monitor the behavior of gilded surfaces with an adhesive based on bovine hide glue compared to that of rabbit glue during the artificial aging process is useful for making a specific assessment of conservation and restoration works.

Acknowledgement
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References
[1] A. Cavalli, D. Cibecchini, M. Togni, H. S. Sousa, A review on the mechanical properties of aged wood and salvaged Timber, *Construction and Building Materials* 114, 2016, 681–687, https://doi.org/10.1016/j.conbuildmat.2016.04.001
[2] J. Mao, H. Abushammala, B. Kasa, Monitoring the surface aging of wood through its pits using atomic force microscopy with functionalized tips, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 609, 2021, 125871, https://doi.org/10.1016/j.colsurfa.2020.125871
[3] K. Kránitz, Effect of natural aging on wood, *Doctoral Thesis*, 2014, 41-73
[4] I. C. A. Sandu, T. Busani, M. H. de Sá. The surface behavior of gilding layer imitations on polychrome artefacts of cultural heritage, *Surface and Interface Analysis* 43(8), 2011, 1171–1181, https://doi.org/10.1002/sia.3796

Ex situ and in situ approach to evaluating crystallinity of Bombyx mori silk fibroin during artificial thermo-ageing.

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A direct motivation for our study was a call for the immediate conservation of precious XVIth-century silk banners from the Wawel Royal Castle in Cracow, Poland.
Semi-crystallite silk is degraded mainly by hydrolysis and oxidation of peptide bonds, which may lead to a decrease in polymerisation degree and the formation of new functional groups on the polypeptide chain together with the liberation of volatile products and recrystallisation. Accelerated ageing tests are the most accepted method for studying the degradation mechanisms of various materials, including silk's fibroin. Therefore, light or/and temperature, different gaseous agents and degrees of humidity are found to be used as ageing stimuli [1]. Those are supposed to lead to changes that reflect naturally occurring degradation reactions.
In our previous work [1], concentrated on the details of the degradation estimators change upon thermal-degradation, we have verified FTIR-derived estimators by XRD, SEC, and UV-Vis techniques. This way, verified degradation markers were put forward to analyse the condition of historic samples [2]. For historical samples, the crystallinity estimator showed incongruous with time trends. This raised our suspicion about the nature of the changes provoked during artificial and natural ageing processes.
Here, we compared crystallinity estimators for the thermo-induced and natural degradation of fibroin calculated from data gathered by XRD and pol-ATR-FTIR techniques. To eliminate the irreproducibility of the sampling spots, we juxtaposed two methods: *ex-situ* ageing in an ageing chamber and closed vials; *in-situ* ageing in airflow and argon flow conditions.
XRD and FTIR analysis for historical samples showed a significant drop in crystallinity. Data indicates that β-sheets pleads of ordered fibroin domains naturally decompose into the non-ordered amorphous and α-helix ones. The *ex-situ* technique of thermo-ageing provoked the breaking of β-sheets into preferably α-helix arrangements that showed some tendency to network with amorphous domains' relative content left intact, unlike in the natural degradation process. *In-situ* experiments provoked the opposite of natural changes, where the β-sheet content seems to grow in time, and the amorphous domains decrease.
The differences between artificial and natural ageing processes described here should be considered when interpreting the results of artificial ageing methods. Thus, the chemical behaviour of silk's fibroin observed during artificial ageing tests should not be understood as a perfect model mimicking the natural changes. Oxidation and hydrolysis provoked during the long-term artificial degradation model natural processes better, but crystalline artificially developed change differs from the natural one.

[1] M.A. Koperska et al., Polymer Degradation and Stability 105, 2014, 185–196;
[2] M.A. Koperska et al., Spectrochimica Acta - Part A, 135, 2015, pp. 576-582.

Artomics: integration of compositional and formal characteristics in the study of artworks. Application to an illuminated cartulary and high-quality glass pieces.

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The Artomics approach aims to identify characteristics voluntarily and involuntarily transferred to the objects due to the cultural, social and economic context of the period they were created in. These characteristics are expressed through the material and formal choices made by the artists or artisans involved, and may include the materials used, the creative processes or techniques applied, decorative styles and calligraphy types amongst others.

Artomics is a novel analytical approach that combines the compositional and formal characteristics describing groups of artworks and their analysis using multivariate techniques. The approach aims to study the "material fingerprints" the creative processes leave on artworks that, in reality, are the fingerprints that a society transmits to the future through the artist and the object.

The methodology includes four main stages: (i) the determination of the composition and structure of the materials used in the object, (ii) the description and parameterization of the relevant formal aspects of the object, (iii) the joint treatment of both information through multivariate methods and, finally, (iv) the interpretation of the observed groupings. The three last steps are the principal innovation of this approach, since it is necessary to define categorical variables from formal aspects, in addition to the application of data processing techniques that include both sources. Of course, interpretation is the final objective and the most complex and critical step.

In this study, we present the results obtained for two types of works: an illuminated cartulary, the *Liber Feudorum Maior*; and a set of glass objects produced by the Royal Glass Factory of Spain. In both cases, X-Ray Fluorescence (XRF) has been used for the compositional analysis.

The *Liber Feudorum Maior* is extensively decorated with miniatures painted in two distinct styles and possibly created by more than two artisans. The data obtained from X-Ray Fluorescence (XRF) analysis is combined with the formal characteristics of the miniatures, previously parametrized using descriptive variables, to classify the illustrations and observe how cultural criteria are projected on the objects. The same approach is applied for the glass pieces, which correspond to a representative sample of the Factory's production (cups, beakers, bottles, jars) across several historical periods (Baroque, Classicist and Imperial), colored and decorated in the style corresponding to each period.

In the case of the *Liber Feudorum Maior*, The joint classification prioritized stylistic variables over compositional ones, most likely because of the limited variety in the materials used and the rules and available materials and knowledge for the creation/production of these objects. Nonetheless, compositional data provided interesting insights regarding execution.

Analysis of oval paintings from the 18th century attributed to the Brazilian painter Leandro Joaquim by XRF and MA-XRF

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In this work, three oval paintings attributed to the painter Leandro Joaquim, who lived between 1738 and 1798 in Rio de Janeiro, became known as one of the most outstanding Brazilian artists of this period for his work considered innovative by historians of the Brazilian art. The oval artworks investigated belong to the collection from the Museu Histórico Nacional, located in Rio de Janeiro, consisting of six paintings in total. According to historical records, these paintings form a collection produced in sequences by Leandro Joaquim. However, the lack of historical records of the artworks raises doubts about whether the six paintings are from the same collection. Therefore, the investigation carried out in this work aims to collect data on the paintings' chemical matrix, which will verify whether the artworks' pigments and creation methods are similar. The paintings were analyzed by macro X-ray fluorescence scanning (MA-XRF) e XRF point analyses. MA-XRF was carried out in the instrument from Bruker, CRONO model that has Rh tube operating with a voltage of 40 kV and a current of 200 µA. Every 1 mm of the paintings was scanned, with 40 ms per pixel dwell time and a translation speed of 20 mm/s. Analyses by XRF point analysis were performed using an instrument from the Bruker TRACER model, with the Rh tube operating at a voltage of 40 kV and a current of 10 µA. In all paintings investigated, elemental maps of Pb-L, Hg-L, Fe-K, Mn-K, and Ca-K were recorded. The Pb-L maps show the presence of Pb pigment throughout the artwork, with some points of loss. This use indicates the use of lead pigment as ground. The Hg-L maps are associated with regions of a red hue. At the same time, the Fe-K maps appear alone in regions with a green hue, while the brown areas appear associated with Fe-K and Mn-K. The results of the elemental maps indicate that the same pigments were used in the three paintings. This information is confirmed by multivariate statistical studies using XRF point analysis data. Because in the Principal Component Analysis (PCA) of the spectra collected on different artworks but in regions with the same hue, they form clusters in score plots. These results, allowing understand the style and materials used in the creation of the paintings, indicate that the three artworks were probably produced by the same method, corroborating the hypothesis of series production.

Portable XRF and Raman spectroscopies to outline the story of Medieval precious objects

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Raman and X-ray fluorescence spectroscopies represent well-established techniques to study gems and jewels. The support of these analytical methods appears particularly relevant during real-time gemological analysis of objects in Museums, especially when studying very unique gold works whose access is limited due to conservation issues. Additionally, it appears fundamental in reconstructing the history of precious objects whose prevenance trajectories have been modified through time.

The case study presented is the diagnostic campaign carried out on four objects with different chronologies and of great interest for reconstructing the technical and artistic development of the Tuscan medieval and modern goldsmithing. The studied gold works, namely the Cintola del Duomo (Opera del Duomo Museum, Pisa), the Holy Cross (Civic Museum, Castiglion Fiorentino, Arezzo), and the Reliquary of the Arm of St. John the Baptist with its case (Siena Cathedral), are among the most famous objects in the history of goldsmithing, both for their manufacturing exceptional quality and for their devotional value.

Gemological analysis of the numerous gems decorating the precious objects has been coupled with an analytical investigation by portable Raman (i-Raman, B&W Tek, excitation source 785 nm) and p-XRF (Elio, Brucker), enabling to reconstruct the complex biographies of the Medieval gold works.

This contribution aims at providing an occasion for discussing how the systematic application of well-established analytical methods in selected contexts can contribute to a deeper understanding of the transmission of technical knowledge. We wish to pinpoint how the application of routine methods in a transdisciplinary framework can lead to solid results for a holistic approach to art-historical objects, proving how stylistic choices can be driven by the symbolic meaning of precious objects.

The authors acknowledge the Opera del Duomo of Pisa and Siena and the Museum of Castiglion Fiorentino for authorizing the present research.

Towards building a CL database for pigments: Characterization of blue pigments

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The identification of individual pigments on Paintings and painted surfaces is considered to be a particularly complex process, due to various factors (e.g. complexity of materials used, alteration processes, etc.) and thus form the basis for particularly intricate Cultural Heritage studies. The combination of Scanning Electron Microscopy (SEM) with Cathodoluminescence (CL) can serve as a powerful new tool for the identification of individual pigments. SEM/CL has the potential of identifying both organic and inorganic pigments and can focus on a micrometer scale. The combination with Energy Dispersive Spectrometry (EDS) allows for robust, cross-checked, elemental and mineralogical characterization of pigments.

In order to apply SEM/CL in a routine-based way for the identification of pigments, it is necessary to have a robust, open-access database of characteristic CL spectra of pigments. A large project has been undertaken to create such a database, focusing primarily at the pigments, both organic and inorganic, which were most commonly used from antiquity until today [1]. In the present work, the CL characterization of common blue pigments (organic and inorganic, based on Cu and Co) is presented.

In most cases, the CL spectra present characteristic bands, which allow the identification of the pigments. Additionally, the potential of identifying the pigments in an actual painting layer, as well as the effect of weathering, was evaluated by comparison to pigments identified on areas of 20th c. paintings. Overall, weathering appears to cause minor differences in the occurring spectra, without preventing the identification of pigments.

These results enrich the available CL database and further support the idea that SEM/CL can serve as a powerful tool for the determination of individual pigments (both organic and inorganic) and the better documentation of the production technology of paintings.

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[1] E. Palamara, P.P. Das, S. Nicolopoulos, L. Tormo Cifuentes, E. Kouloumpi, A. Terlixi, N. Zacharias, Heritage Science, 9:100, 2021.

The newest metal findings from the Early Eneolitic house in South-eastern Serbia

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Velika Humska Čuka is a multi-layered archaeological site near Niš in South-eastern Serbia that was inhabited from the middle of the 5th millennium BC to the 5th century AD. During excavations in 2022, a set of 22 bronze objects was found in a shallow pit dug into the remains of an Early Eneolithic house.

This small hoard consists of 10 circular pendants with a central knob, ten pieces of spirally twisted bronze wire that formed tubes (so-called salteleons), a pin, and a long bronze band that has been folded several times. Pendants and saltaleons once formed a necklace which, together with a pin, were typical for the territory of today's central Europe at the end of the Middle Bronze age and during the Late Bronze age. This type of pendant appeared in the central Balkans at the beginning of the Late Bronze Age, together with other finds that originated from central Europe. Many archaeologists believe such bronze finds reached the central Balkans with the communities of the so-called Tumulus culture, which began to spread from Central Europe in the middle of the 2nd millennium BC. According to the distribution and dating of this type of pendant, the hoard from Velika Humska Čuka belongs to the Br C-D period (14th-13th century BC).

The XRF analysis was performed to reveal the elemental composition of the metal objects. The objects were cleaned before analysis, so only the metal parts were analyzed. The analysis was performed using a hand-held XRF spectrometer Hitachi X-MET8000 Optimum, operating in metallic mode. Additionally, the analysis was performed using an in-house developed pEDXRF spectrometer which consists of a side-window X-ray tube-Oxford Instruments (Rh anode, max. voltage 50 kV, max. current 1 mA, with forced air cooling) as an excitation source and a compact X-ray spectrometer (X-123, AMPTEK Inc. with Si-PIN detector 6 mm^2/500 μm, resolution 160 eV at Mn Kα line, 12.5 μm thick Be window and 1.5" extension). A pinhole collimator was used to focus and reduce the X-ray beam to an approximately 2 mm spot size on the object's surface, which can be precisely aligned to the excitation beam and visualized as the measured spot using two laser pointers. The quantification was done using brass standard reference material-Naval Brass C1108.

The analysis showed that copper, tin, nickel, and arsenic could be found in all analyzed samples, almost in the same quantity, indicating the same raw material origin.

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Optimization of a laser-driven X-ray source for X-ray Fluorescence applications on Cultural Heritage

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Within this study, we present the performance of a laser-driven water-jet target X-ray source for X ray fluorescence (XRF) applications on Cultural Heritage artifacts. Laser-driven X-ray sources are used for X-ray absorption spectroscopy, diffraction, radiography and fluorescence [1]. Nowadays laser driven XRF is applied on archaeological samples and works of art [2-3].

Recently, our department developed a compact liquid target setup for laser-driven ion acceleration and X-ray emission at high repetition rate. Laminar flowing micro-jet of 50 um in diameter is compatible with low-vacuum environment, debris-free, and demonstrate precise dimensional and positional tolerance. The used source was the commercial laser Astrella from the Coherent that delivers maximum 5 mJ laser energy in 30 fs with a repetition rate up to 1 kHz. The interaction of the laser with the water-jet target takes place inside a low vacuum chamber and the produced X-rays are transmitted through a window that was covered with a 25 µm thick Kapton foil.

A silicon drift detector (SDD) (active area: 65 mm^2, energy resolution: 133 eV @ 5.9keV) was used to detect the produced X-rays, placed outside the vacuum chamber. The entrance of the detector was collimated with a 1.2 mm thick stainless steel pinhole with an aperture of 1 mm.

The energy distribution of the X-rays produced by the interaction of the laser with the water-jet target was directly measured by the SDD that was facing at the interaction point. The primary X-ray spectrum was measured at different repetition rates 100, 500 Hz and 1kHz, at different focusing positions of the laser on the water jet target and at different distances from the entrance window. Finally, measurements in 45°-45° XRF geometry of reference materials and application on archaeological samples will be presented.

[1] A. Zymakova´, M. Albrecht, R. Antipenkov, A. Spacek, S. Karatodorov, O. Hort, J. Andreassona, J. Uhli, Journal of Synchrotron radiation, 28, 2021, 1778.
[2] F. Valle Brozas, A. Crego, L. Roso, A. Peralta Conde, Applied Physics B, 122, 2016, 219.
[3] P. Puyuelo-Valdes, S. Vallières, M. Salvadori, S. Fourmaux, S. Payeur, J. C. Kiefer, F. Hannachi, P. Antici, Scientific Reports, 11, 2021, 9998.

The Woven Archive. Material Characterization of Textile Collections in Archives and Libraries.

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Textiles are present in archival and library collections in multiple and sometimes surprising forms: enclosed in letters, in fabric swatch books and as samples in dyers´ notebooks; but also, as wrappings for wax seals, in embroidered bindings or as the substrate of early photographs known as *pannotypes* [1]. Such textiles are a relatively unknown and understudied resource, as often they are not included in public catalogues nor digitized. Interestingly, textiles in archives and libraries are, in general, astonishingly well preserved: their vibrant colours kept away from the light and other environmental factors, which may have degraded to some extent the archaeological textile fragments and historic garments we see in museums. In addition, archival textiles are often accompanied with documentation that allows us to contextualize and accurately date them. All this makes archival and library textile collections an invaluable resource for materiality research.

Efforts are being made to create awareness about the presence of textiles in libraries and exchange knowledge between different professionals dealing with their conservation and material research [2], as well as to capture materiality in ground-breaking digitization projects [3]. This paper introduces three new projects investigating the materiality and conservation aspects of relevant textile collections at The National Archives and beyond:

-Capturing the Materiality of the Prize Papers: a set of 19th century textile samples from Canton and Batavia as a case study.
-Out of the Bag. Unravelling Medieval Seal Bags through Cultural Studies and Scientific Analysis [4].
-From Natural to Synthetic. Analysis of the dyes in the textile samples from the Board of Trade Volumes between 1856 and 1859.

The collections, research questions, methodological approach, preliminary results and next steps will be briefly presented. The analytical techniques used for material characterization of the dyes, mordants, fibres and metal threads include: MSI, VIS-NIR FORS, Raman, SERS, UHPLC-PDA, UHPLC-ESI-Q-TOF-MS/MS, XRF scanning, 3D digital microscopy, MFT.

[1] I. Vasallos, The Pannotype Mystery, *TNA blog*, 2019 https://blog.nationalarchives.gov.uk/the-pannotype-mystery-part-1-historic-photographic-processes-in-design-registers/
[2] VVAA, Textiles in Libraries: Context and Conservation, *The Conv*eyor, 2021. https://blogs.bodleian.ox.ac.uk/theconveyor/tag/textiles-in-libraries/
[3] VVAA, Prize Papers Materiality, 2022 https://materiality.prizepapers.de/
[4] J. Jasperse, L. Pereira Pardo, Beautifully wrapped in silk: Medieval seal bags unravelled, *TNA blog*, 2022 https://blog.nationalarchives.gov.uk/medieval-seal-bags/

ATLAS, a versatile MA-XRF imaging spectrometer and its applications

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A new MA-XRF scanner called ATLAS was constructed for 2D elemental imaging of artworks. It is based on either a micro-focused X-ray tube with polycapillary focusing optics or a collimated low power transmission X-ray tube, and a heavy duty XYZ scanning system, capable of scanning 100x80 cm works of art. The system can either move a MA-XRF measurement head (X-ray tube + 4 SDDs) or the artwork under investigation. A distance sensor is employed to ensure a constant source-surface distance, which is especially useful in the case of curved panels or canvases. The control software exploits multi-threading to efficiently process all detected events. Dwell times per pixel are typically in the 20-100 ms range, recorded count rates are in the range of 50,000-500,000 counts/s.

In this contribution, a number of recent applications of the ATLAS MA-XRF scanner will be discussed related to painted works of art dating from the 15th to the 20th century. The composition of the enameled surface layer of a mid-16th century tile tableau originating from Antwerp was visualized in order to study the difference between original and replacement tiles and the starting materials used for creating the colors. A 15th century wooden panel painted in the style of the Flemish Primitives was investigated to pinpoint the restored areas and to compare the pigments to those found in the works by J. Van Eyck, H. Memling and contemporaries.

Compositional μ-XRF analyses of copper-based coins from Rhodes, Greece, 4th c. BCE to 2nd c. CE

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The present study provides new data on the analysis of 111 copper-based coins from the ancient city of Rhodes, Greece, carried out in the XRF laboratory of the Institute of Nuclear and Particle Physics (INPP), NCSR "Demokritos", as part of the "Rhodes Centennial Project", a scientific collaboration between the University of Copenhagen and the Ephorate of Antiquities for the Dodecanese. This is the first time that elemental analysis is performed on copper-based coins issued by the Rhodian mint from the mid-4th c. BCE to the 2nd c. CE. Based on the μ-XRF results, three different groups of copper-based alloys are formed, with tin and lead as their major alloying components. The elemental composition shows that most of the coins are binary, leaded and ternary bronzes, while only two samples are of different technology—as expected—after it was confirmed that they were imported to Rhodes. All impurities present in the alloys, such as iron, nickel, cobalt, antimony or lead, are typical of copper ores, while the very small amounts of tin, lead and/or arsenic in a few coins could indicate the use of copper scrap-based alloys.

For the purpose of investigating provenance issues and technological aspects the k-means clustering method was used, as it can reveal hidden compositional patterns of the raw material used. Statistical analysis using silhouette analysis for k-means clustering reveals the existence of four distinct clusters (namely 0 to 3), with cluster "0" being distinct from the others due to increased lead content, including leaded bronzes and a leaded copper coin. However, it is interesting to note that all binary and most ternary bronzes are classified into three other groups, namely "1" to "3". The three groups seem to contain a tin content that is limited for each cluster within a certain narrow range with no overlap of tin concentrations. Based on the above statistical results the Common Era (CE) coins have a narrower distribution of tin (> 12.5 wt%) than the Before Common Era group (BCE) (7-24 wt%). However, it is not possible to identify a preferred recipe apart from the 2nd century BCE coins and most of the coins from the period between 350 and 300 BCE which can be considered loosely clustered. Therefore, the statistical analysis confirms that technological aspects of Rhodian coin metallurgy are not stable over a period of six centuries and that different technological choices are made simultaneously and not uniformly, regardless of the chronological framework and under the influence of other criteria e.g. the availability of raw materials at the time. This availability can be related to various factors (finance, politics, physical phenomena, etc.) that can facilitate or disrupt the trade networks of raw materials.

Portable, low-cost, easy-to-use, easily accessible and minimally invasive participatory analytical tools for the diagnosis of metal artefacts

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The *ENDLESS Metal* Innovators Grant (IG16215) project, funded by COST association as a continuation of the PortASAP Action (https://portasap.eu), aims to provide cultural sector professionals with analytical tools that facilitate the diagnosis of metal objects, thus contributing to sustainable decision making. It follows the philosophy of PortASAP action with the development and dissemination of portable, low-cost, easy-to-use, easily accessible analytical tools, adding the important criterion of being minimally invasive.

Two applications offered openly (DiscoveryMat and MiCorr) and an open-source electrolytic pencil (Pleco) will be considered. They allow the identification of the metal families of artefacts studied using a decision chain, the analysis of metals according to their electrochemical behaviour in three solutions, the identification of corrosion products formed on the surface of metals using Linear Sweep Voltammetry plots, and the study of their corrosion structure based on their observation under a stereoscopic microscope. The analysis is carried out by comparison with the tools' databases which are enriched by the users themselves.

After several years of development at Haute Ecole Arc Conservation-restauration, these three tools are currently being disseminated within the framework of the ENDLESS Metal project using all the activities of COST Actions: training schools, workshops, short-term-scientific missions and case studies.

It is expected that through ENDLESS Metal, metal objects will benefit from routine examination and qualitative analyses by the cultural sector professionals responsible for their study and preservation. These professionals will also be better prepared, thanks to the new expertise acquired, to take part in interdisciplinary discussions with the hard science communities. Furthermore, by being closer to the public, cultural sector professionals will be able to raise awareness of the importance of analysis heritage objects.

[1] Degrigny C., Dillmann P., Gaspoz C. and Neff D., Exploitation and dissemination of MiCorr as a diagnostic support tool for heritage metals, Eds. Murray, A., & Vila, A. Diagnosis: Before, During, After. CONSERVATION 360º, 2, 2022, 459.
[2] Degrigny C., Menart E. and Erny G., Easy-to-use, low-cost electrochemical open-source hardware to analyse heritage metals: possibilities and limits, Current Topics in Electrochemistry, 20, 2018, 15-23.
[3] Degrigny C., Jeanneret R., Witschard D., Local cleaning of tarnished Saint Candide reliquary head of the Treasury of Saint-Maurice Abbey, Valais (Switzerland) with the Pleco electrolytic pencil, e-preservation science, 12, 2015, 20-27.

On the application of SmART_scan in the study of the Planisphere mural painting by the Portuguese modernist Almada Negreiros

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Identifying and understanding the materials and painting techniques used by an artist is paramount when developing strategies for the conservation and safeguard of mural paintings. Following the European Standards for the Conservation of Cultural Property, non-destructive methods such as colorimetry/spectrophotometry and handheld-X-ray fluorescence are favored whenever possible, as they can provide crucial information regarding the pigments used in the production of the artworks without compromising its integrity. In this context, the development of X-ray fluorescence (XRF) scanners has provided a straightforward, reliable, and fairly rapid way to acquire compositional data, generating elemental maps of entire paintings or significant sections of these artworks [1-3]. However, the high cost of these systems, as well as their size and weight, can limit the application of XRF scanners in the study of mural paintings, especially those which are only accessible with a scaffold [2]. Therefore, SmART_scan, a computer program that generates false color maps of the distribution of elements (or compounds) in a painting by statistically combining all available data, can be considered a robust and economical alternative to the use of XRF scanners [3,4].

Here we will present the results of the application of the SmART_scan program in the study of a monumental colored planisphere [also known as mapa-mundi] which is the first mural painting commissioned in 1938 to the Portuguese modernist Almada Negreiros at the DN building in Lisbon [5]. By combining information from technical photography in the visible region, ultraviolet fluorescence induced in the visible range and near infrared, colorimetry/spectrophotometry, and handheld-X-ray fluorescence, it was possible to better understand the color materials used by Almada Negreiros and to compared it with tests previously carried out on two working palettes discovered beneath the mural in 1995.

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[1] Martin-Ramos, G. Chiari, Journal of Cultural Heritage 39, 2019, 260-269.
[2] M. Alfed, Microscopy and Microanalysis 26(S2), 2020, 72-75.
[3] A. Mazzinghi, C. Ruberto, L. Castelli, P. Ricciardi, C. Czelusniak, L. Giuntini, P.A. Mandò, M. Manetti, L. Palla, F. Taccetti, X-ray spectrometry 50(4), 2021, 272-278.
[4] D. Miriello, R. De Luca, A. Bloise, G. Niceforo, J.D. Martin-Ramos, A. Martellone, B. De Nigris, M. Osanna, G. Chiari, Mediterranean Archaeology and Archaeometry 21(1), 2021, 257-271.
[5] José de Almada Negreiros: Uma Maneira de ser Moderno [Catálogo da Exposição]; Museu Calouste Gulbenkian: Lisbon, Portugal, 2017.

Water profile distribution inside wall paintings by NMR-MOUSE in combination with evanescent-field dielectrometry technique and near-IR reflectance spectroscopy

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The water inside masonry is one of the major contributors to damage observed on wall paintings, thus a full diagnostics of water content inside represent a key issue for the preventive conservation. Although, for this aim several approaches based on non-destructive techniques are used, but the evaluation of water diffusion inside wall still remains an unsolved problem.

This paper deals with the determination of the profile water content in wall paintings as a function of depth and time by a multi sensors-based approach which includes portable Nuclear Magnetic Resonance (NMR-MOUSE), Evanescent Field Dielectrometer (EFD) system in the microwave range and reflectance spectroscopy in the near-IR region. Each of the selected techniques has a proper investigation depth: the probing of the reflectance spectroscopy in the near-IR region is limited to the surface of the wall painting, the NMR technique can evaluate the presence of water up to 5 mm; while the EFD allows the detection of water up to 2 cm in depth.

The reflectance spectroscopy technique has been employed to assess the amount of adsorbed water from the surface by acquiring the reflectance spectra in the near IR region [1]. The water content is estimated by integration of the absorption band at 1920 nm and at 1450 nm. The NMR-MOUSE allows one to map water in walls and masonries in a non-destructive way preserving the integrity and size of the object under investigation [2]. The collected data on a matrix of points are returned in the form of a contour plot map. Since the intensity of the NMR signal is directly proportional to the water content, the obtained map shows the distribution of moisture content in the first layers of the masonry [3, 4]. While the EFD system in the microwave range, consisting of a resonant probe connected to a network analyzer [5, 6], measures the moisture content inside the wall painting up to 2 cm in depth.

The proposed approach has been applied to investigate the presence of water content on the wall paintings of Brancacci's chapel - painted by Masolino, Masaccio Filippino Lippi between 1425-1485. The investigation became necessary to understand the distribution of water inside the wall in relation with the environmental parameters at seasonally. The intercomparison among the results obtained by the three methods and the environmental monitor inside the chapel are outlined.

[1] D. Magrini, et al. (2017) Measurement Science and Technology, 28(2)
[2] N. Proietti, et al. (2021) Minerals, 11, 406.
[3] D. Capitani, et al. (2009) Analytical and Bioanalytical Chemistry, 395(7), 2245-2253
[4] V. Di Tullio, et al. (2010) Analytical and bioanalytical chemistry, 396(5), 1885-1896
[5] R. Olmi, et al. (2006) Measurement Science and Technology, 17(8), 2281
[6] R. Olmi, et al. (2008) Il Nuovo cimento della Società italiana di fisica, C31(3), 389-402

Use of Mobile All in One Multispectral Devices in the Analysis of Artworks

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The use of light different wavelengths has been used for many years to gain information about the construction technique of the artwork, its layers if there are any, and the restoration they carried out in the next process [1]. Different wavelengths of light such as UVA, UVB, and UVC to investigate the absence of varnish layer in the painting, whether the restoration process has been applied in the next process and this context, and applications such as retouching and patching. Wavelengths of light, defined as IR, are used to check whether there is a preparation for underdrawings in canvas paintings or to check a new painting on a canvas with a different image layer before [2].

When the places where the artifacts are found are such as high-security museum storage spaces or bank vaults, create various problems when examiners enter these areas with heavy equipment. Although multispectral devices have a portable nature, they need a considerable material volume considering the need for an extra light source and connection to a computer. Thus, mobile Multispectral devices, which include a light source with automatically changeable filter keyboards are needed as they are in the form of a tablet, therefore we can examine instantly, which provides advantages in environments where the usage times are not suitable for long working times.

With the ForenScope SmartArt device, Turkish painters Bedri Rahmi Eyüboğlu [3], Eren Eyüboğlu [4] and Gülseren Südor present the executive performance in paintings. In Bedri Rahmi Eyüboğlu's painting, a figure that cannot be seen sufficiently with visible light has become evident by imaging with the 940-960 nm IR light source of the device.

Large areas of Eren Eyüboğlu's painting, which were retouched later, were identified by imaging it with UVA light. In Gülseren Südor's paintings, on the other hand, the figure changes made by the artist in the process became visible in many of her paintings with different combinations of IR and UV filters and lights.

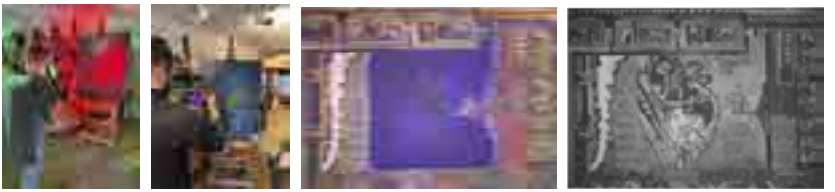

Fig. Working photos with ForenScope SmartArt Tablet.

[1] MacBeth, R., **Conservation of Easel Paintings**, 2012, 291-305.
[2] Mairinger, F., The Infrared Examination of Paintings", **Radiation in Art and Archaeometry**, 2000, 40-55.
[3] Eyuboğlu, H., **Living Under The Shadow of Two Cultures,** 2006, 50-74.
[4] Eyüboğlu, E., Eren Eyüboğlu 1927-1988 Retrospective, 2011.

The Explanation of Crafts: multi-analytical characterization of iron-gall inks prepared following a 12th-century Persian treatise

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The degradation of iron-gall inks (IGI) in manuscripts is a core issue within the conservation community. Identifying the iron gall ink composition is essential to understand the mechanisms of degradation taking place in treasured manuscripts, however, the complexity of their molecular structure is still to be disclosed, which hinders the development of new conservation treatments. In the past few years and within interdisciplinary teams, major breakthroughs were achieved to fill this gap, including detailed molecular characterization of the phenolic extracts of historically accurate reconstructions [1]. By reconstructing historical recipes using ingredients and methods appropriate to their period, we may better understand the complexity behind these inks. However, identifying ingredients and rediscovering ancient techniques may pose a major challenge because of the obscure practices and systems of measures used in the past [2].

This poster will uncover the medieval preparation of iron gall inks found in the Islamic treatise Bayan al-Sana‘at (‘The explanation of crafts’). Written in Persian (or Farsi), Bayan al-Sana‘at is one of the most eminent works of Hobaysh Teflisi, an alchemist, astrologist, and *hakim* (doctor) of the 12th century [3]. There are 10 recipes on the production and performance of iron gall inks encompassing different manufacturing procedures. We have discovered the addition of other elements such as saffron, starch, rose water, and poplar wood besides the common ingredients: a phenolic extract from gallnuts, Fe^{2+} obtained from iron salts and gum Arabic. Rationalization of these recipes will be presented, and a selection will be prepared with as much historical accuracy as possible.

A multi-analytical characterization of these inks and how each ingredient influences the final product will be carried out by colorimetry, high-performance liquid chromatography-diode array detector, Raman and infrared spectroscopies. By combining these techniques, we will relate color with chromatographic and spectroscopic profiles, allowing us to optimize these analytical techniques for identifying iron gall inks in manuscripts. We entail that this study will add knowledge to a better understanding of the historical manufacture and characterization of these precious writing inks, ultimately contributing to the sustainable preservation of our cultural heritage.

References:

[1] R. Díaz Hidalgo, R. Córdoba, P. Nabais, V. Silva, MJ. Melo, F. Pina, N. Teixeira, V. Freitas, Heritage Science 6(63), 2018, p. 1-15.
[2] R. Lucia, Journal of Islamic Manuscripts vol. 7, 2016, p. 294-338
[3] P. Holakooei, Journal of the British Institute of Persian Studies 54:2, 2016, p. 95-106.

Multi-analytical characterization of Woyo masks

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The Woyo people are a prominent cultural group of the Kongo culture in Central Africa in DRC (Banana Area) and Angola (Cabinda province).. During the 15th and 16th century the Woyo emerged as political entity and by the end of 16th -beginning of 17th century became the powerful kingdom Ngoyo. As a result of their geographical location, at the border of the ocean near the city of Cabinda, the Woyo were one of the first central African groups who had contact with the European explorers and merchants, in particular the Portuguese, Dutch, French and English dating back to the 16th-18th century. The connections with these foreign merchants and explorers, which continue during 19th-20th century, have had an influence on the iconography of some of their masks, some of which are comical representations of foreigners. Artistically speaking, the Woyo are known for their so-called "*Ndunga* mask" that were created by a male society called the *Bakama*, a brotherhood that dates, at least, to the 18th century. These masks played a religious, judicial and political role of creating order within the kingdom. Although the function and rituals of the *Ndunga* have changed over time, they still play an important role within the Woyo cultural groups.

These object are still understudied and research on the materials used on these masks will give us not only insight into the use of pigments and colorants within the Woyo culture but might give us further valuable insight in their interaction and trade with foreign visitors. With this aim a series of Woyo masks from the collection of the Royal Museum of Central Africa (Belgium) has been investigated using non-invasive analytical techniques, such as portable X-ray fluorescence (p-XRF) and X-ray powder diffraction (XRPD). Additionally, more detailed information was obtained from a limited number of samples using pyrolysis gas chromatography coupled to mass spectrometry and with synchrotron-based microscopic XRF and XRPD. While mostly natural colorants, such as clays and ochres were found, in some cases also synthetic materials, such as red lead and lead white, were encountered. A curious presence of germanium in the black colorant might form a link to the copper-zinc Kipushi mine, located close to Lubumbashi.

Fusing 3D imaging modalities for the interior and external investigation of cultural heritage objects

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3D imaging methods are increasingly employed to investigate the conservation state, origin and production process of cultural heritage objects [1-4]. Several techniques image the colours and textures of the objects' exterior, such as photogrammetry and structured light scanning. Using X-ray computed tomography (CT) on the other hand, the interior of the object can be visualised. Therefore, these techniques yield complementary information and additional insights can be gained by the fusion of these imaging modalities [5, 6]. However, there is a lack of easy and accessible software to combine these different imaging modalities, especially tailored to the inspection of cultural heritage objects.

We developed an interactive visualisation tool for cultural heritage based on the popular open source 3D software Blender [7]. The tool facilitates the inspection of surface scans and CT scans, registering them in case both are available and making images for research purposes. The CT images can also be shown as slices through the object, and as volume renders (fig 1A,B); the former is useful to investigate internal features in detail, the latter to represent the three-dimensionality of the object. The surface scan (fig 1C) is registered on top, which gives researchers the possibility to relate features on the surface to internal features (fig 1D). The tool will be open access, opening up easy interactive investigation of intricate 3D datasets to a wide range of institutions.

We will discuss the different applications for the fusion of multiple imaging methods and show results on objects from the Rijksmuseum (Amsterdam) and British Museum (London) collection.

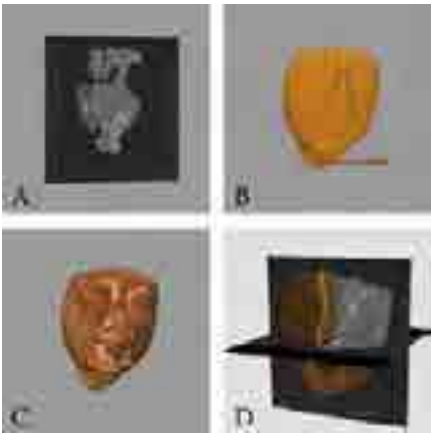

Fig. 1: Combining 3D imaging modalities of an Egyptian wooden mask (private collection). A) a slice through the CT scan, B) CT volume render, C) surface scan, D) registered and combined image modalities.

[1] F.G. Bossema, S.B. Coban, A. Kostenko, P. van Duin, J. Dorscheid, I. Garachon, E. Hermens, R. van Liere, K.J. Batenburg, J. of Cult. Her. 49, 2021, p38-27

[2] M. Domínguez-Delmás, F.G. Bossema, B. Van der Mark, A. Kostenko, S.B. Coban, S. Van Daalen, P. Van Duin, K.J. Batenburg, J. of Cult. Her. 50, 2021, p179-187

[3] I. Garachon, Simiolus Netherlands Q. Hist. Art. 41, 2020, p177-190

[4] J. Dorscheid, F.G. Bossema, P. van Duin, S.B. Coban, R. van Liere, K.J. Batenburg, G.P. Di Stefano, Her. Sci. 10(161), 2022

[5] M. Vandenbeusch, D. O'Flynn, B. Moreno, The J. of Egyptian Arch. 107(1-2), 2021, p 281–298

[6] P. Fried, J. Woodward, D. Brown, D. Harvell, J. Hanken, Digit. Appl. Archaeol. Cult. Herit. 18, 2020

[7] Blender, https://www.blender.org/

A novel multi-modal optical microscope combining Raman and photoluminescence mapping

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In this work we present an innovative multimodal optical microscope that can perform Raman and photoluminescence surface mapping and its exploitation in cultural heritage field.

From a material point of view, Cultural Heritage objects, as paintings, are very complex due to the presence of multiple chemical species, including degradation products, heterogeneously distributed from the surface down to inner layers. To assess their conservation status a multi-modal scientific approach is typically implemented by collecting a variety of spectroscopy and imaging data of the CH object/surface.

The same multimodal approach is effective also in microscopy analysis to analyze microsamples taken from the work of art, as paint stratigraphies. Conventionally, these samples are sequentially investigated with many different techniques, starting from simple optical microscopy observations and then moving to FT-IR, Raman and Scanning Electron microscopies. Nonetheless, the use of different microscopy set-ups unequivocally leads to different sample placement, resulting in difficult overlap of the multiple data collected, an issue that is also hindered by the different sample preparation required by each technique.

The aim of our work is to present the idea, design and development of a novel multimodal optical microscope that combines Raman and laser-induced photoluminescence (PL) spectroscopy within the same set-up to achieve the chemical mapping of a sample.

Indeed, Raman and PL are strongly complementary techniques thanks to their sensitivity to different materials, hence allowing to achieve a thoroughly characterization of the different materials present on a micro-sample.

Following a description of the novel set-up, we will demonstrate its effectiveness in the CH field through examples of analysis on different type of samples, from paint stratigraphies to micro-fragments of historical monuments and buildings. Further, thanks to the multifaceted nature of Raman and photoluminescence spectroscopies, the setup could be exploited in other research fields, as material science and the biological one.

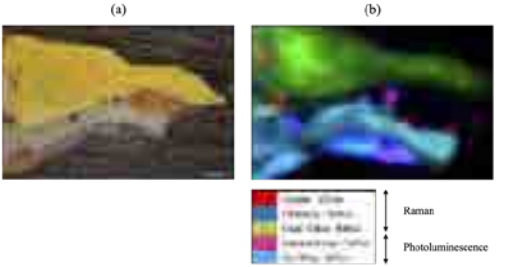

Figure 1: Analyzed stratigraphy sample (L5) from Larionov's painting. (a) Image of the sample. (b) Reconstructed image of Raman and photoluminescence measurements with a legend of the materials retrieved and their main peaks.

New techniques for NMR depth profiles with enhanced resolution and sensitivity and the study of mobile phases in paint layers, applied to a white Nevelson sculpture

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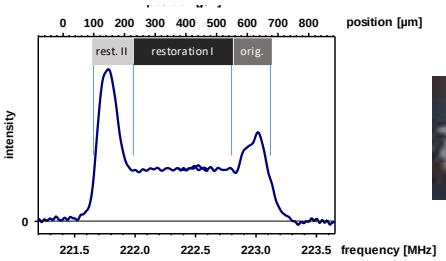
A painted wood work of a chapel (Erol Beker Chapel, St. Peter's Church, Manhattan NY) created by the sculptor Louise Nevelson in 1975 was studied by different NMR techniques in the framework of a restoration project. Original and a previous restoration paint layers were identified as alkyd and polyvinyl acetate, respectively, by solid state ^{13}C NMR spectroscopy, which furthermore showed the migration of pentaerythritol from the alkyd layer to the surface [1]. The effect of the application of cleaning gels has been monitored by means of ^{1}H magnetic resonance profiles acquired with a portable instrument. In order to overcome the limitations in sensitivity and resolution of this instrument, hardware and pulse sequences were developed for the analysis of paint chips flaked off the sculpture by using the gradient of a high field magnet, utilizing the much higher spin polarization [2]. An additional important gain was achieved by a Fourier-transform technique, replacing the scanning over the depth and thus overcoming the problem of achieving high resolution and sensitivity at the same time. Frequency modulated pulses, which have to be very short, allow a uniform excitation over a broad depth range. The technique not only yielded clear images of the original paint layer and that of a previous restoration attempt, but also allowed for the identification of a thin additional paint layer at the surface that has not been visible by microscope. In addition, the data could be analyzed using spin relaxation times (T_2) as contrast criterion. This revealed the concentration and migration of a slowly relaxing component, thus a mobile phase – probably a kind of plasticizer – over the different regions. A particular accumulation of this phase was observed below the interface between first and second restoration layer.



[1] C. Kehlet, S. Nunberg, S. Alcala, J. Dittmer, Microchem. J. 137, 2018, 480-484.
[2] P. Taugeron, S. Bricaud, C. Kehlet, J. Dittmer, Magn. Reson. Chem. 58, 2020, 870-879.

X-ray fluorescence imaging with benchtop devices for scanning and full field techniques

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Investigated historical objects contain often small details which must be analyzed nondestructively using XRF micro-analysis with a narrow excitation beam. In addition, the heterogeneity of these objects requires investigating of larger areas to get much more comprehensible information about the composition and structure. Therefore, mapping XRF techniques have been developed with the aim to visualize surface distributions of individual elements. Such maps can be obtained by means of the scanning of a surface with a narrow excitation X-ray beam or a novel technique, known as full field imaging, can be applied.

The scanning XRF analyses were performed with a device developed and used at the Czech Technical University in Prague. It contains an exchangeable X-ray source, a silicon detector (SDD or Si-PiN), and a positioning system providing an automatic scanning of a selected area with a step down to 5 μm [1]. This device provides us with the macro-XRF scanning using a miniature X-ray tube with a collimator or the micro-XRF scanning is possible with the X-ray tube (XOS) with polycapilly focusing optics.

The XRF system for full field imaging includes a color X-ray camera (CXC) provided by PNDetectors. It is a 264 x 264 pixel detector with an active area of 12.7 mm x 12.7 mm. Its main advantage is its energy resolution of about 140 eV for Mn-Kα line. So, such position sensitive detector provides also X-ray spectrometry with the energy resolution sufficient for energy dispersive XRF. Two miniature X-ray tubes are used for production of characteristic X-rays. Despite their low power (4 W each) they provide sufficient XRF signal because they can be placed very close to an investigated historical object. Thanks to a polycapillary parallel collimator, which is placed between an object and the CXC, the X-rays emitted from a certain position on the object can be transmitted by the X-ray optics of the collimator to a given pixel of the CXC. It means, surface distributions of elements are recorded with the CXC from an area larger than 1 cm^2 without the need to scan gradually the entire area with a narrow X-ray beam. The spatial resolution of this XRF imaging system is limited by the pixel size (48 μm) and it also depends on the distance of an analyzed object from the collimator.

The most frequently analyzed historical materials are metals, inorganic pigments, and siliceous substances. Therefore, our attention was focused on the comparison of these two imaging techniques for pieces of metals, glass and ceramics, manuscripts with ink and illuminations, and paint layers.

[1] M. Hložek, T. Trojek, R. Prokeš, B. Komoróczy, Radiation Physics and Chemistry 167, 2020, 108254

Analytical photography and Macro XRF scanning as tools in the investigation of the Lusina polyptych side-wings

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The two pairs of decorated side-wings of the Lusina polyptych are one of the most enigmatic yet significant objects in the collection of the National Museum in Kraków. They are remains of the only surviving example of a movable winged narrative-painting and sculpture-embellished polyptych in Lesser Poland[1]. Nonetheless, its provenance and authorship are unknown since the first mention of it in 19th-century archives it has become an object of speculation and controversy among contemporary scholars, who tend to link it with the workshop or influence of Veit Stoss. Unfortunately, it had been lost in the maelstrom of World War II when it was seized under Nazi occupation. Once the war ended, only the disassembled wings – missing the most imaginative carved scene - had been recovered. Featuring a relief depicting *The Holy Family*, the main body of the polyptych has never been returned to Poland and continues to be listed in the wartime losses catalogue[2].

The investigation of the polyptych in 2018 has shed some light on its nature. It entailed photographs in various ranges of electromagnetic radiation and macroscopic XRF scanning of all sculpted and painted panels as well as collecting samples for cross-sections and stratigraphic studies. UVF unveiled the extent of overpainting whereas IR photography revealed the preparatory layers, helping determine the technique and follow the artist's or artists' corrections. Mapping of the elemental distribution with MA-XRF (M6-Jetstream Bruker) provided information about gilded and silvered decorations invisible to the naked eye due to their degradation. Analysis of the collected data allowed to discern the consistency of individual panels in the context of its structure and reconstruct the process of executing the polyptych.

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Macroscopic XRF scanning: M. Goryl, M. Walczak, (Academy of Fine Arts in Kraków, Poland)

[1] W. Walanus, MODUS Prace z historii sztuki, II., 2001, p.60.

[2] K. Estreicher jr. Cultural Losses of Poland during the German occupation 1939-1944 with original documents of the looting 2003, pp. 92-93, 601.

Methodological approaches for underwater archeological metals investigation

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The investigation of archeological metals recovered in underwater sometimes is a challenge for a chemist because of the reactions involved in the development of their corrosion and the lack of information about the environmental conditions.
Here, some examples of investigation performed on different underwater archaeological metals are reported: the Montefortino-type helmets and the metals fragments from the Punic Ship exhibited at the Archeological Park Lylibeum (Marsala-TP, Italy) [1-2], the orichalcum ingots recovered in Gela seabed (Caltanissetta, Italy) [3], the roman and punic rostrum from the Egadi battles (second Punic war).
For each this case-study, an appropriate set-up of analysis was developed in order to answer the archaeological questions, and help to reconstruct the history of the objects. In some cases, the main request regards the metal production, while in other cases the interest was mainly devoted to the determination of the processes involved in the deterioration of the metal and to the definition of the conservation state. So, the used multi-analytical approaches were tailored by the application of conventional and non-conventional investigation techniques to determine the chemical composition. In detail, X-ray fluorescence and diffraction, and neutron investigations have been powerful micro and non-invasive means of studying the artifacts, by providing information about the nature and the processing of the metals.
The approaches developed for the investigation of the Montefortino helmets and of the metals findings from the Punic Ship will be presented to describe possible available information and at the same time clearly show the strong impact of the chemical-physical investigations to unveil a kind of degradation processes developed in the underwater archaeological metals.

[1] F. Armetta*, M.L. Saladino, A. Scherillo, E. Caponetti, Microstructure and phase composition of bronze Montefortino helmets discovered Mediterranean seabed to explain an unusual corrosion (2021) Scientific Reports, 11 (1), art. no. 23022.
[2] F. Armetta, R.C. Ponterio, I. Pibiri, M. L. Saladino*, New insight on archaeological metal finds, nails and lead sheathings, of the Punic Ship from Battle of the Egadi Islands (Submitted paper).
[3] E. Caponetti, F. Armetta*, L. Brusca, D. Chillura Martino, M. L. Saladino, S. Ridolfi, G. Chirco, M. Berrettoni, P. Conti, B. Nicolò, S. Tusa, Microchemical Journal, 2017, 135.

Operando monitoring of photo-ageing in hybrid material using a Cultural Heritage dedicated platform

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The understanding of the chemical processes involved in the evolution of a work of art is a long-standing challenge [1]. Indeed, artworks represent dynamic hybrid systems that evolve through time. The scientific community more specifically aims at developing a global study of various alteration phenomena to determine in a systematic way the causes and stages of degradation of the artistic material.

Among them, many historical compounds undergo photo-ageing reactions [2,3] most often associated with a loss of their color, resulting in a browning or fading of the artwork. Although these chemical reactions usually affect a very thin layer of the material surface, they can have a dramatic effect on the rendering of the work. Their study is therefore of prime importance in the field of heritage conservation to develop preventive conservation strategies through the selection of suitable storage and exposure conditions. However, a technological bottleneck to our current understanding of such phenomena is the lack of dedicated operando tool to follow and characterize the kinetic of the degradation processes within hybrid materials. This approach requires in particular to simulate and analyze simultaneously the reactions occurring during the photo-ageing phenomena.

This project proposes to fill this gap, through the development of a dedicated open-access platform for operando characterization of photo-ageing processes of various artistic materials. Accelerated exposure to monochromatic light covering the UV/VIS wavelength range, i.e. 280 to 800 nm, coupled with several measuring instruments (VNIR and SWIR diffuse reflectance spectroscopy, Raman, X-ray diffraction and low field NMR), allow photo-stability study of numerous materials while providing a controlled chemical environment with the development of dedicated environmental cells.

The capabilities of the platform will be illustrated through the time-resolved mechanistic study of the photo-degradation of SrCrO4 and BaCrO4 pigments in oil-paint system.

[1] Walter, P. and L. de Viguerie, Materials science challenges in paintings. Nature materials, 2018. 17(2): p. 106-109.

[2] Miliani, C., et al., Photochemistry of artists' dyes and pigments: Towards better understanding and prevention of colour change in works of art. Angewandte Chemie International Edition, 2018. 57(25): p. 7324-7334.

[3] Degani, L., et al, Stability of natural dyes under light emitting diode lamps. Journal of Cultural Heritage, 2017. 26: p. 12-21.

Seeing through the surface –micro-Spatially Offset Raman Spectroscopy Imaging on paper-based archival documents

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Raman spectroscopy is a well-established method for the characterization of Cultural Heritage (CH) materials such as inorganic pigments, modern synthetic dyes, and gems [1-3]. However, the technique is often limited to materials that are found on the uppermost surface. For hidden information, other techniques are often considered. One of the most used techniques may be MA-XRF which, with its ability to probe through the upper layer, allows to visualize the distribution and hint at the nature of the pigment(s) through their elemental composition. However, XRF does not allow for a complete pigment identification, which can be overcome using molecular spectroscopy such as Raman. Consequently, both techniques are often used in combination, allowing for a complete understanding of the materials and their distribution.

Micro-Spatially Offset Raman Spectroscopy (micro-SORS), which has been applied in the field of CH for almost a decade [4], allows access to the molecular characterization of pigments through opaque layers. Micro-SORS has been applied to several types of materials in the field of Cultural Heritage such as painting, polychrome sculptures, painted plasters, street art mural paintings and decorated porcelain cards [5] but has never been applied to archives-type materials such as closed letters, and or glued pages. Associated with mapping possibilities, the technique allows for both the materials characterization and its spatial distribution to be done at the same time, with the same instrument, rather than relying on two different techniques [6]. With this study, we used micro-SORS for reconstructing hidden images or letters in several case studies representative of what can be found in archives and libraries. Case studies include a 1847 patented playing cards for which the unknown figure is glued to a page, unopened letters and naval notebooks from the 1600s containing blackboard-like pages with friable chalk writings covered by protective paper pages. Here, we will present the results obtained on these objects as well as the limitations that were encountered.

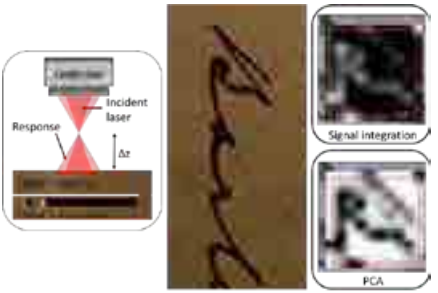

Figure 1. *Schematic representation of the micro-SORS undertaken on a section of a closed letter (red dotted square) and mapping results obtained with signal integration and PCA.*

[1] Bell, I. M., et al. (1997). "Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD)." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 53(12): 2159-2179.
[2] Pause, R., et al. (2021). "Identification of Pre-1950 Synthetic Organic Pigments in Artists' Paints. A Non-Invasive Approach Using Handheld Raman Spectroscopy." Heritage 4(3): 1348-1365.
[3] Bersani, D. and P. P. Lottici (2010). "Applications of Raman spectroscopy to gemology." Analytical and Bioanalytical Chemistry 397(7): 2631-2646.
[4] Conti, C., et al. (2015). "Noninvasive Analysis of Thin Turbid Layers Using Microscale Spatially Offset Raman Spectroscopy." Analytical Chemistry 87(11): 5810-5815.
[5] Conti, C. et al (2020) "Advances in Raman spectroscopy for the non-destructive subsurface analysis of artworks: Micro-SORS." Journal of Cultural Heritage 43: 319-328.
[6] Botteon, A. et al. (2017) "Discovering hidden painted images: subsurface imaging using microscale spatially offset Raman spectroscopy." Analytical chemistry 89(1): 792-798.

Chemical and sensory analysis of a perfume flask with gas chromatography-olfactometry

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Typically, museum objects are appreciated visually, while little or no attention is paid to their smell. However, since the historical value or cultural significance may lie in the olfactory information associated with those objects, it is intriguing that only limited research has so far been conducted to explore the relationship between the volatile organic compounds (VOCs) emitted by objects and their perceived smell. [1]

The aim of the Slovenian/Polish ODOTHEKA project is to explore the research pipeline enabling the collection, characterisation, reproduction, archiving and subsequent delivery of smells to audiences. [2]

Our work so far focused on the first steps in this pipeline: collection and characterisation of smells, focusing on the case study of volatiles emitted by an early 20th-Century perfume flask. The emitted VOCs were collected in passive and active mode using SPME fibres (DVB/CARB/PDMS) and sorbent tubes (Tenax® TA), and then analysed by gas chromatography hyphenated to mass spectrometric and olfactometric detection. [3] This technique integrates chemical and sensory characterisation, which allows for the identification of the main chemical compounds as well as the main odour-active ones. Odour-active compounds are all those volatiles with an odour perceptible by the human nose, therefore characterised by an odour detection threshold - i.e. the lowest concentration perceptible by the human sense of smell. In our analysis these compounds are detected by sensory analysis and identified with mass spectrometer.

The results demonstrate the suitability of the sampling method, coupled with chromatographic, mass spectrometric and olfactory analysis to obtain the olfactory profile of the sample. This output combines the compounds identified in the chromatogram and odour-active volatiles, allowing to determine which molecules are responsible for the overall smell of the object. Once this was known, risk assessment for the VOCs contained in the aroma using Oddy testing was performed. The results for the perfume flask smell have also been compared with similar risk assessments for some of the commercially available aromas for use in exhibitions.

[1] C. B. Jacobo, “Smell of Heritage”, Doctoral thesis, 2020.
[2] https://hslab.fkkt.uni-lj.si/2021/09/24/odotheka-exploring-and-archiving-heritage-smells/.
[3] C. M. Delahunty, G. Eyres, and J. P. Dufour, “Gas chromatography-olfactometry”, *J. Sep. Sci.*, 2006, vol. 29, no. 14, pp. 2107–2125.

Multi-technical approach for the study of the conservation state of mural paintings of Navalcarnero (Spain)

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A multi-analytical investigation was carried out to evaluate the conservation state of contemporary murals and trompe l'oeils painted on the facades of buildings in Navalcarnero by Alberto Pirrongelli, considered the greatest Spanish representative of this pictorial technique, (Madrid, Spain). Portable X-ray fluorescence, Fourier Transform Infrared and Raman spectroscopies were applied for *in situ* analysis of the original materials and the secondary products generated over the years. Successively, in order to clarify some aspects of the obtained results, analyses with benchtop instruments (µ-EDXRF, Raman spectroscopy and ion chromatography, IC) were performed on selected samples.

The results revealed that the preparation layer of all the wall paintings was a mixture of rutile (TiO_2), calcium carbonate ($CaCO_3$) and an organic polymeric binder, probably polystyrene, mixed with a lower amount of dolomite ($CaMg(CO_3)_2$). The pigments identified were phthalocyanine green and blue, barium sulphate (the inorganic part of the lakes), arylamide yellow, hematite, carbon black, ultramarine blue and naphthol red. The state of conservation of the murals was different as a function of the local environment, but three remarkable pathologies were observed The most dangerous damage was the efflorescences formed in a mural that decorate a fountain. The infiltration of water charged with natural and anthropogenic (agriculture activities and a nearby highway) source ions into the mural gave rise to the formation of salts rich in Na^+, K^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} (IC) under the pigment layer and the consequent swelling and loss of the paint layer. The efflorescences were characterized by Raman spectroscopy as gypsum ($CaSO_4{\cdot}2H_2O$), thenardite (Na_2SO_4), potassium nitrate (KNO_3) and sodium carbonate (Na_2CO_3). Another mural showed a *craquelure* on the pictorial film in some black areas, possibly caused by the contraction during the drying process of the polymers or an excess of paint used [1]. In addition, one of the most evident degradation process was an ochre patina composed of iron(III) oxide (hematite) and an iron(III) oxi-hydroxide that appeared in another mural, where the persistent dripping of water through a steel grating placed in the mural caused lixiviation of iron. The patina covered an extensive area of the mural, resulting in an important chromatic variation from the green colour pigment to the ochre colour currently observed

[1] T. Rivas, E. M. Alonso-Villara, J. S. Pozo-Antonio, The European Physical Journal Plus volume 137, 2022, 1257

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Non-destructive and on-site X-ray fluorescence analysis of national treasure glass beads from Okinoshima Island, Japan

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On Okinoshima Island in Japan, sacred rituals were held to pray for safe ocean voyages and national peace from the 4th to the 9th centuries AD. Approximately 80,000 voting offerings unearthed from the island have been collectively designated as national treasures in Japan. Of the 23 ritual sites on the island, 10 produced a large number of glass beads, totaling over 4,000 pieces. This study aims to clarify where and how the glass beads unearthed from Okinoshima Island were produced scientifically, a non-destructive and on-site X-ray fluorescence analysis (XRF) of the glass beads from the island were conducted.

In this study, two portable XRF analyzers (OURSTEX 100FA) were brought to Munakata Taisha and used for chemical composition analysis of a total of 303 glass beads [1]. Except for 13 pieces said to be derived from the Okinoshima island, all other pieces were unearthed from the following 10 ritual sites on the island: sites No.16, 17, 18, 19, and 21 dated to the late 4th-5th century, and sites No. 4, 6, 7, 8, and 23 to the late 5th-7th century. All beads were monochromatic and colored blue, yellow, yellowish green, red, and orange. The oxide concentrations of 22 elements (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Sn, Sb, Ba, and Pb) were quantified.

Based on chemical compositional features, the glass beads were classified into the following composition types: alumina soda-lime glass (m-Na-Al: Na_2O-Al_2O_3-CaO-SiO_2), soda-lime glass (m-Na-Ca, v-Na-Ca: Na_2O-CaO-SiO_2), and potash glass (m-K-Al, m-K-Ca-Al: K_2O-SiO_2). Because these glass types could be associated with different production regions including the Mediterranean region, Western Asia, Central Asia, South Asia, Southeast Asia, and China, the glass beads from Okinoshima Island were thought to be primarily produced in these regions. Colorants of glass were successfully identified as below: blue by Co^{2+} or Cu^{2+}, opaque yellow by lead tin oxide ($PbSnO_3$), yellowish green by $PbSnO_3$ with Cu^{2+}, red by metallic Cu nano colloid, and orange by micro crystal of cuprite Cu_2O. A number of ancient glass beads with similar compositional features have been found broadly along the Japanese archipelago [2].

In conclusion, the use of portable XRF analyzers revealed that a number of colorful beads with various international origins were dedicated to ancient rituals on the sacred island of Okinoshima over a thousand years ago.

[1] Abe, Y., et al., Journal of Archaeological Science: Reports, 40, 2021, 103195.
[2] Oga, K., Tamura, T., *Journal of Indian Ocean Archaeology* 9, 2013, 35–65.

Portable non-destructive techniques applied to the study of the deterioration pattern of partially submerged heritage in reservoirs.

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The DAMAGE project aims to study the deterioration pattern suffered by the built cultural heritage that is partially submerged in freshwater reservoirs. Due to increasing droughts, this heritage is subjected to annual cycles of emersion and submersion, which are believed to damage the structures in a different and more detrimental way than they would in permanent aerial or subaquatic conditions, as the reservoir shore areas are highly dynamic [1]. For this reason, two real case studies of cultural heritage in Spanish reservoirs have been selected where the state of deterioration of the built heritage is being evaluated by applying in-situ a wide variety of portable non-destructive techniques. The results are being compared with those obtained in laboratory tests carried out on similar stone materials obtained from nearby quarries.

Some of the studied properties and the techniques applied are flaw detection by ultrasonic pulse velocity, Leeb rebound hardness, color by spectrophotometry, moisture content by electrical conductivity and capacitance measurements, electrical resistivity tomography, infrared thermography, optical surface microroughness, hydrophilicity by mobile contact angle (water drop/substrate) analyzer and portable digital microscopy. Minimal sampling has been carried out to study the petrological characteristics of the building stones, and chemical analysis of the main materials has been done by powder X-Ray Diffraction (XRD) and portable spectroscopy techniques such as FTIR-ATR, FTIR-Reflection, X-Ray Fluorescence (XRF), and Raman spectroscopy, in addition to LIBS spectroscopy, which is planned to be applied soon.

The joint analysis of all these results allows us to combine and compare hundreds of data to have a complete view of the state of decay of the case studies and to evaluate the information that each technique can provide. By the end of the project and the doctoral thesis involved, the aim is to develop a protocol of analysis and procedures that could be applied to other cases of cultural heritage in reservoirs, which are very common in Spain as it is one of the countries with the largest number of reservoirs [2]. Both the protocol and the doctoral thesis will include recommendations on the techniques that have provided greater value so that other conservation professionals can use them as a reference.

[1] Nicu, I. C., Usmanov, B., Gainullin, I., & Galimova, M. Water (Switzerland), 11(3), 2019.

[2] International Commission of Large Dams (ICOLD): https://www.icold-cigb.org/article/GB/world_register/general_synthesis/number-of-dams-by-country-members. Last access: 17/01/2023.

Research on Near-infrared Spectroscopy and Raman Spectroscopy of Handmade Paper Based on Machine Learning

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Handmade paper is the major carrier and also a widely used restoration material of traditional Chinese books, calligraphies and paintings. In this study, both near-infrared spectroscopy (NIR) and Raman spectroscopy were employed to analyzed 18 types traditional handmade paper samples. The collected spectral data was then processed by 5 different machine learning algorithms: principal component analysis (PCA), support vector machine (SVM), random forest (RF), k-nearest neighbors (KNN), and neural networks. High-accuracy classification and prediction of the handmade paper samples can be achieved by data processing of all the 5 machine learning algorithms with NIR spectral data. However, only PCA combined with linear regression (LR) has high classification and prediction accuracy for Raman spectral data. In order to obtain better machine learning results for Raman data, two novel data preprocessing methods, i.e., cross correlation method (CCM) and two-dimensional correlation method (TDCM) were developed. CCM takes cross correlation between two spectral data of the same category to expand the spectral dimension from 1×N to 1×(2N-1). TDCM includes two-dimensional synchronous correlation method (TDSCM) and two-dimensional asynchronous correlation method (TDACM). TDSCM and TDACM take tensor product between two spectral data and between one spectral data and the Hilbert transformation of the other spectral data of the same category, respectively, to expand the spectral dimension from 1×N to N×N. The results showed that for SVM-LR, KNN and RF models, the R-squared from low to high was basically sorted according to the raw data, baseline removal data, CCM, TDSCM and TDACM processed data. The R-squared for TDACM processed data are nearly approach to 1, which nearly has 100% enhancement of machine learning accuracy for Raman data. However, the CCM and TDCM didn't significantly improve the machine learning accuracy for NIR spectral data. Our results suggest that the machine learning with two-dimensional correlation data preprocessing method can be very useful for the spectroscopic analysis of heritage materials.

Multi-analytical characterization of 19-century bricks and plaster from the Church of Sant Rafael (Barcelona, Spain)

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The Church of Sant Rafael is located in the north of Barcelona (Spain) and is part of the Old Hospital de la Santa Creu which was one of the largest mental hospitals in Europe. This neoclassical church was designed in 1857 by the architect Josep Oriol i Bernadet and built in 1859 by the architects Elies Rogent and Josep Artigas. The main construction materials inside the church are fired bricks covered by a plaster that still preserves some paintings with artistic inscriptions. After the closure of the church the building began a deterioration process until today being affected by the presence of moisture.

Bricks are frequently used in the construction of historic buildings and their durability over time is one of the main requirements as a porous building material. When brick walls are exposed to moisture they become susceptible to weathering processes and damp problems inside the building may appear. The aim of this study is to characterised the original historic fired bricks and plaster of the inner of the Church of Sant Rafael (Barcelona, Spain) in order to assess their susceptibility to deterioration and contribute to the conservation of architectural heritage of the second half of the 19th century.

A multi-analytical approach was carried out to address mineralogical, chemical and physical characterisation of studied materials. Samples were analysed by means of polarized light microscopy (PLM), X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP). Furthermore, Hygric properties were also tested for a better study of the pore system and hydric behaviour of the historic bricks.

Analytical results allowed to distinguish different types of bricks among studied samples. Differences in the hydric behaviour of studied fired bricks were also detected, showing a higher moisture retention capacity in the bricks laid under the tiled floor. Moreover, the results show that the plaster consists of two different layers with different mineralogical and chemical composition.

Going green:

The secret behind a fragile yet remarkable medieval color

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In the last decades, investigations on the manuscripts produced in the scriptoria of three Portuguese monasteries (12th-13th centuries) showed a luxurious palette based on three main colors, lapis lazuli blue, *bottle green*, and red based on vermilion and lac dye [1]. The original *bottle green* was a shiny color, but at present, even though the brightness and the saturation of the deep green have been preserved, the proteinaceous binding media shows extensive chain scission and cross-linking, which is confirmed by the presence of calcium oxalate. The consequences are an extensive loss of paint adhesion to the support. [1,2]. The green color is physically detached and thus lost. Given that green occupies 20% of the entire colored area, it is a critical issue for the preservation of Romanesque Portuguese manuscripts [1,2]. To conduct appropriate conservation treatments, it is fundamental to know the exact structure of the synthetic copper proteinate. So, a set of historically accurate reconstructions was elaborated, and it was found that verdigris, a neutral copper acetate, was necessary to produce the *bottle green* [1,3]. However, by just using verdigris and a protein, the deep glassy green is not achieved, and its infrared spectra did not match those of historical paints [1,2].

In the present work, fourteen treatises/recipe books, from the 9th to the 16th century, were studied and fifty-five recipes dedicated to the making of verdigris paints were collected. This approach allowed us to discover the secret ingredient behind the deep green, missing in the previous databases: an organic yellow described in 70% of the recipes analyzed. The most used organic yellow, present in 72% of the recipes, is saffron (*Crocus sativus*), followed by rue (*Ruta graveolens*) and berries of buckthorn (*Rhamnus* spp.). In these reconstructions, verdigris was dissolved in an acidic solution (vinegar or wine), as described in the recipes, and applied with just the protein binder and, for the first time, with two organic yellows: *Rhamnus spp*. and *Reseda luteola*. Even though these yellows are described in the recipes to a lesser extent, recently they were studied by our research group and their quantum yield of reaction attests to their stability [4]. We will show that, when comparing the *bottle green* reconstructions and the historical paints, the presence of an organic yellow is fundamental to obtaining a deep green. Other characteristics and specificities of the paint that are fundamental to achieving historical accuracy will also be discussed. Finally, we will present the main outcomes of the full characterization of these reconstructions, through synchrotron UV–VIS multi-spectral luminescence, micro infrared spectroscopy, fiber optic reflectance spectroscopy and colorimetry. This methodology will allow us to advance one step further for the preservation of *bottle green* in medieval illuminated manuscripts.

[1] M. J. Melo, R. Araújo, R. Castro, C. Casanova, *Microchemical Journal* 124, 2016, 837-844.
[2] M. J. Melo, P. Nabais, R. Araújo, T. Vitorino, Physical Sciences Reviews 4(8), 2019, 20180017.
[3] J. Buse, V. Otero, M.J. Melo, Heritage 2(2), 2019, 1614-1629.
[4] S. Sharif, P. Nabais, M.J. Melo, F. Pina, M. Conceição Oliveira, Dyes and Pigments 199, 2022, 110051.

Early medieval age glass production techniques evolution : an Inter-laboratory and multi-analytical techniques intercomparison campaign

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One of the most emblematic technical changes occurring in the early Middle Ages particularly in north-western Europe, was certainly the glass industry. The mechanisms that led to this transformation are not yet clear and are a concern for many fields and research groups. To shed light on this change, written documents are scarce and archaeological glass artefacts themselves, their respective elemental and structural fine compositions, are the main and crucial source of information. Thanks to various combinations of analytical techniques available in different institutions studying ancient glass, with different analytical techniques set-ups and methodologies, but now adapted and optimized for the specific constraints of Cultural Heritage artefacts, glass objects are nowadays providing many crucial data to trace the socio-economic history of this proto-industry and understand the evolution of techniques and know-how.

In 2021, a "Studium Consortium Institute for Advanced Studies" funding has been initiated, bringing together three laboratories, respectively from Orléans, Leuven and Liege universities, active in the field of both archaeometry and ancient glass studies [1-5], with the objective to address the key issue of the inter-comparability of results obtained with different combinations of analytical techniques and to propose analytical protocols allowing it.

A large corpus of different historical glass objects namely vessels, tesserae, beads, stained window glass but also sets of certified glass references used to calibrate the different elemental analytical techniques were selected, shared and analyzed during several analysis campaigns, namely, by LA-ICP-MS (Laser Ablation, Inductively Coupled Plasma Mass Spectrometry) in Orléans and by PIXE-PIGE (Particles Induced X-rays Emission and Particles Induced Gamma-rays Emission) in Liège.

In this paper, we will present the results of this intercomparison exercise and will highlight strengths, limitations and complementarities of different combinations of different elemental, structural and isotopic analytical techniques. We will end up by presenting the needs and first steps towards the design and preparation of a new set of adapted calibration glass references to be proposed to all laboratories involved in ancient glasses studies.

[1] N. Schibille, A. Sterrett-Krause, I. C. Freestone, Archaeol Anthropol Sci 9 (6), 2017, 1223–1241.
[2] D. Foy, B. Gratuze, M. Heijmans, J. Roussel-Ode, *J. Glass Stud.* **2017**, *59*, 153–169.
[3] F. Mathis, G. Othmane, O. Vrielynck, H. Calvo del Castillo, G. Chêne, D. Strivay, Nucl. Instr. and Meth. in Phys.Research B,268, (11–12),2010, 2078-2082.
[4] L. Van Wersch, I. Biron, F. Mathis, G. Chêne, and D. Strivay. In *The Saint-Servatius complex in Maastricht. The Vrijthof excavations (1969-1970)* edited by F. Theuws and M. Kars, 316-325., 2017, 316-325.

Searching for a new pozzolanic component for the formulation of compatible preservation mortars

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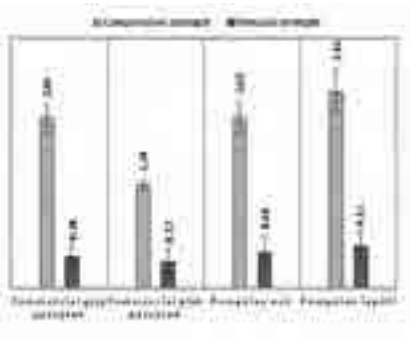
The Vesuvian lapilli and ashes that buried Pompeii in 79 AD were tested as potential natural pozzolanic material for the formulation of conservation mortars. At first, complementary analytical techniques (XRD, FTIR, ICP-MS and IC) were used to evaluate the mineralogy of these volcanic materials.

Initial XRD analyses showed that the mineralogical compositions of both lapilli and ash are very similar to that of the original pozzolanic mortars preserved in the archaeological site. Afterwards, two sets of pozzolanic mortars were prepared using lapilli and ash (particle size of <125µm) as a pozzolanic material and silica sand (p.s. 0.08-2mm) as an aggregate. After curing, the measured compressive and flexural strengths of the lapilli-based mortars were found to be higher than those of the control samples made with commercial pozzolan (see Figure 1). A second set of samples were then prepared by replacing the silica sand with coarse lapilli and ash grains (p.s. 0.5-2mm). Laboratory tests proved the mechanical properties of these mortars were further improved. This effect is probably related to the formation of interfacial transition zones.



The results demonstrate, for the first time, that the volcanic material that buried the archaeological site of Pompeii could be used as a raw material in the formulation of compatible preservation mortars. Further tests are being carried out to optimize the formulation of the mortars and investigate the evolution of their properties with time.

Figure 1: Compressive and flexural strengths of mortar samples prepared by using standard sand as aggregate.

Minero-petrographic characterisation of roman mosaic tiles from Aquileia

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Despite the importance of Romans mosaic of Aquileia, only few works are specifically aimed to their study [1, 2] and there is a strong need to define technology and materials used for their production. In this work, 150 specimens of Roman mosaic tiles (tesserae) are considered. The material under investigation was collected during archaeological field-walking survey of the fields surrounding the center of Aquileia, the capital of the Regio X of the Roman Empire located in NE Italy. Thanks to the large number of selected samples, this research provides a broad study of lithic materials employed for the production of roman mosaic tesserae.
Initial optical investigations (colorimetric and optical microscopy analysis) have enabled to cluster the specimens into 6 groups in relation to their colour. This preliminary characterisation has underlined how burial condition have induced changes in colour of the original material. Afterwards, petrographic characterization was performed in order to assess the nature of the rock types used. Thin sections of specimens were analysed by Microscope Polarized Light (PLM), Scanning Electron Microscopy with EDX probe, in order to investigate the morphology, the mineral phase and the chemical composition of the lithic matrix. Comparison of the results obtained from the analysis of the tesserae with the data present in literature revealed important similarities between the materials. These results confirmed the use of sedimentary rocks as reported in literature [3, 4]: limestone from Trieste surroundings and the Karst area.
To the best of our knowledge, this research represents the widest characterisation analysis of mosaic tesserae from Aquileia ever performed and provides a clear picture of the technology and materials most used by Romans in Aquileia's settlement for the production of mosaics. Moreover, our results constitute a relevant step forward in the understanding of the possible provenience of the raw materials.

[1] M. Bueno, M. Novello, F. Rinaldi, Per un corpus dei mosaici di Aquileia: status quo e prospettive future of L'architettura privata ad Aquileia in età romana, 2011, pp. 195–220
[2] C. Boschetti, S. Dilaria, C. Mazzoli, M. Salvadori, Making Roman Mosaics in Aquileia (I BC – IV AD): Technology, Materials, Style and Workshop Practices of Local Styles or Common Pattern Books in Roman Wall and Mosiacs, 2021, pp. 91-111
[3] J. Bonetto, C. Previato, Trasformazioni del paesaggio e trasformazioni della città: le cave di pietra per Aquileia of Antichità Altoadriatiche LXXVI (2013). Le modificazioni del paesaggio nell'Altoadriatico tra pre-protostoria e altomedioevo, 2013, pp. 141-162
[4] C. Previato, Aquileia. Materiali, forme e sistemi costruttivi dall'età repubblicana alla tarda età imperiale, Padova University Press, 2015

Metalworking influence on the corrosion behaviour of Ag and Ag-coated Cu

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The development of techniques aimed at the understanding of the state of the metallic historical artefacts generally include experiments that are minimally invasive and encompass complementary fields of analysis to provide a complete view of the state of the substrate. Therefore, corrosion science plays an important role in the investigation of metallic artefacts such as silver [1-6]. It addresses the occurrence and progression of corrosion as a function of the particular metalworking methods used, as well as the development of techniques to mitigate corrosion.

In the present work, various surface states were generated on sterling silver dummy coupons as well as silver-plated copper to simulate surface finishing procedures on historical silver artefacts. Coupons were either polished by hand, by a fabric disc on a polishing machine, or submitted to a hammering process in reference to the as-received state. All samples were subjected to various aging protocols (natural aging, TAA test according to NBN EN ISO 4538:1995 and Na_2S immersion test according to NBN EN ISO 8891:1998) [6-7]. The evolution of tarnishing was monitored by colorimetry. The surface condition of the specimens as well as the morphology of the tarnish layers were evaluated by optical microscopy and scanning electron microscopy.

Various surface finishing methods led to marked differences in the tarnishing behaviour. The colorimetric evolution of specimens was monitored. Irrespective of the applied tarnishing procedure, samples that did not receive surface treatment or were hammered showed both accelerated tarnishing. Silver plated copper samples showed tarnishing behaviour that was markedly different from bulk silver samples.

Acknowledgment:
This research is partially funded within the framework of the project PHELETYPIA [8] by the Heritage Science Austria grant program of the Austrian Academy of Sciences.

[1] T. E. Graedel, J. P. Franey, G. J. Gualtieri, G. W. Kammlott, and D. L. Malm, “On the mechanism of silver and copper sulfidation by atmospheric H_2S and OCS”, *Corros. Sci.*, vol. 25, no. 12, pp. 1163–1180, Jan. 1985.
[2] T. E. Graedel, “Corrosion Mechanisms for Silver Exposed to the Atmosphere”, *J. Electrochem. Soc.*, vol. 139, no. 7, pp. 1963–1970, 1992.
[3] G.W. Warren, B. Drouven, and D.W. Price, “Relationships between the pourbaix diagram for Ag-S-H_2O and electrochemical oxidation and reduction of Ag_2S”, *Met. Mater Trans B*, vol. 15, pp. 235–242, 1984.
[4] R. Wiesinger, C. Kleber, and M. Schreiner, “Surface and Interface Analytics as a tool in atmospheric corrosion research”, *Glob. J. Phys. Chem.*, vol. 1, no. 1, pp. 59–78, 2010.

[5] R. Wiesinger, I. Martina, C. Kleber, and M. Schreiner, “Influence of relative humidity and ozone on atmospheric silver corrosion”, *Corros. Sci.*, vol. 77, pp. 69–76, Dec. 2013.

[6] P. Storme, O. Schalm, and R. Wiesinger, “The sulfidation process of sterling silver in different corrosive environments: impact of the process on the surface films formed and consequences for the conservation-restoration community”, *Herit. Sci.*, vol. 3, no. 1, p. 25, Aug. 2015.

[7] O. Schalm *et al.*, “The corrosion process of sterling silver exposed to a Na_2S solution: monitoring and characterizing the complex surface evolution using a multi-analytical approach”, *Appl. Phys. A*, vol. 122, no. 10, p. 903, Oct. 2016.

[8] V. Ljubic Tobisch, A. Artaker, and W. Kautek, “PHELETYPIA,”Project PHELETYPIA “The impact of early photography and electrotyping media on the creation of images and contemporary art" (Heritage 2020-060 PHELETYPIA) by the Heritage Science Austria grant program of the Austrian Academy of Sciences. 2023.

Portable non-destructive techniques applied to the study of the deterioration pattern of partially submerged heritage in reservoirs.

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The DAMAGE project aims to study the deterioration pattern suffered by the built cultural heritage that is partially submerged in freshwater reservoirs. Due to increasing droughts, this heritage is subjected to annual cycles of emersion and submersion, which are believed to damage the structures in a different and more detrimental way than they would in permanent aerial or subaquatic conditions, as the reservoir shore areas are highly dynamic [1]. For this reason, two real case studies of cultural heritage in Spanish reservoirs have been selected where the state of deterioration of the built heritage is being evaluated by applying in-situ a wide variety of portable non-destructive techniques. The results are being compared with those obtained in laboratory tests carried out on similar stone materials obtained from nearby quarries.

Some of the studied properties and the techniques applied are flaw detection by ultrasonic pulse velocity, Leeb rebound hardness, color by spectrophotometry, moisture content by electrical conductivity and capacitance measurements, electrical resistivity tomography, infrared thermography, optical surface microroughness, hydrophilicity by mobile contact angle (water drop/substrate) analyzer and portable digital microscopy. Minimal sampling has been carried out to study the petrological characteristics of the building stones, and chemical analysis of the main materials has been done by powder X-Ray Diffraction (XRD) and portable spectroscopy techniques such as FTIR-ATR, FTIR-Reflection, X-Ray Fluorescence (XRF), and Raman spectroscopy, in addition to LIBS spectroscopy, which is planned to be applied soon.

The joint analysis of all these results allows us to combine and compare hundreds of data to have a complete view of the state of decay of the case studies and to evaluate the information that each technique can provide. By the end of the project and the doctoral thesis involved, the aim is to develop a protocol of analysis and procedures that could be applied to other cases of cultural heritage in reservoirs, which are very common in Spain as it is one of the countries with the largest number of reservoirs [2]. Both the protocol and the doctoral thesis will include recommendations on the techniques that have provided greater value so that other conservation professionals can use them as a reference.

[1] Nicu, I. C., Usmanov, B., Gainullin, I., & Galimova, M. Water (Switzerland), 11(3), 2019.

[2] International Commission of Large Dams (ICOLD): https://www.icold-cigb.org/article/GB/world_register/general_synthesis/number-of-dams-by-country-members. Last access: 17/01/2023.

The 'Madonna delle Grazie' of Andrea del Sarto/Giovanni Antonio Sogliani: a multi-analytical study

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Recent restoration works carried out on the exquisite painting '*The Virgin on the throne with Child, St. John the Baptist, St. Francis, St. Bartholomew and St. Jerome*' (known as '*Madonna delle Grazie*') offered the occasion for a multi-analytical study of this XVI Century masterpiece. In his *Lives of the Artists of the Italian Renaissance*, Vasari informs us that the panel (2.35 m x1.94 m) was committed by the St. Francis's friars of Pisa to Andrea del Sarto (Andrea d'Agnolo, Florence 1486 – Florence 1530). Because of the improvise death of the artist, during the 1530 plague in Florence, the painting was concluded only eight years later by Giovanni Antonio Sogliani (Florence, 1492 – Florence, 1544).

This peculiar four-handed experience leaves some questions on the paternity of the different elements of the composition. Among art historians there is some consensus on the hypothesis that almost all the painted surfaces might be attributed to Giovanni Antonio Sogliani, while the composition seems to reflect the Andrea del Sarto concepts; so far, some compositional elements might be realized also by Giovanni Antonio Sogliani following the imprint of Andrea.

To shed some light on this issue, a new multispectral approach, based on the Interesting Feature Finding (IFF) method, was used to study the art composition; moreover, Energy Dispersive-X-Ray Fluorescence (ED-XRF) and micro-Raman analyses were also performed to characterize the pigments used by the painter(s) in different parts of the panel.

The multispectral analysis revealed the presence of important differences between the underdrawings (reasonably attributable to Andrea del Sarto) and the painted surface, especially for what concerns the background and the figure of St. Francis. However, the XRF and micro-Raman results does not exclude the possibility that some part of the painting would have been realized by Andrea. The IFF method also evidenced in the underdrawings the outline of a small figure, whose interpretation (not straightforward) will be discussed in the presentation.

Modeling water transport phenomena and induced reactivity relevant to oil painting deterioration

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This work is part of the GoGreen project (2022-2026), a Horizon Europe project aiming to develop clear and reliable parameters for environmentally friendly and healthy conservation methodologies for cultural heritage.

A tailored well-researched damage function does not exist for oil paintings, in contrast to other cultural heritage materials like copper and silver. For paintings, water exposure is an important factor, because water absorbed in oil paintings due to environmental humidity or conservation treatments can result in undesirable changes in the materials in an oil painting. Therefore, we aim to develop a damage function for oil paintings to aid decisions on cleaning strategies and designing acceptable indoor climate conditions.

Particularly, our focus is on moisture transport inside a stratified oil painting coupled to induced chemical reactivity. The presence of water can accelerate change inside an oil painting by increasing oil binder hydrolysis, triggering metal soap formation, facilitating ionic reactions, or altering the mechanical properties of layers. As a first step towards this linked computational and experimental research, we showcase our extended water transport model based on absorption isotherms and diffusion coefficients, as well as water transport experiments obtained with time- and spatially resolved transmission FTIR imaging spectroscopy.

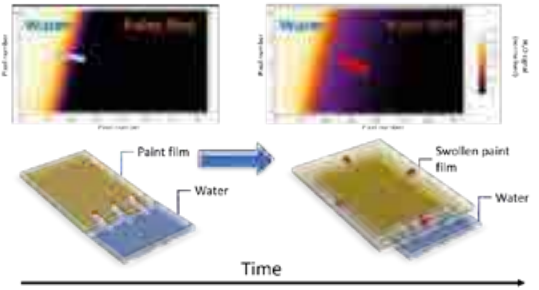

Figure 1. Schematic overview of water-induced swelling of a paint film and a set of spatially-resolved normalized water concentration maps at the paint/water boundary obtained with transmission FTIR imaging spectroscopy.

Revealing unseen evidence of the hand of Masolino, Masaccio and Lippi in the Brancacci Chapel frescoes

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In 2022, an extensive project aimed at analyzing and monitoring the cycle of frescoes in the Brancacci Chapel in Florence began as part of the Collaboration Agreement between SABAP and CNR-ISPC. The frescoes were painted between 1425 and 1427 by Masolino da Panicale and his 21-year-old collaborator Masaccio, and completed by Filippino Lippi about fifty years later. On this unique occasion, the three levels of the cycle were made accessible through an imposing scaffolding, which made it possible not only to admire the painted walls up close, but also to carry out an extensive measurement campaign with transportable instruments.
In this study, we jointly applied two optical imaging techniques, namely laser scanning microprofilometry [1] and reflectance imaging spectroscopy [2], by means of two prototypes developed specifically for in situ measurements. The data obtained through this non-invasive approach allowed us to unveil hidden details that can be traced back to the hand of the different authors, as well as to deepen our knowledge of the painting technique and obtain preliminary information on the pigments used.

The authors wish to thank Opera per Santa Maria del Carmine in Firenze and the Municipality of Firenze in particular to all the staff of the 'Servizio Belle Arti e Fabbrica di palazzo Vecchio' (Resp. Arch. G. Caselli) for valuable and constant support during the organization and execution of the whole diagnostic campaign. The conservation activities, study and research, were made possible thanks to the finance of Friends of Florence and Jay Pritzker Foundation.

[1] Striova, J., Fontana, R., Barucci, M., Felici, A., Marconi, E., Pampaloni, E., ... & Riminesi, C. (2016). Optical devices provide unprecedented insights into the laser cleaning of calcium oxalate layers. Microchemical Journal, 124, 331-337.
[2] Striova, J., Dal Fovo, A., & Fontana, R. (2020). Reflectance imaging spectroscopy in heritage science. La Rivista del Nuovo Cimento, 43(10), 515-566.

Monitoring changes in human activities across the Upper Palaeolithic: a statistical approach for the critical assessment of ancient organic residues through SR-FTIR microscopy

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Residue analysis is one of the most effective ways for directly inferring the technical expertise and adaptability of Palaeolithic human groups. Within its wide range of application, the study of hafting procedures of lithic armatures and the chemical characterisation of the adhesives used for this purpose play a role of particular significance. In this contribution, we present the results of an extensive study conducted on 724 backed pieces from the Epigravettian sequence of Grotta della Cala (Campania, southern Italy), consisting of eight levels related to the evolved and the final phases (evolved phase – layers P, N, O and M; final phases – layers I, L, H and G; available radiocarbon dates: N: 20,826-18,819, M: 18,978-16,863, H: 14,173-13,600, 14,842-14,096, 14,226-13,598, cal BP - 68,3 %). The in-depth analysis of the back of the implements through 3D digital microscopy enabled the identification of dark-coloured residues on 23 of them, which underwent the chemical analysis through Synchrotron Radiation Fourier Transform Infrared (SR-FTIR) microscopy in transmission mode. One to two samples of residue were analysed from each of the selected implements and an average of 20 spectra per sample were collected, for a total of 834 high-resolution spectra. The huge amount of data thus obtained was then processed with a chemometric approach to observe the statistical significance of the results obtained for each sample and highlight potential trends in the stratigraphic sequence. Soil samples from each layer were also analysed by Attenuated Total Reflectance (ATR-) FTIR spectroscopy in triplicate as a negative control, to support the authenticity of our findings. As a result, none of the tested sediment samples contained traces of proteins, adipocere and vegetal substances that we were able to widely identify on the backed pieces analysed. Even though the use of fats and animal glues in the hafting procedures cannot be ruled out, these organic substances could even be related with hunting and other human activities. This is the first extensive study targeted at investigating the occurrence of adhesives on Upper Palaeolithic backed pieces in southern Italy and represents the natural extension of previous works concerning the use of SR-FTIR microscopy for residue analysis [1], with special reference to ancient glues [2].

[1] C. Dominici, C. Stani, M. Rossini, L. Vaccari, Journal of Physics: Conference Series 2204, 2022, 012050.
[2] K. Sano, S. Arrighi, C. Stani, D. Aureli, F. Boschin, I. Fiore, V. Spagnolo, S. Ricci, J. Crezzini, P. Boscato, M. Gala, A. Tagliacozzo, G. Birarda, L. Vaccari, A. Ronchitelli, A. Moroni & S. Benazzi, Nature Ecology and Evolution 3, 2019, 1409-1414.

Electrochemical techniques for patinas and coatings assessment in conservation studies

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Electrochemistry can provide valuable information on metallic artifacts patinas stability and conservation treatments performance. Therefore, the use of electrochemical techniques in multi-analytical studies on the conservation-restoration of outdoor copper statuary alloys has increased over the last two decades. However, despite some recent developments, for reaching their full potential, especially as regards in situ nondestructive testing there is still subject matter to be explored [1-3].

The two case studies included in this communication highlight the usefulness of the non-destructive electrochemical techniques within the framework of conservation studies of copper alloy outdoor monuments.

One case study refers to a 220-year-old bronze monument. Within a multi-analytical approach for the conservation state diagnosis [4], *in situ* measurements of electrochemical potential and resistivity were carried out over representative areas of the surface patinas. The electrochemical test results, in agreement with the other findings, revealed the less protected zones of the statue and contributed to prioritize the required interventions.

The other case study aimed the assessment of conservation treatments developed for outdoor bronze monuments [5]. In this study, the electrochemical impedance spectroscopy (EIS) was used to evaluate the efficacy and the durability of innovative treatments comprising eco-friendly products and procedures, such as organo-silanes coatings, limewater and cuprite deposition. These were applied to copper/bronze (85Cu5Sn5Pb5Zn) substrates with natural and artificial patinas representing urban and marine environments. Electrochemical impedance spectroscopy was carried out before and after weathering, according to the patina type, under natural exposure in a marine environment (C5, Cabo Raso test site) and artificial weathering in UV+sulphate salt spray chambers [6]. Untreated and Incralac® (reference) treated specimens were also evaluated for comparison. The EIS testing results showed that some of the new treatments presented better protective properties (higher and more durable corrosion resistance) than the reference treatment, being a viable eco-friendly option for bronze conservation. EIS is an important tool not only for testing and predicting the corrosion protection performance of conservation treatments applied to copper alloys, but also for understanding the processes involved in their degradation.

[1] P. Letardi, B. Salvadori, M. Galeotti, A. Cagnini, S. Porcinai, A. S. Barbone, A. Sansonetti, Microchemical Journal 125, 2016, 151.
[2] B. R. Barat, B. P. Letardi, E. Cano, Metal 2019: Proceedings of the Interim Meeting of the ICOM-CC Metals Working Group September 2-6, 2019 Neuchâtel, Switzerland, Pulido & Nunes (Eds), 2019, 77.
[3] G. P. Cicileo, M. A. Crespo, B. M. Rosales, Corrosion Science 46, 2004, 929.
[4] M. M. Salta, I. R. Fontinha, Relatório nº313/98 - NQ, LNEC, Lisboa, 1998.
[5] S. Bittner, G. Farron, R. Fontinha, D. Job, E. Joseph, P. Letardi, M. Mach, R. Mazzeo, S. Prati, M. Salta, A. Simon, Conservation Science 2007, J. Twonsend, L. Toniolo, F. Cappitelli (Eds), London, 2008, 40.
[6] I. R. Fontinha, M. M. Salta, Relatório 395/2008-NMM, LNEC, Lisboa, 2008.