Book of Abstracts

InART

6th International Conference on Innovation in Art Research and Technology

4–7 June 2024 – Oslo, Norway

Book of Abstracts

Edited by

Angeliki Zisi

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Archaeopress Archaeology

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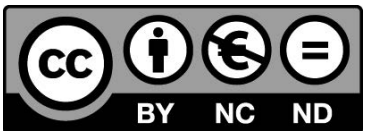

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PRODUCTION BABY

Minnie Minerva

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KEYNOTE SPEAKERS ABSTRACTS

Advanced and intelligent aerial and space-born techniques to safeguard archaeological sites against man-made and natural threats

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Keywords: Cultural property protection, Illicit trafficking, Climate change

Abstract

To safeguard cultural heritage for future generations it is essential to recognize the significant threats from both the climate change and the human activities it faces. Cultural heritage assets, often exposed to direct anthropogenic threats and natural elements, are indeed increasingly endangered. This heightened exposure, leaves these sites highly susceptible to damage and potential destruction, underscoring the urgent need for protective measures.

Anthropogenic Threats: Archaeological Looting

The discovery of a message stating "*With the trafficking of works of art we support our family*", found in Mafia Boss Matteo Messina Denaro's hideout, after his arrest following 30 years on the run, underlines the deep connection between art trafficking and organized crime [1]. Exact figures for the overall illegal revenue streams, are still debatable, due to the challenges in detecting and monitoring these activities [2]. However, estimates suggest that profits from the illicit trade in antiquities can range anywhere between $225 million to $6 billion annually. Such criminal activities deprive humanity of invaluable archaeological insights and artifacts that are part of our shared heritage [3]. Archaeological looting and trafficking present significant challenges for many EU member states. These challenges include protecting widely dispersed and remote heritage sites with only limited resources and funding. First recognized at an international level in 1954 by The Hague Convention [4], the gravity of cultural property crimes has since been emphasized by UNESCO in 1970 [5] and 2001 [6], by UN in 2000 [7] and by the Council of Europe in 2017 [8]. The UN Security Council, views such trafficking as a threat to global peace, infringing on the right to enjoy cultural heritage. It also challenges the 2030 SDG, especially 16 [9] and 11.4 [10]. To combat this phenomenon, a comprehensive approach involving global cooperation at all levels, is essential to protect and preserve the shared heritage. Remote sensing exploiting satellite technologies and aerial platforms has shown great potential for analysing archaeological looting, thanks to the increasingly higher resolution of the sensors, the faster temporal revisiting time and the development of smart and agile aerial vehicles [11]. While earth observations cannot directly prevent illegal activities on the ground, they play a crucial role in identifying new looted areas that may be unknown to local stakeholders, thus raising awareness about potential illegal trafficking and increasing

local ability to introduce new site-level protections in vulnerable locations. Moreover, in recent years, Artificial Intelligence (AI) and Machine Learning (ML) have been increasingly applied across various research domains, including Earth Observations. These technologies are also being adopted by archaeologists for analysing a diverse array of data types, such as geospatial, material cultural, textual, natural and artistic data. Thanks to their capabilities in pattern recognition within satellite imagery for detecting looting and their ability to quickly identify and classify archaeological features and objects, AI and ML have become powerful tools in the fight against illicit archaeological excavations.

Climate Change Threats: Rising Sea Temperatures and Uncontrolled Growth of Seagrass Meadows

Discussions explicitly linking cultural heritage with climate change, first emerged in the literature in the 1990s and have progressively become a focal point [12]. The impact of climate change on cultural heritage is expected to be dynamic and multifaceted. As evidenced by gradual shifts in temperature, precipitation, atmospheric moisture, wind strength, sea level rise and the frequency of extreme events, climate change is already noticeably affecting cultural heritage assets, as recent reviews have highlighted [13]. The UNESCO World Heritage Site List catalogues a total of 1,199 sites (May 2024), with 132 of these being coastal or underwater, comprising approximately 10% of the overall sites. Two of the most significant consequences of climate change are the rising sea level and sea temperature, which have evolved over recent decades, posing a threat to all coastal and underwater cultural heritage sites. One of the effects of rising sea temperatures is the seagrass growth. Seagrass, which is highly sensitive to environmental changes, particularly temperature, may experience enhanced photosynthetic activity and accelerated growth within certain temperature ranges. This can lead to shifts in its distribution, as species may expand into areas that were previously too cold, potentially resulting in an 'uncontrolled' growth in new regions. Furthermore, *Posidonia Oceanica*, a common type of seagrass in the Mediterranean, plays a complex role in underwater archaeological sites. It helps protecting and stabilizing artifacts by anchoring them to the seabed against currents and erosion. However, it can also obscure and entangle ruins, making exploration and preservation efforts more challenging. This dual role further highlights the intricate interactions between marine biology and cultural heritage preservation under ever-changing climatic conditions. Multispectral and hyperspectral sensors can efficiently monitor seagrass growth, serving as powerful means for managing heritage assets over large areas and extended time periods [14]. Although the depth at which the underwater archaeological remains are located, still plays a major role for data capturing and analysis, processing data across different wavelengths of light and applying a series of remote sensing indices, can help improving mapping the underwater ecosystem in proximity of archaeological submerged sites and, therefore, enhance the management and preservation strategies.

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Sustainable management of collection environments

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Keywords: Sustainability, Climate, Risk, Preventive conservation, Standards

Abstract

Sustainable management of indoor environments for art collections has become a top priority for cultural heritage institutions worldwide. The interest in changing strategies for controlling museum climates is, on the one hand, driven by an increasing cost of energy and budget cuts and, on the other, by the national or pan-national strategies of sustainable development. There is a growing expectation that museums will operate according to environmental standards, demonstrating a commitment to respecting the environment and preserving resources for future generations. As stated in the 2021 Joint Commitment for Climate Action in Cultural Heritage by IIC, ICCROM and ICOM-CC, *'We recognize that the climate crisis represents one of the greatest threats to that heritage in a world with depleting natural resources, growing inequality and social injustice. In response to these challenges, it is incumbent on all of us to adapt, innovate and pioneer change.'* Since the mid-1970s, many museums, galleries, archives, and libraries have regarded a narrow set of environmental parameters – temperature of 20°C ± 2°C and relative humidity of 50% ± 3% – as providing optimum conditions for collection preservation. Although never scientifically proved as necessary, these ranges have become a de facto standard and regarded as 'best practice' for appropriate collection care. Achieving such a narrow target range is difficult for many collecting institutions, especially in historic buildings and in non-temperate climates. Moreover, tight control of temperature and humidity is dependent on continued use of HVAC systems, requiring access to reliable and relatively low-cost energy sources, a situation that can no longer be taken for granted. Saving energy and reducing costs of operations can be achieved by measures, such as sealing the building structure, improving insulation to reduce heat gain/loss and optimizing ventilation rates. However, interventions on the building are not always possible and it has been demonstrated that relaxing the parameters of temperature and humidity, also produces a considerable reduction in energy consumption. As a result, many museums, galleries, archives and libraries, are now reconsidering their specifications for collection environments. While some have already accepted a broader climatic range, there is still a reluctance in the heritage field to adopt a less stringent approach to display and storage environmental conditions. From recent studies by the Managing Collection Environments Initiative (MCE) of the Getty Conservation Institute, major obstacles in developing sustainable strategies for environmental management in museums include the following points:

Lack of evidence-based risk analysis of climate-induced damage of collections

Understanding the mechanical properties of heritage materials and how they respond to changes in environmental conditions, is fundamental to establishing acceptable ranges of temperature and humidity for art objects. It also requires shifting attention from the most sensitive to less sensitive objects, those that are more common and more representative of the museum collection. The

sustainable approach is to critically assess the behavior of mixed collections, while individually managing risk for the small subset of high-risk objects.

Lack of expertise and case-studies on energy use for managing sustainably the collection environment

The process of optimizing the operation of climate control systems in museum buildings, is hindered by a lack of knowledge on the potential gains associated with implementing more efficient climate control strategies. As a result, collection care staff tends to focus primarily on the current safety of art objects, without considering if the implemented environmental management strategy is sustainable. This problem can be addressed through cooperation between facilities and collection care staff. An effective approach would involve the pairing of a comprehensive analysis of the economic and energy consequences of a more sustainable climatic control strategy in the museum buildings, with the use of effective object monitoring techniques, to ensure the safety of collections during the subsequent implementation of this strategy.

Lack of cost-benefit analysis between collection risk and resource allocation

Cost analysis of risk mitigation for museum collections is needed to identify the intersection where environmental conditions represent an acceptable level of risk to the entire collection, while achieving the energy and cost savings necessary for more sustainable operations. It is critical for conservation science to address these barriers in order to re-define museum operations and provide tools for museum staff to support their decision-making process. During the presentation, I will discuss studies conducted at the Getty Conservation Institute, which focus on the analysis of safe (from a material standpoint) temperature and relative humidity ranges for mixed museum collections and methods for monitoring climate-induced micro-damage on museum objects. This ongoing research provides a strong scientific background for defining sustainable control of collection environments in museums. However, the development of new preventive conservation strategies for collections, requires not only reliable scientific data on damage mechanisms, but also a practical assessment of the broader risks associated with the implementation or non-implementation of these strategies. It can be demonstrated that, to be effective, the decision-making process must be well organized and the roles and responsibilities of the participants must be clear. Stakeholders must understand and agree on the overarching goals of the institution and have access to the knowledge, expertise and tools to assess the risks and benefits of individual decisions that are part of the institutional strategy.

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Building bridges: integrating conservation and conservation science

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Keywords: Conservation science, Conservation, Heritage science, Analytical methodology, Cooperation

Abstract

The words of Dr. H.J. Plenderleith –who in 1924 was appointed at the Department of Scientific and Industrial Research at the British Museum– encapsulate the essence of this presentation: as one of the pioneers in building bridges between conservation and conservation science [1]:

> '*It was a great privilege to be part of the British Museum. As the laboratory was within the precincts, I had direct access to the national library... Also my colleagues in the Museum were all leading world authorities in their own fields of study, and it was always possible to consult directly on scholarly matters and, with their help, to have access to objects either in the exhibition rooms or in store for comparative purposes.*
>
> *It emerged in time that I could reciprocate their help in a number of ways that had never been anticipated. For example:*
>
> (1) *By making for them simple chemical analyses of materials.*
> (2) *By providing technical description of specimens from excavations useful in their publications.*
> (3) *By preparing objects for exhibitions.*
> (4) *By drawing attention to artifacts on exhibitions or in storage that seemed to require laboratory treatment.*
> (5) *By providing evidence of age, or wear, or by pointing out artificial patinas, etc. not to mention the more mundane matters related to technical correspondence, a time-consuming routine in all large museums.*'

Dr. Plenderleith's words provide both a theoretical framework to think about the interactions between all the disciplines involved in conservation, as well as a practical desideratum towards a more holistic and well-grounded approach in conservation. In this talk I will briefly address the historical underpinnings of the relationship between conservation and conservation science and I will focus on specific contemporary cases, which show the importance of continuously building interdisciplinary and intradisciplinary bridges.

As it is known, conservation encompasses a wide-ranging area focused on preserving Cultural Heritage, including both movable and immovable objects. Initially, conservation was entrusted to unqualified practitioners, who experimented and employed undisclosed formulas for the restoration of artworks. Conservation's significance and professionalization grew with the scientific advancement in this field. Modern conservation practices trace their origin back to 1888 in Germany, with the establishment of

the Chemical Laboratory at the Berlin Museums, at present named after its first director, Dr. Friedrich W. Rathgen. The Society for Rational Painting methods was founded in Munich in 1880, which in 1902 became part of the Technical University of Munich, as a Research Institute and Information Office for Painting Techniques; the Doerner Institute, as well as the National Analysis and Research Institute for Colour Technology, were founded in 1937. In the United Kingdom, the foundation of conservation on a scientific basis emerged shortly after World War I. Dr. Scott was called upon to provide scientific support to the existing restorers at the British Museum. They faced challenges related to degradation, stemming from storing numerous objects in the underground conditions during World War II. To address this urgent issue, a laboratory was established in 1920, initially intended to operate for three years. However, due to the substantial workload and needs, the laboratory's tenure was extended indefinitely, persisting to this day. In the United States, Edward Forbes, the Director of the Fogg Art Museum at Harvard University, established a research department in 1925. It was run by George L. Stout and John Gettens with the aim of examining painting materials, their production process and preservation methods [1,2]. In the same line, in 1898 the first international conference on the preservation of manuscripts was held in Saint Gall, Switzerland. This was a pioneering cooperation employing an interdisciplinary approach, which brought together archivists, conservators and chemists with a common goal: the preservation of archival heritage. During the war period, this international cooperation ceased and the topics discussed in the conference, were forgotten. After the war, a large amount of archival heritage was damaged and entrusted to craftsmen for repair. It was not until the mid-late 20th century when the field of paper conservation regained academic status, even though modern scientific and technical issues related to paper conservation had already been discussed at the Saint Gall conference many years before [3].

Working in tight collaboration with other disciplines is also at the core of each profession. ICCROM and ICOM-CC's definitions of Heritage Science and Conservation profession [4,5], specify that the conservator must work in the Heritage Science field as part of an interdisciplinary team where humanities, science and engineering must co-operate. The work process should be based on the scientific methodology, which involves having a clear goal, contextualizing the object and problem, formulating the questions scientifically and precisely, analyzing data, interpreting results, formulating hypotheses and drawing conclusions based on the original goal and contextualization, the latter taking into consideration historical and archival sources. Therefore, it is essential not only to analyze the constituent materials of the artworks, but to also answer the formulated questions in a humanities context. This often leads to a subsequent phase where questions are refined and different scientific analytical techniques used and/or developed. During the initial phase of the scientific methodology, non-invasive techniques are typically favored. However, in certain cases, where the original research objective necessitates it and information cannot be obtained by other means, micro-sampling may be required already from the first phase, whilst more than one analytical method can be performed. Effective communication between the conservator and the scientist is crucial when selecting the analytical methods, sample size, sample locations and when discussing results. Additionally, documenting the sample sites is essential for ensuring accuracy and reproducibility in the analytical process.

Since the late 19th century, the field of conservation has evolved significantly, marked by the integration of new working models and analytical technologies. This evolution has fostered a close intertwining of conservation with conservation science. Art historians are increasingly integrating insights derived from scientific analysis, into their research. Collaboration between curators and scientists has also become more common in the development of exhibitions and publications. However, despite these advancements, there still exist gray areas between the fields of science and humanities, which require

refinement. This talk will discuss contemporary examples of collaborative conservation, showing methods, processes, outcomes, as well as suggestions on how to improve collaboration. The main goal is to show that embracing a collaborative, team-oriented method, is crucial for achieving success in scientific investigations within this field.

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ORAL ABSTRACTS

Oral Session 1 - Applications of Artificial Intelligence, 3D documentation and Virtual Reality

Tracing forgeries in paintings with attribution markers and artificial intelligence

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Keywords: Artificial intelligence, Authenticity of paintings, Attribution markers, Machine learning

Abstract

Detecting forgeries in paintings can be extremely challenging. There are two main approaches to this task. The traditional method, which dates back to the 17th century, relies on the opinion of a historian or art expert, which by its nature is highly subjective and may not meet the requirements of modern forgery detection methods. The second approach integrates several rigorous physical and chemical examination methods and is a consequence of the scientific discoveries and technological developments of the early 20th century. It has made the assessment of authenticity more objective. However, it has also drastically increased the amount of information available to art experts to consider in the authentication process, putting additional pressure on them. Based on more than 60 authenticity tests [1], a three-stage analysis protocol and authenticity markers were defined. A marker will be understood here as a brief summary of an individual examination procedure carried out within the protocol. Using the authenticity markers specific to the painting in question and the information from previous tests, the expert should be able to determine whether the painting is genuine. However, due to the large amount of data involved, it may not be possible to draw definitive conclusions based on all markers. Machine learning algorithms will be, therefore, used to summarise the results and assist the expert's decision-making process. These algorithms are rooted in computational statistics and can effectively generalize large amounts of data. In particular, decision trees will be used to assess new paintings based on the data from previous authenticity tests. We will present the results of the application of the proposed analytical protocol for the evaluation of the painting attributed to Jan Fyt, one of Antwerp's

most famous Baroque painters, and the analysis of some works attributed to Artur Grottger, a well-known Polish painter of the 19th century. The former was donated to the National Museum in Wrocław (Poland) by a privet collector, making it necessary to analyze its authenticity. The attribution of the other works to Grotger has been disputed since his works are often copied by forgers, sometimes with forged signatures.

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Fusing 3D imaging modalities for the internal and external investigation of multi-material museum objects

[1,2]F. Bossema, [2,3,4]P.J.C. van Laar, [5]K. Meechan, [5]D. O'Flynn, [5]J. Dyer, [2]T. van Leeuwen, [1]S. Meijer, [6,7]E. Hermens, [2,8]K.J. Batenburg

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Keywords: Computed Tomography, Surface scanning, Fusion of 3D imaging modalities, Multi-material objects

Abstract

Several 3D imaging methods (e.g. structured light scanning, photogrammetry) image the outside of the object and have been used to record archaeological and museum objects. X-ray Computed Tomography (CT) on the other hand, captures the interior in 3D and can reveal valuable information about the current state of the object and possible restoration treatments and contribute to unravelling the production process and attribution of objects. A reconstructed CT volume is often represented as a stack of 2D slices, but for art objects, a 3D representation can be more intuitive and informative. Combining various non-invasive 3D imaging techniques is a promising and powerful research tool for object-based investigation, as well as digitization of objects. Overlaying the CT visualizations with a structured light surface scan, which reflects the real colour and texture of the outer surface, takes, therefore, the impact

of visualizations to a higher level. There are several software solutions for 3D visualizations, but there is yet no standard method tailored to cultural heritage. Using the open access software Blender, we provide the first step towards interactive visualization of multiple 3D imaging techniques, by offering software that visualizes and registers surface scans and CT scans [1]. This workflow has been developed and designed in a collaboration between the Center for Mathematics & Computer Science (CWI), the Rijksmuseum and the British Museum. Besides inspection and investigation purposes, these methods can be used for digitization to conserve information about the current state of the object for future generations, as well as for outreach within museums. The interdisciplinary research team consists of (technical) art historians, X-ray imaging specialists, computer scientists, conservators and curators. Our main results are firstly, the development of a workflow to collect 3D CT and surface datasets and their combination and visualisation in an interactive environment and secondly, the application of this tool to museum collection objects from the Rijksmuseum and the British Museum.

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A study of enamels: conservation and history of global transfer of technology

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Keywords: Enamels, Deterioration, Global, Technology, Exchange

Abstract

The Early Modern Period, c.1500-1800 CE, saw the further development of enamelling technologies and the political, socio-cultural and economic global networks through which, enamels and technological developments were exchanged [2,6]. However, questions remain as to the nature of such exchanges within and between different production centres and regions of that period. The study of enamels of this period and prevention of their deterioration, due to humidity and pollutants, is, therefore, of great interest for museums and conservators [2,4,5,6]. As part of an ongoing collaborative PhD project

between Nottingham Trent University (NTU), the British Museum (BM) and the Victoria and Albert Museum (V&A), 16th–18th centuries Chinese and European enamelled objects from the V&A and BM collections have been analysed using a multimodal, non-destructive methodology to better understand and identify the compositions, production technologies and deterioration of enamels in museum collections and inform our knowledge of the global transfers of enamelling technologies in the Early Modern Period. The methodology for this project builds upon one developed for the study of Limoges enamels and includes optical coherence tomography (OCT), shortwave-infrared (SWIR, 1000-2500nm) and visible-near infrared (VNIR, 400-850nm) reflectance spectral imaging and X-ray fluorescence (XRF) spectral imaging [4,5]. Spectral imaging datasets were manipulated using a machine learning-based spectral clustering technique, where pixels with similar spectra are grouped [3]. Computational methods were then used to visualise and analyse the spectral imaging data [1,3]. SWIR analyses have enabled the production of "hydration" maps, mapping deterioration in the form of hydrated areas of the enamels [4,5]. Together with these "hydration maps", XRF mapping data processed using the machine learning clustering code, has revealed how particular compositions correlate to areas of enamel deterioration. Clustering of the VNIR reflectance spectral imaging data, similarly demonstrates how spectral information in the visible range may correlate to that of XRF. The data gained from these analyses has enabled further development of this methodology, while demonstrating the benefits of its application for large collections.

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6th International Conference on Innovation in Art Research and Technology
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Oral Session 2 - Applications of Computed Tomography technology

Unlocking van Goyen´s panels: a comprehensive study integrating dendrochronology, X-ray CT and database comparison for technical art historical paintings insights

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Keywords: Jan van Goyen, Painting, Dendrochronology, Technical analysis, Art history

Abstract

This research project focuses on examining eight paintings ascribed to Jan van Goyen (1596-1656), a renowned Dutch landscape painter of the 17th century, housed in the Medeiros e Almeida Museum, Lisbon, Portugal. The project aims to study the artist's working methods, materials and art historical context through technical analysis of the paintings, including pigment, layer, preparation analysis and dendrochronology. Additionally, the project seeks to identify the wooden panels used by van Goyen's workshop, the assembly techniques employed and their dating. Dendrochronological examination of the transverse edges of individual boards composing a panel, is essential in the dendrochronological analysis of panel paintings. To enhance the visibility of the growth rings, cleaning must be carried out along each board. However, the range of cleaning methods can be considered invasive and, therefore, unfavourable as they may leave certain marks on the cross-sections of the panel paintings. X-ray computed tomography is a non-invasive technique for dendrochronological dating of artworks, which emerged in the last decade [1-3]. Although this method has obvious advantages, its limited availability hinders its applicability in art research. Our approach involves using two methods to compare results and identify the advantages and disadvantages of each, concluding on the possibility of improving the application of non-invasive/non-destructive dendrochronological techniques. The results from dendrochronology will be compared with the RKD database results from 38 paintings in German, American, Swedish and Dutch museum collections. A further aim of the project is to create a FAIR (Findable, Accessible, Interoperable and Reusable) database including the results of this research,

accessible freely to the scientific community and to expand this database to include other unstudied works by Jan van Goyen and more artists from international holdings, such as the two paintings from The National Museum in Oslo, in a near future study.

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Offering bearer statuettes from the Minhotep's Tomb: technical comparison between three Ancient Egyptian funerary wooden sculptures

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Keywords: Ancient Egypt, Wooden sculptures, Micro-CT, Minhotep, Asyut

Abstract

As one can observe from the technical literature actually available, the wooden funerary sculpture is a topic of the Ancient Egypt culture still under-researched, in particular from the point of view of the constructing techniques. For a better understanding of these artefacts, our group, first in the framework of a preliminary study [1] and now of a PhD research, is developing a multidisciplinary study based on the technical comparison between wooden sculptures belonging to the same context. The main goal of the research is to underline similarities and differences among different sculptures in terms of construction techniques and materials used, in order to try to suggest some hypotheses about their history, that might be related to specific production areas or production processes. For this purpose, we selected as a starting point for the study, the funerary assemblage from Minhotep's tomb found during the 1908 excavation season in Asyut necropolis by the Italian Archaeological Mission led by Schiaparelli, and which is nowadays preserved in the Museo Egizio in Turin. It includes, among other objects, thirteen wooden sculptures of different typology: three "offering bearer" statuettes, a bakery model, four boat models, two statues of Minhotep, one sculpture of Upuauthemhat, a male figure and a female figure. These sculptures are stylistically dated back to the early 12th Dynasty. We decided to proceed with the study of the objects by grouping them by typology: in this occasion the first results coming from the comparison between the three painted wooden sculptures representing female offering bearers (nº inv. S. 08794; S. 08795; S. 8796), will be presented. The diagnostic plan developed for the research is based on a multi-technique approach, to support the study of the constructing techniques and the identification of the materials [2]. The non-invasive techniques have a great relevance to this diagnostic plan, in light of the importance of these objects. In particular, the micro-X-ray Computed Tomography (CT) allows us to obtain information about the inner characteristics of the sculptures, as is their wooden structure, the thickness of the decoration materials and previous structural interventions, without the need for sampling or disassembling the object. The painting materials have been studied with both non-invasive and micro-invasive techniques, such as X-Ray Fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), with a particular focus on white and black pigments, which turned out to be very interesting. So far, the research outcomes seem to be encouraging since, despite the same provenance context and iconography of the sculptures, some important differences in terms of manufacturing techniques, use of materials and state of preservation, can be highlighted. This study would like to contribute to the correct understanding of finds coming from the same context, but not necessarily produced by the same artisans, researching features of similarity or difference that could support the Egyptological study for a possible reconstruction of the different workshops active in Asyut in the early 12th Dynasty (1940-1876 BCE). Moreover, our hope for the future is to suggest a different approach for the study of the funerary assemblages, which could include a focus on the construction techniques as a means of trying to reconstruct the production process and the purchase method of these objects by the owner of the tomb.

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A scan of worms

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Keywords: X-ray CT, African heritage, Insect damage

Abstract

The conservation department of the Royal Museum for Central Africa oversees the care and preservation of over 250,000 African heritage objects. The objects in this vast collection are made from a wide variety of materials, ranging from wood, plant fibers, leather, fur, to fruits. Consequently, the collection poses a particular attraction to insects, as evidenced by the large number of objects showing external signs of insect damage. At present, the museum's conservation team focuses its attention mostly on monitoring and eliminating active insect infestations. Yet, a lot is still unknown about past infestations in the museum's 125-year history. There is no clear overview neither of which objects in the collection were infested in the past nor which type of insect was responsible for the damage to the collection and the actual (internal) extent of the material loss the insects caused on the objects. Getting answers to these questions would help the conservation team understand the collection better and would inform on the way they handle and preserve the objects under their care. In the context of a research project centered around identification of materials through X-ray tomography, 129 objects from the collection were scanned since early 2021. These scans offer a unique, three-dimensional insight into the objects, visualizing the entire object inside and out. As such, they allow the conservators of the museum to study and understand the objects to a greater extent. Upon analysis of the scans, half of the scanned objects were documented as showing traces of past insect damage. As such, the scans offered a unique opportunity to gain a deeper understanding of the insects that came into contact with the collection objects and the damage they caused. This paper will present five heritage objects and discuss the information their scans revealed. Notably, some scans proved that there was a discrepancy between the signs of damage visible on the outside surface of the objects and the reality of their internal state: for some objects, undiscovered insect presence could be discovered; for others, the few exit holes that could be distinguished visually on the object's surface, belied a much more extensive network of galleries on the inside. In addition, an attempt was made to identify the insect species active in the scanned objects, based on the dimensions of galleries and exit holes, the composition of frass and in one case, on the eggs preserved inside an object. In differentiating between African and European insect species, the conservators could draw preliminary conclusions about the timeframe of the infestation – whether the objects sustained the insect damage in their home of origin or after they were brought to Belgium. This study will also reflect on the challenges of visualizing and quantifying the information found in the scans. In particular, the presence of 'frass' or processed wood fibers left behind in parts of the insect galleries, proved difficult to isolate from the intact wood structure surrounding the galleries. While the difference in structure could be distinguished with the naked eye, software relying on the attenuation coefficients of the scanned material, could not. In order to visualize the entire network of galleries, hollow and filled with frass, deep-learning software was used. This software could be taught to distinguish between the structure of disintegrated wood fibers and intact wood structure, resulting in a more accurate quantification of the amount of the object's material that had been compromised.

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Oral Session 3 - Data management

Addressing contemporary challenges in art and cultural institutions: exploring the role of blockchain technology in the preservation of digital cultural heritage of Asia

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Keywords: Blockchain, Preservation, Digital cultural heritage, Accessibility, Automation

Abstract

One of the major challenges facing museums in the 21st century is not only the management, long-term preservation and control of the exponentially growing amounts of digital and digitised data, but also the increasing use of this data by external audiences. Given the possibilities now offered by technologies, such as AI, there is a need to develop long-term strategies to protect these digital assets from loss, theft, manipulation and falsification. At the same time, it is imperative to establish balance between preservation and control and accessibility that caters both general and specialised audiences. This paper will, therefore, explore the role of blockchain technology in addressing the challenges encountered by museums, specifically in relation to the safeguarding of their collection assets. Additionally, it seeks to investigate the potential of blockchain in optimizing digital asset management practices and its capacity to contribute to the accessibility and financial resilience of institutions.

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M3R – a multimodal representation for storage and open-access dissemination of data of historical manuscripts

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Keywords: Non-invasive analysis, Medieval manuscripts, Web viewer, METS, TEI

Abstract

During the last decades, collaborations have been established between humanities, such as philology, art history and conservation-restoration, on one side, and natural sciences, such as computer vision and material analysis, on the other. The Centre of Image and Material Analysis in Cultural Heritage (CIMA) in Vienna, is the result of such an interdisciplinary co-operation and represents an interuniversity research institution for the investigation of cultural heritage [1,2]. The research projects have so far focused on the documentation by Multi and Hyperspectral Imaging (MSI and HSI) [3,4] and non-invasive material analysis of medieval manuscripts [5,6] from the 8th to the 14th centuries, written in different languages and scripts. The material analyses are carried out applying three complimentary non-invasive methods for elemental and compound specific analyses: X-ray Fluorescence (XRF), Fourier Transform Infrared spectroscopy with External Reflection (ER-FTIR) and Raman spectroscopy. Furthermore, codicological and conservational descriptions, as well as transcriptions and philological editions, could be performed. Within our research projects, two different categories of objects are preferred: on the one hand, bad preserved sources or manuscripts containing overwritten text (palimpsests), which pose particular challenges to the philological investigation, and, on the other, manuscripts with a remarkable colour decoration (initials, miniatures etc.), which are of interest not only from an art historical and philological point of view, but also from an art technological and chemical point as well. The investigations have yielded that mainly iron gall inks with varying contents of copper, lead and zinc, were applied as writing material, whereas well-known pigments, such as vermilion, red lead, orpiment, lapis lazuli, azurite or indigo, were detected in the miniature paintings. Due to the high amount of data (images and spectra of more than 140 manuscripts and charters), a repository for the archiving and dissemination of research data, the project DiTAH [7] was launched in the form of Multi-Modal Manuscript Representations (M3R), in which the various digital artefacts are spatially and logically related. The various data streams and metadata, are spatially and logically related and combined to virtual objects, which are disseminated via a graphical web viewer and technical interfaces. With respect to the long-term preservation and linked open data, special emphasis is put on the use of established and open standards for data and metadata: IIIF, METS, TEI and SKOS. The resulting virtual objects can be disseminated via technical interfaces, but also via an interactive web viewer. Thus, the data available in the repository is made long-term accessible not only for natural sciences and technologies, but also for research and education in the humanities.

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From the excavations to the lab: cutting-edge strategies in archiving archaeometric research at the Austrian Archaeological Institute/OeAW

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Keywords: Archaeometric databases, Open-access data, Digital collections

Abstract

Archaeometry employs natural science methods to analyse artefacts and structures that constitute our past heritage. Like archaeological excavations, the laboratory analyses generate a large amount of processed materials, samples and data. However, minimal effort is dedicated to tracing the journey that archaeological objects undergo from the excavation sites to the laboratory and beyond. This not only significantly impacts the quality of scientific research in terms of data reproducibility and verifiability, but also hinders public access to and engagement in archaeometry. This paper outlines the OeAI's extensive efforts over the past decades to archive every information, material, data and documentation related to its archaeometric research. We view these elements as integral components of our cultural

heritage. The OeAI's archaeometric collection consists of multi-period ceramic thin sections, sherds and test briquettes, clay samples, plasters, mortars, glasses, metals and stones from Austria, Greece, Turkey, Egypt and Italy, as well as associated petrographic, geochemical and mineralogical data. Currently, the OeAI boasts the widest archaeometric collections of Roman marble and pottery from Asia Minor. Large marble data collections are currently at the ÖAI/ÖAW, including the reference corrections of Prof. W. Prochaska, D. Attanasio and L. Moens, allowing us to establish a strong discipline related to the marble provenance studies. A modular database was created for the research data generated in the course of the multi-year project "Fingerprinting White Marbles" to store the collected specific data on archaeological objects in a structured way, on one hand and on the other hand, to be able to keep the analysis data in the respective samples of the objects and the quarries. Using controlled vocabulary, this information is made available to the scientific community through an application. Based on this system, existing data from other marble provenance research projects will be also recorded and published as individual data sets and collections. Designed as a sustainable solution (FAIR), further projects from all fields of archaeometry will be able to use it in a modified way in the long-term. In the presentation, the status quo will be shown and thus provide a preview that will give rise to discussion about the respective needs of the users – both "producers" and "consumers" of the data.

HERIe – digital preventive conservation platform

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Keywords: Fire risk, Design of museum storage, Digital tools, Sustainable approaches, Sustainable preventive conservation

Abstract

A rational strategy for effective and sustainable collection preservation in galleries, libraries, archives and museums (GLAM institutions), requires an understanding of the relationship between the magnitude of a threat and the damage caused. To support the international community of GLAM institutions and conservation professionals in assessing the safety of display and storage conditions for collections, a digital preventive conservation platform HERIe has been developed. The platform provides remote access to quantitative assessment of risks to heritage assets. So far, it contains modules corresponding to the environmental agents of deterioration: air pollutants, light, incorrect temperature or relative humidity, as well as the module allowing estimation of the magnitude of fire risk. Risks from environmental conditions are assessed by analyzing data uploaded by the user prevailing in a space in which an object is displayed or stored. The effect of moving an object from one environment to another, a frequent problem when loans for exhibitions are made, can be also assessed. The platform includes also

tools allowing to estimate the amount of silica gel for stabilization of lowering RH level in a showcase or dehumidifier capacity. The HERIe is being developed by several institutions with financial support between other from the European Commission and the Getty Conservation Institute. The developed digital solution has been made freely available under the HERIe name at herie.pl to anyone involved in the preservation of collections. The HERIe platform is currently used by more than 2000 users to support decisions in the area of preventive conservation. It was found that approximately 50% of users are educators, exploiting the platform for lectures, classes and professional development courses.

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Oral Session 4 – Case studies

A multi-analytical investigation on darkening of blue pigments in Munch's paintings

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Keywords: Edvard Munch, Paintings, Darkening, Cobalt blue, Ultramarine

Abstract

There are specific deterioration phenomena connected to blue paints used by Edvard Munch, which deserve further investigation, as these occur frequently in paintings in the museum's collection. The phenomena observed include colour changes (both fading and darkening), deep cracks, water sensitivity and adhesion issues. Several studies have been done on these topics, focusing on different pigments and binding media [1-3], but the complete understanding of these phenomena is far from being achieved, especially when considering the darkening affecting oil paints containing blue pigments, such as Ultramarine and Cobalt Blue. In this study, we aim to better understand the physical and chemical mechanisms leading to the progressive darkening of Ultramarine and Cobalt Blue affecting several of Munch's paintings. In these paintings, darkening has been observed and previously reported [2,3] in areas where the paint has been applied in thick brushstrokes, allegedly thought to be squeezed directly from the tubes on the canvas. A multi-analytical approach, combining 3D Hirox microscopy imaging, as well as elemental (pXRF) and molecular characterization (FTIR and μ-Raman Spectroscopy, GC/MS and Py-GC/MS, MID+FAR-IR synchrotron facility) of the paint composition, is being applied on several paintings in the MUNCH's collection in Oslo (including the "Drowned Boy", 1907-1908 and the "Old Man In Warnemunde", 1907, previously investigated in a MOLAB campaign in 2021). The 3D Hirox microscope allows high magnification scans (from ranges between 10x to 90x and 140x to 2500x) and observation of details on the surface of the darkened areas, being also useful for the sampling of micro-fragments and surface deposits. The results from the analyses done on micro-samples of paint layers are compared with those obtained from samples collected from the original paint tubes collection of the museum [4]. New insights are arising from this interdisciplinary and multi-analytical study, pointing towards the cause responsible for the darkening affecting the paintings, which is to be found either in the organic or inorganic components of the paint formulations, in their mutual interactions and, also, in the painting technique.

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A multi-competence and multi-analytical approach to contrast fakes in art

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Keywords: Authentication, Fakes, Raman spectroscopy, SEM-EDS

Abstract

Artworks authentication represents a fundamental step in art and archaeology. The circulation and trade of non-certified or unknown provenance artworks, can be associated to illicit removal from the original contexts or faking manufacture. As well as representing an obvious cultural problem, the fake artifacts can create confusion in art market and enormous economic damages. Moreover, in many countries, falsification of art and archaeology artworks is considered a crime. Historical and stylistic analyses represent a first, effective and well-known approach for the authentication of works of art, which can, in some cases, give rise to ambiguous, if not incorrect, answers. In the last decades, archaeometric approaches have given a huge contribution to the investigation and characterization of works of art and, recently, also in

discriminating between fakes from original ones through a direct or indirect dating, supported by in-depth studies on material composition, execution techniques, degradation processes and ageing products. On the other hand, even the exclusive use of archaeometric investigations can lead to an incorrect assignation to discriminate artwork authenticity. For this reason, a multi-competence approach, combining technical-scientific skills with historical-artistic and archaeological ones, is mandatory to correctly authenticate artworks. Among the huge quantity of works of art, the counterfeiting record goes to Contemporary paintings, prints and drawings, while the most reproduced archaeological objects by forgers are those that best meet the tastes of the buyers, in particular Italic cultures artifacts, such as Magno-Greek, Etruscan and Roman ones. In this work, we present case studies on different typologies of art and archaeological objects, coming from illicit trafficking of cultural goods and stored at the "Laboratorio del Falso", a research and study laboratory for the fight against faking and trade of non-authentic works of art. The "Laboratorio del Falso" is a center of interdisciplinary studies founded in 2017, which follows the agreement between the Carabinieri for the Protection of Cultural Heritage (Comando Carabinieri Tutela Patrimonio Culturale, TPC) and Roma Tre University. A multi-technique approach, based on micro-Raman Spectroscopy, SEM-EDS microanalysis and X-Ray Fluorescence spectroscopy, has been adopted. The main results are reported and discussed, along with the best experimental protocol applied for each specific case-study.

Feathered objects: a multi-analytical study

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Keywords: Structural colors, Feathers, Non-invasive analysis

Abstract

The craft of Tian-Tsui or diancui is the process of decorating objects with Kingfisher feathers. These feathers are painstakingly adhered to metal and wooden materials, creating intricate and complex designs [1]. Typically, Tian-Tsui objects include jewelry, hair pins or headdresses, adorned with bright blue Kingfisher feathers. Some works may incorporate additional colors, such as pink and purple feathers from different Kingfisher species, as well as iridescent greens from peacock and duck feathers [1,2]. Unlike traditional dyes and pigments, Kingfisher feathers have structurally-based coloration resulting from nanoscale features. This type of coloring is known as structural color and is present in many plants and animals, for example the iridescent blue wings of the Morpho Butterfly [3]. These subwavelength mesostructures selectively absorb and reflect light, resulting in the brilliant blue color observed on the Tian-Tsui objects. The morphology and orientation of the nanostructured features influence the observed coloring [3,4]. This study examines a diverse range of artworks, spanning from headdresses and brooches to a 19th century Chinese Calendar consisting of 12 large screen panels. In particular, the examination of these panels, presented a rare opportunity to scrutinize larger-size feathered works not typically available for analysis [2]. Furthermore, the combined examination of various types and categories of objects yielded a more comprehensive understanding

of feathered objects fabricated via the Tian-Tsui technique. Employing a multi-analytical approach, the investigation combined non-destructive and micro-destructive methodologies including Scanning Electron Microscopy (SEM) Hyperspectral Imaging (HSI), Fiber Optics Reflectance Spectroscopy (FORS), Fourier-transform infrared spectroscopy (FTIR) and X-ray Fluorescence (XRF). This comprehensive research shed light not only on the materials and techniques employed by the artists, but also on the diverse colorations present in the studied objects. Beyond material and technique analysis, this research explored the challenges and capabilities associated with utilizing well-established cultural heritage research instrumentation and methods when dealing with structural color-based materials. In doing so, it aims to contribute to the broader understanding of these intricate artworks, highlighting their significance in cultural heritage, while also addressing overarching challenges in collection care and stewardship.

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MeV SIMS – an accelerator-based technique providing new insights into the characterization of ß-naphthol and triarylcarbonium colorants from the INTK materials collection

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Keywords: MeV SIMS, ß-naphthol colorants, Triarylcarbonium colorants

Abstract

The Institute for Natural Sciences and Technology in the Arts (INTK) at the Academy of Fine Arts Vienna, has a valuable materials collection from the 19th and 20th centuries, with about 800 synthetic organic

pigments and dyes among other materials. As such, collections are unique sources of reference material in the field of cultural heritage, an open access web-enabled colorants database containing historically relevant information and analytical results (e.g., main components, trace elements, XRF, FTIR, Raman and MeV SIMS spectra, bottle images, etc.). Several synthetic organic colorants from ß-naphthol and triarylcarbonium pigment classes could not be clearly identified by FTIR and Raman spectroscopies, due to their similar or unclear spectral features. In order to determine the exact chemical composition of these samples, which is essential for materials when used as references, 31 colorant samples were selected for the MeV SIMS analysis. Accelerator-based secondary ion mass spectrometry with MeV primary ions (MeV SIMS), is a highly sensitive method for the analysis of synthetic organic colorants and their mixtures, giving exact molecular compositions without any pre-treatment of the solid samples [1]. Main advantages comparing the SIMS with the primary ions in keV range, are: lower fragmentation, higher secondary molecular ion yields (up to factor 103), higher mass range and primary ion doses below the so-called static limit. MeV SIMS measurements were performed using the set-up with linear TOF spectrometer at the heavy-ion microbeam beamline at the Ruđer Bošković Institute (RBI) [2]. For the analyses, a pulsed 5 MeV Si^{4+} primary ion beam was used. The pigment grains were pressed directly into the indium surface and analyzed in positive and negative ion mode. We derived that the ß-naphthol and triarylcarbonium pigments can be identified in the same straight forward way as already reported by the authors for other synthetic organic pigment classes [1] through their (protonated) molecules and two main fragment ions. Furthermore, MeV SIMS was very successful in the differentiation between triarylcarbonium pigments and their corresponding triarylmethane dyes. The ß-naphthol (PR1, PR3) and triarylcarbonium (PV3, PG1, PB1, PB2, PB3, PB10, PR81) pigments could be obtained in positive-ion mode. An important point is that, due to the high sensitivity of the MeV SIMS, mixtures of two and more pigments were determined in the samples that were not detected by FTIR and Raman. Negative-ion mode led to the identification of ß-naphthol lakes (PR49, PR53:1). Here, also the presence of species specific to heteropolyacids, such as phosphomolybdic acid (PMA), phosphotungstic acid (PTA) and phosphotungsto-molybdic acid (PTMA), were detected. These are precipitating agents, which have been used in the production of triarylcarbonium pigments from dyestuff ever since 1917 [3]. The results emphasize the efficiency of MeV SIMS in providing an unambiguous identification of ß-naphthol and triarylcarbonium pigments/lakes. Consequently, we focus recent MeV SIMS research on its application on samples taken from modern artworks to precisely identify the synthetic organic colorants. Many of the selected colorants have been used in modern inks and as colorants for plastics, thus their MeV SIMS spectra will also enlarge the MeV SIMS spectra database at the RBI, to serve as references in analysis of real samples.

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Exploring monitoring and mould cleaning options for paintings and painted surfaces: a case-study of Andebu church (ca. 1100), Norway

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Keywords: Monitoring techniques, Microclimate, Mould, Cleaning methods, Paintings

Abstract

The growth and proliferation of xerophilic mould on painted surfaces in historical buildings, poses complex challenges. Xerophilic moulds grow at low water activity and low relative humidity (RH). Notably, growth has been observed at RH as low as 58% [1], which falls below the ASHRAE (2019) Control type A threshold (<65% RH) established to prevent mould germination and growth in museum collections. This underscores the need for a deeper understanding of decisive factors for mould growth in different microclimates and for ways of safely removing it from old and vulnerable painted surfaces. The goal of this research is to contribute to the development of methods for monitoring, removing and preventing new mould growth on paintings in historical buildings. Andebu church (ca. 1100) in Vestfold and Telemark County, Norway, serves as an illustrative case of a heated stone building experiencing an outbreak of xerophilic mould with no prior history of reported mould issues. Among the affected objects are a Dutch panel painting (1569) and a portrait painted on canvas (1842). In autumn 2023, the panel painting was moved from the church to a conservation studio for documentation and mould removal. Despite many reported cases of mould growth in historical buildings, there are few recent conservation studies specifically addressing mould growth on paintings or painted surfaces. Some noteworthy exceptions are the studies by Paiva de Carvalho et al. [2] and Kosel et al. [3]. The present study includes visual and archival investigations of Andebu church's exterior and interior and artworks. RH and temperature loggers (Tiny Tag) were initially placed in the church during the February 2023 assessment, later supplemented by small cloud-connected RH and temperature sensors (BevArt/ Disruptive Technologies) mounted near or directly on the front and reverse of the paintings and outside the church. Tape lifts (Mycotape) of the mould on the paintings, were analyzed. A selection of various mould removal methods were reviewed and a selection tested on the panel painting. Climate panels based on the Klima-MOV project [4], this time incorporating painted surfaces on wood and canvas, will be developed to monitor new mould growth in the church, with surface samples collected and analyzed at intervals. Analysis of the tape lifts revealed substantial growth of the xerophilic *Aspergillus penicillioides*. Current measurements indicate a fluctuation in RH within the church, between approximately 30% and 77%. The cloud-connected RH and temperature sensors show promising results for monitoring small, relative differences in microclimates near paintings. The surface sample analysis and painted climate-panels are expected to contribute by enhancing the understanding and potential of age determination and early detection of mould growth on painted surfaces in buildings facing similar challenges to those of the Andebu church.

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A dissemination experiment centered on the scientific analysis of a cat mummy

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Keywords: Museum mediation, Virtual reality, Non-destructive analysis, 3D data

Abstract

This work presents the design and evaluation of a dissemination experience aimed at enhancing the scientific study of a cat mummy. The resulting dissemination environment relies primarily on a virtual reality (VR) experience and complex 3D printing techniques. The mummy belongs to the archaeological collection of the Musée des Beaux-Arts in Rennes, France. This project was carried out after a study conducted by the University of Manchester on around 800 animal mummies which saw that around a third of them were empty [1]. The project led to various discoveries about the mummy [2] and produced a large amount of digital data collected by X-ray, tomodensitometry and photogrammetry. This data was processed for use in various augmented reality, VR and 3D printing productions, first, to support the scientific analysis of the mummy and then to disseminate the findings to the public. The originality of the dissemination approach lies in the choice to highlight the scientific process that led to new knowledge and new unresolved questions, rather than presenting the conclusions in a historical

perspective. The project produced two main media. First, the 3D data obtained from processing the scanner data was used to produce a transparent 3D print on a 1:1 scale. This technique was already proposed as a means of safeguarding the internal spatial organization of archaeological material [3]. This copy of the mummy allows the public to discover its different internal elements. It is now part of the museum's permanent collection, displayed alongside the real mummy. Then, a virtual reality environment, called Secret of Bastet, was set up and presented to visitors to offer an interactive, educational and entertaining experience. The application was designed and produced as part of a collaboration between the museum team, a computer science laboratory, an archaeology laboratory, a VR research team from the international private company Orange Innovation and the graphics studio Polymorph 3D. The experience takes users through the production, exploration and analysis of the data and guides them in its interpretation by counting the number of cat specimens present in the moment by identifying and counting bones of the same type. After a first presentation during an international professional event in 2023, the Bastet experience was presented at the museum during weekly dissemination events. During these presentations, two user studies were carried out using subjective questionnaires to collect and analyze user feedback. The first study focused on the quality of the VR experience in terms of presence, usability and comfort. Thirteen users responded to the questionnaire. The second study examined the impact of the dissemination experience. Seventy people responded to the questionnaire. Both studies received positive and enthusiastic feedback. The results show that users are genuinely interested in discovering and experiencing the scientific approach. The two media offer complementary experiences. The 3D printing gives access to a vast amount of information, otherwise "invisible" on the original artefact. The VR environment proposes a more active experience through a scripted story and interactions with the mummy that are usually inaccessible. User studies carried out during exhibitions of the VR experience, validate the interest of the approach from the public.

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Oral Session 5 – Neutron and Synchrotron light-based techniques

Advances in Neutron Resonance Transmission Imaging for inhomogeneous material characterization in heritage science

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Keywords: Neutron imaging, Resonance absorption, Non-destructive, Elemental analysis, Isotopic analysis

Abstract

Within the field of neutron imaging, significant advances are being made at the ISIS Neutron and Muon Source [1] to improve an innovative imaging technique, named Neutron Resonance Transmission Imaging (NRTI). This method provides both spatial and quantitative information about the elemental and isotopic composition and distribution inside the bulk of an object. NRTI exploits the epithermal portion (0.3 eV < En < 100 eV) of the neutrons available at the ISIS neutron and muon source, on the INES instrument, which is not yet widely used for neutron imaging. This technique is an extension of the better-established Neutron Resonance Transmission Analysis [2-4] and combines the sensitivity of NRTA to elemental and isotopic composition with detailed morphological information obtained through a time and space-resolved detection system [5,6]. The NRTI technique relies on the measurement of the beam attenuation, due to the resonant absorption of epithermal neutrons by the nuclei of a material. Since resonance structures appear at specific energies for each nuclide in their neutron-induced reaction cross-sections, they can be used to identify and quantify elements and also isotopes, in materials and objects. What sets NRTI apart from standard neutron radiography/tomography, is the possibility to locate specific features within an object's volume and identify and localize specific elements and isotopes with enhanced contrast compared to other methods. This contrast enhancement is possible thanks to the fact that each pixel of the detector used for NRTI, contains the full unintegrated transmitted spectrum, preserving detailed time and, therefore, energy information, in contrast to neutron tomography where the spectrum is typically integrated over the energy range by the neutron camera. The availability of the detailed time-of-flight spectrum in each pixel allows the selection of specific resonance dips during post-processing analysis, highlighting the areas where the selected element is present inside the object volume. The striking features of NRTI make it suitable for the characterization of inhomogeneous samples [7,8], 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 conducted with the INES beamline [9] of the ISIS facility.

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Neutron imaging of capillary water uptake in waste-based geopolymers for cultural heritage conservation

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Keywords: Geopolymers, Neutron imaging, Conservation, Capillary water uptake

Abstract

Geopolymers are currently studied as an alternative low-carbon replacement of Portland-based cements for application in the conservation/restoration field and building industry. They can be obtained at room temperature through the mixture of an aluminosilicate powder with an alkaline activator, such as sodium hydroxide and/or sodium silicate solutions. The possibility of employing natural and industrial waste as raw material, makes these products even more suitable in the perspective of green materials development, currently under test for application in cultural heritage conservation [1]. Research in the field of geopolymers applications for cultural heritage conservation, though, is still lacking information about materials durability, an open question related to weathering action, including the possible formation of efflorescence and sub-efflorescence. Consequently, it is important to study the materials porosity in association with water penetration, a physical process that can directly influence geopolymers service life and durability. The unique properties of the neutron – high penetration power and sensitivity to light elements– makes this subatomic particle an ideal probe for studying the structural properties of geopolymers and their interaction with penetrating water. The capillary

water uptake in cement-based materials and in building stones [2], has been studied through neutron imaging and a first attempt on geopolymers has been made on fly ash-based products [3]. This work aims at exploiting the benefits of neutron imaging study during capillary water uptake of geopolymers made with waste Sicilian (Italy) raw materials (volcanic ash, rocks cutting sludges and ceramic waste), for usage in cultural heritage conservation and fully characterized from a chemical and mineralogical point of view. The addition of calcium-based additives or of reinforcing carbon fibres, has been tested too. Comparisons between samples as they are and samples exposed to salts crystallization, has been performed focusing on the mechanism of water filling the pores and the cracks. The neutron imaging study was conducted with the Dingo beamline at ANSTO (Australia) [4]. The experiment consisted of recording a sequence of neutron radiographies of prism-specimens (~2x2x8 cm^3) positioned on a purposedly designed and manufactured imbibition platform. The diffusion of water into the bulk of the samples was visualized with a spatial resolution of about 50 μm and temporal resolution of 60 s for a total irradiation time ranging from 20 minutes to 17 hours. The water uptake velocity curves were extracted from the measured neutron transmittance profiles, averaged through the specimen's height across the radiographic temporal scan. By comparing the behaviour of the same binder with different additives, we were able to evaluate their influence on the geopolymers durability: the presence of fibres caused a general acceleration in water uptake, while deceleration was observed with calcium-based additives. An increase in velocity was observed in geopolymers subjected to salts crystallization, with different rates according to each material tested.

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Deciphering the chemistry and nanostructure of artists' paints with mixed protein-oil binders

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Keywords: Renaissance, Mixed-media paints, Tempera grassa

Abstract

The transition from egg-based tempera to oil painting in quattrocento, was a turning point in art history and influenced the creation of Renaissance masterpieces by renowned artists of the time. Sandro Botticelli, Leonardo da Vinci and many others, continued to use egg in parallel or in combination with oil and prepared paints of great complexity. Protein-oil mixtures, used as paint binders, can result in diverse microstructures based on the sample preparation procedure (i.e. tempera grassa - i.e. egg with oil - oil paints with protein-coated pigments or capillary suspensions) [1-4]. Today, we are still missing critical information on the molecular composition and microstructure of such mixed media paints. Imaging techniques able to map the organic constituents (i.e. proteins, oils) with a nanoscale spatial resolution, are pivotal to tackle the micro-organization of the organic phases within paint media. Atomic force microscopy-based infrared spectroscopy (AFM-IR) is an emerging technique which allows chemical analysis of infrared (IR) spectroscopy with the spatial resolution (<20 nm) of the atomic force microscopy (AFM), which is below the diffraction limit [5]. In this work, we have employed AFM-IR to elucidate the spatial distribution of proteins and lipids at the nanoscale, to contribute to the ambitious objective of understanding the materiality and the technology of a technical revolution in art history: the transition from egg to oil in Renaissance Italy. We also present X-ray Raman scattering (XRS) spectroscopy as an element-sensitive bulk probe for disentangling complex chemical speciation of organic mixed-media paints. In the XRS process, an incident photon is inelastically scattered by a core electron and part of its energy is transferred to excite the inner-shell electron into an empty state, providing X-ray absorption near edge structure (XANES) data comparable to conventional X-ray absorption techniques [6]. In this work, we identify and compare the carbon bonding of paints prepared using diverse formulations, aiming at understanding the chemical structure of the paint binder. We also discuss the main limitations of the approach (i.e. spatial resolution, radiation-induced effects) and we suggest complementary techniques and mitigation strategies to overcome them.

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6th International Conference on Innovation in Art Research and Technology
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Oral Session 6 – New approaches for the study of textiles

New insights on flax fiber durability through the study of ancient Egyptian textiles

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Keywords: Flax fibers, Ancient Egyptian textiles, Biochemical composition, Mechanical properties, Ageing

Abstract

Flax is one of the first domesticated plants and its cultivation goes back to the ancient Egyptian period. At that time, flax textiles were very valued, mostly, due to the comfort and strength provided by the fineness and high mechanical properties of flax fibers. Thus, flax was widely used for clothing, household linen, funerary uses, such as mummy strips or funeral clothes, or even fishing nets and ropes [1,2]. Today, the use of flax fibers for composite reinforcement or textile, is strongly increasing, mostly due to their high average mechanical performance [3]. Nevertheless, flax fibers often exhibit some defects known as “kink-bands”, these being weak points for the fiber itself and, more generally, in the material made out of flax fibers [4]. Thus, the effect of ageing on the characteristics of such defects, remains a fundamental question and is of interest to the present work. Some pieces of Egyptian flax textiles from Pharaonic and Roman periods, have survived for millennia up to the present day, thanks to specific environmental conditions. The samples studied in this work come from Le Louvre Museum, Paris, France (E 27370, E 27376, AF 11260) and from Museo Egizio, Turin, Italy (TUR 2226). These textiles were carefully selected for their archaeological contexts and for the storage conditions they were subjected to. Contemporary samples were also investigated and used as references for the study. Through an original and transdisciplinary approach, this work focuses on the effects of ageing on the composition and mechanical performance of flax fibers from samples of archaeological interest. For this, fiber biochemical composition was investigated through synchrotron deep-UV autofluorescence imaging. A big difference between samples in terms of fluorescence intensity and emission wavelength was observed, illustrating a change in the parietal composition through ageing, depending on the environmental conditions and duration. These results were correlated with mechanical properties evaluated by Atomic Force Microscopy (AFM) in peak-force quantitative nano-mechanical property mapping mode (PF-QNM). If for some ancient fibers, the average indentation modulus of the fiber cell wall remains comparable to average modulus of contemporary fibers, the topography shows additional defects, such as cracks in the cell wall that can be observed on ancient fibers.

Acknowledgments

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Study of the degradation of ancient Egyptian fabrics through synchrotron radiation and cutting-edge techniques

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Keywords: Synchrotron radiation, Textiles, Flax, Ancient Egypt

Abstract

In the fields of art, archaeology and industry, textiles often take a backseat to materials like metals, stones, ceramics and glass. A comprehensive literature on the degradation mechanisms of plant fibers, fiber processing and the interaction between plant fibers and exogenous materials, remains limited. Although

synchrotron radiation has previously played a crucial role in acquiring information on biochemistry [1,2] and plant fiber ultrastructure [3] in botanical and engineering studies, little has been done to study archaeological fabrics [4]. In this study, state-of-the-art characterization techniques, including second harmonic generation (SHG) imaging microscopy and deep-UV (DUV) fluorescence imaging and microspectroscopy, were employed to unravel the degradation mechanisms of linen fibers aged in different archaeological contexts. Five yarns sampled from objects in the ancient Egyptian collections of the Louvre Museum, as well as a sample from the Egyptian Museum of Turin, were selected to represent the degradation of objects in different environments: two linen shrouds (tombs), two votive figurines garments (objects buried in the ground) and a fishing net (object degraded in water). Differences were observed in yarns sampled from the linen garments of the buried figurines, found in the Gebel el-Zeit sanctuary, indicating a certain degree of mineralization and degradation, although one of the yarns was found more mineralized than the other. Minerals were found encrusting the yarn not only on its surface, but also in the inner layers of the fibers. The most degraded fibers showed a loss of their natural shape, increased porosities in the cell wall structure and an increasing roughness of their surface. On the other hand, the two linen burial shrouds from the Pebos and Ini tombs, showed generally high fluorescence emission over the entire observed spectral range. However, contrary to the yarn sampled from the funerary linen of Pebos mummy, which is well-preserved, the yarn sampled from the oldest and most degraded funerary linen, was found with poorly preserved crystalline cellulose. The yarn from the fishing net was found poorly preserved as well, despite the high fluorescence intensity emission. The inner layers of the cells, rich in cellulose, were almost completely degraded and the only layer still preserved was the cell wall layer rich in lignin. This justified a high fluorescence emission of lignin in comparison to proteins and ferulic acid, detectable by the DUV technique. The fishing net also showed some fibers with similar fluorescence emission values to the funerary linens. This similarity can be explained by the presence of an organic coating found in the yarn of the fishing net, hypothesized to be beeswax. This coating makes the fibers comparable to the yarns sampled from funerary textiles that could have been in contact with bitumen, beeswax and resins, following the embalming rituals of the ancient Egyptians. The study emphasizes the potential of interdisciplinary approaches, combining art, archaeology and advanced scientific techniques, to enrich our understanding of the past and address contemporary challenges in materials science and industry.

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Metallic thread lace: unveiling manufacturing techniques via scientific analysis of historic textiles

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Keywords: Metal lace, Cultural heritage, Microscopy, Historic textiles, Spectroscopy

Abstract

Historical textiles adorned with metallic threads, are esteemed for their artistic, cultural and historical significance. One such example is lace, which evolved from cutwork embroidery techniques and gained popularity across Europe in the 16th century [1]. While typically crafted from linen, the introduction of silk and the integration of metal threads, embellished these textiles, sometimes comprising entire lacework made from metallic threads. Research on the physico-chemical attributes of metallic threads within textile-based objects, likely commenced in the late 19th century [2]. Understanding the material composition and production techniques of these artifacts, holds invaluable insights for art historians and textile conservators. The National Museum in Kraków hosts a substantial collection of lace artifacts dating from the 17th to the 19th centuries that employ the bobbin technique, entailing intricate interweaving of numerous threads wound around traditionally wooden or bone bobbins. These objects come in diverse shapes, with many forming bands of varied widths, allowing the creation of captivating aesthetic designs. This synopsis encompasses the findings derived from analyzing 575 samples obtained from 192 lace items. The investigation initiated with optical microscopy (OM) and scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM-EDS) to gain insight into fabrication techniques, object morphology and to align results with prior research. Subsequent analytical work employed X-ray fluorescence spectroscopy (XRF) and Fourier-transform infrared spectroscopy (FTIR). OM facilitated characterizing the metal threads in terms of color, braid direction and metal degradation. Further analysis via XRF and SEM-EDS categorized the objects into four groups based on metal thread composition and stratigraphic layers: Ag/Cu alloy plated with Au, Cu/Zn alloy, Ag plated with Au, and Ag/Cu alloy. Additionally, FTIR spectroscopy identified the textile substrates as either linen or silk.

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Oral Session 7 – Preventive conservation

How the impact of natural ventilation and air pressure affects climate control in historic museum buildings

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Keywords: Preventive conservation, Climate, Historic buildings, Air pressure

Abstract

Climate control and sustainable climatic boundaries for historical objects, is a core issue for how museums safeguard and prolong the life span of their collections. However, while the international standards take into consideration how the natural climate of different countries vary, little is understood about how the natural ventilation of historic buildings affect the building`s capacity to deliver the preferred environmental conditions. Historic buildings are often ventilated through natural pressure systems within the building structure. However, the movement of air changes throughout the building when mechanical climate systems are introduced. The Historical Museum belongs to the University of Oslo. It is located in the city center of Oslo in a purpose built Jugend style building, made by the architect Henrik Bull and constructed between 1897- 1902. The museum opened in 1904 and contained what was then, the Collection of National Antiquities, the Ethnographic collection and the Coin cabinet (numismatic collection). Today, both the exterior and the interior of the Historical Museum are on the list of protected cultural heritage in Norway, whilst the building itself is one of a dwindling number of buildings belonging to the turn of the 20th century buildings in Oslo that still retains its original function. Its roof and facade were renovated between 2018 and 2021. New insulated inner windows were installed and work to protect the interiors from solar gain, was also carried out as part of the renovation. The old building has high air leakage, integrated air ducts and large windows lacking solar and light protection. High infiltration leads to dry air inlet from the ambience during cold periods, whilst solar gain raises indoor temperatures during summertime. This leads to uncontrolled fluctuations of temperature and relative humidity caused by ambient temperature, wind and solar gain, meaning that the building is climatically unstable and challenging to run according to the climatic requirements of a modern museum. It has also a high energy consumption. The building has mechanical ventilation with central humidification, though the need for humidification varies from room to room. Due to the openings between the floors, the situation differs on each floor, due to the stack effect. Method: Pressure loggers were mounted around the museum premises to better understand the movement of air through the building structure. Temperature and relative humidity are logged within the same areas. The ventilation system was inspected and assessed and the real values of the velocity and delivery of air into the different parts of the building, were measured and logged. The building structure was also analyzed

through simulations performed with an IDA ICE-system, including the patterns of use from both the audience and the employees at the museum. Results: The case-study shows that the climatization of a historic building in a Northern cold climate depends on a more intricate web of systems than what is considered normally. It also shows that closed climatized showcases is a necessity for the most delicate and sensitive objects if they are to be kept in a building like the Historical Museum. Results will be presented showing the influence of the outdoor climate on different parts of the building. We will also propose possible ways to provide a better indoor climate and reduce the building's energy consumption.

Analyzing vibration levels in museum collections

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Keywords: Vibration levels and transfer, Museum environments, Paintings, Seismic sensors, Risk assessment

Abstract

The present study analyzes and evaluates the diversity of vibration levels in museum collections resulting from various sources of excitation. These sources include everyday movements and conversations by museum visitors, street traffic, construction work in and around the museum building, as well as internal museum events like music performances. While numerous studies focus on vibrations during art transportation, it is equally important to examine and classify the vibration levels in everyday situations within museums that artworks are exposed to. Vibrations are inevitable and can compromise the material structures of artworks upon prolonged exposure. This study aims to analyze the effects of these external influences on art objects and identify detrimental vibration levels, particularly for canvas paintings. A comprehensive data collection is imperative in identifying potential excitations and thus to understand the response of art objects to these influences. This investigation encompassed diverse spaces and areas in internationally accredited museums, among them the Staatsgalerie in Stuttgart, the Anna-Amalia Library in Weimar, the Schauwerk in Böblingen and the Depot Boijmans van Beuningen in Rotterdam, combining old and modern architecture. In this presentation, a substantial number of measurements, along with subsequent analytical outcomes and ensuing observations, are showcased and compared to draw conclusions. Several comparative measurements were conducted, using highly precise seismic acceleration sensors and Laser Doppler Vibrometry. This extensive data collection captures unknown vibration levels and patterns within exhibition spaces. The study examined the extent of vibration transfer from the excitation sources into the exhibition room and onto painting surfaces by analyzing the occurring amplitudes and frequencies. This approach allows for comprehensive data analysis and aids in establishing complex correlations. The interpretation of the findings provides a better understanding of everyday vibrations in the museum environment. This aids in taking a further step towards identifying risk factors and offers potential recommendations for the

protection and conservation of artworks in museum collections. However, a critical examination of the results is essential for every location separately, due to the unique nature of each environment, making generalizing challenging. The insights derived from this comprehensive study, not only significantly contribute to advancing conservational understanding, but also, facilitate a targeted risk assessment for exhibits in museum displays of global significance. The applied methodology for high-quality vibration measurements represents an approach, identifying potential risk factors and assessing the enduring impacts on artworks within museum collections. This methodological framework broadens perspectives, aiding in the identification of potential sources of danger and capturing the long-term effects on artworks, thereby enhancing our understanding of safeguarding and preserving these invaluable cultural treasures.

Mapping visitor and music related vibrations in Estonian National Museum

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Keywords: Preventive conservation, Vibration damage, Museum

Abstract

Vibration is a considerable risk for museums, which may occur during an earthquake, construction work, public transport or while transporting an artefact itself. But one considerable risk, which has not always been associated with museums, is music. As vibration damage is cumulative in time, objects may show unexpected damage in stable conditions. Many public memory institutions have programmes containing music events, where museum staff has to take into account the risk of vibration and its effect on artefacts. For example, in 2018 the Estonian National Museum (ENM) was visited by 195 000 guests and about 600 events took place inside and outside the museum building, including theatre and music events. This is an upward trend among museums, as it attracts more visitors and new audiences. The competition to gain high visitor numbers is harsh as museums do not compete with each other, but with all other institutions providing leisure activities from social media to sports [1]. ENM's first experience with vibrations affecting artefacts started after the opening of our new building in 2016, mostly because concert areas and exhibitions were planned nearby. After the information that Metallica concert was planned to take place next to the main building, it triggered our sense of danger and we started measuring sound related vibrations in exhibition areas and storages. Today it is clear that vibration measurements made in 2019 were not as precise as we hoped, because of the device chosen at that time (Brüel & Kjaer S313 type 2260 and S308 type WB 3461). The reason why these measurements failed, was because the device used was designed for measuring vibrations affecting humans, not objects. Now,

ENM has a collaborative project with Tartu Observatory, Department of Space Technology in Tõravere. First tests with a new vibration measurement device have been made and expectation for further measurements is high. As of the moment, we tried to assess visitors impact on artefacts on display and evaluate how display cases act on different vibration levels. In the next two months we are planning to map areas exposed to high vibration levels during events, like concerts or events with amplified music. This experiment will give us a good overview on how the building responds to different sound frequencies. In the future, we at ENM have a much better understanding of the risks in our exhibitions during events or even when exhibitions are visited by large groups, for example 32 school children.

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Satellite images and risk management strategies for Cultural Heritage in natural and semi-natural environment

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Keywords: Art-Risk 5.0 Atlas, Cultural landscapes, Geographical Information System, Preventive conservation, Remote sensing

Abstract

Conservation of cultural heritage located in natural and semi-natural environments, represents a technical and logistical challenge for many municipalities. The remote location of these cultural assets from urban centers, complicates their monitoring making it challenging to detect early signs of deterioration that could lead to structural damage. In this context, the use of satellite image series and estimated meteorological products, has emerged as a highly useful tool for implementing remote monitoring strategies and promoting the preventive conservation of heritage resources located in non-urban environments [1-3]. In recent years, different methodological proposals have emerged aiming to facilitate the use of satellite images. One of them is offered by the tool Art-Risk 5.0 Atlas (register number: IPRUPO2023-010 https://artrisk50.users.earthengine.app/view/art-risk5) a freely available computer application developed by the Pablo de Olavide University and the University of Seville. Art-Risk 5.0 Atlas utilizes the Google Earth Engine (GEE) computing platform and the ECMAScript 5 programming language. It leverages GEE's proprietary library to access satellite data and conduct statistical analyses for extracting relevant climate information. This study aims to test the use of Art-Risk 5.0 Atlas to monitor the changes recorded in the climatic hazard of the Spanish territory between

2002-2023, in terms of precipitation, temperature and vegetation. Additionally, it seeks to analyze the climatic characteristics of natural environments with cultural heritage assets, which have been affected by emergencies caused by rainfall, droughts and wildfires. Results have enabled the mapping of the entire national territory with a maximum spatial resolution of 5 km. The precipitation cartography and graphs identify accumulated rainfall values, occurrences of extreme rainfall, droughts and daily precipitation in millimeters. Additionally, temperature maps displaying maximum, minimum and average surface temperatures, showcase fluctuations and daily temperature ranges. Lastly, assessments of vegetation density, health and seasonal changes, have been identified. With an increasing focus on understanding the risks cultural heritage in natural and semi-natural environments is encountering, Art-Risk 5.0 Atlas has emerged as a valuable solution to address this escalating concern. Its capability to identify changes in natural hazards and generate early alerts, promises a positive impact on the management and preservation of cultural heritage at risk. The tool, designed for use without prior programming or remote sensing knowledge, democratizes access to satellite data and its analysis, representing a significant innovation in the conservation of cultural heritage in non-urban settings.

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Oral Session 8 – New approaches for conservation

Initial exploration of surface attached gels for swelling acrylic coatings

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Keywords: Polyacrylamide gel, Acrylic dispersion, Varnish

Abstract

This work introduces surface attached gels (SAGs) [1] as a tool for the removal of degraded acrylic coatings from sensitive acrylic painted surfaces. Conservators can consider removing or thinning acrylic dispersion coatings which have degraded over time causing an unwanted aesthetic impact [2]. However, due to the sensitivity of acrylic dispersion paints/coatings to water and other solvents and the similarity of their chemistry, there is currently no safe and effective technique for this conservation treatment. SAGs are formed of a thin layer of polyacrylamide-based hydrogel, bound to a polyethylene backing [1] and can contain co-polymerised surfactants, which provide compatibility with active agents and affinity with degraded coatings. SAGs have previously been used in the removal of natural varnishes and soiling from a range of coatings on paintings and plaster casts [3]. These materials pose a suitable option for overcoming this challenge, due to their low loading of fluid onto acrylic coated surfaces, thus reducing the fluid volume, which may penetrate and damage the underlying paint film. Gravimetric data has determined that 3 µm thick, 30-min photo-crosslinked SAG films, release less than 0.2 mg/cm^2 water upon contact with the substrate [1]. This study compares a range of SAGs produced with and without co-polymerised surfactant, crosslinked to varying degrees and incorporating a range of fluids containing benzyl alcohol and water in differing quantities. This will allow: evaluation of the wetting of the SAGs, any resulting swelling effect on the acrylic medium and which features of SAGs increase swelling efficacy. These selections are based on initial swab roll swelling investigations, their low impact on human health, as well as environmental acceptability and accessibility to conservators. This study will provide the basis for the development of SAG compatible microemulsions with reduced free surfactant afforded by the gel-anchored surfactants. Digital microscopy, glossimetry, colourimetry, Fourier transform infrared spectroscopy and scanning electron microscopy [4,5], will be employed to characterize the impact of the SAG systems on the surface of mock-up samples produced using paints and coatings selected from two popular and well-studied paint brands, Golden Artist Colors and Liquitex. Prepared samples are subjected to light accelerated ageing and an initial investigation into solvents/solutions known to swell acrylic films, was completed, whilst their swelling power was modelled using HSPiP software.

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Development of an innovative method to stabilize the chemical reconversion of darkened lead white in wall paintings

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Keywords: Darkening, Lead white, Wall paintings, Reconversion, Stabilization

Abstract

In wall paintings, the darkening of lead-based pigments is a widespread alteration process. In particular, the oxidation of lead white (lead carbonate) into brown lead dioxide (β-PbO2, plattnerite), is one of the most common phenomena [1]. This can severely affect the aesthetical appearance of a painting disturbing the light and shadow balance and, therefore, compromise the legibility of the artwork. Although several factors like the alkaline environment, the presence of humidity, light, oxidizing agents and microorganisms, have been investigated as potential responsible for the darkening, the actual causes, mechanism and kinetics of reaction, have not been firmly established [2]. Nevertheless, the need of recovering the original colors to improve the visual appearance of darkened wall paintings, encouraged conservators and restorers to use a chemical treatment known as "reconversion". This method was

specifically developed to transform plattnerite into lead carbonate through a redox reaction, which involves the combined use of hydrogen peroxide and diluted acetic acid. This treatment was successfully applied on darkened portions of several wall paintings proving the immediate recovery of the original appearance [3]. However, in some cases, especially for the wall paintings located in a humid environment, the reconversion was only temporary and darkening reoccurred over time. To fill in the gap of knowledge on the reconversion process in terms of long-term efficacy and stability, a 4-years research project (2023-2027) funded by the Swiss National Science Foundation (SNSF) and entitled "Darkened lead-based wall paintings: innovative treatments to stabilize the recovered original colors", is ongoing [4]. The project involves both in situ and laboratory work. As a first step, a comprehensive survey of wall paintings affected by the darkening phenomena and/or by previous reconversion treatments, was undertaken in Canton Ticino (Switzerland). The visual examination combined with the use of non-invasive analytical techniques (i.e. XRF and Raman spectroscopy), allowed the selection of wall paintings characterized by darkened lead white, as well as an interesting case of re-darkening after past reconversion (Cana wedding scene wall painting in Santa Maria Annunciata Church, Muralto, Ticino). In parallel, systematic laboratory tests in vitro on powdered plattnerite and on wall painting models are ongoing, so to clarify the nature of the reconversion products and to develop innovative stabilization methods. These tests are designed to implement preliminary and promising results obtained using di-ammonium phosphate (DAP), which allows the formation of a more stable white lead-based compound, lead-phosphate, thus making lead ions no longer available for the darkening process. The laboratory tests will involve the assessment of different reagents containing phosphate ions in different application modes on the wall painting models (e.g., use of poultices or gels, different contact times, etc.). The best procedure will be tested in situ on the darkened wall paintings selected as case studies and will be periodically monitored by non-invasive techniques (MA-XRPD/XRF, Raman and FTIR spectroscopy and colorimetry). This assessment will be implemented with invasive, but non-destructive analyses of micro-samples (SEM-EDS, micro-Raman, micro-FTIR and synchrotron X-ray techniques). In addition, the project will involve the environmental monitoring of the selected sites through microclimatic probes and the investigation of possible microorganisms by a technology recently applied to the cultural heritage field, like the Next-Generation Sequencing (NGS). Overall, this research intends to provide a solid scientific understanding of the reconversion process and a reliable system to ensure the durability of the retrieved colors over time.

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Solving microbiological infestation on arctic cultural heritage

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Keywords: Microbiological infestation, Fungi monitoring, ATP tests, Integrated pest management

Abstract

The University Museum of Bergen has an extensive ethnographic collection containing objects of Arctic cultural heritage. The Samic objects come mainly from Northern Norway, whereas the Inuit objects come mainly from Greenland and Alaska. Most artefacts were brought to the museum during the 19th century, thanks to polar expeditions and dedicated collectors. Objects made of organic materials, such as furs, skins, leather and feathers, were kept in special cold storage to receive the best conditions for preservation of the various organic materials. However, in 2012, a serious accident happened. A cooling unit had a defect and a severe microbiological attack developed. The material was cleaned and treated after the accident, improving the situation significantly. It was re-treated in 2020 before it was moved to the central storage. Even though subsequent dry-cleaning projects reduced the fungal activity, thorough ethanol treatments that are usually efficient [1] were excluded due to the nature of the contaminated material. Climate control, as well as the low oxygen environment, contributed to reducing the fungal activity [2]. Since it is not possible to remove the fungal spores from the cultural heritage entirely, the fungal problems must be included as permanent issues in the agenda of Integrated Pest Management. The paper will discuss the risks for the collection in terms of long-term storage and the potential adverse health effects on the museum staff [3]. Various methods to detect, identify and monitor fungi on cultural heritage, including easy microscopic staining tests, microbiological cultivation, ATP tests and DNA analysis, will be discussed [4,5]. The ATP tests seem like the most promising tests for usage within the museum context. These tests, initially developed for the food industry and healthcare, have recently been adopted in the conservation field. They are based on mitochondrial bioluminescence and can thus measure the cell activity of eucaryotes, such as fungi and bacteria. Mitochondria produce energy thanks to Adenosine Triphosphate (ATP) molecules, which can store and transfer energy within cells. ATP, a marker for every living organism, can be detected by an enzyme luciferase containing luciferin molecules. When luciferin reacts with ATP, a bioluminescence occurs. The bioluminescence can thus be exploited as an indicator of fungal and/or bacterial activity. The systematic performance of the ATP test must be methodologically the same when comparing results. The evaluation of the test result needs to be based on robust statistical data from the cultural heritage sector, which is a critical task for future research. The paper is the result of a long-term effort to identify, eliminate and monitor fungi from the University Museum of Bergen collections.

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6th International Conference on Innovation in Art Research and Technology
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Oral Session 9 – Archival and written documents

Archaeometric philology for the study of deteriorated and overlapping layers of ink: the colour-code writing system and afterlife of an early Qur'anic fragment

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Keywords: Archaeometry, Philology, Inks, Qur'an, Parchment

Abstract

Scribes of early Qur'anic manuscripts – from the 7th century onwards - used a mechanism of the Arabic writing system to distinguish homograph letters. Strokes were added to letters as markers of consonantal diacritics. Only later, coloured rounded dots were introduced as part of the writing system to mark vowels [1,2]. After their production, early Qur'anic manuscripts continued to be read, studied and updated to include new mechanisms of the writing system. Deciphering diacritical signs can play a crucial role in the understanding of the making of early Arabic manuscripts, as well as their use and reception [3]. The manuscript condition and deterioration can make the nature and meaning of coloured dots, puzzling for manuscript scholars. In this case, the analysis of the state of conservation is often enlightening, as it allows to determine the exact nature of the colours. At the same time, the philological and paleographical analysis of the dots can make sense of the observations done by conservators, thanks to their interpretation based on the colour code known from the literature on the topic (al-Dani, d.1053). Therefore, bringing together archaeometry, codicology, philology, history of the text and conservation, is crucial when forms of degradation happen to occur on pigments and inks [4,5]. In this study, advanced non-destructive techniques, such as X-ray fluorescence (XRF), μ-Raman spectroscopy, Infrared Reflectography (IRR) and Fourier-transform infrared spectroscopy (FTIR) [6-8], will be employed to examine the chemical composition and materiality of a Qur'anic fragment on parchment, held at the Staats- und Universitätsbibliothek Hamburg Carl von Ossietzky (Cod. in scrinio 153a). These non-invasive techniques will allow for a comprehensive assessment of the layered ink, helping to distinguish between the initial stage of production of the object and its later additions. This analysis will allow to assess the nature of the deteriorated colours, to separate overlapping ink layers, to understand the relative chronology of each stage and to identify the distinct diacritical signs and their meaning, shedding light on the reception history of the manuscript text. The interdisciplinary approach employed in this study has been developed within the framework of FAIR data management and could serve as a model for the investigation of historical manuscripts with overlapping ink layers.

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Alf Bjercke's factory. Comparing ready-made paint and colour swatches with archived recipes from the first half of the 20th century

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Keywords: Identification, Reference sample, Paint binder, FT-IR, GC-MS

Abstract

The importance of the paint material manufacturers' archives in the study of artworks and painted surfaces, has gained more attention internationally in recent years [1,2]. Companies' archives could provide important information about the paint materials and paint formulation. The Norwegian Museum of Science and Technology owns the archive of the paint manufacturer Alf Bjercke, active from

1880 to 1972. A broad range of information is available: ledgers, recipes, laboratory journals, production logbooks, durability tests, catalogues, colour samples, price lists, instruction books, advertising material and original products, such as pigments and ready-made paint cans. Between the two World Wars, there was a rapid and extensive development of new binding media with diverging properties from the traditional ones. To distinguish between new and traditional binders, it is important to be able to identify the new materials in order to develop new conservation strategies for the surfaces painted during the interwar. In this project, analyses of ready-made paint boxes and colour swatches have been performed to compare the analytical results with the archived paint recipes. The aim of the project is to establish a reference collection for the paint media used in early Norwegian ready-made paints. This would also be an important part of the paint material import/export history in Norway. The project is innovative as such binding media references covering Norwegian house and decorative paint products, do not yet exist, whilst previous analyses on foreign paint catalogues have mainly focused on artists' paint tubes, their pigments and dyes. A multi-analytical approach was adopted for the identification of the binding media, both in paint catalogue swatches and original paint materials, produced from the 1910 to 1932 in Alf Bjerke's factory. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was employed for the investigation of the binding media in the swatches, while Gas Chromatography-Mass Spectrometry (GC-MS) was performed on liquid paints. Scanning Electron Microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) was performed to analyze the inorganic content of the liquid paints, while Portable X-Ray Fluorescence Spectroscopy (pXRF) was used for the analysis of the colour swatches. The results from the analyses were compared to the old paint recipes in the archive of Alf Bjerke's factory, to explore the consistency between such sources and the examined catalogues and liquid paints.

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Tracing the author of an iconic Greek Enlightenment book by investigating its printing ink components with infrared spectroscopy and X-ray fluorescence

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Keywords: Printing inks, Historical, Non-invasive, FTIR, XRF

Abstract

Simultaneously with the invention of typography in Europe, a printing technology based on siccative oil-bound carbon-based inks was developed, which survived until the 20th century [1]. At the beginning of the 19th century, a book titled Elliniki Nomarcheia (i.e. The Greek Republic or EN), an epitome of the most advanced liberal ideas of its time, signed by the 'Anonymous Greek' and secretly printed in, presumably, various Northern Italian printing houses in 1806, was carried in the pockets of notable Greek conspirators as the secret intellectual and revolutionary 'cookbook' [2]. Possibly the holy grail of the Greek Enlightenment, is to elucidate the author of EN, for whom many theories have been proposed but remains unproven. This work targets at drastically narrowing down the many possibilities of its authorship, based on the identification of its printing material components. An interesting aspect is that the book is composed of seventeen 16-page booklets (or 266 pages), which, for reasons of secrecy or necessity, appear to have been printed in three different printing houses, presumably in various cities of northern Italy. From this book, several typeface traces on the paper were analyzed. Based on previously published approaches [3], we applied a non-invasive methodology using ATR-FTIR spectroscopy and X-ray fluorescence to investigate the printing ink blend, which was used for the target book. To this end, spectra from several printed traces of carbon-based ink on various pages of the book, were recorded. The infrared spectra of the actual inks were derived after subtracting spectra from the adjacent paper material, which showed prominent organic binder peaks. Of these peaks, the C–H antisymmetric stretch at 2935-2929 cm^{-1} and the C=O stretch at 1735-1710 cm^{-1}, were mainly considered as reflecting the presence of additional resinous components, besides the oily base material. Additional bands, such as those of carboxylates detected in several instances, were also taken into consideration. In addition, elemental analysis showed a variety of metallic elements, such as Fe, Pb and Cu, known to be used as additives in the ink blend for drying and other purposes. Of these elements, Fe and Pb were of the those with the highest abundance and were considered elemental markers of the printing blend. The entire data set was categorized as the 'Elliniki Nomarcheia data group' (EN). For comparison reasons, a large number of books known to have been printed in specific European cities (Vienna, Paris, Venice, Padova, Lucca and Livorno), largely considered as the hotspots of the new liberal European ideals, were also analyzed. The data was collected from several parts of these books for reproducibility and the results were organized accordingly in a reference database for the specific needs of this work, named the 'Historical

Reference data group' (HR). Finally, mock-ups were constructed with paper printed in inks based on several historic recipes, thus composing the 'Mockup Reference data group' (MR). The variabilities of the infrared markers from the molecular analysis, as well as those from the elemental components in the EN, were considered in comparison with those of the MR groups and their conclusiveness was evaluated, significantly narrowing down the possible printing houses. These also helped to dramatically narrow down the possible authors of the EN book, based on historically documented travels in northern Italy during the years 1805-1806.

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Oral Session 10 – New methods for diagnostics

The contribution of multiphoton microscopy to our knowledge of parchments

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Keywords: Multiphoton microscopy, Parchment, Manufacturing, Degradation, Conservation

Abstract

Multiphoton microscopy, also called non-linear optical (NLO) microscopy, is an optical imaging technique widely developed in the biomedical field, but relatively new for the analysis of heritage materials. This technique is particularly efficient in investigating skin-based materials at the microscopic scale, especially parchments, since it can visualise the collagen fibre organisation within the material from the collection of the second harmonic generation (SHG) signal. The simultaneous collection of fluorescence signals by the same NLO microscope, can also reveal the presence of interacting fluorescent materials, such as fat, elastin and keratin, remaining from the skin preparation or gelatin resulting from collagen degradation. Thus, when a skin is transformed into a parchment, NLO microscopy can easily evidence the rearrangement of the collagen fibres in plane and parallel to the skin surface. When applied to historical parchments and manuscripts, NLO microscopy sometimes reveals very different morphology of collagen fibres and signals collected, likely associated with various factors from the life of the object. As a result, experiments have been set up on modern parchments to investigate the impact of manufacturing, degradation and some restoration treatment in the NLO images collected. In the case of manufacturing, the measurements show that the type of animal species and the use of some finishing treatment, can greatly influence the collagen fibres organisation. This new data helped understand the specific morphology of the collagen fibres observed in the sheep parchment of the Mappa Mundi of Albi (8th century, France). During parchment degradation, the damage to the collagen structure is evidenced by the loss of the SHG signal and the onset of a 2PEF signal. The ratio of two-photon excited fluorescence to second harmonic generation signals, can then be used to quantify the collagen state of degradation. This quantitative approach was applied to investigate the collagen degradation state in different historical parchments, including medieval manuscripts from the Chartres' library exposed to fire and water, as a result of the library being bombed at the end the World War II. Lastly, a focus will be given on the parchment transparency to show, thanks to multiphoton microscopy, that transparency is not always

associated with gelatinisation, the extreme degradation of the collagen. A multiphoton microscope optimised and dedicated to the heritage community, was recently installed at the National Museum of Natural History in Paris. We hope that the facilitated access of the community to the instrument, will favour the development of the multiphoton microscopy for other collagen-based materials in collections, such as bone or leather, as well as cellulose-based materials (paper, textile, wood).

From rock to artefacts: investigating the provenance of lapis lazuli in antiquity with μ-PIXE and μ-IBIL

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Keywords: Lapis lazuli, Ion beam analysis, Provenance study

Abstract

Lapis lazuli is a semi-precious blue stone, used since the 7th millennium BCE for the manufacturing of small carved artefacts (such as jewels, decorative and votive objects) in the ancient Middle East and in part of Central and Southern Asia (current Turkmenistan, Afghanistan and Pakistan). The Badakhshan mines in Afghanistan are generally considered the most plausible hypothesis for the origin of the lapis lazuli used in antiquity [1]. However, some other existing and less known sources, have been debated by scholars [2]: Tajikistan, Siberia, Myanmar, Pakistan, Iran and Egypt (the last three possibilities are not geologically confirmed). The limited number of reference samples from well-documented geological sources, the records in ancient written evidence and the provenance studies conducted since the 1960s using various scientific techniques, often invasive or destructive, have shown that the question of the provenance is still unsolved. Driven by the growing interest in adopting conservative methods when analyzing precious artefacts and by the lack of a systematic study of the origin of the raw material of lapis lazuli, the Solid-State Physics group at the University of Torino started in 2008 developing a provenance protocol based on Ion Beam Analysis (IBA) [3,4]. The use of micro-Particle Induced X-ray Emission (μ-PIXE) and micro-Ion Beam Induced Luminescence (μ-IBIL) proved to be effective in finding minerochemical markers (trace elements, peculiar luminescence bands) within reference geological rocks, able to distinguish among five provenances: Afghanistan, Tajikistan, Siberia, Chile and Myanmar. The possibility of applying these techniques both under vacuum and in air (without any sample preparation) ensures at the same time a non-invasive and high-sensitive approach also for archaeological samples. Due to the lapis lazuli heterogeneity, markers are searched inside single mineral phases (wollastonite, pyrite, diopside and calcite, the last one recently included in the study), exploiting the use of a microbeam to investigate single crystals. Some upgrades of the methodology are also under evaluation. Samples from archaeological excavation contexts, frequently

show superficial weathering processes [5] affecting the crystals of the mineral phases, useful for provenance attribution (especially pyrite). In order to try to overcome this issue, we recently started to test micro-cleaning treatments based on the use of micro-pulsed laser source on very small areas (about 100x100 μm^2), strictly targeting pyrite crystals. The aim of this procedure is to create a small breach in the surface layer, allowing the proton beam to reach the preserved crystal beneath. The methodology of the protocol and its future developments will be presented together with some examples of application on lapis lazuli findings coming from archaeological sites from the 2nd to 3rd millennium BCE and located in different areas in the Middle East.

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Analysis of organic residuals found within ceramic vessels using aptamers and immunofluorescence microscopy

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Keywords: Ancient protein analysis, Organic residuals, Ceramic vessels, Aptamers, Immunofluorescence microscopy

Abstract

Archaeological potteries reveal cultural associations of meals that were cooked in them and provide data on human diet in specific socioeconomic contexts. However, comparing the shape of pods does not lead to identification of specific food types and, therefore, commonly results in wrong designations. Because these items are so prolific and because their ceramic structure is very durable, most of them

are stored improperly, which results in microbial degradation of organic residuals within their porous structure. Therefore, unless research methodologies become more accessible and effective in the analysis of ancient organic residuals in the near future, the options to reveal the culinary history of Europe, will become ever more limited. Protein analysis of organic residuals within the porous ceramic structure, provides the opportunity for improved tissue and taxonomic resolution of foodstuffs prepared in ceramics, mainly because they hold rich molecular information encoded within the amino acid sequences. Moreover, the abundance and composition of proteins, makes them more stable in comparison to nucleic acid, such as DNA. ELISA (Enzyme-Linked Immunosorbent Assay) is currently the most accessible methodology for the characterization and identification of ancient proteins found adhered to ancient ceramics. It relies on targeting specific antibodies, which bind to individual protein targets. However, antibodies are easily denatured and commonly suffer from cross-reactivity problems, due to non-specific binding or loss of epitopes. Furthermore, for ELISA analysis, proteins must be extracted from the sample, however, extraction from ancient ceramics is difficult to achieve. Therefore, there is a need to search for alternative molecular recognition elements to antibodies and one promising option are aptamers. These are single-stranded oligonucleotides generated via chemical synthesis, which includes reiterative selection cycles that bind their selected protein targets with high affinities and specificities, via folding into specific secondary ligand binding structures. Aptamers are highly stable at room temperature, have a long shelf-life, no batch-to-batch variability and a reversible denaturation without loss of function. Strict selection using the tailored isolation process, ensures the aptamers' very high affinity and specificity for target proteins. Therefore, 16 aptamers were tested for their potential application in immunofluorescence microscopy (IFM, a technique similar to ELISA). After FT-IR spectroscopy analysis, IFM was directly performed on cross-sections of solid samples, which made it independent of any protein extraction techniques. In this way, we aimed to prove the feasibility of aptamers for the analysis of organic residuals found within the ceramic samples, in future IFM and ELISA applications.

Proteogenomic insights from a waterlogged medieval pelt from Tønsberg, Norway

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Keywords: Proteomics, Genetics, Waterlogged pelt, Species determination

Abstract

Tønsberg, Norway's oldest city, was established before 1130 CE. During the medieval era, it was a significant center of power, trade, whaling and maritime activities, influenced by both the Viking and Hanseatic League cultures. In 2014, an archaeological excavation in Tønsberg unearthed a pelt fragment in a context radiocarbon-dated to circa 1200 CE. The site's exceptionally anaerobic conditions resulted in the fragment's remarkable preservation, offering a more authentic glimpse into the medieval period. Pelt finds from wet archaeological sites are scarce in Scandinavia and rare globally, with limited literature on their deterioration and conservation. Such finds are notably absent from museum collections [1]. This study focuses on the biochemical characterization and species identification of the pelt, as well as the preservation and conservation treatment. Initial analyses involved light and scanning electron microscopy and infrared spectroscopy, comparing the archaeological pelt with known samples from goats and sheep. Proteomic analysis and genetic sequencing, were conducted in a double-blind protocol. Chromatography was performed using a Thermo Fisher EasyLC 1200 and a Q-Exactive "classic" Orbitrap Mass Spectrometer [2]. Concurrently, DNA barcoding was employed to confirm the species identity through Illumina mass sequencing. The raw read-outs were processed with Operational Taxonomic Units (OTUs), following standard metabarcoding protocols [3]. Proteomic analysis showed a high correlation with *Ovis aries* (sheep), with some protein markers also indicating *Capra hircus* (goat). The sequence similarity search, predominantly matched the OTUs to *Ovis aries* with 100% identity, confirming the species and re-opening the debate on the need of databases improvement for archaeological samples.

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Oral Session 11 – New approaches to cleaning: 1st part

Assessment of greener solutions for the cleaning of historical metal heritage

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Keywords: Bio-cleaning, Green gels, Historical metal heritage, Raman spectroscopy, Polarization resistance

Abstract

The advent of the Green Chemistry principles is nowadays a great driving force for the research carried out in the field of Conservation Science to provide safer and more sustainable solutions to conservators [1]. Great is the attention addressed in response to the potential risks derived from cleaning methods conventionally employed in art conservation, which are frequently relying on the use of petroleum-based, toxic and pollutant substances, such as solvents and complexing agents [2]. Within this scenario, the HELIX project seeks to explore greener alternatives for the design of hydro and organo-gels for the cleaning of altered historical metal collections. The core issue with the preservation of metals lies in the spontaneous and irreversible process of corrosion towards which they naturally tend over time [3]. A precaution to such detrimental phenomenon is to shield the metallic surface from external atmospheric agents by means of organic coatings. However, these materials also degrade in the long-term perspective due to several environmental factors, leading to a failure of these protective systems [3]. Consequently, it is common that the appearance, functionality or conservation conditions of metal artworks, are jeopardized by the presence of altered organic coatings associated to corroded underlying metal substrates, leading conservators to opt for cleaning and removal of both these detrimental features. The present work proposes an innovative multi-functional green gelled solution, able to tackle both corrosion and altered organic coatings simultaneously. In particular, the potential of a biodegradable complexing agent, namely ethylenediamine-N,N′-disuccinic acid (EDDS), is investigated for exploring the agent's suitability as a novel candidate for the removal of copper corrosion products present on brass and sterling silver collections [4]. In addition, the bio-solvent ethyl lactate is employed to tackle nitrocellulose-based films, which are mainly present on this class of metals in indoor collections. In particular, this contribution is aimed to show the results obtained from the multimodal analytical protocol performed on both formulation and surface of

treated metal samples, to evaluate the efficiency and the reliability of the newly designed gel. Colour, morphology and chemical composition, are examined before and after cleaning using complementary analytical techniques. Specifically, when focusing on the applied gels, X-ray fluorescence spectroscopy confirmed the successful complexing action of EDDS towards the alteration present on the metal substrates, corroborated by Raman and Fourier-transform infrared spectroscopies. The same spectroscopic techniques were also employed to ascertain the successful removal of both inorganic compounds and organic substances from the metallic surfaces. Assessment by Raman spectroscopy and electrochemical measurements, was performed to verify any potential drawbacks in the use of the developed formulation, also in the long-term, using artificially aged metal samples. Specifically, polarization resistance was examined by means of the agarose-based electrolyte method developed by the research group at the Centro Nacional de Investigaciones Metalúrgicas (CENIM) in Spain [5].

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A comparative study of confined aqueous cleaning systems for water-sensitive painted wood

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Keywords: Damascus Room, Cleaning, Painted wood, Gels, Technical study

Abstract

The Damascus Room at the Los Angeles County Museum of Art, serves as a case-study to evaluate the challenging cleaning of grime and soiling from water-soluble painted surfaces. The room, that dates to 1766, was recently reinstalled at the museum for the first time since its acquisition. The room was treated

over a two-year period from 2014-2015, prior to an outgoing loan and during this treatment the cleaning challenges of water-soluble painted wood became readily apparent. The wood paneling was stabilized, consolidated and mounted for installation, but could only be partially cleaned, due to paint sensitivity. Traditionally, the removal of surface soiling from water-sensitive surfaces has relied on petroleum-derived solvents, such as white spirits, xylene and toluene, often to minimal effect. In the last thirty years, conservators have moved towards aqueous chemistry confined to a dispersed phase in a surfactant-laden microemulsion, to more effectively clean delicate surfaces. Today, several rigid gels and viscosity modifiers have been adopted and/or developed for containment of tailored aqueous and solvent blends for targeted cleaning. This evolution has allowed for greater control and cleaning efficacy, but has also perpetuated a continued reliance on petroleum-based surfactants, polymers and solvents that have a known negative impact on our environment and on the conservator's health. As part of the GREENART EU Horizon Project, panels of the Damascus Room were reassessed to see if newly developed greener nanogels could provide a viable treatment solution for this type of material. This new comparative study looks at the use of aqueous cleaning solutions (pH-adjusted solutions with citric acid, DTPA and EDTA chelators) in different delivery systems. These systems include the traditional approach of cleaning fluid on cotton swabs, established methods, such as xanthan gum as a viscosity modifier and agarose as a rigid gel, as well as newer materials currently in development. These approaches were evaluated using non-destructive and micro-destructive techniques including digital microscopy and cross-section analysis, visible and UVF imaging, FTIR and colorimetry, to supplement the conservator's observations on working properties and efficacy.

Developing environmentally sustainable solutions for cleaning Edvard Munch's monumental Aula paintings: a materials science-driven multi-analytical methodology

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Keywords: µEDXRF, FORS, Canvas paintings, Soiling cleaning

Abstract

Both indoor and outdoor artworks are prone to airborne particulate matter deposition, which affects their aesthetical appearance and contribute to their degradation [1]. Therefore, the study of novel cleaning materials and methods on historical surfaces affected by soiling, deserves the ongoing and relevant research efforts. Edvard Munch's unvarnished monumental oil paintings in the Aula of the University of Oslo, are susceptible to physico-chemical alterations caused by indoor (and, formerly, outdoor) soiling [2,3]. For this reason, Munch's paintings have undergone several conservation campaigns and, fortunately, over the last 20 years, the soiling rate has been reduced [4]. However, particulate matter deposition continues to pose a threat on the Aula and the need for surface cleaning of the paintings remains [2]. VNIR-SWIR hyperspectral imaging was recently used to map cleaning tests on one of Aula's painting, Kjemi [5]. While this methodology showed promise for large-scale treatment mapping, direct detection of bands in the VNIR-SWIR associated with soiling components, was lacking. Consequently, significant post-processing methods were required to indirectly track soiling removal. The ENCLOSURE project aims to develop new sustainable cleaning solutions for painted surfaces and non-destructive methods to monitor their effectiveness [6]. In its framework, this work aims to improve the chemical evaluation of soiling removal by developing a reproducible, non-destructive, multi-analytical methodology utilizing micro-Energy Dispersive X-Ray Fluorescence (μEDXRF) imaging and Fiber Optic Reflectance Spectroscopy (FORS) in the VNIR-SWIR ranges. The goal is to make this methodology accessible, particularly to conservators who have access to such equipment (particularly, if portable), enabling timely on-site decisions regarding the effectiveness of cleaning trials. Tailor-made mock-ups of the Aula paintings, both unsoiled and soiled, were utilized in this study. Artificial soiling was applied to mimic weathering in the Aula and the mock-ups underwent controlled aging. μEDXRF and FORS data processing, supported by chemometrics, facilitated soiling presence monitoring and allowed the classification of canvas painting mock-ups based on materials used and aging procedures. FORS results, augmented by chemometrics, provided chemical signatures of soiling components, aiding a potential transfer of results to hyperspectral imaging. In the future, comparing the chemical composition of artificial soiling in mock-ups with soiling on the Aula paintings, would be valuable. This comparison will help uncover potential limitations in the analytical methodology due to chemical differences in the soiling compositions.

Acknowledgements

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Nonwoven electrospun mats and green solvents: progress in their development as new artwork restoration systems

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Keywords: Nonwoven, Electrospinning, Cleaning, Green solvents, Composite materials

Abstract

Electrospun (ES) nanofiber mats have found application in a broad range of technological fields [1]. Electrospinning is a versatile technique that allows the production of different types of materials, from the most straightforward nonwovens to composite mats (e.g., nanofibers and nanoparticles). Recently, we exploited the microporosity of these materials as support for gels or directly for solvents in the conservation field [2,3]. Indeed, we observed that the sorbent properties of these materials, allow them to effectively retain the solvents used for cleaning, while absorbing swollen/solubilized coatings by capillarity. The possibility of loading the ES nonwovens with several organic and inorganic additives, allows for conferring specific functionalities [4,5]. This work presents progress on developing new and sustainable systems for cleaning cultural heritage using ES mats and green organic solvents in the frames of the European project GOGREEN and the nationally funded project SUPERSTAR. Polyamide (PA) nonwovens coupled with dimethyl carbonate (DMC), were employed to remove dammar coatings from paintings. We observed that fiber diameter and pore sizes affected the cleaning efficacy. The paint absorption within the fabric is favored by capillarity, promoting a peel-off of the unwanted layer, which allows further mechanical surface treatments to be avoided. To meet the demands of sustainability and toxicity, polyamide was replaced by pullulan, a polysaccharide of natural origin [3,4,6,7]. The pullulan-

based system was further implemented by introducing photothermal nanoparticles into the fibers. This allows for an increase in the local temperature by irradiation, facilitating the solubilization/swelling of insoluble layers (e.g., reticulated alkyd spray paints, oxidized natural resins) and reducing the application time [8,9]. ES mats were extensively characterized in their physicochemical properties and optimized for application on model artwork samples. Ad hoc multi-analytical protocols were employed to study the systems' cleaning efficacy and mechanism. Then, when possible, cleaning tests were performed on sacrificial historical artworks, proving their suitability for actual conservation-restoration campaigns.

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Oral Session 12 – New approaches to cleaning: 2nd part

Investigation of non-contact cleaning of typical unstable sensitive cultural heritage materials from fire-born soot using atomic oxygen generated with the radiofrequency cold plasma at atmospheric pressure

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Keywords: Fire, Soot, Non-contact cleaning, Atomic oxygen, Green cultural heritage conservation

Abstract

Ever more frequent fires and wildfires linked to climate change and societal unrest, presage future challenges and the need for effective first-responder technologies for the remediation of fire damage and fire-born soot contamination. Fire-born aerosols and soot are among the most pernicious contaminants and major deterioration factors to all cultural heritage assets, which can quickly be affected on a waste scale. Soot particles are considerably smaller than pores in typical art substrates and will penetrate minor cracks and porosities. Soot's tendency to bond increasingly stronger to surfaces over time, requires an immediate cleaning treatment. However, cleaning soot with the available dry and wet cleaning methods, remains very complicated, due to the soot's miniscule particle size and the risk of disintegrating soot agglomerates into even smaller fragments, which may, therefore, get transported and ingrained in porous substrate, causing permanent change. Atomic oxygen (AO) offers exciting opportunities for non-contact liquid-free cleaning of fire-damaged cultural heritage materials, as AO rapidly reacts with soot and organic carbons, converting them into volatile species, mainly CO, CO_2, and H_2O. Atomic oxygen is found 80-1000 km above the Earth's surface in the outer space. Its use for the non-contact cleaning of fire-born soot and organic carbons from typically unstable, sensitive and porous substrates, offers a breakthrough solution. AO treatment was pioneered by Bruce Banks and

Sharon Miller at NASA in the 1990s, but their experiment was far ahead of its time and the research was left suspended at the concept stage, unavailable to conservators. Today, we understand better the potential of their groundbreaking work, but to bring AO to conservation, significant research and development are required, which is a work in progress by the MOXY project (2022-2026), funded by the Horizon Europe in the call to develop green materials and technologies for cultural heritage. This study experimented with AO for non-contact soot cleaning from several challenging substrates, such as gouache on paper, acrylic paints on cotton duck canvas, plaster gypsum, feathers, glass, high-polish metal, ceramics and glass. Representative soot soiling models were developed by exposing mock-ups to a fire-born soot aerosol, using a custom-designed soot generator, composed of a 90 cm tall and 60 cm in diameter metal cylinder, with a carousel for samples, where soot was produced at controlled conditions using a combustion process. In this study, AO was generated under atmospheric conditions by flowing He and O_2 in He, using radiofrequency field at 13.56 MHz. AO cleaning tests were conducted using an automated XYZ movement stage, custom-programmed for each material to move the AO generator nozzle to guarantee reproducibility. Soot was sampled and characterized by XRD and Raman spectroscopy. AO treatment was assessed using optical and 3D microscopy; surface morphology was assessed using SEM, microprofilometry and atomic force microscopy AFM; optical changes were assessed using reflectance spectroscopy and colorimetry; and chemical changes were investigated with ATR-FTIR microscopy, SEM-EDX and by evolved gas analysis coupled with mass spectrometry (EGA-MS). The results show the potential of innovative non-contact AO cleaning of diverse cultural heritage materials and the feasibility of developing a groundbreaking first-responder technology, which does not raise health or environmental concerns and that can be upscaled and used in synergy with the available cleaning methods. The results, potential and risks associated with AO technology, are discussed, emphasizing the need for innovative, green and sustainable treatment methods to empower the resilience of cultural heritage transitioning through climate change.

Study of the behaviour of pigments of different nature under laser irradiation: comparison between nanosecond and femtosecond domains

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Keywords: Pigments, Cultural heritage, Laser cleaning, Femtosecond, Nanosecond

Abstract

In the current context of global warming, atmospheric pollutants and greenhouse gases contribute to the formation of surface deposits on ancient wall paintings, which prevent their correct reading and compromising their stability. The deontological code for restoration of Cultural Heritage (CH) requires that the method used to remove these deposits respects the integrity of the pictorial layer and its structure. Therefore, there is a need to optimize cleaning procedures for these deposits, which will allow maximum removal without causing damages to the artwork. Among the cleaning methods used in CH, laser ablation is emerging as a technique, which can successfully remove these deposits without endangering the historical-artistic value of the pictorial layer. The scientific literature demonstrates the enormous influence on the response of materials used in CH, by some key parameters of laser cleaning, such as wavelength, frequency and pulse duration. Regarding this last factor, previous works showed that nanosecond (ns, 1 ns = 10-9 s) pulse durations, may induce photothermal and photochemical damages (such as oxidation or melting) and/or physical effects (colour modifications), whereas picosecond (ps, 1 ps = 10-12 s) or femtosecond (fs, 1 fs = 10-15 s) pulsed lasers, induce less photothermal effects [1]. The present study analyses the influence of the pulse duration (ns versus fs) on the response of several raw pigments used in tempera mural paints to laser irradiation, also evaluating, within each domain, the effect of different laser wavelengths. For this, two lasers were used: 1) a nanosecond pulsed Nd:YVO4 laser (Coherent AVIA Ultra 355-200) operating at 355 nm (ultraviolet region) and 25 ns of pulse duration, with a maximum pulse energy of 0.1 mJ and a repetition rate reaching up to 100 kHz; and 2) a femtosecond laser (Spirit system from Spectra Physics) operating at 1040 nm (near to infrared) and 380 fs pulse duration, in which a pulse rate can be selected from single shot to 1 MHz, with a maximum pulse energy of 40 µJ at 100 kHz. Seven pigments used on ancient mural paintings with different composition, were studied: carbonates (malachite, azurite and lead white), sulphides (cinnabar and orpiment), oxides (hematite) and a natural mixture of silicates and oxides (red earth). Pigment pellets were prepared in aluminium moulds and compacted with a 30-tonne pressure press. Irradiation methodology was based on an attempt to identify the range of safety fluences under which insignificant or no changes on the pigment were detected under the naked eye. Then, fluences greater than the safeguarding condition, were applied to the pellets to induce evident changes on the surfaces. Textural, physical and chemical changes of the irradiated surfaces, were evaluated by means of stereomicroscopy, colour spectrophotometry, hyperspectral imaging, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDS). The property that suffered the most change after irradiation, was colour. Thus, depending on the degree to which colour varied, pigments that were more or less resistant to irradiation, could be distinguished. The pigments most susceptible to laser irradiation were the two sulphides (orpiment and cinnabar); cinnabar, for example, experienced an intense darkening even at minimum fluence. The most resistant pigment, which barely suffered colour changes (undetectable by an experienced human eye), was lead carbonate. Sometimes, colour changes were associated neither with chemical nor mineralogical changes, but were, due to textural changes, identified by SEM. These results constitute the essential starting point to investigating the resistance to laser irradiation of tempera made with these pigments, which will allow to know the influence of the pigment-binder interaction on the response to the laser.

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Unveiling radiance: an analytical exploration of laser cleaning efficacy evaluation in contemporary mural restoration

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Keywords: Laser cleaning, Analytical methodologies, Street art preservation, Comparative analyses, Contemporary mural restoration

Abstract

In the realm of cultural heritage, contemporary murals and street arts are increasingly recognized for their accessibility, social impact and role as platforms for activism, making them vital components of modern urban landscapes. However, the conservation of these murals faces persistent challenges from unwanted graffiti and environmental wear. Recovering the original appearance of murals from undesired graffiti, is one of the most vital tasks in urban art restoration. The similarity of synthetic painting materials presents a significant challenge in cleaning these vandalized surfaces, without causing severe damage to the original paint layer. Addressing this complex intersection, we conducted an extensive investigation into the laser cleaning of synthetic sprays on both fresh and artificially aged mock-up samples, presenting a protocol for assessing the effectiveness and selectivity of laser cleaning on contemporary murals. In the context of the SuperStaAr project (Sustainable Preservation Strategies for Street Art, https://prin2020superstar.dcci.unipi.it/), this research incorporates four types of lasers, namely a Q-Switch, a Long Q-Switch, a Short Free Running (all three of them Nd:YAG) and an Active Fiber laser (Ytterbium-doped). In this initial phase of the project, we focus on presenting the results from the first two instruments. The Short Free Running laser has been proven unsuitable for cleaning synthetic paints in our experiments. The Active Fiber laser is currently under testing. This novel laser instrument has never been applied in the field of mural restoration and we will soon present results comparing it with other types of lasers. This study introduces a set of empirical criteria for evaluating the efficacy and possible induced damage of laser cleaning in murals conservation. Five parameters, including the presence of residues, surface roughness, color changes, cleaning effectiveness and pigment pickup, form the basis of a comprehensive assessment framework. Scores assigned by an expert evaluator facilitate a nuanced evaluation, providing a direct and practical insight into the performance of laser cleaning. The protocol is then validated by analytical methodologies. Colorimetric measurements reveal substantial color changes, particularly in samples with styrene-acrylic binders. Residues and effectiveness are investigated with micro ATR-FTIR and Py-GC/MS analyses. While FTIR delivered rapid results that generally correlated with empirical evaluations, Py-GC/MS exhibited superior sensitivity, providing detailed information on the ablated material components. Notably, we introduced a passive sampling system implemented during the laser cleaning process. This system, employing a thermally stable quartz fiber membrane in conjunction with a micro-aspirator, allows Py-GC/MS analysis without the need to sample directly from the artwork. Comparative analyses between Q-Switch and Long Q-Switch lasers, underscore their comparable efficacy

in cleaning vandalized murals, especially in the absence of styrene-acrylic binders. The ageing of the paint film does not significantly influence the effectiveness of cleaning. However, we observed that while the laser adeptly removes unwanted paint, it may erode the superficial layer of the underlying paint. This unveils a surface diminished in binder content, but enriched in pigments and fillers, which requires additional considerations for long-term maintenance. Beyond the immediate findings, this study provides a robust framework for assessing laser cleaning procedures. As laser cleaning technology continues to evolve in the field of cultural heritage conservation, the passive sampling system for Py-GC/MS stands out as a promising avenue, offering detailed insights into ablated material components, while preserving artwork integrity. The study sets the stage for future investigations into the behavior of anti-graffiti coatings under laser cleaning processes, promising continued advancements in the field of cultural heritage conservation.

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Oral Session 13 – New materials for conservation

Learning from Romans: when Vitruvian recipes became the inspiration for new technologies

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Keywords: Mosaic, Mortars, Consolidation, Compatibility, Innovative materials

Abstract

Aquileia is one of the most prosperous cities of the Roman Empire, where the abundance of materials and the exceptional craftsmanship converged to create exquisite decorative artefacts, such as floor mosaics. As reported by Vitruvius [1], Roman mosaics are constructed using a multi-layered system consisting of five different strata. This multi-layer structure, with high material heterogeneity within each stratum, poses a significant challenge for restorers. Traditional restoration methods involve the use of pastes to address damage in mosaic systems, including the consolidation of different strata e.g., grouting, filling of cracks and repositioning lost tesserae [2]. However, contemporary pastes utilized, like lime mortars mixed with acrylic emulsions [3], as well as cement pastes, are predominantly hydraulic or non-hydraulic. These pastes, while widely employed, are not specifically tailored to mosaic preservation. They often lack compatibility with the host material, resulting in only partial substrate repair and leading to secondary degradation effects. Compatibility is the key parameter to consider for defining the materials to use for restoration treatment [4]. This research centres around the development of novel mortar formulations intended for use in mosaic preservation. Their design is based on the results achieved by the analysis of mortars of Roman mosaics fragments and inspired by ancient recipes. The current trend towards greener and more sustainable building materials, has led to the renewed interest in using plant products as additives, drawing inspiration from antique solutions [5]. Therefore, we combine elements of mimesis and innovation of ancient technology, by introducing novel additives, such as natural gel into the ancient formulations, based on both literature records and characterization of archaeological pieces. The chemical composition of both the ancient materials and the formulated ones, was characterized through X-ray diffraction (XRD) and scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) analyses, confirming their complete compatibility. Microstructural features were evaluated using microscopic and colorimetric analyses. The performances of the prepared mortars were assessed through slump test and rheological test of mortar in the fresh state. Additionally, analyses of compressive and flexural strength, water absorption tests and evaluation of the surface hardness of hardened mortars at different curing times, were conducted. Primary results show the enhancement of workability, thanks to the use of natural gel, minimal colorimetric change, modification of strength and

water absorption induced by additives. These findings not only extend a warm invitation to delve into ancient techniques for discovering innovative functional products, but also align with the current trend towards environmentally friendly and sustainable building materials.

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The UNESCO site of Cefalù Cathedral (Sicily) as a pilot site for the application and study of innovative conservation interventions

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Keywords: Conservation, Intervention, Mosaics, Innovation, Geopolymers

Abstract

Cefalù Cathedral entered the UNESCO World Heritage list in 2015 [1] (UNESCO Worlds Heritage Convention). It was built under the Normans and is famous for its magnificent Byzantine mosaic, considered one of the most beautiful in Italy. The mosaic apparatus is currently undergoing an extensive conservation intervention by Piacenti S.p.A. It is in this context of the highest historical, artistic and cultural value, that the present study is set, with the aim to develop substitutional materials, eco-sustainable and compatible with the original ones. For this purpose, alkaline-activated materials, better known as geopolymers, are implemented. The versatility of these materials makes them suitable for various applications on polychrome surfaces, as shown by recent studies in the field of conservation, with

different functionalities [2] in sites of great historical and artistic relevance as the Monreale Cathedral [3]. The present study is divided in two steps: in situ colourimetric analysis of original materials and laboratory experimentation, followed by characterization of the new ones. Thanks to the collaboration with Piacenti S.p.A, it was possible to carry out several surveys to identify missing parts in the huge surface of the mosaic apparatus. At the same time, an in situ campaign of colourimetric measures was conducted on the original tesserae to identify the colour coordinates of the very wide range of colours used. Various formulations of pigmented geopolymers were studied in the laboratories of the University of Catania. The commercial metakaolin (ARGICAL™ M-1000, provided by IMERYS, France), whose use is frequent and was already tested as seen in the literature [4], was selected as the geopolymeric precursor, mainly because of its light colour. Different kinds of commercial inorganic and organic pigments, were directly added into the geopolymer mixture in different percentages (1, 3, 6, 9 and 12%) in order to synthesize preliminary products. Both raw materials and geopolymers were characterized through a combination of spectroscopic (Raman spectroscopy, FTIR-ATR, DRIFT) and diffractometric (XRD) techniques. Geopolymers also underwent colourimetric analysis at regular intervals, compression tests after a month of curing and chemical and physical stability tests, with excellent results in terms of pigment stability in alkaline environment and surface homogeneity. Among all the materials made, it was decided to select for the application tests those which, after a curing time of 28 days, showed colour coordinates more similar to the original tesserae and consequently a minimal colour difference. Once a good aesthetic and material compatibility was assessed, we proceeded with the application of the pigmented geopolymer tesserae on the mosaic apparatus, with an excellent result in terms of aesthetic performance. It now appears necessary to monitor the conservation intervention in order to ensure its long-term success.

Acknowledgements

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Exploring eco-friendly antimicrobial solutions for cultural heritage stone conservation

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Keywords: Essential oils, Green, Stone conservation, Biodegradation, Antimicrobial effect

Abstract

Stone materials can undergo several degradation phenomena, which can be triggered by atmospheric, anthropic or even microbiological factors. When it comes to preserving cultural artefacts, these factors shouldn't be underestimated, since they can be the initial stage of a series of more complex degradation phenomena, which could potentially result in a definitive loss of the artwork. In the restoration field, numerous antimicrobial products are commonly employed and a large amount of them already exists. However, a significant drawback is that many of these products contain hazardous and toxic components, posing risks to both the operator and the environment, particularly when proper disposal of the cleaning water is neglected. While collecting washing water is a relatively straightforward process for small objects, when it is a façade or monument that needs to be cleaned, most of the time the water is just left flowing into the ground. Another main issue, concerning the environmental sustainability of the restoration procedures, is the need to re-apply the antimicrobical product quite often so to maintain the surface free of dangerous microorganisms, hence having an economical and product higher dispense. This study involved the characterization and examination of different natural extracts, with the aim of acting as antimicrobial products against a broad spectrum of microorganisms. We focused on two essential oils, namely *Origanum Compactum* and *Thymus Vulgaris* and the vegetal extract of limonene. Both the essential oils and the limonene are derived from herbs and plants highly diffused in the Mediterranean area and were, hence chosen, due to their sustainability and widespread availability. Concerning the microorganisms to be employed in this study, we focused on fungi collected from real-case sites, both from where a microbiological attack was evident and from where biodegradation was still at its early stage. The microorganisms were isolated and their growth inhibition was tested in the presence of the previously presented natural extracts. Tests have been carried out both in vitro and directly on the stone surfaces of some marble mock-ups. Additionally, scanning electron microscopy (SEM) analyses were performed to investigate the bio-receptivity of the mock-up with the selected microorganisms. During this study, both essential oils demonstrated a significant inhibitory effect in contrasting fungal growth. Particularly, the most promising results were achieved with the essential oil derived from oregano, which exhibited high efficacy even at low concentrations. On the other hand, the vegetal extract of limonene, did not show positive outcomes and was, therefore, considered unsuitable for this application, within the chosen experimental conditions. Concluding, in this work it was possible to investigate greener alternatives to commercial antimicrobial products in the restoration of cultural heritage stone materials.

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Oral Session 14 – Applications of Spectral Imaging techniques

Application of hyperspectral imaging to evaluate cleaning methods for corroded glass

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Keywords: HSI, SWIR, Glass corrosion, Cleaning efficiency

Abstract

Glass cleaning is a complex field in conservation, facing the challenge of removing the corrosion products, while minimising further corrosion. Conservators' responses to our survey show that there isn't a "universal" method for cleaning glass objects. Water, ethanol, acetone and/or mixture of them, are often used, however, the solvents' proportions, sequence and mode of application differ from one conservation laboratory to another. Moreover, very few papers exist dealing with the documentation of the cleaning process and the assessment of its efficiency [1,2]. Hyperspectral imaging (HSI) is a non-destructive and non-invasive imaging technique, acquiring images at contiguous wavelengths to obtain reflectance spectra over a large spatial area [3]. Its application in heritage sciences has mainly focused on the characterisation of pigments in paintings and manuscripts [4-6] and the identification of chromophores in glass [7-10]. Recently, HSI in the short-wave infrared range (SWIR) was successfully applied to detect corrosion in transparent glass objects. The study shows that the water and OH- bands at 1410 and 1906 nm can be used for the documentation of glass corrosion and its temporal evolution [11,12]. In the present paper, we explore the use of the HSI methodology established by Babini et al. [11] and Sharma et al. [12] to evaluate the efficiency of several "conventional" and "exploratory" cleaning methods, based on the use of several solvents and different application methodologies. Cleaning tests were performed on artificially corroded potash-lime silicate glass. Normal photographic documentation and hyperspectral Images in the SWIR domain, were acquired before and after cleaning. Data evaluation should allow the selection of the most suitable cleaning method(s) for glass conservators.

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Silver/dyes decoupling and colour restoration of autochromes using multispectral imaging

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Keywords: Autochrome, Multispectral imaging, Colour restoration, Image preservation

Abstract

The Lumière Autochrome was patented in 1903. It is considered the first commercially successful colour photography process, whilst autochrome plates are held today in a range of museum collections internationally. The process comprises a glass plate on top of which sits a colour filter made of

microscopic starch granules dyed red, green and blue and a panchromatic silver gelatine emulsion. The extreme light-sensitivity of these photographs causes the fading of their colours. Autochromes are also susceptible to damage from humidity and moisture, causing dye bleeding and silver layer alteration. Being a glass-based process, they are prone to cracks and fracturing. Because of this sensitivity and fragility, only facsimiles should be displayed in public institutions. Therefore, it is necessary to develop non-invasive tools and methods that enable new ways for public access. We intend to make use of the possibilities offered by multispectral imaging to reconstruct the original colours of autochromes. Our case-study comprises of 44 autochrome plates from the collection of the Victoria and Albert Museum, London (V&A), which have been already digitized with standard colour imaging. Due to the light sensitivity, no further imaging is allowed by the owning institution. To test a novel colour restoration method, we purchased a test autochrome plate from a private collection to undergo multispectral imaging and, if required, other invasive analyses. This "sacrificial" plate serves to refine our pilot imaging and processing methods and to assess light-induced damage caused by multispectral scanning, potentially shaping new guidelines for autochrome imaging. This effort aligns with the broader PERCEIVE project, an international collaboration aiming to recover lost or altered artwork colours, creating new ways for the perception, preservation, curation, exhibition, understanding and access to Cultural Heritage collections. The colour restoration approach leverages the layered structure of autochromes, comprising two primary overlapping elements: the uniform colour mosaic pattern and the silver-based emulsion containing the photographic image. Dye fading takes place over time, while the photographic emulsion is comparably more stable. As a result, prolonged exposure to intense illumination tends to cause a loss of colour vibrancy, although the image contrast, for which the silver particles are responsible, remains preserved. The dyes constituting the colour mosaic are transparent in the near infrared, while the absorbance of the silver-based photographic image extends in this electromagnetic region. Therefore, infrared imaging allows capturing the photographic image without the absorption of the colour mosaic. A multispectral image is captured using an imaging system with magnification high enough to resolve the individual dye granules (around 10 microns), encompassing the full transmittance information of the autochrome plate in the visible and infrared range. More precisely, we use a camera equipped with a macro-lens with a 5X magnification and a 61-megapixel full-frame sensor. An image-processing technique will be developed, combining the information of the infrared and the visible images in order to separate the silver signal from the rest of the multispectral information, thus obtaining the transmittance information of the sole colour mosaic. The absorbance of the faded colour mosaic can then be numerically increased to reinstate its supposed original colour. By recombining the restored mosaic and the photographic image, a digital representation of the unfaded autochrome, can be displayed. This endeavour will result in a practical methodology developed from the insights gained through the multispectral imaging approach. This methodology will be employed to transform the existing RGB images of V&A autochromes into rejuvenated digital versions, intended for public exhibition.

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A combined study using MSI (Multi Spectral Imaging), HSI (Hyper Spectral Imaging) and chemical analysis to study pigments in ancient art

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Keywords: HSI (hyper spectral imaging), MSI (multi spectral imaging), Pigments

Abstract

Multispectral imaging (MSI) and hyper spectral imaging (HIS) are powerful tools in art analysis [1,2]. They are very simple, low-cost techniques that do not require special skills to be understood. In some specific cases, this kind of techniques turned out to be very powerful methods in order to disclose the chemical nature of pigments. MSI is a non-invasive imaging technique with which images of an illuminated object are captured using ultraviolet, visible and infrared light, allowing the identification of features that are imperceptible to the naked eye. HSI technique allows for a two-dimensional, pixel-by-pixel acquisition of the reflection spectra of a surface, thus allowing a mapping of the pigments present. This approach has been applied to study an Italian painting dated to the beginning of the 15th century. For the pigments identification, the results obtained by MSI, HSI and by colorimetric measurements (reflectance spectra in the visible range), were compared on the painting and simultaneously on Kremer color charts, used as a reference. The use of false-color images (IRRG and IRGB) also helped in pigment identification. Thanks to these comparisons, it was possible to highlight the presence of cinnabar, red ochre and azurite. In addition, some pigments applied during later interventions, such as Prussian blue, were identified. The presence of these pigments was confirmed by Raman analysis [3] using a portable spectrophotometer. Spectra were acquired despite the presence of 19th-century varnish applied to the surface of the painting, which, however, was partially removed duriHiang the restoration. Finally, micro-destructive analysis was performed on some samples for the purpose of identifying the nature of the binder and to investigate the possible presence of dyes, such as indigo. In fact, on the basis of the HSI analysis, this pigment was identified in correspondence as green (thus added to a yellow) and showed a reflectance spectrum similar to that of both synthetic and natural indigo. However, only LC-MS analysis on a micro-sample would allow establishing the exact nature of the dye. In conclusion, the combined approach, including imaging and chemical analysis techniques, both non-destructive/ in situ and micro-destructive analysis, allowed the reconstruction of the artist's palette and the identification of repainting.

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POSTERS

Challenging assumptions about the Sløkkefri drinking horn; a multidisciplinary exploration

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Keywords: Drinking horn, Cultural history, XRF

Abstract

This contribution presents a thorough investigation of the Sløkkefri drinking horn, currently featured in the "HERITAGE" exhibition at the Museum of Cultural History. The project addresses the limited scholarly attention this artifact has received, aiming to bridge existing gaps in knowledge about drinking horns in Norway: the majority of the 58 registered drinking horns at the Museum of Cultural History, remains understudied. Employing a multidisciplinary approach through historical, art historical and material science perspectives, the authors tried to illuminate the origin, alterations and cultural significance of this unique artifact. The study involves the cultural history methodology, building upon past research and employs non-invasive techniques to re-examine this artifact, seeking to expand our understanding and uncover new perspectives on the horn's historical significance. Foundational to our inquiry is previous research, notably Sigurd Grieg's studies [1,2]. Through these methods, the study scrutinizes the horn's original design and attempts to shed light on its evolution over time. Additionally, it aims to contribute to a broader conversation regarding the cultural significance of such artifacts, beyond their conventional use. Hereby, we report the critical examination of the Sløkkefri drinking horn, which identified modifications and later additions contradicting Sigurd Grieg's suggestion that the horn could have been earlier adorned with medieval "claws" instead of wheels. Moreover, the holes were made after the terminal was coated, suggesting sequential mounting, thus differing from Grieg's hypothesis about the concurrent existence of pendants and terminal. Additionally, the X-ray fluorescence (XRF) analyses are challenging Sigurd Grieg's claim of medieval bronze mounts, revealing brass and older pewter plated with brass. Both visual and instrumental analyses refute Grieg's timeline, emphasizing the horn's complex evolutionary history.

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Copper soaps formation in verdigris-linseed oil painting mixtures: a multi-spectroscopic characterization

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Keywords: Verdigris, Metal soaps, Linseed oil, EPR, Raman

Abstract

Copper acetate (also known as verdigris) is a bimetallic Cu(II) greenish pigment widely used in oil paintings. Since ancient times, this pigment was known as a degradation-prone compound, especially when combined with lipidic binders [1]. However, the degradation mechanism and the involved species have not been disclosed yet. In this project, we study verdigris interactions with linseed oil in painting mock-ups stressing out the formation of copper-based complexes and proposing reaction routes. Such complex systems are studied applying a complementary multi-spectroscopic approach: a combination of Continuous-Wave (CW) Electron Paramagnetic Resonance (EPR) [2,3], Electron Spin Echo Envelope Modulation (ESEEM)[4], Raman [5] and Attenuated Total Reflection (ATR) Fourier Transform infrared (FTIR)[6]. Based on the experimental evidence, we propose the following mechanism: the neutral copper acetate shifts to a basic verdigris promoting triglyceride hydrolysis, aided by the coordination of Cu(II) cations towards the carboxylic functions. The increased amount of free fatty acids in the mixtures, triggers the formation of monomeric Cu(II) complexes. Afterwards, the oil polymerization reaction occurs and secondary oxidation species, containing OH groups in the alkyl chain, act as further ligands for copper nuclei. This is the first time, at the best of our knowledge, that a comprehensive view is proposed.

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A comprehensive study on cadmium soaps in oil painting mock-ups

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Keywords: Cadmium soap, SEM-EDS, µ-FTIR, SR-µ-XRPD, GC/MS

Abstract

The formation of metal carboxylates in oil paintings is a well-known issue and has been one of the most recurrent topics in conservation science research for 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 through 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. First, optical Microscopy (OM) and Scanning Electron Microscopy (SEM) - Energy Dispersive spectroscopy (SEM-EDS) were performed both on the paint surface and on cross-sections of the mock-ups, to visualize and monitor the formation of cadmium soaps and study their morphology and distribution in the paint film. 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 [3]. Following this, X-Ray Powder Diffraction (XRPD) was used to gain information on the crystalline phases in these metal soaps, to complement the spectroscopic data. To obtain a more comprehensive and detailed identification and distribution information of the formed crystalline structures, Synchrotron Radiation based µ-XRPD mapping (SR-µ-XRPD) was performed within the Historical Materials block allocation group (BAG) [4]. Cadmium soaps, characterized by diffraction peaks in the low angle 2θ range (1°-4°), were detected as large globules in over the surface SR-µ-XRPD maps. Furthermore, their presence was confirmed in the cross-sections as well, demonstrating their formation both on the paint surface and in depth of the paint. Analyses of the free fatty acids and metal soaps by Gas Chromatography / Mass spectrometry (GC/MS) through two analytical steps, was also

carried out. The results obtained by this research call attention to one of the causes of the appearance of cadmium soaps, together with the possible formation of cadmium oxalates, laurates, myristates, palmitates, stearates and arachidates in oil paintings. Furthermore, it demonstrates that oil paint containing cadmium red and/or yellow aged by LED lighting systems, exhibited larger, more protruding soaps and a greater average distribution of them compared to those aged by halogen lamp or natural light. This research offers a better understanding of recurring metal soap formation in oil paint systems and could potentially become useful for the further development of adequate mitigation and long-term oil paint preservation strategies.

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Synthetic binder identification without sampling? Results from preliminary studies with microscopic and spectroscopic methods

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Keywords: FTIR, Binding media, Non-invasive testing, Paint analysis, Modern materials

Abstract

The use of synthetic resins in paints as binders dates back to the late 1920s. From this point onwards, artists began to use industrial paints containing synthetic binders, often appearing on the market. Synthetic paints became particularly popular in the early 1960s following the introduction of acrylic emulsion paint [1]. The variety of paint types used by 20th-century artists has important conservation implications, as their response to particular treatments and storage conditions is highly diverse. Awareness of the types of modern binders present in works of art and knowledge of methods for their effective identification, is becoming increasingly significant as contemporary paintings created with synthetic paints, increasingly require conservation. Two techniques routinely used to identify binders of modern paints are Fourier transform infrared spectroscopy (FTIR) and pyrolytic gas chromatography with mass detection (Py-GC/MS) [2]. However, both these methods require taking a sample from the painting and, unfortunately, getting approval for such action is impossible in some cases. Hence the idea

of exploring alternative research methods for the non-invasive identification of synthetic binders in paint layers, was born. Paint samples based on acrylic, alkyd, nitrocellulose and polyvinyl acetate resins, were prepared for research. The surfaces of the paint films were observed using a Hirox digital microscope to find the characteristics of each polymer class. In addition, the paint binders were examined using a FTIR spectroscope equipped with a fibre optic probe. In this configuration, no sampling of the object is required. The obtained data was compared with the results from the analysis using a conventional FTIR-ATR spectroscope. Furthermore, the samples underwent accelerated ageing and were examined again. The study also involved the determination of the colour stability of the paint samples through measurements made with a spectrophotometer before and after exposure to ultraviolet radiation. The study identified the changes occurring in time in the spectra and the appearance of the examined paints. Moreover, the possibility of non-invasively identifying paint binders with the Hirox microscope and FTIR spectroscope with a fibre optic probe, is discussed.

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Application of non-destructive techniques to evaluate the image of Our Lady of Good Health

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Keywords: X-Ray fluorescence, Digital radiography, Non-destructive analysis, Polychrome wooden sculpture

Abstract

In this work, the pigments, ground layer and the structure of Our Lady of Good Health, a Portuguese polychrome wooden sculpture from the 18th century, was characterized using X-ray fluorescence and digital radiography techniques. Radiographic images were acquired using a transportable X-rays, model ICM CP120B from Teledyne and flat panel detector, model DXR 250U-W, from General Electric. XRF measurements were performed using a Bruker Tracer-III SD Portable, which has an X-ray tube with

a rhodium target and a Si PIN diode detector, operating at 40 kV and 60 μA. Through XRF analysis it was possible to detect the elements: Ca, Ba, Cr, Ti, Mn, Fe, Cu, Zn, Au, Hg, Pb and Sr and characterize the pigments used in painting. The varied and rich polychromy is composed of lemon yellow, chrome yellow, strontium yellow, yellow ochre, massicot, zinc yellow, red ochre, litharge, vermilion, chrome red, viridian, brown ochre, sienna, umber, azurite, Prussian blue, manganese blue, copper phthalocyanine, calcite, lead white, zinc white, titanium dioxide white and gold foils. In the regions where there were restorations, it was possible to identify the presence of the lemon yellow, strontium yellow, lithopone, titanium dioxide white and zinc white, indicating that these processes occurred from the 19th century onwards. Radiographic analyzes revealed details, such as the glass eyes, fixing and repair nails, restoration regions and a hook at the top of the sculpture's head. Some nails have a modern appearance and the presence of the hook indicates that the sculpture has undergone a restoration process.

A multi-analytical study on two International Gothic paintings

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Keywords: ED-XRF spectroscopy, FORS, NIR reflectography, Pigments, Underdrawings

Abstract

Two panel paintings from the International Gothic period were analyzed to study and compare the materials and the techniques used for their realization. One painting, the Mystic Marriage of Saint Catherine of Alexandria (Siena, Pinacoteca Nazionale), is attributed to Michelino da Besozzo, while the attribution of the other, the Madonna of the Rose Garden (Verona, Museo civico di Castelvecchio), is still debated, with some art historians ascribing it to Stefano da Verona and others to Michelino da Besozzo. Michelino da Besozzo, was a great protagonist of the International Gothic style in Italy. He worked in Lombardy under the patronage of the Visconti dukes and he was celebrated by humanists at the time, particularly as an excellent master of drawing. The paintings were analyzed in situ by means of energy dispersive X-ray fluorescence spectroscopy (ED-XRF) and fiber optics reflectance spectroscopy (FORS). Near infrared reflectography images of the Madonna of the Rose Garden, were also acquired. The combined use of ED-XRF and FORS allowed the identification of the pigments used for the realization of the two paintings. The two palettes confirm the high quality of both paintings and the use of precious pigments, such as lapis lazuli, cinnabar and lakes. The near infrared images of the Madonna of the Rose Garden revealed several underdrawings, which were related to some model book drawings by Michelino and his workshop [1]. The comparison of the pigments used for the realization of the two paintings, together with the study of the underdrawings, provided a strong support to the attribution of the Madonna of the Rose Garden to Michelino da Besozzo.

Acknowledgments

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Application of FTIR spectroscopy technique for studying seals of the Santi Quattro Coronati Complex (Rome, Italy)

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Keywords: FTIR spectroscopy, Seal, Sealing wax, Spectral analysis

Abstract

The seals served as markers to ensure the authenticity of a document and explicitly indicate its potential validity or alteration [1]. The production of seals evolved over the centuries, beginning with the use of beeswax, progressing through the 11th century with the introduction of coloring substances, i.e. lead oxide. By the late 16th century, sealing wax had replaced beeswax [2]. During the excavations of the Quattro Santi Coronati complex in 1996 [3], written fragments of paper and parchment with four red wax seals, were found from various stratigraphic units. The excavation focused on the tower area where, roughly between the 16th and 17th centuries, the first floor had been used as a rubbish dump [4]. In this study, we utilized FTIR spectroscopy to analyze the seals and examined their spectra. Pre-treatment was applied to infrared spectra, exploring various strategies [5]. Our focus was on identifying differences that could reflect changes in production materials and similarities among the seals in different stratigraphic units. The seal analyses provided results that enhanced our understanding of the sample's nature, adding valuable information to the interpretation of the written fragments.

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Non-invasive techniques applied to the study of pigments used by Joan Miró in his paintings on canvas

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Keywords: Miró, Non-invasive techniques, XRF, Pigments, Palette

Abstract

Joan Miró (b. 1893, Barcelona; d. 1983, Palma de Mallorca) was a Catalan artist with a highly productive artistic career. Miró had an enduring interest in experimenting with materials and different artistic disciplines, such as painting, drawing, engraving, sculpture, ceramic and tapestry. A large number of these artworks are, at present, in The Fundació Joan Miró, which opened to the public in 1975 in Barcelona. Miró's desire was to create this centre for the study and research of his work and of contemporary art in global. This research has the main objective to analyse the pigments and filler materials employed by Miró in his paintings. Until now, little attention has been paid to the artist's painting technique and while some technical studies have been carried out on specific artworks, a comprehensive study of Miró's technique as a whole, is still lacking. A detailed summary of art-supply

brands and a chronological list of colours, grounds and canvas types cited by the artist himself in written sources and interviews, have been recently reviewed and gathered by the authors [1]. Nevertheless, it is the first time that many of Miró's paintings (more than 30) covering all his artistic periods (1914–1978), have been studied. Non-invasive techniques, such as X-ray fluorescence (XRF) and Raman spectroscopy, have been used to study the aforementioned group of paintings. The chemical results from this research allowed to identify the pigments used by Miró in his paintings. Results are presented in comparison and dialogue with the chronological list of materials cited by Miró in his personal notes and written sources [1]. Furthermore, this study allowed the grouping of the used materials based on his artistic period, studio location and availability of material. Finally, all this information is of paramount importance as a tool to better understand and act on the pathologies observed in Joan Miró artworks and to design conservation, storage and exhibition strategies for his paintings.

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Discovery of a composition on the reverse of Train du Soir (1957) by Paul Delvaux

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Keywords: Paul Delvaux, Imaging, Ma-XRF, Infrared reflectography

Abstract

As part of the project on the technical study of the works of Paul Delvaux, a Belgian Surrealist painter known for his dreamlike and enigmatic compositions, the painting Train du Soir (Evening Train) from 1957 belonging to the collection of the Royal Museums of Fine Arts of Belgium (RMFAB), was studied in situ with imaging methods (high-resolution photography, infrared reflectography, X-Ray radiography) and non-invasive analytical techniques (MA-XRF and Raman spectroscopy). This composition deals with one of the artist's favorite subjects, a railway station. On its reverse, a composition is hidden under a thick layer of white paint, as revealed by infrared reflectography. Unlike the front painting, the composition of the reverse deals with a subject much less known to the artist: 'Ancient Egypt'. Indeed, out of all his painting work, only one oil painting represents it, the La Légende Egyptienne (The Egyptian Legend) from 1953. The characteristic outline of the hidden composition, leaves no doubt about its painter. In addition, a Paul Delvaux's drawing book dated to 1953 and now belonging to the

RFMAB collection, contains the sketch of the discovered painting. Considering all these elements, an understanding of the process of creation, elaboration and destruction of the painting by Delvaux, will be discussed in this presentation. Furthermore, a virtual colorized reconstruction will be proposed, built based on the infrared reflectography, the elemental information provided by MA-XRF analysis and the microscope examination of the painting surface.

The V&A portrait of Marie Antoinette by François-Hubert Drouais uncovered: materials and conservation

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Keywords: Non-invasive analysis, Oil painting, Marie Antoinette, François-Hubert Drouais

Abstract

Most visitors exploring the Europe Galleries at the Victoria and Albert Museum (V&A) in London, can easily overlook the portrait of Marie Antoinette, by François-Hubert Drouais. The wide and eclectic range of objects and media displayed in the Galleries, can easily distract the eye of the visitor, who will pass by this important oil painting unaware of one of the most recognisable, controversial and influential queens in European history. This relatively small portrait (circa 63×52 cm unframed) was painted in 1773, when Marie-Antoinette was still the Dauphine of France. At the time, she was already married to the heir apparent to the throne of France, the future king Louis XVI, but was not yet queen, as Louis would ascend to the throne only the following year. This portrait is, therefore, one of the few surviving depictions of Marie Antoinette as a teenager. As such, its scientific and technical investigation is considered to be especially desirable. V&A scientists, conservators and curators arranged the study of the portrait to unveil its secrets. The investigation began with a combination of visual observation and research into the portrait's conservation history. The use of visible, raking-light and ultra-violet illumination photography, highlighted areas of interest. High-resolution digital microscopy followed, allowing to capture the state of the pictorial surface and make a note of both the brushwork and any past conservation interventions. Infrared reflectography highlighted the location of the areas where the original paint layers are missing and XRF scanning allowed to uncover details of the materiality of the painting of one of history's greatest fashion icons. Comparisons of both iconography and attire and composition and technique, were made with other portraits of Marie Antoinette, especially the larger portrait of her, painted by Drouais in the same year (Musée Condé, Chantilly) and the tapestry created after this portrait.

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Unraveling the mysteries of the 15th century masterpiece Saint Vincent Panels: a characterization with Raman Spectroscopy (in situ and micro)

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Keywords: In situ campaign, Micro-Raman spectroscopy, Mobile Raman spectroscopy, 15th century polyptych

Abstract

The Saint Vincent panels, painted by the Portuguese artist Nuno Gonçalves (c. 1450 - 1491), is a 15th century polyptych consisting of six paintings. These panels are of high symbolic importance for the Portuguese culture. Originally, the panels were believed to be part of the altarpiece of Saint Vincent in the chancel of Lisbon Cathedral. The painting, in which 58 people are depicted, represents the Portuguese society in 15th century centered around the double figuration of Saint Vicent. Such a group depiction is quite unique in the European painting history [1], highlighting once again the importance of this painting. Nowadays, the six panels are displayed in the Museu Nacional de Arte Antiga (MNAA) in Lisbon. As this painting is quite unique in its kind and of great importance for the Portuguese culture, it is more than evident that the panels are under extensive research to reveal its mysteries and to restore the masterpiece to its original state. This is the aim of 'The Project of Study, Conservation and Restoration of Saint Vincent Panels', sponsored by the Millenium BCP Foundation. This interdisciplinary study is led by three Portuguese institutions renowned in the cultural heritage field, i.e. Museu National de Arte Antiga (MNAA), HERCULES Laboratory of the University of Évora and José de Figueiredo Laboratory. The research has a twofold approach, namely the analysis of the surface and the support of the painting, as well as the material characterization of the painting layers. For this, a vast array of techniques is used including visible and standard light photography, UV fluorescence photography, X-Ray radiography, Infrared (IR) reflectography, IR macrophotography, X-Ray fluorescence (XRF), liquid chromatography-mass spectrometry (LC-MS), scanning electron microscopy-energy dispersive X-Ray spectroscopy (SEM-EDS), Raman spectroscopy (micro and mobile in situ instrumentation) and micro-Fourier Transform Infrared Spectroscopy (FTIR). The application of all these (complementary) techniques will no doubt increase the knowledge about this 15th century masterpiece, as well as the work of Nuno Gonçalves. In

the study presented here, the results obtained with Raman spectroscopy during an in situ measurement campaign of the panels are discussed in regards to the material characterization of the paint layers. In addition, micro-Raman spectroscopy was used for the characterization of microsamples taken during the mobile campaign.

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Paints from palettes – crucial starting point for the paintings research – the case of Jerzy Duda - Gracz (1941-2004)

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Keywords: Modern paints, Palette, Non-invasive methods, Authentication

Abstract

Jerzy Duda- Gracz (1941-2004) is one of the most important painters commenting everyday life and its absurdity under the oppression of the communistic power in the post-war Poland. His big monographic exhibition in 2016 at the Centre of Contemporary Art in Torun, was an opportunity to investigate his paintings. The other fortunate situation was the contact with the artist's wife and daughter that enabled further examinations of his four palettes, from which samples of paints were taken. More than 100 measuring points on palettes and on extracted samples, were executed. XRF measurements were followed by microscopic examination in ViS and UV light, as well as with Hirox digital microscope. Further data was gained using chromatographic analyses on samples. XRF allowed to distinguish non-invasively a significant number of hues of numerous colours on more than fifty investigated paintings. The research has revealed some coloristic habits and characteristic features, which can establish an invaluable tool in the identification and authentication of this popular and commonly falsified artist. It has also shown the value of connecting research executed on paintings with that on the palettes, allowing to fully characterize the paints and identify them later on paintings, often non-invasively,

thus broadening the conservation and research toolkit and supporting studio practice recognition. This approach does not use new methods [1,2], yet, especially in the case of contemporary artists, there is often access to their studios and paintings materials, where a richness of data can be collected, without further sampling from the actual painting, but just by starting with tubes and palettes [3,4]. Whilst pure historical paints from palettes are fully investigated also with destructive methods, it allows the possibly of nearly non-invasive identification of paintings. Following this protocol would protect the objects themselves, allowing extraction of rich information without sampling. Stressing this methodology and using accessible artists' studio materials, strengthens routines favouring non-invasive approaches for the identification of modern and contemporary paintings [5].

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Understanding physical-chemical degradation processes in Antonio Saura's oil paintings on canvas

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Keywords: Saura, Physical-chemical degradation, Spectroscopic analysis, Molecular analysis, Multiband imaging

Abstract

Certain contemporary oil paintings display signs of deterioration, due to various physical and chemical mechanisms. These changes affect the paint film's properties, both in terms of mechanics and dimensions, stemming from interactions with the binder and pigment that can be also influenced by external agents. This article focuses on the study of five oil paintings by Antonio Saura from the Contemporary Art Collection of "la Caixa" Foundation. Antonio Saura (1930-1998) was a Spanish Informalist painter who used, as other coetaneous artists, a limited color palette -black, gray, white and browns- and an independent painting style. Since the late 1950s he exhibited internationally in the Venice Biennale, Kassel Documenta and museums such as the Guggenheim and MoMA. The five artworks of this study were painted with black and white oil paint between the 1950s and 1960s. These paintings exhibit evident localized degradation issues, such as delamination, cracking and alligatoring on selected areas. Different type of crack patterns were observed mainly on the dark areas, but also in some localized white zones. To comprehend these degradation mechanisms, global analyses were conducted alongside an initial exploration of the pigments utilized by the artist. The primary aim of this investigation was to understand the materials employed by Saura in the five chosen case studies and identify similarities and differences among them while documenting the execution technique and existing issues. The examination of these artworks was performed in two stages. In situ non-invasive and micro-invasive campaigns were carried out to identify the artists' materials, to correlate the pigments used on each painting with the different crack pattern, as well as to obtain a final overall comparison among each crack pattern-pigments from the five paintings. For this purpose, multiband imaging evaluation combining trans-illumination in the visible (TI), reflected ultraviolet (UVR), luminescence induced by ultraviolet radiation (UVL), ultraviolet false color (UVFC), infrared photography (IR), infrared transirradiation (IRT), visible induced luminescence (IRL or VIL) and infrared false color (IRFC), were carried out to differentiate the artists' materials and to document surface alterations at a macroscopic and microscopic level. In addition, technical photography, digital portable microscopy and UV-Vis-NIR reflectance spectroscopic technique (FORS), were also used to characterize the investigated paintings and to gain an insight into materials and failure mechanisms involved behind the observed surface alterations. By means of a flow diagram, a joint reading will be presented, allowing the mapping of certain pigments, verified by the spectroscopic response for each case-study. The technical study included the use of elemental and molecular techniques for a more comprehensive understanding of the painting materials, the degradation products and the damage phenomenon.

Acknowledgments

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What do we learn from a mock painting: a case on X-ray fluorescence mapping and technical photography

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Keywords: X-ray fluorescence mapping, Technical photography, Mock painting, Non-invasive techniques

Abstract

Non-invasive techniques, such as imaging, X-ray fluorescence, Raman and fiber optic reflectance spectroscopy, have proved to be useful and preferred methods in the study of historical works of arts and cultural heritage for the identification of the artist's materials and techniques. The information obtained is not only essential in the conservation and restoration processes, but it is also valuable knowledge from an artistic, historical, cultural and archeological perspective. There are many examples of non-invasive scientific analyses, which reveal information which cannot be obtained visually. However, there is still information that cannot be obtained, possibly due to the limitation of the analytical techniques. In this work, we investigated the strengths and limitations of technical photography and X-ray fluorescence mapping, in the analysis of materials and working methods in a mock painting made by an artist. A 210 x 297 mm^2 mock painting of a rabbit and a moon, called "Kiang Chan", was painted by the artist, who was provided with different pigment powders for red, yellow, blue, green, black and white. It was painted on canvas using tempera technique with gilding. Tamarind seed glue was used as a binder for the pigments and fig latex was used for gilding. The artist was advised to paint in layers and intentionally hide some information. The painting was first analyzed by technical photography including visible light, raking visible light, raking infrared, ultraviolet fluorescence, reflected ultraviolet and infrared photography. Areas with different gilding materials, imitation and genuine gold leaves, were differentiated. UV fluorescence photograph showed how zinc white was applied to create detail and dimension to the rabbit's fur. IR reflectance photography showed some of the underdrawings and the hidden signature of the artist. However, most of the hidden pictures and underdrawings were not seen, since they were hidden behind the blue color area. X-ray fluorescence mappings were performed using the M4 Tornado Plus and M6 Jet stream micro-XRF scanner. The elemental mapping results, successfully identified the pigments and gilding material used in each area. They also revealed all the hidden paintings, but not the underdrawings. The mapping of the lighter elements in the area, which was covered by pigment with heavier elements, resulted in shadows or absence of the signal, which can be explained by the lower energy of the secondary X-rays. This showed that not only the knowledge of the elemental composition of pigments, but also the X-ray fluorescence phenomena are important for the interpretation of the results. Due to the limitation of the detection zone of the M4 scanner, the painting was scanned twice, so to cover most of the area of the painting. Part of the hidden painting was missing, due to the incomplete scan of the painting. This was not a problem for the M6 scanner.

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Visualization of partial delamination of wax-resin linings by using active infrared thermography and THz time-domain imaging

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Keywords: Wax-resin lining, Paintings conservation, Delamination, Active infrared thermography, THz time-domain imaging

Abstract

Wax-resin linings are a kind of additional support used to reinforce damaged oil paintings for conservation. They are attached on the reverse sides of the paintings with wax-resin adhesives composed of mainly beeswax and resins. The lining method was frequently employed worldwide in the 20th century. In Japan, a number of oil paintings were treated using the method at the time. While many of them are well-preserved, a few of the linings seem to be partially coming off from the paintings. What highlights the possibilities of the delamination of wax-resin linings (such as bulges or deformation of paintings), is generally detected through visual inspection and palpation by conservators. Since the adhesive interface of lined paintings cannot be observed from the outside, if further treatment is required, the type of treatment required is normally determined based on the conservators' experience and presumption. Considering the situation, this study has attempted to not only find and locate the delamination of wax-resin linings, but also, observe the state of wax-resin lined paintings (that is, how wax-resin linings attach to or delaminate from paintings) by using scientific non-destructive examination methods. Oil paintings on canvases owned by The University Art Museum, Tokyo University of the Arts and The National Museum of Modern Art, Tokyo, which were treated with the wax-resin lining method decades ago, were investigated using active infrared thermography and THz time-domain imaging. These experimental methods have proven their effectiveness in detecting the delamination of wax-resin linings through a preliminary examination, using a mock-up lined painting [1]. In the resulting planar images, the delaminated areas of the wax-resin linings, were mapped. Much of the delamination was under the bulges or deformation of the painting. In one of the case studies, areas other than the delaminated areas (the ones where the lining was properly attached to the painting), were shaped like brush strokes. It is assumed that the lining adhesive was applied on the reverse side of the painting with brushes and was not heated enough to melt and impregnate overall. This suggests that the lining might not had adhered entirely to the painting when it was applied. Besides, cross-sectional images of the lined paintings obtained by using THz imaging, made it possible to observe the layered structure and each of the interfaces. These images disclosed the fact that the reverse sides of the paintings were not always flat and were detached from the linings, even if there were no bulges or deformation of paintings visible from the outside. If they were not flat when lined (although they might have been temporarily alleviated with the lining procedures), it would trigger the delamination of the linings. The resulting images also allowed us to distinguish whether gaps between paintings and linings, was just air or a filling with some type of material (such as wax-resin adhesives). Finally, after the investigation, the

accuracy of those two examination methods was verified through visual observation of the interface, when one of the linings was removed from the painting for restoration. In this study, it was confirmed that the partial delamination of wax-resin linings was visualized by using active infrared thermography and THz time-domain imaging in some case studies. The results allowed us to observe the state of wax-resin lined paintings and set up hypotheses on how the delamination of the linings had developed. It is expected that our findings would help suggest appropriate ways for treating wax-resin lined paintings, whose linings partially delaminate.

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Rediscovering the gilding layers from the 15th century Funchal Cathedral: combined in situ analysis by EDXRF with laboratory research

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Keywords: EDXRF, Gilding, Heritage, Non-invasive techniques, 3D scan

Abstract

The main buildings in the city of Funchal began in the 15th century, the golden age of Funchal's sugar trade. The construction of the Cathedral of Funchal began in 1493 and ended in 1517, when it was consecrated on October 18, in honor of the Blessed Virgin Mary, as it was done in all Portuguese churches at the time. Two of the main constructive and decorative features of this church, are the ceilings of the central nave, side naves and transepts in the Mudejar style. These are unique in Portugal, due to their size and characteristics, as well as due to the 15th Portuguese-Flemish altarpiece, which is the only one in the country still in its original location. The recent discovery of numerous gold leaf-covered elements inside the Cathedral of Funchal, the lack of historical information on the date of their execution and the existence of a record of two major campaigns of work on the church, which are

not described but reported with high costs, one in the 16th century and the other in the 17th century, raise the question of whether the gilding of the columns, arches and ceiling elements, were carried out at the time of the construction of the cathedral and the main altarpiece or later [1,2]. The aim of this project is to identify the materials, origins, period of execution and techniques used in the gilding, focusing on the preparatory layers and gold leaf of the various elements under study. The scientific approach combines in situ analysis by EDXRF of gilding decorations in the eight altars of the Funchal Cathedral and the analysis of micro-samples collected during MoLab campaign by optical microscopy (OM/ stratigraphic analysis), scanning electron microscopy-energy dispersive X-Ray spectroscopy (SEM-EDS), Raman spectroscopy (μ-Raman) and micro-Fourier Transform Infrared Spectroscopy (μ-FTIR). A deep understanding of the golden leaves' composition (including trace elements), thickness and size, combined with the techniques of artistic production in those sets, will introduce a new vision about the Funchal Cathedral, allowing further comparison with other European sets, and, therefore, possible statements about sequences of construction and, on the limit, the chronology of materials and techniques applied. The in situ campaign also included the 3D laser scanning of the entire set, including the recent restored ceiling of the church, that will also integrate the program of digitalization of cultural heritage buildings and masterpieces in Madeira. This research, which is part of the E-RIHS.pt - MoLab platform, together with the study carried out in 2013/2014 for the altarpiece, will provide in depth knowledge of the techniques and materials used in the gilding found at the Cathedral of Funchal.

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Detection, identification and mapping of organic binders used in ancient wall paintings by combined non and micro-invasive mobile spectroscopic techniques

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Keywords: Ancient wall paintings, Organic binders, Non and micro-invasive analytical techniques, LIF, FTIR

Abstract

Identification of organic materials holds significant importance in any conservation program involving wall paintings, as it enhances our understanding in terms of the employed painting techniques and adds valuable insights into the processes of mural deterioration. Moreover, the accurate identification of organic materials is essential for developing appropriate and compatible conservation interventions, particularly prior to consolidation and/or cleaning. As already highlighted in previous studies, several factors may limit the ability of the scientific instruments to accurately identify the presence of organic materials within the complex matrix of wall paintings: the low concentrations of the binder-to-pigment ratio (detection limits); the natural aging/degradation of the organic materials; the vast and porous wall painting system, highly susceptible to degradation and biological contamination; or the complex binder-pigment interactions (matrix interferences). This work outlines the results obtained within the artMAP project on formulating an effective analytical protocol based on non and micro-invasive mobile spectroscopic techniques for the detection, characterization, identification and mapping of key molecular species present in low amounts in ancient wall painting fragments. Up to this date, chromatographic techniques in various detection schemes have been the first-choice methods for the precise identification of organic materials. Despite their high sensitivity and selectivity, these techniques are destructive and require elaborate and time-consuming sample preparation steps, including the use of hazardous solvents. Moreover, given the large surface areas covered by wall paintings in general, best practices recommend a protocol of investigations that favors non-invasive methods (that could ideally provide a spatial distribution of the key chemical species), followed by micro-invasive investigations with minimal sampling carried out in representative areas of the investigated surface. In this study, we propose a green and cost-effective procedure based on a portable laser-induced fluorescence (LIF) system, integrated with Fourier-transform infrared (FTIR) spectroscopy. Specifically, starting from the aforementioned considerations, we developed a custom-made system for advanced fluorescence imaging and spectroscopy, which we used as a first step for remote non-invasive real-time diagnosis and mapping of the organic components, which may be present within the investigated samples. Based on the LIF measurements, which offer a first level of identification, representative micro-samples were taken from the surface areas of interest followed by a refined FTIR procedure (selective extraction method of the organic binder) in order to provide a second level of identification. This combined methodology provides a synergic effect, as the specific chemical identification of the organic components provided by FTIR, can be transferred to the whole painted surface, thanks to the imaging capabilities of the

LIF system, without the need for extensive micro-sampling. The proposed methodology was tested on demonstrative samples, as well as on several 2nd century wall painting fragments with preserved polychromy. The most important results obtained are presented and discussed in terms of sensitivity (level of information obtained: presence, type and nature of the organic compounds), limit of detection, precision and accuracy. The design and development of a spectral library, which facilitates remote identification and mapping of organic compounds in wall paintings, are also presented.

Layers of the past. Non-destructive investigations of the old wall paintings from Râmnicu-Valcea Episcopal Church, Romania

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Keywords: Hyperspectral Imaging, FTIR, XRF, LIF, Photogrammetry

Abstract

In the summer of 2019, during an intervention meant to replace the interior pavement of the 19th century Episcopal Cathedral from Râmnicu Vâlcea (Vâlcea County, Romania), remains from the brick walls of a previous smaller church, were discovered underground. The archaeologists found at a depth of approximately 1.5 m, the original ground level, paved with hexagonal terracotta tiles. According to historical references [1] these walls must have been part of the initial 14th century construction, later rebuilt and repainted in two different historical stages, namely 1576 and 1737. This information is sustained by the on-site observations, where three overlapped painted plaster layers, were highlighted. Two of these layers, placed at the middle and the top (latter interventions) and depicted slightly different, display the same decorative pattern, namely the theme of curtains, which was commonly found in the post-Byzantine iconography, at the lower register of the church walls. The original painting layer, placed directly on the brick walls, is visible only in some small areas. However, it is very different from the other two overlapped layers, depicting highly decorative floral motifs. As part of an emergence plan required by the church administration to document the discovery, a two-days campaign for data acquisition was facilitated on-site using the ART4ART mobile laboratory [2]. Photogrammetry was performed in order to record a high accuracy 3D model of the entire interior structure. SWIR Hyperspectral imaging data (950-2500 nm) acquisition was carried out with a close-up lens, on four fragments of mural painting, the only accessible areas. During the process of archaeological excavation, the microclimate and the water content of the soil in which these fragments were preserved for centuries, changed dramatically, leading to an advanced degradation of the wall paintings, causing lack of adherence and lack of cohesion between the component materials [3]. Small samples were collected from all three layers of the mural painting for microscopy cross-section, FTIR and XRF spectroscopy. For each of these layers, the results

highlighted a rich content of calcium carbonate and the use of traditional fresco pigments, such as iron oxides (mainly yellow ochre and red) and black carbon. On the top layer, characteristic technical features of a fresco painting, such as incisions made on the fresh plaster, preliminary drawing made with yellow ochre, slight traces of trowel marks and specific networks of thin cracks (as a result of water evaporation and contraction of the lime), were clearly visible, especially in ranking light. Although no traces of organic binder were found on any of the three layers of painting, additional mapping using a custom-made set-up for LIF spectroscopy, was performed in order to confirm the results. UV fluorescence examination was also performed on-site. All these results were integrated in a dedicated Web-based platform for 3D visualization of multimodal imaging and spectroscopic data [4], an alternative to H-BIM solutions.

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Multi-modal non-destructive investigation of the wall paintings of the Magdalen Chapel of St. Emmeram, Regensburg. A methodology to address the material complexity of a palimpsest

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Keywords: Wall painting, Palimpsest, Non-destructive, Spectroscopy, Imaging

Abstract

The Magdalen Chapel is a treasure part of the monumental church of St. Emmeram in Regensburg (Germany). It shows a unique palimpsest made of overlapping and unrelated wall paintings from four different painting phases simultaneously visible, dated between the 12th and the 17th centuries. At some point, the walls were whitewashed and only partially uncovered in the 1980s. Nowadays,

the fragmentary status of the wall paintings hinders their readability and poses queries about their conservation. To shed light on such complex artwork, a multi-modal in situ approach was used to identify the materials, understand the art techniques and research the degradation phenomena. The paintings were systematically investigated by a conservator-restorer and documented through photogrammetry, UV- and VIS- induced luminescence (UVL and VIL, respectively) and a visual observation mapping using metigo®MAP software. Moreover, non-destructive, complementary and portable analytical tools, such as a double-sensor hyperspectral imaging system with an extended spectral range (400-2500 nm) and a macro-X-ray fluorescence scanner, were complemented by punctual analytical tools, such as portable Raman and mid-infrared spectrometers. As a result, the figures of three saints hidden by the whitewash were identified and visualized thanks to the UVL images. VIL suggested the presence of Egyptian green as well as organic materials used for consolidation. Pigments such as goethite, hematite, caput mortuum, vermilion, minium and lead-tin yellow were identified by Raman spectroscopy. This technique was also crucial in confirming the presence of carbon black in black leaf-formed decoration elements, thus excluding the degradation of the Cu-based pigments identified by XRF in the same areas. Azurite and malachite were identified by XRF and hyperspectral imaging. No information about possible organic binders for the areas painted by means of secco technique was obtained using FTIR in reflection mode. To this end, further micro-invasive analysis will be carried out. The combination of the object investigation done by the conservator-restorer, mapping, technical photography and analytical results allowed the assignments of the individual painting phases and relative pigment palette, identification of later interventions and visualization of hidden layers. In particular, the chemometric evaluation of the hyperspectral data cube permitted the optimization of a methodology for the automatic selection of the different phases based on their material composition and their visualization. The information gathered using the multi-modal non-destructive approach will serve to implement a conservation strategy. Furthermore, a new concept for the access and readability of the Magdalen Chapel palimpsest by the general public will be developed.

A secret mural painting back to light inside the crypt of the Cathedral of Parma (Italy): discoveries and mysteries hidden behind a wall

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Keywords: Mural painting, Micro-Raman spectroscopy, Chrome yellow, Egg binder media, Beeswax

Abstract

Inside the crypt of the Cathedral of Parma (Italy), a completely unknown mural painting was found very recently, behind a wall. An intentional gap of approximately 12 cm was present between the wall and the painting. The wall is attributed to the 17th century, hiding and protecting the painting for centuries. No documentation was found on this work of art and, therefore, so the artist, as the people who commissioned the work, remain unknown. The painting, which can be dated between the end of the 15th and the beginning of the 16th century, depicts the Madonna enthroned with the Child in the center. On her right, St. Peter and St. John are present. On the opposite side, an anomalous, outsized scene, namely the Presentation of Mary in the Temple, is visible, with Anna and Joachim and the High Priest. The scene is the exact copy of the same episode painted at the beginning of 1400 in the nearby Ravacaldi Chapel. Before the restoration, an analytical campaign devoted to the identification of the painting materials (pigments and binders), finishing surface materials, plaster mortar and efflorescence salts, was carried out on sub-millimetric samples with a multi-technique investigation, by means of micro-Raman spectroscopy, Fourier-Transform Infrared spectroscopy (FT-IR) and Gas Chromatography equipped with Mass spectroscopy (GC-MS). Using FT-IR spectroscopy, the presence of beeswax was highlighted by the vibrational bands, due to methylene symmetric and antisymmetric stretching vibrations (at 2916 and 2848 cm^{-1}, respectively) and out of plane bending modes (at 1472 and 1462 cm^{-1}). Beeswax could have been probably used as a surface finish. The characteristic carbonate and silicate vibrational bands of the substrate, were also found. In the areas affected by efflorescence, the characteristic bands of gypsum were identified. GC-MS investigations revealed the presence of proteinaceous materials in the selected examined specimens. From the determination of the amino acid content, it was found that the proteinaceous fraction is due to the egg used as a paint medium. It was, sequentially, observed that several parts of this mural painting were made with a secco technique, using egg as a binder. A finish layer of the mural painting using beeswax, was also found. The pigments used in the whole palette were identified by means of Raman spectroscopy. Most of them are traditional mineral pigments, including very expensive ones, as cinnabar. The palette is very rich: many different pigments and organic dyes are used to obtain similar hues (e.g., several different blue pigments and dyes). The use of a secco technique was confirmed by peculiar pigments, such as azurite and malachite. Furthermore, mosaic gold, made of SnS_2, was also revealed. Degradation products from the alteration of Cu-based pigments, were observed (e.g., Cu-sulphates, Cu-hydroxy chlorides). In some points, unidentified organic dyes were found. Very interesting is the presence of chrome yellow ($PbCrO_4$), because this pigment was synthetized only after 1800. Its presence as natural crocoite is debated, due to the extreme rarity of this mineral. At the authors knowledge, this is just the third discovery of $PbCrO_4$ used as a pigment before 1800 [1,2]. Remarkably, the rich palette, including precious and rare pigments, underlines the extraordinary value of this work of art. These results are expected to be useful for the current investigations on the technique and identification of the creator of the mural painting of the crypt of the Cathedral of Parma.

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New perspectives for the inhibition of salt damages in mural paintings located in hypogea context: the case of Saint Augustine in the rupestrian church of San Pietro Barisano

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Keywords: Innovative materials, Salt damages, Salt's crystallization inhibition, Mural paintings, Hypogea

Abstract

This paper focuses on the first results of a research aimed at inhibiting the salt's crystallization on the architectural decorated surfaces; the latter was included as part of the conservation project on the fresco painting of Saint Augustine in the rupestrian church of San Pietro Barisano (Matera, Italy). This pilot area was chosen in the pictorial cycle of the Saint Canione's Chapel, as a case-study for on-site testing for the development and characterization of new materials for conservation treatment using salt's crystallization inhibitor products. The outcome of this study has contributed to enhancing the knowledge on crystallization inhibitor products, with a specific focus on the preventive conservation of mural paintings in rupestrian heritage. The experimental campaign was conducted first in the laboratory, in collaboration with the Material Testing Laboratory of the Istituto Centrale per il Restauro of Rome and the CNR-ISPC of Lecce and it was aimed to test the performance of two phosphonate products. Preliminary tests were conducted, in order to determine the optimal concentration of the products to be used with respect to pigments compatibility, as well as to identify the most suitable methodology for the product's application. Mocks-up in stone materials and painted plaster with different shades and colors, yellow ochre and carbon black, were selected in order to study the compatibility of the treatments with the original materials of the mural painting. The behavior of mortar samples, in relation to the treatments, was investigated by performing water vapor permeability test and water absorption test by contact sponge. Color changes, were assessed by colorimetry on samples of painted fresco mortar with two different shades, yellow ochre and carbon black. The latter was also used to investigate the effectiveness of the products in contrasting salt damage and preserving the pictorial films. For this purpose, salt crystallization tests, using sodium sulphate and calcium sulphate solutions, were performed and the effect of the salt inhibitors were evaluated by visual inspection and weight loss. The results obtained for each tested product, were compared and discussed. They encourage the in situ application of salt inhibitors treatments on the original mural paintings damaged by salts, as an innovative approach to the preventive conservation of this heritage, especially in hypogea contexts, where the salt source can hardly be removed. Finally, the product with the best performance was chosen

for the in-situ application. Some sample areas of the mural painting were selected for the treatment, in order to study the effect of the product on the salt damage processes in a real case. In these test areas salts were preliminarily removed during the conservative intervention and monitoring was planned after the application of the salt inhibitor product.

Insights into Leonardo da Vinci's *Monochrome* mural in the Sforza Castle of Milan. A non-invasive approach through model samples

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Keywords: Mural paintings, Model samples, Non-invasive testing

Abstract

The so-called *Monochrome* is a preparatory drawing painted by Leonardo da Vinci on the walls of the Sala delle Asse, in the Sforza Castle of Milan [1]. Together with the Last Supper, it is the only other preserved example of mural painting executed by Leonardo himself. In this study, a broad range of in situ and laboratory analytical techniques were applied to investigate the painting materials of the *Monochrome*, to further knowledge about the painting solutions experimented by Leonardo and get better insight into his painting techniques in the specific case of murals. A first step involved the collection of samples from the Sala to characterize the different painting components of the preparatory drawing and understand its painting technique. The analyses allowed to gain understanding of most of the materials and techniques involved, but still left some open issues. In particular, the nature of the binder and the possible presence of a primer on the plaster surface, were still uncertain. Therefore, a second step consisted of creating model samples, which would simulate the composition of the *Monochrome* for comparing with the real samples. This step became necessary, due to the fragility of the *Monochrome* itself, allowing only limited number of samples and, due to its partial alteration during the consolidation/cleaning works of the late 19th and 20th centuries, which sometimes compromised the correct readability of the original layers. To simulate the mural painting, model samples were set up by applying two layers of plaster, a coarser one at the bottom and a finer "intonachino" on top, on alveolar aluminium panels, commonly used as substrates for detached wall paintings. On top, different combinations of pigments, binders and primers were experimented as painting layers. The range of tested binders and primers included animal glue, egg yolk, linseed oil, ammonium caseinate, lime water and a "tempera grassa" [2]. A visual matching was conducted with micro and macroscopic observations. Then, a compositional matching was carried out by comparing micro-invasive and non-invasive analyses of the *Monochrome* and of the model samples. The selected techniques were SEM-EDS on collected samples and in situ portable FTIR measurements. Overall, the combination of laboratory and field-based analyses on both the *Monochrome* and the model

samples, allowed getting a complete framework of the painting materials and techniques. Two different types of carbon black were employed in black and brown areas, in the latter case in mixture with ochres. The painting layers were applied on the plaster with no ground layer in between and once the plaster had set. The comparison with the model samples proved fundamental to gain insight into the binder and the primer: at present, a plausible hypothesis is that the binder might be lime-based, with addition of organic (probably protein-based) substance. It also seems possible that an organic primer might have been applied on the plaster surface as a form of preparation, although a contribution to the detected signals of organic protein substance might also be due to transport phenomena from the whitewash, which covered the *Monochrome* for centuries. Further analyses on the nature of the binder and the possible primer are due to gain a better understanding of their role and features.

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In situ analysis method for discoloration of pigments and dyes in organic cultural relics based on microfading spectrometry

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Keywords: Pigment, Dye, Discoloration, Microfading spectrometry, SERS

Abstract

Calligraphy, painting and silk objects are the most representative organic cultural relics of the Chinese civilization and are important material witnesses for research on Chinese and world culture. Pigments and dyes as color carriers, are crucial attributes of these two types of cultural relics, reflecting vital information, such as pigment or dye raw materials, dyeing and finishing processes, as well as cultural and technological exchanges, which are indispensable in the value recognition, conservation and restoration of calligraphy, painting and silk objects. The micro in situ online evaluation of the fading degree of pigments on calligraphy and painting and dyes on silk objects, has always been a bottleneck and urgent problem in this field. Recently, microfading spectrometry has been broadly applied for

simulating accelerated photofading process and evaluating if the pigment or dye was susceptible to discoloration [1-3]. However, in most reported cases, although the color difference (ΔE) was provided, it was confusing how the faded color changed and what color it changed to. In this work, a data analytical strategy based on microfading spectrometry has been developed for elaborately evaluating the fading behavior of dyes, including characteristic spectral changes, fading kinetics, photostability and color change trajectory analysis. By using the developed method, the fading behavior of 6 typical calligraphy and painting pigments, and 10 typical textile dyes, was summarized. Additionally, in order to investigate the fading molecular mechanism of easily fading dyes, this study established a dual-mode strategy based on SERS and MALDI-FTICR-MS using core-shell silver nanoparticles for the first time, leading to precise identification and semi-quantitative analysis of mixed dye components [4]. Based on the above, two established methods, the fading evaluation and prediction of 12 dyed silk artifacts unearthed from the Kayakkuduk beacon site in Xinjiang, were studied. The results indicated that archaeological samples unearthed from different places from the same site, faded in a different way, with varied fading rate, manifesting that in-depth photofading behavior studies should be refined and that, only ΔE was not enough for these evaluations. Moreover, combined with the work on dye content analysis, the lightfastness of samples seems to be related to dye content. Summarising, this study will provide a basis for evaluating the color preservation status of these two types of cultural relics and provide scientific support for restoration and conservation.

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Unveiling the chemical signatures of 19th century and 20th century lead white: HR-XRPD, MA-XRPD and SEM-EDS analysis of commercial paints

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Keywords: Munch, Lead white, XRPD, Paint tube formulations, Winsor & Newton

Abstract

The pigment lead white (LW) has been produced since the antiquity and dominated the painter's palette until the 20th century. Therefore, it is present in nearly all European artworks and polychrome finishes created before WWII [1]. Its production method underwent significant changes during the industrial revolution, resulting in an inherently different pigment [2]. This did not only affect the rheological properties and the stability of LW, but might have also enabled chemical discrimination between the various LW types. Preliminary MA-XRPD experiments on historical paintings indicated a clear variation in the mass ratio of the constituting compounds of LW: cerussite, hydrocerussite and plumbonacrite [3]. This variation may assist in establishing 'pallet anachronism', a term referring to declining the authenticity of paint layers based on the identification of pigments that were not in use during the creation of the artwork [4]. Unlike traditional LW, industrial-age LW remains an understudied field. With its broad collection of Edvard Munch's historical paint tubes, the Munch Museum holds a crucial role in defining the chemical fingerprint of industrial-age LW used in modern artworks. Therefore, 23 of Edvard Munch's LW paint tubes were selected from 10 different manufacturers for chemical characterization and quantification with synchrotron-based high resolution X-ray powder diffraction (HR-XRPD). The particle size was investigated with scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS). In addition, the results were compared with macroscopic X-ray powder diffraction (MA-XRPD) analysis of LW paints in 20th century Talens paint sample booklets and Winsor & Newton paint tests. The chemical characterization of LW paints is paired with an investigation of LW production patents, in order to establish a potential correlation between newly developed production methods and the chemical signature of LW in paintings. This work presents the insights gained into: (a) which LW types were used in industrial-age artists' materials (1750-1940) and (b) which LW types can we expect in artworks by Munch (and his contemporaries), in order to better understand degradation phenomena concerning lead white in industrial-age artworks.

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Techniques for analysis of art pigments

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Keywords: Pigments, Art forgery, Raman spectroscopy, SEM-EDS

Abstract

In our forensic practice, we come across case studies that are focused on recognizing whether an object is an original art object or a forgery. Especially in art paintings, we use radiographic methods, like X-ray, as a basic technique. This method already helps us when comparing the questionable work to possible originals made by the artist, but also indicates whether it is the artist's painting technique or whether a different technique is used, e.g., pre-drawing and then filling in, a practice that the artist does not follow, etc. It is very easy to detect re-paintings. Also, high radiographic contrast can inform us about the pigments used. Analysis of pigments is an important part of forensic expertise for the evaluation of authenticity of artworks. Identification is based on similarities or differences in composition between materials detected in questioned artwork and samples, or information in databases of originals from artists. For non-destructive analyses, we mainly use methods like Infrared spectrometers or Raman spectrometers. Modern pigments and other materials are mostly prepared for commercial sale and are easy to use. We know according to analysis, that we can find big differences both in the trace materials, which these pigments contain (they carry them from current production) and the pigments' structure. We focused on cooperation with the National Gallery Prague for investigating artwork from the first half of the 20th century. In the project with the National Gallery in Prague, we embarked on a detailed analysis of the pigments that are currently on the market. We also obtained interesting information about the chemistry and structure of pigment materials from pigments prepared in the chemistry laboratory at the University of Pardubice, Czech Republic. Modern paints are mostly prepared by the

producer to be easily used by the artists. The composition of the paints relates to geological, mining and manufacturing processes and can be unique for each producer. Thus, information about variability and rarity of the composition of available artists' paints, is important for forensic experts and the history of pigments and their production. As part of an extensive project dealing with the detection of counterfeits, emphasis was placed on creating a unique database, relating to the specifics of the artist's painting techniques and the possibility of using period art materials. This significantly expanded the knowledge of art practice from artists of the 20th century and helped to collect a basic database of used art materials. This will make it possible to identify the artist's specific material features, which can be key for effective verification of the original or in the detection of counterfeits. One of the significant methods used to identify the materials used and in this area, especially the analysis of pigments, is X-ray diffraction. However, its significance is far greater than the mere identification of the analyzed material. For some pigments, it is important to determine the structure itself, as historic milestones in the production of these particular pigments. One potentially good feature may be the titanium white occurring in the two structural modifications (anatase and rutile) or Naples yellow, where Bindheimite or Rosiaite might be represented in its structure. The complexity of the issue requires interdisciplinary cooperation of the forensic field with the fields of analytical, scientific and restoration surveys of works of art. The correctness of the procedures and techniques developed, have been already verified in many cases involving controversial cases, which will be presented.

Acknowledgements

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Gouache or not gouache? Inside the "opaque" definition of body colour paintings

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Keywords: Gouache, Body colour painting, Painting technique, ER-FTIR

Abstract

Gouache (or body colour) is a painting technique made similarly to watercolour, but, besides gum Arabic, presents other agents (usually white pigments) added to obtain an opaque and reflective effect. The technique dates back to the 15th century and it can be found in many artworks across countries and centuries, up until the contemporary ones. In addition to the improved covering capacity of

gouache paints, the artists appreciated the final effect of luminosity, which was particularly suitable for illustrations and landscape paintings [1]. However, when looking more closely at the definition and use of the term "gouache", some confusion appears. First, the term can also indicate the resulting paintings executed with this technique. Moreover, it has often been used to describe any painting or detail with a resulting opaque appearance, regardless of the actual technique employed by the artist [2]. In this contribution we will discuss this historical misuse of the terminology and report the results from some analytical campaigns performed on some artworks, made by different artists between the 1920s and 1970s, belonging to the Peggy Guggenheim Collection in Venice. The study originated from a specific request by the Museum, which, thanks to non-invasive scientific investigations, can verify the techniques and materials of the works in the entire collection. The in situ analysis of the artworks was carried out mainly by external reflection infrared spectroscopy (ER-FTIR). In general, the contactless technique provided some useful pieces of information allowing to better contextualize the binding media and technical approach used by the artists. ER-FTIR investigations have properly identified the components of the gouache painted areas. Moreover, the analyses have also showed that, in some cases, a "gouache effect" was obtained by adding an inorganic white pigment to a non-polysaccharidic binder, confirming the potentiality of the contactless technique in discriminating the binder. In addition to the in situ analyses, the assessment of the contactless methodology was evaluated by comparing the spectra collected on reference materials by both ER-FTIR and micro-ATR and/or ATR. This comparison highlighted possible interferences arising from the thinness of the paint layer (i.e. the presence of substrate absorptions) and/or from the fillers used in the paper support. Overall, the possibility of discriminating different binding media and, at the same time, of detecting the inorganic materials issuing the body colour to the paint layer, makes ER-FTIR a suitable tool for identifying gouache according to its proper definition [3].

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High-performance liquid chromatography in an identification of colorants used in color layers of the paintings

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Keywords: HPLC, Red colorants, Paintings

Abstract

Organic colorants of both natural and synthetic origin are widely used for textiles, manuscripts and paintings. The correct identification of a colorant is of utmost importance, as it provides us with information about the history of the object and the culture that produced it. This work focuses on the identification of red colorants in paintings, which can be used for dating, especially in the case of synthetic dyes from the 19th or 20th centuries. Since samples from paintings are usually very small and the amount of colorants is low, precise methods are essential. Today, high-performance liquid chromatography is widely used to identify colorants in various historical materials [1]. Samples from paintings are usually insoluble in common organic solvents, such as methanol or acetone. Therefore, the first step of this project was to find the optimal way to dissolve the samples. The next step was to optimize the conditions of separation and measurement conditions for the UV-Vis and fluorescence detectors. In the first round of experiments, the pigments and pure colorants obtained from Kremer Pigmente, Deffner&Johann or Sigma Aldrich, were used. Several extraction, analytical and detection methods, were tested on a selected group of samples (about fifteen). The method that gave the best results was then used for all the samples studied. In the case of extraction, methods based on various acids (HCl [2], TFA, oxalic acid [3], formic acid) were used together with heat exposure and an ultrasonic bath to fully dissolve the sample. The experiments were performed using Agilent 1260 Infinity II chromatograph with DAD (1260 Infinity II Diode Array Detector WR) and FLD (1260 Infinity II FLD Spectra) detectors. The column used was Poroshell 120 EC-C18. For the mobile phases, either acetonitrile-water or methanol-water was used. The extraction by acid, namely oxalic acid, proved to be the best extraction method for natural pigments. The extracted sample was subsequently dissolved in methanol. Since the synthetic pigments are less soluble in methanol, other solvents, such as acetone or acetonitrile, were tested. For most colorants, the best separation was achieved by using a combination of water and acetonitrile. The UV-Vis spectrum was first measured in all the standards and the optimal excitation wavelength for fluorescence spectrometry was estimated and later adjusted based on the maximum absorption wavelength. A total of fifty types of red colorants were measured. After obtaining an extensive database of red colorants, several samples from actual paintings, were also measured. The results of these measurements were then compared to our database and the composition of the samples was determined.

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Revealing the synthetic organic colorants found in the artists' materials of the renowned Austrian caricaturist Erich Sokol (1933-2003) by MeV SIMS

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Keywords: Modern inks, Erich Sokol, Synthetic organic colorants, MeV SIMS

Abstract

This study presents the use of SIMS with MeV primary ions for the identification of the synthetic organic colorants (SOCs) found in the artists' materials of a renowned Austrian caricaturist, Erich Sokol (1933-2003). Since many SOCs are fugitive upon exposure to light, their proper identification is needed to plan an optimal conservation and display of the artworks. The original artist's materials from Sokol's estate, which are mostly inks kept in glass bottles, now belong to the State Collections of Lower Austria and are stored at the Kulturdepot St. Pölten. Forty-two bottles were selected based on color and the presence of duplicates or even triplicates, which signaled the predilection of the artists for their use. They consisted of liquid watercolors (Ecoline – Royal Talens) and acrylic inks (AeroColor – Schmincke, and ArtiColor – Rotring). The former are known to be dye-based, whereas the latter are pigment-based. However, the information provided by the manufacturers regarding the SOCs, which they included in their formulations, is rather scarce, as no older color charts could be found. The watercolors and inks were applied onto Japanese paper to create mock-ups that mimicked the real caricatures. Preliminary measurements were performed with MeV SIMS on twelve mock-ups to check whether both pigments and dyes could be identified. However, it has been previously proven that this analytical technique is efficient in the simultaneous identification of synthetic organic pigments (SOPs) present in artistic blends [1]. For more details regarding the benefits of MeV SIMS, see the abstract of Jembrih-Simbürger et al. Yet, regarding dyes, MeV SIMS was mostly used to identify the colorants from a single class, namely triarylmethanes, which are present in ballpoint pens [2]. Thus, only a few reference spectra were available for the evaluation. The analysis was carried out at the Ruđer Bosković Institute in Zagreb, Croatia, using 5 MeV Si^{4+} primary ions in positive- and negative-ion modes and following the set-up presented in Tadić et al. [3]. For the MeV SIMS measurements, small samples (inks or watercolors on paper) were removed from the mock-ups using a scalpel and then pressed into indium with a flat aluminum plate. The positive-ion mode proved to be efficient in the identification of the molecular ions and/or protonated molecules of SOPs in the analyzed acrylic inks. The evaluation was made using the reference spectra acquired on the pigment powders presented in Krmpotić et al. [1]. The molecular ion of Pigment Yellow 74, for example, could be detected at m/z 386 in one of the yellow inks from Rotring's ArtiColor line. The negative-ion mode seemed to be more adequate for the identification of the dyes used in the Ecoline watercolors, which were thus expected to be mostly anionic. This confirmed the

results in Zaffino et al. [4], who highlighted the predominance of acid dyes in the colors provided by Royal Talens. Our results show that MeV SIMS is indeed adequate for the analysis of watercolors and acrylic inks containing synthetic organic colorants, since we could identify most SOCs present in the artist's materials of Erich Sokol.

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Blended thitsiol/urushiol Asian lacquers: an in-depth multi-analytical study

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Keywords: Thitsiol-Urushiol lacquer, Ageing, μ-FTIR-ATR, THM-Py-GC/MS, PCA

Abstract

Thitsiol and Urushiol were often blended to produce lacquer for lacquerware imported to Europe from Japan in the 17th century [1]. Nowadays, new lacquer types based on that mixture are produced by the coating industry [2]. Despite the importance of Asian lacquers in Europe, there is a lack of scientific studies aimed at understanding their curing, (photo-)aging and degradation, which are of special interest to indoor collections. For this research and for the first time to date, blends of thitsiol with

urushiol were prepared in different mass ratios to study the aforementioned degradation processes with a multi-analytical approach, supported by chemometrics. Digital optical microscopy, optical coherence tomography (OCT) and color measurements, were employed to investigate stratigraphy, possible morphological changes and alterations in the appearance. In addition to these methods, this study included thermally assisted hydrolysis and methylation mode of pyrolysis, coupled with gas chromatography and mass spectrometry (THM-Py-GC/MS) and micro-Fourier transform infrared spectroscopy in transmission and attenuated total reflection (μ-FTIR-ATR) mode, to evaluate chemical changes. Such chemical variations in the different mixtures, were also explored by the principal component analysis (PCA) and hierarchical clustering analysis (HCA) of the μ-FTIR results (pre-treated with different approach). The specimens were cured 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 highlight the cause of the formation of specific micro-cracks at the surface level and the presence of oxidation markers for the thitsiol-urushiol blends. Degradation pathways can be proposed by analyzing the results from the different techniques used. Finally, the use of chemometric exploratory tools, such as PCA and HCA, has proven effective in distinguishing the different mixtures of these historically relevant lacquers.

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Identifying the dyes from Hauts de la Chapelle necropolis (13th century, France): a reflection on the challenges of transposing a characterisation methodology from model to archaeological textiles

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Keywords: Archaeological samples, Natural dyes, Raman spectroscopy, SERS

Abstract

The archaeological site of Hauts de la Chapelle, a mediaeval necropolis in southern France, provided a large number of textile fragments, including more than 30 pieces exhibiting red hues. The excavation of the necropolis, performed in 2020, benefited from a delicate and fine soil removal, which was partially carried out in the laboratory on the extracted fragments. From their discovery, the textiles have been left untreated and were only minimally cleaned. In this work, we focus on the characterisation of the preserved dyes at the origin of the colouration. In order to limit the invasiveness, the analytical methodology applied was based on vibrational spectroscopic techniques, with infrared and Raman spectroscopy, but also Surface-Enhanced Raman Spectroscopy (SERS) when necessary. Firstly, we approached these materials by infrared spectroscopy in Attenuated Reflectance mode (FTIR-ATR). The spectra obtained revealed the nature of the fiber and, in some cases, the presence of sediment from the burial environment. However, FTIR-ATR is not a suitable technique in detecting dyes when present in very low amounts. Secondly, the samples were analysed by conventional Raman spectroscopy using various excitation wavelengths, as this technique is usually effective in detecting colour molecules via resonance processes. Its major drawback is the strong fluorescence often present for these organic materials, which shadows the characteristic Raman signals. Nevertheless, alizarin was identified in 12 samples with an excitation wavelength of 458 nm. Considering this result in a mediaeval Mediterranean context, we attributed its presence to the use of madder. Therefore, for unidentified samples, we used SERS to increase the Raman signal using a plasmonic metal substrate. As can be seen in the literature, a classical SERS methodology based on Lee and Meisel's silver colloidal suspension, a plasmonic substrate was implemented. Even though this methodology worked on model fibers, it was not successful for the Hauts de la Chapelle archaeological samples. We have, therefore, decided to investigate other strategies for implementing SERS analysis to optimize dye detection in this context. This includes the use of new plasmonic substrates that can be encapsulated to limit invasiveness. These strategies were first developed on alizarin solutions and model fibers of silk, wool and cotton dyed with natural madder or alizarin, using several excitation wavelengths. After a systematic exploration of the best conditions for identifying the dye(s) used, the most efficient protocols were applied to historical samples. Furthermore, the pre-treatment of these complex ancient textile fragments with solvents or acids prior to SERS analysis, was also investigated. The difficulties in transposing these methodologies from model to ancient materials, highlight the specific features of archaeological samples, affected by various types of pollution and specific states of material alteration.

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Discovering the ancient artisan heritage of the Moroccan carpet

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Keywords: SERS, XEF, FORS, Carpet, Dyes

Abstract

Carpets, such as those from Taznakht, Chiadma or the Middle Atlas, are the livelihood of many families in rural Morocco. From a cultural point of view, the ancient know-how of "traditional Moroccan Zarbia" is a tangible and intangible heritage that must be preserved. However, nowadays, the wide availability of chemical dyes, in addition to the ease and speed with which they can be used in wool dyeing, have led to an increase in the use of these chemicals for dyeing to the detriment of the natural products traditionally used by artisans. It is, therefore, necessary to develop rigorous experimental-scientific research in natural dyeing in view of improving young women know-how in rural carpets craftsmanship and also, to preserve ancient carpets housed in the various museums while restoring. This work carries out applied research relating to the sustainable development objectives defined by Morocco. In particular, it implements scientific tools for the characterization of carpets dyed with natural dyes. It provides an opportunity for a systematic study of the Zarbia artworks, by means of non-invasive and non-destructive techniques: SERS, XRF, FORS, 3D Fluorescence and colorimetry, which can identify the natural dyes used, while SEM analysis can highlight significant differences or degradation phenomena in the fibers. Surface enhanced laser-induced breakdown spectroscopy (SENLIBS) has also been used to identify inorganic dye mordants. In this preliminary work, we have studied a selection of wool fibers collected from a selection of ancient carpets belonging to the Oudays museum in Rabat. The focus has been put on the yellow dyes representing the most challenging task of the research and, at the same time, being difficult to identify with a non-destructive approach.

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Reconstructing archaeological textiles from Dunhuang (China, 8th-10th century CE) – a focus on scientific analysis

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Keywords: Natural dyes, Archaeological textiles, Imaging, LC-MS, Silk Roads

Abstract

As part of a collaborative project between the British Museum (BM) and the China National Silk Museum (CNSM), three textiles from the BM collection (accession numbers: MAS.857, MAS.858 and MAS.876/877) found at the archaeological site of Dunhuang (China), were selected for study. The textiles are dated between the 8th and the 10th centuries CE and the aim of the project was to reconstruct these using original materials and weaving/dyeing techniques. The scientific investigation was aimed at obtaining all information necessary to attempt the replication. Analyses included colourimetry of the various colour shades, digital microscopy to measure the threads and their projection width, broadband multispectral imaging (MSI) and fibre optic reflectance spectroscopy (FORS) to map the distribution of the dyes and obtain preliminary identifications non-invasively. In addition, X-ray fluorescence spectroscopy (XRF) and scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDX), were respectively used to, identify the composition of the metal threads and to investigate the fibres and assess the presence of mordants. Finally, high pressure liquid chromatography coupled to diode array detector and tandem mass spectrometry (HPLC-DAD-MS/MS), was employed to identify the dyes at a molecular level. These included sappanwood (*Biancaea sappan*), safflower (*Carthamus tinctorius*), smoketree (*Cotinus coggygria*), Chinese cork tree (*Phellodendron chinense*), pagoda tree (*Sophora japonica*), gromwell (*Lithospermum erythrorhizon*) and indigo, in agreement with the use of typically Chinese dyes. However, the samite border of MAS.858 revealed the presence of the yellow dyes turmeric (*Curcuma longa*) and larkspur (*Delphinium semibarbatum*). This represents the first identification of turmeric in textiles from Dunhuang, whereas the presence of larkspur points to a Central Asian origin of this textile, in agreement with its Sogdian-style motif. Nevertheless, some dyes remain not fully identified, highlighting the need for more research. The identification of light sensitive dyes (safflower, sappanwood, Chinese cork tree, turmeric, etc.) suggested that the original colours of these textiles were significantly brighter, as confirmed when access to the back of the textiles was possible. Although the exact original colours are difficult to recreate, this information was considered during the reconstruction of the textiles.

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Early synthetic dyes: building molecular databases using historic sources of reference materials

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Keywords: Synthetic dyes, HPLC, Mass spectrometry, Database, Reference materials

Abstract

Identifying early synthetic dyes in cultural heritage artefacts, in particular textiles, is challenging for various reasons. During the decades following the first synthesis of mauveine in 1856, hundreds of new and diverse molecular formulations were rapidly developed and commercialized, often using a complex nomenclature. Some of these historic materials are no longer available on the market today and were in use for short periods of time, hence accessing reference materials for their identification is not straightforward. Nevertheless, molecular databases are fundamental for the unequivocal identification of these compounds. Furthermore, the degradation of these molecules can jeopardise their detection in historic objects that have been exposed to light, humidity and temperature fluctuations. For these reasons, around 300 textile swatches present in two historic books, were analysed by high-pressure liquid chromatography coupled to diode array detector and high-resolution tandem mass spectrometry (HPLC-DAD-HRMS/MS). The books are "The Coal Tar Colours of the Farbwerke vorm. Meister, Lucius & Brüning, Höchst on the Main, Germany – A General Part" published in Germany in 1896 and "A Manual of Dyeing: For the Use of Practical Dyers, Manufacturers, Students, and All Interested in the Art of Dyeing" by E. Knecht, C. Rawson and R. Loewenthal, published in England in 1893. The results allowed a molecular database containing more than 500 molecules to be created, as well as degradation pathways to be elucidated. Additionally, around 40% of the labels did not precisely match with the actual composition of the dyes used, thus raising awareness of the importance to characterise these materials before using them for research purposes. This database represents an important research tool. The dates of the first synthesis of early synthetic dyes are often known with precision, hence their detection can be used to refine the production date of objects. Additionally, their trade from Europe to the world and their adoption in artistic practices around the globe, is an active area of research.

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Microfade testing of aniline blue on silk: an investigation of its long-term light-fading characteristics

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Keywords: Aniline blue, Early synthetic dyes, Microfading test, Photodegradation

Abstract

Aniline blue is an early synthetic textile dye first synthesized in 1860, shortly after the discovery of other aniline dyes, mauve and magenta [1]. Despite being observed early on by historical dyers as fugitive [2], aniline dyes remained commercially viable in the late 19th century for aesthetic and economic reasons, until they were overtaken by technically superior dyes at some point in the early 20th century. It is, therefore, likely to find such dyes in historical textiles from the period [3,4]. Literature indicates that aniline blue is fugitive to light and conservators may encounter it in blue or bluish textiles combined with natural or other synthetic dyes [4,5]. In this study, the light-fading characteristics of aniline blue were investigated using both real-time ageing and microfading testing in order to gauge its level of sensitivity to light and to offer collection care recommendations. Model fabrics were prepared by dyeing silk with a modern aniline blue equivalent, following a dyeing recipe from 1885 [2]. Samples were exposed for six weeks to different lighting conditions representing museum environments to which historic textiles are likely to be exposed to (natural light through glazed windows and LED lighting in a conservation workroom and motion-activated LED lighting in object storage), as well as exposed to high levels of illumination (outdoor and indoor). Separate unexposed pieces of model fabric, were tested using a microfader. Weekly visual and instrumental monitoring of real-time aged samples, revealed significant colour changes caused by exposure to high levels of natural lighting. A perceptible change resulted from a combination of natural and artificial illumination inside a conservation workroom, while no significant change was observed after brief exposures to light in the storage room. Colour parameters measured using a spectrophotometer showed that all samples which underwent colour change, became lighter and more neutral, indicating fading. The same fading behaviour was observed during the microfading test simulating prolonged exposure to museum display lighting without UV. Intense illumination with visible light caused a subtle colour change ($\Delta E^* = 0.63$). However, the change continued progressively, without indication of stopping or slowing down within the duration of exposure. In a separate microfading test, the contribution of UV to photodegradation was demonstrated using UV irradiation, which resulted in a significant discolouration ($\Delta E^* = 7.32$) following a direction of change in colour parameters that is different from what was observed in both real-time ageing and irradiation with visible light only. Nevertheless, the observations from both techniques provide insight into the light-fugitive characteristic of aniline blue, which undergoes rapid fading from exposure to natural light containing high amounts of UV and slow, but progressive fading under visible light. It is recommended that the exposure of historical textiles containing aniline blue to light sources, especially those that emit UV, be kept as minimal as possible.

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The Poor Persons Purple. Investigations into a lichen Orcein dye from Norwegian domestic lichen

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Keywords: Lichen dyes, Dye identification, FTIR, Raman Spectroscopy

Abstract

What colors did the Vikings wear? In the mind of most, the palette of the past is one of muted earth-tones and dull browns. But what if the Vikings wore fuchsia? The dyestuff 'Korkje', a Norwegian Orcein dye, which can be produced from a range of lichens native to Scandinavia, have been found in Scandinavian archeological textiles dating back to 3rd - 4th century, whilst toll records in Norway show extensive export from at least the 14th century. The dye yields bright colors ranging from Barbie-pink to imperial purple. Mediterranean lichen purple, as substitute for the fabled Tyrian purple of antiquity, was revered by Theophrastus and Pliny the elder for its beauty. However, the dyestuff is fugitive, thus making identification often difficult. In order to investigate the properties of lichen purple produced in Scandinavia, dyed textiles were prepared according to the HART (Historically Accurate Reconstruction Technique) principles from domestic lichen of the *Ochrolechia* spp. These lichens, harvested in the area of Lista in southern Norway, known for its massive export of color-lichen in the 18th century, were turned into dye using fermented urine according to recipes found in Norwegian Sources dating back to the 17th century. The dyestuff was used to dye yarn and fabric to form a base for creating a reference collection for the identification of the dye through a multi-analytical approach. After dyeing, the dyed yarn was subjected to accelerated light ageing and the

colorimetric changes were recorded in order to evaluate deterioration patterns. Although fugitive fabric dyes are often imperceptible to the naked eye, due to extensive deterioration, traces of the dyestuff might be perceptible using advanced analytical tools. Using a wide range of analytical techniques, a database for future comparison was created. FTIR, Raman, HPLC and molecular fluorescence in the visible, were applied to both fresh and light-aged, dyed textile and pure dyestuff. This will shed light on the use of lichen dyes in cultural heritage by providing a database of analytical information, which will aid in the identification of lichen purple in both archeological and historical materials. In addition, knowledge of the aging processes of the dyestuff could help improve preservation efforts of fragile cultural heritage, such as textiles. The presented work is part of a Master's research project, conducted in the framework of the NorCol research group at the Museum of Cultural History (KHM), which focuses on the production, use and trade of natural dyestuffs and pigments in Norway from the Iron Age to modern times, as well as of the project TexRec, Museum of Cultural History, dealing with the textile artifacts from the Oseberg burial, funded by the Norwegian Research Council (project number 316268).

Oil media on paper: investigating the morphological and chemical changes of linseed oil-impregnated paper mock-ups upon ageing

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Keywords: Linseed oil, Paper, SEM, FTIR, Deterioration

Abstract

Books, archival material and works of art on paper, present specific types of damage, when the oil binders in oil paints and traditional oil-based inks are absorbed by the paper supports, such as discolouration, loss of mechanical strength and drop of pH. These problems have been recorded in diverse case studies, differing in intensity and extent, setting questions for the input of materials, paper and oil type. The combination of paper and oil could raise substantial concerns for the preservation of works upon ageing, since the condition of the oiled areas of the paper support may, deteriorate leading to local or overall fragmentation. A recent PhD research project involved the investigation of the changes in the optical, mechanical and chemical properties that occur on the paper–linseed oil system upon ageing, aiming to the interpretation of damage recorded on works of art and printed materials, due to absorption of oil into the paper substrate [1,2]. Results showed that linseed oil has the predominant role in the changes of the system upon ageing, but the pulp content of the paper has a significant input to changes development. Application of Transmittance Fourier-transform infrared spectroscopy (FTIR) analysis provided more

information on the chemical changes that occur upon ageing and the rate of deterioration, depending both on the linseed oil formulation and the types of paper. Analysis indicated that the presence of an alkaline buffer to the paper pulp, reduces the rate of deterioration, as it deters the formation of acids that are, possibly, consumed to formulate metal soaps of fatty acids [3]. Research also involved the study of the morphological properties of the system, to record the alterations that happen upon the deterioration of the system and support the changes in the optical and mechanical changes. SEM images demonstrated that the application of linseed oil after drying creates a united mass with the fiber net, while a film covers the surface of the impregnated paper, which gradually reduces into the fibre net upon ageing, exposing the fibres at the final stages. However, the rate and the extent of the reduction of the linseed oil, as well as the changes on the surface of the film and the evident deterioration of the system, differ between the sets of mock-ups impregnated, having first been prepared with three linseed oil formulations and three paper types. The results were supplemented by images of optical microscopy and digital microscopy.

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Insights into fluorescent paint conservation: a methodical research plan at LACMA (Los Angeles County Museum of Art)

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Keywords: Fluorescent paint, Mock-ups, Oil-based, Acrylic-based

Abstract

The Los Angeles County Museum of Art (LACMA), established in 1965, stands as one of the largest art museums on the western coast of the United States. Housing nearly 152,000 objects spanning centuries, genres, cultures and materials, LACMA is dedicated to collecting and presenting diverse works of art

that reflect the multicultural essence of Los Angeles. Among the various materials within LACMA's collection, fluorescent paint presents a distinctive conservation challenge. Research on fluorescent paints has focused on a comprehensive examination of daylight fluorescent pigments, exploring their chemical composition, spectral properties and the challenges involved in their display and conservation. Investigators have also considered the ethical and practical aspects of exhibiting a painted leather jacket by Castronovo under UV light, recognizing its potential to expedite the fading of fluorescent colors. To address the challenges faced by conservators in safeguarding artworks with fluorescent pigments, these studies, along with others, collectively aim to advance knowledge in the conservation and understanding of these unique artistic materials. They emphasize the importance of scientific analysis, ethical considerations and ongoing research, as crucial elements for developing effective preservation strategies. When developing a cleaning treatment or considering the removal of retouching, it is crucial to comprehend the potential surface changes to the painted layer. Given that over the years LACMA has acquired a variety of artworks containing fluorescent paints, mock-ups were created using pink and yellow, fluorescent paints, both commercially and laboratory prepared, featuring acrylic or linseed oil as the paint binder. The mock-ups were subsequently soiled and artificially aged. The study ultimately assesses the suitability of different grime removal approaches. The methods tested include more common or traditional approaches, such as dry cleaning and aqueous cleaning systems delivered using a cotton swab and compares these results with the same aqueous systems delivered using rigid hydrogels. The poster will discuss the experimental design and share some preliminary results.

Bast from the past: a crossed approach between ancient Egyptian and Andean civilization fibre processing

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Keywords: *Linum usitatissimum L.*, *Asclepias* sp., Cell wall mechanical properties, Ultrastructure, Bi-photon microscopy

Abstract

Bast fibres have been critical accessories in the evolution of human civilizations. In particular, their uses in fishing technologies, such as nets, traps or lines, as well as in naval gear, such as ropes, sails and sailors' clothing, have enabled mobility and livelihoods. Thus, the use and processing of bast fibres by pre-industrial societies, established the premises of development of cotton textile industry. Here, we compare characteristics of fishing nets from two distant, but almost contemporaneous groups in Predynastic Egypt and on the Peruvian Pacific coast at the end of the 4th millennium BCE, both preserved thanks to arid conditions. We observe substantially similar architectures in the fishing nets, though constructed using very different bast fibres: *Linum usitatissimum L.* (flax linen) and *Asclepias* sp. (milkweed) in the case of the costal Andean and groups, respectively. We examine how these two fibre types, despite having different morphological and ultrastructural characteristics, were used to produce similar fabric products using probably similar chaîne opératoire. Bi-photon and scanning electron microscopy are supplemented by 3D micro-computed tomography to investigate the unique architecture of the yarns and their individual fibres artefacts. These ultrastructural characteristics are discussed in relation to the mechanical performance of the fibre cell walls measured by atomic force microscopy (AFM). Our work demonstrates the use of state-of-the-art micro-spectroscopy techniques for archaeobotanical studies and uses fishing nets as new lenses to unravel the episteme and techne of fibre and textile production in the past.

Assessing the effect of minimally invasive lipid extraction on parchment integrity by artificial ageing and integrated analytical techniques

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Keywords: Parchment, Lipid extraction, SEM, FTIR, Mechanical properties

Abstract

Parchment, a historical writing material made from processed animal skin, has been widely used as a writing surface for manuscripts, religious texts, legal documents and other important writings, for over 2000 years [1,2]. As a result of this, parchment is a ubiquitous resource with millions of well-dated documents held in archives and library collections in Britain and elsewhere. Parchment is primarily composed of collagen, a fibrous, structural protein that is abundant in mammalian skin [3]. Among other components (mineral salts, water), which shape the material's response to ageing and environmental

conditions, parchment has been shown to contain a measurable lipid fraction [4,5]. Here, we recognize the potential for the stable isotopic composition of lipids within well-dated parchments, to offer insights into past environments and historical climate events. Until now, however, their extraction has necessitated the removal of fragments and soaking in organic solvents. Such an invasive approach is unsuitable for most documents, so a minimally invasive vacuum-aided extraction procedure was developed [6]. To apply this technique to historical documents, we assessed its impact on parchment integrity. In this paper, we evaluate the immediate and long-term effects of this newly developed minimally invasive lipid extraction method on parchment integrity. To do so, we performed multiple extractions on four sacrificial parchment samples, which were then subjected to mild artificial ageing to replicate natural degradation. Our assessment employed FTIR to monitor molecular changes, SEM to examine physical alterations and mechanical testing to understand material brittleness and stiffness. Our multimodal analysis did not reveal measurable changes in the structural, molecular or mechanical properties of the lipid-extracted parchment. These findings indicate the suitability of the minimally invasive lipid extraction method for historical parchment records, ensuring their preservation while enabling the analysis of organic constituents. This non-invasive approach, with minimal short and long-term impacts, ensures the future preservation of historic parchment records. By enabling the recovery of lipids non-invasively, we utilize their use as high-resolution recorders of historic climate and environment for the first time, paving the way for future isotopic studies of diet and precipitation.

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

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Keywords: Parchment, Collagen, Nonlinear optical microscopy, Polarimetry

Abstract

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, which 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 destructive. 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 artefacts 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 [2,3]. 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 (I2PEF/ISHG), 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 [4]. We first validate this method rigorously 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 I2PEF/ISHG 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 World War II [4].

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An insight to take away: palaeoproteomics reveals the original binder and modern contaminations in distemper paints from Uvdal Stave Church, Norway

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Keywords: Palaeoproteomics, Distemper paint, Binding medium, Uvdal Stave Church, Norway

Abstract

In this project, we examined two distemper paint samples taken from decorative boards in Uvdal Stave Church (1170 A.D.), Norway, employing palaeoproteomics. Our goal was to characterise the original binder and possible contamination of previous restoration treatments. Examining organic compounds present within paint samples, is analytically challenging mainly due to the degradation processes and complex matrix of the materials. Nonetheless, palaeoproteomics has demonstrated to be a powerful technique in studying protein contents derived from archaeological and historical contexts, especially by providing information about the biological source and species [1,2]. In the present study, we discovered cow collagen proteins (COL1A1, COL1A2, COL3A1), as well as cow keratins and Bovine fetal hemoglobin, suggesting the use of calfskin to prepare the hide glue. This is consistent with the instructions of binder production and resource allocation in the historical records of Norway [3]. We did not detect any protein corresponding to contaminations regarding previous restoration treatments [4]. However, we found other contaminants including abundant traces of human saliva proteins, along with a few proteins corresponding to oats and barley. Although the presence of saliva proteins might appear to be peculiar, using one's own saliva has been one of the most common agents for cleaning a painting's surface. Spit cleaning is still in practice, because salivary enzymes, such as amylase and lipase, can gently help break down surface contamination [5]. On the other hand, saliva could have been employed during preliminary examinations by restorers to test water sensitivity. However, saliva cleaning is not a common practice for the cleaning of wall paintings at NIKU. Therefore, we believe that saliva proteins most likely originate from the time of discovery to remove dust and dirt from the surface of the painting. However, it must be noted that the unexpected presence of saliva in the samples was problematic in interpreting the data, as highly abundant modern proteins can mask the recovery of lower abundance, endogenous proteins and, therefore, hinder the identification. This work highlights the need to fully consider contamination sources in palaeoproteomics and to inform those working with such objects, about the potential for their contamination.

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Mapping of deteriorations and biological factors using optical microscopy, multispectral techniques, SEM-EDS analysis and biological assessment on Greek photographic documents of the period 1938-1948

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Keywords: Historical photographs, Mapping of deterioration, Multispectral techniques, SEM-EDS analysis, Biological assessment

Abstract

The visual observation by the human eye is not sufficient to characterize the preservation state of historical photographs. The purpose of this study is to determine the conservation status of ten historical photographs of the period 1938-1948. These historical documents come from a ten-year unrest period (World War II and the Greek Civil War). They present a very poor preservation state and their fabrication seems to be below the standards of older or newer historical photographs. Mapping using non-invasive multi-analytical methods can give us capable, precise and useful results towards this direction. Multispectral imaging, macroscopically and microscopically, provide valuable information on both the materials and the fabrication technique, as well as on the preservation state of photographs. Microbiological analysis by swab plating on selective growth media and optical microscopy can reveal data for the biological

assessment of the objects. Finally, scanning electron microscope (SEM) using energy dispersion analyzer system (EDS) can yield important information both for the abiotic and biotic factors. Combining the above methods we could verify the active biological attack in suspected areas and identify the materials on which it has been developed. In this way, a damage mapping of the entire surface of each photograph is created, determining the different areas of deteriorations and the agents that have caused the damage. In this study, mapping of the damage was performed, by examining step by step the preservation state of the photographs in order to provide an evaluation of the biological attack. Results of multi-analytical methods showed a significant lack of materials and technical fabrication, making these photographs more sensitive to the various factors of deterioration. The photographs present poor preservation status and extensive biological attack, because they are more sensitive to the effects of environmental conditions. Thus, their substandard state of preservation can be partially attributed to their fabrication done during a very difficult and impecunious time, as the historical events of this decade were accompanied by many deprivations, both in Greece and in the European continent.

Lippmann interferential colour photography and the value of replicas for the understanding of the historic technology and its conservation

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Keywords: Lippmann interferential colour photography, Materials analysis, Mock-ups, Replicas, Non-invasive methods

Abstract

Gabriel Lippmann (1845-1921) presented the first true and permanent colour photographic technique in the history of photography in 1891. Almost immediately after the presentation, several photographers and scientists started to experiment and produced images using the Lippmann method. This fascinating technique depends on the standing wave phenomenon of light and does not require pigments or dyes. On the basis of historical records, it is estimated that several thousand Lippmann interferential colour images were produced. However, today, only a few institutions and collectors worldwide possess original examples of these rare colour images. The Lippmann colour plates appear in a variety of conditions and presentation forms, which significantly affect their vulnerability, permanence and viewing properties.

The Preus Museum – the National Museum of Photography in Norway – has a collection of 12 Lippmann colour plates made by two key pioneers of Lippmann photography: Richard Neuhauss and Hans Lehmann. In addition, it owns a unique historic collection with books, papers and objects concerning the Lippmann process. This collection forms the basis of a four-year research project initiated by the conservation department of Preus Museum. The project aims to investigate Lippmann colour photography in terms of its history and materiality, as well as its preservation and conservation challenges. The interferential colour photographs by Richard Neuhauss, Hans Lehmann, as well as the well-known German photo-pioneer and researcher Hermann Krone [1] and the inventor Gabriel Lippmann himself, are the focus of this research. Previous research has uncovered unknown properties of these rare photographic objects [2]. In this study, we focus on the value of the used replicas and mock-up materials, while investigating the materials, the deterioration, and damaging patterns of these sensitive and rare museum objects with non-invasive analytical techniques. The reasons behind the preparation of these replicas and mock-ups and their comparison to the original, will be illustrated. Finally, results of investigations conducted on original plates, replicas and mock-ups by Micro Energy Dispersive X-ray Fluorescence Imaging, Micro-Raman Spectroscopy, Micro Fourier-transform Infrared Spectroscopy, Fiber Optics Reflectance Spectroscopy and Hyperspectral Image Analysis, will be presented.

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Monitoring degradation and assessing the condition of plastics using spectroscopic methods

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Keywords: Plastics, Polymers, Non-destructive analysis, Condition survey

Abstract

Currently, the physical condition of plastic objects or plastic parts of objects that are part of art collections, is usually classified based on visual assessment. Such an assessment is highly subjective and does not always reflect the actual condition of the object [1]. For this reason, we focused on the possibilities of using non-destructive spectral methods in the assessment of the condition of plastic

objects. The possibility to determine the degree of degradation of objects based on spectral analyses, would reduce errors that may occur in visual assessment and would help to spot degradation early, ideally before degradation manifests itself externally. Determination of the degree of degradation using non-destructive analytical techniques, can greatly assist in designing the next course of action, setting storage conditions and helping identifying objects at risk. Spectral methods are an ideal option for this purpose as they offer the possibility of non-destructive analysis and are often used to identify plastic materials. The main aim of this work is to investigate the possibilities of using non-destructive spectroscopic methods in assessing the condition of original objects with the presence of plastics in the collections of memory institutions. Based on the results of a material survey in the Slovak National Gallery (SNG) and a literature search, several criteria were used to select the types of plastics from which model systems would be assembled. The selected plastic samples were subjected to accelerated thermal and light ageing, under defined conditions. The plastic samples were analyzed gravimetrically and by ATR-FTIR and Raman spectroscopy. The progress of degradation was monitored through detailed analysis of the measured spectra. For the ATR-FTIR spectra, the oxidation indexes relevant to the different types of plastics, namely hydroxyl index, carboxyl index and carbon-oxygen index, were monitored [2]. Simultaneously with the experiment with the model systems, the analysis and evaluation of the condition of real objects made of selected types of plastics in different states of degradation, was carried out. Moreover, real objects in the collections of the Slovak National Gallery were examined to record and evaluate the most frequent manifestations of degradation, emphasising the importance of a systematic approach to the description and characterization of degradation and its specific manifestations using methodological descriptions [3]. Our goal was to find a correlation between the external manifestations and spectral properties of individual types of plastics. The recorded spectra and characteristics of all analyzed samples were compared with each other to find correlations between the external manifestations and spectral properties of the different types of plastics and to evaluate the degree of degradation of the objects in the indeterminate state. The results are used for proposing a methodology for determining the degree of degradation of plastic objects made of selected types of plastics in the art collections of the SNG using spectral methods, thus improving the ongoing control of collection objects.

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Lifetime prediction of cultural heritage objects made of plasticized poly (vinyl chloride)

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Keywords: Plasticized poly (vinyl chloride), Artificial ageing, Cultural heritage, Raman spectroscopy, ATR-FTIR spectroscopy

Abstract

Plasticized poly (vinyl chloride) (PVC-P) is according to material surveys one of the most frequently occurring and least stable synthetic polymeric materials in modern and contemporary art collections. In many cases, the only possible way to slow the deterioration of cultural heritage objects made of PVC-P, is preventive conservation. In order to be able to take action in preventive measures, it is crucial to understand the degradation processes, which occur in PVC-P stored under indoor conditions. Based on previous studies, it is assumed that PVC-P degradation stored under indoor conditions is predominately caused by plasticizer migration and thermal elimination of hydrogen chloride [1-3]. Most of the previous studies on the degradation of PVC-P employ accelerated ageing tests. However, considering the complexity of synthetic polymeric materials and the universality of accelerated ageing tests, it is highly questionable whether these accelerated ageing tests induce the same changes in PVC-P as natural ageing in the indoor environment of galleries and museums does. There is a lack of studies in which PVC-P ageing tests are performed at temperatures below 100 °C and at wavelengths to which PVC-P stored under indoor conditions is normally exposed to. Accelerated ageing tests are a great tool to determine the upper reference usage limit of PVC-P, but their utility in predicting the lifetime of cultural heritage objects made of PVC-P stored under indoor conditions, is rather limited [2,4,5]. Therefore, the aim of our work is to study the influence of accelerated ageing on stability of PVC-P model samples, representing PVC-P commercially produced in the 20th century, performed under various conditions using non-destructive and non-invasive spectroscopic methods of analysis, but also destructive methods of analysis and to compare the spectral data obtained from PVC-P model samples exposed to accelerated ageing with spectral data obtained from specified PVC-P objects of a composition similar to our model samples exposed to natural ageing.

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The degradation processes of celluloid under indoor conditions: preliminary results of a multi-analytical investigation

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Keywords: Celluloid, Degradation, Ageing, Spectroscopy

Abstract

Since it was first introduced in the market in the 1860s, cellulose nitrate (CN) has been widely used for almost a century. With the introduction of camphor as a plasticizer, the formulation was optimized into the so-called celluloid, a thermoplastic material that is recognized as the first commercially successful semi-synthetic plastic. Not only was it employed to produce dentures, everyday-life objects and design items, but it also served as a support for cinematographic, photographic and X-rays films and as compositional medium for artworks [1-3]. Its success was mainly due to its cost-effectiveness combined with an unprecedented versatility: different colours and visual effects resembling those of luxury materials could be attained. Furthermore, it was possible to shape celluloid into thin and flexible films, which constituted tremendously more practical supports for photographs compared to the previously used glass plates. However, the enthusiasm for celluloid progressively ceased, given its unstable nature and flammability. Other safer plastic materials, such as celluloid acetate, were preferred starting from the mid-20th century, while the production of celluloid was gradually abandoned [4]. CN and celluloid have proved to be rather unstable, presenting signs of degradation, such as yellowing, crazing, embrittlement or loss of plasticity after few decades. Such macroscopic evidence is due to physicochemical phenomena as denitration, oxidation, chain scission and plasticizer loss. Not only is the degradation of celluloid autocatalytic, but it also causes the alteration of the nearby materials [4,5].

This is due to the release of volatile organic compounds (VOCs) occurring during the ageing process and makes the storage and display of celluloid artifacts rather problematic. Several heritage objects testifying for the technological and design development of the late 19th – early 20th centuries artworks and historical records, are now in danger of being lost [6,7]. Thereby, the urge for adequate conservation protocols is impelling. A considerable international effort has been devoted to celluloid-related issues in the last decades [1,3,5,6]. Despite the advancement in understanding how the alteration of celluloid unravels, several issues are still open to debate. The present work aims at filling some gaps by further investigating the mechanisms of degradation. In the frames of the project, artificial ageing experiments of different durations and under controlled conditions of light irradiation, humidity and temperature, are conducted. The tested celluloid films are partly purchased and partly synthesized in the laboratory, in order to investigate commercial products and also, to be able to vary some determining parameters (e.g., the quantity of camphor can be modulated to better define its role in the stability of celluloid or the film thickness can be varied to investigate the difference in alteration on the surface with respect to the bulk of the material). The release of VOCs and their impact on the polymeric substrate are also studied, together with the effect of external pollutants. A multi-analytical approach envisaging the study of morphological features (by optical and electronic microscopy) and the molecular modifications (by FTIR, Raman and EPR spectroscopies), is implemented. In this contribution we report the first results and the information obtained on understanding the degradation mechanisms of celluloid.

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Study and conservation of a forgotten heritage. The case-study of Saint Vincent Martyr simulacrum

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Keywords: Portuguese martyrs' simulacra, Roman catacombs, Material and technical characterization, Degradation, Conservation issues

Abstract

Saint Vincent Martyr is one of the four martyrs' simulacra belonging to the Major Seminary of Coimbra (Coimbra, Portugal). The simulacrum is encased in the urn-altar of the Chapel of Saint Miguel. The bones were exhumed from the Catacomb of Priscila and brought to Portugal in 1760 by D. Miguel da Anunciação, the Bishop-Count of Coimbra and founder of the Seminary. Like numerous other simulacra documented in the country, the body of Saint Vincent served as a conduit for devotion to the holy martyrs of the Roman catacombs [1]. Simulacra of martyrs constitute a distinct category of relics/reliquaries, which were popular between the late 17th and the mid-19th centuries. The sacred bones (or *corpi santi*), exhumed from the catacombs of Rome after their rediscovery in 1578, were arranged within a life-sized simulated body representing the martyr. This form was crafted using gauze, papier-mâché, wax and other and was supported by a metallic structure. These simulacra were subsequently adorned in Baroque attire resembling Roman legionaries or virgins and were displayed alongside the symbols of martyrdom in ceremonial exhibitions. The historical and scientific study already carried out on this religious heritage in Portugal, intended to create a national inventory, to confirm the Roman origins of the sacred bones, and to analyze the religious significance and popular devotions linked to them [1]. Besides this, the analytical research has brought attention to the manufacturing techniques and materials employed by devout craftsmen in the material production of these assets. This work endeavours to elucidate the complexity of Saint Vincent's simulacrum from material, technical, decorative and conservation perspectives. For this, a combined multi-analytical approach was employed, encompassing imaging techniques, such as radiography and optical microscopy (OM), as well as vibrational spectroscopic (ATR-FT-IR) and chromatographic techniques (LC/DAD/MS & Py-GC/MS) [2-4]. Moreover, a careful visual examination revealed physical deformities and significant photochemical degradation. These observations were not expected given its current display location, suggesting that the simulacrum may have been moved from its original place in the Seminary.

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The study of two impressive simulacra housed by Santa Casa da Misericórdia de Almada, Portugal

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Keywords: *Corpi santi*, Simulacra, SCMA, Textile evaluation, Analytical characterisation

Abstract

The devotion inspired by the sacred bones, is as old as Christianity. Nevertheless, opposition to relics, propelled by various movements inside and outside the Church, sometimes left devastating consequences. On the other hand, relics could also be a sign of power amongst men. Following the Protestant Reformation, the Council of Trent (1545/1563) triggered a counterattack on the veneration of the relics of the saints and sacred images, which was later emphasised by the fortuitous discovery of an entrance to the Roman catacombs (1578). In subsequent centuries, the catacombs emerged as the primary source of sacred bones for churches, religious orders, civil institutions and nobility. The entire skeletons exhumed from the "*loculi*" in their burial place, piously, but eventually, incorrectly identified as victims of the Roman imperial persecution, were named catacomb saints or "*corpi santi*" (holy bodies). Initially sent in boxes-reliquaries to the Western world (Europe and the Americas), the skeletons were mounted in metallic structures, underneath richly decorated costumes and jewelry

after the 18th century. Face and hands also underwent gauze, paper-maché, wood or wax work, to simulate the human body better (simulacra) [1,2]. Little is known about the simulacra found in Santa Casa da Misericórdia de Almada (SCMA), Portugal, besides the fact that these two bodies belonged to very young children, probably under one year of age. According to developing historical research, Lourenço Pires de Távora received relics from Pope Pius IV in 1562 and housed them in at least two private chapels near Almada until 1799. At the time, the 1st Count of Caparica and Marquis of Valada, a descendant of the Távora, decided to erect a new chapel on his land and asked for new indulgences from the Pope in 1803. It is unknown if Rome sent new relics for this new chapel and how they arrived in SCMA during the 20th century. The set held by the SCMA is magnificent, with several adults, a mother and her child and three isolated children. The two simulacra presented in this work, Saint Theodori and Saint Primogenita (?), are included in this set. The textile evaluation revealed the use of high-quality materials, although they currently suffer from severe degradation, particularly St. Primogenita (?). This work aimed to provide a holistic interpretation of the simulacra. A historical and multi-analytical approach based on in situ microscopic, spectroscopic and radiographic observation, complemented by an in-depth laboratory study of the samples, was carried out to unveil the materials and methods used to produce them.

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Diving into the ancient secrets: unraveling the chemistry of waterlogged Neolithic wood ecofacts

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Keywords: Waterlogged wood, Analytical pyrolysis, Chemical changes, Marsh sediments, Acidic environment

Abstract

The application of analytical techniques for the characterization of wood is currently recognized as an important procedure to get detailed information associated with the type of wood, the degradation processes and further technical details for conservation issues [1-3]. In this respect, the current work focuses on employing the reactive pyrolysis-GC/MS [4-6] with in situ hexamethyldisilazane derivatization, to study ancient wooden elements uncovered from acidic marsh sediment. The application of this analytical technique by the present research, aimed at investigating the lignocellulosic contents to determine the processes that affected the chemical composition of the wooden elements uncovered during an archaeological intervention in September 2022 at the O areal salinae Roman saltwork archaeological site, located in the city of Vigo (Galicia, Spain). The uncovered woods consist of two cherry (*Prunus* sp.) and eight oak (*Quercus* sp.) wooden elements with an estimated radiocarbon age ranging between 6100 and 5990 cal BC. The analytical process was undertaken using milled wood samples from a mixture of wood fragments selected along wood's radial direction to get samples that are representative of the uncovered wooden elements [7]. The obtained results indicated clear changes in the wood's chemical composition [3,6]. All samples presented a very high level of depolymerization process undergone of the polysaccharide contents [2]. However, it was apparent that the degradation process did not equally influence the studied wooden elements. For instance, the values of the holocellulose/lignin ratio, a very important index for estimating the degradation of archaeological wood, were particularly low for the cherry wood and for two of the oak wood samples [2,5]. The polysaccharides, in the ancient cherry wood samples, show appreciable decrease in the level of polymerization, whereas for the ancient oak wood this process is less apparent. Furthermore, the result indicated also the partial oxidation of lignin contents in the ancient oak wood samples, related to the increasing acid functional groups and partial depolymerization of the lignin structure in the oak wood. Despite their surprisingly good visual appearance, it can be concluded that the waterlogged wooden elements underwent an important degradation process. The high depolymerization level could be associated with the occurrence of anaerobic bacterial agents, which especially affect the polysaccharide contents. Furthermore, the observed changes in the lignin structure for some of the oak woods, could be explained by diverse causes related to the sediment, including the mineralogic composition and possible variability of hydraulic flow during the long-term burial period. Further works are planned for further investigation of the environmental influence on wood buried under the O areal salinae archaeological site, which is characterized by acidic, sandy loam and saturated sediments.

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Multi-analytical approach for characterisation of Roman Age stone monuments

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Keywords: Roman stone monuments, Laser spectroscopy, Chemometrics

Abstract

The present interdisciplinary investigation is focused on the characterisation of the polychrome layers present on stone monuments from Moesia Inferior Roman province, dating back to the 2nd-3rd century AD. The monuments, carved in local Turonian stone, were uncovered in a secondary context, reused as building material in Late Roman and Byzantine fortifications. Thus, they provide information on their initial display, layout, making, chronology and dedicant, but also on the value of their lithic material in later periods. The vegetal decoration and the inscriptions, present a visible red pigment layer, whilst preliminary in situ spectroscopic analyses using XRF and LIBS stratigraphy identified Fe present in all red pigment areas, as well as traces of Pb on some of the lower investigation points. The investigations continued using portable Raman and FTIR, as the LIBS stratigraphy peaks were depicting similar spectral abundance of iron and for stone, and the red areas present differentiate from colorimetric point of view. Advanced chemometric analyses were used in order to process the spectral information and correlate the findings to the original or repainted layers and also to detect other paint layers on the surface of the stone monuments.

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Historical and precious ecclesiastical artefacts in Sicily from the 12th to the 19th century: non-invasive gemological analyses

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Keywords: Non-invasive, Raman spectroscopy, X-ray fluorescence, Gemstones, Ecclesiastical jewelry

Abstract

The corpus of ecclesiastical artistic heritage is represented by different types of liturgical furnishings, such as monstrances, chalices, pyxes, but also jewelry and ex-votos. The chronological span related to them, is very broad and covers the centuries between the 12th and 19th centuries. These are very precious objects currently exhibited in numerous Diocesan Museums and Museums of Sacred Art, which stand out in the field for their collections of high historical and cultural value. These objects display exquisite finishes, refined decorations and the presence of precious gems set into the surface, which gives them an inestimable value. But are these works really valuable, apart from their devotional value and historical testimony? Are the records that have come down to us and the stated information on the gemological repertoire, really reliable? Traditional techniques and autopsy observations do not allow for the analysis or classification of set gems, whilst scientific studies are rarely carried out. In contrast, specific studies with non-invasive portable instruments would allow these works to be studied directly in situ. In particular, thanks to a combined in situ approach involving portable Raman spectroscopy (with an excitation wavelength of 785 nm) and portable X-ray fluorescence (XRF), it was possible to confirm the identifications of gems [1] present on some important artefacts from the Treasure of Palermo Cathedral and the Diocesan Museum of Monreale (Italy). The series of objects investigated includes liturgical furnishings of various kinds: reliquaries, chalices, monstrances, ciboria, patens, statues, vases and paci of Sicilian manufacture, especially from Palermo, Spain, Lombardy and Rome, dating from the 12th century to the first half of the 19th century [2]. In addition, an ornament called "*La gioia del Santo Costato*" by goldsmith Francesco Burgarello, dating from before 1782, has also been extensively analysed. In the inventories of Palermo Cathedral from 1848 and 1898, the work is recorded as "a joy of the Holy Rib of the Crucifix" and is described as "set on gilded silver" and decorated with "number three hundred diamonds [...]" [3]. The central red gemstone was the most important object of investigation, as was the presence of numerous colourless gems set in the surrounding radius. The object follows a type of traditional Sicilian production of late Baroque derivation in vogue, especially in the 18th century. The gems mentioned must have been rubies and diamonds.

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Marble inscriptions from ancient Sicily: multi-analytical approach for provenance studies

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Keywords: Marble, Epigraphy, Provenance studies

Abstract

The interdisciplinary project "Crossreads: Text, materiality and multiculturalism at the crossroads of the ancient Mediterranean" aims to incorporate the materials information for the comprehension and discussion of the epigraphic culture in ancient Sicily. Within this framework, crystalline marbles represent the vast majority of the used stones, especially in Roman times. As no exploitable marble outcrops are present in Sicily, all crystalline marbles on the island had to be imported through maritime trade [1]. The aim of the study is to assess the variety of marbles used for inscriptions in Sicily, in order to verify possible local and chronological trends and to verify if a hierarchical use of imported stones can be suggested, following what is observed in sculpture and architectural elements [1]. Unfortunately, only a limited number of archaeological papers deal with such matters concerning inscriptions. Moreover, the correct identification of supports on analytical bases has been completely disregarded by historians and epigraphists, creating a generalized lack of knowledge on the material aspects of such written documents. As no single method is suited for marble provenance [1], a multi-analytical approach is here proposed, based first on a fully non-invasive characterization through portable X-rays fluorescence (pXRF) and digital microscopy carried out in situ and then a micro-destructive one. Small samples were collected from selected inscriptions and prepared both as thin sections and as powders for X-ray diffraction (XRD), geochemical analyses (carbon and oxygen stable isotopes) and electron paramagnetic

resonance (EPR). From the combination of the data coming from all these analyses, a full description of the crystalline marbles could be derived, which allowed, by comparison with the published literature [2-6], to propose the provenance of marbles and to start an interdisciplinary discussion on inscriptions' materiality based on archaeometrical results.

Acknowledgements

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Making magic happen: composite gems from antiquity to medieval age. The art of counterfeiting

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Keywords: Gem analysis, Doublets, Triplets, Spectroscopy

Abstract

From antiquity to modern times, gemstones have been treated to improve or change their aesthetic appearance. Treatments, such as foiling, coating or filling cracks, are some of the most used and fairly accepted in the manufacturing of jewelry [1]. On the contrary, some other type of treatments remains rather understudied, among which, that of composite gem stands out. Composite gems are made up of two or three slices (doublets or triplets) of natural or artificial gem material, glued together with adhesives and layers of pigments or metal foils, a practice quite common in the medieval and modern times, although documents attesting this practice, are quite absent from ancient written sources. Only Pliny describes the practice of imitating sardonyx for the carving of cameos, whilst and with a large timespan in between, the first description of doublets and triplets is found in Cellini [2]. When set in jewelry, the treatment of gemstones can be difficult to study, but, it is very important for aspects, such as dating or manufacturing techniques. In addition, the question of the composite gem opens up a reflection on the concept of counterfeiting. Indeed, gluing together quartz and glass slices has the clear fraudulent intention of making the gem appear bigger or more appealing, or even to deceive the sumptuary laws [3]. The gemological and analytical study by Raman spectroscopy of jewelry dating from the 11th to the 15th century and preserved in some Museums of Tuscany, offered an occasion of analyzing a variety of gemstones, cuts and settings, as well as different types of treatments, among which, the composite gemstones emerged for their peculiar manufacturing technique [4-5]. The analysis of doublets and triplets led to rethinking the manufacturing date, the beginning of the practice and the credibly fraudulent process behind their production, which could justify the absence of references in the literature until the 15th century. The analysis of the cuts and settings in the studied jewelry objects, would suggest a systematic production of doublets and triplets in specialized workshops selling this type of "treated gem" from the 13th century onwards. This would probably be linked to the development of new knowledge and skills in cutting gemstones and glass technology [6-7]. Ongoing analysis on adhesives, natural and artificial portions of these gems and comparative studies among different jewelry, are providing a new and interesting scenario on the beginning of a practice, making some magic happen in gemology.

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Influence of the intrinsic variability of Raman data on the outcome of PCA classification of ancient ceramics

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Keywords: Provenance, Ceramics, Raman spectroscopy, Neolithic, Principal component analysis

Abstract

In the field of archaeological studies, provenance is a topic of continuous growth, especially in the past decades. Although sometimes used interchangeably, the terms "provenance" and "provenience" have slightly different origin and meaning. Regarding archaeological studies, provenance has incorporated both meanings, denoting the real discovery place of an object and its history, as well as its trajectory through time, following its unearthing. The importance of provenance studies comes from the fact that they can shed light on unknown aspects from the history of humanity, such as social, cultural or economic habits pertaining to certain time period or geographical location [1]. Probably the largest part of archaeological provenance studies involved ceramics, which are the most frequent archaeological findings. Most of these studies involve the use of specific features of the ceramic body, relying on the human operator's skills. However, the past years have brought about an increased number of studies trying to improve the process of ceramics' provenance by introducing a more automated approach, through data mining statistical methods. One of the most often used methods is the principal component analysis (PCA), which works really well with infrared or X-ray data [2-5], for example, but fewer studies have involved Raman data. Thus, the aim of this paper was to evaluate the influence of Raman data variability on the outcome of PCA, applied for the study of archaeological Neolithic ceramics. For this, a portable Raman equipment was used to record the Raman signal from 86 ceramics samples coming from the Balkan region, specifically the present territory of Bulgaria. The research showed that the variability associated with both the data set and the Raman data, made it difficult to create a very precise model and that several iterations were needed in order to obtain a satisfactory classification.

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Archaeometric study of ceramic findings from the site of the Roman villa in Fiumana (Italy)

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Keywords: Pottery, Raman, X-Ray diffraction, Roman

Abstract

In the important archaeological site in Fiumana (Predappio, Forlì-Cesena, Emilia Romagna, Italy), where the excavations recently restarted, a villa urbano-rustica dating back to Augustan age and a big late-antique complex, are currently under investigation. The large amount of materials recovered allow us to compare many different types of pottery of the same age, coming from the same place: kitchen pottery, common ware, red painted ceramic, terra sigillata and amphorae. These ceramic findings have

been analysed by a combined use of optical microscopy (OM), X-ray powder diffraction (XRPD) and micro-Raman spectroscopy. Mineral-petrographic observations showed all the main features of samples (matrix, microstructure, inclusions). XRPD analysis allowed identification and quantification of mineral phases suggesting important insight about the technological processes. The support of micro-Raman spectroscopy allowed a more complete recognition of raw materials and firing procedures (atmosphere and temperature). For example, some mineralogical phases are considered temperature indicators, like feldspars, which can be present as raw materials or newly formed minerals during firing. Only through a multi-technique approach, is it possible to correctly examine of various feldspars and their role. Finally, the results obtained by the investigation of different ceramic classes led to a comparative evaluation of different kinds of ceramic materials from the Roman age, on their composition, manufacturing technology, nature and provenance of raw materials.

An analysis of clay samples from Liåker, Lunner municipality, Norway

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Keywords: FTIR-ATR, XRD, Clay, Firing temperature, Prehistoric features

Abstract

The prehistoric everyday activities preserved in the archaeological context, are often fragmented and challenging to understand. This challenge is further raised when the material consists of burned material. However, the data obtained at Liåker, gave important insights into the impact of controlled fire on prehistoric structures and helped to develop a methodology for analysing thermal impact on clays from in situ archaeological contexts. Cooking pits, a typical prehistoric structure occurring in Norway, are usually characterised by a layer of charcoal, ash and fire-cracked stones, often framed by a thin layer of burned, reddish ground, which is a result of the formation of hematite, due to high temperatures. Other changes in the mineral phases of the clay fraction, invisible to the naked eye, occur during the same process. Although challenging to analyse, these changes occur at an expected range and can be, therefore, used in the estimation of temperatures [1] to which the clay in the ground surrounding the pit was exposed. This poster presents an implementation of new routines to understand the material in a new way and develops a methodology for future analyses of similar structures. Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) spectroscopy and X-ray diffraction (XRD), were implemented to estimate the temperatures [2] to which the structures at Liåker were exposed. Samples of raw burned clay from the cooking pits and a sample from a possible oven burned at a significantly higher temperature, gave a great opportunity to obtain data on clay from archaeological in situ contexts at different stages of thermal impact. The samples were successively analysed to determine modifications in terms of structure and mineralogical composition. Despite challenges posed by quartz interference, distinct absorption bands characteristic of clay minerals, were identified through FTIR-ATR, whilst

the mineral composition was confirmed by the XRD analysis. Burned clay samples originating from structures have been compared to raw clay samples from the site. The analysis indicates that the clay ground at Liåker consists of illite, chlorite, muscovite, large quantities of quartz and multiple types of feldspar. Based on the occurrence of muscovite mica and chlorite and the occurrence of absorption bands 875-915 cm^{-1} attributed to clay with structural changes occurring at over 500°C, it has been interpreted that the cooking pits have all been exposed to temperatures under 400°C. Muscovite begins to degrade at temperatures exceeding 300°C, whilst the raw clay samples exhibit higher muscovite content compared to the heat-exposed samples. The structure thought to be an oven, was exposed to higher temperatures than the usual cooking pits, based on the lack of muscovite and high levels of quartz and feldspar. Additionally, the lack of chlorite, stable up to 550-650°C and the lack of mineral phases forming at higher temperatures, suggest that the possible oven was exposed to temperatures at around 700°C.

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Prehistoric cultural changes in the use of fire from foraging to the earliest farming societies: an interdisciplinary archaeological and multi-analytical study of hearths at Riparo Mochi (Ventimiglia)

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Keywords: Archaeometry, Hearths, Bones, Pigments

Abstract

To achieve its main objectives, the Pyro-Transition project, funded by the Italian Ministry of Universities, is developing a "holistic" archeological-archaeometrical approach. The study aims to acquire detailed and innovative information to define as accurately as possible, the evolutionary framework of the main behavioural changes in relation to the use and management of fire, from the end of the Middle Palaeolithic

period to the Early Neolithic period, in one of the most nationally and internationally renowned Italian prehistoric sites, the Riparo Mochi (Ventimiglia). The different scientific fields involved in the project, are interacting in a continuous deductive-inductive relationship between laboratory analyses and field research, which are synergistically developing an accurate reconstruction of the technological and functional characteristics of the combustion structures present at the site [1]. This will improve our knowledge on strategies for using fire as was used by human groups in the past which, although biologically and/or culturally different from each other, exploited the same territories for several millennia, whilst facing important changes in climate, successfully modifying their habits over time. For this issue, a series of radiometric dates will be performed to enable a detailed chronological framework. Furthermore, new, accurate and reproducible research protocols, are being developed to provide answers to some of the specific archaeological questions still unanswered, particularly focusing on the study of those remains that are more likely to be related to the purposeful use of fire by humans in antiquity, with materials, such as bones, lithics, pigments, shells, residues and pottery [2,3]. As far as bones are concerned, they have typically undergone many degradation processes, which have caused chemical and physical changes to the original constituent matter. Indeed, one of the processes that caused these changes is heating, responsible for significant variations in colour and chemical composition, for the study of which, this research is producing one of the main methodological protocols. The first results from the chemical analysis of heated lithic materials, ashes, bones, reddened earths and pigments, performed both in situ and in the laboratory by electron microscopy (SEM-EDXS), infrared spectroscopy (FTIR), colorimetric, visible reflectance and Raman techniques, will be presented and discussed. Especially, the usefulness of employing portable instruments, particularly Raman spectroscopy, whose ability for pigments' and materials' characterisation is widely recognized [4,5], has been emphasised in this work, because of the importance of having available non-destructive and effective characterisation tools when it comes to art objects and archaeological interest.

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Multi-analytical approach for similitude analysis of metal Roman Age findings

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Keywords: Vechten-type helm, Laser spectroscopy, XRF

Abstract

The present study is focused on the characterisation of rare artefacts - two halves of Roman cavalry sports helmet, which were discovered in the area of the Islaz Roman fortifications, at the Olt River Roman frontier. The helmet is Vechten type, thus a rare artefact, since there is only one other known to have been discovered in the world. Both parts of the helmet were accidental discoveries, made by private persons in nearby locations, within a four-months timeframe. The halves are well preserved and present a strong evidence for the Roman presence at Islaz. XRF and LIBS stratigraphy were performed on several areas of interest in order to identify the chemical composition of the two pieces. The spectral data obtained from the core of the material, were processed by advanced methods of statistical analysis and then characterized according to similarities, in this manner obtaining a detailed similitude analysis of the two pieces, based on the elemental composition of the original material. The approach is particularly useful for deepening the knowledge on similar objects typologically, chronologically, however, discovered apart.

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Non-invasive characterisation of tobacco pipes from the National Museum of Slovenia by vibrational spectroscopy

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Keywords Tobacco pipes, Non-invasive techniques, Reflection FTIR spectroscopy, Raman spectroscopy

Abstract

The beginnings of the use of tobacco pipes in Europe can be traced back to the 16th century through interactions between adventurers, seafarers, colonists and indigenous peoples of the Americas, who had already used pipes made out of various materials in prehistoric times. Initially, tobacco pipes in Europe were simply designed, but with the development of smoking culture, tobacco pipes with their unique design gained historical significance. Tobacco pipes usually consist of the chamber and the stem, which can be divided into two parts. However, there are also tobacco pipes that are made entirely from one piece. As far as the chemical composition is concerned, dismantled tobacco pipes are usually made out of two different materials, while one-piece pipes are made out of the same material. In order to determine chemical composition, a large segment of the Nation Museum of Slovenia's (NMS) collection with tobacco objects, was analysed by means of FTIR and Raman spectroscopy in a non-invasive manner. For the analytical approach, three different locations on a tobacco pipe were investigated, namely the bowl, the stem and the mouthpiece. The aim was to determine the material composition of each part of the tobacco pipes, as well as possible degradation products that could occur on the different areas of the tobacco pipe, due to the heavy handling and/or absorption of the tobacco, as well as, due to the impact of high temperatures during their use. The results of the non-invasive analyses showed that one-piece tobacco pipes are in most cases made from the natural material sepiolite or Meerschaum [1], while tobacco pipes that disassemble into chamber and stem, are made from a combination of artificial and natural materials. The chambers are mostly wooden, whilst the stems are made out of synthetic composite materials, such as modified rubbers, styrene-acrylic-copolymer, nylon, etc. As a part of the chemical analysis of the selected objects from the "Smoking Paraphernalia Collection" of the National Museum of Slovenia, other tobacco objects were also non-invasively analysed, such as an ashtray (N 34962), a tobacco pipe stand (318-2022) and a tobacco box (198-2022). The ashtray is most likely made out of hard tissue with animal origin (either ivory, horn or bone). The Japanese lacquer "urushi" was identified as the main component of the tobacco box, while the pipe stand is made out of natural shellac resin and indigo pigment.

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XRF and Raman spectroscopy applied to gemstones study of an image of the 17th century

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Keywords: XRF, RAMAN, Gemstones, Glasses, Cultural heritage

Abstract

The Virgin of the Rosary from the Church of Santo Domingo is an image from the 16th-17th century, that wears a silver dress decorated with near 400 gemstones. A gemological study and chemical analysis of gemstones was carried out by gemological studies and X-Ray Fluorescence and Raman spectroscopy, in a nondestructive way. The 377 gems of the image were classified according to their color, cut, conservation state and response to ultraviolet light, while chemical characterization was carried out by an XRF Elios equipment manufactured by Bruker. All the kinds of cuts and color were studied. The results were compared in some samples with results obtained by a spectrometer SHIBUYA D-1 and the scanning electron microscope JEOL model JSM- 6460 LV, with acceleration voltages of 15 kV and 100 s for the microanalyses. EDS microanalyses were accomplished in an Inca X-Sight instrument Oxford attached to the SEM equipment. The dress of the Virgin is decorated with red, blue, yellow, green, purple, orange and colorless gemstones, whilst the red color is the most common in the dress (30 % of the gemstones), located mainly in the front of the skirt and in the left sleeve. It has been also detected blue, green and yellow pieces unhomogeneously distributed in the dress. Purple, orange, and colorless are less common and appear in the sleeves. Regarding the glasses with gemological quality, most of them show red, blue, green and yellow colors. In the front of the skirt, the red glasses and gems were the most abundant. More than 85 % of the analyzed gems are mounted on their table, with the cullet to air, contrary to the usual way of preparing current jewelry. This mounting could be due to the higher stability of the gem because it was on the largest facet or due to the aesthetic criteria of the lapidarist. The gem cuts were

classified into four different groups: modified emerald, modified brilliant, with facets (modified Dutch) and baguette or carré. Most of the gemstone has emerald cut (≃80 %). The second most abundant cut is the modified brilliant-cut (≃19 %). These pieces have an octagonal perimeter with eight triangular or pentagonal facets and eight rhomboidal facets in their pavilion. Most of these gems are composites, in other words, they are formed by two or three pieces giving the feeling of just one gemstone. Red, blue or green gemstones show an advance alteration of the colored glue, which, in some cases, appears almost translucent due to the loss of the color. In conclusion, the gemstones present a range of colors, where red is the most representative and different cut, that are related to different chemical composition and could be in relationship with different interventions in the dress. The results show that gems with emerald cut were mainly glasses, while doublets or triplets gems are in the brilliant cut.

Acknowledgements

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Design and study of cost-effective conservation of watercolor paper art

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Keywords: Foxing, Acrylic, Watercolor, Paper, Biotic

Abstract

The primary concern with watercolor artworks on paper is the natural oxidation process of the paper, leading to the development of unsightly yellow-brown spots referred to as, foxing. Historically, efforts to preserve watercolor pieces in museums, institutions and private collections, have relied on intricate and expensive techniques. Unfortunately, these methods are not practical for the broader community of artists and less-affluent collectors. Furthermore, the introduction of foreign preservation materials, which can interact with the artwork's components, poses a risk to the original visual appeal. Consequently, watercolor art collections have lost some of their appeal compared to oil paintings on canvases. This study endeavors to offer an alternative, straightforward and cost-efficient approach to safeguard watercolor artworks created on high-quality watercolor paper, a type commonly used by typical watercolorists, making it a suitable candidate for this investigation. This approach also avoids introducing additional substances into the artwork. The protective technique involves the application of commercially available acrylic gesso to a fresh sheet of watercolor paper. This gesso-coated paper

serves as a backing for framing and displaying the original watercolor artwork, without the need for any foreign preservation materials to be added to the artwork itself. To assess the effectiveness of this protection method, a comparison was made between the foxing tendencies of protected and unprotected paper artworks stored for a decade. These samples were subjected to various analytical techniques, including 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 results revealed that, when compared to untreated samples, rarely any foxing spots were observed on any of the treated samples and both the oxidation and degradation of cellulose fibers were diminished. Additionally, the analysis showed that the acrylic gesso comprised inorganic components, such as calcium carbonate ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), rutile (TiO_2) and organic acrylic. The carbonates created a mildly alkaline environment, neutralizing the acidity in the paper. The titanium dioxides exhibited biocidal and fungicidal properties, due to their photocatalytic characteristics. The acrylic component bound and dispersed the inorganic constituents, whilst the coating formed an impenetrable barrier against any invasive chemical or moisture from the external environment. In addition to significantly improving the resistance of the paper to foxing, the methods outlined in this study, are highly cost-effective and readily accessible to artists and collectors. Importantly, they do not add any preservation materials to the original artworks.

The link between water and paper structure to enhance the efficiency of preservation processes

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Keywords: Paper, Water, Sorption isoterms, Conservation

Abstract

A significant part of traditional information carriers (books, archival documents) comprises record, on acid paper. This type of paper is prone to faster ageing and degradation caused by acid hydrolysis of the cellulose chain, which can even lead to complete disintegration and fiber brittleness. The solution is to deacidify the paper and create an alkaline reserve [1,2]. Deacidification processes are based on either aqueous/polar or non-aqueous/non-polar basis. Aqueous deacidification systems are close to cellulose in terms of polarity, efficiency, environmentally benign and safe. However, they are

accompanied by undesirable effects, such as fiber swelling and paper curling, which cause irreversible deformation and are unsuitable for closed book blocks deacidification [3]. Despite these drawbacks, water is crucial in the deacidification process. Water ensures the transport of the active deacidifying agent into the paper structure and removes unwanted acids from the paper. Water in the form of air moisture is commonly added by conditioning to the deacidification process using particle dispersion in a non-polar carrier. Adding air moisture/water improves particle penetration into the paper structure by causing fiber swelling, allowing penetration of the active deacidifying components inside the fiber cell wall [4,5]. Therefore, for the development of a new efficient deacidification/stabilization system, it is important to understand the relationship between paper and water. The interaction of water or air moisture with cellulosic materials, is characterized by sorption isotherms [4,6]. However, because of the complex structure of paper, it is necessary to focus on the paper itself, as a fibrous porous material and also on the correlation of water with this material [4,5]. Each type of paper differs depending on its structure, type of pulp, additives and technology, which affects its interaction with water and consequently the efficiency of deacidification. The lignin and hemicellulose content in paper fiber, the porous structure and the additives, have a major influence on the interaction of water with the paper. Another important factor affecting the structure and properties of the paper, is age. As paper ages, it degrades, causing significant changes in its structure and properties. The aim of this work is to demonstrate the relationship between the structure and the chemical composition of paper and its sorption properties in order to gain important knowledge for improving the efficiency of preservation, namely deacidification processes. Measurements were carried out on four types of model paper - lignin-containing paper, lignin-free paper, Whatman paper and a real paper sample from a naturally aged book containing lignin. Sorption isotherms, Cobb test, contact angle for measuring paper wettability, surface pH, mechanical properties and SEM, were measured.

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Searching for a suitable chromatic reintegration technique for outdoor exposed wall paintings

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Keywords: Wall painting, Chromatic reintegration, Nano-silica, Outdoor, Durability

Abstract

Historical wall paintings are generally inseparable from the building in which they are located. Therefore, their conservation is subjected to the environment that surrounds them. One of their main deterioration forms is the material loss in the form of lacuna [1-2]. Besides impairing the integrity of the artwork, lacunas make it difficult to admire and understand the pictorial image [3]. Conservator-restorers, through the application of chromatic re-integrations (pigment + binder), aim to fill those paint losses [1]. Whilst water-based (i.e. with Arabic gum) and varnish-based (i.e. with natural or synthetic resins) procedures have been widely used [1,3], they only appear to be effective for indoors use, where environmental conditions can be controlled. However, when wall paintings are partially or completely outdoor, they are more prone to decay, due to their exposure to environmental agents, such as relative humidity, UV radiation, soluble salts, pollutants, etc. [1,2]. Therefore, the pursuit of a technique that can resist the deteriorating action of these factors, is seen as paramount. In view of the scarce scientific knowledge in this field, study on the suitability of chromatic reintegration techniques in terms of aesthetic features (colour and gloss) and durability, is considered as an under-researched field of study. In this regard, the use of silica-based techniques has regained popularity in Mediterranean countries. Soluble alkaline silicates (e.g., sodium and potassium) were the first to be used, but have proven to be unsatisfactory in terms of water resistance and freeze-thaw cycles. Thus, aqueous silica nanoparticle dispersions are considered as a possible alternative, due to their apparent inalterability and high resistance properties [4]. In this study, mock-ups were prepared following traditional wall paintings techniques. Nano Estel (an aqueous colloidal silica dispersion of nanometric dimensions) [5], was used as binder for chromatic re-integrations. Three blue pigments were tested: Egyptian blue, lapis lazuli and ultramarine blue. Samples were exposed for a period of a year under two different natural environments: Vigo (NW Spain), under a humid environment, moderate temperatures, marine influence and low levels of pollution; and Granada (SE Spain), under a dry environment, an intense thermal range strongly marked by the season and highly polluted. Colour variations were monitored by spectrophotometry every 50 days and gloss was evaluated before and after exposition. A mineralogical and molecular characterization was carried out by X-ray diffraction (XRD) and Fourier-transform IR spectroscopy (FTIR). Lastly, a study of the surface and cross-sections was performed with stereomicroscopy and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). Overall, colour changes were recorded and generally became stable in time. Gloss also changed, slightly decreasing in both environmental exposures. These chromatic changes can be ascribed mainly to the formation of a thin layer of carbonates on the surface. In general, these colour variations are more intense in samples exposed in Vigo, where the carbonate

layer appeared thicker and more homogeneous. The marine environment and high relative humidity conditions of Vigo, are a determining factor in their deterioration.

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Development of silver test system with bio-based green aging methods and assessment with multi-analytical techniques

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Keywords: Silver, Green, Artificial aging, Raman

Abstract

Several teams have researched ways to produce systems, which mimic the surface of naturally aged historical silver objects, in order to develop appropriate restoration treatments [1,2]. Due to the high value of silver artefacts, such developments are essential to test new cleaning methods. Furthermore, it is often difficult to reliably assess the effectiveness of cleaning treatments on silver objects, due to the complex history of conservation conditions of such objects. We have studied protocols for producing

coupons with a homogeneous tarnish composed of corrosion products, like those found in historical objects, with a high degree of reproducibility. Two artificial ageing methods with bio-based materials were tested, in accordance with the "green" criteria defined in the objectives of the GoGreen project [3]: (i) the boiled egg white method [4] and (ii) the albumin solution method [5], re-investigated by the ASTEC project [6]. Both methods were tested on sterling silver and pure silver coupons with different surface finishes (i.e. polishing). The challenge of evenly polishing a soft metallic material was overcome by using a 3D printed specimen holder to allow uniform pressure to be applied on the coupons. The ageing process was designed to be carried out in a non-laboratory workspace with easily accessible apparatus (e.g., casserole dish). To define the most appropriate protocol, different reagent concentrations and exposure times were tested for each ageing method. Characterization of the aged coupons was carried out using micro-Raman spectroscopy by single point and mapping analysis, supported by linear scanning voltammetry measurements. Typical corrosion products, such as acanthite (Ag_2S), covellite (CuS) and some Ag-Cu-S intermediates, were identified. Compared with Raman spectra collected from naturally tarnished silver objects, the boiled egg white method led to similar corrosion compounds. On the other hand, the albumin solution method gave a more homogeneous tarnishing appearance. Changes in the surface morphology of the aged coupons were observed using optical microscopy and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. The homogeneity and reproducibility of the artificially produced tarnish layers, were assessed using a spectrophotometer. A particular surface microstructure consisting of islands or rings of different sizes was observed on some of the coupons aged with the albumin solution, which is being further investigated with Kelvin probe force microscopy. This work is being developed as part of the EU Horizon project GoGreen, which aims to develop innovative, environmentally friendly methods inspired by nature and historical treatments for remedial conservation [3].

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New sustainable treatment based on chitosan and halloysite nanotubes for the conservation of waterlogged archaeological wood

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Keywords: Archaeological wood, Conservation, Chitosan, HNT, Chemical imaging

Abstract

Chitosan (CHI) is among the most used biopolymers in conservation science due to its antibacterial and antioxidant properties [1,2]. On the other hand, the nanotubes of halloysites (HNT) are used as fillers due to their excellent thermal and mechanical properties besides the possibility of being used as nano-reservoir for sustained release of active agents [3]. In this work, Chitosan/Halloysite Nanotubes dispersion has been designed as a novel green protocol for the conservation of waterlogged archaeological wood. Firstly, CHI/HNT dispersion was prepared at a fixed concentration of chitosan, of 2%, and HNT was added at a concentration from 0 to 3%. The immersion protocol of waterlogged archaeological wood was monitored for 72h and subsequently, it was dried for 24h at room temperature. The percentage of consolidant adsorbed from wood was measured gravimetrically. Colorimetric analysis and optical microscopy revealed the characteristic surface of untreated and treated archaeological wood. Chemical imaging was also applied to determine the spatial distribution of CHI/HNT dispersion on waterlogged archaeological woods. Thanks to this last analytical approach it was possible to assess that a more homogeneous distribution was possible when the concentration of nanotube was increased. However, at the same time, an increase in the aggregations of chitosan were also visible at the maximum concentration of HNT. Meanwhile, a physico-chemical characterization was carried out on wooden samples to investigate the mechanical and thermal properties before and after treatment. A higher thermal and mechanical resistance has been shown in the samples treated with CHI/HNT dispersion compared to the untreated archaeological wood sample. Since wood is a hygroscopic material, it was important to consider water vapor absorption/desorption after CHI/HNT treatment, thus an immersion test and a water uptake measurement were performed. Finally, the aging test of archaeological wood samples led to the examination of the efficacy of CHI/HNT composites as a protective formulation for archaeological wood: lignin index of archaeological wood samples was calculated before and after they were exposed to nitric acid for 72h. In conclusion, the proposed CHI/HNT dispersion presents a promising strategy for conserving waterlogged archaeological wood. This is attributed to the ability of chitosan to form a film with antioxidant and antibacterial properties, serving as a green and sustainable reinforcing coating and the capacity of halloysite nanotubes to enhance the thermal and mechanical resistance of wood samples.

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Archaeological woolen textiles in a fragile state: the potential of polysaccharide based consolidants

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Keywords: Bio-inspired consolidant, Polysaccharide, Archaeological textiles, Wool, Ageing

Abstract

For the preservation of archaeological textiles, there is no one procedure that fits all. Freeze drying of fresh waterlogged finds is a possible choice; however, in cases of very high fragility, it may be insufficient. Moreover, the method is problematic for objects that are dry already or need to be retreated. Similarly, severely degraded textiles in a dry state may benefit from greater cohesion to allow movement for exhibition and research though protection against further physical degradation. As always, risks must be weighed against benefits of a given consolidation measure. The fact that many applications of current consolidation materials show varying drawbacks, has stimulated rich research on alternative conservation treatments. The tremendous progress in the use of bio-inspired materials in many fields of material science and medicinal research, is encouraging for the potential of bio-polymers and their derivatives for the preservation of archaeological textiles. In the current study, investigating a range of polysaccharide/glycan-based compounds for conservation of severely degraded archaeological

wool, the impact of these compounds on modern wool and selected dyes, is examined. In addition, the aim is to understand the impact of ageing on treated textiles, reversibility and if the consolidant impacts future dye analysis. The selected consolidants are biocompatible and sustainable. Three different dyes have been applied, namely madder, weld and woad, which are common dyes found in Europe. Test-pieces made of modern undegraded wool rather than modern degraded fabric, were selected to investigate the consolidants, as the degradation will add variability to the material and could interfere with the interpretation of results. Dimensional changes, colour changes, weight and stiffness impacted by the applied consolidants, were assessed along with accelerated ageing of these treated and untreated fabrics, to understand long-term behaviour under museum conditions. The dyes were analysed by means of various methods, which allows to select the most suitable approaches for future analysis of archaeological textiles. The next step will be to simulate degraded state(s) similar to that found in archaeological textiles. Carbon-containing consolidants may interfere with future analyses, carbon dating in particular. However, analytical methods have improved and continue to do so by passing many previous concerns. For example, compound specific carbon dating could allow for dating despite the addition of a consolidant, as these consolidants are not protein based. Various mass spectrometry methods exist and are advancing which could allow for dye analysis despite the presence of consolidants. The presented work is carried out in the framework of the TexRec project, a project dedicated to studying and preserving the Oseberg tapestries, one of the most important textile artefacts from the Viking Age. The project is funded by the Norwegian Research Council under the number 316268.

Study and development of an innovative consolidating material: the use of Paraloid B72 and Regalrez 1126 in combination with Laponite nanoparticles

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Keywords: Paraloid B72, Regalrez 1126, Consolidation, Wood

Abstract

Consolidation of decayed wooden artefacts consists of reinforcing their physical-mechanical characteristics by impregnation with polymer precursors dissolved in organic solvents, which diffuse by capillarity within the material and subsequently polymerise in situ. Among consolidants, acrylic-based Paraloid® B72 gained enormous success over the past decades thanks to its presumed stability and

ability to reduce micro-porosity, making the object more compact, less friable, reducing the absorption of water both on the surface and in depth. Nevertheless, Paraloid® B72 treatment is responsible for surface saturation and glossy effect and its degradation processes essentially consist of chemical transformations, due to the action of some parameters: light, temperature, presence of oxygen, interactions with the substrate and atmospheric pollution. Recently, a lot of research can be found in the literature dealing with the development of innovative consolidating treatments, which remains an open challenge. Until now, the only effective material able to replace the Paraloid® B72 is an aliphatic resin, Regalrez® 1126, characterised by high solubility in non-polar solvents and smaller molecules, which better penetrate inside the wooden structure. However, the structural reinforcement obtained is significantly lower than the one achieved by the acrylic resin. To ensure high-performance structural reinforcement, the common procedure is a two-step treatment: a first application of Regalrez® 1126 and a second one of Paraloid® B72 [1]. However, even if this procedure is widely employed, the problems related to the use of the acrylic resin still need to be solved. This study deals with the development and characterisation of Regalrez® 1126 and Paraloid® B72 in solution with EP and RD nanostructured Laponite® particles at different percentages, in order to obtain good compatibility, structural reinforcement, penetration capacity and saturation of wood's macro and micro-porosity. Each formulation has been preliminarily characterised from the mechanical point of view by means of tensile test, carried out on film samples and compression test performed on wooden mock-ups. The tensile test of the resin's film containing 3% (w/w) of Laponite® RD and EP, showed a good mechanical behaviour with values of the stress-strain curves almost doubled to those of Paraloid® B72 and Regalerz® 1126. However, due to the precipitation of the laponite nanoparticles added to the aliphatic non-polar resin/solvent solution, the impregnation tests of the wooden mock-ups could not proceed. On the other hand, the solution of acrylic resin with Laponite® RD nanoparticles, proved stable and showed good structural reinforcement performances. In this way, with a lower amount of consolidating material compared to the traditional technique, the consolidation treatment was equally effective. Due to the presence of the laponite's high atomic weight particles, the applicability of micro-CT technique to monitor the penetration of the consolidating material inside the wood, was assessed [2]. Moreover, the possibility to employ a three-dimensional virtual reconstruction by photogrammetry to monitor dimensional variations of the samples before and after the treatment, was also investigated. Finally, the solution of 8% (w/w) Paraloid® B72 and 3% (w/w) Laponite® RD was employed as consolidation treatment of a 16th century wooden sculpture as a first application on a real case-study.

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Innovative phosphonate consolidant: pushing the boundaries of carbonate stone artifact preservation

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Keywords: Phosphonate, Consolidant, Carbonate, Stone, Preservation

Abstract

In recent decades, new synthetic materials have been tested for the protection and restoration of carbonate stone substrates, which are often subjected to deterioration, due to age and weathering [1]. This degradation process results in an evident roughening of the stone surfaces and the partial loss of carved details on artifacts. In this work, an organophosphonate salt has been synthesized as a derivative of the well-known diammonium phosphate, fully characterized by microchemical and spectroscopic means and tested by the immersion method on calcium carbonate powder, white Carrara marble and naturally degraded white marble coming from the early Christian Basilica of San Saturnino in Cagliari (Italy). The characterization of the treated stone samples by diffractometric techniques and microscopy, colorimetric, and porosimetric measurements, showed that this compound reacts on the stone surface to form a passive layer, while preserving the mechanical and chromatic properties of the treated samples. It is noteworthy that the treatment with the novel organophosphonate salt, addresses a significant challenge: overcoming the metastability of the new phases obtained by consolidation with the use of diammonium and ammonium hydrogen phosphate [2]. By employing the proposed derivative, a high selectivity in the consolidation process can be obtained, resulting in the formation of a single, remarkably stable and water-insoluble consolidating phase.

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Preserving Venice's heritage: an innovative safeguarding approach against biodeterioration

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Keywords: Marmorino plasters, Photocatalysts, Biocidal properties, Venetian palaces, Built heritage

Abstract

Venetian marmorino is a traditional plaster, which has been covering the walls of palaces in Venice and in the Veneto region, since the 15th century. Despite its intrinsic durability, susceptibility to surface degradation processes has prompted innovative interventions. Degradation processes can negatively affect aesthetic properties of the surface, leading to the formation of stain deposits of different origins (i.e. pollution, bio-deterioration, vandalism), which can change the material colour and even trigger other severer degradation phenomena. A compelling method to prevent these phenomena, involves employing coatings with photocatalytic properties. This approach ensures that the deposits are chemically removed as soon as they start to deposit on the surface, using only oxygen from the atmosphere and light as an energy source. Through photocatalysis, these materials can break down primary environmental pollutants, both organic and inorganic (VOC, NO_x), grant self-cleaning properties and diminish the likelihood of microorganism attacks, interacting both through optoelectrical and photocatalytic actions. This study investigates an approach employing photocatalytic nanomaterials, featuring titanium dioxide (TiO2) and zinc oxide (ZnO), to enhance the plaster's resistance towards biodeterioration, specifically to microbiological colonization. The integration of TiO2 and ZnO applied both as top coatings (finish layer) and within the mortar matrix, produced compelling results. Notably, these modifications imparted self-cleaning properties and inhibited fungal growth. The study targeted specific microorganisms, sampled from real-case stone materials in Venice, namely *Penicillium italicum* and *Cladosporium spherospermum* fungi. Microscopic observations and electron microscopy (SEM) analyses confirmed the antimicrobial properties of the modified marmorino plaster. The experimentation involved verification of the antimicrobial features through optic microscopic observations, providing insights into fungal colony growth on marmorino mock-ups with distinct compositions and finish layers. The selected fungi served as reference microorganisms for their known impact on wall materials in Venice. The subsequent SEM analysis further corroborated the efficacy of the modified marmorino in inhibiting fungal growth, showcasing its potential in preventing biodegradation, such as spore development or mycelium rooting. The innovative safeguarding approach demonstrated remarkable capabilities, not only in reducing the pollutants present in the environment and preventing surface degradation, but also in inhibiting microorganisms' proliferation, such as fungal growth, resulting in an inhibition of the ability to take root and spore development. Specifically, for both types of fungi, the presence of zinc oxides in the plaster mixture contributed to creating an unfavorable environment for fungal proliferation. Regarding the top coating, the addition of TiO_2 nanoparticles to the traditional soap-based finishing layer, also enhanced the antimicrobial effect. Given the intrinsic properties of the two metal oxides, their antimicrobial activity

was correlated with their photocatalytic and optoelectrical activities. In conclusion, it was possible to confer antimicrobial properties to the Venetian marmorino plaster through photocatalysts, successfully blending a historically traditional material with scientific innovation.

Feasibility study on the application of stone processing wastes for the conservation of archaeological ceramics: the alkali activation technology

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Keywords: Alkali activated binders, Wastes, Conservation, Ceramics, Circular economy

Abstract

Sawing sludges (SS) are the finest rock-waste of industrial processing (i.e. cutting and polishing) of stones which result from the mixing of rock powder (Ø < 50 μm) with the water used to cool down the cutting tools. According to the European List of Wastes (LoW) regulated by EC n. 2150/2002, powders from stone sawing are considered a non-hazardous waste. Unfortunately, this often leads to the mismanagement of the SS, which are abandoned and accumulated in large heaps, creating a significant environmental impact [1,2]. However, it may be possible to make use of this waste material. SS, like those based on aluminosilicates, are suitable as a precursor in the Alkali Activation (AA) materials synthesis, leading to the reorganization of the initial crystalline structures of rocks into a new amorphous or semicrystalline homogeneous 3D network [3]. The process takes place at room temperature and without any energy consumption or precursor pre-treatment, resulting in an eco-friendly procedure [4] with many fields of application [3]. Previous research proved the feasibility of using waste-based AA-materials (AAMs) in the restoration of artworks [5,6]. In this study, the feasibility of using SS-based AA-binders for the conservation of Norwegian archaeological ceramics is investigated. Three types of precursors, varying in mineralogical composition, were initially mixed with a low amount of metakaolin and then, NaOH (8M) and $NaSi_2O_3$ (SiO_2/Na_2O = 2) were added to obtain the AA-binders. The materials were preliminarily characterised using X–Ray Diffraction (XRD), Dynamic Vapor Sorption (DVS), Ultrasonic Pulse Velocity (UPV), colorimetry and Oddy test. Next, AA-binders were used as a filling material on modern ceramics to evaluate the properties of the pastes during application, as well as their aesthetical and physical changes over time. The test revealed some issues related to the paste application, thus permitting the development of a protocol for achieving the best result in terms of conservation outcome. Finally, following the developed application protocol, AA-binders were tested as a filler on Norwegian archaeological ceramics of different shapes and thicknesses, with some

promising results. This work demonstrates that AAMs could be considered an interesting and potentially sustainable alternative to the filling materials traditionally used in conservation, opening up to further studies assessing their applicability on other types of artworks and historical materials.

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Geopolymer waste in a cradle-to-cradle process: new resources for a green conservation of cultural heritage

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Keywords: Conservation, Sustainability, Geopolymers, Ceramics, Waste

Abstract

Industrial, construction and demolition activities are today the responsible for the production of non-sustainable volumes of waste. In the last years, waste management became an economic issue for companies and an environmental priority for policy makers. Waste recycling by using it as secondary raw materials, is the solution most advocated, concurrently reducing waste environmental impact and exploitation of

virgin materials, which are no more abundantly available [1]. By reusing the waste with aluminosilicate composition (ceramics or fly ash, etc.), geopolymers can be obtained. These are new binders resulting from the activation of an aluminosilicate source by an alkaline solution. The chemical reaction determines the aluminosilicate species dissolution and their re-arrangement in an amorphous three-dimensional network by polycondensation. Geopolymers are recognized as promising eco-sustainable alternative to traditional materials for construction and restoration. Their aluminosilicate nature ensures chemical compatibility towards silicate substrates as ceramic materials, which represent one of the most diffused constituting materials of cultural heritage. Geopolymers can be optimized for the kind of intervention needed, satisfying the requirements of physical, mechanical and aesthetical compatibility required by restoration ethics. Today, more than ever, as extensive research on geopolymers proceeds, the generation of geopolymer waste increases. Furthermore, considering them as "the materials of the future", a new kind of global waste arises. Thus, it becomes important to anticipate solutions for the management also of this kind of waste [2]. Nevertheless, few studies are available on geopolymer waste recycling, used as aggregates [3] or partially replacing precursors for new geopolymers [2]. The chance to create novel geopolymer materials by recycling up to 100% of geopolymer waste, is until now, little explored [4]. The present work aims to evaluate the feasibility of using ceramic-based geopolymer waste as precursors for further geopolymer materials, suitable for the conservation of ceramic-based cultural heritage. Following the principle of "cradle-to-cradle", several ceramic-based geopolymers resulting as waste from previous research, were employed as geopolymers precursors, solely or in binary mixtures with metakaolin. After their characterization, their behavior under alkaline activation and their ability to consolidate at room temperature, were evaluated. The evolution of the geopolymer gel was confirmed by ATR-FTIR spectroscopy and X-Ray Diffractometry, whereas preliminary results on mechanical strength showed values comparable to those of the geopolymers from which they originate. Finally, to assess their suitability in the conservation field, their application performance was evaluated by using them on ceramic pottery and bricks as filler, adhesive and pre-casted elements for partially substitutions of missing parts. The workability, adhesion properties and colorimetric parameters, were studied. The research demonstrates the recyclability of geopolymer materials, particularly of those obtained by recycling ceramic waste. The outcomes are promising for ceramics conservation and encourage further research for the development of these innovative green products.

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Reusable aerogels based on functionalized cellulose nanocrystals for desalination of mural paintings

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Keywords: Cellulose nanocrystals, Aerogels, Salt removal, Mural paintings, μEDXRF

Abstract

The development of advanced materials for preserving and restoring cultural heritage poses a significant research challenge. These materials not only have to demonstrate their ability for the purpose they were designed for, but also must align with the goals of the EU Green Deal. Cellulose, known for its renewability, sustainability and eco-friendliness, stands out as a promising biopolymer, due to its inherent compatibility with various substrates. Recent advancements in nanotechnology highlight the potential of nanocellulose as a consolidation agent or reinforcement coating [1]. This material has shown positive contributions to the consolidation of archaeological wood [2] and historical paper [3], the stabilization of damaged painting canvas [4], among other applications. Apart from these purposes, the chemical modification of nanocellulose for stable liquid systems, remains underexplored. Designing self-assembling structures using nanocellulose, with abundant free hydroxyl groups, could lead to sustainable cleaning products. This synthetic strategy can provide new hydrogels and aerogels, which could serve as safe carriers of cleaning agents with the aim to remove exogenous materials (soluble salts, soiling, aged varnishes and so on) from water-sensitive artworks. Within the framework of the project ENCLOSURE [5], this study focuses on developing novel functionalized cellulose nanocrystals-based aerogels. These aerogels, composed of dialdehyde cellulose (DAC) crosslinked with a natural

triol, provide a 3D structure with tailored properties for the removal of external substances. DAC was synthesized via cellulose nanocrystals oxidation and its characterization was conducted using 13C-NMR and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT). Materials with different DAC/triol ratios were thermomechanically and chemically characterized to obtain aerogels with high water uptake capacity, adaptability to irregular and porous surfaces, applicability in both horizontal and vertical orientations, residue-free application and reusability. The most promising aerogel was immersed in Milli-Q water to assess its effectiveness in desalinating wall paintings. Fresco painting mock-ups were prepared following the traditional Roman recipe to test the aerogels. Such mock-ups were then impregnated under vacuum, with chlorides and sulfates to simulate salt degradation. Micro energy dispersive X-ray fluorescence (μEDXRF) imaging allowed to estimate the extent of salt removal. Additionally, the reusability of the aerogels was also demonstrated applying the same aerogel several times by wringing out the aerogel manually after each application. Finally, in the near future, we plan to address environmental and operator health concerns related to these materials, before transferring them to the conservation laboratory.

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Cellulose nanofiber-based hydrogels as a sustainable alternative for soiling removal on canvas paintings

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Keywords: Cellulose nanofiber-based hydrogels, Soiling removal, Canvas paintings, Edvard Munch

Abstract

Hydrogels are three-dimensional structural materials composed of linkages between polymer chains, with a significant water presence within the matrix. Their tunable properties and versatile fabrication techniques have led to a widespread use in various fields, ranging from biomedical to engineering applications [1]. In the field of cultural heritage preservation, the removal of soiling is a prevalent, delicate and fundamental task in preserving artworks. Hydrogels can serve as a vehicle for applying cleaning agents more efficiently, with a longer solution retention time, thereby enhancing the control over the cleaning process [2]. Beyond their capacities, new cleaning materials should align with the requirements of the 2030 Sustainable Development Goals, emphasizing the use of renewable and biodegradable materials. Biopolymers could play a crucial role in achieving the latter. Among various alternatives, cellulose, especially at the nanoscale, stands out for its specific surface area, non-toxicity and – when combined with crosslinkers – notable strength, stiffness and hydrophilicity. These qualities makes it suitable for preparing hydrogels for soiling removal [3]. Within the framework of the project ENCLOSURE [4], the aim of this work is to develop cellulose nanofiber-based hydrogels crosslinked with green amine compounds for the soiling removal from unvarnished canvas paintings. To enhance the selectivity of the cleaning process, different fluids were loaded to remove specific elements without damaging artwork's surfaces. To evaluate the efficacy and innocuousness of the new cleaning alternatives, an artificial soiling mixture was applied to mock-ups reproducing the painting technique of Edvard Munch in the Aula of the University of Oslo [5,6]. Micro-Energy Dispersive X-Ray Fluorescence (μEDXRF) imaging and Fiber Optic Reflectance Spectroscopy (FORS) techniques, in the VNIR-SWIR range, were used to chemically evaluate the removal of the soiling mixture. Additionally, apart from the physical and chemical characterization of the hydrogels, the soiling retained on them was also characterized through μEDXRF. The results indicated that these hydrogels are capable of effectively removing the components in the soiling.

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Exploring the action of fatty acids as green solvents for the removal of hydrophobic paint-layers

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Keywords: Deep eutectic solvents, Fatty acids, Paint removal, Hydrophobic paint surfaces, Green solvents

Abstract

Conservators are often challenged by the need to formulate and apply new methodologies for the removal of paint layers. For this purpose, different approaches are currently available, such as the use

of organic solvents, mechanical and laser cleaning. In the last few years, deep eutectic solvents (DES) [1] have emerged as a new generation of solvents, offering a green alternative to toxic liquids. These compounds are prepared as a mixture of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). In this work, mixtures of saturated fatty acids [2] (ranging from valeric, C5:0, to lauric, C12:0, acid), both as DES and as "standard" solutions, were tested on tailored oil-based paint mock-ups to evaluate their efficacy in removing hydrophobic paint layers. A Design-of-Experiment (DoE) approach, implemented using the "mixexp" package available in the open-source environment R/RStudio [3], guided the selection of mixtures for the study. The mixtures were applied using different supports, such as agar rigid gels and Evolon microfilament fabrics. Results from the mock-ups were evaluated by different conservators for effectiveness and odor. These results were then elaborated with the help of the aforementioned software and a combined response surface was generated to determine the optimal mixture. This investigation was inspired by the study of overpainted wall paintings by the Norwegian artist Peder Balke, located at Billerud in Norway. These were presumably painted in 1834 and overpainted shortly after. Micro-Fourier Transform Infrared analyses in Attenuated Total Reflectance mode showed the presence of oil as a binder in both the original paintings and the overpaint, posing a challenge in removing the overpainted layer without damaging the underlying artwork. To our knowledge this is the first time that such compounds have been adopted for the removal of hydrophobic paint surfaces and that a DoE approach has been employed to systematically address a cleaning problem in conservation.

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Green solvents and green strategies for the cleaning of street art: from molecular to macroscale investigations

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Keywords: Green solvents, Cleaning, Street art

Abstract

Nowadays, in the field of restoration, there is an increasing demand related to the development of new green methods which are safe both for the operator and for the environment. In this context, we have so far developed different formulations obtained with biopolymers, such as polyhydroxybutirate and agar in combination with green solvents of different polarity (Dimethylcarbonate, γ-Valerolactone, Ethyl Lactate, Biodiesel, green Deep Euctetic Solvents) for the selective removal of different types of unwanted coatings from different types of artefacts, such as movable and immovable paintings, metal objects, paper substrates, cinematographic movies [1-4]. In the frames of the Italian-funded project, Superstar (https://prin2020superstar.dcci.unipi.it/), we are developing innovative green cleaning systems for street art in order to remove deposits or paints from acts of vandalism on graffiti. To define the optimal cleaning solution, a preliminary chemical-physical study on a selection of green solvents, was conducted. Binary mixtures of γ-Valerolactone (GVL) and water (GVL/W) and dimethyl carbonate and GVL (DMC/GVL), were considered. Empirical solubility values for the mixtures were determined by Teas Charts and compared/integrated with spectroscopic investigations (UV-Vis fluorescence, micro-Raman and ATR-FTIR spectroscopies) to probe the intra and intermolecular interactions as a function of the solutions molar fractions and deriving the chemical-physical behaviour of the systems. First cleaning tests on test-systems prepared in laboratory, were also performed to correlate the specific chemical-physical properties of the binary solutions to the cleaning performances.

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Perception and objectivation of cleaning of paintings

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Keywords: Material appearance, Varnish removal, Multimodal analysis, Perception

Abstract

Appearance plays a major role in the conservation process. Indeed, the eye is the expert's tool for diagnosis and validation, as well as the observer's path to appreciate the work. In this way, linking visual changes to physical measurements of appearance, is a new subject of research and, for instance, could be useful to select the most suitable method for cleaning [1]. We want to link perceptual measurements from sensory analysis with measurements obtained from optical methods during a specific conservation intervention: cleaning. The aim is to find which attributes of appearance are relevant during this process, in order to design a new tool which could help conservators in decision making and traceability. Mock-ups made of alkyd paints on canvas were varnished and artificially aged before being unvarnished by conservators. The modifications of appearance at each step of the process were studied using objective physical measurements of colour, gloss and surface state. Different instruments were used to analyse these changes: for the colour it was photography, multispectral imaging, hyperspectral imaging and spectrophotometers, whilst for the gloss, the measurements were performed with a simple glossmeter and were compared with BRDF measurements and a study of the surface roughness. These techniques are different in respect to the resolution, the precision and the scale of investigation. This multimodal analysis provides substantial information about the impact of varnish, ageing and varnish removal on the visual aspect of the paintings. The results match with the common knowledge of conservators and heritage scientists. For example, varnish increases the saturation and the gloss, ageing makes surfaces duller and makes the varnish turn yellow. Nevertheless, results differ across all instruments and raise the question about which one is the closest to the conservators' perception. At the same time, a sensory

analysis was conducted. A questionnaire was implemented in order to collect the conservators' opinions on their varnish removal: is the result homogeneous? Is there still varnish on the pictorial layer? By correlating these sensory comments with physical measurements, we identified the combination of attributes that best fit the changes of perception during cleaning. We also characterised the notion of homogeneity and identified the thresholds of perception during the cleaning process. To do so, we used a statistical technique, linear discriminant analysis (LDA), which is a common method in the food-processing industry in order to cluster products [2,3] and, therefore, allowing us to understand which physical parameters classify perceptual groups.

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Varnish removal from works of art on paper, a controversial matter. Recent reflections on the materials and methodology used for the treatment of the varnish layer

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Keywords: Varnish, Works of art on paper, Removal, Analysis, Green materials

Abstract

The practice of varnishing works of art on paper, in particular prints, to provide a glossy finish, was developed for two main reasons: to imitate oil paintings, so the works of art on paper could mingle with them, as well as to avoid the high cost of the glass on the frame [1]. Varnishing was also applied to make maps and drawings more durable for handling and display [2]. Commonly, works of art on paper were coated with oil-based and alcohol-based varnishes. Upon ageing, the varnish layer becomes brittle and hard, cracks and discolours [3]. Consequently, the deterioration of the varnish promotes severe damage

to the works, such as the loss of the mechanical strength of the paper support or the flaking of the media [4]. This process can lead to the complete loss of the image, especially when exposed to aggravated environmental conditions. Removing a varnish coating is a challenging procedure in the field of paper conservation, with questionable results. There are concerns about the impact of the varnish removal procedures on the paper support, the media and the binding agents, as well as the possible residues of the reagents used in the cleaning solutions or the alterations caused to the media and the paper support and the long-term stability and aesthetics of the works. Within the framework of the EU funded project GreenArt, the application of green cleaning liquids and gels was studied and compared to solvents using swabs and other alternative techniques, gel and cleaning fluids available in the market, as well as laser cleaning on two 18th-century varnished black and white prints, which were used as sacrificial objects. Research methodology included the identification of the materials using imaging techniques (VIS, UVL, UVR, FCIR and multispectral imaging), optical microscopy and ATR-FTIR. In order to record and evaluate the results from the application on various materials, imaging techniques, colorimetry, glossimetry, microscopy on the original works and ATR-FTIR, were employed. This methodology recorded the changes and the results from the application and indicated the presence of residues.

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New atomic oxygen technology for non-contact cleaning of cultural heritage materials from carbon-based contaminants: approaches to atomic oxygen generation pathway, characterization of effluent and potential for greener cleaning methodology

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Keywords: Non-contact cleaning, Atomic oxygen, Cold atmospheric plasma, Green materials, Sustainable conservation

Abstract

The paper discusses atomic oxygen (AO) as an innovative green material for non-contact cleaning of unstable and sensitive cultural heritage objects and a new approach to AO generation at atmospheric pressure, tailored to cultural heritage needs, currently in development by the MOXY Horizon Europe project (2022-2026) in the context of green technologies for cultural heritage (CH). AO, found in outer space in the Low Earth Orbit (LEO), 80-1000 km above the Earth's surface, offers the possibility of non-contact liquid-free cleaning of soot, hydrocarbons and organic and biological contaminants from many problematic cultural heritage surfaces. AO reacts with soot and carbon-based contaminants, converting them into volatile species, mainly CO, CO_2, and H_2O vapors. AO can be used as a cleaning agent with high chemical selectivity, which can be tailored to the composition of the material to be treated. AO in conservation originates from a serendipitous invention, necessary due to the defacement of a lipstick kiss on Andy Warhol's 1961 painting "Bathtub". Having exhausted the available means for removing it, conservators turned to NASA, where B. Banks and S. Miller pioneered an atmospheric AO apparatus. AO was formed by flowing O_2 in He gas through a high-voltage, low-current DC arc, placed a few millimeters from the surface, removing the lipstick without touching the surface. To use AO for surface cleaning treatments, it must be produced in high fluences and then transported to the surface. This is challenging

because AO is extremely short-lived in atmospheric conditions. Moreover, in atmospheric conditions, a higher frequency of collisions causes undesirable gas heating. For conservation, an AO generator needs to produce high concentrations of AO, while limiting the yield of ozone, NOx, radical species, heat and UV-VUV radiation. To tailor AO parameters to conservation, the He/O_2 gas phase composition, the pulsed operation, the waveform of applied voltage and the geometry of the nozzle, need to be finely tuned to achieve the desirable performance. The poster describes a novel approach adapted for conservation for producing AO by flowing He and O_2, using a radio frequency (RF) at 13.56 MHz plasma and applying a secondary flow of Ar or He as a shield gas, aimed to protect the AO from the environment. The AO method in development can generate an AO effluent at a sufficient distance from the treated surface (3–20 mm) and at the 1-6 W power needed to create AO. Low power was essential to maintain safe low effluent temperatures (30-60°C) during the treatment. The AO effluent was investigated using optical emission spectroscopy (OES) and FTIR. Ozone and NOx were measured using respective analyzers. The quartz crystal microbalance (QCM) method was tested for the AO source evaluation. Preliminary findings indicate that AO is a radical improvement over the current state-of-the-art cleaning methods. The poster discusses the challenges in developing an AO process appropriate for CH conservation. It presents the optimization of the AO generation and the transport flow required to create an effective non-contact cleaning process for the removal of carbon-based and organic contaminants (fire-born soot, environmental pollution, biological contaminants, degraded conservation materials, biocides) from sensitive porous CH materials. To fully assess the new AO material and technology, consideration was given to comply with the Safe & Sustainable by Design (SSbD) framework and the Life Cycle Thinking, highlighting the need for investment in developing new green materials and sustainable conservation practices in cultural heritage.

Cleaning soot-contaminated silk textiles using plasma generated atomic oxygen, a new technological approach

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Keywords: Plasma technology, Cleaning, Fire soot, Textile

Abstract

The cleaning of soot from historical textiles is one of the most intricate challenges for conservators [1]. Soot can be electrostatically bonded to the surface and penetrate the substrate following fire damage. Conventional contact cleaning treatments, such as dry and solvent cleaning often result in compacting

the particles deeper into the fibrous structure, giving rise to an incomplete and unsatisfactory outcome [2,3]. Plasma technology has been utilized for surface cleaning in industries, due to its contactless, non-toxic and residue-free characteristics [4,5]. In our current projects, a novel non-thermal plasma generated Atomic Oxygen (AO) is developed for removing carbon-based contaminations from a series of substrates [6-8]. Specifically, when operated in ambient air, highly reactive AO was able to oxidize superficial soot deposits into non-toxic H_2O and CO_2 rapidly, without causing visible damage. This was achieved when enhancing the AO generation from the plasma jet and, meanwhile, confining the surface temperature under 60°C. In this work, we report the development of a set of optimized parameters allowing the cleaning of soot from silk fabrics. Silk was selected as it is a widely used protein-based fibre known to be more prone to organic solvents, high temperatures and oxidizing agents than are cellulosic materials, such as cotton [9]. Nevertheless, there are relatively few publications targeting soot removal from textiles. The generation of AO and temperature control is further optimized by changing the He/O_2 gas admixture and the voltage amplitude. The cleaning results were assessed at different stages by optical microscope (OM), scanning electron microscope (SEM), fibre optics reflectance spectroscopy (FORS), colorimetry and ATR-FTIR. The results indicate that soot can be safely removed from undyed silk fabric with AO when keeping the parameters below certain damage thresholds, as will be demonstrated during the present contribution. Further mechanical and molecular analysis of silk samples exposed to variable doses of AO, will be performed in the near future. This research is a part of the EU funded MOXY project (ID: 101061336), as well as of the Plasmart (FWO grant OZ9056).

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Nature self-printing: multidisciplinary study bridging history of technology, experimental reconstruction and artistic research

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Keywords: Electrotyping, Nature self-printing, Experimental reconstruction, Graphic techniques, Artistic research

Abstract

This study provides the missing cornerstones for understanding early Austrian electrotyping history [1], based on archival and scientific research on original objects and on electrochemical and self-printing experiments, which mimic and reproduce the historical processes. Electrotyping enabled unlimited duplication and was successfully used in arts and graphics [2]. The historical findings form a bridge to the issues facing modern society in the age of the digital, in which the distinction between original and copy is increasingly fading. Nature self-printing is a graphic art technique developed and patented by Alois Auer and the Austrian National Printing Office (k. k. Hof- und Staatsdruckerei) in 1852 [3]. The Department of Botany and Biodiversity Research of the University of Vienna [4], still owns 515 original copper plates, i.e. patrices, from the largest and most prominent Austrian nature self-printing project in history from 1856, the "Physiotypia plantarum austriacarum" [5]. This technique was developed by Constantin Freiherr von Ettingshausen and Alois Pokorny in Vienna for the electrotyping reproduction of e.g., dried natural objects, fabrics, lace samples or embroideries. The possibility of duplicating preparations of unmistakable and authentic prints of natural objects, which were very time-consuming to produce, must have seemed particularly appealing. Three original patrices from the Physiotypia printing project were investigated by digital optical microscopy, which provided information about the production methods, as well as the surface properties. These are essential for conservation considerations regarding the sensitive surface of the printing plates. Of great interest was also the accuracy of the faithful transfer of the plant objects by the historical process. The technique of natural self-printing that has fallen into oblivion, was revived and experimentally reconstructed. The reconstruction of the historical process started with the impressing of plant motives onto a lead plate. A negative of this was produced using siloxane and was mounted on a stable support plate of acrylic glass. The siloxane surface was made electrically conductive with a thin coating of graphite powder. Copper was electrodeposited on this to form a sufficiently stable printing plate, which was then used to produce a series of prints. In the cross-thinking process of researching and experimentally reconstructing the technique of natural self-prints, the past and the present encounter with each other. From different perspectives, it is exciting to see what technical hurdles had to be overcome in the production of the natural prints and how such a process can be recreated today. The present heritage science study relies on and strengthens the synergies between art history, historical techniques, conservation science and contemporary artistic research, as they all have a part to play in researching, preserving and imparting cultural heritage and can mutually benefit from each other.

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Long-term microclimate monitoring using a wireless sensor system for the conservation of cultural heritage sites: the case of a Byzantine Hermitage in Thessaly, Greece

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Keywords: Wireless sensors, Monitoring, Microclimate, Temperature, Humidity

Abstract

Climate change, beyond threatening infrastructure, ecosystems and social structures, is also exacerbating the physical deterioration of cultural heritage sites, raising in this context various concerns about their conservation. Given the observed and projected trends in the main meteorological parameters, the harmful and destructive effects of climate change on cultural heritage sites are expected to increase. Indeed, as indicated in literature, degradation and erosion of cultural heritage sites, including in particular, stone and brick structures, is further intensified by changes in air temperature and humidity in the atmosphere. In this respect, assessing the performance of microclimate variables within these structures themselves, as well as analysing the conditions for effective conservation of artefacts, are both challenging endeavours. To this end, this work presents an approach for the long-term monitoring of the variables affecting the microclimate of a Byzantine Hermitage, which extends into a small cave located on the southwestern side of Mount Olympus in the district of Thessaly in Greece. Specifically, the Hermitage, which is dedicated to the Holy Cross, is dated back to the 14th century and its structure extends in a small cave following naturally the rock and

the vertical walls, as well as on the narrow platform formed by the rock in front of it. The interior of the Hermitage comprises a complex of three chambers, that is the chapel inside the cave, as well as the narthex and the hermit's cell on the platform, which was covered by a single wooden roof that has been destroyed and not restored up to present. Beyond the structure of the Hermitage, what is of particular interest are the remarkable frescoes preserved in its interior, depicting saints and hierarchs, as well as scenes from the life of Jesus Christ, all dated back to 1339 AD during the reign of the Emperor Andronicus III Palaiologos and his wife Anna. Based on the structure and the specificities of Hermitage, a wireless sensor system was integrated in its premises, consisting of a network of battery-powered sensing nodes deployed at the most critical and accessible points, for the long-term monitoring and assessment of microclimate variables, namely temperature, relative humidity (RH) and carbon dioxide (CO_2) concentration. The data acquired by the system's sensor nodes, constituting a wireless sensor network (WSN), is stored in the cloud, where it is managed, allowing the long-term monitoring and assessment of microclimate conditions in the Hermitage. The evaluation of the system indicated that the methodology adopted was quite effective in terms of the long-term monitoring process and the assessment of the microclimatic conditions in the Hermitage, allowing the early diagnosis of imminent risks and taking the required maintenance actions. The future directions of this work are oriented towards the integration of the wireless sensor system into the Internet of Things (IoT) to allow the remote control of the microclimatic conditions of the Hermitage through real-time monitoring and management of the relevant parameters.

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Pedological rectification offering better environmental systems (PROBES): a novel method to mitigating deterioration of earthen archaeology

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Keywords: Environmental monitoring, Earthen archaeology, Conservation management, Statistical analysis

Abstract

Exposed in situ earthen architecture is extremely prone to accelerated deterioration [1]. Environmental cycles that cause swelling, salt efflorescence and biological decay, are but a few ways this breakdown is exacerbated, resulting in earthen archaeological remains rapidly losing coherence, shape and ultimately, cultural value. Several invasive methods have been attempted to cessate this process, to varying effectiveness. However, only recently has quantified site deterioration been correlated with environmental data [2]. Results from these reports showed that the soil moisture of walls and profiles could potentially be used as an indicator of earthen archaeology deterioration rates. The site of Vésztő-Mágor is the largest prehistoric tell on the Great Hungarian Plain with ~7 m of stratified cultural layers dating to the Neolithic, Copper and Bronze Ages. The tell features a unique, in situ exhibition of a stratigraphic snapshot of Hungarian prehistory and is a valuable cultural commodity for the local community. The 19m x 4.5m trench was opened in 1986 in the central part of the tell and was later covered with a permanent, closed structure to facilitate public access. In the decades since, fluctuating environments have caused deleterious erosion to the site. In 2022, a program was launched to mitigate deterioration, rejuvenate the site and increase visitor engagement. As the bottom of the trench sits immediately above the water table, it was unknown how the surrounding soil affected the atmosphere of the exposed environment. This would need to be determined prior to any shelter modification, such as the installation of a sustainable HVAC system, as failure to characterise this relationship could result in the continued rapid erosion of the trench. To determine this depositionally stable environment, a novel method was devised to understand the relationship between the pedological and atmospheric environments. Four Delta-T PR2/6 soil profile probes were vertically installed in intervals into an exposed 5-meter profile wall. These one-meter-long probes monitor soil moisture content at 10, 20, 30, 40, 60 and 100cm. These allow for a nuanced analysis of how moisture movement throughout the pedological section impacts – or is impacted by – atmospheric fluctuations in relative humidity and temperature. This data is measured against temperature and humidity data collected by seven TinyTag Plus 2 – TPG-4500 environmental monitors. Environmental patterns can then be used in determining and employing future modifications to the atmosphere and shelter. Data for this pilot study was collected from July through October 2022. Initial analysis showed that, although the resolution of the probes is insufficient to determine any diurnal correlation between soil moisture and relative humidity, data trends over the entire collection period suggest that the humidity of the trench is impacting the moisture content of the profile. Additionally, a desiccating event was observed at 40cm, as the 40cm sensors on every probe returned drier results than either 30cm or 60cm. This aligns with Heller's model [3] of two-phase evaporation occurring between saturated and unsaturated soils, with a 'bone-dry front' forming where these phases meet. This paper will discuss the implementation of this method, the statistical analysis of the data and its implications on managing the environment of Vésztő-Mágor.

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Analysis of fire effects on cultural heritage

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Keywords: Fires, Cultural heritage, Stone, Painted sculptures

Abstract

FENIX is a Spanish project which tries to develop methodologies to evaluate fire hazards and consequences in cultural heritage. Fires are one of the most dangerous hazards for cultural heritage and their occurrences are mainly due to anthropogenic agents as armed conflict, lack of maintenance of electric net or gas pipeline systems, employment of candles, etc. and could destroy complete or partially buildings and their movable heritage. The approach employed for vulnerability analysis is based on ART-RISK 3.0, an AI tool for preventive conservation [1], where the main factors for buildings and special zones are evaluated. The model was applied at three churches of Seville in different periods. The results show that maintenance and preventive conservation actions are key strategies to prevent fires. When the fire occurs, the project evaluates the damage by chemical characterization of samples. In this paper, two polychrome wood sculptures of the 20th century affected by fire were studied. Cross sections were prepared to determine the stratigraphic sequence and thickness of layers and were analysed by optical microscopy (Leica DM5500) and scanning electron microscopy with energy dispersive X-ray spectroscopy (JEOL model JSM-5400 and EDX-Oxford with software INCA Energy 200). Samples with different degrees of alteration were studied from burned sculptures. One of the sculptures was only partially affected by the fire. This made it possible to compare areas affected by the direct action of the flames and other unexposed areas, although they have also been subjected to high temperatures, potentially affecting their components. The other sculpture was severely damaged and the structure had almost completely collapsed; a dramatic transformation of the materials occurs at the structural and chemical level. Generally, this is manifested in the form of chromatic alteration where the preparation layer changes from brownish to totally darkened tones and the polychrome layers exhibit a range from gray to completely black. The presence of internal cavities, pores, fractures, superficial cracks and deformations of the layers, caused the structure to partially or totally collapse as a consequence of the thermal shock.

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Rescuing documents and books from earthquake, fires and floods. The drills in the Archive and Library of Antequera (Malaga, Spain)

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Keywords: Plans for safeguarding, Drills, Rescue

Abstract

FENIX and FENIX 4.0 are Spanish research projects aimed at developing new technologies for the prevention and management of fires and natural disasters affecting both movable and immovable cultural heritage. Protecting our cultural heritage against disasters is a core principle of the Spanish National Plan for Cultural Heritage Research. Safeguarding cultural heritage not only preserves a significant source of income for urban and rural areas, but also enhances our resilience. Within this framework, these projects implement best practices for decision-making models and develop tools for preventive conservation, emergency response and resilience policies. In November 2022 and November 2023, two comprehensive drills (earthquake and flood; earthquake and fire) were conducted at the Archive and Library of Antequera in Spain. These drills involved activating both the emergency plan and the provincial plan, which included the support of a cultural heritage evaluation and rescue unit. The drills mobilized firefighters, civil protection personnel, medical staff, police officers, restorers and conservators. The software ART-RISK 4 Mission Track was customized for use by the cultural heritage evaluation and rescue unit (UB) to facilitate the rescue of five types of documents, papers and books, each with varying levels of damage. Mission Track was implemented on the mobile phones of the UB team and configured in two phases: rescue and triage. The analysis of the results enables the assessment of the time required to rescue each document, conduct triage and georeference both the items and the teams during the rescue operation. Additionally, it provides insights for improving emergency plans for future drills or actual emergencies. It is the first time, through these two R&D projects (FENIX and FENIX 4.0) that this mobile technology-based emergency management software was employed for the conservation of cultural heritage in Spain.

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Towards a FAIR data management in heritage science research: updates and progress on the INFRA-ART Spectral Library

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Keywords: Spectral library, Spectroscopy, Art materials, Heritage science, FAIR data

Abstract

Data policies are relatively new to the heritage science sector. FAIR data management in heritage science research refers to the adoption of principles and practices that make data Findable, Accessible, Interoperable and Reusable. This approach facilitates the discovery and utilization of data, accelerates research progress and ensures that heritage science remains a dynamic, transparent and collaborative field. The European Commission has been actively involved in recent years in promoting open data policies and initiatives to improve data accessibility and sharing. Inspired by the FAIR data principles and the European Commission's recommendation on access to scientific information, several resources, which facilitate online access to tools and data hubs for heritage research, have been developed within the last years. To address the need for online spectral databases relevant to conservation and heritage science research, an open-access spectral library exclusively dedicated to art and cultural heritage materials, has been developed. The INFRA-ART database (https://infraart.inoe.ro/) is an open-access integrated spectral library of artist paint materials that was designed as a digital support tool for research specialists and other heritage-related professionals, who work with non or minimally invasive spectroscopic techniques. Developed as an easy-to-use web-based resource that offers open-access to good-quality spectral data for the scientific analysis of pigments and other art-related materials, the INFRA-ART Spectral Library contains, at this moment, over 1600 ATR-FTIR, Raman and XRF spectra linked to over 800 known reference materials. Starting September 2022, the INFRA-ART Spectral Library is registered as a resource within the Open Science Cloud (EOSC) Portal for higher visibility and increased FAIRness. Likewise, starting recently, the INFRA-ART Spectral Library is part of the services offered by the Romanian hub within E-RIHS (European Research Infrastructure for Heritage Sci-ence) DIGILAB. In this paper, we present the latest updates and progress on the INFRA-ART Spectral Library, including: the integration of new data types, the design and development of several web-based analytical tools (advanced search, peak search, etc.) and the design and development of educational resources. Data management practices for increased and sustainable accessibility within the field of heritage science, are also discussed.

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Hyperlyse – an open-source intuitive-user interface for viewing and analyzing hyperspectral images

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Keywords: Hyperspectral imaging, Vis/NIR, Open-source software, Data cube analysis, Multifunctional tool

Abstract

Hyperspectral imaging has gained increasing attention during the last years in the field of manuscript research. A new software tool for the evaluation of hyperspectral data cubes was developed within the course of an interdisciplinary cooperation of researchers from the humanities, computer sciences and natural sciences (Digital Transformation of the Austrian Humanities, DiTAH [1]). It was designed to provide an open-source [2] intuitive-user interface for viewing and analyzing hyperspectral images not only for spectroscopy experts, but also for using this kind of data in humanist research. Hyperlyse supports the ENVI format. The user interface has an image display showing a visualization of the currently loaded data cube, which is used to select single points or rectangular areas of interest. Furthermore, a spectrum display shows the spectrum of the selected point or area. The image controls allow to adjust the brightness of the image and to zoom in for a precise selection of the area of interest. Four modes of visualization are available: a) RGB image, b) single spectral layers at chosen wavelengths, c) similarity to a currently selected point or a database spectrum and d) the results of a principal component analysis. All results can be exported as .png images. The software further allows creating spectral databases (JCAMP-DX format) by exporting a spectrum from a selected area or importing spectra from external sources. The spectra controls allow to compare the spectrum from a selected area with selected spectra from databases or to search in databases in a specified spectral range based on the comparison of either gradients (first derivatives) or computation of squared errors. Hyperlyse was used for the evaluation of hyperspectral data cubes obtained from investigations on medieval manuscripts dated from the 15th and 16th centuries. It allowed to characterize various pigments used for illuminations by comparison to database spectra obtained from color charts and moreover, a comparison of the colors used in different manuscripts in order to detect similarities between them. Furthermore, retouches with a blue cobalt pigment on a layer of azurite were detected in one manuscript, by using the similarity visualization mode of Hyperlyse. Last, but not least, the single spectral layer visualization mode allowed discovering pentimenti in one case. We conclude that Hyperlyse is an efficient software for the evaluation of hyperspectral data cubes, which offers a set of tools with the potential to answer various scientific questions connected to material analyses and painting techniques.

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Evaluation of historical buildings using laser scanning - a case-study of Funchal Cathedral in Madeira (Portugal)

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Keywords: Laser scanning, Geospatial methods, Heritage assessment, Identification of superficial pathologies, Non-invasive and non-destructive methods

Abstract

Non-invasive and non-destructive procedures offer a benefit over standard methods of chemical analysis in the study of heritage. Unlike intrusive sampling, which involves removing a sample for examination, these approaches do not cause any damage to the materials being studied. The utilization of laser scanning enables the generation of a three-dimensional point cloud representing the object under investigation. In addition, the color and energy reflection of the objects are measured as a percentage of the energy emitted by the laser beam at the time of acquisition. Generating point clouds to document heritage structures, including individual objects or entire buildings, aids in the preservation of detailed information regarding their three-dimensional composition. If there is a loss, it is feasible to recreate the information from this source. Conversely, these can serve as the foundation for generating augmented reality content, allowing users to digitally explore a location and potentially aid, in the conservation of vulnerable sites. When applied to altarpieces, this technique enables a comprehensive examination of the painting's central area in three dimensions. This study helps identifying any potential issues with the wood, such as deformations in the wooden boards. The energy represented by the textural aspects of the painting can be divided into many value ranges. This division allows us to link a certain range to specific design elements of the painting and it may also be associated with the materials employed. The objective of the study conducted on the Funchal Cathedral in Madeira, Portugal, is to analyze the interior of the building, by examining the point cloud data. Additionally, the study seeks to analyze the altarpieces of different altars and establish a correlation between the reflection values and the materials used in the paintings.

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3D printing and 3D scanning: Preservation and protection of our cultural heritage

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Keywords: Three-dimensional scanning, 3D printing, Heritage preservation, Digital representations

Abstract

The utilization of three-dimensional scanning and 3D printing has gained significant prominence within the field of cultural heritage preservation. The application of three-dimensional scanning is employed to generate intricate digital representations of cultural heritage locations, objects and monuments, hence facilitating their utilization in research, repair and virtual exhibition. In contrast, three-dimensional printing facilitates the production of tangible replicas of cultural heritage artifacts, hence enabling their utilization in educational, exhibitionary and preservation contexts. The utilization of these technologies offers numerous benefits, such as the capacity to record and safeguard cultural heritage places, artifacts and monuments in a method that does not cause harm, alongside the capability to generate digital and tangible replicas, which can be employed as educational and exhibition objects. Nevertheless, several obstacles exist in the pursuit of this endeavor, including the requirement of specific equipment and experience, alongside apprehensions regarding the preservation of the authentic artifacts. Notwithstanding these obstacles, the utilization of 3D scanning and 3D printing has demonstrated its worth, offering advantageous instruments in the realm of cultural heritage conservation, projecting an expansion of their application in the forthcoming years.

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Virtual reconstruction of historical textiles using graph neural networks

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Keywords: Virtual reconstruction, Historical textiles, Graph neural networks

Abstract

Archaeological artifacts are often found in a fragmentary state and archaeologists need to identify matching fragments and reassemble a puzzle to reconstruct the original and analyze its motifs. The process resembles jigsaw puzzle solving; puzzle solving is challenging for archaeological textiles, which are especially prone to fragmentation, degradation, fading and deformations [1]. A vivid example of such an open puzzle problem, is the Oseberg Tapestry from the Viking Age [6]. Previous works [2,3] used classical texture classifiers, as well as pre-trained neural networks to extract features from fragments and feed the feature vectors to clustering algorithms to identify similar fragments, but the performance was not deemed satisfactory (see [1] for full overview). In this work, we take an alternative approach and use Graph Neural Networks (GNN) for puzzle solving process. The eventual intended application is the case of the Oseberg Tapestry, which tells interesting stories from the Viking Age, but has many highly fragmented and missing pieces with irregular shapes [6]. However, due to its complexity and lack of complete reference, our study uses well-preserved, but stylistically similar textile. Using artificially fragmented textile allows us to evaluate the accuracy of puzzle solving, which is harder for the Oseberg Tapestry, due to lack of the ground truth. By artificially fragmenting the textile, we simulate an unrestricted pictorial puzzle [4], a type of puzzle where pieces are arbitrarily shaped, forming a complex planar adjacency graph that demands sophisticated reconstruction techniques. As mentioned in Harel and Ben-Shahar [4], there have been a few solutions for this type of puzzle, due to its complex nature. In recent years, one notable work comparable to our problem is a work on fragment assembly using graph neural network-based (GNN) reconstruction of papyrus fragments [5]. By virtually segmenting the textile imagery data (RGB and depth maps) into non-adjacent, different sizes of square patches, we construct a dataset needed for our GNN reconstruction model. The core of our reconstruction process involves extracting features from these tapestry patches using a pre-trained neural network. The extracted feature vectors form the nodes of fully connected graphs, encapsulating the relationships between tapestry segments. Using graph neural network's pooling techniques, we can dynamically exchange information between nodes and update node embeddings containing visual and geometric data. Lastly, using the updated graph, we predict the edge connections information used to reconstruct the fragmented tapestry accurately. This methodology aims to predict the puzzle's assembly, laying a foundation for future work in the virtual reconstruction of fragmented historical textiles.

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Automatic thread counting for archaeological textiles

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Keywords: Thread counting, Archaeological textiles, Computer vision, Image processing, Edge detection

Abstract

Archaeological textile artifacts are often fragmented and human experts need to solve a puzzle to find matching pieces and reconstruct the original. This is a challenging task due to missing or degraded fragments, deformations and fading. Often it is not even known whether fragments come from the same object or not. A good example is the Oseberg Tapestry from the Viking Age [1]. Matching is usually done by experts who rely on technical analysis of the textile. One important criterion for identifying fragments from the same object is thread count (i.e. number of threads per centimeter) in the warp and weft directions. This is a tedious and time-consuming process. Computer science literature shows that current algorithms are not robust enough to solve the puzzle of archaeological textiles and proposes taking inspiration from the criteria that humans use [2-4]. To address this, we propose a framework for automatizing thread counting in textile images. We created a feature extractor, which captures thread count in vertical and horizontal directions. Thread count is usually measured by selecting several 1x1cm areas on the tapestries (we refer to this area as a patch), counting the threads and averaging the results. Archaeological textiles often have holes where threads are missing due to decomposition. The experts take this into account when they decide where to count. We modeled the thread count extraction as a pulse-counting process, inspired by how we intuitively count threads. For counting vertical threads, we trace the patch in the horizontal direction and count the thread by finding the number of occurrences of two consecutive vertical edges. Similarly for the horizontal threads we trace the patch in vertical directions. Our proposed thread flow begins with applying Otsu's binary thresholding to the patch. Then we take all the pixel values for all columns in the same row to model the horizontal tracing of the patch. The pulse front is obtained by calculating the absolute approximate derivative of the trace. The number of pulses, which represent the number $X(2:n) - X(1:n-1)$ of thread, is obtained by the number of non-zero elements of the absolute approximate derivative divided by two. This operation is repeated all the way from the top to bottom patch and the majority thread count is returned as the thread density of the patch. We compared our algorithm with the ground truth counted by experts. The preliminary results show that our method overestimates thread count. The final results will be presented at the conference. However, thread count features extracted with our method, provided promising results when used for clustering. Twelve out of 27 fragments clustered using thread count alone, were aligned with archaeologists' hypotheses on which fragments belong together. The Oseberg Tapestry is a challenging case-study also because its thread systems consist of double threads, which introduces an additional complexity to the machine. The result for simpler scenarios will be also presented. Future work should explore more sophisticated methods for thresholding, such as Sobel to expose edges, and STRESS (Spatio-Temporal Retinex-inspired Envelope with Stochastic Sampling) enhancement pre-processing, to make them more separable.

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Synergistic use of non-destructive analysis and deep learning for the study of Coptic textiles

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Keywords: Coptic textiles, Dyes, Hyperspectral imaging, Computer science, Non-destructive analysis

Abstract

Coptic textiles are defined as “clothes and furnishing fabrics found in burial environments in Egypt and dated from the Roman times to the medieval period from 1st BC to 16th century AD” [1]. These textiles, usually made from linen and dyed wool, are monochrome in the oldest examples or polychrome in most recent ones. This project focuses on the examination of 42 Coptic textiles from the Art Institute of Chicago’s collection, whose dating and geographical origin remain uncertain. Through the identification of the dyes present and their molecular composition, we aim to provide a more precise dating and determination of the geographical area [1-4]. This large corpus of objects was primarily analyzed using two non-destructive analytical methods: X-ray Fluorescence mapping spectroscopy (ma-XRF) and Hyperspectral Imaging in the visible and IR range (HSI-VIS and SWIR). This analytical approach allowed us to identify, for the most part, the presence of the mordant and dye used either individually or in a mixture. However, conducting this analysis on a large collection of objects, yields a significant volume of data, making processing time intensive. Specifically, processing hyperspectral data necessitates handling each data cube individually to extract the average spectrum representative of each dye present. Given this challenge, we implemented contrastive learning on the HSI data to expedite the identification process. Contrastive learning is a

relatively new deep learning technique, wherein a neural network learns a mapping of high-dimensional data to a lower dimension specifically optimized for clustering. While it has been applied in the classification of HSI surveillance data, to our knowledge, it has not been employed for dye clustering [5]. Finally, some of these results were confirmed or extended upon using more traditional micro-destructive methods, such as Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and Liquid Chromatography coupled with Mass-Spectrometry (HPLC-MS). These micro-destructive methods allowed us then to assess the accuracy of our contactless approach.

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Computational simulation clarifies the coloration mechanism of ancient copper red glaze

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Keywords: Copper red glaze, Reflection spectra, Mie scattering, Multi-scattering model

Abstract

For several decades, the coloration mechanism of copper red glaze has been disputed in the academic field, which mainly focuses on whether the color agent is metallic copper nanoparticles or cuprous oxide (Cu_2O) nanoparticles. Modern analytical methods, such as XRF, XANES, SEM and TEM, have greatly

promoted our understanding of copper red glaze, but they are still insufficient to solve this problem completely, whilst these methods are often invasive, because cross-section samples are needed. Reflection spectrum is indeed a genuine non-invasive method, but standard samples with pure metallic copper/cuprous oxide nanoparticles uniformly dispersed, are really difficult. Therefore, it is not easy to quickly determine whether a given copper red glaze sample, especially an unbroken artifact, is colored by metallic copper particles or cuprous oxide particles. In this work, a numerical calculation framework based on Mie scattering theory and multiple scattering model was established [1]. The reflection spectra of transparent glazes with uniformly dispersed nanoparticles of different sizes, different volume fractions and different materials, were simulated under two-channel approximation and the corresponding L*a*b* values were calculated. Calculation results show that the metallic copper particles with diameters in the range of 20~200 nm, may make the glaze behave as a good copper red glaze, but the volume fraction requires changes as the size changes: when the diameter of copper particles is 20~50nm, good coloration effect can be achieved with the volume fraction in the range of 0.003%–0.03%; when the diameter is 100 nm, good coloration effect can be achieved with the volume fraction exceeds 0.03%; and when the particle size is 200 nm, the volume fraction of particles needs to be at least 0.1%. When cuprous oxide nanoparticles are used as scatterers, the corresponding spectral characteristics and chromaticity values are obviously different from that produced by metallic copper particles, so it is difficult to realize the effect of copper red glaze. Using the chromaticity values of sacrificial red glaze reported in the literature as a reference, a practical criterion was given: if the sample's reflection spectrum rises rapidly near 600nm and the chromaticity value $a^* > 3b^*/2$, its colorant is mainly the metallic copper particles, even if both metallic copper particles and cuprous oxide particles exist in the system simultaneously. If the increasing interval of the reflection spectrum is wide and the chromaticity value $a^* < b^*$, cuprous oxide is likely to play a role in coloration. As an application, one furnace transmutation copper red glaze sample, unearthed from the Nandaku Site in the Palace Museum, which was produced during the Qianlong reign period in the Qing Dynasty, was analyzed. The reflection spectra of this sample are consistent with our simulation and its chromaticity values are also consistent with the criterion raised above. In this sense, our numerical calculation framework gives an elegant answer to the long-term unsolved coloration mechanism of copper red glaze and makes it possible for us to quickly determine the coloration mechanism of any copper red artifact, by analyzing its reflection spectrum. Nevertheless, this is still far away from its capability boundary. With great extensibility, this numerical calculation framework can also be used to study the coloration of different kinds of ancient ceramics and may even be used to study the reflection spectra at different reflection angles.

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Robotic and non-destructive analysis of 3D objects - new possibilities

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Keywords: Multimodal non-destructive analysis, Robotic scanners, XRF, XRD, Multispectral imaging

Abstract

Complex multimodal non-destructive analysis and characterisation of 3D objects, are always a great challenge in the field of forensics and objects of art analyses. One of the options is the use of robotic scanners. A new system is currently being developed, which integrates the existing X-ray scanner with other analytical modalities (XRF, XRD, multispectral imaging and other). The development of this system is currently being finalised in cooperation with Radalytica company. The system is based on Radalytica's multi-robot imaging platform, referred to as RadalyX. The system measures nearly all conventional 2D and 3D trajectories of X-ray imaging with precisely calibrated and reproducible geometrical accuracy, leading to a spatial resolution of up to 50 μm. The system opens the door to exploring new approaches to both 2D and 3D X-ray imaging, especially in combination with photon-counting detectors. The platform allows combining several imaging modalities with any required number of robots. Such modalities range from visible light imaging, UV and IR, to 3D surface profiling, air-coupled ultrasound to 2D X-ray imaging and CT. The key parts of the scanner are two robotic stations. One robot carries an X-ray tube, whose emission spot size range is 8 – 40 μm and the operating voltage range is 10 – 130 kVp, whilst the other robot holds a photon-counting imaging detector of the Widepix MPX3 family. Robots can move and rotate freely about the sample in a precisely synchronised movement. It provides almost absolute flexibility of viewing angles. The very high sensitivity, spatial resolution and dynamic range of the used detectors, allow us to push the X-ray image quality to its physical limits. The system is equipped with accurate geometrical calibrations, which allow positioning both robots precisely, yet, arbitrarily. Therefore, the robots can be moved to different locations during on-site inspections. The system is equipped with 6-joint robotic arms, which can position the detector and X-ray tube independently and freely around the scanned objects. The robotic arms are functional scanning elements for both 3D translation and rotation. They are used to measure the CT projections at different angles and positions. This flexibility of positioning allows new types of scanning trajectories or even a combination of 2D scan strategies at multiple angles and positions to form optimal CT projections, given the partial accessibility and inner structure. The different tomosynthesis scan trajectories, to resolve depth information when the accessibility is limited, was introduced. The resulting images have corrected absolute dimensions for all object depth slices. The method is described as a way to 'focus the X-ray image to a selected depth'. The full depth data is measured in one scan and the focused depth is selected easily in the visualization. The projection angles are achieved by either rotating the X-ray tube and the detector or only by the cone-beam angle itself without rotation. The integration of different imaging modalities allows giving

detailed information on possible defects in analysed objects. Other modalities as macro-photography, SWIR and VNIR imaging modules, are highly desired for technical art analysis and forensics. Properties of the photon-counting detectors make them suitable also for methods like X-ray fluorescence imaging (XRF), which provides information on chemical elements present in the object or X-ray diffraction (XRD), which gives data on crystalline structures of inspected materials.

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From dream machines to scream machines: an exploration of art, perception and multisensory experiences

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Keywords: Degradation processes, Multidisciplinary exploration, Psychology of perception, Emotional responses, Technological tools

Abstract

This paper embarks on an interdisciplinary journey at the crossroads of art, psychology and perception. It investigates the phenomena of phosphenes, color psychology and emotional responses to art, with a particular focus on Edvard Munch's masterpiece, "The Scream." A central aspect of this exploration is the introduction of the "Screambox," a multimedia art installation designed to immerse participants in a dynamic visual symphony inspired by the colors of "The Scream" and to integrate both visual and auditory stimuli. By transcending conventional art appreciation, the Screambox re-imagines classic art in an immersive, interactive and emotionally charged manner, thereby expanding our comprehension of color perception. Future research endeavors will involve empirical studies assessing the emotional and psychological impact of the Screambox on participants, alongside investigations into the construction of the Dreamachine and the development of a computer application replicating its effects, enabling the examination of variations in the quality of phosphenes.

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Performance assessment of portable light dome systems for surface characterization in heritage objects

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Keywords: Portable Light Dome (PLD), Reflectance imaging, Multispectral imaging, Surface characterization, Non-invasive analysis

Abstract

The field of cultural heritage is standing at an exciting crossroad with the emergence of innovative technologies. Among these, Portable Light Dome (PLD) systems present a promising non-invasive method for documenting and understanding heritage objects. Using the multi-light reflectance techniques, these systems employ an array of light sources to illuminate and capture an object's surface from multiple angles, thereby enabling the generation of detailed and comprehensive images, which reveal information about the content, condition, material properties, production techniques and damage patterns, which are unidentifiable or invisible to the naked eye. This capability empowers heritage professionals to significantly enhance their ability to document, analyze and preserve cultural heritage [1]. In recent years, KU Leuven Core Facility for Heritage Science and Digitisation Technologies (VIEW), developed several PLD systems in various sizes and equipped with different types of cameras and lenses [2]. To support their efficient use and further developments, this poster presentation highlights an ongoing project focused on a comparative performance analysis of PLDs. This project is centered on evaluating how PLDs of different designs compared to each other and to benchtop reflectance and multispectral imaging equipment. It emphasizes the influence of size and optical variations on the effectiveness of PLDs. Furthermore, the project investigates specific challenges and devises potential strategies for the optimal use of PLDs in studying and preserving heritage objects, tailored to meet unique research objectives. A variety of heritage objects featuring diverse materials, scales and surface characteristics, are selected for this project. This selection specifically includes painted and engraved surfaces exhibiting characteristic features. Images are captured using a multispectral micro-dome (a suitcase-sized PLD), a white light nano-dome (a backpack-sized PLD), a conventional Reflectance Transformation Imaging (RTI) set-up and a well-established narrowband multispectral imaging system. After processing, the images are analyzed in the Pixel+ viewer, which generates textured color, shaded, automated sketch and normal map images for interactive comparative analysis. Image analysis includes qualitative and quantitative assessments of surface geometry. Qualitative assessment involves visual comparison of images to determine the extent of finely-crafted features identified by each technique. Quantitative assessment includes measurements of surface roughness, engraved depth and dimensions and geometric features. Technical specifications of the different PLD systems, such as size, weight, energy

consumption, assembly time, flexibility, resolution, acquisition time, processing time, repeatability and reproducibility, are also evaluated. This poster presentation provides a comprehensive evaluation of the performance of PLD systems with different designs in heritage science. It underscores the versatility and potential of PLDs in revealing intricate details, identifying materials and monitoring the condition of heritage objects, deepening on our understanding of their preservation needs. The implications of these findings for the development of preservation strategies in heritage conservation, will be discussed to highlight the impact of PLD systems in the field of cultural heritage.

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Condition assessment scanner (CAS): a fast, high precision scanner to assess and monitor the topography of paintings

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Keywords: Topography mapping, Condition assessment, Painting cracks

Abstract

Condition assessment of a painting is a standard prerequisite for its preservation, treatment, exhibition or loan. It is carried out by trained professionals, generally by conservators, who use examination tools and techniques to evaluate and document the overall and detailed condition of the painting. This can include an evaluation and documentation of the overall structural and esthetical condition of the painting, detailed assessment of the condition and evolution of cracks, blisters, dents, adhesion issues, presence of accretions, stains or degradation products, chromatic changes etc. It can be a painstaking, time-consuming and repetitive activity, which could benefit from a level of systematization and automation

for speed, accuracy and consistency. In 2019 the Van Gogh Museum and ASML entered a Partnership in Science to promote and conduct research dedicated to the preservation and appreciation of Van Gogh's legacy. One of the ongoing projects aims at supporting the museum conservators, by developing an instrument to assess and monitor the condition of paintings in the collection. The Condition Assessment Scanner (CAS) will support two sensors to register, evaluate and monitor the topography and fulfill the conservators' requirements for speed, accuracy and precision. In this presentation, we will report on the current design of the condition assessment scanner and on selecting, implementing and testing the topography probe. The Keyence XT-024 –a probe that uses pattern projection lighting– was selected for fast and high-accuracy 3D imaging, complemented with 2D color inspection. Post-processing algorithms to register and stitch images, are being developed alongside AI-based methods to detect, classify and monitor cracks and will be validated using naturally and artificially aged test paintings. In addition, a visualization platform to handle the resultant gigapixel images, is being built to allow conservators to interactively explore detected cracks and enrich their condition assessments. These large datasets (image acquisition, registration and crack detection and monitoring) also require smart data management to store and easily retrieve relevant information. By scanning a painting at different time intervals (e.g., 2 years or before and after loans), the topography maps can be compared and conservators will be able to detect and record changes in a fast, thorough and efficient manner that will support their visual examination.

Testing the approach applied for theoretical research on inks and parchment interaction

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Keywords: Parchment, Degradation, EPR, Spectroscopy, MHT

Abstract

In the frames of the studies conducted within the FWF-P35484 project 'Synergetic Interaction of Writing Materials' and the fruitful cooperation with the Austrian National Library in Vienna (ÖNB), it was possible to incorporate the data of case studies for testing the approach applied in the frames of a theoretical research. This work presents some preliminary results related to the analysis of the materiality of medieval manuscripts by the application of non-invasive analytical methods, such as X-ray, Raman and FT-IR spectroscopies [1,2] in combination with micro-invasive methodologies, such as Micro Hot Table

(MHT) and Electron Paramagnetic Resonance spectroscopy (EPR) [3]. One of the manuscripts that we investigated during our research, was the black Book of Hours (Horarium Galeazzii Mariae Sfortiae V. ducis Mediolanensis, Vienna, Austrian National Library, Codex 1856; 1450 – 1474, Bruges). The peculiarity of this manuscript is the completely black-colored parchment folios, on which the text was written in silver and gold ink. The complementarity of the techniques allows not only to determine the materials used for its production, but will help to assess the fragile condition of the thin parchment. The detection of iron gall ink used as a colorant, probably applied by brush, was important information acquired for the study of the interaction between this acidic material and the proteinaceous support and crucial for the evaluation of the deterioration of the parchment. A thorough characterization of the degraded parchment is the first step in the development of preservation methods for this endangered manuscript.

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The Vanvitelli's ink recipe

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Keywords: Ink, Raman spectroscopy, Gas chromatography, Microscopy

Abstract

The correspondence of Luigi Vanvitelli (1700-1773) stored in the Palatine Library of the Royal Palace of Caserta, is composed of 1,624 documents. The letters are almost all addressed to his brother, Urbano

Vanvitelli, abbot of the church of San Giovanni dei Fiorentini in Rome and cover a period from 1751 to 1768. The rich collection of letters is unique evidence and allows to know his thoughts and his passions as a politician and a man of culture. Therefore, the letters represent a source of information on the activity of the architect during its permanence in the Kingdom of the Two Sicilies, performed under the commission of King Carlo of Borbons. Moreover, they speak about the fine material used in the 18th century, when written documents were mainly made from paper supports, inks and waxes. The composition of the inks is incredibly varied along the centuries, but possibly divided into two main categories: coal-based ink and iron gallates-ink [1]. However, rarer logwood inks are also used [1]. Literature reports a lot on the identification and use of ink composition, but relatively less on their degradation mechanism. In fact, the letters show clear degradation phenomena, from discoloration to holes. Preventive conservation requires the knowledge on both the composition of inks and papers, as well as their interrelated mechanisms of degradation. Ink analysis has been carried out via OM, Raman microspectroscopy, ATR-FT-IR and gas-chromatography. Particularly, Raman microspectroscopy identified three major components: amorphous carbon, an aromatic compound (possibly due to some tannins related species [2] and metallic sulphates [3], in a variable relative amount. Based on the spectroscopic screening, some of the samples were investigated by GC-MS for their organic content. The detection of fatty acids and monosaccharides allowed to speculate on the composition of the ink. Fatty acids detected (i.e. linoleic, myristic, stearic and palmitic acids) suggested the use of vegetable oils as binders of the ink, possibly ascribable to a coal-based ink. The detection of glucose, mainly indicative product of cellulose hydrolysis, could be also supporting evidence of an iron gallates-ink, as natural gallotannins always yield significant amount of glucose on acid hydrolysis. The detection of glucose together with the absence of arabinose and galactose, further allowed to exclude the presence of arabic gum, thus excluding the use of a logwood ink. This is also in accordance with results from ATR-FT-IR analyses, which did not detect hematein. Neither gallic acid nor its degradation products, were detected. However, the absence of these compounds does not exclude the use of an iron gallates-ink: previous studies have demonstrated that the concentration of gallic acid with respect to that of glucose, consistently decrease with time, from major abundance in gall nuts, to a very small amount in the oldest manuscripts. A quantitative estimation of such components will provide a recipe of the Vanivitelli's ink. Mock-ups will be prepared according to this recipe to study the degradation mechanism of the ink with different paper supports as a function of several physico-chemical parameters.

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A systematic and multi-analytical approach in the in-depth characterisation of iron gall inks

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Keywords: Iron-gall inks, Ancient manuscriptts, EPR, Raman Spectroscopy, Coordination compounds chemistry

Abstract

Iron gall inks (IGI) are one of the most used inks in ancient times. A great variety of recipes have been developed throughout the centuries, but in all of them three "ingredients" are common: an oak-gall extract rich in tannins, an iron salt and a binder (such as Gum Arabic). The chemical reaction between the first two ingredients, results in the formation of insoluble fine particles of a dark bluish coordination compound. These particles are kept dispersed in the binder and constitute the main component of IGI [1]. In the last decades, IGI have been studied from different perspectives to better understand their strong degradation patterns, such as ink staining, but also formation of holes, embrittlement of the support etc. [1-3]. In fact, IGI are well known to have a corrosive-like behaviour, due to their acidity and the presence of iron in its oxidized form (Fe^{3+}). However, various aspects about their chemistry must still be understood. In this study we have approached the research of IGI with a systematic and multi-analytical investigation, starting with the characterisation of iron-polyphenolic coordination compounds without other components. We have focused our attention on the control of three important variables in the formation of such complexes: (a) the nature of the polyphenolic ligand, (b) the pH of the polyphenolic solution, as the protonation state of the ligands within the final complexes, and (c) the iron to ligand ratio. To consider the great intrinsic variability of this materials, a large set of samples consisting of pellets of iron-polyphenolic complexes, was prepared in the laboratory. Each sample was analysed with Raman and Attenuated-Total Reflectance Infra-Red (ATR-FTIR), two of the most used non-invasive techniques in the study of ancient manuscripts. The innovative aspect of the work is the application of electronic paramagnetic resonance spectroscopy (EPR) to gain useful information regarding the coordination state of the paramagnetic metallic center (Fe^{3+}) in the different complexes. The big set of spectroscopic data obtained, allowed the clarification of important aspects about the chemistry of these inks. The role of the pH in the definition of the complex structure and the unexpected coordination geometries of Fe^{3+} centres, are just some of the outcomes of this study. All new pieces of evidence obtained, are important to describe better the variability of this class of inks, giving an important support to the studies of the degradation processes occurring in IGI. Moreover, this work will contribute to defining molecular models more realistically than the ones previously described in the literature [4,5]. A general aim of the work is to further explore the potential and limitations of each technique in the study of IGI, exploiting a rational multi-analytical approach to overcome problems and limitations from using just single techniques.

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Material analysis of papyri from the chancellery of Qurra b. Sharik

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Keywords: Ink analysis, Papyrus, Egypt, XRF

Abstract

An important corpus of administrative texts from the early Islamic Egypt is the Qurra dossier, which contains letters sent by Qurra b. Sharik (709 - 714 CE), the governor of Egypt, to his pagarchs (heads of districts), mostly Basilios, the pagarch of Aphrodito. These letters were written in Arabic, Greek and occasionally Coptic, following a similar structure, reflecting the multilingual environment in Egypt. The Qurra dossier also includes bilingual texts. Most of these letters concern public law including tax collection and provide information about early Islamic administrative practices in multilingual Egypt [1,2]. The papyri forming the Qurra dossier, are now preserved among various libraries and institutes worldwide. While a majority of these texts has been carefully studied by manuscript scholars in recent years, these papyri have never been investigated from the perspective of material analysis. These documents can provide us with insights into scribal practices in early Islamic Egypt, specifically at the chancellery of Qurra b. Sharik. In this study, we carried out in situ material analysis of Qurra papyri preserved at the Institut de Papyrologie de la Sorbonne. Three Arabic, four Greek and two bilingual papyri from the Qurra dossier, were investigated using equipment from the CSMC mobile lab. The analytical protocol, developed by the Centre for Study of Manuscript Culture (CSMC), Universität Hamburg and Bundesanstalt für Materialforschung und -prüfung (BAM) for the study of inks in written artefacts, was followed for investigating the fragments [3,4]. This includes: 1) an initial screening using

a digital microscope (DinoLite AD4113T-I2V) under ultraviolet (395 nm), near infrared (940 nm) and visible (white) light source to discriminate between the ink types; 2) Infrared Reflectography using APOLLO Infrared Reflectography Imaging System (IRR) from OPUS instruments in combination with a Long Wave Pass Filter (LWP1510, range 1510–1700 nm) to confirm the presence of carbon; and 3) elemental analysis of inks and supports using X-ray fluorescence (XRF) spectroscopy, using Bruker Crono XRF spectrometer. The results indicate the use of carbon-based inks in all nine papyri. Two out of the three Arabic fragments were penned with pure carbon ink, while the third contains traces of copper. Two out of the four Greek fragments contained traces of iron. The Arabic-Greek bilingual document was written using carbon ink containing copper for the Arabic sections and pure carbon ink for the Greek section. The Greek-Coptic bilingual document was written using carbon-iron gall mixed ink for the Greek sections and pure carbon ink for the Coptic section. No distinct pattern could be identified, due to the limited number of fragments analysed, however, the trace elements, when present, seem to be related to the language. Further papyri from the Qurra dossier will be studied in the future.

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Investigating degradation processes of documents written in the 18th century

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Keywords: Inks, Degradation mechanisms, Raman spectroscopy, Gas chromatography, Biodeterioration

Abstract

The conservation and restoration of paper works play a fundamental role in the field of cultural heritage. In fact, the characterization and study of inks composition, as well as of their mechanisms of degradation, is of greatest interest for the identification of the most suitable restoration processes for the preservation of artistic and historical manufactures [1]. The composition of the inks is incredibly varied, but it is possible to divide them into two main categories: those based on coal and those based on iron gallates. However, rarer wood-based inks are also used [2]. The interest in the analysis of paper and ink heritage arises from the significant destructive effects observed in the use of inks on parchment and paper substrates. In addition, books, parchments and manuscripts, consist also of materials, which have their own structure and different degradation mechanisms. In many cases, these degradation processes end with paper fragmentation and the creation of holes or gaps [3,4]. The Royal Palace of Caserta stores in its historical archive several written documents, both letters and official documents, dated from the 18th to the 19th centuries. The correspondence of Luigi Vanvitelli is located in the Palatine Library and it is mainly composed of letters addressed to his brother, covering a period from 1751 to 1768. The analysis of the inks and paper supports was performed using a chemical and a microbiological diagnostic approach. Particularly, ink analysis was carried out via optical microscopy, Raman microspectroscopy, ATR-FT-IR and gas-chromatography. Using Raman microspectroscopy, three major components were identified: carbon, an aromatic compound (probably due to some tannins related species) and metallic sulphates in a variable relative amount [5]. The analysis of the organic content detected fatty acids and monosaccharides and allowed to speculate on the composition of the ink. In degraded areas, the ink's chemical composition is highly variable in the sulphates content and in its metallic counterpart, as well as in the organic compounds. To elucidate the possible degradation mechanisms happening to the inks and the paper surface, mock-ups prepared according to the Vanvitellian recipe, are currently under investigation.

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Spectroscopic analysis of mixtures of iron gall inks and logwood

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Keywords: Inks, Iron gall, Logwood, Spectroscopy

Abstract

Iron gall ink was one of the most important inks for centuries, being used until the 19th or even 20th centuries [1]. The main ingredients are organic material – galls (polyphenols- gallotannic/gallic acids), vitriol (sulphates of various metals) and binder (gum arabic). It may take some time for iron gall inks to develop their full colour/hue, depending on the ratio (concentration) between the components. For this reason, other dyes, such as madder, indigo or logwood, were often added to improve the colouring properties. Iron gall ink is usually characterised as a metal complex with polyphenol [2]. However, full characterisation is still incomplete, due to the complex structure of natural materials, which is further complicated by a variety of chemical processes, which can occur, especially when the ink is applied to the paper and is subjected to ageing and degradation. One disadvantage of iron gall inks is their corrosive properties. To prevent the corrosion of metal nibs, chromium-logwood inks were, therefore, developed in the 19th century [3]. Logwood inks are made from (extract of) logwood (a hematein source) with various metal salts; the colour depends on the choice of metal. With iron salt it forms a black ink. But even though a decoction or extract of logwood can be used to make ink with iron salt, it was preferably used as an additive to tannin inks, which were not black enough [3]. Many recipes mention the use of mixtures of galls and logwood for inks, with the mass ratio between galls and logwood varying [3]. In this study, an ink from a mixture of galls, logwood and ferrous sulphate, was prepared following a historical recipe [3]. The inks were analysed in liquid and dried form and applied to the paper. As a reference set, various mixtures were also prepared in different proportions of tannic acid and hematein with ferrous sulphate. The samples were analysed using Raman spectroscopy (portable spectrometer and Raman microscope with different excitation lines). It was found that the spectral response depends on the ratio between tannic acid and hematein. In addition, the spectra recorded at 785 nm, show a larger contribution of the iron-polyphenol (tannic acid) complex, while the spectra recorded at 532 nm contain more information about the hematein-based species. The study was also complemented with surface-enhanced Raman spectroscopy. Furthermore, reflection FTIR was used for non-invasive characterisation of inks on paper. The investigations were complemented by computational methods to investigate the strength of the interaction between iron ions and tannic acid and hematein. The most favourable positions for binding iron ions were calculated, followed by theoretical comparison of acidic properties of the compounds. Lastly, electron paramagnetic resonance spectroscopy was used to evaluate the coordination and crystal structures.

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Micro-XRF and micro-CT data fusion for the analysis of cultural heritage objects

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Keywords: Computed microtomography, X-ray fluorescence, Data fusion

Abstract

Imaging techniques are important tools for the analysis of artworks and are increasingly applied in the investigation of cultural heritage. Each technique is capable of generating specific data, such as composition/distribution of pigment, topography or internal structure of the objects, whilst generally, the analysis is done separately to make up the entire evaluation. In this work, a methodology is proposed to merge the data provided by two imaging techniques, micro-XRF and micro-CT. Both techniques were applied for analyzing wooden boards artworks in different sizes. The elemental mappings were carried out using the M4 Tornado (Bruker) and Crono (Bruker) micro-XRF equipment for the small and large samples, respectively. The micro-CT scanning was performed using the Phoenix VTomex (BHGE) system and the data was reconstructed with the Datos Reconstruction software. Images of the main elements' distribution on the surface of the boards, were merged with the 3D data using image processing tools. The result was data fusion from both internal and external images, where the elemental composition of each pigment could be correlated with its distribution

in the volume space. Furthermore, the XRF intensity of the elements can be analyzed together with the gray value of the micro-CT data at each pixel, making it possible to establish a density calibration. The visualization of the combined data in the same 3D software, provided a more precise analysis of the characteristics of the objects, generating important information for the research in the cultural heritage field.

Computed tomography 3D imaging as a non-invasive bookbinding evaluation tool for the restoration of the prayer book of Mary Stuart, Queen of Scots

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Keywords: Computed tomography, Non-invasive tests, Historical bookbinding, Historical book restoration

Abstract

In 2022, the prayer book of Mary Stuart, Queen of Scots, was delivered for conservation. Having a wonderful history and conservation-restoration technological challenges, it was decided that the object was to constitute a PhD project topic. In 2026, the manuscript will be an important part of the exhibition about Stuarts and Sobieski's connections at Princes Lubomirski's Museum in Poland. A question was raised if the binding of the prayer book can be restored to enable opening it more easily, hence hindering the sewing from distorting the vellum, whilst misplaced pages could return to the right position. The aim was to apply as many non-invasive tests as possible, before physically touching the precious book itself and for this reason it was decided to focus on CT imaging [1]. The objectives of the project and the book itself attracted multiple professionals willing to collaborate and explore proposed research possibilities. Nuclear physics professor, Chiara Mazzocchi from the University of Warsaw, Poland, is supervising the tomography during the project. Professor Ville-Veikko Telkki from NMR Department of the University in Oulu, Finland, is helping us explore the possibility of using NMR in this context. Since it is planned to perform comparative study and CT-scans of similar bookbindings/prayer books [2], queries will be further conducted at the Bodleian Library, Oxford, Bibliotheque Nationale in Paris and the Morgan Library, NY. Multiple historical custodians and consultants provided their expertise: Dr Anna Groundwater from the National Museums of Scotland, Dr Emily Wakefield from the University of Birmingham and Eugenio Donadoni from Christie's. Considering the conservation-restoration procedure of such a valuable object, as is the prayer book of Mary Stuart, it is vital to apply every non-destructive assessment test and method available [3]. Physics imaging methodologies, such as CT and NMR are going to be applied for the purpose of this conservation project [4]. Combining scientific

disciplines and technologies in artwork evaluation, offers incredible amounts of previously unknown information and data. Implementing them as full-fledged diagnostic tools, wouldn't be possible without interdisciplinary partnerships and collaborations. Exchanging and joining experiences from different research fields, advances potential knowledge base about the examined art object. Defining new analytic possibilities by means of non-invasive test methods, is of great importance to the research conducted by art historians and conservators. Works of art, such as manuscripts, has already been tested with CT worldwide. Implementation of these methods is widely appreciated by many specialists, due to their non-invasiveness and useful values [5]. They provide insight into these objects' structures, support their return to a stable, restored state and condition, pertinent to their historical value. These methods can serve in analysing and documenting without any actual interference. They allow access to every layer of the object without compromising its safety, it being an original object.

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Under the surface: condition assessment of archaeological metal objects by µCT scanning

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Keywords: Metals, µCT scanning

Abstract

Everyday condition assessment of archaeological objects relies largely on visual observation combined with the conservators' experience and their theoretical knowledge. As such, the condition assessment is based on a personal interpretation of the general appearance of the objects' outer surface, as well as assumptions of their inner nature. Moreover, depending on equipment access, the assessment may

also be supported by X-ray imaging and surface analysis. The only of these approaches which more readily provides information on the inner nature of the object, is X-ray imaging. Yet, X-ray images may be limited in resolution and are two-dimensional; although the latter can be compensated by obtaining multiple X-ray images from different angles of an object. This project wishes to turn the condition assessment focus from the outer to the inner, bulk material of an object and explore the use of computed tomography (µCT) as the basis for condition assessment. It also wishes to understand how the inner structural condition relates to the outer appearance of an object. The research will focus on the investigation of objects made from copper alloy and iron; however, the approach may be also appropriate for other inorganic and organic materials, such as other type of metals, wood, bone and antler, answering similar research questions. The research and testing material for this project will be provided by the Museum of Cultural History (MCH) and the Norwegian Institute for Cultural Heritage Research (NIKU) and includes objects discovered using metal detector, as well as discarded archaeological material from excavations run by MCH and NIKU. The selection of objects will be based on visual condition assessment and will ensure inclusion of objects with a present type of corrosion commonly encountered on metal objects coming from archaeological burial contexts and which is characteristic to the object and material type. The project seeks to visualise, identify, trace and thereby get a better understanding of different corrosion phenomena and their extent whilst occuring in the inner structure of an object. Furthermore, the project investigates how this knowledge may correlate to the corrosion phenomena identified on the object's outer surface. For the chemical identification, instrumentation, such as SEM-EDS, µRaman, FT-IR and XRF, will be used. Given the nominal resolution of 1.3 microns of the µCT scanner, which is going to be used in this research, this project will also explore the possibility of not just identifying different regions and phenomena of interest within the bulk of an object, but also explore the possibility of monitoring changes taking place within the material, due to either conservation treatment or storage under unstable conditions. This will be done by exposing modern iron test coupons and discarded archaeological iron objects to an artificial environment optimised for iron carbonate crystal growth. Micro-CT scanning will be used to discover any likely changes happening at the object's corrosion crust and to investigate their possible impact on the object as a whole; any further information within the object's corrosion crust will be also reported.

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