7th International Congress

CHEMISTRY FOR CULTURAL HERITAGE

(ChemCH)

https://chemch2024.educell.sk

Winter Riding Hall, Bratislava Castle, Bratislava, Slovakia.
2–5 July 2024

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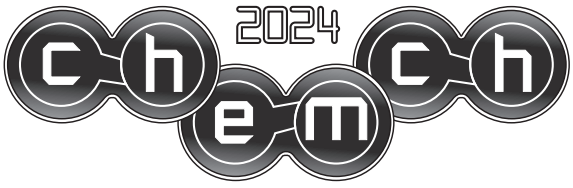
9 788082 081247
ISBN 978-80-8208-124-7 (print)
ISBN 978-80-8208-125-4 (PDF)

Foreword

Since the very beginning of conservation and restoration concepts and practice, different branches of **Chemistry for Cultural heritage**, such as **physical**, **analytical**, **organic**, **inorganic**, **environmental chemistry**, have been playing a pivotal role in diagnosis, understanding causes and state of conservation, studying ancient production techniques, developing and evaluating restoration materials and methods, guiding conservators in the planning and execution of conservation-restoration interventions of both movable and immovable cultural heritage as well as in the education and training of conservation professionals.

The last decades have seen the introduction of new and advanced chemical technologies applied to the different fields mentioned above, which have marked a substantial improvement in the capability of the Chemistry discipline to answer specific conservation-restoration needs raised by the cultural heritage preservation international community.

The **7th International Congress on Chemistry for Cultural Heritage**, organized by the **Slovak University of Technology**, **Slovak National Museum** in collaboration with the **Slovak Chemical Society (SCHS)** and its **Division of Chemistry in Cultural Heritage**, under the patronage of **Slovak Commission for UNESCO** is aimed at providing an international platform for presentation and discussion on all the above-mentioned issues.



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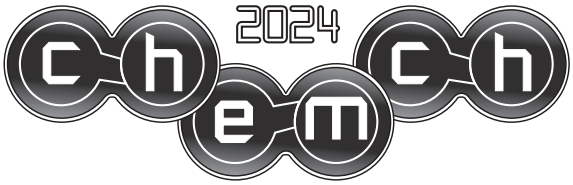

Oral presentations

Dealing with Complex Data in the Characterisation of Cultural Heritage Materials: the Power of Multivariate Analysis

Paolo Oliveri

University of Genova, Department of Pharmacy, Viale Cembrano, 4 – 16148 Genova (Italy);
paolo.oliveri@unige.it

Keywords: chemometrics; multivariate analysis; artworks; spectroscopy; imaging.

In the last decades, chemometrics has played a crucial role in the interpretation of analytical data and it has been increasingly employed in the conservation science to overcome drawbacks and limitations related to the application of univariate approaches for the study of complex and heterogeneous cultural heritage materials. Complexity of analytical data obtained from the investigation of artworks and archaeological samples is related not only to the heterogeneity of materials (usually complex mixtures that undergo modifications over time) but also to the fact that multiple analytical platforms are often required to perform thorough characterisations. This often leads to the production of a considerable amount of multi-block data during a diagnostic campaign.
Univariate analysis is the simplest form of processing data, considering one variable at a time independently of the others, without considering intercorrelation – a feature that can be very informative, if recognised and properly interpreted.
On the contrary, multivariate methods play a crucial role for the development of adequate and increasingly automated tools for efficient analytical characterisations of complex systems. Indeed, an appropriate use of chemometric tools involves the overall analytical approach: from the definition of the problem to the choice of samples and the type of analysis. Among the multivariate tools most widely used in the field of cultural heritage, there is certainly principal component analysis (PCA), an exploratory technique that extracts the highest information contained in the data, looking for their maximum variability.
Multivariate analysis proved to be very useful for the evaluation of spectroscopic data obtained through classical spectroscopies and spectral imaging, operating in different spectral ranges, where problems related to bands deformation and overlapping, as well as changes in relative intensities of analytical signals may occur, hampering a correct evaluation of big datasets.

Funding

Financial support provided by the Italian Ministry of Universities and Research – MUR (Research Project PRIN 2022 n. 20223WBTH8, CUP: D53D23008950006) is gratefully acknowledged.

Thermal and Thermooxidative Stability of Materials - Assessment and Predictions

Peter Šimon, Tibor Dubaj and Zuzana Cibulková

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia;
peter.simon@stuba.sk

Keywords: stability, materials, thermooxidative, assessment, prediction

Mechanisms of the processes in condensed phase are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, the rate of the complex multi-step condensed-state process can be formally described as [1]

$$d\alpha/df = k(T)f(\alpha) \quad (1)$$

Eq. (1) is called the general rate equation. It resembles a single-step kinetics equation, even though it is a representation of the kinetics of a complex condensed-phase process. Kinetics of a complex process should be described by a set of rate equations. The single-step approximation thus resides in substituting the set of kinetic equations by the sole single-step kinetics equation [1]. The temperature function k(T) in Eq. (1) is mostly expressed by the Arrhenius equation. It has been justified [1] that the temperature function can hardly be considered the rate constant so that another function may be applied. The Berthelot-Hood temperature function was found being highly suitable:

$$k(T) = A_k e^{DT} \quad (2)$$

where A_k and D are adjustable parameters.

Isoconversional methods represent the most widely employed category of methods based on Eq. (1). Their basic idea is that the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion. Under these conditions, the value of conversion function $f(\alpha)$ in Eq. (2) is constant and the reaction rate is a function of temperature only. The isoconversional methods can be crudely divided into two groups, i.e., the isothermal methods and the methods at linear heating [1].

The oxidation processes occurring in the condensed phase exhibit an induction period (IP) which is determined as a point of sudden increase in the rate of oxidation [2]. At the end of IP, a sudden change in material characteristics mostly takes place so that the length of induction period is considered a relative measure of material stability. To estimate the stability of materials, a sample is mostly subjected to an accelerated test under standardized conditions where heating is the most common means of accelerating the oxidation. The end of IP is determined indirectly as the time/temperature of a sudden increase in the rate of the main oxidation stage [2], i.e., as the oxidation induction time (OIT) in the case of isothermal measurements and the oxidation onset temperature (OOT) in the case of measurements with linear heating [2]. Oxidation (and other degradation processes) are accompanied with the release of

heat or sample mass so that thermoanalytical methods such as differential scanning calorimetry or thermogravimetry can be applied for its study.
Denote α_i the conversion of the reactions occurring during IP and corresponding to the end of IP. Since the processes occurring during IP are not registered, the value of α is not known. Nonetheless, as for all isoconversional methods, it is assumed that the conversion α_i is always the same irrespective of the temperature regime employed during ageing stress [2]. Combining Eqs. (1) and (2), after a sequence of manipulations [2] one can get the relationship for the dependence of oxidation onset temperature, T_i, on the heating rate, β:

$$T_i = (1/D)\ln(AD\beta + 1) \quad (3)$$

where the parameter A is given as:

$$A = (F(\alpha_i) - F(0))/A_k \quad (4)$$

The function $F(\alpha)$ is the integral of the inverted function $1/f(\alpha)$, A and D are adjustable parameters in the procedure of minimizing the sum of squares between the experimental and calculated values of T_i. Hence, T_i is the temperature at which the fixed conversion α_i is reached, i.e., the oxidation onset temperature. Knowing the parameters A and D, the isothermal induction period, i.e. the oxidation induction time for a chosen temperature can be assessed:

$$t_i = Ae^{-DT} \quad (5)$$

Application of the theory will be demonstrated on the case studies of the curing of sandstone consolidant [3], beeswax degradation [4, 5], stability of fillings employed in the restoration of a baroque painting [6] and the role of thermooxidation and depolymerisation in the ageing of systems paper/gum arabic/historical ink [7].

Funding

Financial support from the Slovak Scientific Grant Agency (VEGA 1/0498/22) and from the Slovak Research and Development Agency (APVV-20-0410) is greatly acknowledged.

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When Chemistry Meets Other Disciplines in Heritage Science

Łukasz Bratasz

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, 30-239 Kraków, Poland, lukasz.bratasz@ikifp.edu.pl

Keywords: degradation mechanism, preventive conservation, museum environment

Effective preservation of cultural heritage collection requires an interdisciplinary approach as usually degradation processes are of a complex nature and their manifestation impacts objects' composition, appearance, mechanical stability, ability to be used etc. All those changes need to be evaluated in terms of change of value – the decisive factor in preventive conservation decision-making. Despite unquestionable developments in the understanding of the degradation mechanisms of heritage objects, several significant gaps in this knowledge still exist particularly at the interface between various disciplines.

The presentation aims to identify some of these gaps and suggest future directions in heritage science. One area in need of further study is the interface between the chemical degradation of modern materials and their mechanical properties. The pressing need for further research in this area is illustrated in the case study of two identical cellulose acetate objects 'Little large glass' made by Marcel Duchamp. After being housed in two different environments the objects arrived at dramatically different states of preservation. Unexpected material shrinkage in one of the objects stored in an airtight enclosure was observed. It was related to a change of mechanical properties due to a drop in glass-transition temperature caused by acetic acid released during the chemical decomposition of the cellulose acetate. The effect was confirmed by the artificial ageing of samples prepared in the laboratory [1].

Another area requiring further study is the understanding of oil paintings' vulnerability to relative humidity (RH) variations. It has been shown that drying oils used as binders in oil paints are glycerolipids based predominantly on polyunsaturated fatty acids. Drying oils solidify and harden through chemical reactions with oxygen, entailing two main paths – oxidation and crosslinking [2]. All paints show a rapid initial oxygen uptake followed by mass loss due to the decomposition of oxygenated compounds with low-molecular-weight molecules lost by evaporation [3]. Crosslinking is fundamental in the formation of a durable paint film and the degree of crosslinking and types of crosslinks promoted by different pigments are important contributors to the long-term chemical and mechanical stability of the oil paint layer. In parallel to oxidation, hydrolysis of ester bonds takes place yielding di- and monoglycerides and free fatty acids. Metal ions released from pigments and additives, that improve the optical properties and workability of the paint, react with free fatty acids to form metal soaps or with carboxylic groups present in the cross-linked polymer transforming it into an ionomer. As a result, the molecular composition of the oil binder evolves.

Understanding how the evolving molecular composition of an oil paint layer on its transition to an aged solid film affects its dimensional change and mechanical properties is fundamental to the assessment of material durability and more broadly

risk of degradation of oil paintings. Tensile properties – modulus of elasticity and strain at break – as well as cumulative shrinkage, were determined for a selection of oil paints from Mecklenburg's Paint Reference Collection now after approximately 30 years of drying. The oil paints were found to get stiffer and more brittle with diminishing plastic deformation and increasingly elastic behaviour. The shrinkage of paints due to molecular relocation and/or evaporation of organic medium as they dry and age can be very significant. This shrinkage can exceed their strain at break and lead to fracturing of the oil paint layer if it is restrained by a dimensionally stable substrate. Consequently, after long-term drying, the cumulative shrinkage can cause oil paints to crack even in the absence of fluctuations in RH or temperature. The physical model of panel painting showed that paintings with a developed cracks system, called craquelure pattern, due to the chemical evolution of oil paints, are much less vulnerable to RH variations than previously assumed. This naturally opens doors for more rational and sustainable management of the museum environment, particularly in terms of reducing energy use and carbon emissions.
Last but not least, an important issue is the effective translation of scientific results. A new preventive conservation platform HERIe supporting the decision-making process of managing the collection has been developed for museum professionals recently and will be presented. A list of gaps in knowledge impeding the reduction of energy consumption will be discussed. The case of low-energy museum storage illustrating the win-win situation when preservation is not in conflict with environmental care will be presented.

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Dynamic mechanical properties of heritage materials

Katarzyna Poznańska, Sonia Bujok, Łukasz Bratasz

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland; katarzyna.poznanska@ikifp.edu.pl

Keywords: DMA, mechanical properties, paintings

A significant part of heritage objects are made of materials of biological origin, i.e. as wood, linen, vegetable oils or animal glues. Such materials often contain natural polymers that may be sensitive to temperature and humidity variations. Dynamic mechanical analysis (DMA) enables the study of the temperature-, humidity- and time-dependent viscoelastic behavior of materials, in which the response of the material depends on the rate of applied stress. This makes it possible to predict the mechanical properties and damage conditions of the material as a result of long-term processes. The research covers materials typical of panel paintings, i.e. glue-based ground and tempera paints. Historical materials were reconstructed by mixing a binder (egg yolk, rabbit skin glue) with pigments (chalk, yellow ochre, azurite, lead white). Reference samples of unpigmented binders were also investigated. Using DMA, it is possible to test paint samples with a thickness corresponding to layers in real objects, e.g. hundreds of micrometers in the case of paints, and thus verify previous measurements often obtained on large samples [1,2,3]. The results show how the properties of the binder itself change with the addition of pigment. The stiffness of the material can be predicted depending on the amount of pigment used. The values of temperature and humidity corresponding to alpha (glass) transition were determined as values at which the material changes from the brittle to a rubbery state. Thermal and moisture expansion coefficients of materials were determined for predicting mechanical stresses originating from climatic fluctuations in the decorative layers. The aim of this research is to complement the knowledge obtained in traditional static mechanical tests characterizing the behavior of materials under conditions of rapid deformation. The research progressed towards understanding pigment-binder interactions and the implications of microstructural-level interactions on macroscopic mechanical properties. The determined properties of materials will be used to evaluate the behavior of objects in different climatic conditions and to estimate the risk of mechanical damage caused by humidity fluctuations. This will allow to verify the safe humidity ranges for storing paintings in museums and may contribute to the reduction of energy consumption related to less strict climate stabilization.

Funding

The research leading to these results has received funding from the Norwegian Financial Mechanism 2014–2021, project registration number 2019/34/H/HS2/00581, and the statutory research fund of the Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences.

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ODOTHEKA
Olfactory heritage research: capture,

reconstruction and conservation of historic smells

Tomasz Sawoszczuk[1], Matija Strlič[2], Julio Cesar Torres Elguera[1], Justyna Syguła – Cholewińska[1], Emma Paolin[3], Fabiana Di Gianvincenzo[3], Irena Kralj Cigić[3],

[1]Department of Microbiology, Institute of Quality Sciences and Product Management; tomasz.sawoszczuk@uek.krakow.pl
[2]Heritage Science Laboratory Ljubljana, University of Ljubljana, Slovenia, University College London, UK: matija.strlic@fkkt.uni-lj.si
[3]Heritage Science Laboratory Ljubljana, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

Current museum experience is predominantly visual, although historically, museums were places of learning where objects were admired from close distance, touched and smelled. Only with the increasing number of visitors in the 19th century, their experience was slowly reduced to a single sense. In parallel, our sense of the wider environment was slowly anaesthetised as well. Although we now associate cleanliness with the absence of smell this was not always the case. The past was a cacophony of odours. Contemporary museum interpretation is becoming increasingly multisensory and there are isolated examples of successful olfactory engagement. However, there is currently no clear understanding or best practice of development of olfactory displays. Often, curators rely on industrially designed interpretative smells, with no direct link to the object, therefore the authenticity of such displays is questionable.

The central research premise of ODOTHEKA is that smells of objects require a much more systematic approach in order to develop olfactory displays that are authentic. ODOTHEKA will carry out research into how the smells of museum objects could be retrieved, characterised, described, reproduced, displayed and conserved. This is a ground-breaking proposal in collaboration between research teams in Poland and Slovenia, leading in the field of smell characterisation, indoor air analysis and conservation. In collaboration with curators from the National Museums in Krakow and Ljubljana,

we will select 10 case studies of exceptional national importance, such as Da Vinci's Lady with the Ermine or the personal belongings of the Slovenian national poet, and explore their historical, societal, aesthetic and other values, aswell as olfactory significance, i.e. any references to odours associated with the objects. In parallel, the smells will be captured non-destructively and non-invasively, and scientifically characterised using state-of-the-art olfactory and chemical analyses, and historic odour wheels will be developed. These will describe the individual components of the aromas, and their chemical and olfactory properties. In the next step, the smells will be reproduced on the basis of the constituent volatile organic compounds (VOCs) such that a matching composition, as well as a matching sensory perception will be

achieved. This will again be assessed with the help of odour panels. The reproduced smells will be displayed in museum environments as 'points of interest', i.e. requiring active participation in order to access olfactory information. The conservation risks of this approach will be assessed in situ due to the fact that the introduction of VOCs could be seen as a conservation risk. We will do so by monitoring the air quality (particularly the concentrations of organic acids and aldehydes that can have corrosive impacts on museum materials) around the displays, as well as by carrying out so called Oddy tests – tests of corrosivity of complex mixtures of volatiles. In the museums, we will carry out audience research during, as well as three months after the visit to comparatively explore memory retention as a consequence of increased interest in the case study objects due to multisensory engagement. The process described above will thus be validated through sensor panels and through visitor engagement, and will represent best practice.

ODOTHEKA is a fundamental interdisciplinary and collaborative research project in the field of conservation research and will result in a number of publications in highly ranking peer-reviewed journals as well as in conferences. A significant media impact is also likely, and we will ensure that the research is adequately presented and communicated to the public.

The significance assessments providing material for historical and contextual understanding of odours, the historic odour wheels, the reproduced smells themselves, as well as all the analysis and assessment data will constitute archival records constituting objects in the ODOTHEKA – International Archive of Historic Smells. This will the first such collection that we will share through the European Research Infrastructure for Heritage Science, within which there is currently no

similar ongoing initiative. In this way, ODOTHEKA will achieve lasting impact both nationally and globally.

The authors gratefully acknowledge the financial support from the National Science Centre, Poland which has allowed implementing the project entitled Olfactory heritage research: capture, reconstruction and conservation of historic smells, reference number 2020/39/I/HS2/02276.

Nine principles of green heritage science for sustainable practices and quantifiable impacts

Abdelrazek Elnaggar & Matija Strlic

Heritage Science Lab Ljubljana (HSLL), Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia.

abdelrazek.elnaggar@fkkt.uni-lj.si & matija.strlic@fkkt.uni-lj.si

Keywords: Life cycle methods, green chemistry, energy consumption, stakeholders, decision making

The importance of sustainability in the context of climate change and understanding the relationship between cultural heritage and its physical and social environment is often stressed ([1], [2], [3]). This encompasses environmental, social, and economic dimensions and requires addressing the interconnected challenges posed by e.g. climate change, resource depletion, and social inequities. Sustainable heritage science practices would minimise environmental impact, respect local cultures, and promote community involvement which is vital for preserving heritage assets while supporting economic development. To enable the green transformation of heritage science and heritage conservation, a new, 'green' paradigm would promote the use of renewable or recycled natural sources, minimal intervention, minimal use of toxic chemicals, energy-efficient solutions and minimal waste generation, taking into account socio-economic aspects. Inspired by the twelve principles of green chemistry (4), nine principles of green heritage science were recently formulated ([5]) to initiate a broader debate. These take into account the global cultural and economic contexts as well as the different perceptions of value and availability of conservation resources. While there are guidelines and standards for environmental management in the field of conservation with environmental and collection considerations, heritage professionals still lack a sustainability analysis tool with quantifiable indicators[6].

Solutions such as green chemistry-based conservation products and processes or renewable energy-based storage can help to ensure more sustainable management of cultural heritage. To evaluate the effect of such solutions, we need sustainability analysis tools, such as life cycle-based methodologies[7], that involve quantifiable cultural and social indicators and models. Life Cycle Assessment (LCA) is at the centre of a fast-developing research domain informing and promoting green solutions and sustainable decision-making as a standardised, structured, comprehensive, and internationally comparable assessment tool, often complemented by Life Cycle Costing (LCC), and Social-Life Cycle Assessment (S-LCA). It is argued that life cycle methods could work as advanced tools to enable the green transformation of heritage science.

Funding:

Funding provided by the European Union (GREENART project, Horizon Europe research and innovation program under grant agreement no. 101060941). Views and opinions expressed are, however, those of the author only and do not necessarily reflect those of the European Union or the European Research Executive Agency (REA). Neither the European Union nor the granting authority can be held responsible for them.

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Unlocking the manufacturing secrets of Maison Goupil's prints: Non-Invasive Analysis of its Mechanical Reproductions

F. Galluzzi[1], D. Abilmazhinova[2], G. Sciutto[2], R. Chapoulie[1], R. Bigorne[3], A. Mounier[1]

[1]Archéosciences Bordeaux (UMR CNRS 6034), University Bordeaux Montaigne, 33607 Pessac Cedex – France
[2]Department of Chemistry "G. Ciamician", University of Bologna, Via Guaccimanni 42, 48121, Ravenna, Italy
[3]Museum of Aquitaine, 33000 Bordeaux
francesca.galluzzi@u-bordeaux-montaigne.fr

Keywords: multi-analytical study, non-invasive techniques, colored print reproductions, engraving techniques

In the 19th century, social, economic, and political changes, together with advances in printing technology, promoted the democratization of art, broadening access to a wider audience and breaking down previous barriers that limited the production, consumption, and appreciation of art exclusively to the aristocracy. Maison Goupil, one of the leading printmakers and art dealers of the time, played a major role in this "revolution" in art production. Founded in Paris in 1829 and active until 1921, Goupil & Cie. purchased paintings or reproduction rights and produced high-quality prints at affordable prices, utilizing both traditional and innovative techniques. In particular, the company was a pioneer in the use of photogravure, photoglyptie, and chromotypogravure. Some prints were then embellished with manual additions of color and localized varnishes. Through its national and international distribution, Goupil popularized the painters of its time and the masters of the past. It participated in the spread of taste, serving as a source of inspiration for many artists, and, most importantly, exerting a decisive influence on the globalization of the art market.
Fourteen hitherto unstudied artworks were selected from the extensive collection of the Goupil Museum (comprising 46,000 prints), housed by the Musée d'Aquitaine in Bordeaux, France, to gain a deeper understanding of their printing techniques and state of preservation. To characterize the coloring materials (dyes and pigments) and binders, a multi-analytical approach was adopted based on non-invasive, contactless, and portable techniques, including portable optical microscopy, Vis-NIR imaging spectroscopy, FORS, XRF, and FTIR. The comprehensive analysis conducted allowed for the elucidation of the unique characteristics inherent to various printing techniques such as lithography, burin engraving, photography, chromotypogravure, and photogravure, as well as different coloring methods. For instance, it was noted that certain lithographs (e.g., three engravings from the collection of "Costumes Historiques de Ville ou de Théâtre et travestissements" by A. Devéria) underwent a first step of coloring using a specific ink (printing coloring), followed by the selective addition of a second pigment to specific areas at a later stage (most likely handmade coloring).
Furthermore, examining reproductions of the same subject with different analytical techniques revealed differences in materials, properties, and preservation status. It will

presented as example the comparison of the three prints “Enfin… seuls!” (burin of 1881, photogravure of 1883, and miniature proof printing of 1892), where the burin was sold 10 times more expensive than the miniature. The presentation will also explore the characterization of the natural cellulosic fibers of the paper support, the sizing used, and the assessment of the state of conservation (i.e., paper yellowing, foxing, etc.).

Acknowledgements

The authors would like to thank the musée Goupil and the musée d’Aquitaine (MAQ), in particular the director Laurent Védrine to provide the access to the collection.

Funding

This study received financial support from the French government in the framework of the University of Bordeaux’s IdEx “Investments for the Future” program / GPR “Human Past”.

Inside the Patina of Archaeological Metal Coins: LA-ICP-MS as a Micro-destructive Method to Study Corrosion Evolution

Edoardo Tartaglia[1,2], Francesco Abate[1,2], Roberta Zanini[2] , Maria Antonietta Baldo[1], Chiara Zanardi[1] , Arianna Traviglia[2]

[1]Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, Venezia, Italy

[2]Center for Cultural Heritage Technology (CCHT), Istituto Italiano di Tecnologia (IIT), Via Torino 155, Venezia, Italy

Keywords: archaeological metal coins, micro-destructive technique, LA-ICP-MS, 3D mapping

The conservation of ancient metal artifacts requires continuous innovations for the development of new methods to ensure minimal invasivity during a targeted diagnostic actions. Recently, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has been used as a micro-destructive analytical technique for the quantitative determination of major, minor, and trace elements in heritage metals. [1-2]. LA-ICP-MS is widely adopted for the investigation of the bulk alloy in highly corroded metals, thanks to its capability to first locally ablate the corroded layer, and then analyze the uncorroded original alloy by mass spectrometry [3]. The capability of this technique to conduct micro-destructive depth-profiling and fast 3D-mapping analyses [4] represents an innovative way to characterize small objects that cannot be sampled. In particular, this technique allows to perform several micro-spots collecting information on the heterogeneuos patina layers of archaeological metal samples.

The aim of this study is to demonstrate the potentiality of a LA-ICP-MS approach applied to both artificially aged mock-ups and archaeological copper-based coins , as well as to counterfeited coinage, to provide diagnostic elemental trends of multi-layered structures. In order to assess the effectiveness of the laser ablation process on sample compositional and structural heterogeneities, preliminary drilling tests coupled with optical profilometric analysis were carried out on aged mock-ups. Consequently, elemental analysis in depth-profiling was performed on corroded coins as well as on counterfeited coinage for the conservation and the authentication studies. These outcomes have been further validated by SEM-EDS analyses on cross-sections. In particular, depth-profiling and SEM-EDS data have shown consistent outcomes referred to a Sn enrichment in the inner layer and the clustering of Pb corrosion products. Finally, here we report, for the first time, 3D-elemental mapping of the corrosion patina of archaeological metal objects, achieved by multiple sequential ablations over the same area (Fig. 1). This contribution highlights the employment of LA-ICP-MS for conservation purposes, emphasizing its advantages in obtaining 1D, 2D and 3D information on stratified and inhomogeneous samples such as highly corroded archaeological metals.

Acknowledgements

We acknowledge Dr. Marco Roman from Ca' Foscari University of Venice for his useful support during LA-ICP-MS measurements, and the staff of the scientific laboratory of the "Opificio delle Pietre Dure", Firenze, for the preparation of the micro-sections and for performing SEM-EDS analysis.

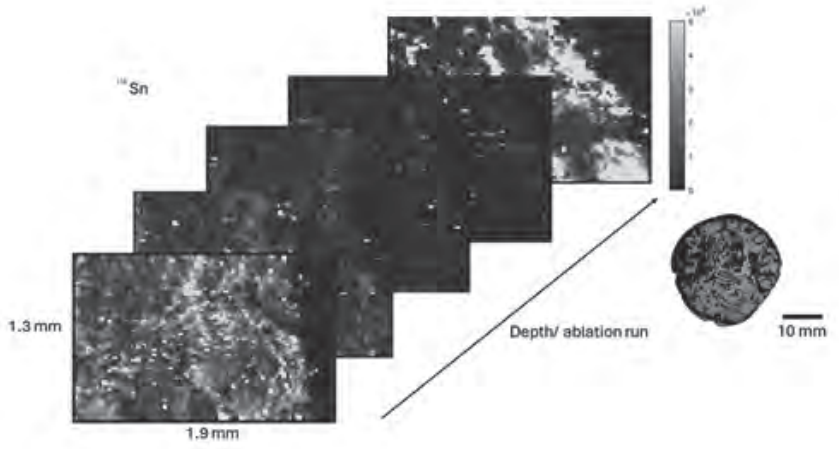

Fig. 1 LA-ICP-MS datacube, exploded layer by layer. Each box represent one ablated layer

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The Potential of ORBI-SIMS for Investigating Dyes in Archaeological Textiles

Jennifer M.K. Wakefield[1,2] and Line Flo[1], Chas Jones[3], Stephen E. Harding[2], Hartmut Kutzke[1]

[1]Musuem of Cultural History University of Oslo, Kabelgata 340580 Oslo; hartmut.kutzke@khm.uio.no; jennifer.wakefield1@nottingham.ac.uk

[2]University of Nottingham. The National Centre for Macromolecular Hydrodynamics, University of Nottingham, University of Nottingham, Sutton Bonington Campus, Sutton Bonington, Leicestershire, LE12 5RD; steve.harding@nottingham.ac.uk; jennifer.wakefield1@nottingham.ac.uk

[3]Independent

Keywords: ToF-SIMS, Orbi-SIMS, Dye analysis, Textiles, Mass Spectroscopy

Analyses of dyestuffs are an essential part of studying historical textiles. Characterization of the used dyestuffs and their composition improves not only our knowledge of historical manufacturing techniques, but may also help in a better understanding of the societies where the fabrics have been produced.
LC-MS and GC-MS are the most common methods and reveal to most information for dye analysis. However, these techniques require quite large sample sizes which in many cases cannot be provided. Although advancements in liquid chromatography had reduced the required amount of material, there are still samples of a significant size needed. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an alternative: it is non-invasive and minimally destructive technique and where sampling is required, requires only sampling on a microscopic scale. However, it does not separate components but rather produces a 'fingerprint' consisting of all compounds present. As a drawback, a layer of consolidant or other contaminations on the surface of the artefact could block this method from working. It is a pure surface technique,
Also, TOF-SIMS does not have MS/MS capabilities which allows to look at fragmentation patterns in order to identify unknown compounds. Therefore it relies on knowledge of expected molecular ions of known compounds from dyes and reference material. A new instrument that has become available is Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS) with hybrid OrbiTrap™ (Orbi-SIMS). Orbi-SIMS is a high resolution method with MS/MS capabilities and with the ability to depth profile or 3D map selected ions. These increased capabilities are anticipated to aid in identification chromophores and, in addition, degradation products. The vertical profile and 3D map capability may allow for identification of a dye even if a consolidant has been applied, and without having to remove the consolidant prior to analysis. To investigate the potential of this method, selected freshly dyed wool and consolidated freshly dyed wool were investigated alongside archaeological textile artifacts samples from the Oseberg finds as a case study.

Acknowledgements

The Orbi-SIMS analyisis is to be carried out at the Nanoscale and Microscale Reserach Centre at the University of Nottingham. Hanna Lukesova aided us with the sampling of the Oseberg artefacts.

Funding

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 artifacts from the Viking Age. The project is funded by the Norwegian Research Council under the number 316268.

Non-Destructive Dating of Medieval Manuscripts with Infrared Spectroscopy

Hend Mahgoub[1], Sonja Svoljsak[2], Jasna Malešič[2], Bernhard Spangl[3], Johannes Tintner[4,5], Nataša Golob[2] and Matija Strlič[1]

[1]Heritage Science Lab Ljubljana (HSLL), Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia; hend.mahgoub@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si
[2]National and University Library of Slovenia (NUK), Ljubljana, Slovenia; sonja.svoljsak@nuk.uni-lj.si, jasna.malesic@nuk.uni-lj.si, natasa.golob@ff.uni-lj.si
[3]Institute of Statistics (STAT), University of Natural Resources and Life Sciences (BOKU), Vienna, Austria; bernhard.spangl@boku.ac.at
[4]Natural Sciences and Technology in the Art, Academy of Fine Arts, Vienna, Austria; j.tintnerolifiers@akbild.ac.at
[5]University of Natural Resources and Life Sciences (BOKU), Vienna, Austria.

Keywords: machine learning, regression modelling, dating, historical paper

Non-destructive Infrared (IR) techniques enable the non-invasive characterization of various cultural heritage materials such as paper [Mahgoub et al, 2016], plastics [Rijavec et al, 2022] and paintings [Oriola et al, 2014]. Moreover, they have proven successful in dating organic materials, particularly cellulose-based objects [Coppola et al, 2023]. Due to the complexity of spectral data, integrating with machine learning methods is essential for the construction of dating models. This involves correlating specific production dates with spectral information that reflects chemical identity and interrelated changes influenced by factors such as material composition, manufacturing techniques, environmental conditions during storage. The general workflow for developing dating models using Infrared spectroscopic techniques is similar starting from selecting a representative, well-dated calibration set from the target material (e.g. paper), choosing the appropriate IR technique with a specific spectral range and selecting machine learning methods for data preprocessing and modelling to achieve the highest accuracy which means minimizing the difference in years between actual and predicted dates.

In this research, the use of three IR spectroscopic techniques was investigated for dating historical paper in the Medieval era, spanning the 13th to the 19th century. These techniques included Near-infrared (NIR) in the range of 350-2500 nm and Fourier Transform Infrared (FTIR) in the spectral range of 4000-400 cm-1 using two modules: Attenuated Total Reflectance (ATR) and Reflectance (RF). The selected well-dated dataset is part of the collection of the National and University Library (NUK) in Slovenia, which includes manuscripts and printed documents. Each methodology presents advantages and disadvantages regarding contact with samples, spectral resolution and range, penetration depth, etc. A methodological comparison is conducted to evaluate the impact of these factors on prediction accuracy. Various models are developed using regression methods and the evaluation of the models is based on the root mean square error of prediction (RMSEP) and correlation coefficient (R^2).

The research is part of the European project named Ancient Book Craft (ABC, 2022-2025) project (N1-0271) which aims to systematically explore the potential of non-destructive IR spectroscopic methods to date library materials. It involves BOKU (University of Natural Resources and Life Sciences, Austria), ÖAW (Institute of Medieval Research, Austria), NUK (National and University Library, Slovenia) and UL (Heritage Science Laboratory at the Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia). The project also collaborates with NLCR (National Library of the Czech Republic) and KN (Abbey Library and Archives of Klosterneuburg), where various collections will be measured for calibration and validation purposes. This will facilitate comparative studies of methods and calibrations, contributing to the assessment of the analytical robustness of the developed dating methods. It will also involve investigating the influence of storage environments, material types and properties, spectroscopic approaches, and the transferability of the developed methods.

Funding

The ABC project (N1-0271) is funded through the WEAVE program in collaboration between FWF (The Science Fund – Austria) and ARRS (Slovenian Research Agency).

This research is underpinned by the Research Programme Group N-DAD.

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Pre-Historical Mobility And Interaction Networks – A Non-Destructive Methodological Approach To Carbonate-Rich Remarkable Artefacts

Ana Luísa Rodrigues[1], Rosa Marques[1], Maria Isabel Dias[1], Maria Isabel Prudêncio[1], Dulce Russo[1], António Valera[2,3], Andrea Martins[4,5], César Neves[4,5], Mariana Diniz[4,5], José M. Arnaud[5], Zsolt Kasztovszky[6], Ildiko Harsányi[6], Veronika Szilágyi[6], B. Maróti[6], Imre Kovács[7] and Zoltán Szőkefalvi-Nagy[7]

[1]C2TN/DECN, Instituto Superior Técnico - Universidade de Lisboa, Campus Tecnológico e Nuclear, EN 10, km 139.7, 2695-066 Bobadela-LRS, Portugal; analuisarodrigues@tecnico.ulisboa.pt
[2]Era Arqueologia, Núcleo de Investigação Arqueológica—NIA. Cç. de Santa Catarina, 9C, 1495-705 Cruz Quebrada—Dafundo—Portugal.
[3]Interdisciplinary Center for Archaeology and Evolution ofHuman Behavior (ICArHEB, Universidade do Algarve, Campo de Gambelas, Faro, Portugal Institution
[4]UNIARQ – School of Arts and Humanities-University of Lisbon, 1600-214 Lisbon, Portugal
[5]Associação dos Arqueólogos Portugueses-Largo do Carmo, 1200-092 Lisbon, Portugal
[6]Nuclear Analysis and Radiography Department, Centre for Energy Research, 29-33 Konkoly-Thege street, 1121 Budapest, Hungary
[7]Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics, Budapest, Hungary

Keywords: Non-destructive analyses; pre-historical artefacts; Mobility and interaction networks

Interaction always assumed a relevant role in the explanation of social organization and social change. During the Chalcolithic, Southwest Iberian societies were engaged in a social trajectory of increasing complexity where regional and interregional interaction was a major element. In this context, idols and symbolic artefacts, one of the most impressive features of this period, which tend to assume explicit anthropomorphic aspect, have an important role on the understanding of this communities and their interactions [1]. Only non-destructive methods are suitable for the analysis of remarkable archaeological artefacts. The chemical characterization of Chalcolithic symbolic stone artefacts of Portuguese National Monuments (Vila Nova de São Pedro – VNSP and Perdigões – PRD), and its potential raw-materials was performed for the first time by using non-destrutive X-ray and neutron-based techniques, allowing the determination of numerous chemical elements contents [2,3].
In general, and comparing the artefacts with potential raw materials, the artefacts show signs of local/regional and long-distance procurement for both sites. The idea of VNSP as a limestone idols production center [4] was reinforced, and trade networks with PRD is suggested. This work impacts on the pre-historic study of interaction network in the Chalcolithic (Southern Iberia).

Acknowledgements

The authors are grateful to ERA-Arqeuologia S.A. and Museu Arqueológico do Carmo for the access to the archaeological artefacts. C2TN authors gratefully acknowledge

the Portuguese Science and Technology Foundation—FCT support through the UID/Multi/04349/2013 and UID/Multi/04349/2020 projects.

Funding

Projects supported by the European Commission under CHARISMA (GA No. FP7-228330) and
HORIZON 2020 Program through the Key Action Integrated Platform for the European Research Infrastructure on Cultural Heritage IPERION CH (Project Nr. 654028 - BRR_586_IP).
Ana Luísa Rodrigues and Andrea Martins research works are supported by post-doctoral grants SFRH/BPD/114986/2016 and SFRH/BPD/108951/2015, respectively, from Portuguese Science and Technology Foundation—FCT.

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Evidence of Transverse Ion Migration Mechanisms in the Early Stages of Drying Oil Paint Films Using Complementary Analytical Techniques

M. Gnemmi[1], L. Fuster-Lòpez[2], M. Mecklenburg[3], A. Murray[4], S. Sands[5], G.Watson[5], F.C. Izzo[1]

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, Venice, Italy; margherita.gnemmi@unive.it, fra.izzo@unive.it
[2]Universitat Politècnica de València, Instituto Universitario de Restauración del Patrimonio, Camì de Vera edificio 8B, Valencia, Spain; laufuslo@crbc.upv.es
[3]Smithsonian Museum Conservation Institute, Silver Hill Road, Suitland, USA; mecklenburgm224@gmail.com
[4]Queen's University, Art Conservation Program, Department of Art History and Art Conservation,15 Bader Lane, Kingston, Canada; alison.murray@queensu.ca ,
[5]Golden Artists Paints, Bell Rd 188, New Berlin, USA; sarahsands2@gmail.com
GWatson@goldenpaints.com

Keywords: Ion migration, oil paint, drying, film formation, material degradation.

This research provides evidence of the mechanisms involved in the migration of ions into adjacent pigmented oil paints, from the first hours after casting during frying and curing, over 24 months.
Two sets of samples were prepared with oil paints manufactured ad hoc by Golden Artist Color Inc. USA. A representative range of traditional and colors commonly used by artists was selected: SET1 consisted of a single layer of cobalt blue, earth colors (burnt and raw umbra and sienna) and whites (zinc, titanium, lead white); SET2 consisted of two layers of oil paint, with the just mentioned colored oil paint layer applied next to a lead white oil paint layer. Systematic investigations, supported by experimental chemo-physical techniques, were carried out on both the surface and the bulk of the painted systems: scribe tests, percentage weight variation (ΔW%), attenuated reflectance Fourier transform infrared spectrophotometry (ATR-FTIR), gas chromatography-mass spectrometry (GC-MS), thermal analyses with differential scanning calorimetry (TG-DSC). The results demonstrated the pigment-dependent transverse migration of metal ions and its effect on the drying, film formation and degradation phenomena observed on pigmented oil films. The chemical nature of the pigments and the composition of the oil binder were shown to play a role in the time taken to dry to touch as a function of the pigment present and how the presence of a lead white oil paint film influenced such drying and degradation products [1-3]. This provides an insight into the early drying stages and the migration mechanisms of material curing and degradation, such as metal soaps, between adjacent paint films, with particular emphasis on the influence of lead white [4-5]. This study allowed the interactions between oil and pigment, and between pigments in a paint film, to be monitored from the first hour after casting to the point of material degradation. It also showed how long selected colors took to dry to the touch, depending on the

pigment present, and how the presence of a lead-white oil paint film affected these drying and degradation products. Ions capable of promoting both oxidation and polymerization of the oil, such as lead, migrate transversely into the adjacent paint film and influence its drying through a catalytic reaction capable of accelerating the autoxidation reactions of unsaturated lipids. The results also showed that the effect of lead white on the reactivity of polyunsaturated triglyceride fatty acids was pigment-dependent: in paint layers containing earth or cobalt blue pigments (made from primary metal ions), oxidative reactions increased more rapidly. The study presented here highlights that unravelling and sequencing the factors that influence the physico-chemical mechanisms that take place in the early stages of film formation, curing and degradation of oil paint films has made it possible to design informed conservation strategies to mitigate such degradation [6].

Acknowledgements

The authors acknowledge Golden Artist Colours, Inc. for supplying paint samples for the preparation of the mock-ups.

Funding

This research was carried out in the framework of PID 2019- 106616GB-100 project granted by MCIN/ AEI /10.13039/501100011033 (Ministerio de Ciencia e Innovación/ Agencia Estatal de Investigación, Spain).

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An Optimized Multi-analytical Protocol for Identifying Colorants in p-PVC: Focus on the Hangings Series by Kiki Kogelnik

Teodora Raicu[1], Dubravka Jembrih-Simbürger[1], Matea Krmpotić[2], Iva Bogdanović Radović[2], Zdravko Siketić[2], Maresa Gerlach[3], Katja Sterflinger[1], Valentina Pintus[1,3]

[1]Institute for Natural Sciences and Technology in the Arts, Academy of Fine Arts Vienna, Augasse 2-6, Vienna, A-1090, Austria
[2]Division of Experimental Physics, Laboratory for Ion Beam Interactions, Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, HR-10000, Croatia
[3]Institute for Conservation and Restoration, Academy of Fine Arts Vienna, Augasse 2-6, Vienna, A-1090, Austria

Keywords: synthetic colorants, colored p-PVC, Kiki Kogelnik

Synthetic colorants, including pigments and dyes, are frequently used to color plastics. Pigments are preferred over dyes since dyes tend to migrate in polyvinyl chloride (PVC) and polyolefins, which are common types of plastics. Both inorganic and organic pigments are widely used, primarily selected based on their lightfastness. Although the concentration of pigments in plastic formulations may be relatively low, such as 0.75% in plasticized PVC [1], they significantly impact the photoaging of plastics. To mitigate this, companies add titanium white (TiO2), as it absorbs UV light. Despite this effort, museums and collections often report the fading of the colorants present in plastic cultural heritage objects. Thus, it is essential to identify the colorants to ensure appropriate display and storage conditions. However, since colorants are present in less than 1% within a complex matrix, their identification is a challenging task.

To address this issue, we developed a novel multi-analytical protocol for identifying colorants in p-PVC, focusing on the Hangings series (1968-1986) by Austrian pop artist Kiki Kogelnik. We examined seven p-PVC colored sheets from Kogelnik's estate, preserved by the Kiki Kogelnik Foundation. The sheets, in colors matching the Hangings (red, pink, yellow, orange, green, cerulean blue, and turquoise), appeared to be leftover materials from Kogelnik's original works. To identify the colorants, we employed XRF (X-Ray Fluorescence) and Raman spectroscopies combined with high-sensitivity Mass Spectrometry techniques, such as MeV SIMS (Secondary Ion Mass Spectrometry with MeV primary ions), DTMS (Direct Temperature Mass Spectrometry), EGA-MS (Evolved-Gas Analysis Mass Spectrometry), and HC/EGA-GC/MS (Heart-Cut/EGA - Gas Chromatography/Mass Spectrometry).

Firstly, XRF analysis was carried out to determine the elemental composition of the samples. Titanium (Ti) was detected in all samples, suggesting the use of TiO2 as a colorant and UV absorber. Lead (Pb) and chromium (Cr) were prevalent in the yellow and orange sheets, which were associated with chrome yellow/orange. Raman spectroscopy yielded conclusive results only when using an instrument equipped with an autofocus function. The results revealed the presence of chrome yellow in a monoclinic phase in the yellow and orange samples, according to the $\nu1(CrO_4^{2-})$ mode at 841 cm-1 and $\nu4/\ \nu2(CrO_4^{2-})$ modes at 400-358 cm-1 [3]a class of pigments frequently

used by painters of the Impressionism and Post-impressionism period, are known for their different chemical stability; the latter depends on the chemical composition ($PbCrO_4$, $PbCr_1?xSxO_4$. TiO_2 in the anatase form was found in all samples, with higher abundance in the pink and cerulean blue sheets. Synthetic organic pigments from the phthalocyanine class were identified in the blue, turquoise, and green samples, whereas β-naphthol lakes were detected in the red sample. PB15 (likely PB15:3) was identified in the cerulean blue sheet, and PG7 in the green sheet. The turquoise p-PVC consisted of a mixture of PG7 and PB15. The red sheet contained a mixture of PR53:1 and PR57:1. Due to the high abundance of TiO2 in the pink sample, the pigment could not be clearly determined.

MeV SIMS, an accelerator-based and surface-sensitive technique, was chosen for its efficiency in identifying molecular ions of synthetic organic colorants even at low concentrations [2]. Despite extensive analysis, only species corresponding to PVC and phthalates were observed, except in the turquoise sheet, which showed a low-intensity peak at m/z 575, possibly PB15:3. Additional information about colorants was obtained through DTMS, EGA-MS and HC/EGA-GC/MS, particularly in the red sheet. HC/EGA-GC/MS, by separating compounds according to the temperature zones determined by DTMS and EGA-MS, detected products of β-naphthol pigments/lakes in the zone of 288-384°C with a ramp of 10°C/min. Identified products included: m-toluidine/p-toluidine (m/z 77, 106), m-toluidine, 4-chloro (m/z 77, 106, 141), and 2-naphthol (m/z 115, 144).

The proposed multi-analytical protocol successfully addressed issues like low concentration and matrix effects, identifying colorants in six out of seven p-PVC sheets from Kiki Kogelnik's original materials. Among the various techniques used, Raman spectroscopy proved to be the most suitable for detecting synthetic inorganic and organic pigments in p-PVC.

Acknowledgements

The authors are grateful to Anna Sauer from the Kiki Kogelnik Foundation for providing the p-PVC samples from the original materials of Kiki Kogelnik.

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Influence of Tin Weighting on Silk Acidification, Colour Change and Structural Modification Induced by Accelerated Degradation

Ibrahim Elrefaey, Matija Strlič, Irena Kralj Cigić, Andraž Pezdirc, Anton Meden, Matija Tomšič

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna Pot 113, Ljubljana (Slovenia); ibrahim.elrefaey@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si, irena.kralj-cigic@fkkt.uni-lj.si, ap7195@student.uni-lj.si, Anton.Meden@fkkt.uni-lj.si, Matija.Tomsic@fkkt.uni-lj.si

Keywords: silk, varying content of tin-weighting, degradation, acidity, structure

This study investigates the effects of varying content of tin weighting on the acidity and colour properties, as well as the structural changes of silk fabrics induced by accelerated degradation. Previous research has shown that silk degradation leads to increased acidity [1] while tin salts can buffer this effect [2]. Colour change or yellowing has been considered a marker for underlying chemical changes [3]. However, the correlation between the content of tin salts and colour change upon degradation needs further investigation. In this study, mock-up silk samples, both unweighted and weighted with increasing tin metal salt contents using the tin-weighting technique [4]and especially costume, collections often contain weighted silks. The fabrics are generally in poor condition as a result of the weighting agents that were added, and conservation treatments are often difficult. The wide variety of silk weighting methods that have developed since the latter part of the nineteenth century has led to the state of deterioration of the textiles that have survived being equally diverse. To date there are no standard conservation treatments for weighted silks, although various chemical and physical\nmethods have been tested. The problem of fastdecaying silks has stimulated research within the silk industry since the late 1800s. This review focuses on information relating to the history, identification, degradation and stabilisation of Western weighted silks found in the English and German literature from the 1870s onwards.","container-title":"Studies in Conservation","DOI":"10.1179/sic.2009.54.Supplement-1.3","journalAbbreviation":"Studies in Conservation","page":"3-15","title":"Weighted silk: History, analysis and conservation","volume":"54","author":[{"family":"Hacke","given":"Marei"}],"issued":{"date-parts":[["2009",6,1]]}}}],"schema":"https://github.com/citation-style-language/schema/raw/master/csl-citation.json"} , were utilized. These samples underwent accelerated degradation via UV radiation, heat, and combined heat/humidity exposures. After degradation, acidity was assessed by measuring the pH of the extracts. Colour difference was calculated between reference samples and degraded ones subjected to several stressors. It was hypothesized that lower tin content may not fully buffer acidification, while higher tin weighting better maintain a neutral pH. However, extensive degradation could overwhelm the buffering capacity. The correlation between weighting, acidity, colour change, and degradation extent was examined. Structural analysis techniques such as XRD, SAXS, and WAXS revealed that tin weighting and accelerated degradation induce changes predominantly in the amorphous regions of silk, altering the nanostructure. These results provide insights into preserving both non-weighted and tin-weighted

silk artifacts by understanding how metal salt loading and different degradation environments impact silk acidity, colour, and structure.

Acknowledgements

Funding through the SAFESILK project (N1-250, FWO (The Research Foundation – Flanders) and ARIS (Slovenian Research and Innovation Agency), N-DAD Programme group and I0-012 E-RIHS.SI (both ARIS) is acknowledged.

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The Interaction between Musical Instrument Steel Strings and Cellulose Nitrate

Vera de Bruyn-Ouboter[1] and Hartmut Kutzke[2]

[1]Ringve Music Museum, Lade Allé 60, 7041 Trondheim, Norway / Norwegian University of Science and Technology, Department of Materials Science and Engineering, 7491 Trondheim, Norway; vera.de.bruyn.ouboter@mist.no
[2]Museum of Cultural History, University of Oslo, Postboks 6762 St. Olavs plass 0130 Oslo, Norway; hartmut.kutzke@khm.uio.no

Keywords: musical instrument, cellulose nitrate, steel string, corrosion, conservation

In collections of historical musical instruments, contact and atmospheric corrosion are challenges for conservation. Steel strings of stringed instruments are severely exposed to corrode in contact with the sound body's materials. The aim of this project is a better understanding of the degradation mechanisms and the development of methods for conservation.
Within a survey, 1200 musical instruments were investigated in 12 European museum collections, and contact corrosion could be reported on 10 % of the instruments. Metal strings corrode in contact with wood, sound damping fabric, leather or plastic. An intense corrosion process was observed on strings mounted close to cellulose nitrate (CN) parts (Figure 1).
Three stringed instruments from the collection of Ringve Music Museum / Rockheim, Trondheim, Norway, have continually been observed since 2009 and form the basis for this project. Our objective is to investigate the corrosion products and the mechanisms of the corrosion process of the steel strings in contact with the volatile emissions of the degrading CN. Nitrogen oxides emitting from the degrading CN are expected to be dominant reaction partners for the steel to oxidise [Chavez Lozano 2023]. FTIR confirmed the presence of CN in samples taken from the three different instruments. The strings and the corrosion products were investigated by SEM–EDS to detect their microstructure and elemental composition. Bubble-formed and elongated structures dominated, whereby the elongated structures grow out of the bubbles (Figure 2). EDS revealed a relatively small amount of nitrogen beside the main components, iron and carbon. (Figure 3).

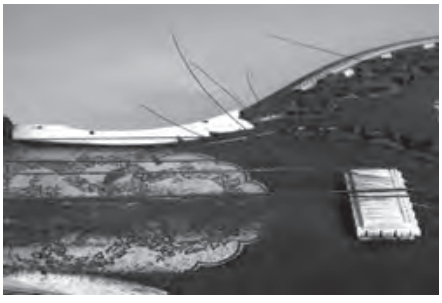

Figure 1
Corroded steel strings mounted close to a decoration element made of cellulose nitrate (CN) (Bass sitar, India, 20th century)

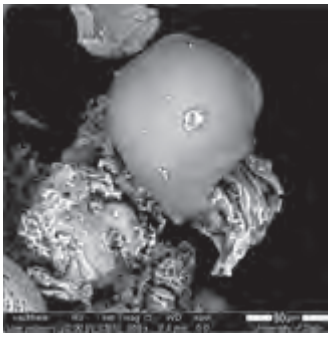

Figure 2 – Bubble-formed corrosion product with a developing elongated shape; SEM image

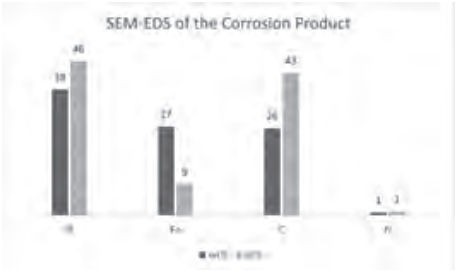

Figure 3 – EDS measurement revealing the nitrogen content in the corrosion product

IR and Raman spectroscopy pointed to a ferric nitrate and an iron hydroxy hydrate. The accurate composition of the corrosion product is still under investigation, focusing on the question of whether the product consists of a mixture of, for example, Fe(NO3) 9H2O (ferric nitrate nonahydrate) and -FeO(OH) (goethite) or if it represents an uncommon Fe-NO-OH species. The presence of nitrous compounds in the corrosion product of the steel strings indicates the involvement of nitrogen oxides emitted from CN [Leygraf 2016].

The volatile compounds emitted from the CN were captured by solid-phase-microextraction (SPME) and analysed by gas chromatography-mass spectrometry (GC-MS). The preliminary results of the SPME-GC-MS show a broad spectrum of compounds, including acetates, carbonic acids, aldehydes, camphor, sulphur- and nitrogen-containing compounds.

Attempts to protect the surface of the strings have been made, and SAMs (organic thin-film layers) have been tested in laboratory experiments.

Funding

The project is funded by the Research Council of Norway.

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Cumengeite Formation in Model Samples Investigated by Synchrotron Micro-X-ray Diffraction

Ermanno Avranovich Clerici[1], Steven de Meyer[1,2], Frederik Vanmeert[1,5], Letizia Monico[1,3], Costanza Miliani[4] and Koen Janssens[1,5]

[1]AXIS Research group, NANOlab Center of Excellence, University of Antwerp, Belgium
[2]Paintings Laboratory, Royal Institute for Cultural Heritage (KIK-IRPA), Brussels, Belgium
[3]CNR-SCITEC and SMAArt Centre (University of Perugia), Perugia, Italy
[4]CNR-ISPC, Napoli, Italy
[5]Rijksmuseum Amsterdam, The Netherlands
ermanno.avranovichclerici@uantwerpen.be

Keywords: Synchrotron, degradation, cumengeite, model samples.

In a medieval painted fragment from the vault of the Upper Basilica of Saint Francis of Assisi, the atypical mineral cumengeite ($21PbCl_2{\cdot}20Cu(OH)_2{\cdot}6H_2O$), a mixed (Pb,Cu) basic chloride salt, rarely found in paintings, was identified by means of synchrotron radiation-based X-ray powder diffraction at the micro-scale (SR-μ-XRPD) [1]. In the field of heritage science, cumengeite has been identified previously in historical bronzes and Roman coins as part of the degradation patina. On painted surfaces, up to now, this compound was only detected by Hradil et al. in a series of wall paintings [2]. In that specific case, its presence was interpreted as an intentionally applied blue pigment: since the presence of lead-containing compounds in the vicinity of cumengeite lacked, the possibility of its in situ formation as result of paint degradation processes was therefore excluded. Nevertheless, because of its rare occurrence in nature, a historical recipe for the preparation of this blue pigment was proposed to explain its presence in mural paintings [2]. In this study an extensive series of model samples containing Pb- and Cu-carbonates were prepared, employing different substrates, and exposed to chlorine under alkaline conditions before accelerated aging (light and high relative humidity) was performed to mimic the in vitro formation of cumengeite. The path for its formation as a secondary product and the pictorial techniques that most simply allow and favor its development have been investigated (Fig 1): these include fresco, tempera, semi-fresco and the use of skin glue as a binder. Not only was the distribution of cumengeite observed but alongside it other Pb- and Cu-containing chlorinated compounds such as laurionite Pb(OH)Cl and/or clinoatacamite $Cu_2(OH)_3Cl$ were identified employing specific distribution maps of crystalline compounds. In the samples from the Basilica of Assisi, these degradation products are also spatially correlated with cumengeite.

Acknowledgements

The authors also express sincere gratitude to the European Synchrotron Radiation Facility (ESRF) for providing access to their synchrotron radiation resources, and are grateful to Marine Cotte, Manfred Burghammer, Clement Hole, Jiliang Liu and Ida Fazlic for assistance in using beamline ID13 (proposal HG-172, pilot of a BAG project

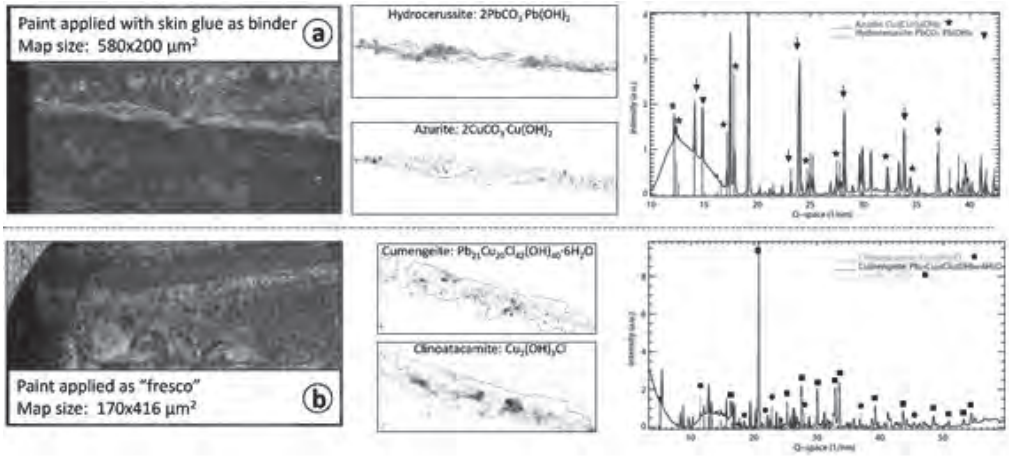

Fig 1:Microphotographs, XRPD distribution maps and 1D XRD patterns collected at ESRF (ID13) from two model samples exposed to chlorine in alkaline conditions before accelerated aging (light and high RH).
(a) a model sample painted with skin glue as binder and still showing the presence of the originally applied pigments azurite ($2CuCO_3{\cdot}Cu(OH)_2$) and hydrocerussite ($2PbCO_3{\cdot}Pb(OH)_2$).
(b) a second model sample painted using slack lime ($Ca(OH)_2$) as binder showing the presence of calcite $CaCO_3$ and the formation of the secondary compound: cumengeite ($Pb_{21}Cu_{20}Cl_{42}(OH)_{40}{\cdot}6H_2O$) and clinoatacamite ($Cu_2(OH)_3Cl$)

supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No 870313, Streamline).

Funding

The authors acknowledge the financial support from the following sources Smart*Light 2.0 funded by the Interreg V Flanders-Netherlands program with financial support from the European Regional Development Fund ERDF. Letizia Monico acknowledges the EU project IPERION-HS (H2020-INFRAIA-2019-1, GA no. 871034).

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Chemical Evolution of Oil Paints Under Different Hygrothermal Ageing Conditions

S. van Lith[1], J. Hermans[1,2,3] and K. Keune[1,2]

[1]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands; s.vanlith@uva.nl
[2]Conservation & Science, Rijksmuseum, Ateliergebouw Rijksmuseum, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands; k.keune@rijksmuseum.nl
[3]Amsterdam School for Heritage, Memory and Material Culture, Conservation and Restoration of Cultural Heritage, University of Amsterdam, PO Box 94552, 1090 GN, Amsterdam; j.j.hermans@uva.nl

Keywords: Oil paint, linseed oil, humidity, hygrothermal ageing, ester hydrolysis

Oil paints absorb water from their surrounding environment. The presence of water inside an oil paint is a driver for, among other things, oil binder hydrolysis [1] and metal soap formation [2]. Museums and private collectors attempt to slow down these processes by firmly controlling climate conditions, i.e. temperature and humidity. Despite a growing understanding of oil paint degradation pathways [3], a direct translation of knowledge to the prediction of degradation kinetics as response to environmental conditions is still missing. These predictions are powerful for determining optimal storage conditions for different types of paints, but also to assess (un)foreseen risk factors during storage. As a step closer to understand oil paint degradation kinetics under different environmental conditions, we have studied the chemical evolution of linseed-oil based paints under different humidity conditions at elevated temperature using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy. This study highlights the effect of dynamic and static humidity along with pigment type, and pigment concentration on ester hydrolysis of these oil paints. The findings were compared with dynamic vapor sorption (DVS) measurements of these oil paints (Figure 1A) in order to relate the initial water sorption to the ester hydrolysis of the binder material. Ultimately, the findings of this study help to define a computational chemical model for oil paint degradation which will aid future decisions on cleaning strategies and designing acceptable indoor climate conditions.
Interestingly, although the amount of absorbed water in the oil paint is determining the rate of ester hydrolysis, we also observed phenomena which may be associated with an ester hydrolysis equilibrium. We have found the hydrolysis rate is decreasing over time until the oil paint barely hydrolyzes further. In addition, ester hydrolysis is reversible in case the oil paint is stored in a dynamic environment changing from a high to a low humidity environment (Figure 1C). This chemical concept can shift perspective on oil paint degradation kinetics and resultantly preventive conservation. Given this insight, phenomena distorting this equilibrium and further promoting ester hydrolysis, e.g. evaporation of volatile organic compounds or metal complexation, may prove to be very important for the long-term degradation of an oil paint. Conversely, humidity fluctuations and water sorption of an oil paint could have less impact in the long-term than previously thought.

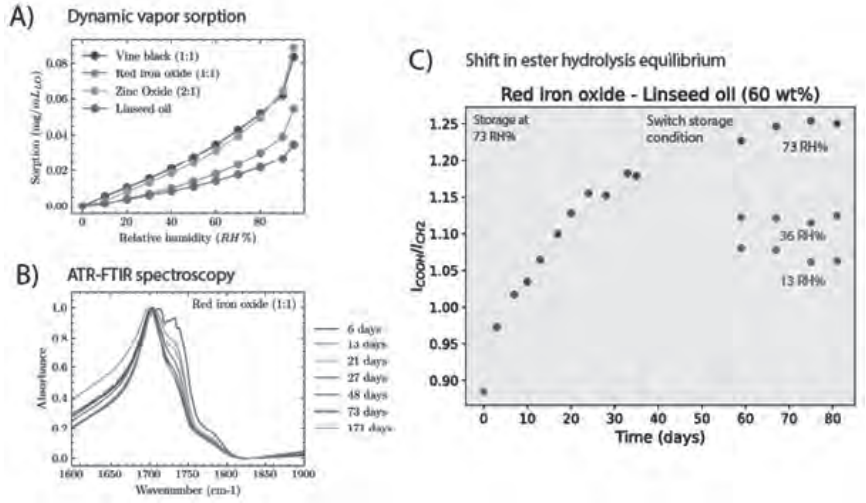

Figure 1. A) Dynamic vapor sorption of vine black (1:1), red iron oxide (1:1), zinc oxide (2:1) pigment particles mixed with linseed oil in given mass ratios and pure linseed oil. B) Infrared spectra (1600-1900 cm-1) of red iron oxide paint film stored under high humidity condition (73 RH%) measured at different time intervals. C) Time evolution of peak ratio (I1410/I1456) of red iron oxide pigmented paint film (60 wt.% red iron oxide) preconditioned for 35 days at high humidity condition (73 RH%) and afterwards stored under other (13 and 36 RH%) or the same humidity conditions.

Acknowledgements

The authors thank Jorien Duivenvoorden (The Rijksmuseum, the Netherlands) and prof. Piet Iedema (University of Amsterdam, The Netherlands) for fruitful research discussions during this research project.

Funding

This work is part of the GoGreen project (Grant Agreement Number: 101060768), a Horizon Europe project funded by the European Union aiming to develop clear and reliable parameters for environmentally friendly and healthy conservation methodologies for cultural heritage.

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Evaluating the Light-Induced Damage of Dyed Silk Textiles

Ludovico Geminiani[1,2], Cristina Corti[2,3], Moira Luraschi[2,4], Sandro Recchia[1], Laura Rampazzi[2,3,5]

[1]Department of Science and High Technology, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como; L.G. lgeminiani@uninsubria.it; S.R. sandro.recchia@uninsubria.it
[2]Centre for Cultural Heritage Studies, Università degli Studi dell'Insubria, via Valleggio 9, 22100 Como, Italy
[3]Department of Human Sciences and of Innovation for the Territory, Università degli Studi dell'Insubria, Via Valleggio, 9, 22100 Como; C.C. cristina.corti@uninsubria.it; L.R. laura.rampazzi@uninsubria.it
[4]Museo delle Culture, Villa Malpensata, Riva Antonio Caccia 5, Lugano, Switzerland; moira.luraschi@lugano.ch
[5]Istituto per le Scienze del Patrimonio Culturale, Consiglio Nazionale delle Ricerche (ISPC-CNR), via Cozzi 53, 20125 Milano, Italy

Keywords: silk, silk degradation, light-induced damage, dyes

Silk has always been considered one of the most precious yarn, due also to the rich hues which were obtained after dyeing. In particular, Asian textiles show one of the widest ranges of colours, which were traditionally obtained from a lot of different plants extracts [1]. Different mordants were used to obtain different hues from the same dye too. The present work studies how the various combination of dyes and mordants influence the degradation rate of dyed silk textiles. While the mordant-induced damage is commonly recognized [2], it seems that some dyes can accelerate or slow down the rate of the light-induced degradation, but there is no specific research on this issue. Light damage is not only limited to fading: overexposure can also cause weakening, discoloration, yellowing and embrittlement of the fibre [3]. Raw silk was obtained and underwent a controlled degumming process to eliminate sericin. 4 replicated samples of silk were dyed using traditional recipes and different dyeing bath, to assess the reproducibility of the dyeing conditions. 9 traditional dyes extracted from Asiatic plants were tested with 4 commonly used mordants (alum, potassium tartrate, iron sulphate and tannic acid). Indigo and safflower were also tested as direct dyes. Two sets of dyed silk mock-ups were artificially aged using either UVA or visible light to reproduce and compare the light-induced damage obtained with UVA respect to visible light. A similar set of mock-up samples of raw silk was aged under the same conditions. UV-Vis reflectance spectroscopy was used to evaluate the colour variations during the accelerated ageing test. A protocol based on attenuated total reflectance and external reflection Fourier-transform infrared spectroscopy [4], X-ray diffraction [5], and thermal gravimetric analysis [6] was used to monitor the degradation extent. Data were manipulated by means of peak fitting analysis and chemometric tools. The crystallinity index was calculated from both X-ray diffraction, and thermal gravimetric analysis, showing a loss of crystallinity as degradation took place. FTIR spectroscopy permitted to study the ageing mechanism. The results of this research are valuable in order to evaluate the light-induced

damage on silk textiles. Some combination mordant/dye are particularly dangerous for the conservation of silk textiles. Thus, the information about the mordant and the dye, which can be obtained through commonly available and portable analytical techniques, can help evaluating the risk associated to the exhibition of particular kind of artifacts and planning the best preventive conservation practices.

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Proteomic Approaches for Studying the Degradation of Egg Proteins in Polychrome Layers

Elena C. L. Rigante, Cosima D. Calvano, Simona A. Riganti, Tommaso R. I. Cataldi

University of Bari Aldo Moro, Department of Chemistry, via E. Orabona 4, 70125, Bari (Italy); elena.rigante@uniba.it, cosimadamiana.calvano@uniba.it, simona.riganti@uniba.it, tommaso.cataldi@uniba.it.

Keywords: MALDI, mass spectrometry, painting binders, aging

Among the ancient protein-based binders, egg was widely used in the tempera technique thanks to its good resistance and stability to aging [1]. The present study was designed to investigate the effect of artificial aging on egg white proteins in order to better understand the process of protein degradation and the role of pigments in real works of art. Oxidation of serine, phenylalanine, and cysteine as well as deamidation of asparagine and glutamine are reported as the principal proteins deterioration events in historical samples [2]. Additionally, several studies have demonstrated that certain inorganic pigments affect the proteinaceous binder's network stability [3, 4].
The following samples were prepared: beaten egg white, egg white mixed with ematite and with calcium carbonate each spread with a brush on glass microscope slides. All samples underwent artificial aging with a solar lamp (300 W, 230 V, 280-2000 nm) at 50°C for a maximum of 864 hours.
Sampling (1 mg) was carried out on freshly prepared samples and after 30, 72, 144, 288, 576 and 864 hours of artificial aging to perform in solution enzymatic digestion with three types of enzymes: trypsin, GluC and AspN. These last two enzymes are typically employed for middle-down proteomics since they allow for the formation of higher molecular weight peptides which can be useful to study the occurrence of PTMs (post-translational modifications). Trypsin was chosen as the conventional enzyme for bottom-up proteomics. Analysis were performed with ATR-FTIR (attenuated total reflectance - Fourier transform infrared spectroscopy) directly on microscope slides, while two mass spectrometry techniques, LC-ESI-MS (Liquid Chromatography-Electrospray Ionization-Mass Spectrometry) and MALDI-TOF-MS (Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry), were used to investigate the enzymatically digested samples. With the aid of bioinformatic software, we found that the number of specific peptides increases with artificial aging time, suggesting that a protein structural degradation occurs, regardless of the enzyme employed. This is also confirmed by the PMFs (peptide mass fingerprinting) which show a progressive decreasing of S/N ratio with aging especially for heavier peptides. The main results obtained during the present work will be discussed in this communication.

Funding

This work was supported by Progetto di Ricerca di Interesse Nazionale—PRIN 2022CNNRWZ-REActiveGElfororgaNicbindERsrecognitioninArtworks(REAGENERA),

financed by the Italian Ministero per l'Istruzione, l'Università e la Ricerca (MIUR).

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Degradation by Dehydrochlorination of Poly(vinyl chloride) Heritage Objects

Špela Pok, Tjaša Rijavec, Irena Kralj Cigić, Matija Strlič

Heritage Science Laboratory, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana; spela.pok@fkkt.uni-lj.si, tjasa.rijavec@fkkt.uni-lj.si, irena.kralj-cigic@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si

Keywords: PVC degradation, HCl emissions, yellowing

Poly(vinyl chloride) (PVC) is one of the most commonly used polymers in everyday life due to its good properties and low production costs. It can be found in various areas, from packaging to construction. Due to its intriguing nature and easy handling, PVC has also become an important means of expression for various artists and today represents a large part of the material cultural heritage of the 20th and 21st centuries. Due to the signs of rapid degradation, PVC objects pose a major challenge for conservators and curators. The need to understand this material and thus prevent the loss of culturally important objects is therefore of the paramount importance [1, 2]. One of the most visible indicators of degradation is the yellowing of PVC, as polyene sequences are formed after the dehydrochlorination reaction. Hydrogen chloride (HCl) is formed as a by-product, the fate of which at the room conditions is not yet fully understood [3]. The aim of our experiments is therefore to determine the extent of HCl emissions from PVC and the consequences for the material itself and the environment around the PVC objects.

As a part of ongoing research work, the gaseous HCl emissions were determined in various experiments using the Markes Micro-Chamber/Thermal Extractor CTE120 in surface emission mode with the air flow of 100 mL/min at a temperature of 80 °C to 120 °C and without controlling the relative humidity. Emissions from new, old (> 25 years) and new PVC after accelerated degradation were investigated by sampling on specially cleaned silica gel sorbent tubes, followed by extraction from the sorbent in sodium hydroxide and analysis of the solutions using an ion chromatograph with conductivity detector.

A series of experiments were done at 110 °C. This showed that the HCl emissions from the new PVC decrease in the first 12 to 24 hours, whereas this is not the case with the old PVC. We concluded that this observation is due to HCl accumulation in the material as a residue from the production of the material itself. After 24 hours, the amount of HCl starts to increase, and this is the result of the HCl produced during the experiment. At lower temperatures the emission rates become smaller, so the sampling times are much longer – three weeks were needed to detect and quantify the HCl emissions from the new PVC at 80°C.

The cross-infection of the polymer samples was also studied with the piece of PVC and the piece of reference cellulose (Whatman filter paper) in the same Schott glass vial. Degradation of the cellulose was evaluated after 14 days at 80 °C as the degree of polymerisation (DP) determined by viscometry. The results showed that the DP decreased significantly in the experiments with old PVC samples, but further

experiments need to be conducted to better understand the degradation of these materials.

Acknowledgements

The authors would like to acknowledge Maja Šubic for her work done on the topic.

Funding

This work was supported by the Slovenian Research Agency (ARIS) project N1-0241 (PVCare) and by the Programme Group N-DAD.

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Mercury Soaps in Paintings: from Suspicion to Analytical Confirmation and Risk Assessment

Silvie Švarcová[1], Ruslan Barannikov[1,2], Petr Bezdička[1] and Janka Hradilová[1]

[1]ALMA Laboratory, Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec 1001, 250 68 Husinec-Řež, Czech Republic; svarcova@iic.cas.cz, barannikov@iic.cas.cz, petrb@iic.cas.cz, hradilova@iic.cas.cz

[2]Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, 128 43 Prague 2, Czech Republic

Keywords: mercury carboxylates, XRPD, FTIR, ssNMR, thermal analysis, paintings

Saponification of paint layers often induces undesirable changes of the original appearance of paintings caused by the increased transparency and/or opacity of the affected paint layers. In addition, the growing soap aggregates threaten the stability of works of art when the protruding and efflorescing soaps result in the loose of paint layers' adhesion. [1] In the research of saponification phenomena, the attention is paid predominantly to zinc and lead-based pigments which are apparently the most prone ones to interact with fatty binding media under formation of metal soaps. However, our research of portrait miniatures has revealed presence of different types of crystalline metal carboxylates frequently in a conjoined occurrence of lead white ($2PbCO_3 \cdot Pb(OH)_2$) and cinnabar (HgS) in paint layers, exceptionally even without presence of any lead-based pigment, indicating that HgS assisted to the formation of Pb and/or Hg carboxylates. [2] Nevertheless, the paucity of reliable reference structural data for mercury carboxylates limited both their proper identification in artworks and the experimental research of HgS interactions with binders on molecular level.

Therefore we synthesized long chain simple and mixed mercury (II) carboxylates of the general formula $Hg(C16)_x(C18)_{2-x}$ (where C16 and C18 stand for palmitate and stearate, resp., and $0 \leq x \leq 2$) in the form of pure polycrystalline powders and characterized them by XRPD, ssNMR, FTIR and DSC. The crystal structure description of the synthesized mercury carboxylates [3] enabled us the successful distinguishing of mercury and lead carboxylates in miniature portraits [4]. Furthermore, application of the Rietveld refinement on the collected XRPD patterns provided a detailed insight into the chemical composition of detected crystalline mercury and lead carboxylates, showing their mixed character (i.e., both palmitate and stearate anions are incorporated in one compound). In addition, specification of chemical composition of detected mercury and lead soaps allowed us to estimate consumption of cinnabar and lead white by saponification reaction based on mass balance relations, indicating the original composition of degraded paint layers.

Moreover, the pigment-binder interactions with fatty binders were studied in the series of model experiments simulating egg and/or oil-based paint systems consisted of mercury and/or lead-based pigments. The preliminary results show the susceptibility of cinnabar to form crystalline mercury carboxylates (in egg-based systems) and also its tendency to accelerate the formation of lead carboxylates in mixtures with lead-based pigments.

Finally, we studied thermal behaviour and stability of mercury palmitate and mercury stearate and their respective mixtures with linseed oil in the temperature range of 25 to 150 °C using DCS, TG-MS, FTIR, XRPD, including in situ high-temperature FTIR and XRPD. The results clearly show that being mixed with linseed oil, mercury carboxylates decompose rapidly at relatively low temperature around 100 °C under formation of metallic mercury, a volatile toxic substance, and free fatty acids, reactants capable of further development of saponification in paint layers.
The contribution summarizes the fundamental structural and thermal characteristics of synthesized reference mercury carboxylates and their application into the identification of mercury soaps found in painted artworks as well as into the experimental study of pigment-binder interactions.

Acknowledgements

The authors thank to all colleagues who participated in the research and analyses, namely Eva Kočí, Silvia Garrappa, Michal Pech, David Hradil, Jiří Plocek, Libor Kobera, Jan Rohlíček, Anna Vykydalová and Joen Hermans, as well as to restorers, curators and artworks' owners collaborating in the investigation of paintings.

Funding

This work was supported by the Academy of Sciences of the Czech Republic within the frame of the research programme Strategy AV21 No. 23 - City as a Laboratory of Change; Historical Heritage and Place for Safe and Quality Life.

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Study of Degradation of Mixed Model Systems Consisting of Plasticised Poly (vinyl chloride) and Lignocellulosic Material

Simona Klempová[1], Petra Urbanová[1], Lucia Mencáková[1], Katarína Kučíková[1], Michal Oravec[2] and Katarína Vizárová[1]

[1]Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Radlinského 9, 812 37 Bratislava; simona.klempova@stuba.sk, petra.urbanova@stuba.sk, xmencakoval@stuba.sk, katarina.kucikova@stuba.sk, katarina.vizarova@stuba.sk

[2]Slovak National Gallery, Riečna 1, 815 13 Bratislava; michal.oravec@sng.sk

Keywords: plasticised poly (vinyl chloride); lignocellulosic material; accelerated ageing; cross-infection; spectroscopic analysis

Considering the material diversity of modern and contemporary artworks, there is a high probability of the co-existence of various incompatible materials in one collection or even in one single artwork. One of these unsuitable material combinations is plasticised poly (vinyl chloride) (PVC-P), the most common malignant synthetic plastic in modern and contemporary art collections, with cellulosic or lignocellulosic materials [1, 2, 3]. The main degradation pathway of PVC-P is most probably the migration of plasticiser and dehydrochlorination, leading to the release of HCl and the formation of conjugated polyenes in the PVC chain, which are responsible for the colour changes in PVC-P [4]. Since cellulosic and lignocellulosic materials are intrinsically sensitive to acid hydrolysis, there is a great need for studies dealing with the influence of PVC-P and its main degradation product – HCl, on the stability of these materials [5].

The present study focuses on the influence of PVC-P on the stability of cellulosic and lignocellulosic material and vice versa. The PVC-P model samples represent a simplified PVC-P formulation widely used in the 2nd half of the 20th century. The prepared PVC-P formulation is composed of polymer–suspension poly (vinyl chloride), plasticiser–dioctyl phthalate (35 wt%) and thermal stabiliser–calcium and zinc stearate in a ratio of 1 to 1 (3.8 wt%). Whatman paper (pure cellulose) model samples (WP) were the representatives of cellulosic materials. NOVO paper (17 % lignin, rosin-type sizing agent and kaolin-filler) model samples (LP) were the representatives of lignocellulosic materials. Three one-component model systems (PVC-P, WP, LP) and two two-component model systems (PVC-P with WP and PVC-P with LP) were exposed to accelerated thermal ageing at 90 °C in airtight glass bottles for the duration of 5/10/15/25/30/35 days. The changes in properties of PVC-P model samples were studied using UV-Vis and ATR-FTIR spectroscopy. The changes in the properties of WP and LP model samples were studied using ATR-FTIR spectroscopy, colourimetry (calculation of colour difference E), viscometry (determination of the degree of polymerisation is only applicable to WP model samples) and surface pH measurements.

The UV-Vis and ATR-FTIR spectra of PVC-P model samples show that degradation of PVC-P (dehydrochlorination and loss of plasticiser) is significantly faster and more intense in the presence of the Whatman paper in comparison with the other model systems.

The results of colourimetry, viscometry and surface pH measurements led to the conclusion that the presence of PVC-P encourages the degradation of the Whatman paper. The results of ATR-FTIR spectroscopy also suggest that the migration of thermal stabiliser to the Whatman paper is possible. The results of colourimetry and surface pH measurement are, in the case of NOVO paper, comparable for both model systems (LP alone and PVC-P with LP), and therefore, inconclusive what is probably given by the high heterogeneity of NOVO paper; however, ATR-FTIR spectroscopy shows that the presence of PVC-P promotes the degradation of NOVO paper resulting in its faster and more intense oxidation.
In conclusion, PVC-P has an undesirable effect on the stability of both cellulosic and lignocellulosic material and vice versa. The differences between the intensity of the degradative effect of cellulosic and lignocellulosic materials on PVC-P will be subject to future research.

Funding

This work was supported by the Slovak Research and Development Agency under the contract No. APVV 20-0410.

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The Power of Swabs: Non-Destructive Surface Analysis of Heritage PVC

Tjaša Rijavec[1,2], Irena Kralj Cigić[1], Matija Strlič[1], G. Asher Newsome[2]

[1]Heritage Science Laboratory Ljubljana, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia; tjasa.rijavec@fkkt.uni-lj.si, irena.kralj-cigic@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si
[2]Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746-2863, United States of America; newsomeg@si.edu

Keywords: plasticizers, poly(vinyl chloride), exudates, mass spectrometry

Poly(viny chloride) (PVC) objects constitute a significant part of heritage collections due to their diverse properties and ease of production.[1] These artifacts are prevalent in both contemporary artwork and industrial heritage collections. The versatile material properties are achieved by incorporating plasticizers to enhance flexibility and stabilizers to improve thermal and oxidative stability. Unfortunately, heritage PVC items often display pronounced signs of degradation, with gradual yellowing resulting from dehydrochlorination, is predominantly influenced by storage temperature.[2,3]as relevant to room conditions during long-term storage of heritage collections. Degradation was quantified as increase in the b* colour coordinate during accelerated degradation at 50 and 70 °C as a function of temperature, relative humidity, plasticizer content, and polymer molecular weight. The significance of each variable was investigated with multiple linear regression. Lower temperature, lower relative humidity, higher polymer molecular weight and higher plasticizer content were associated with lower degradation rates. The activation energy of 86 kJ/mol was calculated. The concept of '1- °C-equivalent' is introduced to enable variable prioritisation from a heritage management aspect. The resulting model can be used to shape environmental management guidelines and identify the most vulnerable objects in heritage collections. Damage function for poly(vinyl chloride Loss of plasticizers occurs by diffusion, migrating from the bulk to the surface, where they can either evaporate or accumulate at the surface. Exudation of plasticizers and other additives causes the appearance of 'sticky' and 'tacky' surface which is commonly associated with damaged plastic objects. This poses a significant challenge in conservation and research because the compromised surface tends to attract dust and pollutants.

This research aimed to establish and validate a non-destructive methodology for analysing the surface of PVC using swabs. Although there are case studies documenting plasticizer pooling,[4] the chemical composition of most surface exudates remains unknown. Working with objects of heritage value requires non-destructive in-situ sampling, so a methodology based on dry swabbing was developed. The swabs were directly analysed with non-proximate desorption photoionization (NPDPI) with high resolution mass spectrometry (Orbitrap), enabling non-targeted identification with high sensitivity.[5]

Furthermore, the research demonstrated that the surface concentration of di(2-ethlyhexyl) phthalate (DEHP), as the most common plasticizer, can be quantitatively determined based on the same sampling methodology. For this purpose, a known surface area of an object was swabbed in triplicate, and the analytes were extracted with a solvent before quantification using an GC-MS in SIM mode.
The methodology was developed and validated on sacrificial PVC samples and deployed for use on selected objects at the Smithsonian American Art Museum (SAAM) and the Cooper Hewitt, Smithsonian Design Museum (CHDM). The chemical composition of the investigated objects ranged from simple to complex. The measured surface concentration of DEHP ranged from 1.5 mg/m^2 to 102 mg/m^2.
The non-destructive surface analysis methodology was designed to be accessible to all museums, requiring no advanced equipment for sampling, and provides comprehensive information on the chemical composition of surface exudates, currently unknown for many plastic heritage objects.

Acknowledgements

The authors thank Jessica Walthew and Kira Eng-Wilmot from the Cooper Hewitt, Smithsonian Design Museum (New York, United States of America) and Leah Bright from the Smithsonian American Art Museum (Washington DC, United States of America) for their help with conservation assessments and sampling. The authors thank Sarah Barack (Cooper Hewitt, Smithsonian Design Museum) as well as Amber Kerr and James Concha (Smithsonian American Art Museum) for their help with organizing the museum survey.

Funding

This work was supported by the Slovenian Research Agency (ARIS) through the project N1-0241 (PVCare) and Research Core Funding (P-NDAD). TR acknowledges support through the Smithsonian Institution Predoctoral Fellowship and GAN acknowledges the support from Smithsonian federal funds.

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Stabilization of Verdigris Pigment on Paper Documents

Jasna Malešič[1], Klara Retko[2,3] and Irena Kralj Cigić[3]

[1]National and University Library, Turjaška 1, 1000 Ljubljana; jasna.malesic@nuk.uni-lj.si
[2]Institute for the Protection of Cultural Heritage of Slovenia, Research Institute, Poljanska cesta 40, SI-1000 Ljubljana, Slovenia, klara.retko@zvkds.si
[3]University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana; Irena.Kralj-Cigic@fkkt.uni-lj.si

Keywords: paper, Verdigris, copper, pigment, degradation, stabilization

Copper-based pigments, such as Verdigris, cause severe damage to many important historical documents. This pigment was widely used from antiquity until the 19th century and can be found in illuminations, book illustrations, and maps. The extent of damage caused by green copper-based pigments ranges from colour changes in painted areas to the complete degradation of both the pigment and the carrier material, whether it be papyrus, parchment, or paper [1]. This phenomenon, known as "copper corrosion," is induced by the presence of soluble copper ions [2], which are known to catalyse the oxidative degradation of cellulose in an alkaline environment. Studies have shown that copper ions are significantly more catalytically active in the oxidative degradation of cellulose compared to several other transition metal ions, including iron [3]. Additionally, acids may also be present in the paper carrier, leading to the acid hydrolysis of cellulose [4].

Despite the subject of Verdigris stabilization receiving considerable attention in research in recent years, it remains an ongoing concern for paper conservators and researchers. Until recently, little was known about the degradation pathways of Verdigris under various conditions, which are necessary for paper stabilization studies. Studies of various stabilization processes usually take place under conditions of accelerated thermal or light degradation, namely at elevated temperature and relative humidity and/or exposure to light of different wavelengths. For paper, temperatures equal to or higher than 80°C are usually employed for thermal accelerated degradation tests, either without humidification or with humidification up to 65% relative humidity (RH). Additionally, studies on paper stabilization with Verdigris have typically been conducted under these conditions.

Based on research by Brostoff et al. [5,6], studies on paper stabilization were conducted in accordance with the new accelerated degradation protocol (50°C and 65% RH). Mock-up samples were prepared with historically significant neutral Verdigris. In addition to Whatman filter paper, Verdigris paint films were also applied to handmade paper sheets. The efficacy of two promising antioxidants as stabilization agents, previously studied under elevated accelerated degradation conditions—tetrabutylammonium bromide (TBAB) [7] and benzotriazole (BTA) [8]—was re-evaluated.

The concentration of copper ions on paper samples was determined using AAS (Atomic Absorption Spectroscopy). To assess the stability of mock-up papers, colour, molecular weight (Mw), and pH value during accelerated degradation were determined. The pH values increased during accelerated degradation experiments, most likely due to

the formation of basic Verdigris from neutral Verdigris, indicating that stabilization treatment may not necessarily include a deacidification agent. Both antioxidants delayed the degradation of cellulose under mild accelerated degradation conditions compared to untreated samples. SEC (Size Exclusion Chromatography) measurements of Mw during accelerated degradation experiments confirmed that the stabilization effect of tetrabutylammonium bromide was superior to that of benzotriazole. Additionally, colour changes were slightly more noticeable after the addition of BTA compared to TBAB. However, during degradation, some paper samples containing a high amount of pigment exhibited pronounced black and brown spots on all three types of samples (untreated, treated with BTA, and TBAB), which were analysed using Raman spectroscopy and resulted in detection of copper oxide and will be further investigated using XAS (X-ray Absorption Spectroscopy).

Acknowledgements

The authors gratefully acknowledge Ana Šiško for technical support. The authors acknowledge the CERIC-ERIC Consortium for the access to experimental facilities.

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Nanocellulose-Stabilized Oil-in-Water Pickering Emulsions for Removing Natural Resin Varnishes From Canvas Paintings

Maria Rita Caruso[1], Olivia Gómez Laserna[2], Giuseppe Cavallaro[1], Francesco Caruso[3], Giuseppe Lazzara[1], Maite Maguregui[3]

[1]Department of Physics and Chemistry "Emilio Segrè", University of Palermo, Viale delle Scienze, Ed. 17 Stanislao Cannizzaro, 90128 Palermo, Italy. mariarita.caruso02@unipa.it, giuseppe.lazzara@unipa.it.
[2]Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain, olivia.gomez@ehu.eus.
[3]Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain, Francesco.caruso@ehu.eus maite.maguregui@ehu.eus.

Keywords: Cellulose nanocrystals, oil-in-water pickering emulsion, varnish removal, green conservation

The removal of the yellowing varnish layer is considered asone of the most complex steps in conservation. Key requirements are homogeneous treatment, absence of residues, and minimal (if any) alterations to pictorial layers. Therefore, the development of advanced solutions to remove varnish should not only demonstrate effectiveness but also include a testing phase that ensures the artwork preservation, as well as address concerns related to human health and the environment [1].
In various fields such as food industry, cosmetics, pharmaceutics, and medicine, Pickering Emulsions (PE) have gained widespread use due to their stability and formulation versatility [2]. Recently, PEs have also emerged in the field of art conservation as a safe alternative to conventional surfactant-based emulsions to provide a controlled and effective cleaning of artworks [3-5]. PEs demonstrate the ability to encapsulate cleaning agents, which can be then applied in a controlled way onto the painting layer to softly remove soiling or varnishrelease residius.
Cellulose, the most abundant biopolymer on earth, is renewable, nontoxic, and biodegradable. It can be employed for the stabilization of PEs, ensuring safety for both the operators and the environment. Among others, cellulose nanocrystals (CNC) are the main stabiliser used for oil-in-water (o/w) PE [6].
This work presents the use of CNCs to create PEs for the removal of yellowed natural resin varnishes on canvas paintings. For the o/w PEs, green solvents (such as ethyl acetate) have been integrated as an alternative to traditional petroleum-based solvents.
The influence of various CNC concentrations and ratios between oil and water phases on the formation, stability, dimensions, and viscosity of PEs were was investigated by optical microscope microscopy and Confocal Laser Scanning Microscopy. Rheological, zeta Potential and Dynamic Light Scattering measurements complement this study.
The effectiveness of the most promising formulations was tested on canvas paintings using a non-invasive analytical approach to monitor the cleaning. Initially, observations under the stereo-microscope and colorimetric analyses were carried out. Eventually, the use of more advanced techniques, like Fiber Optics Reflectance Spectroscopy and

Hyperspectral Imaging in the Vis-NIR-SWIR range (400-2500 nm), among others has been implemented.
The results demonstrate the capability of CNCs as stabilizers in the formation of new ethyl acetate o/w PEs. The concentration of CNC plays a crucial role in particle aggregation or repulsion at the o/w interface, due to its electric charge, thereby influencing the hydrodynamic radius of nanoparticles and the formation of PEs. Additionally, the addition of NaCl reduces the electrostatic forces that contribute to the PE formation. The testing phase of stable formulations revealed the potential of ethyl acetate within the PE system, with the best-admitted ratio between oil-in-water phase, for removing the aged varnish layer.
Based on the positive results obtained from this initial study, we aim to provide a range of tailored alternatives for different types of varnishes and painting supports.

Acknowledgements

M.R. Caruso acknowledged the University of Palermo, Department of physics and Chemistry. O. Gómez-Laserna acknowledged her contract funded by grant TED2021-129299A-I00 and F. Caruso acknowledges his Maria Zambrano fellowship from UPV/EHU, funded by MICIU and the European Union NextGenerationEU/PRTR.

Funding

This work has been supported by by grant TED2021-129299A-I00, funded by MCIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR and by PON “Research and Innovation” 2014-2020, Asse IV “Istruzione e ricerca per il recupero”, all’Azione IV.5 “Dottorati su tematiche green”. DM 1061/2021, by the University of Palermo.

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Development of Novel Green Cleaning Systems for the Removal of Dammar Varnish from Paintings

Burcu Keser[1], Francesca Ramacciotti[2], Chiara Gualandi[2], Maria Letizia Focarete[2], Valentina Sabatini[3], Manuele Colombo[3], Thomas Della Vedova[3], Carmine Lucignano3, Paolo Canonico[3], Giorgia Sciutto[1], Rocco Mazzeo[1] and Silvia Prati[1]

[1]Department of Chemistry "Giacomo Ciamician", Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), University of Bologna, via Guaccimanni 42, 48121, Ravenna, Italy; burcu.keser2@unibo.it, giorgia.sciutto@unibo.it, rocco.mazzeo@unibo.it, s.prati@unibo.it,
[2]Department of Chemistry "Giacomo Ciamician", University of Bologna, via Selmi 2, 40126, Bologna, Italy; francesc.ramacciott2@unibo.it, c.gualandi@unibo.it, marialetizia.focarete@unibo.it,
[3]Saati S.p.A., Via Milano, 14, 22070, Appiano Gentile, Italy; vsabatini@saati.com, mcolombo@saati.com, tdellavedova@saati.com, clucignano@saati.com, pcanonico@saati.com

Keywords: electrospinning, green solvent, cleaning of the paintings

The traditional methodology used for removing old varnish from paintings is based on applying cotton swabs soaked with a volatile organic solvent. However, this approach may result in reduced integrity of the paint layer due to leaching and swelling [1]. Moreover, substituting toxic organic solvents with greener alternatives is necessary to prevent health effects on the operators during restoration interventions [2]. This research aims to develop selective and sustainable cleaning systems using green solvents along with advanced electrospun fabrics [3]. The electrospinning process is an effective way to produce fibers in the nanometer range, with tunable properties such as surface/volume ratio, porosity, morphology and flexibility in surface functionalities [4]. In particular, this research aims to propose new electrospun materials for work of arts restoration and consolidation that can be industrially scalable, enabling new uses and expanding application areas, thus opening the door to new sources of growth for Cultural Heritage sector. The new materials were obtained by coupling a thin recycled-based PA6 electrospun membrane in the order of a hundred nanometers with a sustainable nonwoven thicker absorbent material (made with bamboo or viscose) that acts as a solvent reservoir. The combined materials have been characterized by analyses of porometry, air permeability, gravimetry, water contact angle, SEM, and tested on model painting systems. The cleaning performances have been compared with what obtained using cotton swabs, gels [5] and lab scale thick PA6,6 electrospun self standing mats [6] with the same solvents (gamma valerolactone and dimetylcarbonate).

Funding

This research has been funded by the Horizon Europe project GoGreen, "Green strategies to conserve the past and preserve the future of cultural heritage" (G.A. no. 101060768) and ESF REACT-EU funds (PON „Ricerca e Innovazione" programme).

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Nanocellulose Aerogels and Hydrogels as New Generation Materials for The Green Transition in Painting Conservation

Olivia Gómez Laserna[1], Iratxe Zarandona[1], Martina Romani[1], Francesco Caruso[2], Anna Nualart-Torroja[3], Africa Pitarch Martí[3,4], Tine Frøysaker[5], Jan Dariusz Cutajar[5], Erlantz Lizundia[6,7], Maite Maguregui[2]

[1]Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain; olivia.gomez@ehu.eus, iratxe.zarandona@ehu.eus, martina.romanir@ehu.eus

[2]Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain; francesco.caruso@ehu.eus, maite.maguregui@ehu.eus

[3]Arts and Conservation Department, Fine Arts Faculty, University of Barcelona, C/Pau Gargallo 4, 08028 Barcelona, Spain; anualart@ub.edu, africa.pitarch@ub.edu

[4]Institut d'Arqueologia de la Universitat de Barcelona, c/Montalegre 6-8, 08001 Barcelona, Spain;

[5]Conservation Studies, Institute of Archaeology, Conservation and History (IAKH), University of Oslo (UiO), Postboks 1008, Blindern, 0315 Oslo, Norway; tine.froysaker@iakh.uio.no, j.d.cutajar@iakh.uio.no

[6]Department of Graphic Design and Engineering Projects, Faculty of Engineering in Bilbao, University of the Basque Country UPV/EHU, 48013 Bilbao, Spain; erlantz.liizundia@ehu.eus

[7]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Scientific Park, 48940 Leioa, Spain;

Keywords: nanocellulose aerogels and hydrogels, green conservation, soiling, varnish, paintings

Developing advanced materials for conserving and restoring cultural heritage present a significant research challenge. These materials must demonstrate efficacy and comply with restoration standards to ensure the safety of the artwork, conservator, and the environment. Furthermore, they should align with green chemistry principles and undergo rigorous validation procedures before potential use. Cellulose, recognized for its renewability, sustainability, and eco-friendliness, emerges as a promising biopolymer due to its inherent compatibility with various substrates. Recent advancements in the field of cultural heritage have showcased its advantages at the micro- and nanoscale, serving as a protective coating and consolidant for archaeological wood [1,2], historical paper [3], or in the stabilization of damaged painting canvases [4], among other applications. However, the use of micro- and nanocellulose has not been thoroughly explored to clean canvas paintings.

This work presents new generation nanocellulose-based materials that aim to contribute to the conservation of paintings. Nanocellulose aerogels have been developed in the context of ENCLOSURE project [5] using dialdehyde cellulose (DAC) cross-linked with glycerol as green alternative to the non-environmentally sustainable glutaraldehyde. This aerogel exhibits high water uptake capacity, adaptability to irregular porous surfaces and applicability in both horizontal and vertical orientations, without leaving residues. Additionally, it can be reused after each application. Its potential application in painting conservation has been tested by loading green solvents to remove natural resin varnishes on canvas paintings.

To remove soiling on canvas paintings, cellulose nanofiber-based hydrogels crosslinked with

sustainable amine compounds have also been generated in this project. To enhance the cleaning ability of the hydrogel, various green fluids were incorporated to selectively remove the soiling without causing damage to the artwork.
After conducting physico-chemical and mechanical studies on the nanocellulose-based materials, their cleaning ability was tested on oil painting mock-ups. For the soiling removal, a synthetic mixture that simulates soiling was sprayed on both varnished (natural resin varnishes) and non-varnished mock-ups. This experiment aimed at evaluating the effectiveness of the nanofiber-based hydrogels in removing soiling on a less water-sensitive surface (varnished) and more sensitive ones (non-varnished). The non-varnished mock-ups replicated the painting technique of Munch in the oil paintings of the Aula of the University of Oslo.
The ENCLOSURE project not only aims to generate new materials but also to develop appropriate non-invasive methodologies for assessing the cleaning ability of new materials and ensuring that they do not adversely affect the paintings. In addition to microscopic observations and colorimetric analysis, other analytical approaches based on chemical imaging were developed. For the soiling removal, micro-energy dispersive X-ray fluorescence imaging and hyperspectral imaging in the NIR-SWIR range (1000-2500 nm) were employed. Furthermore, the evaluation of varnish removal was conducted under UV light, and changes were monitored through reflectance in the Vis-NIR-SWIR range (point-by- point and hyperspectral imaging).

Acknowledgements

O. Gomez-Laserna, I. Zarandona and M. Romani acknowledge their research contracts to the grant TED2021-129299A-I00. F. Caruso acknowledges his Maria Zambrano fellowship from UPV/EHU, funded by MICIU and the European Union NextGenerationEU/PRTR. A. Pitarch Martí is a Serra Húnter fellow.

Funding

This work has been supported by grant TED2021-129299A-I00, funded by MCIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR.

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Preserving Carbonate Rocks Surfaces: A Novel Organophosphonate Approach

Simone Murgia[1], M. Carla Aragoni[1], Paola Meloni[2,3], Enrico Podda[1,5], Anna Pintus[1], Gianfranco Carcangiu[4], Domingo Gimeno Torrente[6] and Massimiliano Arca[1]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, 09042 Monserrato (Cagliari), Italy.
[2]Dipartimento Ingegneria Meccanica Chimica e dei Materiali, Università degli Studidi Cagliari, 09123 (Cagliari), Italy
[3]Laboratorio di Restauro Colle di Bonaria, Università degli Studi di Cagliari, Via Ravenna snc, 09125(Cagliari), Italy
[4]CNR-ISAC, Dipartimento di Fisica, Università degli Studi di Cagliari,09042 Monserrato (Cagliari), Italy
[5]Centro Servizi di Ateneo CeSAR, Università degli Studi di Cagliari, 09042 Monserrato (Cagliari), Italy
6Universitat de Barcelona, Faculty of Earth Sciences, Dept de Mineralogia, Petrologiay Geologia Aplicada, Spain

Keywords: Consolidation, Organophoshonate, Carbonatic rocks

In recent years, there has been a growing interest in exploring novel synthetic materials for preserving carbonate stone, substrates prone to deterioration over time and exposure to the elements.[1] This degradation often results in noticeable roughening of the stone surfaces and partial loss of intricate details in historical artifacts.
The primary objective of this study is to synthesize an organophosphonate salt derivedfrom the well-established diammonium phosphate.[2] The synthesized compound undergoes a fully microanalytical and spectroscopic characterization before being subjected to immersion testing on various substrates, including calcium carbonate powder, white Carrara marble, and naturally weathered white marble of historical interest.
Subsequently, the treated stone samples were analyzed using techniques such as SEM microscopy, mercury intrusion porosimetry, X-ray diffraction, and NIR spectroscopy. Furthermore, post-treatment changes in hydric, structural, colorimetric, and rugosimetric properties were assessed. These investigations show that the synthesized compound interacts with the stone surface to form a protective layer, effectively preserving the mechanical and chromatic properties of the treated samples.
Significantly, the novel organophosphonate salt effectively addressesa key challengeby mitigating the metastability issues associated with the use of the traditional diammonium andammonium hydrogen phosphate for consolidation purposes. Through the use of this derivative, a high degree of selectivity in the consolidation process is achieved, resulting in the formation of a single, remarkably stable consolidating phase that is insoluble in water.

Funding

This presentation was produced while attending the PhD programme in Chemical Sciences and Technology at the University of Cagliari, Cycle XXXVIII, with the support

of a scholarship financed by the Ministerial Decree no. 351 of 9th April 2022, based on the NRRP - funded by the European Union-Next Generation EU-Mission 4 "Education and Research", Investment 4.1 "Extension of the number of research doctorates and innovative doctorates for public administration and cultural heritage.

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Assessment of Tarnished Silver Test Systems Prepared with Bio-based Green Aging Methods

Qing Wu[1], Han Zhou[2], Kirill Gubanov[3], Arianna Passaretti[1,4], Jorge Gonzalez Frutos[1,5], Christian Degrigny[1], Loïc Bertrand[6], Maartje Stols-Witlox[2], Laura Brambilla[1], Edith Joseph[1]

[1]Haute Ecole Arc Conservation-Restauration, HES-SO University of Applied Sciences and Arts Western Switzerland, Espace de l'Europe 11, 2000 Neuchâtel, Switzerland; qing.wu@he-arc.ch, arianna.passaretti@he-arc.ch, laura.brambilla@he-arc.ch; christian.degrigny@he-arc.ch, edith.joseph@he-arc.ch

[2]University of Amsterdam, Turfdraagsterpad 15-17, P.O. Box 94551, 10op GN Amsterdam, The Netherlands; h.zhou5@uva.nl, M.J.N.Stols-Witlox@uva.nl

[3]Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany; kirill.gubanov@fau.de

[4]University of Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland;

[5]Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland; jorge.gonzalez-frutos@empa.ch

[6]Université Paris-Saclay, ENS Paris- Saclay, 4, avenue des Sciences, 91190 Gif-sur-Yvette, France; loic.bertrand@ens-paris-saclay.fr

Keywords: silver, green, aging, Raman, KPFM

Several teams have researched ways to produce systems that mimic the surface of naturally aged historical silver objects and allow to develop appropriate conservation treatments [1,2]. We developed protocols to produce coupons with a homogeneous tarnish layer similar to that found on historical silver objects and with a high degree of reproducibility. Two green ageing methods were tested using bio-based materials: (i) boiled egg white [3] and (ii) albumin solution [4,5]. Sterling silver and pure silver coupons with different surface finishings were employed. An even polishing was obtained by using a 3D printed specimen holder that allows an uniform pressure to be applied on the soft metal. The ageing procedure was designed to be carried out in a non-laboratory workspace with easily accessible apparatus (e.g. casserole dish). Different concentrations and exposure times were evaluated.

Characterisation of the aged coupons was carried out using micro-Raman spectroscopy, supported by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) and linear scanning voltammetry measurements. In addition to the typical corrosion products found on tarnished silver objects, e.g., acanthite (Ag_2S), chalcocite (Cu_2S) and covellite (CuS), Ag-Cu-S intermediates were also identified on aged sterling silver coupons. The boiled egg white method led to similar corrosion compounds as those identified on naturally tarnished silver objects. The albumin solution method resulted in a more homogeneous surface appearance. Colour measurements showed that the artificially created tarnishing was homogeneous and highly reproducible. During optical microscopy observations, some of the coupons aged with the albumin solution method showed peculiar surface microstructures consisting of various sized islands or rings. EDS analysis showed the same elemental

composition in and out of the islands. Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) mapping suggested a dependence between the islands' thickness and surface potential, but not with the nature of the corrosion products present on the surface. As regards rings, KPFM measurements demonstrated that their formation is linked to an accumulation of corrosion products.
This study is carried out in the framework of the European project GoGreen, which aims to develop innovative and environmentally friendly methods, inspired by nature and historical recipes, for remedial conservation [6].

Acknowledgements

We thank the Pollux beamline at Swiss Light Source for the 3D printing of the coupon holders for polishing. We thank Dr. Benjamin Watts from the Paul Scherrer Institute for writing the script for the automatic production of weighted integration maps based on PCA analysis of Raman spectra. Part of the SEM-EDS measurements was implemented at the Swiss Center for Electronics and Microtechnology (CSEM).

Funding

This study is funded by Horizon Europe (GoGreen: Green strategies to conserve the past and preserve the future of cultural heritage (Project No.: 101060768).

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Study of Sustainable Corrosion Inhibitors in New Acrylic Coatings for Outdoor Bronze Artworks

Giulia Pellis[1] , Barbara Giussani[2], Paola Letardi[3], Paola Rizzi[1], Barbara Salvadori[4], Antonio Sansonetti[5], Fabrizio Caldera[1], Francesco Trotta[1] and Dominique Scalarone[1]

[1]Department of Chemistry, University of Torino, Via Pietro Giuria 7, Torino, Italy; giulia.pellis@unito.it; paola.rizzi@unito.it; dominique.scalarone@unito.it; fabrizio.caldera@unito.it; francesco.trotta@unito.it

[2]Science and High Technology Department, Università degli Studi dell'Insubria, Via Valleggio 9, Como, Italy; barbara.giussani@uninsubria.it

[3]Institute of Anthropic Impacts and Sustainability in the Marine Environment, CNR, Via De Marini 6, Genova, Italy; paola.letardi@ias.cnr.it

[4]Institute of Heritage Science, CNR, Via Madonna del Piano 10, Sesto Fiorentino, Italy; barbara.salvadori@cnr.it

[5]Institute of Heritage Science, CNR, Via Roberto Cozzi 53, Milan, Italy; antonio.sansonetti@cnr.it

Keywords: corrosion inhibitors, bronze artworks, sustainable coatings, ageing studies

The most commonly used conservation method for outdoor bronzes is the application of transparent coatings. The main aim is to protect the artwork from weathering and reactive compounds in the atmosphere. This is defined as a passive approach to prevent degradation; it can be converted in an active one by adding corrosion inhibitors, that can slow down or prevent further corrosion.[1] The most used inhibitor in this field is benzotriazole; however, due to its suspected carcinogenicity[2], further studies are currently underway to find safer solutions. The main class of corrosion inhibitors is that of heterocyclic compounds since the presence of heteroatoms such as nitrogen, sulphur and phosphorus in the organic molecule improves the corrosion inhibition action. [3] Despite this, a critical limitation of this class of substances is their photosensivity which can be overcome including light stabilizers in the coating formulation. [4] Another problem is the loss of the inhibitors, which leave the coating over time and are released into the environment.

This contribution is part of a project that aims to develop a more sustainable coating using an acrylic resin-namely Paraloid® B44- with a corrosion inhibitor, having a low-toxicity profile, and a light stabilizer. Two types of corrosion inhibitors [5-mercapto-1-pheniltetrazole (MPT) and 5-ethyl-1,3,4-thiadiazol-2-amine (AEDTA)] and two types of light stabilizers (Tinuvin® 312 and Tinuvin® 5050) were tested comparing their performances. Several coatings were formulated with different concentrations of the corrosion inhibitors. They were applied on inert supports and on bronze polished mock ups, and they were light aged to simulate the outdoor exposure. Since various properties had to be considered, the coatings were monitored using a multi-analytical approach in order to optimize the coating performances.[5] Particular attention will be given here to the study of the permanence and stability of corrosion inhibitors over time; the permanence of both additives in the coating was monitored by FTIR and the stability was assessed by double-shot Pyrolysis-Gas Chromatography/ Mass Spectrometry (Py-GC/MS). AEDTA was found to perform better than MPT: it

does not change colour over time, it interacts preferentially with the bronze surface and it is photochemically stable. However, it is partially lost over time. To overcome this issue, an inclusion complex of methyl-β-cyclodextrin (MeβCD) and AEDTA was prepared and then incorporated in Paraloid® B44 coatings in different concentrations. The preliminary results obtained so far demonstrate a longer permanence within the coating of the MeβCD-AEDTA complex compared to AEDTA alone.

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Tărtăria - A Everlasting Story

Mihai Straticiuc[1] , Malvinka Urák[2], Melania Istrati[1], Dragoș Mirea[1] and Regina Anna Uhl[3]

[1]Horia Hulubei National Institute for Physics and Nuclear Engineering, Magurele, Romania; mstrat@nipne.ro
[2]The National Museum of History of Transylvania, Cluj, Romania; themalvinka@gmail.com
[3]Deutsches Archäologisches Institut – Eurasien Abteilung, Berlin, Germany; regina.uhl@dainst.de

Keywords: archaeological discovery; Tartaria Tablets; ion beam analysis, PIXE

Among the most captivating archaeological discoveries, some have emerged from the mist of accidental unearthing, adding a mythical aura to their narrative. Yet, this very mist can cast doubt on their credibility and authenticity. One such enigmatic find is the trio of clay tablets from Tărtăria (Figure 1), discovered in a so-called ritual pit during a test excavation in 1961 in the Lower Mureș Valley, Transylvania, Romania. These tablets, presenting a series of incised symbols that might resemble pictograms, were considered the cornerstone of many scientific debates concerning the European Neolithic and were initially interpreted as evidence of an early writing system, surpassing in time even the cuneiform writing of the Near East or the Egyptian hieroglyphs.
These artefacts have sparked a deluge of scholarly discourse, measured in linear meters [1-7], dividing renowned scholars and the general public. Following the publication of the findings [8, 9], a period of intense academic polemics ensued. Today, the debate may have subsided, but it has left behind a palpable caution, a distress that, in Madame Bovary's words, could be expressed as the fear of having the gliding sticking to our fingers if we touch our idols. However, the same cannot be said for the work of amateurs and believers, who continue to produce questionable publications and documentaries, even claiming to have decoded the incised symbols on the clay tablets.
With the alarming number of pseudo-scientific publications and the more widespread use of AI technology, often used to create content relying on unverifiable data, the risk of losing control of the matter is imminent. It is our duty, as scholars, to employ modern scientific methods to get closer to a series of events that happened in a past not that far behind us yet covered by darkness.
Thanks to the technological advancements of recent decades and the application of interdisciplinary methods in archaeological analysis, long-time untouchable tangible heritage is being brought closer to us. Non-invasive methods have revolutionized our exploration, allowing us to delve beyond the visible and pushing the boundaries of our empirical knowledge. This paper, the first part of a series, aims to systematically approach a topic that has long been emotionally rather than scientifically explored.
This experiment's scope was to understand the clay tablets' physical and chemical properties using atomic and nuclear analytical techniques like X-ray Fluorescence (XRF) and Particle Induced X-ray Emission (PIXE). As these artefacts are unique, invasive procedures are not suitable. The main objective is to determine if the three

discoveries show similar microscopic and technological characteristics, indicating that they belong to the same batch.
Our findings revealed twelve trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr and Zr) that are present in various concentration for each tablet, offering a fair perspective of the fabric and helped us to decipher a first pattern for the raw material source. Matrix components (Na, Mg, Al, Si, K and Ca) oxides attributed to common feldspars were also detected by XRF and PIXE, together with other five major chemical elements (P, S, Cl, Ti and Fe).

Acknowledgements

This work was supported under the "Nucleu" Programme PN 23210201. Experiments were carried out at 3 MV Tandetron™ accelerator from "Horia Hulubei" National Institute for Physics and Nuclear Engineering (IFIN-HH) and were supported by the Romanian Government Programme through the National Programme for Infrastructure of National Interest (IOSIN).

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GREENART Project: Environmentally Friendly and Low Impact Materials for Cultural Heritage Conservation

Piero Baglioni , Giovanna Poggi, David Chelazzi and all participants to Greenart EU project (https://cordis.europa.eu/project/id/101060941/en)

CSGI - University of Florence, Department of Chemistry via della Lastruccia 3, 50019 Florence, Italy; baglioni@csgi.unifi.it

Keywords: Nano-, meso-materials, green materials, cleaning, consolidation, art restoration

European Cultural Heritage (CH) is a crucial resource that must be maintained, preserved and made accessible, to counteract degradation enhanced by unfavorable environmental conditions and climate changes. Some of the conservation methodologies nowadays available lack sustainability and cost-effectiveness, and are typically based on energy-consuming processes or non-environmentally friendly materials. This contribution will report on the main results so-far achieved in the EU-funded project GREen ENdeavor in Art ResToration (GREENART), coordinated by the Center for Colloid and Surface Science of the University of Florence (CSGI). Coping with the imperatives of EU Green Deal, the project proposes new solutions based on green and sustainable materials and methods, to preserve, conserve and restore CH. In particular, several innovative materials have been developed and tested: 1) Protective coatings based on green materials from waste and plant proteins, with self-healing and reversibility character, possibly functionalized with organic/inorganic nanoparticles to impart VOC capture, anti-corrosion and barrier behaviors. 2) Foams and packaging materials made by biodegradable/compostable polymers from renewable sources (polyurethanes and natural fibers) to control temperature and relative humidity. 3) Consolidants based on natural polymers from renewable sources, to mechanically strengthen weak artifacts. 4) Gels and cleaning fluids inspired by the most advanced systems currently available to conservators, which will be improved according to green metrics and circular economy requirements. 5) Green tech solutions for monitoring CH assets non-invasively against pollutants and environmental oscillations. Life Cycle Assessment and modeling favor the “safe-by-design” creation of affordable solutions safe to craftspeople, operators and the environment, and minimize energy-consumption in monitoring museum environments. Such holistic approach is granted in GREENART by a multidisciplinary partnership that gathers hard and soft sciences and engineering, including academic centers, innovative industries and SMEs, conservation institutions and professionals, museums whose collections hold absolute masterpieces in need of conservation, public entities and policy makers. Innovative materials and products have been assessed at the lab scale on representative mock-ups of works of art (remedial conservation), or in simulated museum/archive environments (preventive conservation). The project intends to transfer the most promising systems to field assessment on actual artefacts and museums/archives, in cooperation with conservator partners. The best products are also fed into a

GREENART open repository and an App to illustrate the new solutions and involve citizens in good preservation practices. Constant feedback from conservators (internal or external to the partnership) can stimulate iterative refinement of the products, triggering a positive loop in this methodological approach. Covering these topics, this talk provides an overview of some of the most advanced green materials for art conservation that can be useful to end-users in this field.

Acknowledgements

CSGI and the European Union (GREENART project, Horizon Europe research and innovation program under grant agreement no. 101060941) are gratefully acknowledged for financial support. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Executive Agency (REA). Neither the European Union nor the granting authority can be held responsible for them.

Erratic Cultural Heritage as a Monitoring Tool for Environmental and Anthropic Impact in the City of Venice

Margherita Zucchelli[1], Aurora Cairoli[1,2], Elisabetta Zendri[1]

[1]Department of Environmental Sciences, Informatics, Statistics, Università Ca' Foscari di Venezia, Via Torino 155, 30170, Mestre, Venice, Italy, margherita.zucchelli@unive.it, elizen@unive.it
[2]Department of Science of Antiquities, La Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy, aurora.cairoli@uniroma1.it

Keywords: Venice, Cultural heritage, Environmental impact, Physical transformation, Degradation Map

Air quality and climate have relevant impacts on the exposed cultural heritage and architectural surfaces, increasing degradation phenomena such as erosion, detachments, and biological growth. In Venice the climatic effects are further enhanced by the presence of lagoon water since the soluble salts therein are responsible for significant further degradation processes in materials [1], [2], [3], [4], [5]. The huge tourism increase is bringing, in its turn, a transformation of the city, in terms of values and authenticity, but also in terms of enhanced material degradation. Warnings regarding the threats of climate change and mass tourism to cultural heritage in Venice came recently also from the World Heritage Centre of UNESCO, which stated that "The effects of the continuing deterioration due to human intervention, including continuing development, the impacts of climate change and mass tourism threaten to cause irreversible changes to the outstanding universal value of the property" [6], [7], [8].

Monitoring is one of the most important instruments to preserve cultural heritage, avoid expensive intervention for its maintenance and restoration and develop cost-effective strategies However, monitoring generally focuses on single case study with their own specificity, the results of which are often difficult to be applied to other assets. Even prediction models do not always consider all the variables involved in the degradation processes observed on the manufacts [3], [4], [9], [10], [11]

This project aims to use "minor" cultural heritage spread throughout the historic centre of Venice to evaluate the decay evolution on an urban scale considering the intrinsic characteristics of the materials and the surrounding environment.

In the context of PNRR CREST (Cultural Resources for Sustainable Tourism) project and thank to the collaboration with the volunteers of the Nucleo Tutela Beni Culturali of Venice Civil Protection, we accessed a repository of more than 900 assets (sculptures, decorative and architectural elements, religious shrines, etc.) spread only over the Cannaregio Sestiere. These artworks, even if not belonging to the most recognized ones in the city, are important elements of Venice's heritage, since they build a part of every-day life and identity of the citizens. Moreover, beside their socio-cultural meaning, they represent an invaluable asset which tells the city's transformations over time related to environmental factors and voluntary or involuntary anthropogenic activities.

Many photographs of these so called "erratic heritage", have been collected. The material gathered comprises recent and archive photographs which belong to the

repository of the Civil Protection, to several private and public archives or taken from books.
For several heritage surveyed it was possible to retrieve archive photographs older than thirty years and visually evaluate the physical transformation upon time, since they were covering a prolonged time span.
To assess the presence of any recurrent transformation patterns and the relationship between the observed modification and the surrounding environment, several parameters were considered for each heritage: the material, the position with respect to the canals (nearby or far away from it) and to the ground level and the specific exposure of the heritage (exposed to rains or sheltered).
First results show similar decay evolution for exposed (not sheltered) heritage, regardless of whether they are facing the canal or located on intern calli or courts.
An overall decrease of gypsum black crusts is observed for several of the considered heritage, reflecting the reduced presence of SO_2 as degradation factor with respect to the past. Black crusts decrease and limited impact of SO_2 over stone material is confirmed by in situ Raman spectroscopy analyses, while run-off impact caused a loss of legibility of the single artifact and it is here evaluated according to a scale of value from 1 to 3 (1=still readable, 2=partial loss, 3=unreadable) [2], [12], [13], [14].
In addition, religious shrines represent an interesting example of how the presence of people influences the conservation state of these heritage, they are usually at head height, and they are among the most deteriorated ones due to the rubbing action of the faithful.
In conclusion, the aim of this work is the development of a methodology to read at the environmental impact observed on the surface of these heritage through non-invasive monitoring systems (validated with diagnostic instruments) applicable on a large scale at urban level.
Data acquired from this study will allow the construction of a detailed map of the most affected areas of the city. The heritage located in these areas should be then monitored with more attention above all with respect to the most important ones sited in their surrounding (i.e. churches, buildings, statues).

Acknowledgements

Ricerca finanziata grazie al Piano Nazionale di Ripresa e Resilienza, Missione 4 “Istruzione e ricerca” – Componente 2 “Dalla ricerca all’impresa” finanziato dall’Unione europea – NextGenerationEU) - progetto “CHANGES - Cultural Heritage Active Innovation for Sustainable Society” –PE_00000020 - CUP: H53C22000850006

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A Comparison Among TGA, SEM-EDX and Raman Spectroscopy to Assess PVC Plasticizer Loss in the Presence of Various Wrapping Materials

Emilande Apchain, Adeline Royaux, Odile Fichet and Sophie Cantin

CY Cergy Paris Université, LPPI, F-95000 Cergy, France; cantin@cyu.fr

Keywords: PVC, storage, wrapping material, plasticizer migration

Silk paper, LDPE or PET are commonly used as wrapping materials for the transport or storage of PVC contemporary art heritage collections without knowing exactly their effects. That is why the loss of plasticizer in PVC, when in contact with these wrapping materials, was evaluated over a period of 17 months of artificial aging using temperature cycles of 2 days at 80 °C then 1 day at 25 °C under a relative humidity of 65 % [1]. This study was made on model PVC containing 31.6 wt% of di-isononylphthalte (DINP) and 3.2 wt% of epoxidized soybean oil (ESO). We combined three different techniques, ThermoGravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) images coupled to Energy Dispersive X-ray (EDX) analyses and Raman spectroscopy. SEM was chosen to reveal the evolution of the surface morphology. TGA and EDX analysis allow the evaluation of the plasticizer loss, while Raman Spectroscopy is used to deepen the understanding of the two plasticizers, DINP and ESO, migration. While TGA probes both the volume and the surface of the PVC samples, Raman spectroscopy and EDX provide information essentially from the surface, i.e. a few µm-thick layer. The interpretations of these various analyses initially underscored both the strengths and limits of each technique. TGA analysis provided the evaluation of the overall plasticizer loss without differentiation of ESO and DINP, showing some limits of the technique in the widespread case of a plasticizer mixture. In addition, the dehydrochlorination observed during the analysis was found to be significant, thereby affecting the quantification of plasticizers. EDX analyses allow evaluation of the plasticizer loss during aging only if a particular atom can be used as plasticizer marker like the oxygen atom in this study. These analyses coupled with SEM images confirmed the presence of plasticizers on the PVC surface and revealed a kinetics of plasticizer migration controlled by evaporation rather than by diffusion. However, quantification of sample plasticizer loss after surface cleaning was difficult due to the high sensitivity of the method and detection of oxygen that may come from external contamination. Finally, Raman analyses performed on PVC samples allowed the quantification of DINP and ESO precisely and separately. The relative speed mass loss was observed to be similar for DINP and ESO plasticizers but significant differences were revealed depending on the wrapping material in contact with PVC during aging. Indeed, silk paper and LDPE slowed down the plasticizer loss while PET accelerated it. However, aging with silk paper would be recommended to be used as wrapping material for plasticized PVC objects since in contrast to LDPE, it does not stick to the PVC surface.

Acknowledgements

This work was supported by the Paris Seine Graduate School Humanities, Creation, Heritage, Investissements d'Avenir ANR-17- EURE-0021 –Foundation for Cultural Heritage Science.

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Revolutionizing Art Authentication with Artificial Intelligence

Barbara Łydżba-Kopczyńska[1] and Janusz Szwabiński[2]

[1]University of Wroclaw, Faculty of Chemistry, Cultural Heritage Research Laboratory, F. Joliot-Curie 14, 50-383 Wroclaw, Poland
[2]Wrocław University of Science and Technology, Hugo Steinhaus Center, Faculty of Pure and Applied Mathematics, Wyb. Wyspiańskiego 27, 50-370 Wroclaw, Poland

Authenticating a painting can be extremely challenging. Typically, an art expert makes decision regarding a piece of art after meticulously examining various forms of evidence. The study of the painting style, scrutinizing correspondence from the artist's lifetime and tracing the painting's ownership history for may already provide some clues. Material analyses involving the pigments and materials used, along with the method of their preparation, painting techniques as well as the study of the creative process through examination of underlayers using X-ray and infrared imaging, are often conducted. Additionally, the visual aspects encompassing the appearance and style of the work are compared with those of the artist's other creations. However, even with these combined analyses, determining authenticity may remain inconclusive, prompting art experts to seek additional viable sources of evidence.

In the recent years, machine learning techniques and computer vision methods have become increasingly important tools for analysis in many domains, including fine art authentication. In one of our recent papers, we tested already whether the decision process involved in authenticity evaluations may be supported by machine learning algorithms [1]. The results were promising, however the applicability of the method used in that study was limited by the availability of data from already finished authentication and attribution procedures(Fig.1).

In the presented study a slightly different approach to fine art authentication with

Fig 1 Machine learning algorithms use attribution markers for authentication.

machine learning tools and computer vision techniques will be presented. High resolution images of paintings of a given author (both authentic and potentially forged) will be analysed first to determine a series of features (e.g. texture, colour, brushwork). Then, a clustering algorithm will be used to group the images with similar features together. The aim of this method is not to replace authenticity studies or to provide certainty that an image that stands out from the others is forged. However, it can be a useful diagnostic tool to support the authentication process by indicating which images require further examination. The method will be tested on a collection of baroque paintings by Michael Willman, known as the Silesian Rembrandt and 19th-century artworks by Artur Grottger. The studies are supported by a database containing information on the materials and techniques used by these painters. This information has been gathered through authentication studies carried out by Cultural Heritage Research Laboratory over the last decade[2,3,4]

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Lanolin, a Possible Archaeological Biomarker of Ancient Sheep Shearing

Claudia Adsuar Fuster[1], Francesco Caruso[1], Enmanuel Cruz Muñoz[2], Martina Romani[3], Olivia Gómez-Laserna[3], José Manuel Amigo[3,4], Leire Kortazar[3], Ramón J. Barrio[1], Josep Maria Vergès[5,6], Vincenza Forgia[7], Maite Maguregui[1], Asier Vallejo[1]

[1]Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain; cadsuar002@ikasle.ehu.eus, francesco.caruso@ehu.eus, r.barrio@ehu.eus, maite.maguregui@ehu.eus, asier.vallejo@ehu.eus
[2]Department of Earth and Environmental Sciences, University of Milano-Bicocca, Piazza dell'Ateneo Nuovo 1, 20126 Milan, Italy; e.cruzmunoz@campus.unimib.it
[3]Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain; martina.romanir@ehu.eus, olivia.gomez@ehu.eus, josemanuel.amigo@ehu.eus, leire.kortazar@ehu.eus
[4]IKERBASQUE, Basque Society for the Promotion of Science, Plaza Euskadi 5, Bilbao 48009, Spain
[5]Institut Català de Paleoecologia Humana i Evolució Social (IPHES-CERCA), Zona Educacional 4, Campus Sescelades (Edifici W3), 43007 Tarragona, Spain
[6]Departament d'Història i Història de l'Art, Universitat Rovira i Virgili, Avinguda de Catalunya 35, 43002 Tarragona, Spain; jmverges@iphes.cat
[7]Dipartimento Culture e Società, Università degli Studi di Palermo, Viale delle Scienze Edificio 15, 90128 Palermo, Italy; vincenza.forgia@unipa.it

Keywords: Atapuerca, Vallone Inferno, Flint, Obsidian, Cutting tools, Wool

The use of flint and obsidian blades as cutting tools was common until the Copper Age (ca. 5000 BC). The use of these cutting tools was varied but most likely, they were also used as shearing tools. Sheep were sheared to keep them cool in the warmer months and to reduce the presence of parasites. This activity likely began with the domestication of the animals in the Neolithic age. During shearing, a natural wax called lanolin accumulates in the blades. This wax may be persistent and could be used as an ancient shearing biomarker.

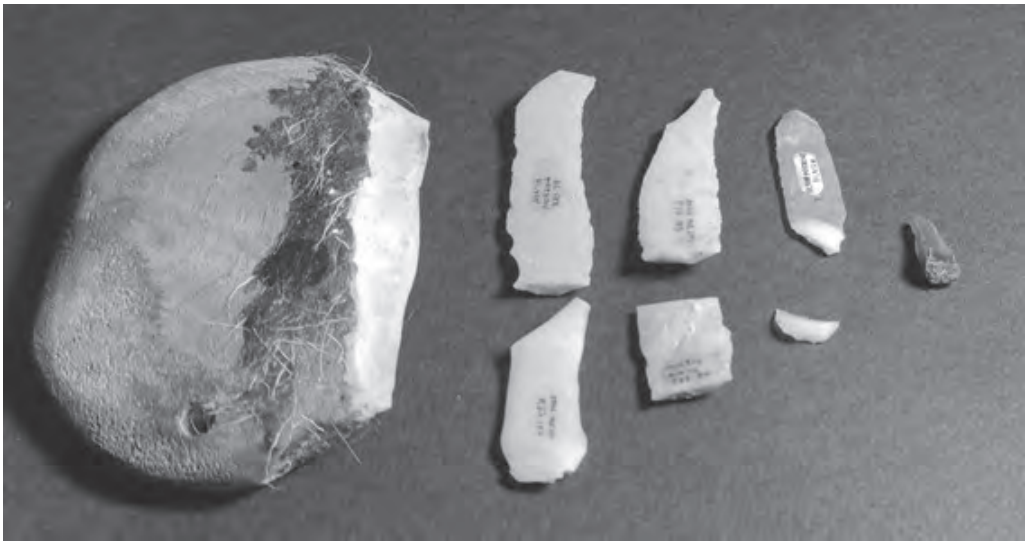
Biomarkers are persistent organic compounds capable of determining their origin and, therefore, are useful to describe the development of Pre/History. DNA, proteins, or lipid compounds are the most used biomarkers. However, research for new biomarkers continues, since finding DNA and proteins is not always possible and many lipid compounds do not have a single source.

In this case, lanolin's main source is wool. Therefore, its presence (and that of possible degradation products) may be used as an ancient shearing biomarker.

Consequently, the main objective of this work is to characterize lanolin and its degradation products with several analytical techniques to obtain a clear spectrum of this wax and use it as shearing biomarkers of flint and obsidian blades from El Mirador cave (Sierra de Atapuerca, Burgos, Spain) and Vallone Inferno rock-shelter (Scillato, Sicily, Italy) respectively.

To do this, we have studied lanolin with an experimental archaeology approach. We have applied lanolin on contemporary clean flint, silex and obsidian fragments.

The analytical approach has been non-destructive and micro-destructive. We have employed micro-FTIR (Fourier Transformed Infrared Spectroscopy) in reflection, NIR-HSI (Near Infrared - Hyperspectral Imaging combined with chemometrics and GC-MS (Gas Chromatography coupled with Mass Spectrometry). We have characterized the mock-ups with fresh application and after the aging in a climatic chamber. In this way, the degradation compounds of lanolin on these fragments have also been identified. The biomarkers found are being sought in archaeological samples and, therefore, could give valuable indications about the ancient shearing technology.



Acknowledgements

F. Caruso acknowledges his Maria Zambrano fellowship from UPV/EHU, funded by MCIU and the European Union NextGenerationEU/PRTR. O. Gomez-Laserna acknowledges her postdoctoral research contract to the grant TED2021-129299A-I00, funded by MCIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR. The authors thank the technical and human support provided by the Alava Central Service of Analysis of SGIker (UPV/EHU, MINECO, GV/EJ, ERDF, and ESF). This work was funded by the Spanish Ministry of Science, Innovation and University (PID2021-122355NB-C32 project), by the Basque Government, Research Groups of the Basque University System (Project No. IT1492-22) and by AGUR-DGPC Dept. Cultura. Government of Catalonia (CLT009-22-00024).

Characterisation of the Tin Relief Decorations on the Van Eyck's Ghent Altarpiece as Part of the Third Phase of Restoration: a Study by Ma-Xrf, Sem-Edx, Sr-Xrd, and Sr-Xrf.

Sophie Kirkpatrick[1,2], Jana Sanyova[1], Koen Janssens[2], Hélène Dubois[1], Ingrid Geelen[1], and Geert van der Snickt[2]

[1]Royal Institute of Cultural Heritage (KIK-IRPA), 1 Parc du Cinquantenaire, 1000 Bruxelles, Belgium
[2]University of Antwerp (UA), 9 Blindestraat, 2000 Antwerpen, Belgium
sophie.kirkpatrick@kikirpa.be

Keywords: Applied brocades, tin, Ghent Altarpiece.

The Ghent Altarpiece, a large 15th c. polyptych painted by the brothers Jan and Hubert Van Eyck, is now in its third phase of restoration. This comprises the treatment of the large central panels of the upper register, showing the enthroned figures of the Deity, the Madonna and John the Baptist. Richly decorated cloths of honour are draped behind each of these almost life-sized figures . They consist of "applied brocades", a gilded tin-relief technique imitating luxurious silk and gold thread fabrics This technique consisted in pressing tin foil into a mould in order to give them a relief. A filler was applied on the tin before these three-dimensional surfaces were attached to the painting, gilded, and painted..

The applied brocade areas suffered serious damage, partly due to decomposition of the tin layers and have been partially repainted. By employing Macroscopic X-Ray Fluorescence scanning (MA-XRF) on the panels as a whole and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX), Synchrotron X-Ray Diffraction (SR-XRD), and Synchrotron Radiation Induced X-Ray Fluorescence (SR-XRF) on a limited number of paint samples, this study aims to provide conservation restoration scientists with important, objective information on the current state of conservation of these zones.

Used together, these analytical methods allow to collect valuable information regarding the characterisation of the materials and their associated degradation products. A first assessment of the complexity of the local stratigraphy and the state of conservation of the applied brocades is made and the first hypothesis regarding their degradation processes are raised.

Acknowledgements

The authors acknowledge the team of conservators restorers of the Ghent Altarpiece, Griet Steyaert, Marie Postec, Natalie Laquière, Laure Mortiaux, Kathleen Froyen, Cécile de Boulard and Françoise Rosier for their contribution to this research, their support and advices. They also warmly thank Cécile Glaude and Martina Stillhammerova from the laboratory of KIKIRPA, as well as Ermanno Avranovich Clerici from the University of Antwerp, for their collaboration in the characterisation of the Ghent samples with FTIR, Raman, GC-MS, SR-XRF, and SR-XRD.

Funding

This PhD research is supported by the Gieskes-Strijbis fund and the Research Foundation Flanders (FWO) through its program on PhD Fellowships in Fundamental Research (application number 1181221N and 1181223N). In addition, this research was also part of the activities of the Chair on Advanced Imaging Techniques for the Arts, established by the Baillet Latour fund.

Toratom Device in Conservation Services – Case Studies of a Recent X-Ray Investigation Into Baroque Oil

Luboš Machačko[1] and Michal Vopálenský[2]

[1]University of Pardubice, Faculty of Restoration, Jiráskova 3, 570 01 Litomyšl, Czech Republic; lubos.machacko@upce.cz
[2]Czech Academy of Sciences, Institute of the Theoretical and Applied Mechanics, Centre Telč, Batelovská 486, 588 56 Telč, Czech Republic; vopalensky@itam.cas.cz

Keywords: X-ray transmission radiography, pixel detector, baroque oil painting

The Twinned Orthogonal Adjustable Tomograph (TORATOM) device in Centre Telč, Institute of Theoretical and Applied Mechanics, Czech Academy of Sciences,[1] helps conservators gain an in-depth understanding of the structure and the manner of execution of artworks to be restored. TORATOM is an in-house made experimental device with two orthogonal optical axes and 16 computer-controlled manipulators, which allow a wide range of choice in setting the geometry measurements. The device is equipped with a reflection type XWT-240-SE X-ray tube, achieving an acceleration voltage of 240 kV at the target power of 250 W, and a transmission type XWT-160-TCHR tube with a nanofocus feature (both tubes supplied by XrayWorX, Germany).
The maximum source-to-detector distance is 1300 mm, with the minimum source-to-object distance limited only by the dimensions of the object itself. The projection magnification can thus be adjusted in a wide range from approx. 1.2× to 200×. Since the position of the tube as well as the detector can be controlled both in horizontal and vertical axes, the device can be used for high-resolution radiographical scanning based on the exposure of a grid of adjacent tiles, which are then stitched together. In this way, flat objects, such as paintings, up to the dimensions of approx. 1000 × 1000 mm^2 can be scanned with an arbitrary pixel size (down to approx. 5 m/px). The reflection type X-ray tube XWT-240-CT (XrayWorX, Germany) with the acceleration voltage of 100 kV and target power of 50 W is usually employed. The large-area, flat panel XRD 1611 CP (Varex Imaging, USA) with the GOS scintillator is used as the detector. The active area of the detector is 409.6 × 409.6 mm, the pixel pitch is 0.1 mm.
Several Baroque oil paintings by renowned masters active in Moravia, Jan Kryštof Handke (1694–1774) and Gabriel Müller (1688-1764), were examined by this device [2] to provide a greater insight into the state of preservation of the artworks, past treatments, and the painting technique. Thanks to the results, the authorship and dating of two paintings by the above-mentioned authors were determined. A significant change in the composition of the painting Madonna and Child dating to 1753 was revealed by X-ray. (Fig. 1) The figure of St. Joseph originally painted on the background and later overpainted was revealed.[3] The manner of execution discovered by X-ray helped to attribute the painting to Jan Kryštof Handke, an important Moravian painter. (Fig. 2) Fragments of a signature and dating on the reverse side of the portrait of Maria Antonia of Questenberg,[4] (Fig. 3, Fig. 4) hidden by relining during the treatment in the 1980´s, were discovered and helped to confirm the authorship of Gabriel Müller, the court painter of the Questenbergs.[5]

In addition to the above, the X-ray radiography, with the help of the optical and electron (SEM-EDS) microscopy and the Fourier transform infrared spectroscopy (FTIR), enabled the identification of materials containing heavy metals, the visualization of the craquelure of the painted layers, the character of the underlying textile, and the type and the extent of secondary treatments.

Acknowledgements

The authors thank Petra Lesniaková and Radka Šefců for performing the instrumental analyses.

Fig. 1 Madonna and Child at the TORATOM X-ray unit. Photo Luboš Machačko

Fig. 2 Madonna and Child. X-ray image. Photo Michal Vopálenský.

Fig. 3 Maria Antonia of Questenberg. Visible light. Photo Luboš Machačko.

Fig. 4 Maria Antonia of Questenberg. X-ray image. Photo Michal Vopálenský.

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Cerulean Blue. Not a Simple Story

Václava Antušková[1], Jana Luxová[2], Radka Šefců[1], Žaneta Dohnalová[2], Petra Šulcová[2], Ivana Turková[3] and Marek Kotrlý[3]

[1]Chemical-technological Laboratory, National Gallery Prague, Staroměstské náměstí 12, 110 15 Prague 1, Czech Republic; vaclava.antuskova@ngprague.cz
[2]Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 95, 532 10 Pardubice 2, Czech Republic
[3]Institute of Criminalistics, Strojnická 27, 170 89 Prague 7, Czech Republic

Keywords: cerulean blue, Czech painting, pigment composition, pigment identification

Cerulean blue (Ceruleum blue, Coelin blue) is listed in Colour Index as Pigment Blue 35. The composition is usually given as $CoO \cdot SnO_2$ (cobalt tin oxide, cobalt stannate). The first pigment based on cobalt and tin was prepared by Höpfner at the end of the 18th century, but it seems that it was not widely available and was of little use. It was reinvented at the edge of the 1850s and 1860s when it was introduced to the art market [1]. In Taylor's revisited edition of Field's Chromatography from 1885, cerulean blue is described as a relatively new pigment with a good colour hue, but inferior workability compared to the more common cobalt blue (cobalt aluminate, $CoO \cdot Al_2O_3$) [2]. Standage (1887) states that the pigment may contain an admixture of calcium sulphate. Its advantages are permanency under the influences of heat, light, and atmosphere. It is more suitable for use in watercolour, fresco, and enamel than in oil where it becomes greenish in time [3]. Several methods of preparation of the pigment are presented in books by Terry (1895) and Church (1901). The procedure described by Church results in pigment containing silica as an admixture which may be replaced by calcium sulphate or lead sulphate. Both authors mention the greenish tint of the pigment and its good stability [4, 5].

Samples of cerulean blue were synthesized following the methods of preparation written by above mentioned authors. Because the procedures are not always described clearly different raw materials and reaction conditions were tested. Prepared pigments had a dark greenish hue, no clear blue colour was obtained. Their composition and structure were characterised using scanning electron microscopy coupled with energy dispersive spectroscopy, Raman spectroscopy and X-ray powder diffraction. Raman spectroscopy was chosen for characterisation because it is widely used for pigment identification in artworks. Obtained spectra may serve as a comparative material for spectral libraries.

Commercially available cerulean blue pigments with proper hue were analysed to find out any differences. Elemental analysis of pigments supplied by Kremer Pigmente and Winsor & Newton reveals a considerable amount of magnesium with a minor admixture of chromium, aluminium, and other elements. Findings were compared with results obtained on real artworks from the collection of the National Gallery Prague. Cerulean blue was used by Czech painters from the end of the 19th century and the first half of the 20th century. On Raman spectra, a characteristic band at ~ 660 cm^{-1} was observed. Extended supplemental elemental analysis showed besides cobalt and tin considerable amount of magnesium.

From the obtained data, it seems that the composition of historical cerulean blue was more complex than commonly mentioned $CoO \cdot SnO_2$. Preparation methods described in 19th century books are probably not accurate. Other artworks with cerulean blue will be subjected to more thorough research focused on the elemental composition to find out any possible admixtures. Differences among individual pigments will be noticed as they may be characteristic features specific for distinct periods. New pigments will be synthesized reflecting the results acquired on paintings and afterwards characterized. The obtained data will serve as a comparative material for further analysis. The knowledge of slight differences in pigment composition related to material characteristics of the pigment used by individual artists may facilitate the process of artwork authentication.

Acknowledgements

This work has been financially supported by the project of the Ministry of the Interior of the Czech Republic: The Development of a Strategic Cluster for Effective Instrumental Technological Methods of Forensic Authentication of Modern Artworks (VJ01010004).

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Shedding Light on the Waterproofing Technology of Historical Carriages, a Multianalytical Approach

A. Marchetti[1,2], V. Beltran[3,4], A. Krotova[1,5], H. Cosemans[1], F. Borondics[6], G. Van der Snickt[1,5] and E. Van Binnebeke[2]

[1]University of Antwerp, ARCHES Group, Mutsaardstraat 31, B-2000 Antwerp, BE; Andrea.Marchetti@uantwerpen.be
[2]Royal Museums of Art and History, Cinquantenaire Park 10, 1000 Brussels, BE
[3]University of Antwerp, A-Sense Lab, Groenenborgerlaan 171, B-2010 Antwerp, BE
[4]Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, 30172 Venice, IT
[5]University of Antwerp, AXIS Group, Groenenborgerlaan 171, B-2010 Antwerp, BE
[6]Synchrotron SOLEIL, F-91192 Gif-sur-Yvette, FR

Keywords: hippomobile heritage, lacquer, waterproofing technology, analytical methods, degradation

Despite carriages and sledges occupying a central role in society for several hundred years and being present nowadays in a great number of museum collections all over the world, hippomobile heritage remains a heavily understudied field in Conservation Science. Throughout history, horse-drawn vehicles represented not only functional objects and a popular means of transport, but were also a fashion statement and a symbol of social status. As such, the materials, technology and overall expertise employed in the production of these objects, faithfully reflect technological, scientific and societal developments. Due to a lack of research, this knowledge potential remains mostly untapped.

The Belcaire (BELgian CArriage Interior REsearch) project, a collaboration between the Antwerp Cultural Heritage Science (ARCHES) group and the Royal Museum of Art and History (KMKG) of Brussels, aims at shedding light for the first time on this unique type of cultural heritage. In particular, research of historical sources and state-of-the-art analytical techniques are combined to study the unique collection of historical carriages and sledges of KMKG. This includes outstanding pieces, such as a stunning 18th century Portuguese "Coupé de gala" (Fig.1a) and the whole collection of Belgian Royal carriages.

In this work, we present the first results obtained from the multi-analytical investigation (handheld XRF and FTIR-ATR, MA-XRF, SEM-EDX, SR- FTIR and O-PTIR) of a selection of top pieces of the collection, including the "Coupé de gala" and the Belgian Royal carriages. The focus is put on the characterization of the paint and lacquer coatings used to protect the exterior of the carriages against outdoor environmental conditions. Given the key twofold function of these coatings on carriages and sleighs, i.e., protective and decorative, their degradation can have dramatic consequences on the overall condition of the objects and cause a severe loss of aesthetical, historical, scientific and educational values (Fig.1b). Thus, shedding light on the historical technology, material composition and chemistry of these complex coatings is a first key step towards enabling a correct preservation of hippomobile heritage.

Our multianalytical approach allowed to collect some first key information on the materials and techniques employed, highlighting the complex nature of the coatings. In particular, several overlapping layers of transparent oil-resin varnishes were employed to achieve the characteristic glossy effect on the lacquer finishes (Fig. 1c). Interestingly, differences in composition between the single varnish layers were observed. Moreover, many different pigmented layers and semitransparent velature were overlayed to decorate and contribute to the final chromatic appearance of the vehicles. These layers contained both inorganic (e.g. lead white, vermilion, bone black, viridian, ...) and metal-organic pigments (mostly red lakes), as well as siccatives and other additives. These results enable a first discussion on how provenance, time period, manufacturer and social status are reflected in the materials and techniques employed.
Relevant insights were collected also on the reactivity and degradation of the coatings. In particular, the distribution of metal soaps and oxalates within the layers was studied and linked to macroscopic degradation phenomena on the lacquer.
Given the severe lack of information on these topics, the results obtained in this study represent a first crucial step towards a deeper understanding and an improved conservation of hippomobile heritage, while also supplying first insights into the evolution of historical waterproofing technology.

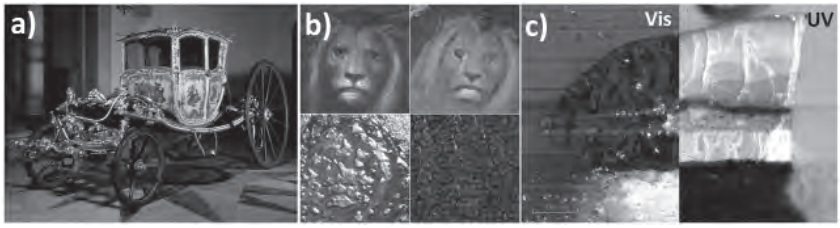

Fig.1_a) Coupé de gala, 1750-1770; b) examples of degradation phenomena of lacquer coatings on carriages; c) cross-section of a microsample of lacquer showing a complex layered structure (OM, polarized visible light and UV light).

Acknowledgements

The authors acknowledge SOLEIL Synchrotron for provision of synchrotron radiation facilities (Proposal No. 20231812) and Ms. Nina Deleu for the support with MA-XRF analysis.

Funding

This project has received funding from the The Belgian Science Policy Office (BELSPO) through the FED-tWIN program (Belcaire).

A Multidisciplinary Approach Combining Sensory and TD-GC-MS-O Analysis to Characterise the Smell of Ancient Egyptian Mummified Bodies

Emma Paolin[1], Cecilia Bembibre[2], Fabiana Di Gianvincenzo[1], Julio Cesar Torres-Elguera[3], Randa Deraz[1], Ida Kraševec[1], Ahmed Abdellah[4], Asmaa Ahmed[4], Irena Kralj Cigić[1], Abdelrazek Elnaggar[1,5], Ali Abdelhalim[4,5], Tomasz Sawoszczuk[3], Matija Strlič[1]

[1]Heritage Laboratory Ljubljana, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, Ljubljana, Slovenia; Emma.paolin@fkkt.uni-lj.si, fabiana.digianvincenzo@fkkt.uni-lj.si, randa.deraz@fkkt.uni-lj.si, ida.krasevec@fkkt.uni-lj.si, irena.kralj-cigic@fkkt.uni-lj.si, abdelrazek.elnaggar@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si
[2]Institute for Sustainable Heritage, University College London, London, UK; cecilia.bembibre@ucl.ac.uk
[3]Department of Microbiology, Institute of Quality Sciences and Product Management, Cracow University of Economics; email: torresj@uek.krakow.pl, sawoszct@uek.krakow.pl
[4]The Egyptian Museum of Cairo, Cairo, Egypt; asmaahmed82@hotmail.com, ali.abdelhalim@arch.asu.edu.eg
[5]Faculty of Archaeology, Ain Shams University, Cairo, Egypt

Keywords: Mummified bodies, olfactory analysis, GC-MS-O

Ancient Egyptian mummification is a mortuary practice with spiritual significance that aims to preserve the body for the successful transition of the soul into the afterlife [1]. Mummification was practised in Ancient Egypt for more than 3000 years and embalming is one of the most important steps in the process. Various balms, oils, gum resins and waxes were used to preserve the body and its organs, and different techniques were used between and within historical periods and social classes [2]. Nowadays, a large number of mummified bodies is being excavated and stored, and most of the ones in museum collections have been treated. As a result, the presence of conservation products and/or pesticides, which include plant oils and various synthetic pesticides, is added to the presence of original materials such as oils and resins [3].
This study explores a selection of nine Ancient Egyptian mummified bodies, dating from the New Kingdom to the Bizantyne period with a non-invasive methodology. The work proposes an innovative multidisciplinary approach to study the volatile organic compounds (VOCs) emitted from ancient mummified bodies by combining traditional techniques with olfactory analysis [4]. In particular, we combined sensory analysis with evaluators, chemical analysis with thermal desorption-gas chromatography coupled with mass spectrometric and olfactory detection (TD-GC-MS-O), and microbiological investigation. The main result from the study is the different type and concentration of volatiles emitted by the mummified bodies stored in different areas of the museum, highlighting higher amounts and variety of volatiles for those stored in the display cases in the exhibition area. The sensory analysis shows an average medium-low intensity of smell in the storage area, while a medium-high intensity in the display area. In both environments the main descriptors are woody (78%), spicy (67%), and sweet (56%).

The chemical analysis with TD-GC-MS-O analysis allows to classify the volatiles into four main categories based on their origin. The emissions originate from: the original mummification materials and their degradation (Acetic acid, -Pinene); plant oils used for conservation treatments (D-Limonene, (E)-Cinnamaldehyde); synthetic pesticides (1,2-Dichlorobenzene, 1,4-Dichlorobenzene); and microbiological deterioration (Octanol, 2-Heptanone). Although some compounds can be assigned to more than one group, as some oils used in the embalming process have recently also been used as insect repellents, this study demonstrates the possibility to classify the different compounds on the basis of chemical and olfactory analysis of the volatiles. The majority of the compounds identified with mass spectrometry were also identified with olfactory detector, allowing to determine the olfactory profile of each mummified body under investigation.
This work demonstrates the possibility to investigate the differences in mummification techniques and the state of preservation of mummified bodies using a non-invasive approach and highlights the importance of olfactory analysis, which can lead to a more comprehensive understanding of the cultural heritage [5].

Acknowledgements

The authors would like to acknowledge the Leads of the El-Hibe Coffins Project (2020–2023) funded by the German Archaeological Institute in Cairo.

Funding

The authors acknowledge the financial support from EU research project GREENART (Horizon Europe research and innovation program under grant agreement no. 101060941), ODOTHEKA project (the Slovenian Research Agency project No. N1-0228 and the Polish Narodowe Centrum Nauki project No. UMO-2020/39/I/HS2/02276), the Slovenian Research Agency research Core Funding No. 20-MR.55995-122 and N-DAD programme group.

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Trace Elements Analysis in Provenance Studies of Pigments in Paint Layers: Examples of Application

Zdeňka Čermáková[1], David Hradil[1], Janka Hradilová[1] and Jitka Míková[2]

[1]ALMA Laboratory, Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec 1001, 250 68 Husinec-Řež, Czech Republic; cermakova@iic.cas.cz, hradil@iic.cas.cz, hradilova@iic.cas.cz
[2]Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic; jitka.mikova@geology.cz

Keywords: LA-ICP-MS, provenance studies, azurite, smalt

Laser Ablation – Inductively Coupled Plasma – Mass Spectroscopy (LA-ICP-MS) is a powerful technique of trace elemental analysis capable of detecting even ones ppm. Such precision enables a detailed comparison of (trace) elemental record of the samples, which may allow to establish a so-called fingerprint, a set of parameters typical for source localities or production technologies. While LA-ICP-MS is a well-established technique in geological science, the examples from cultural heritage, especially focused on painting materials, are much rarer. [1, 2]

This study focuses on two blue pigments, azurite and smalt (cobalt-coloured glass). While azurite elemental composition is directly related to its forming geological environment, smalt, an intensely Co-coloured glass is a man-made material, yet its trace elemental composition may retain indicators related to the origin of the cobalt ore. The study included i) German glass smalt samples originating from the 16th century containing most probably cobalt from Schneeberg, Germany, one of the most prolific cobalt-rich deposit, and ii) smalts collected on the Czech side of the Ore Mts. (e.g. from Horní Blatná, known for smalt production since the 16th century). In case of azurite, geological samples from four localities including three historical Central European sites with potential of being azurite pigment source in the Middle Ages were studied (Brixlegg, Austria, Piesky, Slovakia, Rudabánya, Hungary).

In addition, micro-samples from painted artworks were analysed in order to apply the method in practice and formulate its benefits and limits. The interpretation of the results has to take into account that the obtained trace elemental record may be influenced by impurities introduced by contamination from adjacent layers, potentially admixed other pigments or even binding media (such as phosphorous from egg tempera). Nevertheless, it was possible to establish a pattern and several elements were pinpointed as very useful provenance indicators. For example in azurites, in addition to the frequently described minor components such as As, Zn, Ba, Sb, some of them contained also trace amounts of lanthanides, yttrium or uranium. Based on the content of these elements, Hungarian Rudabánya was ruled out as a possible source of azurite in late Gothic painting from Lipany, Slovakia, while Brixlegg, Austria, was selected as the most probable locality of origin (Fig. 1).

These results show possible ways of interpretation; definitive conclusions will be drawn after studying a larger number of samples. In conclusion, while not widely used, LA-ICP-MS showed its capability to provide a detailed trace elemental composition in pigment samples and micro-samples and together with careful interpretation of the results may provide an insight into provenance of the pigment or its raw materials. As

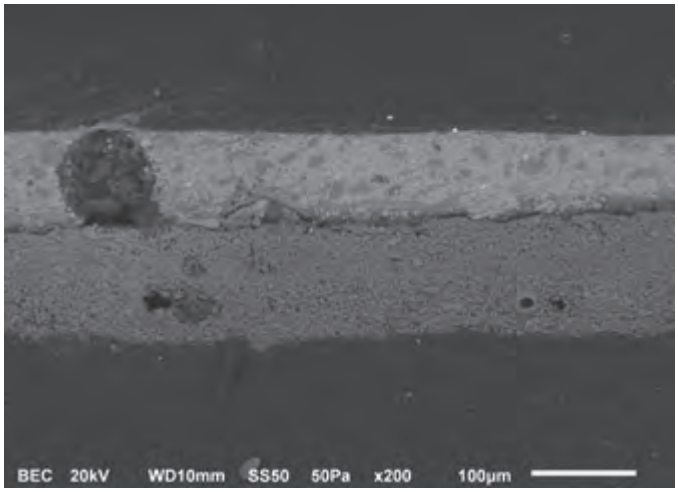

Fig. 1 SEM-EDS photograph of a micro-sample from Altarpiece of St. Martin in Lipany, Slovakia, dated 1526, with a nicely visible crater after LA-ICP-MS analysis of the upper azurite-rich layer

a part of a broader discussion, such knowledge can also help in determination of origin of the whole artwork.

Acknowledgements

The authors are grateful to Mike Haustein, Martin Gelnar and Martin Ševko for providing some of the reference samples, to all the colleagues who participated in the research, as well as to art historians and artworks' owners collaborating in the investigation of the paintings.

Funding

This research was supported by Czech Science Foundation, grant No. 22-17966S.

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Multi-Scale Multi-Technique Characterization Approach to Reveal the Secrets of Corami (gilt and painted leather) Wall Coverings from Chigi Palace, Italy

Elena Badea[1,2], Cristina Carsote[2,3], Noemi Proietti[4], Valeria Di Tullio[4], Marianne Odlyha[5], Chloe Pearce[5], Ilaria Quaratesi[2], Genoveva Burca[6,7], Stefan Michalik[6], Bogdan-Florin Rusu[2]

[1]Department of Chemistry, Faculty of Sciences, University of Craiova, Calea București 107, Craiova, Romania; elena.badea@edu.ucv.ro
[2]Advanced Research for Cultural Heritage Group (ARCH Lab), National Research and Development Institute for Textiles and Leather, ICPI Division, Strada Ion Minulescu 93, Bucharest, Romania
[3]Center for Research and Physical-Chemical and Biological Investigations, National Museum of Romanian History, Calea Unirii 12, Bucharest, Romania; criscarsote@yahoo.com
[4]Institute of Heritage Science (ISPC), CNR, Area della Ricerca di Roma 1 , Monterotondo Stazione (Roma) – Italy; noemi.proietti@cnr.it; valeria.ditullio@cnr.it
[5]Birkbeck College, University of London, Malet Street, Bloomsbury, London WC1E 7HX4, United Kingdom; m.odlyha@bbk.ac.uk; cpearc03@mail.bbk.ac.uk
[6]STFC, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK
[7]Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, OX11 0DE, United Kingdom; genoveva.burca@diamond.ac.uk; stefan.michalik@diamond.ac.uk

Keywords: gilt leather, manufacturing, degradation mechanisms, conservation

Leather with a gilded or silvered background, tooled and painted in bright, transparent colors is called “corami” (from the Latin corium), “cuoi d’oro,” or “cuoridoro” (gold leather). Corami manufacturing in Italy peaked in the XVIth and XVIIth centuries. The most important production centers were Naples, Rome, Venice, Bologna, Ferrara and Modena. It is known that gilt leather rarely survives in its original state due to the inherent problems caused by overlaying layers of leather, animal glue, silver leaf, oil paints, glazes and varnishes. One of the most spectacular examples of corami wall coverings from the XVIth century is conserved in Palazzo Chigi, located in Ariccia, near Rome. The collection was the subject of comprehensive in situ and ex situ analysis campaigns intended to study the materials used for manufacturing, assess their deterioration and evaluate the overall conservation condition of the wall panels. Both the manufacturing process itself and the multitude and complexity of degradation mechanisms, which likely occur simultaneously in such sophisticated artefacts, require a characterization approach that can explore surfaces and interfaces at a range of length-scales to probe chemical, morphological, and structural changes of constituents, their dynamics and interactions with past and present conservation material. A number of micro samples were analyzed by Fourier transform infrared (FTIR-ATR) spectroscopy, Raman microscopy, optical microscopy, SEM-EDX, micro-differential scanning calorimetry (micro-DSC), ^{1}H NMR and ^{13}C CPMAS NMR spectroscopy [1]. X-ray diffraction was performed at the I12 Joint Engineering, Environmental and Processing (JEEP) beamline of Diamond Light Source to unambiguously identify the inorganic materials and show how the collagen conformation was still preserved in

the structure of the corami. Controlled environment neutron radiography of moisture sorption/desorption was performed at the pulsed neutron spallation source ISIS in the United Kingdom to get insight in the damaging effects of relative humidity fluctuations. The findings we present would not be possible without such a systematic, multi-scale, multi-technique characterization approach, which highlights the critical importance of detailed analysis of structure, composition and degradation patterns to propose conservation strategies to extend the life and use of gilt leather artefacts.

Acknowledgements

UKRI Grant "Monitoring effects of RH fluctuations on leather based cultural heritage objects". Experiments RB2320345 (ISIS Neutron and Moun Source) and MG35634 (Diamond Light Source).

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Ritual Revealed: Psychotropic Substances in a Ptolemaic Egyptian Vase

Davide Tanasi[1], Branko F. van Oppen de Ruiter[2], Fiorella Florian[3], Radmila Pavlovic[4,5], Luca Maria Chiesa[4], Igor Fochi[6], Chiaramaria Stani[7], Lisa Vaccari[8], Dale Chaput[9], Giorgio Samorini[10], Alberto Pallavicini[3], Sabrina Semeraro[11], Anastasia Serena Gaetano[11], Sabina Licen[11], Pierluigi Barbieri[11], Enrico Greco[11]

[1]Department of History, University of South Florida, 4202 E Fowler Ave, Tampa, FL 33620, US; dtanasi@usf.edu
[2]Tampa Museum of Art, 120 W Gasparilla Plaza, Tampa, FL 33602, US; branko.vanoppen@tampamuseum.org
[3]Department of Life Sciences, University of Trieste, via Licio Giorgieri 5, 34127, Italy; florian@units.it, pallavic@units.it
[4]Department of Veterinary Medicine and Animal Science, University of Milan, via dell'Università 6, 26900 Lodi, Italy; radmila.pavlovic@unimi.it, luca.chiesa@unimi.it
[5]ProMeFa, San Raffaele Scientific Institute, via dell'Olgettina 60, 20132 Milan, Italy
[6]Thermo Fisher Scientific S.p.A., 20090 Rodano, Milan, Italy; igor.fochi@thermofisher.com
[7]CERIC-ERIC S.S. 14 - km 163,5 in AREA Science Park 34149 Basovizza Trieste, Italy; chiaramaria.stani@ceric-eric.eu
[8]Elettra-Sincrotrone Trieste S.C.p.A., S.S. 14 - km 163,5 in AREA Science Park 34149 Basovizza Trieste, Italy; lisa.vaccari@elettra.eu
[9]Department Molecular Biosciences, University of South Florida, Tampa, FL 33620, USA; chaput@usf.edu
[10]Ethnobotanist, independent researcher, Bologna, Italy; giorgio@samorini.it
[11]Department of Chemical and Pharmaceutical Sciences, University of Trieste, via Licio Giorgieri 1, 34127, Trieste, Italy; anastasiaserena.gaetano@phd.units.it; slicen@units.it; barbierp@units.it; enrico.greco@units.it

Keywords: Psychedelics, Ptolemaic Egypt, Biomolecular Archaeology, LC-MS/MS Orbitrap

This study [1] presents a comprehensive multimodal analytical study of an Egyptian ritual Bes-vase [2,3], of the 2nd century BCE employing cutting-edge proteomics, metabolomics, genetics techniques, and synchrotron radiation-based Fourier Transformed Infrared microSpectroscopy (SR μ-FTIR) to characterize organic residues of its content. We successfully identified the presence of various nutraceutical, psychotropic, medicinal, and biological substances, shedding light on the diverse components of a liquid concoction used for ritual practices in Ptolemaic Egypt. Using LC-MS/MS with a new methodological approach, we identified key proteins and metabolites, enabling the identification of botanical sources, also confirmed by genetic sequences. Our analyses revealed traces of Peganum harmala [4,5], Nimphaea nouchali var. caerulea [6,7], and a plant of the Cleome genus [8,9], all of which are traditionally proven to have psychotropic and medicinal properties. Additionally, the identification of human fluids suggests their direct involvement in these rituals. Furthermore, metabolomics and SR μ-FTIR analyses also revealed the presence of

fermented fruit-based liquid and other ingredients such as honey or royal jelly. The identification of specific chemical compounds, such as alkaloids and flavonoids, provides insight into the psychoactive and therapeutic uses of these in ancient ritual practices. This multidisciplinary study highlights the complexity of ancient cultures and their interactions with psychoactive, medicinal, and nutraceutical substances. These findings contribute to our understanding of ancient belief systems, cultural practices, and the utilization of natural resources, ultimately enhancing our knowledge of past societies and their connection to the natural world.

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Unveiling the Material Evolution of Urban Art: Analyzing Mural Stratigraphies from the Graffiti Alley (Ghent, Belgium) and the Galeria de Arte Urbana (Lisbon, Portugal)

Jacopo La Nasa[1], Silvia Pizzimenti[2], Chloë Coustet[3], Mathieu Thoury[3], Ilaria Degano[1], Francesca Modugno[1]

[1]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy; Center for the Integration of Scientific Instruments of the University of Pisa (CISUP), University of Pisa, Pisa, Italy; jacopo.lanasa@unipi.it, ilaria.degano@unipi.it, francesca.modugno@unipi.it
[2]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy; Department of Pharmacy, University of Pisa; email: silvia.pizzimenti@unipi.it
[3]Université Paris-Saclay, CNRS, ministère de la Culture, UVSQ, MNHN, Institut photonique d'analysenon-destructive européen des matériaux anciens, Saint-Aubin, France; emails: c-coustet@ipanema-remote.fr; mathieu.thoury@ipanema-remote.fr

Keywords: Street art, material evolution, analytical pyrolysis, infrared spectroscopy, elemental analysis

Visual art in urban contexts consists of both commissioned and often non-commissioned street art. The ephemeral character, free access, and exposure to the environment and anthropic actions, make public paintings vulnerable to removal, vandalism, and degradation. Urban art is at present widely recognized by art history and by the wide society as an important part of contemporary cultural heritage, and a historical perspective on the evolution of materials and techniques is highly needed to gain a better knowledge of this form of art and to contribute to sustainable preservation strategies [1,2]. The synthetic paint materials used by street artists in the last decades, such as spray paints, have undergone a fast evolution in their compositions. This aspect is related both to the implementation of new health regulations, leading to substances being banned from commercial use, and to the continuous improvement and evolution of commercial formulations. Targeted analytical experiments have been carried out to contribute to a comprehensive understanding of the chemical composition of paint materials used by street artists over the past decades, by studying samples which contain stratigraphies representing over 20 years of paint materials. Two case studies of great importance are presented: the Graffiti Alley (Ghent, Belgium) and Galeria del Arte Urbana (Lisbon, Portugal). These two locations are characterized by up to 25 years of repaintings on the same paint supports, giving a unique point of view on the evolution of the materials in a specific and well-defined time segment. The use of traditional analytical approaches on these samples did not provide an accurate evaluation of the distribution of the materials due to the thinness of the paint layers. In the presented preliminary study carried out at IPANEMA, a state-of-the-art European facility renowned for its expertise in multiscale and multispectral approaches in heritage science, we conducted Multi-spectral Luminescence Microscope (MSLM), Mid-infrared Hyperspectral Imaging (MIRHSI), and combined Micro-XRF analysis to obtain an exhaustive spatial resolution apt to study the stratigraphy of both the organic and inorganic materials. Moreover, FEG-SEM was carried out in Pisa to provide the

elemental composition of the different paint layers. Subsection of the stratigraphies were also analysed by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) to obtain a more detailed molecular composition of the samples. By applying this multiscale and multispectral approach combined with the micro destructive Py-GC-MS, we were able to obtain detailed chemical information about the different paint layers in the cross-sections. This allowed us to gain insight into the paint binder stratigraphy, differentiating between various classes of organic polymers, such as alkyds, acrylics, and nitrocellulose resins, present in each layer, and the evolution of their use in formulation during time. Additionally, the analysis provided valuable information about the inorganic content of the paint layers, revealing not only the presence of pigments and inorganic fillers. While some elements such as calcium and titanium were homogenously present in all the layers, specific metal were detectable only in the oldest paint layers. In particular, the presence of lead was highlighted only in the oldest layers. A detailed microscale element distribution can be crucial in the comparison with relevant literature (patents, European health regulations, peer-reviewed journals, etc.) to tentatively date the different paint layers. The research has been carried out in the framework of the Italian PRIN2020 project SuPerStAr - Sustainable Preservation Strategies for Street Art.

Funding

Italian PRIN2020 project SuPerStAr - Sustainable Preservation Strategies for Street Art; Financial support by the Access to Research Infrastructures activity in the H2020 Programme of the EU (IPERION HS Grant Agreement n. 871034)

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Complimentary Documentations and Multi-modal Representations of Written Heritage

Simon Brenner[1], Hans Clausen[2], Gerlinde Schneider[2], Ivana Dobcheva[3], Wilfried Vetter[3], Manfred Schreiner[3] and Robert Sablatnig[1]

[1]Computer Vision Lab, TU Wien, Favoritenstrasse 9-11, 1040 Vienna, Austria; simon.brenner@cvl.tuwien.ac.at; r.sablatnig@cvl.tuwien.ac.at
[2]Centre for Information Modelling, University of Graz, Elisabethstrasse 59/III, 8010 Graz, Austria; hans.clausen@uni-graz.at ; gerlinde.schneider@uni-graz.at
[3]Institute of Natural Sciences & Technology in the Art, Academy of Fine Arts Vienna, Augasse 2-6, 1090 Vienna, Austria; w.vetter@akbild.ac.at; m.schreiner@akbild.ac.at

Keywords: medieval manuscripts, non-invasive analysis, data dissemination

During the last decades collaborations have been established between humanities such as philology, art history, and conservation-restoration on the 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]. The research projects have focused so far on the documentation by Multi- and Hyperspectral Imaging (MSI and HSI) [2, 3] and non-invasive material analysis of medieval manuscripts [4, 5] 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. Mainly Slavic (Glagolitic and Cyrillic), Greek and Latin manuscripts of the Austrian National Library and various Austrian monasteries from the 8th to the 14th centuries have been analysed. Furthermore, investigations could be carried out in the St. Catherine Monastery in Sinai (Egypt), the Rila Monastery (Bulgaria), National Library Sofia and Plovdiv (Bulgaria), the Vernadsky National Library of Ukraine, Biblioteca Comunale Trento (Italy), National and University Library Ljubljana (Slovenia), National Library Budapest (Hungary), National Library Zagreb (Croatia) and finally in the Biblioteca Apostolica Vaticana (Vatican).

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. Additionally, a system for increasing the readability of poorly preserved manuscripts or documents containing overwritten text (palimpsests), which pose particular challenges to the philological investigation, could be designed and assembled. The acquisition setup consists of an achromatic middle format camera (PhaseOne IQ 260 Achromatic) and a conventional RGB camera (Nikon D4) mounted next to each other. A linear unit allows for automatic shifting between the two cameras.

Due to the high amount of data (images and spectra of more than 120 manuscripts and charters) a repository for the archiving and dissemination of research data, the project DiTAH [6] was launched in the form of Multi-Modal Manuscript Representations (M3R), in which the various digital artifacts 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 long-term preservation and linked open data, special emphasis is put on the use of established and open standards for data and metadata such as IIIF, METS, TEI, and SKOS. Thus, the data available in the repository are made long-term accessible not only for natural sciences and technologies, but also for research and education in the humanities.

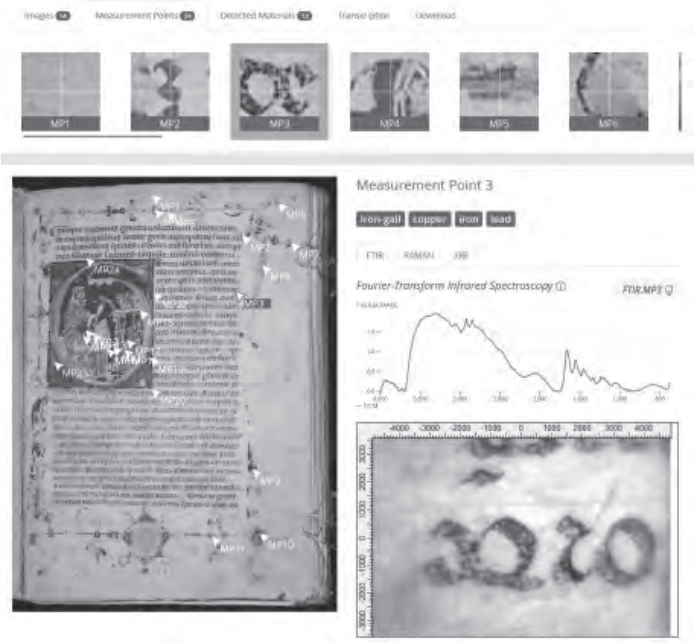

Figure: Browsing measurements in the web viewer.

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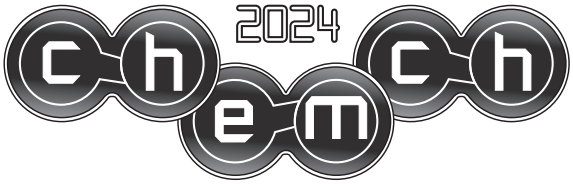

Poster presentations

Exploring Historical Development and Analyzing Properties of Paper: Advances in Data Processing Methods

Mgr. art. Martina Šottová, ArtD.

Academy of Fine Arts and Design in Bratislava, Hviezdoslavovo nám. 18, Bratislava 814 37, Slovakia;
sott.martina@gmail.com

Keywords: handmade paper, structure, digital recording

Within the scope of our research, our primary focus was on the manual production of paper in Europe. Craft production during the medieval and early modern periods was characterized by workshop secrecy. [1] In our region, the research on handmade paper production was conducted by Viliam Decker (1907-2000). Thanks to his monographs, we have access to dozens of studies on the history of papermaking in Slovakia. [2]
Rags (flax, hemp, later cotton) served as the fundamental material for European paper. Characteristic features of handmade paper include its unique watermark visible in the translucent parts, which is its structure. This distinct individual feature is shared by all products of European handmade paper production. Therefore, the paper form has therefore become the most important tool determining the surface and internal structure, as well as the format and thickness of the produced sheet. [3] Researcher Viliam Decker extensively studied handmade paper production in Slovakia and outlined the basic classification of papermaking forms. According to Decker's interpretations, the papermaking form consists of stretched fabric on a wooden frame shaped from wires, with thicker wires forming the warp at a greater distance from each other than the weft, for which thinner wires were used. Decker examined the distance between individual wires on papermaking forms. The subject of the study was the papermaking form and the structure of paper. For the research needs of the structure, GMB Bratislava provided materials. The available material provided a sufficient basis for the research goals. As part of the data collection process for the paper substrate structure, the study of individual graphics in terms of authorship, dating, and, if possible, determining the circumstances of the creation of individual cycles was conducted. Detailed information is included in a separate catalog published in the dissertation. [4] Concurrently, the description and documentation of technological and visual properties of substrates on the transparency of the scanner (Epson Perfection V850 Pro), and measurements feasible by the naked eye were performed. Criteria for collecting data on the structure of handmade paper:
- Visual properties of paper
- Technological properties of paper
- Fiber distribution and orientation
- Examination of substrate thickness and its variability
- Examination of subsequent restoration interventions
- Selection of sampling location (if necessary)

In the realm of technological development, data obtained from the analysis of 151 works of European origin dating back to the 16th and 17th centuries were utilized. During measurements of individual differences in the structure of handmade paper,

we monitored the categories of mode, median, and mean. In the 16th century, the most common structure comprised 30 horizontal lines per 3 cm and 4 warp lines per 10 cm. Conversely, in the 17th century, the structure exhibited 24 horizontal lines per 3 cm in measurement, along with 4 warp lines. The spacing in the most commonly occurring structure from this century was approximately 1.25 mm between the lines in the warp and 25 mm in the weft. Upon comparing the range of spacing of lines between the 16th and 17th centuries, we confirmed a consistent increase in spacing between the lines in both the warp and the weft. In the theoretical research section, we learned that Viliam Decker [5] mentions a typical distance between the tensioning of warp wires of 20-25 mm for the period spanning the 15th to 17th centuries. This data was corroborated in our research. According to William Decker, 100-120 wires were placed per 10 cm in the warp during the 16th-17th centuries. In our measurement, there are 87-100 lines (wires) per 10 cm in this period.

The primary objective of the research is to enhance the current database by incorporating fresh data obtained through further measurements. These additional measurements will be carried out on the areas of the paper that have been supplemented or modified. Our aim is to guarantee that the supplemented paper aligns with the technical parameters and specifications of the original paper.

By conducting additional measurements and ensuring that the supplemented paper meets the standards set by the original, we strive to maintain the integrity and authenticity of the paper. This meticulous approach is crucial, especially in fields where historical documents or artworks are involved, as it ensures that any alterations or additions are seamlessly integrated without compromising the overall quality or characteristics of the original material.

Moreover, expanding the database with new data not only enhances our understanding of the paper's structure and properties but also enriches the resources available for future research and preservation efforts. By continuously updating and refining our database, we contribute to the advancement of knowledge in the field of paper studies and facilitate the preservation of valuable historical artifacts for generations to come.

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16. Century	3 cm	10 cm
average	29,42	4,09
median	29	4
mode	30	4

Tab. N. 1. Containing values with the number of lines in the attack at 3 cm and the number of lines in the warp at a span of 10 cm from the 16th century

17. Century	3 cm	10 cm
average	27,43	4,03
median	26	4
mode	24	4

Tab. N. 2. Containing values with the number of lines in the attack at 3 cm and the number of lines in the warp at a span of 10 cm from the 17th century

Proposal for a Remediation Method for the "Vinegar Syndrome" in Cellulose Acetate-based Motion Picture Films

F. Porpora[1], A. Maiano[1], C. Forcellini[1], C. D'Aleo[1], L. Lisi[1], L. Dei[1], M. De Sanctis[3], E. Carretti[1,2]

[1]University of Florence and CSGI, Via della Lastruccia 3-13, 50019, Sesto Fiorentino, Italy
[2]CNR-INO, Largo E. Fermi 6, 50125 Florence, Italy
[3]L'Immagine ritrovata SRL, Via Riva di Reno, 72, 40122, Bologna, Italy

Motion picture films made of cellulose acetate (CA) are subjected to chemical degradation mainly due to the "vinegar syndrome". It concerns the cleavage of the ester bonds between the acetate group and the cellulose chain through ester hydrolysis (deacetylation), with the formation of hydroxyl groups and the release of acetic acid. It is strictly influenced by temperature, moisture and acidity: the released acetic acid acts as a catalyst for the reaction. By-products of deacetylation can promote, also, the hydrolysis of the glycosidic bonds of the cellulosic backbone. The consequent deformation and embrittlement of the films can strictly compromise their usability [1,2].

The most important goal of this project is to set up innovative, cheap, easy-to-produce and handle and possibly reusable chemical inhibitors. We proposed and characterized several systems based on two strategies: the use of sponge-like systems (1) made of polyethyleneimine (PEI) and/or (2) uploaded with metal oxide nanoparticles. The intent was to use free amino groups, in the first case, and inorganic nanoparticles, in the second case, to convert acetic acid into ammonium carboxylate and acetate salt, respectively, through an acid/base reaction. The evaluation of the efficacy of the above-mentioned systems in inhibiting the vinegar syndrome was performed both on real motion picture films on which the deacetylation process has been artificially induced with an innovative degradation protocol and on films naturally affected by the "vinegar syndrome". The different behaviors of untreated and treated films have been evaluated through an innovative multi-analytical protocol able to monitor the chemical alterations of the supports connected with the occurrence and the evolution of the "vinegar syndrome".

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Tărtăria – A Everlasting Story

Mihai Straticiuc[1] , Malvinka Urák[2], Melania Istrati[1], Dragoș Mirea[1] and Regina Anna Uhl[3]

[1]Horia Hulubei National Institute for Physics and Nuclear Engineering, Magurele, Romania; mstrat@nipne.ro
[2]The National Museum of History of Transylvania, Cluj, Romania; themalvinka@gmail.com
[3]Deutsches Archäologisches Institut – Eurasien Abteilung, Berlin, Germany; regina.uhl@dainst.de

Keywords: archaeological discovery; Tartaria Tablets; ion beam analysis, PIXE

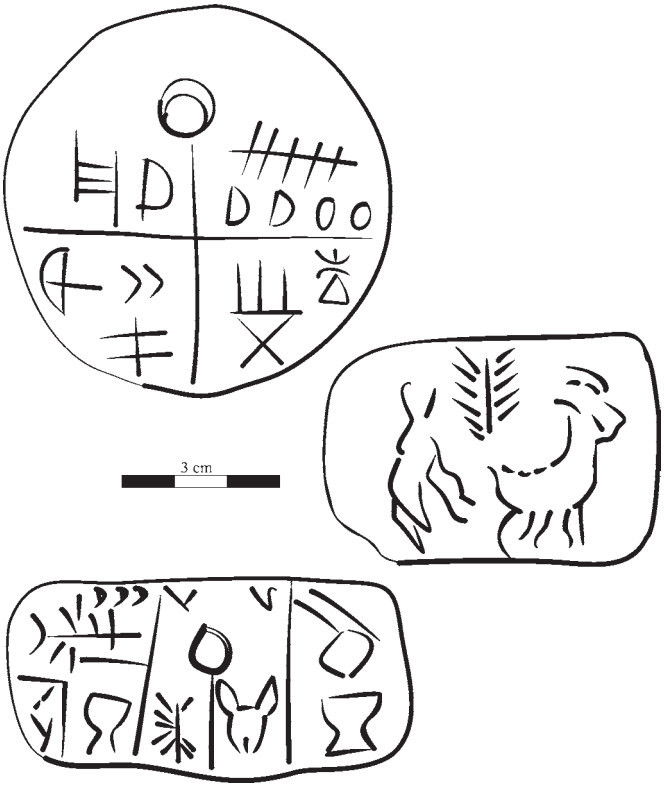
Among the most captivating archaeological discoveries, some have emerged from the mist of accidental unearthing, adding a mythical aura to their narrative. Yet, this very mist can cast doubt on their credibility and authenticity. One such enigmatic find is the trio of clay tablets from Tărtăria (Figure 1), discovered in a so-called ritual pit during a test excavation in 1961 in the Lower Mureș Valley, Transylvania, Romania. These tablets, presenting a series of incised symbols that might resemble pictograms, were considered the cornerstone of many scientific debates concerning the European Neolithic and were initially interpreted as evidence of an early writing system, surpassing in time even the cuneiform writing of the Near East or the Egyptian hieroglyphs.

These artefacts have sparked a deluge of scholarly discourse, measured in linear meters [1-7], dividing renowned scholars and the general public. Following the publication of the findings [8, 9], a period of intense academic polemics ensued. Today, the debate may have subsided, but it has left behind a palpable caution, a distress that, in Madame Bovary's words, could be expressed as the fear of having the gliding sticking to our fingers if we touch our idols. However, the same cannot be said for the work of amateurs and believers, who continue to produce questionable publications and documentaries, even claiming to have decoded the incised symbols on the clay tablets.

With the alarming number of pseudo-scientific publications and the more widespread use of AI technology, often used to create content relying on unverifiable data, the risk of losing control of the matter is imminent. It is our duty, as scholars, to employ modern scientific methods to get closer to a series of events that happened in a past not that far behind us yet covered by darkness.

Thanks to the technological advancements of recent decades and the application of interdisciplinary methods in archaeological analysis, long-time untouchable tangible heritage is being brought closer to us. Non-invasive methods have revolutionized our exploration, allowing us to delve beyond the visible and pushing the boundaries of our empirical knowledge. This paper, the first part of a series, aims to systematically approach a topic that has long been emotionally rather than scientifically explored.

This experiment's scope was to understand the clay tablets' physical and chemical properties using atomic and nuclear analytical techniques like X-ray Fluorescence (XRF) and Particle Induced X-ray Emission (PIXE). As these artefacts are unique, invasive procedures are not suitable. The main objective is to determine if the three discoveries show similar microscopic and technological characteristics, indicating that they belong to the same batch.



Our findings revealed twelve trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr and Zr) that are present in various concentration for each tablet, offering a fair perspective of the fabric and helped us to decipher a first pattern for the raw material source. Matrix components (Na, Mg, Al, Si, K and Ca) oxides attributed to common feldspars were also detected by XRF and PIXE, together with other five major chemical elements (P, S, Cl, Ti and Fe).

Acknowledgements

This work was supported under the "Nucleu" Programme PN 23210201. Experiments were carried out at 3 MV Tandetron™ accelerator from "Horia Hulubei" National Institute for Physics and Nuclear Engineering (IFIN-HH) and were supported by the Romanian Government Programme through the National Programme for Infrastructure of National Interest (IOSIN).

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Reverse Glass Paintings and How to Study Them

Markéta Dumpíková[1], Anastasiia Ivanova[1], Gabriela Vyskočilová[1], Romana Kirchnerová[2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno; gabriela.vyskocilova@mail.muni.cz
[2]National Museum, 2, Václavské náměstí 1700/68, 110 00 Praha 1; romana.kirchnerova@nm.cz

Keywords: reverse glass paintings, FTIR, MS, SEM-EDX analyses

The reverse glass painting is a kind of painting made of very thin glass (app. 2 mm). The painting is created in reverse order - the contours are made first while the background is made last. The colour layers are thin and usually only in one layer, so the stratigraphy of the cross-section is poor and not useful. The most often technique should be distemper, sometimes oil painting, using natural resin or gum. The painting is only applied on the glass, any other varnish, (eg. enamel) or other techniques are not used. It was necessary to use appropriate colour binding which would be able to connect the colour and glass.

Apart from the colour layer on the glass, reverse glass painting contains other materials (e.g. paper or wood covers, wood frames, wood or metal nails and hook nails etc.) which are used as protective materials. All these materials affect the state and degradation processes.

The Czech National Museum has a collection of approximately 2,000 pieces of different kinds of reverse glass paintings. Some of them are very simple folk paintings while others are masterpieces. Usually, the paintings are colourful but it can be found a few so-called mirror reverse glass paintings. These mirror paintings are usually gold-black, silver-black or a combination of these materials.

The research aimed to investigate the materials used for making these types of paintings and find the most useful techniques for their characterisation. We compared FTIR, ATR-FTIR and ATR-FTIR for the bindings characterisation. For more specific results of animal bindings LC-ESI-Q-TOF/MS was applied. SEM-EDX was used for the characterisation of gilding materials on the mirror painting while the Raman spectroscopy was used for the detection of black colour on the same pieces. Optical microscopy as well as UV light were used for the detection of some data, repainting or painting techniques.

Based on the infrared techniques, it is possible to recognize if the binding has an animal or plant source. Because of the sample character, the best technique is ATR-FTIR which does not destroy or distort the results. The infrared techniques can determine if the painting is bound by the resins, oils, gums or animal binding. Unfortunately, IR is not a useful technique for the precise determination of animal binding (gelatine, mucilage, casein and egg tempera). As a very sensitive and useful technique for their determination LC-ESI-Q-TOF/MS was used.

Due to the combination of methods we can say that some colours were bind by temper emulsion (drying oil with animal glue), oils, natural resin, animal glue-starch emulsion, polysaccharides gum or only by animal glue.

We exclude the egg or casein temper (which are mentioned most often in the literature) as the colour bindings on the reverse glass paintings.
Except for the colour bindings, we investigate the materials used for mirror glass paintings. UV light and X-ray methods were used for revealing the re-painting or secondary interventions. Optical microscopy is exploitable for the determination of the techniques of mirror reverse glass painting. We recognize many techniques such as the eglomisé (translucent arish underlaid with metal foil), engraving into the gold, silver, their combination, silver layer with washgold, gilding or amalgam gilding.
SEM-EDX helped us to recognize the inorganic composition of colours and their damage. By the EDX we were able the recognise the materials used for mirror reverse painting – if the metals are pure gold or silver or if they are substituted by cheaper materials, eg. a combination of gold, copper, silver, zink or at least only colour varnish. SEM scanning is useful for recognition of the type of gilding – if the gold slice or gold coat was applied. Moreover, the SEM revealed the mechanism of decomposition or degradation of mercury amalgam layers. During the maturation of the amalgam layer, the composition of the liquid and solid phases are changed. The restorers describe that mirror glass reverse painting evolved the mercury globule. Under the SEM it is possible to see the „craters" which release the mercury globules which can be removed from the colour layers.
Due to our works, we understand better the reverse glass paintings and their degradation mechanisms. The knowledge about the composition, as well as the degradation, is useful for restorers as well as curators.

Acknowledgements

We would like to thank Š. Kučková, D. Pavliňák, Z. Moravec and K. Rapouch.

Funding

CzechNanoLab (ID LM2018110, MŠMT, 2020–2022), CEITEC University of Technology Brno; Ministery of Culture for the institutional support of National Museum (DKRVO 2019-2023/8.III.e, 00023272),

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Study of Paint Layers Using MA-XRF analysis

Michal Oravec[1], Stanislava Trginová[2], Boris Blatný[1]

[1]Slovak National Gallery, Riečna 1, 815 13 Bratislava; michal.oravec@sng.sk
[2]Slovak National Gallery, Námestie SNP 1, 960 01 Zvolen; stanislava.trginova@sng.sk
[1]Slovak National Gallery, Riečna 1, 815 13 Bratislava; boris.blatny@sng.sk

Keywords: elemental analysis, Ladislav Mednyánszky, pigment analysis

In this work, the study of paint layers was realized using elemental analysis – scanning macro X-ray fluorescence (MA-XRF) technique. Analyzed artwork is part of Slovak National Gallery collection, named Boy on the porch (1895–1900) by impressionistic author Ladislav Mednyánszky (1852 – 1919). The aim of the work was to visualize unfinished lower painting subsequently overpainted by the same author, which was partly visible by daylight. The painting is made on the thin wood support without priming layer, painted on the raw wood. Acquired data from elemental composition paint analysis can be usefully employed to define the pigments present in the paint layers. Since IR cameras or medical X-ray machines seem to be preferred in the case of analyzing paintings "pentimenti" – alterations that show artist change of mind during the composition of the artwork. These methods do not offer exact information about chemical elements. The MA-XRF instrument (M6 JetStream, BRUKER) is a relatively new technique, although it has prominence in paint analysis [1], due to the possibility of making high-resolution images of the elemental map distribution of relatively large areas in artworks non-invasive and autonomously. Acquired data from elemental composition paint analysis can be usefully employed to determine the pigments present in the paint layers [2]. Figure 1A represents the actual paint after restoration. It is evident the lower part of the paint contains visual indications that another painting is presented. This was confirmed after displaying the elemental map of zinc, which is a component of zinc white used as an admixture with lead white in the lower painting. (Figure 1B). The lead element analysis in various energy levels is depicted in Figure 2 A-C. Since the lead element was presented in pigments of both of the paint layers, it is possible to separate two paints.

Fig. 1.: Comparison of the original (A) [3], and MA-XRF image of the Zn-Lα element (B) 180 degrees rotated. Both of the images were processed using graphic software.

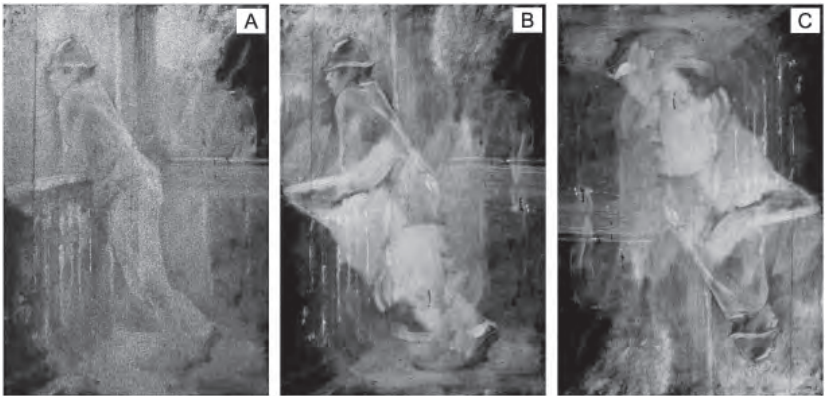

Fig. 2.: Comparison of the MA-XRF images Pb-Mα (A) Pb-Lα (B), and Pb-Lα 180 degrees rotated.

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Icon of Our Lady of Jerusalem "Merciful" from the Beginning of the 15th Century AD: Study of the Paint Layers and Gesso Using Optical Microscopy, XRD, SEM / EDS Analysis and Raman Spectroscopy, Dendrochronological and Radiocarbon AMS Dating of the Wooden Panel of the Icon.

Konstantin Voronin[1] and Mariya Kabanova[2]

[1]Institute of Archeology of the Russian Academy of Sciences; Dm. Yljanova street, h.19, 117292, Moscow; volter1707@gmail.com
[2]Yaroslavl State Technical University; Moskovskiy prosp., h.88, 150023, Yaroslavl, Russia; mariya_vk02@mail.ru

Key words: icon, XRD, SEM/EDS, Raman Spectroscopy, dendrochronology

This icon (123.5 cm x 90.3 cm x 3.2 cm) is an aristocratic work of art from Veliky Novgorod of the late 14th - first third of the 15th century AD, with a Gothic influence in the style of engraved ornaments applied on a gilded background. In the author's painting palette, consisting of 7 colors, 10 pigments were used (optical microscopy, XRD, SEM/EDS, Raman Spectroscopy). Red is cinnabar. Yellow - ocher. Green - glauconite, copper resinate. Blue is azurite. Brown - ocher, hematite. Black - soot, coal. White - lead white. The original coating of the background of the icon is thin sheets of pure gold without impurities, which probably indicates the native origin of this metal. The original gesso of the icon is made on the basis of chalk. The pine panel of the icon is made from trees grown in the north-west of Russia, harvested in the summer of 1410 AD. (dendrochronological dating). The wiggle-match dating procedure using 6 AMS radiocarbon dates showed that in three cases the radiocarbon age of the annual rings of the wooden panel of the icon coincided with the dendrochronological one, and in the rest it turned out to be younger than the dendrochronological one with a maximum difference of about 40 years. According to the written sources of the 14th century AD.., the wood harvested for panels of paintings was stored until the moment of use, as a rule, no more than two years. Therefore, based on the natural-science age of the icon panel, it can be argued that the icon of Our Lady of Jerusalem "Merciful" was painted around 1412 AD. This icon is the earliest known copy of the Byzantine icon of the Mother of God "Korsun" - the famous lost shrine, according to legend, brought to Russian lands in 988 AD under Grand Duke Vladimir Svyatoslavich.

Determination of the Cause of the Freshwater Reservoir Effect During Radiocarbon Dating of Ceramic Paste of Two Vessels of the Textile Ceramics Culture from the Bronze Age Hearth Complex.

Konstantin Voronin

Institute of Archeology of the Russian Academy of Sciences; Dm. Yljanova street, h.19, 117292, Moscow; volter1707@gmail.com

Key words: 14AMS, XRD, SEM/EDS, Bronze Age

Radiocarbon dating of ceramic paste of two vessels of the textile ceramics culture from the complex of Bronze Age hearth from the prehistoric settlement of Pesochnoye 1 (Russia, Yaroslavl region) showed that at the 2nd sigma level their radiocarbon age was about 2900 - 2100 years BC. Thus, the radiocarbon age of these vessels determined from ceramic paste turned out to be 800 - 1000 years older than the radiocarbon age determined from samples of the cultural layer taken near the hearth in which they were part of the complex. The reason for the older radiocarbon age of the dated vessels undoubtedly lay in the physicochemical properties of their ceramic paste. Also, based on the research practice of colleagues, the most likely reason for the older radiocarbon age in this case was the manifestation of freshwater reservoir effect associated with the presence of a carbon-containing substance of aquatic origin in the dated matters. In Lake Nero, on the shore of which the prehistoric settlement of Pesochnoe 1 is located, sapropel is the only substance whose texture is similar to the texture of ceramic paste of dated vessels. Based on this, to determine similarities and differences in phase and elemental composition, XRD and SEM/EDS studies of ceramic paste samples of the dated vessels and the sapropel sample from Lake Nero were carried out. Radiocarbon AMS dating of the sapropel sample was also done. In order to identify the degree of manifestation of a potentially expected freshwater reservoir effect in the water area of the lake in the immediate vicinity of the prehistoric settlement of Pesochnoye 1, a sample of modern days sapropel was selected. The use of a sapropel sample formed in modern days made it possible to create a correct research model, which made it possible to determine the degree of manifestation of the freshwater reservoir effect in counting down from present days.
XRD study showed the identity of the mineral phases in the vessels ceramic paste and the sapropel sample, and SEM/EDS analysis stated the similarity of their elemental composition. At the 2nd sigma level, the radiocarbon age of the modern days sapropel sample was 1000 – 1200 years. The presence of the mineral phase of calcite in the samples of ceramic paste of dated vessels and in the studied sample of sapropel explains the older radiocarbon age of the ceramic paste of vessels and the sapropel sample precisely by the freshwater reservoir effect, and more specifically by the “hard water effect”, the cause of which is ancient calcium carbonates dissolved in water.

A Comparison Among TGA, SEM-EDX and Raman Spectroscopy to Assess PVC Plasticizer Loss in the Presence of Various Wrapping Materials

Emilande Apchain, Adeline Royaux, Odile Fichet and Sophie Cantin

CY Cergy Paris Université, LPPI, F-95000 Cergy, France; cantin@cyu.fr

Keywords: PVC, storage, wrapping material, plasticizer migration

Silk paper, LDPE or PET are commonly used as wrapping materials for the transport or storage of PVC contemporary art heritage collections without knowing exactly their effects. That is why the loss of plasticizer in PVC, when in contact with these wrapping materials, was evaluated over a period of 17 months of artificial aging using temperature cycles of 2 days at 80 °C then 1 day at 25 °C under a relative humidity of 65 % [1]. This study was made on model PVC containing 31.6 wt% of di-isononylphthalte (DINP) and 3.2 wt% of epoxidized soybean oil (ESO). We combined three different techniques, ThermoGravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) images coupled to Energy Dispersive X-ray (EDX) analyses and Raman spectroscopy. SEM was chosen to reveal the evolution of the surface morphology. TGA and EDX analysis allow the evaluation of the plasticizer loss, while Raman Spectroscopy is used to deepen the understanding of the two plasticizers, DINP and ESO, migration. While TGA probes both the volume and the surface of the PVC samples, Raman spectroscopy and EDX provide information essentially from the surface, i.e. a few m-thick layer. The interpretations of these various analyses initially underscored both the strengths and limits of each technique. TGA analysis provided the evaluation of the overall plasticizer loss without differentiation of ESO and DINP, showing some limits of the technique in the widespread case of a plasticizer mixture. In addition, the dehydrochlorination observed during the analysis was found to be significant, thereby affecting the quantification of plasticizers. EDX analyses allow evaluation of the plasticizer loss during aging only if a particular atom can be used as plasticizer marker like the oxygen atom in this study. These analyses coupled with SEM images confirmed the presence of plasticizers on the PVC surface and revealed a kinetics of plasticizer migration controlled by evaporation rather than by diffusion. However, quantification of sample plasticizer loss after surface cleaning was difficult due to the high sensitivity of the method and detection of oxygen that may come from external contamination. Finally, Raman analyses performed on PVC samples allowed the quantification of DINP and ESO precisely and separately. The relative speed mass loss was observed to be similar for DINP and ESO plasticizers but significant differences were revealed depending on the wrapping material in contact with PVC during aging. Indeed, silk paper and LDPE slowed down the plasticizer loss while PET accelerated it. However, aging with silk paper would be recommended to be used as wrapping material for plasticized PVC objects since in contrast to LDPE, it does not stick to the PVC surface.

Acknowledgements

This work was supported by the Paris Seine Graduate School Humanities, Creation, Heritage, Investissements d'Avenir ANR-17- EURE-0021 –Foundation for Cultural Heritage Science.

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Exploring Exchange Routes Of Schist Artefacts In Iberian Chalcolithic By X-Ray And Neutron-Based Non-Destructive Analytical Methods

Ana Luísa Rodrigues[1,2], Rosa Marques[1,2], Maria Isabel Dias[1,2], Maria Isabel Prudêncio[2], Dulce Russo[1,2], Paula G. Fernandes[2], Andrea Martins[3,4], César Neves[3,4], Mariana Diniz[3,4], José M. Arnaud[4], Patrícia Jordão[3], Zsolt Kasztovszky[5], Ildiko Harsányi[5], Veronika Szilágyi[5], B. Maróti[5], Imre Kovács[6] and Attila Németh[6]

[1]DECN, Instituto Superior Técnico - Universidade de Lisboa, Campus Tecnológico e Nuclear, EN 10, km 139.7, 2695-066 Bobadela-LRS, Portugal; analuisarodrigues@tecnico.ulisboa.pt2 C
[2]TN - Instituto Superior Técnico - Universidade de Lisboa, Campus Tecnológico e Nuclear, EN 10, km 139.7, 2695-066 Bobadela-LRS, Portugal; analuisarodrigues@tecnico.ulisboa.pt
[3]UNIARQ – School of Arts and Humanities-University of Lisbon, 1600-214 Lisbon, Portugal
[4]Associação dos Arqueólogos Portugueses-Largo do Carmo, 1200-092 Lisbon, Portugal
[5]Nuclear Analysis and Radiography Department, Centre for Energy Research, 29-33 Konkoly-Thege street, 1121 Budapest, Hungary
[6]Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics, Budapest, Hungary

Keywords: Non-destructive analyses; Chalcolithic Iberian artefacts; Exchange routes of schist

The Iberian Peninsula boasts a wealth of symbolic artifacts from the Chalcolithic period, including idols, schist plaques, and small statuettes. One of the most impressive examples comes from Vila Nova de São Pedro (VNSP) in Azambuja, Portugal. This massive hilltop settlement has yielded a vast collection of symbolic tools unearthed over years of archaeological excavations. VNSP's significance extends beyond its size, as it has been identified as a potential production center based on finds of metalwork, bone ornaments, and other prestigious symbolic items like limestone cylindrical idols [1].
Among these artifacts, a prominent category directly linked to the funerary sphere are schist plaques. Dating from the mid-4th millennium BC to the end of the 3rd millennium BC, these rectangular plaques, polished on both sides, primarily feature geometric designs like reticulated patterns and zigzags, alongside some anthropomorphic motifs. These motifs include depictions of body parts like eyes, facial tattoos, arms, hands, and the pubic triangle. Found throughout Portugal, from Serra de Aire e Candeeiros to the Algarve, schist plaques are particularly abundant in Alentejo's megalithic monuments, with their distribution extending into southwestern Spain. While primarily associated with funerary contexts, schist plaques have also been unearthed in settlements like VNSP.
The VNSP schist plaques exhibit significant fracturing. This damage likely stems from a combination of post-depositional processes, past excavation methods, and potentially even intentional reuse within domestic contexts. The assemblage, comprising roughly 50 fragments that may represent around two dozen complete plaques, includes pieces with both geometric and anthropomorphic decoration. Notably, the artisans employed different types of schist in their creation. The decorative technique involved filiform incision, likely executed with a flint tool.

Crucially, the schist used in these plaques is not locally sourced. Situated within a limestone massif, VNSP lacks readily available schist, with the nearest sources located kilometers away. Determining the likely origin of the raw material used in these plaques holds immense potential for understanding not only the exchange networks associated with these artifacts but also the routes traversed by people, materials, artefacts, and ideas during the 3rd millennium BC. Unlike other artifact categories like the cylindrical limestone idols and flint tools, schist plaques were demonstrably not produced at VNSP, making them exogenous elements within the settlement. The absence of a known necropolis at VNSP further underscores the intriguing questions surrounding the presence of these funerary-related artifacts in a domestic context.
For the first time, a non-destructive approach combining bulk prompt-gamma activation analysis (PGAA) with external milli-beam particle induced X-ray emission spectroscopy (PIXE) has been applied to characterize the composition of the VNSP schist plaques. This compositional analysis will be used to infer the provenance of the schist plaques by comparing the obtained results with potential source materials. Thus, this research aims to elucidate the probable exchange routes of these plaques, shedding light on the networks for raw materials, objects, and symbolic elements within the Iberian Chalcolithic period.

Acknowledgements

The authors are grateful to ERA-Arqeuologia S.A. and Museu Arqueológico do Carmo for the access to the archaeological artefacts. C2TN authors gratefully acknowledge the Portuguese Science and Technology Foundation—FCT support through the UID/Multi/04349/2020 project.

Funding

Projects supported by the European Commission under HORIZON 2020 Program through the Key Action Integrated Platform for the European Research Infrastructure on Cultural Heritage IPERION HS (Grant Agreement Number 871034 – fix_123 - EXPLORSCHIST).

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Investigation of the Gothic Relief Sculpture of the Holy Trinity from Poloma from the Workshop of Master Paul from Levoča

Eva Bezúchová[1], Michal Oravec[2] and Stanislava Trginová[3]

[1]Slovak National Gallery, Námestie SNP 1, 960 01 Zvolen; eva.bezuchova@sng.sk
[2]Slovak National Gallery, Riečna 1, 815 13 Bratislava; michal.oravec@sng.sk
[3]Slovak National Gallery, Námestie SNP 1, 960 01 Zvolen; stanislava.trginova@sng.sk

Keywords: gothic relief sculpture, workshop of Master Paul, color modifications

The object of material survey is the late-gothic wooden relief named The Holy Trinity from Poloma from the workshop of Master Paul from Levoča, dated to around 1520. It is a specific type of the Holy Trinity, where the God The Father holds the bluish dead body of Jesus Christ in his arms. The dove of the Holy spirit was not preserved. The two angels are from both sides of God the Father and they uncover his coat, like an opening curtain (1).
The object has a significant degree of damage, the wood material was attacked by wood-decay insects and the original color layers are preserved only in fragments. In the latest restoration intervention were applied thick coatings of colored waxes, which significantly suppressed the aesthetic qualities of the artwork and they had to be removed from the surface. Based on the stratigraphic analyses of cross-sections of color layers by using SEM-EDS analysis was found, that the relief went through with several color modifications during the centuries. The knowledge, how the colors of individual parts of the relief were changing, is crucial for another cleaning and removing overpaintings in the restoration process.
A part of the research is also a comparison of technological painting specifics used on the relief with the specifics of workshop of Master Paul from Levoča (2).

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Investigating Polysaccharide Based Consolidants for Fragile Archaeological Woollen Textiles

Jennifer M.K. Wakefield[1,2], Line Flo[1], Chas Jones[3], Hanna Lukesova[4], Stephen E. Harding[2], Hartmut Kutzke[1]

[1]Musuem of Cultural History University of Oslo, Kabelgata 340580 Oslo; hartmut.kutzke@khm.uio.no; jennifer.wakefield1@nottingham.ac.uk
[2]University of Nottingham. The National Centre for Macromolecular Hydrodynamics, University of Nottingham, University of Nottingham, Sutton Bonington Campus, Sutton Bonington, Leicestershire, LE12 5RD; steve.harding@nottingham.ac.uk; jennifer.wakefield1@nottingham.ac.uk
[3]Independent
[4]University Museum of Bergen, University of Bergen, Hana.Lukesova@uib.no

Keywords: Sustainable consolidants, Textiles, polysaccharide

There has been great interest in the past decade into green/sustainable consolidants. There are numerous reasons for this: one is the pressing need to move away from fossil fuels in all aspects of life. Another reason is the aim to use at these polymers in conservation that are biocompatible and reversible from the object, if needed
Wool is a material that had received less attention, compared with materials such like wood or cellulose based textiles. The present study aims to investigate several polysaccharides such as funori, microfibrillated cellulose, hydroxy propyl cellulose (Kucel G) and hydroxy propyl chitosan (not previously used in conservation) specifically for treatment of highly friable woollen artefacts. Textile artifacts are often dyed and, in order to avoid damages, the interaction between dyed fabric and potential consolidants have to be investigated. Therefore, four modern wool fabrics were dyed using three different dyeing techniques: Vat dyes, direct dyes and mordant dyes with woad, lichen, weld and madder. As reference an undyed wool fabric was treated in the same way.
The impact of the consolidants were assessed by measuring weight gain, dimensional change, water isothermal adsorption, colour changes, stiffness, and reversibility. Scanning electron microscopy (SEM) showed the behavior of the consolidant within the fabric, and artificial ageing (UV, temperature, humidity) simulated long-time museum storage of the treated fabrics to investigate stability of the treatment.

Funding

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 artifacts from the Viking Age. The project is funded by the Norwegian Research Council under the number 316268.

X-ray Methods For Assessing Desalination Efficiency and Reusability of Microcellulose Foams and Nanocellulose Aerogels in Mural Paintings

Martina Romani[1], Francesco Caruso[2], Olivia Gómez Laserna[1], Pascale Sénéchal[3], Hannelore Derluyn[3,4], Anna Nualart-Torroja[5], Àfrica Pitarch Martí[5,6], Erlantz Lizundia[7,8], Maite Maguregui[2]

[1] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain; martina.romanir@ehu.eus, olivia.gomez@ehu.eus
[2]Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain; francesco.caruso@ehu.eus, maite.maguregui@ehu.eus
[3]Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, DMEX, Pau, France; pascale.senechal@univ-pau.fr
[4]Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, LFCR, Pau, France; hannelore.derluyn@univ-pau.fr
[5]Arts and Conservation Department, Fine Arts Faculty, University of Barcelona, X/Pau Gargallo 4, 08028 Barcelona, Spain; anualart@ub.edu, africa.pitarch@ub.edu
[6]Institut d'Arqueologia de la Universitat de Barcelona, c/Montalegre 6-8, 08001 Barcelona, Spain
[7]Department of Graphic Design and Engineering Projects, Faculty of Engineering in Bilbao, University of the Basque Country UPV/EHU, 48013 Bilbao, Spain; 8 BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Scientific Park, 48940 Leioa, Spain; erlantz.liizundia@ehu.eus

Keywords: micro X-ray fluorescence, X-ray micro-tomography, nanocellulose aerogels, microcellulose foams, desalination, mural paintings

One of the primary challenges in the conservation of mural paintings is salt crystallization. Traditionally, cellulose poultices have served as the main option for salt removal in mural paintings. However, in recent decades, there have not been excessive efforts to provide new advanced cellulose-based materials for desalination of mural paintings.
Cellulose-based foams and aerogels have attracted significant attention recently, thanks to their high adsorption efficiency, eco-friendly prospects and cost effectiveness. While they have been extensively employed for pollutant removal [1], there is no existing literature reporting their potential application in the desalination of mural paintings. Foams and aerogels present significant advantages over traditional cellulose poultices in terms of water retention and reusability due to their chemically crosslinked micro- and nano-structure, respectively. Therefore, their application can minimize prolonged water exposure to the porous substrate while enhancing the capacity for salt removal. Besides formulating novel desalination solutions for mural paintings, an essential aspect involves establishing an appropriate analytical methodology to evaluate their efficacy. Usually, ion chromatography is the preferred technique for quantitatively evaluating the salt removal capacity. However, being a destructive technique, it is not possible to use it to monitor in the same painting the removal of salts before and after the desalination treatment application. Furthermore, this technique cannot offer insights into changes in the spatial distribution of salts within the painting stratigraphy. An alternative to monitor salt removal non-invasively could be micro-energy dispersive X-ray fluorescence (μ-EDXRF) imaging. However, using this technique, obtaining

information on the entire volume of a mural painting is not possible. Being able to directly monitor the removal of salts, and the evolution of their spatial distribution, without manipulating the sample would be essential to design-controlled protocols that avoid partial desalinization, the formation of salt fronts in the painting or even back diffusion problems..

For all the mentioned above, this work focuses on the validation of a new methodology based on μ-EDXRF and X-ray micro-tomography (μ-CT) to monitor, in the whole volume of a mural painting, the desalination ability of novel microcellulose foams and nanocellulose aerogels developed in the context of ENCLOSURE project [2]. To achieve this, replicas, mocking up ancient Roman wall paintings, were vacuum-impregnated with chlorides and sulfates, two of the main types of salts affecting mural paintings, to simulate salt attack. An experiment including both salts was also considered.

To monitor the desalination capacity of the foam and aerogel, each cellulose-based material was applied on a mock-up several times over a determined period. An additional experiment was conducted using traditional cellulose poultices to demonstrate the added value of the new materials proposed. Each cellulose-base material was applied several times to evaluate the progressive desalination. After each application, desalination rate was determined by μ-EDXRF imaging and the salt removal on the whole volume of the mock-ups was evaluated using μ-CT. For the successive applications of foams and aerogels on each mock-up, the same cellulose-based material subjected to a manual squeezing was employed to demonstrate their reusability.

Acknowledgements

M. Romani and O. Gomez-Laserna acknowledge their research contracts to the grant TED2021-129299A-I00. F. Caruso acknowledges his Maria Zambrano fellowship from UPV/EHU, funded by MICIU and the European Union NextGenerationEU/PRTR. Access to the DMEX Centre for X-ray Imaging from UPPA through the EXCITE Transnational Access Call 2023 (EXCITE_TNA_C4_2023-65) is gratefully acknowledged. H. Derluyn acknowledges the support from the ERC Starting Grant PRD-Trigger (grant agreement No 850853). Alvaro Tejado and Jaime García from Construction and biobased products – Energy, Climate and Urban Transition Division in Tecnalia are gratefully acknowledged for providing the microcellulose foams.

Funding

This work has been supported by grant TED2021-129299A-I00, funded by MCIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR.

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Air Quality in the Depositories of the National Library of the Czech Republic or Prevention of Book Damage

Jitka Neoralová[1], Petra Vávrová[1] , Jan Francl[1], Magda Součková[1], Rebeka Zembjaková[1], Nikola Šipošová[1] and Ludmila Mašková[2], Jiří Smolík[2]

[1]National Library of the Czech Republic, Mariánské nám. 190/5, 110 00 Praha 1, Czech Republic; jitka.neoralova@nkp.cz
[2]Institute of Chemical Process Fundamentals AV ČR, v. v. i., Rozvojová 1/135, 165 00 Praha 6-Suchdol, Czech Republic; maskova@icpf.cas.cz

Keywords: Monitoring of climatic parameters, preventive conservation, temperature, relative air humidity, air pollutants

In 2023, a professional publication summarizing the results and procedures of measuring and monitoring climatic conditions in the objects of the National Library of the Czech Republic was published. The book is intended for employees of libraries and other cultural institutions to improve the conditions of storage of written heritage. The results of long-term measurements, the development of methods for monitoring climate parameters, the possibilities of their regulation and case studies are presented. The book also contains dozens of illustrative photos of the equipment and graphic processing of the results, which illustrate overall approaches to preventive conservation and understanding the results of long-term measurements and monitoring of conditions in depositories. It is also important to compare the various types of depositories that the National Library of the Czech Republic has, where approaches for different types of buildings and interiors of depositories or storerooms are illustrated. The types of library fund materials and their degradation changes caused by the influence of the surrounding environment are also presented.
The poster presents an overview and specification of the depository buildings of the National Library of the Czech Republic, a basic overview of the procedures for measuring and monitoring climatic conditions and an example of protective measures for the preventive care of library collections.

Funding

This article was created with the institutional support of The National library of the Czech Republic for the long-term conceptual development of a research organisation provided by the Ministry of Culture of the Czech Republic.

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History and Present of Multispectral Imaging in the National Library of the Czech Republic.

Jitka Neoralová, Andrei Kazanskii

National Library of the Czech Republic, Mariánské nám. 190/5, 110 00 Praha 1, Czech Republic;
jitka.neoralova@nkp.cz

Keywords: non-invasive survey, video spectral comparator, multispectral analysis, radiography, monochromator

The use of multispectral methods for image analysis of illuminations, written texts or already invisible drawings and writings has a long tradition in the National Library. The principle of multispectral analysis is based on the possibility of observing a historical document in a wide range of wavelengths, namely in the UV region, in the visible light region, or even in the near IR region. Thanks to photographing the document in different areas of radiation, we obtain several images in which the searched elements are displayed very differently, which facilitates their interpretation. The acquired images are compared and processed using specialized software for image analysis, which allows various operations and combinations with the acquired records (image segmentation, thresholding, addition or subtraction of individual images, etc.). In this way, the maximum amount of information can be extracted and a significantly better result can be achieved, for example in making unreadable text visible [Cosentino 2015]. The poster presents the development of multispectral analyzes in the National Library of the Czech Republic. From color filters on light sources on the microscope, monochromator, infrared camera to today's equipment Videospectral comparator, forensic lamps and X-ray.

Funding
This article was created with the institutional support of The National library of the Czech Republic for the long-term conceptual development of a research organisation provided by the Ministry of Culture of the Czech Republic.

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Neutron RADIOGRAPHY of Moisture Sorption/Desorption in Halloysite Nanotube-Treated (New and Historical) Leather in a Controlled Environment

Elena Badea[1,2], Cristina Carsote[2,3], Marianne Odlyha[4], Chloe Pearce[4], Genoveva Burca[5,6], Bogdan-Florin Rusu[2]

[1]Department of Chemistry, Faculty of Sciences, University of Craiova, Calea București 107, Craiova, Romania; elena.badea@edu.ucv.ro
[2]Advanced Research for Cultural Heritage Group (ARCH Lab), National Research and Development Institute for Textiles and Leather, ICPI Division, Strada Ion Minulescu 93, Bucharest, Romania
[3]Center for Research and Physical-Chemical and Biological Investigations, National Museum of Romanian History, Calea Unirii 12, Bucharest, Romania; criscarsote@yahoo.com
[4]Birkbeck College, University of London, Malet Street, Bloomsbury, London WC1E 7HX4, United Kingdom; m.odlyha@bbk.ac.uk; cpearc03@mail.bbk.ac.uk
[5]STFC, Rutherford Appleton Laboratory, Didcot, OX11 0QX, United Kingdom
[6]Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, OX11 0DE, United Kingdom; genoveva.burca@diamond.ac.uk

Keywords: historical leather, consolidation, halloysite nanotubes, moisture sensitivity, neutron radiography

Halloysite nanotubes (HNTs) are natural nano clays with a large aspect ratio that are effective for reinforcing polymeric matrixes, such as collagen, that need strengthen due to ageing-induced degradation [1-2]. Leather is sensitive to moisture and especially susceptible to environmental fluctuations in temperature and relative humidity (RH). Uncontrolled environments found in historic houses and palaces can cause hydrolytic degradation and mechanical damage to leather. To simulate this situation in an experimental setting, leather samples were mounted in a custom-made closed-cell and subjected to programmed cycles of RH at a controlled temperature while exposed to the neutron beam. We report results for untreated (new and historical) and treated samples treated with HNTs in aqueous (hydroalcoholic urea-sodium chloride solution) and nonaqueous (PEG 400) media. Urea facilitated moisture diffusion, while PEG showed a tendency to slow it. The results were compared with the changes in the hydrothermal denaturation of collagen (shrinkage activity), molecular structure (FTIR-ATR) and relaxometry parameters (^{1}H NMR). The changes in storage and loss moduli as measured by Dynamic Mechanical Analysis (DMA) with the same cyclic RH program and temperature were also determined. Treated samples shown higher hygroscopicity than the new ones, while the historical samples are less hygroscopic than the new ones. This behaviour was correlated with the hydrothermal denaturation of collagen-tannin matrix and changes in its triple helix structure as revealed by X-ray diffraction (XRD) pattern. The experimental setup and resulting data provide a pilot study demonstrating the potential of neutron radiography in following and comparing real-time moisture diffusion dynamics in untreated and HNT-consolidated leather and assisting in

validating the overall benefit of the treatment. Besides, leather moisture sorption/desorption behaviour is a critical parameter to be taken into account when setting the environmental parameters of the ehhibition/storage spaces.

Acknowledgements

UKRI Grant Monitoring effects of RH fluctuations on leather based cultural heritage objects. Experiments RB2320345 (ISIS Neutron and Moun Source) and MG35634 (Diamond Light Source).

Funding

Eureka Project PN-III-P3-3.5-EUK-2019-0211 „IoT-based system for monitoring museum environment (MUSEION)".

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Protection of Bronze and Its Black and Green Patina from Atmospheric Corrosion by Polymer Nano-thick Coatings

H. Bach-Rojecky[1], D. Šatović[2], E. Pezić[1], V. Desnica[2], B. Markulić[1], M. Mirosavljević[1], D. Kralj, K. Marušić[1]

[1]Ruđer Bošković Institute, Division of Materials Chemistry, Laboratory for Precipitation Processes, Bijenicka cesta 54, Zagreb, Croatia
[2]Academy of Fine Arts, Department of Conservation and Restoration, Ilica 85, 10000 Zagreb, Croatia

Keywords: Bronze, patina, nano-coatings.

Most of the outdoor bronze sculptures are covered with various patinas, which emphasize the aesthetics of the object and at the same time provide protection from the environment to which they are exposed. Patinas can be formed naturally as the bronze is exposed to its environment over time, or they can be formed synthetically, with the recipe for synthesis chosen according to the desired effect and colour. Naturally, the protection and stabilization of the bronze and its patina is of utmost importance. However, the protection used today is short-term and must be repeated at short intervals. However, the development of new protection systems is very challenging, as the protection must not only be protective and stable, but also environmentally friendly and should not alter the aesthetic appearance of the sculpture.
In this work, we investigate the possibility of protecting bronze and two types of patinas from simulated atmospheric conditions using extremely thin polymer nano-coatings based on behenic acid. A black patina was created on the RG7 bronze by applying a K_2S solution and a green patina from a (NH4)2CO3 + NH4Cl solution. Behenic acid was applied to both the bronze and the patinas by spontaneous adsorption from an ethanol solution. The molecular layer formed was further polymerized by gamma irradiation. The protective properties of the coatings were investigated by electrochemical methods, while the patinas were characterized by SEM/EDX, XRF, Raman spectroscopy, colorimetry and contact angle measurements.

Funding

Authors thank the Croatian Science Foundation (HRZZ IP-2020-02-4344) for supporting the research.

Study of Degradative Effects of Low-temperature Plasma on Objects of Heritage Made from Natural and Synthetic Polymers

Dominika Smatanová

Department of Wood, Pulp, and Paper, Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia; dominika.smatanova@stuba.sk

Keywords: plastics in objects of heritage, plasma, degradation

Plastics have become an integral part of cultural heritage, yet misconceptions about their durability have led to neglect in their conservation. This oversight has resulted in the rapid degradation of materials such as cellulose nitrates, acetates, polyvinyl chloride (PVC), and early polyurethanes. The degradation of these materials stems from various internal and external factors, including temperature, light, air pollution, manufacturing processes, storage conditions, and microbial attacks.

Cleaning and sterilization of plastics present significant challenges due to their sensitivity to high temperatures and solvents. Low-temperature plasma, an ionized gas, offers a promising solution—a safe, environmentally friendly, and efficient technology. While plasma treatment has been explored in heritage conservation for materials like wood, paper, and silk, research in plastics conservation remains scarce, with only limited studies focusing on changes in adhesion properties during the repair of plastic objects. Conversely, the application of plasma sterilization has been studied in medical and biomedical fields.

This study aims to investigate the effects of plasma treatment on selected synthetic materials—PVC, polyurethane (PUR), and polyethylene (PE)—with a focus on degradation. The examined parameters include plasma gas, exposure time, and power.

Funding

This study was funded by the Slovak Research and Devolepment Agency under contract No. APVV-20-0410, project PolArt.

Diversity of Chemical Composition of Synthetic Paints Present on Polish Painters' Pallettes

Magdalena Wróbel-Szypula

Laboratory for Research and Protection of Museum Collections, National Museum in Warsaw; email: mwrobel@mnw.art.pl

Keywords: synthetic paints, palettes, 19th/20th century art, FTIR-ATR, XRF

Palettes are very important memorabilia that allow to analyse deeper the workshop of each artist. The first synthesis of organic dye that took place in the middle of the 19th century [1] had diametrically changed the technology of paints' production. Since then the composition of painters' palettes has been considerably increasing. This fact is perfectly illustrated by identification and comparison of components of paints belonging to 3 Polish artists: Tadeusz Makowski (1882 – 1932), Xawery Dunikowski (1875 – 1964) and Monika Żeromska (1913 – 2001) by ATR – FTIR (attenuated total reflectance Fourier – transform infrared) and XRF (X-ray Fluorescence) spectroscopy.
In each palette 4 colours were compared: red, blue, yellow and green. In case of blue colour synthetic ultramarine was used by two of artists. This pigment, which replaced its natural equivalent, has been produced since 1828 [2]. On the other hand Xawery Dunikowski used even more modern synthetic dye, namely phtalocyanine blue which has been synthesized from 1930s [3]. Cadmium yellow was used in all palettes. It is also a synthetic pigment that has been very popular among painters even starting in 19th century since its discovery in the mid 1840s [4]. Each of the artists used different synthetic red paints: organic alizarin, eosin (geranium lake) and inorganic cadmium sulfoselenide. All of them have been manufactured synthetically since the second half of 19th century [4, 5, 6]. Identification of green paints' composition allowed to confirm dating of the palettes as in Makowski's paints emerald green was found. Production of this pigment was discontinued in the first decades 20th century because of the toxicity of acetoarsenite [7]. On the contrary, in Dunikowski's palette green paint consisted of phtalocyanine dye, which overlaps with the blue paint on the same palette. Sample of Żeromska's green paint could be an example of a chrome pigment undergoing ageing reaction from lead chromate to chromium oxide, sulphate and acetates [8].
These results are the beginning of complex studies on the development of workshops of painters that were using modern synthetic paints from the industrial revolution in the 19th century until contemporary art in the 21st century using FTIR-ATR and XRF spectroscopy.

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Development of Green Strategies for the Cleaning of Street Art and Paintings

S. Prati[1], F. Ramacciotti[1-2], A. Menichetti[2], G. Di Cara[1], B. Keser[1], G. Sciutto[1], C. Gualandi [2], M. Montalti[2], M.L. Focarete[2], R. Mazzeo[1]

[1]Università di Bologna, Microchemical and Microscopy Art Diagnostic Labratory, Department of Chemistry G. Ciamician, via G. Guaccimanni 42 Ravenna,
[2]Università di Bologna, , Department of Chemistry G. Ciamician, Via Selmi 2 Bologna

Keywords: green restoration, cleaning, paintings, street art

In the field of restoration, there is a growing demand for the advancement of eco-friendly methodologies that ensure safety for both operators and the environment. To this aim gels produced using biopolymers such as polyhydroxybutyrate and agar, in conjunction with green solvents (including Dimethylcarbonate, γ-Valerolactone, Ethyl Lactate, Biodiesel, and green Deep Eutectic Solvents) have been used to remove different unwanted coatings from artistic artifacts, encompassing movable and immovable paintings, metal objects, paper substrates, and cinematographic films [1-4]. More recently electrospun nonwoven (ES)s have been proposed as carriers of green gels [5] and solvents [6].
Under the auspices of the Italian-funded initiative Superstar (https://prin2020superstar.dcci.unipi.it/), we are developing innovative green cleaning systems tailored for street art, aimed at eliminating deposits or vandalic paints superimposed upon graffiti, while in the frame of the European project GOGREEN, we are studying suistanible methodologies for the removal of aged varnishes from paintings and the treatment of tarnished metals.. To this extent a biobased ES mat obatined with pullulan has been tested as carrier of gamma valerolactone. The pullulan based non wovens have been also functionalized with a photoactive materials capable to produce a localized increase of temperature when enlighted with a LED source with the aim of favoring the removal of high insoluble coatings such as alkyd sprays and aged natural resins.

Acknowledgements

Sustainable Preservation Strategies for Street Art (SuPerStAr) funded by MUR, PRIN; Green Strategies To Conserve The Past And Preserve The Future Of Cultural Heritage (GOGREEN); financing institution: EUROPEAN COMMISSION (HORIZON EUROPE)

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Investigation of the Effects of Ion Beams Techniques on Parchment: Using FTIR Imaging System Coupled with Advanced Data Processing Methods

Mingchi Ma[1], Giorgia Sciutto[1], Emilio Catelli[1], Zelan Li[1], Rocco Mazzeo[1], Boglárka Döncző[2], Zita Szikszai[2], Silvia Prati[1]

[1]University of Bologna, Department of Chemistry "G. Ciamician", Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), via Guacciamnni 42, Ravenna, 48121, Italy; mingchi.ma2@unibo.it
[2]HUN-REN Institute for Nuclear Research (ATOMKI), Bem tér 18/c, 4026, Debrecen, Hungary; szikszai.zita@atomki.hu

Keywords: Proton beam irradiation; Parchment degradation; Fourier Transform Infrared Spectroscopy; Principal Component Analysis

Ion beam analysis (IBA) has been proven to have distinctive capabilities for the non-destructive analysis of the elemental composition of artifacts, particularly its efficacy in light element detection. External beam IBA techiniques such as particle induced X-ray emission (PIXE), particle induced gamma-ray emission (PIGE), and Rutherford or elastic backscattering spectrometry (RBS/EBS) enhance the measurement and quantification of light elements that cannot be easily achieved by many conventional methods [1]. One limitation of these techniques may concern the effects on organic-based objects, and recently, attention has been devoted to the evaluation of the effects on protein-based materials, such as parchment. Indeed, high dose exposure may cause the break of collagen molecules implying denaturation, hydrolysis, and oxidation processes [2–4]. These chemical effects pose a great concern for scientists, as they modify the chemical structure of the material and result in visible damages such as yellowing and darkening of the analyzed area. Therefore, it is vital to determine the exposure limits of the technique, both in terms of duration and ion beam dosage, to avoid any damage to the sample and ensure a safe application for users.

This study presents an in-depth evaluation of the effects of ion beams technique on plain parchment, using Micro Fourier Transform Infrared Spectroscopy mapping (μ-FTIR). The objective is to identify the main chemical variation related to ion beam dosage and the resultant color modification. A series of parchment samples were exposed to varying doses of proton beam irradiation (from 0.125, up to 20 μC/cm^2, provided by ATOMKI), with evident yellowing areas related to the highest dose exposure, and then submitted to both Mid-Infrared (MIR) and Near-Infrared (NIR) (7000–675 cm^{-1}) analysis. The utilization of micro infrared spectroscopy in mapping mode aims to understand the extent of degradation and structural alterations that occur in response to different levels of proton beam dosage, and to generate chemical maps of the degradation markers. The parchment fragments were positioned at the center of a lighter and smoother surface, measuring approximately 8 x 8 mm^2. Sample subjected to higher dosage exhibited a noticeable yellowing at the center spot.

The data obtained by performing infrared mapping on both damaged and undamaged parchment samples were processed through multivariate analysis in order to consider

all the variables and their related modifications within the NIR-MIR region. Principal Component Analysis (PCA), in particular, facilitates effective data dimension reduction and the extraction of the most useful information to unveil the degradation patterns [5]. It was also used to highlight the most important variables involved in the modification of the chemical structure induced by the irradiation process.
Preliminary results from this study provide valuable insights into the vulnerability of parchment to proton beam irradiation and contribute to a better understanding of the degradation mechanisms of parchment-based cultural heritage materials subjected to ion beam irradiation.

Funding

This research has been funded by the H2020 European project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science, GA 871034).

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Proteomics for SafeSilk: Mass Spectrometry-based Protein Sequencing to Study the Effect of Weighting on Museum Silk Objects

Fabiana Di Gianvincenzo[1], Ibrahim Elrefaey[1], Aya Osama[2], Ida Kraševec[1], Sameh Magdeldin[2], and Matija Strlič[1,3]

[1]Heritage Science Laboratory, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna Pot 113, Ljubljana (Slovenia); fabiana.digianvincenzo@fkkt.uni-lj.si, ibrahim.elrefaey@fkkt.uni-lj.si, ida.krasevec@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si
[2]Children's Cancer Hospital Egypt 57357, 1 Seket Al-Emam Street – El-Madbah El-Kadeem Yard – El-Saida Zenab – Cairo; aya.osama@57357.org, sameh.magdeldin@57357.org
[3]University College London, Institute for Sustainable Heritage, 14 Upper Woburn Place, London (UK)

Keywords: silk, proteomics, mass spectrometry, protein damage

Silk is a protein-based fabric, first produced in China about 7000 BCE from the cocoons of the wild species Bombyx mandarina, and later from other species of silkworm, such as the domesticated B. mori and various Antheraea species. The different species are used to produce different types of silk: for example, Bombyx species are used to produce Mulberry silk, whereas Antheraea species to produce Tasar silk. The physical and mechanical qualities of the fabric will differ based on the type of silk, also due to differences in the primary structure of the proteins, that is the amino acid sequence of the proteins produced by different silkworm species. The production technique and treatments applied to silk fibres or fabric will also influence the characteristics of the final material. A notable example is represented by weighting procedures, used in the 19th- and 20th-century Western world mainly to increase the weight of the material, and thus its price, and in connection with dyeing and mordanting processes. Various organic and inorganic substances, and in particular metallic salts have been used as weighting agents. Besides modifying the mechanical properties of the fabric, conservators have suggested that weighting accelerates and accentuates the damage of silk artefacts in museum collections, albeit the connection between weighting and damage is still not clear [1].

The SafeSilk project [2], a collaboration between research institutions in Slovenia and Belgium, aims at investigating the impact of weighting on the preservation of silk objects from museum collections. In this context, the investigation of silk samples with tandem mass spectrometry-based proteomics can be extremely informative. This technique investigates the primary sequence of all the proteins present in a sample, thus allowing to accurately identify the species of origin of the material by comparing the experimental data to public databases of protein sequences. In addition, the presence of modifications throughout the sequence can be investigated, revealing the chemical reactions occurred in the material, which can be connected to the display and storage conditions of the object (for example, photo-oxidation due to exposure to light), as well as to the presence of weighting agents.

Thus far, proteomic research on archaeological and historical silk has focused mostly on the identification of the species of silkworm, with a few studies also looking into protein damage [3]. In this project, a protocol adapted from literature [4] was used

to extract and characterise proteins from silk mock-ups subjected to weighting and artificial ageing in controlled conditions of UV-light exposure, temperature, and relative humidity. The results indicate that the protocol can successfully lead to the identification of the species of silkworm, even when different types of silk are mixed to produce the fabric. Moreover, damage patterns such as (photo-)oxidation can be detected in aged silk proteins, in connection with the ageing conditions and the presence of weighting agents. Future applications of the protocol to real museum samples will allow to connect the damage modifications to display and storage conditions, macroscopic damage, and the presence and type of weighting agents.

Funding

The SAFESILK project (N1-250) is funded through the WEAVE program in collaboration between FWO (The Research Foundation – Flanders) and ARIS (Slovenian Research Agency). Further funding by the ARIS Programme group N-DAD is acknowledged. Fabiana Di Gianvincenzo is funded by the Slovenian Research Agency Core Funding (project P1-103).

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MA-XRF Study of van Gogh' use of Geranium Lake

Teresa Scovacricchi[1], Elvira Scialla[2], Alba Alvarez-Martin[3], Matthias Alfeld[4], Geert Van der Snickt[1] and Koen Janssens[1]

[1]AXIS group, Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium, teresa.scovacricchi@uantwerpen.be
[2]Department of Mathematics and Physics, University of Campania 'Luigi Vanvitelli', Viale Lincoln 5, 81100 Caserta, Italy, elvira.scialla@unicampania.it
[3]Conservation and Science, Rijksmuseum, Amsterdam, 1071ZC Amsterdam, The Netherlands, a.alvarez.martin@rijksmuseum.nl
[4]Materials Science and Engineering, Delft University of Technology, Delft, The Netherlands, m.alfeld@tudelft.nl

Keywords: Van Gogh, MA-XRF, Geranium Lake

The artistic production of Vincent Van Gogh(1853-1890)is usually divided into sections based on his stays in The Netherlands, Belgium and France within the time period November 1881- July1890. His activities not only put him in contact with the color theory of Delacroix and Le Blon but also with innovative artistic materials of his time such as emerald green, chrome yellow and geranium lake [1].
Historical geranium lake recipes describe the precipitation of the eosin dye (a tetra-brominated xanthene) onto aluminum or lead salts to form an insoluble pigment, the result of which is an aggregate of eosin molecules complexed to the metal substrate. However, despite its brightness and beautiful hue, from purple to pink, this family of brominated lake pigments tends to rapidly fade under the influence of light. The identification and distribution mapping of these lake pigments, either in faded or unfaded state, is possible by means of scanning macro-XRF (MA-XRF) via the use of the Br-K emission signals, but poses a challenge at low concentration levels [2]. The characteristic Br lines overlap with those of other elements commonly present in paintings such as lead, mercury and arsenic. Further difficulties arise in the case of overpainted works of Van Gogh with complex stratigraphy.
In this study, MA-XRF data obtained from 22 Van Gogh paintings, part of different museum collections and dated between the 1885 till 1890, were (re)considered. An overview of the artist's palette can be obtained through which we can validate previous studies and expand the knowledge gathered so far. From the processed data, it is possible to conclude that Van Gogh already incorporated geranium lake in his palette during the Neunen period. The MA-XRF data reveals that geranium lake was used throughout his period of production for various purposes such as shading or contouring;various (pink to dark-red) tints were obtained by mixing the geranium lake with other pigments.

Acknowledgements

The authors wish to acknowledge the help and assistance received from various individuals in the Van Gogh Museum (Ella Hendriks), the Kroeller-Mueller museum

(Luuk Van der Loeff, Margje Leeuwenstein), the Museum of Modern Art (Ana Martins) and others during the collection of the MA-XRF data used in this study.

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Sustainable Archival Materials for Historical Paper Collections: A New Protocol for Characterizing and Assessing the Impact of Volatile Organic Compounds

Fabiana Di Gianvincenzo[1], Randa Deraz[1], Ivan Mitevski[2], Manfred Anders[3], Katharina Schuhmann[3], Jasna Malešič[4], Irena Kralj Cigić, Abdelrazek Elnaggar[1], Matija Strlič[1,5]

[1]Heritage Science Lab Ljubljana (HSLL), Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia;
Fabiana.DiGianvincenzo@fkkt.uni-lj.si, Randa.Deraz@fkkt.uni-lj.si, irena.kralj-cigic@fkkt.uni-lj.si, Abdelrazek.Elnaggar@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si.
[2]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia;
im5543@student.uni-lj.si.
[3]ZFB – Zentrum für Bucherhaltung GmbH, Germany; anders@zfb.com, k.schuhmann@zfb.com.
[4]National University Library (NUK), Slovenia; jasna.malesic@nuk.uni-lj.si.
[5]UCL Institute for Sustainable Heritage, University College London, United Kingdom.

Keywords: formic acids, degree of polymerization, preventive conservation.

The long-term storage of historical paper collections is a critical issue for decision-makers in museums, libraries, and archives which significantly affects the conservation management of paper collections. It is still unspecified which packaging material (plastic/cardboard, lignin-free/lignin-containing boxes) is more protective, cost-effective, and environmentally preferable for the long-term storage of paper collections. The quantitative measurement of emissions of acetic and formic acids from storage materials is very important because of the known risks to heritage preservation associated with the presence of these acids [1], [2], [3]. This research aims to determine the volatile organic compounds emitted by different types of cardboard and plastic-based storage archival materials and evaluate how deacidification and coating treatments affect volatile organic compound (VOC) emissions of recycled archival boxes. The amount of total volatile organic compounds (tVOCs) emitted by the Air-tight boxes storage archival materials has been measured (in parts per million – ppm) during a temperature cycle from 15 °C to 35 °C, to estimate the quantitative variation of emissions in changing temperatures, but with constant relative humidity. Two sampling approaches were used to qualitatively evaluate the VOC emissions from a subset of the studied boxes: (1) Solid Phase Micro-Extraction (SPME), and (2) Tenax® TA sorbent tubes. A new methodology for quantitative measurement of emissions of acetic and formic acids from storage archival materials was also tested based on the official protocols for the analysis of emissions of acetic and formic acids [4], [5]. The analytes were then extracted and quantified using ion chromatography (IC). To assess the impact of VOCs emitted by the tested archival boxes on the paper collections, a modified Oddy test protocol [6], where the effect of volatile emissions on reference paper materials is tested, was used to test a subset of the studied materials.
Preliminary data analysis shows that results obtained with Tenax sampling were overall similar to those obtained from the SPME analysis, and most of the identified compounds were hydrocarbons. The results from the materials examined show that

the amount of tVOCs emitted is higher when the temperature rises, as expected, and decreases when the temperature is lowered again. The VOCs emissions from the polypropylene (PP) archival boxes are higher than all cardboard samples, both in intensity and in number of identified compounds. The effect of emissions from different materials is evaluated based on quantified changes of the degree of polymerization (DP) of reference cellulose paper. For the cardboard and PP samples, there is little effect on the DP, indicating a preservation effect or moderate cross-infection for the recycled samples, the results indicate significant cross-infection when compared to the protocol blank. This effect is probably due to emissions of acetic and formic acids, highlighting the importance of optimising a protocol to detect such emissions. Further experiments are ongoing to optimise the detection of acetic and formic acid emissions, as well as the interpretation of the detected organic emissions.

Acknowledgements

The authors acknowledge Ms. Marta Kozole, Faculty of Chemistry and Chemical Technology, University of Ljubljana, for her contribution to the analysis of organic emissions from cardboard boxes. Also, the authors acknowledge Ms. Ivana Štular, Heritage Science Lab Ljubljana (HSLL), Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia for her help with tVOCs emission tests.

Funding

Funding provided by the European Union (GREENART project, Horizon Europe research and innovation program under grant agreement no. 101060941). The work supported by the programme group of "N-DAD: Non-destructive Analysis and Diagnostics".
Fabiana Di Gianvincenzo is funded by the Slovenian Research Agency Core Funding (project P1-103).

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Microorganisms Assisted Formation of Calcium Oxalate on Cultural Heritage Materials

Ludovico Geminiani[1,2], Cristina Corti[2,3], Antonella De Stefano[1], Laura Rampazzi[2,3,4], Giancarlo Ranalli[5], Elisabetta Zanardini[1]

[1]Department of Science and High Technology, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como; L.G. lgeminiani@uninsubria.it; E.Z. elisabetta.zanardini@uninsubria.it
[2]Centre for Cultural Heritage Studies, Università degli Studi dell'Insubria, via Valleggio 9, 22100 Como, Italy
[3]Department of Human Sciences and of Innovation for the Territory, Università degli Studi dell'Insubria, Via Valleggio, 9, 22100 Como; C.C. cristina.corti@uninsubria.it; laura.rampazzi@uninsubria.it
[4]Istituto per le Scienze del Patrimonio Culturale, Consiglio Nazionale delle Ricerche (ISPC-CNR), via Cozzi 53, 20125 Milano, Italy
[5]Dip. di Bioscienze e Territorio, Università degli Studi del Molise, C.da Fonte Lappone snc, 86090 Pesche (Is); ranalli@unimol.it

Keywords: calcium oxalate, biodeterioration, calcium soaps

There is still debate about the origin of calcium oxalate films, a significant contributor to the colour change of stone materials [1]. The suggested origins include the biogenic production by oxalic-acid-generating microorganisms and the chemical development of oxalic acid through the oxidative breakdown of biological coatings on stone surfaces, a consequence of previous polishing and restoration works involving natural materials such as lipids, proteins, and carbohydrates [2]. Recent research works [3] showed that oxalate salts could be also the decay product of the Japanese lacquer (urushi), which is a natural polymer obtained from the exudate of the tree Rhus Verniciflua. This lacquer is widely employed in East-Asian art for finishing wood and metallic surfaces. Historical texts and contemporary analyses also mention the incorporation of calcium carbonate powder as a filler in lacquer, providing a straightforward explanation for the presence of calcium ions. The present work aims to clarify the mechanisms leading to the formation of oxalate films due to microbial metabolic products. In literature, previous experiments investigating the biological formation of calcium oxalate revealed that various fungi, as well as bacteria, can produce organic acids, notably oxalic acid [4]. This acid reacts with carbonate substrates to yield calcium oxalate. Unlike many studies using liquid cultural media and non-environmental conditions, the experimental design which was developed in this study aimed to replicate real-world conditions as closely as possible.

Both stone and lacquered specimens were subject to microbial growth tests. Stone substrates received various organic treatments (whole egg, linseed oil, and gum arabic), both fresh and artificially aged. For Japanese lacquers, three different mixtures were employed, incorporating filler ($CaCO_3$) and two types of additives (perilla oil and rice starch). Bacterial and fungal inocula were obtained from the microbiological sampling of a bas-relief (located at the external façade of Pisa Cathedral) and of some Japanese urushi-lacquered armors (Morigi Collection, Museo delle Culture, Lugano, Switzerland). Both the sampling contexts showed the presence of calcium

oxalate. After the inoculation, the mock-up samples underwent high humidity and ambient temperature conditions. The microbial growth was assessed over time through microscopic observation (SEM), while the formation of organic acids and of oxalate salt was monitored by Fourier transform infrared spectroscopy (ATR-FTIR and external reflection-FTIR) and by X-ray diffraction (XRD).
Results on stone specimens revealed that added organic substances served as favorable microbial growth substrates, promoting chemical reactions leading to the formation of calcium oxalate and unexpected compounds, such as metal soaps, commonly found in oil paintings due to fatty acid saponification. The presence of organic substances may affect microbial production of hydrolase enzymes, potentially leading to the formation of calcium soaps. In particular, mycetes exhibited substantial growth and adaptation capabilities, hydrolyzing triglycerides from egg and linseed oil through metabolic enzymes.
This study underscores the significant influence of microbial growth on the formation of decay products like calcium oxalate and calcium soaps. It happened significantly using an experimental design which was developed to replicate real-world conditions as closely as possible. Infrared spectroscopy and X-ray diffraction proved valuable in characterizing substrates, organic substances, and inocula. In particular, portable external reflection infrared spectroscopy was able to detect bacterial and fungal growth in real time. That suggests a possible use of the technique as a mean to evaluate the presence of biological colonization on cultural materials surfaces and remnants of microbiological activity after biorestoration and biocleaning works.

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Analytical Evidence and Imitation of "Hungarian Mountain Green", a Semi-natural Cu Pigment from Banská Bystrica (Neusohl) Region

Markéta Žůrková[1], Silvie Švarcová[1], Janka Hradilová[1], Petr Bezdička[1], Miroslav Lacko[2] and David Hradil[1]

[1]ALMA Laboratory, Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec 1001, 250 68 Husinec-Řež, Czech Republic; zurkova@iic.cas.cz, svarcova@iic.cas.cz, hradilova@iic.cas.cz, petrb@iic.cas.cz, hradil@iic.cas.cz

[2]Friedrich-Christian-Lesser-Kolleg für Ostmitteleuropa, Friedrich-Schiller-Universität Jena, Fürstengraben 1, 07743 Jena, Germany; mir.lacko@gmail.com

Keywords: copper pigments, Upper Hungary, polychromies, panel paintings

In the past, various copper compounds have been used as blue and/or green pigments, including copper carbonates such as natural minerals malachite and azurite or their artificial analogues (the so-called verditers), intentionally prepared copper acetates (Verdigris) or various basic copper chlorides and/or sulphates of ambiguous origin. The increasing number of detected copper sulphates (such as brochantite, posnjakite or langite), e.g., in Dutch paintings from the late 15th to 16th century [1], implies they were probably more common than considered previously. The con-joint occurrence of copper sulphates with spherulitic malachite ($Cu_2(CO_3)(OH)_2$) might indicate their precipitation either following some synthetical procedure [2] or from water drained from copper mines [3] (Heydenreich et al., 2005).

Within the contribution, new evidences of copper sulphates found in various medieval polychromed sculptures or panel paintings will be presented, including, e.g., pieces of Master Paul of Levoča, the significant carver of the early 16th century in Upper Hungary (currently Slovakia).

Recently, the history of semi-natural formation of copper sulphates and/or malachite, intentionally collected from reservoirs of copper sulphate rich mine drainage water leaking from abandoned galleries located for example in the Banská Bystrica region, Slovakia has been examined [4]. The historic documents evidence a significant production of green colour known as "Schifergrün" or "Berggrün") gained as a secondary product of copper mining in Piesky (near Špania Dolina) and Lubietová at least from the second half of the 15th century to 1950 as well as the trading in this commodity across the Europe. However, from the chemical point of view, the composition of this semi-naturally produced green has not been specified satisfactorily.

Considering this green pigment consisted of both basic copper sulphates and malachite (as it is indicated by their con-joint presence in paintings), the simulation reactions were carried out to define the conditions of the chemical conversion from Cu(II) sulphate-based compounds to malachite in laboratory conditions. Since the effort was to simulate the conditions in the locality of the green colour production, the particular attention was paid to chemical composition of mine drainage water (reported for example for Lubietova by Majzlan et al. [5] with respect to variation of concentrations of the key ions for this conversion, i.e., Cu^{2+} and CO_3^{2-}. The final and/or intermediate products of experiments were characterised by X-ray powder diffraction

and vibrational spectroscopic techniques in order to determine the effect of different conditions on the final chemical composition of the product. Furthermore, the morphology of products was studied by scanning electron microscopy with the aim to identify possible morphological features suitable for distinguishing semi-naturally formed malachite and copper sulphates from the synthetic ones.

Acknowledgements

The authors thank to all colleagues who participated in the research and analyses, to scientists, restorers, art historians, curators and artworks' owners collaborating in the investigation of paintings.

Funding

The research was funded by Czech Science Foundation, project no. 22-17966S.

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Optimization of Scanning Parameters for Non-invasive Image Analysis Using MA-XRF Spectrometry

Michal Pech and Janka Hradilová

ALMA Laboratory, Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec 1001, 250 68 Husinec-Řež, Czech Republic; pech@iic.cas.cz, hradilova@iic.cas.cz

Keywords: imaging methods, MA-XRF scanning, painting, pigments

MA-XRF spectrometry is a rapidly developing non-invasive technique that is particularly useful for the identification of inorganic pigments [1] and the visualisation of a painting technique and hidden structures [2]. This method offers the possibility of high resolution and scanning of large images, but it poses the challenge of large data volumes and long measurement times.

The main measurement parameters that affect the overall time are the size of the area to be measured, the pixel measurement time and the pixel size. The choice of these parameters is crucial according to the objectives of the analysis. For studying techniques and fine details, it is advisable to choose a higher resolution, but at the cost of longer measurement time. Conversely, a longer measurement time yields higher quality spectra and more reliable trace element detection and resolving spectral overlaps.

Exceeding certain parameter limits only increases the overall measurement time without providing additional information. Consequently, the correct choice of parameters has also economic benefits, as the measurement time of the instrument is expensive. In some cases it may even be more advantageous to perform an indicative lower quality scan and then supplement it with higher quality details, spot measurements or analysis by other methods. Such an approach allows efficient use of available resources and optimal analysis results.

Operators often base their choice of measurement parameters solely on their experience. However, in practice, it is often advantageous to perform a series of tests with different parameters, evaluate their quality and select the optimum settings based on this. [3-5]

In this study, the procedure for optimizing measurement parameters was firstly carried out on technological copies of paintings with a known composition and stratigraphy of layers and then applied to actual artworks‘ investigation. This example allows to assess whether the measurement provides maximum information. The subsequent analysis of the results helps to identify the ideal combination of parameters for a given situation and ensures the effective use of MA-XRF spectrometry in the study of artworks.

Acknowledgements

The authors thank to all colleagues who participated in the research. Further they thank to the Academy of Fine Arts in Prague and artworks‘ owners collaborating in the investigation of paintings.

Funding

The research was funded by Czech Science Foundation, project no. 22-17966S.

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Identification of Textile Fibers of Funerary Textiles from Different Burial Contexts

Zuzana Machatová[1], Ingrid Ondrejičková-Soboslayová[2] and Sylvia Birkušová[1]

[1]Department of Conservation and Restoration, Academy of Fine Arts and Design in Bratislava, Drotárska 44 811 02 Bratislava, machatova@vsvu.sk
[2]Department of Textiles, Academy of Fine Arts and Design in Bratislava, Drotárska 44 811 02 Bratislava

Keywords: funerary textiles, identification, bast fibres,

Differentiation between various sources of bast fibers represents one of the major challenges in fiber identification protocols, even if ample amount of intact sample is avalilable for the analysis. The analysis of textile fragments from archaeological textile is complicated by limited size of sample and often significant degradation of the fibre. However, the characterization of funerary textiles may contribute to interpretation of social and ethnographic contexts and contributes to elucidation of the details of funeral rites and spiritual beliefs.
Morphological analysis using optical and polarizing microscopy is one of the basic methods of fiber identification and characterization. The modified Herzog test is often cited as one of the most effective protocols for identification of bast fibers [1].
In this study, performance of the identification protocol based on optical and fluorescence microscopy, polarization microscopy and the modified Herzog test, Raman and FTIR spectroscopy and microchemical staining for identification of severly degraded textile fibers, was tested.
Fragments of funerary textiles from Žilina (cleaned as well as non cleaned fragments from ossarium, exhumed and relocated from individual grave sites) and Church of st. Egidius in Bardejov (well preserved individual graves) were analysed. The results were compared according to several parameters: survival of different types cellulose fibers, presence of fiber modification (sizing) and fibrillation indices of individual fiber types.
The extreme conditions determined by the processes of decomposition of soft tissues often lead to significant degradation of cellulosic fibers and often the subsequent manipulation with the excavated fragments facilitates further degradation. There are many factors that affect the rate of decomposition in a grave site in temperate zone – e.g. climatic conditions, depth of the grave, characteristics of the soil (e.g. pH, moisture, pedological profile) and method of burial (e.g. clothing and textiles with ritual significance). The presence of sawdust and straw in coffins, which can significantly increase the temperature and affect the circulation of liquids in the system. This complexity makes designing of funerary textiles model systems very challenging. In this study, we decided to focus on basic preliminary model experiment, based on modifiying one variable at a time. Fragments of silk, hemp and flax textiles were buried in sandy subsoil (correlation with fragments from Bardejov) and clay subsoil (correlation with fragments from Žilina), without presence of carcass. After three months, first extraction of samples took place and the fibers were characterised by identification and characterization protocol used in fragments of funerary textiles. Th experiment is designed as long term, with extraction procedures once a year in

september. Even with significant limitations, first extraction proved model systems represent a valid strategy a we hope to extend the experiment adding other variables in the future.

Acknowledgements

We would like to thank the Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology and the Slovak National Gallery for kindly sharing FTIR spectrometer.

Funding

The study was supported by KEGA 002VŠVU-4/2023.

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Cleaning Albumen Photographs with Locally Available Materials and Its Impact on Albumen Properties

Barbora Palatínusová, Zuzana Machatová and Janka Blaško Križanová

Academy of fine Arts and Design in Bratislava, Hviezdoslavovo nám. 18, 814 37 Bratislava; barbora.palatinusova@student.vsvu.sk, machatova@vsvu.sk, krizanova@vsvu.sk

Keywords: albumen photography, dry and wet cleaning treatment, albumen stability

The protection and care of cultural heritage in Slovakia have been constantly improving. A measurable indicator of this trend is the increased number of professional employees in museums, galleries and archives, new investments in depositories and exhibition spaces, not only in the capital, but also in other regions. Despite multiple efforts to improve the quality of conservation practices, it is not possible to make the change immediately, due to the long neglected conditions. Photographic collections form a large part of Slovakia's cultural heritage, not only as artworks, but also as documentary sources. The long-term absence of photograph conservators in Slovakia has resulted in several deficits in the care of photographic material held in this region. Proper care for photographs presents a challenge for conservators, especially those from smaller regional institutions. Even basic conservation treatments such as dry and wet cleaning may become a challenge for those conservators due to lack of equipment and experience needed in this field.

The aim of this paper was to study several dry and wet surface cleaning techniques using locally available and less expensive materials. The intention was to study their impact on albumen photographs and changes in their properties. Dry cleaning done with several rubber erasers archival and non-archival quality and microporous sponges was tested, as well as human saliva cleaning and its synthetic alternative done with cotton swabs. It is well known that alpha-amylase is the main cleaning agent of human saliva and can be obtained artificially [1]. However this practive is still not spread among local conservators. An image analysis protocol was developed, in order to evaluate changes after cleaning model samples of albumen prints. The aim was to estimate changes in albumen layer, the extent of albumen cracks and the residues of rubber erasers and saliva using image analysis protocols based on optical and fluorescence microscopy, gloss meter, VIS and UV photography, as well as FTIR analysis.

The results show particular changes in albumen quality and cracks developing. Those changes are at the resolution limit and barely impact the stability of the albumen layer. Saliva cleaning with cotton swabs is an effective cleaning method, however it should be consider in the context of its ephemeral nature. More hygienic and less mutable synthetic saliva is an appropriate, but not always locally available option.

Acknowledgements

We would like to thank the Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology and the Slovak National Gallery for enabling FTIR measurements.

Funding

The study was supported by KEGA 002VŠVU-4/2023.

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Synthetic Organic Pigments in Postwar Artists' Paints: Analytical Results in the Context of Archival Documents

Sarah Critchley and Gunnar Heydenreich

Cologne Institute of Conservation Sciences, University of Applied Sciences Cologne; Ubierring 40, D-50678 Köln, Germany. Email: sarah_ann.critchley@th-koeln.de

Keywords: Synthetic organic pigments; artists' paint manufacturer archives; multi-analytical approach

In the 1950s and 1960s, six new classes of synthetic organic pigments (SOP) were introduced by pigment manufacturers [1]. However, there is currently little knowledge about how long it took for these pigments to find their way into artists' paints, and therefore to potentially have been used in paintings. Researching the development of pigment use in artists' paints is important to better understand the properties and characteristics of the pigments; to provide information for the dating of paintings and related attribution questions [2]; to understand the pigments' sensitivities and develop suitable conservation strategies for paintings [3]; and to shed light on artists' processes and practice [4].

Previous work on understanding the history of pigment use by paint manufacturers in other time periods [5,6] has highlighted the benefits of a combined approach comprising of multi-analytical chemical examination of paint samples and research on documentary evidence from paint manufactuers. In recent years great progress has been made on identifying SOP using analytical methods [7,8]. However, without documentary evidence it is possible to miss pigments, either because they are not active in the techniques used, or because the interpretation of analytical results can be influenced by the analysts' expectations [9].

Therefore the aim of this project is to gain knowledge on the SOP used in artists' paints in the 1950s and 1960s using the archives of LUKAS/Schoenfeld and Schmincke, two of the leading artists' paint manufacturers in Europe in this period. Chemical analysis (principally micro-Raman Spectroscopy, Transmission FTIR Microscopy and XRF) on paint-out charts and paint tubes is combined with research on documentary evidence (including recipe books, product catalogues and laboratory tests) to identify the pigments.

In this first stage of the project results for purple paints are presented. The use of various purple pigments from the triarylcarbonium, anthraquinone and dioxazine SOP classes could be tracked across the time period. Significant is the dating of the use of the dioxazine pigment PV23, which first came into use in this period.

Acknowledgements

Dr. Wolfgang Müller, Dr. Heike Stege, Diana Blumenroth, Inken Maria Holubec and Luisa Kahnert (Restaurierungszentrum Düsseldorf, LUKAS-Archiv), and Heiko Alzer (H. Schmincke & Co. GmbH & Co. KG).

Funding

This research is funded by the Konrad Adenauer Stiftung.

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Multi-Analytical Assessment of Archaeological Wood Preservation: A Case Study from La Draga, Spain

Deborah Roversi[1,2], Kirsty Penkman[1], Isabelle Théry-Parisot[2] and Kirsty High[1]

[1]Department of Chemistry, University of York, York, YO10 5YW, UK. kirsty.penkman@york.ac.uk, kirsty.high@york.ac.uk, deborah.roversi@york.ac.uk
[2]French National Centre for Scientific Research | CNRS · CEPAM UMR 7264. isabelle.thery@cepam.cnrs.fr

Keywords: archaeological wood, degradation processes,

The presence of well-preserved wood in archaeological sites is a rare occurrence, with wood materials being vulnerable to chemical and biological degradation during both burial and post-excavation phases. Despite its fragile nature, archaeological wood provides valuable insights into past societies, including environmental management and technological skills in crafting wooden artefacts.[1]
To effectively plan conservation and display conditions for such artefacts, a thorough understanding of the preservation state is crucial. Given the complexity of wood materials, a multi-analytical approach is vital in obtaining a clear picture of the present state of decay of wooden materials.
Wood morphology is examined through optical and scanning electron microscopy (SEM), offering insights into biological attacks and structural integrity. The integration of SEM with energy-dispersive X-ray spectroscopy (EDS) enables targeted analysis of inorganic content on sample surfaces. That in many cases may lead to further degradation.[2,3]
Chemical degradation is assessed through molecular techniques such as attenuated total reflectance infrared spectroscopy (ATR-FTIR), pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), and evolved gas analysis/mass spectrometry (EGA-MS). These techniques provide molecular-level information on wood components [4], aiding in understanding decay degree and establishing preventive conservation measures.
This multi-method approach was applied to archaeological wood samples from La Draga (Banyoles, Spain), a lake dwelling dating from 5300–4900 cal BC, which shows exceptional wood preservation. This case study provides insights into the preservation of different taxa, and their potential variations across diverse site areas characterised by distinct soil conditions. Additionally, analysis trials were conducted on wood that had undergone already standard conservation practices with PEG/Paraloid. Aiming to better understand the current state of preservation and anticipate potential degradation patterns that may arise in the future for these artifacts.
This emphasises the approach's applicability to assess the preservation of archaeological wood and other lignocellulose-derived materials, offering valuable insight for future archaeological investigations and conservation efforts.

Acknowledgements

I would like to express my gratitude to Erika Ribechini for giving me access to laboratory facilities at the University of Pisa to conduct Py-GC/MS and EGA-MS analyses, and for her support in interpreting the data. I am also grateful to Oriol Lopez for guiding me

through the La Draga site and its archive, for the selection and collection of samples.

Funding

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie, ChemArch project, grant agreement No 956351.

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Archaeometric Analyses of Medieval Pottery from the Lower Danube Region, Romania

Roxana Bugoi[1], Cristina Talmaţchi[2], Constantin Hait[3], Ana-Maria Banici[4], Daniele Ceccato[5,6]

[1]Horia Hulubei National Institute for Nuclear Physics and Engineering, 30 Reactorului street, M□gurele 077125, Romania; bugoi@nipne.ro
[2]Museum of National History and Archaeology, Piaţa Ovidiu 12, Constanţa 900745, Romania; ctalmatchi@gmail.com
[3]National Museum of Romania's History, Calea Victoriei 12, Bucharest 030026, Romania; costel_haita@yahoo.com
[4]National Institute for Laser, Plasma and Radiation Physics, 409 Atomiştilor Street, M□gurele 077125, Romania; ana.niculescu@inflpr.ro
[5]Università di Padova, Dipartimento di Fisica e Astronomia "Galileo Galilei", Via Francesco Marzolo 8, Padova 35131, Italy
[6]INFN – LNL, Viale dell'Università 2, Legnaro 35020, Italy; daniele.ceccato@lnl.infn.it

Keywords: ceramic, Byzantine, petrography, PIXE, XRD

Thirty-two ceramic fragments discovered in the excavations from the settlement from Pantelimonu de Sus, Romania, dated to the 8th-10th century AD, were subjected to archaeometric investigations, trying to evidence the raw materials and manufacturing techniques used by the potters from the Lower Danube region during the Medieval period.

The shards were initially grouped according to stylistic and granulometric criteria by the archaeologist. Afterwards, it followed the examination using Optical Microscopy (OM) used to detail the fabric characteristics – texture, porosity and microstructure, as well as surface treatments and firing of the potteries. The petrographic observations agreed with the initial division of shards into fine and coarse fabric, but showed an increased variability in terms of mineral composition, homogeneity and porosity. The mineralogy of the ceramic fragments was further refined by XRD measurements on powders from selected shards.

PIXE analyses on all pottery fragments were conducted at the AN2000 accelerator of LNL, INFN Italy, to get information on the chemical composition of ceramic body. The Principal Component Analysis (PCA) of the PIXE data evidenced two main categories of shards with distinct compositional signatures. Thus, the potteries supposedly made of kaolinitic clays were clearly dissimilar from the rest of the samples.

The results of the investigations reported in this communication were compared to those previously obtained on coeval ceramic items from several relatively nearby archaeological sites [Bugoi et al., 2015; Bugoi et al., 2018; Bugoi et al., 2019; Bugoi et al., 2020] in a trial to provide hard science evidence for the trade networks in the Lower Danube region during the Medieval period, or, alternatively, for the spread of a certain know-how in pottery making.

Acknowledgements

Leonardo La Torre is gratefully acknowledged for his contribution in performing the experiment at LNL/INFN.

Funding

Work performed with the financial support of ENSAR EU FP7 Programme project ENSAR (2007–2013) – Grant Agreement No. 262010.

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Ion Beam Analyses on Late Iron Age Glass Finds Excavated at Tinosu, Prahovia County, Romania

Roxana Bugoi[1], Despina Măgureanu[2], Mariana-Cristina Popescu[3], Žiga Šmit[4,5], Kristina Isaković[4]

[1]Horia Hulubei National Institute for Nuclear Physics and Engineering, 30 Reactorului street, Măgurele 077125, Romania; bugoi@nipne.ro
[2]Vasile Pârvan Institute of Archaeology, 13 Calea 13 Septembrie, Bucharest 050711, Romania; despinamagureanu@yahoo.com
[3]The National Museum of Transylvanian History, 2 Constantin Daicoviciu street, Cluj-Napoca 400000, Romania; marianacristinapopescu@yahoo.com
[4]Jožef Stefan Institute (JSI), Jamova cesta 39, 1000 Ljubljana, Slovenia; Kristina.Isakovic@jsi.si
[5]Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia; ziga.smit@fmf.uni-lj.si

Keywords: glass, Hellenistic, Ion Beam Analysis

This communication reports the results of Ion Beam Analyses (IBA) measurements on 21 glass fragments dated to the 2nd century BC-2nd century AD excavated in a Late Iron Age site from Tinosu, Prahova County, Romania. Most vitreous fragments stem from intentionally colored tableware: monochrome (green or blue), millefiori glass (brown, black, red, yellow and/or white), splashed glass (blue and white). The analyzed items were identified as originating from several Isings forms (2, 5, 37, 81) [Isings 1957], a blue bracelet and two beads. Chemical composition revealed typical Hellenistic glass recipes, suggesting long range commercial and cultural exchanges.

Funding

The experimental work at JSI has been supported by the RADIATE project (Grant Agreement 824096 from the EU Research and Innovation programme HORIZON 2020)

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Archaeometric Characterisation of Reduction-fired Polished Jugs from the Early Modern Period Belgrade

Ljiljana Damjanović-Vasilić[1], Milica Kašanin-Grubin[2], Danica Bajuk-Bogdanović[1], and Vesna Bikić[3]

[1]University of Belgrade-Faculty of Physical Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia; ljiljana@ffh.bg.ac.rs
[2]University of Belgrade-Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia; milica.kasanin@ihtm.bg.ac.rs
[3]The Institute of Archaeology, Kneza Mihaila 35/IV, 11000 Belgrade, Serbia; v.bikic@ai.ac.rs

Keywords: grey metallic ceramics, production technology, XRF spectroscopy, XRPD, FTIR spectroscopy

Reduction-fired jugs, also known as grey metallic or grey-polished ware (GPW) due to their glossy surface, represent a specific class of pottery from the Early Modern period. In addition to the distinctive surface treatment, the class is characterized by a compact, hard grey fabric, and shaping on a kick wheel [1, 2]. Archaeological and ethnographic records offer valuable data on the types of jugs, their chronology and distribution in the core areas in the Danube regions and the Great Hungarian Plain [3]. As a result of the research of Hungarian ethnologists, the technique of firing these jugs in ovens and pits has also been reconstructed [4]. Notwithstanding, this pottery class remained insufficiently known. This work presents the results of the first multianalytical approach employed to provide insight to the mineralogical and chemical composition and production technology of the Early Modern period reduction-fired jugs. The samples originate from the 17th century context from the Belgrade Fortress. 15 pottery shards have been studied using optical microscopy, X-ray powder diffraction (XRPD), petrographic thin-section analysis, Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy and energy dispersive X-ray fluorescence (EDXRF) spectroscopy.

Qualitative EDXRF spectroscopy revealed very similar elemental composition for 14 investigated samples. The presence of the following elements has been detected: Fe, Ca, K, Ti, Mn, Ni, Cu, Zn, Rb, Sr, Y and Zr. In addition, XRD analysis of these samples identified high-temperature silicate minerals diopside and gehlenite, whereas calcite has been detected by FTIR spectroscopy for 7 out of 14 samples. In the investigated assemblage, only one sample had different elemental composition, with abundant presence of Pb besides other detected elements which were the same as for other investigated shards. Moreover, this sample has poor mineralogical composition since only quartz and feldspar have been detected by XRPD analysis.

Characteristic Raman broad doublet for amorphous black carbon was identified for all investigated samples, indicating firing in a reducing atmosphere. Based on the mineralogical composition the firing temperature was estimated to be 800–900 °C.

The obtained results reveal important details about technology which, in correlation with morphological features, shed light on the origin of grey-polished ware in which pottery traditions from the northern Transdanubian region and the Balkans, i.e. the

Ottoman regions south of the Danube, are mixed with the local tradition of the Great Hungarian Plain area.

Acknowledgements

The authors acknowledge contribution of undergraduate student Luka Golubović during sample prepration.

Funding

The financial support was provided by Ministry of Education, Science and Technological Development of Republic of Serbia Contract numbers: 451-03-65/2024-03/200146 and 451-03-66/2024-03/200001.

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Degradations of Phosphate-plasticized PVC Under Artificial Aging at Low Temperature

Mathilde Larrieu[1,2], Sophie Cantin[1], Odile Fichet[1], Nathalie Balcar[2], Gilles Barabant[2] and Maroussia Duranton[2]

[1]CY Cergy Paris Université, F95000 Cergy, France
[2]Centre de Recherche et de Restauration des Musées de France (C2RMF), 14 Quai François Mitterrand, 75001 Paris, France, mathilde.larrieu@cyu.fr

Keywords: plasticizer migration, phosphates, colorimetry, FTIR, mass loss

The use of various plasticizers, in different rates, has led PVC to become the third most used plastic for commodity applications and can be found in objects from toys to furniture, including fashion. This wide range of use has allowed PVC objects to enter museum collections. Unfortunately, previous studies have shown that museum objects in plasticized PVC (p-PVC) are often in a state qualified as mediocre [1]. The most often observed degradations are a yellowing of the object, which is due to dehydrochlorination, and an exudation and fouling accompanied by a loss of flexibility, due to the loss of plasticizer.

Among the artificial thermal aging studies conducted on p-PVC degradations, only a few have been carried out at low temperatures, and are thus applicable to conservation methodology [2-3,5]. In addition, to our knowledge, the specific case of the degradation at low temperatures of PVC plasticized with phosphates has received little attention [4], while such p-PVC are found in public areas furniture, for example, where phosphates are used as a flame retardant.

Thus, the goal of this study is to evaluate the long-term degradation comportment at low artificial aging temperatures of PVC plasticized with phosphates, and to assess the influence of pigmentation on the degradation of such materials.

For this study, PVC films, plasticized with Diisodecyl Phthalate (DIDP, 17.52%), Epoxidized Soybean Oil (ESBO, 1.75%) and a phosphate plasticizer (DISFLAMOLL TPLXS 51036, 17.52%), containing or not containing a pigmentation paste (TiO2 with DINCH, 2.5%), have been artificially aged placed on microscope slides in a climatic chamber. A temperature cycle consisting of 2 days at 80°C followed by 1 day at 25°C [5] was applied under 65% relative humidity and under forced convection for 90 cycles, i.e. 270 days. These have been both sampled regularly, weighted, and characterized through spectrocolorimetry and ATR-IRTF.

The first observable degradation is the yellowing of the material, quantified by spectrocolorimetry. A change of colour is visible to the naked eye after only 2 to 4 aging cycles (figure 1). In addition, this colour change is less important for pigmented samples.

To confirm that the yellowing of the material is due to PVC dehydrochlorination, samples were analysed by ATR-FTIR as function of the aging time. But since the C-Cl absorption band at 630 cm-1 and the C=C absorption band at 1590 cm-1 overlap with other bands, only the evolution of the C-H absorption band at 960 cm-1 was studied (figure 2). A significant decrease of the area of this band during aging was observed, until its stabilisation beyond around 40 cycles. In addition, contrary to the observations

made with the spectrocolorimeter, it seems that pigmentation has no effect on dehydrochlorination. This suggests that the yellowing effect of dehydrochlorination is only less visible, and not slowed down, in the presence of a pigment.
The second characterized degradation is the loss of plasticizer, mostly demonstrated through mass loss. It is illustrated by figure 3, showing a continuous mass loss until a plateau is reached beyond around 40 cycles of aging. ATR-IRTF spectra analysis also proves that the phosphate plasticizer leaves the samples first, followed by DIDP and HSE plasticizers (figure 4). This mass loss is accompanied by a loss of flexibility, which demonstrates the loss of plasticizer. Moreover, pigmentation does not seem to have any influence on the plasticizer migration. Sample manipulation also shows that the aged p-PVC films are not sticky, meaning that under forced convection, the plasticizers migrate towards the surface and evaporate, thus diffusion is the limiting mechanism of plasticizer loss. The colour variation was then correlated with the loss of mass and compared to that observed when phosphates are absent in the p-PVC.
To conclude, pigmentation does not have any impact on the degradation of PVC films plasticized with phosphates: it only affects the yellowing perception of the film, but does

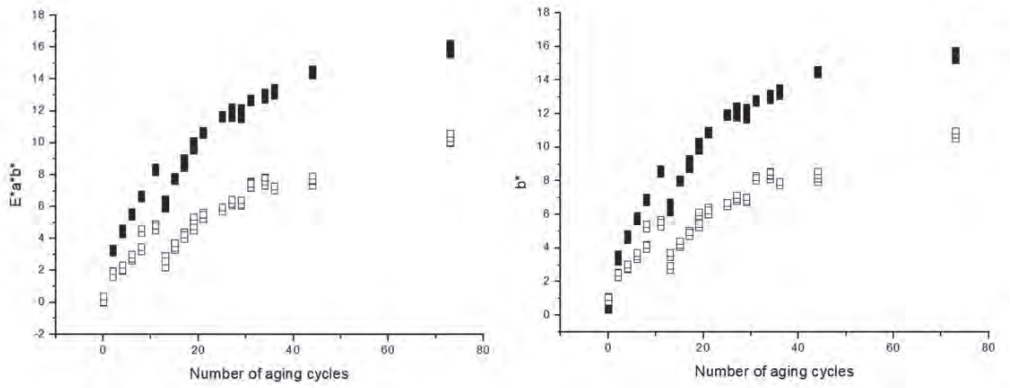

Figure 1: Colour variation (left) and b* variation (right) of unpigmented PVC (■) and pigmented PVC (□) as a function of the number of aging cycles.

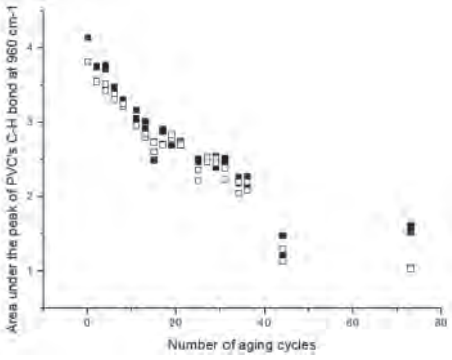

Figure 2: Area under PVC's C-H bond peak at 960 cm^{-1}, for unpigmented PVC (■) and pigmented PVC (□), as a function of the number of aging cycles

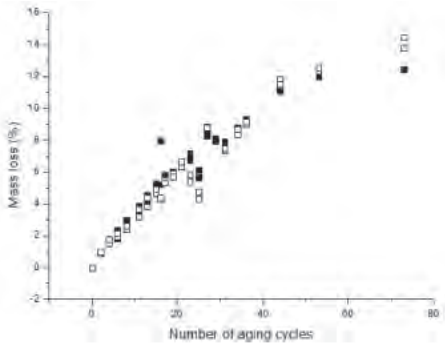

Figure 3: Mass loss of unpigmented PVC (■) and pigmented PVC ( ) as a function of the number of aging cycles

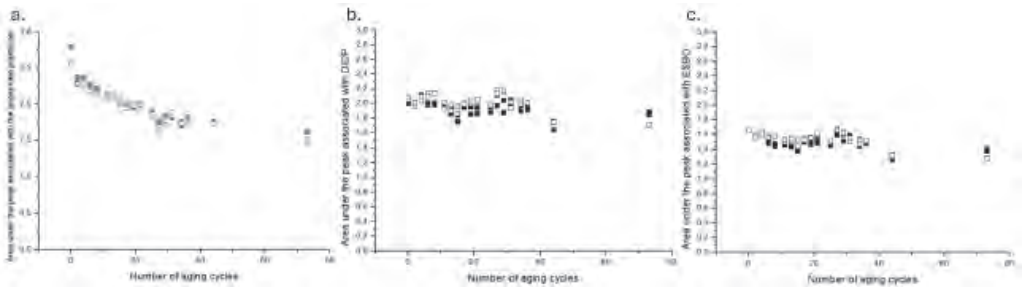

Figure 4: a. Area under phosphates plasticizer's P-O band at 946 cm^{-1}, for unpigmented PVC (■) and pigmented PVC (□) as a function of the number of aging cycles
b. Area under DIDP's associated band at 1721 cm^{-1}, for unpigmented PVC (■) and pigmented PVC (□) as a function of the number of aging cycles
c. Area under ESBO's associated C=O band at 1731 cm^{-1}, for unpigmented PVC (■) and pigmented PVC (□) as a function of the number of aging cycles

not slow down its degradations. Furthermore, has been demonstrated that in case the PVC film is co-plasticized with phosphates and phthalates, first will leave the phosphate plasticizer, then the phthalate plasticizer. Lastly, since it is industrial knowledge that phosphates create a "greasy fog" when evaporating, it would be recommended to separae phosphate plasticized PVC objects from other objects to avoid contamination.

Acknowledgements

The authors wish to thank Kamal MERGOUM, R&D director of Griffine Industries, who has provided the samples.

Funding

This work has benefited from State support managed by the Agence Nationale de la Recherche under the integrated investment program for the future included in France 2030, bearing the reference ANR-17-EURE-0021 Ecole Universitaire de Recherche

Paris Seine Humanities, Creation, Heritage – Heritage Science Foundation

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Mineological Studies of Red Pottery from the Neolithic and Bronze Age on the Korean Peninsula

Young Rang Uhm[1], Hyunkyung Choi[1], and Min Su Han[2]

[1]HANARO utilization division, Korea Atomic Energy research institue (KAERI), Daejeon 34057 Republic of Korea ; uyrang@kaeri.re.kr
[2]Department of Cultural Heritage Conservation Science, Korea National University of Cultural Heritage, Buyeo 33115, Republic of Korea; dormer@korea.kr

Keywords: Iron oxide, Firing environment, Red pottery, Mssbauer spectroscopy

The mineological characteristics of red pigment in surface and body of pottery of the neolothic and bronze age excavated from South Korean Peninsula, have been investigated using multiple analyses (SEM–EDS, XRD, Raman and Mössbauer spectroscopy). The color factors of the reddish yellow body were estimated to be hematite and maghemite, and those of the black body were estimated to be amorphous carbon and magnetite. Though the Neolithic and Bronze Ages, which are the periods before the use of kilns, used open-air firing with an uneven firing atmosphere thus, samples of the same object may exhibit differences depending on the firing method. Through analyzing the type of Mössbauer spectrum, it is possible to obtain information regarding the firing conditions of pottery, which can then be compared with XRD results to determine the environmental conditions during the firing process. It is assumed that clay soil with high Fe contents as its main ingredient was used in the red pigment layers on the surfaces of the Neolithic Age Red Painted pottery and the Red Burnished pottery in the Bronze Age that were excavated from the southern areas of the Korean peninsula. In particular, the Mössbauer spectra of surface layers in this study showed a higher spectrum area ratio of sextet by ferrihydrite than that by hematite, implying that ferrihydrite in reddish-brown might have played a significant role in developing its color.

Acknowledgements

The Red Burnished pottery JJ-1 and other Bronze Age pottery samples excavated from Sancheong were provided by Jinju National Museum. Kyungnam University Museum provided the Red Burnished pottery JJ-7, and the Neolithic pottery samples from Geoje and Tongyeong were provided by Gimhae national Museum. The Neolithic pottery sample UJ-1 excavated from Jukbyeon-ri site was provided by Samhan Institute of Cultural Properties.

Funding

This work was supported by the National Research Institute of Cultural Heritage grant funded by the Cultural Heritage Administration (No. 2021A01D03-001).

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Integrated Spectroscopic Analysis of Perugino's Masterpieces in Central Italy: Non-Invasive Multi-Technique Investigations

Volpi Francesca[1,2], Amadori Maria Letizia[3], Anselmi Chiara[4], Azzarelli Michela[5], Clementi Catia[6], Malagodi Marco[1,2], Mengacci Valeria[3], Romani Aldo[6], Vagnini Manuela[5]

[1]University of Pavia, Department of Musicology and Cultural Heritage, Corso Garibaldi 178, 26100 Cremona, Italy; francesca.volpi@unipv.it; marco.malaodi@unipv.it
[2]University of Pavia, Arvedi Laboratory of non-Invasive Diagnostics, CISRiC, Via Bell'Aspa 3, 26100 Cremona, Italy
[3]University of Urbino, Department of Pure and Applied Sciences, piazza Rinascimento 6, 61029 Urbino, Italy; maria.amadori@uniurb.it; valeria.mengacci@uniurb.it
[4]CNR-IRET, Viale Guglielmo Marconi 2, 05010 Porano, Italy; chiara.anselmi@cnr.it
[5]Laboratorio di Diagnostica per I Beni Culturali, piazza Campello 2, 06049 Spoleto, Italy; m.vagnini@diagnosticabeniculturali.it; m.azzarelli@diagnosticabeniculturali.it
[6]University of Perugia, Department of Chemistry Biology and Biotechnology, Via Elce di Sotto 8, 06123 Perugia, Italy; claudia.clementi@unipg.it; aldo.romani@unipg.it

Keywords: non-invasive; spectroscopic methods; Perugino; painting materials

The presented work discusses the significant contribution of a non-invasive multi-technique approach within the extensive diagnostic project titled "Luce e colore nel rinascimento umbro: da Perugino a Raffaello. Indagini diagnostiche su Materia e tecniche esecutive". The main objective of this contribution is to present the scientific outcomes achieved during an extensive analytical campaign on a specific selection of artworks attributed to Pietro Vannucci (1446-1523, Città della Pieve, Italy), commonly known as Perugino, one of the most renowned painters of the Italian Renaissance [1]. Among the 35 artworks analyzed within the project, the contribution focuses on seven paintings that have never undergone comprehensive study before. These seven paintings, which include five wall paintings and two panel paintings located at the Nobile Collegio del Cambio in Perugia, the Oratorio dei Bianchi and the Cathedral of Saints Gervasio and Protasio in Città delle Pieve (Fig.1), were selected on the basis of their chronology, artistic technique and patronage. The selection provided a unique insight into Perugino's technique and artistic awareness painter between the last years of the 1400s and the first decade of the 1500s.

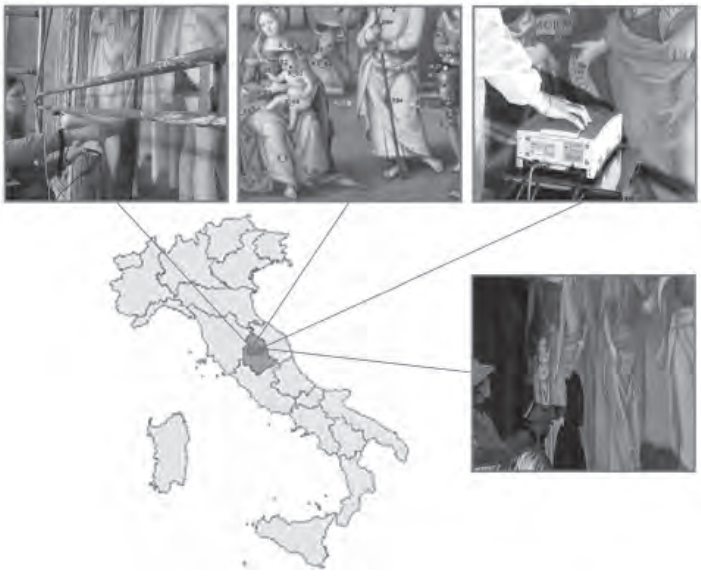
The analytical campaign combined multi-analytical methods, utilizing portable, non-invasive, and complementary techniques to understand the materials and painting techniques employed by Perugino [2-3]. Imaging systems (UV-Vis photography and IR reflectography), visible reflectance spectroscopy (FORS) both in absorption and emission, Raman spectroscopy, Energy-Dispersive X-ray Fluorescence (ED-XRF), and external reflection infrared spectroscopy (ER-FTIR) were applied in situ to reveal underdrawings, pigments, dyes, binders and varnish layers, and their mindful use by Perugino on his artworks.

The proposed approach permitted the chemical differentiation of pigments, identifying a widespread use of smalt for blues, while natural ultramarine and azurite

were recognized by ER-FTIR only on specific paintings and for specific details. Reds, yellows, and greens were characterized and discriminated by Raman, UV-Vis-NIR spectroscopy and XRF as primarily iron-based earths, while ER-FTIR revealed possible insight on the green earth provenance [4]. The use of gold and vermillion suggested a deliberate choice to enrich the garments with multiple decorations, implying the quality of the representations and wealth of patronage. The same analytical protocol was successfully performed on the panel paintings which revealed some differences in the selection of the pigments and a more complex stratigraphy. Measurements on the lacunas permitted the characterization of the ground layer consisting of gypsum and glue. In blue and green areas azurite or verdigris were identified by ER-FTIR, sometime mixed with lead white or lead-tin yellow, respectively, depending on the final hue. In red areas not only inorganic but also organic pigments, such as red lake, were revealed by fluorescence spectroscopy indicating a thoughtful selection of materials by the artist. Additionally, a lipidic binder was recognized.
The integration of results from multiple non-invasive techniques allowed the researchers to answer crucial research questions about the execution processes and composition of Perugino's paintings. Furthermore, it is worth emphasizing the significance of this comprehensive study in providing the first non-invasive examination of the artist and his connection to his homeland. Indeed, the data collected from the entire set of 35 artworks analyzed in Umbria will enable a comparative statistical study with artworks from outside this territory and those of coeval Italian artists, offering a complete understanding of Perugino's artistic practices and influences.

Acknowledgements

We would like to thank the Rector of the Nobile Collegio del Cambio for permitting the



analysis of the paintings and the Municipality of Perugia and Città della Pieve for the logistic support.
Inizio modulo

Funding

The project has been funded by Fondazione Perugia and Comitato Perugino Cinquecento.

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Ammonia-oxidation and De-carbonation Detected on Stone of Angkor Monuments and Implications for Conservation

Ji-Dong Gu[1] and Youfen Qian[2]

[1]Environmental Science and Engineering Program, Guangdong Technion – Israel Institute of Technology , 241 Daxue Road, Shantou, Guangdong 515063, China; jidong.gu@gtiit.edu.cn
[2]Environmental Science and Engineering Program, Guangdong Technion – Israel Institute of Technology , 241 Daxue Road, Shantou, Guangdong 515063, China; youfen.qian@gtiit.edu.cn

Keywords: Stone, Deterioration, Ammonia-oxidation, Nitrate Accumulation, De-carbonation

World cultural heritage sites are important record of civilization and humanity, but they suffer from destruction due to natural and anthropogenic causes, among them microbes and their biochemical reactions play an indispensable role. Under the tropical conditions in South Asia, stone monuments are de-stabilized by visible growth and extension of plants and, at the same time, invisible microorganisms cover the surfaces with various colors over time and seasons (Liu et al., 2020; Gu and Katayama, 2021)(Figure 1). Obviously, water contents on the surface and inside the stone materials are key factors directly contributing to the damage through temperature and moisture interactions. For water or moisture content of stone, the specific physical state of it is the most important one to the surface colonization and biofilm formation of the microbiome. At the same time, the composition as well as the physical and chemical properties of the stone influence the consequently interactions between water and moisture, and the stone integrity. Because of this, water cycle and damage are critically important process to stone under tropic conditions, but the involvement of the soluble salts, and their mobility and crystallization and re-crystalization are phenomena contributing to the delamination and defoliation of stone (Liu et al., 2020; Gu and Katayama, 2021).
Sandstone is susceptible to acidity and both natural and biological processes can acidify the local conditions over time. In the N cycling reactions, ammonia-oxidation by both ammonia-oxidizing archaea (AOA) and ammonia-oxidizing bacteria (AOB) are recently found to lower the pH condition and the nitrate as a product of this reaction has been detected at higher concentrations on Angkpr monuments in Cambodia (Meng et al., 2016, 2017). Further analysis also confirm the existence of complete ammonia oxidation to nitrate (Comammox) bacteria on Angkor monuments for the first time (Ding et al., 2021). This collection of information enriches our current understanding on the microbiome and their physiological functions to the destruction of sandstone monuments. In addition, chemical and mineralogical compositions of the stone used to build the cultural heritage has shown a clear de-calcification of carbonat minerals, e.g., calcite (Qian et al., 2022). During microbial community development on stone surface and initiation of any decay, the biochemical reactions from the microbial growth and development are responsible for the dissolution of selective minerals and some of the most prevalent ones include metabolic reactions of carbon, nitrogen and sufur. Using N as an example, several different reactions are involved for ammonia oxidation by AOA, AOB and Comammox bacteria. By coupling with the local climate and ecological variables, these biochemical reactions through water and salt mobility play an indispensable role in the destruction of sandstone.

Figure 1 Micobial colonization, colors and deterioration of sandstone wall at the Angkor Bayon temple gallery

Acknowledgements

Permission for sampling of this project was granted by the APSARA Authority of the Kingdom of Cambodian Government.

Funding

This project was supported by the Safeguarding of Bayon Temple of Angkor Thom (JASA, Japan) and my laboratory operation budget.

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Organic Acids and Degradation of Lignin-containing Paper

Ida Kraševec, Nik Nikolić, Jan Ocepek, Aleksander Kravos, Hend Mahgoub, Irena Kralj Cigić, Matija Strlič

Heritage Science Laboratory, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, Ljubljana, Slovenia
ida.krasevec@fkkt.uni-lj.si, jan.ocepek@gmail.com, nik.nikolic18@gmail.com, aleksander.kravos@fkkt.uni-lj.si, hend.mahgoub@fkkt.uni-lj.si, irena.kralj-cigic@fkkt.uni-lj.si, matija.strlic@fkkt.uni-lj.si

Keywords: lignin, cellulose, organic acids, degradation

Paper has for centuries been one of the humanity's most important information carriers, but its composition changed during the ages. Evolving from the pure cellulosic fibres of the past centuries, the onset of the industrial revolution established wood as the main source of fibres in papermaking from mid-19th century onwards. Because groundwood is a mixture of various substances including cellulose, hemicelluloses and lignin, this lead to an increase of lignin content in paper, recently content of up to 35 % was measured in paper samples from 1350-1990 [1].

Hydrolytic degradation of cellulose chains accelerated by low pH [2] is well known to be the cause of long-term paper degradation. Paper produced from groundwood is usually characterised by acidic pH values and it is among the most fragile types of paper due to the hydrolysis and the consequential loss of mechanical properties. It has been estimated that up to 80% of library and archival material is prone to rapid embrittlement [3].

The possible sources of acidic compounds in paper include: the manufacturing process, which in the past included sizing with resin acids and alum (aluminium sulphate); acidic air pollutants, present in archives and libraires; and the degradation products of cellulose and lignin [4]. However, the effect of the lignin on cellulose degradation remains debated, due to the dual effects of carboxylic acids forming during its degradation and its antioxidant properties that slow cellulose oxidation [5].

In this work, a collection of one hundred naturally aged samples of European paper produced between 1844 and 1990 (a part of the SurveNIR reference collection) was investigated. An extraction method was optimized to quantify the organic acids in the paper using two different separation methods: anion-exchange chromatography with conductivity detection and ion-exclusion chromatography with UV detection. Acetic, formic, lactic, glycolic, glyoxylic, succinic, maleic, and oxalic acid content was determined, and their presence was correlated with the pH of the paper, as well as age, lignin and resin acid content, molecular weight and the degree of polymerisation. A strong correlation between the paper pH and the oxalic acid concentration was noticed, which could be due to the low volatility of this acid in comparison to monocarboxylic acids such as acetic and formic acid (that are traditionally considered as the reason for the low pH of paper).

Additionally, a selected subset of samples was further artificially degraded under increased temperature and relative humidity both as free sheets of paper and in the

form of stacks, mimicking closed books. The additionally degraded samples were further characterised through changes in colour, molecular weight and organic acid content. Preliminary results show that the paper in stacks degrades at higher rates than the free sheets, but the mechanisms remain to be investigated.

Funding

This work was funded by the Slovenian Research and Innovation Agency as a part of the Project LIGNIN (J4-3085) and the Programme group N-DAD.

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Degradation and Chemical Properties of Vincent van Gogh's Prussian Blue Oil Paints Investigated Through Paint Reconstructions

Suzanne Reus[1,2], Lise Krebbers[3], Maarten van Bommel[2,4], Klaas Jan van den Berg[3,4]

[1]Van Gogh Museum, P.O. Box 75366, 1070 AJ, Amsterdam, the Netherlands
[2]University of Amsterdam, Faculty of Science, van 't Hoff Institute for Molecular Sciences, Analytical Chemistry Group, Science Park 904, 1098 XH, Amsterdam, the Netherlands
[3]Cultural Heritage Agency of the Netherlands, Hobbemastraat 22, 1071 ZC, Amsterdam, the Netherlands, s.reus@uva.nl
[4]University of Amsterdam, Faculty of Humanities, Amsterdam School for Heritage, Memory and Material Culture, Conservation and Restoration of Cultural Heritage, P.O. Box 94552, 1090 GN, Amsterdam, the Netherlands

Keywords: Oil paints; Prussian blue; mechanical degradation; historical reconstructions

Several degradation phenomena have been observed in very dark blue, almost black paint strokes in Vincent van Gogh's oil paintings. The phenomena are mostly of a mechanical nature, including different types of cracking, delamination and paint loss and appear to be specific to the dark blue strokes. The paint has also been found to be solvent sensitive, its blue colour bleeding from cracks upon contact with solvent. X-ray fluorescence spectroscopy (XRF) of the dark blue paint strokes, as well as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and optical microscopy of samples taken from these areas have been used to confirm that the paint is an almost pure Prussian blue oil paint, mixed with very little or no lead white or zinc white and containing only a few differently coloured pigment particles.
The cause behind the formation of these phenomena and why they appear to be specific to this dark blue paint is not yet understood, and requires further investigation of the mechanical and chemical properties of Prussian blue oil paints. To be able to study changes in the properties of this paint over time, without excessive sampling of Van Gogh's paintings, Prussian blue oil paint reconstructions were prepared and artificially aged. Paints were created as historically representative as possible, based on SEM-EDX, microscopic and pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) analyses of samples taken from Van Gogh's paintings. The Prussian blue pigments used for the paints were specifically prepared following late 19th-century recipes as well [1].
Multiple variables were included in the preparation of the reconstructions to investigate their influence on the ageing of the paint outs. These include the type of Prussian blue pigment, the pigment volume concentration (30% or 39%), the addition of 2 vol% beeswax, and the thickness of the paint outs (50 μm or 200 μm). The employed pigments are a commercial Prussian blue and two pigments prepared according to 19th-century recipes, one for so-called "soluble" ($KFe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$) and one for "insoluble" ($Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot xH_2O$) Prussian blue. Paint outs were prepared on polyester support and, after being dry to the touch, artificially aged for up to 16 weeks at elevated temperature and fluctuating relative humidity. The ensuing optical, mechanical and chemical changes of the paints were monitored using microscopy,

SEM-EDX and ATR-FTIR analyses. After 16 weeks of ageing, extensive cracking was observed in all paint outs. However, the different compositions of the reconstructions were found to influence when these cracks first appear, as well as the visual appearance and chemical properties of the paints.

Acknowledgements

The authors would like to thank Bart Ankersmit of the Cultural Heritage Agency of the Netherlands for his help in regards to the artificial ageing of the oil paint reconstructions.

Funding

This work was supported by ASML – Van Gogh Partners in Science.

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A Systematic Study of Iron-gall Inks: How their Variability Affects the Degradation Processes

Salvatore Caterino[1], Iulia Caniola[1], Marc Pignitter[2], Alfonso Zoleo[3], Santiago Sanchez-Cortes[4], Katja Sterflinger[1] and Federica Cappa[1]

[1]Academy of Fine Arts – Institute of Natural Sciences and Technology in the Arts, Wien, Austria; s.caterino@akbild.ac.at
[2]University of Wien – Institute of Physiological Chemistry, Faculty of Chemistry, Wien, Austria; marc.pignitter@univie.ac.at
[3]University of Padua – Department of Chemical Sciences, Padua, Italy; alfonso.zoleo@unipd.it
[4]Consejo Superior de Investigaciones Científicas – Institute of optics, Madrid, Spain; s.sanchez.cortes@csic.es

Keywords: iron-gall inks, ageing, manuscript, systematicity

Iron-gall inks (IGI) are among the most diffused and popular inks in antiquity. Although commonly associated with Middle Age manuscripts, evidence suggests their usage in much earlier periods as well.[1] The preparation of such inks generally followed two main steps: the preparation of an oak-galls extract, the addition of green vitriol ($FeSO_4 \cdot 7H_2O$) and Arabic gum, and eventually other additives.[1,2] From a chemical point of view, the formation of the dark insoluble particles, constituting the IGI main component, results from the interaction between the polyphenols contained in the oak-gall extract and the iron(II) cations. The polyphenols, mainly gallotannins, can create stable coordination compounds with metal cations. The oxidized forms of these complexes are insoluble and, once dispersed in a suitable medium, like Arabic gum, constitute a very good dark permanent ink.[1–4] Due to their characteristic acidity and the presence of iron in its oxidized state, manuscripts containing IGI are often subjected to severe degradation forms ranging from the embrittlement of the support to the formation of proper holes.[5]particularly the cellulose-based support. Intending to stabilize it, we have come a long way from the nineteenth-century cellulose nitrate laminations to the relatively recent phytate treatments; nevertheless, less invasive treatments are needed. To pave the way for developing safer and more sustainable treatments, tailored as much as possible to the object, this paper reviews the conservation treatments and the advances that have taken place over the last decade in our understanding of the degradation mechanisms of iron-gall inks, based on a careful selection of references to support a concise microreview. This discussion is based on the currently accepted models based on the Fe3+-gallate and the identification of degradation products for iron-gall inks observed in heritage objects, including manuscripts dating from the fourteenth to seventeenth centuries and drawings from the fifteenth to nineteenth centuries. The degradation promoted by iron-gall inks induces scission of cellulose through acid catalysis and/or redox reactions. The causes of these acid-base and redox reactions are also assessed. Finally, we detail the state-of-the-art conservation treatments used to mitigate iron gall ink deterioration, covering treatments from the late nineteenth century to the beginning of the twentieth century, followed by the presentation of current phytate treatments

and new postphytate treatments.","container-title":"Heritage Science","DOI":"10.1186/s40494-022-00779-2","ISSN":"2050-7445","issue":"1","journalAbbreviation":"Herit Sci","language":"en","page":"145","source":"DOI.org (Crossref The main challenge in the in-depth study of the IGI degradation processes is the variability deriving from their great diffusion. Their popularity is reflected in the huge number of historical recipes which included the use of different aqueous solvents for the extraction of the tannins (like vinegar and wine), the presence of additives (such as other pigments or components to modulate the viscosity), secondary sources of tannins (like pomegranate peels and chestnuts shells), etc.[1]

For a deeper understanding of the degradation processes occurring in IGI, the variability of the chemical structures of the various IGI components has to be addressed. One of the novelties of this research is the approach used for the preparation of mock-up samples done in a systematic and controlled manner allowing one to study the main parameters affecting the structure of iron-polyphenolic compounds. For this purpose, iron complexes of tannic acid and gallic acid (here functioning as model ligands) were prepared and isolated in three pH conditions (pH2, 4, and 6) and using different iron to ligand ratios. Furthermore, for a more realistic simulation, iron-polyphenolic complexes using oak-gall extracts were additionally prepared. All the obtained samples were subjected to artificial ageing with UV-A radiations and two relative humidity conditions (80 and 30%). Raman Spectroscopy, Infrared spectroscopy (IR) and electron paramagnetic resonance (EPR) were used to characterize all the samples before, during and after the ageing.

The approach adopted for the preparation of the mock-ups together with the complementarity of the results obtained revealed to be a valid approach to better understand the degradation of IGI-containing manuscripts. The use of both gallic and tannic acid enabled to clarify that their respective iron complexes are subject to different degradation processes and most importantly with different speed. The role of the pH in these modifications has been demonstrated to be crucial, while the iron concentration effect resulted to be effective just above a certain threshold.

The use of Raman, EPR and IR helped to synergistically understand different aspects of the molecular mechanisms of the degradation. The validity of the methodological approach concluded from this study has therefore to be considered as the second important outcome of this study.

Funding

This project is funded by FWF project no. P35484-N.

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Effectiveness of Different Chemical Cleaning Methods to Remove Graffiti from Ornamental stones: the Case of Varying Organic Solvents Concentrations and Poultices.

Ricci, C.[1]; Calvar-Santamaría, A.[2]; Pozo-Antonio, J.S.[3]

[1]Centro per la Conservazione ed il Restauro dei Beni Culturali "La Venaria Reale", 10078 Venaria Reale, Torino, Italy. chiara.ricci@ccrvenaria.it
[2]CINTECX, GESSMin group. Dpt. of Natural Resources and Environmental Engineering, School of Mining and Energy Engineering, University of Vigo, 36310 Vigo, Spain. angela.calvar@uvigo.gal
[3]CINTECX, GESSMin group. Dpt. of Natural Resources and Environmental Engineering, School of Mining and Energy Engineering, University of Vigo, 36310 Vigo, Spain. ipozo@uvigo.gal

Keywords: stone cleaning, graffiti, cultural heritage, conservation, chemical cleaning, low toxic solvent.

The removal of graffiti from ornamental stones through chemical cleaning procedures is a common practice in conservation of cultural heritage. It is based on the interaction between a chemical product and the paint, achieving its dissolution and extraction. Cleaners can be applied on the stone surface directly by brush or as poultices. Recently, owing to the hazard posed using mostly harmful solvents, the use of mixture of organic solvents with low toxicity (replacing solvents with higher toxicity commonly used) have been implemented and promoted in conservation as an alternative cleaning approach. Thickeners and gels can be used as delivery system to retain large amount of cleaner on the surface to be cleaned (increasing the performance time), to decrease diffusion rate and to control the cleaning action.
In this research, to replace toxic solvents commonly used as cleaners, low toxic organic solvents (ethyl alcohol, isooctane and acetone) were mixed under different concentrations to extract a black graffiti from four stones with different composition and texture (Pietra di Luserna-a orthogneiss-, Baveno granite, Vico diorite and Roman travertine). Four mixtures were applied directly with a brush or with different delivery systems: Nevek® (gel), laponite (clay) or a mixture of paper pulp, sepiolite (clay) and Klucel® G (hydroxypropylcellulose) to know the influence of the delivery system on the cleaning achieved. After the application of the different delivery systems, surfaces were evaluated with stereomicroscopy to detect appearance changes of the stones, spectrophotometry to know the possible color changes of the surfaces, Raman spectroscopy to identify graffiti remains and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray analysis (EDX) to identify graffiti remains and textural and/or mineralogical changes and/or chemical contamination.
In general terms, it was identified that the performance of each delivery system clearly depends on the texture of each stone: orthogneiss and travertine, both with an uneven surface, showed a higher amount of graffiti remains regardless of the ternary solvent mixture applied for cleaning. Indeed, there were more remains for gneiss into fissures, while for travertine in the characteristic pores of this stone. Graffiti removal appeared more successful on granite and diorite, which showed a polished surface. In most cases (for diorite, granite and gneiss), the best results were mainly obtained using

a solvent mixture composed of 51% ethyl alcohol, 38% isooctane and 11 % acetone, while for travertine the best results were obtained with a mixture of 1% ethyl alcohol, 96% isooctane and 3% acetone. Regarding the delivery system, the best results were obtained on diorite by using a mixture of paper pulp, sepiolite and Klucel®, on granite with laponite and on gneiss and travertine by direct application through cotton swab.

Acknowledgements

Thanks are given to .Arianna Scarcella, from Centro per la Conservazione ed il Restauro dei Beni Culturali “La Venaria Reale”, for her technical assistance.

Funding

This research has been funded by the Spanish research projects CNS2022-135645 and RYC2020-028902-I.

TiO_2 Enriched SiO_2 Nanocontainers for the Protection of Stone Surfaces

Andrea Campostrini, Teresa Botrè, Elena Ghedini, Michela Signoretto, and Federica Menegazzo

CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice and INSTM RUVe, Via Torino 155, 30172 Venice, Italy; andrea.campostrini@unive.it

Keywords: Silica NPs, TiO_2, sustainable, antimicrobial, pollutants abatement

Even though stone heritage artworks might seem made of very resistant material, they still undergo several degradation phenomena, which are strictly related to the environment they are exposed to. These phenomena can derive from different sources: chemical, physical-mechanical, or biological. In the latter case, it is referred to as biodeterioration, which usually begins with microorganisms' colonization, then followed by bigger organisms till plants and trees [1]. To avoid such degradation phenomena, preventive actions must be considered, such as the application of antimicrobial protective coatings [2].
This work presents indeed a green nanoparticle-based system aimed at developing a protective coating for stone surfaces exposed outdoors. Specifically, the silica (SiO_2) porous material MCM-41 was synthesized and characterized by different techniques (i.e., N_2 physisorption, XRD, FT-IR, TPO, TG-DTA) and employed as a nanocontainer to host and subsequently release antimicrobial products. Furthermore, the system was enriched by adding Titanium dioxide (TiO_2) nanoparticles to increase the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms [3]. In addition, the presence of a photocatalyst in the mixture would ensure an air pollutants abatement, such as NOx and VOCs, and a correlated self-cleaning effect on the surface [4].
In detail, the MCM-41 nanocapsules were impregnated with different TiO_2 nanoparticles, varying in size and crystalline phase. They were subsequently characterized by N_2 physisorption and electron microscopy analyses (SEM/TEM) to assess the position of TiO_2 in the porous MCM-41 matrix. To evaluate the Silica-TiO_2 photocatalytic activity, tests on plaster mock-ups were carried out, simulating organic deposition using Methylene Blue as a model stain compound.
In conclusion, it was possible to develop a multifunctional sustainable protective system, able to maximize the efficacy and the self-cleaning action through the combination of SiO_2 and TiO_2 nanoparticles.

Funding

Funded by the European Union – NextGenerationEu, by the PON R&I 2014-2020/ IV.5 – GREEN action, and the Unione Stuccatori Veneziani – Uni.S.Ve. s.r.l. company

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Design & Study of Cost-Effective Conservation of Watercolor Paper

Woon Lam Ng, Zeyan Zhuang and Huanlong Hu

Nanyang Technological University, 81 Nanyang Drive, #2-10, 637458 Singapore ;
ngwoonlam@ntu.edu.sg

Keywords: Foxing, Acrylic, Watercolor, Paper, Biotic

One of the concerns of 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 impractical 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 appeal compared to oil paintings on canvases. This study offers an alternative, straightforward, and cost-efficient approach to safeguarding 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 to 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 (CaCO3), dolomite (CaMg(CO3)2), rutile (TiO2), 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, and 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 involve the addition of any preservation materials to the original artworks

Acknowledgements

The authors gratefully acknowledge support from the Nanyang Technological University for funding the project and providing chemical and biological lab access. The authors also like to thank the artist Mr. Jack Tia Kee Woon for providing acrylic-coated samples aged more than 10 years for the study.

Funding

This work was supported by Nanyang Technological University, Singapore [grant number #021456-00001].

Analysis and Treatment of the Alien from The Stuff

Rebecca Ploeger[1], Pilar Brooks[2], Sophie Hunter[3], Rio Lopez[3]

[1]SUNY Buffalo State University, 1300 Elmwood Ave., Buffalo, NY, USA; ploeger@buffalostate.edu
[2]Getty Post Baccalaureate Intern in Art Conservation; 1200 Getty Center Dr, Los Angeles, CA 90049, pilarbrooks96@gmail.com
[3]Academy Museum of Motion Pictures, 6067 Wilshire Blvd, Los Angeles, CA, 90036, USA; shunter@oscars.org; rdlopez@oscars.org

Keywords: phthalate plasticizer; poly(vinyl chloride); movie prop; multi-lobe acrylic; preventive conservation

According to the movie trailer, ‚THE STUFF is a product of nature... a deadly, living organism.“ [1]; however, it is not according to scientific analysis, at least in the case of the movie prop in the collection of the Academy Museum of Motion Pictures. The object in question is a flexible blob-like alien special effects sculpture, that is taller in the centre and thins out into a pool with rounded irregular edges. On film it appears to have a marshmallow-like consistency. It entered the conservation lab with tears and a detachment, along with a thick layer of sticky plasticizer and grime across the surface (Figure 1). There was also some cellulose nitrate based red paint accretions along one side, and evidence of burns, both believed to have occurred during the creation of the film (THE STUFF, 1985, dir. Larry Cohen; special effect artist Bret Culpepper; model maker Ted Rae). The exact scene in the film that features this prop could not be identified.

Based on visual and tactile observations, the object was originally thought to be silicone – it was a flexible off-white material with a glossy (almost greasy) porous skin-like surface texture, that had been shaped by pouring it into a single-sided mold. Several small pieces were collected for Fourier transform infrared spectroscopy (FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis, as well as microchemical testing.

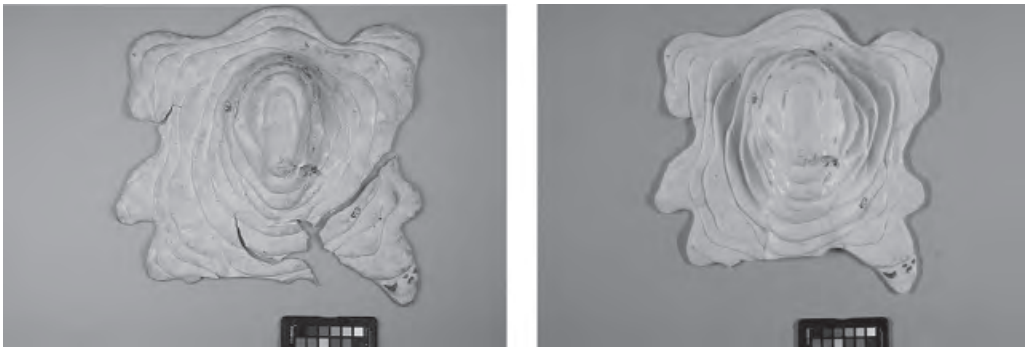

Figure 1 – Left: before treatment image; right after treatment image. Dimensions: approximately 38 cm W x 38 cm D x 9 cm H. ©Academy Museum Foundation

Analyses showed that it was poly(vinyl chloride) (PVC) heavily plasticized with phthalate plasticizers. This changed the trajectory of the treatment, handling, and storage, but also brought health and safety considerations into the picture with the large amount of phthalate plasticizers. The phthalates identified were primarily diheptyl phthalate, dinonyl phthalate and diundecyl phthalate. None are specified in California regulatory laws; however, their respective GHS information listed all of them as harmful to human/animal health and/or aquatic life.

The conservation treatment was tricky and required adhesive testing; plasticized PVC fishing lures were used as mock-ups. A range of adhesives were investigated, including a series of acrylic-based products, BEVA® 371, animal glues, and Aqauzol. Rhoplex™ Multilobe™ 200 (The DOW Chemical Company) was ultimately selected; this waterborne acrylic system is a combination of spherical an lobed particles to enhance brush drag [2]. The unique lobed geometry of the particles, with a high surface area, alters the rheology properties and may also help with adhesion performance [3]. It also has a reported glass transition temperature of 9 °C [2], which ensures that it is flexible in room temperature.

Tears were repaired with Rhoplex™ Multilobe™ 200. As there was no way to clamp the broken pieces, small strips of Hollytex were used to create temporary bridges across the tears while the adhesive dried. The bridges were then removed using heat. The underside of the blob was lined with Rhoplex™ Multilobe™ 200 on Tengucho paper. A custom support was created with Ethafoam and Volara® foam since supporting the object was critical to maintaining the repairs. The Stuff was also cleaned; plasticizer was reduced from the surface, and it was in-painted where necessary (Figure 1). Reducing the plasticizer led to the leaching of more plasticizer. The removal of any original material is controversial; however, for this object it was necessary in order to remove the grime. The long-term storage of the Stuff is still under investigation – the foam support is hoped to be replaced with a non-absorbent material, and cool storage conditions are being considered, being mindful to the glass transition of the repair, to slow the migration of the plasticizer. The Stuff must also remain covered to reduce dust and debris from imbibing into the plasticizer, and any handling must be done with gloves to prevent skin exposure and accidental transfer of the plasticizers.

This treatment is a cross-disciplinary blend of cultural heritage expertise, where scientific knowledge helped with the treatment of an unusual object. As well, it demonstrates a fun, yet very complex treatment experience for a pre-program conservation student, and for the experienced supervising conservators. Everyone involved gained valuable insight into the conservation of heavily plasticized PVC, and the additional considerations and precautions that needed to be reviewed and followed.

Acknowledgements

Getty Post Baccalaureate Internship in Art Conservation

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Preliminary Results on Cleaning of Urban Art Murals

Varvara Marazioti[1,2], Antonios M. Douvas[2], Stamatios Boyatzis[1], Yorgos Facorellis[1]

[1]Department of Conservation of Antiquities & Works of Art, University of West Attica, 12243, Egaleo, Attica, Greece
[2]Institute of Nanoscience and Nanotechnology (INN), National Centre for Scientific Research (NCSR) "Demokritos", 15310, Agia Paraskevi, Attica, Greece
v.marazioti@gmail.com

Keywords: urban murals; conservation; cleaning; green solvents; sustainability

Contemporary outdoor murals are frequently vandalised by graffiti artists [1],[2], a phenomenon that poses challenges to potential cleaning interventions, due to the chemically similar material i.e. spray paint [3], [4]. The complexity associated with achieving optimal cleaning treatments stems from the necessity to selectively remove or eliminate undesirable material without compromising the integrity of the underlying paint layers [5].
This study explores whether there are effective means for the preservation of contemporary murals and optimises cleaning treatments on painted mock-ups, using physical and chemical hydrogels loaded in green solvents and nanostructured fluids (NSFs), as an alternative approach to sustainable preservation of cultural heritage. The surface examination was realised with optical microscopy (OM) and Fourier Transform Infrared spectroscopy (FTIR), while colour and gloss measurements complemented the cleaning assessment methodology. The research is supplemented by the findings of cleaning interventions conducted on a contemporary mural executed by Stelios Faitakis in Athens (Greece). This study provides important information for the conservation field regarding the effects of the selected green materials, their application method and their effectiveness in removing various types of overpaintings on urban murals.

Funding

The research was partially funded by the Special Account for Research Grants, University of West Attica.

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Characterisation of the Building Granites and Surface Finishes of the Chapel of Nossa Senhora dos Prazeres in the Casa Mateus Palace Complex (Vila Real, Portugal).

Vendula Natherová[1,2], Ana J. López[1], Alberto Ramil[1], Andrea Mariani[3,4], and David M. Freire-Lista[5,6]

[1]Laboratorio de Aplicacións Industriais do Láser, Campus Industrial de Ferrol, Universidade da Coruña, 15471 Ferrol, Spain.
[2]Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 00, Prague 2, Czech Republic.
[3]Fundação Casa de Mateus, Casa de Mateus, Mateus, 5000-291, Vila Real, Portugal.
[4]CITCEM. Centro de Investigação Transdisciplinar «Cultura, Espaço e Memória», Faculdade de Letras da Universidade do Porto, Via Panorâmica s/n, 4150-564 Porto, Portugal.
[5]Universidade de Trás-os-Montes e Alto Douro. Quinta de Prados. 5001-801 Vila Real, Portugal.
[6]Cgeo. Centro de Geociências da Universidade de Coimbra, Universidade de Coimbra—Polo II, Rua Silvino Lima, 3030-790 Coimbra, Portugal.

Keywords: Granite, aplite, historical quarries, bush hammered, surface finish, integrity

The conservation and restoration of built heritage involves the location and study of its historical quarries, the characterisation of its building stones and deterioration, as well as its enhancement (Freire-Lista et al. 2022a). Building stones must meet high-quality standards to ensure the best behaviour in all situations (Sousa, 2013).
The first step in protecting cultural heritage is the need to define parts of the building that are considered historically valuable and their conservation is important. This requires a multidisciplinary team with a broad criterion of inclusion. Variables such as rarity, accessibility, demand and territorial insertion must be considered when designing a conservation strategy for each asset. In this way, a cultural diversity attractive to a wide range of audiences can be generated.
The ashlars of historic buildings provide very useful information for built heritage professionals. The materials, surface finish, deterioration and stratigraphy of the walls must be taken into account for a rigorous study of the conservation and enhancement of stone heritage (Freire-Lista et al. 2022b).
The palace complex of the Casa de Mateus, in Vila Real, Northern Portugal, is one of the most important Baroque monuments in Northern Portugal. With the construction of its chapel in the mid-18th century, the palace took on its current form. The symmetrical façade of this chapel has two pairs of lateral columns supporting a lintel that ends in a central semi-circular arch. The space between the columns and the arch is occupied by the main entrance door, a window above the door and a shield between the window and the arch. The upper part is decorated with scrolls and lateral vases, and in the centre there is the inscription of the foundation of the chapel. The chapel is crowned by a cornice with broken arches on the sides and a cross in the centre.
The aim of this work is to characterise the main building stones, to locate their quarries of origin and to digitise their surface finishes for the conservation of the chapel.
Two types of building granite were sampled from the chapel and its original historic

quarries. Thin sections were made according to UNE-EN 12407, 2020, which allowed the petrographic characterisation of both granites and the ratification of their original quarries. In addition, X-ray diffraction and X-ray fluorescence were used for mineralogical identification.
The ultrasonic pulse velocity was measured according to UNE-EN 14579, 2020 and the colour of the granites was expressed using the three chromatic coordinates of the CIE-L*a*b* parameters, according to UNE-EN 15886, 2011.
The surface topographies of the ashlars were obtained using a MEL M2DW laser line scanner connected to a laptop computer via an Ethernet BlueBox. The surface roughness was obtained according to UNE-EN 25178-2, 2013.
The main building stone is a fine-grained aplite with frequent pseudospheric mafic enclaves of turmaline, mostly between 1 cm and 2 cm in diameter. Its average colour is L*= 77.35 ± 2.2; a*= 1.04 ± 0.2; b*= 11.85 ± 1.11. Intrusion of turmaline group aplites can result from metasomatic processes, where H_2O-rich residual fluids exsolve from pegmatitic melt and infiltrate fractures and fissures in granitic rocks.
Loss of H_2O-rich fluids and rapid cooling of the melt upon contact with already rocks then lead to significant undercooling of the melt, resulting in the formation of aplitic features (Roda-Robbles et al., 2018). Schorl, which is found in the masonry of Nossa Senhora dos Prazeres Chapel, occurs under reducing conditions in Sn-W-rich veins (Nieva et al., 2007). Another much less used building stone is a two-mica granite of coarse to medium crystal size with elongated pseudo-oriented feldspars. Its average colour is L* = 62.16 ± 5.4; a* = 2.82 ± 0.8; b* = 11.27 ± 2.9.
The microroughness of the aplite surface is defined by areal roughness parameters Sa= 0.091 ± 0.011 μm; Sq= 0.114 ± 0.014 and that of the granite by Sa= 0.217 ± 0.017 μm; Sq= 0.278 ± 0.019 μm.
The localization of historic quarries of the granites used in Nossa Senhora dos Prazeres Chapel will guarantee the use of the original building stones with the same physical properties. This will allow the restorers to achieve quality results in the conservation of the chapel. The digitalisation of the surface finishes of the historic ashlars will allow scientists and stonemasons to reproduce them in a sustainable way, using resources efficiently and preserving the regional architectural identity.

Acknowledgements

Grant PID2021-123948OB-100 funded by MCIN/AEI/10.13039/501100011033 and by ERDF "A way of making Europe", by the European Union.
Fundação para a Ciência e a Tecnologia (Lisboa, PT) , GRANT_NUMBER: CEECIND/03568/2017.
Erasmus consortia "HERDADE" (2021-1-ES01-KA131-HED-000009095) Funding.

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Unveiling the Chemistry of Street Art by a Multi-technique Approach

Cosima D. Calvano[1,2], Elena C. L. Rigante[1], Francesca Modugno[3], Jacopo La Nasa[3], Silvia Pizzimenti[3], Tommaso R. I. Cataldi[1,2]

[1]Department of Chemistry, University of Bari Aldo Moro, via Orabona 4, 70126 Bari (Italy);
[2]Centro Interdipartimentale SMART, University of Bari Aldo Moro, via Orabona 4, 70126 Bari (Italy);
[3]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa.
cosimadamiana.calvano@uniba.it

Keywords: street art, pigments, mass spectrometry, binders, Py-GC/MS

In recent years, graffiti and street art have been recognized as artistic movements due to their growing popularity, so that these new forms of art are also deemed worthy of diagnostic campaigns. Indeed, the creation of murals serves to foster a sense of community and enhance the aesthetic appeal of suburban areas. Today, great attention is paid not only to their protection from vandalism and deterioration, but also to the definition of standardized guidelines for their cleaning, conservation and restoration. Various techniques, including infrared (IR) and Raman spectroscopies, as well as pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), have been employed to identify both inorganic and organic pigments, along with binders [1–3]. In this study, we examined different spray varnishes from several brands using multiple analytical techniques, including attenuated total reflection Fourier-transform (ATR-FT)-IR, reversed-phase liquid chromatography (RPLC) coupled with UV-Vis and electrospray ionization (ESI) MS, and laser desorption ionization (LDI)-MS. Employing small amounts of samples, approximately 1 mg each, collected from three of the ten murals created in 2021 by local and international street artists, such as Hogre, Ozmo, and David Pompili, within the Quartiere Museale (Bari, Italy), very useful information were obtained regarding binders and pigments used. ATR-FTIR spectroscopy and Py-GC/MS proved valuable in identifying the primary binder used, while a combination of UV-Vis and mass spectrometric techniques was helpful to identify the organic pigments. In this communication, we will discuss the most noteworthy findings derived from these analyses.

Acknowledgements

This work was supported by Progetto di Ricerca di Interesse Nazionale—PRIN 2020MNZ579—"Sustainable Preservation Strategies for Street Art - SuPerStAr", financed by the Italian Ministero per l'Istruzione, l'Università e la Ricerca (MIUR).

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Unveiling the Painting Technique of the Gallo-Roman Wall Paintings of Limonum: a Multi-analytical Study

Adriana Iuliano[1], Francesca Galluzzi[1], Isabelle Pianet[1] and Mathilde Carrive[2]

[1]Archéosciences Bordeaux, CNRS/Université Bordeaux Montaigne/Université de Bordeaux, Maison de l'Archéologie, Pessac, France; adriana.iuliano@u-bordeaux-montaigne.fr, francesca.galluzzi@u-bordeaux-montaigne.fr, isabelle.pianet@u-bordeaux-montaigne.fr
[2]Hellénisation et romanisation dans le monde antique (HeRMA), Université de Poitiers, 15 Rue de l'Hôtel Dieu, Poitiers, France; mathilde.carrive@univ-poitiers.fr

Keywords: Roman Gaul, wall painting, pigments, spectroscopy, multi-analytical approach

Roman influence expanded in Gaul from the 3rd century B.C. and culminated with the conquest and administration of the region under Augustus, bringing with it new construction and decoration techniques, including wall painting. Gallo-Roman decorative traditions, initially strongly influenced by Italian models and techniques, are known for gradually acquiring a certain stylistic autonomy and originality in the second half of the 1st century A.D. [1]. This raises questions on possible changes in the choice of pigments and painting technique made by craftsmen of the time.
Painting production in Gaul is well studied and documented from an archaeological and artistic point of view [2], [3]. In the last ten years, archaeometric studies have also been carried out, although often limited to a single building or a group of close and/or contemporary buildings, therefore not allowing a comprehensive study of the practices employed in ancient painting [4]. For this reason, this research focuses on the investigation of a larger corpus of wall paintings in the Roman province of Gallia Aquitania, that of the painted plasters of the ancient city of Limonum (modern-day Poitiers, France). Several lots of painted fragments were selected, dating from the 1st to the 3rd century A.D. and coming from diverse excavation sites such as the ones of the Chambre de Commerce, 10 Rue de la Bretonnerie, and 13 Rue des Carmes. The plasters were analysed in order to identify the colour palette and understand the evolution of the painting technique used in the wall paintings.
A multi-analytical approach consisting of imaging and physico-chemical techniques was followed. A first step involved the use of non-invasive techniques on wall painting fragments, such as portable digital microscopy, hyperspectral imaging (HSI) in the Vis-NIR (350 - 1000 nm) and SWIR range (950 - 2500 nm), portable x-ray fluorescence (pXRF) spectroscopy, micro-XRF mapping, and x-ray diffraction (XRD) analysis. The first part of the protocol allowed for the characterisation of red and yellow ochres, green earths (celadonite), Egyptian blue, cinnabar, carbon black, as well as for the identification and selection of sampling areas. Further investigations with micro-invasive non-destructive analytical techniques were carried out in a second step, including optical microscopy (OM) on micro-samples and cross-sections, scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDS), micro-Raman spectroscopy and Fourier-transform infrared (FTIR) spectroscopy. Punctual and molecular analyses confirmed previously obtained results, while

stratigraphic observations gave some insights on the painting technique employed, determining the presence of pigments mixtures and complex paint layers. Finally, the comparison and combination of information obtained from different lots and analyses showed the importance of complementarity in multi-analytical approaches for a complete understanding of the artworks of Limonum.

Acknowledgements

The authors would like to thank the Centre de Conservation et d'Etude (CCE) of Poitiers, in particular Axelle Chabroux, conservator in charge of the CCE, as well as Flavien Bambagioni and Jérôme Defaix.

Funding

This study received financial support from the French government in the framework of the University of Bordeaux's IdEx „Investments for the Future" program / GPR „Human Past", and from the Nouvelle-Aquitaine region in the framework of the Programme de recherche „Aquitania Ornata. Formes, matériaux et techniques du décor pariétal en Aquitaine romaine."

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Crystal Palace Dinosaurs: A Picture of the Past Through the Study of the Sculptures' Painting Materials

Francesca Gherardi[1], Tom Bardwell[2], Rachel Lawson[2] and Karen Morrissey[3]

[1]Historic England, Fort Cumberland laboratories, Portsmouth (UK); francesca.gherardi@historicengland.org.uk
[2]Sally Strachey Historic Conservation Ltd, Wells (UK); bardwell.thomas@gmail.com, rachel@sshconservation.co.uk
[3]Hirst Conservation Ltd, Sleaford (UK); karen@hirst-conservation.com

Keywords: outdoor sculptures, 19th century, micro-XRF, SEM-EDS, metal soaps

The Crystal Palace Dinosaurs are the first full-scale sculptural reconstructions of extinct animals from fossil remains. They were designed and sculpted between 1852 and 1855 by Benjamin Waterhouse Hawkins and placed in the Crystal Palace Park (London, UK) in the ‚Geological Court' [1].
The sculptures (about 30) were made from a clay model, then moulds were taken in sections and the final model cast using Portland cement. They were then painted.
After 1936, the park fall into disrepair and the sculptures were cleaned, stripped and repainted several times, with significant changes in the colour schemes.
To develop a long-term preservation strategy, a condition survey of the statues was carried out in 2023, and this research focused on the study of the materials and the stratigraphy of the original paint schemes.
Samples collected from the sculptures during a conservation intervention in 2000 [2] were investigated using 3D digital microscopy, micro-XRF spectroscopy and SEM-EDS.
The results indicate that the original paint includes a red primer and a secondary white preparation layer made by using red and white lead, respectively, in an oil binder.
In the statues of dinosaurs, reptiles and amphibians, a green/turqoise coat was applied using green earth mixed with lead white and barite as an extender, while shading of the skin was created using brown ochres in an oil medium. Finally, a beige/brown paint finish, prepared by mixing different ochres with lead white and barite, was applied on the mammals to simulate the presence of fur.
Several degradation compounds (carboxylates and oxalates) were also found in the paint layers, and their production might have lead to detachment of the early paint layers from the substrate of the aquatic animals.
The study of these samples is very valuable because, in many cases, they represent the only evidence of the original paint applied on the sculptures and the resuts will be used to match the colour of future repaints and, together with the condition survey, inform a holistic repair strategy of the sculptures.

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Unveiling Provenance and Production Technologies of Chalcolithic Loom Weights from Vila Nova de Sao Pedro (Portugal) – A Multi-analytical Approach

Rosa Marques[1,2]; Ana Luísa Rodrigues[1,2]; Maria Isabel Dias[1,2]; Maria Isabel Prudêncio[1,2]; Dulce Russo[1,2]; Paula G. Fernandes[1]; Mariana Diniz[3,4]; Andrea Martins[3,4]; César Neves[3,4]; José M. Arnaud[4]; Pedro Cura[5]; Joana Carrondo[5]; Zsolt Kasztovszky[6]; Ildiko Harsányi[6]; Veronika Szilágyi[6]; Imre Kovács[7]; Attila Németh[7] and Katalin Gméling[8]

[1]C2TN, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 (km 139,7), 2695-066 Bobadela, Portugal; rmarques@ctn.tecnico.ulisboa.pt
[2]DECN, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 (km 139,7), 2695-066 Bobadela, Portugal
[3]UNIARQ – School of Arts and Humanities, Universidade de Lisboa, 1600-214 Lisboa, Portugal
[4]Associação dos Arqueólogos Portugueses, Largo do Carmo, 1200-092 Lisboa, Portugal
[5]Pre-Historic Skills
[6]Nuclear Analysis and Radiography Department, Centre for Energy Research, 29-33 Konkoly-Thege street, 1121 Budapest, Hungary
[7]Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics, Budapest, Hungary
[8]Centre for Energy Research, Nuclear Analysis and Radiography Department, Budapest, Hungary

Keywords: Iberian Chalcolithic; Vila Nova de São Pedro; Loom weights; Micro-invasive methods

The Vila Nova de São Pedro (VNSP – Azambuja, Portugal), considered a national monument, is one of the biggest settlements of Iberian Chalcolithic (3rd millennium cal BC). It is well-known by the three identified walls, bastions and a high number of archaeological records recovered during the 31 archaeological campaigns directed by Afonso do Paço in 1937-1967 [1] and, since 2017 by the VNSP3000 research project [2]. This settlement sets on Miocene-Pontian limestone and sandstones and clays also occur. Compositional analyses of symbolic artefacts were already done and published [3].

One of the most iconic artifactual categories of VNSP are the loom weights, whose number ascends to 800 elements, mostly deposited in the Carmo Archaeological Museum (Lisbon, Portugal). These ceramic artefacts, with a square or rectangular shape, have four perforations, one in each end, showing their function of suspension on a loom. These plates also present decorative motifs incised on one or both sides.

The iconography is diverse: anthropomorphic, zoomorphic, solar and geometric motifs [4-6]. The collection of VNSP is the largest in Iberia, and the morphology of these weights is a regional specificity. The high number of loom weights identified, together with the presence of linen seeds and sheep faunal remains (wool extraction?), lead us to assume that local production of fabrics (cloths and/or strips) would be one of the central economic occupations at the settlement.

Through the experimental archaeology program (VNSP3000 project), several loom typologies were possible to recreate, were produced using local clays taken from the existing clay pits near the settlement and following the parameters of the original artifacts (size, weight, thickness).

For the first time, micro and non-destructive methods were applied to perform the mineralogical and chemical characterization of archaeological loom weights, experimental replicas, and local raw materials. These analyses will be crucial in identifying the raw materials used for loom weights in Vila Nova de São Pedro and understanding their production technology. The archaeometric results will be discussed in the context of the artifacts' diverse styles, decoration, usage, and manufacturing processes. These findings are significant for evaluating the significance of local textile production, trade networks, and consumption patterns.

Acknowledgements

C2TN authors gratefully acknowledge the Portuguese Science and Technology Foundation (FCT) support through the UID/Multi/04349/2020 project.

Funding

Projects supported by the European Commission under HORIZON 2020 Program through the Key Action Integrated Platform for the European Research Infrastructure on Cultural Heritage IPERION HS (Grant Agreement Number 871034 – fix_113 - CHALCLOOM).

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On Etching and Reproduction of Daguerreotypes: Comparison and Characterization of Prints

Valentina Ljubić Tobisch[1,2], Wolfgang Kautek[2]

[1]Technische Universität Wien, X-Ray Center, Getreidemarkt 9, 1060 Vienna - Austria;
valentina.tobisch@tuwien.ac.at
[2]University of Vienna, Department of Physical Chemistry, Währingerstrasse 42, 1090-Vienna, Austria;
wolfgang.kautek@univie.ac.at

Keywords: daguerreotypes, photomechanical reproduction, prints, etching

Two crucial techniques were developed in the late 1830s that significantly influenced the graphic arts and the quantity of print runs. Electrotyping [1] was successfully used for the production and reproduction of printing plates shortly after its invention by the German physicist Moritz Hermann von Jacobi in 1838. Photography [2] is the second pioneering innovation within this context, co-developed and published by Louis Jacques Mandé Daguerre just one year later in 1839, which soon enabled the development of photomechanical and photochemical reproduction processes [3–4]. Joseph Berres and his photography-enthusiastic contemporaries worked on the first photomechanical reproduction processes in Vienna. By the early 1840s, they were already able to produce a large number of prints from daguerreotypes through the direct application of the etching technique on daguerreotypes or through their galvanic reproduction[5]. These and other printing processes enabled automated reproduction techniques and facilitated the rapid development of photographic prints.

The Heritage Science Austria project PHELETYPIA is researching the early Viennese photographic processes and the first photomechanical reproduction processes using printing on paper. In many museum and archive collections, prints from this very early phase of photography can still be found, but often cannot be identified as such. Some details, which are often difficult to recognize, can provide information about their production method on closer inspection and help to identify the early photomechanical prints.

This work compares early photomechanical prints from different international collections and points out their detailed characteristics. The scientific analysis of the surface characteristics enables the identification of manufacturing features caused by etching as well as by subsequent processing by engravers, thus contributing to an easier identification of the prints.

Funding

The funding is acknowledged by the project PHELETYPIA, “The impact of early photography and electrotyping media on the creation of images and contemporary art“ (Heritage 2020-060 PHELETYPIA) in the Heritage Science Austria grant program of the Austrian Academy of Sciences.

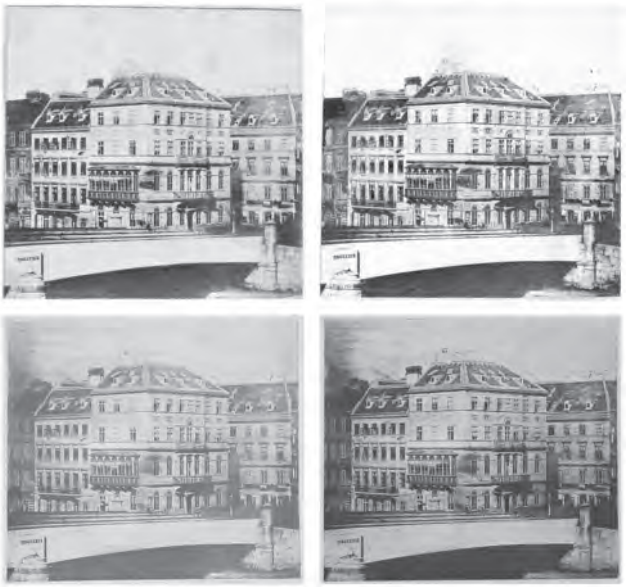

Fig. 49 Ferdinand's Bridge in Vienna 1840, Joseph Berres, print from etched daguerreotype. Upper left: Technisches Museum Wien, Vienna, Austria, BPA-015565-05_32. Upper right: Helfried Seemann Collection, Vienna, Austria; inscribed: Nach der Natur. Bottom left: Albertina, Vienna, Austria, FotoGLV2000/1717, inscribed: Die Ferdinandsbrücke. Bottom right: George Eastman Museum, Rochester, NY, 1980.0276.0001, inscribed: Heliogravure auf geätzter Daguerreotypplatte von Joseph Berres 1840, (Courtesy of the George Eastman Museum).

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The Appeal of Pigments and Gold Colouring on a Daguerreotype from the Varaždin City Museum, Croatia

Valentina Ljubić Tobisch[1], Dieter Ingerle[1], Peter Wobrauschek[2], Christina Streli[1,2], Karin Whitmore[3], Qaisar Maqbool[4], Günther Rupprechter[4], Klaudia Hradil[1,] Wolfgang Kautek[5]

[1]Technische Universität Wien, X-Ray Center, Getreidemarkt 9, 1060 Vienna, Austria; valentina.tobisch@tuwien.ac.at
[2]Technische Universität Wien, Atominstitut, Stadionallee 2, 1020 Vienna, Austria
[3]Technische Universität Wien, USTEM, Wiedner Hauptstraße 8-10, 1040 Vienna, Austria
[4]Technische Universität Wien, Institute of Materials Chemistry, Getreidemarkt 9/165, Vienna, Austria

Keywords: daguerreotypes, pigments, SEM/EDX, μXRF, μIR

As part of the Heritage Science Austria project PHELETYPIA[1], the surface morphology and elemental composition of daguerreotypes (first photographic technique developed in 1839) from museum collections is being analysed. The results should provide information about the manufacturing processes as well as the ageing phenomena in relation to the long-term preservation of these extremely sensitive artefacts[2]. In this paper, the results of three analytical methods - scanning electron microscopy, μXRF[3] and μIR - applied on one daguerreotype from the collection of the Varaždin City Museum, Croatia were applied to visualise the pigments and gold-based coatings.

Daguerreotype showing a young woman with a Biedermeier hairstyle in a pink dress with a matching jewellery set consisting of a brooch, a necklace and a bracelet. The picture was taken in a studio, probably in front of a tapestry showing a landscape with a tower in the background. The woman is sitting turned slightly to the right, her head and gaze are directed to the left towards the photographer, her right hand is resting on a small table. The daguerreotype is coloured. Light microscopy, SEM/EDX and μXRF analyses revealed an unusual colouring technique. The jewellery set was painted with gold (gold flakes) applied with an organic binder. This physical application of colour makes the jewellery appear almost three-dimensional. The green gemstones were painted on with pigments containing copper and arsenic. Moreover, the infrared reflectivity and the properties of other pigments used were determined with a μIR.

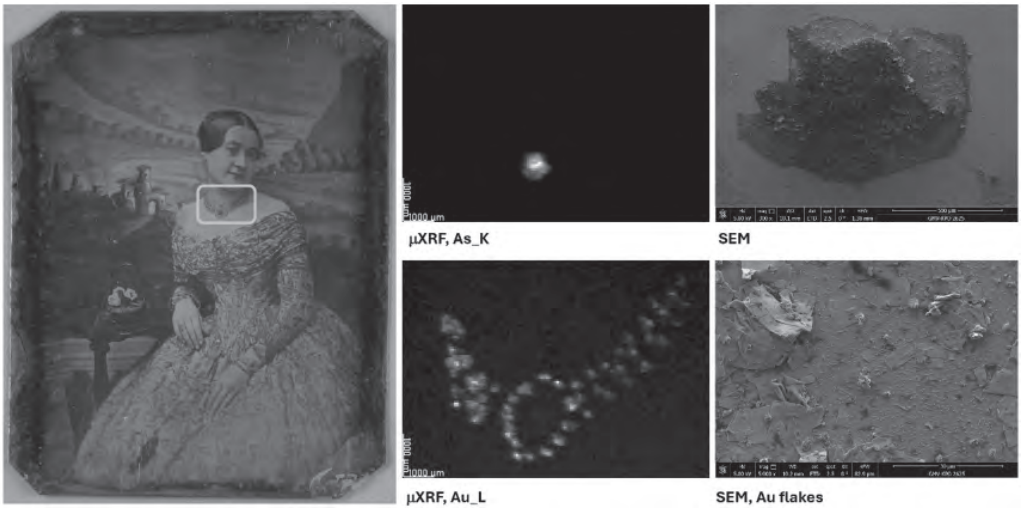

Figure 1. Portrait of a lady with a gold necklace with a green gemstone, Varaždin City Museum, Croatia

Funding

The funding is acknowledged by the project PHELETYPIA, "The impact of early photography and electrotyping media on the creation of images and contemporary art" (Heritage 2020-060 PHELETYPIA) in the Heritage Science Austria grant program of the Austrian Academy of Sciences.

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Study of Degradative Effects of Low-temperature Plasma on Objects of Heritage Made from Natural and Synthetic Polymers

Dominika Smatanová, Radko Tiňo

Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia; dominika.smatanova@stuba.sk, radko.tino@stuba.sk

Keywords: plastics in objects of heritage, plasma, degradation

Plastics have become an integral part of cultural heritage, yet misconceptions about their durability have led to neglect in their conservation. This oversight has resulted in the rapid degradation of materials such as cellulose nitrates, acetates, poly(vinyl chloride) (PVC), and early polyurethanes. The degradation of these materials stems from various internal and external factors, including temperature, light, air pollution, manufacturing processes, storage conditions, and microbial attacks [1, 2, 3].
Cleaning and sterilization of plastics present significant challenges due to their sensitivity to high temperatures and solvents. Low-temperature plasma, an ionized gas, offers a promising solution—a safe, environmentally friendly, and efficient technology [4]. While plasma treatment has been explored in heritage conservation for materials like metals, wood and paper, research in plastics conservation remains scarce, with only limited studies focusing on changes in adhesion properties during the repair of plastic objects [5, 6, 7]. Conversely, the application of plasma sterilization has been studied in medical and biomedical fields.
This study aims to investigate the effects of plasma treatment on selected PVC with a focus on degradation. PVC used in experiments contains 40% (w/w) plasticizer (dioctyl phthalate) and 3.8% (w/w) heat stabilizer (zinc stearate). The study employs a Design of Experiment (DoE) approach to explore the mentioned effects of plasma and its optional parameters, time of plasma exposure (1–15 minutes), frequency (500–2000 Hz), and energy (0.10–1.24 J/s), on the selected plastic material resulting in 20 experimental conditions. Other parameters, which are constant, include voltage (set at 150 V) and type and flow of working gas (saturated air, 6 l/min).
Each polyvinyl chloride sample is analysed using ATR–FTIR spectroscopy and optical microscopy. Changes in material composition of selected samples are mapped from surface to bulk using FTIR-imaging. Alterations in stability are monitored through thermal analysis. To determinate the effect of low-temperature plasma on prevention of plasticizer leaching, untreated and treated samples were extracted with hexane, and the loss of mass after extraction was evaluated.

Funding

This study was funded by the Slovak Research and Devolepment Agency under contract No. APVV-20-0410, project PolArt.

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New Processes for the Stabilization of Lignocellulosic Materials Developed in last 5 years

Eva Guzikiewiczová, Soňa Malečková and Katarína Vizárová

Slovak University of Technology, Faculty of chemical and food technology, Radlinského 9, Bratislava, 812 37, Slovak Republic, eva.guzikiewiczova@stuba.sk

Keywords: stabilization, deacidification, processes, paper

Traditional stabilization techniques often struggle with limitations such as the need to sort documents prior to modification, the inability to mass deacidify books for aqueous systems, economic difficulty, environmental concerns etc [1, 2]. The period in recent years on which the paper focuses highlights the current efforts to advance the resolution of these challenges through innovative approaches. These newer methods encompass a range of techniques including the utilization of nanotechnology, environmentally friendly chemicals, and advanced mechanical processes to ensure the deacidification, antioxidation, and reinforcement of paper materials.

One of the traditional methods works on the basis of dispersions. The particle size of these dispersions is on the micrometer level. Standout features of the new developments is the use of nanotechnology in the conservation process. Nanoparticles, such as calcium hydroxide and magnesium oxide, have been modified to improve their efficiency in deacidification and paper strengthening. These nanoparticles exhibit unique properties that allow for a deeper penetration into the paper matrix and a more uniform distribution, thereby ensuring a comprehensive stabilization effect without compromising the paper‘s structural integrity.

A emphasis is also placed on the ecological and health safety of these methods, alongside their effectiveness in preserving the integrity and extending the lifespan of paper-based information carriers. The advancements discussed in this article not only offer more efficient and safer alternatives for paper conservation but also underline the ongoing need for research in this vital field of heritage preservation.

This contribution aims to summarize the main findings, methodologies and advantages of the 16 newly developed procedures. The paper presents in detail results of one of the newly developed methods whose deacidifying agent is hydrotalcite dispersed in a mixed solvent (prefluoroheptane (PFH), isopropanol (IPA) and water). The effectiveness of the method to stabilise the lignocellulosic material during accelerated ageing is evaluated by measuring chemical (surface pH, glycosidic bond cleavage), mechanical (folding ndurance - coefficient of relative increase of the lifetime), optical (colorimetry) and spectral properties (FTIR) [3, 4].

Funding

This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-18-0155 MUFUSCEM.

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Effect of Low-temperature ADRE Plasma on Photographic Negatives

Dušana Grešová[1,2], Viera Jančovičová[1], Zuzana Hámorová[1]

[1]Department of Graphic Arts Technology and Applied Photochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava; dusana.gresova@stuba.sk

[2]Department of Preservation, Slovak National Archives, Drotárska cesta 42, P.O.Box 115, 840 05 Bratislava 45; Dusana.Gresova@minv.sk

Keywords: ADRE plasma, photographic negatives, cellulose acetate, decontamination

All film-based negatives consist of several layers. The number and thickness of the layers may vary according to the type of film. Photographic film is a complex, multi-component system generally composed of a flexible polymer base (the largest part of the film [1]), a gelatin binder, and an image-forming agent. Several polymer bases have been used throughout history, including cellulose nitrate (CN), cellulose acetate (CA), and polyethylene terephthalate (PET) [2].

Majority of black and white photographic films stored in the collections of archives and other memory institutions (libraries or museums) are made on cellulose acetate base [3]. This statement corresponds with the results of a material survey of the film collection of the Slovak National Archives. The results of the survey confirmed that more than 80 % of almost 16 000 microfilms1 have a cellulose acetate base.

Despite controlled conditions in archival depositories, fungi is a widespread cause of biological degradation of photographic film, resulting in significant cultural and historical loss to society. Organic cellulosic materials and gelatin used in the production of photographic negatives are sensitive to a variety of factors (such as humidity, temperature, etc.) and provide a suitable culture medium for fiber fungi and other microorganisms [2].

When microbiological contamination of the material is proven, it is important to proceed with disinfection or sterilisation. A wide range of chemicals in gaseous, vapour and liquid form can be used in cultural heritage conservation. In the field of photographic and cinematographic film disinfection there are two current studies; the first one deals with the effect of gamma and electron beam irradiation for conservation treatment of CA films [3] and the second one studies four types of disinfectants: butanol vapours, Bacillol®, Septonex® and ethylene oxide suitable for mass disinfection [1]. In the practical consideration of any disinfection or sterilization product or process, antimicrobial efficacy, compatibility with the material being treated, and any potential safety concerns should be considered [4]. Low temperature ADRE plasma generated at atmospheric pressure meets the following requirements.

This study describes the possibility of using low-temperature atmospheric discharge runaway electrons (ADRE) plasma in order to decontaminate photographic negatives. Electrical discharges and the plasma generated by them has the potential to destroy

1 a film strip on a polymer base bearing a miniature photographic copy of printed or other graphic matter, usually of a document, newspaper or book pages, etc., made for a library, archive, or the like.

fungi, bacteria and viruses [5]. The study investigates the influence of ADRE plasma on the optical and spectral properties of CA film and its long-term stability.
The prepared samples of CA negatives were characterized using densitometry, colorimetry and FTIR spectroscopy. The selected samples were exposed to the ADRE plasma treatment. The ADRE plasma treatment conditions (working gas air, device power 1 W/cm2, exposure time 15 minutes, total exposure 0.6 kJ/cm2) were selected based on previous results obtained in the decontamination of black and white gelatin photographs [6]. To test the effect of the ADRE plasma on the aged samples, the samples were subjected to accelerated aging in a Q-Sun chamber. To test the effect of sterilization on the long-term stability of the samples, samples treated with ADRE plasma were also subjected to accelerated aging. The use of ADRE plasma did not have a significant effect on the polymer base but caused oxidation processes in the image layer of the film, which were monitored using FTIR spectroscopy. After accelerated aging, ADRE plasma treatment showed no significant deterioration in the long-term stability of the film in terms of optical and spectral properties [7].

Acknowledgements

We would like to thank the management of the Slovak National Archives for their cooperation, also for the opportunity to publish the results of the material survey.

Funding

The study was supported by APVV-20-0410, project PolArt.

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Migration of Additives in PVC-P Induced by Accelerated Ageing

Katarína Kučíková, Katarína Vizárová, Soňa Malečková, Simona Klempová, and Radko Tiňo

Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia; katarina.kucikova@stuba.sk

Keywords: Polyvinyl chloride, migration of additives, plastic objects, FTIR imaging

Plastic production has more than doubled in the last two decades and its application is everywhere, even in the art. Over the years, we can now see, how short lifetime compared to traditional materials used for the century's plastic has. No long-term research has yet been devoted to the preservation of plastic objects in memory institutions, but it is developing rapidly. Polyvinyl chloride (PVC-P) is the third most widely produced synthetic polymer in the world and is also part of many cultural heritage objects [1]. It is classified as a malignant plastic and can be potentially dangerous for other materials in close contact. Malignant plastics consist of various groups or types of plastic that release corrosive or toxic substances as they degrade. In the case of PVC-P, it is known that the degradation processes that are applied during aging consist mainly in dehydrochlorination and migration of plasticizers from the internal structure to the surface of the material. The aim of the work was to describe the changes in the chemical structure of the cross-section of PVC-P samples exposed to accelerated aging, coinciding with the migration of phthalate plasticizer and heat stabilizer to the surface. FTIR spectroscopy appears to be a suitable method, because we can identify the bands of the plasticizer (1790 - 1660 cm-1) and the bands of the used stabilizer (1620 - 1520 cm-1). The ongoing dehydrochlorination in PVC-P can be seen by the FTIR method by the decrease in the intensity of the absorption band of the valence vibration of the C-Cl bond at 670-570 cm-1. For our research, the FTIR technique in combination with mapping seems interesting, which gives us new information about the changes in the chemical structure of the material caused by aging.Analyses were made on a set of PVC-P samples that were in contact with Whatman paper (W) and were subjected to accelerated aging in closed bottles in a drying oven at a temperature of 90 degrees for 35 days. The samples were previously conditioned at a temperature of 23 ± 1 °C, relative humidity of 50% ± 1% for 24 hours. The results confirm the migration of additives (both plasticizer and stabilizer) across the structure of the PVC-P sample, while the influence of the adjacent porous cellulosic material on the course of this process was revealed. The results of the analyses were also supported by microscopy. The gained knowledge will be applied to setting up the preventive protection of cultural heritage objects containing PVC-P.

Acknowledgements

The authors thank Zuzana Nagyová Menyhártová for her help in making the microscopic images.

Funding

This study was funded by the Slovak Research and Devolepment Agency under contract No. APVV-20-0410, project PolArt.

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EXCITE Network: European Union-funded Platform Offering Access to Structural and Chemical Imaging Techniques

Eva Zikmundová[1], Tomáš Zikmund[1], Pavel Pořízka[1], Jozef Kaiser[1], Geertje ter Maat[2], Oliver Plümper[2] and the EXCITE team

[1]Central European Institute of Technology (CEITEC), Brno University of Technology, Purkyňova 656/123, 61200 Brno, Czech Republic; eva.zikmundova@ceitec.vutbr.cz
[2]Utrecht University, Heidelberglaan 8, 3584 CS Utrecht, The Netherlands; g.w.termaat@uu.nl

Keywords: imaging techniques, spectroscopy, free-of-charge access

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Funding

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Using Green Solvents to Enhance the Bioavailability of Xenobiotics and thus Favour their Removal from Built Heritage

Fabiana Martín-Caramés, Dafne K. Quintero and Patricia Sanmartín

CRETUS, GEMAP (GI-1243), Departamento de Edafoloxía e Química Agrícola, Facultade de Farmacia, Universidade de Santiago de Compostela, 15782 - Santiago de Compostela, Spain

Keywords: biodegradation; environmentally sound; sustainable development; synergistic processes; synthetic materials.

Biocleaning (bioremoval) has the advantage over many of the physical and chemical cleaning protocols used in cultural heritage conservation of being a non-invasive, non-toxic, sustainable green technology. However, it also has some drawbacks, such as the longer time needed for biological transformation (relative to cleaning with chemical solvents and ablative processes) and the (as yet) scarce use of the technique for the removal of xenobiotics (synthetic chemical substances that are resistant to degradation). Xenobiotics are difficult to remove from substrates because of their molecular complexity. The key step in the biological degradation of these substances is to increase their bioavailability, ultimately making the substrate more susceptible to microbial attack.

This study aimed to explore the use of green solvents to increase the bioavailability of xenobiotics before their removal from built heritage. The green solvents used were dihydrolevoglucosenone (Cyrene™), dimethyl carbonate (DMC), chitosan (D-glucosamine and N-acetyl glucosamine) and ethyl lactate. All of the solvents degraded the xenobiotic material (plastic resins and graffiti paints applied by brush), as indicated by the results of analysis by infrared (ATR-FTIR) spectroscopy and surface microtopography. The next step (currently in progress) is to determine the specific impact that the four solvents being assessed have on the effectiveness of the subsequent biocleaning.

Funding

This study was conducted in the framework of the BIOXEN project: BIOcleaning of XENobiotic materials in granite stone heritage (PID2021-123329NA-I00) financed by the Spanish State Research Agency (AEI) of the Ministry of Science and Innovation (MCIN). P. Sanmartín acknowledges receipt of the Ramón y Cajal contract (RYC2020-029987-I) financed by the Spanish State Research Agency (AEI) of the Ministry of Science and Innovation (MCIN).

Migration of Additives in PVC-P Induced by Accelerated Ageing

Katarína Kučíková, Katarína Vizárová, Soňa Malečková, Simona Klempová, and Radko Tiňo

Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia; katarina.kucikova@stuba.sk

Keywords: Polyvinyl chloride, migration of additives, plastic objects, FTIR imaging

Plastic production has more than doubled in the last two decades and its application is everywhere, even in the art. Over the years, we can now see, how short lifetime compared to traditional materials used for the century's plastic has. No long-term research has yet been devoted to the preservation of plastic objects in memory institutions, but it is developing rapidly. Polyvinyl chloride (PVC-P) is the third most widely produced synthetic polymer in the world and is also part of many cultural heritage objects [1]. It is classified as a malignant plastic and can be potentially dangerous for other materials in close contact. Malignant plastics consist of various groups or types of plastic that release corrosive or toxic substances as they degrade. In the case of PVC-P, it is known that the degradation processes that are applied during aging consist mainly in dehydrochlorination and migration of plasticizers from the internal structure to the surface of the material. The aim of the work was to describe the changes in the chemical structure of the cross-section of PVC-P samples exposed to accelerated aging, coinciding with the migration of phthalate plasticizer and heat stabilizer to the surface. FTIR spectroscopy appears to be a suitable method, because we can identify the bands of the plasticizer (1790 - 1660 cm-1) and the bands of the used stabilizer (1620 - 1520 cm-1). The ongoing dehydrochlorination in PVC-P can be seen by the FTIR method by the decrease in the intensity of the absorption band of the valence vibration of the C-Cl bond at 670-570 cm-1. For our research, the FTIR technique in combination with mapping seems interesting, which gives us new information about the changes in the chemical structure of the material caused by aging.Analyses were made on a set of PVC-P samples that were in contact with Whatman paper (W) and were subjected to accelerated aging in closed bottles in a drying oven at a temperature of 90 degrees for 35 days. The samples were previously conditioned at a temperature of 23 ± 1 °C, relative humidity of 50% ± 1% for 24 hours. The results confirm the migration of additives (both plasticizer and stabilizer) across the structure of the PVC-P sample, while the influence of the adjacent porous cellulosic material on the course of this process was revealed. The results of the analyses were also supported by microscopy. The gained knowledge will be applied to setting up the preventive protection of cultural heritage objects containing PVC-P.

Acknowledgements

The authors thank Zuzana Nagyová Menyhártová for her help in making the microscopic images.

Funding

This study was funded by the Slovak Research and Devolepment Agency under contract No. APVV-20-0410, project PolArt.

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Characterization of the Unique Attributes of Extra Thin Washi Papers

Aldona Jedrusik[1] and Ida Skotnicova[2] and Milena Rehakova[3] and Michal Durovic[4]

[1]Slovak University of Technology in Bratislava, Institute of Natural and Synthetic Polymers, aldona.jedrusik@stuba.sk;
[2]Slovak University of Technology in Bratislava, Institute of Natural and Synthetic Polymers, ida.skotnicova@stuba.sk;
[3]Slovak University of Technology in Bratislava, Institute of Natural and Synthetic Polymers, milena.rehakova@stuba.sk;
[4]Univeristy of Chemistry and Technology in Prague, Department of Chemical Technology of Monument Conservation, michal.durovic@vscht.cz;

Keywords: Japanese Tissue, Low-Density, Physical Properties, Tensile Strength

The project presents the characterization of the physical properties of low-density Washi papers. Traditional Japanese paper, also known as Washi, is famous for its unique properties. Despite its low weight and thin sheet formation, the mechanical properties of Washi can surpass those of conventional papers. The study provides an evaluation of the tensile properties of low grammage Washi papers to better understand their performance. The research focuses on the mechanical properties of Washi papers, particularly examining aspects such as sheet density and tensile strength, as well as elastic modulus and fiber bonding.
By employing advanced analytical methods such as microscopy, spectroscopy and several different mechanical testing instruments, we unravel the underlying principles dictating the behavior of low-density Washi papers under particular environmental conditions.
Analysis of the physical properties of low-density Washi papers enhances our knowledge of this traditional material's mechanical behavior and potential applications. The findings from this study can offer valuable insights into the unique qualities of Washi papers and their suitability for various artistic, cultural and practical uses in the conservation of art.

Acknowledgements

The authors would like to acknowledge the significant and much appreciated contribution from the National Archives in Prague for providing assistance, support and access to their resources.

Funding

This work was carried out within the framework of Visegrad Fellowship Program under the project no. 62320195 and was funded by Visegrad Fund.

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Identification of varnished plastic objects in the collections of the Musée des Arts Décoratifs (MAD Paris)

Mathilde Larrieu[1,2], Héloïse Tessier[3], Nathalie Balcar[2], Florence Bertin[3], Gilles Barabant[2], Vincent Detalle[1], Maroussia Duranton[2], Odile Fichet[1] and Sophie Cantin[1]

[1]CY Cergy Paris Université, F95000 Cergy, France, mathilde.larrieu@cyu.fr
[2]Centre de Recherche et de Restauration des Musées de France (C2RMF), 14 Quai François Mitterrand, 75001 Paris, France
[3]Musée des Arts Décoratifs, 107 Rue de Rivoli, 75001 Paris, France

Keywords: conservation, material identification, ATR-FTIR, OCT

A collection survey in the Musée des Arts Décoratifs (MAD Paris) was carried out in 2023 on a selection of around 300 objects containing plastics, in order to register their degradation in a database and improve their storage conditions [1]. 188 pieces from the fashion (28%), toy (41%), advertising (9%) and design (22%) departments were analyzed to answer the one of the first questions that always arises in this case: which plastic is present or constitutive of the object?

Since ATR-FTIR spectroscopy has proven its efficiency as a non-destructive characterization technique [2], [3], [4] it has been used to identify the materials, using the database built during the POPART project [4]. This allowed to identify that, for example, PVC represents around 30% of the chosen degraded artefacts. However, decorative and/or protective layers are often applied on leather, as well as on fake leather items, especially on PVC. These coatings are in many cases polyurethane and polyester based, with thicknesses from 10 μm and above. As the ATR-FTIR wave's penetration depth into the samples is usually under 5 μm for polymers [5], the varnish has great chances of being misinterpreted as the object's core material, especially when a polyurethane-based material is identified. To distinguish coated from uncoated objects, it is thus essential to implement a reliable methodology, to then be able to establish suitable conservation conditions.

The first step of the methodology aimed to build an ATR-FTIR database containing unvarnished and varnished materials. Starting with PVC, the previous database was supplemented with polyurethane, vinyl acrylic and fluorocarbon -based varnishes, coated on unpigmented and pigmented PVC samples. The results obtained with this new completed database were compared with previous results. This first step identified reliably 5 PVC objects coated an acrylic-based product, either a varnish or a paint.

If/when the doubt persisted, a micro-sampling of the object was performed. The sample was then characterized on both sides, still using ATR-FTIR: if the FTIR spectra were different, it was concluded that the object has a minimum of one surface coating. However, if the spectra were the same, we could not necessarily conclude, especially when polyurethane was identified because it could be either the unvarnished material or a polyurethane covered with a polyurethane varnish.

In such cases, another method was used: Optical Coherence Tomography (OCT),

which allows detecting the number and thickness of layers in transparent to opaque materials, to a depth up to a couple of millimetres. Indeed, this interferometry technique, used in the medical field, takes advantage of the reflectivity properties of an incident optical beam at the interface of a layered object. OCT can be used on micro-sample if analysing the object is too complex (large or curved objects for example). Potentially varnished objects from the MAD's collections are still under study.
To summarize the identification method of varnished objects, an ATR-FTIR analysis is done, and a closest match is given using a database containing varnished samples. If the match score is too low, the object is micro-sampled. The micro-sample is analysed on both sides using ATR-FTIR, identifying the surface and core materials. And if the identification is still questionable, the OCT is used on the object or micro-sample to assess the number of layers. This method allows a deeper understanding of coated objects, and allow conservators to implement the best conservation protocol.

Acknowledgements

The authors wish to thank Kamal MERGOUM, R&D director of Griffine Industries, who has provided the samples that were used to expand the database. They lastly wish to thank Xueshi BAI for her insight on the use of OCT.

Funding

This work has benefited from State support managed by the Agence Nationale de la Recherche under the integrated investment program for the future included in France 2030, bearing the reference ANR-17-EURE-0021 Ecole Universitaire de Recherche Paris Seine Humanities, Creation, Heritage – Heritage Science Foundation

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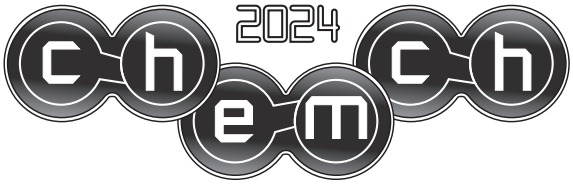

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Laboratory of Conservation Science and Technology
Contact: Assoc. prof. Katarína Vizárová, PhD., phone: +421 918 671 215, e-mail: katarina.vizarova@stuba.sk

Contact us
Assoc. prof. Katarína Vizárová, PhD., ODCP FCHPT STU, Radlinského 9, 812 37, Bratislava, Slovak Republic, phone: +421 2 5249 5381, mobile: +421 918 671 215, e-mail: katarina.vizarova@stuba.sk, web: http://www.fchpt.stuba.sk

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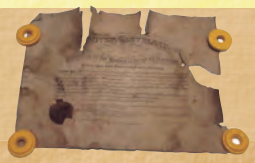

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Katarína Vizárová, Radko Tiňo
Katarína Kučíková, Milena Reháková

7th International Congress
Chemistry for Cultural Heritage

Abstract Proceedings

Published by Faculty of Chemical and Food Technology Slovak University of Technology in Bratislava in Slovak Chemistry Library FCHPT STU, Radlinského 9, 812 37 Bratislava in 2024.
Printed in Slovenská Grafia, a. s., 232 pages, 13,39 AH.
1. edition, Slovak Chemistry Library FCHPT STU in Bratislava.
Cover design, page layout:
Vladimír Dvonka and Miroslav Kováč
Impression: 200 pieces
ISBN 978-80-8208-124-7 (print)
ISBN 978-80-8208-125-4 (PDF)

Organizers:

STU FCHPT

SLOVAK NATIONAL MUSEUM

Slovak national gallery

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