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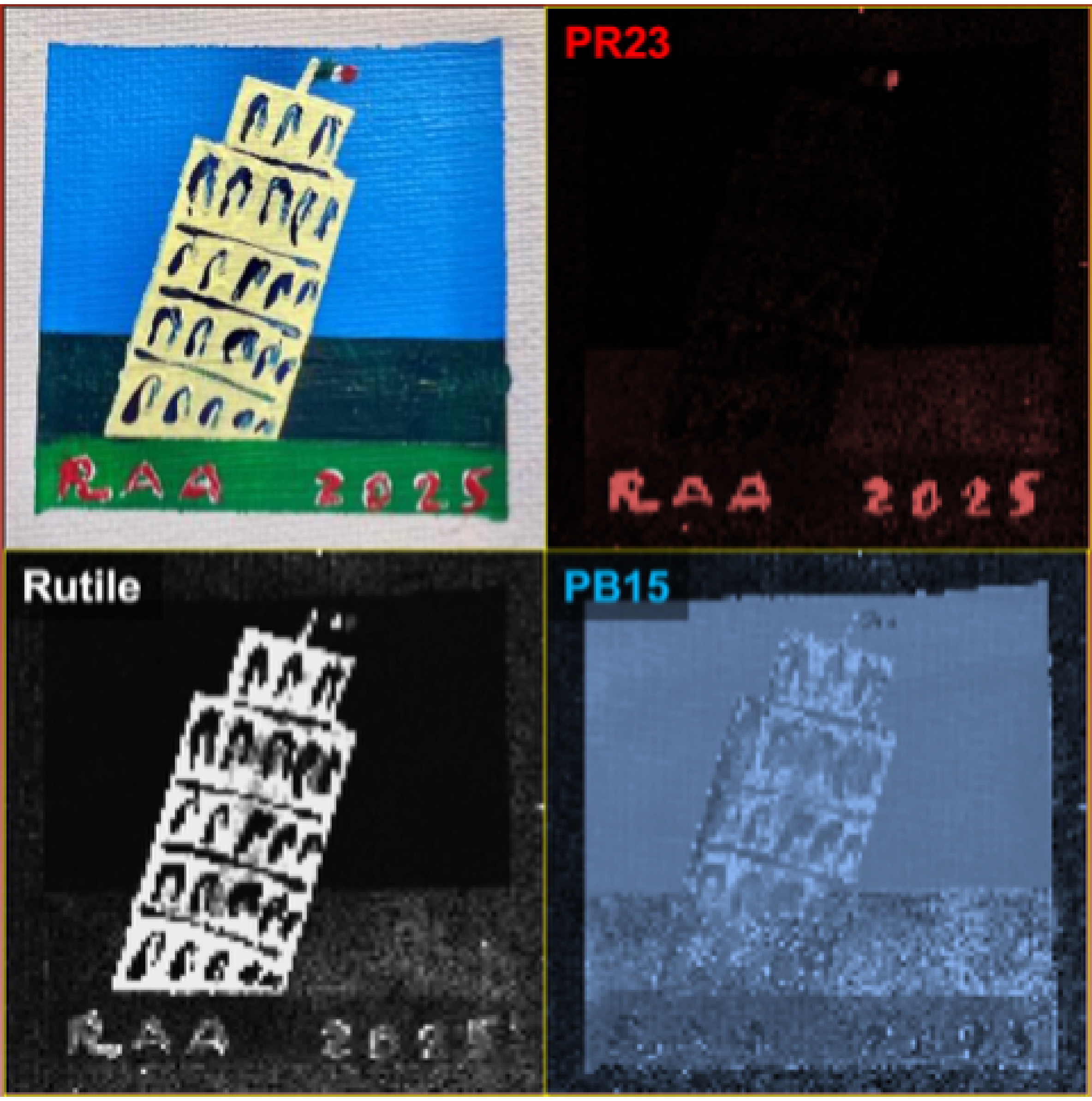
RAA 2025
International Conference on the Application of
Raman Spectroscopy in Art and Archaeology
Pisa, 1-6 September 2025

Abstract Book for

International Conference on the Application of Raman Spectroscopy in Art and Archaeology



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Abstract Book for the International Conference on the Application of Raman Spectroscopy in Art and Archaeology 2025

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COVER PHOTOGRAPH: P. Vandenabeele | Micro-Raman mapping on special painting dedicated to RAA2025.

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Table of Contents

Editorial

School Lectures

Plenary Session

Scientific contributions

Sponsor Talk

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
DOI: doi.org/10.19276/PLINIUS.2025.SI.019

Editorial

Illuminating the Past: The 12th International Raman Spectroscopy Symposium on Art and Archaeology in Pisa

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The International Conference on the Application of Raman Spectroscopy in Art and Archaeology (RAA) is a biennial event that brings together scholars and young researchers from a variety of humanities and science backgrounds. With a focus on Raman spectroscopy's ability to solve the mysteries of art and archaeology, the conference fosters interdisciplinary connections and advances the field of archaeometry.

After 14 years, the conference is returning to Italy for the third time. It is being hosted by the University of Pisa and organised by the Italian National Research Council's Institute of Chemistry and Organometallic Compounds (CNR-ICCOM), in collaboration with the Departments of Earth Sciences of the University of Florence, and the Departments of Civilisation and Forms of Knowledge and Chemistry and Industrial Chemistry at the University of Pisa. A two-day school hosted by the University of Pisa at the Collection of Plaster Casts and Antiquities will introduce the conference. This school will focus on the application of Raman spectroscopy techniques in art and archaeology. The training school is aimed at Master's and PhD students, as well as early career researchers. Participants will have the opportunity to use mobile/portable Raman equipment and learn methods for data acquisition and processing through a combination of theoretical sessions and practical workshops.

During the RAA 2025 conference, researchers from Europe and further afield will discuss a variety of themes through keynote lectures, poster presentations and social events. These topics have been organised into five sessions presenting studies that demonstrate the significant role of Raman spectroscopy in answering specific research questions. Often, these studies combine Raman spectroscopy with traditional methods or complementary techniques, both elementary and molecular, such as LIBS/XRF and Raman, and FTIR/HPLC and Raman, to exploit the strengths of each approach. The conference will explore new frontiers in non-traditional Raman spectroscopy applications, such as SORS (Spatially Offset Raman Spectroscopy) and SERS (Surface-enhanced Raman Spectroscopy), as well as methods involving synchrotron radiation Raman spectroscopy. In the era of open data and collaborative digital infrastructures, significant attention will be given to standardising data to enable the effective sharing of spectral information correlated with metadata, as well as to recent advances in chemometric approaches. Six sponsors with extensive experience in Raman spectroscopy will also present innovations aimed at enhancing its use in the cultural heritage field.

The Journal of Raman Spectroscopy (JRS) continues its long-standing tradition of supporting the Raman in Art and Archaeology (RAA) conference series with a special issue; it will feature a selection of extended papers presented at the 12th International RAA meeting, showcasing the diversity and depth of current research in this field.

The high quality of contributions to this Plinius special edition has enabled us to develop a rich scientific program complemented by glamorous social activities in the vibrant city of Pisa. This collection of abstracts highlights how Raman spectroscopy continues to provide valuable insights into the materials, techniques, and history of cultural heritage objects.

We hope that these contributions will inspire further dialogue and discovery at the intersection of science and the arts.

We would like to acknowledge the support of the Italian Society of Mineralogy and Petrology (SIMP) for the 12th RAA School and Conference, and all the patronages and the sponsors of the event.

School lectures

Basics of Raman Spectroscopy

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Raman spectroscopy is a widely employed method for materials analysis and has been shown to be a useful tool in the context of art conservation and archaeological science. The Raman bands in the spectrum correspond to vibrational modes which oscillate at specific frequencies. Rich, clear and often critical analytical information derives from Raman spectra obtained in the investigation of diverse types of objects and finds, which permit researchers to identify various materials, for example, pigments, minerals, corrosion products or even detect forgeries. Progress in instrumentation has led to the development of mobile Raman spectrometers that facilitate significantly analytical campaigns in museums, monuments or excavation sites. In this talk, the basic principles of Raman spectroscopy, the part of a Raman spectrometer, the analysis of a Raman spectrum and finally the different applications of Raman scattering in the field of cultural heritage will be discussed.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Deep Raman methods for Cultural Heritage

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The lecture will provide an overview of the rapidly advancing Deep Raman field and its impact on Heritage Science. Conventional Raman studies generally use a backscattering setup, in which the illuminating laser and detector for measuring the scattered Raman light partially follow the same optical path and target the same area. With opaque materials, as those encountered in Cultural heritage, this approach is limited to surface observations due to the diffusion process of photons from deep into the material. Over the last 20 years, time and spatial domain Raman methods paved the way for a non-invasive analysis of opaque materials, influencing several fields of high societal impact. Micro-Spatially Offset Raman Spectroscopy (micro-SORS), a Raman method specifically developed for the non-invasive investigation of deep portions of Cultural Heritage materials, will be illustrated and potentials in art field demonstrated.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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An Overview of Chemometric Approaches in Raman Studies of Cultural Heritage Materials

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In the last 20 years, chemometrics has gained significant importance in the field of cultural heritage research, particularly in managing the large volumes of multivariate data generated by various analytical instruments. It allows for the creation of easily interpretable graphs that encapsulate all the relevant information simultaneously.

This lecture aims to discuss the applications of chemometrics and multivariate statistical algorithms in cultural heritage studies using Raman spectroscopy. The goal is to present practical applications with examples drawn from the literature. Additionally, the lecture will provide essential theoretical insights necessary for a comprehensive understanding of the fundamental algorithms used. The focus will be on fundamental qualitative and quantitative models capable of addressing the most common challenges encountered when studying historical or artistic artifacts, with particular attention to data pre-processing.

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Exploring Mineral Identification in Cultural Heritage Using Raman Spectroscopy

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The study of cultural heritage materials requires an interdisciplinary approach that combines scientific analysis with historical and archaeological perspectives. Minerals, whether used as pigments, formed as degradation products, or present in the structure of an object, can provide valuable information about its history. Their identification through Raman spectroscopy helps to trace raw material sources, understand manufacturing techniques, and reveal patterns of trade, mobility, and cultural exchange. Additionally, mineralogical analysis contributes to assessing an object's state of conservation and reconstructing its historical trajectory.

This session will explore different approaches to mineral identification using Raman spectroscopy, focusing on spectral interpretation, complementary analytical techniques, and methodological considerations. Key factors influencing Raman spectra will be discussed, including crystal structure, fluorescence, and degradation processes, as well as the integration of Raman data with other analytical techniques. Through case studies from art, archaeology, and historical heritage, the session will address the challenges and possibilities of mineral characterisation in cultural heritage research.

Plenary session

Innovative methodological and technological insights to Raman spectroscopy applied in the field of Cultural Heritage (in the memory of Prof. Austin Nevin)

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Raman is a well-established spectroscopic technique which has found its place in many analytical laboratories dedicated to different fields of application. In particular, the capability to recognise the molecular composition of a great variety of materials in a non-destructive and non-invasive manner makes Raman spectroscopy a leading technique in the field of Cultural Heritage. However, the low signal intensity, the interference with other emission sources, and the risk of inducing photothermal effects during measurements push always scientists to find innovative solutions to make this technique more efficient and widely applied.

A selection of some significant published and unpublished (recent) research works and projects will be discussed in detail considering the five Raman sessions proposed at the conference: the application of chemometrics to Raman data to highlight subtle differences among the spectra as well as the conceptualization of innovative technological and instrumental solutions to solve specific conservation issues will be presented. Moreover, non-conventional analytical approaches and protocols of measurements to improve the identification and characterisation of problematic artistic materials to be detected by using Raman spectroscopy will be discussed. Most of these research works bring the significant contribution of Prof. Austin Nevin, who passed away last year. This plenary is also the occasion to celebrate his memory by recalling his research activity focused mainly on Raman spectroscopy applied to the Cultural Heritage field and to try to transmit to the audience his professional attitude capable of addressing complex technical and conservative issues due to his strong scientific background.

Scientific contributions

Preparative technique of Polychrome Floors at the Royal Palace of Caserta

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A painting should not be considered solely as a visual artwork created on canvas; artists also use various other surfaces, such as wood panels, walls, floors to cite a few. Painted and decorated floors, for instance, can often be found in royal residences. A remarkable example is the Royal Palace of Caserta that show marble-like painted terracotta floors. The art of painted terracotta is typical of the Neapolitan area and has historical roots dating back to the Renaissance. It involves different types of decoration, from geometric to cultural motifs. Among them, there is the marble-like painted terracotta that represents a decorative effect that imitates the veins and colors of marble, giving the rooms an elegant and refined appearance. Despite this widespread use, in literature the terracotta decorated floors, their chemical nature and preparation technique are still very poorly characterised. Spectroscopic techniques can be useful in analysing the composition of the colors used for the painted floors, identifying the preparation technique but also degradation mechanisms that can be induced by environmental, physical and chemical factors (Ntasi et al., 2024).

These decorated floors show evident signs of wear and degradation, which suggested the presence of a complex stratigraphy. Their analysis can reveal hidden history, providing insights into the restoration interventions undertaken, through observation of the number and composition of the various layers composing the paint. After careful inspection, 28 floor fragments were sampled from the apartments of the Museum Reggia di Caserta, of which 11 samples were investigated focusing on the organic and inorganic chemical composition. Several decoration units, composed of both preparation layers and pictorial ones, were studied by using optical microscopy.

The obtained stratigraphy was sometimes really complicated, ranging from a minimum of 3 up to 14 different layers (Fig. 1). Primarily results were obtained, that revealed information on the colour shades of the pictorial layers, the stratigraphy of the preparation layers and the decoration units related to restoration interventions.

Handheld X-ray fluorescence (hXRF) data were acquired in support to the pigment identification by micro-Raman spectroscopy. The latter allowed the identification of several pigments composing the color palette, varying from inorganic ones as red, white and greyish to the green, brown and yellow shades composed of phthalocyanine based pigments (Bersani & Lottici, 2016; Christie & Abel, 2021). Moreover, next to the pigment identification, micro-Raman spectroscopy allowed also to study some recurring layer sequences providing an interpretation for the floor preparation.

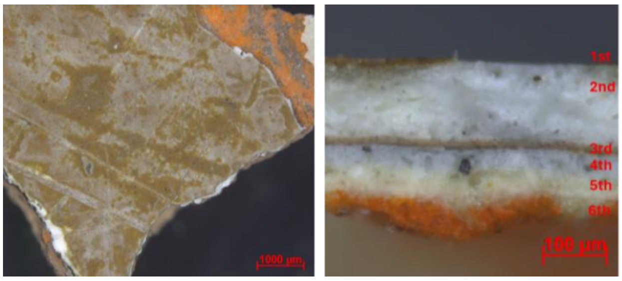

Figure 1 *Representative sample of decorated floor with six layers. On the right side a stereomicroscopy image of the sample surface. On the left side, one of the stratigraphy.*

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

References

Bersani, D., & Lottici, P.P. (2016) - Raman spectroscopy of minerals and mineral pigments in archaeometry: Raman spectroscopy of minerals in archaeometry. J. Raman Spectrosc., 47, 499–530.

Christie, R., & Abel, A. (2021) - Phthalocyanine green pigments. Phys. Sci. Rev., 6, 665-669.

Ntasi, G., et al. (2024) - On the Identification of the *a fresco* or *a secco* Preparative Technique of Wall Paintings. Heritage, 7, 3902.

How „Bravo" is the handheld Raman? A critical evaluation of its efficiency on investigating the facades of the Berlin Modernism Housing Estates

Alp Z.[1,2]*

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The handheld Raman spectrometer Bravo by Bruker Optics is a powerful, non-invasive and rapid alternative to benchtop Raman instruments. The instrument utilizes a Sequentially Shifted Excitation (SSE) technology, combined with a dual laser system operating at wavelengths of 785 nm and 853 nm. The patented SSE algorithm effectively eliminates fluorescence by applying slight shifts in sequential excitations, enabling rapid measurements. This technology merges three spectra from both lasers to produce a final spectrum that is free from fluorescence interference. While the Raman bands measured may shift with varying excitation wavelengths, undesired spectral intensities can persist (Cooper et al., 2013).

Research has demonstrated that BRAVO is highly effective for examining artworks and museum objects in situ (Pozzi et al., 2019). In this study, we assessed its efficiency on the painted facades of the UNESCO-listed Berlin Modernism Housing Estates, built between the First and Second World Wars. These estates have been continuously restored in accordance with preservation orders since the 1980s and 1990s. The inventories compiled by architects H. Pits and W. Brenne from the late 1970s onward were archived. We analysed the material samples from this archive, including original fragments from Gartenstadt Falkenberg and Waldsiedlung Zehlendorf. Furthermore, we conducted on-site investigations in Waldsiedlung Zehlendorf where construction phase paint layers were still present. Non-invasive results obtained using the BRAVO instrument were compared with laboratory-based μ-Raman spectroscopy on the same samples.

Our results indicate that the handheld Raman spectrometer Bravo, successfully identified the primary pigment composition of the exposed layers in many cases. The detected pigments were mainly inorganic. Chrome oxide yellow and green, ultramarine, calcite, titanium oxides, carbon blacks, and some synthetic organic pigments were detected with great precision. However, certain iron oxide minerals (particularly goethite), zinc oxide, and lead-based pigments required further examination with μ-Raman. In certain instances, pigments could not be detected due to poor Raman scattering properties, which limited the efficiency of identification. Additionally, some indicative bands fell below the instrument's spectral range limit of 300 cm^{-1}, which can be extended to 170 cm^{-1} with an additional package from Bruker. Furthermore, a low signal-to-noise ratio in some measurements affected the clarity and reliability of pigment identification. The large (apx. 1 mm) measurement area of the instrument presents both advantages and limitations. On uniform surfaces such as painted facades, the results represent a sum of the predominantly present materials, which is valuable for rapid examinations. However, this can obscure minor yet crucial components in the paint. Additionally, because the instrument measures the surface layer, investigating deeper layers requires sampling for analysis.

A combined approach using Bravo and portable X-ray fluorescence has proven beneficial in estimating the presence of underlying components in situ and for the decision making for potential sampling. On-site, a practical drawback was the need for a stable surface to hold the instrument, which directly influences the quality of the spectra. This issue was particularly evident when working on scaffolding, where the use of a tripod was not possible. In conclusion, Bravo's technology offers a valuable tool for non-invasive pigment analysis on the painted surfaces of Berlin Modernism Housing Estates. However, in some cases, its limitations necessitate complementary analytical methods for comprehensive material characterisation.

Figure 1 *Application in-situ of the handheld Raman spectrometer Bravo on the painted facade of Waldsiedlung Zehlendorf, Hochsitzweg 81, image courtesy: Jana Hainbach.*

References

Cooper, J.B., et al. (2013) - Sequentially Shifted Excitation Raman Spectroscopy: Novel Algorithm and Instrumentation for Fluorescence-Free Raman Spectroscopy in Spectral Space. Appl. Spectrosc., 67, 973–984.

Pozzi, F., et al. (2019) - Evaluation and optimization of the potential of a handheld Raman spectrometer: in situ, noninvasive materials characterisation in artworks. J. Raman Spectrosc., 50, 861–872.

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A rare medieval palette: identification and provenance of natural crocoite ($PbCrO_4$) in the wall paintings of Brandenburg Cathedral Cloister (Germany)

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The fragmentary and barely decipherable condition of the late medieval wall paintings (c. 1440s) in the former library of the Brandenburg Cathedral Cloister (Germany) presents significant challenges to their interpretation and readability. Since 2017, the wall painting cycle depicting the Liberal and Mechanical Arts has been under investigation by an interdisciplinary team of art historians, conservators, and heritage scientists to improve the visualisation of the motifs, understand the constitutive materials and assess the degradation stage (Schädler-Saub & Noll-Minor, 2022). Results of an in situ analytical campaign from 2024 shed light on the presence of a rare and unusual pigment, crocoite (lead chromate, $PbCrO_4$), used to paint the yellow frame of the books held by the clerical scholars in dialogue (Fig. 1).

Crocoite was uniquely identified using Raman spectroscopy, with its presence further confirmed by portable MA-XRF. Based on the reconstruction of the figurative motifs, the yellow layer is confirmed as original, suggesting the use of natural crocoite. It has been reported as a pigment in only three known instances across continental Europe—specifically in wall paintings from Prague (Czech Republic) and Siena and Parma (Italy), dated between the 13th and 16th centuries (Potenza et al., 2025). Its identification in the wall paintings of the Brandenburg Cathedral Cloister marks both the first in situ detection of natural crocoite using portable analytical equipment and the first documented occurrence of this rare natural yellow pigment in Germany. Crocoite is abundant in nature only in Tasmania (Australia). Before the advent of synthetic lead chromate in the 19th century, the use of natural crocoite as a pigment was not only uncommon in Europe due to its scarcity but, until recently, was generally regarded as improbable or accidental—and in some cases, even attributed to modern retouching. Therefore, this study aims to present and compare results obtained through a multi-analytical approach on mineralogical crocoite samples from known sources with those collected at Brandenburg. Bench-based Raman microscopy, employing multiple laser wavelengths, supports the identification of secondary lead chromate minerals and associated phases characteristic of natural crocoite. In parallel, quantitative trace element analysis via LA-ICP-MS is used to establish their geochemical "fingerprints" with the aim of highlighting compositional differences among the various mining sources. Mineralogical samples from various continental European deposits—including Callenberg (Saxony, Germany), the Berezovsk district (Russia), and, for comparison, Tasmania—are considered in this study. Comparing these reference materials with microsamples from Brandenburg aims to support provenance analysis and contribute to understanding the origin of the crocoite used in the wall paintings and, in turn, clarify the much-debated question of its use as a pigment.

The present investigation offers a valuable addition to previous research (Schädler-Saub & Noll-Minor, 2022), contributing to a deeper understanding of the palette employed at Brandenburg. In addition, it marks a significant step in the history of art technology by uncovering the use of natural crocoite.

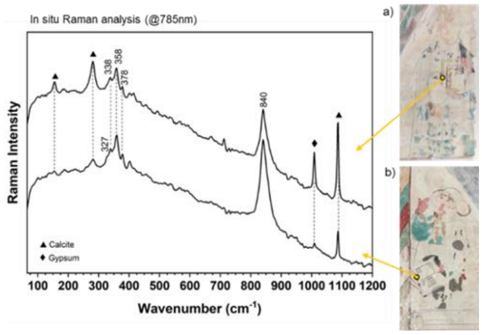

Figure 1 *Raman spectra collected in in situ with B&WTek i-Raman® Plus spectrometer (Metrohm group) of crocoite (ν_4 327, 338, 358, 378 cm^{-1}, ν_4 840 cm^{-1}) on the southern wall paintings of former Cloister of Brandenburg Cathedral: bay 7, eastern part (a) and bay 6, western part (b). Contours of the figures are displayed to improve their readability.*

References

Potenza, M., et al. (2025) - A Mural Painting Discovered in the Crypt of the Cathedral of Parma (Italy): Multi-Technique Investigations for the Conservative Restoration Project. Heritage, 8, 87.

Schädler-Saub, U., & Noll-Minor, M. (2022) - Der Wandmalereizyklus zu den Wissenschaften und Künsten in der Domklausur zu Brandenburg. Hendrik Bäßler verlag, Berlin.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Archaeometric analysis of medieval enamelworks from Hungary (Árpádian period, 10th-13th century)

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Enamelworks were considered among the most valued creations of the Byzantine Empire. For many centuries, Byzantium almost exclusively produced cloisonné enamel on gold, a technique that became strongly linked with Constantinople. These enamelled items represented the power of the imperial court, which were often used as tools of diplomacy and sent as gifts to other monarchs and churches. Despite their rarity and significance, modern archaeometric studies in the literature is scarce (Biron, 2015), and on pieces found in Hungary is completely missing. The aim of our research is to assess the provenance and possible raw materials for secular Byzantine enamels proving or disproving long-lasting hypotheses on the recycling of Roman tesserae; and to reveal the provenance of enamelworks from the Árpádian period. The study of enamelworks from the Árpádian period provides a unique opportunity to gather valuable data on these pieces of art. This dataset would provide a base for further studies of the most valuable Byzantine enamels of Hungary: the Monomachos Crown and the Holy Crown of Hungary. Only non-destructive, non-contact methods were used: after 2D and 3D microscopy we identified regions of interest for the analyses. μ-XRF was carried out to reveal the distribution of major and trace elements in the enamels and to map out the heterogeneities inside the glasses. Raman microspectroscopic analyses were conducted on the glassy matrix of the enamels to provide additional chemical information on pigments and opacifiers used. Based on the major and trace elements of the base glasses, combined with the identification of pigments and opacifiers in the enamels, may enable to reconstruct the recipes of the studied enamels. Measurements were carried out on the following enamelworks:

- A Byzantine-style enkolpion from the grave of Béla III of Hungary (reign: 1172-1196);
- A breast ornament with shape of a tetrafoil, one side still retaining the original enamels covered with white vine motives in front of blue background, with separate red enamels in the bends. These enamels are analogous to the vines next to the plates of the apostles on the hinges of the Holy Crown of Hungary. The enkolpion is often thought to have been made in Sicily, where the Norman monarchs from the 1070s until the 12th century united the Byzantine and Arabic heritage with their own Franco-Latin culture.
- A Byzantine style enameled disc (probably a brooch originally), now made into a bracelet recovered from Székesfehérvár. The "bracelet" is thought to be an important parallel of the Holy Crown with its enamelled plates and filigree decorations.
- A ring with a king's head: a cloisonné enamel depicting a head of a king or a queen. Its creation can be hypothetically placed in Hungary, where at the time of the foundation of Hungary craftsmen from many areas came to the kingdom to fulfil the orders of the court (Kiss, 2020).

Based on the combined μ-XRF and Raman measurements all enamels were made of soda-lime glass. On the enkolpion a natron-type base glass (opacified with cassiterite) can be assumed, but on the other items addition of plant-ash is highly likely based on their elevated phosphorous and potassium contents. On the bracelet the white enamel is opacified with hexagonal Ca-antimonate ($CaSb_2O_6$), meanwhile on the ring both antimonates and cassiterite (SnO_2) were used. Light yellow enamel only appears on the enkolpion, where its colour and opacity are caused by Pb-antimonate (Naples Yellow) and cassiterite. Opaque red enamels are usually the most altered ones, but it could be still determined that on all three enamelworks they were coloured and opacified by iron and copper. Green enamels, found on the bracelet and the ring, were coloured by pure copper, as suggested by the lack of tin in the glasses. All blue enamels are coloured with cobalt, and opacified with both orthorhombic ($Ca_2Sb_2O_7$) and hexagonal Ca-antimonates together with cassiterite. In all blue enamels the Co-contents correlates with copper, implying a similar geological source for cobalt. Our preliminary data indicate that the enamels were indeed made using Byzantine glass recipes known from the literature. Based on the scarce data on Byzantine enamels, glasses on all three items fits the Composition groups 1, 2 and 3 of Biron (2015), which represent soda-lime enamels from the 9th to the 13th centuries. To determine the exact timing and to narrow down to exact provenance and workshops of the studied enamelworks, further data is needed.

References

Biron, I. (2015) - Émaux sur métal du IXe au XIXe siècle: histoire, technique et matériaux. Faton, Dijon.

Kiss, E. (2020) - Ut mos est grecorum – Byzantine Heritage and the Era of the Árpád Dynasty. In „The Light of Thy Countenance, Greek Catholics in Hungary", S. Terdik, Debrecen, 20-35.

Garnet Provenance of Polychrome Jewellery from the Migration Period in the Carpathian Basin: the role of Raman spectroscopy

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Polychrome jewellery with red garnet inlays was widespread during the Hellenistic, Roman and Migration Periods. These fine metalwork pieces were characteristic for around three centuries in the Carpathian Basin (late 4th – 7th century AD) from the Hunnic Period through the age of the Gepidic and Langobardic kingdoms, up until the Avar Period. From the late 4th to the mid-5th centuries AD garnets were mainly used to decorate unique, prestigious items. In contrast, more simple artefacts from the 6th century AD reflect mass production and standardised designs. From the late 6th and 7th centuries AD, garnet jewellery saw a resurgence, marked by exquisite pieces worn by the elite. Tracing the provenance of the used gemstone inlays, based on their chemical composition, enhances the understanding of the garnet supply chains and trade networks, the production organisation, potential workshop connections and their changes during the Migration Period. Not only the quality of the jewellery, but also the sourcing of the garnets varied during this period. Due to the nature and value of the studied objects their investigation is only possible with careful non-destructive and non-invasive methods. Raman spectroscopy is one of the most suitable methods (Nasdala et al., 2023) for the archaeometric study of garnet-inlaid artefacts, as it is the most accessible method for analysing these artefacts even on-site in the museum collections. Raman is also the best tool for identifying inclusions in the garnet gemstones, which is crucial for determining their provenance. Raman data on garnets from jewellery are still growing (e.g. Nasdala et al., 2023; Gilg et al., 2024; Horváth et al., 2024), but still not available in the literature on all possible garnet sources, classified into 9 clusters and groups by Gilg et al. (2024). Thus, our goal is to build a comprehensive database of inclusion data, chemistry (SEM-EDS/WDS, μ-XRF) and Raman spectra of garnet inlays from various artefacts from the Migration Period. Ultimately, our aim is to be able to determine the provenance of garnets from polychrome jewellery solely based on Raman spectroscopy, including both tabletop and mobile instruments.

Raman spectra of more than two thousand garnet inlays from Migration Period artefacts from several localities were collected. Most data are also supported by optical observations and Raman spectra of their inclusions, mineral chemistry (SEM-EDS/WDS) and occasionally with μ-XRF measurements. Using principal component analysis (PCA), we identified the best Raman bands that can be used to estimate the major element components (i.e. almandine, pyrope and grossular content) of the garnets; these are Band IX (470-490 cm^{-1}), Band VIII (495-510 cm^{-1}), Band V (625-645 cm^{-1}) and Band I (1040-1050 cm^{-1}). Based on these bands most garnet clusters can be distinguished, but some clusters, which overlap in major element content (e.g. Clusters A and B), are still challenging to recognize without additional data (e.g. inclusions or trace elements). We also carried out comparisons between mobile and tabletop Raman measurements, which suggest that mobile Raman instruments may be able to determine the provenance of garnets, despite their lower resolution and smaller detection windows, even in the case of garnets, which show a wide chemical variation within a cluster. Our robust dataset reveals the most important changes in garnet supply in early medieval Europe. Mainly Clusters A, 'J' (unknown origin) and H (Sri Lanka) garnets were in use from the early 5th century AD. Cluster B (Northern India) garnets became widespread later, from the early 6th century, but only in the former Roman province of Pannonia. Clusters of garnets, which were widespread in late 6th-7th century Western Europe (Cluster E, Bohemia) and during Antiquity (Clusters D, F and G with Portuguese/Nigerian, unknown and Eastern Indian origin, respectively), appear only in small quantities during the Migration Period.

References:

Gilg, H.A., et al. (2024) - Four millennia of garnet trade in Northeast Africa–chemical analysis of ancient and Late Antiquity beads from Lower Nubian sites. Archaeometry, 66, 4, 860-876.

Horváth, E., et al. (2024) - Production perspectives of a high-status polychrome jewellery set from the Hunnic period (mid-5th century AD) Carpathian Basin. J. of Archaeol. Sci., 171, 106085.

Nasdala, L., et al. (2023) - The Imperial Crown of the Holy Roman Empire, Part I: Photoluminescence and Raman Spectroscopic Study of the Gemstones. J. of Gemmology, 38, 5.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Multilayered secrets of the past: non-invasive material analysis of Egyptian scarabs, scaraboids, and shabtis through XRF, Raman spectroscopy and CT scanning

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Scarabs, scaraboids and shabtis are among the oldest rock-based inscribed amulets from the ancient Egyptian culture. These portable historical objects were first introduced during the Old Kingdom (ca. 2575-2130 BCE), but it was not until the Middle Kingdom (ca. 2000-1550 BCE) that their production increased significantly. While the production of shabtis was predominantly confined within the Egyptian territories, from the Third Intermediate Period (ca. 1069-664 BCE) scarabs and scaraboids quickly spread beyond the borders of Egypt and began to appear throughout the Mediterranean region. As a result, their increasing popularity led to the gradual establishment of production centers outside of Egypt, as evidenced by the wide range of specimens found in Carthage, Tharros, Ibiza and other sites (Gorton, 1996).

The design and engravings of scarabs, scaraboids and shabtis reveal sociocultural characteristics that might otherwise have been lost to history. Alongside royal and non-royal names, scarabs and scaraboids unfold a wide range of funerary and religious texts and figurative motifs, while shabtis disclose to us particular funerary practices, in which they acted as magical substitutes for the deceased when called by the gods to undertake menial activities in the netherworld. Similarly, significant insights can be gained on the production and use of these artefacts by studying their mineral-phase composition, since they are predominantly made of rock fragments or powdered minerals mixed with binding and fluxing agents, before being fired at high temperatures to produce a characteristic glazed surface.

Traditional gemological techniques for identifying these artifacts rely on visual inspection, which is often inconclusive or yields too generic results due to the glazed surface. Given the uniqueness and historical value of these objects, which prohibit sampling, non-destructive and non-invasive analytical techniques that can determine the chemical composition and crystal structure of the writing supports, are becoming increasingly popular. X-ray fluorescence (XRF) and Raman spectroscopy have been successfully used to determine the structure, elemental composition and firing conditions of glazed scarabs (Costa et al., 2015) and glazed ceramics (Colomban & Paulsen, 2005), but not yet combined with computed tomography (CT) scanning.

Our investigation makes use of XRF, Raman spectroscopy and a portable high-resolution CT scanner to analyse selected scarabs, scaraboids and faience shabtis from the Ancient Art and Antiquities collection of the Museum für Kunst und Gewerbe (MK&G), Hamburg. We demonstrate that the combination of Raman spectroscopy with complementary XRF and CT scanning analysis can (i) determine the major, minor and trace element composition within the mineral phases of the rock-based substrate and of the glazed surfaces, (ii) differentiate among glazing techniques and specify firing conditions specifically for glazed steatite-based scarabs, and (iii) uncover the structural features of the glaze and inner core of shabtis and scarabs.

References

Colomban, P., & Paulsen, O. (2005) - Non-destructive determination of the structure and composition of glazes by Raman spectroscopy. J. Am. Cera. Soc., 88, 390-395.

Costa, M., et al. (2019) - A micro-analytical study of the scarabs of the Necropolis of Vinha das Caliças (Portugal). Microsc. Microanal., 25, 214-220.

Gorton, A.F. (1996) - Egyptian and Egyptianizing Scarabs: A typology of steatite, faience and past scarabs from Punic and other Mediterranean sites (Oxford University Committee for Archaeology, Monograph 44). Oxford University Committee for Archaeology. Oxford.

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Development of a multi-analytical database, enhanced motorization for in situ techniques, and open-source workflows for the study of historical pigments by Raman spectroscopy

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This work presents the development of a detailed, open-access database of over 70 historical pigments that includes not only their historical information but also a complete analytical characterisation using techniques of interest in the study of heritage due to their safety and portability, such as Raman spectroscopy, infrared spectroscopy (ATR and DRIFT modes), X-ray fluorescence, colorimetry, and hyperspectral cameras. A fundamental aspect of this work is implementing this database as an open-access, multiplatform application. Its easy accessibility and diverse search and comparison functionalities are designed to provide a valuable tool for studying heritage, particularly when used on portable devices such as smartphones or tablets. Although the development of the database is the core of this project, a broader approach has been considered to enhance the study of historical pigments on heritage. On the one hand, the limitations of conventional in situ experimental devices, particularly Raman spectrometers, were assessed, leading to the design of two multi-technique motorization devices. One of the devices is designed to be employed on small objects, whereas the other can cover regions up to 50 x 50 cm². Raman spectroscopy can be utilized with these systems in both macro and micro modes. Moreover, when using Raman spectroscopy in microscopic mode, the motorization systems and associated software allow for performing in situ XY mapping with autofocus capabilities. On the other hand, open-source Quasar spectroscopic software has been employed to ensure broad compatibility of experimental data with the developed database and related data treatment procedures. Specific workflows have been designed to compare experimental results with the database's reference values. Moreover, these workflows were designed and adapted to be compatible with any other free spectral database, aiming to provide a universal tool to expand the usefulness of existing resources. Finally, to test the project results and its impact on the heritage sector, the database and its implementation were validated with a selection of heritage assets. Training materials and activities were also created to introduce its use to sector professionals.

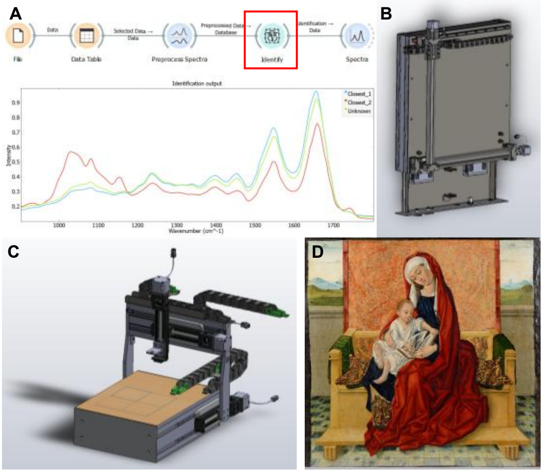

Figure 1 a) *Example of a simple Quasar workflow using the AHMat's Identify tool and the provided results.* ***b,c)*** *Design of motorization setups for large (b) and small (c) samples.* ***d)*** *Madonna (Maestro de los Luna, 1488) is the central piece of the altarpiece of the church of El Muyo (Segovia, Spain). This was one of the artworks studied by Raman spectroscopy during the development of this project.*

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References

Eastaugh, N., et al. (2007) - Pigment compendium: a dictionary of historical pigments. Routledge.

Edwards, H.G.M., et al. (Eds.) (2005) - Raman spectroscopy in archaeology and art history. Royal Society of Chemistry.

Toplak, M., et al. (2021) - Quasar: Easy Machine Learning for Biospectroscopy. Cells, 10, 2300.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Polychromy, classification, and firing temperature of pre-Roman glass beads in the Iberian Peninsula and Balearic Islands

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Glass pieces were highly appreciated goods in the Protohistory of the Mediterranean. Regarding the Iberian Peninsula, the specialized production of these glass pieces seems non-compatible with local workshops. Therefore, they are proof of commercial relationships with other cultures with the technical capability to produce such pieces. Thus, developing a comprehensive study with statistical relevance of a wide collection of glass beads throughout Iberia constitutes an opportunity to widen the knowledge about our history and cultural heritage. An ongoing research project, "Líthos chytós (éx tês) Iberías. Physico-chemical analysis of preroman glass beads: a window into Iberia's past (LITHOSCHYTOS)", intends to carry out the largest and more detailed study of pre-Roman glass beads recovered in the Iberian Peninsula and Balearic Islands.

This project considers a multi-technique approach, with Raman spectroscopy as an essential tool required to fulfill the objectives of the project. This work presents the preliminary results of the ongoing research project, currently including more than 350 glass beads recovered from over 20 archeological sites at the center and west of the Iberian Peninsula and the Balearic Islands. Among the impressive glass beads collections studied, it can be highlighted the study of glass beads from the necropolis of Puig de Molins (Ibiza, Spain), one of the most important necropolises in the western Mediterranean, a World Heritage Site with more than 3,000 rock-carved tombs and burial sites from the Phoenician to the Roman period. Moreover, the selected samples also comprised over 15 phoenician glass pendants. These kinds of glass beads are the summit of pre-Roman glass craftsmanship. However, only 6 pendants have been studied till now from an archaeometric perspective (only 3 using Raman spectroscopy) at the international level. Thus, this work included the most extensive archaeometric study on these extraordinary archaeological findings performed up to date.

In particular, the study of this large set of samples by Raman spectroscopy has allowed the identification of the most common pigments employed in polychrome samples, and surface alterations, as well as studying their manufacturing (e.g., estimating the firing temperatures from the characteristics of the ν(Si-O) stretching and δ(Si-O) bending vibrational bands) and classifying them by the features of their Raman spectra (e.g., taking into account the relationships between their polymerization index, and the νmax(Si-O) versus δmax(Si-O) values). Finally, the results obtained by Raman spectroscopy were contrasted or compared with the elemental composition of the samples determined by X-ray fluorescence.

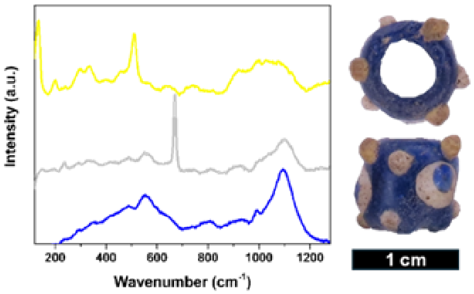

Figure 1 *Raman study of a polychrome bead, showing Naples yellow and calcium antimoniate as pigments respectively on yellow and white regions and the glass Raman bands on the blue regions.*

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References

Barroso-Solares, S., et al. (2024) - A multi-technique approach to unveil the composition and fabrication of a pre-Roman glass masterpiece: a double-faced human-head shape polychrome glass pendant. Archaeol. Anthropol. Sci., 16, 9, 153.

Colomban, Ph., (2013) - Non–destructive Raman analysis of ancient glasses and glazes. In: "Modern methods for analysing archaeological and historical glass", 275-300.

Pinto, J., et al. (2021) - Investigating glass beads and the funerary rituals of ancient Vaccaei culture (S. IV-I BC) by Raman spectroscopy. J. Raman Spectrosc., 52, 1, 170-185.

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Dye analysis on historical textiles by Raman and Surface-Enhanced Raman Spectroscopies: a focus on resonance phenomena

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Dyes have been employed in the past to colour historical textiles, and their detection and identification are essential to a thorough understanding of the history of dyeing craftsmanship. In this work we focus on the detection of red and yellow dyes, which are widely used across cultures and time periods, and are particularly challenging to characterise using minimally invasive analytical approaches. Textiles displaying these colours can be found in museum collections or unearthed during archaeological excavations. By documenting the natural resources (plants and insects) exploited and the know-how used to dye textiles, we can understand the history of these techniques, which require empirical knowledge of complex chemistry.

In most cases, these organic molecules have a skeleton based on light-absorbing cyclic rings. This property makes them good candidates for Raman spectroscopy analysis, however their detection remains a challenge. Despite the widely recognized strengths of this technique, such as minimal invasive character and suitability for organic analytes, the analysis of these ancient materials requires adjustment of the analytical conditions or sample pre-treatment. This is due to the strong fluorescence produced by the dye or associated textile and the low initial or residual concentration of the molecules to be detected. To improve dye detection, two paths can be explored: implementing Resonance Raman Spectroscopy (RRS) or adding plasmonic metallic nanostructured substrates to obtain the conditions for Surface-Enhanced Raman Spectroscopy (SERS). In both cases, selecting a specific excitation wavelength is crucial for signal enhancement. However, although these approaches are regularly applied to the identification of dyes on heritage objects, no study provides a full experimental understanding of enhancement efficiency depending on excitation wavelengths and dyeing molecules, and similarly, very few studies have explored the information that theoretical modeling approaches could provide (Pagliai et al., 2018). This highlights a lack of understanding of the phenomena involved in enhancing the Raman response, which could help in guiding and rationalizing the analytical conditions to be implemented for optimal detection performance depending on the targeted molecules.

To reduce this gap, in this study we have focused on the analysis of three major anthraquinone dyes, alizarin, purpurin and carminic acid, which are representative of red dyes, and two flavonoid dyes, luteolin and quercetin, representative of yellow dyes. The dyes responses with conventional Raman spectroscopy were studied by tuning the excitation wavelength from blue to infrared. The aim was not only to observe experimentally varying fluorescent backgrounds specific to each dye as a function of wavelength, but also to determine variations in the intensity ratio of Raman scattering characteristic bands. These variations are therefore correlated to a particular activity of certain vibrational modes depending on the laser. In order to better understand the latter phenomenon, ab initio DFT calculations were performed and the results compared with experimental data. The analytical approach adopted was to analyse pure dyes, but also mock-up dyed textiles (wool, silk and cotton), in order to approximate as closely as possible the historical samples of interest. All these samples were studied using conventional Raman spectroscopy and excitation wavelengths from blue to infrared corresponding to resonant or non-resonant conditions. As these fibers generally exhibit high fluorescence with conventional Raman spectroscopy, we also deployed SERS analyses, using Lee-Meisel silver colloid as SERS substrate (Lee & Meisel, 1982). These experiments and calculations allow to better understand the spectra obtained, the effects of wavelength selection and the resulting resonances in these complex samples.

To summarize, the results presented, combining the study of experimental and theoretical data will shed light on the physical phenomena leading to Raman scattering enhancement, while rationalizing the selection of optimal analysis conditions for the study of historical textile dyes. This final point will be illustrated by the presentation of measurements highlighting the performance of the recommended conditions for dyes identification in medieval textiles.

References

Lee, P.C., & Meisel, D. (1982) - Adsorption and surface enhanced Raman of dyes on silver and gold sols. J. of Phys. Chem., 86, 3391-3395.

Pagliai, M., et al. (2018) - DFT calculations of the IR and Raman spectra of anthraquinone dyes and lakes. J. of Raman Spectrosc., 49, 668-683.

Comparative Analysis of Data Processing Techniques for Macro-Raman Mapping in Art Analysis

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Raman spectroscopy is a valuable technique in cultural heritage research because it can non-destructively obtain molecular information. When analysing an array of spectra, it is important to combine molecular information with spatial information, which is where macro-Raman mapping comes in.

Macro-Raman mapping is a non-invasive technique that provides spatially resolved, high-resolution molecular maps of artifacts, which is crucial for material identification and conservation. It acquires and analyses thousands of Raman spectra over vast surface regions, which can be over several square centimeters. However, the quality and interpretability of Raman maps are highly dependent on the data processing methods used.

The approach to this study is to evaluate data processing techniques—such as baseline correction, noise reduction, and scaling— and outline the pros and cons of each method to evaluate their impacts on data quality and interpretability. By comparing these methods, this research will highlight each method's advantages, limitations, and the influence of applying specific corrections on Raman maps. These techniques will be examined for their effectiveness in enhancing image clarity and distinguishing between different materials.

Ultimately, this research aims to optimize Raman mapping analysis and promote more informed and effective strategies for preserving cultural heritage. In situations where it is crucial to integrate molecular data with spatial information, the analysis of an array of spectral data becomes pertinent. This is the primary application of macro-Raman mapping.

References:

Ropret, P., et al. (2010) - Advances in Raman mapping of works of art. J. Raman Spectrosc., 41, 1462-1467.

Ryabchykov, O., et al. (2019) - Analyzing Raman spectroscopic data. Physical Sci. Rev., 4, 2, 20170043.

Vandenabeele, P., & Rousaki, A. (2021) - Developing Macro-Raman Mapping as a Tool for Studying the Pigment Distribution of Art Objects. Anal. Chem., 93, 46, 15390-15400.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Synthesis of Egyptian Blue starting from Roman coins: characterisation of modern products and comparison with archaeological samples

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The reconstruction of the raw materials used and of the whole chaîne opératoire employed by the ancient people to produce Egyptian Blue is at the basis of the many attempts of modern synthesis started at the beginning of the 20th century and constituting a challenge for researchers still nowadays. Actually, the attempts made up to now are mostly successful, but among the many possible variables that can be changed in the hypothesized recipes and firing conditions, the source of copper, though crucial, has not been taken sufficiently into account. The pigment, one of the first synthetic ones in the history, owes its blue colour to cuprorivaite ($CaCuSi_4O_{10}$) and the copper present in its structure. The origin of this copper used in the mixture should be, according to Vitruvius, copper filings. Nevertheless, only one work in the literature (Nicola et al., 2019) basis the synthesis on scrap metals instead of malachite or commercial CuO.

With the present work we aim at going in the direction of Vitruvius' recipe, using ancient alloys filings obtained from two damaged Roman coins of private collection to reproduce the synthesis of Egyptian Blue. Another expedient employed that differs from literature is the introduction in the batch of original Egyptian Blue powder to check if its grains could act as nucleating agents during the firing. The materials obtained were compared with syntheses classically carried out with malachite, with different amounts of water, and with two samples of archaeological origin (Fig. 1). A combined analytical approach was adopted for the study of synthesised and ancient products. The preliminary observation of the results had the aim of discarding the worse products with a gradual selection of those most similar to the ancient pigment. Therefore, to start, optical microscopy, spectro-colorimetry and Visible Induced Luminesce (VIL) were employed. The selected products were then subjected to the analysis by means of Raman spectroscopy. Finally, the product that was judged the most closely related to the ancient pigment, was analysed also by means of X-ray Diffraction (XRD), high-resolution Raman mappings and SEM-EDS. This was the pigment produced with one of the two coins, Egyptian Blue grains, addition of water and 8 hours firing in muffle at 900°C. The Raman mappings and the SEM-EDS observations and analyses showed their complementarity in the obtained results; analogously it was underlined the benefit of coupling global (XRD) and local structural characterisation (Raman spectroscopy). Concerning Raman, the acquisition of high-resolution mappings could overcome some of the limitations in terms of representativeness of the local analysis. Furthermore, based on previous indications of the literature (Dariz & Schmid, 2022), Raman spectroscopy was employed also in situ during the firing of the raw materials within a Linkam heating stage associated to the spectrometer, in order to highlight the possible formation of intermediate products. This approach brough to light some evident experimental challenges, but its future employment, coupled with small-scale mappings at selected temperature steps, would provide a way of complementing the current results.

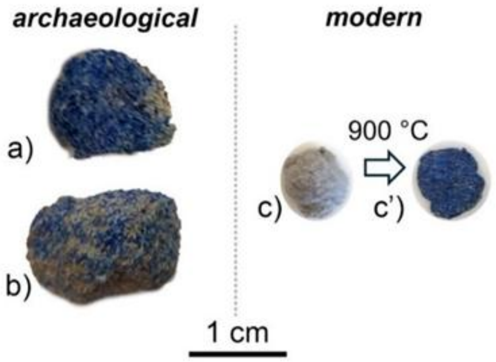

Figure 1 *Egyptian Blue archaeological samples (a, b) and modern synthesis before (c) and after (c') firing in muffle at 900°C.*

References

Dariz, P., & Schmid, T. (2022) - Raman focal point on Roman Egyptian blue elucidates disordered cuprorivaite, green glass phase and trace compounds. Sci. Rep., 12, 15596.

Nicola, M., et al. (2019) - Late production of Egyptian blue: synthesis from brass and its characteristics. Archaeol. Anthropol. Sci., 11, 713,5377-5392.

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Raman investigation on *Abies alba Miller* wood samples to test cellulose nanocrystalline (CNC) as a sustainable material for the conservation of ancient wood

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Cellulosic artworks exposed to high humidity levels and UV component of light are subjected to various forms of degradation such as the oxidation of the main constituents of wood fibers like lignin and cellulose, acidification and hydrolysis phenomena of cellulose, with progressive loss of mechanical properties of wood.

Here, we present a preliminary investigation study through Raman Spectroscopy, performed on a set of Abies alba Miller wood samples, to test cellulose nanocrystalline (CNC) as a possible sustainable material for the conservation of ancient wood. CNC can be obtained through acid hydrolysis of cellulose sources, followed by dialysis purification. Firstly, Raman, FTIR spectroscopy and SEM-EDS Microscopy allowed a characterisation of materials and technique of the case study: “Christus Patiens“, an important XVI century wood and "mistura" crucifix from south-western Sicily, as a preliminary study for the restoration intervention. Then, spectroscopic investigations were performed to assess the experimental application of CNC as a potential product for the conservation of ligno-cellulosic materials, both on the accelerated aged wood samples and on the crucifix.

Wood samples, cut longitudinally (L) and transversally (TR), were subjected to accelerated aging for 144 hours under UVA 340 nm irradiation (0.7 W/m2) at 30°C, and then treated by brush with 1% nanocrystalline cellulose. The Raman spectra were acquired at different laser wavelengths: 780 nm, 532 nm and 473 nm. Photoageing of wood mainly involved lignin components (Kanbayashi et al., 2018). As evident in the Raman spectra (Fig. 1a, b) after UV irradiation the peak at 1660 cm^{-1}, attributed to the ring-conjugated C=C stretching of lignin, decreased, whereas a new peak increased gradually with increased exposure time: the appearances of the band at 1555 cm^{-1} represents the formation of lignin oxidation products, such as quinone-type structures.

CNC was applied to wood samples previously cut in both directions (transverse and longitudinal to the fibers). Results showed different CNC penetration degrees according to cutting direction. When applied in the transverse direction, CNC penetrated the wood, whereas when applied in the longitudinal direction, it remained on the surface and formed a compact and homogenous film. In the Raman spectra recorded on the CNC-treated samples, the characteristic peaks of cellulose at 1095 cm^{-1} and 1122 cm^{-1} remain substantially of the same intensity as those present in the wood in the TR-samples (Fig. 1c) while they are very strong in the L-samples (Fig. 1d). Such observations suggest novel perspectives and studies for the evaluation of different CNC application methods for wood artworks.

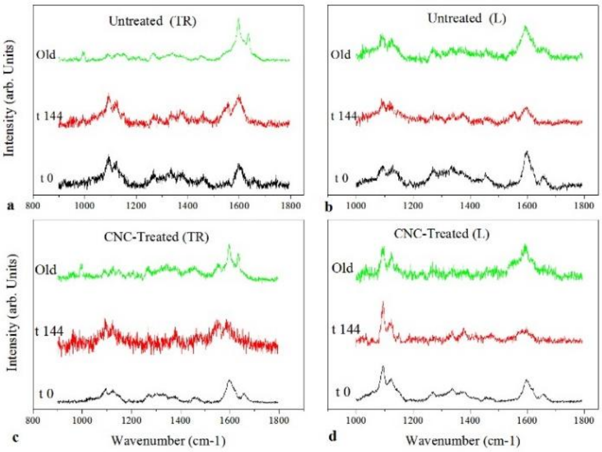

Figure 1 *Raman spectra acquired on untreated and CNC-treated samples.*

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References

Kanbayashi, T., et al. (2018) - Confocal Raman microscopy reveals changes in chemical composition of wood surfaces exposed to artificial weathering. J. Photochem. Photobiol. B: Biol., 187, 136-140.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Expanding SORS frontiers: new perspectives for Heritage Science

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In recent years, the Raman Spectroscopy Lab at ISPC-CNR has experienced significant methodological and technological advancements. These include the ability to distinguish geological and anthropogenic calcite based on spectral features combined with machine learning methods; the capability to reconstruct images and read texts concealed beneath layers of paper, as in the case of sealed historical letters, using alternative phenomena to Raman scattering, such as absorption and fluorescence; the extensive non-invasive mapping of degradation compounds diffusing beneath painted surfaces; and the development of innovative prototypes and methods for in-situ non-invasive measurements, such as a portable micro-SORS prototype and the combination of SORS with SERDS and Charge Shifting techniques.

In this contribution, we present a recent study carried out at Rutherford Appleton Laboratory where the capabilities and constraints of SORS were tested in an innovative application: assessing preservation liquids in the "wet collections" of natural history museums.

Maintaining and analysing these preservation fluids is fundamental for ensuring the long-term stability of specimens housed in fluid-based collections. However, their evaluation presents considerable analytical obstacles, as traditional invasive techniques necessitate opening containers, potentially endangering specimen integrity. Jars from historical collections may contain diverse chemical substances in both liquid and solid forms, some of which could be hazardous. Altering fluid composition or adjusting concentration levels may compromise conservation, while rehydrating desiccated specimens introduces further complications. Accurately identifying and maintaining the correct chemical balance of these solutions is key to their effective conservation.

A portable SORS instrument was utilized to examine preservation fluids non-invasively through their original glass enclosures, and data were treated using Principal Component Analysis (PCA). This approach enabled the detection of chemical constituents and the differentiation of fluid compositions and concentrations without requiring direct sampling. Compared to conventional Raman spectroscopy, SORS offers a distinct advantage by minimizing interference from container walls, thereby enhancing sensitivity and discrimination capability. This technique provides a viable, on-site analytical solution, eliminating the necessity for specimen relocation and reducing potential risks. By improving the monitoring and management of preservation fluids, SORS supports the sustainable conservation of wet collections, highlighting its significant impact on modern museum preservation practices.

Figure 1 *Example of a wet collection object (left); portable SORS used for the study (right).*

References

Botteon, A., et al. (2024) - Advanced Microspatially Offset Raman Spectroscopy for Noninvasive Imaging of Concealed Texts and Figures Using Raman Signal, Fluorescence Emission, and Overall Spectral Intensity. Anal. Chem., 96, 4535-4543.

Lux, A., et al. (2025) - Shifted-excitation Raman difference spectroscopy and charge-shifting detection coupled with spatially offset Raman spectroscopy for heritage science. Analyst, 150, 1140-1150.

Mosca, S., et al. (2025) - Noninvasive Characterisation of Preservation Fluids through Glass Container Using Spatially Offset Raman Spectroscopy: Potential in Heritage Science. ACS Omega, 10, 8, 8658–8664.

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Degradation of the Herculaneum dagger due to an obsolete conservation treatment

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In the early 1980s, the archaeologists working on excavations in the ancient city of Herculaneum found around 300 skeletons in the beach area. They belonged to people trying to escape following the eruption of Mount Vesuvius in 79 CE. Among them, the skeleton of a soldier was found together with his weapons, a sword, a dagger, and his belt in an excellent state of conservation. The soldier's set, preserved in the museum of Archaeological park of Herculaneum, was analysed by the IBeA research group during an in situ analysis campaign by means of Raman and X-ray fluorescence spectroscopies. In addition, some micro fragments were analysed in the laboratory.

Undoubtedly, the results obtained from the analyses of the dagger stand out due to the decay products related to its state of preservation. The dagger sheath consists of a metal exterior and a wooden interior part, which was visible at naked eye due to a degradation phenomenon that is causing its fragmentation.

In situ analyses of the exterior of the artefact identified iron degradation products such as the iron(III) oxide-hydroxide goethite (α-FeO(OH) and traces of red pigment cinnabar (HgS), suggesting that it probably had red decoration. Raman analyses of some micro-fragments (iron and wood fragments) carried out in the laboratory, showed the presence of numerous secondary products. Specifically, Raman spectra of boussingaultite [$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$], ammoniojarosite [$(NH_4)Fe_3(SO_4)_2(OH)_6$], anhydrous sodium sulfate [thenardite, Na_2SO_4], sodium sulfate decahydrate [mirabilite, $Na_2SO_4 \cdot 10H_2O$], ammonium sulfate [maskaganite, $(NH_4)_2SO_4$], magnesium sulfate heptahydrate [epsomite, $MgSO_4 \cdot 7H_2O$] were recorded (Fig. 1).

The identified degradation products could be related to the burial condition of the artifacts. However, they could have formed as a result of an obsolete consolidation treatment with potassium alum solution ($KAl(SO_4)_2 \cdot 12H_2O$) which was applied to waterlogged archaeological wood. In fact, this compound was identified by means of XRD analysis on a micro-sample. This conservation method was common in the early 20th century and it has had dramatic long-term consequences for historical wooden artifacts. Considering the obtained results, we can state that the fragmentation of the dagger is caused by the formation of salt efflorescence in the wooden sheath.

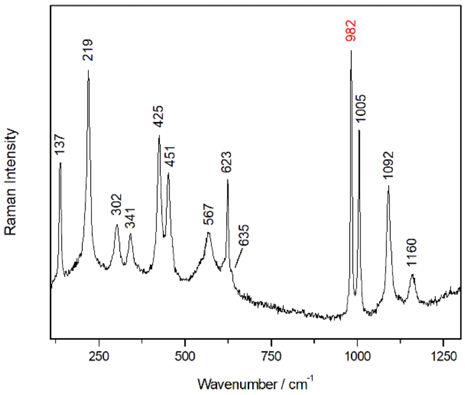

Figure 1 *Raman spectrum recorded on the dagger microfragments shows the presence of amoniojarosite (in black) and epsomite (in red).*

This research provides highly relevant information about the artefact, not only regarding its state of conservation but also concerning the previous procedures performed. In this way, the restores will be able to find the best conservation method for this unique piece.

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References

Häggström, C., & Sandström, T. (2013) - Alum-treated archaeological wood: Characterisation and re-conservation. Riksantikvarieämbetet, Sweden, 131.

Catelli, E., et al. (2016) - Salt efflorescence in historic wooden buildings. Herit. Sci. 4, 31.

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Raman micro-analysis for discriminating superimposed historical inks in a non-invasive and multi-analytical approach

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In historical manuscripts, documents, and letters, it is common to find textual parts modified or added after the original draft. In some cases, chemically similar inks to those used in the original text have been employed to erase or overwrite it, affecting its legibility and understanding of the writing process. Over the centuries, inks have shared many material components (e.g., similar polyphenols found in galls and logwood, metal salts for ink formation, etc.), resulting in analogous material properties when analysed.

In this research, Micro-Raman spectroscopy was employed to characterise and discriminate between inks of these textual parts to support comprehension at the writing stage. This technique is an established method for characterising the molecular composition of inks, generating a vibrational spectrum that acts as a specific structural fingerprint (Retko et al., 2024; Colantonio et al., 2018).

A methodological approach was employed to evaluate the varying responses of point and mapping Raman analyses using both bench-top and portable Raman set-ups. Laboratory samples (Fig. 1a) were prepared using inks produced according to historical recipes dating from the 15th to 18th centuries (i.e. carbon, iron-gall, and logwood). Different experimental parameters (laser wavelength and intensity, laser spot diameter) were tested to define an effective analytical protocol.

Raman microscopy enabled the discrimination of iron-gall and logwood inks by distinguishing spectral details in the characteristic bands of the metal-polyphenol complex within specific spectral ranges and identifying their mixture in overlapping areas (Fig. 1b).

Raman micro-analysis was tested in synergy with a novel multispectral method, called Hypercolorimetric Multispectral Imaging, supported by traditional spectroscopic techniques, including single-point and mapping X-Ray Fluorescence (XRF), and Fourier Transform Infrared (FTIR) spectroscopy, using both External Reflection and Attenuated Total Reflection modalities. After being tested on laboratory samples, the multi-analytical and non-invasive approach was applied to selected original manuscripts from the University Library of Pavia (Pavia, Italy).

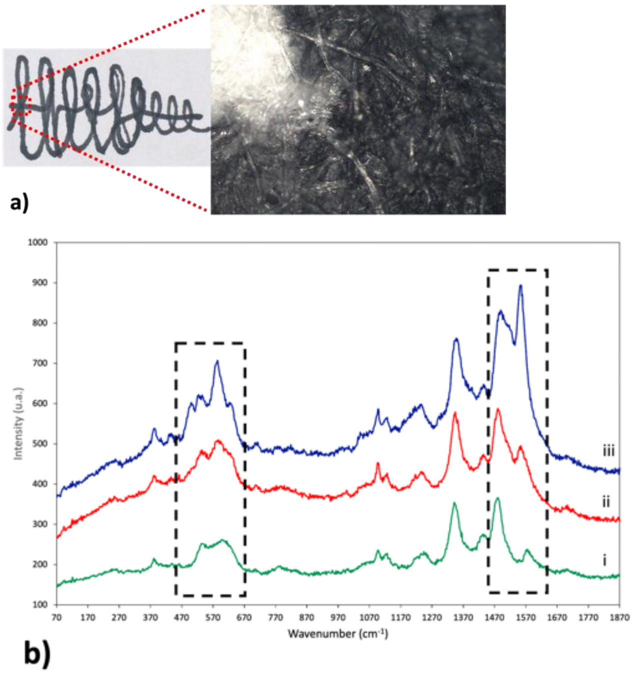

Figure 1 a) *Visible image of a laboratory sample made with logwood ink, crossed out with a stroke of iron-gall ink, and magnified 10X around the overlapping area where the Raman mapping analysis was performed.* ***b)*** *Raman spectra excited at 638 nm of (i) iron-gall ink, (ii) iron-gall ink on logwood ink, and (iii) logwood ink.*

References

Bicchieri, M., et al. (2008) - All that is iron-ink is not always iron-gall. J. Raman Spectrosc., 39, 1074-1078.

Colantonio, C., et al. (2018) - Hypercolorimetric multispectral imaging system for cultural heritage diagnostics: an innovative study for copper painting examination. Eur. Phys. J. Plus, 133, 526.

Retko, K., et al. (2024) - Identification of iron gall inks, logwood inks, and their mixtures using Raman spectroscopy, supplemented by reflection and transmission infrared spectroscopy. Herit. Sci., 12, 212.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Portable Raman spectroscopy and X-ray fluorescence for the in situ characterisation of the parchment, inks, and pigments of medieval manuscripts at the Bulgarian National Library

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The physical preservation of the material carriers of the written heritage in good condition forms the basis for its successful preservation and transmission to future generations. A significant role in this process is played by the study of these carriers using modern non-invasive analytical techniques. With this work, we present analytical data obtained for the first time in Bulgaria through in situ research using Raman spectrometry and portable X-ray fluorescence (pXRF) of five valuable medieval manuscripts from the collection of the Bulgarian National Library (BNL), made of parchment and dated to the 9th-12th centuries CE. Of particular interest is the 12th-13th century codex 880 as consisting of two parts written both in Greek and Cyrillic and including palimpsest folios as well (Fig. 1).

The Raman analysis of the valuable manuscripts was performed using a specially purchased Drawell ATR 3000 spectrometer (in the frame of the Project No. КП-60-Н06/9, funded by the Bulgarian National Science Fund) with the ability to adjust the power of the excitation laser between 50 and 500 mW. For the in situ measurements of the elemental composition of the parchment and inks/pigments a pXRF spectrometer Bruker S1 Titan was used, kindly provided by the Center of Archaeometry with Laboratory of Conservation and Restoration (CALCR) at the Sofia University „St. Kl. Ohridski". Analytical information was obtained both for the parchment itself and for the inks and pigments used. On the one hand, this allows the selection of the most appropriate methodology for the restoration and conservation of the manuscripts. On the other hand, it allows for the distinction between original and palimpsest parts of the medieval manuscripts based on the analytical information.

Due to the different chemical structural and elemental characteristics of the two types of parchment in the Greek and Cyrillic palimpsest-parts of codex 880, Raman spectroscopy can precisely identify their nature as well as their composition. Furthermore, portable Raman spectrometer allowed the in situ analysis of rare and valuable manuscripts in a non-destructive and noninvasive way. Raman technology for manuscript analyses provide much greater accuracy during the stage of preliminary manuscript assessment and allows for accumulation of comprehensive information about the physical and chemical properties of each individual manuscript, the history of its treatment, the origin of materials it is made of, and provides the basis for comparative research perspectives. The application of new non-invasive methods of analysis as a methodology for comprehensive study of the material body of parchment manuscripts contributes to their more precise historical, codicological and linguistic research and helps for their reliable digitalization, conservation and restoration. Moreover, creating a digital catalog using the analytical data from the studied material body of the medieval manuscripts using Raman spectrometry allows for the comparison of quantitative and qualitative parameters. This is a big step toward figuring out where manuscript monuments of cultural heritage came from and when they were made.

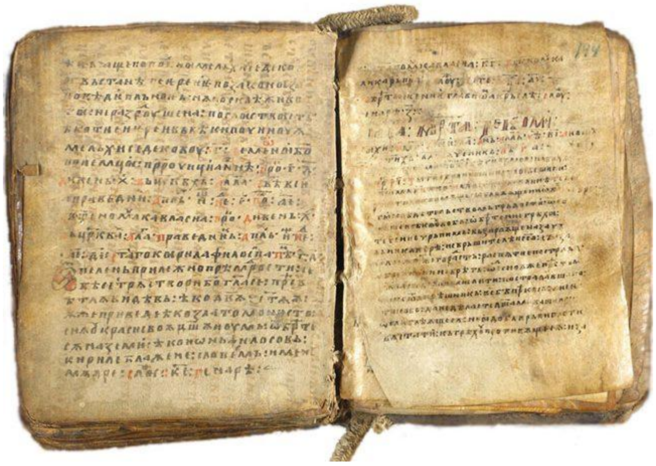

Figure 1 *Codex 880 stored in the Bulgarian National Library, dated to the end of 12th-beginning of the 13th centuries.*

Acknowledgements: This study and participation to the RAA 2025 are funded by the Bulgarian National Science Fund under the Contract No. КП-60-Н06/9. The Bruker S1 Titan pXRF spectrometer at the CALCR was provided with the financial support of the INFRAMAT Project.

PLINIUS 51 | 2025 | Special Issue | Raman Spectroscopy in Art and Archaeology
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Raman Data Processing for Large Maps of Iron Corrosion Using Non-Negative Matrix Factorization

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The CORINT project focuses on elucidating the corrosion of iron in opaque and porous media, such as archaeological iron in soil, by employing non-invasive, quasi-in situ bimodal neutron and X-ray tomography (NX-CT). A specific goal is to develop, by the end of the project, a fully non-intrusive protocol, based solely on tomography (Granget et al., 2024a).

The protocol integrates multimodal and multiscale data, including XCT 3D, NCT 3D, optical microscopy 2D images, and Raman-labeled datasets, to train a machine learning model. The trained model learns from labeled zones on a Raman mapping, and applies this knowledge to predict and characterise the uncharacterised volume in the tomograms. Once trained, the model will be capable of characterising corrosion layers using only NCT and/or XCT data.

This method requires, in the development phase, using traditional invasive approaches, such as Raman spectroscopy on cross-sections, to provide ground-truth data. Thus, after NX-CT imaging, Raman spectroscopy using the Renishaw Virsa™ Raman Analyser is performed on cross-sections of Roman nails from an archaeological site in Avenches, Switzerland. Each cross-section is mounted inside a custom 3D-printed sample holder to maintain anoxic conditions (Granget et al., 2024b), preventing oxidation of reactive compounds during extended mapping. For each nail, typically eight cross-sections are analysed, with four maps per section. Each map spans 1000 × 1000 microns, with a step size of 50 microns, using a 20× LWD objective. This approach collects 441 data points per map and 14112 data points per nail, necessitating efficient data processing and labeling.

Spectral preprocessing, conducted using the Wire5 software, includes cosmic ray and baseline removal, Savitzky-Golay smoothing, and normalization. Processed files are exported alongside images of the mapped zone, and used as input for the data processing in an in-house Python script. This script incorporates a user interface to set parameters, visualise results, and label components.

Non-negative matrix factorization (NMF) was chosen for spectral decomposition (Pauca et al., 2006). By approximating the data matrix into weight and component matrices, NMF identifies components corresponding to expected Raman spectra or noise. Once the operator approves the NMF results for a map, component profiles (pseudo-spectra) and weight tables (indicating each component's contribution to individual spectra) are exported. This workflow enables efficient labeling and characterisation of corrosion products, providing critical data for training the tomography-based machine learning model.

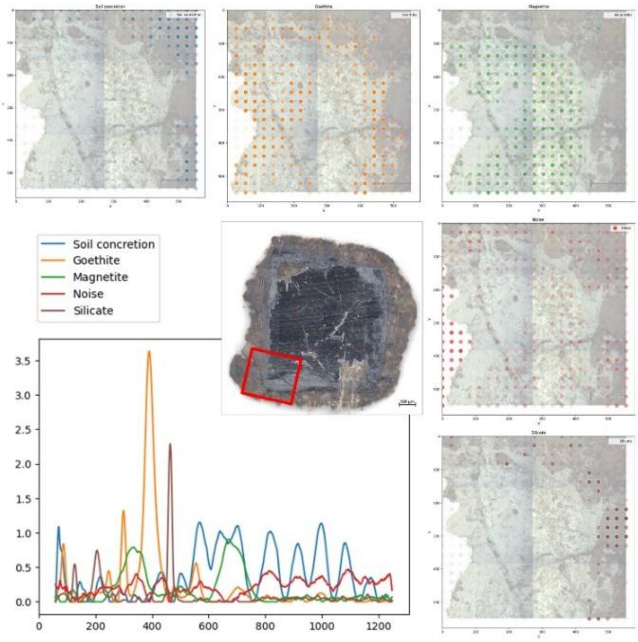

Figure 1 *Visualisation of the NMF results for 1 map on a nail cross-section. Components were found for: blue) poor Raman signal on soil concretion, yellow) main bends for goethite, green) main bends for magnetite, red) noise, brown) main bends of silicate representing sand inclusions.*

References

Granget, E., et al. (2024a) - Developing a quantitative multimodal and multi-scale, fully non-destructive technique for the study of iron archaeological artefacts. Acta IMEKO, 13, 2, 1799.

Granget, E., et al. (2024b) - Raman Mapping in Anoxic Conditions for Multimodal Analysis of Iron Archaeological Artifacts. Poster available online in book of Abstracts of ICORS 2024, 570.

Pauca, V.P., et al. (2006) - Nonnegative matrix factorization for spectral data analysis. Linear Algebra and its Applications, 416, 29-47.

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µ-Raman surface mapping of antique silver coin

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Coins are valuable archaeological objects, extensively documented across time periods and geographic areas. They offer direct evidence of the constituting power and reflect political and economic evolutions of their related societies. Silver coins were the most widely produced in the Greek world during antiquity and are preserved in large amounts in public and private collections, whereas gold and bronze were usually produced in smaller quantities. Numismatic studies mostly rely on stylistic, weight, and die analyses. These criteria are however limited to subjective interpretation and require the tedious examination of large quantities of coins. Elemental and isotopic analyses have been developed as complementary methods to assess the composition and provenance of the coins and ores. The elemental analysis of silver coins can reveal subtle variations in the alloy composition and detect trace elements. However, the elemental characterisation of the alloy using techniques such as PIXE is limited by several effects, such as the silver enrichment of the surface, or the presence of corrosion products on the surface. Raman spectroscopy is known to be a powerful tool for the characterisation of corrosion products on archaeological objects. Combining a Raman spectrometer with a microscope allows for the chemical mapping of large areas. However, mapping the corroded silver surfaces of archaeological coins faces several challenges. This work presents the development of µ-Raman mapping of the surface of ancient silver coins. Silver tarnishes with time, leading to the formation of a thin Ag_2S black layer. This phase is more stable than Ag_2O, which does not naturally occur. When exposed to a laser, Ag_2S is subject to photoinduced decomposition to metallic silver and sulfur oxide, even using a low power density. This patina is often retained by curators and collectors, but is sometimes removed —alongside other corrosion products, dirt, and surface grime— using mechanical, chemical, or electrochemical cleaning. Each method results in a different surface morphology at the nanoscale. Antique coins are usually handled without gloves by historians, inevitably depositing contaminants on their surfaces. Those contaminants can appear in Raman spectra of silver usually handled without gloves by historians, inevitably depositing contaminants on their surfaces. Those contaminants can appear in Raman spectra of silver surfaces, and are often carbonised by the laser, leading to one or two broad bands at 1400-1600 cm^{-1}. These bands can cover vibrational modes associated with Ag_2S or other corrosion products. Cleaning techniques have therefore been compared to remove adsorbed species from silver surfaces, without removing the tarnished layer which would modify the visible appearance of the coins. Antique silver coins usually contain a very high amount of silver, but other metals such as copper, lead, tin, zinc, and gold are often present alongside the silver due to the metal origin or intentionally added to reduce the cost of minting. These secondary constituents, even in small amounts, can lead to the formation and accumulation of corrosion products such as what we report for a tetradrachm from Alexander the Great.

These corroded surfaces were found to be very inhomogeneous and to impact elemental measurements using p-XRF. Like Ag_2S, some of these corrosion products, such as Pb_2O_3, exhibit high thermal sensitivity. Finally, the uneven topography of archaeological silver surfaces requires special mapping processes. A Horiba LabRAM Soleil Raman microscope was used with custom acquisition processes to perform Raman mappings on uneven surfaces. We hope the characterisation of the coin surfaces will allow a better consideration of the surface for elemental analysis of the bulk using PIXE.

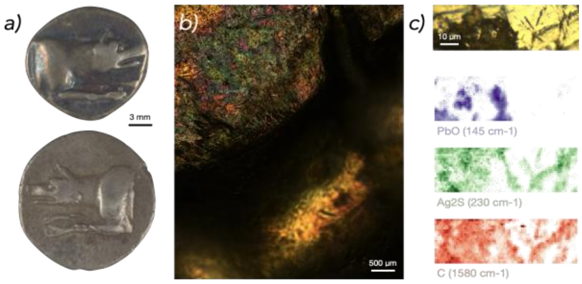

Figure 1 ***a)*** *Two silver coins with different patinas (the upper one has probably been electrolysed),* ***b)*** *microscope image of the upper coin's surface,* ***c)*** *µ-Raman cartography of corrosion products on another coin's surface. The colour scales go from white (min) to intense shade (max).*

References

Costa, V. (2001) - The deterioration of silver alloys and some aspects of their conservation. Studies in Conserv., 46, 18–34.

Flament, C. (2014) - Premier bilan des méthodes de laboratoire appliquées au monnayage argien tirant notamment parti de résultats inédits d'analyses par activation neutronique menées en 1979 à l'instigation de Tony Hackens. Revue Belge de Numismatique et de Sigillographie, 160, 203–216.

Passaretti, A., et al. (2024) - multi-analytical characterisation of Art Déco dinanderie: Single-point and map analysis of Jean Dunand's metal artworks. J. Raman Spectrosc., 55, 1289–1299.

The combined use of Raman and FTIR Spectroscopies assisted by Machine Learning Algorithms for the quantitative analysis of minerals in Archaeological Bones and Ashes

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Bones are composite materials composed of approximately equal volumetric fractions of mineral (apatite) and organic materials (collagen). Their Raman and infrared spectroscopic features reflect this specific composition.

According to the literature, burned bones and ashes found in archaeological sites underwent a range of different degrees of calcination, basically depending on firing temperature and duration. Raman spectroscopy and Fourier Transform Infrared spectroscopy (FTIR) have proven to be valuable tools for determining the qualitative and quantitative composition of fired bones, ashes, and pigments that may be found among these archaeological materials. Moreover, the unique capability of Raman spectroscopy for the analysis of carbon and iron-based compounds makes the combined use of those techniques a powerful method for the recognition of archaeological samples.

After a survey of the main mineralogical phases present in the samples, the objective was the quantification via FTIR and Raman spectroscopy of those compounds.

In our study, the possible post-burial alteration, including the adsorption or incorporation of carbonates from the surrounding soil, was taken into account. To reduce the influence of these potential alterations in the interpretation of data, the samples were in some cases pretreated with sodium hypochlorite and acetic acid before analysis.

As an initial approach, reference standards of calcite, hydroxyapatite, and quartz, along with mixtures of these components, were subjected to the pretreatment to assess the effectiveness of the technique and to verify that hydroxyapatite, the key constituent of bones, remained unaltered.

Those reference materials were then prepared KBr pellets and analysed through FTIR and Raman spectroscopy. The protocol was then applied to a set of 9 samples from the archaeological site Riparo Mochi (Ventimiglia), which is one of the most important sites in Europe concerning the use of fire since the stratigraphy covers the cultural and technological transition from the prehistoric to the earliest farming societies' use of fire.

Particle size and degree of crystallinity affect the spectroscopical response of compounds, therefore. A great effort was made to standardise the grounding and mixing of the samples, both reference materials and archaeological soils.

It is a matter of fact that one of the main issues in quantifying an unknown mixture of clay and minerals is calibrating the method. This involves preparing and measuring a training data set of reference materials with a known concentration of the four identified substances, i.e. calcite, silicate, hydroxyapatite and quartz.

To improve the quantitative process, the available data was post-processed using artificial intelligence (AI) strategies. The original dataset was expanded using an appropriate algorithm that employed the actual spectra to generate an augmented set of artificial spectra. The whole data-set (original+artificial spectra) was then utilised to train and validate a neural network (NN), which revealed good performance in predicting the concentration of the target minerals in samples.

In light of the positive results of this study, future research will concentrate on applying Raman and FTIR techniques directly at the Riparo Mochi archaeological site.

Acknowledgements: *This presentation is part of the project Pyro-Transitions: prehistoric cultural changes in the use of fire from foraging to the earliest farming societies, funded by MUR - PRIN 2022 (project code 2022PWY2YS, CUP Master no. E53D23000300006, CUP G53D23000310006).*

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New findings in Levantine rock art: The case of the Rambla de la Huerta de Mateo II rock shelter, Minglanilla, Cuenca (Spain)

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Levantine rock art is a unique prehistoric graphic production in Europe that depicts actions such as hunting, rituals, war, or dance in the eastern area of the Iberian Peninsula. This artistic expression extends along most of the Mediterranean coast, with manifestations also found in countryside locations.
In 2022, a new open-air rock shelter was discovered in the so-called "Rambla de la Huerta de Mateo II", located in Minglanilla, province of Cuenca, Spain. Remarkably well-preserved Levantine rock art decorations were identified on three fallen blocks detached from the wall (see Fig. 1a), as well as a small depiction of a goat on the shelter's wall (see Fig. 1b). The paintings were created by the nomadic hunter-gatherers that were periodically occupying the rock shelter from the very Late Upper Magadalenian through early Mesolithic periods. Neolithic remains are limited to some pottery fragments located on the surface of the site.

The red and white pictographs in the three detached blocks and the goat that still remains on the wall of the rock-shelter were analysed by non-destructive analytical techniques, including X-ray fluorescence (XRF), Diffuse Reflectance Infrared Fourier Transform (DRIFT), Raman spectroscopy, and Visible and Near-Infrared spectroscopy (VIS-NIR). Raman spectroscopy revealed the use of hematite (Fe_2O_3) for the red figures and dolomite ($CaMg(CO_3)_2$) for the white ones, while the walls contain mainly calcite (see Fig. 1c) with some amounts of silicate (probably the responsible of the fluorescence background observed in some Raman spectra) and iron as detected by XRF. DRIFT and VIS-NIR records were consistent with those findings.

In addition to the rock shelter pictograms, a workshop area was found nearby the rock shelter. Here, possible remains of the raw materials used for the paintings were investigated. Raman analysis revealed the presence of hematite, used in the red samples, and different calcite/dolomite mixtures used for white samples. Moreover, analyses revealed the presence of goethite heated to form hematite.

The discovery of white minerals is particularly significant, as their use in Levantine rock art is scarce, and is completely absent in the south-eastern area of distribution. It is abundant just in the area of Albarracín, with some minor examples in the northern Cuenca region. The unique compound found in the pictograms was dolomite. In contrast, in the rocks found in the possible workshop calcite was the main compound with few traces of dolomite. Archaeological evidences suggest that the shelter was "reused" over time, as the head of a goat figure was repainted in red over the original white, while the horns retain their white color. Furthermore, the absence of organic degradation suggests that decorated rocks detached relatively soon after their creation. The detached blocks fell face down on the ground, shielding the artwork from external erosion and preserving it for thousands of years.

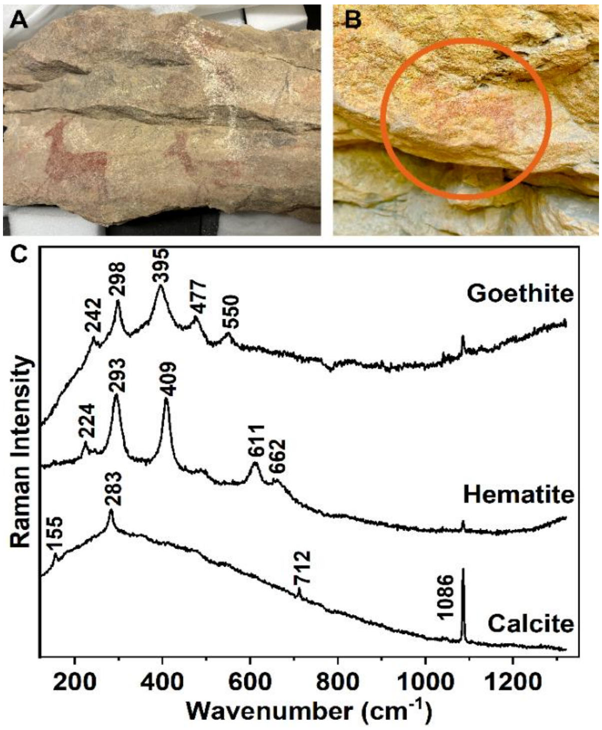

Figure 1 a) *One of the blocks detached from the rock shelter;* ***b)*** *Goat figure from rock art in the rock shelter of Minglanilla;* ***c)*** *Raman spectra of goethite, hematite and calcite.*

References

Rogelio-Candelera, M.A. (2015) - Digital image analysis based study recording, and protection of painted rock art. Some Iberian experiences. Digital Applications in Archaeology and Cultural Heritage, 2, 68-78.

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Sulfates in Cultural Heritage: Raman spectroscopy as a key analytical tool

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Sulfates are among the most harmful soluble salts, affecting cultural heritage (CH) by deteriorating wall paintings, archaeological and historical artifacts, and built materials. This work summarises the IBeA research group's experience in sulfate detection using Raman spectroscopy. In Atlantic wall paintings, gypsum [$CaSO_4·2H_2O$] mixed with calcite is the most common mortar, as seen in the mural paintings of the Romanic Santa María de Hermo Church, Asturias. Gypsum can be altered by microorganisms to bassanite [$CaSO_4.½H_2O$], and then to anhydrite [$CaSO_4$] as observed in the Romanic church of San María de Lemoniz, Biscay (Spain). This degradation is comparable to that observed three decades ago in the tomb of Nefertari in the Valley of the Kings, Luxor, Egypt (Corzo, 1993), where the climate is characterised by temperatures of 30°C and relative humidity of 30-40%. However, the occurrence of such dehydration in the Atlantic environment, with an average temperature of 18°C and relative humidity of 80%, requires further investigation.

Reactions between gypsum-mortars and pigments also resulted in the formation of new sulfates, such as the iron sulfate para(conquimbite) [$Fe_2(SO_4)_3·9H_2O$], derived from the blackning of hematite, a phenomenon observed in the House of Marcus Lucretius in Pompeii (Italy). A similar phenomenon occurred in the Lemoniz church, where posnjakite [$Cu_4(SO_4)(OH)_6·H_2O$] and antlerite [$Cu_3(SO_4)(OH)_4$] are altered products of malachite (Pérez-Alonso, 2006).

Sulfate decay also affects metal artifacts, such as the copper based sculpture like the one studied in the Getxo graveyard, Biscay (Spain), where brochanite [$Cu_4(SO_4)(OH)_6$], posnjakite and langite [$Cu_4(SO_4)(OH)_6·2H_2O$] were detected. In building materials, calcium-rich stones react with H_2SO_4 aerosols to form gypsum, bassanite or anhydryte, while sodium-rich bricks produce mirabilite [$Na_2SO_4·2H_2O$] and thenardite [Na_2SO_4]. Other sulfate neominerals (salts), including aphthitalite [$(K,Na)_3Na(SO_4)_2$] and syngenite [$K_2Ca(SO_4)_2·H_2O$] were found in the Pompeian House of the Gilded Cupids and picromerite [$K_2Mg(SO_4)_2·6H_2O$] in the degraded yellow tuff used in the houses of Herculaneum (Vázquez-de la Fuente, I. 2025) due also to the SO_x acid gases interaction. Moreover, mascagnite [$(NH_4)_2SO_4$] and epsomite [$MgSO_4·7H_2O$] in La Galea Fortress, Getxo (Spain) were found due to marine aerosol depositions. Finally, (ground)water contamination by agricultural practices has also led to ammonium sulfate crystallization in the foundations and wall paintings of the romanic church of Alaiza, Araba (Spain) (Veneranda, 2014).

Based on all these studies, Raman spectroscopy has played a fundamental role in the identification of over 15 different sulfates in Cultural Heritage materials, providing valuable insights into sulfate-related degradation. Its non-destructive nature and portability make it an essential tool for heritage conservation efforts, especially to detect well Raman scattered minerals like sulfates.

Acknowledgements**:** This work was supported by SIDIRE project (PID2023-146230OB-I00) funded by the Spanish Agency for Research AEI (MICIU/AEI/10.13039/501100011033/FEDER/UE).

References

Corzo, M.A. (1993) - Afshar Art and Eternity: the Nefertary Wall Paintings Conservation Project 1986-1992, Getty Conserv. Inst., Los Angeles.

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Contribution of Raman Spectroscopy in the Physicichemical Documentation of the Paintings; The collection of the National Gallery – Alexandros Soutsos Museum, Greece

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Raman spectroscopy has become an indispensable tool in the study of cultural heritage, offering non-destructive insights into the molecular composition of artworks.

This study presents the application of Raman spectroscopy in the physicochemical documentation of selected artworks from the collection of the National Gallery of Greece, focusing on pigment identification, degradation mechanisms, and material characterisation.

By employing a portable (Fig. 1) and a high-resolution laboratory Raman system, we have the chance to analyse a selection of artworks spanning different artistic periods and techniques.

The spectral data reveals crucial information about pigment composition, binder interactions, and the presence of degradation products, enabling a deeper understanding of the materials and techniques used by artists. Furthermore, Raman analysis contributes to the characterisation of inks and the differentiation of original pigments from later restorations and guided conservation strategies. The information obtained from selected cases, underscore the significance of Raman spectroscopy in heritage science, reinforcing its role as a key analytical technique for the preservation and authentication of paintings.

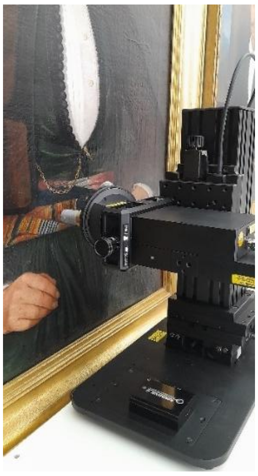

Figure 1 *Raman analysis on a canvas painting from the National Gallery collection.*

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References

Kouloumpi, E., et al. (2012) - Canvas and the Panel Paintings: Techniques and Analyses. In „Analytical Archaeometry Selected Topics“, H. G. Edwards & P. Vandenabeele, The Royal Society of Chemistry Publishing, Cambridge, 361-398.

Rousaki, A., & Vandenabeele, P. (2021) - In situ Raman spectroscopy for cultural heritage studies, J. of Raman Spectrosc., 52, 12, 2178-2189.

Stamp decorated black and red late antique pottery from Bulgaria characterised by Raman and pXRF spectrometry

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The black and red stamp-decorated Late Roman pottery is most often referred to as the term gray Macedonian terra sigillata, which was introduced by J. Hayes, noting the similarities with Gallic terra sigillata grise. Its presence has been established throughout the Central Balkan region. The ancient city of Serdica (present-day Sofia, Bulgaria) is one of the places where stamped tableware is frequently found during archaeological excavations. All vessels were made on the potter's wheel, but the use of moulds for some of them cannot be excluded, especially for the decoration. The leading physical characteristic of these vessels is the stamped decoration, but other techniques were also used - incised, rouletting, appliqué, and casted in a mould. The vessels, after firing, have a gray/black and red color on the surface. Some of the sherds are covered with a very high-quality varnish slip, in some cases - with a silvery metallic shine (Fig. 1). Studying the composition and technological issues of the production of this varnish slip is the main aim of the present investigation. The analytical techniques applied are Raman spectroscopy and X-ray fluorescence. For the non-invasive Raman spectroscopy measurements, both Bruker Bravo and Drawell ATR 3000 portable instruments were used to obtain more representative data. The ATR 3000 spectrometer allowed for the adjustment of the power of the excitation laser between 50 and 500 mW. Elemental concentrations, on the other hand, were determined nondestructively by a portable Bruker Titan S1 X-ray fluorescence spectrometer (pXRF). The analyses were accomplished at the Sofia University's Centre of Archaeometry with Laboratory for Conservation and Restoration (CALCR) 33 ceramic fragments dated to the end of the 3rd-5th centuries CE were studied, including seven that were red in color, one that had a black exterior and a brown inner, and the remaining 25 that were completely black. Statistical processing of the elemental compositions data reveals that the analysed samples are almost indistinguishable in terms of the clays used to fabricate the ceramic body or apply the outer layer. However, the increased contents of iron and titanium in the outer smoothed layers of the black sherds attest to the addition of a mineral layer, possibly carrying Ti-bearing iron oxides or contributing to their formation during the wares' high-temperature treatment.

The Raman spectra obtained for the polished outer surface of the black sherds are especially intriguing. Approximately more than 70% coincidence with the typical Raman spectrum of natural graphite is observed in practically all specimens analysed. These samples also show resemblance with carbon black and hematite, with a coincidence of roughly 40-65%. Therefore, the results imply that the characteristic gray-black color with a metallic shine was most probably achieved by coating and polishing with a graphite-containing material. Moreover, the Raman spectra of the black sherds' cores do not show coincidence with the graphite characteristic bands. For the red ceramic samples, the presence of hematite is notable. Hematite is responsible for the distinctive reddish hue and suggests an oxidizing atmosphere during firing. The absence of graphite bands on the polished outer surface of the red sherds is a distinguishing feature compared to the black samples.

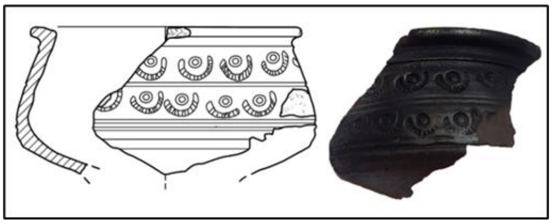

Figure 1 *Example of the analysed black stamp decorated pottery, covered with a polished varnish slip with metallic shine.*

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References

Hayes, J.W. (1972) - Late Roman Pottery. British School at Rome, London, 402-407.

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Machine Learning Approach to Amber Provenance: Bridging Traditional Analytical Methods and Advanced Computational Techniques

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Determining the geographical and geological origin of archaeological amber artefacts is a fundamental archaeometric study (Peris-Díaz et al., 2018). Traditional methods of determining the provenance of archaeological amber have relied on a combination of physical, chemical and microscopic analyses, including visual morphological examination, molecular analysis based on spectroscopic methods, elemental composition analysis and isotope ratio measurements (Bielińska-Majewska & Łydżba-Kopczyńska, 2025). While these approaches have provided valuable insights, they often require extensive sample preparation, which is often limited in the study of historical objects, is time consuming, and may lack the comprehensive discriminatory power required for accurate provenance determination.

Due to the advent of relatively cheap, powerful computers and the recent advances in algorithms, machine learning (ML) has become an interesting alternative in data analysis. ML revolutionizes the way the computers learn, i.e. not by memorizing instructions, but by discovering patterns hidden in the data and making decisions on their own. Being the state-of-the-art method in many domains, it may also become a transformative approach to amber provenance studies, since it allows the integration and analysis of multiple complex datasets with unprecedented sophistication (Zhang & Chignell, 2021).

In this contribution, the application of advanced computational techniques to amber provenance investigation will be explored, with the goal to demonstrate how ML algorithms can overcome the limitations of traditional analytical methods. By leveraging techniques such as supervised classification, unsupervised clustering, and predictive modeling, machine learning can potentially synthesize multidimensional data from spectroscopic, chemical, and isotopic analyses to identify subtle geographical and geological signatures that may be imperceptible to human researchers. Thus, it may help develop more robust and rapid classification models for amber origin determination. In the present study, the Raman spectra of reference amber samples from various geological ages and with different geographical origins in Europe, Asia and America are utilised. These samples are drawn from the laboratory's spectral database, along with the data collected during the projects carried out for the Polish National Node of E-RIHS ERIC (European Research Infrastructure for Heritage Science). Our preliminary investigations suggest that hybrid ML approaches, combining multiple algorithmic strategies, may provide the most reliable provenance classification models. By treating amber provenance as a complex multidimensional classification problem, we can potentially overcome the inherent variability and complexity of amber formation processes. The method will also demonstrate the broader potential of machine learning in material science and archaeological investigations.

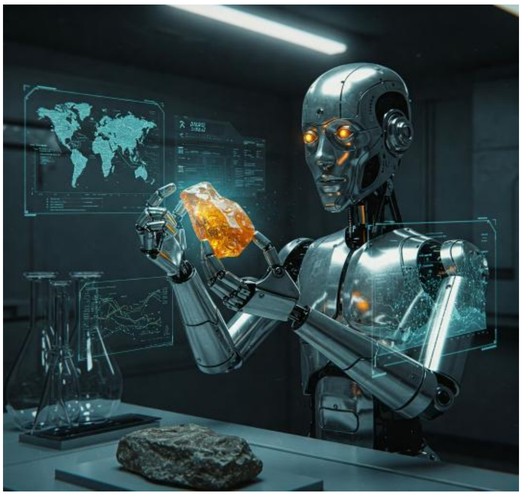

Figure 1 *A visual summary of the contribution: an AI investigating the provenance of amber samples with ML methods. Drawing generated with Google's Gemini.*

References

Bielińska-Majewska, B., & Łydżba-Kopczyńska, B. (2025) - Provenance study of amber discovered in the Toruń Basin on Late Palaeolithic site 50 in Brzoza (Poland). Praehistorische Zeitschrift.

Peris-Díaz, M.D., et al. (2018) - Raman spectroscopy coupled to chemometrics to discriminate provenance and geological age of amber. J. Raman Spectrosc., 49, 1-10.

Zhang, B., & Chignell, M. (2021) - Reshaping human factors education in times of big data: practitioner perspectives. Proceedings of the Human Factors and Ergonomics Society Annual Meeting, 65, 1574-1578.

Raman analysis assisted by invasive TLC and LC-MS in categorisation of red inks

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The writing materials market has been rapidly evolving, with an increasing variety of inks available in different colors. This growing diversity highlights the need for a standardized database of their components, such as pigments and dyes, which determine the color of writing materials. Although blue and black-colored inks have received significant attention, leading to numerous studies on their composition and degradation processes, writing materials in other colors remain an open field for research (Łydżba-Kopczyńska et al., 2021; Biernat et al., 2024). Red-colored inks are widely used in ownership and identity documents, as well as in official stamps and markings on legal records. They are also commonly found in corrections and decorative writing. Various applications of red inks call for analytical methods that enable easy data collection for database purposes.

Raman spectroscopy is widely recognized as a valuable method for examining inks in documents (Łydżba-Kopczyńska et al., 2021). Its non-destructive nature makes it particularly useful in forensic investigations, allowing for the direct identification of inks on documents and requiring no sample preparation. Moreover, this method is well suited to detect pigments, which is challenging for chromatographic techniques. However, Raman analysis provides spectra of all components contained in the ink mixture as well as the document background, which can complicate the identification of dyes in pens that use multiple dyes.

Thin Layer Chromatography (TLC) and Liquid Chromatography coupled with UV-Vis and Mass Spectrometry detection (LC-UV-Vis-MS) require the extraction of ink from paper thus being invasive methods. As these methods provide selective separation of components of multidye inks they seem to be optimal techniques for analysis of complex dye mixtures. They allow the separation and structural identification of red ink components leading to categorisation according to dye type, which complements Raman spectroscopy (Han et al., 2023).

The combination of Raman analysis with TLC and LC-UV-Vis-MS in a diverse group of 49 red-colored writing tools (pens, markers, fineliners, felt-tip pens) available on the Polish market will facilitate the categorisation of red inks and enable the development of a database that can serve as a useful tool in comprehensive ink analysis. Creating such database, in which dye groups identified through invasive techniques (TLC and LC-MS) are assigned to characteristic Raman signals, allows rapid comparison of spectroscopic results with reference patterns. Therefore, the questioned inks could be associated with specific dye groups without damaging the document. As Raman spectroscopy is a fast, noninvasive analytical tool, it could be used as preliminary screening procedure for questioned documents.

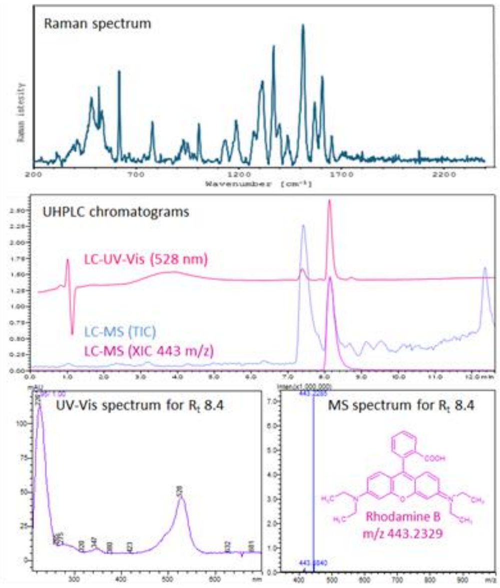

Figure 1 *Multidisciplinary analysis of red Rhodia pen.*

References

Biernat, M., et al. (2024) - The effect of storage conditions on preservation of writing inks - physicochemical study. 21st Wrocław Symposium on Questioned Document Examination, Wrocław, Poland.

Han, C., et al. (2023) - Thin layer chromatography coupled with surface enhanced Raman scattering for rapid separation and on-site detection of multi-components. J. Chromatogr. A, 1706, 464217.

Łydżba-Kopczyńska, B., et al. (2021) - Application of chemometric methods for the determination of fading and age determination of blue ballpoint inks. J. Raman Spectrosc., 52, 159-169.

Assessing copper-based and lead-based pigments deterioration in Early Islamic manuscripts by means of Raman spectroscopy

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Coloured inks have been employed since antiquity for various purposes. In the Islamic world, their use was often definite and systematic, particularly for the production of Qur'anic manuscripts. Contrasting colours were often used for highlighting certain sections of the text, for the addition of decorative elements and as coloured dots for the voweling system. Coloured inks were also used to add certain sections of the text, albeit less systematically, in Arabic papyrus protocols. The materials used for the manufacture of a vast majority of these pigments have been transmitted in technical handbooks, and treatises on scribal practices (Fani et al., 2023).

Among these, red and green inks are two colours we encounter commonly in both Qur'anic manuscripts on parchment and Arabic protocols on papyrus, that often exhibit signs of deterioration, making them difficult to identify and characterise. This deterioration of inks is influenced by multiple factors including the continuous use, exposure and mobility of manuscripts throughout centuries. Another determining factor influencing the type of deterioration is the composition of the writing materials used; the coexistence of organic and inorganic materials can lead to changes in the chemical and optical properties of both components. This is particularly evident in the case of verdigris (copper acetate), wherein the use of vinegar for its production can result in the formation of various unstable copper acetates. (Knipe et al., 2018; Fani et al., 2023). Additionally, the role of raw materials in combination with atmospheric pollutants in influencing the alteration of colour of lead -based pigments has been widely studied. In the case of Arabic manuscripts from early centuries of Islam, both these pigments were widely used, however they now appear to be in various stages of degradation. Verdigris usually presents an alteration in colour and ink corrosion, while red lead, particularly on papyrus, exhibits signs of colour alteration and fading. Both these pigments also feature prominently in the Arabic treatises on the \`art of the book', providing us with a pathway to reproduce the pigments and understand the mechanism of degradation.

In this study the pigment degradation observed on historic materials was investigated and compared with artificially aged mock-up samples, produced according to recipes reported in historical treatises. The pigments, of both historical manuscripts and mock-up samples, were then characterised using Raman spectroscopy, the most common and successful technique for the identification of pigment compositions. The application of Raman spectroscopy also proved to be a useful tool for the assessment of the degree of deterioration of the two pigments, enabling a deeper understanding of the pigments' production techniques and degradation processes. In the case of a deteriorated verdigris pigment, peaks at ~ 1592 cm^{-1}, 1486 cm^{-1}, and 1351 cm^{-1} were observed with the 532 nm laser operated in the extended mode (0-3000 cm^{-1}). These peaks can be associated with the formation of organo-copper complexes resulting from a verdigris alteration due to the combination of copper acetate with proteinaceous media (Brostoff et al., 2020). The detection of markers for alteration products associated with specific manufacturing processes also facilitates the correlation of the recipes with the behavior observed in the case of historical samples. This can help shedding light on scribal practices and on the material, choices adopted during the manuscript production during the Early Islamic centuries.

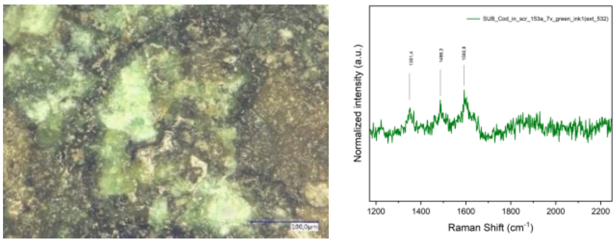

***Figure 1** Left: Microscopic image of a degraded copper-based pigment surface (Keyence digital microscope, Rx100 x700, full coaxial, fine depth composition with 1 μm step). Right: Raman spectrum obtained on the same pigment, acquired with the 532 nm laser in the extended mode, baseline corrected.*

References

Brostoff, L.B., et al. (2020) - Tracing the Alteration of Verdigris Pigment through Combined Raman Spectroscopy and X-ray Diffraction, Part I, Restaurator. International Journal for the Preservation of Library and Archival Material, 41, 1, 3–30.

Fani, S., et al. (2023) - Prendi, aggiungi, mescola, scrivi. Ricettari arabi sulla preparazione di inchiostri, Editrice Bibliografica, Milano.

Knipe, P., et al. (2018) - Materials and techniques of Islamic manuscripts. Herit. Sci., 6, 55.

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Peridots from Zabargad. The journey of these green gems from the Crux Vaticana (Città del Vaticano, Italy) to the Holy Cross in Castiglion Fiorentino (Italy)

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Peridot has been esteemed since antiquity, with some of the earliest and most prized specimens originating from the volcanic island of Zabargad in the Red Sea, whose ancient mines yielded gemstones of exceptional clarity and carat weight (Fig. 1). During the medieval period, the gem experienced a resurgence in prominence across Europe, largely due to the influence of the Crusaders, who played a significant role in reintroducing it and reviving the potent, mystical and protective lore associated with it (Thoresen & Harrel, 2014).

Figure 1 *Sample from the collection of Natural Museum La Specola, Florence, Italy (courtesy of Natural Museum La Specola).*

Within this historical framework, two reliquary crosses of particular scholarly and cultural interest—each set with green stones identified as peridot—have been examined through the application of portable, non-invasive, and non-destructive analytical techniques, namely Raman spectroscopy and X-ray fluorescence (XRF). The Vatican Crux, dated to the 6th century and preserved at the Museum of Saint Peter in Vatican (Rezza et al., 2009); and the Holy Cross, which is dated to the 13th century and is preserved at the Pinacotheca of Castiglion Fiorentino (Arezzo, Italy).

The gemological and analytical analysis of the gemstones mounted on the reliquaries has yielded numerous useful elements in reconstructing the complex and debated provenance of the goldworks. Indeed, the multidisciplinary approach has facilitated the acquisition of valuable information regarding the history, execution techniques, and the geology of the gems. In particular, the presence of peridots (Fig. 2) facilitated a comparative analysis of the gems from the two reliquaries and the reference gems with known provenance.

Figure 2 *Peridot in (sx) Holy Cross in Castiglion Fiorentino and (dx) Crux Vaticana (© Fabbrica di San Pietro in Vaticano).*

This analysis was facilitated by the fact that the peridots in question date back to the time of the works' execution. The present study validates the efficacy of gemology, Raman and XRF technology in facilitating the in situ analysis of museum artefacts.

References

Rezza, D., et al. (2009) - Archivum Sancti Petri. Studi e Documenti sulla Storia del Capitolo Vaticano e del suo Clero, La Crux Vaticana o Croce di Gistino II, collana a cura da Mons. Prof. Dario Rezza, Edizioni Capitolo Vaticano, Città del Vaticano.

Thoresen, L., & Harrel, J.A. (2014) - Archaeogemology of peridot, in "Twelfth Annual Sinkankas Symposium, Peridot and Uncommon Green Gem Minerals, April 5, 2014", GIA, California.

Torriti, P. (2010) - Sacra Mirabilia, tesori da Castiglion Fiorentino, catalogo della mostra, Roma, Museo Nazionale di Castel Sant'Angelo, 18 febbraio – 11 aprile 2010. Edifir, Firenze.

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Different colors, same pigment: the antique science beyond the lead-antimoniate used by ancient Roman glass-makers revealed by a study of Aquileia archaeological Museum's *glass-gems* collection

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Aquileia, in northeastern Italy, is one of the most important ancient Roman archaeological sites worldwide. To deepen our knowledge about the conservation and valorization of the glass-gem collection in the National Archeological Museum of Aquileia, a specific project was designed called "Glass-Gems Exploration Using Multidisciplinary Methods, Analyses, and Experiments" (GEMMAE). During several on-site and off-site campaigns (Marcucci et al., 2025), it was possible to deepen the results of previous campaigns by selecting peculiar specimens and performing in-depth optical microscopy analysis, colorimetry measurements, and recording further micro-Raman spectra (Fig. 1).

Particular interest has been focused on the opaque glass, where peculiar mineral phases and pigments have been used by the ancient Roman glass-makers to obtain specific colors and transparency effects. Thanks to the on-site micro-Raman investigation, the glass opacifies and the pigments have been both well characterised. In fact, in several gemstones made of artificial glass, the Yellow (Y) and greenish-Yellow (gY) hues have been correlated to the presence of lead-antimoniate, a well-known artificial pigment in yellow, and green archeological glasses (Basso et al., 2014).

Lead-antimoniate ($Pb_2Sn_2O_7$), also known as "Naples yellow", consists of a cubic pyrochlore structure with a typical Raman spectrum showing characteristic bands at about 139, 340 and 510 cm^{-1}; its crystal lattice is able to host also other cations, such as zinc and tin. Therefore, the Raman bands will show shifting and broadening effect on the basis of the combination of Pb-Sn in binary ratio and/or the presence of a third cation, as demonstrated by Rosi et al. (2009).

In our case, we had the chance to correlate the differences between the position and aspect of the Pb-antimoniate Raman bands with the ancient roman glass hue of the archaeological gems.

Finally, this is a preliminary work: more laboratory investigations will be carried out on synthetic materials and artificial reproduction, in order to better understand the correlation between the hue and the lead-antimoniate structure, including the processing temperature. Thanks to this, we will be able to unveil the technology as well as the raw materials employed by the roman glass-makers for glass-gems preparation.

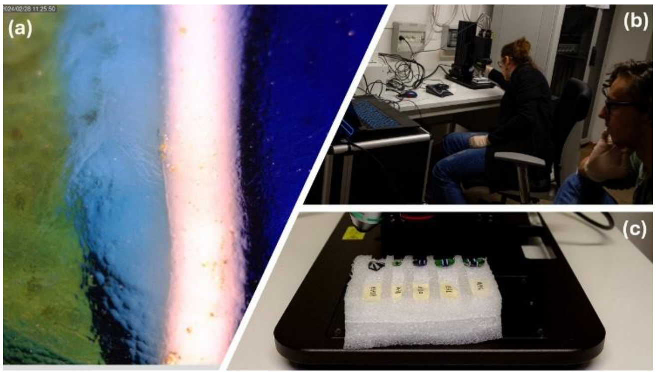

Figure 1 *Working on-site:* ***a)*** *Detail of polichrome glass-gem from Aquileia (Museo Archeologico Nazionale di Aquileia), observed by the digital microscopy during one of the on-site characterisation campaigns, showing Blue, White, Light Blue and yellowish Green colors [catalogue ref. 48446];* ***b)*** *The Renishaw VIRSA™ Raman system's set up at the museum;* ***c)*** *detail of several glass-gems ready for the Raman analysis.*

References

Basso, E., et al. (2014) - Characterisation of colorants and opacifiers in roman glass mosaic tesserae through spectroscopic and spectrometric techniques. J. Raman Spectrosc. , 45, 238–245.

Marcucci, G., et al. (2025) - Submitted to the European Physical Journal Plus.

Rosi, F., et al. (2009) - Raman scattering features of lead pyroantimonate compounds – Part I. J. Raman Spectrosc., 40, 107–111.

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Geology straddling art: a multi-technique study of the Taramelli's watercolors

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2022 marked the centenary of Professor Torquato Taramelli's death, a renowned Italian geologist, cartographer, passionate naturalist, and amateur painter. Above all else, Taramelli was one of the founding fathers of geological and seismic cartography (Gortani, 1922-23).

His ability to describe nature from a scientific perspective has been passed down to us not only through his extensive scientific and academic production, but also thanks to his artistic works, especially landscape watercolors.

In commemoration of this event, within other scientific and didactic initiatives, the restoration and the exhibition of Taramelli's watercolors collection, given to the University of Pavia by the author, have been realized and promoted.

The collection consists of a set of thirty-three views; all painted between about the middle and the end of the XIX century. The restoration also represented a privileged opportunity to carry out a characterisation study, performed using a multidisciplinary approach that focused on identifying pigments, the conservation state of the artworks, and techniques used by the author. Indeed, selected watercolors have been studied by combining micro-Raman Spectroscopy, portable X-ray Fluorescence (p-XRF) and multispectral imaging techniques (UV-Vis-IR). Here, we will discuss the protocol adopted to study these artworks. Indeed, several issues have been faced during the analyses, mainly correlated with the complexity of the watercolors' stratigraphy (Fig. 1), the different penetration capabilities of the analytical techniques applied, and the fading of the pigments, due to their degradation and altered conservation state, unfortunately typical for historical watercolors (Brosseau et al., 2011).

Moreover, in the watercolors the final hues consist of a complex mix of different pigments, which means that the same pigments can be used to reproduce different colors (Frausto-Reyes et al., 2009). This is particularly notable where the color is spread with a peculiar purpose, as made by Taramelli in his watercolors. The main pigments identified were cinnabar and ochre for reds, chromium yellow, cobalt blue and Prussian blue; all quite usual for the time. On the other hand, the aim of the author was extremely interesting, as demonstrated thanks to this characterisation study. Indeed, the identification of the pigments/hues and the techniques used by the author has supported the hypotheses that, as a scientist, Taramelli applied a sort of "scientific painting" with a geological educational use of the color. Therefore, his watercolors can be considered a hybrid tool between scientific geological notes and a rudimentary geological map of the landscapes but revealing an artistic approach.

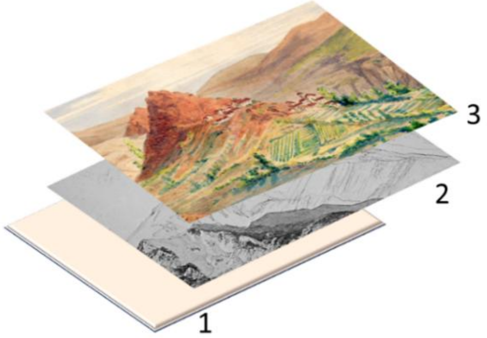

Figure 1 *T. Taramelli, Picco di Pregola 1896. Watercolors stratigraphy's composition: 1 Paper support; 2 IR imaging revealing the sketching preparation phase performed by the author by pencil and carbons; 3 Visible image showing the watercolors pigments, studied by micro-Raman spectroscopy and p-XRF.*

References

Brosseau, C.L., et al. (2011) - Revealing the invisible: using surface-enhanced Raman spectroscopy to identify minute remnants of color in Winslow Homer's colorless skies. J. Raman Spectrosc., 42, 1305–1310.

Frausto-Reyes, C., et al. (2009): Raman spectroscopy for the identification of pigments and color measurement in Dugès watercolors. Spectrochim. Acta A, 74, 1275–1279.

Gortani, M. (1922-23): Torquato Taramelli. Necrologio nell'annuario Università di Pavia.

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XRF, XANES and Raman combined for chromophore quantification in tourmaline gemstones

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Tourmalines belong to a supergroup of borosilicate minerals, typically represented by the formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, with various elements occupying each site.

The diverse elements present in tourmaline gemstones, which can function as chromophores, allow them to exhibit a broad spectrum of colours, making them fascinating for gemological purposes.

Among the various colours that tourmalines can exhibit, green and pink elbaite tourmalines are the most common and may also display colour variations within the same specimen. The observed chromatic variation appears to be linked to varying concentrations of iron and manganese, which account for the green and pink colouration, respectively (Pezzotta & Laurs, 2011).

Raman spectroscopy exhibits variations in the OH stretching modes, along with the emergence of additional bands associated with the presence of iron, and can thus be correlated to the relative content of these two chromophores (Pasetti et al., 2023). Nonetheless, a clear relationship linking colour, chromophore concentration, and the intensities of the OH Raman band has yet to be established.

We conducted XRF (X-ray Fluorescence) and XANES (X-ray Adsorption Near Edge Structure) at the synchrotron SOLEIL, specifically at the Puma beamline (Schöder et al., 2024), to analyse the concentrations of iron and manganese in various pink and green elbaite samples. This investigation also considered the oxidation states of these two elements, as they can influence the evaluation of their concentrations.

The findings indicate a clear relationship between variations in Raman spectra and the relative amounts of iron and manganese, enabling rapid identification of chromophore concentration from the Raman spectrum. This approach overcomes the need for lengthy and potentially damaging measurements on precious gemstones.

Figure 1 *Pink and green tourmaline gemstones.*

References

Pasetti, L., et al. (2023) - Identification of Some Gem Quality Blue to Green Li-Tourmalines. Minerals, 14, 44.

Pezzotta, F., & Laurs, B.M. (2011) - Tourmaline: The kaleidoscopic gemstone. Elements, 7, 333-338.

Schöder, S., et al. (2024): Heritage research at the PUMA beamline. Appl. Phys. A, 130, 848.

Biochemical Signatures of Historical Parchment: Insights into Parchment Origin and Degradation

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Parchment, a biomaterial derived from processed animal hides, has been a primary medium for written records for centuries. Typically, is sourced from sheep (*Ovis aries*), calves (*Bos taurus*), and goats (*Capra hircus*) but, over time, processing methods, environmental exposure, and ageing compromise the preservation and molecular integrity of these materials, making species identification challenging (Pangallo et al., 2010, Malissa et al., 2023; Malea et al., 2024). Traditional approaches often struggle to deliver accurate results without compromising the physical integrity of these valuable artefacts.

This study introduces a multi-technique analytical framework combining non-destructive spectroscopic methods and genetic analysis to improve species attribution in parchment samples. We combined Raman spectroscopy and FTIR-ATR (Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance) to analyse the molecular composition and establish spectral fingerprints specific to parchment of different animal origins. These spectral non-destructive analyses were further validated and complemented using mitochondrial DNA (mtDNA) analysis, targeting multiple loci to confirm species identity even in highly degraded samples.

To enhance interpretability, chemometric techniques were applied to integrate and analyse the spectral datasets, allowing for pattern recognition and differentiation between animal species based on subtle molecular variations.

The combined approach not only strengthens species attribution but also reveals how historical processing techniques impact the molecular integrity of parchment over time.

The findings of this research contribute to the field of heritage science by advancing non-invasive and minimally destructive diagnostic tools for the study and conservation of historical manuscripts. Additionally, this work provides a deeper understanding of parchment as a complex biomaterial.

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References

Malissa, A., et al. (2023) - Spectral Features Differentiate Aging-Induced Changes in Parchment - A Combined Approach of UV/VIS, µ-ATR/FTIR and µ-Raman Spectroscopy with Multivariate Data Analysis. Molecules, 28, 12.

Malea, E., et al. (2024) - The Complementary Use of Raman, ATR-FTIR Spectroscopy, and Chemometrics for Investigating the Deterioration of Artificially Aged Parchment. J. Raman Spectrosc., 55, 12, 1266–1280.

Pangallo, D., et al. (2010) - Identification of animal skin of historical parchments by polymerase chain reaction (PCR)-based methods. J. Archaeol. Sci., 37, 6, 1202–1206.

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Studying light-induced alterations in inorganic pigments through Raman microscopy

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This study examines how laser light interacts with inorganic pigments during their analysis by Raman spectroscopy. Lead and iron based pigments such as, red lead (Pb_3O_4), massicot (PbO), red ochre (Fe_2O_3), yellow ochre ($FeOOH$) and prussian blue ($Fe_4(Fe(CN)_6)_3$) known since antiquity have been studied. Three different Raman spectrometers were employed: a mobile one equipped with a diode laser source with an excitation wavelength λ_{exc}=785 nm and two laboratory microscopes with excitation wavelengths of λ_{exc}= 473 nm and λ_{exc}= 532 nm, respectively. The pigments were analysed both in their pure powdered form, and when dispersed in a binder, then coated with a layer of varnish.

The study investigated key irradiation parameters, including laser power, focusing conditions, exposure time of the sample to the laser beam, and the excitation laser wavelength. The main goal of this research was to develop irradiation protocols and guidelines for the safe application of Raman microscopy in the analysis of common pigments frequently used by artists. It is crucial for the analyst to obtain accurate results and maximize signal to noise (S/N) ratio in the Raman spectra while ensuring that no damage occurs to the pigment during exposure to the laser beam.

In most cases, the Raman spectrometer was used for irradiation and for monitoring of the samples. However, in some cases, a pulsed laser (λ_{exc}:1064 nm) was applied also for irradiating the samples.

The different pigments showed varying interactions with the laser light, including the appearance of new Raman bands, the elimination of others, or changes in the intensity of existing bands as the laser power increased. In most cases, a noticeable darkening of the pigment surface occurred beyond a certain laser power threshold.

Despite the protection provided by the presence of the binders and the additional layer of varnish to the specific pigments examined, it is highly recommended that during Raman analysis, the laser power density be maintained below the pigment alteration threshold values established for the neat pigments.

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References

Bertrand, L., et al. (2015) - Mitigation strategies for radiation damage in the analysis of ancient materials. Trends in Anal. Chem., 66, 128-145.

Philippidis, A., et al. (2021) - Determining optimum irradiation conditions for the analysis of vermilion by Raman spectroscopy. Eur. Phys. J. Plus, 136, 1194.

Exploring the Photodegradation of Purple Textiles via SERS and Steady State Spectroscopy

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The use of natural purple dyestuffs for textiles dates back to ancient times, thus making the photodegradation of historical artifacts a longstanding concern. Accurate dye identification depends on the knowledge gathered of its chemical behavior. As such, the present study investigates the photodegradation in textiles dyed with the purple dye extracted from the roots of Alkanna tinctoria, which contains the naphthoquinones chromophores shikonin (S-enantiomer) and alkanin (R-enantiomer) (Cardon, 2007).

Several studies have investigated the (photo)stability of this dye either in solution or paint-layer mock-ups (Cheng et al., 1995; Pinto et al., 2024). Given the historical significance of shikonin/alkannin as a purple dye in oriental culture, a detailed investigation of its photochemical behaviour in textiles was considered historically relevant to establish a comprehensive database to provide insights into the preservation and degradation of valuable cultural artifacts. Here, the color changes induced by artificial light exposure were investigated in two different textiles – cotton and wool – and characterised by SERS, UV-Vis and colorimetric techniques.

SERS characterisation at neutral pH, combined with UV-Vis and fluorescence data, reveals differences between non-mordanted and mordanted textiles before and after light exposure. SERS identified shikonin and alkannin peaks, highlighting variations across different conditions. On aging, an overall loss of intensity and resolution of peaks across the entire spectral range was observed correlating to the formation and stability of photoproducts as detected in solution. 3 From UV-VIS, fluorescence emission spectroscopy and colorimetric data, the spectral dye colour degradation was characterised. Thus, the combined spectroscopic data allowed to identify the dyed source of a Japanese purple textile from the Bunsei period, bridging the laboratory mock-up knowledge to a historical artifact.

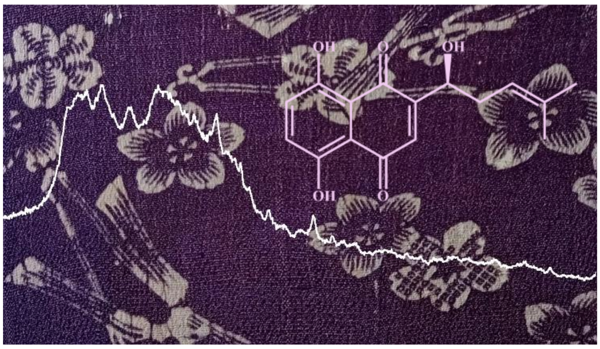

Figure 1 *Japanese textile, textile mock-up SERS spectrum and shikonin molecular structure.*

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References

Cardon, D. (2007) - Natural Dyes: Sources, Tradition, Technology and Science: Archetype.

Cheng, H.W., et al. (1995) - Photochemical decomposition of alkannin/shikonin enantiomers. Int. J. Pharm., 120, 2, 137-44.

Pinto, C.M., et al. (2024) - Unveiling the photostability of the molecule of colour shikonin: From solution to the solid state. J. Mol. Struct., 1316, 138898.

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Raman Spectroscopy for Identifying Pigment Compounds: A Case Study of White Inlaid Pottery Decoration from Bulgaria at the Beginning of the First Millennium BC

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The practice of inlaying white material into pre-prepared grooves or depressions on ceramic vessels in the Balkan Peninsula began at the end of the Late Neolithic (late 6th–early 5th millennium BC) (Boyadziev, 1995). This decorative technique became widespread during the Chalcolithic (5th–early 4th millennium BC), where it was favored by local potters. The use of white inlay persisted through the Bronze Age (3rd-2nd millennium BC) and into the Early Iron Age (first half of the 1st millennium BC). While ornamental styles and groove-making techniques evolved, the application of white paste remained consistent for nearly five millennia.

Archaeometric analyses of white pigments from Southeastern Europe reveal a diverse range of minerals used across different periods, including calcite, dolomite, aragonite, apatite, talc, gypsum, and kaolinite clays. Although only a limited number of samples have been analysed, discernible trends and regional variations in raw materials and pigment recipes can be identified. These variations suggest differences in pigment selection based on cultural preferences and functional distinctions between ritual and utilitarian ceramics (Pirovska, 2021).

This study examines the mineral composition of white inlaid paste in Early Iron Age ceramics from Bulgaria. Ceramic fragments with characteristic stamped and incised decorations filled with white paste were analysed using Raman spectroscopy (Bravo, Bruker) and X-ray Fluorescence (pXRF, S1 Titan, Bruker) at the Center of Archaeometry with Laboratory of Conservation and Restoration (CALCR) at Sofia University. The results reveal a high degree of continuity in pigment recipes, along with specific variations likely influenced by the availability of local raw materials. This research is part of a broader project and serves as an initial contribution to a more comprehensive investigation of white pigments used in Early Iron Age ceramic decoration in Bulgaria.

***Figure 1** A fragment of a ceramic vessel featuring characteristic Early Iron Age stamped decoration with inlaid white pigment. Micrograph of the white pigment.*

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References

Boyadziev, Y. (1995) - Chronology of prehistoric cultures in Bulgaria. In "Prehistoric Bulgaria. Monographs in World Archaeology №22", D. W. Bailey & I. Panayatov, Madison, Wisconsin, 149-191.

Pirovska, A. (2021) - White Pigments Used for Inlay and Painting on Pottery Dated Back to the Neolithic and Chalcolithic Period (Archaeometric Study), Bulgarian e-Journal of Archaeology Supplements | Българско е-Списание за Археология, 8, 19–32.

Surface Enhanced Raman Spectroscopy of drying oils

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Surface Enhanced Raman Spectroscopy (SERS) has been applied in the last decades as a sensitive technique for the detection of highly fluorescent compounds investigated in conventional Raman conditions.

So far, SERS has been mainly adopted for the analysis of several classes of natural organic dyes employed in the past for the dyeing of textiles or as lake pigments in painted objects.

However, applications of SERS for the investigation of binding media is still unexplored and only one contribution in literature has dealt with the SERS analysis of linseed oil.

This work focuses on the application of SERS for the investigation of three types of drying oils widely employed in both ancient and modern paint. Respectively, linseed oil, stand oil and tung oil have been analysed in SERS conditions. SERS is explored as a potential methodology to identify spectral markers able to differentiate successfully and unambiguously these compounds.

Both fresh and aged oil samples have been analysed in SERS conditions and compared.

References

Carlesi, S., et al. (2018) - The ageing of model pigment/linseed oil systems studied by means of vibrational spectroscopies and chemometrics. Vib. Spectrosc., 99, 86-92.

Gomez, M., et al. (2019) - Linseed oil as a model system for surface enhanced Raman spectroscopy detection of degradation products in artworks. J. Raman Spectrosc., 50, 242-249.

Leona, M., et al. (2006): Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art. J. Raman Spectrosc., 37, 981-992.

Raman Spectroscopy combined to hyperspectral image to evaluate the consolidation efficiency of nanoparticle-based formulations

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The NanoCult Project (Advanced Nano-solutions for consolidation and multifunctional protection in Cultural Heritage) aimed to develop nanoparticle-based formulations for consolidating stone materials used in cultural heritage contexts. To this end, Lurederra Technological Centre has developed different silicon formulations, with the objective of identifying the most effective option for consolidating degraded stony materials. Several mock-ups of sandstone and natural limestone were treated with the silicon nano-particles formulations, to optimize the most adequate application method. The mock-ups were characterised before and after the treatments by using different analytical techniques, such us Raman spectroscopy (Figure 1 shows the spectrum of the consolidant), micro X ray fluorescence (μ-XRF) and scanning electron microscope coupled with energy dispersive spectrometry (SEM-EDS) to evaluate the efficiency of the proposed consolidation method, concluding that the consolidation was successful on the mock-ups.

To test the consolidation capability on real marly limestones, naturally degraded samples from the Azkorri site (near Bilbao, Spain) were used. These real samples, exposed for decades to a rural environment affected by diffuse pollution from the surroundings of Bilbao's outer harbour, were characterised before and after the consolidation process, adding hyperspectral imaging to the previous mentioned techniques. This combination of Raman spectroscopy and hyperspectral imaging enabled the identification of the treated sample and the identification of the areas where the consolidation was most efficient, as demonstrated in Figure 2.

This combined approach has the potential to identify consolidated pieces in large areas and even evaluate the efficiency of consolidation over time using Raman spectroscopy and scanned hyperspectral images.

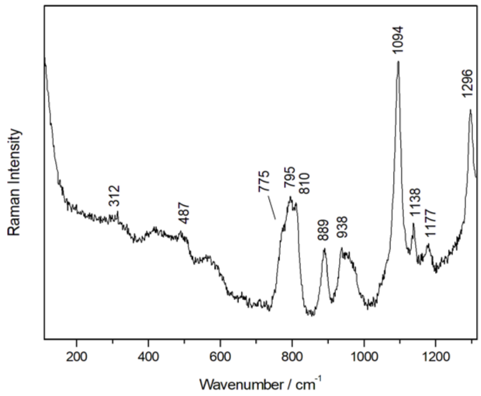

Figure 1 *Raman spectra of the nanoparticle-based consolidant used to consolidate both the sandstone and the marly limestones.*

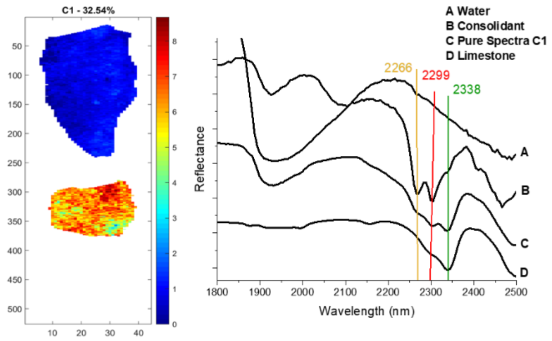

Figure 2 *(left) Distribution map of the first component obtained by MCR that discriminates an untreated sample from a consolidated one and (right) the NIR spectra obtained by hyperspectral imaging.*

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Tikuna Blue: Chemistry of an Unknown Colorant from the Amazon Forest

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The Amazon Forest is home of an immense cultural and biological diversity. Hundreds of Indigenous groups have been using several materials still understudied in conservation science and technical art history (Puglieri & Maccarelli, 2023). One example are colorants produced by the Tikuna people, who live near the borders of Brazil, Colombia, and Peru. The Tikuna people is also known as Magüta and Tukuna, and the terms Tikuna and Tukuna are also written as Ticuna and Tucuna, respectively.

Of special interest is a blue colorant produced through the engagement of the Tikuna people with chemical reactions. Curt Nimuendajú (1883-1945) reported that "the juice of one fleshy fruit (T., na'inku) furnishes a dark violet which, upon contact with iron, changes into a clear blue" (Nimuendajú, 1952). This suggests the involvement of chemistry in its production. Na'inku, naīcü, and other associated terms, are related with plants from the family Zingiberaceae, genus Renealmia L.f., including, for instance, Renealmia alpinia (Rottb.) Maas, Renealmia alpinia, and Renealmia sp.

In a previous work, Tikuna masks from two US and two Brazilian museums were investigated to search for the blue produced with naīcü (Puglieri & Maccarelli, 2024). The colorant was not detected, and the authors proceeded the research through a bigger initiative based on community-engaged approaches. In this work, collaboration with the Tikuna community was considered for the production and naming of the blue colorant. Mockups were prepared by Wilder and his family, Josi Tikuna, and Mercedes Tikuna, and the name "Tikuna blue" was suggested by three Tikuna artisans' associations: Associação das Mulheres Indígenas Artesãs (AMATU), Associação das Mulheres Indígenas Ticuna (AMIT), and Associação das Mulheres Indígenas de Porto Cordeirinho (AMIPC).

Investigations aiming at determining the Tikuna blue chemical composition, color, and colorfastness were conducted with colorimetry, FORS, SEM-EDS, normal and resonance Raman, Fourier transform infrared micro-spectroscopy (μ-FTIR), and microfading tester. Computational calculations were used to aid electronic and vibrational spectra interpretation.

The results revealed Tikuna blue to be a supramolecular structure based on anthocyanins, pectin, and iron ions, produced by the Tikuna people with a strategy analogous to one of those used by nature to fix blue color in flowers. The limited number of scientific investigations on Indigenous materials and the need to reevaluate Western canonical values that usually guide materials investigations in technical art history and conservation science are addressed, as well as how the results of this research are been currently used in other activities with bigger community engagement and mutual benefits.

References

Nimuendajú, C. (1952) - The Tukuna. University of California Press, 42.

Puglieri, T.S., & Maccarelli, L. (2023) - Paint and Coloring Materials from the Brazilian Amazon Forest: Beyond Urucum and Jenipapo. Heritage, 6, 5883–98.

Puglieri, T.S., & Maccarelli, L. (2024) - Blues from Tikuna/Magüta Masks and a Still Unknown Blue Colorant in Technical Art History and Conservation Science. Heritage, 7, 4697–711.

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Mixing Colours: a multi-analytical study of roman pigments from a coastal and an island archaeological site

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In the field of cultural heritage diagnostics, no single analytical technique can comprehensively address all questions related to material characterisation. Consequently, the integration of complementary spectroscopic methodologies, both elemental and molecular, is essential for achieving a more thorough and reliable understanding. Within this framework, Raman spectroscopy is widely employed for pigment identification; however, it presents certain limitations, particularly when applied to complex samples such as painted plasters, which often comprise mixtures of different components.

This study introduces a multi-analytical approach for the characterisation of pigments used in painted plasters from two Roman-period archaeological sites: the maritime villa on the island of Gorgona (LI) and Domus B in Luni (SP), both dated to the 1st century BCE. Rather than focusing on stylistic and decorative aspects—already extensively examined in Dr Ilaria Benetti's doctoral thesis—this work adopts a production-oriented perspective, tracing the materials from the raw materials used in pigment manufacture to their application in wall paintings.

The materials were classified according to their state of findings and examined at both macroscopic and microscopic levels. The most representative samples were selected for analysis using a combination of elemental and molecular techniques, including Raman spectroscopy, X-ray fluorescence (XRF), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and fibre optics reflectance spectroscopy (FORS). These analyses facilitated the identification of pigments and informed hypotheses concerning the nature of the raw materials employed.

Furthermore, this study addresses critical challenges associated with the application of Raman spectroscopy to these materials and demonstrates how its integration with XRF and FTIR mitigated issues related to surface colouration and chemical composition.

The integration of multiple datasets enabled a more robust characterisation of the production processes underlying the painted layers, revealing both commonalities and distinctions between the two archaeological contexts. Variations in pigment use across the sites are likely indicative of the preferences of patrons operating within a specific and contemporaneous historical milieu. Consequently, the findings are interpreted from an archaeological perspective, considering their historical, cultural, political, and economic implications.

In conclusion, this study underscores the value of a multi-analytical approach in the detailed characterisation of ancient pigments and reflects on the most effective strategies for integrating data from different techniques, highlighting their potential for advancing the understanding of complex ancient production and artistic practices.

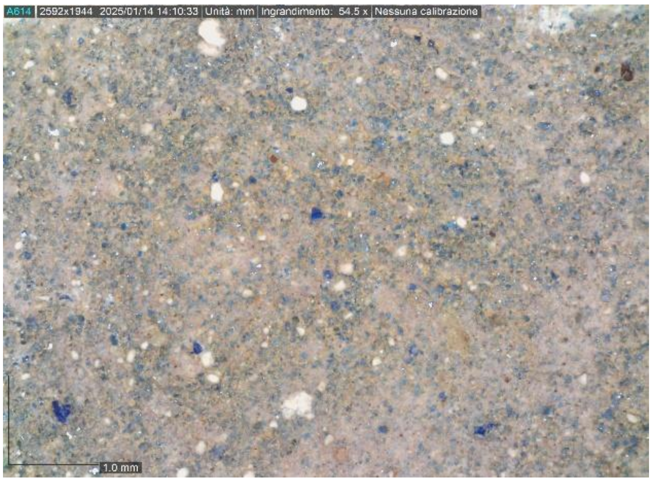

Figure 1 *Digital microscope image of a mixture of red ochre and Egyptian blue.*

References

Alderighi, L. (2018) - Gli intonaci dipinti delle villae maritimae dell'arcipelago toscano (Gorgona, Capraia, Elba, Pianosa). In "Pictores per provincias II", Y. Dubois & U. Niffeler, Archéologie Suisse, Basel, Germany, 567–574.

Grifa, C., et al. (2025) - Pompeian pigments. A glimpse into ancient Roman colouring materials. J. Archaeol. Sci., 177, 106201.

Menchelli, S. (2020) - Luni. Gli scavi nel quartiere di Porta Marina. Atti della Pontificia Accademia Romana di Archeologia. Rendiconti, 369–415.

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Artificial arsenic sulfide pigments used in Juan Bautista Maíno's *Pentecostés* (1612-14): new findings revealed with the aid of Raman micro-spectroscopy

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Detailed cross-sectional analysis of a paint sample from the yellowish-orange garment of Saint Peter in Juan Bautista Maíno's painting Pentecostés (1612-14, Museo del Prado, Madrid) was carried out with aid of optical microscopy, scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) and Raman micro- spectroscopy (RMS). The following results were obtained: a) natural and artificial arsenic sulfides; b) lead white; and c) brownish-yellow iron hydroxide pigments (yellow ochre). With the aid of Raman micro-spectroscopy it was possible to identify dry-process x-ray amorphous orpiment glass (g-As_2S_3) with particle sizes ranging between 3 to 70 µm. Two of the larger particles show clear evidence of gas bubbles and pores of up to 2-3 µm Ø which developed during dry process preparation of natural orpiment at high temperatures. SEM-EDX analyses confirm the chemical composition of amorphous orpiment glass (g-As_2S_3) identical to natural orpiment (As2S3). Equally important is the presence of numerous thin-foliated and kinked fragments of natural orpiment crystals between 5 and 40 µm in size throughout the whole layer which suggests that the mineral was most likely the starting material to produce the roasted orpiment glass pigment (Fig. 1). Interestingly, both Francisco Pacheco (Arte de la pintura, 1649) and Antonio Palomino (El Museo pictórico y escala óptica, 1715–24) describe the preparation of exactly this type of pigment. Raman analysis proved to be an indispensable tool for this study, particularly for the differentiation between x-ray amorphous yellow arsenic sulfide glass (g-As_2S_3) and natural crystalline orpiment (As_2S_3). The value of this specific analytical technique has also been confirmed in previous studies on different types of dry-process artificial arsenic sulfide pigments. The identification of a dry-process artificial yellow arsenic sulfide pigment in Maíno's Pentecostés does not come as a complete surprise due to the artist's close association with Italy and the fact that various Italian sources such as Cennino Cennini's Il Libro dell'Arte (c. 1400) prized this artificial product for its bright yellow colour. Juan Bautista Maíno (1581-1649), one of the most original but least known figures in Spanish painting at that time, was highly regarded. This is shown by the fact that he was the drawing teacher of King Philip IV. The son of a Milanese merchant, he travelled to Italy at a very early age, where he received intense artistic training in the circles of Italian naturalism and classicism. Once back in Spain, he carried out various works until, in 1612, he was commissioned to paint the main altarpiece of the church of the convent of San Pedro Mártir in Toledo, where he ended up becoming a Dominican friar in 1613. The themes of the altarpiece were related to important episodes in the life of Jesus, currently preserved in the Prado Museum. The Pentecostés painting is one of the most clearly Caravaggist compositions contrasting lighting and a colouring where the yellowish-orange, reddish-orange, red, blue and green tones stand out.

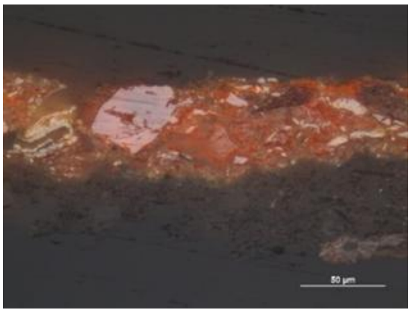

Figure 1 *Sample M-I2, large x-ray amorphous particle of orpiment glass. To the left of this particle is a crystal of natural orpiment exhibiting thin-foliated and kinked fragments. Vertically reflected light, 500x magnification.*

References

Grundmann, G., et al. (2011) - The rediscovery of sublimed arsenic sulphide pigments in painting and polychromy: applications of Raman microspectroscopy, Studying Old Master Paintings – Technology and Practice, Postprints of National Gallery Technical Bulletin 30th Anniversary Conference, 16-18 September 2009, London. Archetype Pub. Ltd., London, 269-276.

Grundmann, G, & Richter, M. (2008) - Current Research on Artificial Arsenic Sulphide Pigments in Artworks: A Short Review. Chimia, 62, 903-907.

Grundmann, G., & Richter, M. (2012) - Types of dry-process artificial arsenic sulphide pigments in cultural heritage. In „Fatto d´archimia: Historia e Identificación de los Pigmentos Artificiales en las Técnicas Pictóricas", M. del Egido & S. Kroustallis, Ministerio de Educación, Cultura y Deporte, Madrid, 119-144.

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Hardware-Registered Sequentially Shifted Excitation™ Macro-Raman and 3D Mapping System for the Characterisation of Artwork Surfaces

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The analysis and characterisation of cultural heritage artefacts present significant challenges due to the complexity, heterogeneity, and fragility of the materials involved. Traditional analytical methods often fall short in providing comprehensive, non-invasive insights. Consequently, in recent years scientists produced an increasing development of more sophisticated, multicomponent analytical systems (Striova et al., 2021) designed to enhance data quality and access previously unresolvable material information.

Raman spectroscopy (RS) has long proven to be a valuable technique for the surface characterisation of artworks, owing to its non-invasive nature and its suitability for portable, in situ investigations. Beyond conventional single-point measurements—commonly used for identifying specific materials at discrete locations—Raman mapping has emerged as a powerful method for visualising the spatial distribution of chemical components across larger areas of an object (Vandenabeele et al., 2021).

Raman mapping techniques can be categorised as either micro- or macro-scale, depending on the size of the mapped area and the step size of the acquisition grid. Micro-Raman mapping is a common practice for the characterisation of sample cross-sections or small, flat art objects that fit on the motorized stages of optical microscope coupled with spectrometers. Although macro-Raman mapping may involve trade-offs in resolution and acquisition times, it remains particularly effective for analysing extended regions.

At the National Institute of Optics (CNR-INO, Florence, Italy), we have developed a new three-axis scanning platform for hardware-registered multi-instrument acquisition. We used the platform to couple a Sequentially Shifted ExcitationTM (SSE) portable Raman spectrometer (Bruker BRAVO) with a 3D camera. This automated system enables accurate focus adjustment at each measurement point and appropriate registration of Raman spectral data on a 3D map.

To the best of our knowledge, this is the first time SSETM RS has been successfully employed for the spectral mapping applications in heritage science. This represents a major advancement given the efficient removal of fluorescence and other background signals with this method.

This study demonstrates the application of such automatic and synchronized macro-Raman and 3D mapping system on several case studies comprising contemporary paintings. The retrieved information regarding the surface topography, the spatial and chemical distribution of pigments within the painted surfaces through multivariate analytical methods, demonstrates the efficacy of this integrated approach for advanced heritage science research.

References

Striova, J., et al. (2021) - Synchronized Hardware-Registered VIS-NIR Imaging Spectroscopy and 3D Sensing on a Fresco by Botticelli. Sensors, 21, 4, 1287.

Vandenabeele, P., et al. (2021) - Developing Macro-Raman Mapping as a Tool for Studying the Pigment Distribution of Art Objects. Anal. Chem., 93, 46, 15390-15400.

https://www.bruker.com/en.html.

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The extraordinary richness of pigments in Flemish miniatures on parchments. Non-invasive analysis with Raman spectroscopy, XRF, and RIS

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The collection of the National Museum in Kraków includes Flemish Early-modern miniatures depicting landscape motifs. They are made using the watercolor and gouache technique on parchment, which refers to the traditional method of making miniatures. Two of them, dated to the late 16th century, have been attributed to a pupil and his master, namely Jacob Savery and Hans Bol. The first of them is "The siege of Jerusalem with small figures of Roman soldiers" (Inv. no. MNK-III-min-425), on which a monogram evidencing the authorship of Jacob Savery (1566-1603) was identified during research. It is a miniature with a diameter of about 6 cm. The second object, "Spring in the Castle Garden" (Inv. no. MNK XV-1981) by Hans Bol (1534-1593), is larger, with dimensions 11.3 x 17.7 cm, and is dated to 1584.

The research was concerned with identifying the artist's workshop, considering the master-apprentice relationship. Conservation requirements did not allow sampling, but non-destructive examinations were performed to identify the pigments. We performed point measurements using Raman spectroscopy (RS) and elemental mapping using macro-scanning X-ray fluorescence imaging spectroscopy (macro-XRF) as well as reflectance imaging spectroscopy (RIS) in the spectral range 400 – 2500 nm.

The analysis allowed to identify the richness of the pigments used. RS is particularly useful for distinguishing pigments characterised by similar elemental composition (e.g., Cu pigments). Macro-XRF and RIS techniques showed the distribution of pigments throughout the object. Macro-XRF is a more sensitive technique than RS which made it possible to complement the results obtained with RS. RIS spectroscopy allowed to identify organic pigments and areas of conservation interventions. In this way, the range of use of organic pigments was determined.

The miniatures were made using a large palette of pigments. At least two different pigments are present in each colored area. We identified red hematite, cinnabar and cochineal lake, green malachite and brochantite, lead-tin yellow with massicot and blue azurite together with indigo. In addition, traces of conservation interventions and repainting obtained using Prussian blue, cobalt blue, and titanium white, among others, were also identified. The research showed that the chosen techniques are adequately complementary for pigment detection and the possibility of making a chemical distribution map enhanced the interpretation of the results.

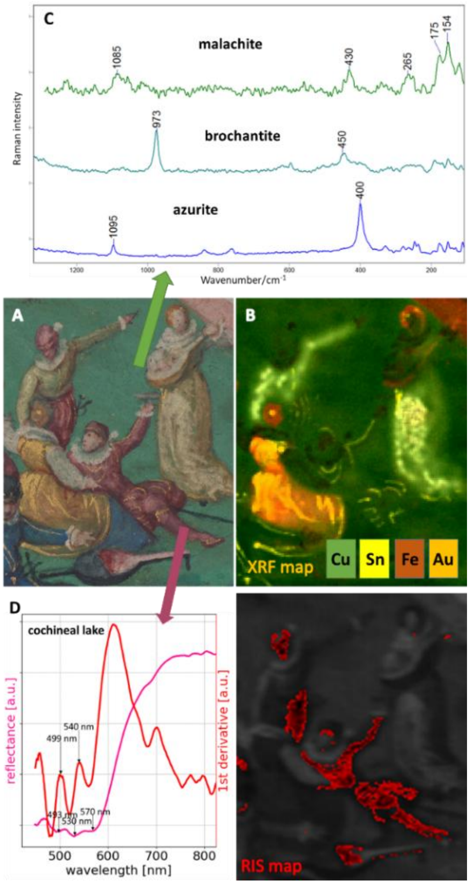

Figure 1 *Analysis of a fragment of the Hans Bol's miniature (1584).* ***a)*** *macro-photography (1.6 x 1.2 cm);* ***b)*** *Macro-XRF map presenting the distribution of Cu, Au, Fe, and Sn;* ***c)*** *Raman spectra of various pigments found in a green colored area;* ***d)*** *RIS spectra of cochineal lake along with its distribution map.*

References

Maniakowska-Jazownik, Z., et al. (2023) - The Siege of Jerusalem and Mount Golgotha: Bemmel, Brueghel and Savery: Case Study of a Miniature from the Collection of the National Museum in Cracow. AUNC ZiK, 54.

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MRS and µXRF for the analysis of vitreous lead slags reused in the production of Roman mosaic tesserae in the Upper Guadalquivir Valley (Jaén, Spain)

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This work presents the analysis of the chemical composition of a set of black vitreous tesserae, which verifies, for the first time, the reuse in Roman times of slags resulting from the galena smelting process in the production of black tesserae used in various Roman mosaics of the province of Jaén (Spain).

This study is part of the research project 'Geochemical analyses for the research and enhancement of the Roman mosaics of the Upper Guadalquivir Valley (GeoChemMos),' funded by the Andalusia Regional Government and with the collaboration of the Department of Archaeology of the University of Ghent (Belgium) and the Hercules Laboratory of the University of Évora (Portugal). Its fundamental objective is twofold: the archaeometric analysis of a set of 13 mosaics located in the Upper Guadalquivir Valley dated between the 1st and 5th centuries AD and, with the new repertoire of data related to the raw materials used, their evolution over time, their singularity and significance, to enhance their conservation and valorisation as a cultural, social and tourist resource. The working methodology has been structured around several phases. A first phase of sample selection, followed by spectroscopic analysis of the selected tesserae using micro-Raman spectroscopy (MRS) and micro-energy dispersive X-ray fluorescence (µEDXRF) jointly. The sampling of the 13 mosaics has revealed the presence of black vitreous tesserae only in the mosaics of Los Amores (Cástulo, Linares), Cerrillo del Cuco (Vilches) and El Altillo (Rus). The analysis of these has been complemented with that of a set of vitreous slags recovered near the Los Amores mosaic of Cástulo and the mining area of El Centenillo (La Carolina).

The results of the analyses point to a type of material not generated in a standardized glass melting process, that is, these are not tesserae made with an allochthonous glass manufactured following a classic process. The analytical data determine compositions and suggest formation processes for these glasses that could be considered characteristic of vitreous slags: (i) Raman spectra related to lead glass (470-490 cm^{-1} and 960-990 cm^{-1}; (ii) high and variable concentrations of Pb; (ii) presence of lead oxide particles (81, 145, 289, 343 cm^{-1}); (iii) persistence of quartz (129, 204, 267, 355, 395, 464, 811, 1160 cm^{-1}) and β-cristobalite grains (112, 228, 282, 416, 792 cm^{-1}); (iv) absence of chromophores and opacifiers related to Pb. As mentioned, the three mosaics in which these types of materials have been identified are located in or in the immediate vicinity of the mining district of Linares-La Carolina, which, from Roman times until the mid-20th century, was characterised by the extraction and smelting of galena to obtain lead and silver. The intense Roman mining and smelting activity would have generated large quantities of black vitreous slags, from which the artisans would have carved the tesserae. The confirmation of the use of these waste products as raw material in the elaboration of mosaics in Roman times gives the mosaics located in this territory a unique originality. The use of this type of tesserae should be analysed both in the context of its aesthetic appeal and in that of the abundance of this raw material and the scarcity of others for these same purposes.

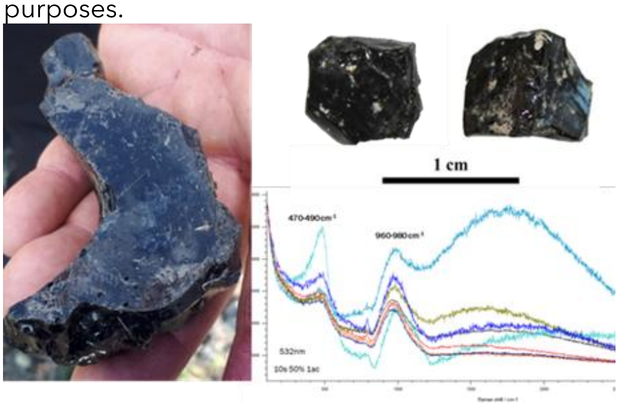

Figure 1 *Vitreous lead slag. Black tesserae. Raman spectra of black teserae.*

References

Colomban, P., et al. (2006) - Raman identification of glassy silicates used in ceramics, glass and jewellery: a tentative differentiation guide. J. Raman Spectrosc., 37, 841-852.

Sánchez, A., et al. (2021) - First insights into the archaeometric analysis of the Los Amores Mosaic in Cástulo (Linares, Spain): the Judgement of Paris. Herit. Sci., 9, 8.

Advanced Raman Analysis of Textile Fragments from the Ryazan-Oka Culture: Application of the SERS Technique for Archaeological Study

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The analytical methods currently used for textile characterisation are based on chromatographic techniques, which are highly sensitive and selective but require the chemical extraction of a few milligrams of sample, making them a destructive technique. Raman spectroscopy has therefore efficiently evolved as a non-destructive and in situ technique for the identification of inorganic pigments and other materials in works of art. However, the application of this technique to organic pigments is limited by two main challenges: the strong fluorescence emission from organic pigments, which typically obscures the Raman signals in the spectra, and the extremely low concentration of the dye, which is often below the detection limit of the low-sensitivity Raman technique (Jurasekova et al., 2008).

Surface-Enhanced Raman Spectroscopy (SERS) is increasingly being used to identify natural organic dyes, both of plant and animal origin, in archaeological artifacts and works of art. The SERS effect is based on the enhancement of the Raman signals of a given molecule, which occurs when the molecule is in proximity to or adsorbed onto a nanostructured metallic surface (Zaffino et al., 2014).

During the study of the monuments of the Ryazan-Oka culture (5th-6th centuries AD), a large number of textile fragments from the garments in which the buried individuals were dressed were discovered. These findings mainly come from the Undrich and Borok-2 burial sites (Ryazan Region, Central Russia). The artifacts were analysed using various spectrometric and chromatographic methods, as well as scanning electron microscopy coupled with an EDS microprobe (SEM-EDS) and vibrational spectroscopic techniques such as ATR-FTIR and Raman spectroscopy. Through Raman spectroscopy, it was possible to identify certain dyes (such as indigo) and to gain insights into some of the dyeing techniques used for textiles in Central Russia during the 5th-6th centuries AD.

This preliminary study enabled the creation of an extensive database containing all the data obtained from chromatographic and spectroscopic analyses. Furthermore, SEM-EDS analysis revealed the presence of copper and copper-tin particles, appearing as small granules embedded in the Fibers.

To achieve a more in-depth identification of the dyes present in the various samples, and therefore a better understanding of the historical dyes used by the populations of Central Russia, the SERS technique was chosen. This method enhances the signal-to-noise ratio, allowing for the acquisition of more detailed information. For the application of the SERS technique, it was decided to synthesize two types of nanoparticles: the well-known and widely used silver (Ag) nanoparticles, synthesized through the Lee-Meisel method, and gold (Au) nanoparticles, synthesized using the Turkevich method, which are commonly employed in the biomedical field. Both methodologies were used to analyse reference samples, obtained by dyeing wool fibers with different dyes, as well as samples from the archaeological site.

Figure 1 *A photo of Borok 2-236.*

Given the promising results, it is essential to emphasize the importance of a synergic approach that combines two complementary techniques to facilitate the identification of different dyes. Furthermore, the absence of written records makes this study a significant step toward a deeper understanding of the customs and traditions of the ancient populations of this region.

References

Jurasekova, Z., et al. (2008) - In situ detection of flavonoids in weld-dyed wool and silk textiles by surface-enhanced Raman scattering. J. Raman Spectrosc., 39, 1309-1312.

Zaffino, C., et al. (2014) - Fourier-transform surface-enhanced Raman spectroscopy (FT-SERS) applied to the identification of natural dyes in textile fibers: an extractionless approach to the analysis. J. Raman Spectrosc., 45, 211-218.

Multi-analytical approach for the characterisation of earthy encrustation collected from authentic and forged ceramic vessels for artworks authentication

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The market of archaeological forgery is a highly lucrative criminal business, which causes economic losses, estimated in millions of euros annually only in Italy (A.O., 2023) along with a cultural contamination. The recognition of fakes is therefore of fundamental importance and scientific investigations can deeply contribute to prevent the counterfeiting crime. Nowadays forgers have refined their skills, producing fake archaeological objects convincing in terms of iconography, raw materials, and manufacturing techniques. Moreover, to further enhance their perceived authenticity and market value, forgers mimetically reproduce on the surface the signs of burial which are considered a key feature of genuine archaeological finds (Privitera et al., 2024, 2025). Given the increasing sophistication of forgeries, there is the need of advanced protocols and the study of earthy encrustations as authentication tool is a novel and promising criteria. In this work, earthy encrustations collected from authentic museum collection ceramics, as well as artificially reproduced encrustations on two typologies of counterfeit pottery (bucchero and attic pottery) are investigated and our preliminary results are encouraging.

An integrated analytical procedure, based on the use of non-invasive and micro-invasive techniques, has been developed by providing a comprehensive insights into the mineralogical and textural features necessary for a systematic comparison between natural and fictitious encrustations. Preliminary in situ investigations have been carried out by portable X-Ray Fluorescence (p-XRF) spectroscopy and colorimetry. Further analyses on selected samples have been performed by using μ-Raman spectroscopy, Synchrotron X-ray powder diffraction (SR-XRPD), and Fourier Transform Infrared Spectroscopy, the last aimed at detecting organic binders. The dataset of Raman spectra and diffractograms processed with Rietveld refinement was subjected to multivariate statistical analysis (clustering and PCA). By comparing the Raman and XRPD data of natural and fictitious encrustations, it was possible to distinguish four different groups: a homogeneous one in which the natural encrustation falls and three different types of counterfeit encrustations. The criterion that enabled the identification of the aforementioned clusters was the $CaCO_3/SiO_2$ ratio, which is very high for natural encrustations with quartz as dominant phase (Fig.1: blue cluster C1), and very low for artificial ones. Regarding the composition of counterfeit encrustations, the first type, characterising the findings on bucchero-type artifacts, consists of a lime-based inorganic binder mixed with sand (Fig.1: green cluster C2). The other two groups correspond to the encrustations found on pseudo-Attic pottery. The second type of fictitious encrustations is composed of a cement-based mortar, in which alite ($(CaO)_3 \cdot SiO_2$)) and larnite (Ca_2SiO_4) phases, typical markers of Portland cement, were identified (Fig.1: orange cluster C3). The last type does not contain any inorganic binders (Fig.1: red cluster C4). Micro-Raman spectroscopy addressed the identification also of some organic and poorly crystalline compounds, barely or not detectable by diffraction, obtaining a representative Raman database useful for authentication purposes and to reconstruct the methods used by the forgers.

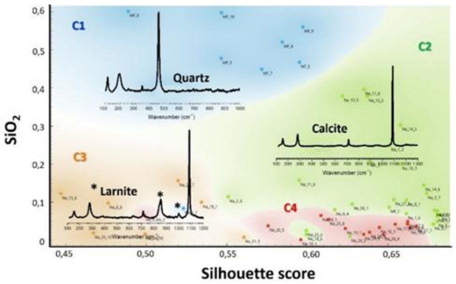

Figure 1 *Cluster analysis results plotted as quartz content (%) versus silhouette scores, obtained by multivariate statistical analysis of Raman and XRPD dataset. Differently colored areas indicate the four distinct clusters identified. Raman spectra, describing the characteristic mineral phase, are also reported: quartz for the blue cluster of natural samples, calcite for the green cluster of bucchero-type fictitious encrustations, and larnite for the cluster related to Attic fictitious encrustations. The red cluster, which is not accompanied by a spectrum, is still under analysis.*

References

Attività Operativa 2023, Comando Carabinieri Tutela Patrimonio Culturale, Rome 2024.

Privitera, A., et al. (2024) - A multi-analytical approach to unmask two Etruscan-Corinthian fake vases: A contribution to the illicit trafficking of cultural goods. J. of Raman Spectrosc., 55, 2, 216-226.

Privitera, A., et al. (2025) - Raman approach to investigate painted decorations and manufacture technology of fake Greek and Italic pottery: a contribution to authentication. Eur. Phys. J. Plus, 140, 3, 234.

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Shedding light on Medieval Burial vaults from Bruges, Belgium: A combined Raman spectroscopy approach (*in situ* and laboratory) for pigment characterisation

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In Flanders, painted burial cists are a unique, late medieval burial form rarely found outside the specific geographical region of Bruges and the adjacent Zwin area (in Belgium and the Netherlands). These vaults occur from the late 13th century to the 17th century, with a notable peak in the 14th and 15th centuries. They consist of single or double brick graves, plastered and painted on the inside. The depictions are always of catholic nature and were made with the aim of ensuring the journey to the afterlife. Even though that these decorations had to be applied in a hurry, as burial had to be performed fast in Medieval times, the depictions can be quite elaborate and detailed. It is thus clear that these burial vaults were typically reserved for the clergy, nobles and wealthy patricians.

Figure 1 *In situ measurement on an illustration of the burial vaults.*

Even though many painted burial cists have been excavated, research on this subject has been limited. The burial vaults share stylistic motifs and subjects, but little is known about the artists' palette. To this day, only limited literature on the pigment analysis can be found (Janssens et al., 1982; Hoffman-Klerkx, 1987). Therefore, more elaborate research on this interesting subject can add to the knowledge on this burial practice.

In this study we present the results obtained with Raman spectroscopy of the illustrations on the internal walls of three burial cists from the former Eekhout Abbey in Bruges, Belgium. Both *in situ* measurements with mobile Raman equipment as well as micro-Raman measurements with a benchtop instrument were applied to unravel the colour palette.

Mobile Raman instrumentation was able to characterise and identify vermilion (HgS), haematite (Fe_2O_3), calcite ($CaCO_3$), quartz (SiO_2) and goethite (FeOOH). However, to have a more precise idea about the different colourants, small samples were taken of regions of interest, to account for micro-Raman analysis. This resulted in the identification of whewellite (calcium oxalate) which could suggest biodegradation. However, the most fascinating result was the identification of indigo as a blue colourant.

Raman spectroscopy was able to extend the knowledge on the colour palette used in Medieval burial vaults.

Acknowledgements: The authors would like to thank Raakvlak for their cooperation in this project and for the interesting objects.

References

Hoffman-Klerkx, E.L. (1987) - Sprekende Graven. Kwadraat, Utrecht.

Janssens P., et al. (1982) - Maria van Bourgondië: Brugge: een archeologisch-historisch onderzoek in de Onze-Lieve-Vrouwekerk. Brugge: Westvlaamse Gidsenkring.

Non-destructive analysis of Roman rings with gems coming from the necropolis of Lovere (North of Italy)

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The glyptic corpus returned from the necropolis of Lovere (Bergamo, Lombardia, Italy), thanks to the findings from 1907, 1996 and 2015, stands out in the panorama of the Lombardy region, for the abundance of rings with gems, their general good/high level, and the high percentage of material in silver/silver alloy, instead of the usual iron or bronze; furthermore, there are four rings in gold. This glyptic set is diversified by chronology (from the middle/end of the 1st century BC to the 4th century AD), typologies, material, representations, more or less accurate execution. Thus, two types of representations can be found. The first one is part of a common, uniform, widespread figurative repertoire and language, it is part of the imperial glyptic koiné, like Tyche / Fortuna, Hermes / Mercury, Nike / Victory, Ceres-Fides, the animals. The second set does not belong to the series production, but presents unusual, rare, even unique motifs and/or styles. In order to identify the materials and to have some clues about the origin of manufacture of the gems and glass found in Lovere, a completely non-desctructive, mobile, multi-technique campaign of measurements was carried out.

The gemological observations, as well as those related to the goldsmith techniques, were conducted using a Dino-Lite digital microscope model AM7915MZT, with a magnification of 10 to 220X, 5 Megapixel Edge Sensor, Extended Depth of Field (EDOF) function, Extended Dynamic Range function, automatic magnification reader (AMR), integrated polarizer and Flexible LED Control (FLC).

Elemental analysis have been performed on the metals of the rings using a portable X-ray fluorescence 'Elio' energy dispersive instrument from Bruker Co. The instrument is equipped with a 50 keV, 200 µA (max) X-ray tube with Rhodium anode and a 17 mm2 Si-drift detector.

Raman analysis have been performed on the gems using a handled Raman spectrometer Enspectr Raport, equipped with a 532 nm emission laser. The measurement range covers 100-4000 cm^{-1}. The composition of the garnets present was then estimated using the new version of the Miragem program running under Matlab ® environment.

In addition to different glasses, chalcedony and quartz varieties, many precious stones, ranging from garnets and pearls to sapphires and emeralds have been identified. Different consideration on the provenance of some stones and the production technology have been drawn.

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A multidisciplinary study for the identification and characterisation of the repaint layers from the Viceroys gallery in Goa: the contribution of Raman Spectroscopy (*in situ* and micro)

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The Viceroy's gallery is a collection of 120 portraits depicting the Portuguese India Viceroys and Governors who administrated this territory between 1505 and 1961. These paintings were made by local artists and are quite unique since (in most cases) they are the only known representation of the sitters and their iconography, so their documental value is very important for the history of that period. 88 painting are on wood and 32 on canvas and, unfortunately, the panels are covered with several layers of repaints. The extension of the repaints is not even, from partial areas in just 16 panels to two full overpaints in 54 panels. In the 50's of the 20th century, seven of these paintings were taken to Portugal for restoration and the complexity of such intervention was well documented in the technical reports. The study of three of these paintings which were incorporated in the Museu Nacional de Arte Antiga (MNAA), in Lisbon, also revealed important information such as cases of panels reused to depict more than one sitter and how an eventual removal of repaints could lead to loss of historical information without a scientific study to support decision-making (Reis et al., 2023).

The aim of Project Old Goa Revelations (Reis et al., 2021) is to understand the historical context of these interventions and collect scientific data for their characterisation. The goal is to differentiate original compositions from intervention layers, supporting the current custodian with interpretation tools towards best practices in the preservation of this shared heritage. This joint interdisciplinary study with the Archaeological Survey of India (ASI) is led by HERCULES Laboratory (University of Évora), with cooperation of José de Figueiredo Laboratory, the Art Studies Research Center of the University of Lisbon and Ghent University.

This project has allowed the integrated research of almost a third of the collection by three scientific in-situ campaigns (2013, 2019 and 2023). For this, a set of multi-analytical techniques were used including visible and raking light photography, UV fluorescence photography, X-Ray radiography, Infrared (IR) reflectography, point and mapping X-Ray fluorescence (XRF) and mobile Raman spectroscopy. Destructive analyses were only conducted in the MNAA portraits, namely scanning electron microscopy-energy dispersive X-Ray spectroscopy (SEM-EDS), Raman spectroscopy (micro) and micro-Fourier Transform Infrared Spectroscopy (FTIR).

This research has allowed to contextualize in place and time interventions occurred in 1581, 1825, 1839, 1894 and 1953-55 (Reis et al., 2024). Still, the restorer's pallet of each phase is still incomplete, and one can detect the same elements repeated in more than one layer. To be able to comprehend the formal and material composition of each intervention, would be a very useful tool for any future conservation procedure. In the study presented here, we co-relate the results obtained with Raman spectroscopy during an in-situ measurement campaign in Goa with the results from micro-Raman spectroscopy, micro-FTIR and SEM-EDS made in the samples collected from the Lisbon portraits towards new steps in the characterisation of the painting materials used in the original compositions and the different restorations.

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References

Reis, T., et al. (2021) - Old Goa Revelations: A collaborative project on the shared heritage between India and Portugal. In „Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, 17–21 May", J. Bridgland, ICOM, Paris, 1–13.

Reis, T. (2023) - A Galeria de retratos dos vice-reis e governadores do Estado da Índia. Percurso para a sua reinterpretação e salvaguarda [Ph.D. thesis], Faculty of Fine Arts, University of Lisbon.

Reis, T., et al. (2024) - Em busca do retrato original de Afonso de Albuquerque: Novas revelações na Galeria dos Vice-Reis de Goa. Conservar Património, 46, 43–59.

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Macro-Raman Mapping of artworks

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Raman spectroscopy is a well-appreciated approach in cultural heritage research. Indeed, the technique has several favourable characteristics, including its non-destructive character, the possibility to obtain molecular information of inorganic as well as organic molecules, and the overall speed of analysis. Moreover, the method exhibits excellent spatial resolution, and by using a Raman microscope, one can record a spectrum of particles down to 1 µm.

Raman mapping allows for obtaining an image that represents the molecular distribution in a sample. One can record a series of Raman spectra in a structured way, to obtain a 3-dimensional data cube, that relates the Raman spectral information with the spatial coordinates. By using appropriate data extraction methods, it is possible to plot the spectral information in an image, showing the concentrations of the molecules in the sample. Until recently, this approach was limited to small samples or areas, as a Raman microscope was used. Macro-Raman mapping uses a larger set-up, that allows to analyse objects, typically covering an area of several tens of cm².

However, whereas the approach may seem pretty straightforward, several hindrances might hamper the broad application of the technique. On the one hand, there are physical constraints during set-up, involving stability and the need to focus the laser beam on the artwork. Furthermore, there is the concern that recording thousands of spectra is very time consuming. An obvious way to reduce the over-all time that is required for recording the map, is by reducing the number of spectra (Vandenabeele, 2024a). By selecting a larger step size, the number of spectra is reduced. However, there is a trade-off between the number of spectra and the image resolution.

Another approach to reduce the over-all measurement time is achieved by reducing the measurement time for each spectrum (Vandenabeele, 2024b). However, there is a limit to this approach: a minimal time is needed to obtain Raman spectra that are of sufficient quality to make a Raman map. On the other hand, not every molecule is equally Raman active. By applying an algorithm that is able to modulate the measurement time as a function of the spectral quality, a qualitative Raman map can be obtained, while reducing the measurement time.

Moreover, Raman mapping is usually limited to relatively flat objects. However, as the distance to the surface of the artefact is measured, when applying 3-dimensional macro-Raman mapping, it is possible to relate the spectral information to the surface of a 3-dimensional object (Vermeersch & Vandenabeele, 2025). By combining measurements under different angles, it is possible to combine different data cubes to achieve a complete 3-dimentional Raman image of an object.

Macro-Raman mapping is an interesting technique that allows to combine the spectroscopic and spatial information for relatively large artefacts. It is without doubt that this methodology can be of wide interest for scientists studying cultural heritage objects.

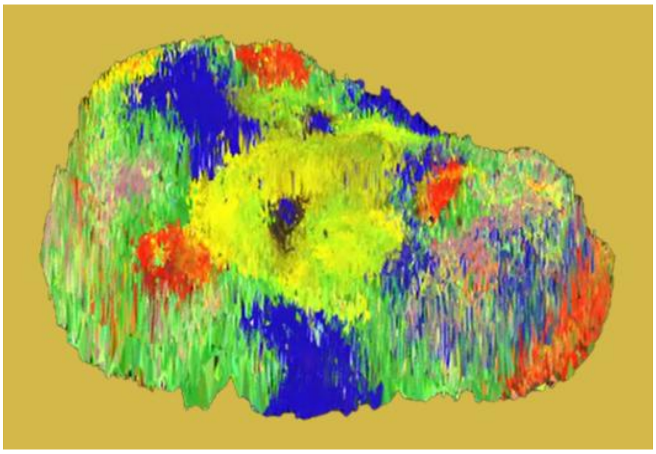

Figure 1 *Macro-Raman map of a 3-D object: a painted head of Dionysos.*

References

Vandenabeele, P. (2024a) - Evaluating the influence of step size in macro-raman mapping experiments. Eur. Phys. J. Plus, 139, 915.

Vandenabeele, P. (2024b) - An alternative macro-Raman mapping algorithm, adapting the numbers of accumulations. J. Raman Spectrosc., 55, 1067-1079.

Vermeersch, E., & Vandenabeele, P. (2025) - Proof of Concept: Macro-Raman Mapping of a Three-Dimensional Object. J. Raman Spectrosc., 56, In Press.

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Exploring the use of Bravo (Bruker) instrumentation for *in situ* measurements

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Recently, Raman spectroscopy has grown as a highly valued analytical technique in archaeometrical research. Especially the ability to use mobile instrumentation for in situ measurements, has generated some interest. Mobile instruments were developed and became increasingly more user-friendly and easier to operate.

One of these instruments is the Bruker spectrometer Bravo, a handheld instrument (Bruker Optik GmbH, Ettlingen, Germany), that weighs around 1.5 kg and has a fixed optical head. It is equipped with two laser, a 785 and 853 nm, yielding a bigger spectral range. The system can suppress the fluorescence by using a sequentially shifted excitation mode (SSE). The laser power of the system is automatically chosen and has a maximum of 100 mW. In addition, the integration time and accumulations are also automatically chosen based on the signal it retrieves. However, it is possible to select the integration time and the accumulations, but this is only available when the instrument is put on its docking stage and is connected to the software on a computer or via a Bluetooth connection to an electronic device.

All these features make the instrumentation very straightforward to use and applicable for routine analysis. However, these same properties/qualities can also be seen as drawbacks of the instrumentation.

The automatization of the system is often regarded as an advantage. However, when working with materials that are precious and/or brittle this automatization could lead to damage of the object, which is something to avoid at all costs when working with vulnerable artefacts. The laser power chosen by the system could be too strong and as such even visually impare the artwork. It could also lead to misidentification if the materials are susceptible to the laser light. A transformation or degradation of the original material could occur. In addition, the fixed optical head requires contact with the surface to obtain well defined spectra, but this is not favored for archaeometrical research. Focusing of the laser is always a crucial part of acquiring Raman spectra.

However, keeping the Bravo instrument stable, which weighs 1.5 kg, can be quite hard over time and too much force cannot be put on the surface it is touching (e.g. the artwork). It is evident that the Bravo instrumentation has some limitations when used in the field.

As such, a set-up specifically for the Bruker Bravo instrumentation for in situ measurements has been explored. The fixed optical head that required contact with the surface has been removed and the optimal focusing distance for the instrument was determined. In addition, a positioning stage with more stability and precise movements has been constructed. This all to make the Bruke Bravo instrument more versatile for in situ measurements.

Figure 1 *Bravo instrument on the docking stage while performing a measurement.*

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Through the looking glass: pigment characterisation of an Archaic Female Head Statue (late 6th BC)

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Raman spectroscopy has grown over many years as a versatile technique, with applications in multiple research fields, of which archaeometrical applications form an important branch. This is due to its non-destructive nature and the possibility to perform the measurements in situ. However, due to the value and brittleness of the artefacts, often artworks are stored behind glass or in a glass display case, securing them from the environment and entrapping them in controlled surroundings to prevent further degradation. Unfortunately, this intervention has its implications on the archaeometrical research and the techniques that can be used for identification.

Many of the techniques that can be applied in situ require approaching the artefact or making contact with it, which cannot be obtained when it is stored behind glass. Typically, mobile Raman instrumentation with a probe has a working distance of several millimeters. Which is insufficient to cross the distance caused by the glass. Long working distance lenses could be an option, however the range in which they work is still not enough. Coupling the laser probe of the instrument to a zoom lens with a larger working distance (several centimeters) has been performed and showed promising results (Vandenabeele et al., 2022). For the very first time, in situ Raman spectroscopy was applied for the pigment characterisation of an Archaic Female Head Statue (Late 6th BC) inside a glass casket. A BWTek instrument, equipped with a 785 nm laser was coupled with the RTS201-NIR zoom lens (Metrohm), that has a working distance ranging from 6 cm to 60 cm. As such, focusing through the glass could be achieved (Fig. 1). The set-up was able to characterise and identify the two main colouring components (calcite $CaCO_3$ and vermilion HgS). The results are part of a collaboration with multiple international research groups on studying the polychromy in ancient architectural monuments and as such were confirmed by the other techniques applied, such as optical microscopy, MA-XRF, hhXRF and HSI.

Figure 1 *Image of the in situ Raman measurement in action.*

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References

Vandenabeele P., et al. (2022) - On the use of a zoom lens for remote Raman measurements: Application in cultural heritage research. J. Raman Spectrosc., 54, 68–75.

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Complementary use of the Raman and XRF techniques for in situ non-destructive analysis of the architectural decorative patterns of Prince Kung's Palace (Beijing, China)

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Prince Kung's Palace in Beijing, built in 1780 by Heshen, is a Qing Dynasty architectural masterpiece and now a national museum and 5A tourist site. There are decorative patterns of various historical periods in the palace.

The research focused on eight representative decorative patterns within Prince Kung's Palace, as shown in Fig. 1, including the Baoguang Hall, the First Palace Gate, East Imperial Gate Two, West Imperial Gate Two, the Hall of Mental Purification, the aisle of Baoguang Hall, and the Duofu Hall. These structures are located on the east, west, and middle roads of the palace, as well as in the gardens, encompassing a broad area. The in-situ measurement locations were carefully selected to encompass most of the observable colors, including red, yellow, white, black, blue, and green.

This study employed portable Raman spectroscopy and X-ray fluorescence (XRF) for an in-depth, nondestructive in-situ analysis of the pigments within the architectural colored paintings of Prince Kung's Palace. Raman spectroscopy, a rapid, non-destructive, and micro-regional analytical technique, was combined with XRF to enable the swift and precise identification of the molecular fingerprints and elemental composition of materials. The Raman spectroscopic analysis was conducted using a portable spectrometer from EmVision LLC., equipped with a thermoelectrically cooled charge-coupled device (CCD) detector and a 785 nm semiconductor laser. The XRF analysis was performed using a Thermo Scientific Niton XL3t spectrometer, which employs a miniature X-ray tube with a gold target as the excitation source.

The study successfully identified a complex palette of painting materials ranging from historical mineral pigments to modern synthetic pigments. The mineral pigments identified include cinnabar, red lead, hematite, orpiment, lead white, chalk, carbon black, azurite, and atacamite. The synthetic pigments include Hansa yellow, chrome yellow, titanium white, Prussian blue, ultramarine blue, phthalocyanine blue, emerald green, and phthalocyanine green. Additionally, the plant-derived pigment indigo was detected in certain areas. Degradation products, such as lead sulfate and gypsum, were also identified. Figure 2 shows part of the Raman spectra measured in situ.

The application of various pigments with similar hues suggests several periods of creation for the murals, offering evidence of the historical restorations of the decorative patterns in Prince Kung's Palace. The pigment analysis, correlated with architectural history, indicates that some patterns can be dated to around the 45th year of the Qianlong period (1780 CE), while others might be painted during the Republic of China period (1912–1949 CE).

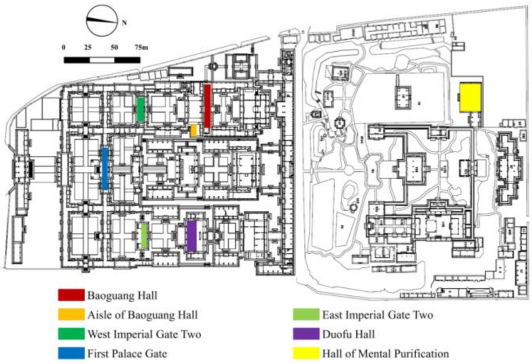

Figure 1 *Architectural plan of Prince Kung's Palace. Architectures that have undergone non-destructive investigation are marked with colored boxes.*

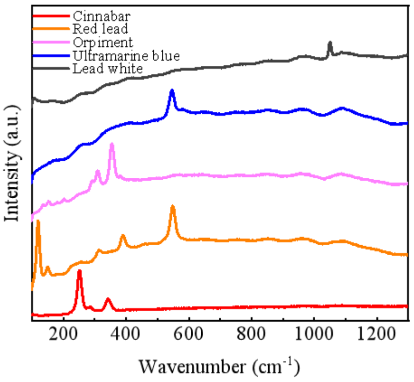

Figure 2 *A part of the Raman spectra measured in situ.*

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A spectroscopic study on the painting materials and technique in a frontal panel wall of a festival chariot from Kerala, South India

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In a recent attribution study in the National Gallery, Sofia, six polychrome wood panels, initially documented as separate artworks in the gallery's collection, were identified as parts of a single composition representing frontal panel wall of a festival chariot (ratha) from Kerala, South India. Rathas were used for transportation of deities' figures in festival processions. Over time, the ratha structure has evolved to an increasingly complex and decorated form.

The panel composition from the National Gallery represents one of the most popular subjects associated with Krishna – "The Thief of Clothes". The narrative flows symmetrically in panel pairs following from the outermost to the innermost direction. The attribution of the middle pair to particular deities was especially challenging due to the lack of specific defining marks or attributes. A specific feature of the entire composition, exemplified by the details of the flute-playing Krishna, the Gopis and Garuda, is the use of point and line decoration. Additionally, the mythical bird Garuda is depicted with peacock plumage rather than as an eagle. The few surviving examples of ceremonial chariot panels in museums and private collections worldwide date back from the 17th-19th centuries, and their dating is generally provisional (Agrawal, 1971).

The stylistic comparison of the composition from the National Gallery with examples from Kerala region showed the closest similarity with those from the period of the XVII - XVIII century. The panel composition was also compared with many later examples. However, the later compositions are characterised by the introduction of new ornamental forms alongside the old; deepening of the stylization; and simplification of the details compensated by a more varied pictorial palette. In addition to the stylistic study, the chariot elements from the National Gallery have been extensively investigated by analytical methods prior the restoration and exhibition in the gallery. The composition of the painting materials was identified by vibrational and micro-Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. When examining the details of the depicted textile patterns of the three loincloths (dhotis) of the god figures of the National Gallery composition, the analysis revealed lazurite (natural ultramarine), orpiment, cinnabar, green earth and gypsum in the green body parts of Krishna. These findings correlate with the old traditional historical pigments used throughout Central and South Asia: lapis lazuli (natural ultramarine) was found in abundance throughout present-day Afghanistan, orpiment was widely used in Central and East Asia (Asma et al., 2019) and cinnabar – frequently used in Ayurveda, although its ore is not found in India and the pigment was usually synthesized. The mineral cinnabarite and the raw material for the synthetic pigment were mined in China and probably shipped by sea trade to South India (Sharma & Singh, 2021).

In the samples taken from the primer, the composition was found to be calcium carbonate and protein binder with added oil. According to the IR spectra of the paint samples, the painting was executed in tempera technique with a protein binder with added oil – materials used also in the mural painting of the 17th century and earlier. The micro-Raman identification of Prussian blue, albeit in very small quantity, only in some of the leaves of the trees – a component of green colour in combination with yellow orpiment, dates back the work to the first half of the 18th century. Since Prussian blue was discovered in the early 18th century and after the first quarter of the 18th century the synthesized pigment spread in European countries, it seems that it probably reached Kerala, India, very soon due to the highly developed trade relations. The minimal presence of Prussian blue and its co-use with a large amount of lapis lazuli in the same composition may indicate an early use of the new material, while iconographically the composition fully adheres to the stylistics of the end of the previous century.

References

Agrawal, O.P. (1971) - A Study of Indian Polychrome Wooden Sculpture. Stud. Conserv., 16, 2, 56-68.

Asma, P., et al. (2019) - A conceptual review on Hingula (Cinnabar-HgS). Int. J. Ayurveda Pharm. Res., 7, 6, 32-39.

Sharma, A., & Singh, M.R. (2021) - Review on Historical Earth Pigments, Heritage, 4, 1970-1994.

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Reconstructing blue pigment production technology in the 17th-18th centuries Pavia majolica manufacture: a multi-technique approach

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The study of ceramic glazes provides important information about the technological development level of societies and the trade of specific raw materials that cannot be found locally (Pradell & Molera, 2020). However, technology reconstruction is a quite challenging task, since literary sources are often incomplete and characterised by an archaic terminology, sometimes difficult to clearly understand. To overcome these limitations, a deep characterisation of the artefacts, in terms of texture observation, mineral phases and pigments identification with elemental composition information (including traces), is required as a necessary step.

Micro-Raman spectroscopy can be a powerful tool to deepen this comprehension, by allowing the identification of mineral phases within the glazes. Nevertheless, it should be combined with other complementary techniques, in order to retrieve additional information for a thorough characterisation of the glaze under study.

This study deals with the glazes of a Northern Italy majolica production from the 17th-18th centuries, the so-called „latesini“; these are white-body majolica artefacts, manufactured in Pavia (Lombardy, Italy) (Pelizzoni et al., 1997), which have not been studied from a petro-archaeometric point of view yet. In particular, the focus will be on the blue decorations of some light blue-glazed samples, discovered in 1976 in Pavia during the excavation procedures of the sewer.

Micro-Raman spectroscopy has been a fundamental part of the adopted analytical protocol, which involved also optical microscopy, colorimetry, Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM/EDS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Invasive analyses, such as SEM/EDS and LA-ICP-MS, have been carried out on some production wastes (Fig. 1a), while Raman spectroscopy has also been applied, with a non-destructive approach, to some samples belonging to the high-quality production (Fig. 1b).

The analytical procedure allowed to identify the pigment used to obtain blue colour (Co^{2+}), as well as to make some hypotheses about its provenance and production technology. Particularly, different steps in the manufacturing technology of both the glaze and the overglaze have been hypothesized, on the basis of the results obtained by the micro-Raman and SEM/EDS characterisation of the samples cross-sections. The identification of some silica polymorphs in the overglaze, enabled by micro-Raman spectroscopy, also allowed to gain some insights into the firing temperatures involved in these production processes.

Finally, the presence of some peculiar mineral phases within the overglaze, combined with trace elements composition of the glassy matrix, obtained by LA-ICP-MS, have also enabled to formulate a preliminary hypothesis about the cobalt pigment provenance. This has been traced back to Erzgebirge region (Saxony, Germany), probably the most important cobalt extraction site in the 17th-18th centuries.

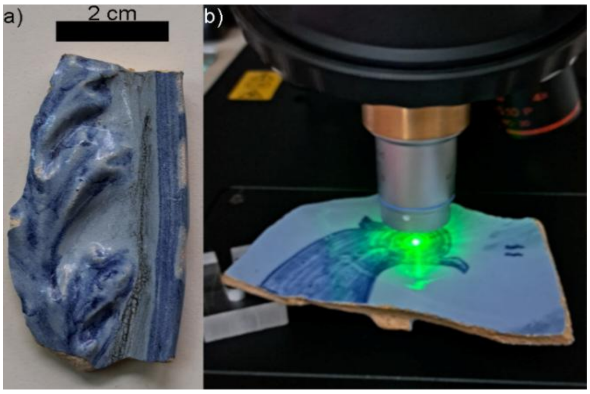

Figure 1 a) *Image of one of the production wastes analysed in the study;* ***b)*** *Raman spectroscopy analysis, with a non-invasive approach, on a majolica artefact.*

References

Pelizzoni, E., et al. (1997) - La Maiolica di Pavia tra Seicento e Settecento. Amici del Museo e della Scuola d'Arte Applicata del Castello Sforzesco di Milano.

Pradell, T., & Molera, J. (2020) - Ceramic technology. How to characterise ceramic glazes. Archaeol. Anthropol. Sci., 12, 189.

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Deep learning-assisted portable Raman spectroscopy for wood identification in historical wooden collections of the Palace Museum

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The origin discrimination of wood is the core in the study of the wooden artifacts, as it helps reveal regional resource utilization strategies during specific historical periods and the evolution of ancient making procedures. More importantly, the physicochemical properties (e.g., decay resistance, density gradients) of various wood species demonstrate significant correlations with microstructural degradation, which is directly responsible for the preservation status of artifacts. Therefore, species identification of wood not only provides an evidentiary foundation for historical interpretation, but also delivers indispensable scientific basis for formulating preservation strategies. The Palace Museum stands as the world's largest wooden architectural complex, housing a collection of nearly 160,000 wooden artifacts that urgently require conservation efforts. This need demands rapid, non-invasive and in situ analytical methodologies for wood characterisation. However, current approaches rely on destructive techniques: micromorphological analysis of anatomical features or chemical profiling via py-GC/MS and LC-MS, which are constrained by the experience of operators and laborious sampling pretreatment procedures.

Raman spectroscopy has emerged as an effective tool in heritage science owing to its rapid analysis, non-invasive nature, micro-scale spatial resolution, and molecular fingerprint recognition, which has been widely used in inorganic materials analysis. However, for organic substrates like wood, two critical challenges persist: (1) intense matrix-induced fluorescence interference under conventional visible-wavelength lasers (532/633 nm) and (2) the combined complexity of Raman spectral signatures and high chemical similarity among wood species. Here, we proposed a novel protocol integrating a portable 1064 nm Raman spectrometer with an innovative deep learning algorithm (CNN-Peak) for in situ wood species characterisation. The 1064 nm near-infrared laser configuration addresses enhancing penetration depth, suppressing fluorescence background, and minimizing photothermal degradation during detection. The developed CNN-Peak algorithm integrates convolutional neural networks with spectral fingerprint recognition to realize the distinction of similar Raman spectra. This protocol was applied to 50 kinds of wood analysis, among which five species were difficult to identify by naked eyes. By using CNN-Peak algorithm, 96% overall identification accuracy was achieved, rising to 99% for fresh wood surfaces. The methodology preserves non-invasive advantages while achieving enhanced classification accuracy between proximate species.

Guided by the principle of minimal intervention in heritage conservation, we applied our protocol to a typical wooden furniture, which is a late Qing Dynasty (1856-1912) square table with "Xi(囍)"character, originally housed in the Palace of Earthly Tranquility of the Palace Museum. This table exhibited visible restoration marks, so the spectra were collected from both the bare original material and the repaired areas. Subsequent identification of wood species was conducted by the CNN-Peak algorithm. As a result, the original material was identified as Dalbergia cochinchinensis Pierre, while the repaired material was Dalbergia odorifera T. Chen with the prediction accuracy of 95% and 80% respectively. The results are inconsistent with the imperial court archives, suggesting it may not be the original object of the Palace of Earthly Tranquility. Traditional micromorphological analysis further confirmed the findings, which proved it is a highly promising method for non-invasive species identification in wooden artifacts.

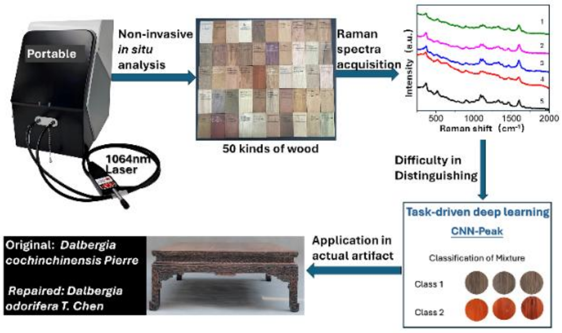

Figure 1 *Analysis protocol for the species of wooden artifacts.*

References

Chiriu, D., et al (2020) - Application of Raman Spectroscopy to Ancient Materials: Models and Results from Archaeometric Analyses. Materials, 13, 2456.

Multi-analytical approach for the identification of organic material stored at ceramic pots from the Antiquity – a case study from South-West Bulgaria

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Archaeological pottery is a rich and durable source of information about the daily life, technological achievements, trade contacts, etc., in the past times. Identification of materials stored in ancient vessels is necessary to give additional knowledge about the ancient communities.

In the present investigation, we applied a multi-analytical approach to identify the organic material stored at the bottom of two ceramic pots found at the Antique Roman city of Heraclea Sintica (modern southwest Bulgaria). The initial hypothesis was that the original content stored at the pot included bitumen or colophony, or a mixture of them, as well as other pine residues. The analytical techniques used included Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS/MS), high-performance liquid chromatography with diode-array detection (HPLC-DAD), and portable X-ray fluorescence (p-XRF). The measurements were carried out at the Center of Archaeometry with Laboratory of Conservation and Restoration (CALCR) and Faculty of Chemistry and Pharmacy (FCP) at Sofia University “St. Kliment Ohridski”. The archaeological samples were mechanically cleaned from the surface contaminations (soil, oxidation products, etc.), and contemporary samples of colophony and bitumen were used as reference materials.

The results from Raman and FTIR spectroscopy show a very good coincidence between archaeological samples and the contemporary bitumen material. On the other hand, the data obtained by GC-MS/MS and HPLC measurements indicate the presence of colophony or other pine plant residue. The practice of using and trading with bituminous mixtures was well known during ancient times in the Near East. Therefore, future investigations on the archaeological organic materials found at Heraclea Sintica and other Roman sites from Bulgaria have to be performed in order to clarify their exact content and origin.

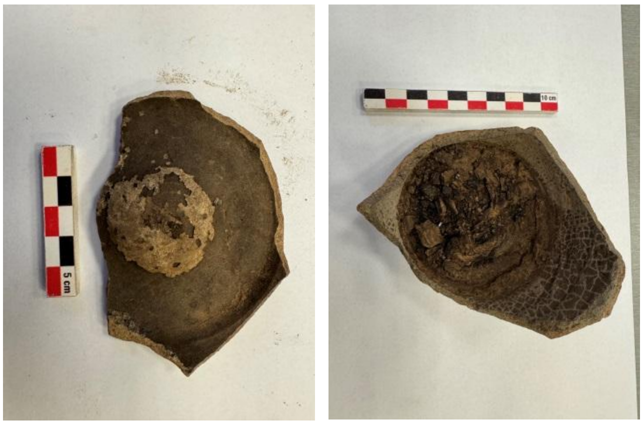

Figure 1 a, b) *Bituminous mixture stored in a jar bottom found at the Roman city of Heraclea Sintica.*

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References

Connan, J., & Van de Velde, T. (2010) - An overview of bitumen trade in the Near East from the Neolithic (c.8000 BC) to the early Islamic period. Arabian Archaeology and Epigraphy, 21, 1-19.

Sponsors talk

Basics of Raman Spectroscopy

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Portable Raman Spectroscopy is widely used for the analysis of paintings, ceramics, statues (surface coatings), and other artifacts. The flexibility of fiber optics in conjunction with the non-destructive and non-contact nature of Raman spectroscopy allows measurements to be made in-situ. The chemical information gained from Raman analysis can guide conservation work, and verify authenticity.

Our lightweight rugged design, various laser excitation and battery options allow you to carry these high performance systems into the field, thus allowing you to maintain the integrity of important heritage sites, and is in line with requirements of conservationists and archaeologists.

Our i-Raman series has been widely implemented in the fields of art, archeology and geology for applications such as:

- Analysis of pigments in tapestries, and on artwork in caves, ceilings, and other structures;
- Analysis of organics and inorganics in ancient paintings to determine authenticity and guide conservation work;
- Analysis of environmental effects such as corrosion, oxidation and degradation of artwork;
- Analysis of archaeological artifacts in difficult to reach places with a tripod-mounted video microscope .

Figure 1 *iRaman Plus 785 nm with video microscope.*

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Enhancing Raman Analysis with Compact, Microscopic, and Ultrafast Tools

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This workflow enables high-resolution Raman analysis by combining compact spectrometers, microscale imaging, and ultrafast laser sources for versatile research and industrial applications.

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Multimodal Spectroscopic Analysis of Egyptian Royal Sarcophagi Samples Using Shimadzu AIRsight

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This study presents an advanced spectroscopic investigation of samples taken from Egyptian royal sarcophagi dating between the 1st and 4th centuries BCE. The analysis was conducted using the Shimadzu AIRsight system, which integrates Raman and FTIR microscopy to enable comprehensive chemical and mineralogical characterization. The primary focus was on identifying pigments, organic binders, and surface treatment residues.

The multimodal approach allowed for detailed mapping of the analyzed surfaces, revealing the presence of both natural and synthetic compounds, as well as traces of ancient conservation practices. The findings offer new insights into the materials and techniques used in Egyptian royal funerary art, contributing to the broader understanding and preservation of archaeological heritage.

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Resolving the Arts: Applications of Confocal Raman Imaging and Portable Raman Microscopy

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The analysis of pigments in historical art objects provides profound insights into the methods of their creation. The information obtained can help classify the artifacts in terms of historical context, support their conservation, or even reconstruct the palettes of past eras. Alongside XRF and IR, Raman spectroscopy is one of the most important tools for identifying color pigments.
However, measurements integrated over large areas provide only an average spectrum, making it easy to overlook smaller components within a mixture. Additionally, fluorescence often originates from a larger volume than the Raman scattering due to diffusion effects, further complicating analysis. Confocal Raman spectroscopy and confocal Raman imaging offer solutions to these challenges. By confining the collection volume within the optical system's diffraction limit, significant amounts of fluorescence can be eliminated. The higher spatial resolution also allows for the differentiation of individual pigment particles within a mixture, enabling the acquisition of clearer and more distinct spectra for each compound.

These advantages will be demonstrated through a range of applications, including confocal Raman imaging on a cross section of an oil painting, where the technology reveals the detailed composition and arrangement of its distinct layers. By employing topographic Raman imaging, the surface of the cross section can remain in perfect focus throughout the measurement process, even if the sample is tilted or uneven. This ensures accurate and high-resolution results, even with challenging surface textures.

The capabilities of a portable confocal Raman microscope will be highlighted with the analysis of a classical Roman fresco, providing insights into the pigments and materials used by artists of the period. This system enables on-site investigations of delicate or immovable objects, eliminating the need to transport fragile artifacts to a laboratory. Furthermore, additional case studies will demonstrate the versatility of Raman spectroscopy for the analysis of ancient materials, showcasing its potential to uncover hidden details and contribute to the preservation and understanding of cultural heritage.

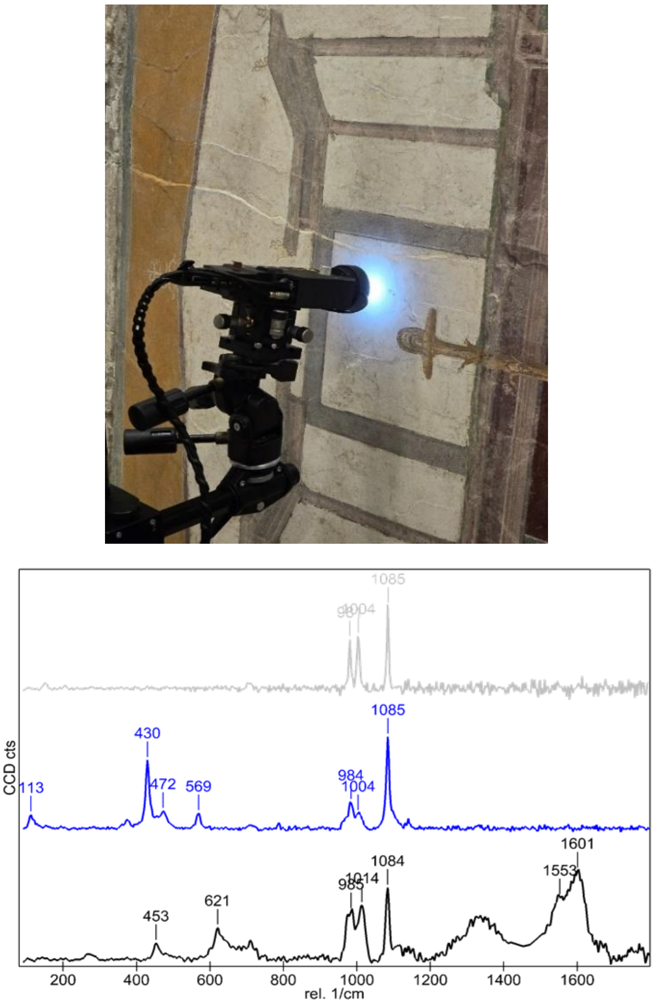

Figure 1 *Confocal Raman spectroscopy on a Roman Fresco (top) and resulting spectra (bottom).*

References

Nasdala, L., et al. (2023) - The Imperial Crown of the Holy Roman Empire, part 1. J. of Gemmol., 38, 5, 448-473.

Maragh, J.M., et al. (2019) - Large-scale micron-order 3D surface correlative chemical imaging of ancient Roman concrete. PLoS ONE, 14, 2.

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Raman Imaging Spectroscopy: future is now

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Molecular spectroscopy is an important analytical area with wide impact and extent. In this field, Raman and Infrared spectroscopies are powerful and complementary techniques, with an extensive use spanning from biomedical, pharmaceutical and material sciences, to name a few.

In last decades applications related to Geological, Mineral and Art samples have become more and more demanding about several topics, like the possibility to perform in situ analysis of organics and inorganics in an easy way with a non invasive and non destructive approach and the possibility to get precise information on micro-scale of layered materials when it is possible to have a sample to be analysed into the laboratory.

The request to perform Raman imaging on large areas (keeping the high lateral resolution) and to overcome the fluorescence in order to get a fast and clear response when a portable (or handheld) device has used are continuously increasing.

Today all the latest technologies (both hardware and software) have been applied by Bruker to all the Raman Spectrometers, both for portable and in lab instrumentations, both for dispersive and FT solutions, showing a unique portfolio on the market.
So, latest innovations will be presented in terms of commercial products, with the state of the art compromise between sensitivity and effective usability. In particular, the unpredictable capability to perform large Raman Chemical Images, on centimeters scale, will be shown.

References

Conti, C., et al. (2016) - Portable Sequentially Shifted Excitation Raman spectroscopy as an innovative tool for in situ chemical interrogation of painted surfaces. Analyist, 141, 4599.

Jehlicka, J., et al. (2017) - Comparison of seven portable Raman spectrometers: beryl as a case study. J. of Raman Spectrosc., 48, 10.

Vagnini, M., et al. (2017) - Handheld new technology Raman and portable FT-IR spectrometers as complementary tools for the in situ identification of organic materials in modern art. Spectrochim. Acta Part A: Molecular and Biomolecular Spectrosc., 176, 174.

Simultaneous and colocalised Raman and SEM imaging for correlated multimodal analysis

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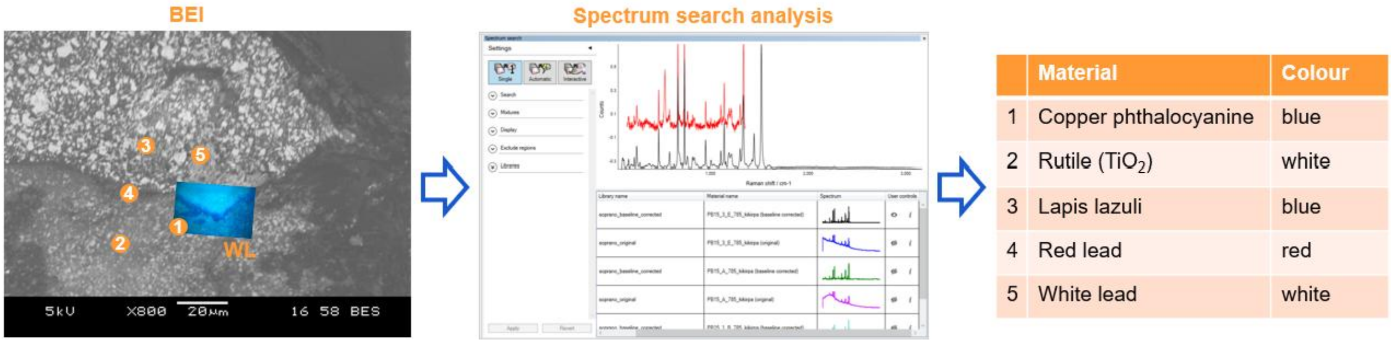
We introduce the inLux SEM Raman interface, a novel solution that can be attached to new or existing SEM microscopes to enable colocalized and simultaneous SEM and Raman imaging. The analysis is performed simultaneously on the same sample region (without moving the sample), thus avoiding correlation errors and the labor-intensive process of transferring samples between different instruments. The inLux interface allows you to combine Raman, optical, and cathodoluminescence methods with standard SEM techniques such as SE, BSE, and EDX.

We will explore the potential applications of correlative SEM and Raman imaging using the inLux interface on various samples, including pigments, polymers, oxidation products. Through these examples, we demonstrate how multimodal correlative analysis can enhance our understanding of materials, showcasing the power and ease of use when these techniques are seamlessly integrated within a SEM using this innovative technology. Figure 1 highlights the advantages of the multimodal approach on a paint chip, showing the clear and precise overlay BEI images with individual Raman spectra and white light image from the Raman interface with SEM. The complementary nature of the analysis revealed species detected by Raman and their identification through spectral libraries.



	Material	Colour
1	Copper phthalocyanine	blue
2	Rutile (TiO_2)	white
3	Lapis lazuli	blue
4	Red lead	red
5	White lead	white

Figure 1 *Example shows the surface morphology of small paint chip collected from a modern piece (1970s?). Mixture of mainly contemporary pigments and dyes, rapidly identified by spectra databases (Renishaw, Soprano, ST-Japan).*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