



16th Conference and Workshop of the Infrared and Raman Users Group

OCTOBER 6 – 9, 2026



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Welcome to Winterthur

On behalf of our staff, trustees, volunteers, and supporters, it is my privilege to welcome you to Winterthur for the 16th Conference and Workshop of the Infrared and Raman Users Group. Our guests are familiar with the amazing decorative arts collection here at Winterthur Museum, Garden & Library; or perhaps they are lovers of the garden and wider estate; or they have had the opportunity to enjoy one of our specialized tours or educational programs. But few of our general visitors are aware of the very thing you are here to study and share with your colleagues: the art and science of conservation and the broader field of study around material culture that finds a home in Winterthur's conservation laboratories and in our graduate programs.

It is our pleasure to welcome you to Winterthur for this IRUG conference, and we are very grateful to host such a distinguished group of researchers as you share your insights and research with one another in infrared and Raman spectroscopy. We are thankful to IRUG for your leadership in this field and so glad that our scientists Rosie Grayburn and Catherine Matsen are here to welcome you and to introduce you to our work here at Winterthur.

While I know that you will be fully immersed in your lectures and workshops, I hope you will take a moment to enjoy the American "country place museum" Henry Francis du Pont created for you and all of our visitors here at Winterthur.

Warmly,

A handwritten signature in cursive script that reads "Chris Strand".

Chris Strand

Charles F. Montgomery Director and CEO
Winterthur Museum, Garden & Library



IRUG Board Welcome

On behalf of the IRUG Board of Directors, it is my pleasure to welcome our global community of scientists, conservators, educators, and students to the IRUG16 Conference at Winterthur. IRUG's core mission is to support the professional development of its participants by providing a forum for the collaborative exchange of IR and Raman spectroscopic information and reference data. Through our conferences and peer-reviewed database, we strive to enhance the analytical tools available for the study of the world's cultural heritage. This gathering embodies our mission.

This 16th conference holds historic significance as we meet at Winterthur Museum for the second time since IRUG was founded. We first convened on these grounds in 1998. Returning almost three decades later allows us to reflect on how IRUG and our field have grown and how the partnership between spectroscopic research and institution-led conservation continues to flourish.

The IRUG16 organizing committee has assembled a rich and diverse technical program featuring presentations and poster sessions that span a range of IR and Raman applications. We are pleased to offer a specialized pre-conference workshop on reflectance FTIR, designed for hands-on training and to address common challenges in data collection and interpretation.

An event such as this relies on the dedication of many individuals. We extend our deep gratitude to our host institution, Winterthur Museum, Garden & Library. Special thanks go to our lead conference organizers, Rosie Grayburn and Catherine Matsen at the Winterthur Scientific Research and Analysis Laboratory. Their planning and ambition have brought IRUG16 to fruition. We also thank Aniko Bezur from the IPCH at Yale University and Liora Mael from Mount Holyoke College for leading the workshop. We are very grateful for the generous funding and support provided by the Department of Art Conservation at the University of Delaware; Renishaw, plc.; Agilent Technologies, Inc.; White Bear Photonics, LLC; Metrohm AG; Thermo Fisher Scientific, Inc.; Manifest Technical, LLC; and the Conservation Department at Winterthur.

Lastly, we thank you—our presenters, attendees, and database contributors. Your intellectual curiosity and commitment to cultural heritage research and preservation are what sustains the IRUG initiative. We encourage you to engage in discussions and explore new collaborations. Sharing is the spirit of IRUG, and we especially invite you to volunteer as a contributor or reviewer of spectra for the IRUG Spectral Database.

Please enjoy IRUG16 and the inspiring backdrop of Winterthur!

Suzan de Groot

Acting President, IRUG Board of Directors

Senior Scientist, Cultural Heritage Agency of the Netherlands, NL



The Infrared and Raman Users Group

The Infrared and Raman Users Group (IRUG) is a public charity recognized under section 501(c)(3) of the United States Internal Revenue Code. It is dedicated to advancing scientific and educational purposes, as described in its mission statement. Incorporated in 2001 in the Commonwealth of Pennsylvania, IRUG is governed by a Board of Directors.

Mission Statement

IRUG is dedicated to the support and professional development of its members by providing a forum for the exchange of infrared and Raman spectroscopic information and reference spectra for the study of the world's cultural heritage. This initiative is sustained at conferences, where participants share information and present papers on a range of topics. A primary goal of IRUG is to improve and expand the data generated and shared by its members. Toward this end, a cooperative database of peer-reviewed IR and Raman reference spectra relevant to cultural heritage materials has been undertaken.

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 Europe and Africa (irug.chair.europeafrica@irug.org): Boris Pretzel
 Asia, Australia, and Oceania (irug.chair.asiapacific@irug.org): Marcello Picollo

IRUG16

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Catherine Matsen, Winterthur Museum, Garden & Library, US

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Marcello Picollo, Institute of Applied Physics “Nello Carrara” - CNR, IT

Aleksandra Popowich, The Metropolitan Museum of Art, US

Brooke Russell, EverGreene Architectural Arts, US

David Thickett, English Heritage, UK

Masahiko Tsukada, Tokyo University of the Arts, JP

Greg Smith, Indianapolis Museum of Art at Newfields, US

Zach Voras, West Chester University, US

Marcie Wiggins, Museum of Fine Arts Boston, US

Conference Program

All timings and presentations are subject to change

Wednesday Morning, October 7, 2026 Visitor Center	
Time	Event
8:00–9:00 am	Registration & Coffee
9:00–9:30 am	Welcome, Opening Remarks & Conference Overview Rosie Grayburn and Catherine Matsen, Winterthur
	IRUG Board of Directors Welcome David Thickett, English Heritage
	Winterthur Welcome Catharine Dann Roeber, Director of Academic Affairs, and Brock W. Jobe Associate Professor of Decorative Arts and Material Culture, Winterthur
9:30–10:30 am	Keynote Lecture: Spectroscopy as Cultural Heritage Dr. Roger Turner, Curator of Instruments and Artifacts, Science History Institute in Philadelphia
10:30–11:00 am	Coffee
11:00 am–12:00 pm	Posters Lightning Round (see list of posters) Chair: Greg Smith, Otto N. Frenzel III Senior Conservation Scientist, Indianapolis Museum of Art at Newfields
12:00–1:30 pm	Lunch Break

Wednesday Afternoon, October 7, 2026 Visitor Center	
Time	Event
1:30–3:00 pm	Session 1. Case Studies: Works on Paper Chair: Annette Ortiz, Conservation Scientist, The Walters Art Museum <i>Non-invasive Paper Analysis: External Reflection Fourier Transform Infrared Spectroscopy and Chemometrics (PCA) Applied to the Study of Cultural Heritage Collections</i> Arthur McClelland, Center for Nanoscale Systems, Harvard University <i>Identification of the Papers Used in Edvard Munch's Prints by ER-FTIR</i> Katherine Eremin, Harvard Art Museums <i>Spectroscopic Evaluation of tert-Butylamine Borane (TBAB) and Sodium Borohydride in Stain-Reduction Treatments: A Ten-Year Natural Aging Study of 19th-Century Didactic Prints</i> Diógenes Vedoy, Canadian Conservation Institute
3:00–3:30 pm	Coffee Break and Posters
3:30–4:30 pm	<i>Decoupling Diffuse and Specular Reflection Contributions to External Reflectance FTIR Signals of Pigments on Paper</i> Erin Mysak, Harvard Library Session 2. IRUG Database Presentation <i>The IRUG Spectral Database Initiative: Update & Tutorial</i> Suzan de Groot, Cultural Heritage Agency of the Netherlands
4:30–7:00 pm	Conference Reception (Reflecting Pool)
7:00 pm	Bus departs Winterthur for downtown accommodation (outside Dorrance Gallery)

Thursday morning, October 8, 2026 Visitor Center	
Time	Event
9:00–10:30 am	Session 3. Databases and Data Science Chair: David Thickett, Senior Conservation Scientist, English Heritage <i>Enabling ATR Library Matching for Delicate Samples: Machine Learning Conversion of External Reflectance FTIR Data</i> Arthur McClelland, Center for Nanoscale Systems, Harvard University <i>What's in a Color? Building a Reference Pigment Database Comparing Transmission, ATR, DRIFT and ER-FTIR Methods</i> Amanda K Satorius, Library of Congress <i>Identifying Historical Lippmann Color Emulsions: A Non-Invasive Approach Using Micro-FTIR in Reflectance and Machine Learning</i> Francesco Caruso, Conservation Center of the Institute of Fine Arts, New York University
10:30–11:00 am	Coffee Break and Posters
11:00 am–12:00 pm	Session 4. Case Studies: Modern Materials Chair: Abed Haddad, Assistant Conservation Scientist, The Museum of Modern Art <i>Plastic Personalities: Non-destructive Identification of Plastics in Dolls</i> Suzan de Groot, Cultural Heritage Agency of the Netherlands <i>Optimising Non-invasive FTIR Identification of Unstable Cine Films</i> David Thickett, English Heritage
12:00–1:30 pm	Lunch Break

Thursday afternoon, October 8, 2026 Visitor Center	
Time	Event
1:30–3:30 pm	Session 5. Case Studies: Painted Surfaces Chair: Marcie Wiggins, Schorr Family Associate Research Scientist, Museum of Fine Arts, Boston <i>Scientific Study of Surface-transferred Crayon Wax in a 20th-Century Painting by Clyfford Still</i> Hitomi Fujii, Department of Scientific Research, The Metropolitan Museum of Art <i>Bocour Casein Colors and the Making of Jacob Lawrence's Hospital Series</i> Abed Haddad, Museum of Modern Art <i>Tradition and Transformation: Colorant Use in the Work of Woo Chong Yung and the Modern Guohua Movement</i> Joan M. Esson, Otterbein University <i>The Application of Confocal Raman and ATR-FTIR Mapping Techniques in the Scientific Analysis and Study of Painting Techniques in Qing Dynasty Imperial Oil Paintings</i> Guanghua Li, The Palace Museum
3:30–4:00 pm	Coffee Break and Posters
4:00–5:00 pm	Session 6. Pigment Studies, Part 1 Chair: Alexandra Popowich, Associate Research Scientist, The Metropolitan Museum of Art <i>Characterization of Emerald Green Synthesis and Degradation by FTIR and Raman Spectroscopy</i> Jasper Montgomery, Queen's University <i>Early Technologies of Lead-tin Yellow Pigments: An Experimental Materials Study</i> Maia Hannahs, California Institute of Technology
5:00 pm	Poster Session and Refreshments
7:00 pm	Bus departs Winterthur for downtown accommodation

Friday morning, October 9, 2026 Visitor Center	
Time	Event
9:00–10:00 am	Session 6. Pigment Studies, Part 2 Chair: Alexandra Popowich, Associate Research Scientist, The Metropolitan Museum of Art <i>One Pigment With Two Types: Infrared and Raman Analysis of Cobalt Yellow</i> Stephanie J. Poland, Rose Hulman University <i>Mortar Than Meets the Eye: A Technical Examination of Carthalite Colourants Used in the Minisa Bridge, Wichita, Kansas</i> Kyna Biggs, Los Angeles County Museum of Art
10:00–10:30 am	Coffee Break
10:30 am–12:00 pm	Session 7. Instrument Innovations Chair: Suzan de Groot, Conservation Scientist, Cultural Heritage Agency of the Netherlands <i>Conservation Science on Wheels: Bringing the Lab to Dutch Museum Collections</i> Olivia van Rooijen, Cultural Heritage Agency of the Netherlands <i>In-Situ Raman Imaging: From Stone Monuments to Paintings</i> Jennifer Ferguson, Renishaw plc. <i>NIR and Mid-IR Reflectance Imaging Spectroscopy of Paintings to Map Artist Materials</i> John K Delaney, National Gallery of Art
12:00–1:00 pm	Roundtable Discussion Closing Remarks Greg Smith, Otto N. Frenzel III Senior Conservation Scientist, Indianapolis Museum of Art at Newfields
1:00–2:00 pm	Lunch Break

Friday afternoon, October 9, 2026 Visitor Center	
2:00–4:00 pm	Optional Tours of Winterthur conservation labs (40 people maximum). Sign up in advance at the registration desk.
4:00 pm	Bus departs Winterthur for Wilmington accommodation

Posters

Title	Corresponding Author
Development of collaborative, course-based technical analysis projects as a teaching tool in an upper division chemistry course	Stephanie Zaleski
Preparation of Standards and Spectroscopic Analysis of Wooden Furniture Finishes for Determining Period of Manufacture	Ethan Radcliffe
Identification of 5th millennium BC stone beads from Pahlevan Hill (Jajarm) in Iran using micro-Raman spectroscopy	Nazli Darkhal
Alum-tawed skin identification by ATR-FTIR and Raman spectroscopy	Laurianne Robinet
Application of surface-enhanced Raman spectroscopy (SERS) for the identification of cochineal in the illuminated parchments from Metropolitan Cathedral of Mexico City	Daniel Meléndez García
Assessment of Discrimination Conditions between Azurite and Lapis Lazuli by On-Site Micro-Raman Spectroscopy for Non-Destructive and Accurate Analysis of Murals	Mizuki Osako
Watercolor Pigments in Context: Raman analysis of Emily Sargent's selected works	Marcie Wiggins
Out of the Blue: Discovering Brominated Indigo in a Hand-Colored Photograph	Joan M. Walker
The House of Many Colors and its Colorants (Olynthus, Greece)	Hilary Becker
Early Synthetic Organic Pigments: Occurrences in the Works of Art	Ekaterina Morozova
Hue knew! - Characterization of rarely used chrome yellow in 20th century African textiles	Kyna Biggs

Posters (continued)

Title	Corresponding Author
Looking past the lustre: Unraveling the materiality of modern Japanese metallic threads	Kyna Biggs
Image Identification and Pigment Analysis of Nineteenth-Century Japanese Utagawa School Prints: An Interdisciplinary Study at Rutgers University–Camden	Georgia Arbuckle-Keil
FTIR and Raman analysis of early printing inks	Jennifer Giacca
Spectroscopic investigation of the printing inks and applied paints in Edvard Munch's prints	Katherine Eremin
Fantastic Beasts: Analysis of a 13th century Spanish fresco to inform conservation treatments	Katherine Eremin
Unmixing Carbon-based and Metallo-tannate Historical Inks in Middle Eastern and Northern African Written Heritage	Lynn Brostoff
Identification of organic material on wall paintings and stone sculptures – paint or/and biogenic structures?	Elke Cwiernia
Characterization of the materials and technology used in XVI-XVIII century tapestries by spectral and microscopic methods	Denitsa Yancheva
Spectroscopic Characterization of 2,5-Hexanediol as a Treatment for Mitigating Copper Ion-Induced Paper Deterioration	Gustė Rudaitytė
Investigating long-term outdoor weathering of a polymeric coating on a contemporary mural	Camilla Tartaglia
UV/Vis/NIR Fibre Optics Absorption Spectroscopy (FORS) for Cultural Heritage: A Validated Spectral Reference Database and Non-Destructive Diagnostic Practice	Philipp Heinrich Westebbe

Workshop on Reflectance Fourier Transform Infrared (rFTIR) Overview

Workshop Instructors

Dr. Liora Mael, Mount Holyoke College

Dr. Anikó Bezur, Institute for the Preservation of Cultural Heritage, Yale University

Dr. Greg Smith, Otto N. Frenzel III Senior Conservation Scientist, Indianapolis Museum of Art at Newfields

This experiential learning workshop focuses on helping participants gain experience and confidence with external reflectance FTIR spectroscopy.

The workshop has several components:

1. a series of pre-workshop video lectures on the theory of vibrational spectroscopy and FTIR,
2. presentations and discussions on external reflectance,
3. coordinated case studies, and 4. time for independent exploration.

Schedule

Tuesday, October 6, 2026 Brown Horticultural Center	
Time	Event
8:30 – 9:00 am	Registration and coffee
9:00 – 9:30 am	Welcome and Introduction General review of FTIR and Reflectance
9:30am – noon	Group case studies 1. Rough vs. smooth surfaces 2. Searching libraries 3. Detection limits
noon – 1:00 pm	Lunch Break
1:00 – 2:15 pm	Hands-On Sample Analysis and Case Studies (Group A) Guided Tours of the Winterthur Conservation Labs (Group B)
2:15 – 2:45 pm	Refreshment break
2:45 – 4:00 pm	Hands-On Sample Analysis and Case Studies (Group B) Guided Tours of the Winterthur Conservation Labs (Group A)
4:00 – 5:00 pm	Discussion
5:00 pm	Departure by bus to Wilmington (Visitor Center)

Keynote Lecture

Spectroscopy as Cultural Heritage

The history of spectroscopy is much more than a timeline of landmark papers and advances in instrumentation. Scientific instruments can also be markers that people use to organize themselves and define systems of meaning. What does spectroscopy look like when we view it as a set of cultural practices and social groups? While celebrated figures like Bunsen and Kirchhoff still matter, a social and cultural perspective reveals significant contributions by less famous, and sometimes minoritized, individuals. Women played crucial roles by coordinating groups to create shared community resources, like Clara Smith Craver's work in building spectra libraries. Communities of spectroscopists were created through short courses like the Fisk University Infrared Spectroscopy Institute founded by James Raymond Lawson and Nelson Fuson. The Science History Institute's collections offer a window on spectroscopy's surprising and playful cultural heritage, from a 1954 photo of brawling spectrophotometer salesmen to an aftermarket label warning users about an NMR spectrometer's "Emotional Crisis Detector."



Roger Turner

Dr. Roger Turner is the curator of instruments and artifacts at the Science History Institute in Philadelphia. He enjoys translating the history of science for different audiences, from chemists at Pittcon to museum visitors and students of all ages. He has recently written museum displays that situate spectroscopy as part of the Institute's temporary exhibits Downstream and Lunchtime. He holds a Ph.D. in the History and Sociology of Science from the University of Pennsylvania.

Abstracts

Oral Presentations

**NON-INVASIVE PAPER ANALYSIS: EXTERNAL REFLECTION FOURIER-
TRANSFORM INFRARED SPECTROSCOPY AND CHEMOMETRICS (PCA)
APPLIED TO THE STUDY OF CULTURAL HERITAGE COLLECTIONS**

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This study evaluates a non-invasive analytical protocol for identifying paper fiber composition and sizing materials in culturally significant objects using external reflection Fourier transform infrared (ER-FTIR) spectroscopy combined with principal component analysis (PCA). The primary objective is to determine whether ER-FTIR–PCA can reliably distinguish paper fiber types and sizing without sampling, thereby enabling broader and more ethical analysis of fragile or restricted heritage materials.

ER-FTIR spectra were collected with a Bruker LUMOS I FTIR microscope. Spectra were preprocessed by baseline correction, mean centering, and global least square weighting and then modeled with PCA to differentiate papers. Reference datasets were built with historically relevant papers, whose fibers were independently identified by polarizing light microscopy (PLM). These reference models were then applied to spectra from collection materials.

PCA score plots show clear clustering of papers according to fiber type demonstrating that ER-FTIR data contains sufficient spectral information for robust classification. A key result is the demonstration that flax and hemp papers—challenging to separate with PLM—can be distinguished using this approach. Three case studies illustrate the method’s applicability: (1) writing papers used by Emily Dickinson in ca. 1860 letter-poems; (2) printing papers associated with Albrecht Dürer and contemporaneous German artists from the late 15th and early 16th centuries; and (3) book papers from the 1st edition of George Eliot’s *Middlemarch* (1871). In each case, non-invasive analysis yielded fiber identifications consistent with historical expectations and known practices.

These results demonstrate that ER-FTIR combined with chemometrics provides a practical, non-invasive approach to paper characterization that significantly expands sampling coverage and has the potential to reshape paper analysis workflows in libraries, archives, and museums.

IDENTIFICATION OF THE PAPERS USED IN EDVARD MUNCH'S PRINTS BY ER-FTIR

Rayner, G.¹, Eremin, K.¹, Schleicher, A.¹, McClelland, A.², and Hossack, A.³

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1. INTRODUCTION

The Harvard Art Museums houses one of the largest collections of works by Edvard Munch in the United States. This collection includes 134 prints which demonstrate Munch's use of different imagery and printing methods (Figure 1). Of particular interest for this study was the variety of papers used across the print collection. Munch's print production was rarely straightforward, spanning many years and involving multiple printers across Europe, so it is unclear how often he chose the papers himself (Landro, 2013; Hettner, n.d. and Munch, 1897). The objectives of this study were to document visual and structural variations in the papers, identify fiber types using polarized light microscopy (PLM), and evaluate in-situ external reflectance Fourier transform infrared spectroscopy (ER-FTIR) combined with principal component analysis (PCA) as a non-destructive tool for paper classification. A more in-depth description of the complete study can be found in Schleicher, Eremin, McClelland et. al (2026).



Figure 1. Selected prints from the study. a) Melancholy II, 2023.592; b) Desire, M20595; c) Two Human Beings (The Lonely Ones), 2023.600; d) Old Man Praying, M21542 and e) Fertility, 2023.603. © President and Fellows of Harvard College

2. MATERIALS AND METHODS

Visual and microscopic examinations in transmitted, normal, and raking light were carried out on 121 of 134 prints. Differences in paper structure, surface texture, thickness, and fibers were assessed and compared to standard samples from *The Print Council of America Paper Sample Book* (Lunnings 1986). PLM was performed on samples taken from 55 prints to identify fiber species, preparation, and additives. Samples were mounted in water for initial observation using plane polarized light and crossed polars before the introduction of Graff ‘C’ stain. ER-FTIR spectra were collected from 115 prints and reference papers. Using a Bruker Lumos I FTIR microscope, more than twenty different points, with sixteen measurements averaged together at each point, were collected to capture the heterogeneity of the paper. A selection of Asian and European reference papers was also analyzed by both PLM and ER-FTIR.

3. RESULTS AND DISCUSSION

Visual grouping identified six internally consistent Asian paper categories and seven more heterogeneous European groups. A small group of miscellaneous papers, which seemed to be a hybrid of Asian papers and European papermaking methods, was also identified. PLM identified that Munch’s papers were typically composed of complex mixtures, unlike the conservation reference grade papers which only included one fiber type. Fibers identified include gampi, kozo, bamboo, straw, cotton, bast, and softwood. Each print was dominated by one fiber type which generally agreed with visual examination.

An initial ER-FTIR/PCA model created using the single fiber reference papers was found to be a poor match for the Munch papers and was revised using PLM-defined fiber mixtures as class labels. This new model successfully separated Asian from European papers and differentiated bamboo-, kozo-, and gampi-rich mixtures. When this model was applied to unsampled prints, the resulting fiber attributions agreed with and refined visual assessments, demonstrating its value for extending identifications without destructive sampling. A separate model was also created to separate out papers that had the addition of clay based-fillers based on the OH bands.

4. CONCLUSION

Overall, the combination of PLM with ER-FTIR and PCA was shown to provide a robust framework for classification of historic print papers. The created PCA model successfully separated Asian from European papers and differentiated bamboo-, kozo-, and gampi-rich mixtures. When this model was applied to unsampled prints, the resulting fiber attributions agreed with and refined visual assessments, demonstrating its value for extending identifications without destructive sampling. This work overall revealed Munch’s extensive and experimentally diverse use of both Asian and European fiber mixtures for his prints.

5. ACKNOWLEDGMENT

The authors thank our Harvard Art Museums colleagues, particularly Penley Knipe and Elizabeth Rudy for their support of the research, which stemmed from their exhibition, *Edvard Munch: Technically Speaking*. A heartfelt thank you to everyone in Collections Management who facilitated movement of the many prints for examination and analysis. Thank you to Kim Schenck for looking at Chinese prints together, Debora Mayer for enthusiastic discussions of PLM of Asian paper fibers and providing reference papers. This work was performed in part at the Harvard University Center for Nanoscale Systems (CNS); a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. ECCS-2025158.

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SPECTROSCOPIC EVALUATION OF TERT-BUTYLAMINE BORANE (TBAB) AND SODIUM BOROHYDRIDE IN STAIN-REDUCTION TREATMENTS: A TEN-YEAR NATURAL AGING STUDY OF 19TH CENTURY DIDACTIC PRINTS

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Stain reduction in the conservation of works on paper is often necessary, yet it raises ethical and material concerns, particularly regarding potential long-term effects on cellulose stability. Reducing agents are theoretically preferable to oxidizing systems because they can diminish discoloration without accelerating cellulose oxidative degradation. This study presents a spectroscopy-centered evaluation of tert-butylamine borane (TBAB) and sodium borohydride (NaBH_4) through their application on two 19th-century prints. Although NaBH_4 has long been the primary reducing agent used by paper conservators, its practical limitations—e.g., hydrogen gas evolution and high working pH—can complicate treatment. TBAB offers several advantages, including improved handling, reduced bubbling, and reduced impact on gelatin sizing. However, limited quantitative analysis exists to assess the long-term impacts of these treatments on paper. Here we employ vibrational spectroscopy to study changes to cellulose following treatment and aging. Measurements were collected after treatment using multiple concentrations of each reducing agent and after ten years of natural aging, providing rare long-term insight into treatment impact. To assess chemical changes in the cellulose substrate, ATR-FTIR and Raman spectroscopy were employed, focusing on oxidation- and hydrolysis-related vibrational markers, especially carbonyl growth ($1730\text{--}1740\text{ cm}^{-1}$), conjugated $\text{C}=\text{O}$ changes ($1650\text{--}1680\text{ cm}^{-1}$), and cellulose fingerprint bands ($1000\text{--}1150\text{ cm}^{-1}$). We expect the results to reveal measurable spectral differences between TBAB- and NaBH_4 -treated papers after aging, including variations in carbonyl development, backbone-related bands, and Raman-accessible cellulose modes. These spectroscopic data, combined with colorimetric measurements collected immediately after treatment and again ten years later, allow comparison of the long-term impact of each reagent on paper stability and stain-reduction efficacy.

DECOUPLING DIFFUSE AND SPECULAR REFLECTION CONTRIBUTIONS TO EXTERNAL REFLECTANCE FTIR SIGNALS OF PIGMENTS ON PAPER

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External reflection Fourier-transform infrared spectroscopy (ER-FTIR) is an attractive, noninvasive method for pigment identification in works on paper, but its broader adoption is limited by the scarcity of spectral libraries and concerns about instrument-dependent differences arising from mixed diffuse and specular reflection contributions to the signal. This study aims to (1) experimentally decouple diffuse and specular contributions to ER-FTIR spectra of pigments on paper and (2) assess the compatibility of spectra acquired on two commonly used FTIR microscopes.

Paint outs of eleven pigments of varied chemical classes from the Forbes Pigment Collection and Mapping Color in History project were prepared in gum Arabic on paper. Purely diffuse and purely specular reflectance spectra were collected on a Nicolet iS50 FTIR using an integrating sphere (with specular port open) and a VeeMAX II specular accessory at 45° incidence, respectively. ER-FTIR spectra were also acquired on a Bruker LUMOS and a Nicolet Continuum FTIR microscope. Surface roughness of the samples was quantified by white-light interferometric profilometry.

Diffuse reflectance spectra consistently enhanced pigment bands, whereas specular spectra emphasized gum Arabic features and showed derivative-like band shapes. ER-FTIR spectra from both microscopes closely resembled the diffuse reflectance spectra. These results are probably because the measured surface roughness values (average RMS $\approx 11 \pm 4 \mu\text{m}$) are comparable to mid-IR wavelengths. Instrumental differences did not preclude comparison of ER-FTIR spectra.

These results demonstrate that, for painted works on paper, ER-FTIR signals are dominated by diffuse reflection, and that ER-FTIR spectral libraries can be broadly applicable across instruments. A simple diagnostic is proposed: if paper fibers or pigment particles are visible at 10× magnification, diffuse reflection is likely to dominate, and diffuse-reference spectra are appropriate.

THE IRUG SPECTRAL DATABASE INITIATIVE: UPDATE & TUTORIAL

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BACKGROUND

Since its inception in 1993, the Infrared and Raman Users Group (IRUG) has facilitated the exchange of spectroscopic information and reliable reference spectra for research and analysis of the world's cultural heritage. Throughout the Group's 33-year history, a primary focus has been developing and distributing the IRUG Spectral Database, which has become a valuable resource for the international cultural heritage community. Along the way, IRUG has achieved several milestones in improving the quality, uniformity, and distribution of the spectra in its database. In pursuit of these objectives, IRUG developed a customized, platform-independent JCAMP-DX (ASCII) spectral file format in 1998, along with guidelines for spectrum submission and peer review to ensure data quality and accurate material identification. (Pretzel 1998; Price, Pretzel, Lomax, et al. 2016)

The first published compilations of spectra were infrared only and distributed by post. By 2001, with an IMLS Leadership grant, IRUG constructed a MySQL web-enabled spectral database on its website, IRUG.ORG. This meant that all spectra transactions, such as submission, peer-review, formatting, and download, could take place electronically via individual user accounts and all spectra were safely archived in the web-enabled database. Next, a 'Structures Index' was added. In 2009, the first fully digitized spectra compilation was released as 'Edition 2007.' That same year, the website database version with online functionality debuted, accompanied by a 'Keyword Search' with an 'Interactive Spectrum' for public access. The next major milestone was realized in 2016, when a Raman JCAMP-DX file format was adopted and Raman spectra were added to the database. Today, the IRUG Spectral database holds 3,625 spectra (2,618 infrared, 1,007 Raman) contributed by 216 individuals representing 137 institutions. These spectra will be included in the next digitized release Edition 2027 slated for January 2027.

SPECTRAL SEARCH FOR IRUG.ORG

IRUG has been developing a spectral search/matching functionality for the IRUG.ORG website. This feature will permit end-users to directly compare their own JCAMP-DX spectra of unknown materials against the IRUG Spectral DB for characterization. Users with internet access will connect from any computer, reducing the need for proprietary instrument search

software. The user will go to the IRUG web page, select 'Spectral Search', and be prompted to enter a JCAMP-DX file for the unknown they wish to search. The user will search the entire IRUG library or a subset selected by parameters such as datatype, material type, color, search algorithm (correlation or first differential), and excluded region (if desired). After initiating the search, the user will receive a 'hit' list (up to 20 entries) with a status string indicating success/failure (match quality and % overlap) and the best spectral matches. The user will click a row in the list to view a plot with the corresponding library entry overlaid on the unknown spectrum. IRUG has collaborated with DLS Solutions, Inc., Endertech Corporation, and Zing Studios for this work, funded by IRUG and the Bank of America.¹

CALL FOR PARTICIPATION

This presentation will provide a brief tutorial on submitting and reviewing spectra for the IRUG Spectral Database, including a glance at the 'Spectral Search' feature.

The success of IRUG and its Database relies on the community's participation and ongoing support. IRUG welcomes new submitters and reviewers interested in participating in the highly valuable collaborative effort to share scientific information on the world's cultural heritage materials. Individuals in the non-profit sector who contribute 10 or more accepted spectra or participate as reviewers are eligible to download the entire digitized spectral database.

Developing and expanding the Database, along with the Spectral Search feature, is a vital mission currently driven by a small team consisting of the IRUG Board of Directors and the Advisory Committee. At present, over 1,100 files await final submission and peer review before they can be released. To foster sustainable growth and development, we wholeheartedly invite your support — your participation can make a significant difference! Please speak with a Board member at the conference to volunteer as a reviewer or submitter, or complete the forms included in the conference materials and submit them to the author, another attending Board member, or the conference hosts.

ACKNOWLEDGEMENTS

IRUG expresses its gratitude to the numerous individuals, institutions, granting agencies, and corporations that have generously contributed their time, expertise, and resources to support and advance IRUG and its Spectral Database initiative over the past three decades.

NOTES

1. Company information is as follows: DLS Solutions, Inc., Trumbull, CT, <https://www.dlssolutions.com>; Endertech Corporation, Los Angeles, CA; <https://endertech.com>; Zing Studios, Longmont, CO. <https://zingstudios.com>

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ENABLING ATR LIBRARY MATCHING FOR DELICATE SAMPLES: MACHINE LEARNING CONVERSION OF EXTERNAL REFLECTANCE FTIR DATA

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Fourier-transform infrared (FTIR) spectroscopy is a cornerstone technique for material identification across diverse fields, including heritage science and art conservation. In the analysis of delicate or irreplaceable samples, such as historical artifacts, paintings, and manuscripts, minimizing or avoiding physical contact is paramount to prevent damage. External reflectance (ER) FTIR offers a non-invasive, contactless means of acquiring spectral information, making it ideal for sensitive objects. However, the vast majority of spectral reference libraries are collected with an attenuated total reflectance (ATR) geometry, creating a significant barrier to identification when only ER data is available.

This research develops a deep learning framework to convert ER spectra to their equivalent ATR spectra, enabling direct comparison with established reference databases. Using a Bruker LUMOS FTIR microscope, paired ER and ATR spectra were acquired from 133 samples, with twenty points collected per sample. Data preprocessing included baseline correction, Savitzky-Golay derivative transformation, and appropriate scaling.

The system employs U-Net convolutional neural networks augmented with multi-head self-attention mechanisms for key spectral regions, critical for identifying pigments, binders, and varnishes. The architecture combines encoder-decoder pathways with skip connections, spectroscopic region-aware attention, and adaptive loss functions maintaining uniform accuracy across diagnostic peaks.

The optimized ensemble model achieved mean absolute error of 0.053, root mean square error of 0.111, and correlation coefficient (R^2) of 0.659 across validation samples.

This framework enables conservators to leverage non-invasive ER measurements while accessing comprehensive ATR reference libraries, facilitating accurate material identification while preserving irreplaceable cultural materials.

WHAT'S IN A COLOR? BUILDING A PIGMENT DATABASE COMPARING TRANSMISSION, ATR, DRIFT AND ER-FTIR METHODS

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1. INTRODUCTION

For over 50 years, Fourier Transform Infrared (FTIR) spectroscopy has been integral in advancing the study of cultural heritage materials. In recent years, External reflectance (ER) FTIR has become an accessible non-destructive method for gathering information, but requires important considerations, such as the difference in spectral characteristics seen from the detection of both diffuse and specular reflection signals (Pozzi, Rizzo, Basso, et. al. 2021). Although there are many readily available resources and online databases that are centered around transmission and attenuated total reflectance (ATR) FTIR, fewer sources contain diffuse reflectance (DRIFT) and ER data (Price, Pretzel, Lomax 2007; Jiménez-Desmond and Pozo-Antonio 2025; Silva, Silva, Edwards, et.al. 2006; Cosentino 2026). Those that do have limited heritage reference spectra available (Buti, Rosi, Brunetti, et. al. 2013; Nodari and Ricciardi 2019; Volpi, Vagnini, Vivani 2019). As a result of the limited ER-FTIR databases, especially references for historical pigments, research was undertaken to compare all methods of FTIR analysis to aid in creating a database of pigments and to ensure accuracy in identification and interpretation when looking at specific classes of pigments. Since FTIR is a non-invasive technique, it is especially important for rare and special collections. As well as exploring the impact of each method of FTIR analysis to compare the results, the authors were interested in fully characterizing the pigments to inform whether specific pigment groups and intensities/thicknesses, may provide better identification results from different modalities.

2. MATERIALS AND METHODS

SAMPLE SELECTION

Around 50 common pigments (pre-1800 to modern) were selected from the over 500 pigment reference collection within PRTD's Center for Heritage Analytical Reference Materials (CHARM). The selected pigments are commonly available and historically relevant and span various broad classifications of pigment types (clay mineral, natural dye, ash-based, copper complex, iron complex, carbon-based). An additional set of samples include reference paint-outs. Each of the 50 pigments was painted out in a grid on a starch sized cotton rag paper. Each patch was a mixture of the pigment with a different binder types (gum arabic, tempera, glair, acrylic, starch paste, linseed oil) on paper substrates, this information being integral to not only understand how the signal is affected by binder and substrate, but also to improve the

Preservation Research and Testing Division's (PRTD's) ability to identify unknown pigments found on collection items, often found on paper based material.

INSTRUMENT

The instrument used was the Bruker ALPHA II Compact FT-IR Spectrometer that has a DLaTGS detector and a KBr beam splitter. Spectra were captured average of 64 scans, a resolution of 4 cm^{-1} , and from 8000 cm^{-1} to 400 cm^{-1} . Initial transmission measurements on the collection were captured with this range, and it was decided to maintain a consistent range as we moved through the other modalities. Raw pigments were sampled and prepared in accordance with the method of analysis used. All four modules were used to analyze the raw pigments. Only the ER module was used to analyze the reference card paintouts.

MODULES

Transmission analysis was completed using the Transmission module with a 7 mm sample pellet holder. Pigment samples were prepared using a 1% or 2% mixture, dependent on tinting strength, of Pigment to potassium bromide powder (KBr) compressed under 10 tons of pressure for 60 seconds in a 7 mm pellet form. A background was captured of the empty pellet holder.

ATR analysis was completed using the ATR module with the diamond crystal attenuation plate. Using a spatula, a small amount was deposited on the crystal and clamped to the surface using the pressure pin. The crystal and pressure pin was cleaned in between each pigment using ethanol and a cotton swab. A background was captured of the cleaned crystal with no sample.

DRIFT analysis was completed using the DRIFT module and the 7 mm sample cup. Two sample preparation methods were used. Each pigment was placed in the 7 mm sample cup, both mixed at a 1% or 2% mixture, dependent on tinting strength, of Pigment to KBr powder and pure powder form. The top was scraped flat using a spatula, no pressure was applied. A background was captured using a gold reflectance standard to ensure consistency when comparing the mixture and pure pigment powder spectra.

ER analysis was completed using the Front External Reflectance Module. For raw pigment analysis, the same sample already prepared for DRIFT in the 7 mm sample cup was also used for this method. No aperture was used on the module to ensure nothing disturbed the surface during analysis. The paintout cards were also analyzed, but the set-up included using the 3mm aperture on the various pigment/binder swatches.

3. RESULTS AND DISCUSSION

This study was significant in being one of the first FTIR projects to carefully assess the impact of different FTIR modalities. The impact of each of the four modules is outlined in the points below

and will be described in greater detail in the presentation. The utilization of some modes would be more beneficial to specific types of heritage materials, so it is important to explore each module. Several consistent trends are readily apparent and can be noted, in no specific order.

- Overall, many pigments show consistent band locations across methods that should correlate to the pigment type, despite intensity differences.
- DRIFT and ER spectra are mostly consistent and comparable in band location and intensity. This is expected due to sample preparation and similarity in data capture, resulting in similar specular and diffuse radiation scattering effects.
- DRIFT sample concentration, 1-2% mixture versus 100% pure pigment preparation methods, influenced the spectra, seen in intensity differences and spectral scattering features. Similar features are seen in ER spectra.
- ATR spectra show fewer bands overall, with areas of minimal to non-existent bands, where bands show prominently using other modules.
- Noise level and baseline distortions correlate to some extent to the darkness of the pigment. Though DRIFT showed a lower band to noise ratio.

Comparison of the raw pigment spectra to the reference paint out cards will be defined in detail during the presentation.

4. CONCLUSION

The findings from the comparison of the four modules are promising, with several spectral features seeming to correlate to pigment color, pigment structure, and light scattering. While there are many pigments that show consistent band locations, additional analysis of the results will explore the impact of specific pigment groups as well as the benefits of each setup and the influence from the orientation of each module. Further work includes completing full comparisons and research of raw pigment spectra. In addition to the pigments, the presentation will review contributions from the base substrate, in the case of these paper samples cellulose and any sizing present, identifying what bands, if important, the paper substrate may be influencing.

5. ACKNOWLEDGMENT

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IDENTIFYING HISTORICAL LIPPMANN COLOR EMULSION TYPES: A NON-INVASIVE APPROACH USING MICRO-FTIR IN REFLECTANCE AND MACHINE LEARNING

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1. INTRODUCTION

A non-invasive analytical study identified emulsion types and coating materials used in Lippmann interferential color photography. In contrast to most previous studies, which have focused on the color properties of Lippmann color photography or its relation to holography, this study forms part of a larger PhD project addressing the material characteristics, preservation, and conservation challenges of Lippmann color photographs. This research was initiated by the Preus Museum, Norway's National Museum of Photography, and the University of Oslo. The analytical part of the project focused on the silver-based image record and its carrier materials from a photograph conservation perspective.

The primary aim was to distinguish between the most common protein-based binders in Lippmann photography, gelatin, and albumen. These are chemically similar and visually indistinguishable once coated on glass. The identification of photographic binders becomes even more challenging as the emulsion ages, or when the individual design of the presentation format restricts physical access to the area of examination (Oravec et al. 2019; McClelland et al. 2020; Estupiñán Méndez and Allscher 2022; Liu et al. 2024).

This investigation focused on the most vulnerable historical Lippmann color plates: those left unprotected by a sealed cover glass, mounted prism, or applied varnish, which represent about one third of the existing Lippmann color heritage. Because the interferential image information

lies very close to the emulsion surface, it is very sensitive to mechanical stress and to changes in temperature and/or relative humidity.

Furthermore, given the small size, fragility, and rarity of these early, 19th-century color photographic objects, sampling is not permissible. A thorough understanding of the material composition of the historical Lippmann color photographs examined is essential for their study and conservation. Although some information can be obtained from historical and technical literature, a museum collection survey conducted as a part of this research on over 341 of the roughly 500 surviving historical Lippmann color plates revealed that most carry very little or no documentation regarding their manufacture or composition. Consequently, non-invasive analytical approaches are essential for characterizing these objects. By obtaining the information of their constituent materials without sampling, this study contributes to a better understanding of these historical objects, their history, and development of informed conservation strategies. Among these key pieces of information is the type of photographic emulsion, which can help narrow questions such as whether a plate was handmade or manufactured commercially by one of the few industrial producers. It may also provide clues about when, within the short Lippmann color era during which it may have been made (Gold 2024; Hannouch 2025).

2. MATERIALS AND METHODS

To answer questions about the type of binder, the overall analytical goal was to apply a completely non-invasive approach that did not feature any contact with the extremely vulnerable emulsion surface. The strategy was to examine the accessible original Lippmann color materials side by side with Lippmann color replicas, mock-ups, and raw materials. The application of replicas and mock-ups served to compensate for the relatively low number of accessible original Lippmann color plates. The Lippmann color replica materials were manufactured according to the original formulas and descriptions by some of most central figures of Lippmann photography around 1900, Richard Neuhauss, Hans Lehmann, Eduard Valenta, and Hermann Krone.

Initially, several non-invasive analytical methods were selected and tested on the Lippmann color replicas made for this purpose. These included Fiber Optic Reflectance Spectroscopy (FORS), Hyperspectral Imaging (HSI), micro-Raman spectroscopy, and micro-Fourier Transform Infrared Spectroscopy (micro-FTIR) in reflectance mode. Contact methods were excluded after the first experimental attempts after their probes left marks on the image surface (FORS with contact probe and handheld XRF). Some methods applied using non-contact probes (FORS with non-contact probe), the scanning of the entire image surface by HSI, or the examination of microscopic areas of the emulsion surface by micro-Raman spectroscopy yielded very unclear data, making the effort time-consuming and the outcome inconclusive. Furthermore, the setup of two methods (HSI and FORS) used strong halogen light as radiation sources, heating the image surface up to 50 °C and above, posing thermal risk to the image surface and to the

adhesion of the emulsion on the carrier glass. Ultimately, these three methods were set aside. However, with further refinement and adjustments in future, these methods may also have the potential to yield better results when applied to sensitive material like Lippmann color plates. Micro-FTIR showed promising results in the first measurements on replica materials, due to its complete non-invasiveness on the very sensitive photographic materials.

Ultimately, to determine the emulsion type, we employed micro-FTIR in reflectance mode, a technique not previously used on historical Lippmann color materials to the best of our knowledge. Six original color plates from the Preus Museum collection (Figure 1) and one from the collection of the Museum for Science and Technology in Oslo were analyzed: five well-documented plates by Richard Neuhauss and two-color plates with unknown emulsion types by John Hertzberg and Neuhauss. Modern replicas prepared for this project (Figure 2), together with raw materials (gelatin, albumen, collodion, and Canada balsam), served as a reference library.



Figure 1. Richard Neuhauss spectra plates without cover glass, Preus Museum collection, Horten Norway. Photo: Ana Gonçalves, Preus Museum.



Figure 2. Replica made after original formula by Richard Neuhauss, without cover glass made for the micro-FTIR investigation. Photo: Jens Gold, Preus Museum.

3. RESULTS AND DISCUSSION

The initial examination of the micro-FTIR spectra provided some insight into emulsion types and coatings. The evaluation of the reflectance FTIR spectra clearly distinguished Canada balsam and collodion but failed to distinguish the closely related binders of gelatin, albumen, and mixtures, especially on the historical color plates. To address the challenges of the noisy spectra caused by the carrier glass, the binder aging, and inhomogeneity (Figure 3), the raw data underwent spectral preprocessing using Standard Normal Variate and Savitzky-Golay smoothing. This approach proved, however, insufficient for clearly distinguishing the protein-based materials in question (albumen, albumen-gelatin mixtures, and gelatin) primarily used in Lippmann photography.

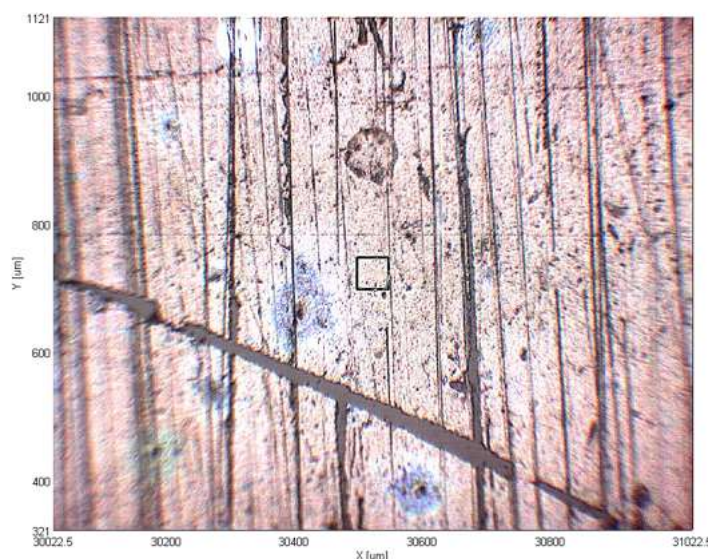


Figure 3. Image from the μ FTIR Instrument camera. Deep scratches and possible polishing marks. Richard Neuhauss, original spectra plate 4, gelatin emulsion, lab. no.: 02_231011_plate4_01_FTIR. The square in the middle represents the area of measurement with $50\ \mu\text{m} \times 50\ \mu\text{m}$. Image taken by: Francesco Caruso and Jens Gold.

Additionally, Principal Component Analysis (PCA) with different pre-treatment strategies (i.e., reduction of the spectral window, differentiating and smoothing with Savitzky-Golay method, and so on), was applied to investigate potential underlying patterns, or trends in the micro-FTIR measurements of originals, replicas, and mock-up materials, with the aim of clarifying the origin of the unknown coatings or emulsions analyzed. Even though some clustering of data was present, the results were more puzzling than clarifying (see, as an example, Figure 4).

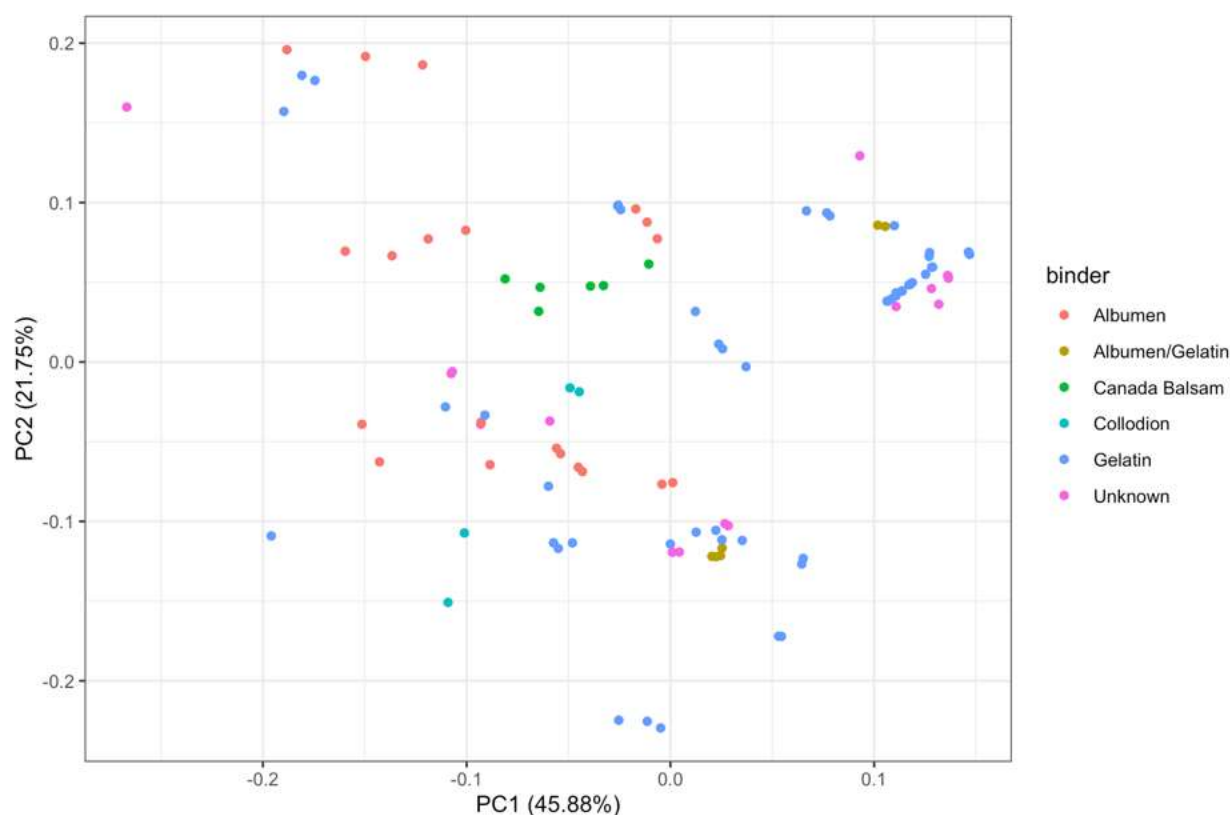


Figure 4. Score plot of the Principal Component Analysis (PCA) of the scaled micro-FTIR reflectance spectra in the region between 1800 and 1300 cm^{-1} . Standard Normal Variate pre-treatment was applied prior to PCA.

Ultimately, the identification of protein-based coatings remained difficult. Advanced supervised machine learning techniques, K-Nearest Neighbors (KNN) and Random Forest (RF) classification implemented in R/RStudio, were then applied to the pre-processed spectra to successfully predict the emulsion types of the unknown originals with a classification error between 3.9 and 25%.

4. CONCLUSION

Machine learning models successfully classified the unknown emulsions. The KNN and RF models identified the unknown emulsion type on the original Neuhauss and Hertzberg Lippmann color plates as gelatin-based. The RF method was particularly reliable, providing a high degree of statistical confidence in the predictions regarding the identification of these over 120-year-old Lippmann color emulsions.

The success of this interdisciplinary approach, integrating analytical chemistry, data science, and photographic conservation, provides a novel non-invasive methodology for identifying historical

photographic processes where traditional, standard identification methods used by photograph conservators reach their limits and provenance and manufacturing records are missing.

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PLASTIC PERSONALITIES: NON-DESTRUCTIVE IDENTIFICATION OF PLASTIC DOLLS

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Dolls form a significant component of museum collections because they offer valuable cultural, technological, artistic, and educational insights into both historical and contemporary societies. They not only illustrate the history of dolls as toys but also function as mannequins for historic clothing and as representations of diverse cultures.

From the late nineteenth century onwards, plastics increasingly replaced traditional natural materials in doll production. Early plastic dolls were made from cellulose nitrate, a material that was inexpensive and easy to manufacture. By the mid-1950s, cellulose nitrate was largely replaced by newer synthetic materials such as polyamide, polystyrene, polyvinyl chloride, polyester, and synthetic rubber. These plastics age and degrade differently when exposed to light, heat, and humidity. Common degradation phenomena observed in dolls include severe discoloration or darkening, efflorescence, and the appearance of liquid exudates caused by migrating plasticizers. Knowledge of the specific plastic composition is therefore essential for determining appropriate storage conditions and ensuring long-term preservation.

Portable FTIR-ATR analysis is widely used for in situ plastic identification and can, depending on object geometry, be applied non-invasively. However, a fully non-invasive technique suitable for complex three-dimensional objects such as dolls would be particularly advantageous. For this reason, the potential of the Bruker Bravo portable Raman system—less commonly used in museum plastic analysis—was investigated.

Following this research phase, the Bravo system proved suitable for the safe and non-destructive identification of plastics in museum collections. Dolls from the Amsterdam Museum and the Wereldmuseum (Amsterdam, Leiden, and Rotterdam) were analysed, enabling accurate plastic identification and the formulation of preventive conservation recommendations. This approach supports the long-term preservation of dolls, ensuring that they remain accessible as storytellers of material culture and history for future generations.

OPTIMISING NON-INVASIVE FTIR IDENTIFICATION OF UNSTABLE CINE FILMS

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1. INTRODUCTION

An important contribution to sustainability, especially global warming mitigation, is the identification of individual object materials and targeting environmental control. This is part of the approach in the Horizon Europe funded GoGreen Project. Cine films provide a dramatic example. Only storage under freezing conditions has been shown to sufficiently extend lifetime for cellulose acetate and nitrate films. This is energy-intensive, and such films are only a portion of any institution's cine collections. Such analysis is frequently confronted with the scale of collections – thousands and even hundreds of thousands of films – are common. Hence, fast methods are needed to survey a collection.

Motion picture films are multi-layered structures in which a photosensitive emulsion, typically composed of silver halides dispersed in a gelatine binder, is coated onto a polymeric support that constitutes approximately 90% of the film's mass [Ciliberto et al 2013]. Cellulose nitrate, cellulose acetate and polyester are the main supports.

Both cellulose nitrate and cellulose acetate films are subject to severe autocatalytic hydrolytic degradation, which occurs at ambient temperature and humidity [Nunes et al 2020]. Cellulose nitrate, in addition to being extremely flammable, degrades by releasing nitric acid and nitrogen oxides, while cellulose acetate produces acetic acid. Other materials stored in close proximity are also at risk of damage, making rapid identification and isolation of degrading films essential to preserve the integrity of entire collections. Both polymers undergo plasticizer migration, resulting in sticky or crystalline surface deposits. The combined effects of acid emission, plasticizer loss, and embrittlement lead to dimensional changes and ultimately render the films unusable. In contrast, polyester-based films demonstrate superior long-term stability. Given this differential degradation behavior, accurate identification of the polymeric support is crucial for implementing appropriate conservation strategies.

The British Motor Museum (BMM), located in Gaydon, Warwickshire, is home to one of the world's largest and most significant collections of historic British motor vehicles and associated archival materials. The museum's archive, managed by the British Motor Heritage Industry Trust Archive (BMHITA), holds approximately 7500 reels of unique and nationally significant motion picture films. Despite their significance, a comprehensive survey of the film preserved in the archive had not previously been carried out. This gap poses critical conservation and safety

challenges, as the collection is known to contain different types of polymeric supports – cellulose nitrate, cellulose acetate, and polyester – each requiring distinct storage conditions and handling protocols. Actively degrading cellulose acetate films have been identified in parts of the collection, while the current storage environment will not be able to slow down the inherent deterioration mechanisms. Rapid, non-invasive identification of the film bases was therefore recognized as an urgent conservation priority, enabling decisions regarding long-term management.

Fourier-transform infrared spectroscopy (FTIR) is established as a method for this, usually by ATR which requires contact. External Reflection mode overcomes this limitation, enabling contactless polymer identification on intact film reels [Carter et al 2020, Mendez and Alscher 2022] without unspooling the reels before analysis. Two spectrometers with the potential to identify a film through the holes in the spool have been investigated, optimized, and proven with a five-day measurement campaign at the BMM. This was part of a UK Arts and humanities Research Council, Research infrastructure for Conservation and Heritage Science (RICHeS) Catalyst Fund project.

2. MATERIALS AND METHODS

Two portable FTIRs were used to trial and develop the new method on eight films transported to the Rangers House facility. An Agilent 4300 was used with an external reflection module. Diffuse reflection was also trialed but produced lower-quality spectra. The analytical window had to be in full contact with films to generate good quality spectra. Even small inconsistencies in the sample geometry had notable effects on data collection. A Bruker Optics ALPHA with external reflection module, probing an area of approximately 6 mm diameter at 1 cm working distance, with sampling positioning monitored via an integrated video camera.

Measurements were performed directly on intact film reels without sampling. Normally, this would be done by analyzing the frontal side of the film leader (the length of empty film used for loading into the projector). Previous analyses removed the gelatine binder layer of the film to expose the base material, a specialist and time-consuming process. The leader could also be made using different materials. To circumvent this, spectra were acquired from the lateral edge of the films, through holes in the spools. This approach has not been reported previously and significantly increases the speed of analysis by removing the need to unspool each film.

At the BMM, films selected for analysis were primarily those not yet identified, as a significant portion of the collection had previously been characterized with polarized light. Priority was given to reels showing visible signs of advanced deterioration and to those suspected of being cellulose nitrate-based, given the associated fire hazards.

Two spectrometers and four scientists travelled to the Gaydon site for analysis, with films provided by four BMM staff and Lux and Liuvre contractors.

Occasionally, multiple film reels were stored in a single container under one accession number. In those cases, full spectral readings were taken on one or two reels while the instrument ‘preview’ mode was used to individually examine the composition of the other reels. Multiple measurement locations per film were acquired in cases where visual heterogeneity was observed.

3. RESULTS AND DISCUSSION

Representative FTIR spectra for each identified polymer class are shown in Figure 1.

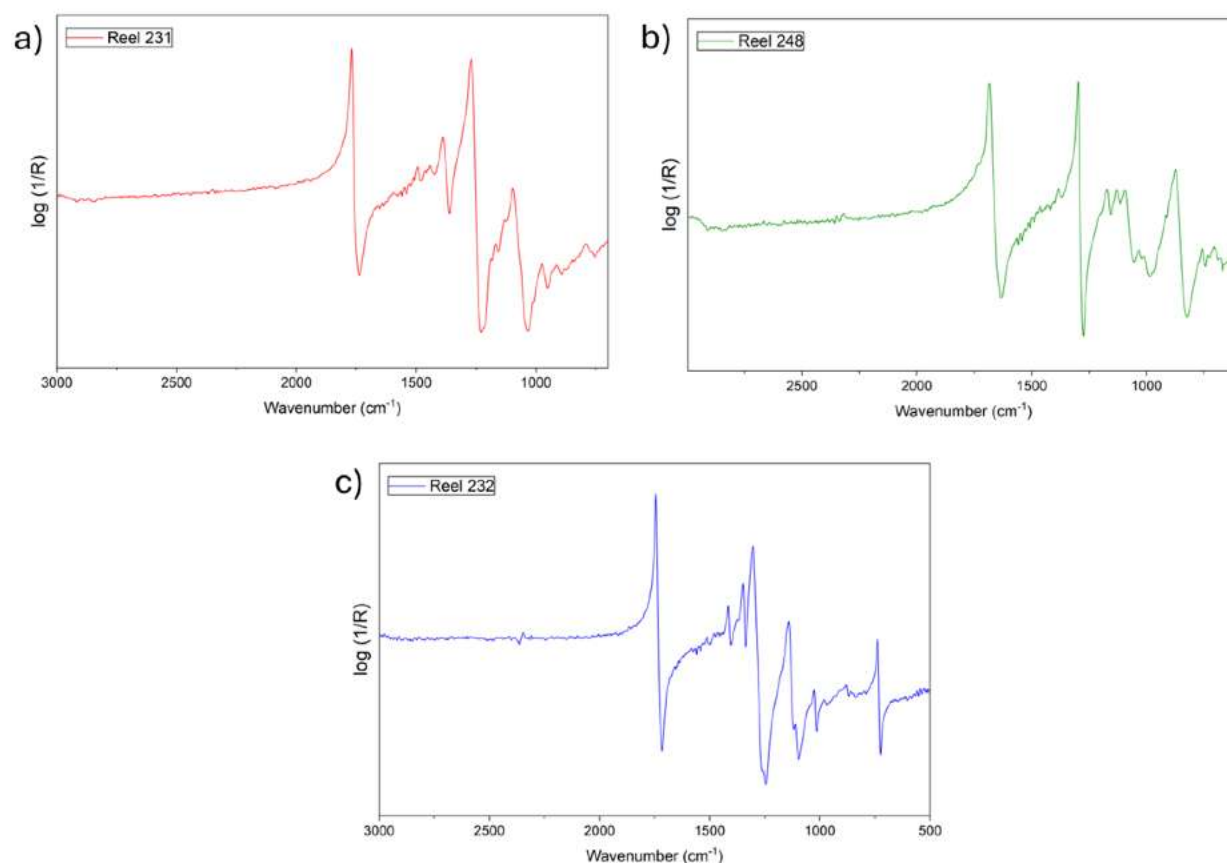


Figure 1 External reflection FTIR spectra of three polymeric supports in the BMHITA collection: (a) cellulose acetate (reel 231); (b) cellulose nitrate (reel 248); (c) polyester (reel 232).

Both instruments produced good quality spectra at comparable speeds, provided the opening in the sides of the reels were large enough to accommodate the analytical head. The Bruker FTIR had a higher tolerance for larger working distances or imperfect surface geometry, while the movable Agilent could be used for more complex cases where a smaller analytical area was available or multiple small reels had to be analyzed. The characteristic spectra of the three film

bases were visually distinct. With few exceptions, the general composition could therefore be immediately determined by the operator, considerably accelerating the survey process.

Overall, the analysis revealed that out of the 891 individual films analysed, 90% were composed of cellulose acetate, 8% of polyester, and less than 1% were cellulose nitrate. As it had been previously assumed that all nitrate materials had been removed from the collection, the detection of several instances was unexpected.

In some instances, material heterogeneity occurred within single reels, with portions identified as cellulose acetate and other as polyester. Where multiple reels were stored within the same can, their base material was generally consistent across all reels. There were some cases where reels with different polymeric base materials were found in the same can.

FTIR results were reported, including a comprehensive methodology and a large table of results. This and all the spectra were submitted to the Heritage Science Data Service (HSDS) RICHES archive in JCAMP format. The archive will be freely publicly accessible, and allows unrestricted access to the work.

4. CONCLUSION

This study successfully applied portable non-invasive External Reflection FTIR spectroscopy to characterize a total of 891 films from the British Motor Heritage Industry Trust Archive (BMHITA) at the BMM without sampling. The analysis revealed that collection is dominated by cellulose acetate-based supports, followed by polyester. Although cellulose nitrate was only identified in a small number of reels, this has implications for fire safety and storage management. In several cases, material heterogeneity was detected within individual reels or between reels stored in the same can, underlining the importance of reel-level identification over can-level assessment. Both instruments provided spectra of sufficient quality for identification. This novel, non-invasive methodology proved suitable for the rapid survey of a large and heterogeneous film collection and provides a robust evidence base to guide conservation interventions, storage management decisions, and prioritization of digitization efforts for the most at-risk materials.

5. ACKNOWLEDGMENT

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SCIENTIFIC STUDY OF SURFACE-TRANSFERRED CRAYON WAX IN A 20TH-CENTURY PAINTING BY CLYFFORD STILL

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1. INTRODUCTION

Clyfford Still, a central figure in post-World War II Abstract Expressionism, redefined modern painting through his bold use of color and materials. While aspects of his painting techniques, including the use of oils, alkyd resins, and pigments, are widely acknowledged, his colored inscription material employed to inscribe titles and notes on the reverse of his canvases remains largely unexamined.

An unexpected visual phenomenon observed in PH-254 (1945), first exhibited as *Buried Sun* in 1946, brings this material into focus: inscriptions originally made on the reverse have ‘transferred’ through the paint layers and become visible on the surface. Understanding the composition of the inscription medium is therefore essential for interpreting both the artist’s working methods and the mechanisms responsible for this alteration.

This study combines Raman and surface-enhanced Raman spectroscopy (SERS), Fourier transform infrared spectroscopy (FTIR), and gas chromatography–mass spectrometry (GC/MS) to characterize the inscription materials and associated paint media, providing new insight into the materials used by Still and the processes underlying this unexpected transfer phenomenon.

2. MATERIALS AND METHODS

Three colored inscription samples (pink, violet, and green) on the reverse of the canvas were analyzed using a multi-analytical approach combining Raman spectroscopy, surface-enhanced Raman spectroscopy (SERS), Fourier transform infrared spectroscopy (FTIR), attenuated total reflectance FTIR (μ -ATR-FTIR), and gas chromatography/mass spectrometry (GC/MS).

Dispersive Raman spectroscopy was employed for the identification of pigments and dyes in samples, while SERS was used to further characterize the violet sample. Bulk FTIR and μ -ATR-FTIR analyses were used to characterize organic and inorganic components, in the surface coating materials and colored inscription materials, using both bulk samples and cross-sections. Spectra were interpreted through comparison with published literature, the reference spectral database of The Metropolitan Museum of Art, and the IRUG 2000 and 2007 databases (Price, Pretzel and Lomax 2007).

GC/MS was used to characterize the organic components of the surface coating materials and colored inscription materials following solvent extraction and derivatization. Chromatographic data were interpreted through comparison with reference materials, the NIST 2023 mass spectral library, and published literature.

3. RESULTS AND DISCUSSION

The pink (S2) and green (S4) samples were identified as Pigment Red 57:1 (Lithol Rubine) and Pigment Green 7, respectively, by Raman spectroscopy (Cwiertnia and Bosi 2022). SERS analysis of the violet (S3) sample revealed bands at approximately 1622 cm^{-1} and 1592 cm^{-1} , with the latter being more intense. This spectral pattern is consistent with the photo-induced N-demethylation of Crystal Violet (Cesaratto, Lombardi, Leona 2017). However, the presence of Methyl Violet cannot be excluded, as spectral bands observed in the $1389\text{--}1341\text{ cm}^{-1}$ region suggest contributions from both Crystal Violet and Methyl Violet.

Methyl Violet (C.I. 42535) and Crystal Violet (C.I. 42555) are among the earliest synthetic triarylmethane dyes developed following the introduction of mauveine in 1856 (Color Index 1971a). Pigment Red 57:1 and Pigment Green 7 are synthetic pigments widely used in twentieth-century artists' materials (Cwiertnia and Bosi 2022; Color Index 1971b).

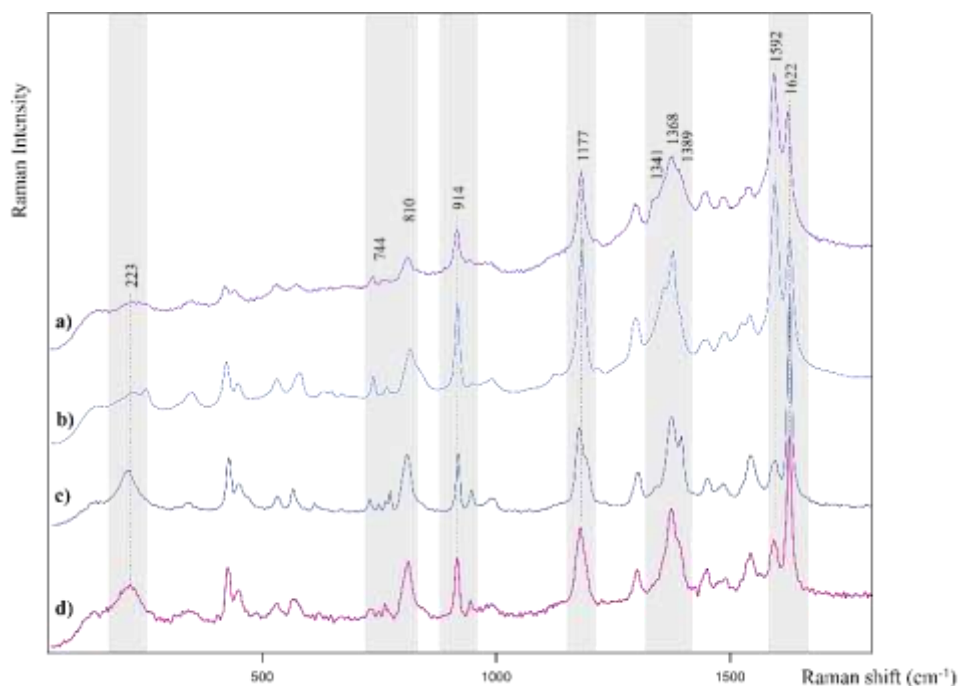


Figure 1: Raman spectra a) PH-254 S3, b) Crystal Violet aging, c) Crystal Violet, and d) Methyl Violet from the reference spectral database of The Metropolitan Museum of Art

FTIR analysis identified two principal binding components. Paraffin wax was confirmed by characteristic hydrocarbon absorption bands at $3000\text{--}2800\text{ cm}^{-1}$, $1480\text{--}1300\text{ cm}^{-1}$, and $750\text{--}700\text{ cm}^{-1}$ (Derrick, Stulik, Landry 1999). A prominent absorption band at 1702 cm^{-1} was attributed to the C=O stretching vibration of palmitic and/or stearic acids, accompanied by additional bands in the $1500\text{--}800\text{ cm}^{-1}$ region (Robinet and Corbeil 2003). These findings were supported by GC/MS analysis, which detected a homologous series of long-chain n-alkanes (C24–C39), dominated by C29 and C31 hydrocarbons (Lawrence, Iyengar, Pag, et al. 1982), characteristic of paraffin wax, along with fatty acid components consistent with palmitic and stearic acids. These results indicate a formulation closely related to historical “crayon waxes” described in early U.S. patents (United States Patent 1976). The Si–O absorption band observed between 1200 and 800 cm^{-1} appears as two distinct peaks in samples S3 and S4.

In addition, O–H stretching bands observed in the 3700–3600 cm^{-1} region suggest the presence of kaolinite, a silicate mineral commonly used as an extender and rheology modifier in artists' materials (Buyondo, Kasedde, Kirabira 2022).

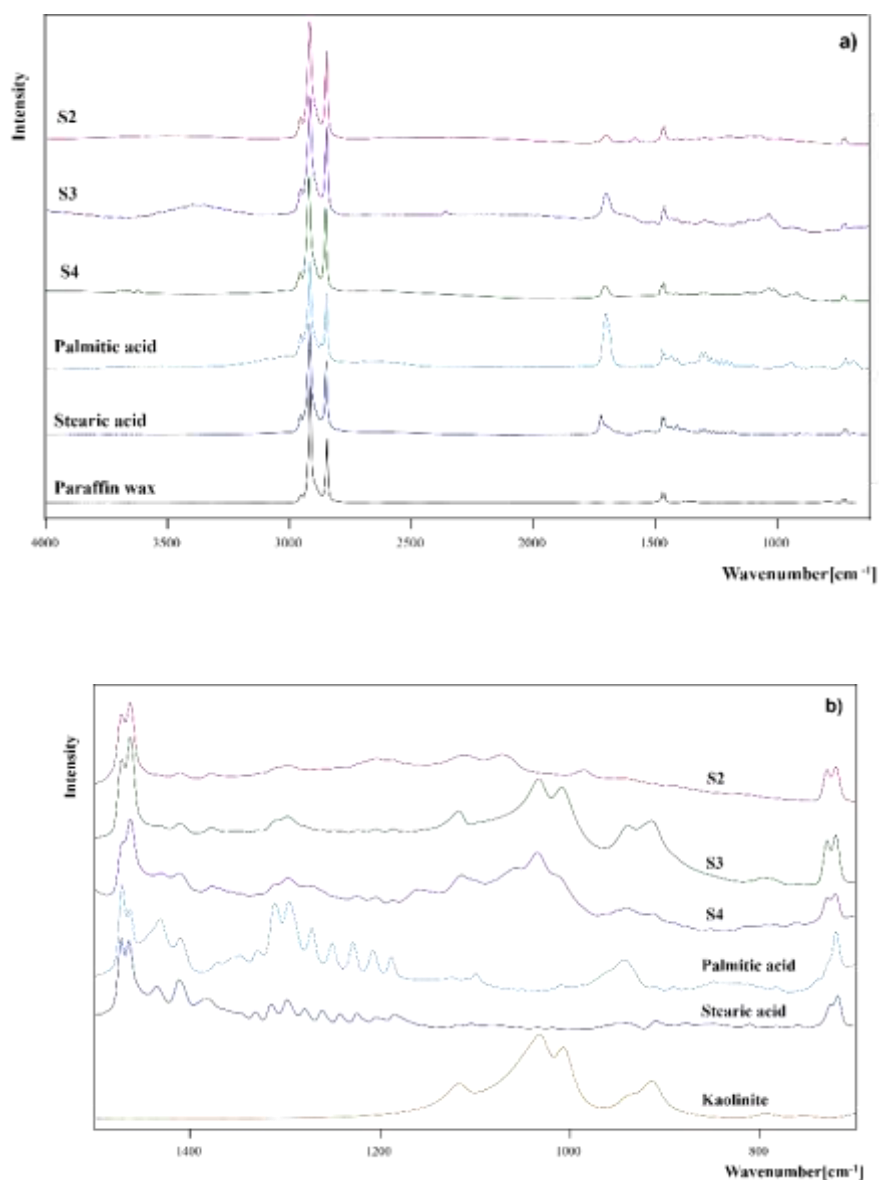


Figure 2: a) FTIR spectra of PH-254 S2, S3, S4, along with palmitic acid, stearic acid, and paraffin wax from the IRUG 2000 and 2007 databases, b) Enlarged view between 1750 and 500 cm^{-1} with spectrum of kaolinite

The surface coating materials on the recto were identified as alkyd resin and oil components through FTIR and GC/MS analyses. As Still is known to have reworked and recoated his

paintings over time, the appearance of the reverse inscriptions on the painted surface may be related to interactions between the wax-based inscription material and subsequent coating layers. Rather than the physical transfer of material through the paint structure, the wax may have functioned as a resist, locally altering drying, curing, or solvent-evaporation behavior within the coating system. This hypothesis is consistent with the sharp boundaries of the writing and similar visual effects observed along the upper edge of the painting, where the stretcher bar may have impeded solvent evaporation.

4. CONCLUSION

This study represents the first scientific characterization of crayon wax materials used by a major modern American artist. Although the mechanism responsible for the appearance of the reverse inscriptions on the painted surface remains unclear, the results provide a foundation for future investigations into this phenomenon, offering insight into both Still's material practice and the long-term behavior of mixed-media paintings.

5. ACKNOWLEDGMENT

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BOCOUR CASEIN COLORS AND THE MAKING OF JACOB LAWRENCE'S HOSPITAL SERIES

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1. INTRODUCTION

Jacob Lawrence (1917-2000) had long transformed contemporary and historical Black life into carefully structured narrative images. Between 1949 and 1950, Lawrence produced eleven paintings on paper that have come to be known as the Hospital series, depicting his time at Hillside Hospital in New York City. However, contradictory accounts of the circumstances surrounding the making of the series have led to speculation about whether the works were produced while Lawrence was a patient. This question carries significant interpretive weight because it affects how the series is situated within Lawrence's career and practice.

Of these works, *Sedation* (Figure 1) is in the collection of The Museum of Modern Art (MoMA) in New York, and its color palette has been compared to the hues found in a contemporaneous brochure of Bocour casein with hand-painted swatches (Figure 2) (Steele 2000). These paints were made by Bocour Hand Ground Colors, a well-known New York City supplier run by Leonard Bocour.



Figure 1. Jacob Lawrence. *Sedation*. 1950. Casein tempera on paper. 20 × 15 in. (50.8 × 38.1 cm). The Museum of Modern Art, New York. Gift of Philip C. Johnson, 15.1951.



Figure 2. Bocour casein brochure showing labeled paint-outs produced by Bocour Hand Ground Colors.

To assess whether Lawrence had used Bocour casein paints, the brochure and *Sedation* were

analyzed using micro-Fourier-transform infrared (μ -FTIR) spectroscopy, reflectance Fourier-transform infrared (RFTIR) spectroscopy, Raman spectroscopy, and large area μ -X-ray fluorescence (XRF) scanning to identify pigments, fillers, and binders. Although visual and scientific analysis cannot definitively establish when or where Lawrence made this work, scientific analysis of the paint, considered alongside existing archival and anecdotal information, can help determine whether the series aligns closely with Lawrence's established artistic practice and milieu.

2. MATERIALS AND METHODS

RFTIR was carried out using a portable Bruker ALPHA spectrometer equipped with an external reflection module and a DTGS detector. Spectra were collected in the 4000–400 cm^{-1} range at a resolution of 4 cm^{-1} over 64 scans, with a spot size of approximately 4 mm in diameter. Both original and Kramers–Kronig (KK) transformed r-FTIR spectra were evaluated.

Samples taken from the edges of *Sedation* and from the paint swatches in the brochure were analyzed using μ -FTIR in transmission mode with a Nicolet iS50 FTIR spectrometer, paired with a Thermo Nicolet Continuum infrared microscope equipped with an MCT–A detector. The spectra were collected in the range 4000–650 cm^{-1} at a resolution of 4 cm^{-1} over 128 scans.

Both were also analyzed using a Renishaw InVia Raman system equipped with a Leica confocal microscope and a 50 $\times$ long-working-distance objective, which was mounted on a flexible sampling arm for the analysis of *Sedation*. Two laser lines were used: a 785 nm diode laser operated at 0.3–3 mW with a 1200 lines/mm grating, and a 532 nm diode laser operated at 0.5–1 mW with an 1800 lines/mm grating. Spectra were acquired between 10 and 30 seconds and averaged over 3–5 accumulations using WiRE V.4.1.

All FTIR and Raman spectra were analyzed using Thermo Scientific OMNIC 9.0 software, and sample identification was performed by comparing the unknown spectra with published references.

Elemental distribution mapping with XRF Scanning was conducted using a Bruker M6 Jetstream with a rhodium target and a 30 mm^2 SDD operated at 50 kV and 600 μA . Scans were collected using a 300 μm spot size, 350 μm pixel size, and a 10 ms/pixel dwell time under ambient conditions.

3. RESULTS AND DISCUSSION

In The Downtown Gallery's presentation of the series, the medium was listed as casein.

Lawrence's gallerist, Edith Halpert, reportedly purchased art supplies for Lawrence while he was

hospitalized, but no receipts or other documentation have been identified that verify that account (Nesbett, Dubois, and Hills 2000). In a likely staged 1950 photograph of Lawrence painting the series, some tubes appear on a table in the foreground. A logo is partially visible on one tube, but the image is too blurry to clearly identify the brand.

Analysis of samples from *Sedation* and the brochure using μ -FTIR confirmed the presence of a protein-based binder, likely casein, with amide I, II, and III bands at around 1650, 1535, and 1450, respectively (Figure 2); amide I and II bands were observed in RFTIR (Barth 2007). Earlier in his career, Lawrence mixed his own paints with a casein binder and powdered pigments, and used inexpensive casein-based poster paints (Steele 2000). His use of casein in *Sedation* therefore continued an established approach to painting.

However, unlike hand-mixed paints, the ones studied here contain fillers and modifiers that are more consistent with commercially prepared paints. μ -FTIR analysis identified a natural wax, likely beeswax, with characteristic bands at 2918, 2850, and 1735 cm^{-1} in both *Sedation* and *Bocour* paints (Figure 2); in the latter, additional bands at 1472, 1463, 729, and 720 cm^{-1} were also observed (Bergamonti, Cirlini, Graiff, et al. 2022). This is characteristic of *Bocour* paints, where Beeswax was also identified in their acrylic and oil paints (Rogge and Epley 2017).

μ -FTIR further identified two silicate-rich clay extenders by characteristic Si–O stretching bands between 1169 and 1048 cm^{-1} and between 798 and 779 cm^{-1} , accompanied by Al–OH deformation near 920–918 cm^{-1} and Si–O deformation between 888 and 846 cm^{-1} ; in RFTIR, this interpretation was further supported by Si–O bending bands near 525–521 and 468–464 cm^{-1} (Nayak and Singh 2007). O–H stretching bands at approximately 3692 and 3620 cm^{-1} are consistent with kaolinite, while a band near 3624 cm^{-1} possibly suggests the presence of bentonite (Madejová 2003). Silicon was also observed in all samples with XRF.

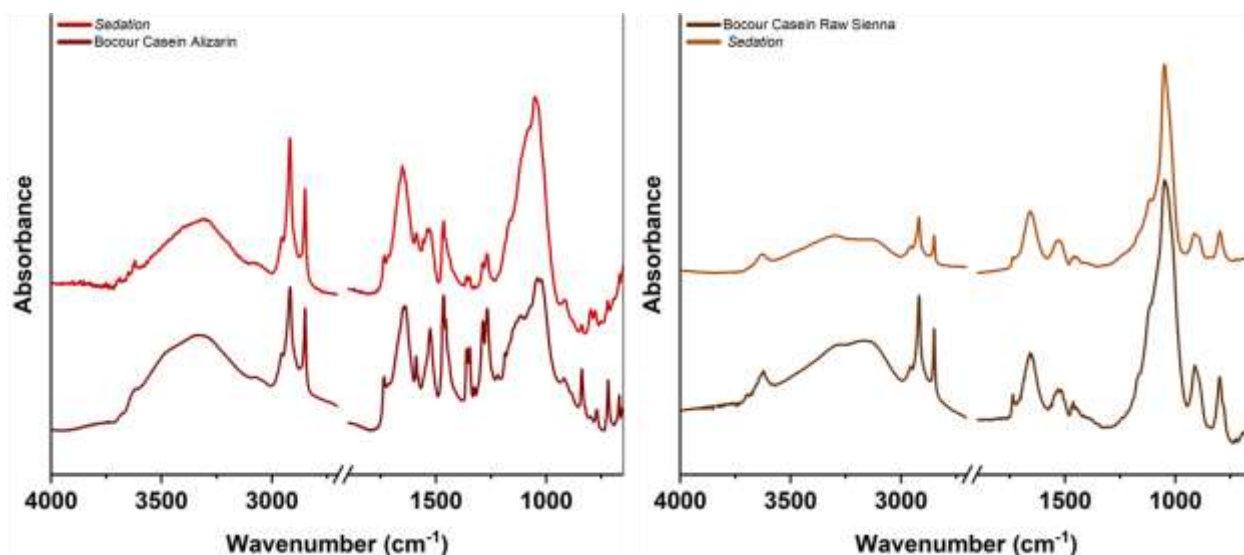


Figure 3. Example μ -FTIR spectra of red (left) and brown (right) samples from *Sedation*, with the corresponding colors identified in the Bocour casein paints brochure.

Raman spectroscopy was also carried out to definitively identify the pigments in *Sedation* and in the brochure. RFTIR further confirmed the presence of specific inorganic pigments due to a broader mid-IR range compared to μ -FTIR. The results suggest a strong correlation between them. The pigments identified in *Sedation* include toluidine red (corresponding to the Bocour paint color *Bocour Red*), alizarin lake (*Alizarin Crimson*), iron-based red pigment (*Indian Red*), iron-based yellow pigments (*Raw Sienna*), cadmium red cadmium yellow (*Cadmium Yellow Pale*), cadmium red or orange (*Cadmium Orange* or *Cadmium Red Light*) iron-based brown pigments (*Raw Umber*), phthalocyanine green (*Bocour Green*), chromium oxide green (*Oxide of Chromium Opaque*), green earth (*Green Earth*), and ultramarine (*Ultramarine Blue*), and along with titanium white and bone black.

XRF analysis complemented pigment identification with spectroscopic techniques. For example, in the Bocour paints, cadmium yellow pale has considerably more zinc than cadmium yellow medium, and cadmium red light and orange have higher amounts of barium.

Nevertheless, there are some discrepancies between *Sedation* and the brochure. The green background contains green earth (celadonite), whereas the visually comparable green paint-out in the brochure also contains viridian. The black paint in the brochure does not include bone black, unlike the black in *Sedation*. There are also some inconsistencies in the silicate fillers. Although Lawrence could have used other brands, the paints in *Sedation* contain beeswax and silicates, and the difference between the brochure and the work could indicate bespoke paints or a change in formulation.

The case for Bocour casein is supported by anecdotal evidence that places the paints within Lawrence's New York milieu. Leonard Bocour maintained close personal friendships with many artists, and his shop on 15th Street functioned as both a supplier and a gathering place. Bocour developed paints for some of the best-known New York artists of the period, including Helen Frankenthaler and Jackson Pollock, and Grace Hartigan (Gabriel 2018). Artists also requested adjustments to existing paints; Kenneth Noland, for example, asked for paints without beeswax (Stoner 2004).

Lawrence was part of Bocour's social circle, attended parties at his home, and later confirmed that he received painting supplies from Bocour, at times in exchange for artwork (Steele 2000). A Bocour promotional brochure also highlighted Lawrence, identifying him as a user of their paints (Bocour Artist Colors n.d.). In a later interview, Lawrence's enthusiasm for Bocour casein may have shaped his memory; although inaccurately, he recalled that Leonard Bocour "was the only one who sold casein at that time" (Steele 2000).

4. CONCLUSION

Although it remains uncertain whether Lawrence had access to comparable artist-grade materials at Hillside, the paints used for *Sedation* connect the work to professional New York art suppliers and to Lawrence's broader artistic network. At the same time, *Sedation* still demonstrates Lawrence's close observation of Hillside's culture and environment and described it as "a continuation of always painting out of my own personal experiences" (Lawrence 1971). Together, these choices support an understanding of *Sedation* as a work shaped by Lawrence's professional practice and social networks, even as it remained grounded in his experience at Hillside.

5. ACKNOWLEDGMENT

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TRADITION AND TRANSFORMATION: COLORANT USE IN THE WORK OF WOO CHONG YUNG AND THE MODERN GUOHUA MOVEMENT

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1. INTRODUCTION

The introduction of new pigments and dyes in the nineteenth and twentieth centuries coincided with profound political, economic, and cultural change in China, including the collapse of the Qing dynasty, expanding international trade, civil and international wars, and the emergence of new artistic movements. Although technical studies of East Asian paintings have expanded in recent decades, the material practices of modern *guohua* (Chinese ink-and-color painting on paper or silk) remain understudied (McCarthy and Giacciai 2021). Consequently, how twentieth-century artists adopted modern pigments, retained traditional materials, or combined both remains poorly understood.

The work of Woo Chong Yung (Wu Zhongxiong, 吳仲熊, 1898–1989), also known in the U.S. as C. Y. Woo, provides a unique opportunity to investigate how artists navigated these changes. Trained within literati traditions, Woo had strong connections to the Shanghai School through a familial relationship with founder Ren Yi. He was also associated with important twentieth-century artists, including Wang Yachen and Xu Beihong. Woo left China before the Cultural Revolution and immigrated to Ohio, USA. Thus, his career spanned Republican China, wartime Shanghai, and the United States, exposing him to multiple artistic communities and material markets. The Frank Museum of Art at Otterbein University houses more than 1,500 works by Woo, including about five hundred firmly dated paintings, providing an exceptional resource for examining changes in artistic materials.

This study investigates colorant use in over one hundred modern *guohua* works and compares Woo's palette to his mentors and contemporaries. Non-destructive Raman spectroscopy, fiber optic reflectance spectroscopy (FORS), and X-ray fluorescence (XRF) were used alongside limited scanning electron microscopy with energy dispersive spectrometry (SEM-EDS). Analytical results were interpreted alongside archival evidence of pigment availability in twentieth-century Shanghai to illuminate how artistic choice, material availability, and geographic mobility influenced colorant selection in modern *guohua*, with implications for dating and authentication.

2. MATERIALS AND METHODS

Artwork. Examined works include 100 bird-and-flower paintings by Woo Chong Yung, including a substantial number of securely dated works from his Chinese (pre-1962) and American periods (post-1966), and 33 paintings by his mentors and contemporaries from the Indianapolis Museum of Art (IMA) collection.

Raman. Spectra were acquired using a Bruker Senterra microspectrometer with OPUS software, 3 selectable lasers (532, 633, and 785 nm), a 50X ultra-long working distance objective, and 5 or 10 sec integrations with 5-30 coadditions. The analysis spot size was about 1 μm , spectral resolution in the range of 9 – 18 cm^{-1} , and laser power at the sample generally below 5 mW.

XRF. A Bruker Tracer 5i handheld XRF was used with 50 keV tube voltage, 10 μA current, and 30 sec live time acquisitions. Point analyses and elemental maps were acquired on a Bruker M6 Jetstream MA-XRF using 50 keV tube voltage, 600 mA current, 45 msec/pixel scan rate, and 540 μm spot size.

FORS. Spectra were collected with an Ocean Optics system using a halogen light source, USB2000+ diode array spectrometer, and fiber optic reflectance probe.

SEM-EDS. Electron micrographs were created using a Zeiss EVO MA15 scanning electron microscope and a Bruker XFlash 6 energy dispersive spectrometer at 20 keV, 1.2 nA beam current, and 8.5 mm sample working distance.

3. RESULTS AND DISCUSSION

Traditional colorants remained dominant throughout the study corpus, while modern pigments appeared first as isolated introductions before becoming widespread in Woo's American-period paintings.

The multi-analytical approach identified a remarkably consistent traditional palette across artists and time periods, including cinnabar/vermilion, red ochre, red lead, and cochineal for reds; gamboge and yellow ochre for yellows; malachite or mixtures of indigo and gamboge for greens; azurite, indigo, and/or Prussian blue for blues; and lead white (Table 1). These findings show traditional colorants remained central to modern *guohua* throughout the twentieth century, even as industrial pigments became increasingly available (Watson, 1930), suggesting that access to materials did not guarantee their use. However, there was gradual and limited incorporation of modern pigments. Consistent with previous studies (McCarthy and Giaccai 2021), chrome yellow was found in an early 20th century work by Zhang Shuqi (Figure 1). Pigments not previously found in *guohua* were also identified – viridian and alizarin, possibly synthetic

PR83:1, in a 1930 painting by Shi Zhen, and emerald green in Woo's 1947 *Duck Looking Back*.

Table 1. Major colorants in selected paintings by Woo Chong Yung, his mentors, and contemporaries.

Painting	Red / Orange	Yellow	Green	Blue	Brown	White
Ren Yi, <i>Flower and Bird</i>, 1860-1896, 73.61.10	cochineal, vermilion (XRF, FORS)	gamboge (FORS, Raman)	indigo + gamboge (FORS, Raman)	indigo (FORS, Raman)	iron ochre (XRF)	lead white (XRF, Raman)
Zhang Shuqi, <i>Young Blackbird in Tree</i>, early 1900s, 56.146	red lead (XRF, Raman)	chrome yellow (XRF, Raman)		indigo (FORS, Raman)	iron ochre (XRF)	lead-based white (XRF)
Xu Beihong, <i>Two Horses on Hillside</i>, early 1900s, 56.149	PO5 (Raman)					
Shi Zhen, <i>Seven Sages of the Bamboo Grove</i>, 1930, 1984.65	vermillion (XRF)	gamboge (Raman)	viridian (XRF, FORS, Raman)	viridian + Prussian blue, indigo (XRF, Raman)	vermillion + PR83:1 (XRF, Raman)	lead-based white (XRF)
Qi Baishi, <i>Lotus and Dragonfly</i>, 1900-1945, 2007.43	vermillion + PR83:1 seal –PR49.1 (XRF, Raman)	gamboge (Raman)			iron ochre (XRF)	
Woo Chong Yung, <i>Duck Looking Back</i>, 1947, 2011.07.515	vermillion (XRF)		emerald green (Raman)	indigo, azurite (XRF, Raman)		lithopone (XRF, Raman)

Qi Baishi, <i>Plate of Cherries</i>, 1948, 64.789	vermillion + PR8 (XRF, Raman)				iron ochre (XRF)	
Woo Chong Yung, <i>Bird on Flowering Branch</i>, 1949, 2011.07.576.	PR83:1 (Raman)			indigo, azurite (XRF, Raman, FORS)	iron ochre (XRF)	lithopone (XRF, Raman, FORS)
Wang Yachen, <i>Mountain Landscape</i>, 1960, 2010.308			copper-based green (XRF)	indigo (Raman)	iron ochre (XRF)	anatase, lead- based white (XRF, Raman)
*Woo Chong Yung, <i>Bulbuls and Loquats</i>, 1962, 2011.07.566	vermillion (XRF)	gamboge (Raman, FORS)	gamboge + indigo (Raman, FORS)	indigo (Raman, FORS)	iron ochre (XRF)	lead white, lithopone (XRF, Raman, SEM-EDX)
Woo Chong Yung, <i>Rooster</i>, 1972, 2011.07.595	cadmium red + PR4 (XRF, Raman)	PY176 (Raman)			iron ochre (XRF)	anatase (XRF, Raman)
Woo Chong Yung, <i>Untitled</i>, 1975, 2011.07.754				indigo (FORS)	iron ochre (XRF)	titanium white, zinc white (XRF)
Woo Chong Yung, <i>Bird and Loquats</i>, 1982, 2011.07.579.	PR4, PR83:1 (Raman)	PY6 (Raman)	indigo + PY6 (Raman)	indigo, PB 15:4 + PY32 (Raman, XRF)	iron ochre (XRF)	
Woo Chong Yung, <i>Sparrows in Wisteria</i>, 1984, 2011.07.545	PR83:1 (Raman)	PY3 (Raman)	indigo + PY3 (Raman)	indigo, PV23 – purple (Raman)	iron ochre (XRF)	anatase (XRF, Raman)

*The inscription is dated 1962 but indicates the work was created 10 years earlier.

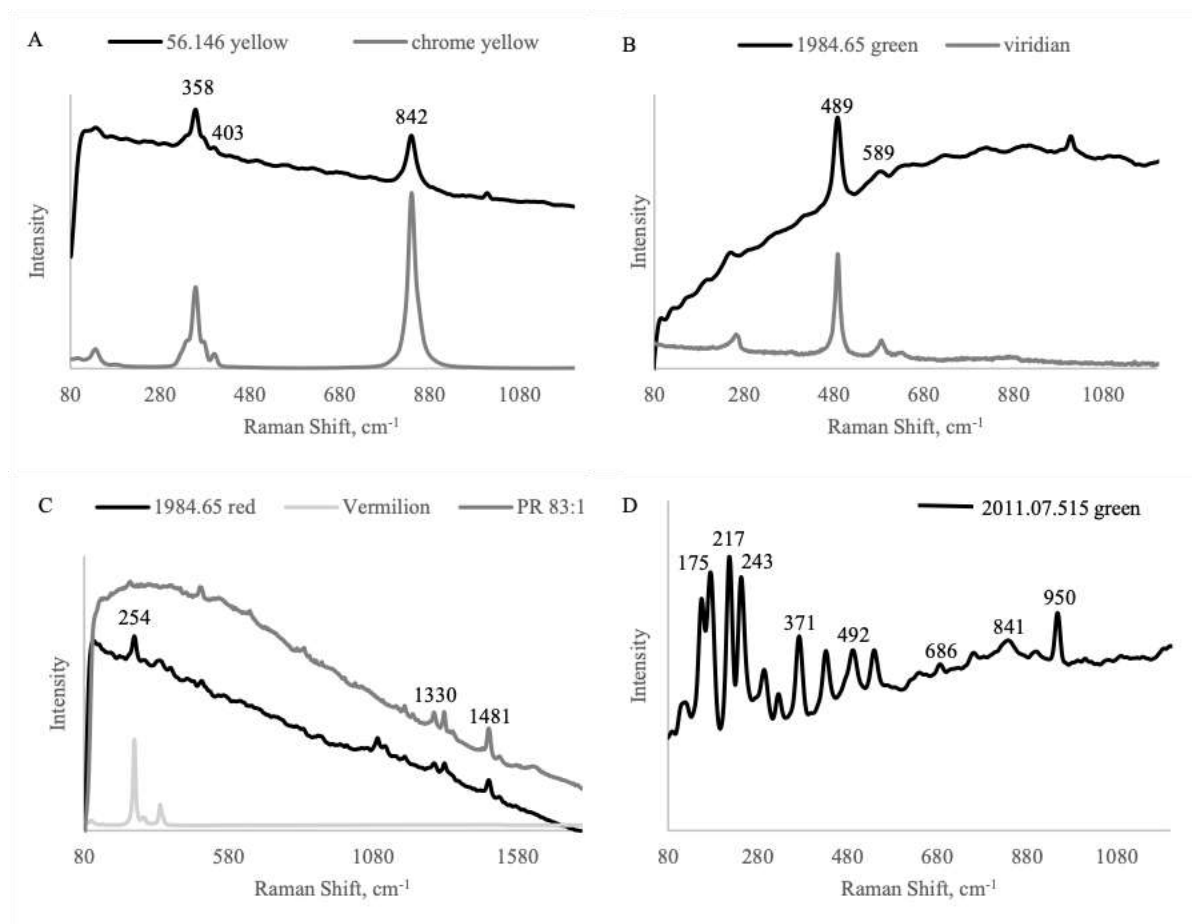


Figure 1. Raman spectra of pre-1950 paintings (black line) compared to standards (grey line). (D) Peaks are consistent with emerald green.

White pigments provide one of the clearest indicators of material transition. Lead-based whites dominate most of Woo's Chinese-period paintings and all pre-1960 works by his mentors and contemporaries, whereas titanium white (anatase) first appears as the dominant pigment in 1960 and only in works by Woo and Wang Yachen produced in the United States (Table 1). However, several works exhibit Raman and XRF signatures consistent with lithopone (Figure 2A), supported by co-localization of zinc and barium in SEM-EDS analysis. Although lithopone was not found in a broad study of Chinese paintings (McCarthy and Giacciai 2021), it is documented in Shanghai trade publications and municipal records, supporting its presence in the studied works (Circular telegram 1936). FORS spectra (Figure 2B) provide information about domestic production by showing the absence of a composite absorption band between 650–750 nm, indicating that cobalt, added elsewhere beginning in the 1920s to stabilize the ZnS crystal lattice and reduce darkening, was absent (Bacci, Picollo, Trumpy, et al. 2007). Surprisingly, zinc white

was the dominant pigment only in Woo's *Untitled* 1975 painting and an undated work, despite a mid-twentieth-century art treatise describing its availability (Feian 1988).

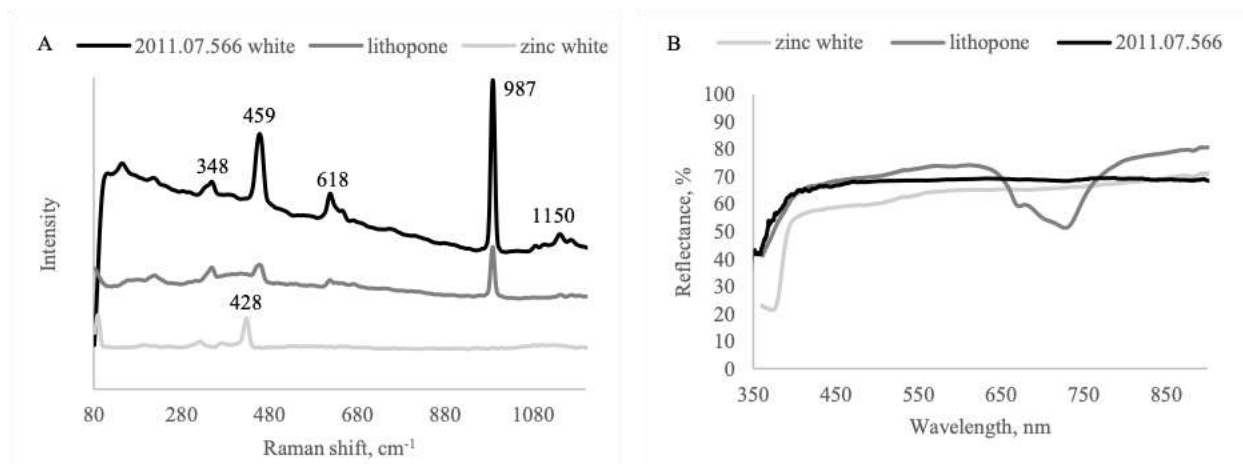


Figure 2. Comparison of (A) Raman and (B) FORS spectra of white pigment in Woo's *Bulbuls and Loquats* to standards of lithopone and zinc white.

The variety in composition suggests Woo experimented with or had differing access to white pigments (Figure 3). Archival records describe postwar shortages of imported pigments and the closure of several paint merchants and pigment dealers, suggesting that availability may have fluctuated considerably during the late 1940s (Shanghai Municipal Archives 2026). These findings reinforce the idea that colorant selection was shaped not only by artistic preference but also by broader commercial conditions.

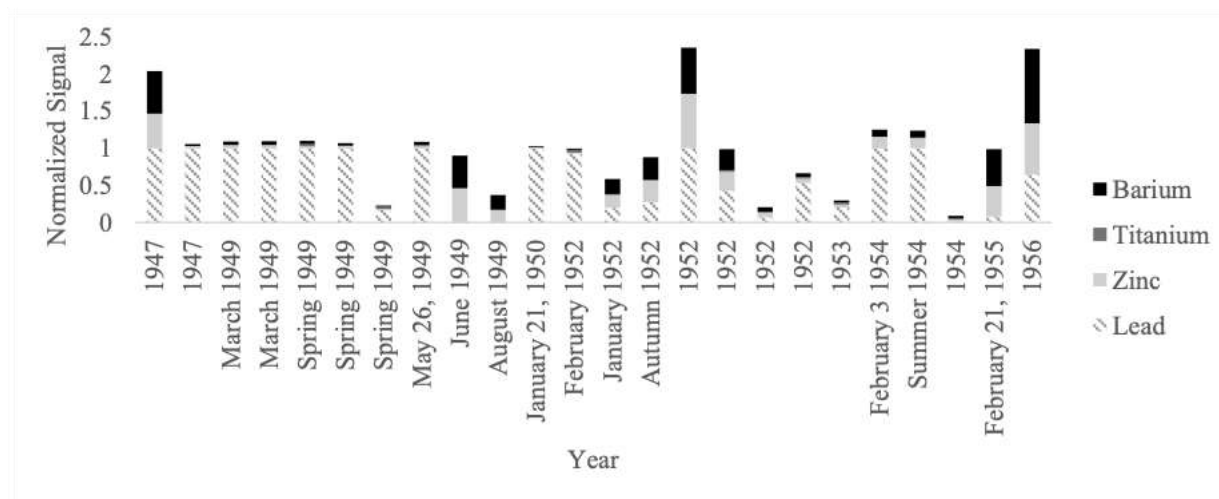


Figure 3. Changes in white pigment use over time. Normalized XRF signal relative to the most dominant element plotted by date.

Comparison between Woo's Chinese- and American-period paintings reveals a significant shift toward modern pigment use. For example, Woo's 1972 painting *Rooster* was made with anatase, diarylide yellow PY176, and cadmium red mixed with PR4 (Figure 4). These changes coincide with Woo's migration to Ohio, where he likely had more limited access to traditional Asian colorants. Instructional materials preserved in the Woo collection suggest intentional substitution of modern pigments for traditional colorants, while other documentation implies he used Kissho pigments from Japan. Indeed, some of the colorants identified in the 1984 *Sparrows in Wisteria* are consistent with modern Kissho pigments (Figure 4).

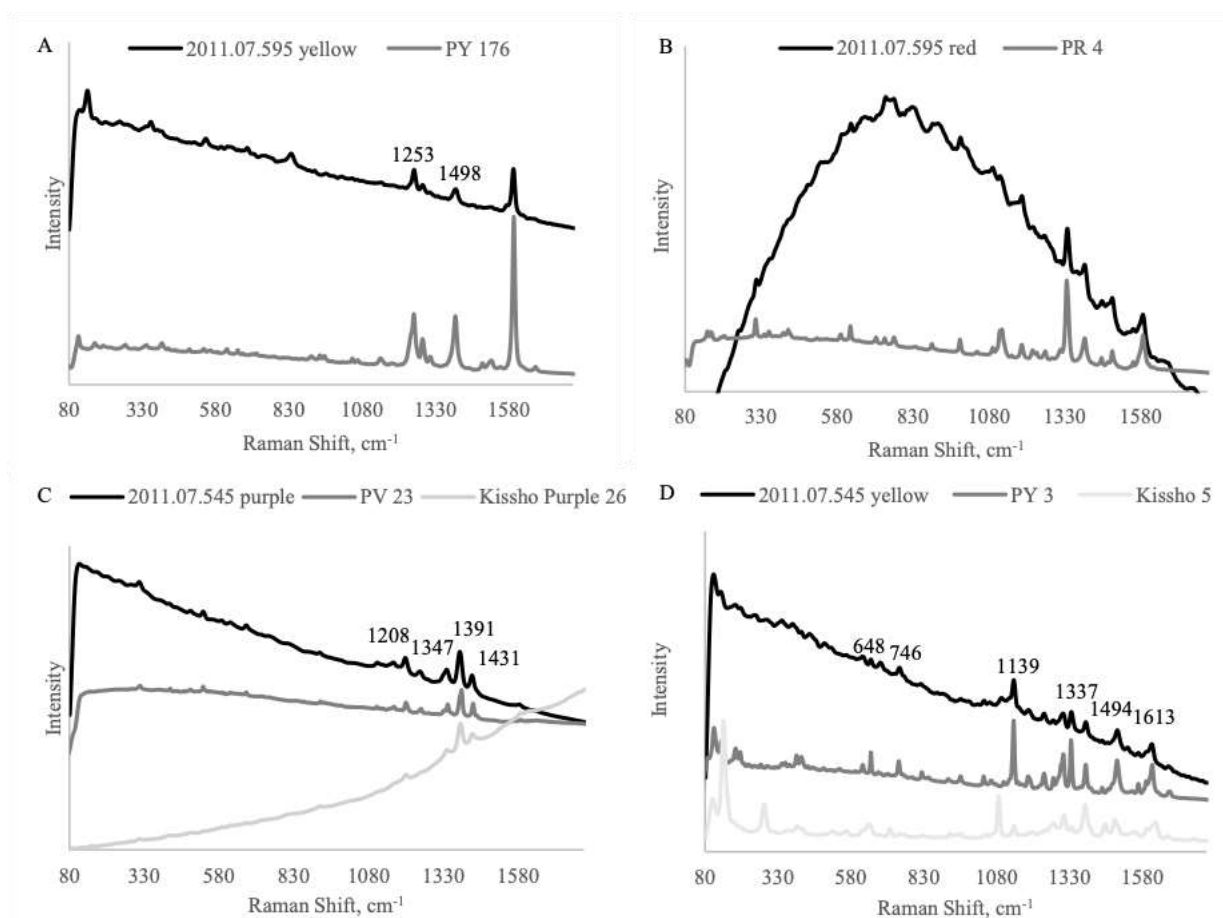


Figure 4. Raman spectra from Woo's American period works, *Rooster*, 2011.07.579 (A-yellow, B-red) and *Sparrows and Wisteria* (C-purple, D-yellow) compared to standards and Kissho pigments.

Colorants in three paintings are different from the pigment profiles in the comparative corpus, emphasizing its value for authentication and dating. The sole colorant in the early 20th century painting *Two Horses on Hillside* by Xu Beihong is PO5 (Figure 5); however, PR83:1 was the only red synthetic organic pigment found in Chinese works. Unexpected synthetic organic pigments were identified in two works by Qi Baishi – PR8 in *Plate of Cherries* and PR49:1 replacing cinnabar/vermillion in the seal imprint of *Lotus and Dragonfly*. Synthetic organic reds were identified in two previously studied Baishi forgeries (McCarthy and Giacciai 2021), warranting further investigation of these works.

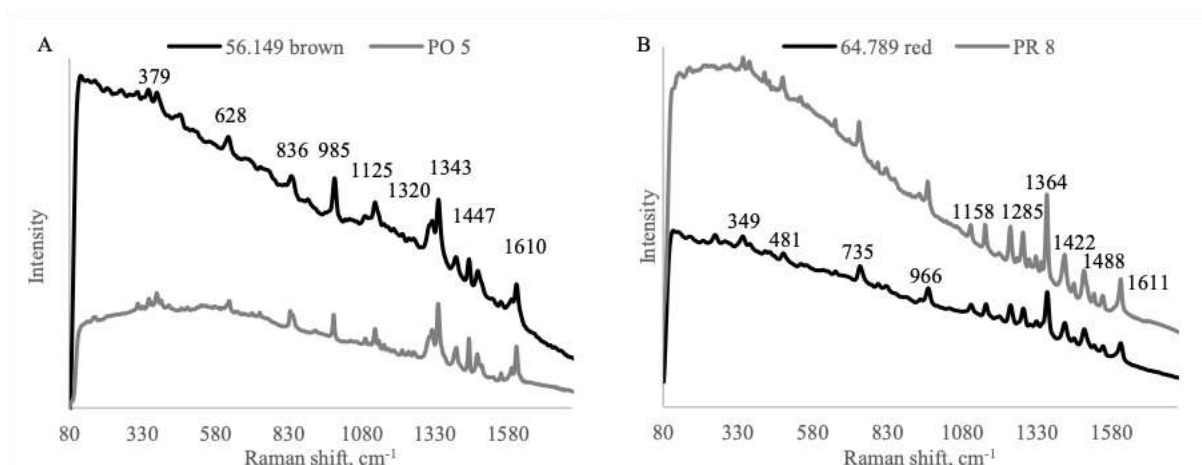


Figure 5. Raman spectra of (A) brown passage in Xu Beihong's *Two Horses on Hillside* and (B) red passage in Qi Baishi's *Plate of Cherries*.

4. CONCLUSION

Technical examination of over 100 works by Woo Chong Yung and his contemporaries reveals that twentieth-century *guohua* artists selectively incorporated modern colorants while maintaining traditional materials. Colorant use differed markedly between Woo's Chinese and American periods, aiding chronological assignment of his undated works. These findings provide a foundation for improved dating, authentication, and technical study of modern *guohua*.

5. ACKNOWLEDGMENT

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THE APPLICATION OF CONFOCAL RAMAN AND ATR-FTIR MAPPING TECHNIQUES IN THE SCIENTIFIC ANALYSIS AND STUDY OF PAINTING TECHNIQUES IN QING DYNASTY IMPERIAL OIL PAINTINGS

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1. INTRODUCTION

During the Qing dynasty, European oil-painting techniques were introduced into the imperial court through Jesuit missionaries, and in 1701 the “Oil Painting Workshop” was formally established under the Imperial Workshops of the Imperial Household Department. Drawing on both European models and Chinese traditions, court painters developed a distinctive practice that combined Chinese paper and silk supports with a mixed palette of indigenous mineral pigments and newly imported Western pigments. Over nearly two centuries, this hybrid system produced large numbers of imperial portraits and ceremonial paintings that served both decorative and documentary functions at court. Against this historical background, a systematic understanding of the materials and techniques of Qing imperial oil paintings is still limited, especially with regard to how Western oil-painting practice was adapted to Chinese supports and workshop routines.

In this study, four Qing dynasty imperial oil portraits from the Palace Museum collection were investigated using a suite of non-invasive analytical methods, including optical microscopy, fibre-optic reflectance spectroscopy and portable infrared reflectance spectroscopy, and one painting was further examined through cross-section analysis, confocal Raman spectroscopy, ATR-FTIR mapping and Py-GC-MS. By correlating these results with archival records from the Imperial Workshops, we aim to clarify the support structures, ground compositions, pigment use and binding media of these paintings, and to assess the nature of their technical hybridity between Chinese and Western traditions.

2. MATERIALS AND METHODS

Materials

Four Qing dynasty imperial oil portraits were selected for this study: hanging-scroll portraits of the Kangxi Emperor (Xuanye) and Consort He, an imperial portrait of the Jiaqing Emperor (Yongyan), and a half-length portrait screen of Noble Consort Wan in ceremonial attire. All four works are executed in oil on silk or paper supports and show varying degrees of cracking, loss and surface wear. The Xuanye portrait, which is in poor condition with extensive flaking and detached fragments, was chosen for micro-sampling to investigate its stratigraphy and binding media in greater detail.

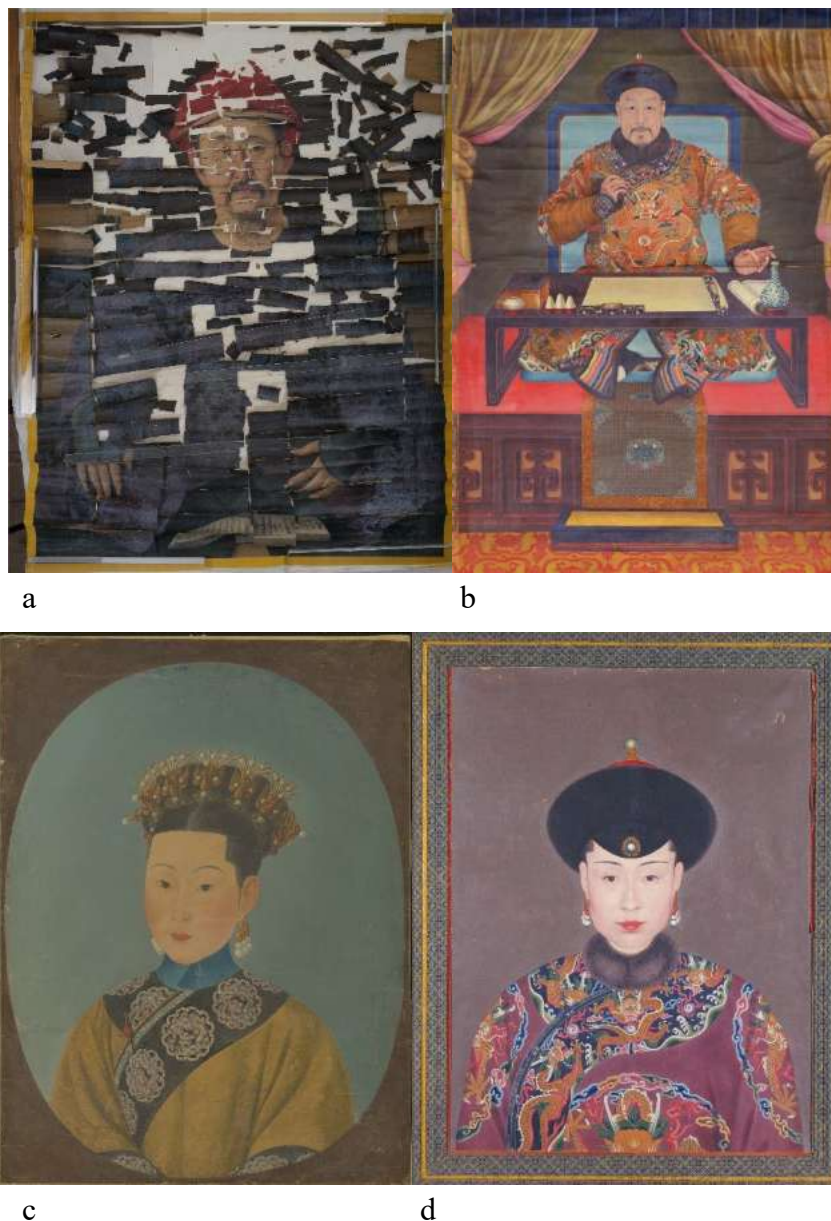


Figure 1. (a) Hanging scroll portrait of Xuanye (Kangxi Emperor); (b) Hanging scroll portrait of Consort He; (c) Hanging scroll portrait of Yongyan (Jiaqing Emperor); (d) Half-length portrait screen of Noble Consort Wan in ceremonial attire.

Methods

To avoid causing damage to the oil paintings, non-destructive analytical methods-including microscopic observation, fiber optic reflectance spectroscopy (FORS), and portable infrared reflectance spectroscopy-were employed to examine the four paintings.

For the Xuanye portrait, which exhibits detached fragments, selected fragments were subjected to cross-sectional microscopic analysis, confocal Raman spectroscopy, ATR-FTIR mapping techniques, and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS).

3. RESULTS AND DISCUSSION

Results of Non-Destructive Analysis

Microscopic observation shows that the four paintings employ traditional Chinese supports: the portraits of Xuanye and Consort He are on silk, while the Yongyan portrait and the Noble Consort Wan screen are on paper. All works display a glossy paint surface with visible brushwork and impasto, clearly distinct from the matte appearance of animal-glue-bound pigments in traditional Chinese paintings. Fibre-optic reflectance spectroscopy and portable infrared spectroscopy indicate the use of indigo as the blue pigment in the Xuanye portrait, whereas Prussian blue is identified in the other three paintings. In addition, ochre, cinnabar and organic dyes are detected in the Yongyan portrait and the Noble Consort Wan screen, reflecting a palette that combines Chinese mineral pigments with imported synthetic pigments.

Results of the analysis of the hanging scroll portrait of Xuanye (Kangxi Emperor)

Cross-sectional analysis of the Xuanye portrait (Fig.2) reveals a composite support consisting of a thin bamboo paper layer (approximately 15 μm) adhered to a silk fabric of about 150 μm thickness. The bamboo paper was confirmed by Herzberg staining and microscopic observation of bamboo fibre vessels, while the silk shows the characteristic triangular cross-sections of *Bombyx mori* filaments. This composite mounting reflects traditional Chinese painting practice and differs from the canvas or wooden panels typical of Western oil paintings.

-Two types of preparatory ground are observed: a dark grey ground and a greyish-white ground. SEM-EDS elemental mapping shows that both grounds contain potassium, aluminium, silicon, magnesium and titanium, consistent with clay minerals, together with lead. Confocal Raman mapping further identifies carbon black and the lead oxides massicot and litharge in the dark grey ground (Fig3), whereas the greyish-white ground lacks carbon black. These results indicate that both grounds are clay-based and enriched with lead compounds, with carbon black used to tone the darker ground. The materials correspond closely to archival records from the Imperial Workshops, which mention red and yellow “gold earths”, litharge, “ding fen” and minium as priming materials.

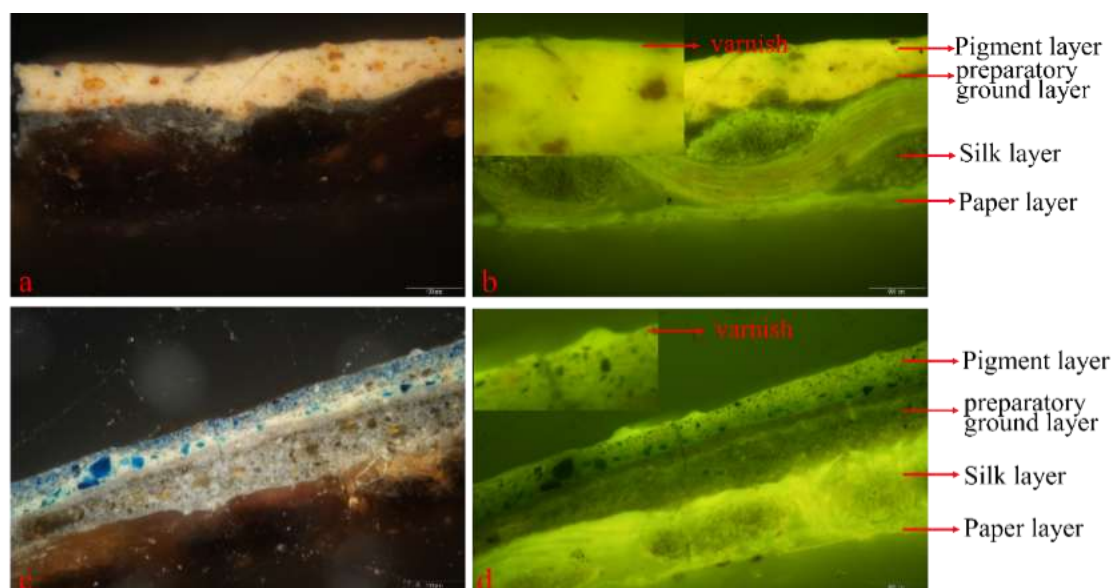


Figure 2. Microscopic cross-sectional stratigraphy of the Xuanye portrait: the “ab” image corresponds to the flesh-tone region, and the “cd” image to the green sleeve region; “ac” represents the image recorded under visible light, whereas “bd” shows the fluorescence image obtained under blue-light excitation.

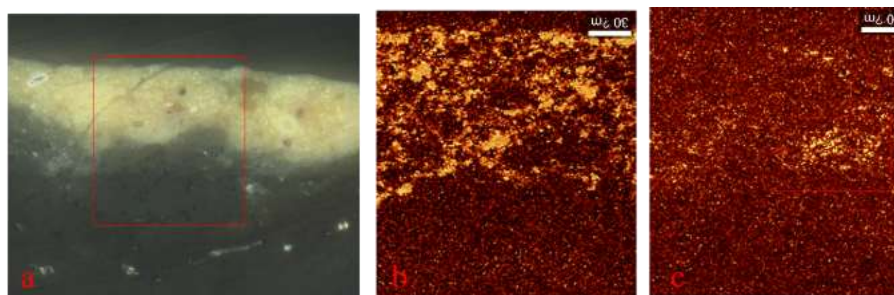


Figure 3. Raman spectral mapping of the cross-sectional sample taken from the flesh-toned area of the Xuanye portrait: (a) overall scanned area; (b) distribution of massicot and litharge; (c) distribution of carbon black.

Based on SEM-EDS and Raman spectroscopy, the pigments identified in the Xuanye portrait include cinnabar, ochre, lead white, massicot, litharge, azurite and lapis lazuli. In the green areas, Raman mapping (Fig.4) shows that azurite forms an underlayer beneath lapis lazuli, a practice comparable to Western oil-painting techniques in which a less expensive blue is used to support a thin layer of the more costly ultramarine. This layered arrangement not only economises materials but also reflects the adoption of Western chromatic strategies within a Chinese workshop context.

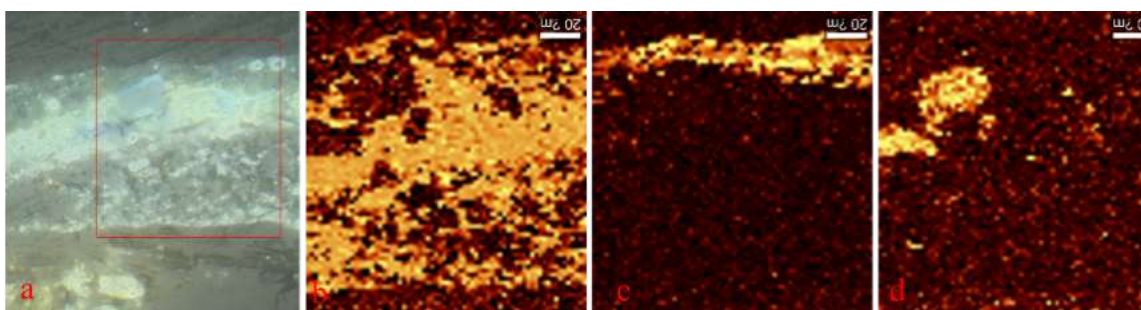


Figure 4. Raman spectral mapping of the cross-sectional sample taken from the green area of the Xuanye portrait: (a) overall scanned area; (b) distribution of massicot and litharge; (c) distribution of lapis lazuli; (d) distribution of azurite.

ATR-FTIR mapping of the cross-section (Fig.5) indicates that the support fibres and certain layers at the interface between the ground and paint contain protein, consistent with a silk substrate and the presence of a proteinaceous sizing or intermediate layer. Bands associated with aliphatic C-H stretching and carbonyl groups are concentrated in the paint and ground layers and in the surface coating, suggesting a drying oil binding medium and an oxidised resin varnish. Combined with the Py-GC-MS results, these data support the identification of a drying oil medium and a rosin-type natural resin varnish applied as a protective layer.

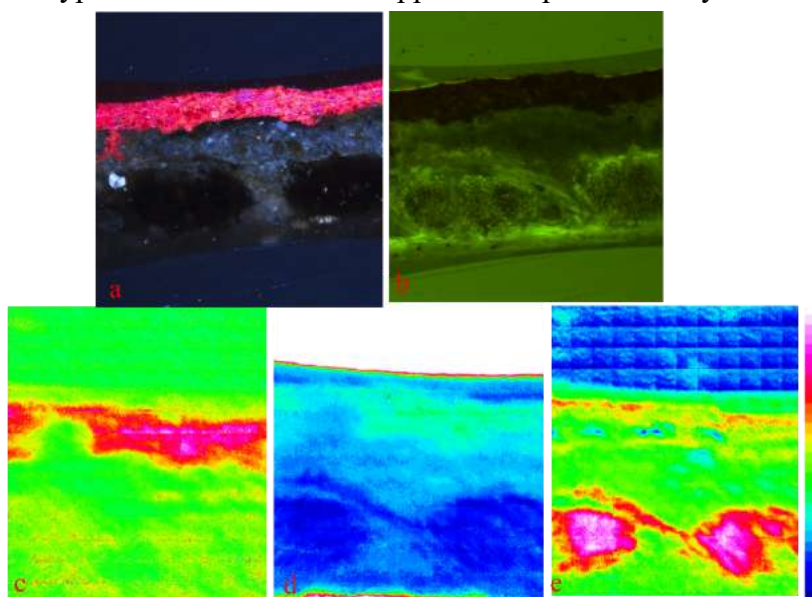


Figure 5. ATR-FTIR analysis of the red cross-section sample from the Xuanye portrait: (a) visible light image; (b) blue-light-excited fluorescence image; (c) integrated intensity map for 2836-2969 cm^{-1} ; (d) integrated intensity map for 1690-1730 cm^{-1} ; (e) integrated intensity map for 1589-1659 cm^{-1} .

4. CONCLUSION

This study, combining non-invasive spectroscopy with cross-sectional analysis, confocal Raman mapping and ATR-FTIR imaging, clarifies the material system and painting techniques of Qing dynasty imperial oil portraits. The four case studies show the consistent use of traditional Chinese supports of silk and bamboo paper, clay-based grounds containing lead compounds, and a palette that integrates Chinese mineral pigments such as azurite and cinnabar with Western pigments including Prussian blue. In the Xuanye portrait, the stratigraphy reveals a composite mounting, a clay–lead ground toned with carbon black, and an azurite underlayer beneath lapis lazuli, echoing both archival prescriptions and Western practice. Identification of a drying oil medium and a rosin-type natural resin varnish further refines our understanding of these hybrid systems and provides a methodological reference for the examination and conservation of similar works.

5. ACKNOWLEDGMENT

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CHARACTERIZATION OF EMERALD GREEN SYNTHESIS AND DEGRADATION BY FTIR AND RAMAN SPECTROSCOPY

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1. INTRODUCTION

Emerald green, or copper (II) acetoarsenite, was a brilliant green pigment widely used by Impressionist and Post-Impressionist artists until equally vibrant, non-toxic alternatives were introduced in the 1930s. Many late 19th and early 20th century oil paintings containing emerald green have since exhibited color alteration, prompting extensive research into its degradation pathways.

The manufacture of emerald green was highly variable, and numerous production methods yielded pigments with differing hues and particle morphologies. (Zerr et al. 1908; Rose and Woringer 1916). Larger particles produced brighter hues but required dilute reaction conditions and longer crystallization times to develop well-formed spherulitic crystals (Bersch 1901). Faster syntheses prioritizing chemical yield resulted in smaller particles and paler tones. An informal survey of oil paintings at The Barnes Foundation suggested that patchy lightening associated with emerald green degradation occurs predominantly in works containing finer-grained particles, observed qualitatively and validated by backscattered electron micrographs.

This study investigates the influence of historical preparation methods, selected to manipulate particle size and paint stratigraphy, on the degradation behavior of emerald green oil paint. Three preparations were investigated with attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and Raman spectroscopy. Paint mockups were aged in a thermal and humidity chamber, and changes associated with degradation were monitored with ATR-FTIR, external reflection FTIR (ER-FTIR), and fiber optic reflectance spectroscopy (FORS).

2. MATERIALS AND METHODS

Emerald green was synthesized to produce nominally small, medium, and large particle sizes using three recipes: Gmelin 1965, Bersch 1901, and Ehrmann 1834 (*Scott 2002; Bersch 1901; Hills 1876*). The precipitates were collected by paper filtration, washed with deionized (DI) water, and dried overnight. Dry pigments were characterized using ATR-FTIR and Raman spectroscopy.

Mockups were made using the three emerald green preparations bound in cold pressed linseed oil (Rublev Colours) layered over lead white (Atlantis Art Materials), zinc white (Kremer), French ultramarine (modern, Kremer), or hide glue (see Figure 1). The 50 x 80 mm mockups were split

in half, resulting in one set of 25 x 80 mm mockups reserved for natural aging in the dark and another set for accelerated aging in a thermal and humidity chamber at 50 °C and 80% relative humidity for 29 days. Changes associated with aging were monitored using ATR-FTIR, ER-FTIR, and FORS.

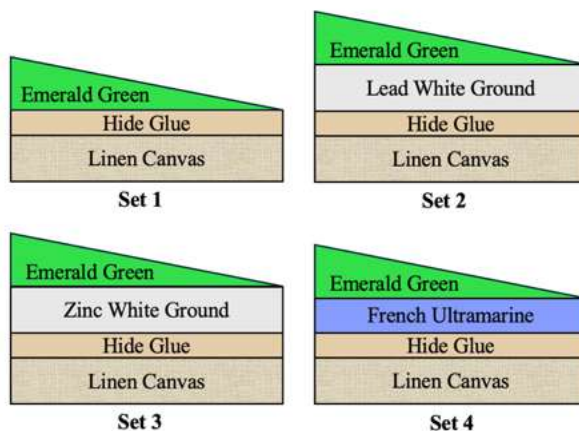


Figure 1. Mockup layer structures for accelerated aging experiments. Each set had three mockups, one for each emerald green preparation.

Infrared spectra were collected using a Nicolet iS5 FTIR spectrometer (Thermo Scientific) with a ConservatIR external reflection accessory or a Thermo Scientific iD7 ATR accessory. Samples were sliced from the mockup surface and analyzed by pressing them against the diamond ATR crystal. Spectra were collected from 4000-400 cm^{-1} and are the average of 32 scans for ATR-FTIR and 64 scans for ER-FTIR at 4 cm^{-1} spectral resolution.

Raman spectra were collected using a Bruker Senterra dispersive Raman microscope. Sample spots were selected using the 50x objective, producing a spot size of approximately 2 μm . A 20 mW diode 532 nm laser was used, and samples were irradiated at 2 mW with a 5 second integration time for 30 co-additions. Spectra were recorded using a grating and CCD detector combination that produced a spectral resolution of approximately 3-5 cm^{-1} .

FORS spectra were acquired using a Spectral Evolution oreXplorer™ Portable UV-Vis-NIR Spectrometer. The spectrometer operates in the range of 350–2500 nm and is equipped with three detectors: a 1024-element UV-enhanced Silicon detector (350–1000 nm), and two 512-element extended TE-cooled InGaAs detectors ((1000-1630 nm, and 1630-2500 nm). The instrument has a spectral resolution of 2.7 nm at 700 nm and 5.5 nm at 1400 nm and 5.8 nm at 2100 nm. The illumination source was a Spectral Evolution contact probe. The fiber optic cable produced a ~1 cm diameter spot size with the illumination source at 90° and the detector at 30° relative to the sample surface at ~5 mm standoff distance. Each scan averaged 80 spectra. Data was collected in the DARWin SP software (v1.5) and processed using the Spectragryph™

software.

3. RESULTS AND DISCUSSION

The three emerald green preparations – approximately 5, 10, and 15-20 μm as determined by scanning electron microscopy – were readily distinguished by differences in the As–O stretching region ($750\text{--}850\text{ cm}^{-1}$) of the ATR-FTIR spectra. Gmelin samples exhibited peaks at 874 (vw) , 816 , and 760 cm^{-1} , Bersch samples showed peaks at 816 and 760 cm^{-1} , and Ehrmann samples displayed a broad band centered at 759 cm^{-1} with a shoulder at 817 cm^{-1} . Raman spectroscopy indicated the presence of residual Scheele's green in the Gmelin preparation, evidenced by additional bands at 782 , 660 , 446 , 277 , and 193 , and 136 cm^{-1} (see Figure 2) (Herm 2021; Pantoja Munoz 2024). These spectral differences likely reflect variations in residual reaction products, including Scheele's green in the Gmelin preparation and unreacted As_2O_3 in the Ehrmann preparation, which was visible microscopically and likely contributed to broadening in the As–O stretching region.

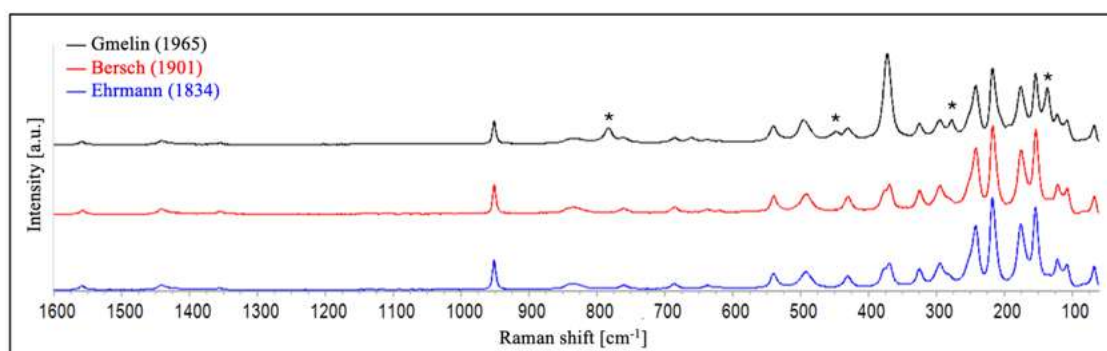


Figure 2. Raman spectra of emerald green preparations as the raw pigment. Asterisks denote peaks attributed to Scheele's green in the Gmelin batch.

Following accelerated aging, degradation was accompanied by visible darkening and decreases in intensity of bands near 1550 , 630 , and 590 cm^{-1} , attributed respectively to COO^- stretching, COO^- rocking, and Cu–O stretching modes (see Figure 3). Aging also caused broadening of the As–O stretching region ($750\text{--}850\text{ cm}^{-1}$) and a shift to higher wavenumbers, consistent with the formation of secondary arsenite and/or arsenate species (As(III) or As(V)) (Carboni Marri et al. 2025). The extent of these spectral changes varied with the synthesis method. Gmelin samples exhibited the greatest broadening, with peaks of comparable intensities spanning $840\text{--}726\text{ cm}^{-1}$, whereas Ehrmann and Bersch samples retained clearer separation between bands near 820 and 755 cm^{-1} .

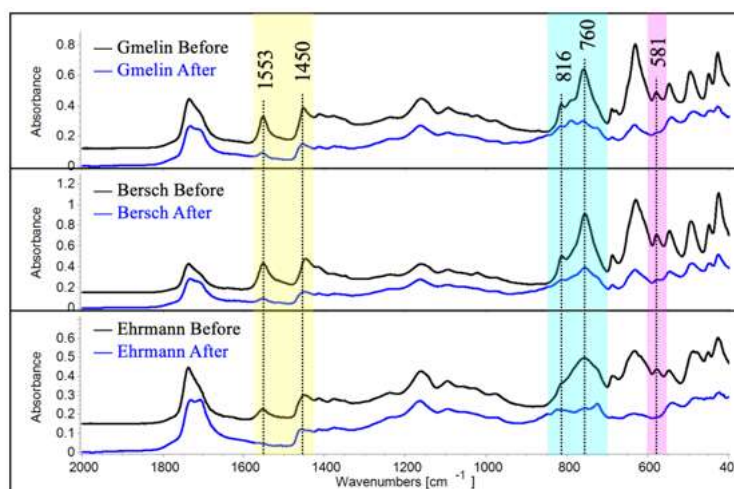


Figure 3. ATR-FTIR spectra of emerald green preparations on hide glue before and after accelerated aging with significant areas of change highlighted.

No significant differences were observed among support systems, suggesting that surface degradation is governed primarily by the pigment itself rather than by paint stratigraphy. The darkening was likely due to the crystallization of As_2O_3 , which occurs preferentially at the surface of paint structures (*Carboni Marri et al. 2025*). Any formation of insoluble arsenates (As(V) species) from interactions with other pigments was likely isolated to the base of the emerald green layer and undetectable from the surface (*Broers et al. 2023*).

FORS showed limited sensitivity to degradation-related chemical changes and revealed no clear trends related to pigment preparation or underlying paint layer. Accelerated aging caused the emission peak at 508–513 nm to decrease in signal and red shift around 41–60 nm (see Figure 4). Absorptions in the SWIR region attributed to emerald green include 1421–1424, 1999–2004, 2142–2143, and 2185–2187 nm, which were largely unaltered after accelerated aging.

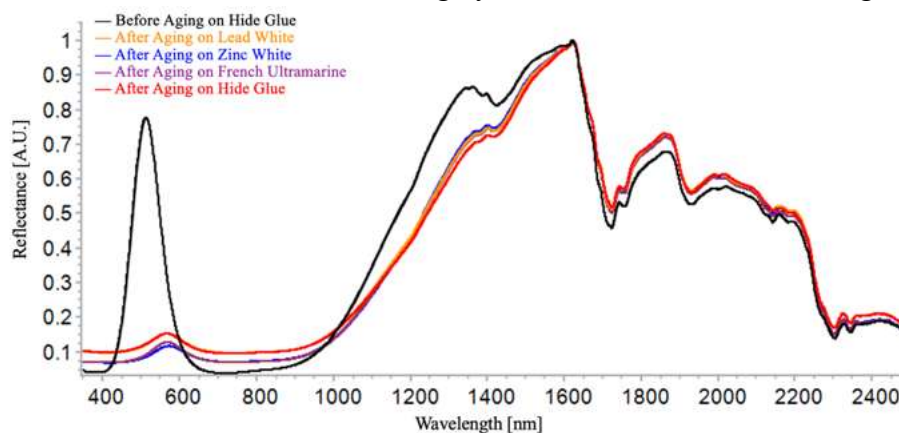


Figure 4. Reflectance spectra for Gmelin (1965) emerald green on various supports before and after accelerated aging. No absorption bands appeared or disappeared; only small shifts occurred.

4. CONCLUSION

ATR-FTIR and ER-FTIR were the most effective techniques for characterizing degradation in emerald green paints. While Raman spectroscopy was valuable for identifying residual Scheele's green impurities, it was less sensitive to changes occurring within the arsenic-oxygen stretching region. Degradation that occurred due to the thermal and humidity aging was undetectable by FORS, except for information about color shifts. As such, FTIR provided the clearest evidence of surface degradation through decreases in carboxylate bands and systematic broadening and shifts within the As-O stretching region. However, to more thoroughly characterize the degradation phenomena, especially for sub-surface changes, additional techniques like scanning electron microscopy or X-ray absorption near edge structure spectroscopy (XANES) are necessary.

5. ACKNOWLEDGMENT

The authors thank Stephanie Barnes from the Canadian Conservation Institute for collection of Raman spectra and Scott Williams from Queen's University for help in FTIR spectra interpretation. Collaborators at The Barnes Foundation and Scientific Analysis of Fine Art are acknowledged for useful conversations.

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EARLY TECHNOLOGIES OF LEAD-TIN YELLOW PIGMENTS: AN EXPERIMENTAL MATERIALS STUDY

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Lead-tin yellow is among the most prevalent of historic yellow pigments, known particularly for its use in 15th-17th century oil painting, and commonly found in 14th century European manuscripts. There are two types of lead-tin yellow that are differentiated by the presence of silicon; type I (Pb_2SnO_4) and type II ($\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$). Typically, analyses of works of art find only one of the two phases, with type II being the prevalent form before the 15th century.

Raman spectroscopy of an illuminated Byzantine manuscript dated to the 12th century unexpectedly identified the co-presence of both phases in the same spot. This unusual finding both predates the earliest known date of use of type I and raises questions about how a mixed phase material may have been produced. Traditional understanding of lead-tin yellow production stems from recipes dating to the 15th century, which describe using type I as a precursor in the production of type II, suggesting that both forms were available by that time. To date, no pre-medieval recipe has been found.

This project seeks to identify production methods that could have led to the formation of both types of lead-tin yellow in a single synthesis. Experimental work has explored whether a mixed phase can be produced from incomplete transformation of type I (testing changes in relative composition, temperature and firing duration), but also whether a mixed phase pigment can be produced in a single step from pure oxides. Early results using scanning electron microscopy and Raman microscopy suggested that the two-step synthesis resulting in incomplete reaction of type I is the most likely pathway. Additionally, the relationship between pre-medieval vitreous materials and pigment production is being examined. These results contribute to our understanding of the Byzantine and medieval history of this pigment.

ONE PIGMENT WITH TWO TYPES: INFRARED AND RAMAN ANALYSIS OF COBALT YELLOW

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There has been much debate historically regarding the lightfastness of aureolin (cobalt yellow, PY40, $K_{3-x}Na_x[Co(NO_2)_6] \cdot nH_2O$), with some saying the yellow pigment holds its color well while others say it quickly fades to grey or brown. In this study, PY40 was synthesized according to historic recipes providing both potassium-only and sodium-containing varieties. Notably, these products that can be differentiated utilizing vibrational spectroscopy based on a band shift of the $\delta(NO_2)$ scissoring vibrations near 830 cm^{-1} . Two subcategories of PY40 have been established: potassium-rich Type A and Type B with increased sodium content. Historical and current commercial cobalt yellow samples readily divide into the two subcategories. Analysis of aureolin pigments and paints via infrared, Raman, and X-ray fluorescence reveals a varied and unpredictable commercial market with a diversity of cobalt yellow formulations.

Lightfastness testing was performed on seventeen commercial paints where PY40 was identified through analysis as the only colorant. Paints that spectroscopically matched potassium-rich aureolin, Type A, were very lightfast ($\Delta E_{2000} = 1.3\text{-}3.1$; Lightfastness I) while those employing Type B varied more significantly but were broadly more fugitive ($\Delta E_{2000} = 2.4\text{-}9.3$; Lightfastness I-III). No correlation between paint medium and lightfastness was observed. This difference in pigment Type thus provides an explanation for the longstanding confusion over cobalt yellow's stability.

MORTAR THAN MEETS THE EYE: A TECHNICAL EXAMINATION OF CARTHALITE COLOURANTS USED IN THE MINISA BRIDGE, WICHITA, KANSAS

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The Minisa Bridge is a historic landmark in Wichita Kansas that traverses the Little Arkansas River. It depicts Native American busts along with buffalo and floral reliefs, serving as a reminder of Wichita's Native American history. Designed by architect Glen H. Thomas and constructed in 1932, the bridge is a significant example of Carthalite, a decorative precast concrete technique unique to Wichita, Kansas. This coloured cast concrete technique was developed in the early 20th century by the Cement Stone & Supply Co., and was primarily used from the 1920s to 1940s. It uses crushed glass and mineral pigments in a Portland cement matrix which is then molded into custom casts. From 2007-2009, a large restoration effort was undertaken to address significant structural and decorative deterioration. Apart from addressing the deterioration and stress to the bridge's structure, the restoration project is focused on repairing losses to many of the decorative elements. As the bridge is emblematic of a unique characteristic of Wichita's decorative arts history, there was particular interest in the material nature used to create the colourful Carthalite designs. The Scientific Research Department at the Los Angeles County Museum of Art (LACMA) was contacted to assist in the material characterization of these elements. Samples of different coloured masonry were analyzed with microscopy, micro-Raman spectroscopy, and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) to identify the aggregates and colourants used. As the samples were a complex mix of different elements, micro-Raman spectroscopy was of particular use and allowed for individual elements within the matrix to be analyzed. Results from this study will inform the restoration of the Minisa Bridge, ensuring that historically appropriate materials are used. Furthermore, this technical study contributes to the growing knowledge of Carthalite and provides insight into its production process.

CONSERVATION SCIENCE ON WHEELS: BRINGING THE LAB TO DUTCH MUSEUM COLLECTIONS

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At the Cultural Heritage Agency of the Netherlands (RCE), we aim to connect science, art, and culture. In addition to conducting research at our heritage laboratory, we also bring our mobile lab to museums and collections across the Netherlands, allowing us to conduct hands-on material analysis directly at the site. This approach helps us provide deeper insights into objects and demonstrates the important role that science plays in preserving cultural heritage to a broader audience. Furthermore, the connection between the (smaller) museums and the RCE is improved as result of better insight in how the Cultural Heritage Laboratory can help them with questions they have regarding our heritage.

We address a wide range of questions, such as: Was this painting created in the 16th century? Is this hairpin made of ivory? Does this silver spoon have a coating? The diversity of objects we work with is truly fascinating, ranging from archaeological finds to deteriorating shoe soles. To explore these questions, we use several advanced analytical techniques, including ATR-FTIR, Raman spectroscopy, microscopy, XRF, and a multispectral camera. In this presentation, we will give you a closer look at our mobile lab and share examples of the objects we have studied. We will discuss our findings, the advantages of using multiple techniques, and some of the challenges we face. While some answers are straightforward, many are surprising and reveal unexpected details.

IN-SITU RAMAN IMAGING: FROM STONE MONUMENTS TO PAINTINGS

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The need to analyze cultural heritage objects and artwork comes with many challenges. Priceless artefacts cannot be modified and may be impossible to move. Therefore, scientific analysis should be accomplished using non-destructive techniques, and with transportable instrumentation. Raman analysis is a non-destructive optical technique that requires no sample preparation. Accordingly, scientists and curators are taking Raman spectroscopy beyond the laboratory, to immobile objects in museum collections or to outdoor archaeological sites.

In this presentation, we discuss how the transportable Virsa™ Raman analyser has been used to study:

The composition of the Altar Stone at Stonehenge

Raman analysis is sensitive to the chemical and mineralogical composition of geological samples, which can provide clues to the provenance of the Altar Stone. We discuss *in-situ* and *ex-situ* single point spectra and Raman images, confirming the presence of a suite of heavy mineral grains. The Raman data agrees with previous petrographic analysis of fragments, matching the mineralogic fingerprint of the stone (Bevins, 2023). By correlating Raman data acquired *in situ* at Stonehenge with previous studies, this study aids the ongoing investigations into the origin of the Altar Stone (Figure 1).

Paint and pigments within artworks at the National Gallery-Alexandros Soutsos Museum in Athens (Rousaki 2025)

This study is one of the first testimonies of *in situ* Raman mapping of easel paintings, while the museum was open to the public. Analysis was performed on two influential 19th century paintings: ‘Fishing Captain’ by Andreas Kriezis (Figure 2), and ‘Boats in the waters of the Bosphorus’ by Symeon Savvidis. The identification of pigments in each artwork allowed a comparison of painting styles and an understanding of application techniques.



Figure 1. Using a Virsa analyser on the Altar Stone at Stonehenge.

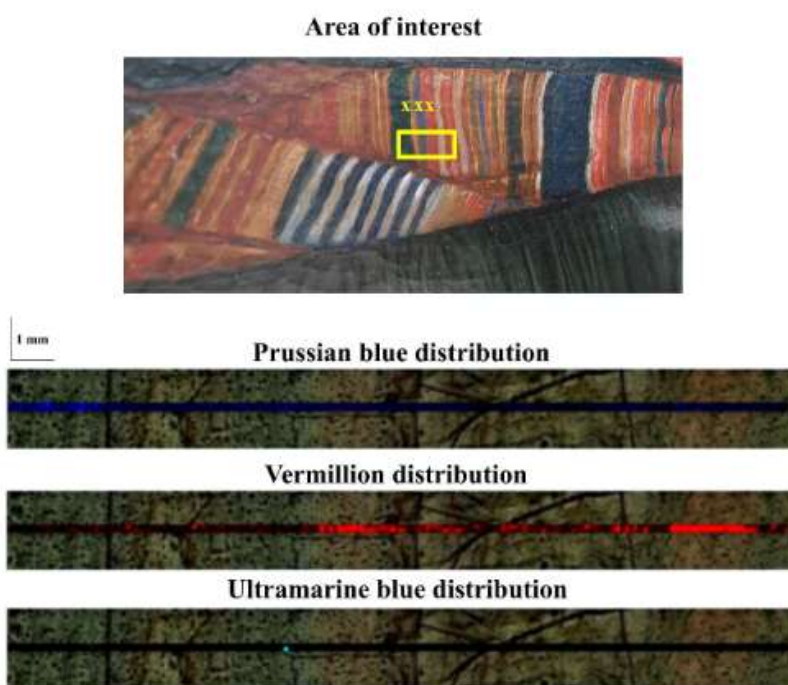


Figure 2. Raman maps from the colourful cummerbund of 'Fishing Captain' from Andreas Kriezis, collected within the yellow rectangle. Maps contained 354 data points and were generated using the Principal Component Analysis (PCA) function in WiRE™ software.

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NIR AND MID-IR REFLECTANCE IMAGING SPECTROSCOPY OF PAINTINGS TO MAP ARTIST MATERIALS

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The spectral region between 10,000 and 650 cm^{-1} (1 and 16 μm) is rich in vibrational features that can aid in the identification and mapping of various artist materials, including pigments, paint binders, and degradation products. The near-infrared region (10,000 to 4000 cm^{-1} or 1 to 2.5 μm) is readily accessible with imaging spectrometers, yielding high-resolution image cubes of paintings. However, the increased transparency of the paint layers in this spectral region, along with the limited number of vibrational features, can hinder material identification and separation. The mid-IR region (4000 to 650 cm^{-1} , 2.5 to 16 μm) has a greater number of vibrational features, which aids material identification, but it is difficult to access without high-cost, complex imaging spectrometers. Slow, low-spatial-resolution single-pixel mid-IR scanners using FTIR spectrometers have been shown to provide a low-cost solution for collecting useful data cubes. In the imaging lab at the National Gallery of Art, we have set up both a NIR and mid-IR reflectance imaging spectrometer to scan paintings. The NIR line-scanning imaging spectrometer has a spatial sampling of 0.21 mm per pixel and a spectral sampling of 2.5 nm over the 1.1 to 2.5 μm spectral band. The mid-IR single-pixel imaging spectrometer has a spatial sampling of 1.5 mm per pixel and a spectral sampling of 4 cm^{-1} in the 4000 cm^{-1} to 650 cm^{-1} spectral region.

In this paper, we explore the utility of fusing NIR and mid-IR image cubes to produce moderate spatial-resolution material maps (better than mid-IR alone) of a mockup painting and a 14th-century Florentine illuminated manuscript.

Abstracts

Posters

DEVELOPMENT OF COLLABORATIVE, COURSE-BASED TECHNICAL ANALYSIS PROJECTS AS A TEACHING TOOL IN AN UPPER DIVISION CHEMISTRY COURSE

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One of the capstone courses in the Chemistry BS and MS degree programs at CSU East Bay is Instrumental Analysis, where students learn about the fundamental principles and basic instrument design of spectroscopic and spectrometric techniques including, but not limited to, Raman, FTIR, NMR, HPLC and GCMS. Despite the inclusion of a weekly laboratory section in the course, students have limited hands-on experience with the instruments. Starting in 2023, the course was redesigned such that students are given three lab sessions at the end of the semester to conduct a technical analysis research project. This project gives chemistry students the experience of working with real world samples and exposes them to the field of conservation science. Importantly, students develop communication skills related to presenting technical results to non-chemists through an oral presentation and a written technical analysis report. Students propose two analysis techniques for their chosen sample to answer the primary research questions. Many students choose FTIR and/or Raman for analysis due to the techniques' chemical sensitivity and non-invasiveness. Most samples analyzed were provided by conservators at the Fine Arts Museums of San Francisco (FAMSF) and SFMOMA. This presentation will showcase the results from select student analysis projects between 2023-2025, focusing on Raman and FTIR analysis of objects in the collections of the FAMSF and SFMOMA, as well as accelerated aging and FTIR analysis of a commercial Cd red oil paint. Overall, this course-based research project has provided chemistry undergraduate and graduate students with an impactful educational experience and strengthened ongoing research collaborations between CSU East Bay, FAMSF, and SFMOMA.

PREPARATION OF STANDARDS AND SPECTROSCOPIC ANALYSIS OF WOODEN FURNITURE FINISHES FOR DETERMINING PERIOD OF MANUFACTURE

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In the field of art conservation, spectroscopy is the ideal method for non-invasive analysis of art and artefacts. Although there are compendiums of spectral data for natural and synthetic organic compounds, they are mostly limited to pure substances and so the art conservation community lacks a database of spectra for complex mixtures. Because traditional wood finishes are often mixtures of several resins or gums in a solvent, their spectral analysis cannot be easily compared to the existing literature for pure substances (such as CAMEO).

This study seeks to characterize various ingredients common in 18th century wooden furniture finishes using Raman and FTIR. Prior research of period recipes informed preparation of an array of standards of about twelve different resins/gums that are dissolved in two different solvents (ethanol and turpentine), and then binary and ternary combinations of each solvent system made prior to analysis. Standards, applied to a wood substrate and scanned, were compared against scans of an unknown wood finish and an attempt was made to identify the wood finish make-up of the unattributed object.

These results are consistent with the Department of the Treasury records for the cabinet shop that manufactured the 1880's facsimiles, and failed to find any evidence inconsistent with manufacture in that period. The data collected for binary and ternary mixtures of natural resins builds upon existing spectral databases, such as CAMEO, referenced by conservators in spectral analyses of museum artefacts.

IDENTIFICATION OF 5TH MILLENNIUM BC STONE BEADS FROM PAHLEVAN HILL (JAJARM) IN IRAN USING MICRO-RAMAN SPECTROSCOPY

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1. INTRODUCTION

Pahlevan Hill, located in the Jajarm plain of North Khorasan Province, northeastern Iran, is a key archaeological site with remains from the New Neolithic, Transitional Chalcolithic (5200–4800 BC), and Middle Islamic periods. Although initially visited and reported by Spooner (1965) and Masuda (1976), systematic archaeological investigations were not conducted until 2014 and 2017 (Azizi Kharanaghi et al. 2016). The most significant feature of this site during the Transitional Chalcolithic period is the stone bead industry. A large number of beads, along with evidence of all stages of the production chain—from raw stone blocks and semi-finished beads to perforating tools and finished or broken beads—have been recovered from the excavations. This study applies micro-Raman spectroscopy, an advanced, rapid, and non-invasive analytical tool, for chemical and structural analysis of these archaeological finds. The primary objectives are: (1) to identify the mineralogical composition of approximately 60 samples including stone beads, raw stones, and related tools; (2) to establish correlations between finished beads and raw materials; and (3) to provide insights into the chaîne opératoire of bead production and the technological capabilities of the Chalcolithic inhabitants. The research addresses critical questions regarding the relationship between beads and raw materials, the efficacy of Raman spectroscopy with different laser wavelengths for identifying such stones, and the role of recovered tools in the manufacturing process.

2. MATERIALS AND METHODS

A total of 60 samples, including 35 stone beads, 6 raw stone pieces, and 15 stone tools (Figure

1), were selected from the excavated assemblage at Pahlevan Hill. Sampling followed a purposive strategy based on macroscopic criteria including color variation (white, blue, green, reddish-brown), functional variety (beads, tools, raw stones), and relative physical integrity. All selected samples were analyzed using a Takusan Apus micro-Raman spectrometer equipped with a 532 nm green laser. Spectra were recorded in the range of 200–2000 cm^{-1} using a 40× objective lens. The measurement conditions were kept consistent across all samples to ensure data comparability. Data processing and baseline correction were performed using Tensuo software. Mineral identification was achieved by comparing the obtained spectra with reference standards from the RRUFF database (Lafuente et al. 2015). For the blue-colored samples, which exhibited strong fluorescence under the 532 nm laser, supplementary analysis was conducted using a 785 nm laser (Horiba Scientific company and using a 10× objective lens) at a collaborating institution to obtain interpretable spectra.



Figure 1 - Raw stones, stone beads that were broken when making holes, as well as complete rounded beads and various types of stone drills in different sizes recovered from the excavation. A: Stones of the area; B: Types of complete and semi-finished and broken beads; C: Complete and semi-finished white seals with stones similar to them; D: Types of almost shapeless complete and semi-white beads; E: Types of stone tools; F: Types of complete and semi-finished blue seals and stones ready to be cut

3. RESULTS AND DISCUSSION

The Raman analysis revealed three distinct mineralogical groups among the samples:

Group A: White Beads and Raw Stones (Calcite – CaCO_3)

This group comprised 24 beads and 4 raw stone samples. All spectra displayed a strong, sharp peak at approximately 1085 cm^{-1} , corresponding to the symmetric stretching vibration (ν_1) of the carbonate group (CO_3^{2-}), along with smaller peaks at 713 cm^{-1} and 283 cm^{-1} associated with bending and lattice vibrations of calcite (Rull et al. 2007). The spectral patterns showed a complete match with calcite reference spectra in the RRUFF database. The consistent match between the beads and the locally-sourced raw stone samples strongly suggests the use of local carbonate sources (limestone or travertine) in the vicinity of the site. Calcite's moderate hardness (3 on Mohs scale) makes it amenable to working with stone tools, indicating a rational choice by the artisans balancing ease of manufacture and aesthetic quality.

Group B: Blue Beads and Raw Stones (Serpentine-Group Minerals)

Ten blue-green beads and two raw stone samples were analyzed. Due to strong fluorescence interference with the 532 nm laser, representative samples were re-analyzed using a 785 nm laser, yielding clear spectra. The spectra revealed a distinct triple-peak pattern at approximately 228 , 381 , and 687 cm^{-1} , which falls within the range characteristic of serpentine-group minerals (Rinaudo et al. 2003). However, while these peaks are broadly consistent with serpentine minerals, they show minor shifts from the diagnostic positions reported for pure chrysotile (692 , 388 , and 231 cm^{-1}). Given the close similarity in Raman signatures among serpentine varieties (chrysotile, antigorite, and lizardite) and the possibility of mixed-phase compositions, we conservatively identify the material as a serpentine-group mineral, rather than assigning it definitively to chrysotile alone. Critically, the complete spectral match between the beads and the local raw stone demonstrates that the beads were manufactured from locally available stone. This finding is particularly significant, as it indicates the use of a local blue-green serpentine source rather than imported lapis lazuli from Badakhshan, Afghanistan, which was commonly used for blue beads at contemporaneous sites. This suggests a preference for locally accessible materials and points to a self-sufficient economic strategy at Pahlevan Hill during this period.

Group C: Stone Tools (Quartz/Chalcedony – SiO₂)

Fifteen tools, including scrapers, perforators, and blades, exhibited a dominant and very intense peak in the 464–468 cm⁻¹ range, characteristic of the Si-O-Si bending vibration in quartz and its cryptocrystalline varieties such as chert, agate, and chalcedony (Kingma and Hemley 1994). The exclusive use of this material for tool-making demonstrates the inhabitants' deliberate selection of raw materials based on optimal physical properties—high hardness (7 on Mohs scale) and conchoidal fracture—ideal for producing sharp, durable cutting edges.

4. CONCLUSION

This study successfully identified the mineralogical composition of the 5th millennium BC stone bead assemblage from Pahlevan Hill using micro-Raman spectroscopy. The findings demonstrate a coherent and technically sophisticated subsistence and production strategy: calcite was used for white beads due to its local availability and ease of working; chrysotile, a locally sourced serpentine mineral, was used for blue-green beads, challenging the conventional assumption of imported lapis lazuli; and quartz/chalcedony was exclusively selected for functional tools due to its superior mechanical properties. The complete matching of finished beads with local raw stone samples provides strong evidence for the production hypothesis and suggests a self-sufficient, locally-oriented economy. The study further confirms that Raman spectroscopy, particularly when combined with appropriate wavelength selection, is a highly effective non-destructive method for analyzing archaeological stone artifacts, and opens new perspectives for comparative studies on contemporaneous sites in northeastern Iran and beyond.

5. ACKNOWLEDGMENT

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ALUM TAWED SKIN IDENTIFICATION BY ATR-FTIR AND RAMAN SPECTROSCOPY

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1. INTRODUCTION

In cultural heritage, most research and development on leather tannin identification has been focusing on vegetable tannins, and much less attention was given to other tanning technologies, in particular alum tawed skins, also highly represented in collections. Few characterization methods could be applied to evidence the use of alum in skin preparation, but these approaches proved sometimes complex to interpret due to the fact that aluminium is a light element difficult to detect with XRF spectroscopy or the possible interference of other elements in the aluminon spot test. Therefore, the present study investigates the potential of infrared and Raman spectroscopies to identify the use of alum in skins.

2. MATERIALS AND METHODS

FTIR and Raman measurements were applied to modern and ancient alum-tawed skins, as well as other leathers displaying similar visual and flexibility characteristics, such as zirconium and chrome tanned leathers. The measurements were carried out either directly onto the skin comparing the grain and flesh sides, whenever suitable, or on the dried residue of the skin water extract. Water extract was considered as it can be recovered from two analytical approaches commonly used on leather, differential scanning calorimetry (DSC) and pH measurement, which requires the immersion of a skin sample in water. Reference spectra of alum and hydrated aluminum sulfate, both raw and dehydrated at 110°C for a few hours, were also recorded for comparison. Infrared spectroscopy measurements were carried out using a Bruker Alpha FTIR spectrometer equipped with a diamond ATR. Raman spectroscopy measurements were carried out on a Renishaw inVia microspectrometer using a laser excitation at 532 nm, and a 50× or 100× objectives.

3. RESULTS AND DISCUSSION

The study showed that when the aluminium content was high in the skin, it could be easily evidenced non invasively by XRF and infrared spectroscopies of the leather, with the presence of two different characteristic ATR-FTIR spectra profiles. Nevertheless, difficulties in its identification arise when the aluminium content is low in the skin or when it is used in combination with other tanning method or manufacturing compound (eg. chromium and zirconium tannins or kaolinite), as the aluminium markers are weak or inexistent both in XRF and infrared spectroscopies. In that case, the infrared or Raman spectroscopy analysis of the leather dried water extract residues, recovered from pH or DSC analysis, can be used to precise

the identification. Thanks to its high solubility, aluminium sulfate salts are extracted in water and can be analysed without interference from the other compounds present in the skin such as collagen, zirconium or kaolinite). For these aluminium sulfate water extracts, two slightly different ATR-FTIR spectra profiles, similar to the spectra of dehydrated alum or aluminium sulfate, are obtained. The different spectra profiles are likely due to variable hydration of the aluminium sulfate residue. Although, it might be slightly more time consuming to record a spectrum due to the presence of a fluorescence background, Raman spectroscopy can also be used to evidence the presence of aluminium sulfate salts in the water extract dried residue.

4. CONCLUSION

The study investigated the possibility to use vibrational spectroscopy to evidence the use of alum or aluminium sulfate in the skin tanning process. The analyses revealed that the use of aluminium sulfate salt can only be confirmed by direct ATR-FTIR measurement when the aluminium content is high and that no other mineral compound was used during the manufacturing (tannin or dryer). In the case of skin with mixed tanning or when the aluminium content in the skin is low, the present study shows the benefit of applying the vibrational techniques to the skin dried water extract residues to precise the identification. Although this methodology is invasive, it can be considered as a complementary approach when DSC and/or pH measurements are carried out on the skin, as immersion of the sample into water is required. Information about the use of alum in the tanning process will be beneficial in the study of ancient skins to learn about ancient technology, but also in the case of modern commercial skins prior to its use for conservation.

5. ACKNOWLEDGMENT

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APPLICATION OF SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS) FOR THE IDENTIFICATION OF COCHINEAL IN THE ILLUMINATED PARCHMENTS FROM METROPOLITAN CATHEDRAL OF MEXICO CITY

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During the restoration works carried out at the Metropolitan Cathedral in 2023, a significant discovery was made in the central dome: twenty-three lead boxes containing wooden and palm crosses, clay fragments, and illuminated parchment were uncovered. The National Coordination for the Conservation of Cultural Heritage (INAH) conducted the diagnosis, stabilization, and material study of these religious relics. The present work focuses on the application of Raman spectroscopy, specifically surface-enhanced Raman spectroscopy (SERS) for the identification of colorants in the illuminated parchments. SERS analysis was carried out on a paper fragment that protected the illuminations, which exhibiting red–violet color migration. Complementary, we employed non-destructive and in situ analytical techniques, including surface optical microscopy (SOM), X-ray fluorescence (XRF), and infrared false-color imaging (FCIR).

The Raman spectra obtained from colorant extraction revealed characteristic vibrational bands corresponding to cochineal, a dye of great historical importance in Mesoamerican territory. This finding constitutes one of the most significant results of the study, as it provides direct evidence of the use of organic colorants in illuminated parchments, which may represent some of the earliest examples produced in New Spain. The identified inorganic pigments include azurite, malachite, vermilion, minium, white lead, carbon black, and iron oxides. These results demonstrate the use of mineral and organic materials in the artistic techniques associated with illuminated parchment production during the 17th and 18th centuries, objects poorly documented and insufficiently studied in Mexico. This research represents a significant contribution to the understanding of historical artistic materials and techniques within the context of cultural heritage conservation.

ASSESSMENT OF DISCRIMINATION CONDITIONS BETWEEN AZURITE AND LAPIS LAZULI BY ON-SITE MICRO-RAMAN SPECTROSCOPY FOR NON- DESTRUCTIVE AND ACCURATE ANALYSIS OF MURALS

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1. INTRODUCTION

Raman spectroscopic analysis is a useful technique for material characterization; however, its application to cultural heritage objects raises concerns regarding potential laser-induced damage (Smith, Burgio, Firth, et al. 2001). Furthermore, the cultural heritage material is not always a pure substance, and fluorescence emission from associated materials may interfere with the intended analysis. Previous studies on the distinguishability of target pigments and risk assessments have mainly focused on pure pigments or simplified mock-up samples (Burgio, Clark and Firth 2001; Ciofini, Agresti, Giamello, et al. 2025), leaving a gap in our understanding under authentic heritage conditions, where surface contaminants (e.g., particulate soiling, soil deposits, and/or conservation materials) may be present. We plan to perform an on-site Raman spectroscopy study to distinguish between azurite and lapis lazuli in the mural painting of Takamatsuzuka tumulus. The mural is designated as a National Treasure, the highest level of cultural property designation in Japan; therefore, a particularly rigorous evaluation is required to assess whether the two pigments can be reliably distinguished and whether the analysis is safe for the painting. This study reports the results of investigating optimal conditions, using mock-up samples that closely replicate the target.

2. MATERIALS AND METHODS

Mock-up Preparation

The mural paintings of Takamatsuzuka Tumulus (late 7th-early 8th century) is one of two examples of polychrome tumulus murals in Japan. A lime plaster was applied to the stone chamber, upon which images were painted. Previous studies suggest that lead-based white pigment was used as an underlayer. The mural to be investigated in future studies is *Azure Dragon* on the east wall. Recent X-ray diffraction analysis identified malachite in the green-colored body. Additionally, blue pigment particles were observed in this feature. To distinguish between azurite and lapis lazuli, micro-Raman spectroscopy is being considered. As the mural is designated as a National Treasure, non-destructive and non-contact analyses are strictly required. Furthermore, its surface exhibits soil contamination acquired during burial, and synthetic resin was also used during past conservation treatments. This indicates that the analysis faces significant challenges from both analytical ethics and the feasibility of pigment identification. Here, mock-up samples closely replicating the mural were prepared for rigorous evaluation of measurement conditions (Table 1). Japanese lime plaster was prepared from calcium hydroxide, funori (a seaweed-derived adhesive), and distilled water and subsequently carbonated. Azurite and lapis lazuli pigment particles (approximately 20–30 μm in size) were applied using animal glue as a binder ([S0]). Mock-ups with simulated soil contamination, conservation materials, and layered paint structures with lead white and malachite were also prepared ([S1], [S2]). Rammed earth from the tumulus, $\alpha\text{-FeOOH}$, and Paraloid B-72 were used as the soil contaminant, deposits of iron oxide, and conservation material, respectively.

Table 1. Details of the mural mock-up samples.

Mock-up details				
S0	Simplified mock-up			
Overview	Azurite and lapis lazuli particles applied to Japanese lime plaster			
Purpose	Discriminability			
	Layer structure	[L1]	Azurite/ Lapis lazuli	
		[B]	Japanese lime plaster	
S1	Mock-up simulating surface soiling and conservation material effects			
Overview	Surface soiling and conservation material applied to pigment particles on a lead white ground over Japanese lime plaster			
Purpose	Discriminability			
			[Type A]	[Type B]
		[L4]	None	Paraloid B-72
		[L3]	Rammed earth/ α -FeOOH/ Paraloid B-72	Rammed earth/ α -FeOOH
	Layer structure			
		[L2]	Azurite/ Lapis lazuli	
		[L1]	Lead white ground	
		[B]	Japanese lime plaster	
S2	Mock-up simulating the mural's paint layer structure			
Overview	Pigment particles applied to a malachite layer on a lead white ground over Japanese lime plaster			
Purpose	Discriminability and risk assessment			
		[L3]	Azurite/ Lapis lazuli	
		[L2]	Malachite painted layer	
	Layer structure			
		[L1]	Lead white ground	
		[B]	Japanese lime plaster	

Instrumentation and Analytical Conditions

To analyze microscopic pigment particles, a micro-Raman spectrometer (VisHead+MacroRAM, HORIBA, Kyoto, Japan) with a coaxial optical configuration, sharing the same optical path for observation light and excitation laser, was employed. To avoid fluorescence interference, a 785 nm excitation laser was selected. Laser power was attenuated using ND filters with 1% and 10% transmittance. A 50 $\times$ objective lens was used, resulting in a laser spot size of $\phi 2\ \mu\text{m}$.

Discriminability and Risk Evaluation

Azurite and lapis lazuli can be distinguished by Raman spectroscopy (Bicchieri, Nardone, Russo, et al. 2001). Here, discriminability was examined by assessing whether the characteristic Raman bands of each pigment are subject to overlap or fluorescence interference from coexisting

materials. Laser-induced damage was evaluated based on pigment discoloration and spectral changes during Raman signal integration. The laser power at the sample was measured, and the condition enabling discrimination of both pigments without damage was considered optimal.

3. RESULTS AND DISCUSSION

Discriminability between Azurite and Lapis Lazuli in Mock-ups

Before investigating the effects of surface contamination, a simple mock-up [S0] was measured. A peak corresponding to the Cu-O bond was detected at approximately 400 cm^{-1} for azurite, whereas a strong peak originating from the S-S bond associated with coloration was identified at approximately 540 cm^{-1} for lapis lazuli. The laser power used in this experiment was 0.65 mW at the sample, and no laser-induced damage was observed. By selectively measuring the target particles, the two blue pigments were successfully discriminated even on a Japanese lime plaster. Using mock-ups [S1], the effects of fluorescence and peaks derived from surface contaminations were investigated. As a result, the two blue pigments could be discriminated under all tested surface conditions. However, the Raman spectrum of α -FeOOH showed a characteristic band at approximately 400 cm^{-1} , and in samples coexisting with azurite particles, spectral overlap was observed. Since the α -FeOOH peak is located at slightly lower wavenumber than that of azurite, the coexistence of the two results in a broadened peak profile. Caution is required when identifying an unknown blue pigment associated with deposits of iron oxide as azurite; however, the respective peaks can be distinguished, and the presence of α -FeOOH peak is considered not to affect the discrimination between azurite and lapis lazuli. Furthermore, provided that the laser can be solely focused on the pigment particles, these overlaps can be avoided. These results indicate that the two pigments can be distinguished even in the presence of surface contaminants.

Discriminability and Risk Assessment Using a Mock-up Simulating the Mural's Paint Layer

Under a laser power of 0.5 mW at the sample, the characteristic bands were observed for each pigment, demonstrating that discrimination was possible without laser-induced damage (Fig. 1). Under these conditions, malachite, which occupies most of the area, was also unaffected. However, when the laser power was increased to 4.6 mW, localized thermal damage occurred in the malachite-painted region, resulting in observable damage. The integration time was evaluated up to 900 seconds at 0.5 mW, and no laser-induced damage was observed. These results suggest that the 0.5 mW condition is appropriate for measurements on the actual mural.

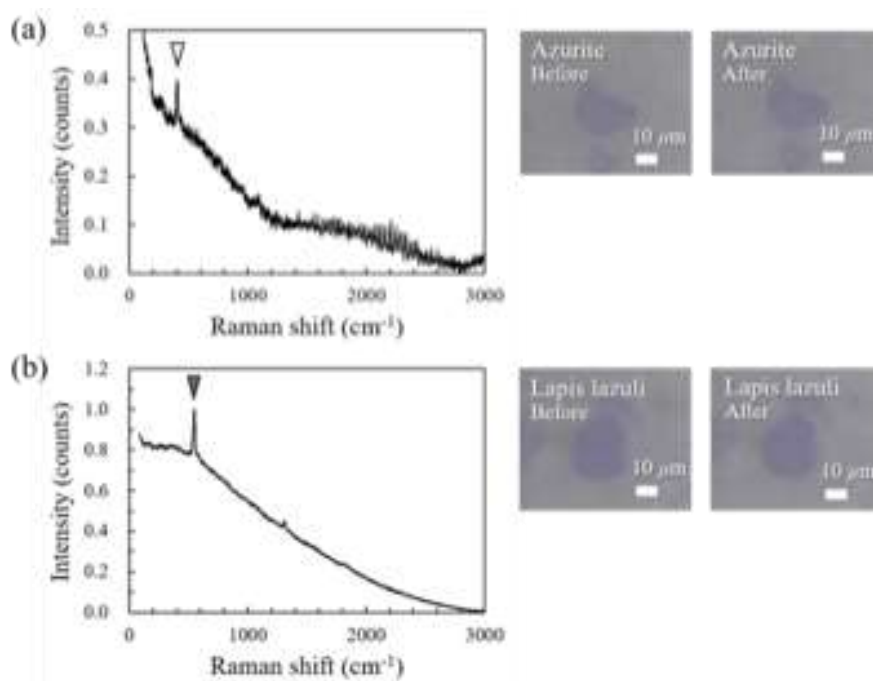


Figure 1. Raman spectra of the mock-up simulating the mural's paint layer.

(a) azurite; (b) lapis lazuli

Insets: microscopic images before and after measurements.

Triangles indicate characteristic Raman bands of the pigments.

4. CONCLUSION

Even when impurities were present on the plaster surface, azurite and lapis lazuli were successfully distinguished by selectively irradiating the particles with a laser. For practical applications, considering the risk of sample damage, a laser power of 0.5 mW at the sample was determined to be appropriate (laser spot size: $\phi 2 \mu\text{m}$). The feasibility of discrimination and risk assessment in this study considered not only the target pigment but also the influence of related materials. In future work, we plan to conduct experiments using the original mural plaster to investigate factors that cannot be reproduced with a mock-up, including effects of biofilm formation.

5. ACKNOWLEDGMENT

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WATERCOLOR PIGMENTS IN CONTEXT: RAMAN ANALYSIS OF EMILY SARGENT'S SELECTED WORKS

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1. INTRODUCTION

Emily Sargent (1857–1936) was an avid watercolorist whose work has been largely overlooked in art historical scholarship. Best known as the sister of John Singer Sargent (1856–1925), Emily traveled extensively with her family and produced a substantial body of watercolors over a career spanning more than fifty years. Over 50 works from her oeuvre are a part of the Museum of Fine Arts collection, along with a large portion of her writings, letters, and archives. This study is the first technical investigation of the materials used in her watercolors.

2. MATERIALS AND METHODS

A representative subset of seven watercolors, spanning approximately her entire career (1877 to 1929), were analyzed with in-situ techniques. Raman spectroscopy served as the primary method for identifying the pigment palette, due to its ability to identify inorganic and some organic pigments in situ and to target particles in both thin washes and more heavily applied media. Point fiber optics reflectance spectroscopy (FORS), reflectance imaging spectroscopy (RIS) and point X-ray fluorescence spectroscopy (XRF) were used to supplement and corroborate pigment identifications.

Initial examination of the watercolors relied on multispectral imaging (MSI), microscopic investigation, and XRF point analysis. XRF analysis was completed with a Bruker ARTAX XRF spectrometer with a rhodium anode x-ray tube operating at 40kV accelerating potential and 400μA current. Follow up point analysis was done with reflectance and Raman spectroscopies. A Thermo Scientific DXR3 Raman microscope with an external arm using a 10× objective was used to focus on the surface of the paintings held upright on a tabletop easel. Two excitation lasers, 532 and 785nm, were used for collection depending on the materials. FORS was carried out with an Ocean Optics halogen light source and Ocean Optics Flame miniature spectrometer (400-980 nm range). One watercolor was also analyzed by RIS, using a Nireos HERA visible/near-infrared (400-1000 nm) hyperspectral camera and HERA analysis package which utilized the Spectral Angle Mapping (SAM) algorithm.

3. RESULTS AND DISCUSSION

Analysis of seven watercolors reflects her frequent use of and the broad availability of both traditional and synthetic pigments in the late nineteenth and early twentieth centuries.

Some findings include:

- The blue pigments found were most often cobalt blue and ultramarine and slightly less frequently cerulean blue and Prussian blue. When one of the latter pigments was detected, it would be in addition to the presence of one of the former blue pigments. One unique pigment found in a mixture of blue and green pigments in *The Grand Mosque of Tangier* (1900) in the dark teal of the mosque's shadow is crystal violet (PV27), a triarylmethane dye. While it is similar to reference materials, the slight variation in Raman spectra suggests this pigment has altered and degraded over time (Cesaratto, et al. 2017).

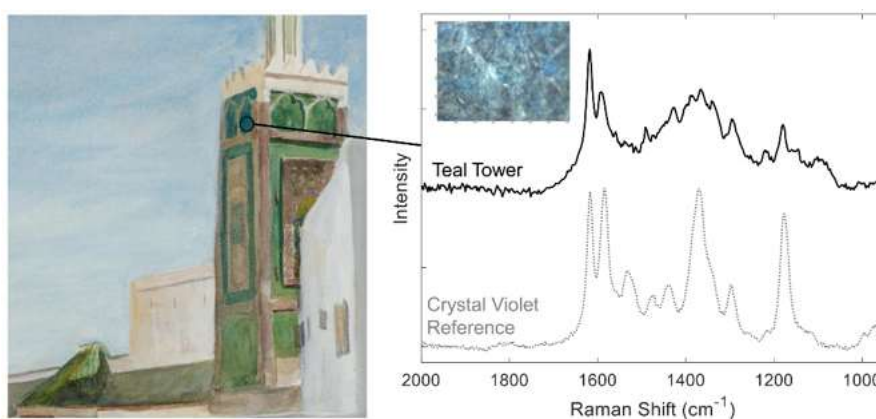


Figure 1. Raman spectra of the teal area compared to reference spectra of crystal violet (PV27). The analysis location is indicated on a detail of *The Grand Mosque of Tangier* by Emily Sargent, 1900. (MFA 2021.97)

- In several watercolors, zinc white is a major material used, mostly as a paint opacifier. However, it is noticeably absent in two of Emily's works, *Buildings, Genoa* (1877) and *Statue of the Madonna* (1908), in favor of lead white. *Buildings, Genoa* is the earliest dated work analyzed and lacks the addition of opacifiers; the white pigment is very minimal in this work. It is only present in the pink of the tower along with vermilion to provide a lighter color. *Statue of Madonna* also does not use white as a major opacifier and instead it is used in areas of white or gray. The lead white paint in this case also contains blixite ($\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$) in addition to hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) (Eastaugh, et al. 2008).
- Several synthetic yellow and orange pigments were found in Emily's watercolors, showing an adoption of newer pigments that offered brighter tones. In addition to strontium yellow, cobalt yellow, chrome yellow, and cadmium yellow/orange, a notable find was an early use of an azobenzene dye, determined by Raman, and a relatively late use of arsenic sulfide pigments, determined by XRF. Both of these pigments were found in *The Grand Mosque of Tangier* (1900) and *The Dogana* (about 1908). While an exact match of the yellow or orange azobenzene dye could not be found, the spectra do show similarities to Mordant Orange 1 and Disperse Red 1 (Pause, et al. 2021; Bintinlaiye 2023), neither of which has previously been reported in watercolor painting. While these two watercolors are believed to be painted about 8 years apart, the overlap in unique pigments used in their creation is prompting reexamination of the dates.

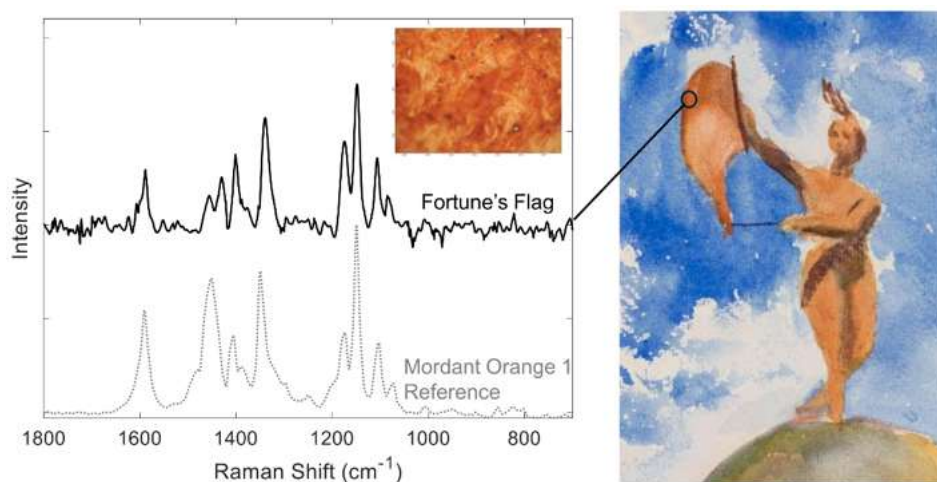


Figure 2. Raman spectra of the orange area compared to reference spectra of Mordant Orange 1. The analysis location is indicated on a detail of *La Dogana* by Emily Sargent, 1908 (MFA 2021.90)

4. CONCLUSION

This technical study is conducted in conjunction with archival research, including Emily Sargent's extensive correspondence documenting her travels. Together, these sources offer points of comparison with her brother's watercolors and his materials, contribute to establishing a chronology of her watercolors, and provide insight into her working practices as they evolved over a fifty-year career.

5. ACKNOWLEDGMENT

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OUT OF THE BLUE: DISCOVERING BROMINATED INDIGO IN A HAND-COLORED PHOTOGRAPH

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Non-invasive analysis of hand-colored photographs presents considerable challenges due to the small amount of colorant, fragile surface, and potential interference from the photographic support. Nevertheless, the combined use of external-reflectance Fourier transform infrared (ER-FTIR), Raman, and X-ray fluorescence (XRF) spectroscopy can enable pigment identification. This approach was applied to several hand-colored photographs by James Van Der Zee in the collection of the National Gallery of Art. The investigation of *Violinist* (2019.127.3) resulted in the identification of a brominated indigo species not previously described in the cultural heritage literature.

The identity of the blue colorant used by Van Der Zee remained elusive, despite distinctive Raman and XRF spectra. A breakthrough occurred when a match for these spectral signatures was found among a study collection set of photo-coloring pencils, permitting more invasive analyses. Current evidence indicates that the major species in both pencil and artwork is 5,5',7,7'-tetrabromoindigo (Ciba Blue 2B). A corroborating example of the dye on cotton was found in a historic Ciba sample book, and a commercial sample of the dye powder was also obtained. Chemical separation by chromatography and molecular weight confirmation through mass spectrometry is pending.

THE HOUSE OF MANY COLORS AND ITS COLORANTS (OLYNTHUS, GREECE)

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The House of Many Colors at Olynthus is often used as the textbook example demonstrating the plan and appearance of a late Classical Greek house. The house seems to have been in the course of being painted just at the time when Philip II of Macedon, Alexander the Great's father, besieged and set fire to the city in 347 B.C. David M. Robinson collected samples of the pigments and wall plasters during the excavations of this house in 1938, a fortunate circumstance since the house was thereafter backfilled. These materials, now held in the collection of the University of Mississippi Art Museum, provide an opportunity to analyze the range of colors once in use, thereby making it possible to finally define the “many colors” of this famous house. Modern archaeometric analysis of these materials, using XRF, Raman, FTIR, and SEM-EDS will be assessed in order to explore the pigments used on site and compare them to contemporary pigment use from this era. In addition, Robinson experimented with the pigments by painting “samplers”, a destructive choice also worth examining. The colorants of the House of Many Colors provide an opportunity to explore the life of these materials before they were put on the walls, how they were used on the walls, and their use in poor experimental archaeology in the modern era.

EARLY SYNTHETIC ORGANIC PIGMENTS: OCCURENCES IN THE WORKS OF ART

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The second half of the 19th century marked a turning point in dye chemistry with the synthesis of numerous organic compounds, primarily developed for dyeing textile. However, historical and analytical data indicate that some of them were also used as artistic pigments. Among them were Basic Fuchsin (1856), Acid Fuchsin, Methyl Violet (1876), Methylene Blue (1876), Victoria blue (1882), Naphthol Green B (AG 1 or PG 12; 1883), Tartrazine (1884), which are the subject of this report.

This study is devoted to the identification in authentic and dated artworks of above-mentioned organic pigments some of that have not previously been found in painting. The examined artworks were created by well-known artists, including Aristarkh Lentulov and Nicholas and Svyatoslav Roerich. Most of the paintings were executed in tempera technique, while one work by A. Lentulov was created using artistic ink. The primary methods used to identify organic pigments and dyes were Infrared and Raman spectroscopy, but in some cases, the use of physical-optical methods was essential in the study of multicomponent paint samples. For example, polarized light microscopy made it possible to establish the presence of a small amount of organic pigment in the green paint layer of a work by Nicholas Roerich.

The obtained results expand our understanding of the use of early SOPs in painting and refine the chronology of their application.

HUE KNEW! - CHARACTERIZATION OF RARELY USED CHROME YELLOW IN 20TH CENTURY AFRICAN TEXTILES

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Chrome yellow (lead chromate, PbCrO_4), a well-documented artist pigment, is also noted to have been used as a textile colourant. Though mentioned in 19th-century dyeing manuals as superior to vegetal dyestuffs due to its lightfastness, there are few confirmed examples of its use on historic textiles. This is likely due to its limited use for cotton fibres, since it is highly damaging to proteinaceous fibres. Additionally, the earliest commercial availability of chrome yellow was 1818; however, the introduction of aniline yellows after the 1860s appears to have quickly replaced it in textile dyeing, possibly due to the complications and hazards of the chrome yellow dyeing process. As such, only a few case studies have identified its use sparingly, often as embroidery threads. In preparation for exhibition in the new David Geffen Galleries at the Los Angeles County Museum of Art (LACMA), X-ray fluorescence (XRF) analysis identified Cr and Pb in the prominent yellow weaving of a 20th-century prestige garment from the Ewe people of West Africa. The rarity of chrome yellow in historic garments, as well as the unexpected use of this dyestuff much later than the 1860s combined with few dye studies of West African textiles prompted an analytical survey of similar 20th-century West African textiles in LACMA's collection. In situ XRF analysis, combined with micro-samples, analyzed using optical microscopy and Raman spectroscopy allowed for lead chromate to be conclusively identified and characterized on all studied textiles. The results contribute to the growing case studies identifying the use of chrome yellow as a fibre colourant that was used in historic textiles, acting as one of the first studies showing the longevity of the practice, as well as gives insight into the material availability and practices of 20th-century West African textiles.

LOOKING PAST THE LUSTRE: UNRAVELING THE MATERIALITY OF MODERN JAPANESE METALLIC THREADS

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Metallic threads have been used as ornate decorations in textiles by many cultures for centuries. They were most commonly created using precious metals, such as gold, silver, or copper, and were either drawn into wires or beaten into thin sheets. They could then be used on their own or twisted around other textile fibers. While this was a common method to create luminous threads, other cultures developed different techniques to achieve a similar outcome. Though Japanese lacquerware is most often connected to furniture and objects, the use of urushi has also been applied to textile threads. “Urushi threads” describe the process of applying lacquer to silk, paper, or other fibers to create a reflective surface that could be further altered by applying metallic or pigmented powder to achieve different colours. While this is a known craft, there are limited studies focused on the full material characterization of these threads. As such, a technical study was undertaken on a kimono-style coat from the 1960s in the collection at the Los Angeles County Museum of Art (LACMA). The lustrous patches of gold, silver, blue, and red that decorate the garment were of particular interest in determining how these metallic-looking threads were constructed. A multi-analytical approach was conducted to fully characterize the materials used to create these threads including attenuated total reflection-Fourier transform infrared (ATR-FTIR) and Raman spectroscopies, pyrolysis gas chromatography-mass spectrometry (py-GC-MS), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), and optical microscopy. Results indicated that urushi lacquer was applied to a cellulosic substrate and powdered pigments were applied on top. The obtained results will shed light on the craftsmanship used to create these threads and contribute to the growing literature, allowing for further comparative studies on production methods used over time to be made.

**IMAGE IDENTIFICATION AND PIGMENT ANALYSIS OF 19TH CENTURY
JAPANESE UTAGAWA SCHOOL PRINTS: AN INTERDISCIPLINARY STUDY AT
RUTGERS UNIVERSITY**

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Among the artworks archived at the Rutgers University-Camden Center for the Arts (RCCA) is a collection of sixteen Ukiyo-e Japanese polychrome woodblock prints donated by an emeritus Rutgers–Camden art history professor. The collection is the focus of an interdisciplinary research project led by Professors Arbuckle (Chemistry) and Wu (Visual Media and Performing Arts) and supported by Rutgers Camden Chancellor funding. The project has enabled undergraduates in chemistry and art history to engage in cultural heritage research, investigating the materials, techniques, and historical contexts of the woodblock prints.

One key print studied is *Story of Cherry Blossoms on Higashiyama* (c. 1851) by Utagawa Kunisada (1786-1864). Selected in part for its depiction of kabuki actors, the print reflects the cultural significance of kabuki theater in Edo-period Japan (1603-1868). Part of a triptych depicting a scene from a play inspired by *The Rustic Genji*—a parody of the canonical *Tale of Genji*—this work demonstrates innovative approaches to *Genji* iconography and exemplifies the intertwined histories of image-making across literature, the visual arts, and the performing arts.

Chemical analysis of the prints was undertaken non-invasively via external reflectance (ER) Fourier transform infrared (FTIR) spectroscopy. Microscopic samples were utilized for transmission FTIR and Raman microspectroscopy. Upon arrival at the RCCA, the prints exhibited curled and damaged edges with some loose fragments from which the micro-samples were carefully acquired.

Initial characterization of the colorants using ER revealed the presence of Prussian blue pigment (distinct cyanide band at 2096 cm^{-1}). Subsequent analysis of the red pigments necessitated Raman to distinguish the presence of red iron oxide pigment (bengara). The latter pigment has a long history of use in Japanese prints, while Prussian blue is noted in later Edo-period works. The full findings of this research project will be jointly presented, along with commentary on the student experience.

FTIR AND RAMAN ANALYSIS OF EARLY PRINTING INKS

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The composition of early printing inks is uncertain. In East Asia, while it has been presumed that the inks used for woodblock printing are identical to the inks used for calligraphy and painting, modern practitioners add rice starch (nori 糊) to the ink to improve handling characteristics of the ink. Although regarded as traditional it is unclear when the addition of nori to printing inks became common practice. In Korea, printing on movable metal type was common for certain documents from the 15th century, however it has commonly been thought that the water-based inks commonly used for woodblock printing, painting, and calligraphy would not be suitable for use on metal type. FTIR and Raman are able to identify the two main components of printing inks, proteinaceous glue and soot. Peaks for both are the only components found in the movable metal type Korean documents from the 15th to 17th centuries that were analyzed, demonstrating that even for movable metal type, Koreans used a water-based ink similar in composition to that of the inks used for calligraphy and painting.

SPECTROSCOPIC INVESTIGATION OF THE PRINTING INKS AND APPLIED PAINTS USED IN EDVARD MUNCH'S PRINTS

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1. INTRODUCTION

Inks and applied colors on Edvard Munch prints in the Harvard Art Museums' collections were analyzed as part of a study to investigate the printmaking materials and techniques used by Edvard Munch (1863-1944). Technical analysis was undertaken on most of the 134 Munch prints in the collection, which includes woodcuts, lithographs, and intaglio prints. Munch used a jigsaw technique for his woodcuts, cutting the woodblocks into irregular shapes and reassembling them to create varied multicolored compositions, as seen in Fig. 1 for three versions of *Woman's Head Against the Shore*. The use of different printing inks or applied color for prints within a series further increased the variations possible. This presentation focuses on the printing inks and applied paints. An overview of the complete study can be found in Schleicher et al 2026.



Figure 1: Three versions of *Woman's Head Against the Shore*. Left-right: 2012.261; 2012.272; 2023.597: although the image size is similar for the three versions, the sheet size varies. © President and Fellows of Harvard College.

2. MATERIALS AND METHODS

The printing inks and applied colors were analyzed in-situ with Raman spectroscopy, external reflectance Fourier transform infrared (ER-FTIR) spectroscopy, x-ray fluorescence (XRF) and fiber optic reflectance spectroscopy (FORS) to determine the materials used. Rare samples were taken from areas of thicker applied color for transmission Fourier transform infrared (TR-FTIR) and Raman spectroscopy for more accurate identification.

3. RESULTS AND DISCUSSION

The most common colors for the printing inks were black, blue, green, red, orange and yellow, with most white areas found to be unprinted paper. In-situ analysis by all techniques revealed a limited palette of pigments within the printing inks. Prussian blue was the most common blue pigment used, both alone and in mixtures. Prussian blue was mixed with carbon black for the black ink on over half the prints analyzed, presumably to modify the tone. Different shades of blue and green were obtained by varying the amount of Prussian blue in the printing ink and by mixing it with chrome yellow in differing proportions. Only three prints contained ultramarine, mixed with Prussian blue in one print and with chrome yellow and chrome green in another. Analysis of red printing inks showed that vermilion and organic red pigments were most common, with alizarin identified by TR-FTIR in a rare sample. TR-FTIR also indicated an oil binder in this sample, as expected for printing inks. In addition, red ocher was identified in a few prints, often mixed with organic red. Orange printing inks were found to contain various mixtures of organic red, vermilion, red ocher, and chrome yellow or orange. Chrome yellow was used for nearly all yellow printing inks, with only one instance of yellow ochre. Complex mixtures of organic red, ultramarine and cobalt violet (cobalt arsenate) were identified in rare pink-violet and purple-red inks, with the proportions of the different pigments adjusted to control the desired shade.

A much wider variety of pigments were identified in the applied colors, which included watercolor, crayon and oil paint. Small samples were taken of some watercolor and oil paints where possible, but it was not possible to sample the crayon. However, in-situ analysis of prints with applied crayon identified Prussian blue in blue crayon, a mixture of Prussian blue and chrome yellow in green crayon, chrome yellow in yellow crayon, and a mixture of red lead and lead white in orange crayon.

In-situ analysis of applied watercolor on several prints identified Prussian blue, vermilion and cadmium yellow as the main colorants. TR-FTIR of a sample from one print identified gum as the binder, confirming the use of watercolor.



Figure 2: *Fertility*, 2023.603, showing extensive handcoloring of the original monochrome print. © President and Fellows of Harvard College.

One originally monochrome print, *Fertility*, shown in Fig. 2, was extensively hand colored several years after printing. In-situ analysis of this print indicated a wide variety of pigments including Pigment Red 3 (PR3), Pigment Green 1 (PG1), cadmium yellow, cobalt blue, Prussian blue, zinc yellow, and likely zinc white. One area of red paint is noteworthy for the glossy, red appearance, which suggested it may have a different binder than the other applied paints. However, TR-FTIR analysis of a small sample identified gum binder, showing this was also watercolor paint, and confirming the use of PR3. Both PG1 and PR3 were developed in the early 20th century during Munch's lifetime, consistent with application by the artist.

In-situ analysis of applied oil paint on Munch prints identified a wide range of pigments, including Prussian blue, ultramarine, cobalt blue, cobalt violet, lead white, zinc white, organic red, cadmium red, cadmium yellow, chrome green and bone black mixed with organic red and cadmium red for dark red. TR-FTIR and Raman analysis of samples confirmed the pigments obtained with in-situ analysis and the use of an oil binder.

Comparison of prints from a single set, such as the three versions of *Woman's Head Against The Shore* (shown in Fig. 1), reveal how Munch manipulated different printing inks and applied color to create strikingly different art works from the same blocks. The variety of printing inks used for *Woman's Head Against the Shore* is shown in Table 1.

Table 1: Pigments identified in printing inks used in versions of *Woman's Head Against the Shore*

Accession Number	Red	Orange	Peach	Dark blue	Light blue	Grey green
2012.261		organic red	Organic red	Prussian blue, chrome yellow		
2012.272	vermilion	organic red		Prussian blue, ultramarine	Prussian blue	unknown
2023.597	vermilion	organic red, (hematite)		Prussian blue	Prussian blue	

4. CONCLUSION

A combination of in-situ analysis and analysis of selected samples identified many of the pigments used for printing inks and applied color on Edvard Munch prints in the collections of the Harvard Art Museums. Further analysis is required to identify some pigments which cannot be sampled, for example colorants used in grey-green areas. Comparison of prints made from the same blocks shows how Munch manipulated both the woodblocks and the materials to create unique works within a series. The prints analyzed in this study represent only a fraction of those created by Munch, and it is hoped that this will prompt analysis of works in other collections.

5. ACKNOWLEDGMENT

The authors thank our colleagues at the Harvard Art Museums, particularly Penley Knipe and Elizabeth Rudy for their support of the research, which stemmed from the exhibition, Edvard Munch: Technically Speaking. We also thank everyone in Collections Management who facilitated movement of the many prints for examination and analysis. This work was performed in part at the Harvard University Center for Nanoscale Systems (CNS); a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. ECCS-2025158.

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UNMIXING CARBON-BASED AND METALLO-TANNATE HISTORICAL INKS IN MIDDLE EASTERN AND NORTHERN AFRICAN WRITTEN HERITAGE

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The identity of black-brown inks in hand-written heritage from the ancient to pre-modern Middle East is a subject of on-going interest. Studies include new translations of historical Arabic treatises, along with research on replicate inks and new categorization as carbon, metallic, tannin, metallo-tannate, or mixed compositions. Consistent with a de-colonialization of historical narratives, there is interest in tracing the origin of iron gall ink (IGI), metallo-tannate inks which dominated hand-written heritage in Western Europe from the Middle Ages to the 19th century. Increasing evidence shows that Western ink technology spread from the Middle East with Christianity. Analysis of historical inks from ancient Egypt and Israel support the earliest inks being carbon-based, similar to predecessors from Asia; however, the history of changeover to metallo-tannate inks remains murky.

Common analytical techniques for identifying Middle Eastern inks are based on XRF and multi-spectral imaging (MSI). The latter methods stem from well-known observations that IGI becomes transparent in the near and short-wave infrared (NIR, SWIR), while carbonaceous materials remain dark. However, MSI methods are far from standardized and often used without an understanding of device limitations or properties of inks that affect their responses.

This poster summarizes recent work at the Library of Congress that evaluated methods for distinguishing mixed inks by XRF, Raman spectroscopy, MSI, and Vis/NIR/SWIR fiber optic reflectance spectroscopy (FORS). Historical materials from the Library of Congress included an Al Burdah manuscript on paper (15th century?) and a collection of Qur'anic folios on parchment (7th – 12th centuries). Mock-up samples of mixed carbon black and IGI were also examined. Results indicated that these techniques are fairly reliable in combination, but not alone. Furthermore, FORS revealed details about the ink behavior in an accessible and easy to process method.

IDENTIFICATION OF ORGANIC MATERIAL ON WALL PAINTINGS AND STONE SCULPTURES – PAINT OR/AND BIOGENIC STRUCTURES?

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1. INTRODUCTION

Various wall paintings and sculptures are created using secco techniques with organic binding media. Art historians and conservators are interested in learning more about the materials applied by artists and craftsmen throughout the centuries. Conservation materials are sometimes added, but without documentation, they are often difficult to identify. Degradation processes over centuries can alter the chemical composition. Organic matter due to biological growth presents additional challenges. Identifying biological residues from fungi and/or algae and distinguishing them from paint residues is difficult when the material is completely dried and cellular structures are not visible. Proteins are known to be found in glue, egg, and casein tempera, as well as fungi. Cellulose and its derivatives indicate plant growth such as algae and lichens but can also be present in binders. Chitin is found in fungi and insects.

2. MATERIALS AND METHODS

Several colored layers on walls and stone sculptures were analysed to identify organic matter on inorganic structures using optical microscopy (Zeiss Axio Imager.A2m), Fourier Transform infrared spectroscopy (Bruker Alpha II and Bruker Invenio-S IR spectrometer with Hyperion 3000 microscope), and pyrolysis-gas chromatography-mass spectroscopy (EGA/Py-3030D by Frontier Laboratories Ltd. attached to an Agilent GC/MSD System (5977A Series)).

3. RESULTS AND DISCUSSION

Typical FT-IR bands of proteins, cellulose and its derivatives, lignin, and chitin were studied (Figure 1) and identified on paint layering systems of wall paintings, secco paint reconstructions, and soiled surfaces.

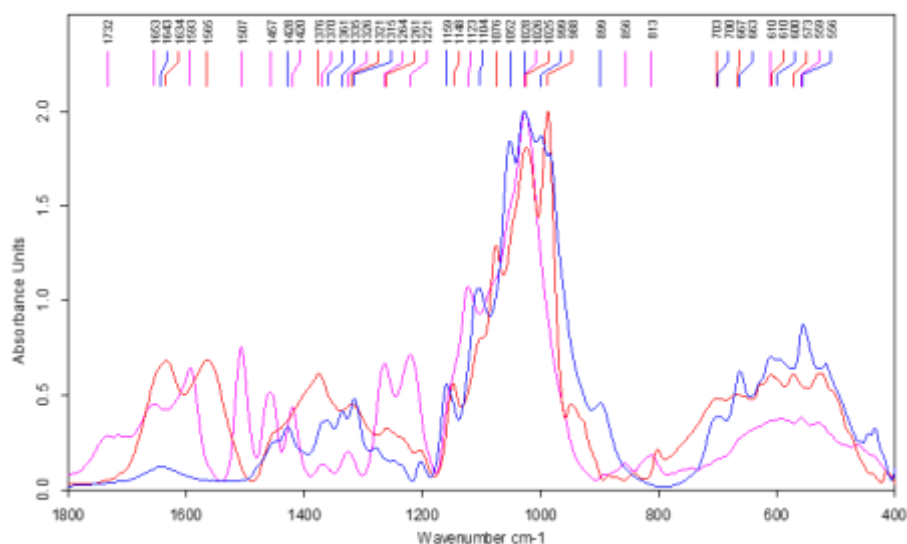


Figure 1. FT-IR spectra of cellulose (blue), chitin (red), and lignin (pink)

Most different between cellulose, lignin, and chitin were bands between 1200 cm^{-1} and 1800 cm^{-1} in reference samples. However, in original old samples, these bands were often covered by matrix. Therefore, Py-GC-MS analysis was carried out (Figure 2) in addition to microscopy and IR spectroscopy. This added information and often helped with interpretation. Nevertheless, not only the identification of a material in a sample, but also its exact location in it, are often crucial pieces of information, leading to a better understanding of the paint and layering system and any biological contamination. FT-IR imaging and traditional staining of cross-sections gave further information and helped in the process of interpreting data.

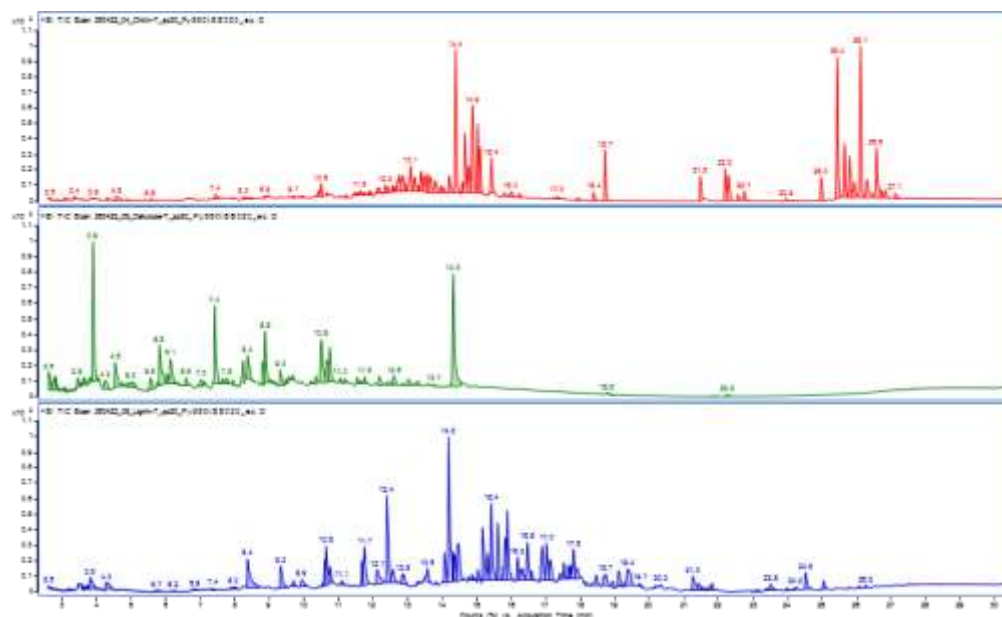


Figure 2. Chromatograms of chitin (red), cellulose (green), and lignin (blue) references

4. CONCLUSION

Achieving conclusions requires a multi-analytical approach. Analytical results of a complex system together with historical context information, interpreted collaboratively by conservators, biologists, and historians, often provides valuable insights into the composition of paint systems and the probable ageing of coloured layers. However, conclusive identification is not always possible. Organic binders may be severely degraded, obscured by previous conservation treatments, or contaminated by environmental deposits, limiting the interpretability of analytical results. In such cases, acknowledging uncertainty is not a weakness but an essential aspect of rigorous scientific practice. Fostering a culture in which doubt and analytical limitations are communicated transparently strengthens the credibility of heritage science. It also encourages the continued development of improved methodologies and closer collaboration among experts employing complementary analytical techniques.

5. ACKNOWLEDGMENT

I thank the team of the Rathgen-Forschungslabor, especially Betül Sezgin, for taking FT-IR reference spectra and Bill Landsberger for discussing ideas regarding biological growth on stones.

CHARACTERIZATION OF THE MATERIALS AND TECHNOLOGY USED IN XVI-XVIII CENTURY TAPESTRIES BY SPECTRAL AND MICROSCOPIC METHODS

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The focus of the study is 11 tapestries and 6 sets of upholstery from the National Gallery Sofia, inventoried under provisional titles, without dating or relevance to a school, defined only as Western European textiles. The identification of stylistic and iconographic characteristics was carried out in parallel with instrumental analyses. The weaving materials were studied by scanning electron microscopy energy dispersive X-ray spectroscopy (SEM–EDS), attenuated total reflectance Fourier transform infrared (ATR–FTIR) and surface-enhanced micro-Raman spectroscopy (SERS). Broader ATR-FTIR analysis differentiated dyed wool and silk weft threads, undyed original wool and secondary cotton warps in historical repairs. SEM-EDS showed the yarns' morphology and identification of metal salts applied for pretreatment of the textile fibers and mordants – alum, blue and green copper sulfate, tin salts. The analysis of the blue, red, and yellow dyestuff was carried out by the ATR–FTIR and SERS methods directly on the threads or after microextraction with solvent mixtures. The blue colorant was identified as indigotin-based, while the red threads indicated cochineal and alizarin (madder) dyes. The micro-Raman spectrum of some yellow dyed threads showed the closest similarity to the Persian berries dye. The combined visual and material identification led to the attribution of the tapestries. They were determined to belong to the 16th–18th centuries golden periods of the Flemish and French tapestry tradition and shown in an exhibition in March – October 2025.

Acknowledgments: Research equipment of Distributed Research Infrastructure INFRAMAT, supported by the Bulgarian Ministry of Education and Science is used in a part of this investigation. The exhibition, conservation and attribution is executed with funding from the Ministry of Culture of Bulgaria under project contracts № RD 11-06-761/13.12.2024 and № RD 11-06-239/12.12.2023.

FANTASTIC BEASTS: ANALYSIS OF A 13TH CENTURY SPANISH FRESCO TO INFORM CONSERVATION TREATMENTS

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1. INTRODUCTION

The Harvard Art Museums' collections include a rare early 13th century fresco (Figure 1) that previously decorated the wall of the chapterhouse of San Pedro de Arlanza monastery in Burgos, Spain, as part of a larger group. These frescos were covered by plaster during remodeling of the monastery and were only exposed in the late 19th century due to damage to the building. In 1929 the entire fresco cycle was removed from the monastery walls by the *strappo* technique and dispersed between different collections, including the Harvard Art Museums, the Metropolitan Museum of Art, and the Museu Nacional d'Art de Catalunya.



Figure 1. Fresco from San Pedro de Arlanza Monastery, Harvard Art Museums 1938.124, before conservation © President and Fellows of Harvard College

The *strappo* method involved attaching fabric to the painted surface with animal glue, mechanically removing the pigment layer, and transferring it to a new canvas support, reputedly using lime casein. This resulted in a powdery and fragile surface, altered the stratigraphy and introduced new materials. Subsequent conservation treatments caused further deterioration and disfigurement. Current conservation treatments require a better understanding of the materials present and their distribution within the new stratigraphy. This presentation presents the analysis of the frescos to determine the materials and stratigraphy. For more details on the study, see Morilla et al. (forthcoming).

2. MATERIALS AND METHODS

To aid the planned conservation and display of the fresco and ascertain the materials and stratigraphy present, samples were taken from the Harvard Art Museums' fresco, mock-ups produced to test different conservation treatments, and a rare sample from a remaining in-situ fresco fragment. Samples were analyzed using transmission Fourier transform infrared (FTIR) and Raman spectroscopy and scanning electron microscopy with energy dispersive microanalysis (SEM-EDX). Larger samples were mounted as cross-sections to reveal the complete stratigraphy of paint and ground layers. The materials and stratigraphy were compared with those of samples from remaining in-situ frescos in the monastery and from mock-ups produced for testing different conservation treatments. Point analyses and mapping were undertaken to gain a thorough understanding of the stratigraphy and organic media. Mapping was undertaken in external reflectance FTIR and attenuated total reflectance FTIR modalities to compare the results and principal component analysis (PCA) investigated to discriminate between different organic media.

3. RESULTS AND DISCUSSION

Analysis revealed a thin surface layer of whewellite (calcium oxalate monohydrate), variations in stratigraphy from samples across the fresco, concentrations of calcium sulfate versus calcium carbonate, likely from remnants of plaster remaining after the frescos were uncovered and pulled off the walls. Cross-sections from the Harvard mural showed that the layers were highly porous and disrupted, contrasting with the solid coherent layers of the cross-section from the in-situ fresco. As a result, ATR-FTIR mapping from cross-sections was dominated by the mounting resin, necessitating spectral decomposition. The combination of optical and SEM imaging, FTIR, Raman and SEM mapping of the cross-sections helped isolate the location of organic layers within the transferred fresco, showing the complex stratigraphy. However, although protein-rich layers were identified, there was no evidence for a distinct casein layer as opposed to animal glue.

4. CONCLUSION

The combination of spectroscopic techniques, with both point analysis and mapping, and data

processing techniques revealed the complex stratigraphy and materials and identified key differences between the Harvard murals, mock-ups and in-situ samples. Although casein had been proposed as the material used for the transfer, no clear evidence was found for casein rather than animal glue. Subsequently, the use of cattle glue was confirmed by matrix assisted laser desorption-time of flight-mass spectrometry (MALDI-TOF-MS) analysis of a sample from the Harvard mural. The use of cattle glue rather than casein may partially explain the poor preservation of these frescos. Identification of the surface efflorescence enabled development of a conservation strategy for cleaning the fresco for exhibition

5. ACKNOWLEDGMENT

We are grateful to our colleagues at the Straus Center for Conservation and Technical Studies for their support and to Dan Kirby for analyzing a sample with MALDI-TOF-MS. We also thank our colleagues in Barcelona for their assistance with the comparative study of the Spanish also fragments: Sílvia Yagüe, Núria Oriols, Carme Ramells, Jorge Otero, and Carlos Rodríguez Navarro. We likewise thank our colleagues at the Metropolitan Museum of Art: Julia Perratore, Kristin Holder, and Alan Miller. Finally, we are grateful to our colleagues at Harvard University: Felipe Pereda and Jeffrey Hamburger.

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SPECTROSCOPIC CHARACTERIZATION OF 2,5-HEXANEDIOL AS A TREATMENT FOR MITIGATING COPPER ION-INDUCED PAPER DETERIORATION

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1. INTRODUCTION

The long-term preservation of historical and cartographic materials in archival collections is challenged by chemically induced degradation associated with traditional inks and pigments. Copper-containing paints and inks accelerate the deterioration of paper and related substrates. Copper-containing paints and pigments, as well as historical ink formulations containing copper, accelerate the deterioration of paper and related substrates. Copper ions present in these materials catalyze the oxidative degradation of cellulose in paper-based cultural heritage. These Cu²⁺ ions participate in Fenton-type reactions, generating highly reactive hydroxyl radicals that cleave the β-1,4-glycosidic bonds in cellulose, thereby accelerating material deterioration (Jablonsky and Šima 2021; Yan 2023). This study investigated the potential of 2,5-hexanediol (2,5-HDO) as a stabilizing treatment for copper-containing paints and inks on paper.

2. MATERIALS AND METHODS

To evaluate the effectiveness of 2,5-hexanediol (2,5-HDO), model paper samples were prepared using copper sulfate-containing ink formulations and malachite and verdigris paint analogs prepared with gum Arabic or fish glue. The samples were divided into untreated controls and samples treated with an aqueous 2,5-HDO solution, followed by accelerated aging under controlled temperature and relative humidity conditions. Degradation processes were characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and pH measurements.

3. RESULTS AND DISCUSSION

Artificial aging resulted in decreased pH values in paints on paper, indicating degradation-related chemical changes. No significant FTIR spectral changes were detected in malachite-containing samples, whereas verdigris-containing samples exhibited additional absorption bands consistent with copper formate formation. X-ray diffraction analysis confirmed the formation of copper formate in verdigris-containing samples after artificial aging. Samples treated with inks and 2,5-HDO exhibited smaller decreases in pH during artificial aging.

4. CONCLUSION

The results provide some evidence that 2,5-HDO can mitigate copper-catalyzed degradation, supporting the development of new conservation strategies for irreplaceable historical documents and artifacts. However, further research is required to assess the long-term performance of 2,5-HDO and validate its applicability to a broader range of historical materials and conservation conditions.

5. ACKNOWLEDGMENT

The author thanks the Wroblewski Library of the Lithuanian Academy of Sciences for providing access to research resources and archival materials.

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INVESTIGATING LONG-TERM OUTDOOR WEATHERING OF A POLYMERIC COATING ON A CONTEMPORARY MURAL

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1. INTRODUCTION

Protective coatings for modern and contemporary murals exposed outdoors serve fundamental functions, including acting as a physical barrier to environmental agents, providing protection against photo-degradation, modulating water ingress, enhancing color saturation, and facilitating graffiti removal (Pagnin, Goidanich, Guarnieri, et al. 2025). Investigating coating deterioration is critical to inform long-term conservation strategies, and to reduce the potential onset of color alteration and material degradation.

This study focuses on *Inner Resources*, a large (25x11m) outdoor mural painted in 2000 by artist Paul Botello on the south-facing wall of a gym in City Terrace Park, East Los Angeles (Barnet-Sanchez and Drescher 2016) (Figure 1). It was conceived as a community-based project: the artist actively involved local residents during the design phase, integrating their input into the mural's iconography, and collaborated with neighborhood participants throughout its execution. As a result, the work has become a meaningful and cherished landmark within the local community.



Figure 1. Orthorectified photo of *Inner Resources* (©Site&Studio Conservation, 2024).

Inner Resources was painted with commonly used materials for modern muralists: artist-grade

acrylic paints on a concrete-based support, and a protective coating on top. Based on direct communication with the artist, the coating has been identified as a commercial acrylic copolymer widely employed for outdoor mural protection across the LA area. As a result of the long-term outdoor exposure, the coating had developed significant degradation patterns, including cracking, detachment, and loss of transparency. Similar patterns have been observed on coating-protected murals subjected to comparable challenging outdoor exposure conditions throughout the Los Angeles County area, characterized by year-long intense solar radiation, direct rain exposure, and atmospheric pollution.

Due to the severity of the deterioration, the Los Angeles County Department of Arts and Culture commissioned a conservation intervention for the mural, which was carried out in 2024 and integrated a diagnostic campaign to support the treatment. The objective of the scientific work was to answer relevant conservation questions on materials characterization and treatment performance, thus effectively informing the conservation work. In particular, a key research question focused on investigating the physicochemical changes in the coating and the potential mechanisms responsible for them through an integrated laboratory- and field-based approach. Here, we present the chemical characterization of the deteriorated coating after more than 20 years of natural exposure, investigated via FTIR.

2. MATERIALS AND METHODS

Micro samples were collected from the mural's surface in areas showing significant coating deterioration.

A Dino-Lite 5MP Edge AM7915MZT Digital Microscope was used to conduct a preliminary investigation of the surface, identify representative surface conditions (different colors and states of conservation of the coating), and document each sampling area. An external LED light was used for consistent raking light illumination.

A Bruker Hyperion μ -FTIR with a Vertex 70 spectrometer was used to analyze the samples. The spectrometer is coupled with a Hyperion 3000 microscope, equipped with an MCT detector and a 15X IR Cassegrain objective for micro-IR measurements. Analyses were carried out in transmission mode working on micro-fractions of samples after preparation in a diamond compression cell. For each sample, 64 single scans were averaged within the 600-4000 cm^{-1} spectral range.

Laboratory reference samples of the same commercial acrylic coating, prepared at the Getty Conservation Institute (GCI) in 2009 as part of a treatment study on coatings for modern and contemporary murals (Macdonald-Korth, Rainer, and Learner 2015) and stored away from natural light, were analyzed to provide comparative data from long-term cured, not UV-aged

materials.

3. RESULTS AND DISCUSSION

Micrographs acquired from the sampling areas allowed the identification of surface features responsible for the degradation patterns observed macroscopically, such as the overall loss of transparency, which impacted the readability of the mural, as well as flaking, bursting, and peeling (Figure 2). The microscopic observation of the coating in areas of severe deterioration revealed extensive cracking, soiling, localized loss of adhesion from the paint substrate, and consequent material loss.

FTIR spectra of the coating were evaluated against an array of acrylic resin references. Best matching spectral features were found with Paraloid B48, a poly(methyl methacrylate) (Figure 3), with some significant differences: the peak at 1633 cm^{-1} and a broad absorption around $3600\text{--}3100\text{ cm}^{-1}$. Both can result from photoaging of the polymer. The band at 1633 cm^{-1} is ascribed to the stretching of double bonds: it is associated with the formation of conjugated double bond chromophores due to the crosslinking responsible for the formation of the polymer film at first, and for its discoloration later during ageing (Domenech Carbo, Bitossi, Yusa Marco, et al. 2006). The band at $3600\text{--}3100\text{ cm}^{-1}$ is due to the absorption of the hydroxyl group (OH): increased absorption in the hydroxyl region is typical in acrylic polymers, due to the loss of the R' part in correspondence of R-C-O-O-R' ester bonds (here, the methyl group) caused by photo-induced oxidation occurring on the side chains. For example, in the case of B67, which shares compositional similarities to the best-matching B48, a very broad absorption is documented,¹ with two relative maxima at ca. 3500 and ca. 3250 cm^{-1} , visible also here (Lazzari and Chiantore 2000).

Other signs of aging of the *Inner Resources* coating observed here are the broadening of the carbonyl band (1737 cm^{-1}), and an overall loss of structural resolution and sharpness of peaks in the fingerprint region ($1500\text{--}600\text{ cm}^{-1}$) (Lazzari and Chiantore 2000).

Overall, FTIR analysis therefore confirms that the visible deterioration pattern of the original coating can be attributed to photoaging of its polymeric structure. These chemical alterations are consistent with the physical deterioration patterns observed in the micrographs, which are typical manifestations of embrittlement in photoaged acrylic films.

Additional analysis compared the *Inner Resources* coating with a sample of the same commercial resin from the GCI archive described above, which underwent a similarly long curing (≈ 15 years) but without being exposed to UV and pollutants (Figure 4). The absence of ageing-related features in the reference sample confirms that the observed spectral differences in the *Inner Resources* sample result from long-term outdoor exposure and the consequent weathering.



Figure 2. Micrographs on representative areas of the mural showing recurring weathering patterns of the coating: cracking, detachment, and loss of transparency.

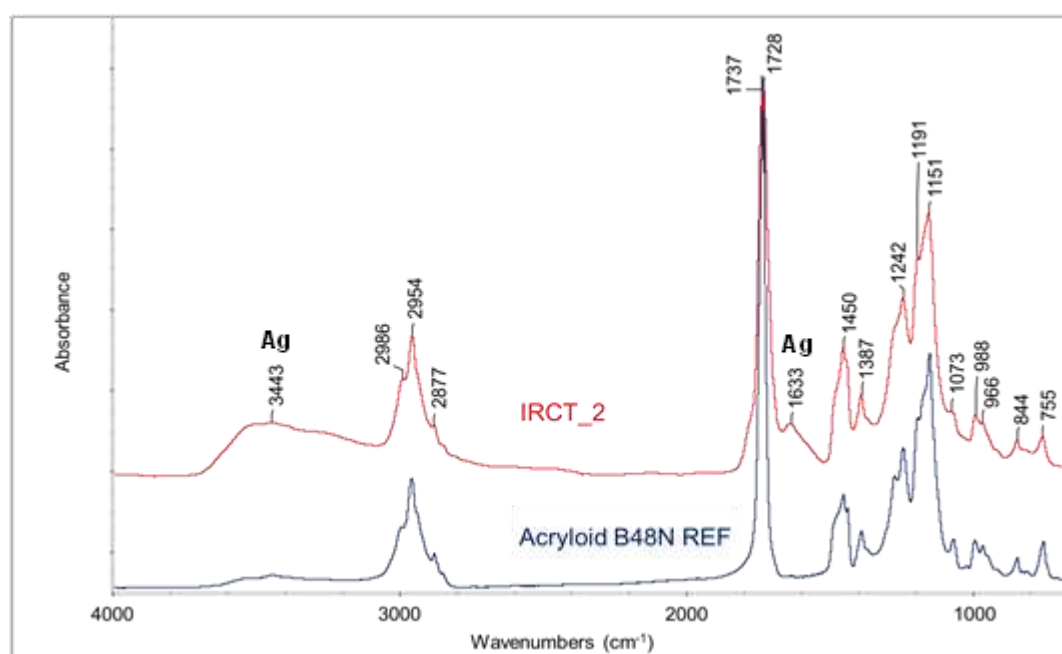


Figure 3. FTIR spectrum of a sample of the aged coating (“IRCT_2”, in red) compared to a reference Acryloid/Paraloid B48 resin. Peaks labelled with “Ag” indicate spectral changes associated with ageing of the coating.

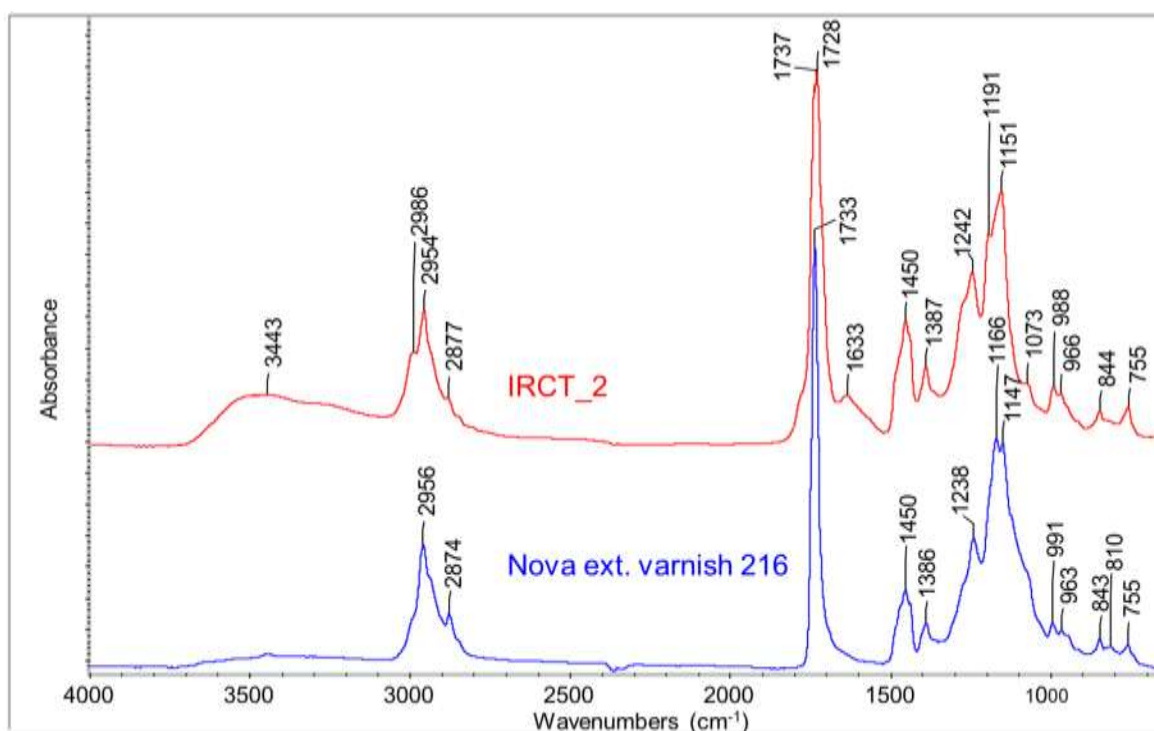


Figure 4. Experimental spectra of the aged coating (“IRCT_2”, in red) and a reference sample of the same commercial acrylic coating from the GCI archive (blue). Bands attributed to ageing of the *Inner Resources* coating are labelled with “Ag”.

4. CONCLUSION

The effects of weathering of the coating (cracking, loss of transparency, peeling) were visually observed during site surveys, documented via digital microscopy, and investigated through FTIR to characterize the chemical deterioration patterns of the polymeric matrix. FTIR analysis identified the coating as a poly (methyl methacrylate)-based polymer and highlighted chemical transformations associated with photo-oxidative degradation phenomena typically occurring in UV-aged acrylic paints and coatings and commonly associated with outdoor exposure. These molecular changes can be directly correlated with the macroscopic deterioration patterns observed in situ, caused by long-term exposure to solar radiation and environmental stressors. Comparison with a reference sample of the same coating subjected to long-term curing, comparable in duration to the *Inner Resources* ones but protected from exposure to solar radiation, confirmed that these alterations are primarily driven by outdoor exposure, highlighting the critical role of photoaging.

The results underscore that durability of acrylic copolymer coatings in highly exposed environments such as Los Angeles is challenging, with implications for similar outdoor murals in comparable climatic conditions. From a conservation perspective, these findings support the need to advance the research and on-site testing of alternative and innovative solutions with

enhanced UV stabilization for improved resistance to photo-oxidation.

More broadly, this study demonstrates the value of combining field observations with laboratory analysis and reference materials to better understand long-term material behavior and inform conservation strategies.

5. ACKNOWLEDGMENT

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UV/Vis/NIR FIBRE OPTICS ABSORPTION SPECTROSCOPY (FORS) FOR CULTURAL HERITAGE: A VALIDATED SPECTRAL REFERENCE DATABASE AND NON-DESTRUCTIVE DIAGNOSTIC PRACTICE

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1. INTRODUCTION

At the end of this presentation, you will know where the largest unresolved gap in non-destructive cultural heritage analysis lies — and what a validated UV/Vis/NIR spectral reference database covering the complete Kremer Pigmente colourant range can do to close it.

Fibre Optics Absorption Spectroscopy (FORS) in the UV/Vis/NIR range (300–1,100 nm) is today an accepted method for the in-situ, contact-free identification of colourants on polychrome surfaces, wooden objects, textiles, and canvas — without sampling, without laboratory preparation, directly on the object. The instrumentation exists. The methodology is established. The practice is international.

What does not exist is the reference data to match it.

No comprehensive, commercially available spectral reference database for UV/Vis/NIR absorbance data of historical colourants exists anywhere in the world. The IRUG database — the field's most recognised resource — provides over 3,600 peer-reviewed FT-IR and Raman reference datasets, oriented toward non-profit institutional access. UV/Vis/NIR is absent. The consequence is systematic: results cannot be compared across institutions, pigment identification remains experience-dependent, and the diagnostic potential of an established method goes structurally underused.

This project addresses that gap directly. In scientific collaboration between ZRW Berlin / artLABOR® (Westebbe) and Independent Conservator-Scientist Dr. Heinrich Piening — whose foundational dissertation established the methodological framework for mobile UV/Vis/NIR spectroscopy in conservation science (Piening 2008) — a validated spectral reference database is under construction, based on the complete Kremer Pigmente colourant range (~2,500 colourants, target: ~9,000 validated spectra). Project partners are Chroma Art Consulting and Kremer Pigmente GmbH & Co. KG.

The database does not exist yet. That is precisely why it matters.

2. MATERIALS AND METHODS

The project operates on three integrated levels: instrumentation, reference material, and data architecture.

Instrumentation. All UV/Vis/NIR measurements are performed with the TIDAS® S 300 MMS VIS/NIR 3011 by J&M Analytik AG (Essingen, Germany) — a transportable fibre optics diode array spectrometer (Hamamatsu S3904-256Q NMOS, 256 pixels, wavelength range 300–1,100 nm, optical resolution ca. 10 nm FWHM, wavelength accuracy <0.5 nm, weight ca. 8 kg), equipped with a diffuse reflectance measuring head (REFH/045J, 45/0 geometry) and 2 m UV-grade silica fibre optics (600 μ m, 190–1,000 nm). The system enables direct in-situ, contact-free measurement on object surfaces across all substrate materials without sample extraction. White reference calibration is performed before each measurement session following standardised protocol. Complementary FT-IR analysis (binding media, varnishes, waxes) is planned via BRUKER ALPHA II Compact FT-IR Spectrometer (350–8,000 cm^{-1} , ATR and KBr transmission); Raman extension via BRUKER BRAVO handheld (DuoLaser 785/852 nm, 300–3,200 cm^{-1}) is in preparation.

Reference material. The colourant archive is based on the complete Kremer Pigmente range — approximately 2,500 individual colourants, spanning historical inorganic pigments, organic dyes, lakes, and modern synthetic colourants. To date, approximately 1,000 colourants have been acquired, archivally filled, and inventoried in a systematic drawer system at artLABOR® Berlin. Systematic spectroscopic measurement of the full archive is being conducted June–August 2026 by Eva Bermont, Heritage Science student (Northwestern University, Weinberg College), during her research internship at artLABOR®.

Data architecture. Spectral data is managed and analysed within KnowItAll Analytical Edition by Wiley Science Solutions — a platform integrating UV/Vis/NIR, FT-IR, and Raman in a single environment, supporting over 130 instrument formats. The software enables one-click identification, mixture analysis, quality control, and the construction of proprietary pigment reference libraries. Dr. Heinrich Piening contributes over 4,000 UV/Vis/NIR spectra from decades of conservation practice at the highest institutional level, forming the scientific backbone of the database alongside the Kremer-based measurements.

The methodology was first presented publicly at the VDR Specialist Conference *Analyses in Practice — Examination Methods for Wooden Objects in Conservation Science*, HAWK Hildesheim, November 2025 (Westebbe and Piening 2025).

3. RESULTS AND DISCUSSION

The database does not exist yet. That is the finding — and it is the point.

What exists today is the infrastructure, the methodology, the reference material, and a growing body of validated spectral data that together constitute the first systematic attempt to close a gap the field has treated as acceptable for too long.

Current database status. As of June 2026, the artLABOR® spectral archive contains approximately 680 UV/Vis/NIR spectra measured and validated by Westebbe, complemented by over 4,000 spectra contributed by Piening from decades of conservation practice — totaling more than 4,600 validated UV/Vis/NIR reference datasets across the Kremer Pigmente colourant range. Spectral acquisition is actively ongoing: intern Eva Bermont (Northwestern University, Weinberg College) is conducting systematic measurement of approximately 1,000 further inventoried colourants at artLABOR® Berlin between June and August 2026, contributing an estimated additional 1,000 validated spectra to the archive within the internship period. Full coverage of the complete Kremer Pigmente range of approximately 2,500 colourants and the target of approximately 9,000 validated spectra is projected for completion by end of 2027. In parallel, all validated datasets are being continuously integrated into the KnowItAll Analytical Edition by Wiley Science Solutions, building a structured, searchable proprietary spectral reference library directly linked to the Kremer colourant inventory.

Spectral reliability and validation. All spectra are acquired under standardised conditions (white reference calibration, defined fibre optics geometry, controlled ambient light exclusion) and validated against published reference data where available — principally Piening (2008), Longoni, Genova, Marzanni, Melfi, Beccaria, and Bruni (2022), and Cosentino (2014). Systematic cross-validation between independently measured spectra of identical colourants (Westebbe vs. Piening datasets) provides an internal consistency check not previously applied at this scale for UV/Vis/NIR cultural heritage reference data.

Diagnostic performance. Preliminary results confirm that the database enables reliable pigment group identification across all major colourant classes — lead white, iron earth pigments, copper-based pigments, carbon blacks, organic lakes, and synthetic colourants — directly from absorbance curves without sampling. Spectral signatures show sufficient inter-class discrimination for unambiguous identification in the majority of cases examined to date. Overlap zones — principally among certain iron oxides and between some organic lakes — are documented systematically and flagged within the KnowItAll environment as requiring complementary FT-IR confirmation.

The gap this fills. The IRUG database provides over 3,600 peer-reviewed FT-IR and Raman entries. No comparable UV/Vis/NIR resource exists in institutional or commercial form. The present database, upon completion, will represent the first publicly accessible, instrument-validated UV/Vis/NIR spectral reference collection for historical colourants at this scale — directly applicable to non-destructive in-situ diagnosis on cultural heritage objects worldwide.

4. CONCLUSION

FORS in the UV/Vis/NIR range is an established method without an established reference. This project changes that.

The systematic development of a validated UV/Vis/NIR spectral reference database — based on the complete Kremer Pigmente colourant range, grounded in the methodological framework of Piening (2008), and built through rigorous cross-validated measurement protocol — addresses the most consequential structural gap in non-destructive cultural heritage diagnostics today. A method used internationally, in museums, conservation studios, and research laboratories across Europe and beyond, has until now depended on institutional memory and individual expertise where it should depend on shared, validated reference data.

Upon completion, the database will offer the conservation and heritage science community a resource that does not currently exist: approximately 9,000 validated UV/Vis/NIR spectra of historical colourants, integrated within a professional spectral analysis environment, applicable across all substrate materials, and designed from the outset for cross-institutional use.

The contributions of this project are three:

First, a validated spectral reference archive of a scale and systematic coverage not previously achieved for UV/Vis/NIR cultural heritage data. Second, a reproducible measurement and validation protocol applicable beyond the Kremer range — establishing a transferable standard for future UV/Vis/NIR reference database development. Third, a demonstration that independent conservation practice, in scientific collaboration with institutional expertise, can produce infrastructure-level research outputs of direct relevance to the international field.

The database is under construction. The method is ready. The field has waited long enough.

5. ACKNOWLEDGMENT

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Eva Bermont (Northwestern University, Weinberg College, Heritage Science Program) contributed systematic spectral measurement and data entry during her research internship at artLABOR® Berlin, June–August 2026. The project was first presented publicly at the VDR Specialist Conference *Analyses in Practice — Examination Methods for Wooden Objects in Conservation Science*, HAWK Hildesheim, November 2025.

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