IRUG15

Infrared & Raman Users Group

Conference & Workshop

東京（Tokyo, Japan）

26 - 29 September 2023

TOKYO GEIDAI

東京文化財研究所

Tokyo National Research Institute for Cultural Properties

Organised by Conservation Science Laboratory, Tokyo University of the Arts (Geidai) and the Tokyo National Research Institute for Cultural Properties (Tobunken)

Organisers: Boris Pretzel and Masahiko Tsukada

Sponsorship Acknowledgements

IRUG would like to acknowledge the generous support it has received for IRUG15 from its industrial sponsors.

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Bronze level sponsors

We would also like to acknowledge Thermo Fisher Scientific and Bruker for the support they are providing for the reflectance spectroscopy workshop (27 September 2023)

Boris Pretzel Masahiko Tsukada

IRUG 15 Conference Organisers
Conservation Science Laboratory Tokyo University of the Arts
and
Tokyo National Research Centre for Cultural Properties

Editors: B Pretzel, M Tsukada, B Price 2023.
Abstract evaluation: IRUG Board.
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Conference schedule (summary)

Date/Time†	26-Sep	27-Sep	28-Sep	29-Sep
08:00	Registration			
08:15				
08:30				
08:50	Welcome	08:50 start	08:50 start	08:50 start
09:00		Posters 7 - 9	Oral 12	Oral 24
09:15	Oral 1	Posters 10-13	Oral 13	Oral 25
09:30	Oral 2	Sponsors talk	Oral 14	Oral 26
09:45	Oral 3	(09:35 -10:05	Q&A	Q&A
10:00	Q&A	T/C/P/S	Oral 15	T/C/P/S
10:15	T/C/P/S		Oral 16	
10:30		Sponsors	Q&A	Oral 27
10:45	keynote		T/C/P/S	Oral 28
11:00		Workshop		Oral 29
11:15		(free / tea	Oral 17	Q&A
11:30		ceremony)	Oral 18	Oral 30
11:45	Q&A		Oral 19	Oral 31
12:00			Oral 20	Oral 32
12:15			Q&A	Q&A
12:30	Lunch			
12:45	posters		Lunch	Lunch
13:00	sponsors		posters	posters
13:15			sponsors	sponsors
13:30	Oral 4			
13:45	Oral 5			
14:00	Oral 6		Oral 21	Oral 33
14:15	Q&A		Oral 22	Oral 34
14:30	Oral 7		Oral 23	Oral 35
14:45	Oral 8		Q&A	Q&A
15:00	Oral 9		T/C/P/S	T/C/P/S
15:15	Q&A			
15:30	T/C/P/S		Tours	IRUG
15:45				Summary
16:00	Posters 1-3			closing
16:15	Posters 4-6			
16:30	Oral 10			**Close**
16:45	Oral 11			
17:00	Q&A	Close of		
17:15	Sponsors	Workshop		
17:30		Tea	**Close day 3**	
17:45		ceremony		
18:00			Sake tasting	
18:15				
18:30	**Close day 1**	**Close day 2**		

† **Times are approximate - see detailed schedule for more info**

Tuesday 26 September

08:00	Registration			
		Name	**Organisation**	**Title**
08:50	Welcome	Welcome statements from Tobunken and Geidai and introduction to conference		
09:00				
	Session chair: Professor Boris Pretzel, Geidai			
09:15	Oral 1	Dr Marcello Picollo	IFAC CNR, Florence, IT	Total reflectance FT-IR spectra: impact of the support on paint layer analysis
09:30	Oral 2	Dr Arthur A. McClelland	Harvard University, US	Using principal component analysis and specular reflection FTIR to model chemical tests and fiber identification
09:45	Oral 3	Professor Lijiang Yang	Peking University, Beijing, CN	Computational chemistry simulations of molecular structures in different ageing silk textiles using ATR-FTIR
10:00	Q&A	Q&A Papers 1 -3		
10:15	T/C/P/S	Break for tea / coffee / posters / sponsors		
10:30				
10:45	Keynote	Professor James de Haseth	University of Georgia, Athens, Georgia, US	Infrared reflection spectrometries
11:00				
11:15				
11:30				
11:45	Q&A	Q&A for keynote talk		
12:00	Lunch / Posters / sponsors	Lunch break with time for posters and sponsors		
12:15				
12:30				
12:45				
13:00				
13:30	Oral 4	Ms Catherine Matsen	Winterthur Museum, Garden & Library, US	The Need for Speed: a success story of couture, exhibition and catalog deadlines, and ATR/DRIFTS
13:45	Oral 5	Dr Elizabeth Carter	Sydney Analytical, University of Sydney, AU	Raising of the Sun and the Moon: the Sydney Opera House tapestries
14:00	Oral 6	Dr Ashley Freeman	LA County Museum of Art (LACMA), US	Maria Kipp and Dorothy Wright Liebes: exploring the use of metallic threads in mid-20th century textiles

		Name	Organisation	Title
14:15	Q&A	Q&A for papers 4 – 6		
	Session chair: Professor Masahiko Tsukada, Geidai			
14:30	Oral 7	Drs Abed Haddad and Corina Rogge	Museum of Modern Art (MoMA) and The Menil Collection, US	Is there an International Klein Pink?
14:45	Oral 8	Joan M. Walker	National Gallery of Art, Washington DC, US	ER-FTIR spectroscopy of coated silver gelatin photographs: applications to the works of Dorothea Lange
15:00	Oral 9	Ekaterina Morozova (virtual)	The State Research Institute for Restoration, Moscow, RU	Natural and synthetic organic pigments in the palette of Nicholas and Svyatoslav Roerich
15:15	Q&A	Q&A for papers 7 – 9		
15:30	T/C/P/S	Break for tea / coffee / posters / sponsors		
15:45				
		Quickfire poster presentations 1 - selected posters only		
16:00	Poster 1	Dr Lynn Brostoff	Private conservation scientist, US	Identification of colorants in an 18th century Torii Kiyonaga hashira-e
16:05	Poster 2	Dr Catherine Cooper	National Center for Preservation Technology and Training, LA, US	Testing the sustainability of washing and reusing conservation cleaning sponges
16:10	Poster 3	Dr Abed Haddad	Museum of Modern Art (MoMA) New York, US	Rainbow treasures: multi-analytical characterization of Ronan Superfine Japan Colors
16:15	Poster 4	Clare Kim	Australian Museum, Sydney, AU	Investigation of unknown substances from entomology collection using ATR-FTIR spectroscopy
16:20	Poster 5	Nara Lee	National Research Institute of Cultural Heritage, KR	Application of handheld Raman spectroscopy for pigment ID of a large Buddhist painting in Janggoksa Temple
16:25	Poster 6	Dr Yufang Li	Northwest University, Xi'an, CN	Infrared spectrum identification of liquor residues in ancient China
		Late afternoon paper session		
16:30	Oral 10	Dr Qian Cheng	China National Centre for Archaeology, CN	Colours transferred along the Silk Road: the manufacture of glass beads from Qiemo cemetery, Xinjiang Region, during first millennium CE…
16:45	Oral 11	Dr Louisa Campbell	University of Glasgow, UK	Polychromy and portable Raman spectroscopy: identifying degraded pigments on roman sculpture
17:00	Q&A	Q&A for papers 10 – 11		
17:15	Sponsors	Time for delegates to interact with sponsors and/or look at posters		
17:30				Ueno Park tour and orientation
17:45				
18:00				
18:15				
18:30	**Close day 1**			

Wednesday 27 September

		Name	Organisation	Title
08:50	start			
	Quickfire Poster presentations 2 (selected posters only)			
	Session chair: Dr Suzan de Groot, Rijksdienst voor Cultureel Erfgoed (RCE)			
09:00	Poster 7	Dr Lamprini Malletzidou	Adv. Materials & Devices lab., Aristotle University, GR	Assessing the effects of a fire protocol on wall painting mock-ups
09:05	Poster 8	Shinnosuke Ono	Toyo Institute of Art & Design, JP	Prediction model for paper degradation using FT-IR spectra
09:10	Poster 9	Dr Corina E. Rogge	The Menil Collection, Texas, US	Blurred lines: issues distinguishing between alkyds and oils
09:15	Poster 10	Seka Seneviratne	Grimwade Centre, University of Melbourne, AU	Preliminary FTIR microscopic analyses coupled with SEM-EDX for the identification of microbes on lab. made modern paintings from Thailand
09:20	Poster 11	Dr Gregory Dale Smith	Indianapolis Museum of Art, US	Curious corrosion at Centre College: chalconatronite, antlerite, and tenorite on bronzes in rural Kentucky
09:25	Poster 12	Dr W. Vetter (Prof. Schreiner)	Akademie der Bildenden Künste, AT	Manuscript illumination at the court of Emperor Maximilian I (1459-1519): a multianalytical study using ER-FTIR, XRF, and Hyperspectral Imaging
09:30	Poster 13	Dr Jia Yu	National Research Institute of Cultural Heritage, KR	FTIR as a method to estimate the combustion atmosphere of ancient cremated human bone: Korean cremation burials in the Baekje period
	Silver level sponsor's talk - Thermo Fisher Scientific			
09:35	Sponsors talk	Stephan Woods (virtual)	Thermo Fisher Scientific	Vibrations throughout history- Insights into the past by vibrational spectroscopy
10:05	T/C/P/S	Break for tea / coffee / posters / sponsors		
10:20	Sponsors	Sponsors / Posters		
11:00	Workshop	Workshop / free time		Tea Ceremony group 1
12:00				
14:00				

14:00		
17:15	Close of workshop 17:30	
17:30		Tea Ceremony group 2
17:45		
18:00		
18:15		
18:30	**Close day 2**	Sake tasting Groups 1 &2: 18:00 - 20:00 and 20:00 - 22:00

Thursday 28 September

		Name	Organisation	Title
08:50	start			
	Session chair: Dr Greg Smith, Indianapolis Museum of Art			
09:00	Oral 12	Michael Doutre	Getty Conservation Institute, US	An FTIR-ATR Survey of German Democratic Republic Plastics in Design
09:15	Oral 13	Dr Suzan de Groot	Rijksdienst voor Cultureel Erfgoed (RCE), NL	On the road with a portable Raman system: Identifying plastics in Dutch collections
09:30	Oral 14	Dr Eleonora Del Federico (virtual)	Pratt Institute, New York, US	Non-invasive multi-analytical studies of early Licio Isolani paintings and fiberglass polyester resin sculptures
09:45	Q&A	Q&A for papers 12 – 14		
10:00	Oral 15	Dr Tai-Sheng Yeh	Meiho University, TW	Application of open-source software for spectra analysis of pigments
10:15	Oral 16	Mike Lo	Photothermal Spectroscopy Corp.	Sub-micron infrared analysis of painting cross-section for accurate identification of paint layer compositions
10:30	Q&A	Q&A for papers 15 - 16 (10 minutes)		
10:40	T/C/P/S	Break for tea / coffee / posters / sponsors		
	Session chair: Herant Khanjian, GCI			
11:10	Oral 17	Nasim Koohkesh	University of Melbourne, AU	Application of r-FTIR in pigment identification of white and green pigments in a Persian illuminated manuscript
11:25	Oral 18	Stephanie Barnes	Canadian Conservation Institute (CCI), Ottawa, CA	Non-invasive study of hand-painted illustrations from an early 19th century manuscript using ER-FTIR, Raman and other methods.
11:40	Oral 19	Jennifer Giaccai	National Museum of Asian Art, Smithsonian, Washington DC, US	Infrared and Raman analysis of black East Asian printing inks
11:55	Oral 20	Professor Manfred Schreiner	Akademie der Bildenden Künste, AT	Multidisciplinary studies of medieval manuscripts
12:10	Q&A	Q&A for papers 17 - 20 (20 MINUTES)		
12:30	Lunch / Posters / sponsors	Lunch break with time for posters and sponsors		
14:00				

		Name	Organisation	Title
14:00	Oral 21	Luís Manuel de Almeida Nieto	Delft University of Technology, NL	Flexible method for feature isolation and analysis in IR reflectance data for pigment and binder identification
14:15	Oral 22	Dr Gianluca Pastorelli	National Gallery of Denmark, DK	Combining multiple NUV-MIR spectral unmixing techniques for identifying mixtures of colorants in art and cultural heritage
14:30	Oral 23	Dr Celia Chari (virtual)	Harvard Art Museum, Harvard University, US	Non-invasive Identification of pigments in Indian manuscripts using principal component analysis and specular reflection FTIR data
14:45	Q&A	Q&A session for papers 21- 23		
15:00	T/C/P/S	Break for tea / coffee / posters / sponsors		
15:30	Visits	Visit around Tobunken facilities (prebooked groups only)		
17:30	**Close day 3**			
17:45				
18:00	Sake tasting	Prebooked only	Session 3 18:00 - 20:00 Session 4 20:00 - 22:00	

Friday 29 September

		Name	Organisation	Title
08:50	start			
	Session chair: Professor Manfred Schreiner, Akademie der Bildenden Künste, Wien, AT			
09:00	Oral 24	Dr Aditya Prakash Kanth	Centre for Heritage Mgmt., Ahmedabad University, IN	ATR -FTIR and μ-Raman based analysis for detection of chemical transformation in Indian wall paintings
09:15	Oral 25	Dr Shuxuan Shi	University of Science and Technology, Beijing, CN	Studies on Chinese architectural pasting ornament in the Forbidden City by Raman spectroscopy
09:30	Oral 26	Georgina Rayner (virtual)	Harvard Art Museum, Harvard University, US	Polychrome decoration on wooden Prince Shōtoku sculptures and associated miniature deities from C13th
09:45	Q&A	Q&A for papers 24 – 26		
10:00	T/C/P/S	Break for tea / coffee / posters / sponsors		
10:30	Oral 27	Celia Cramer	University of Sydney, AU	Investigating the potential of NIR spectroscopy to provenance natural history museum specimens
10:45	Oral 28	Mr An Gu	The Palace Museum, Beijing, CN	Revealing recipes of ancient Chinese lacquer process techniques by non-invasive quantitative method: near IR spectroscopy and chemometrics
11:00	Oral 29	Dr Yingchun Fu	University of Science and Technology, Beijing, CN	Quantitative study of oils in ancient lacquer objects by near-infrared spectroscopy
11:15	Q&A	Q&A for papers 27 – 29		
	Session chair: Dr Marcello Picollo, IFAC-CNR			
11:30	Oral 30	Dr Flavia Fiorillo	Fitzwilliam Museum, University of Cambridge, UK	Novel insights from the study of Isaac Oliver's portrait miniatures
11:45	Oral 31	Erin Mysak and Christy Gratini	Museum of Fine Arts (MFA) Boston, US	Characterization of artists' materials from 20th century Mexican ex-voto paintings
12:00	Oral 32	Sawako Sentoku	Tokyo University of the Arts, JP	FTIR analysis of the blue restoration of cyanotypes decolorized after alkalis
12:15	Q&A	Q&A for papers 30 – 32		
12:30	Lunch / Posters / sponsors	Lunch break with time for posters and sponsors		
14:00				

14:00	Oral 33	Herant Khanjian	Getty Conservation Institute, US	Analytical studies of light aged Asian lacquer boards
14:15	Oral 34	Mingrui Zhang	Zhengzhou University, Henan Province, CN	Leather deterioration: insights for the conservation of collagen-based cultural heritage
14:30	Oral 35	Dr Rebecca Ploeger	University at Buffalo (SUNY), US	The value of degraded polymers - representing degraded polymers in IRUG
14:45	Q&A	Q&A for papers 33 – 35		
15:00	T/C/P/S	Break for tea / coffee / posters / sponsors		
15:15				
15:30	IRUG	Boris Pretzel	Tokyo University of the Arts / IRUG	30 years on – IRUG in the past, present, and future
15:50	Summary	Conference summary		
16:00	closing	closing remarks and close		
16:30	**Close**			
16:45				
17:00				
17:15				
17:30				
17:45				
18:00				
18:15				
18:30				

Papers accepted for IRUG 15

Papers are listed alphabetically by presenting author. Titles are taken from IRUG15 registration information and should not be relied upon to determine academic or professional positions or qualifications. Ctrl + Click on author or title to go to the abstract.

Author(s)	Institution	Paper titles
Stephanie Barnes et al	Canadian Conservation Institute, Ottawa, CA	Non-invasive study of hand-painted illustrations from an early 19th century manuscript using ER-FTIR, Raman and other complementary methods – successes and challenges
Dr Louisa Campbell	University of Glasgow, UK	Polychromy and portable Raman spectroscopy: identifying degraded pigments on roman sculpture
Dr Elizabeth Carter et al	Sidney Analytical, University of Sydney	Raising of the Sun and the Moon: The Sydney Opera House Tapestries
Dr Celia Chari et al (v)†	Harvard Art Museum, Harvard University, US	Non-invasive identification of pigments in Indian manuscripts Using Principal Component Analysis and Specular Reflection FTIR data
Dr Qian Cheng et al	China National Centre for Archaeology, CN	Colours transferred along the Silk Road: slight on the manufacture of glass beads from Qiemo cemetery site, Xinjiang region, during the first millennium CE by Raman micro-spectroscopy and SEM-EDS
Celia Cramer et al	University of Sydney, AU	Investigating the potential of NIR spectroscopy to provenance natural history museum specimens
Michael Doutre et al	Getty Conservation Institute, US	An FTIR-ATR survey of German Democratic Republic plastics in design
Dr Eleonora del Federico et al (v)†	Pratt Institute, New York, US	Non-invasive multi-analytical studies of the early paintings and fiberglass polyester resin sculptures by artist Licio Isolani
Dr Flavia Fiorillo et al	Fitzwilliam Museum, University of Cambridge, UK	Novel insights from the study of Isaac Oliver's portrait miniatures
Dr Ashley Freeman et al	LACMA	Maria Kipp and Dorothy Wright Liebes: exploring the use of metallic threads in mid-20th century textiles
Dr Yingchun Fu et al	University of Science and Technology, Beijing, CN	Quantitative study of oils in ancient lacquer objects by near-infrared spectroscopy
Jennifer Giaccai et al	National Museum of Asian Art, Smithsonian Institution, Washington DC, US	Infrared and Raman analysis of black East Asian printing inks
Dr Suzan de Groot	RCE The Netherlands, NL	On the road with a portable Raman system: Identifying plastics in Dutch museum collections

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Mr An Gu et al	The Palace Museum, Beijing, CN	Revealing the key recipes of ancient Chinese lacquer process techniques by non-invasive quantitative method: near infrared spectroscopy and chemometrics
Drs Abed Hadad and Corina Rogge	Museum of Modern Art (MoMA) and The Menil Collection, Texas, US	Is there an International Klein Pink?
Professor James de Haseth	University of Georgia and Light Light Solutions LLC, US	Keynote talk: Infrared reflection spectrometries
Dr Aditya Prakash Kanth et al	Centre for Heritage Management, Ahmedabad University, Gujarat, IN	ATR -FTIR and μ-Raman based analysis for detection of chemical transformation in Indian wall paintings
Herant Khanjian et al	Getty Conservation Institute, US	Analytical studies of light aged Asian lacquer boards
Nasim Koohkesh et al	University of Melbourne, AU	Application of r-FTIR in pigment identification of white and green pigments in a Persian illuminated manuscript
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Dr Arthur A McClelland et al	Harvard University, US	Using principal component analysis and specular reflection FTIR for paper fiber identification
Ekaterina Morozova (v)†	The State Research Institute for Restoration, Moscow, RU	Natural and synthetic organic pigments in the palette of Nicholas and Svyatoslav Roerich
Erin Mysak and Christy Gratini	Museum of Fine Arts Boston, US	Characterization of artists' materials from 20th century Mexican ex-voto paintings
Luís Manuel de Almeida Nieto et al	Delft University of Technology, NL	Flexible method for feature isolation and analysis in infrared reflectance data for pigment and binder identification
Dr Gianluca Pastorelli et al	National Gallery of Denmark, DK	Combining multiple NUV-MIR spectral unmixing techniques for identifying mixtures of colorants in art and cultural heritage
Dr Marcello Picollo et al	IFAC CNR, IT	Total reflectance FT-IR Spectra: Impact of the support on paint layer analysis
Professor Boris Pretzel	Tokyo University of the Arts / IRUG	30 years on: IRUG in the past, present, and future
Dr Rebecca Ploeger et al	University at Buffalo (SUNY), US	The value of degraded polymers - representing degraded polymers in IRUG
Georgina Rayner et al (v)†	Harvard Art Museum, Harvard University, US	Polychrome decoration on wooden Prince Shōtoku sculptures and associated miniature deities from the 13th century
Professor Manfred Schreiner et al	Akademie der Bildenden Künste, AT	Multidisciplinary studies of medieval manuscripts

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Joan M. Walker et al	National Gallery of Art, Washington, US	ER-FTIR spectroscopy of coated silver gelatin photographs: applications to the works of Dorothea Lange
Stephan Woods	Thermo Fisher Scientific (Silver level sponsor's talk)	Vibrations throughout history- Insights into the past by vibrational spectroscopy
Professor Lijiang Yang et al	Peking University, Beijing, CN	Computational chemistry simulations in the deep understanding of molecular structures in different ageing silk textiles using ATR-FTIR spectroscopy
Dr Tai-Sheng Yeh et al	Meiho University, TW	Application of open-source software for spectra analysis of pigments
Mingrui Zhang et al	Zhengzhou University, Henam Province, CN	Leather deterioration: insights for the conservation of cultural heritage

† (v) signifies a presentation given virtually

Posters accepted for IRUG15

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Dr Catherine Cooper et al	National Center for Preservation Technology and Training (NCPTT), LA, US	Testing the sustainability of washing and reusing conservation cleaning sponges
Dr Abed Haddad	Museum of Modern Art (MoMA), US	Rainbow treasures: multi-analytical characterization of Ronan Superfine Japan Colors
Clare Kim	Australian Museum, Sydney, AU	Investigation of unknown substances from Entomology collection using ATR-FTIR spectroscopy.
Nara Lee et al	National Research Institute of Cultural Heritage, KR	Application of handheld Raman spectroscopy for pigment identification of a large Buddhist painting in Janggoksa Temple, South Korea
Dr Yufang Li et al	Northwest University, Xi'an, CN	Infrared spectrum identification of liquor residues in ancient China
Dr Lamprini Malletzidou	Laboratory of Advanced Materials & Devices, Aristotle University of Thessaloniki, GR	Assessing the effects of a fire protocol on wall painting mock-Ups
Mariko Nakao et al	Archaeological Institute of Kashihara, Nara, JP	An analysis of Lacquer layers adhering to excavated potteries using FTIR
Masayoshi Okuyama et al	Archaeological Institute of Kashihara, Nara, JP	Research on textile material from Kofun period (4th century to the middle of the 6th century) in Japan - a study of cultural properties using a FT-IR photoacoustic spectroscopy
Shinnosuke Ono	Toyo Institute of Art & Design, JP	Prediction model for paper degradation using FT-IR spectra and its explainability
Dr Corina E. Rogge et al	The Menil Collection, Texas, US	Blurred lines: issues distinguishing between alkyds and oils
Seka Seneviratne et al	Grimwade Centre for Cultural Material Conservation, Melbourne University, AU	Preliminary FTIR microscopic analyses coupled with SEM-EDX for the identification of microbes on laboratory made modern paintings from Thailand
Dr Gregory Dale Smith et al	Indianapolis Museum of Art, US	Curious corrosion at Centre College: chalconatronite, antlerite, and tenorite on bronze sculptures in a rural Kentucky setting
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Dr Jia Yu et al	National Research Institute of Cultural Heritage, KR	FTIR as a necessary method to estimate the combustion atmosphere of ancient cremated human bones: A case of cremation burials in the Baekje period, Korea

‡ presented by a colleague.

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Foreword

The following texts are the abstracts accepted for presentation as papers and as posters at the 15th Infrared and Raman Users Group International Conference, hosted by the Conservation Science Laboratory at Tokyo University of the Arts (Geidai), and the Tokyo National Research Institute for Cultural Properties (Tobunken). This is the first IRUG conference to be held in Asia and it is our great honour to have been involved in the organisation and running of this important milestone meeting.

The conference focuses, as always, on all aspects of IR and Raman spectroscopies and their application to the study of the world's cultural heritage, but with particular emphasis on reflectance mode and ATR techniques, and work on Asian cultural heritage. It is accompanied by a workshop on reflectance infrared data acquisition, processing, and interpretation. We are indebted to Professor James de Haseth for his keynote talk *Infrared reflection spectrometries*; to Drs Marcello Picollo (workshop lead); Suzan de Groot, and Manfred Schreiner for their aide in running of the workshop; and to Thermo Fisher Scientific, Bruker, the Conservation Science Laboratory at Geidai, and the Conservation Science Center at Tobunken, for loan of equipment for the workshop. We are also indebted to Tobunken, and particularly Dr Toru Tateishi, the Director of the Conservation Science Research Center there, for hosting the conference and workshop in their wonderful facilities.

This 15th IRUG conference is dedicated to the memory of Professor Masanori Sato, a long-time supporter and early advocate of IRUG and recipient of the 2008 IRUG Career Achievement Award, who sadly passed away in 2022.

Editing of the abstracts has been confined to be as light as possible a touch and is typically applied for stylistic consistency and to improve clarity and impact. The first section contains abstracts of the papers presented orally (together with the keynote talk and the silver level sponsor's talk) and the second, those for the posters.

Boris Pretzel Masahiko Tsukada

Organisers

Conservation Science Laboratory, Tokyo University of the Arts

1. Paper abstracts, in alphabetical order by presenting author(s)

Presenting author(s) are indicated by an * (asterisk) by their name

1.1. Non-invasive study of hand-painted illustrations from an early 19th century manuscript using ER-FTIR, Raman and other complementary methods – successes and challenges

Stephanie Barnes*, Jennifer Poulin, Kamila Bladek
Canadian Conservation Institute (CCI), Conservation Science Division, Ottawa, Ontario, CA

The *Buttrey manuscript of Military and Social Tunes* is a handwritten manuscript from the earth 19th century, containing over 1000 military fife tunes, alongside several painted illustrations on both military and non-military themes. The volume may have been compiled by several people over a number of years, including John Buttrey (1784-1854), who, as a young man, served as a drummer in the 34th Foot Regiment of the British military. Buttrey emigrated to Canada in 1849, and the manuscript remained within his family for six generations before being donated to the City of Toronto Museum and Heritage Services Unit in 2019.

The Buttrey Manuscript has already been the subject of significant research by music and military historians. The pages have been digitized and the songs have been transcribed and recorded. The manuscript arrived at the Canadian Conservation Institute (CCI) in 2020 for conservation treatment.

Analysis was carried out to identify components of the paints and inks, including areas of colour change and degradation. Key illustrations from the manuscript were analyzed using a suite of non-invasive techniques – XRF, Raman microscopy, and portable FTIR with an external reflectance module. Select analysis of binding media and organic pigments using Py-GC-MS was carried out using magnesium oxide sticks for microsampling. Key phenomena of interest included staining on the verso of certain areas of green pigment, and fading and blackening of some areas of red pigment but not others.

ER-FTIR spectroscopy on this paper object presented many challenges. Many areas of paint application were thin and watercolour-like in their application, and peaks for cellulose overwhelmed the spectrum. Areas suitable for analysis were also limited by the large spot size of the instrument relative to the small colour areas on the manuscript. More generally, interpretation of ER-FTIR spectra is challenging due to a relative lack of available reference spectra for comparison compared to more established techniques, and the wide variability in the appearance of spectra with dependence on surface gloss, roughness and other factors. Despite these factors, azurite could be readily identified and indigo and gamboge tentatively assigned.

Raman microscopy, using a 785nm laser, was the ideal technique to identify several of the pigments present in the manuscript, including vermillion, red lead, azurite and indigo. However, the use of a Raman system set up for the analysis of samples rather than objects presented many challenges for working with the manuscript. Given the size and depth of the object, the stage had to be removed from the microscope to allow it to fit safely beneath the objectives. This removed the ability for fine, computer controlled movement of the object in the x,y directions, and the use of fine and coarse focus knobs for adjustments in the z-direction. Improvements to this improvised setup are being investigated for future projects.

1.2. Polychromy and portable Raman spectroscopy: identifying degraded pigments on Roman sculpture

Dr Louisa Campbell*
Lord Kelvin Adam Smith Leadership Fellow in Archaeology,
University of Glasgow, UK

Portable Raman spectroscopy has immeasurably enhanced our ability to fingerprint pigments and surface treatments on works of art. Alongside complementary mobile instrumentation, including pXRF, Microscopy, FTIR and others, Raman permits the in situ non-invasive analysis of precious curated artefacts without risk to their integrity or the need for their removal from the safety of museum spaces.

The clarity of data provided by Raman is particularly invaluable for identifying pigments that have been mixed or applied in layers since pXRF provides only cumulative results from samples, regardless of their stratigraphic sequence. That said, the technique is most effective in 'clean' samples where sample material is visible to the naked eye. This inevitably presents challenges unique to archaeological artefacts, such as Roman statuary, that have been subject to taphonomic processes over millennia. My recent research has found that pigments degrade very differently on sculptures from antiquity, resulting from post-depositional processes that alter their structure and appearance, both at the visible and microscopic level. This is exacerbated by their application to sandstone statuary buried in acidic soils and harsh environmental conditions such as those associated with Scotland on the Empire's north-western frontier.

This paper presents some comparative results from 'clean' pigments and archaeological samples to share the challenges inherent in working with polychromy on ancient statuary and to highlight to curatorial and conservation colleagues that surface treatments may not present in a way that is recognisably pigment in some archaeological contexts. Through this, I will demonstrate the value of using Raman as part of a suite of analytical techniques for recognising, fingerprinting and preserving this irreplaceable material for posterity.

1.3. Raising of the Sun and the Moon: the Sydney Opera House tapestries

Dr Elizabeth Carter*[1], Prof. Daniel Dias da Costa[2], Ms Mary-Anne Gooden[3], Ms Kristin Phillips[3], Ms Thérèse Harrison[4], Mr David James[5], Ms Christina Ritschel[6], Dr Jeffrey Shi[7], Dr Brad Swarbrick[8], Dr Xia (Rachel) Zhong[9]

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In 1969, John Coburn, one of Australia's best-known modern artists of the time, was commissioned to design theatre curtains for the newly built opera and drama theatres in the Sydney Opera House. The majestic tapestries named the *Curtain of the Sun* and *Curtain of the Moon* (Figure 1) were woven with Australian Merino wool by the Pinton Frères atelier (Aubusson) in France. The *Curtain of the Sun* is dominated by a large sun with metal thread and surrounded by shapes depicting natural elements and the Australian landscape, the *Curtain of Moon* with its eye-catching shimmering moon finished in deep blue, purple, green and silver. The tapestries were hung for the opening of the Opera House in 1973.

Figure 1: (LEFT) *The Curtain of the Sun* installed in the Joan Sutherland Theatre and (RIGHT) *The Curtain of the Moon* installed in the Drama Theatre, Sydney Opera House – Photo Credit: Jacquie Manning.

The manufacture of the tapestries was not straightforward, with New South Wales (NSW) fire regulations requiring that both the cotton warp and wool weft to be treated with fire retardants before weaving and after completion. In the early 1990s a large tear in the Curtain of the Moon was repaired, a lining attached due to concerns about the strength of the warp, and analysis performed to determine if the fire retardant had caused damage. The tapestries have remained in storage since

they were decommissioned in the 1980s and have been occasionally displayed in their original locations for public exhibition.

The Sydney Opera House is committed to ensuring the conservation of these magnificent tapestries. This has included re-examination of the tapestries to determine the frequency and duration of public display. Over the past few years, they have been successfully hung for short periods. Scientific analysis was recently undertaken to better understand the exact nature of the fire retardants and the tensile strength of the warp and weft to determine if they can be displayed for longer periods.

A suite of complementary analytical techniques was used to investigate the chemical (ATR and NIR spectroscopy/Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)), mechanical (Tensile strength/Digital image correlation) and physical (SEM) properties of forty-two woollen weft fibres sampled by Artlab Australia conservators from the Sydney Opera House Coburn Tapestries. Correlation of the chemical (ATR/EDS) and mechanical data (Tensile) with the NIR spectroscopic findings were investigated to determine if it was possible to build a predictive model to assess structural integrity, allowing for future in-situ analyses that required only NIR spectroscopy.

Figure 2: Artlab Australia senior textile conservators Kristen Phillips and Mary-Anne Gooden removing woollen weft fibres for scientific analysis.

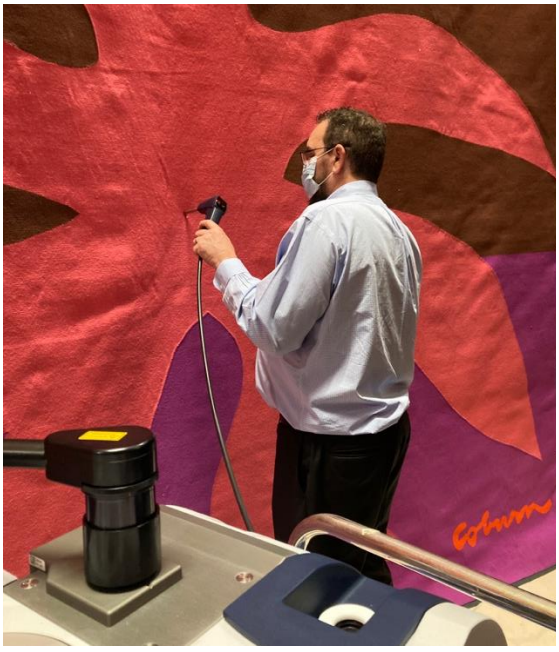

Figure 3: Dr Brad Swarbrick collecting NIR spectroscopic data from the Curtain of the Sun.

1.4. Non-invasive identification of pigments in Indian manuscripts using principal component analysis and specular reflection FTIR data

Celia S. Chari*[1], Katherine Eremin[1], Arthur A. McClelland[2], Nicholas S. Colella[2] Georgina Rayner[1], Jinah Kim[3], Anjali Jain[4], Narayan Khandekar[1]

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Harvard University's Mapping Color in History (MCH) is a Digital Humanities project that brings together scientific data drawn from existing and ongoing material analyses of pigments in Asian paintings, all within a historical perspective. Currently, the project is working to establish a library of spectral data that documents pigments used in Indian and related manuscripts based on new non-invasive analyses of works in the collections of the Harvard Art Museums. A group of fifty mineral and organic pigments, including a variety of red, yellow, green, blue, brown, black, and white colorants, are included in this study, originating from both the Forbes Pigment Collection and a traditional miniature painting workshop based in Jaipur, Rajasthan. A series of paint outs were prepared using said pigments, gum Arabic and jute paper, resembling the artists' materials that would be expected in Indian manuscripts, and subsequently analyzed using non-invasive spectroscopic techniques. In this presentation, we discuss how specular reflectance FTIR measurements of reference pigments can be processed using principal component analysis and describe how this technique allows us to distinguish between pigments through clustering algorithms. Ultimately, this analysis will allow us to build a three-dimensional reference library of pigments, which can be applied to non-invasively identify pigments in Indian manuscripts in the Harvard Art Museums collected with the same analytical techniques.

1.5. Colours transferred along the Silk Road: shedding light on the manufacture of glass beads from Qiemo cemetery site, Xinjiang region during the first millennium CE by Raman micro-spectroscopy and SEM-EDS

Qian Cheng*[1 2], Jinlong Guo[3], Thilo Rehren[2]

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As one of the latest artificial materials, glass was an intriguing product, that not only encompasses symbolic and practical functions but also represents the intelligence and creativity of glass artisans within the past three and half millennia. As a trade and cultural hub between the East and the West, the Xinjiang region in the west of China used to enjoy wide commercial exchanges with other contemporary civilizations. Glass beads, regarded as luxury commodities, were widely distributed along the Silk Road. Various kinds of glass ornaments in the form of necklaces, earrings and pendants have been discovered from cemetery sites dated between the Chinese Han and Weijing dynasties (2nd century BCE to 6th century CE).

This paper will focus on an assemblage of representative glass beads excavated from Zhagunluque cemetery site on the edge of the Takalamagan desert, which is generally accepted as part of the ancient Qiemo (且末) kingdom on the southern line of the Silk Road. In order to identify the colorants and opacifiers of glass samples, scientific analysis using Raman microscopy and scanning electron microscopy equipped with energy-dispersive spectrometry (SEM-EDS) were carried out for those colourful beads ornaments, which were used to be deposited around the mummies as funerary objects.

According to published results by LA-ICP-AES (Cheng, Q., 2021), these glass ornaments can be classified into two main types, i.e. soda-lime-silica glass and lead-barium glass. Those samples were examined non-destructively with a HORIBA XploRA Raman microscope. A HR460 spectrometer, coupled with an Olympus BX-41 microscope, was used after surface analysis had been performed at a magnification of 50X. Raman spectra were collected by means of a liquid nitrogen-cooled charge-coupled device (CCD) camera. The two laser sources were: a 100 mW, 532 nm, frequency-doubled Nd: YAG; and a 100 mW, 785 nm diode.

Results and Discussion

1. Soda-lime-silica glass

Four representative beads, including Z-8 yellow, Z-15 white, Z-19 green, and Z-1eye bead (Figure 1), have been selected from the soda-lime-silica type made by using plant ash flux. Typical colorants from these western glasses, such as lead-tin yellow for yellow, tin oxide for white (Figure 2), and cuprite for red (Figure 3), etc., have been detected by Raman microspectroscopy.

Figure 1: Blue eye bead excavated from Tomb M133

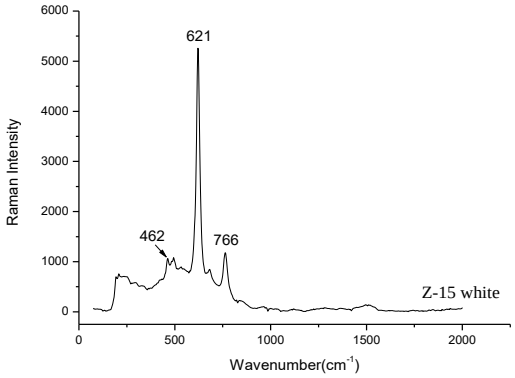

Figure 2: Raman spectrum of tin oxide in the white crystals of glass bead Z-15; excitation wavelength λ= 532nm

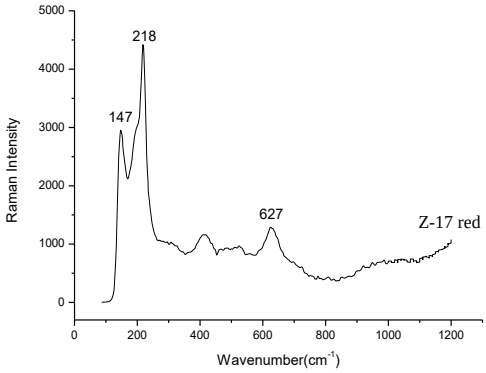

Figure 3: Raman spectrum of cuprite in the red crystals of the glass bead Z-17; excitation wavelength λ= 532nm

Combined with morphological analysis by SEM-EDS, the samples are quite similar to Sasanian glass (Mirti et al. 2008, Mirti et al. 2009) in terms of chemical composition, colorant, and manufacture. Those beads dated between the 1st and 6th century CE and were possibly made by Sasanian craftsmen who specialized in plant ash glassmaking. Although the location of the primary glass manufacture is uncertain, it can be assumed that this eye bead was probably produced in Western Asia during the Sasanian period, and transferred from Western Asia to the ancient Qiemo kingdom along the ancient Silk Road.

2. Lead-barium glasses

There are two green beads, Z-4 and Z-6, that were discovered in Tomb M2. In Figure 4, on the left side is an opaque light green bead, and on the right side is a translucent green bead, both in a donut shape.

Figure 4: Sample Z-4 (left) and Z-6 (right)

These two green beads have concentrations of elevated levels of lead oxide (43.8% and 48.4%) and barium oxide contents (16.2% and 12.8%), showing a typical lead-barium glass composition that is dated from 206 BCE– 24 CE. By means of a 532 nm laser, the Raman spectra showed peaks of 991 cm^{-1} and 457 cm^{-1} (Figure 5), and this indicates the presence of barite ($BaSO_4$) crystals within the glass. Furthermore, the opacification extents of the two beads may result from the unequal ratios of BaO/PbO for Z-4 and Z-6 of 0.37 and 0.26, respectively. It is very likely that the barite was intentionally added as an opacifier into the glass matrix in order to obtain distinct visual effects as artisan designed, mostly to imitate jade worshipped by ancient Chinese people for five millennia.

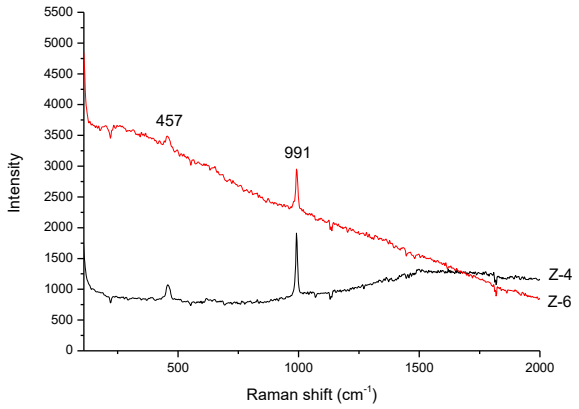

Figure 5: Raman spectra of barium sulfate in the white crystals of the glass bead Z-4 and Z-;: excitation wavelength λ= 532nm

Lead-barium glass was a unique type of glass specifically produced during the Warring States period and the Han Dynasty (ca. 400 BCE–200 CE). Due to its high sensitivity to weathering, lead-barium glass, which was popular among noble families during the Han Dynasty, gradually faded out of use when the Eastern Han Empire collapsed in 220 CE. Thus, with regard to archaeological finds discovered from the tomb sites, including silk, iron, and lead-barium glass beads, it can be presumed that the ancient Qiemo kingdom on the southern line of the Silk Road had an intimate relationship with Central China.

The study has demonstrated that when the traditional soda-lime-silica glass was produced and transferred along the Silk Road, simultaneously an exclusive type of lead-barium glass was manufactured in the east and concentrated to the southern branch of the Silk Road. The Qiemo kingdom had wide commercial and social interactions with both the East and the West before and in the first millennium CE.

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1.6. Investigating the potential of NIR spectroscopy to provenance natural history museum specimens

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Introduction

The "period of enlightenment" was characterised by a surge in enthusiasm for the natural world and the plants, animals and people within it. This enthusiasm was reflected in the establishment of natural history collections, which soon evolved into Public Museums and places of knowledge-making and natural sciences. Novelty and opportunity were the criteria for these early collections (Ville), and record keeping and specimen contextual data were barely developing notions. Consequently, natural museum collections throughout the world hold specimens that are missing part or all of their contextual data [Burgess, 2022].

Zoological specimens with invalid or missing contextual data have limited use in scientific and historical research, yet it is these very specimens that are typically the oldest and most rare. Residues of the preservatives applied by field collectors as they gathered natural history specimens from the wild may offer clues from which to rebuild contextual data. This study explores the potential of NIR spectroscopy for investigating skin preservation mixtures using replica skins treated with preservatives commonly found in 19th century zoological specimens.

Methods and materials

Materials: replica preserved skin specimens were developed to represent common preservatives that were applied to mammal and avian natural history specimens in the 19th century. Additionally, three natural history specimens collected before 1900 were sampled from the Macleay Collection at the University of Sydney.

Spectroscopy: Diffuse Reflectance NIR Spectra collected using a Bruker MPA II Fourier Transform Near Infrared spectrometer over the spectral range of 12490-3996 cm^{-1} (c2500-800nm), at 16 cm^{-1} resolution and 128 co-additions. Specimens were mounted directly above the integrating sphere. OPUS (version 7.5.18 Ettlingen, Germany) was used to collect a minimum of 6 spectra over each specimen.

Analysis: Spectra truncated to 9604-6166cm^{-1} (1041.23- 1621.80nm). Raw spectra were atmosphere corrected and processed using OPUS 8.2.21. Using VEKTOR DIREKTOR (version 1.1 KAX Group, Australia), spectral data were transformed using Savitzky-Golay second derivative and normalised using the standard normal variate before performing principal component analysis (PCA).

Results

Analysis of data collected from replica preserved skin specimens revealed unique bands identified as markers for the presence of specific preservatives. The spectra of lime (CaOH) treated replica specimens were characterised by a peak at 7083 cm^{-1} (Figure 1A). This band was weaker in the spectra of replica specimens treated with arsenical soap - a mixture that included sodium hydroxide (NaOH).

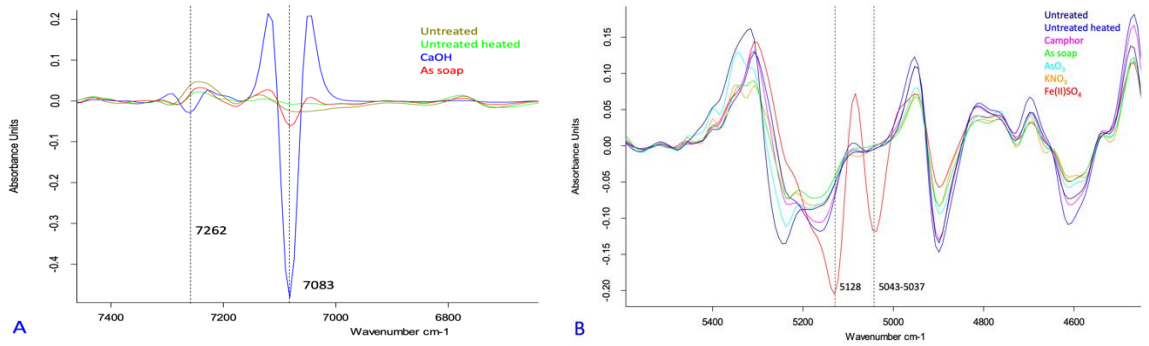

Figure 1: NIR-DR spectra shaowing (A) peaks attributed to hydrolysation as a result of treatment with lime. (B) Iron sulfate treatment producing peaks attributed to metal-collagen complexation

Replica specimens treated with iron(II) sulfate ($Fe(II)SO_4$) can be distinguished from other treatments by bands at 5129 and 5045 cm^{-1} (Figure 1B). These may be attributed to the complexation of iron with collagen carboxyl groups, causing changes in both ν(CO) (5129 cm^{-1}) [Beć et al, 2020] and COOR vibrations (5045 cm^{-1}) [Duki et al, 2013; Covington, 2006; Bruker, 2001].

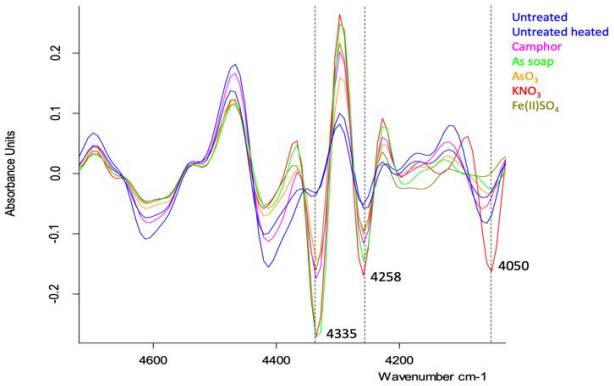

Figure 2: NIR-DR spectra of skin sampes in the region of 4600-4000 cm^{-1}

Bands at 4335 and 4258 cm^{-1}, attributable to proteins [Beć et al, 2020] were observed to increase in intensity when treated with camphor, potassium nitrate, iron(II) sulfate, aluminium sulphate, arsenic trioxide and arsenical soap. Potassium nitrate also interacts with lipids as is evidenced by the intense band at 4050 cm^{-1} (Figure 2).

Principal Component Analysis revealed that the combinations region (around 5000-4400 cm^{-1}) and the second overtone region (7100-6400 cm^{-1}) describe changes in protein structures in response to preservatives and aging.

Conclusions

This study suggests that NIR spectroscopy may be useful for non-destructive and non-invasive identification of a number of skin preservatives and in describing the degradation of skin's protein structures. Such information has the potential to contribute to the understanding of the provenance of zoological specimens and may be used to inform the selection of specimens for exhibition.

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1.7. An FTIR-ATR survey of German Democratic Republic plastics in design

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Shortly after World War II, in 1946, the nation of Germany was split in two: the Federal Republic of Germany, occupied by the United States, England, and France, and the German Democratic Republic (GDR), under Soviet influence. These two regions, commonly referred to as West Germany and East Germany within Western culture, underwent distinct political, economic, and social transformations. These changes were a result of their differing ideologies and the influences of their respective occupying powers. This situation continued until 1989, with the fall of the Berlin Wall, the reunification of Germany in 1990, and the dissolution of the Soviet Union in 1991. Beginning in the 1950s, the GDR developed into one of the leading plastics-producing nations and exported its products to almost all countries of the Eastern Bloc. As the GDR was a closed cultural and economic system, the production of plastics in the GDR was characterized by groundbreaking and technologically independent developments, distinct from those in Western countries. Consequently, there is a lack of knowledge about the various types of plastics that were produced in this region.

In this research, several hundred plastic components of GDR design objects from the collection of the Wende Museum (Los Angeles) were examined using portable Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR). This research revealed that polystyrene was the dominant polymer used in GDR design from very early in the country's history up to its fall, with an increasing use of copolymers in the later periods. This work is part of a larger investigation into plastic in GDR design in collaboration between the Getty Conservation Institute, Wende Museum, TH Köln–Cologne Institute of Conservation Sciences, and Die Neue Sammlung–The Design Museum (Munich) and is the first systematic examination and assessment of these objects regarding production history, material use, and aging.

1.8. Non-invasive multi-analytical studies of the early paintings and fiberglass polyester resin sculptures by artist Licio Isolani

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This work involves a non-invasive multi-analytical study of twenty paintings and five colored fiberglass polyester resin sculptures created between 1957 and 1965 by artist Licio Isolani (1931-2015) through the use of portable instrumentation. The goal of this work was to investigate the evolution of Isolani's materials and techniques over time in a non-invasive fashion as the collection and archive donated to Pratt Institute by the artist were being inventoried. Portable X-Ray fluorescence (XRF), macro X-ray fluorescence (MA-XRF), external reflectance Fourier transformed infrared spectroscopy (FTIR), Raman, and unilateral nuclear magnetic resonance (NMR) were employed. The results of the study reveal that the artist's early painting palette (1957-1962) involved mixtures of ground metals (copper, aluminum, zinc, tin, lead, and gold) of varying particle size, along with the use of lead-based pigments, Prussian and ultramarine blue, bone black. Titanium, lead, and barium whites were used either as pigments or in the ground preparation of the paintings. Lead chromate yellow and red were found in his latest paintings (1962). The absence of cobalt and cadmium-based pigments throughout all his paintings was also noted. External reflectance FTIR suggests that the artist's binding media involved the possible use of acrylics, alkyds, oil, and natural and synthetic resins applied either to a canvas or to aluminum-gilded linoleum, cardboard, or wood surfaces. The possible presence of modern organic dyes was inferred through the absence of an inorganic chromophore, as they were difficult to identify otherwise through this non-invasive approach. Moreover, the unusual presence of high amounts of chlorine was observed by XRF in most of his aluminum-gilded paintings, which suggests the possible use of chlorinated rubber resins [Miliani et.al, 2015]. The presence of such resin agrees with entrances in the artist's notebooks stating his use of samples obtained from Monsanto and DuPont in 1959. Five of Isolani's fiberglass polyester resin sculptures were also analyzed. The results show that the artist achieved intentional translucency versus opacity effects on the sculptures by "color-matching" lead-based pigments and organic dyes, either embedded in the resin or painted on top. Areas of high opacity also show the presence of high-density fiberglass, suggested by the high intensity of silicon and calcium in the XRF analysis, whereas transparent areas are mainly composed of dyed polyester resin and low-density fiberglass (low silicon and calcium signals and the absence of an inorganic chromophore). This preliminary study through the use of portable instrumentation showed the complexity and richness of Isolani's materials and techniques and his experimentation with "new materials", juxtaposing them with "traditional" ones in both his paintings and sculptures.

Reference

Miliani et.al, 2015, *Chlorinated rubber film on an asbestos support* in "Conservation Issues in Modern Contemporary Murals" pp. 286-298, T. Lerner, M. Sanches-Pons and W. Shank editors.

1.9. Novel insights from the study of Isaac Oliver's portrait miniatures

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Scientific analyses for the characterisation of materials and techniques of cultural heritage have been in continuous development in recent years. FTIR and Raman spectroscopies, often used as part of a multi-modal analytical approach, have been increasingly applied to objects preserved at the Fitzwilliam Museum to gain new insights into the collection.

The Museum owns an important set of portrait miniatures, known at the time as 'limnings', painted in England in the 16th and 17th centuries. In this type of art, a portrait is painted with finely ground pigments bound in gum Arabic, applied on vellum glued to a card support, often a playing card. The object is then enclosed within a locket made of turned wood, ivory, or metal inset with enamels and gems and worn on the body as a piece of jewellery. These sophisticated items were often imbued with highly personal significance, sometimes incorporating the sitter's emblem and motto, sometimes serving as commemorative pieces, and often given as gifts. However, compared with large-scale painting and portraiture of this period, limited technical research has been carried out on these minute objects.

Starting with seven portrait miniatures from the Fitzwilliam Museum in 2018, and since then expanding the research to include works from many other collections across the UK, Europe and Canada, we have gathered technical data on over 90 objects. The focus of this research project has been to extensively investigate and characterise the materials and painting techniques of miniatures attributed to Isaac Oliver (c. 1565-1617), a highly skilled artist originally from Rouen who established himself within the artistic emigree community of London.

A non-invasive analytical protocol was employed to investigate these fragile and small-scale objects, which are usually less than 10 cm in height. The systematic approach started with technical imaging (visible and raking light, UV, near-infrared) and X-ray radiography to document the state of preservation, visualise pentimenti and localise retouched areas. Optical microscopy was undertaken to observe and capture the minute detail of the paint work. Macroscale XRF scanning was used to gain unprecedented insights into the distribution of chemical elements in maps with a high spatial resolution, and spectroscopic techniques (UV-VIS-NIR reflectance spectroscopy, FTIR spectroscopy and Raman microscopy) enabled the identification of original and retouching pigments, colourants, and binders.

The rich body of objects in this research and the in-depth analysis undertaken allowed us to gain a broad understanding of the materials and working techniques of Oliver and to reveal changes in the palette over time, such as the presence or absence of indigo in the shaded areas, arsenic sulfides in the orange grounds under shell gold detailing, and vermilion in the flesh tones.

Among the wide range of pigments used by the artist, the green and white ones are of particular interest. Analysing minute details on a surface that was not always flat proved challenging for the use of FTIR in reflectance mode, but the combined results obtained with FTIR and Raman spectroscopies were able to characterise pigments in the green areas. The extensive use of brochantite in specific

paint passages, such as details in clothing and hair ornaments or landscape backgrounds, in contrast to mixtures of blue and yellow pigments used in other areas, is an explicit choice made by Oliver that shows a connection to the art produced elsewhere in Europe and in particular in Flanders at that time. Critically, these artistic choices allow us to differentiate Oliver's technique from his contemporaries.

The unusual discovery of a mercury-based white pigment (the mercury(I) chloride known as mercury white, or calomel) by Raman microscopy was first detected on a miniature from the Fitzwilliam Museum and subsequently found on a growing number of objects associated with Oliver and his followers, adding to and refining the information hitherto available on this artist's palette.

The research presents new technical insights into this under-explored art form, in particular a comprehensive characterisation of Isaac Oliver's palette and working technique. In the context of the continental training he received, and the materials described in contemporary treatises, the discoveries made in this work could also have an impact on the attribution of other objects to Isaac Oliver or his workshop and/or followers.

1.10. Maria Kipp and Dorothy Wright Liebes: exploring the use of metallic threads in mid-20th century textiles

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Metal threads have been used in textiles for centuries by various cultures to create ornate and luxurious fabrics. Over time, the use of precious metals in garments, draperies, and furnishing fabrics became more widespread and sophisticated. Even today, metal threads continue to be employed for decorative purposes in textiles. However, in the twentieth century, new methods of production emerged to meet the ongoing demand for metallic accents in textiles. One of these methods involved laminating aluminium foil with a polymer film, resulting in coated fibers with a metallic appearance. Building on this innovation, the introduction of vacuum metallization advanced the production of coated monofilament polymer fibers. Vacuum metallization is a process in which a thin layer of metal, such as aluminum, is deposited onto the surface of a polymer film using a vacuum chamber. This breakthrough expanded the possibilities of incorporating metallic elements into textile designs. In 1946, in between these two stages of development, the Dobeckmun Company trademarked a metallic fiber as Lurex (later acquired by Dow Chemical Company in 1957). Today, the term "Lurex" is widely used to refer to similar treatments of metallic fibers or fabrics outside of its trademark. However, the use of "Lurex" as a common descriptive term can cause some confusion, especially for objects that predate the trademark's registration. The use of metallized threads, including Lurex®, can be found in costumes and textiles displayed in various museums and cultural institutions, including those focused on modern and contemporary art. Notably, both the Los Angeles County Museum of Art (LACMA) and the Museum of Modern Art (MoMA) have textiles in their collections that feature these threads. This pioneering technique of using laminated metallized aluminum fibers during the mid-20th century pushed the boundaries of traditional textile art. Renowned artists Maria Kipp (1900-1988) and Dorothy Wright Liebes (1899-1972) were known for incorporating these fibers into their works during the same period. To gain a better understanding of the history of metallic threads used by Kipp and Liebes, a collaboration was undertaken between LACMA and MoMA.

This study focuses on 24 textiles by Kipp and six textiles by Liebes, utilizing a range of methods to investigate the metallic fibers present in these works. Comparisons are drawn with two spools of Lurex® obtained from online sources, which can be dated back to the initial production phase (ca. 1946-1957). The investigation is divided into two stages. Initially, the overall condition of the textiles is studied, and microscopic evaluations of the sampled fibers are conducted. The second stage involves fiber characterization using Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR), Raman spectroscopy, X-ray fluorescence (XRF), and scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS). The findings from this investigation will contribute to the development of a comprehensive preservation plan for these textiles and provide insights into the availability and use of Lurex® during its initial production phase.

1.11. Quantitative study of oils in ancient lacquer objects by near-infrared spectroscopy

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Oils were the most common additives in lacquer objects, which can increase the glossiness and elasticity of lacquer film. Qualitative and quantitative analysis of oils in ancient lacquer film is crucial for revealing lacquering materials and techniques in ancient times and supporting the conservation and restoration of lacquer objects. Through pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), which is an extremely effective method for analyzing organic lacquering materials, perrilla seed oil, linseed oil, and tung oil were identified as oil additives in ancient lacquer films. However, the severe aging and degradation of lacquer and oil make quantitative analysis of oil in lacquer objects very difficult.

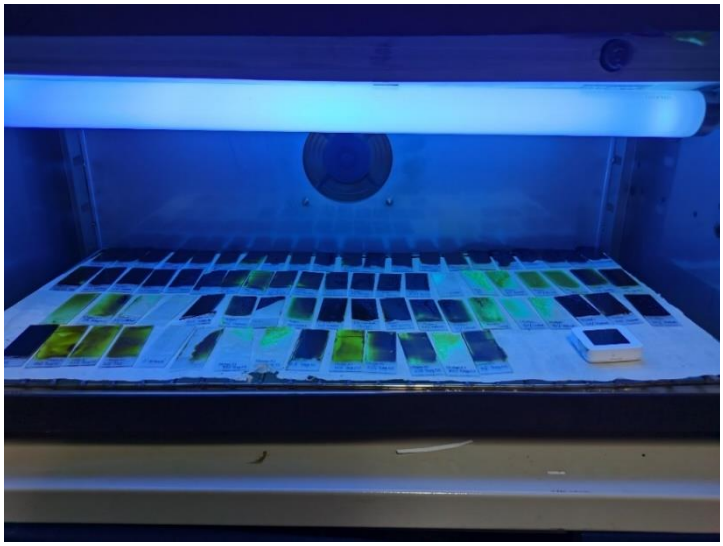

Figure 1: Reference samples for mixtures of lacquer with perilla seed oil, linseed oil and tung oil

In order to quantitatively analyze the proportion of oil to lacquer in the ancient lacquer objects, Near-infrared spectroscopy (NIRS), a non-destructive method was studied. In this research, partial least squares (PLS) models of reference samples for quantitative analysis of lacquer films were established, including perilla seed oil - lacquer PLS model, linseed oil - lacquer PLS model and tung oil - lacquer PLS model. When evaluating a model, factors such as correlation coefficient (R) and the root mean square error of prediction (RMSEP) were considered. The final optimal results of the PLS model showed that RMSEP and R in the calibration set were below 3 and above 0.97, respectively, demonstrating that NIRS can be used for the quantification analysis of lacquer film.

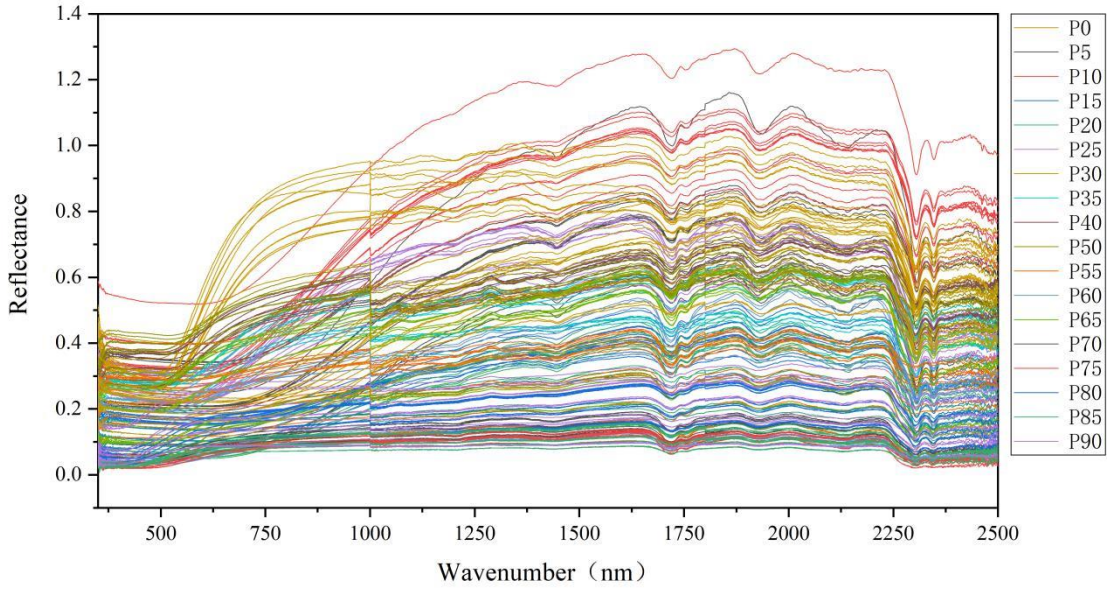

Figure 2: Original near-infrared spectra of reference samples composed of different ratios of perilla seed oil and lacquer

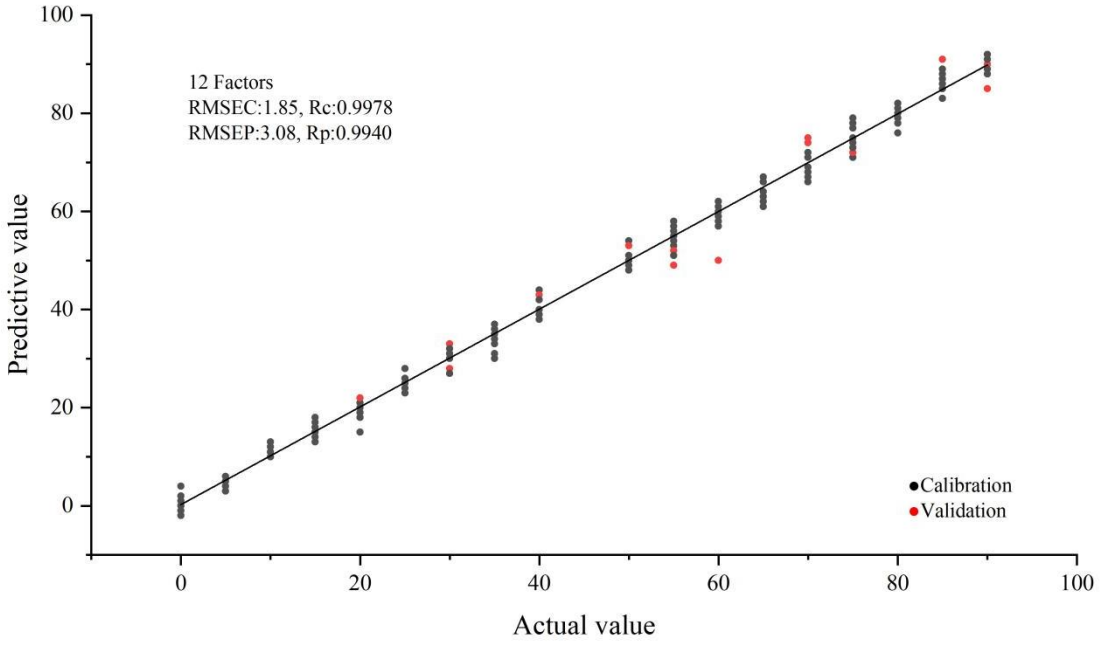

Figure 3: The perilla seed oil - lacquer PLS model

Subsequently, the established PLS models were applied to the quantitative analysis of oil in the lacquer films of lacquer Dou from Zaoshulin Zeng State Tomb in the Spring and Autumn Period, lacquerware from Chengyangcheng tomb in the Warring States Period, lacquer screen from the Mawangdui Han tomb, lacquer Zhu from Gufenyuan Han tomb, and six lacquer samples from the Buddhist statue and altar of Qing Dynasty, while thermally assisted hydrolysis–methylation for pyrolysis-gas chromatography-mass spectrometry (THM-Py-GC/MS) was applied for the qualitative analysis. The results showed that perilla seed oil was used in two lacquer films from tombs of the Spring and Autumn Period and Warring states Period, and their ratios were about 13%, while linseed

oil was used in two lacquer films from Han tombs and their ratios were about 25%, which indicated that the ratios of oil in lacquer films of Eastern Zhou Dynasty and Han Dynasty might be different. In addition, tung oil was used in six lacquer films of the Qing Dynasty, and the ratios of oil were varied between 20% ~ 36% in different objects for special purposes.

For the first time, the proportions of oil to lacquer were revealed in the ancient lacquer objects, which is significant in enhancing the knowledge about lacquering techniques in ancient times.

1.12. Infrared and Raman analysis of black East Asian printing inks

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Printing has occurred in East Asia (China, Japan, and Korea) for centuries, using both woodblock printing since the Tang dynasty in China and movable metal type printing since at least the 13th century, primarily in Korea. Woodblock printing has been used not only for the production of books but also as an art form that remains in practice today. Infrared and Raman spectroscopies are complementary analytical techniques for the examination of black East Asian printing inks. Raman spectroscopy is particularly sensitive to the polycyclic aromatic hydrocarbon structures in the soot pigments that color the inks but is very insensitive to the binding materials of the inks, while infrared spectroscopy is able to identify the binding materials in the inks.

Raman spectroscopy of the pigment used in black printing inks has been able to differentiate between two different black inks used in printing a Japanese printing of *Jieziyuan Huazhuan* [Mustard Seed Garden Manual of Painting], as well as to differentiate between traditional Asian lamp black and pine soot pigments. Infrared spectroscopy has been used to examine both printing inks and written commentary in several early movable type printed specimens, confirming the use of a protein-based binding medium and suggesting the absence of a starch-based binding medium.

1.13. On the road with a portable Raman system: identifying plastics in Dutch museum collections

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The Plastic Identification Tool (PIT) presented at IRUG13 has proved to be successful for the identification of plastics in museum collections without analytical equipment in many cases [Cultural Heritage Agency]. In cases where the PIT is not conclusive, FTIR-ATR analysis using a portable system is very useful for the identification of plastics on site and, depending on the geometry of the object this can be performed non-invasively. However, a non-invasive technique that can be applicable for a range of 3D objects containing plastics will be very useful. Therefore, it was decided to explore the possibility of using the Bruker Bravo portable Raman system for non-invasive analyses of plastics. The Bravo uses a DuoLaser system excitation, 785 nm and 852 nm, recording spectra in two separate spectral ranges of 170–2200 and 1200–3200 cm^{-1}. This instrument affords automatic fluorescence mitigation, thus proving valuable or the analysis of the highly fluorescent materials present in some of the samples.

The patented sequential shifted excitation (SSETM) works by temperature-shifting the lasers over a small wavelength range and recording three spectra per laser, finally merging them into a seventh averaged spectrum. In this way, and through the use of near infrared lasers, the system is able to reduce fluorescence [Pause, 2021].

To verify if the Bravo system can be used safely for the identification directly on plastic objects, the use of the system on plastics was evaluated. First, the Raman spectra of the plastic references from the POPART SAMCO reference collection were recorded using different combinations of settings. Afterwards, the samples were checked for laser induced damages [POPART, 2012]. To evaluate the Bravo's performance for the identification of plastics, the acquired Bravo spectra were compared to the spectra of the same references recorded with a benchtop micro-Raman instrument, a RamanMicro 300 in combination with a RamanStation 400F (Perkin Elmer) and an Olympus BX51M microscope. The Bravo spectra of the SAMCO collection could then be used to build a plastic reference library. Finally, the Bravo – library combination was tested by analyzing a large number of objects from the van Oosten collection, which is the RCE plastics reference and study collection.

After completing the steps mentioned above, the Bravo system was ready for the road to identify plastics in Dutch museum collections. The tour of the Bravo included visits to several museums in the Netherlands:

- the Boerhaave Museum in Leiden, where the embedding resin for moonstones could be identified
- the National Museum of World Cultures in Amsterdam, for identifying different plastics in the collection during a collection survey
- the Stedelijk Museum in Amsterdam, for identifying the plastics in 'La-Boîte-En-Valise', Marchel Duchamps, 1936-1949

the Stedelijk Museum in Amsterdam, for identifying plastics in 'Angel', Simone Forti, 1975-1977

and

a Naum Gabo from a private collection that visited the RCE laboratory to be analyzed using the Bravo: 'Bas-relief on a circular surface, semi-spheric', Naum Gabo,1938.

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POPART 2012, https://popart-highlights.mnhn.fr/wp-content/uploads/2_Identification/1_What_plastics_are_in_my_collection/2_2_NeedForAPlasticReferenceSampleCollection.pdf (accessed 26 September 2023).

1.14. Revealing the key recipes of ancient Chinese lacquer process techniques by non-invasive quantitative method: near infrared spectroscopy and chemometrics

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Keywords: Lacquer; tung oil; non-invasive; quantitative; near-infrared spectroscopy; chemometrics

Introduction

Lacquer sap is a kind of raw liquid material secreted by Anacardiaceae plants. The solidified lacquer has a high strength and is resistant to heat, corrosion, and water. Its performance is better than most modern synthetic materials. Archaeological evidence suggests that lacquer has been used as a coating material in ancient China for more than 8000 years [Wu, 2018]. Since then, the lacquer handling process has developed continually and has become a unique and flourishing Asian art. In addition, Chinese lacquerware was popular in Europe in the 16th–18th centuries and influenced the aesthetics and handicrafts of Europe [Honour, 1973; Webb, 2000; Buonanni, 2009].

The process of mixing Tung oil in lacquer sap was a milestone in lacquerware history. It ensured that craftsmen could easily adjust the color and mechanical properties of lacquer film by changing the Tung oil content. Furthermore, abundant types of lacquer art forms appeared over the past thousands of years. However, it is unfortunate that the rules of Tung oil content for different types of art forms are still unclear and disputed. The main reason can be concluded as the lack of quantitative testing methods, especially non-invasive ones, which are friendly to precious arts.

In this research, a breakthrough in solving this problem was made based on near infrared spectroscopy (NIR) and chemometrics. The oil ratios of 55 ancient Chinese lacquerwares with different kinds of process techniques were analyzed by this new method and the rules of oil content in different types of ancient lacquerwares were discussed.

Standard samples preparation

To ensure representativeness, the four types of Urushi lacquer were used, which were obtained from 4 main producing areas in China, namely Chengkou in Chongqing province (重庆城口), Bijie in Guizhou province (贵州毕节), Maoba in Hubei province (湖北毛坝), and Langao in Shaanxi province (陕西岚皋). The oils used were 3 commercial stand Tung oil products. Then, 140 samples (including 100 calibration samples and 40 validation samples) with different oil ratios (between 0%–80% by weight) were made for every combination. Cinnabar is commonly mixed in lacquer as a pigment. Therefore, cinnabar was randomly added in the samples to simulate an actual situation. Mixed sample saps were painted on glass sheets and laid in a room environment for 2 years for solidification.

Collection of NIR spectra

A Thermo Antaris II FT-NIR analyzer with a white light source and InGaAs 2.6 µm detector was used and scanned 16 times with a resolution of 8 cm^{-1} in the spectral range of 4000–10000 cm^{-1}. Data were collected from the standard samples and artworks using a fiber-optics probe (Figure 1). The standard samples were thin and could be penetrated by NIR. So, they were placed on a gold coated mirror that reflects the NIR back in to the sample without any characteristic absorption. In contrast, the ancient objects were analyzed directly.

Chemometrics modeling

TQ Analyst software was used for chemometrics calculation. Several methods were used for the pretreatment of NIR spectra, such as SNV, NDF, second derivative, mean centering technique, and variance scaling technique (Figure 2). PLS was used for modeling based on the full spectrum (4000–10000 wave number). As shown in Figure 3, the root mean square error of calibration (RMSEC) is 1.95, and the root mean square error of prediction (RMSEP) is 2.09. These two values are similar, which means that the model will be stable for unknown samples.

Results discussion and conclusion

Fifty-five Chinese lacquer artworks with different periods and process techniques (Figure 4) were selected to analyze the rules of oil ratio. The results were divided into groups for discussion according to the research purpose. Details are as follows:

1. Four black lacquerwares, two colorful lacquerwares and twelve carved lacquer of the Qing Dynasty were statistically studied together to discuss the relationship between lacquer process types and oil ratios. The results show that there is a clear correlation between them. The oil ratios of black lacquers are the lowest (7%~13%). The oil ratios of colorful lacquers are higher (16%~34%), probably because adding oil can make the lacquer film more transparent to ensure that the color of pigments is bright and vivid. The oil ratios of carved lacquers are the highest (50%-69%). The main reason might be that carved lacquerwares consist of dozens of lacquer layers. Adding oil decelerates the speed of drying, keeping the lacquer film soft and easy to carve for a long time.

2. Thirty typical lacquerwares of the Han Dynasty (BC202 – AD220) were statistically studied together to discuss the oil ratios of the early lacquer process. The results show that: (1)The oil ratios of these lacquerwares are in the range of 17.4% - 40.2% and that most of the data is concentrated in 25% - 35% range. It indicates that the process of adding oil in lacquer was very popular in this period. (2) The average oil ratio of black positions is 24.5% and of dark brown positions 25.7%, which are very close. It shows that the reason for the color difference is not oil ratios. (3) The average oil ratio of red positions is 32.6% and is apparently higher than the black and dark brown positions. This could be evidence that the craftsman acquired the technology to increase the saturation of the color by adding oil as early as the Han Dynasty.

3. Seven typical carved lacquerware of the Ming Dynasty (AD1368 – AD1644) and twelve typical carved lacquerware of the Qing Dynasty (AD1636 - AD1912) were statistically studied together to discuss the difference in oil ratio between these two dynasties. The oil ratios of the Ming Dynasty are in the range of 38% - 48%. The oil ratios of the Qing Dynasty are in the range of 50% - 69%, which is apparently higher than for the Ming Dynasty. On one side, this phenomenon may explain the reason why the carved lacquerwares of the Ming Dynasty are generally darker and tend to crack more easily than those of the Qing Dynasty. On the other side, this phenomenon could be essential in separating the generation of carved lacquerwares.

Figure 1: Collecting the NIR spectra noninvasively from a carved lacquerware of Qing Dynasty by a fiber-optics

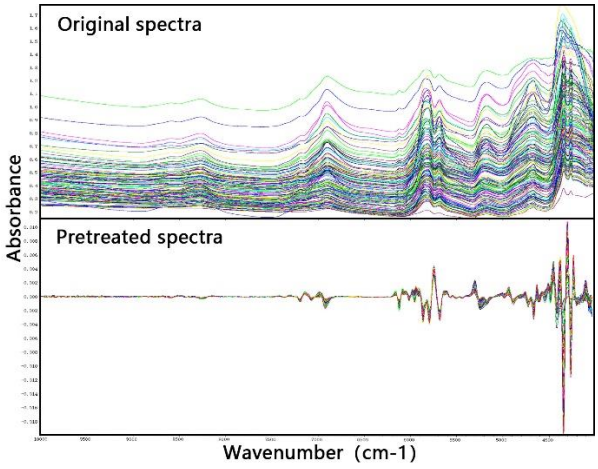

Figure 2: The original and pretreated NIR spectra of

probe. standard samples with different contents of oil.

For the NIR spectra (Figure 2), the difference of the characteristic bands in the original spectra is not clear. And the problem of baseline shift was also found. The pretreatment enhances the feature information and mitigates baseline shift.

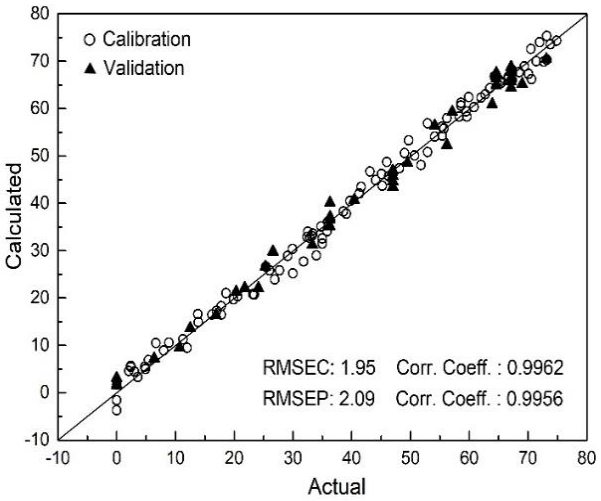

Figure 3: Calibration and validation result of the PLS model. The X axis is for actual values of tung oil content of samples. The Y-axis is for calculated values of tung oil content of samples. Circles indicate calibration samples. Triangles indicate validation samples. The closer a sample point get to the diagonal, the less is the error calculated by the model

(a) Fragments from typical lacquerwares of the Han Dynasty (oil ratio of dark brown position: 28.5%, oil ratio of red position is 34.1%)

from

(b) One of typical black lacquerwares of the Qing Dynasty: “Throne with black lacquer and golden paint” (oil ratio of black position is 14.4%)

(c) One of typical colorful lacquerwares of the Qing Dynasty : “Colorful painted box for Guqin” (oil ratio of red position is 22.9%, oil ratio of red position is 27.8%)

(d) One of typical carved lacquerwares of the Qing Dynasty: “Floral pattern plate” (oil ratio is 57.1%)

(e) One of typical carved lacquerwares of the Ming Dynasty: “Floral pattern bowl” (oil ratio is 42.4%)

Figure 4: A part of tested typical ancient Chinese lacquerwares and the testing result of oil ratios. 55 ancient Chinese lacquerwares were tested in total. The Periods of manufacture include the Han, Ming and Qing Dynasties. The lacquer process techniques include black lacquer, colorful lacquer and carved lacquer.

Funding

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1.15. Is there an International Klein Pink?

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Yves Klein (1928-1962) was an artist who sought to free painting from historical constraints of subject matter, media, and methods of paint application. In the early 1950s, he began experimenting with monochromatic works in green, yellow, blue, pink, red, and orange. These works were first publicly presented in his 1954 books *Yves Peintures* and *Haguenault Peintures*. As Klein continued to create monochromes, he became frustrated that the color of pure pigments altered upon mixing with a binder, saying:

> "*I did not like colors ground with oil. They seemed to be dead… What upset me was to see this incandescent powder lose all its value and become dulled and lowered in tone once it was mixed with glue or whatever medium was intended to fix it to its support.*" [Stich 1994, 59-60]

Although best known for his IKB paintings, Klein never abandoned other colors and eventually came to favor a monochromatic 'trinity' created through the use of blue, pink, and gold [Stich 1994]. Unlike his IKB, Klein provided very little information about these materials. In his self-published newspaper *Dimanche: Le Journal d'un Seul Jour*, he indicated that the term "IKP" ("International Klein Pinck"[sic]) referred to a pink madder lake (lacque de garance rose), but this has not been confirmed through scientific analysis of his artworks. It is also unclear if he used a single pigment across all his pink works, similar to his use of a single blue pigment, and if the colorants in his red and pink works are the same, with tonality differences arising from different pigment to filler ratios.

To address this void, we undertook an investigation of five red and pink works by Klein [Haddad and Rogge, 2023]: *Untitled Red Monochrome (M 63)* (1959) at the Solomon R. Guggenheim Museum, New York, US; *Grand Monopink (MP 16)* (1960) at the Louisiana Museum of Modern Art, Humlebaek, Denmark; *Red Rain (Pluie Rouge) (S 37)* (1961) and *Untitled Shroud Anthropometry (ANT SU 4)* (*Anthropométrie suaire sans titre [ANT SU 4]*) (ca. 1960), both at the Menil Collection, Houston, US; and a pink silkscreen print from 1961 held by The Museum of Modern Art (MoMA), New York, US. While these works were made within a short time frame of only three years, they nevertheless present a variety of formats in which Klein used the colors red or pink. These five works thus offer a chance to interrogate Klein's pink and red color choices through a variety of artistic creations that encompass much of his oeuvre.

Binders were identified by micro-Fourier transform infrared spectroscopy (μ-FTIR) and additional filler materials through x-ray fluorescence spectroscopy and scanning electron microscopy coupled with energy dispersive x-ray spectrometry, in addition to μ-FTIR in some cases. The pigments, many of which were highly fluorescent under ultraviolet illumination, were identified by Raman and surface enhanced Raman spectroscopy. The results show that while the binders for the paintings and sculpture are all polyvinyl acetate (PVAc), Klein used a variety of different pigments, including Para red (PR1), rhodamine 6G (PR81), rhodamine B (PR173), eosin Y (PR90:1), and alizarin lake (perhaps PR83:1). The binder in the screenprint in the collection of MoMA was identified as oil-based printing ink. In at least two cases, Klein either altered the colors in his works from pink to red or made deliberate use of layering to manipulate the visible color. These findings paint a more complex

picture of Klein's working practice with the color and have significant implications for the longevity of these works. The pigments found range in lightfastness from Blue Wool Scale 2-3 (eosin Y and rhodamine B) to 6 (synthetic alizarin), which indicates that, even under normal museum display conditions, significant color change can be anticipated within a relatively short period of time. Many of these pigments are also solvent-sensitive, which could limit future treatment possibilities.

The diversity of pigments identified in this study suggests Klein had not settled on a singular "IKP'' pigment. Perhaps, had Klein lived longer, this exploration of the color pink would have led to the same standardized practice he arrived at with IKB, or perhaps for reds and pinks he had no clear vision of what the ideal color was, unlike his strong vision of a single, perfect blue.

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1.16. Infrared reflection spectrometries (keynote)

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Keynote talk

Spectral analysis of irreplaceable works of art presents important technical challenges due to the need for minimally invasive or non-invasive methods. The artworks should, as much as possible, remain intact. For mid-infrared spectrometric analyses, reflection methods, that is, specular reflection, attenuated total reflection, and diffuse reflection, present attractive options. Still, each of the three spectrometric techniques presents its own issues with respect to sensitivity and spectral anomalies. The gold standard for infrared spectra is regarded as transmission spectrometry, which requires (micro) invasive sampling of the original item to be analyzed. Transmission spectra, if collected carefully, have no band distortions or band shifts, if the instrument is operating correctly. The reflection methods have distinctly different characteristics, for which the theoretical aspects are quite well understood. To understand the differences, the optical constants, refractive index and absorption index must be considered. The different reflection methods are affected in different ways by the optical constants. A theoretical discussion of optical constants is beyond the scope of this presentation, and only a brief introduction will be given.

Attenuated Total Reflection (ATR) spectrometry has become the most popular general sampling technique for infrared spectra due to the lower sample preparation requirements compared to other techniques. The drawback, particularly with samples that cannot be damaged, is that the sample must be in intimate contact with the ATR internal reflection element (or IRE, sometimes erroneously called a “crystal”). Intimate contact can be an issue, as the infrared radiation only extends a few micrometers beyond the surface of the IRE, and often some pressure must be exerted to record a good spectrum, which could damage the sample. While ATR spectra are straightforward to collect, there are anomalies associated with the spectra. The “depth of penetration” of the infrared radiation into the sample is a function of wavenumber and refractive index of the sample. The refractive index is generally around 1.5 for most organic compounds, but that is true only where there is no absorption. Inside an absorption band, the refractive index can vary greatly, and the band intensities, shapes, and even positions can be distorted. There are algorithmic corrections that may be applied to the spectra, but care must be taken to ensure no additional anomalies are introduced.

Specular reflection spectrometry overcomes at least some of the issues of ATR spectrometry because it is a non-contact technique. Distinction has to be drawn between bulk samples, where the sample thickness is greater than or equal to the incident wavelength, and thin samples, where the sample is thinner than the wavelength. Thin samples need a reflective surface upon which the sample sits, or the radiation will not readily be reflected back to the spectrometer. Bulk samples are more directly measured, but the refractive indices and the absorption indices of the sample affect the spectrum. For most organic molecule samples, the refractive index dominates the reflection spectrum, and as such, the resulting reflectance spectrum appears as a refractive index spectrum. (Reflectance is the intensity of the reflected radiation ratioed by the incident radiation.) The refractive index across absorption bands varies with wavelength, and the spectral features are similar to first derivatives of the spectral bands. Judicious application of a Kramers-Kronig (KK) transform can yield the true refractive index spectrum and the absorption index spectrum. The absorption index spectrum is related to the absorption spectrum. An issue that can arise with reflection spectra of bulk samples is

in the measurement of some pigments. If pigments contain minerals, which are largely composed of oxyanions, the absorption index can be very high. If the absorption index is sufficiently high, no radiation can be propagated into the sample, and the reflectance is largely or completely reflected. This reflectance radiation is known as “residual rays” or, more frequently, as Reststrahlen bands.

Diffuse Reflection (DR) spectrometry is a suitable technique in some cases. In the mid-infrared region, the sample must be diluted into a solid solution to produce a good spectrum. Typically, this is done in a salt such as KBr. This requires that the sample be extracted and pulverized to a small particle size and mixed carefully with the ground salt. Fortunately, an alternative sampling technique can be used to scrape the surface of the sample very lightly with a small piece of silicon carbide paper. An advantage of DR spectrometry is that the analyte produces better spectra when its concentration is very low. As such, minimal damage to the original sample may result. The raw spectrum is measured in reflectance. It is common practice to convert the reflectance spectrum to absorbance; however, the spectrum may represent a true absorption spectrum better if converted to Kubelka-Munk units.

There are several other issues that can be examined; that is, what else may be used to enhance the results without the introduction of anomalies? It is not always apparent that infrared spectra, or any optical spectra, may not correctly represent band intensities and shapes. Beers Law fails at high absorbances in such a way that band intensities and even shapes may be distorted. It is not uncommon to measure samples that are too concentrated or thick, and sometimes there is no alternative. The definition of high absorbance is subject to a number of factors, but most prominently, the apodization function or line shape function of the spectrometer determines the limit at which Beers Law fails. A simple rule of thumb is to keep the strongest absorbances below 1 absorbance unit (AU). Why is adherence to Beers Law important? If spectral subtraction is needed to resolve components of a mixture spectrum, then if the reference spectrum and the sample spectrum have different non-linear absorbances, the difference spectrum will have anomalies. The same criterion applies to spectral searching; poor search results will occur if the spectra do not obey Beers Law. Other standard computer operations, such as baseline correction, may distort spectra and actually shift band centers. Even spectrometer calibration is important to assure instrumental errors do not introduce anomalies into spectra.

1.17. ATR –FTIR and μ-Raman based analysis for detection of chemical transformation in Indian wall paintings

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Wall paintings are exposed to all vagaries of the environment, such as uncontrolled humidity, temperature, growth of biological organisms, etc., apart from man-made factors. Preservation of such painted surfaces requires a holistic approach to address the causes of such decorative surfaces. In the present paper, wall paintings of two sites from north India, one an 18th century living Shiva temple and the other an early 16th century Raj Mahal of Orcha fort, were investigated using predominantly attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR) and micro-Raman spectroscopy. For the wall paintings, a correct physical and chemical characterisation of pigments is crucial to their appreciation and conservation. The major advantage of ATR infrared spectroscopy is that it gives the opportunity to retrieve the samples for other further analyses. We used the same samples for ATR examination followed by Raman spectroscopy, with neither process requiring any sample preparation. In this paper, we demonstrate the complementarity of ATR-FTIR and μ-Raman in investigating the wall painting materials, specifically the inorganic materials used in Indian paintings, and highlight the chemical transformations detected during the analysis using these instruments. ATR enabled reliable identification of the molecular composition of the surface layer and identified secondary species and impurities present in the painted layer in the pigment of both wall paintings.

All the pigments in both sites have been badly affected due to the formation of calcium oxalate by biological colonisation, and the damage is continuing. The transformation of the calcitic layer via sulphation into the calcium oxalate has been clearly observed in ATR and Raman analysis. There was a slight deviation in the Raman bands of red colour, probably due to calcium sulfate and calcium carbonate in the ground, which has created fluorescence in Raman spectra. It was interesting to see that in all FTIR spectra there was a band present around 1316-1320 cm^{-1} and one at780 cm^{-1}, which indicated that some of the proteinaceous parts of the binding medium might have converted into calcium oxalate. The approximate amount of calcium oxalate formation in all the samples was calculated by analyzing the ratio of calcite, gypsum and calcium oxalate obtained through ATR analysis of all pigments. For this purpose, the intensities of absorbance of the carbonate band centered around 1405 cm^{-1}, sulfate band centered around 1114 cm^{-1} and oxalate band around 1320 cm^{-1} were taken for measuring the concentration of the individual components in the samples. However, the high heterogeneity of the samples does not allow the precise quantitative comparison using this method. Fungal contamination is a global problem existing not only in houses but also in museums, art galleries and monuments. Prevention of mould growth is a common concern in most of the museums, monuments and historic buildings. Due to the oxalate formation, green pigments, especially malachite, suffer chromatic alterations. Fungus, bacteria, algae and lichens have been responsible for the transformation of calcium carbonate to calcium oxalate. During metabolism, these micro-organisms secrete oxalic acid ($H_2C_2O_4$), which can react with the calcite ($CaCO_3$) present in the painting giving rise to calcium oxalate (CaC_2O_4), in different states of hydration whewellite ($CaC_2O_4.H_2O$) and weddellite ($CaC_2O_4.2H_2O$), which are very insoluble, leading to the formation of efflorescence and consequent deterioration of the paintings.

In the Orchha fort wall painting pigments, a chemical transformation of gypsum into anhydrite was detected which could be due to long hot summers in the area. When the white area of pigmented plaster was targeted under 785 nm laser, the peaks of calcite at 1086 cm^{-1} in association with a peak at 280 cm^{-1} were observed. In addition to this, several bands in Raman spectra considered as diagnostic bands of anhydrite were observed, suggesting this as a major component in the white area. We observed a strong, intense peak at 1016 cm^{-1} and other peaks at 168, 235, 415, 498, 608, 627, 674, 1102, 1128, and 1160 cm^{-1}, clearly indicating the transformation of gypsum to anhydrite. Raman spectroscopy is a most useful technique to differentiate between different polymorphs of sulfates of calcium. Gypsum is the most common phase of calcium sulfate. On dehydration, the hemihydrate product bassanite (also known as plaster of Paris) is formed. The transition from gypsum to bassanite to anhydrite is temperature dependent and when the anhydrite is reheated the band of 1016 cm^{-1} {$v_1(SO_4^{2-})$} shifts further to the high-frequency region and appears at ~1026 cm^{-1}. On cooling, this peak again disappears and re-appears at 1016 cm^{-1}, the characteristic peak of low-temperature insoluble anhydrite.

When the black pigment from Orchha fort was examined by Raman with 785 nm laser, only three peaks at 222, 290 and 546 cm^{-1} were observed. The bands at 222 and 290 cm^{-1} indicate the presence of haematite, which was primarily natural red ochre. The bands at 222 and 546 cm^{-1} are characteristic peaks of red lead. The possibility of the presence of the red lead was also corroborated by the EDX analysis in which lead is present as one of the major elements. Thus, the finding of red ochre and red lead inclusion indicates the presence of red pigment in the black area. This implies that the black area does not contain any characteristic black minerals, but the black hue may be due to the growth of microorganisms on the painted surface.

The analysis of painted surfaces helped in identifying the deterioration process that guides the future course of conservation. The red pigment in Orcha was totally transformed into a black colour due to microbial growth, which disfigured the paintings. The formation of calcium oxalate formed a veiled appearance on all pigments. The calcium oxalates, which were found in pigments of both sites, gradually develops on the painted surface and becomes problematic as they are resistant to organic solvents and other cleaning agents. The mineralization of organic components in the paintings poses significant practical and ethical challenges in the development of cleaning strategies for such painted surfaces. The alteration products in the form of oxalates have been of great interest to scientists and conservators.

1.18. Analytical studies of light-aged Asian lacquer boards

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The systematic study of light aging behavior of Asian lacquers is an important step in the understanding of physio-chemical changes to the decorative surfaces and aiding in the development of appropriate treatment methods. Of primary concern are changes resulting from exposure to photo-oxidative inducing light radiation and potential influences on the material's sensitivity to aqueous solvents. Many published aging studies on Asian lacquers have been carried out on dried tree saps only. Unfortunately, the one-dimensional approach has limited the more comprehensive understanding of changes to the lacquer mixtures. To simulate the synergistic influence of additives, lacquer replicas with known formulations containing urushi, laccol and thitsi were applied to wood boards and allowed to cure. Light aging experiments were carried out in an Atlas Ci4000 Weather-Ometer (WOM) housing a Xenon arc lamp, a sodium borosilicate inner filter and a CIRA soda lime outer filter, simulating the influx of natural light through window glass. The output of the lamp was set at 0.5 W·m−2 at 340 nm. The temperature and relative humidity inside the chamber during light aging were set at 50°C and 35%, respectively. Following light aging, the panels were exposed to relative humidity cycling between 80% RH and 20% RH in humidity chambers for 12 weeks.

FTIR-ATR mapping studies on surface samples and embedded cross-sections were conducted to help determine the extent of light induced alterations. The observed changes were primarily limited to the top few micrometers of the lacquer films. THM-Py-GC/MS analysis was also conducted on samples scraped from the top surface and soluble residues extracted with water applied to the surface. A marked increase in the formation of acid catechols produced from the unsaturated sidechains of substituted catechols was observed. In addition, di, tri and tetra-carboxylated benzene isomers were detected in the water extracts, likely influencing pH conditions on the surface.

Results from the study of replicas have furthered the understanding of the chemistry of Asian lacquer surfaces and, in turn, have assisted in the development of treatments for the removal of degraded lacquer layers and helped improve the long-term appearance of lacquered objects.

1.19. Application of r-FTIR in the identification of white and green pigments in a Persian illuminated manuscript

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Pigment identification challenges

Correct identification of materials, including pigment, is crucial for the conservation of cultural materials. Illuminated manuscripts pose a particular challenge with materials analysis due to sample size limitations. When studying illuminated manuscripts, methods requiring sampling are often not permitted as historical manuscripts are usually fragile, with intricate calligraphy and fine painting limiting the amount of material available for samples, making it difficult to remove a sample without damage. Therefore, in-situ non-destructive analysis is preferred [Aceto et al, 2012]. Several non-destructive spectroscopic methods are available that can be used for in-situ pigment studies, such as X-ray fluorescence spectroscopy (XRF), Raman microscopy (RM) and Fourier Transform Infrared Spectroscopy (FT-IR) [Burgio, 2021].

The complexity of the paint layer composition can make it challenging to identify pigments using XRF. RM may also be challenging when the paint layer fluoresces. FT-IR spectroscopy and the development of ATR-FTIR have enabled researchers to identify various materials non-destructively [Bruni et al, 1999; Creagh et al, 2000; Giacometti et al 2017]. However, some limitations remain with the use of ATR-FTIR for illuminated pages as the requirement for close contact between the ATR crystal and the area being analysed can result in pressure on the surface of the object, and this can damage fragile paper, cracking brittle pigment layers or create indentations on its surface [McClelland et al, 2020].

On the other hand, reflection infrared spectroscopy (r-FTIR) is a non-invasive tool that enables the material to be studied without contact. In r-FTIR microscopy, a microscope is coupled to the FTIR spectrometer, and the specimen is analysed in reflectance mode [McClelland et al , 2020;Bitosi et al, 2005; Katon, 1996]. Researchers have been using r-FTIR for conservation purposes, such as pigment investigation [Bruni et al, 1999; Holakooei et al, 2018; Miguel et al, 2009; Bruni et al, 2008]. Despite the potential of r-FTIR spectroscopy for non-invasive analysis, this technique is not yet routinely used to analyse artworks. This is because the spectra produced by r-FTIR differ from those produced by conventional FTIR or ATR-FTIR modes. Differences in relative band intensities are typically observed due to variations in the scattering factor and absorption coefficient, which are affected by the surface reflection and volume (diffuse) reflected radiation, producing strange distortions in the band's shape, position and intensity, all making spectral interpretation challenging [Miliani, 2012].

Aim

This research aimed to identify white and green pigments applied in a treatise of *Yūsuf and zulaykhā (MUL 76)*, a 17th-century Persian illuminated manuscript held at the University of Melbourne Middle Eastern Manuscript Collection. This manuscript has opening pages (*sarlawh*) illuminated in gold, ultramarine, black, red, yellow, white and green ornaments. Utilising a combination of RM and XRF, the composition of all the paint layers was identified, with the exception of white and green, since

these colours exhibited intense fluorescence during RM analysis. As a result, there remained the need to find additional non-destructive, non-damaging methods that might prove useful.

Figure 1: *Yūsuf and zulaykhā (MUL 76)*, opening page

Methods

This research explores the application of in situ non-contact r-FTIR spectroscopy to identify white and green pigments in the studied manuscript, MUL 76, utilising a LUMOS FTIR microscope (Bruker) operated in reflection mode in the spectral range of 7000–450 cm^{-1} at a resolution of 4 cm^{-1}, with a background taken against the built-in gold reference mirror. The accompanying Bruker OPUS (v7) software, was used to collect IR spectra. X-ray fluorescence microscopy (XFM) was employed to confirm the composition of the pigments.

Materials

A particular benefit for researchers working on the history of Persian book production is the large number of historic treatises and manuals that are available from different periods. These are especially useful for researchers undertaking materials analysis as they provide information of the materials used in the production of manuscripts during particular periods. In Persian treatises, materials such as lead white ($2PbCO_3.Pb(OH)_2$) and calcined eggshells have been mentioned as the white pigment [Afshar, 1601; Qumi, 16th Century; Purinton et al, 1991]. As lead white and calcined eggshell, ($Ca(OH)_2$), which is slowly reconverted to calcium carbonate ($CaCO_3$) on exposure to the air [Gettens et al, 2018], are both carbonate-based pigments, the spectral region of the carbonate functional group in the FTIR spectrum is of interest. Samples of lead white pigment (sourced from Kremer Pigments) and calcium carbonate (sourced from Sigma Aldrich) in a solution of gum Arabic

(source from Persian local market) in distilled water (20% m/V) were applied on Winslow watercolour paper and used as a reference of white. Identifying green pigments entails comparing the r-FTIR spectra of the area in question to the spectra of verdigris, malachite, and azurite as established by prior research [Miliani, 2012; Buti et al, 2013; San Andrés 2010].

Results and conclusions

- White pigment identification:

R-FTIR spectrum of lead white displays an intense absorption in the 1450-1420 cm−1 region because of the antisymmetric CO_3^{2-} stretching (v3), which is inverted by the Reststrahlen effect. Additionally, lead white reveals the carbonate anion's v1 + v3 combination band, which appears around 2400-2420 cm^{-1}, and the combination band of the v1 + v4 modes, which occurs at 1733 and 1740 cm^{-1} for anhydrous (cerussite) and hydrous (hydrocerussite) forms of lead white, respectively [Miliani, 2012]. Regarding calcium carbonate, a sharp peak can characterise it at 1800 cm^{-1}, corresponding to the combination band at v1 + v4 mode, and a combination band at v1 + v3, centred at 2516 cm^{-1}, with a shoulder at 2594 cm^{-1}[Miliani, 2012].

Analysis of the white paint layers in the treatise of *Yūsuf and zulaykhā (MUL 76)* revealed that the r-FTIR spectrum of white colour matches the characteristic peaks of lead white, and the absence of peaks at 2500 and 1790-1800 cm^{-1} indicates the sample does not include calcium carbonate.

- Green pigment identification:

Green was also applied to depict different ornaments in the illumination of MUL 76. Various materials have been historically found as green pigments in Persian paintings, including verdigris ($Cu(CH_3COO)_2H_2O$) [Clark et al, 1998], malachite ($CuCO_3.Cu(OH)_2$) [Muralha et al, 2012; Bruni et al, 2001], and an admixture of indigo and a yellow pigment [Clark et al, 2006; Jurado-López et al, 2004]. XRF analysis of the *sarlawh* of MUL76 revealed that the green contains copper, a key component of copper-based pigments such as verdigris, malachite, and azurite [Purinton et al, 1991; Buti et al, 2013].

FTIR peaks primarily associated with verdigris correspond to acetate groups (CH_3–COO), hydroxyl (–OH), and water of hydration. The acetate group exhibits the most significant bands, which include those related to the methyl group (–CH_3), the carboxylate group (COO), and the C–C vibrations [San Andrés et al, 2010]. In verdigris, the carboxylate groups display symmetric and antisymmetric stretching vibrations at around 1420 and 1600 cm^{-1}, respectively. The CH_3 groups show C-H bending modes at 1032, 1051, 1354, and 1444 cm^{-1}, usually overlapping with C–H bending vibrations from the binder [Buti et al, 2013]. Moreover, the combination of -CH stretching and bending modes exhibits three peaks between 4450-4300 cm^{-1} [Buti et al, 2013], and the hydroxy group not involved in hydrogen bonding exhibits a stretching vibration of the -OH at around 3450-3600 cm^{-1} [Clark et al, 1998].

Regarding malachite, the r-FTIR spectrum shows bands related to CO_3^{2-} and O–H. The v3 antisymmetric stretching bands of CO_3^{2-} occur at 1389 and 1494 cm^{-1}. Bands correspond to the stretching vibration of the carbonate group (v1), and the bending vibration of the carbonate group (v4) appears at around 1800 cm^{-1} [Miliani et al, 2012; Buti et al, 2013]. Another distinctive CO_3^{2-} band appears at around 2537 – 42 and 2422 cm^{-1} (v1+v3). In addition, malachite shows spectral bands at around 4506 and 4405 cm^{-1}, indicative of the second-order overtone of v3 CO_3^{2V}. Malachite also

shows two peaks at around 4241 and 4166 cm^{-1}, attributed to the combination of O–H bending and stretching [Miliani et al, 2012; Buti et al, 2013].

Azurite is a blue carbonate pigment. Azurite's combination band of v1+v4 modes appears broad at about 1860 cm^{-1}. The combination of v1 + v3 happens at 2500, 2553, and 2587 cm^{-1}. Another region of interest is where overtone of 3v3 and v + δ (OH) occur as a strong doublet at around 4380 and 4244 cm^{-1}, respectively [Miliani et al, 2012; Vetter et al, 2019]

Analysis of the green paint layers in the treatise of *Yūsuf and zulaykhā (MUL 76)* involved comparing the r-FTIR spectra of the green colour in MUL 76 with characteristic peaks of verdigris malachite and azurite. The absence of carbonate peaks indicated that the paint composition does not include malachite and azurite. The stretching vibrational bands of CH_3 in the verdigris acetate group's asymmetric and symmetric stretching vibration and the combination of -CH stretching and bending modes in verdigris reveal the presence of verdigris.

Conclusion

In summary, r-FTIR reveals that the white pigment in MUL 76 is lead white, and the green pigment is verdigris demonstrating the effectiveness of r-FTIR in conducting non-invasive pigment analysis of illuminated manuscripts. This complementary non-destructive technique for pigment identification provides an alternative option to analyse composition accurately when fluorescence prevents the use of Raman spectroscopy.

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1.20. Sub-micron infrared analysis of painting cross-section for accurate and rapid identification of paint layer compositions

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Chemical analysis of historical paintings has always been a challenging task due in part to the intricate yet complex nature of the paint layers. The cross-sections revealing these layers provide not only the history of the valuable artwork but also serve to confirm or deny its authenticity. Such analyses commonly make use of infrared and Raman techniques, which could give direct identification of unknown materials by interpreting vibrational modes of chemical bonds (Griffiths, 2007). Using conventional FT-IR, an infrared signature can readily identify the local composition of the layers, but the long infrared wavelengths cannot spatially resolve layers narrower than 20 µm unless an attenuated total reflectance probe is pressed against the sample. With the latter method, the specimen could be damaged due to the intimate contact requirement; further, inconsistent contact will also affect the band shape of the resulting ATR-FTIR spectra. It is possible to conduct non-contact reflection mode FT-IR, but the spatial resolution would still be limited to at least 20 µm, and the rough sample surface would cause scattering artifacts distorting the band shapes of strong infrared absorption modes. Those band distortions may misidentify unknowns. Raman microspectroscopy represents a valuable alternative to infrared as it provides high spatial resolution in the range of 1 – 3 µm without contacting with sample surfaces. Thinner layers, in the order of less than 10 µm in the cross-section, could be sufficiently analyzed by the high spatial resolution of Raman microscopy. Further, with its standoff data collection method, there is no contact with the sample specimen; as a result, Raman microscopy has been a go-to technique. Nevertheless, most paint layers contain pigments that could strongly absorb visible wavelengths, leading to rapid laser-induced degradation of the specimen. Further, strong visible absorption would also lead to strong emission, also known as auto-fluorescence, upon illumination, thus leading to the overshadowing of inherently smaller Raman scattering cross-sections.

In recent years, the novel optical photothermal infrared (O-PTIR) technique has demonstrated its ability to analyze very small organic specimens into sub-micron without physically contact of the same, while offering femtogram-level sensitivity [Lo, 2022] and sub-micron spatial resolution [Kansiz, 2020]. Further, a few recent articles have cited the application of paintings towards soap heterogeneity [Ma, 2022], rough degraded surface features [Marchetti, 2022], and small pigment particle identification [Beltran, 2021]. The high spatial resolution of O-PTIR affords excellent capability in analyzing the cross-section of historical paintings, where the layers may be too thin (< 10 µm) to be successfully analyzed by conventional FT-IR spectroscopy. The standoff collection method of the O-PTIR instrument requires no contact while outputting distortion-free infrared spectra, thus yielding high confidence in the spectral analysis of chemically complex paint. These O-PTIR spectra could be directly searched against classical infrared spectra databases to identify unknown materials within the paint layers.

In this contribution, we illustrate the identification of components that are present over the entire stratigraphy (from varnish to canvas) of an old painting, identified as *Cobaye_one* [Calligaro, 2022], with sub-micron O-PTIR infrared analysis. The sample has been retrieved from one side of the

painting, followed by embedding in epoxy and polishing with a microtome. The resulting surface is on the top surface of the block, which could be accessed in reflection mode by the O-PTIR infrared microscope. The sub-micron resolution of the O-PTIR provides detailed chemical analysis of varnish and paint material near the surface of the painting while retaining the structural arrangement. The cross-section analysis enables direct observation of the structure of the painting without significant concerns of miscounting and preserving the order of the layers. Those O-PTIR spectra from the varnish in Figure 1 illustrate nearly pure spectra of amide-I and amide-II, which are consistent with proteins that have been applied during the lining process of the painting [Calligaro, 2022]. The indirect detection of photothermal signals due to infrared absorption in non-contact reflection mode enables quick interpretation of undistorted infrared bands. The broad 1732 cm^{-1} ($\nu_{C=O}$) infrared absorption likely corresponds to the partially degraded triacylglycerol (TAG) Paint Layer 1 and appears to be uniformly composed of lead carbonate. A clearly distinctive boundary can be observed in the corresponding overlaid O-PTIR image collected at 1660 (green), 1460 (red), and 1066 cm^{-1} (blue) in Figure 2.

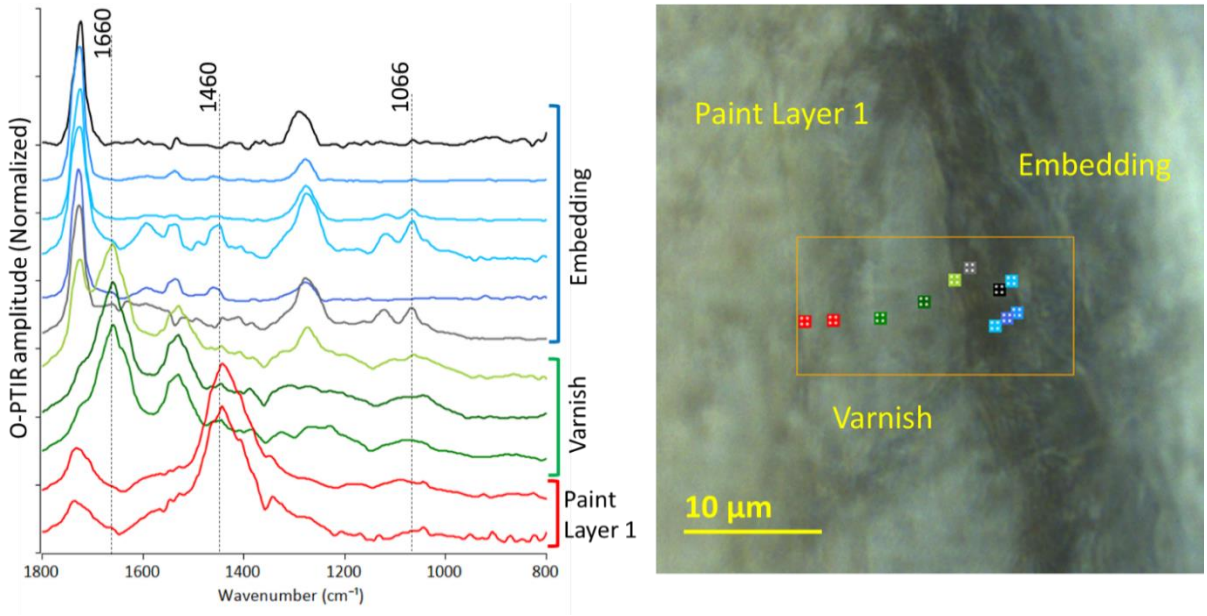


Figure 1: Optical image showing the location of the thin proteinaceous varnish on top of the Paint Layer 1 and examples of O-PTIR spectra collected from the spots marked in selected areas

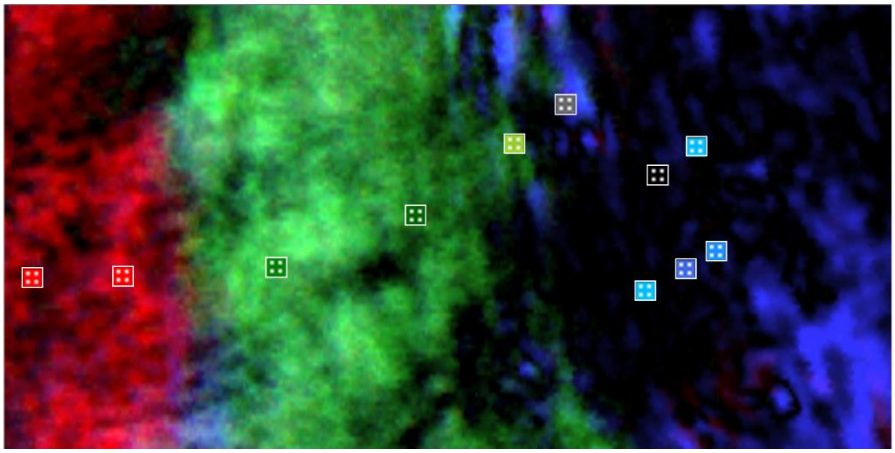


Figure 2: An overlaid of sub-micron O-PTIR images collected at 1660 cm^{-1} (green), 1460 cm^{-1} (red), and 1066 cm^{-1} (blue)

The wavenumber-independent sub-micron spatial resolution of the O-PTIR technique simplifies the identification of complex mixtures within the paint layer. The large spot size of conventional FT-IR spectroscopy would have averaged signals at varying extents from multiple paint species over the mid-IR. Spectra from the small sampling spot are likely representing fewer number of chemical species, thus improving the confidence of de-mixing spectral components. Major component analysis of Paint Layer 2, *Imprimatura*, and Ground Layer 1 can be performed with spectra collected nearby (Figure. 3). From the *Imprimatura*, SP23 could be de-mixed with SP12 as the component that comes up with a result best consistent with lead carbonate [1410 cm^{-1}, $\nu_{as}(CO_3^{-})$] (Figure 4); and from the Ground Layer 1, SP10 may also be decomposed with SP12 to reasonably suggest of a monoglyceride ($\nu_{C=O}$, 1736 cm^{-1}), which is a partial breakdown product from the corresponding triacylglycerol. All layers contain significant degradation product between lead white and triacylglycerol in the form of carboxylates (1530 cm^{-1}, broad, ν_{as} (COO^{-})), which is further supported by O-PTIR image collected at 1530 cm^{-1} (Figure 5).

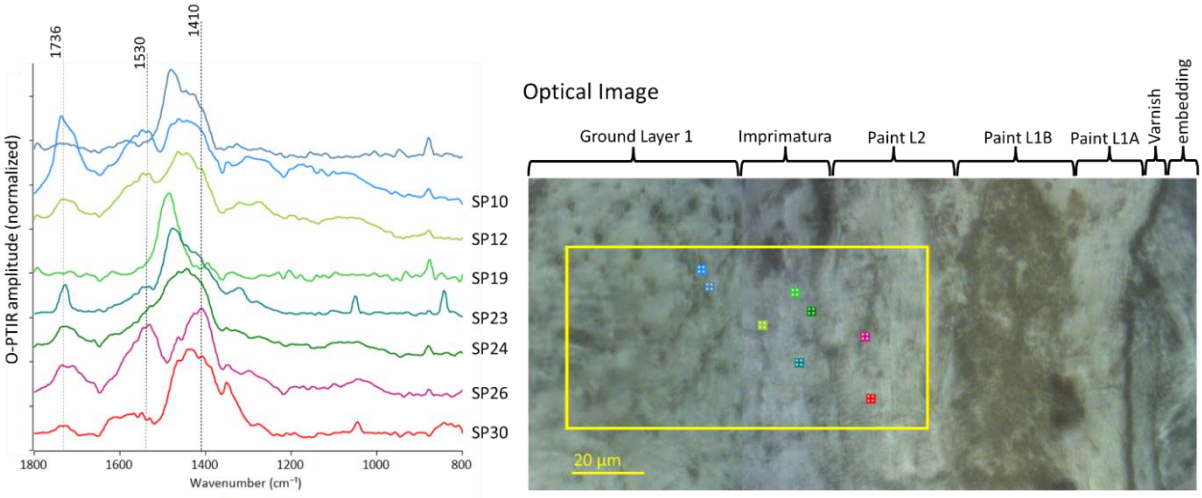
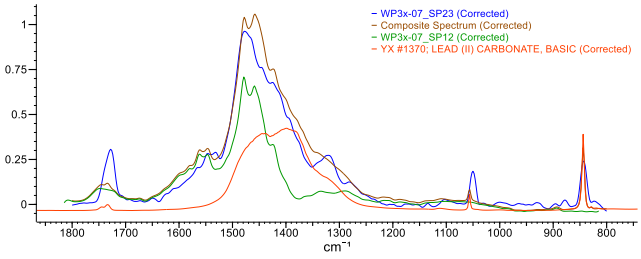


Figure 3: Optical image of the specimen showing the area imaged by O-PTIR technique within the yellow box and the corresponding sub-micron infrared spectra



HQI	Ratio	Excluded	ect	DB	ID	Name	Chemical Structure	Spectrum
87.71	N.A.					Composite Spectrum	$PbCO_3$	
	0.62					WP3x-07_SP12		
	0.38			YX	1370	LEAD (II) CARBONATE, BASIC	$PbCO_3$	

Figure 4: Spectral de-mixing of SP23 with SP12 as a component suggests the remaining component to be consistent with a lead carbonate

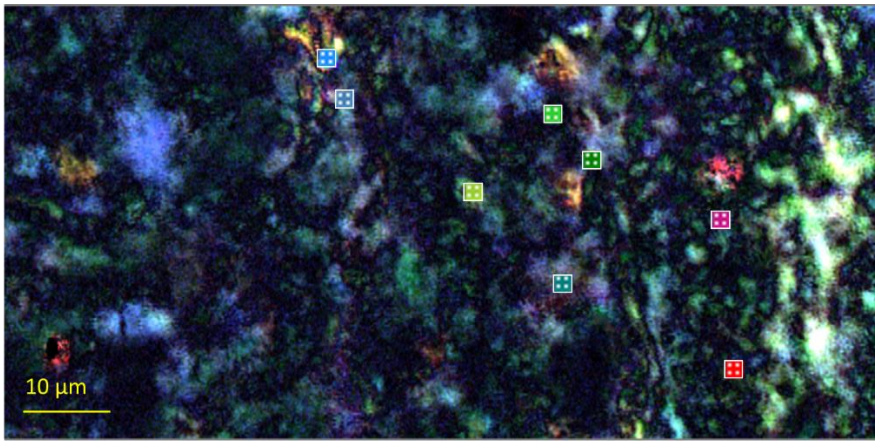


Figure 5: Overlaid O-PTIR images collected at 1730 (red, TAG), 1530 (green, carboxylates), and 1410 cm^{-1} (blue, carbonates) over the yellow rectangular region highlighted in Figure 3

With the novel sub-micron O-PTIR analysis, we have obtained confident identification of components in the painting's cross-section in a non-contact operation mode. The varnish layer of *Cobaye_one* is composed of a chemically uniform proteinaceous matter likely originated from egg white. The small spot size of the O-PTIR technique extracts photothermal infrared signal from limited number of chemical species, thus readily separating the unknown compositions, which are best consistent with lead carbonates, carboxylates, and degradation products of triglycerides. Since the sample would remain pristine even after a thorough O-PTIR analysis, additional confirmatory procedures can be performed, thus significantly reducing sampling requirements and enhancing analysis for discoveries previously not possible.

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Ma, et al, 2022. *Micro to nano: multiscale IR analyses reveal zinc soap heterogeneity in a 19th-century painting by Corot*. Anal. Chem. 2022, **94**, 3103.

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1.21. The Need for Speed: a success story of couture, exhibition and catalog deadlines, and ATR/diffuse reflectance IR

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Tight museum exhibition schedules often necessitate accelerated turnaround times for conservation scientists to provide materials identifications to conservators and curators. The fortuitous acquisition of a portable ATR and diffuse reflectance mode IR spectrometer coincided with conservation of gowns and research for the catalog of Winterthur Museum's exhibition "Ann Lowe: American Couturier" (September 9, 2023–January 7, 2024). Museum scientists were able to non-destructively analyze twelve couture gowns on loan for the exhibition in order to confidently identify fabrics as either natural or synthetic fibers, identify specific synthetic fibers such as rayon, nylon and cellulose acetate, as well as identify the polymer compositions of sequins. The choice between ATR or reflectance mode was based primarily on the weave structure of the fabric, but also the accessibility to specific fabrics given the complicated layering and designs of the gowns. Reflectance mode measurements were successful with the use of magnets to hold the fabric steady and provide good contact with the instrument; however, most sheer fabrics, because of their thinness, were difficult to analyze in reflectance mode and were only successful with ATR. Only on one occasion was a sample required for fiber microscopy, after FTIR could not differentiate between cotton and viscose. The project was completed over the course of one month with interpretation aided by reference spectra provided in publications and those authors' digital file sharing of their reference libraries. Results allowed textile conservators to make better informed treatment decisions, specifically regarding cleaning and choice of support materials. The results also provided additional context for the material choices by designer Ann Lowe, such as that the majority of dress linings were made with synthetic fibers which would have helped support the desired drape and silhouettes of the gowns. This presentation will highlight the relative ease with which ATR and reflectance mode IR spectroscopy analysis was successfully utilized to identify fabrics in a fast-paced museum exhibition and catalog timeline.

1.22. Using principal component analysis and specular reflection FTIR for paper fiber identification

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Works of art and archive collections on paper, like drawings, watercolors, prints, books, and manuscripts, represent many cultural heritage collections. The paper substrates or supports are infrequently the subject of technical studies. This is due to inherent limitations, such as the fragility of the paper substrate, a lack of suitable sampling opportunities and preference for non-destructive sampling, and the presence of mixed, but chemically similar cellulosic materials.

The first sample set for this research consisted of the Paper and Mediums Study Collection from Legacy Press compiled by Cathleen Baker (http://www.thelegacypress.com/studycollection.html). The collection consists of American and European book and writing papers ranging from the 18th to the 21st centuries. The collection had previously been subjected to fiber analysis and chemical tests for gelatin, starch, and lignin, following standard methods in the field of paper conservation, though all tests involved some degree of destructive sampling. The Legacy Press collection was supplemented with sets of known alum sized papers and pure fiber pulp stock.

The reflectance FTIR spectra were collected with a Bruker LUMOS FTIR microscope with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector in the range from 4000 to 600 cm^{-1} at the Harvard Center for Nanoscale Systems (CNS). The background was taken against a gold reference mirror on the instrument sample stage. Data collection was carried out using the accompanying Bruker OPUS software. Spectra were baseline corrected in Opus using the rubber band method. The reflectance FTIR technique is fully non-contact. The LUMOS microscope system allows for multiple points in the analysis area to be selected and scanned. An 8x optical microscope and color camera allowed the close examination of the analysis area and documentation of its visual appearance.

The resulting reflectance spectra were almost impossible to distinguish by human eye as the chemistry of the samples were all very similar. Correlation matching algorithms commonly used in spectral library searches were also not very helpful in classifying the different papers based on sizing materials or fiber type as they are strongly biased towards the most intense peak in the spectrum, which would be common cellulose peaks across all these objects.

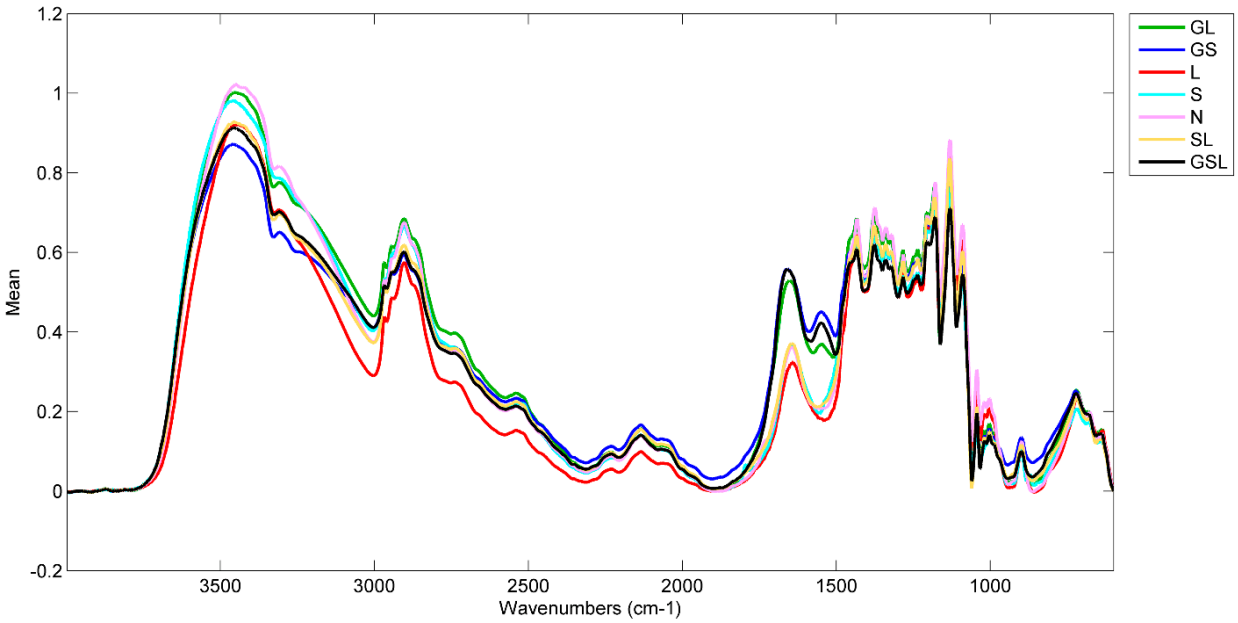

Figure 1: The average reflection FTIR spectra of gelatin-lignin (GL), gelatin-starch (GS), Lignin (L), starch (S), nothing (N), starch-lignin (SL), and gelatin-starch-lignin (GSL) papers, plotted with Absorbance on the y axis

However, the application of principal component analysis (PCA) modeling to the reflection FTIR data allowed for the distinguishing of paper sizing materials and fiber types in the papers. The clear advantage of this approach is as an alternative method for the identification of paper materials in collection objects without the need for destructive testing or sampling of the object.

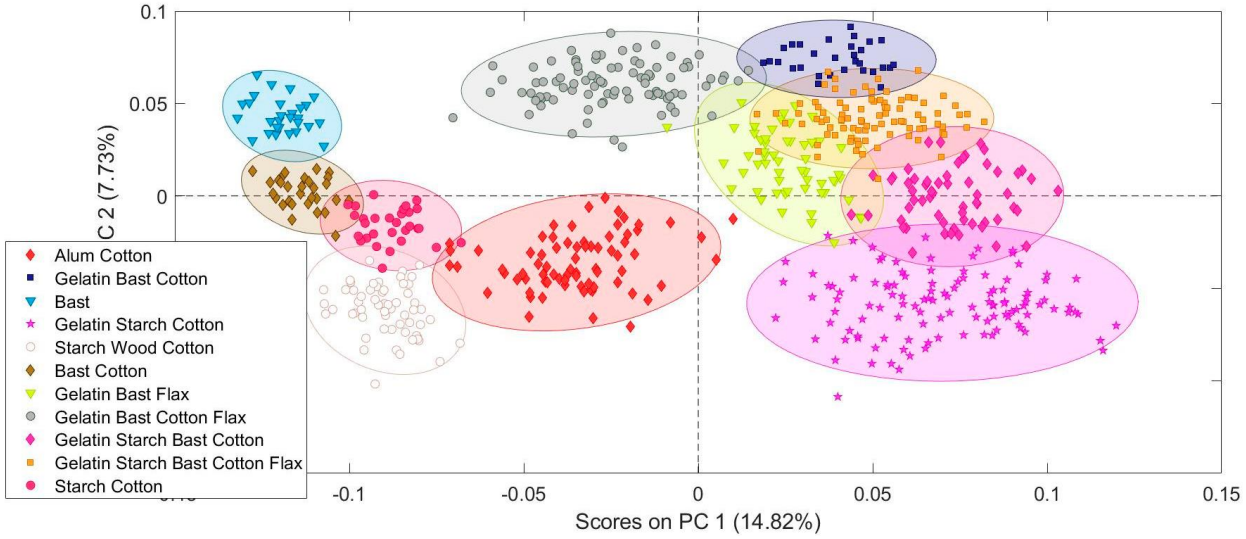

Figure 2: Principal component plot showing that papers of different fiber and sizing materials can be distinguished using reflection FTIR data and principal component analysis

To build a useful PCA model, the data must be preprocessed to emphasize the differences between samples that are of interest. The “rubber band” baseline correction, mentioned above, takes out spectral variation due to infrared light being scattered out of the optical collection path. With papers of different textures and roughness, there will be different amounts of scattered light leading to baseline offsets that do not contain information of interest for this study.

Next, in the Solo + MIA software package by Eigenvector Research Inc., a multiplicative signal correction (MSC) was applied as a weighted normalization treatment to remove magnitude variability. The MSC algorithm also performs baseline removal, but better results were obtained on this data using the OPUS baseline removal tool prior to importing the data into Solo + MIA.

Next, the generalized least squares weighting (GLSW) was applied to the data. GLSW is a decluttering treatment. "Clutter" is variance in the data that is not relevant to the question at hand. For example, in the question about sizing material, the fiber type information would be "clutter" in the data. The weighting factor can be adjusted, with lower thresholds going further into the features from minor components. A GLSW threshold of 0.05 was found to give the tightest clustering of the classes with this data set. The order of operations is important in preprocessing data from PCA models.

Finally, the dataset was mean centered. Mean centering is a data processing method where the mean of the entire data set is subtracted from each column of the matrix. This allows the model to capture variance around the mean of the data, emphasizing differences while eliminating what is the same across all the spectra.

In summary, the full preprocessing treatment for the data was rubber band baseline correction in OPUS and in Solo + MIA MSC (mean), GLSW (clutter source x-block classes, threshold 0.05), and mean centering preprocessing.

Including both the information about the fiber types and the sizing material gave the most robust model in the end. The model was tested against Alexander Gardner's *Photographic Sketch Book of War* (Harvard Art Museum object number 2013.6.1), which was identified as starch sized cotton paper. This work was published in the open access journal Heritage **2022**, 5, 1960–1973.

The use of PCA with reflection FTIR data was also applied to second set of papers. This time Asian paper samples from 2016 joint AIC-CAC workshop on East Asian Paper for Conservation, presented by Nancy Jacobi and Megumi Mizumura. The east Asian papers were provided by The Japanese Paper Place.

It was found that *kozo, gampi*, and *mitsumata* paper fibers were well separated in PCA space based with a specular reflection FTIR data set.

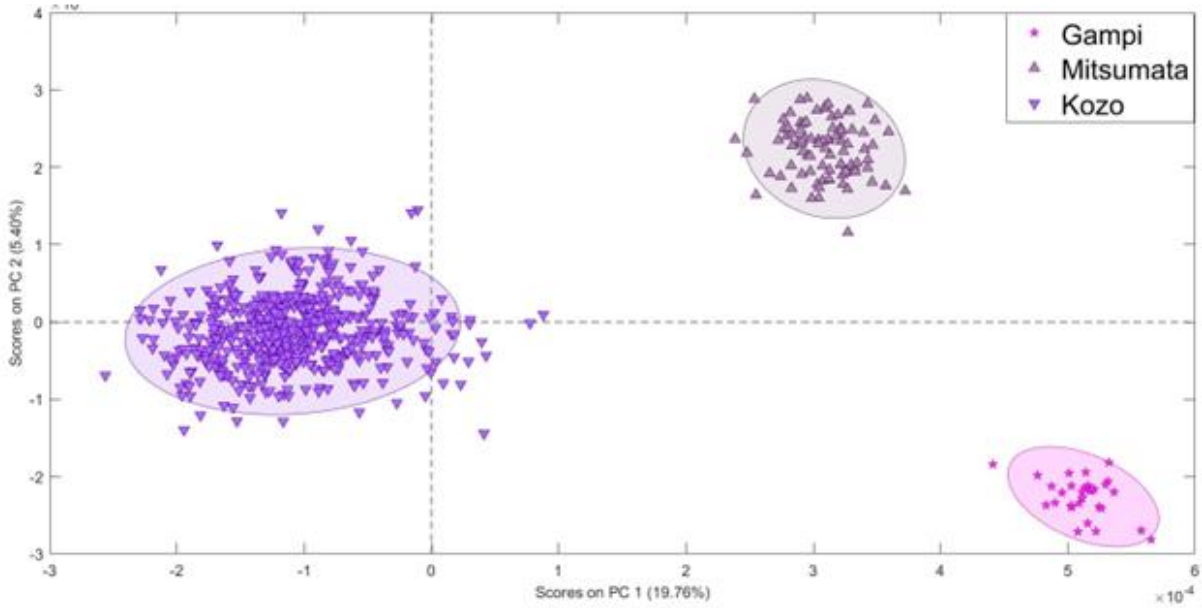

Figure 3: PCA plot for pure *kozo*, *gampi*, and *mitsumata* paper fibers

Kozo paper is made from the "inner bark", botanically known as the phloem, of the mulberry tree. The phloem has three distinct layers, an innermost white layer, a middle green layer, and a closest to the bark black layer. Shirokawa kozo paper uses just the inner white layer. Nazekawa kozo paper uses both the white and green layers. Kurokawa uses all three layers. Further refinement of the PCA model allowed for the discrimination of different types of kozo paper.

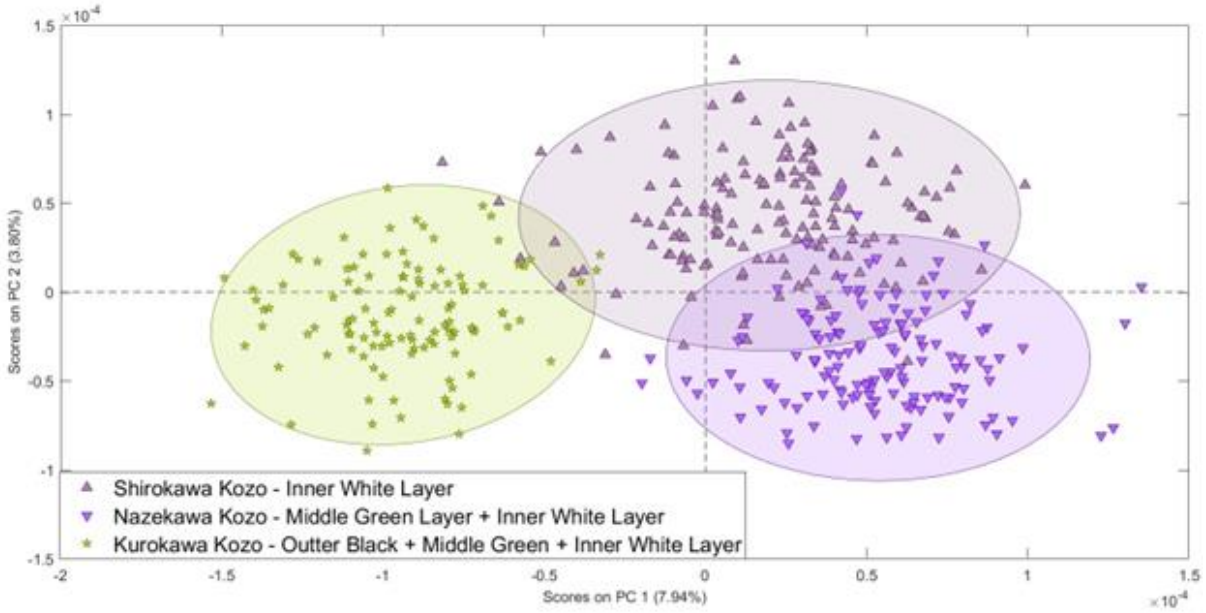

Figure 4: PCA plot for three types of *kozo* paper; Shirokawa, Nazekawa, and Kurokawa

In conclusion, we demonstrate reflection FTIR and principal component analysis can be used to distinguish paper fiber types in a non-contact, non-sampling way.

1.23. Natural and synthetic organic pigments in the palette of Nicholas and Svyatoslav Roerich

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The work of Nicholas Roerich (1874–1947) and his son Svyatoslav Roerich (1904–1993) is still of great interest to art historians, as well as researchers of other related fields, who note that the Roerichs' painting is "a unique and timeless phenomenon that opens up new horizons and carries new meanings" [Demenko, 2021]. Undoubtedly, such a high appreciation of the artists' work is due to their highest professionalism, deep knowledge of the principles of color, composition, rhythm and tone, as well as the properties of artistic materials. In his book "Art and Life" [Roerich, 2007], Svyatoslav describes the technical aspects of his creative process as follows: "Only with practice and a thorough experience with the materials used, we can learn to understand the behavior of certain pigments. Each pigment behaves in a specific way depending on its density, weight, covering power and a variety of other characteristics. Profound knowledge of all the properties and characteristics of a particular paint is necessary to take full advantage of all its possibilities". It is known [Roerich, 2007; Tsesulevich, 2012] that the Roerichs frequently purchased pigments in Paris, and occasionally in London. Like the old masters, they preferred to prepare emulsion for tempera paints themselves, thus achieving an extraordinary brightness of their colors. Along with tempera, Svyatoslav, for example, also resorted to the oil technique of painting, mainly in portraits and sketches [Tsesulevich, 2012].

Despite the extensive knowledge of the oeuvre of Nicholas and Svyatoslav Roerich, there is no reliable data on what kinds of pigments they used. Since the artists lived in Europe and America, and a prolonged period of their work is associated with life in India, their color palette can be quite diverse. All these aspects make the study of the Roerichs' artwork technology important to holistic understanding of the artists' creativity process.

This report presents the results of the technological examination of two paintings by Nicholas Roerich dated 1922 and 1940 and seven paintings by Svyatoslav Roerich executed in 1920s, 1936, 1954 and 1974 from the collection of The State Museum of Oriental Art (Moscow, Russia). As it turned out, the extraordinary color of certain paint layers in the artists' works is caused by the use of organic pigments both synthetic and natural origin. For example, in the painting by Svyatoslav Roerich *Portrait of Mrs. Campbell in a striped dress* (1926) an Al(III)-complex with hematein was found in the purple paint layer (Figure 1). The source of hematein is a tree *Haematoxylon campechianum*, a species indigenous to Mexico, Central America, and the West Indies. When combined with alum salts, the saturated red color of hematein solution changes to a deep violet - black [Golikov, 2020; Centeno et al, 2009]. There is very scarce information about the use of this dye in art. It is known [Centeno et al, 2009] that the dyestuff from the logwood was already used in pre-Columbian times for dyeing textiles. In the 16th century it was discovered by Europeans, and no later than the 18th century it began to be used in manuscripts as an ink substance [Centeno et al, 2009]. To date, no published evidence of its use as a pigment in the pictorial art has been found.

Another unusual pigment that was discovered in two paintings of Svyatoslav is the dye methylene blue. This pigment was first synthesized in 1876 and was commonly used for dyeing fabrics [Golikov, 2020], however, there are no confirmed cases of its use in painting.

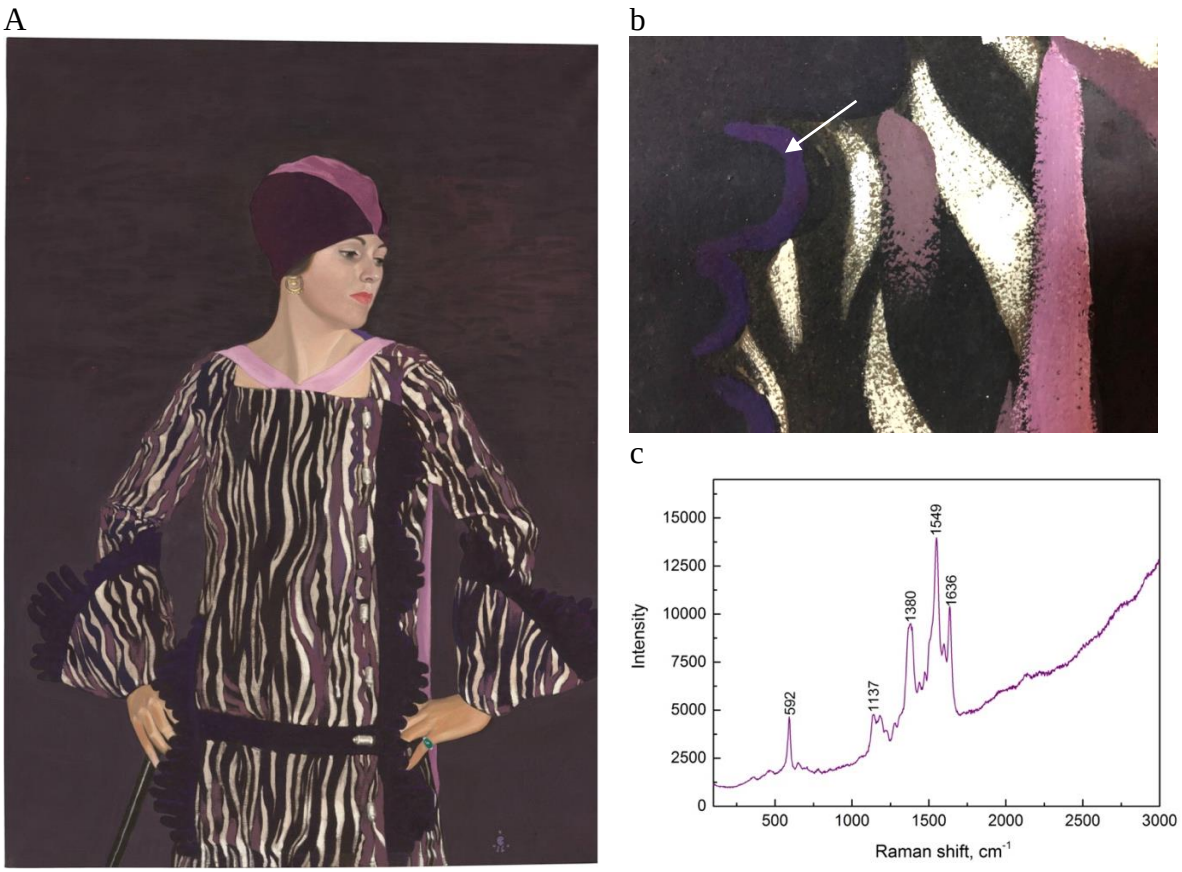

Figure 1:Svyatoslav Roerich. *Portrait of Mrs. Campbell in a striped dress*. 1926. Tempera and oil on canvas. 122 × 91.5 cm. © The State Museum of Oriental Art, Moscow; (a) General view of the painting, (b) A fragment of the dress image; an arrow shows where the purple paint sample was taken from (c) μ-Raman spectrum of violet organic pigment, the main coloring matter in the purple paint layer (λ_0 = 532 nm, incident power 40 mW); the characteristic spectroscopic bands corresponds to hematein–Al(III) complex prepared by mixing hematein and alum solutions [Centeno et al, 2009]

The yellow organic pigment tartrazine (PY 100), obtained in 1884 [6-8], was identified in the painting *Message to Tyrone* (1940) by Nicholas Roerich. Tartrazine was one of the replacement pigments for Indian yellow, which production was banned in 1920s. Since synthetic analogue was sold under "Indian Yellow" trade name it lead to the confusion for modern analysts as the characteristic Raman spectroscopic bands for tartrazine were erroneously attributed to the latter one [de Faria et al, 2016]. Although the use of tartrazine in artistic paints is mentioned in the literature [de Keijer, 2014; Berrie and Lomax, 1997], we failed to find any cases of its occurrence in the works of art. The same concerns to the red organic pigment PR 122 from Quinacridone class [de Keijer, 2014], found in the latest of studied paintings by Svyatoslav Roerich *Karma Dorje* (1974). Thus, to date, these are the earliest instances of the discovery of these pigments in painting.

In present study for the identification of organic pigments the methods of vibrational spectroscopy were applied. Infrared spectra were collected on a LUMOS microscope (Bruker) in the attenuated total reflection (ATR) mode with a Ge ATR crystal, from 4000 to 600 cm^{-1} and for 64 scans with a resolution of 4 cm^{-1}. Raman spectra were recorded using a Renishaw InVia Qontor Raman microscope equipped with linearly polarized lasers 532 and 785 nm, 1200 lines/mm diffraction grating and 50× objective (N.A.=0.8). The spectrometer was as well used to collect a fluorescence emission spectra of some fluorescent dyes (λ_{ex} = 325 nm)

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1.24. Characterization of artists' materials from 20th century Mexican ex-voto paintings

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This project involves the technical examination and conservation treatment of a set of Mexican ex-voto paintings newly acquired by the Museum of Fine Arts, Boston. From the Latin phrase "in accordance with a vow", ex-voto paintings depict often visceral scenes of survival and healing attributed to divine intervention. The ex-voto painting tradition in Mexico dates back to the 16th c. and was popularized by Frida Kahlo, Diego Rivera, and other Modernists who collected and depicted them. However, very limited research has been devoted to conservation and materiality of ex-votos, both historical and modern. The artists who make them come from a range of self-taught and traditional painting backgrounds, and this is reflected in the diverse and innovative materials they employ.

This collection presents an opportunity for a small-scale survey of materials used to create the objects, including analysis of paint layers and in some cases support substrate. The techniques used for this examination include multimodal and computational imaging techniques and other non-invasive analysis, such as FORS, Raman, XRF and reflectance mode FTIR. Where appropriate, small samples were removed from the verso of objects and samples were analyzed with FTIR transmission mode, GC-MS and SEM/EDS for comparison to in-situ results. As the objects' time period spans the early to late 20th century, the painting materials range from oil, alkyd, and nitrocellulose and pigments such as iron oxides and zinc white to rutile and synthetic organic pigments. This analysis will be a milestone for our understanding of the 20th century Mexican ex-voto painting tradition.

1.25. Flexible method for feature isolation and analysis in infrared reflectance data for pigment and binder identification

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Nowadays, many reflectance methods, like fibre optic reflectance spectroscopy (FORS, 400 - 2500 nm), external reflection Fourier transform infrared spectroscopy (ER-FTIR, 400 -7000 cm^{-1}), and reflectance imaging spectroscopy (RIS, 400 -2500 nm), investigating the infrared spectral region (Near- to Mid-IR), are routinely used for the analysis of cultural heritage objects. However, the processing and analysis of the infrared reflectance data produced by these methods remains a challenge. The investigated objects have large material heterogeneity, which results in very complex spectral data with overlap of different vibrational modes. These overlaps can prevent the identification of different components, such as a pigment and its binding media. The deconvolution of these bands is not trivial and cannot be done by a user without help of labour-intensive processing methods.

We propose a method for the analysis of infrared reflectance data to address these challenges, and with less user intervention. The method makes use of the SNIP algorithm [Ryan et al, 1988] to isolate specific target reflectance features. These isolated features can then be further processed, by gaussian fitting, region of interest (ROI) integration, or other methods, to provide feature-specific information.

In this paper we apply this method to two cases. First is the identification of egg yolk (or any lipid containing binder) as a binder when used with certain pigments like azurite ($Cu_3(CO_3)_2(OH)_2$) and malachite ($Cu_2CO_3(OH)_2$), that also present features in that spectral area, and can complicate its identification. We use the lipid combination band ($\nu_a+\delta)CH_2$ feature around 2309 nm (4330 cm^{-1}), which falls in the vicinity of one of the $3\nu_a(CO_3)$ and $\nu a+\delta(OH)$ features of azurite around 2285 nm (4380 cm^{-1}). This is, in general, a useful feature as it distinguishes egg yolk from other common binders, like egg white and gum Arabic. Examples of the method application can be seen in Figure 1.

The second case is on the identification and mapping of lead white (hydrocerussite, $Pb_3(CO_3)_2(OH)_2$) and azurite as pigments through their respective 2ν(OH) features around 1447 nm (6910 cm^{-1}) and 1497 nm (6680 cm^{-1}) using RIS-SWIR (short-wave IR) data. These features partially overlap, which can make their identification difficult when one is more prominent. An example of the resulting distribution maps can be seen in Figure 2.

The method is demonstrated on test samples and historical paintings and is found to provide useful classification results in both cases, and to provide semi-quantitative information for the pigment concentration for the second case.

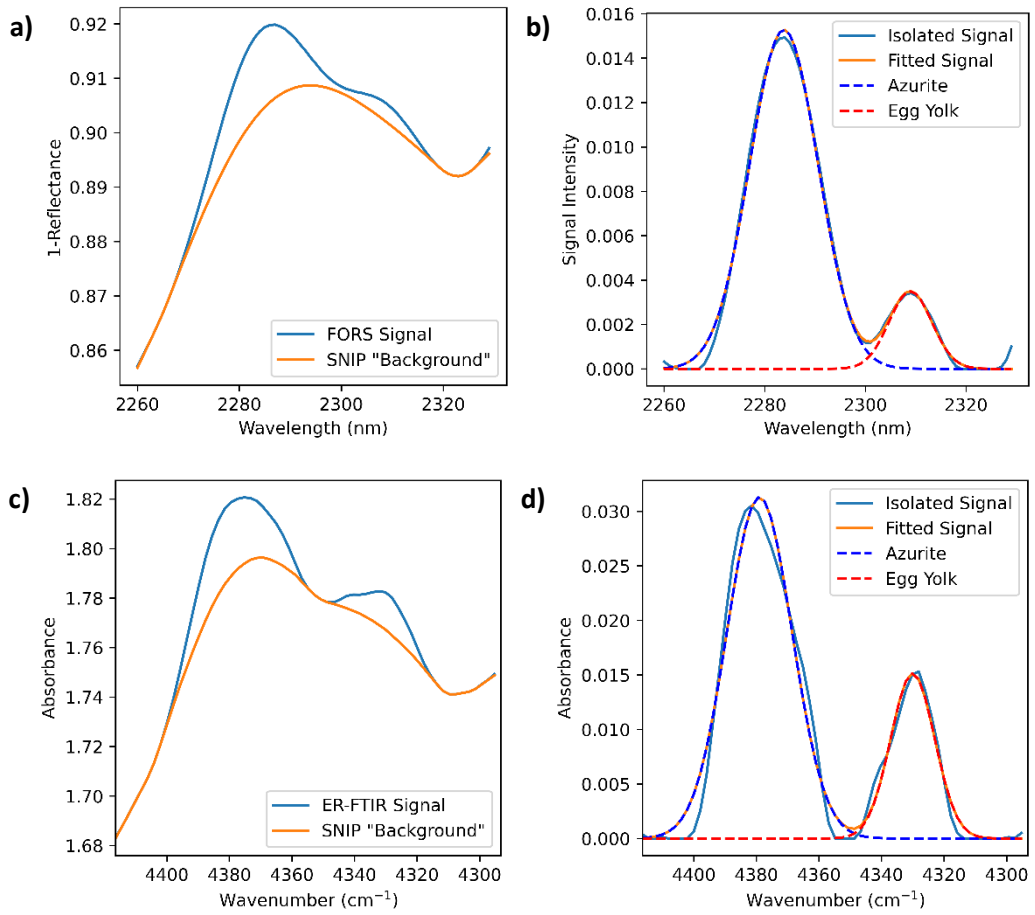

Figure 1: Example of the method applied for the identification of egg yolk as a binder. a) FORS signal and output of SNIP algorithm. b) Guassian fitting of the isolated features of azurite and egg yolk. c) ER-FTIR signal and output of SNIP algorithm. d) Gaussian fitting of the isolated features of azurite and egg yolk

Figure 2: Example of the method applied for the identification of azurite in a historical painting. (Jacob Cornelisz van Oostsanen's Portrait of Jan Gerritsz van Egmond van de Nijenburg (oil on panel, h 42.4cm × w 32.8cm, c. 1518, Rijksmuseum Collection (SK-A-3838)) a) Photograph of the painting. b) Azurite distribution map

Reference

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1.26. Combining multiple NUV-MIR spectral unmixing techniques for identifying mixtures of colorants in art and cultural heritage

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Reflectance spectra in various frequency ranges (near-UV, visible and IR) are widely used in cultural heritage studies to characterize colorants (pigments and dyes) in paintings, manuscripts, and other artefacts. However, identifying the constituents of a paint mixture can be challenging, as the spectral features of a mixture may not match those of the individual substances. In conventional colorant analysis, a spectrum measured from a painted object is compared to reference spectra of known mixtures to identify the constituents of the paint examined. However, the number of reference spectra needed for a reliable mock-up based identification method depends on the research question, mixture complexity, and data quality. For complex mixtures, up to 500 distinct spectra may be needed, making this approach time-consuming and expensive.

To overcome these challenges, spectral unmixing techniques, which can decompose the spectrum of a mixture into its individual components, have been used. Spectral unmixing is based on the principle that a mixture spectrum is a linear or nonlinear combination of the spectra of its individual components. The method requires a library of reference spectra for the individual components, which are typically obtained by measuring the spectra of pure pigments and dyes or by using computational methods to simulate their spectra. Linear mixture analysis (LMA), non-negative matrix factorization (NMF), and vertex component analysis (VCA) are some of the techniques that have been successfully applied to identify colorants in paintings. These techniques can be used for data pre-processing, endmember extraction, and abundance estimation.

Despite their success, the accuracy of these techniques can be impacted by the presence of other compounds not considered during the analysis, such as extenders, mordants, and binding media. These compounds can interfere with the spectral features of the individual components and can lead to inaccurate estimates of their spectra and abundances. To address this issue, a new method for identifying paint mixtures using machine learning and multiple spectral unmixing techniques is proposed. This method consists in applying a variety of unmixing techniques simultaneously, evaluating and interpreting the performance of each technique, and validating and combining the results. The proposed method was trained on a number of swatches of historical and modern colorants, bound in different media, produced by various paint manufacturers between the second half of the 20th century and the early 2000s, and was applied to a dataset of NUV-MIR (350-25000 nm) reflectance spectra collected from a set of selected European paintings and Japanese prints. The spectral data was acquired using a combination of UV-Vis-NIR reflectance spectroscopy and external reflection (ER)-FTIR spectroscopy.

The results showed that all three unmixing techniques were able to identify the major colorants and binding media present in the mixtures with relatively high accuracy. LMA and NMF were particularly effective in estimating the abundance of the individual colorants, while VCA was more robust to the presence of noise and other interference. Additionally, the combination of the three techniques provided a more comprehensive and accurate identification of the materials in the mixtures, as each technique captured different aspects of the spectral data. To validate the results, the estimated compositions of the paint layers were compared with the compositions determined by Raman and X-

ray fluorescence (XRF) spectroscopies. The comparison showed a high degree of agreement between the estimated and actual compositions, indicating the reliability of the proposed method.

One limitation is that the accuracy of the method is strongly dependent on the quality of the spectral data, which may be affected by factors such as the surface unevenness of the object, the presence of varnish and retouching, and the measurement conditions. To address this weakness, future research will focus on developing more efficient and automated procedures for data acquisition, as well as on integrating the proposed method with other analytical techniques for a more comprehensive and multi-scale characterization of pigments and other materials in art and cultural heritage.

In conclusion, the proposed method for identifying mixtures of artist's materials in cultural heritage studies using machine learning and spectral unmixing techniques has been demonstrated to be effective and reliable for the analysis of paints containing various amounts of pigments and dyes. By carefully selecting and applying suitable techniques, it is possible to obtain accurate and meaningful results in relation to the identification and quantification of colorants in mixtures, which can provide valuable insights into the materials and techniques used by artists as well as their historical and cultural context.

1.27. Total reflectance FT-IR spectra: impact of the support on paint layer analysis

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Unravelling pigment compositions in artworks is key for the restauration and conservation of cultural heritage objects. For the study of these objects, a non-invasive in situ analysis with a portable device is highly recommended, as sampling of cultural heritage objects and displacement and handling of museum objects is most of time undesired. [Picollo et al, 2014; Cucci et al, 2016] Fourier transform infrared spectroscopy (FT-IR) is a useful and fast technique for the study of artists' materials. Transmission and attenuated total reflection FT-IR have been extensively used for the study of pigments, but have limitations as sampling and intimate contact with the art object is required, which is always undesired. In contrast, in situ total reflection (or external reflection) FT-IR is a technique that does not need sampling or contact with the artwork and provides useful information about the pigments used [Miliani et al, 2012; Angelin, 2021]. The interpretation of total reflectance FT-IR spectra is very challenging due to the presence of distortions, such as derivative-like spectral features, inverted bands (Reststrahlen effect), broadening and change in the relative band intensities. These distortions are, among other things, influenced by the surface roughness of the artwork [Miliani et al, 2012; Angelin, 2021]. In this research, mock-ups varying in roughness of support, pigment and paint layer thickness were made to examine their influence on total reflectance FT-IR pigment spectra. Principal component analysis (PCA) showed that total reflectance spectra of pigments are mostly influenced by support (Figure 1), which increases with support roughness and decreases with paint layer thickness. PCA was able to discriminate the mock-ups according to different pigment, but this classification at the present stage was unsuccessful to predict pigments in a real-life artwork case study. This research demonstrates the enormous complexity and dependence on surface roughness of using total reflection FT-IR for the examination of works of art and holds promise for the identification of pigments in cultural heritage objects.

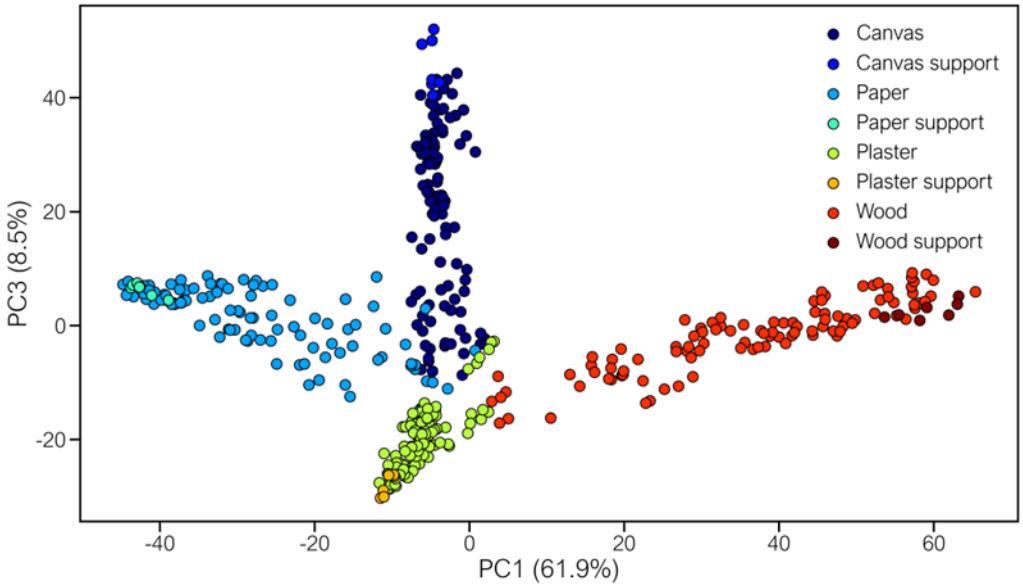

Figure 1: Principal component analysis exposed the enormous dependence on surface roughness of using total reflection FT-IR for the examination of works of art

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1.28. The value of degraded polymers – representing degraded polymers in IRUG

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A challenge for many cultural institutions are polymers – whether they are part of a cultural object, work of art, or a conservation material – understanding their stability over time is critical for collections care. From foams, to films, to coatings, to 3D objects – they are everywhere, and can show a wide breadth of issues. The collection at the Academy Museum of Motion Pictures is no exception, and contains a century worth of movie props, costumes and movie-making objects (as well as pre-cinema objects) that were not designed with the intention of a long-life, but instead as objects to last the span of creating a film.

The caretakers of the collection are tasked with ensuring that these objects continue to amaze and entertain, despite their delicate and fragile nature, and understanding materials and their compositions is an important part. As many collection materials have aged, their FTIR spectra show evidence of oxidation and other degradation mechanisms and phenomena. One continuously finds themselves diving into the academic literature (which often requires a subscription and is not feasible for many cultural institutions) searching for reference spectra of degraded materials for comparisons. So, why not add these spectra to a database? IRUG does contain some aged materials, but it could be valuable to have a section to help guide cultural heritage professionals through the identification of older degraded materials. As analytical tools become portable, and more accessible in conservation departments, it would be helpful for all users to have access to this information. At the Academy Museum of Motion Pictures, as aged materials are identified, when appropriate, their spectra are being added to an in-house database for future ease of identification.

This talk will focus on foam objects in the Academy Museum of Motion Pictures' collection, in particular a natural rubber foam product that can be applied and used in multiple ways. It can be difficult to handle and to identify visually, especially once degraded; however, the spectra of the aged foam are similar. The foam was successfully identified over a range of objects using a Bruker Alpha II Compact FT-IR Spectrometer with a Platinum ATR module. Though out of the scope of this paper, the chemical composition of an aged reference foam sample was confirmed with pyrolysis – gas chromatography – mass spectrometry, complementing and confirming the accuracy of the FTIR results. It is hoped that this example can initiate a discussion about a degraded materials section of the database, recognizing the positive aspects that it can provide as well as limitations.

1.29. 30 Years on: IRUG in the past, present, and future

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[3]National Gallery of Art, US (retired); IRUG Raman committee chair

2000 2004 2009 -

Figure 1: IRUG website home page and website iterations, 2000 – present

The Infrared and Raman Users Group (IRUG, www.irug.org) is celebrating its thirtieth (and 1/3) birthday as we open the 15th IRUG biennial international conference (IRGU15) here in Tokyo, Japan, the first IRUG conference to be held in Asia.

IRUG was born following a meeting of interested scientist discussing the sharing of infrared spectral data at the 21st annual meeting of the American Institute of Conservation in Denver CO, US in June 1993. Shortly thereafter, the group had compiled its first collection of spectral data (Derrick, M. 1993. Infrared spectral library of artist and artisan materials, hard copy only, 777 spectra contributed by 7 institutions) and held its inaugural meeting (Philadelphia Museum of art, 1994).

Early compilations existed in hard copy only and underwent little if any peer review or quality control. IR spectra were printed together with limited accompanying metadata, but spectra and meta data were accepted as provided by contributors. Laudable as these initial efforts were, it soon became clear that the database contained many irregularities and errors and that a more formal editorial process was very much desired. Furthermore, limiting the compilation of data to hard copy only, with no digital spectral data, severely limited the potential use of this compendium.

At the end of the third IRUG conference (IRUG3, Winterthur Museum, Garden, and Library, Delaware, US, 1998), the group adopted a formal committee structure with Beth Price, Janice Carlson, and Boris Pretzel as IRUG regional chairs at the helm. The same year, IRUG published the first version of the IRUG JCAMP format (Pretzel, 1998) and formalized the decision that spectral files should be kept in a JCAMP compliant format with all pertinent metadata accommodated within the file – hence making the finalised spectral file the primary source for all information pertinent to the material, its spectrum, and how the data was collected and processed. By 1999, the group launched its first simple website on www.irug,.org and formed an editing committee, with some 15 members meeting in Florence that year to start the arduous process of sifting through all of the contributions to the hard copy database and work towards a fully peer revied, high-quality collection of reference spectra with good supporting metadata and full availability of supporting digital spectral data. The

group also formally extended its name from the “Infrared Users Group” to the “Infrared and Raman Users Group” (same acronym – IRUG) in recognition of the growing importance of Raman data in the field.

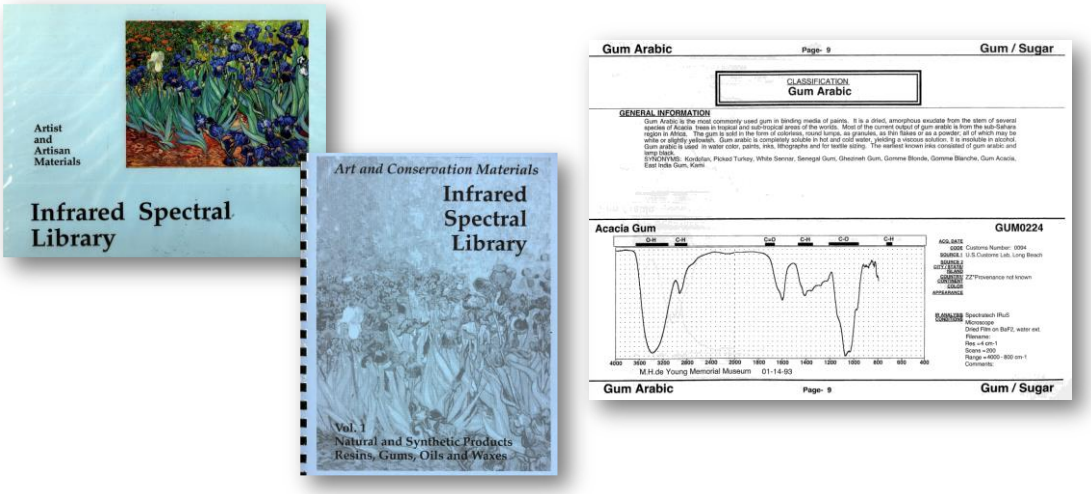

Figure 2: 1993 and 1995 hard copy releases of IRUG reference spectral databases with an example

The editing process continued for some two years, in which time the group also extended the IRUG JCAMP file format to include Raman spectral data (Pretzel et al, 2001; Price et al, 2010). Although only 25% of the original 1259 hard copy spectra contained in the 1995 IRUG hardcopy release passed the editorial process and remained incorporated in the version 2000 reference database, this database version (released at the end of 2001) was augmented with new contributions, and contained 1,258 quality assured and peer reviewed spectra (to match, almost exactly, the number of spectra in the earlier hard copy release). The group also started development of its website to include a MySQL compatible database containing the spectral data accepted and incorporated in to the IRUG reference spectral database, and website software to coordinate the submission and review of spectral data, and to store and distribute the IRUG reference spectral database.

In 2009, an updated database, optimistically called “version2007”, was released to members. This version now contained 2,128 reference IR spectra. The release was still distributed with an accompanying hard copy book (in 2 volumes) but for the first time also downloadable by contributors directly from the website. At the same time, the website was enhanced to include a ‘Key-word Search’ with an ‘Interactive Spectrum’ for public access, and a “structure index” was added to the spectral database.

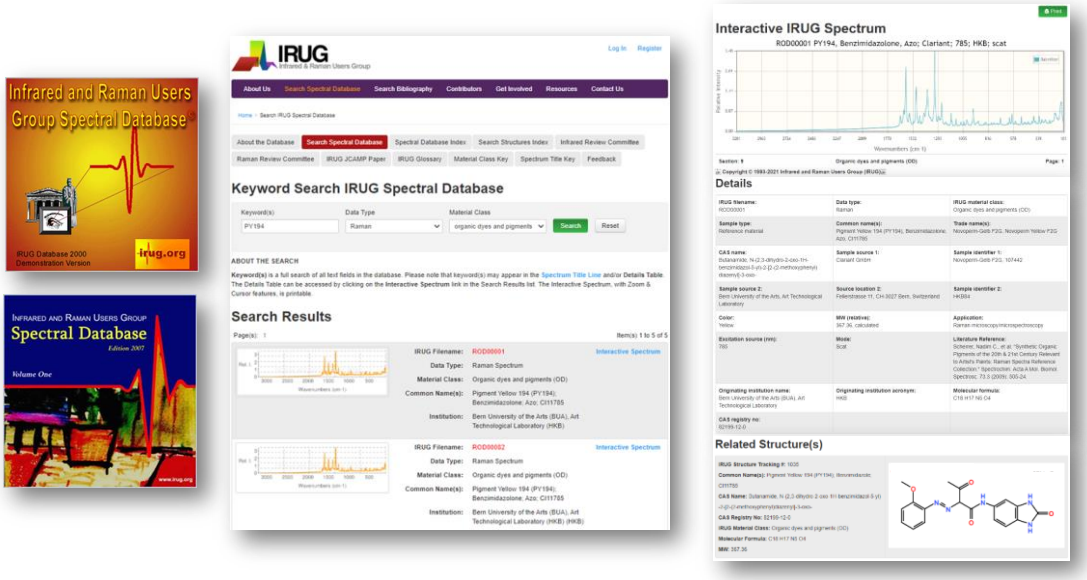

Figure 3: CDs with digital spectral data for IRUG Edition 2000 and Edition 2007 spectral databases, the key word spectral search, and example interactive spectrum plus supporting information on www.irug,org

Other milestone initiatives include:

- 2009 - 2011
  - the IRUG JCAMP format was revised with more fields, to correlate more rigidly to a database structure, expand on metadata for Raman files, and add fields for additional data pertaining to the material sample, source, and location [Price et al 2010]
  - development an off-line IRUG JCAMP-DX building tool in 2009 [Pretzel 2009]. designed principally for IRUG editors, reviewers and submitters with limited interned access, this tool imports 3rd party JCAMP files, shows a thumbnail spectrum of the data, parses out all included meta data and allows input of any missing key IRUG supporting data and generate an IRUG Camped format spectral file with all supporting data included in the appropriate data fields

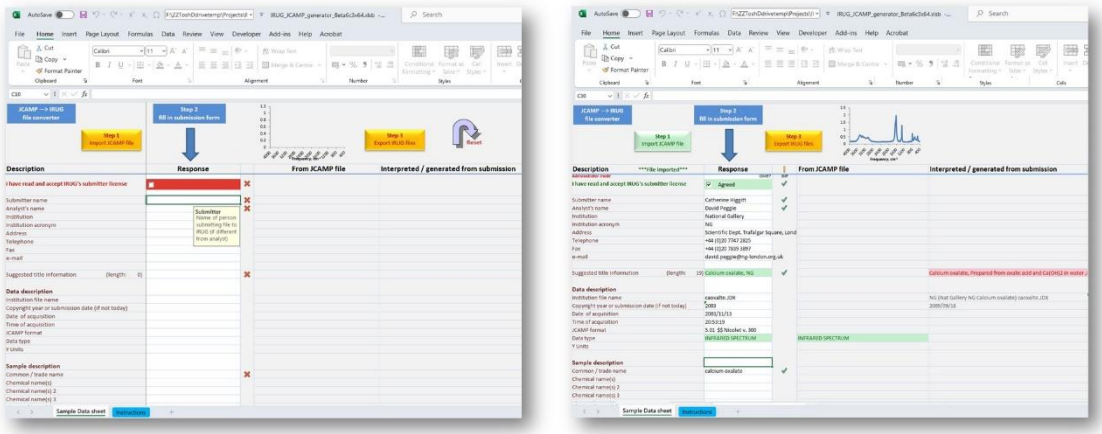

Figure 4: RIUG JCAMP Generator; excel bases utility to interrogate, format and manipulate JCAMP.DX formatted spectral files and generate IRUG format compliant output with meta data correctly embedded in the file. Left before, and right after import of JCAMP file and adding meta data.

- IMLS Leadership grant awarded to IRUG to development a Raman spectral library an enhance its website features, giving open access to IRUG reference spectral data to the general public and centralising the platform for IRUG spectral review activities.

- 2012 - 2013
  - IRUG online spectral search discussions were initiated
  - IRUG PMA Raman spectral web database project launched [Lomax, S., et al, 2013]
- 2014 - 15
  - Spectral search algorithms and approaches were optimized and a formal proposal for developing the on-line spectral was developed
  - IRUG JCAMP Raman file format formally adopted and the first (small) test Raman database released on IRUG website (limited to 36 files)
- 2017- 18
  - first early beta versions of the on-line spectral search utilities were initiated
  - Raman data solicited and submitted

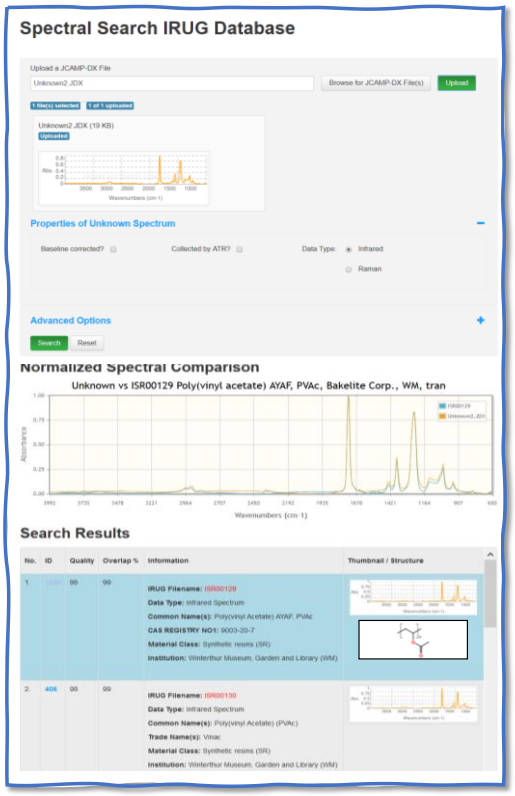

Figure 5: beta version for the IRUG web spectral search utility

- 2019 an on –
  - continued significant Raman data review and enhancements to metadata
  - increasing emphasis on the collection and review of Raman spectral data alongside the already well-established infrared data

As IRUG turned 30, the reference collection totaled 3601fully revied and quality assured spectra with:

- 2601 IR spectra available for interactive spectral viewer via key word search utility
- 1004 Raman spectra available for interactive spectral viewer via key word search utility
- In addition, there were 177 spectra under active review and a further1031 spectra pending completion of submission and / or review! (30% the size of data already in live database)

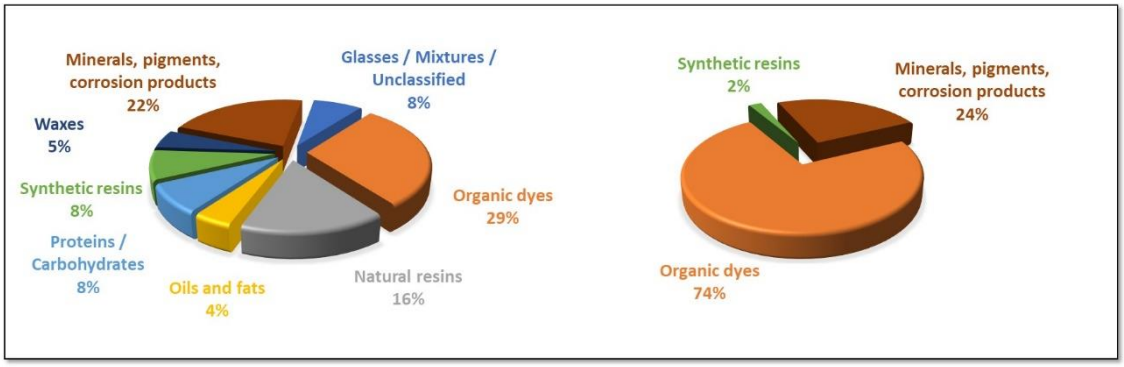

Figure 5: 2023 IRUG database compositions by materials class; IR left (2601 files), Raman right (1004 files)

Forthcoming initiatives include

- release of a 2023 beta version of the Raman spectral database with over 1000 spectra for comprehensive testing and review to identify any missing or incorrect data, unacceptable or unidentified contaminants / spectral features, and any excess fluorescence or unacceptably poor signal to noise
- release spectral search functionality to reviewers for beta testing to identify issues of specificity and usability and consider any redundant or missing feature.

The developments for IRUG and growth of the collection of reference data is an arduous task and is currently driven by ta small team, mainly consisting of the IRUG board of directors. Over 1000 files are waiting work to complete submission and peer review before being added to the reference collection -a daunting task! To develop and grow at a sustainable pace, we need your help.

So please join us!

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1.30. Polychrome decoration on wooden Prince Shōtoku sculptures from the 13th century and associated dedicatory deities

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The collections of the Harvard Art Museums include a unique 13th century wooden sculpture known in English as “Prince Shōtoku at Age Two” that depicts Shōtoku Taishi (c.574-622), often described as the father of Buddhism in Japan. The statue shows him as a two-year-old the moment after he stood up, chanted the name of the Buddha, and manifested a relic between his hands. This is the earliest datable example of a sculpture of the two-year old prince and is superbly carved and decorated with pigments and lacquer. The sculpture was acquired from a Japanese dealer in 1936 by Ellery Sedgwick; it was gifted to the Harvard Art Museums in 2019 by his grandson, Walter Sedgwick. In the late 1930s, the hollow sculpture was opened through the base at the MFA, Boston, and was found to contain many devotional objects including six smaller wooden sculptures of Buddhist deities with polychromy, prayers, charms, and scriptures. Collaborative art historical and technical research was undertaken by an international team to learn more about the context and origins of the sculpture, the materials and techniques used, and how these compare with other examples in Japan and the USA. Technical study of the large wooden sculpture and miniature figures included conventional x-radiography and CT-scanning to understand the structure and construction methods, and materials analysis of the polychrome surface. In-situ analysis was undertaken with x-ray florescence spectrometry (XRF) and Raman spectroscopy (Raman), followed by removal of small samples for analysis with Fourier transform infrared spectroscopy (FTIR), Raman, scanning electron microscopy with energy dispersive microanalysis (SEM-EDX) and gas chromatography mass spectrometry (GC-MS). Analysis identified a diverse palette that included vermilion, hematite, red lead, indigo, azurite, malachite, kaolin, lead white, lead chloride (most likely from alteration) and lacquer. The specific pigments used varied between the sculpture of Prince Shōtoku and the six smaller dedicatory sculptures. FTIR analysis of adhesives on the deities identified two different types: most were proteinaceous, but a carbohydrate-based adhesive was found on one miniature figure. Samples from the “Prince Shōtoku at Age Two” sculpture at the Cleveland Museum of Art (dated to the early 1300s) were analyzed with the same techniques for comparison. This presentation will focus on the Raman and FTIR analysis of the two Prince Shōtoku sculptures and the smaller dedicatory deities and discuss how this was complemented by the other techniques.

1.31. Multidisciplinary studies of medieval manuscripts

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During the last decades collaborations have been established between humanities such as philology, art history, and conservation-restoration on the one side and natural sciences such as computer vision and materials science on the other. The Centre of Image and Material Analysis in Cultural Heritage (CIMA, https://cima.or.at) in Vienna is the result of such an interdisciplinary co-operation and represents an interuniversity research institution for the investigation of cultural heritage. The research projects have focused so far on the documentation and material analysis of medieval manuscripts written in different languages and scripts. Mainly Slavic (Glagolitic and Cyrillic), Greek and Latin manuscripts of the Austrian National Library and various Austrian monasteries from the 8th to the 14th centuries have been analysed. Furthermore, investigations could be carried out in the St. Catherine Monastery in Sinai (Egypt), the Rila Monastery (Bulgaria), National Library Sofia and Plovdiv (Bulgaria), the Vernadsky National Library of Ukraine, Biblioteca Comunale Trento (Italy), National and University Library Ljubljana (Slovenia), National Library Budapest (Hungary), National Library Zagreb (Croatia) and finally in the Biblioteca Apostolica Vaticana (Vatican).

Multi- and Hyperspectral Imaging (MSI and HSI) support the recovery of degraded or deliberately removed contents [Tonazzini et al, 2019; Camba et al, 2014] and spectroscopic analysis methods [Schreiner et al, 2017; Fruehmann et al, 2018] are applied for the identification and characterization of inks, pigments, and binding media used for the text and the illuminations, as well as the characterization of the writing support (mainly parchment) and remains of conservation-restoration treatments. These material analyses are carried out with the aid of three complimentary non-invasive methods for elemental and compound specific material analyses: X-ray Fluorescence (XRF), Fourier Transform Infrared spectroscopy with External Reflection (ER-FTIR) and Raman spectroscopy. This combination has yielded the maximum of information, as there are several limitations in the application of e.g. just XRF for the identification of inks and pigments. Mainly inorganic components can be identified, but no compound specific information is obtained. For these reasons, Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy are valuable complementary techniques, which also can be carried out non-destructively.

Within our research projects, two different categories of objects are preferred: on the one hand badly preserved sources or manuscripts containing overwritten text (palimpsests) which pose particular challenges to the philological investigation, and, on the other, manuscripts with a remarkable, colour decoration (initials, miniatures, etc.) which are of interest not only from an art historical and philological, but also an art technological and chemical point of view. The investigations have yielded that mainly iron gall inks with varying contents of copper, lead and zinc were applied as writing material, whereas well-known pigments such as vermilion, red lead, orpiment, lapis lazuli, azurite or indigo were detected in the miniature paintings. In some cases, a mixture of the various pigments with lead white was verified, likely to achieve a brighter tone. Additionally, the identification of iron gall inks is useful not only from a historical perspective but also for conservation and preservation purposes due to its corrosive nature to the support.

Due to the high amount of data (images and spectra) a repository for the archiving and dissemination of research data a project was launched in the form of Multi-Modal Manuscript Representations, in which the various digital artifacts are spatially and logically related [DiTAH, 2021]. With respect to long-term preservation and linked open data, special emphasis is put on the use of established and open standards for data and metadata. The resulting virtual objects can be disseminated via technical interfaces but also via an interactive web viewer (Figure 1). Thus, the data available in the repository is made long-term accessible not only for natural sciences and technologies, but also for research and education in the humanities.

Figure 1: Browsing measurements in the web viewer

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1.32. FT-IR analysis of the blue restoration of cyanotypes decolorized after alkalis

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Research aims

This research follows the discoloration and subsequent recoloration of cyanotypes using FT-IR and UV-Vis spectroscopy. Discoloration happens on exposure of the cyanotype to alkaline environments. Restoration of the blue color can be achieved by treating the bleached cyanotype with strong acids. The visible spectrum shows the extent to which the blue color is restored, while the FT-IR follows molecular changes occurring on bleaching and subsequent recoloration of the samples.

Background

Cyanotypes are a solar printing method from the 19th and 20th centuries, often seen as photographs and architectural plans. The process utilizes the light sensitivity of ammonium ferric citrate: by mixing this with potassium ferricyanide and exposing it to light, the iron of ammonium ferric citrate reduces from Fe^{III} to Fe^{II}, creating Prussian blue. The parts exposed to light turn blue; therefore, the lines of the original sketch remain white, printing a negative image. Cyanotypes are known to decolorize in the presence of alkalis, and the following reaction has been proposed [Ware 2003].

$$Fe^{III}[Fe^{II}(CN)_6]^- + 3OH^- \rightarrow FeO(OH) + H_2O + [Fe^{II}(CN)_6]^{4-}$$

Equation 1: decolorization by alkalis

Additionally, it is known that cyanotypes recolor by treating with acids [Tsubokura 2010]. However, they conclude that the decolorization by alkalis is irreversible because the blue does not return completely to its original state.

Cyanotypes can be exposed to alkaline environments from many sources: adhesives found in architectural and marine fields, products of deacidification, and buffers in storage materials found in museums. If the color can be reestablished by treatment with acids, the treatment could possibly be developed into a method of their conservation.

Methods and results

In order to observe the color changes with alkalis and acids, a cyanotype was immersed in alkali and then in acid. Cyanotype samples were made with Whatman No. 1 paper, following the recipe of “traditional cyanotype process” [Ware 2014]. The cyanotype first decolorized to yellow after treating with 0.25M sodium carbonate, and then the blue was brought back with 0.1M hydrochloric acid (Figure 1)

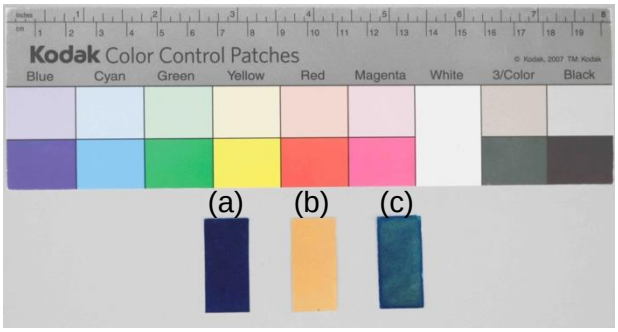

Figure 1: cyanotype before and after immersion
(a) untreated cyanotype
(b) decolorized with alkalis
(c) recolored with acids

However, both visually and by UV-Vis spectroscopy analysis (FORS Ocean USB 2000+), the blue did not completely return to its original color but to a lighter greenish blue (Figure 2).

Additionally, the reaction was examined using FT-IR spectroscopy analysis in ATR and reflectance modes.

Each measurement of "untreated cyanotype," "cyanotype decolorized with alkali," and "cyanotype recolored with acid" was taken 3 times each from 4 different samples (N=12).

In ATR mode, the samples were analyzed with Thermo Scientific (now Thermo Fisher Scientific) Nicolet iZ10 with Smart Miracle Accessory ZnSe under the conditions: 4 cm-1 resolution, 64 scans, and air as background. The results showed the peaks of cellulose of the paper substrate and the stretching cyanide (around 2100cm-1) included in the structure of Prussian blue. No differences were seen in the peaks of cellulose between samples, so the peak of cyanide was closely examined (Figure 3).

As indicated in Figure 3, the cyanide peak first observed in the untreated cyanotype largely decreased after immersing in alkalis and reappeared after the acid treatment.

The same observation was seen with the reflectance mode. The measurements were taken with Bruker Alpha under the conditions: 4 cm^{-1} resolution, 64 scans, and gold mirror background. The measurements were also taken with an FT-IR microscope (Thermo Scientific Nicolet iN10); however, the results were seen with larger noise, so the results from Bruker Alpha will be discussed here.

Besides the same observation of the inhibition and the reappearance of the cyanide, a small peak was observed at 2040 cm^{-1} after decolorization by alkalis, which could possibly be attributed to cyanide.

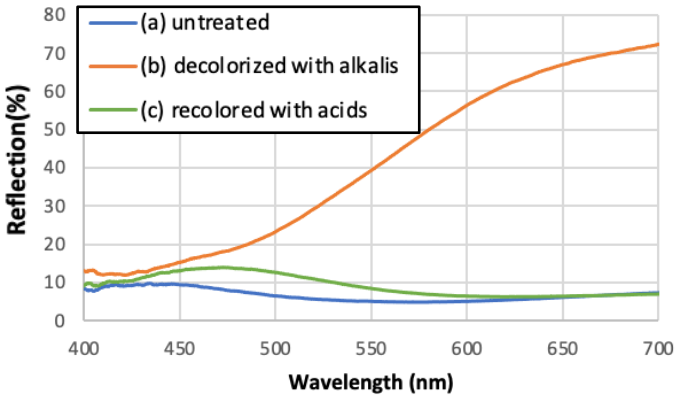

Figure 2: UV-Vis spectrum before and after treatments on cyanotype

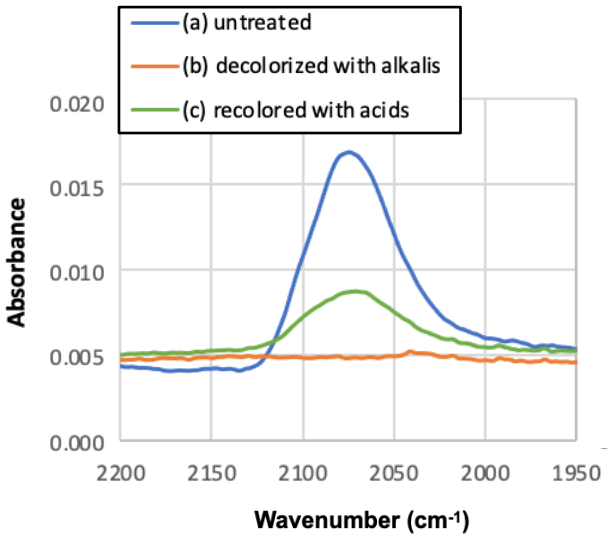

Figure 3: FT-IR ATR mode spectrum before and after treatments on cyanotype

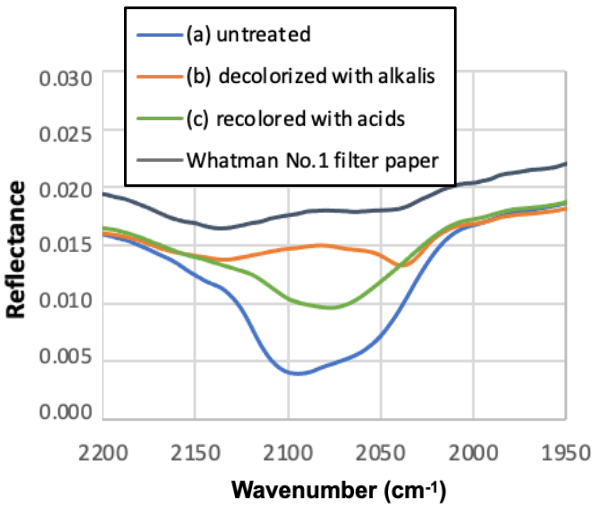

Figure 4: FT-IR reflectance mode spectrum before and after treatments on cyanotype

In order to observe the cyanide in closer detail, the material was measured in transmission mode. Prussian blue precipitate collected from sensitizing the cyanotype sensitizer solution without applying it on paper was measured as the sample.

In comparison, the precipitate after decolorization was prepared by adding sodium hydroxide to the Prussian blue solution. The measurements were taken under the condition of 4 cm^{-1} resolution, 64 scans, and KBr background, and the result obtained is shown in Figure 5.

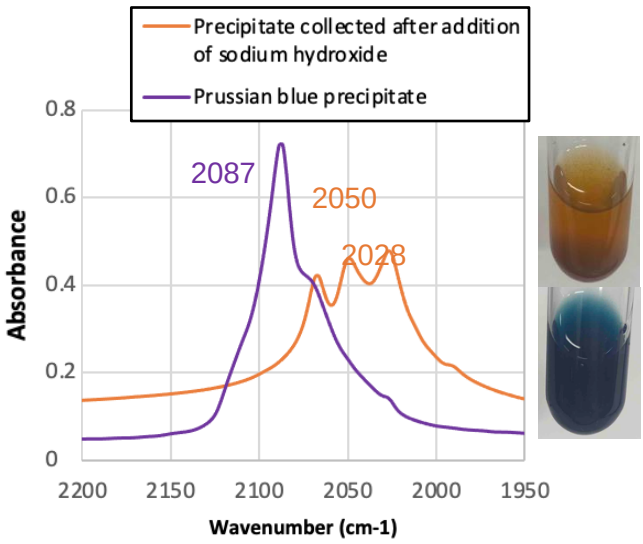

Figure 5: FT-IR absorbance spectrum before and after treatments on Prussian blue precipitate

A peak shift of the cyanide was observed from 2087 cm^{-1} to 2028 cm^{-1} ~ 2050 cm^{-1} range after the addition of alkali, near the peak location of $K_4[Fe^{II}(CN)_6]$. The same material is expected to be formed on cyanotypes; however, the question is brought back to the observation of why the peak of cyanide is inhibited and then reappears.

Conclusion

In this research, the blue could only be seen when the vibration of the triply bonded cyanide was active. The blue that decolorized after treating with alkalis was brought back to some extent after treating with acids. At the same time, the stretching of the cyanide became nearly inactive after the treatment with alkalis, and then again active after treating with acids.

Discussion

The fact that the two observations were seen at the same time suggests that the blue coloring seems to be related to the state of cyanide. However, it is also known that cyanide itself does not create the color blue. Generally, the blue of the Prussian blue is known to originate from its charge transfer transition, having both states of Fe^{II} and Fe^{III} in its structure. The blue of the cyanotype and the recoloration must be originating from the same mechanics. The fact that the decolorization occurred together with the inhibition of the cyanide suggests that the structure is somehow rearranged, affecting the absorption occurring in the charge transfer transition and effecting the color of cyanotypes.

This research leaves many questions on the chemistry of this reaction unanswered. The mechanics of how the stretching of the cyanide is inhibited and then reappears must be important in understanding how alkalis cause the decolorization of cyanotypes and the role of the acid treatment in the reformation of the color. Although the method itself is still unrealistic, as the cyanotypes must be soaked in acid to regain the blue, the fact that the blue could be brought back is one significant achievement of this research as it opens up the possibility of regaining lost images. Further work is needed to explain the observation of the inhibition of the cyanide vibration on removing the color of cyanotypes.

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1.33. Studies on Chinese architectural pasting ornament in the Forbidden City by Raman spectroscopy

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Architectural Pasting Ornament is an important decorative craft in ancient Chinese official architecture, which began in the late Ming Dynasty and became popular in the northern regions of the Qing Dynasty (1636AD-1912AD). Architectural Pasting Ornament refers to several layers of plain paper or paper with colored patterns, as well as textiles pasted on interior walls, roofs, doors, and windows for decorating and keeping the rooms warm. The craft has high historical and artistic value.

There were different styles of Architectural Pasting Ornament, with large white paper used to cover the roofs and walls of the emperor's administrative spaces, chambers, Buddhist halls, study rooms etc., while the concubines' rooms mostly were pasted with silver molded paper of various patterns, which is the main subject of this study. Silver molded paper usually has two layers: the priming layer and the molded pattern layer. In this study, there are three kinds of silver molded paper:

1) peony pattern paper has a silver background and white *Wanzi* and peony pattern on it (Figure 1a).
2) green pattern paper has silver background, on which white *Wanzi* and green wrap-around Passiflora\groups of dragon patterns are molded(Figure 1b)
3) Cherry pattern paper, blue priming layer with a golden cherry blossom pattern. (Figure 1c)

Figure 1: Three kinds of silver molded paper a) peony pattern paper; b) green pattern paper; c) cherry pattern paper

In order to study the materials of the silver molded papers, the main techniques applied to investigate the pigments of silver molded paper include SEM-EDX and Raman spectroscopy, as well as pyrolysis with gas chromatography and mass spectrometry for detecting the binding media used.

Through analyses by using multi-techniques, it was found that the peony pattern paper was produced in the process: calcium carbonate was used for the background, while mica was used as pigment to mold the pattern of the *Wanzi* and peony patterns on the surface, with animal glue was as the binding media.

A more exquisite type is the green pattern paper, for which the study of green pigment was complicated. The green pigment's main elements are Cu and O through SEM-EDX analysis. Through Raman analysis, the spectrum of green pigment is consistent with copper resinate. Moreover, the Raman spectrum of the green pigment has more details than the standard spectrum of copper resinate. (The bands at 225, 547, 1233, 1299, 1442, 1626, 2931 cm^{-1} are consistent with copper acetate.) THM-Py-GC/MS was applied to detect the organic compounds. The detection of methyl dehydroabietate, methyl abietate and 15-methoxydehydroabietic proved the use of rosin resin,

which is additional evidence that the green pigment is copper resinate. It is noteworthy that copper resinate is a Western pigment popular in the Renaissance Period, with a transparent light green color. The detection of it in the pasting ornament samples is important, and is the first time that copper resinate has been found in Chinese heritage relics. By combining the history of the pigment and Chinese archives, it can be inferred the green pigment was probably imported from Europe. After analyses, the fabrication process of green pattern molded paper can be concluded follows: firstly, animal glue and mica were used for laying primer, on the surface of which lead white was applied to mold *Wanzi* pattern and then copper resinate was used to mold wrap-around Passiflora patterns or groups of dragon pattern.

The blue ground with cherry blossom pattern silver molded paper.was also studied with Raman spectroscopy. The Raman spectrum of blue pigment is consistent with indigo. The golden pigment is a mixture of iron red, mica and calcium. It can be observed that the production process is: firstly, indigo was applied on the surface of the bamboo paper to make the blue background. Afterwards, a mixture of mica, calcium carbonate and iron red was blended into the golden drawing of Japanese characteristics of cherry blossom pattern. According to the Qing Dynasty imperial archive, cherry paper was produced by the craftsman of the Jiangnan region of China by using Japanese paper.

The above three types of silver molded papers in architectural pasting ornament have high historic and artistic values. Through this study, the results not only revealed information on the pasting materials used in the Qing Dynasty, but also provided evidence of exchanges between China and Japan as well as the West in th Qing Dynasty.

1.34. ER-FTIR spectroscopy of coated silver gelatin photographs: applications to the works of Dorothea Lange

Joan M. Walker*, Laura Panadero, Emily Mercer

National Gallery of Art, Washington, DC, US

Silver gelatin photographs, the most common type of black and white photograph in the 20th century, consist of several layers: a cellulose paper support, a barium sulfate-containing baryta layer, and an image-bearing gelatin emulsion layer. There may also be present an additional protective coating of gelatin. Photographic paper manufacturers manipulated the chemical and physical properties of each of these layers to create a fascinating diversity of final print appearances to meet photographers' needs. A photographer or printer would choose a suitable photographic paper on which to print and could adjust processing in the darkroom to achieve a desired aesthetic effect. Moreover, a coating could be applied after processing to further refine the surface texture and appearance of the photograph.

During preparations for an upcoming exhibition of photographs by Dorothea Lange at the National Gallery of Art, conservators noted the presence of a clear coating on some of the prints, initially recognized only because it exhibited flaking at the edges. A small sample of the flaking coating was identified as polyvinyl acetate (PVAc) by transmission FTIR spectroscopy. To confirm the presence of PVAc or other coating materials on additional prints without sampling, analysis by external reflectance (ER)-FTIR was performed.

ER-FTIR spectroscopy can non-invasively identify materials present at the surface of an object. In multilayer structures, additional information from beneath the surface may be encoded in ER-FTIR spectra due to the penetration depth of the infrared radiation. Interactions between reflections from the surface and sub-surface layers can generate spectra that are challenging to interpret. For silver gelatin photographs, spectrum information may derive from several layers within the structure, although the extent to which each layer contributes depends on its optical properties, thickness, and roughness.

To address some of the analytical challenges presented by silver gelatin prints in ER-FTIR spectroscopy, sample photographs were prepared using papers with a variety of surface finishes (matte, semi-glossy, and glossy) and were subsequently coated with synthetic polymer varnishes, including the most common polymer classes (acrylic, cellulose nitrate, and PVAc) in several formulations. Application methods used included spraying, rubbing, and brushing to replicate approaches recommended by product manufacturers. These samples were analyzed using ER-FTIR spectroscopy and complementary techniques, including ATR-FTIR and SEM-EDX, to understand how the chemical and physical structure of the photographs influence the ER-FTIR spectra acquired.

In all cases, the coating material on the sample photographs could be positively identified with ER-FTIR spectroscopy. Nuances in the spectra reveal additional details about the photographic paper, surface finish, and application method. Applying this knowledge to the ER-FTIR spectra of the Lange photographs allows for a fuller appreciation of the materials used to create them and adds to the understanding of the aesthetic choices of this consequential artist.

1.35. Vibrations throughout history- insights into the past by vibrational spectroscopy

Stephan Woods* (silver level sponsor's talk)

Thermo Fisher Scientific

The preservation and restoration of cultural heritage artifacts represent an essential aspect of our cultural identity and history. Vibrational spectroscopy is well known as a powerful analytical technique in the field of art restoration, offering non-destructive and high-resolution insights into the composition, degradation, and authenticity of artworks.

Due to the non-invasive nature of vibrational spectroscopy, it is particularly valuable for delicate and valuable artifacts. We will discuss how these techniques have been employed across a wide variety of samples to identify pigments, binders, and varnishes in paintings, as well as to assess the chemical changes occurring due to aging, environmental factors, previous restoration attempts and detecting forgeries or alterations in artworks.

Advancements in chemometrics and small form factor spectroscopic devices have facilitated on-site analysis in museums and galleries and expedited the decision-making process during restoration projects. As technology continues to advance, these techniques hold the promise of further enhancing the accuracy and efficiency of art restoration efforts, ultimately preserving our rich cultural heritage for future generations. This presentation will provide an overview of the applications of vibrational spectroscopy techniques, including reflective FTIR and Raman spectroscopy, in the context of art restoration.

1.36. Computational chemistry simulations in the deep understanding of molecular structures in different ageing silk textiles using ATR-FTIR spectroscopy

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Archaeological and biochemical evidence shows that the silkworm, which were completely domesticated and entirely dependent on humans for survival, originated in the middle and lower reaches of the Yellow River [Lee et al, 2022; Tong et al, 2022] and directly prove that the silk civilization came from China. The Silk Road and the subsequent Maritime Silk Road are shown as vital bridges between East and West, embodying the important contribution of Chinese silk culture in ancient civilizations. Meanwhile, organic dye analysis covering aspects of textile history, color and dyeing has been a very hot topic and also plays an important role in cultural heritage.

The evaluation of the ageing degree of silk fabrics is one of the main difficulties and is extremely worthy of in-depth research. FTIR characterization using attenuated total reflection (ATR) has been widely used in textile heritage [Liu and Kazarian2022]. With this analytical technique, the Palace Museum (Beijing) has conducted qualitative and semi-quantitative assessments of various components of the museum textile collections and their deterioration over the past 15 years [Wei et al, 2022; Wei et al, 2022b]. Computational chemistry is a powerful technology platform to reveal silk properties and predict their ageing extent [Barreiro et al, 2019]. The advantage of computational simulations is that the data library could be added and evaluated their different ageing degree continuously, repeatably, and practicably, and could be expected to bring new ideas and perspectives for the non-destructive analysis of precious silk textiles.

In this experiment, differently aged silk samples, including artificial ageing analogues dyed by indigo (before and after ageing), safflower (before and after UV and LED light ageing), sappanwood (ageing time ranging from 0-16 weeks and corresponding undyed silk control check), and yellowing silk sample with unknown ageing time, respectively, as well as two Thangka relic samples from the Qing Dynasty, were analyzed with using a Thermo Fisher Nicolet iN10 Mx FTIR spectrometer. IR spectra of all samples were collected by smart iTR diamond ATR using traditional single point detection. Every spectrum was composed of 32 scans, ranged from 4000 to 400 cm^{-1}, and was analyzed with OMNIC software. The spectral resolution was about 4 cm^{-1}, and the absorbance was acquired.

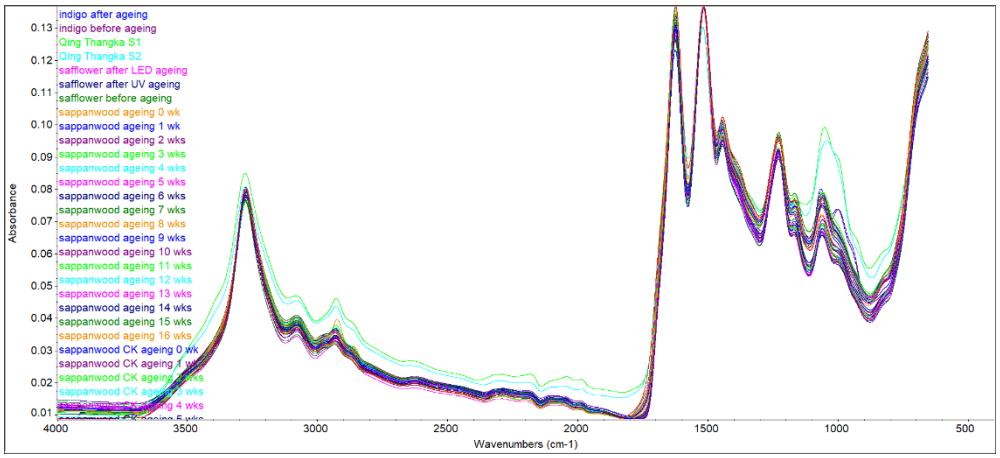

Figure 1: ATR-FTIR spectra of all analyzed silk samples in this experiment

To characterize the chemical alterations induced by the ageing process, we developed a strategy combining ATR-FTIR spectroscopy and multi-scale molecular simulations. Silk samples were analyzed using ATR-FTIR at first (Figure 1). There were three main characteristic infrared absorption peaks of silk protein polypeptide backbone at around 1625 cm^{-1}, 1520 cm^{-1}, and 1230 cm^{-1}, corresponding to amide I, II, and III bands, respectively. The spectra suggested that the chemical composition of the silk samples with different ageing levels might not be changed. Therefore, the major alterations during the ageing process could be the conformational change of the polypeptide which makes up the silk samples. In order to clarify the chemical alterations at the atomic level during ageing, we further applied enhanced sampling molecular dynamics simulations and quantum chemistry calculations to a modelled molecular system that is composed of the major chemical composition of silk fiber. Since the conformational change of polypeptide chain is hard to capture by conventional quantum chemistry calculations, enhanced sampling molecular dynamics simulations were performed to obtain an ensemble of conformations of the polypeptide at a relatively lower precision. Then, the structures were optimized using quantum level calculations. Finally, by matching up the computed spectra using the structures obtained in molecular simulations to the spectra obtained in FTIR measurements, detailed molecule conformations could be retrieved (Figure 2). This strategy also may be useful in characterizing molecule level chemical alterations during the ageing of fibers other than silks and help us to thoroughly comprehend the chemistry of the ageing of materials in cultural heritage.

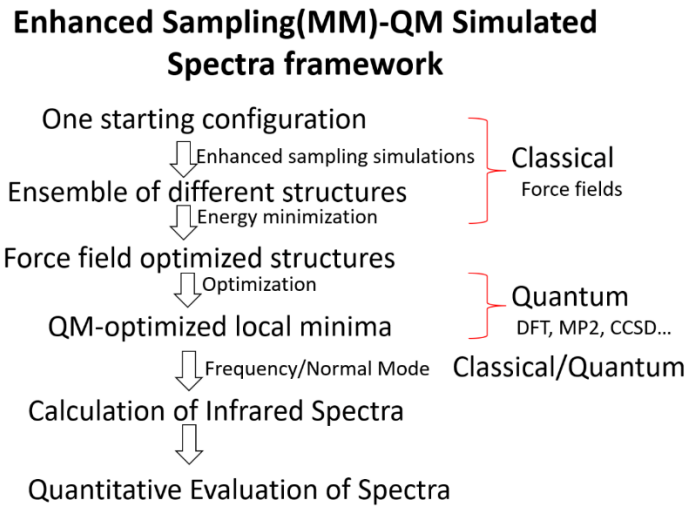

Figure 2: The research protocol of MM-QM Infrared Spectra calculation

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1.37. Application of open-source software for spectra analysis of pigments

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The prominent imagery of Door Gods (Menshen, 門神) in many traditional temples is an important part of Taiwanese folk culture and "religious" culture. These paintings feature a wide variety of colors and rich hues. Many paintings embody the cultural characteristics of Taiwanese Buddhism and Taoism, including their customs, beliefs, and aesthetics, and are therefore of significant cultural heritage value. Identification of pigment and binder in the artefact could provide vital information for future conservation and restoration of these paintings [Rousaki and Vandenabeele, 2021]. Due to the lack of a suitable pigment database in Taiwan, the Ministry of Culture Taiwan initiated a research project to establish the FORS, FTIR, XRF and Raman multi-analytical techniques pigment database and the pigment identification analysis techniques in 2022. For this initial project, five Door Gods paintings from each of the five traditional painters Liu Jia-Zheng (劉家正), Liao Qing-Zhang (廖慶章), Hong Ping-Shun (洪平順), Pan Yue-Xiong (潘岳雄) and Xu Liang-Jin (許良進) were selected for spectra analysis by FORS,FTIR, XRF, and Raman techniques. The FORS data was obtained from ARCoptix ArcSpectro using fiber optics with an integrating sphere. The FTIR analysis was performed using a Shimadzu AIM-9000 spectrometer. The XRF analysis was performed with a Bruker Tracer 5G spectrometer. The Raman spectra were obtained using a Bruker Bravo spectrometer. For each Door Gods painting, at least six pigment colors - black, blue, red, green, yellow, and white - were labelled and measured by the FORS, XRF, and Raman spectrometer. Figure 1 shows an example of a pigment sample analysis spot on the Door God painting by Pan Yue-Xiong (潘岳雄) at Kai Ji San Guan Miao (開基三官廟), Tainan, Taiwan.

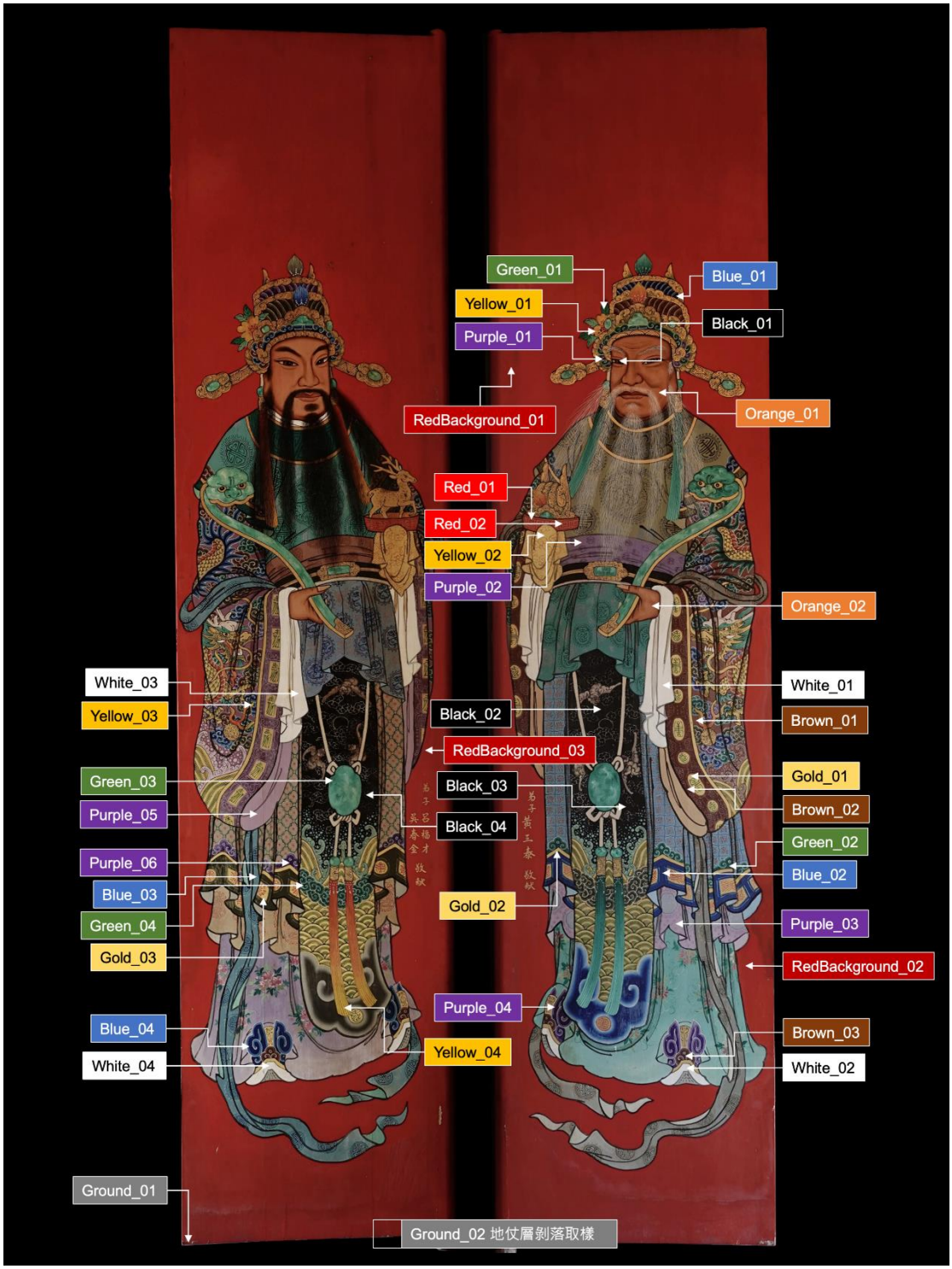

Figure 1: Example of pigment sample analysis spot in Door God painting by Pan Yue-Xiong (潘岳雄) at Kai Ji San Guan Miao (開基三官廟), Tainan, Taiwan

The successful identification of pigment and binder relies heavily on three important pillars: spectroscopic instruments, a comprehensive pigment database and chemometrics techniques. With the help of modern spectroscopic instruments, different pigment and binder databases have been

established [Bell et al, 1997; Scherrer et al, 2009; Burgio and Clark, 2001; Fremout, and Saverwyns, 2012]. Chemometric software plays a detrimental role in pigment spectra data preprocessing, data analysis and spectra searching. Luckily, due to the advances in data science, nowadays, we have many free and open-source tools available for spectroscopic analysis. For example, there are many useful R packages like hyperSpec, ChemoSpec, and spectacles for displaying spectra and comparison of spectra data. For comparison of multiple spectra, multiple spectra plots with offset and stacked spectra plots are very useful. Figure 2 is an example of stacked spectra plot produced by spectacles R package.

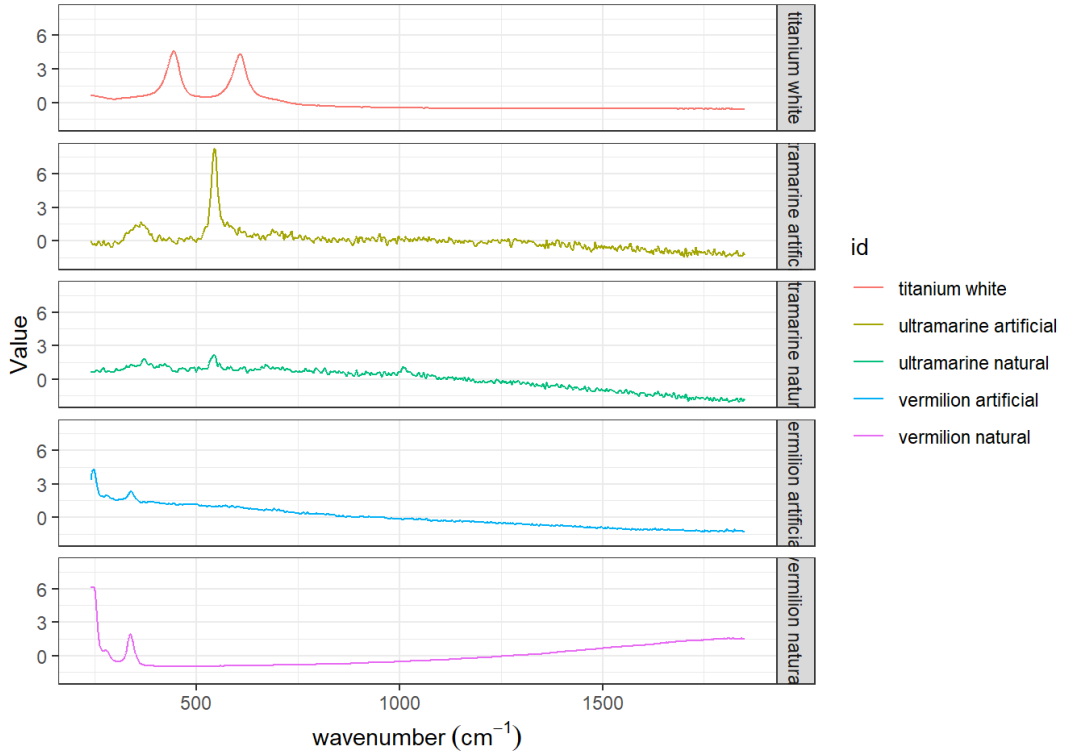

Figure 2: Stacked spectra plot by spectacles R package

Prior to chemometric modeling, spectra preprocessing is often performed to increase the model performance [Martyna et al, 2020]. The *prospectr* package provides miscellaneous functions for processing spectroscopic data. As is very common for Raman spectra, the notorious fluorescence background appeared, and baseline correction may be be required. The R package *airPLS* is very useful for removing Raman fluorescence signal from baseline. Figure 3 provides an example of fluorescence signal baseline correction for PW6 using the *airPLS* package.

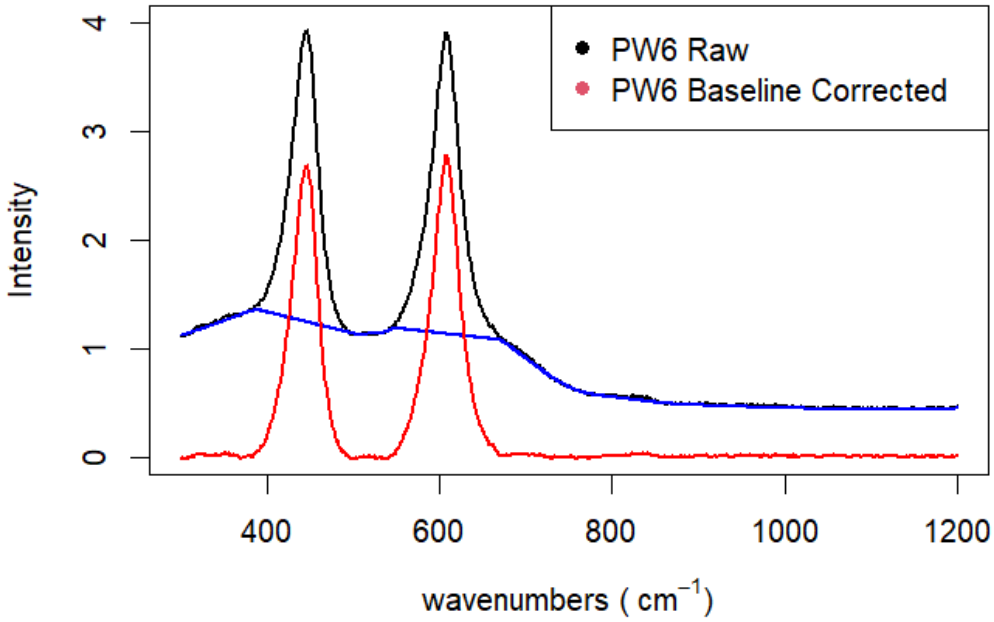

Figure 3: Raman fluorescence signal for PW6 using airPLS R package

The following R code is used to produce the result in Figure 3.

```
library(airPLS)
zc=airPLS(PW6_df$intensity,40)
plot(PW6_df$wavenumber,PW6_df$intensity,
     type="l",lty=1,lwd=2,
     xlab=bquote('wavenumbers ('~cm^-1*')'),
     ylab="Intensity",ylim=c(0,4))
lines(PW6_df$wavenumber,zc,col="blue",lwd=2)
lines(PW6_df$wavenumber,PW6_df$intensity-zc,col="red",lwd=2)
legend("topright",legend=c("PW6 Raw","PW6 Baseline Corrected"),
       pch=19,col=1:2)
```

For spectra searching and pigment identification, peak finding is an important operation. Finding a peak by visual inspection can be very tedious and time consuming. For Raman Spectra, a very useful *RamanMP* R package is useful for automatic peak finding and unknown identification. Figure 4 is a plot of a peak finding result from the peak.finder function in the *RamanMP* R package for PG7. From the found Raman peak position, comparison can be made to a reference pigment spectrum.

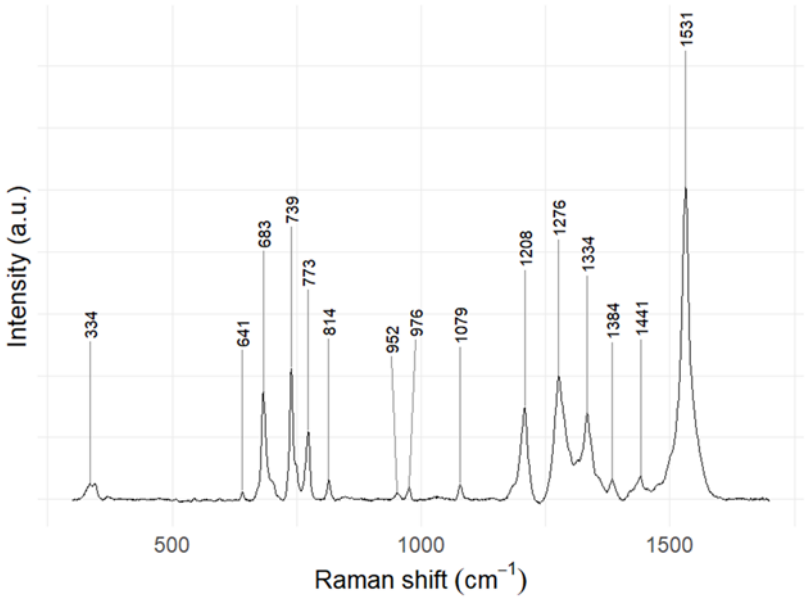

Figure 4: Peak finding for PG7 pigment by peak.finder function in *RamanMP* R package

The following R code is used to create reference green pigment database extracted from the SOPRANO Raman spectra database [Fremout and Saverwyns, 2012] and perform peak finding of PG7 in Figure 4.

```
library(RamanMP)
PG_database <- data.matrix(cbind(wavenumber,t(kikirpa_spc)))
colnames(PG_database)[1] <- "freq"
PG_database <- data.frame(PG_database)
PG7peak.data<-peak.finder(PG_database[,c(1,6)], threshold = 2500, m=15)
```

Browsing through reference Raman spectra databases and find matching spectra is very time consuming. *RamanMP* provides two search methods for spectrum identification: 1. based on Euclidean distance, and 2. based on Pearson correlation coefficient. Figure 5 shows spectrum identification result based on Euclidean distance for KJSGM_02 which is the spot corresponding to the White_02 in the bottom right-hand side of Figure 1. From Figure 5, we can also see that baseline corrected spectrum PW6_bc has higher similarity score 0.95 compared to 0.83 for PW6 raw spectrum. The search function in *RamanMP* successfully identified the blue, green, red, yellow, and white pigments in the Door Gods painting in the current study. For the black pigments, due to the relatively weak signal from 785 nm laser excitation [Marucci et al, 2018], the identification is not easy in the current study. As for the pigment mixture that appeared in the Door Gods paintings, more sophisticated machine learning techniques will be required [Fan et al, 2023].

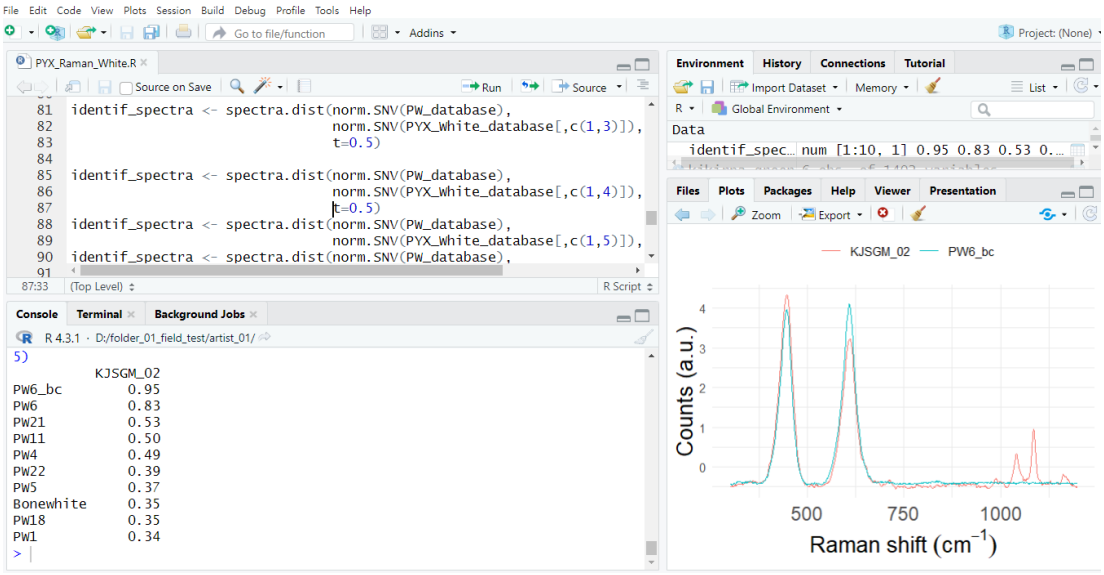

Figure 5: Spectrum identification based on Euclidean distance for KJSGM_02

Besides text based open-source package, the visual programming software Orange Data Mining was very useful for spectra analysis. An example will be given for the chemometrics analysis of Raman spectra of a different class of blue pigments from SOPRANO spectra database. The program workflow for PCA, tSNE, MDS analysis is shown in Figure 6 and the result of PCA, t-SNE, MDS analysis is shown in Figure 7. With powerful interactive graphic visualization, *Orange Data Mining* can help the user understand their data better.

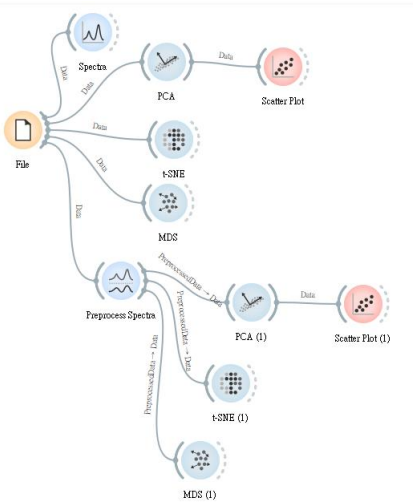

Figure 6: Workflow of Orange Data Mining for chemometric analysis of different class of blue pigment

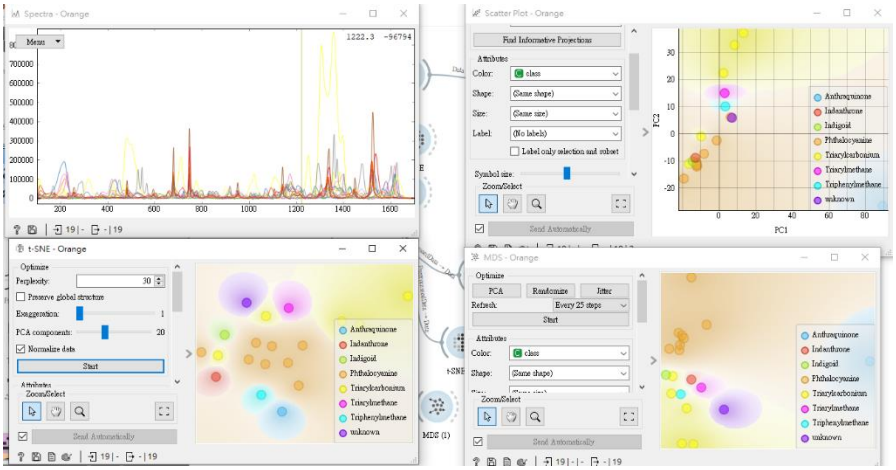

Figure 7: Result of PCA, tSNE, MDS analysis of blue pigment Raman spectra by Orange Data Mining Software

It is hoped that this work helps to illustrate the usefulness of open-source software for the spectra analysis of pigments in cultural heritage artefacts. Both the R software and Orange Data Mining software can be useful for education and research purposes.

Acknowledgements

This work was supported by the Ministry of Culture Taiwan. The authors are very grateful for the funding and the analytical instrument support of FORS, FTIR, XRF, and Raman from the Ministry of Culture Taiwan. The authors are also grateful to Dr. Wim Fremout of Royal Institute for Cultural Heritage (KIK/IRPA), Belgium for providing the whole SOPRANO Raman spectra data which is employed as a reference database in this work.

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1.38. Leather deterioration: insights for the conservation of cultural heritage

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Cultural relics made of leather are vulnerable to microbial attack, especially fungi. In this study, we used *Aspergillus niger* to simulate the aging process of tara-tanned leather and quebracho-tanned leather and analyzed the changes in the leather before and after aging using various techniques. The results revealed significant changes in the composition and structure of the leather by aging. Py-GC-MS showed changes in the leather components, including protein, tannin, fat, and unknown sources. In addition, 8 amino acid DKPs and 2 DKP derivatives in the samples were identified. DKP formation, a common reaction that occurs in protein molecules in leather over time, is considered a critical indicator of leather aging. By ATR-FTIR, alterations in the secondary structure of collagen were found, with a decrease in α-helix structure, resulting in the leather's hardening and embrittlement. Through the study, a comprehensive understanding of the mechanism of biodeterioration was provided, which might offer important scientific insights for the protection and restoration of leather cultural relics.

Key words: Cultural relics, leather, *Aspergillus niger*, ATR-FTIR.

2. Poster abstracts, in alphabetical order by attending author(s)

Attending author(s) are indicated by an * (asterisk) by their name

2.1. Identification of colorants in an 18th century Torii Kiyonaga *hashira-e*

Gwenanne Edwards[1], Cyntia Karnes[2], Lynn Brostoff*[3]

[1]Paper Conservator, Library of Congress, Washington DC. US
[2]Head of Paper Conservation, The Fine Arts Museums of San Francisco, US
[3]Independent Conservation Scientist

This poster compares three methods that were used to identify the colorants in a Japanese woodblock pillar print (*hashira-e*) in the collections of the Library of Congress: *Two Beauties Under a Cherry Tree*, from 1872-73, by artist Torii Kiyonaga. As a case study, the work demonstrates the usefulness and limitations of spectral imaging with false color processing (SI-FCSI) for colorant assessment, compared to information provided by X-ray fluorescence spectroscopy (XRF) and in-situ (non-invasive) µRaman spectroscopy. SI-FCSI was accomplished using the commercial Art Innovation Artist® multispectral imaging system outfitted with a digital camera that captures spectral responses from 300-1100 nm: visible, near-UV induced fluorescence, near-UV reflectance, reflected IR 1 (700-950 nm), reflected IR 2 (1000-1100 nm). False-color images were produced by combining UV or IR images and adjusting in Adobe Photoshop following AIC (American Institute for Conservation) published protocols [Frey, 2017].

Results show that in the case of this *hashira-e*, standardized SI-FCSI of the object compared to a set of references allows conservators to successfully identify red lead, indigo, and also (tentatively) safflower, while the presence of orpiment or gamboge may remain ambiguous. Supplementary XRF is useful in confirming the presence of a Pb-based red and As sulfide-based pigments, while in-situ µRaman spectroscopy validates the identification of red lead and indigo and firmly identifies natural orpiment (with no gamboge), in addition to lead white and carbon black. SI-FCSI shows a distinct advantage in the identification of safflower. Furthermore, in-situ µRaman analysis allows specific characterization of the red lead, which contains a litharge/massicot (PbO) component that signals incomplete synthesis and apparently explains its partial instability [Aze et al, 2008]. µRaman investigation of darkened red lead areas before and after treatment with H_2O_2 suggests that alteration to brown-black $Pb(IV)O_2$ had taken place and that reversion to $Pb(II,IV)_3O_4$ was enabled by the application of dilute H_2O_2 (without pH adjustment).

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2.2. Testing the sustainability of washing and reusing conservation cleaning sponges

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[2]RISD Museum, Providence, Rhode Island 02903 US

One of the common, routine tasks of conservators is to clean materials for preservation and/or display. When preparing historic wallpaper for exhibition at the Rhode Island School of Design (RISD) Art Museum, conservators used non-latex hydrophilic polyurethane foam sponges from University Products (Item no. 708-13708). This study examines the potential of being able to wash and reuse cleaning sponges to reduce waste in conservation labs and presents the cleaning and analytical methods.

Literature about historic painted wallpapers indicates the probability of heavy metals being present, including mercury, arsenic, and lead [Costantini et al, 2021]. Reuse of sponges requires that the washing process remove any heavy metal toxins so that they are not spread from one object to another or to the conservator. Sponges were washed with hot tap water in a small bucket after cleaning the wallpaper.

This experiment used FTIR ATR (Perkin Elmer Spectrum 2) and pXRF (Bruker Trace Vi) to 1) identify any toxins that were taken up by the dirty sponges and 2) check to see whether the washing procedure was sufficient to clean dirty sponges. Samples for analysis were prepared at RISD by cleaning neighboring locations on the wallpaper using two sponges; one was left dirty and the other washed. This was done for six locations with different colors and created a total of six dirty sponges and six washed sponges. Two sponges from the same batch were also set aside unused as controls. The results from both FTIR and pXRF indicate that the washing procedure followed at RISD successfully removed toxins from the sponges. pXRF analysis confirmed that the toxins present in the wallpaper included lead (Pb), iron (Fe), copper (Cu), and mercury (Hg).

Reference

Costantini, I.; Castro, K.; Rodriguez-Laso, M.D.; Madariaga, J.M.; Arana, G., 2021. *Non-destructive analytical investigation of decorative wallpapers samples of the nineteenth century before their restoration*. Sensors **21**, 4416. https://doi.org/10.3390/s21134416

2.3. Rainbow treasures: multi-analytical characterization of Ronan Superfine Japan Colors

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An investigation into the primary palette used by Alexander Calder in painting the large outdoor sculpture Man-Eater with Pennants (1945) shined the spotlight on a near-complete trove of Ronan Superfine Japan Color paints in the reference collection of The David Booth Conservation Center at The Museum of Modern Art (MoMA). The group of paints in the reference collection was purchased in 1984. Historically, Calder favored matte finishes for his outdoor sculptures, as was certainly the case with Man-Eater with Pennants, especially those produced by T. J. Ronan Co. In an undated note in MoMA's object records, Calder specifies his preference for Ronan's "Coach Colors (in Japan Drier)" for repainting the sculpture, in particular the primary colors of "Sign Writers Red, Ult. Blue, and Chrome Yel." Japan Superfine Color paints were first manufactured in New York by The Egan-Ronan-Hausman Co. at the turn of the 20th century. Later, Thomas J. Ronan ventured out to form his own T. J. Ronan Co. in 1920 and continued to manufacture a line of Japan colors. These paints yield a matte surface due to a heavy pigment load and result in saturated, rich colors; the pigments are ground in Japan, which gives them their name.

The paints were confirmed as oil-alkyd enamels using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), whereas pigments and characteristic fillers were identified by a combination of ATR-FTIR, Raman spectroscopy, and portable X-ray fluorescence spectroscopy (p-XRF). The presence of calcium carbonate, identified definitively by ATR-FTIR and Raman spectroscopy, and a strontium filler, identified by p-XRF, proved characteristic for this selection of paints and could aid with future dating and identification. This is importantly the case for the "Signcraft Red" paint, which has been cited over the years as Calder's choice of red and is a cause of great debate; here, it was identified as the organic β-naphthol pigment PR4. Moreover, the presence of trace amounts of lead in many of the paints analyzed raises the importance of safety precautions when treating works where Ronan colors were used.

2.4. Investigation of unknown substances from entomology collections using ATR-FTIR spectroscopy

Clare Kim*

Collection Care & Conservation, Australian Museum Research Institute, Australian Museum, Sydney NSW, AU

The study of unknown substances found within the Australian Museum entomology collection has been investigated by the use of Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy. The entomology collection currently consists of over 1.8 million specimens, which includes 5,035 primary types and 17,362 secondary types, with the oldest registered specimen dated 1850. The majority of the specimens are housed in shallow glass-lidded wooden cabinet drawers. Drawers in the older cabinets commonly have cork-lined bases and often include fumigants such as naphthalene.

The investigation involved visual examination, microscopic examination, photographic documentation, and sampling, followed by ATR-FTIR analysis. ATR-FTIR spectroscopy is a useful analytical tool for identifying unknown substances, both organic and inorganic. Knowing the substances associated with specimens is a crucial step in determining the best preservation and treatment options. Both ATR and reflectance spectroscopic techniques were explored initially. Due to the tiny sizes of the substances, it was challenging to obtain spectra in-situ. The ATR technique proved to be more effective because small samples can be clamped in direct contact with the crystal window, resulting in better spectral data.

Over 150 samples have been obtained, analysed, and databased. This includes unknown substances that had formed on specimens and their enclosed collection drawers, as well as old adhesives and housing materials found within various Entomology collection stores. Results indicate the presence of fatty acids, phthalic acid, verdigris, fungal growths, naphthalene, and a diverse range of adhesives and housing materials, including cellulose acetate.

Challenges include: (a) obtaining adequate sample sizes, (b) interpretation of spectra from heterogeneous multicomponent samples, (c) having limited reference spectra provided by commercial libraries and databases, and (d) limited previous research and a general lack of information on this topic. While the research project is still in an early stage, the results have already yielded positive outcomes for the conservation and care of the insects in the entomology collections.

Keywords: ATR-FTIR spectroscopy, entomology collections, materials conservation, natural sciences conservation

2.5. Application of handheld Raman spectroscopy for pigment identification of a large Buddhist painting in Janggoksa Temple, South Korea

Na Ra Lee*, Young Mi Yoo, So Jin Kim

Conservation Science Division, National Research Institute of Cultural Heritage, Daejeon 34122, KR

A *gwaebul* is a large Buddhist painting of the Sakyamuni Buddha in the form of a hanging scroll that is used during special Buddhist ceremonies. These large paintings are colored with pigments on base materials, such as fabric or paper [Lee, 2004]. An in-situ analysis was carried out using p-XRF and handheld-Raman spectroscopy to identify the pigments of a South Korean national treasure known as the "Hanging Painting of Janggoksa Temple (Maitreya Buddha)" (Figure 1).

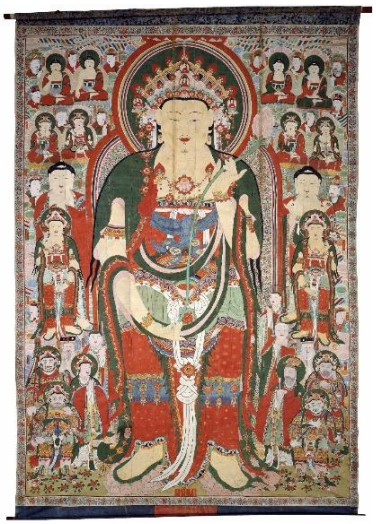

Figure 1: Hanging Painting of Janggoksa Temple (Maitreya Buddha); South Korea, 1673, 599 cm x 869 cm

In the past, the pigments of large Buddhist paintings were identified by elemental analysis using a p-XRF in the field and an XRD analysis in the laboratory based on a small amount of collected samples. However, there are detectable limitations to using a p-XRF when analyzing colored pigments composed of light elements or organic compounds. In addition, a precise analysis of inorganic pigments is possible through an XRD. However, there are restrictions on the size of the sample collection and the representation of the samples. Therefore, handheld-Raman spectroscopy, which enables non-destructive and portable analysis in-situ, minimizes sample collection and complements the limitations of p-XRF.

The results of our analysis identified various coloring materials: inorganic pigment, such as white lead, minium, cinnabar, and orpiment, as well as organic pigment, such as gamboge and indigo. Therefore, it is possible to obtain more information for the identification of pigments while at the same time minimizing the collection sample and simplifying the analysis procedure compared to previously used methods.

Acknowledgement

This study was supported by the Cultural Heritage Research and Development (R&D) project of the National Research Institute of Cultural Heritage of the Cultural Heritage Administration (Daejeon, South Korea).

Reference

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2.6. Infrared spectrum identification of liquor residues in ancient China

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[2]Key Laboratory of Vertebrate Evolution and Human Origins, Institute of Vertebrate Paleontology and Paleoanthropology, Center for Excellence in Life and Paleoenvironment, Chinese Academy of Sciences, Beijing 100044, CN
[3]University of Chinese Academy of Sciences, 100049, CN

The technological analysis of liquor residue is of great significance to archaeology. At present, the main scientific and technological analysis method of liquor residues is the detection of biomarkers. The detection of polyphenols, organic acids and other substances in samples by HPLC-MS is difficult to operate, and the detection period is relatively large. Compared with HPLC-MS, infrared spectroscopy has the characteristics of simple operation, fast detection and non-invasive to the samples, which is very suitable for the preliminary identification and analysis of liquor residues at the archaeological site, and the results can also be verified with other detection methods.

In this study, the Fisher discriminant method was used to classify the infrared data of modern samples obtained and to try to identify the artificial aging samples and the liquor residues excavated from the ancient Chinese cemetery. The results showed that the infrared spectrum combined with the Fisher discriminant could effectively identify the species of the residues with a relatively shallow aging degree. The liquid samples from three ancient Chinese archaeological excavations are highly likely to be beer.

Key words: Liquor residues; Infrared spectrum; Fisher discriminant method

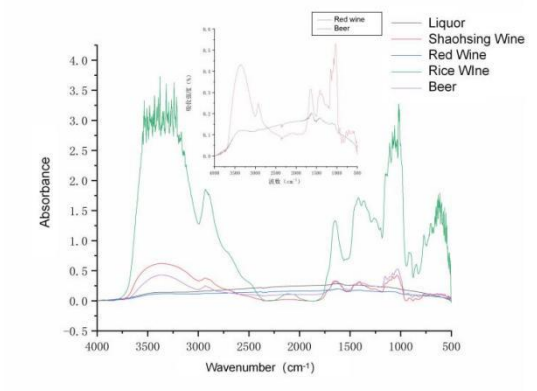

Figure 1: Infrared spectrum of five standard reference sample

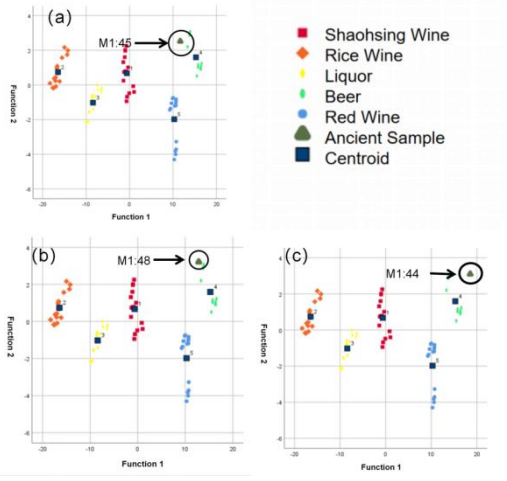

Figure 2: Scatter diagram of ancient residue samples classification results

2.7. Assessing the Effects of a fire protocol on wall painting mock-ups

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Fires pose a significant threat to artifacts, including wall paintings, causing damage ranging from surface deposits to total collapse. The severity of the damage depends on factors such as the duration of exposure to the fire and the temperature it reaches. This study aims to investigate whether it is possible to detect the presence of organic binders in the paint layers of wall paintings based on the maximum temperature reached during a fire. Identifying organic binders is crucial for accurately determining the painting technique used, as the presence or absence of organics is a key factor in this analysis. Without this information, characterizing a wall painting that has undergone a fire may lead to incorrect conclusions about the presence of organic binders. By exploring the detectability of organic binders, this study sheds light on a crucial aspect of wall painting criteria of technique identification.

To investigate the effects of fire on wall paintings, mock-ups were prepared using traditional recipes for *fresco* and *secco* techniques. The painting layer of the secco mock-ups was composed of egg yolk, linseed oil, gum Arabic, and casein binders with yellow ochre. The mock-ups were then subjected to a fire protocol designed to simulate temperatures and durations typical of compartment fires [Hajpál and Török, 2004; Hajpál, 2010]; the mock-ups were heated from room temperature to a maximum temperature (T_{max}) within 60 minutes, held at T_{max}, for 6 hours, and then cooled down in the oven. The mock-ups were analyzed using several techniques, including Fourier transform infrared spectroscopy (FTIR), micro-FTIR imaging, DRIFT spectroscopy with a climatic chamber, X-ray diffraction (XRD), thermogravimetry (TGA), UV-Vis spectrophotometry, and X-ray photoelectron spectroscopy (XPS).

Under the applied fire protocol, the upper temperature limit for maintaining the integrity of plaster and -consequently- is between 400-500 °C. Beyond this threshold, mock-ups start to exhibit severe splitting before collapsing completely. The pigment's analysis shows that yellow ochre can serve as a marker for identifying T_{max} during a fire, as FeOOH transforms to Fe_2O_3 at about 250-300 °C. FTIR results demonstrate that the presence of organic binders can be detected up to a T_{max} of ~350 °C. XPS analysis reveals the presence of phosphates in the painting layer containing egg yolk. Phosphates were also detected in the painting layers containing casein and linseed oil, but only after annealing at a T_{max} of 700 °C. These findings suggest that a wall painting that has survived a fire could provide valuable information about the painting technique and applied binder.

Acknowledgments

All measurements were conducted in the facilities of the Laboratory of Advanced Materials and Devices (AMDE Lab), School of Physics, Aristotle University of Thessaloniki, Greece; the corresponding author acknowledges all its members. Part of this work was supported during the Ph.D. research of the corresponding author by the General Secretariat for Research and Technology (GSRT) and the Hellenic Foundation for Research and Innovation (HFRI) (Fellowship Number: 22).

References

M. Hajpál, Á. Török, 2004. Mineralogical and colour changes of quartz sandstones by heat, in: Environ. Geol., Springer: pp. 311–322. https://doi.org/10.1007/s00254-004-1034-z.

M. Hajpál, 2010. Fire Damaged Stone Structures in Historical Monuments . Laboratory Analyses of Changes in Natural Stones by Heat Effect, in: 18th CIB World Build. Congr., CIB General Secretariat, Rotterdam: pp. 164–173.

2.8. An analysis of lacquer layers adhering to excavated potteries using a FT-IR spectroscopy

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In Japan, it is considered that the culture of using lacquer developed about 7,200 years ago [Kudo, 2021]. Pottery coated with lacquer or adhering lacquer has been excavated from a wide range of eras in Japan. The use of lacquer on pottery is manifold, including lacquer ornaments, lacquer storage containers, and pallets. However, the pottery excavated from ancient sites is degraded and has delaminated lacquer layers. We research the causes of delamination and appropriate conservation methods.

In this study, we analyzed the delaminated lacquer layers using a FT-IR spectroscopy. We used lacquer samples from Sue ware (unglazed stoneware) and Haji ware (low fired brown pottery) excavated from the site.

We analyzed lacquer samples using photoacoustic spectroscopy (PAS), attenuated total reflection measurement (ATR), and FT-IR micro-spectroscopy. We also obtained the PAS spectra shown as an example below (Figure 3 from (a) to (g)). Spectrum (a) is a modern lacquer. Spectra (b) to (e) show adhered lacquer on Sue wares. Spectra (f) and (g) show adhered lacquers on a Haji ware. Spectra (b), (d), and (e) were measured on the surface in contact with the pottery. Spectra (c), (f), and (g) were for the surfaces that were not in contact with the pottery. Additionally, we analyzed three different locations on each lacquer sample; they were not different from each other. We thought they showed a similar trend. We confirmed that soil was affected samples, but we were not able to see significant differences between the surfaces in contact with the earthenware and those that are not. However, since the number of analyses is small, we will need to continue accumulating data.

Figure 1: Sue ware No.1 (Spectrum (b),(c)).

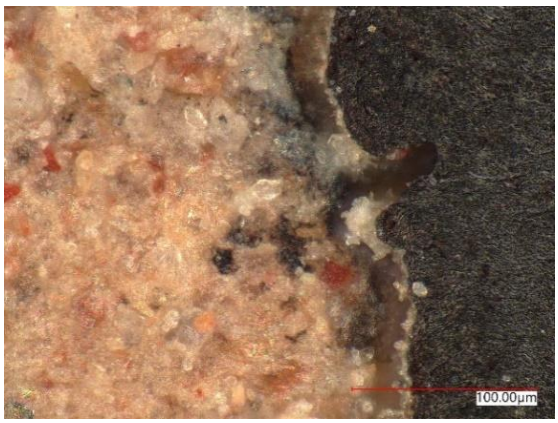

Figure 2: Haji ware No.1 (Spectrum (f),(g)).

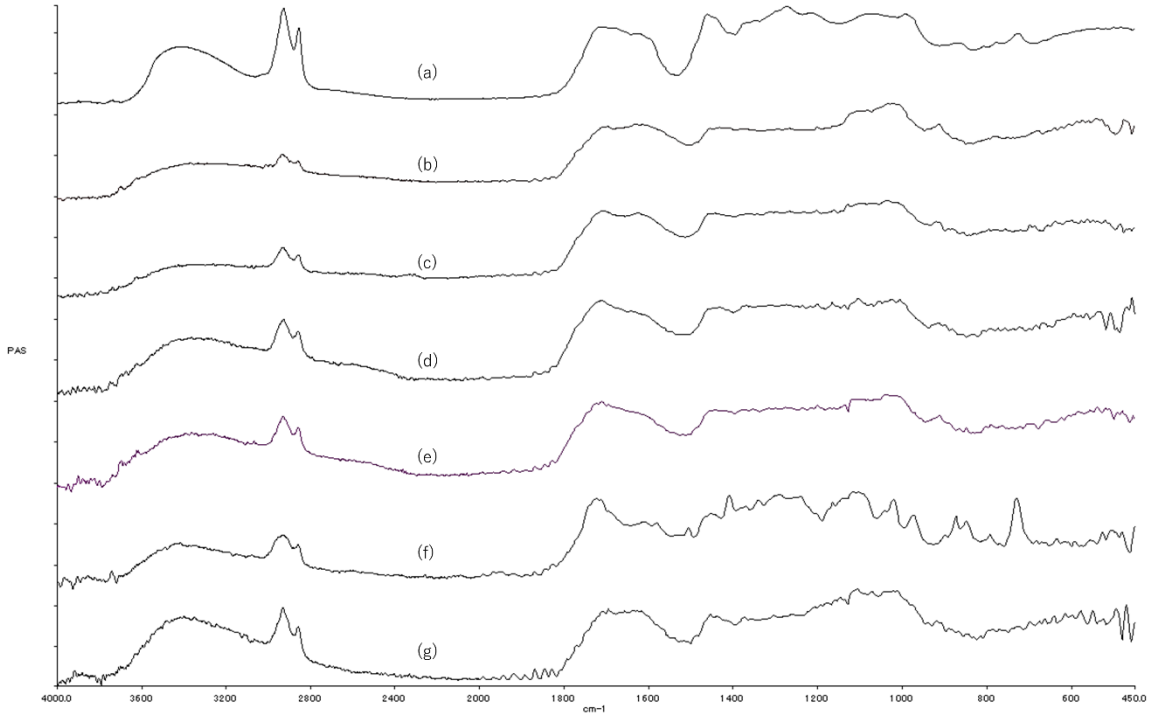

Figure 3: Results of PAS
(a) modern lacquer
(b) Sue ware №1 [measurement not in contact with pottery]
(c) Sue ware No.1 [measurement in contact with pottery]
(d) Sue ware №2 [measurement in contact with pottery]
(e) Sue ware No.2 [Measurement in contact with pottery]
(f) Haji ware №1 [measurement not in contact with pottery]
(g) Haji ware No.1 [measurement in contact with pottery]

Reference

Y. Kudo, 2021. Bulletin of the National Museum of Japanese History225

Acknowledgment: This work was supported by Yura Yamato Ancient Culture Research Association Research Grant Program

2.9. Research on textile materials in the Kofun period (4th century to the middle of the 6th century) in Japan - a study of cultural properties using FT-IR photoacoustic spectroscopy

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[2]Fukushima Prefectural Culture Foundation, Fukushima Cultural Property Centre,Shirakawa Branch, JP

It is already known that infrared spectroscopy is one of the most useful methods for the identification of cultural properties, especially for organic materials. However, usual analytical procedures, such as transmission (TR) or attenuated total reflection measurement (ATR), requires preliminary treatment of sampling and sometimes damages valuable samples by mixing or pressing. Contrary to this, photoacoustic spectroscopy (PAS) [Okuyama and Sato, 2015] uses totally non-destructive procedures. To clarify the advantage of PAS compared with other procedures, some kinds of objects (textiles, pigments and others) were investigated in this study using PAS, TR or ATR.

In this research, we show results of analyzed an ancient textile excavated from a tomb in Japan. It was excavated from Shimanoyama tomb (end of 4th century - the beginning of 5th century, located in Nara Prefecture) together with a bronze mirror (Figures 1 - 4). We analyzed it using PAS (Figure 5). As a result, we confirmed that the textile was made from plant fibers and contained copper corrosion and soil. We could see the material of excavated textiles using the non-destructive method. We are further continuing the PAS study using various kinds of cultural properties.

Figure 1: Map of Japan, Nara prefecture

Figure 2: Map of Nara prefecture and Shimanoyama tomb

Figure 3: bronze mirror excavated from Shimanoyama tomb (diameter ≈14cm)

Figure 4: sample for PAS measurement – a part of textile attached to the mirror excavated from Shimanoyama tomb.

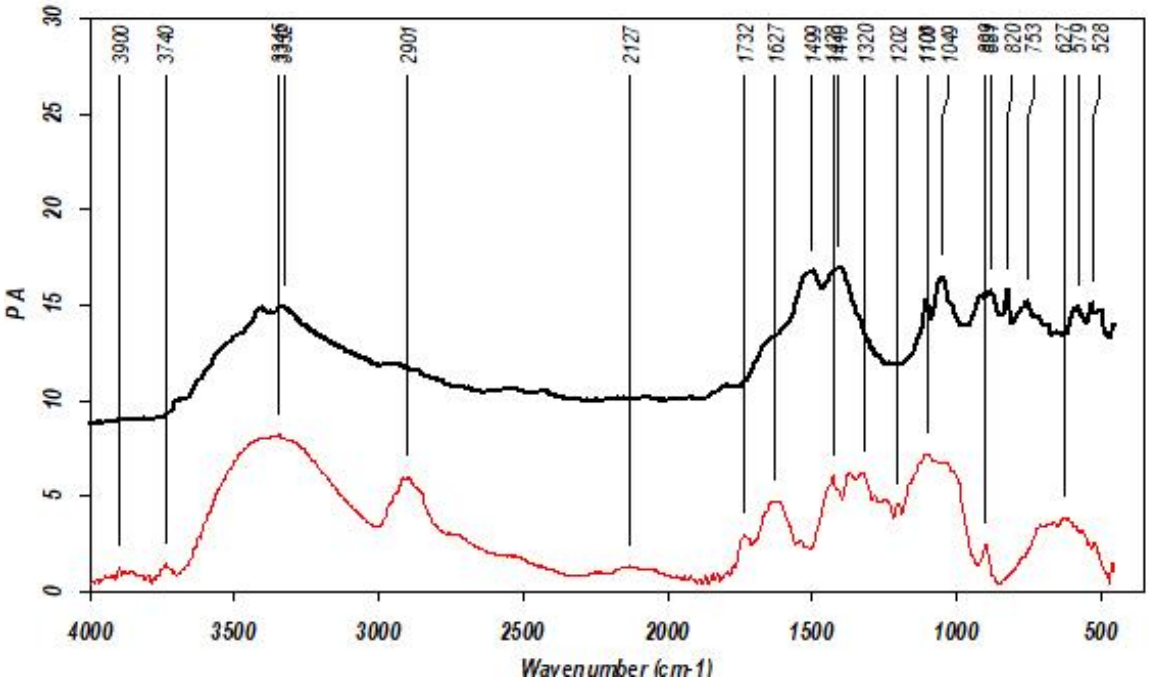

Figure 5: Result of PAS. Top: excavated sample, bottom: modern Ramie

Reference

M. Okuyama, M. Sato, 2015. SEN'I GAKKAISHI **71**(1), 6

Acknowledgment: This work was supported by JSPS KAKENHI Grant Number 17H02023

2.10. Prediction model for paper degradation using FT-IR spectra and its explainability

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In order to construct a model for predicting cellulose degree of polymerization (*DPv*) of paper using ATR-FTIR spectra, manuscript paper and other papers distributed in Japan since the 1950s were prepared without limitation of fiber type, sizing agent, or filler type. In addition, samples simulating manuscript paper of that era were newly made from NBKP and LBKP in an acidic environment. These samples were subjected to accelerated degradation tests, and samples with different *DPv* were prepared depending on the degradation period. Spectra were measured by ATR-FT-IR (single reflection diamond crystal) with Bruker ALPHA, wavenumber range 4000~400cm^{-1}, wavenumber resolution 4 cm^{-1}, integration frequency 24 times (some 100 times), and 330 spectral data sets were prepared. The measured reflection spectra were converted to absorbance, second differentiated by the Savitzky-Golay method, and vector normalized so that the Euclidean norm of each spectrum was 1. The regression model was constructed by [LightGBM], one of the gradient boosting methods, using 1472 features (left side of Figure 1). The prediction accuracy is not bad, but it is questionable why it is possible to predict molecular weight from the vibrational pattern of the molecular structure. The right side of Figure 1 shows the results of a model in which Lorentzian Curve Fitting was performed on the fingerprint region of cellulose (1500~850 cm^{-1}); 26 major peaks were assigned, and the ratio of these areas was reconstructed as a new feature value. The role of each peak in predicting *DPv* was determined using SHAP (SHapley Additive exPlanations), a global and local evaluation method based on Coalitional Game Theory (Figure 2). The SHAP data revealed that there are two types of peaks, one with an increasing trend with decreasing *DPv* and the other with a decreasing trend. In particular, a decrease in peak area with decreasing *DPv* is observed at the lower wavenumber side of Peak 18 at 1027 cm^{-1}. This region contains C-O stretching vibrations corresponding to the GG and GT conformations of C6-OH, which are closely related to the surface chains of cellulose microfibrils. When air-dried paper pieces were subjected to hydrothermal sonication and dehydration with acetone displacement to inhibit reaggregation of the microfibrils during the drying process, the spectral shape characteristics observed at the *DPv* decrease indicated by SHAP were also observed. In this model, the IR spectra capture the decrease in interaction, mainly hydrogen bonding, on the surface of cellulose microfibrils as the *DPv* decreases (microfibril bundle dissociation).

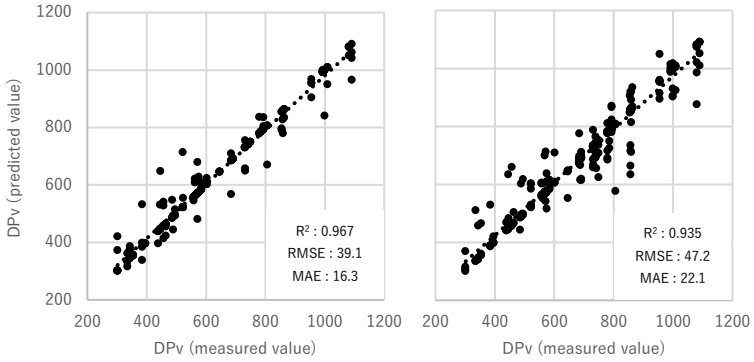

Figure 1: Accuracy of *DPv* Prediction Model
left: with 1472 features, right: with 26 features

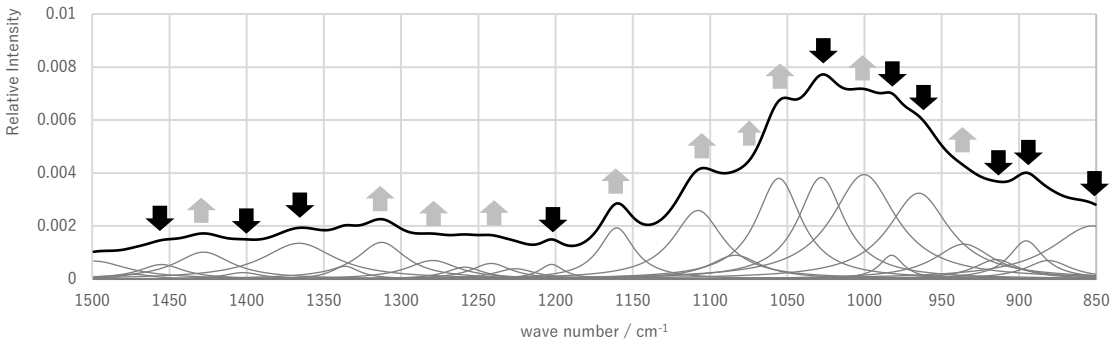

Figure 2: Behavior of the top 20 peaks when *DPv* decreases

2.11. Blurred lines: issues distinguishing between alkyds and oils

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Alkyd paints are oil-modified polyesters manufactured from poly-ols, aromatic polybasic acids (PBAs), and fatty acids or oils. Fourier transform infrared spectroscopy (FTIR) is often used to identify alkyds, although fillers and extenders can obscure the characteristic ester and aromatic peaks. Solvent micro-extraction of the media can remove these interferences, and FTIR is often considered a reasonably reliable means to identify alkyds. Recent work on a collection of studio materials from Hélio Oiticica samples from Edward Kienholz sculptures has called this reliability into question. Comparison of FTIR data with GC/MS data processed using Synthetic ESCAPE revealed that the former method failed to identify some paints as alkyds that were subsequently shown to be alkyds by GC/MS. Synthetic ESCAPE, which creates an overview of oils and alkyds by breaking their main constituents down into four main material categories (oils, polybasic acids, polyols, and pine resin), provides an assessment of relative amounts through the summation of peak areas. While FTIR was able to reliably identify paints as alkyds that contained high amounts of PBAs (<20% as assessed by Synthetic Escape), paints with lower amounts of BPAs were often misidentified by FTIR. Therefore, FTIR analysis alone cannot be considered reliable when distinguishing between these media.

2.12. Preliminary FTIR microscopic analyses coupled with SEM-EDX for the identification of microbes on laboratory made modern paintings from Thailand

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Biodeterioration is the physical or chemical damage caused by biological agents on materials and occurs through the formation of biofilms. An appropriate evaluation of biodeterioration requires a combination of microbiological and materials characterization techniques and knowledge of the substrate. It requires to investigate of elemental analysis of the substrate and the identification of the main types of microorganisms present. The principal aim of this study was to determine microbial activity within 20th century modern paint surfaces in tropical climates. As the first approach, sample collection was conducted in Thailand, and future studies will be expanded further using the metagenomic approach. These paintings were made by laboratory chemists to find the proper formula to make the paints at the Centre for Excellence for Color and Coating at Silpakorn University, Thailand. These works of art were painted with Silpakorn University artist's paints, a known formulation for hot, humid tropical climates. Sample paints with and without biocide also were prepared and analysed. Made by Silpakorn University, Thailand, the biocide content is higher than that of artist's paints formulated in the global north. Consequently, the long-term ageing effects of the biocide content on the Silpakorn artist's paints also were examined.

This poster offers an overview of techniques, and only two are mentioned for materials characterization, such as scanning electron microscopy with energy dispersive X-Ray analysis (SEM-EDX) and micro-Fourier transform infrared spectroscopy (FTIR). The elemental data obtained with SEM-EDX provided information on the paint substrate and its potential susceptibility to biodeterioration. Possible biodeterioration on the paint surface was examined with FTIR-ATR and the amide bonds, while the effects of the biocide on the ageing of the artist’s paint focussed on the carbonyl peaks.

2.13. Curious corrosion at Centre College: chalconatronite, antlerite, and tenorite on bronze sculptures in a rural Kentucky setting

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Centre College is a liberal arts school in a rural area of Kentucky. Samples of corrosion from two bronze sculptures on Centre's campus, Figure 1, were investigated as a preliminary step in planning a conservation intervention and preparing a routine maintenance plan for the artworks. Lincoln, a bronze statue of the former US President commissioned in 2012, sits in front of the library; law books borrowed by a childhood friend enrolled at the school and given to a young Abraham Lincoln were integral to the President's early career as an attorney. The sculpture has quickly become part of student tradition, with pennies placed on his shoe ensuring good grades on exams. The Flame, a stylized triad of flickering flames, evokes the College's motto, Doctrina Lux Mentis (Learning is the Light of the Mind), and the college seal, a lit torch. This 1969 sculpture, too, is an important part of college traditions, both sanctioned and illicit [Urban Dictionary, 2008].

Figure 1: The Flame and Lincoln (left and right respectively) at Centre College in Danville, KY with green corrosion highlighted in the insets

In summer 2022, deep patches of bright green corrosion encircling white nodules of crystalline growth were noted on The Flame. Fearing bronze disease, Raman analysis was undertaken of the white and green crystals to guide further conservation efforts. These components were instead identified as antlerite ($Cu_3(SO_4)(OH)_4$) surrounding gypsum ($CaSO_4{\cdot}2H_20$). In other areas, whitish patches associated with black corrosion were identified as aragonite (ortho. $CaCO_3$) and tenorite (CuO). Both antlerite and tenorite are less common corrosion products for bronze, with the lower

sulfate species brochantite ($Cu_4(SO_4)(OH)_6$) being the more usual copper sulfate outside of polluted urban centers prone to acid rain and cuprite (Cu_2O) forming in preference to tenorite except in certain situations involving heat or high alkalinity [Scott, 2002; Lins and Power, 1994]. Patches of bright green corrosion on Lincoln were observed only in protected areas under his coat tails, with exposed areas of the sculpture in good condition. In this instance, the water-soluble corrosion product chalconatronite ($Na_2(CuCO_3)_2{\cdot}3H_2O$) was identified. It has so far only been observed in a handful of instances related to the reaction of uncleared conservation chemicals formed on copper in proximity to corroding glass or a result of sodium carbonate rich burial soils in archaeological settings [Scott, 2002]. All of the assignments based on vibrational spectroscopy were confirmed by powder x-ray diffraction, which provided further phase information.

The causes of these unusual corrosion products are under investigation. It is hypothesized that plaster investment erupting from the interior of The Flame gives rise to localized high concentrations of sulfate ions on the metal surface, resulting in the unusual formation of antlerite. Tenorite may form as a result of an alkaline environment resulting from the eruption or formation of aragonite; the source of this carbonate is not yet known. Being that Lincoln has never been treated by a conservator, chalconatronite cannot have been formed by the use of sodium sesquicarbonate for treating bronze disease [Scott, 2002], nor can it have formed under any of the other conditions reported in the literature. Rather, we postulate that this first observation of a natural occurrence of chalconatronite on sculptural bronze may be due to local hard water used in routine groundskeeping on the sculpture patio or in its vicinity.

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Scott, DA, 2002. Copper and Bronze in Art: Corrosion, Colorants, Conservation. Los Angeles: Getty Conservation Institute.

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2.14. Manuscript illumination at the court of Emperor Maximilian I (1459-1519): a multianalytical study using ER-FTIR, XRF, and hyperspectral imaging

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This paper discusses the contribution of ER-FTIR (external reflection FTIR) to an interdisciplinary cooperation of researchers from the humanities, computer sciences and natural sciences, aiming to elucidate the conditions of manuscript production at the court of Emperor Maximilian I in the late 15th and early 16th century. Within this cooperation [DiTAH, 2021], the diversity of measurement and descriptive data will be linked and archived in a repository, which will be an available open source for further research and academic teaching.

Fifteen illuminated charters and manuscripts were selected based on stylistic, temporal and local proximity and investigated in ten archives, libraries and museums in Austria and Germany. The manuscripts dated from 1480 to 1515, and additionally, a control group of four more manuscripts from the same period was analysed for comparison. The analyses included microscopic observation, ER-FTIR, XRF (X-ray fluorescence), and HSI (hyperspectral imaging). The selection of single measurement points was limited by the dimensions of the utilized spectrometer and the surface properties (uneven or rough surfaces) of the manuscripts in the case of ER-FTIR, whereas XRF was limited by the fact that also materials from the backside may contribute to the detected signal. In most of the cases, XRF and HSI data were already available when ER-FTIR was performed, which simplified the evaluation of the reflection spectra. On the other hand, ER-FTIR contributed significantly to a deeper interpretation of the XRF and HIS datasets. The objects were analysed in a horizontal position by using a tetrapod, except in the case of a sensitive book where a tripod was used to prevent damage (Figure 1).

Figure 1: ER-FTIR analysis of manuscripts by using either a tripod or a tetrapod

The ER-FTIR spectra obtained were evaluated after Kramers-Kronig transform and baseline correction by using the IRUG Database. In the case of lead-tin yellow, a mockup of the pigment on parchment

was applied as a reference for a reliable identification, as characteristic bands lie outside the spectral range of the IRUG reference below 600 cm^{-1} (Figure 2).

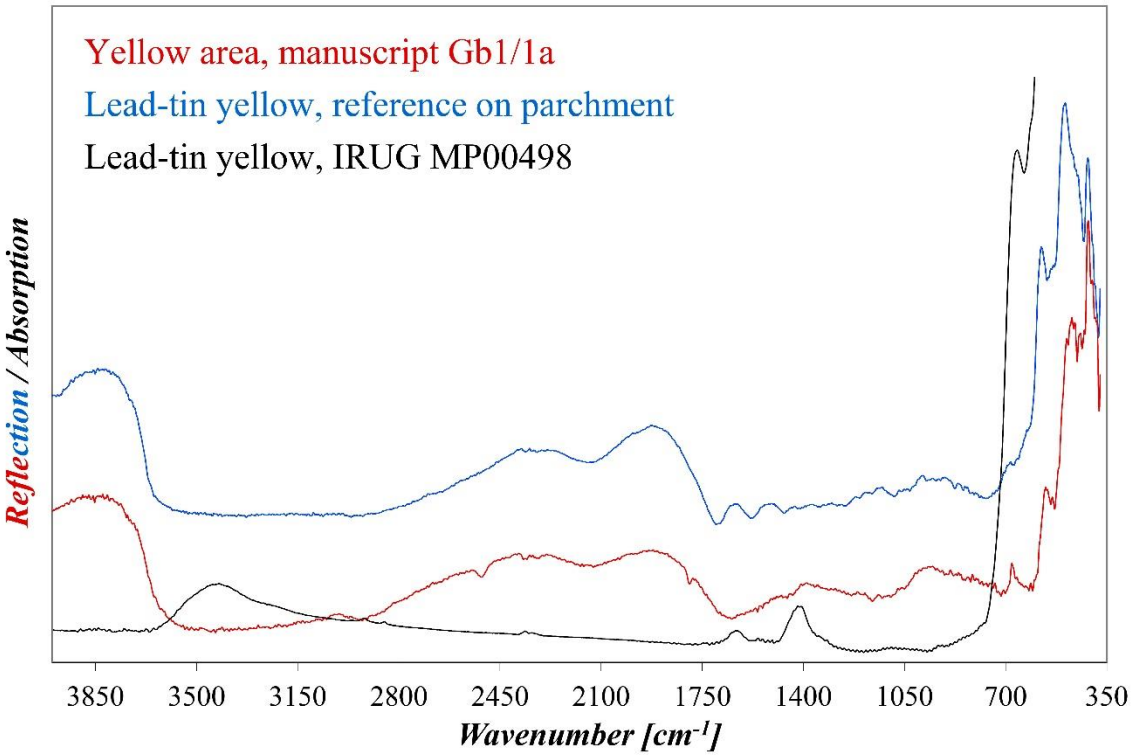

Figure 2: ER-FTIR spectrum obtained from a yellow area (red line) in comparison to a lead-tin yellow reference on parchment (blue line) and IRUG lead-tin yellow reference IMP00498 (black line)

The results showed that ER-FTIR enabled to detect a set of inorganic pigments and fillers (lead white, azurite, brochantite, malachite, lead-tin yellow, kaolinite, chalk, and gypsum), whereas indigo was the only organic pigment detected. The XRF and HSI results suggested the presence of red and violet lake pigments on most of the objects. However, the corresponding ER-FTIR spectra generally did not show features usable for an identification.

ER-FTIR further helped to characterize the parchments and brown/black inks used for the manuscripts. The parchments contain, e.g., chalk resulting from manufacturing processes utilizing lime or from whitening with chalk powder, whereas various contents of calcium oxalates indicate oxidative degradation of the inks. Moreover, the spectra of inks of two different manuscripts showed similar triplets (1140, 1123, and 1094 cm^{-1}), which could not be attributed to a specific compound. Therefore, it remains unclear, whether there is a closer relationship between the inks or the similarity results, e.g., from conservation-restoration treatments.

Small quantities of Prussian blue were detected by ER-FTIR in a grey colour on one manuscript. The pigment has been available to art since 1724, and hence, this result indicates most probably a retouching carried out after this date.

Based on the ER-FTIR data and under consideration of XRF and HSI results, a cluster was identified, including six manuscripts showing high chemical similarity. In particular, the combined utilization of brochantite, led-tin yellow, azurite, lead white, and brown iron oxide pigments containing kaolinite

led to this classification. Furthermore, red lake pigments and vermilion (detected by XRF and HSI) were additionally used for the illuminations.

We conclude that ER-FTIR, in combination with element specific XRF and HIS, is a useful tool for the classification of cultural heritage objects, particularly illuminated manuscripts. The results of the study are currently being discussed within the interdisciplinary cooperation and provide an additional basis for further historical and stylistic research [Hofer, 2023].

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Digital Transformation of Austrian Humanities (DiTAH) 2021 – a research project funded by the Federal Ministry of Education, Science and Research in Austria.
https://www.ditah.at/projects/m3r.html accessed 26/09/2023

Katharina M. Hofer, 2023. These Investigations will be part of a dissertation in humanities written by Katharina M. Hofer. The results will shed light on the court of the Emperor Maximilian I from a different perspective. Existing research results in the humanities and cultural studies will be reviewed, confirmed or modified and extended by the results of the material analyses.

2.15. FTIR as a necessary method to estimate the combustion atmosphere of ancient cremated human bones: A case of cremation burials in the Baekje period, Korea

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Cremation is historically one of the most common funeral cultures in ancient civilizations. In Korea, the earliest evidence of cremation is the burned bones found at an archaeological site from the Neolithic period. The cremation custom was prevalent throughout the Three Kingdoms period (B.C. 1st~7th century).

The only way to investigate ancient cremation culture is to analyze the remains of cremated bones since many organic substances have been incinerated. The color, deformation, and cracking of the cremated bones can provide significant scientific evidence to estimate the cremation atmosphere at the time, as they vary depending on the treatment of the bones. Analytical methods, such as Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), are very useful when estimating combustion temperatures by measuring the bonding and crystal structure of the molecules in the bone minerals. In particular, FTIR is a powerful tool for obtaining more in-depth evidence on the combustion environment, including the burning time, oxygen conditions, the fuel of the pyre, and the presence of fleshed bones or not before burning (secondary funeral).

We present the results of our estimation of the cremation temperature and oxygen conditions of human bones excavated from a royal tomb from the Hanseong Baekje Period (18 B.C.–475 A.D.). We applied various techniques based on XRD and FTIR (destructive and non-destructive for XRD, ATR and transmission for FTIR). In addition, we introduce briefly the analytical protocols and precautions of sample selection used to analyze the excavated bones using FTIR and XRD. All the analysis results attempted in various analytical modes clearly show that the cremated bones of the Beakje period were combusted at 700 to 1,000 ℃ under closed reduction conditions. This temperature range suggests the presence of separate facilities in Baekje for raising the temperature and controlling oxygen. We can also assume that there were people with professional cremation skills at that time. This research provides clues about Korea's ancient cremation culture.

Acknowledgments

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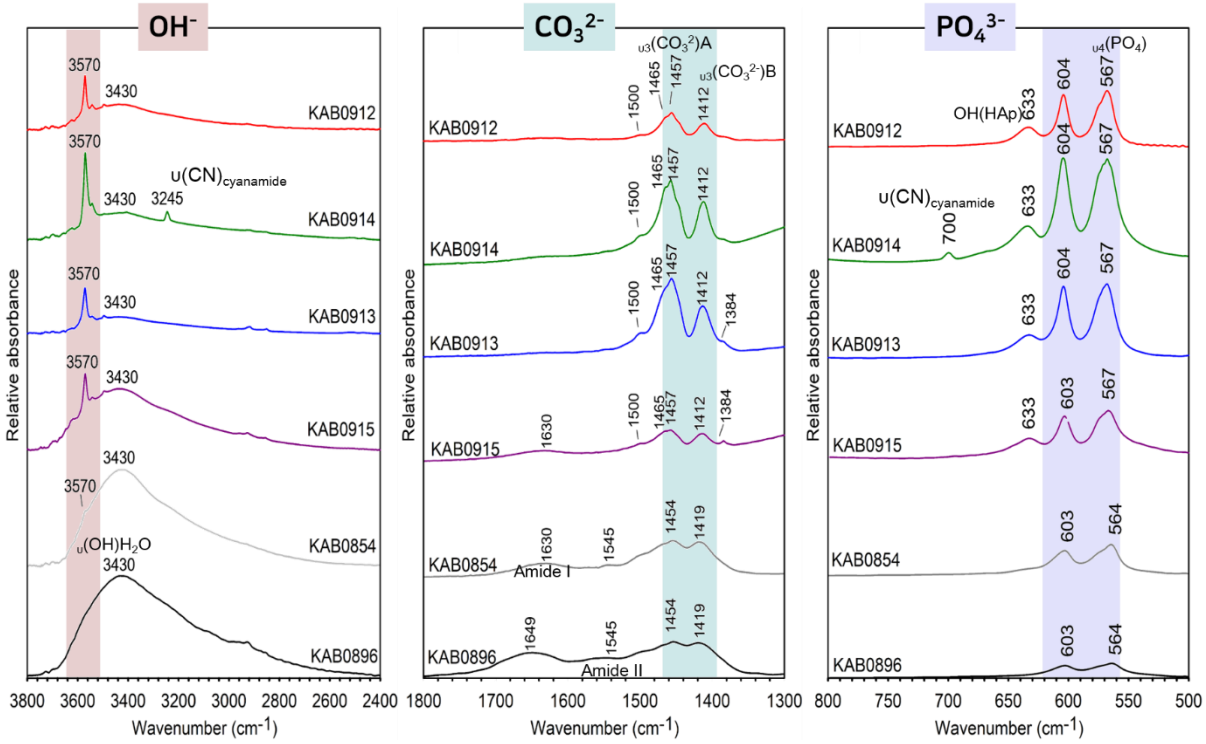

Figure 1: Infrared spectrum of ancient human bones

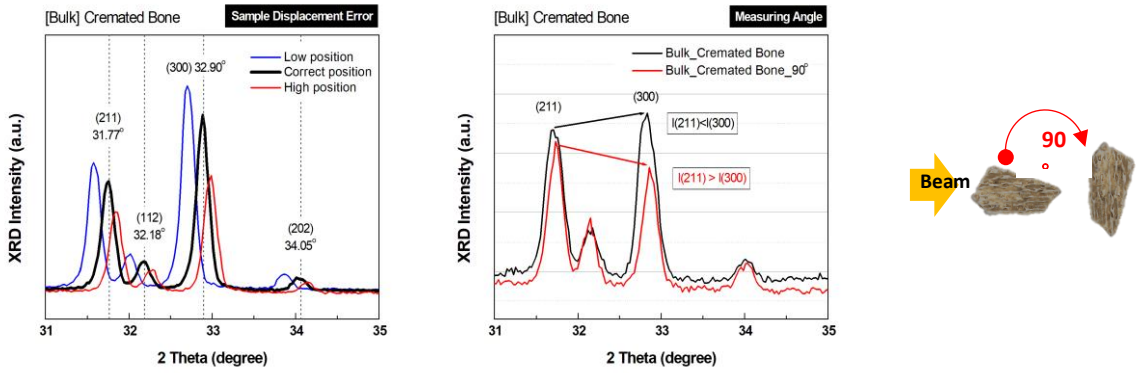

Figure 2: XRD pattern of ancient human bones

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	Joan M. Walker	National Gallery of Art, Washington DC, US	jm-walker@nga.gov	Presenter
	Chiung-Hsia Wang	National Taiwan Normal University, TW	besttime0713@gmail.com	Delegate
	Kazuki Watanabe	ST Japan	watanabe@stjapan.co.jp	Sponsor
	Julia Weber	Conservation Science Laboratory, Tokyo University of the Arts (Geidai), JP		Local organiser
Dr	Le Wei	The Palace Museum, Beijing, CN	lelewendy@gmail.com	Presenter
	Lee Wen-Hsuan	National Taiwan Normal University, TW		Delegate
	Kana Yamabe	ST Japan		Sponsor
	Asuka Yamato	Tokyo National Research Institute for Cultural Properties (Tobunken), JP		Local organiser
Prof	Lijiang Yang††	Peking University, Beijing, CN	yanglj@pku.edu.cn	Presenter
	Norio Yasuda	ST Japan		Sponsor
Dr	Tai-Sheng Yeh	Meiho University, TW	x00010091@meiho.edu.tw	Presenter
	Pan Yi-ling	Research Centre for Conservation of Cultural Relics, National Taiwan Normal University, TW	b8921009@gmail.com	Delegate
Dt	Jia Yu	National Research Institute of Cultural Heritage, Daejeon, KR	yujia@korea.kr	Presenter
Ms	Kaoru Yui	Kyoto Costume Institute, Kyoto, JP	yui@kci.or.jp;kyui.kci@gmail.com	Delegate
	Mingrui Zhang	Zhengzhou University, Heman Province, CN		Presenter

†Title, where given ‡ with permission †† not physically present