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IRUG 13

5-7 December, Sydney, Australia

25 Years Supporting Cultural Heritage Science

This conference is proudly funded by the NSW Government in association with ThermoFisher Scientific; Renishaw PLC; Sydney Analytical Vibrational Spectroscopy Core Research Facility, The University of Sydney; Agilent Technologies Australia Pty Ltd; Bruker Pty Ltd, Perkin Elmer Life and Analytical Sciences; and the John Morris Group.

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PROGRAM

(Presenting author only; see abstracts for full author listing)

All presentations will be held at the Art Gallery of NSW in the Domain Theatre, Lower Level 3.

Morning, afternoon tea & lunches with poster sessions and trade displays will be held in Function Space, Ground Level.

Day 1 – Wednesday 5 December 2018

8:30-9:30 **Registration & poster installation**

9:30-9:40 **Welcome to country**
Uncle Chicka Madden, Elder from Gadigal Country

9:40-9:50 **Welcome to Art Gallery of NSW**
Dr Michael Brand, Director of Art Gallery of NSW

9:50-10:00 **IRUG welcome**
Dr Marcello Picollo, IRUG region chair

10:00-10:40 **Keynote speaker**
Dale Harding, artist: in conversation with Anneke Jaspers

10:40-11:10 **Morning tea & poster display**
Sponsored by Sydney Analytical Vibrational Spectroscopy Core Research Facility, The University of Sydney

11:10-12:45 **Session I**

Non-destructive characterisation of Aboriginal Australian mineral pigments by near-IR HyLogger™ colour and mineral analysis
Rachel Popelka-Filcoff, College of Science & Engineering, Flinders University, Australia

The identification of blue pigments on artefacts in the Sydney University Museums collections
Elizabeth Carter, Sydney Analytical Vibrational Spectroscopy Facility, University of Sydney, Australia

New insights into the material culture of the American Southwest
Christina Bisulca, Detroit Institute of Arts, USA

The application of FTIR microspectroscopy to the study and conservation of excavated textiles
Christina Margariti, Centre for Textile Research, Denmark

Analysis of textile fibres using ATR-FT-IR spectroscopy, reflectance IR spectroscopy and chemometric methods
Pilleriin Peets, University of Tartu, Estonia

12:50-13:50 **Lunch**
Sponsored by Renishaw PLC

13:50-14:20 **Session II- Quick poster presentations**

Neutron techniques for heritage materials
Floriana Salvemini, Australian Institute of Neutron Scattering, Australian Nuclear Science and Technology Organisation, Australia

Optimising an FTIR analysis methodology for identifying polymers in cultural heritage collections
Julianne Bell, Grimwade Centre for Cultural Materials Conservation, University of Melbourne, Australia

An FTIR survey of contemporary pre-primed artist canvases
Gillian Osmond, Queensland Art Gallery|Gallery of Modern Art

Investigating Chinese tradeware ceramics from Angkor with FTIR spectroscopy
Lorraine Leung, Department of Archaeology, University of Sydney, Australia

Spectroscopic analysis of pigments from the coffin of the 2500-year-old Egyptian mummy Mer-Neith-it-es for digital recolouration
James Fraser, The Nicholson Museum, University of Sydney

14:20-15:20 **Session III**

IRUG Spectral Database: Spectral Search Feature & Tutorial
Beth Price, Philadelphia Museum of Art, USA; Suzanne Lomax, National Gallery of Art, Washington, USA; Jeff Levi, DLS Solutions, Inc., USA

Characterizing the physical and chemical alterations in Asian lacquer films
Herant Khanjian, Getty Conservation Institute, USA

Analysis of naturally- and artificially- aged paper using variable angle ATR infrared spectroscopy
Karin van der Pal, School of Molecular and Life Sciences, Curtin University, Australia

15:20-15:50 **Afternoon tea & poster display**
Sponsored by Bruker Pty Ltd

15:50-16:50 Session IV

ALD coatings to protect metal art objects from atmospheric corrosion
Rita Wiesinger, Institute of Science & Technology in Art, Academy of Fine Arts, Austria

Terahertz spectroscopy applied to pigment identification
Andrew Squires, Institute for Superconducting and Electronic Materials and School of Physics, University of Wollongong, Australia

Reassessing reference materials: surprises encountered when building a spectral library
Gregory Smith, Indianapolis Museum of Art at Newfields, USA

17:00-18:30 **Welcoming drinks**
Sponsored by ThermoFisher Scientific
(Art After Hours continues to 22:00)

Day 2 – Thursday 6 December 2018

9:30-10:10 Keynote speaker
Materials and techniques of traditional Aboriginal bark paintings
Narayan Khandekar, Straus Center for Conservation, Harvard University

10:10-10:50 Session V

Project plastics: How to identify plastics without a lab
Suzan de Groot, Cultural Heritage Agency of the Netherlands (RCE), The Netherlands

Assessment of chemical ageing of cellulose acetate
Sue Gatenby, Museum of Applied Arts and Sciences, Australia

10:50-11.30 Morning tea

11.30-12:15 Session VI

Application and advantages of external reflection in the material determination of photographic materials, negatives and film for a fast material testing via FTIR spectroscopy
Thorsten Allscher, Institute for Conservation and Restoration, Bayerische Staatsbibliothek, Munich, Germany

A spectroscopic investigation of Paraloid blends for use as archaeological adhesives
Barbara Stuart, Centre for Forensic Science, University of Technology Sydney, Australia

12:15-13:00 Lunch
Function space, Ground Level

13:00-17:00 Excursions
Derivan Paint factory, Rhodes
ANSTO, Lucas Heights
iCinema, University of NSW, Randwick
Sydney Observatory, The Rocks

18:00-21:00 Conference dinner
Athol Hall, Mosman

Day 3 – Friday 7 December 2018

9:30-10:50 Session VII

A case study: two newly discovered Jackson Pollock paintings?
John Knowles, MicroVisionLabs Inc, USA

Macro-X-ray fluorescence in combination with micro-Raman spectroscopy in the battle against forged paintings: a powerful synergy
Steven Saverwyns, Royal Institute for Cultural Heritage, Belgium

Handheld FTIR spectroscopy for non-invasive screening and identification of varnishes in painting collections. A pilot study on six works by Edvard Munch
Thierry Ford, The National Museum of Art, Norway

Raman Spectroscopy and Laser Desorption Ionization Mass Spectrometry (LDI-MS) as complementary editors of structures of historical and novel azo-pigments
Suzanne Lomax, National Gallery of Art, USA

10:50-11:30 Morning tea & Trade exhibition
Sponsored by Agilent Technologies Australia Pty Ltd

11.30-13:00 Session VIII

Study of metal soaps protrusions in Georgia O'Keeffe oil paintings by FESEM-EDX and FTIR spectroscopy
Annette Ortiz Miranda, Center for Scientific Studies in the Arts, Northwestern University, USA

Investigation into the behaviour of hydrogenated castor oil in modern oil paints
Kim Vernon, Grimwade Centre for Cultural Materials Conservation, University of Melbourne, Australia

Surface analyses for conservation
David Thickett, English Heritage, UK

A spectroscopic look at Indian yellow pigment and related compounds
Gregory Smith, Indianapolis Museum of Art at Newfields, USA

13:00-14:10 Lunch & trade exhibition

14:10-15:30 Session IX

Characterisation of contents from the coffin of the 2500-year-old Egyptian mummy Mer-Neith-it-es
Therese Harrison, Sydney Analytical Vibrational Spectroscopy Facility, University of Sydney, Australia

Identification and characterisation of faience beads from the coffin of the 26th dynasty Egyptian mummy Mer-Neith-it-es
Michelle Wood, Sydney Analytical Vibrational Spectroscopy Facility, University of Sydney, Australia

Infrared chemical imaging of degradation products in cross-sections from paintings and painted objects
Eric Henderson, Canadian Conservation Institute, Canada

Infrared microspectroscopy of cultural heritage materials at the Australian Synchrotron
Mark Tobin, Australian Synchrotron

15:30-16:10 Afternoon tea & trade exhibition
Sponsored by Perkin Elmer Life and Analytical Sciences

16:10-16:50 Session X

FTIR and Raman Spectroscopy in combination with XRF for the characterization of medieval manuscripts on parchment
Manfred Schreiner, Institute of Science & Technology in Art, Academy of Fine Arts, Austria

Salvator Mundi: an investigation of the materials and techniques
Nica Gutman Rieppi, Art Analysis & Research, New York, USA

16:50-17:00 Closing

Posters:
(Presenting author only; see abstracts for full author listing)
*Poster oral presentation

Optimising an FTIR analysis methodology for identifying polymers in cultural heritage collections
Julianne Bell, Grimwade Centre for Cultural Materials Conservation, University of Melbourne, Australia

Rapid identification of cellulose nitrate film in the historic photograph collection of Sydney University Museums
Elizabeth Carter, Sydney Analytical Vibrational Spectroscopy Facility, University of Sydney, Australia

An Overview of the Use of Raman Microspectroscopy for the Identification of Gemstones in Museum Objects
Michelle Derrick, Museum of Fine Arts, Boston, USA

Spectroscopic analysis of pigments from the coffin of the 2500-year-old Egyptian mummy Mer-Neith-it-es for digital recolouration*
James Fraser, The Nicholson Museum, University of Sydney

Problems with obtaining good quality degradation spectra on three dimensional museum items
Rosemary Goodall, Museums Victoria

Assessing portable Raman spectroscopy for testing ethanol content in specimen jars of the natural history collection
Therese Harrison, Sydney Analytical Vibrational Spectroscopy Facility, University of Sydney, Australia

Combined FTIR and Pyrolysis GC/MS for the identification of challenging fibre sub-types
Jurian Hoogewerff, National Centre for Forensic Studies, University of Canberra, Australia

Investigating Chinese tradeware ceramics from Angkor with FTIR Spectroscopy*
Lorraine Leung, Department of Archaeology, University of Sydney, Australia

An FTIR survey of contemporary pre-primed artist canvases*
Gillian Osmond, Queensland Art Gallery|Gallery of Modern Art

Vibrational analysis of β-naphthol colorants: a comparative study through IR and Raman spectroscopy
Marcello Picollo, IFAC-CNR, Sesto Fiorentino, Italy

Japanese Sugito in the Philadelphia Museum of Art: investigation of painted decorations and soluble nylon coatings
Beth Price and Katie Shulman, Philadelphia Museum of Art, USA

The IRIS beamline: applications to cultural heritage materials
Ljiljana Puskar, Helmholtz-Zentrum for materials and energy, Berlin

An indigo we didn’t know: characterization and first identification of 5,5’-dibromoindigo dye in a Japanese yukata
Gregory Smith, Indianapolis Museum of Art at Newfields, USA

Neutron techniques for heritage materials *
Floriana Salvemini, Australian Institute of Neutron Scattering, Australian Nuclear Science and Technology Organisation, Australia

Application of ATR/FTIR to case studies in preventive conservation and novel conservation treatments
David Thickett, English Heritage, UK.

A spectroscopic investigation of sculptural modelling clay materials for conservation purposes
Barbara Stuart, Centre for Forensic Science, University of Technology Sydney, Australia

Characterisation and quantification study of lacquer materials by FTIR analysis
Shuya Wei, Institute of Cultural Heritage and History of Science & Technology, Beijing University of Science and Technology, Beijing, China

Neutron, proton and ion based techniques for heritage materials: a synergistic approach at ANSTO
Rachel White, Australian Institute of Neutron Scattering, Australian Nuclear Science and Technology Organisation, Australia

The potential of IR and Raman spectroscopy to determine pigment and binder concentration in modern paint samples
Rita Wiesinger, Institute of Science & Technology in Art, Academy of Fine Arts, Austria

Identifying the origins of Chocolate-on-White ware, a Bronze Age ware from Jordan
Michelle Wood, Sydney Analytical Vibrational Spectroscopy Facility, University of Sydney, Australia

KEYNOTE PRESENTATION

Dale Harding, artist: in conversation with Anneke Jaspers.

Dale Harding is a Brisbane-based artist and descendant of the Bidjara, Garingbal and Ghungalu people of Australia's North-East. His practice explores the histories and lived realities of his community, with a focus on his matrilineal elders. Harding's current research is engaged with the extraordinary historical rock art galleries that exist on his Country at Carnarvon Gorge in what is now Central Queensland. These sites encompass a range of artistic traditions – including stenciling, petroglyphs and positive mark making – and are also indexes of Aboriginal material culture specific to the region. This research has informed a body of work that utilises sovereign techniques of image and object making, as well as a broad range of organic and synthetic materials, from Central Queensland ochres, plant resins, gums and timbers, to commercial pigments, silicon and lead.

Anneke Jaspers is curator of contemporary art at the Art Gallery of New South Wales where she works across the collection and exhibitions. Her focus is on research based, socially engaged and interdisciplinary practices. For the biennial survey *The National 2017: new Australian art*, Jaspers commissioned a major installation by Dale Harding – the catalyst for an ongoing conversation and, recently, a shared journey to Carnarvon Gorge. She is currently completing a doctorate at the University of New South Wales looking at how contemporary artworks engaged with colonial histories might inform new approaches to institutional curating.

FULL PAPER

Non-destructive characterisation of Aboriginal Australian mineral pigments by near-IR HyLogger™ colour and mineral analysis

R. S. POPELKA-FILCOFF,[1] A. MAUGER,[2] C. E. LENEHAN,[1] K. WALSHE,[3] A. PRING[1]

[1] College of Science and Engineering, Flinders University, GPO Box 2100 Adelaide, 5001, SA, Australia
rachel.popelkafilcoff@flinders.edu.au
[2]Department of Premier and Cabinet, Adelaide, 5001, SA Australia
[3]College of Humanities and Social Sciences, Flinders University, GPO Box 2100 Adelaide, 5001, SA, Australia

Natural mineral pigments on Aboriginal Australian artefacts present a challenging case for non-destructive mineralogical analysis. Red, yellow and brown pigments are composed of iron oxides such as hematite and goethite, as well as white pigments which are composed of aluminosilicates such as kaolinite and others. In many cases, the pigment colour has a specific cultural meaning when applied to the object, and materials were sought from particular quarries for not only their physical and colour properties, but also connection to country. Natural pigments are inherently composed of mixtures of other mineral phases, which also complicates pigment characterisation. These mineral pigments are primarily applied to wood, fiber, bark, resin or other organic substrates, making non-destructive in-situ scientific analyses challenging.

High-resolution, automatic infrared and visible light spectroscopic analyses and imaging of minerals and geological materials for the mining industry have been routinely accomplished by the use of the CSIRO developed HyLogger™ (commercialised by Corescan Pty Ltd). This presentation presents the novel application of the HyLogger™ technology to Australian Aboriginal artefacts for characterisation and high-resolution spectroscopy of applied pigments. The HyLogger™ technology allows high-resolution, high-throughput non-destructive characterisation of pigments in less than 1x1 cm spot size (spectral pixel) on Indigenous Australian objects, along with visual imaging of the spot analysis.

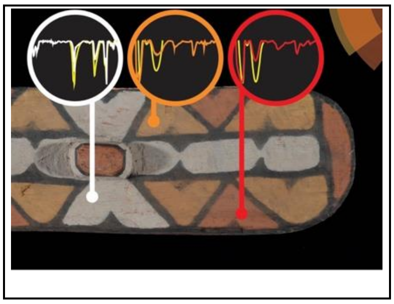

Fig. 1. Spectral images from different regions on an artefact. From Popelka-Filcoff et al. 2014.

A case study of 12 artefacts was analysed and evaluated using the HyLogger™ instrument and The Spectral Geologist (TSG™) software analysis package. The spectral range (250-2500 nm) of the instrument allows identification of multiple minerals in the pigment. In addition, the software quantifies colour for each spectral pixel in Munsell and L*a*b colour. While many identified pigments such as hematite and goethite were expected for the red and orange and yellow pigments, other white minerals such as pyrophyllite and gypsum were identified. These results challenge and add to prior knowledge about the mineralogical composition of Aboriginal Australian mineral pigments. The use of the HyLogger™ technique leads to a more comprehensive understanding of cultural uses and technology of natural mineral pigments in Australia and worldwide.

Acknowledgement
We acknowledge staff at the DMITRE Core Library, Glenside, South Australia, South Australian Museum Board and South Australian Museum Aboriginal Advisory Group, Gary Toone and Tara Dodd of South Australian Museum, Anne Dineen and Liz Murphy of Artlab Australia. The project has approval number 4670 from the Social and Behavioural Research Ethics Committee of Flinders University. Funding is gratefully acknowledged from the AINSE Fellowship and ARC LP0882597. HyLogger™ development was initially funded by AMIRA, with NCRIS and AuScope providing funding for the acquisition of the current equipment, and co-funded by the South Australian Government.

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FULL PAPER

The identification of blue pigments on artefacts in the Sydney University Museums collection

E. A. CARTER[1], J. PHILP[2], M. FOLEY[3], J. SALAMA[4], R. ARMSTRONG[4]

[1]*Sydney Analytical Vibrational Spectroscopy Facility & School of Chemistry, The University of Sydney, 2006, NSW, Australia*
elizabeth.carter@sydney.edu.au
[2]*Macleay Museum, Macleay Building, The University of Sydney, 2006, NSW, Australia*
[3]*Australian Centre for Microscopy & Microanalysis, Madsen Building, The University of Sydney, NSW 2006*
[4]*School of Chemistry, The University of Sydney, 2006, NSW, Australia.*

Previously the authors have used Raman spectroscopy to identify the vibrant blue pigment found on a painted and incised shield shown in Fig. 1 as ultramarine blue. The Australian Aboriginal shield (63 x 24 cm) is thought to be of the Gugu-Badhun people, Townsville, Queensland, and was collected by J. A. Boyd c.1888 and is part of the W. J. Macleay Collection. The shield is decorated with red, brown and blue pigments that are arranged into a squared pattern across the face of the shield. The front surface is decorated with linear and curved lines painted in blue together with a series of incised, parallel lines on both sides.

Fig. 1. Australian Aboriginal Shield. Gugu-Badhun people, Townsville, QLD.

The Raman spectra provided no indication as to whether the pigment was synthetic (possibly Reckitt's blue) or natural ultramarine (lazurite, the main mineral component of lapis lazuli), as their spectra are identical. Lapis lazuli is typically identified using either optical or scanning electron microscopy (SEM) with the morphology and particle size of lapis lazuli being distinctly different from the uniform, small and rounded particles of the synthetic ultramarine blue pigment. Recent literature has indicated that using a combination of laser induced breakdown spectroscopy (LIBS) and Raman spectroscopy together with chemometric analysis allows differentiation between the natural and artificial blue pigments [2].

In this study the authors re-visit our original research and used the additional techniques of scanning electron microscopy and principal component analysis (PCA) to re-examine the blue pigment on the Australian Aboriginal Shield to establish its origin. This work will then be extended to investigate blue pigments on a range of other artefacts from the Sydney University Museums Collection including the icon painting Madonna and Child with saints and angels c. 1450-60.

Acknowledgement
The authors thank Susie Davies, Vanessa Mack and Rosemary Stack from the Macleay Museum, The University of Sydney for providing the Shield and samples for this project. Thanks to Lydia Bushell for the gift to the Macleay Museum of samples of Reckitt's Blue. The authors also thank Dr Ross Pogson from the Australian Museum for the loan of lapis lazuli samples.

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FULL PAPER

New insights into the material culture of the American Southwest

C. Bisulca[1,2], M. Pool[2], M. MgGath[3,4], A. Hall[3], M. Dawley[4], and N. Odegaard[2]

[1] *Detroit Institute of Arts, 5200 Woodward Ave, Detroit MI 48202, USA* cbisulca@dia.org
[2] *Arizona State Museum, University of Arizona, Tucson AZ 85719 USA*
[3] *Heritage Science for Conservation Laboratory, Johns Hopkins University, Baltimore, MD 21218 USA*
[4] *Department of Conservation, The Mariners' Museum and Park, Newport News, VA 23606 USA*

The American Southwest is a unique desert environment that has a rich cultural history. This region includes the Sonoran and Chihuahuan deserts of Arizona, New Mexico, and Northern Mexico and extends upward to its northern boundary in southern Colorado and Utah on the semi-arid Colorado Plateau. In the material culture of the Southwest, numerous plant and insect exudates were utilized as adhesives, coatings, paints, dyes, as well as for medicinal purposes. This includes pine terpenoid resins, both the kino (polyphenolic) and polysaccharide gum from the mesquite tree, exudate from the brittlebush, and various starches and mucilages from seeds, roots and cacti. In addition, these cultures utilized the polyester (shellac) exudate from an American lac insect endemic to the desert lowlands.

The Arizona State Museum (ASM) has been identifying these materials in its collections primarily with Fourier transform infrared spectroscopy (FTIR). To date this work has shed light on how these adhesive materials were used, processed and traded throughout the greater Southwest [1-3]. This research has been comprehensive and includes all artifact types for each major cultural group of this region. This study has recently been expanded to include analysis on additional artifacts at the National Museum of Natural History (NMNH) and the Detroit Institute of Arts (DIA). Importantly, this includes raw materials collected by early anthropologists studying the tribes of this region. To date over 300 artifacts with these adhesive materials have been characterized.

Alongside the study of artifacts, separate studies in experimental archaeology to reproduce adhesive use in artifacts as well as materials testing of their physical properties are being conducted. Natural adhesives available in the Southwest were collected and tested using differential scanning calorimetry and tack testing at the Heritage Science for Conservation Laboratory at Johns Hopkins University. The understanding of their materials properties combined with use patterns in artifacts as determined by FTIR was critical to a holistic understanding of materials selection, and how peoples utilized the natural resources of these arid environments.

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The application of FTIR microspectroscopy to the study and conservation of excavated textiles

C. MARGARITI

Centre for Textile Research, SAXO Institute, University of Copenhagen, Karen Blixens Plads 8, Copenhagen 2300, Denmark, e-mail.christinam@hum.ku.dk

The potential of Fourier Transform Infrared (FTIR) microspectroscopy to the study and conservation of excavated textiles is discussed, through two case studies of 5th c. BCE mineralised finds. Mineralisation is the process when the organic fibres of a textile are gradually replaced by the metal corrosion products of objects nearby. In both cases the textiles are funerary from pyre burials, used to wrap the remains of the incinerated bones of the deceased, and placed inside copper urns, to be buried.

FTIR spectra can be acquired in the context of excavated textiles by an FTIR microscope reflectance mode, as this is a non-destructive method, since it does not apply any pressure, nor does it require pressing. A drawback is that the infrared beam might be scattered due to the cylindrical shape of the fibres. Experiments were carried out to compare FTIR in reflectance and transmission modes with ATR. Generally, some of the characteristic peaks shifted towards the higher end of the spectrum. Spectra were acquired over the range of 4000 to 500 cm^{-1}, with 32 scans at 4 cm^{-1} resolution.

Case study A was excavated in 1936 at Athens [1]. In the 1960s the find was reported as silk of the cultivated *Bombyx mori* species [2], which was used as evidence of the presence of silk in Classical Greece [e.g. 3, 4]. In later years the find was identified as wild silk [5, 6] and later as wool [7]. FTIR was applied and indicated the fibres were cellulosic [8, 9], since they showed two of the signature peaks of cellulose (1635 cm^{-1} and 1124 cm^{-1}) but none of proteins (Fig. 1).

Case study B was retrieved in 1983 at Piraeus. One of the textiles bearing evidence of embroidery [10]. FTIR identified the fibres as cellulosic, and showed that the organic matter had been preserved (signature peaks of cellulose (2900 cm^{-1}, 1635 cm^{-1}, 1173 cm^{-1}, and 1124 cm^{-1}) [11, 12]. Therefore, they could withstand partial unfolding without damage [13]. The unfolded parts revealed an additional pattern, and fragments of the embroidery thread.

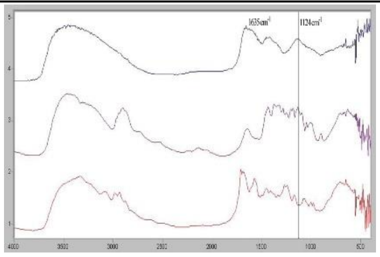

Fig. 1. The excavated textile spectrum (top) shows two characteristic peaks of cellulose (middle 1635 cm^{-1}, 1124 cm^{-1}), but none of proteins (bottom).

FTIR microspectroscopy enhanced fibre identification of a rare excavated textile find, and informed the conservation decision making of another unique find, therefore it can be applied successfully to excavated textiles in a completely non-destructive way.

Acknowledgement
Dr Leonidas Bournias, Archaeologist, and Mr Fotis Katevas, conservator, Archaeological Museum of Kerameikos. Dr Elena Papastavrou, Archaeologist and Dr Eftyhia Lygkouri, former director, Ephorate of Antiquities of Peiraeus and Islands, Hellenic Ministry of Culture.

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Analysis of textile fibres using ATR-FT-IR spectroscopy, reflectance IR spectroscopy and chemometric methods

P. PEETS[1], S. VAHUR[1] AND I. LEITO[1]

[1]*University of Tartu, Institute of Chemistry, 14a Ravila str., Tartu, 50411, Estonia pilleriin.peets@gmail.com*

Textile fibres are complex polymeric materials with diverse properties and usage. Besides traditional natural fibres, during the last century numerous artificial and synthetic fibres have been developed. Due to their abundance and many similar properties, identification of fibres with traditional methods like microscopy, dissolving and burning can be impossible. In this field less-destructive, easy and quick identification methods must be used. Identification of textile fibres and dyes can be helpful in conservation and archaeology, but also in industry (quality control) and forensic science.

In this study, method development for analysis of textile fibres was carried out using infrared spectroscopy and chemometric methods. With attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectroscopy different types (11 single- and 15 two-component) of textiles were measured, the spectra were thoroughly interpreted and classification methods were developed. Discriminant analysis, based on principal component analysis (PCA), was used for classification (see Fig. 1). Additionally, the possibility of semi-quantitative analysis with PCA graphs was tested. Nicolet 6700 FT-IR spectrometer with a Smart Orbit micro-ATR accessory was used for the analysis. [1,2]

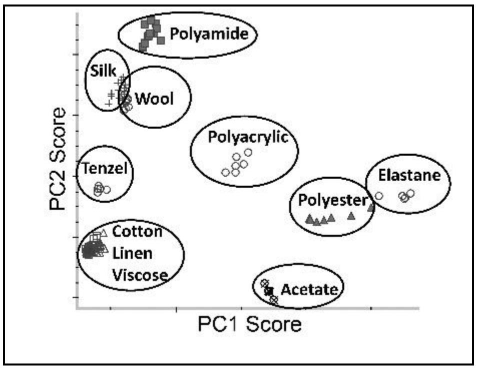

Fig. 1. PCA graph of pure fibres using two principal components (PC1 and PC2)

Additionally, homogeneity of the textiles was studied using the mapping function of Nicolet iN10 MX FT-IR microscope and Leica optical microscopy [1]. For the non-destructive measurements, textile fibre analysis with reflectance infrared spectroscopy was tested using Nicolet FT-IR microscope. Spectra from different fibres were registered and classification method was applied to these results.

The developed methodology was used to analyse different samples from Estonian National Museum, Conservation and Digitization Centre Kanut and archaeology department of University of Tartu.

Acknowledgement
This work was supported by the Personal Research Funding PUT1521 and Institutional Funding IUT20-14 from the Estonian Research Council, as well as by the graduate school „Functional materials and technologies“ receiving funding from the European Social Fund under project 1.2.0401.09-0079 in Estonia.

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POSTER PRESENTATION

Neutron techniques for heritage materials

F. SALVEMINI[1]

[1] *Australian Institute of Neutron Scattering, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234 Australia*
Filomena.salvemini@ansto.gov.au

Neutron radiation techniques are an established means for the non-invasive investigation of objects of art, museum pieces and archaeological findings [1]. Compared to other sub-atomic particles, i.e. electrons or protons, neutrons are uncharged; they can deeply penetrate deeply into matter and interact with the nucleus of an atom rather than with the diffuse electron cloud. These fundamental properties make neutrons the ideal probe to survey the bulk of dense materials and highlight the presence of light elements [2].

In particular, neutron imaging has proven to be a valuable scientific analytical tool to extract and quantify information such as morphology, porosity, and inclusions about the object under investigation. It detects the presence of composite structures with acceptable resolution and accuracy [3]. Complementary, neutron diffraction methods can provides qualitative and quantitative data about phase composition, (residual) microstrains and macrostrains, and crystallographic texture [4].

Several neutron techniques are available at the Australian Centre for Neutron Scattering (ACNS) at the Australian Nuclear Science and Technology Organisation (ANSTO) - Sydney. In collaboration with Australian museum institutions and universities, and international experts, a series of forensic studies involving the neutron instruments will be showcased. Neutron methods were successfully used to characterise the structure, morphology and composition of cultural heritage objects without the need for sampling or invasive procedures. Integrated data were able to shed light on the most advanced manufacturing processes developed by different cultures over time, determine the authenticity of work of art or provide information on the conservation status.

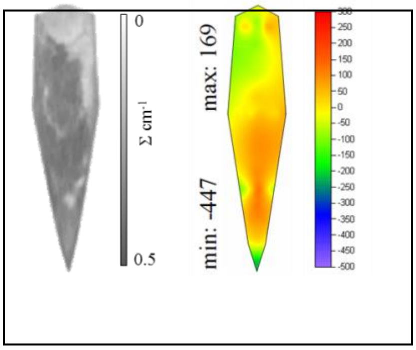

Fig. 1. On the left, neutron tomograph, and on the right, residual stress map of a samurai sword. MAAS collection, Sydney.

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POSTER PRESENTATION

Optimising an FTIR analysis methodology for identifying polymers in cultural heritage collections

J. BELL[1] AND P. NEL[1]

[1]*Grimwade Centre, University of Melbourne, Thomas Cherry Building, Parkville, Victoria 3010. jebell@student.unimelb.edu.au*

Fourier Transform Infrared (FTIR) Spectroscopy is a useful analytical tool for identifying and classifying polymeric materials. The diamond attenuated total reflection (ATR) window accessory allows high-quality spectra to be recorded non-destructively on a wide range of materials in a short space of time, crucial for analysing cultural heritage objects. However, collection items range in shape, size, and fragility, and thus frequently cannot be clamped onto the diamond window. So instead an IR spectrum can be obtained by pressing the object onto the diamond window using handheld manual pressure. Alternatively use of an external reflection module removes the need for contact with the object.

The collaborative national project, PolyMuse, is bringing together data and resources from eight organisations to develop a consistent methodology for managing plastics in Australian gallery, library, archive and museum (GLAM) collections. A key aim is to collate object-oriented descriptive and analytical data from each partner organisation via the development of a relational database. However, accurate comparisons of scientific data across the project partners require consistent data collection and analysis procedures. For this paper an investigation was conducted into the development of a project reference collection and FTIR measurement process for identifying three dimensional polymeric objects in the museum context. Assumptions about the measurement process, including the use of reference databases and collections, number of scans, difficulties in accessing measurement locations, time taken to conduct measurements and comparison of different spectral modes were investigated.

A variety of reference databases and reference collections were scrutinised, with a comparison made of commercial, published and in-house databases. Commercial reference collections were also compared to those obtained from plastics workshops run in Australia and objects obtained from antique stores. As a consequence, a process was developed for building a reference collection that can be used by all partners to build robust in-house databases for identifying plastics in collections. Four case study objects were selected from the plastics research collection to develop the FTIR measurement process with representative qualities including different polymers, ages, colours, shapes and hardness.

The relationship between spectral resolution and signal to noise ratio (S/N) is an increase in S/N with decreased resolution, which may be improved by signal accumulation, or an increased number of scans (Blitz & Klarup 2002, p.1358). However, there is a trade-off between resolution, S/N and time taken to conduct the increasing number of scans. This paper investigated the impact of number of scans on the S/N when measuring different plastic objects to justify a consistent scan number. As collection objects are often unable to be clamped onto the ATR window, both handheld and clamped methods were analysed and compared. Other FTIR options for analysing hard, dark polymers such as phenol formaldehyde, using an external reflection module, and how to compare these with ATR spectra, was also evaluated. Results from these investigations were used to produce a standardised, project wide FTIR analysis methodology for conducting collection surveys.

Acknowledgements
This research is supported fully by the Australian Government through the Australian Research Council's *Linkage Projects* funding scheme (project LP160100160).

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POSTER PRESENTATION

An FTIR survey of contemporary pre-primed artist canvases

G. OSMOND[1], L. CHUA[2], A. CARTER[1], R. AWBURN[3], F. MOHD AMIR[2]

[1] *Queensland Art Gallery/Gallery of Modern Art, PO Box 3686, South Brisbane 4101, Australia; gillian.osmond@qagoma.qld.gov.au*
[2] *Heritage Conservation Centre (National Heritage Board), 32 Jurong Port Road, Singapore 619104*
[3] *Private Conservator, Melbourne, Australia*

Historically, fabric supports for easel paintings have been made from linen or cotton fibres and primed using glue or oil based layers. More recently synthetic fibres have become available for canvases, and synthetic polymer primers are now commonly used as preparatory layers. Many commercially pre-primed canvases are marketed with a 'universal primer' – intended to be suitable for both water and oil based paints.

The characteristics of local and internationally produced pre-primed canvases currently available in Australia and Singapore are being investigated by the Queensland Art Gallery/Gallery of Modern Art and the Heritage Conservation Centre. The study aims to enhance understanding of potential influences of canvas and priming type on conservation care. This presentation reports initial findings for binder and fibre type for 53 samples, including four oil-primed canvases.

ATR-FTIR spectra were obtained from both exposed canvas and primed surfaces of each sample using a Thermo Scientific iN10 microscope with DTGS room temperature detector coupled to an iZ10 diamond ATR bench accessory. Scrapings of priming were also analysed using Py-GC/MS with a Shimadzu GC/MS QP2020 combined with a Frontier PY3030D pyrolyser unit.

Fibre analysis supported by optical microscopy showed good correlation with the information provided by manufacturers. Most canvases (31) were cotton. Linen was used in 17 samples. Polyester (polyethylene terephthalate) was found in 5 samples, including 2 as a cotton blend.

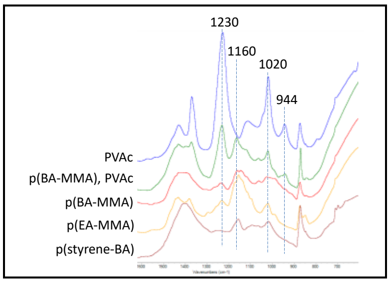

Fig. 1. ATR-FTIR fingerprint region for primings highlighting key Acr/PVAc bands

ATR-FTIR analysis of priming allowed characterisation of oil, acrylic, PVAc, and PVAc/acrylic copolymers with and without styrene. Further detail was provided with Py-GC/MS (including presence of additives). Low amounts of acetic acid (PVAc marker) were detected in 14 samples where no PVAc was seen in FTIR. This may reflect levels of PVAc below the limit of detection of FTIR but it is also likely that Py-GC/MS results include some lower priming layers (i.e. primer layers were not easily separated), in contrast to the surface only analysis of ATR-FTIR. Acetic acid traces may also derive from impurities, rather than intentional addition of PVAc.
The percentage representation of each binder category as determined by the two analytical techniques are tabulated below:

Samples (%)	**Acrylic**		**Acrylic/PVAc**		**PVAc**		**Oil-based**		
	Acr/sty	Acr	Acr/PVAc	Acr/PVAc/sty	PVAc	PVAc/sty	oil	Oil+sty/acr/PVAc	Oil+sty/acr
ATR-FTIR	41.5	20.8	11.3	9.4	7.5	1.9	7.5	-	-
PyGCMS	24.5	17	15.1	26.4	7.5	1.9	1.9	3.8	1.9

- Acrylic based binders predominate regardless of analytical technique. Py-GC/MS identified numerous combinations of seven acrylic monomers. The most commonly represented copolymers were styrene-BA followed by BA-MMA.
- A confident attribution of acrylic/ PVAc using ATR-FTIR required an acrylic peak at c. 1160 cm^{-1} together with PVAc peaks at c. 1230, 1020, and 944 cm^{-1}. Fig. 1 illustrates the potential for confusion in copolymers with MMA.
- Styrene was prevalent, detected in 62% of primings with Py-GC/MS (two more samples than identified with FTIR).
- FTIR detected amorphous zinc carboxylates at the top surface of one sample primed exclusively with oil where zinc oxide was only present in an underlayer. Crystalline zinc soaps were detected at the surface of two oil-primed canvases with acrylic/PVAc underlayers and no zinc oxide; zinc stearate was likely a constituent in the priming formulation.

Initial binder results indicate most preprimed canvases are acrylic. The significant variability in their formulation and the high incidence of styrene and PVAc contrasts with a 2008 study of acrylic emulsion grounds [1] and invites further research.

Acknowledgement
This research is supported by QAGOMA Centre for Contemporary Art Conservation and QAGOMA Foundation

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POSTER PRESENTATION

Investigating Chinese tradeware ceramics from Angkor with FTIR spectroscopy

L. LEUNG[1], E. A. CARTER[2] AND R. FLETCHER[1]

[1]*Department of Archaeology, The University of Sydney, Sydney, NSW, 2006, Australia. lleu4057@uni.sydney.edu.au*
[2]*Sydney Analytical Vibrational Spectroscopy Facility and School of Chemistry, The University of Sydney, Sydney, NSW, 2006, Australia*

The application of FTIR spectroscopy for the analysis of potential archaeological organic residues from 11th-16th century CE Chinese tradeware ceramics from Angkor, Cambodia is presented and discussed. There have been vast amounts of archaeological organic residue analysis research into ceramics, however, little is known about its application to glazed ceramics.

This study aimed to explore whether archaeological organic residues could be detected from high-fired porcelain surfaces and whether this type of data can give insight into the past use(s) and function(s) of vessels. The presentation will provide an overview of the archaeological samples analysed, reference materials analysed and present significant results from the study. Results highlight the successful application of chemical analysis techniques for the detection of extant residues on high-fired porcelain and stoneware.

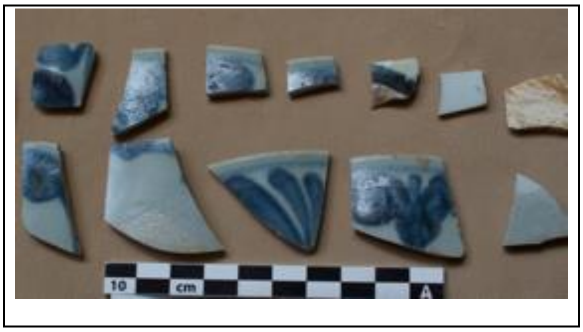

Fig. 1. Chinese tradeware ceramics excavated from Angkor, Cambodia. Image courtesy of Dr Alison Carter (University of Oregon).

Acknowledgements
This study was funded by the Greenwell Carlyle Bequest and the Greater Angkor Project. LL and RF would like to thank Dr Joonsup Lee and Dr Michelle Wood at the Sydney Analytical Vibrational Spectroscopy Facility (SAVSF) for their assistance during the project. Acquisition of reference material thanks to the Chinese Herbal Medicine Clinic, University of Technology. Acquisition of artefacts thanks to the Ministry of Heritage and Culture of the Kingdom of Cambodia and the National Authority for the Protection, Management of Angkor and the Region of Siem Reap (APSARA), Dr Alison Carter (University of Oregon) and Prof Miriam Stark (University of Hawai'i at Manoa).

POSTER PRESENTATION

Spectroscopic Analysis of pigments from the coffin of the 2500-year-old Egyptian mummy Mer-Neith-it-es for digital recolouration

J. R. FRASER[1], T. M. HARRISON[2], M. L. WOOD[2], C. LORD[1] AND E. A. CARTER[2]

[1]The Nicholson Museum, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia, james.fraser@sydney.edu.au
[2]Sydney Analytical, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia

In 1860, Sir Charles Nicholson donated an Egyptian coffin to the University of Sydney that he had purchased from the antiquities market in Saqqara, Egypt. The coffin is constructed from cedar wood imported from Lebanon and carved in a style consistent with the 26th Dynasty (664-525 BC). Hieroglyphic texts painted on the side of the coffin name its occupant as the woman Mer-Neith-it-es, who worked in the Temple of Sekhmet. Although once elaborately decorated, these painted motifs and texts have faded over time, partly a reaction of the copper-based pigments with the oils present in the cedar-wood, and partly due to its exposure to sunlight after robbers removed it from the tomb.

Researchers from the Nicholson Museum and Sydney Analytical are using a combination of Raman, IR (including a range of MIR sampling techniques and NIR) and XRF analysis to determine the chemical composition of these faded pigments. This study will enable us to colour a digital model of the coffin that will be displayed in a dedicated Mummy Room alongside the coffin itself in the new Chau Chak Wing Museum that will open in 2020 at The University of Sydney. This display will help people understand what the faded coffin would have once looked like and showcase how sciences and the humanities work together to help researchers understand the ancient past.

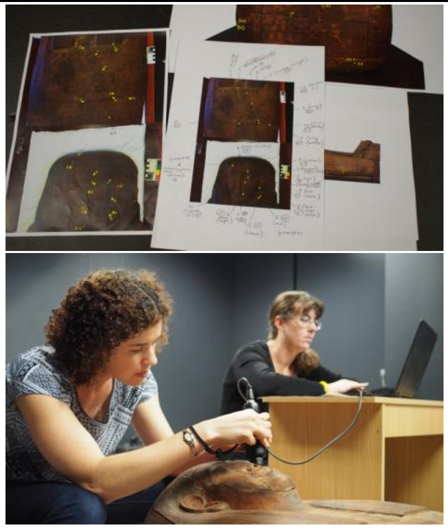

Fig. 1. (top) Photograph marked with regions of interest for analysis. (bottom) Contactless NIR analysis of the cedar coffin of the woman Mer-Neith-it-es; 26th Dynasty (664 BC - 525 BC, Saite Period); Saqqara, Lower Egypt (NMR.29.1-2) Nicholson Museum, the University of Sydney.

Acknowledgements
The authors would like to acknowledge the support provided by the Core Research Facilities (CRF), at The University of Sydney, for funds provided to purchase the equipment used in this study

FULL PAPER

IRUG Spectral Database: Spectral Search Feature & Tutorial

B. A. Price[1], S.Q. Lomax[2], J. Levi[3], B. Pretzel[4], C. Davis[5], F. Pease[3], G. Richards[6] and A. Lins[1]

[1]Philadelphia Museum of Art, PO Box 7646, Philadelphia, PA 19101, USA bprice@philamuseum.org
[2]National Gallery of Art, 6th Street and Constitution Ave NW, Washington, DC 20565, USA
[3]DLS Solutions, P.O. Box 110228, Trumbull, CT 06611 USA
[4]Victoria & Albert Museum, Cromwell Rd, SW7 2RL, London, UK
[5]Retired, The Dow Chemical Company, Independence Mall, Philadelphia, PA, 19106 USA
[6]Endertech Corporation, 400 Crenshaw Blvd., Torrance, CA 90503, USA

Background

Since its inception in 1993, the Infrared and Raman Users Group (IRUG) has worked to facilitate the exchange of spectroscopic information and reliable reference spectra for the research and analysis of the world's cultural heritage. Throughout the group's history, a primary focus has been the development and distribution of the IRUG Spectral Database, which has become a valuable resource for the cultural heritage community. During its 25 years, IRUG has achieved a number of milestones in efforts to improve the quality, uniformity, and distribution of the spectra in its database. With these objectives in mind, IRUG developed a customized, platform-independent, JCAMP-DX spectral file format along with guidelines for submission and peer-review of spectra.[1] The first published compilations of spectra were infrared only and distributed by post. By 2001, IRUG had constructed a MySQL web-enabled spectral database available on IRUG.ORG. This meant that all spectra transactions, such as submission, review, formatting, and download could take place electronically via individual user accounts and all spectra safely archived in the web-enabled database. A 'Structures Index' was added next. In 2009, the first database version from the online functionality debuted, accompanied by a 'Key-word Search' with an 'Interactive Spectrum' for public access. The next major milestone was realized in 2016, when a Raman JCAMP-DX file format was adopted and Raman spectra were added to the database. The first Raman DB release is slated for December 2018.

Spectral Search for IRUG.ORG

IRUG now is developing a spectral search/matching functionality for the IRUG.ORG website. The specialized software will permit end-users to directly compare their own JCAMP-DX spectra of unknown materials against the IRUG spectral DB for characterization. Users with internet access may connect via any computer, thus reducing the need to access costly, proprietary vendor search software. IRUG has partnered with DLS Solutions, Inc., Trumbull, CT, and Endertech Corporation, Torrance, CA, to develop the library search function and user interfaces, respectively.[2]

User Scenario

The user will go to the IRUG web page, select 'Spectral Search' and be prompted to enter a JCAMP-DX file for the unknown they wish to search. The user will search the entire IRUG library or a subset selected from various parameters, such as datatype, material type, colour, search algorithm (correlation or first differential) and excluded region (if desired). The user then will initiate the search and receive a 'hit' list (up to 20 entries) with a status string indicating the success/failure (match quality and % overlap) and library entries that are the best matches spectrally. The user will click a row of the list to view a plot with the corresponding library entry overlaid on the unknown spectrum.

Benefits and Participation

This paper will introduce the new 'Spectral Search' feature and provide a brief tutorial on the submission and review of spectra for the IRUG Spectral Database. The 'Spectral Search' feature is being funded by the Bank of America and IRUG. It is the first of its kind for the cultural heritage community and is expected to significantly advance access to high-quality spectra. The success of IRUG and its database relies on the participation and ongoing support of the community. IRUG encourages and welcomes new spectra, and members and reviewers interested in participating in IRUG's highly valuable collaborative effort to share scientific information on the world's cultural heritage materials.

Notes:

[1] See http://irug.org/uploads/documentation/irug-jcamp-dx-revised-white-paper-text-only-with-2b-version-1-26-sept-2013.pdf for complete descriptions and guidelines.

[2] For information about DLS Solutions, Inc. spectral library search components, see www.dlssolutions.com; for software development by Endertech Corporation, see www.endertech.com.

FULL PAPER

Characterizing the Physical and Chemical Alterations in Asian Lacquer Films

H. KHANJIAN[1], M. SCHILLING[1], AND J. HAN[1]

[1]Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles, 90049, CA, USA hkhanjian@getty.edu

The understanding of light aging behavior of Asian lacquers is an important step in the development of successful cleaning treatments. There are many challenges in finding appropriate cleaning methodologies for different lacquer formulations. The difficulties rest in not only characterizing the complex mixture of materials but also comprehending the degrees of surface and in-depth degradation profiles. Of primary concern are changes resulting from exposure to photo-oxidative inducing light radiation and potential influences on the materials sensitivity to aqueous solvents.

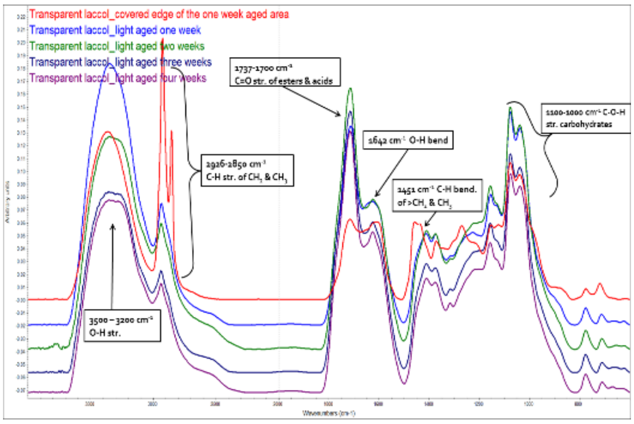

Fig. 1. Accelerated light aging behaviour of laccol lacquer.

In recent years, the GCI's Materials Characterization Laboratory has been researching the physical and chemical changes to lacquer films exposed to accelerated light aging conditions. Lacquer replicas with known formulations applied to wood boards have been prepared for light aging experiments under a xenon arc lamp and full spectrum fluorescent light, simulating indoor aging conditions. Microscopic, FTIR, Py-GC/MS and LC/MS methodologies were utilized in characterizing the changes to aged lacquers. After a period of four weeks of aging in an Atlas Weather-Ometer, ATR-FTIR analysis of the top surface showed reductions in the C-H stretching bands accompanied by broadening of O-H and increases in C=O groups, supporting the formation of photo-oxidative by-products. 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 side-chains 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.

Current and future findings from the study of replicas will further the understanding of the chemistry of Asian lacquer surfaces. In turn, they will assist in the development of treatments for removal of degraded lacquer layers and improve the long-term appearance of lacquered objects.

FULL PAPER

Analysis of naturally- and artificially- aged paper using variable angle ATR infrared spectroscopy

K. J. VAN DER PAL[1,2], R. S. POPELKA-FILCOFF[3], G. D. SMITH[4], M. J. HACKETT[1,2], W. VAN BRONSWIJK [1,2] AND S. W. LEWIS[1,2]

[1]School of Molecular and Life Sciences, Curtin University, GPO Box U1987, Perth, 6845, WA, Australia
karin.vanderpal@postgrad.curtin.edu.au
[2]Curtin Institute of Functional Molecules and Interfaces, Curtin University, Perth, WA, Australia
[3]College of Science and Engineering, Flinders University, GPO Box 2100, Adelaide, 5001, SA, Australia
[4]Indianapolis Museum of Art at Newfields, 4000 Michigan Road, Indianapolis, IN, 46208, USA

The aging mechanisms of cellulose in paper have been thoroughly researched, with literature agreeing that oxidative reactions cause the yellowing colour change and that acid-catalysed hydrolysis makes the paper brittle by shortening fibre lengths [1]. Cellulose is not the only component in paper, and the effects of additives such as fillers, whiteners and binders on aging processes have not been extensively investigated. The Committee on Production Guidelines for Book Longevity determined that "paper should last at least several hundred years without deterioration under library use and storage conditions." [2] However paper manufacturers only monitor the longevity of their product for short periods.

As optical brighteners have only been used in paper manufacture since the 1950's, knowledge on how these additives influence long term aging is limited to the last 70 years [3]. Only recently have issues relating to the inclusion of optical brighteners been acknowledged, with a correlation to decreasing cellulose fibre length [4]. There are concerns that without establishing the longer-term survivability issues with conserving paper products, a "legacy of decaying books and paper documents … [will be left behind] for future generations" [2].

Paper samples of known composition dating back to the 1970s were collected from the Shoalhaven paper mill (NSW). In addition to these naturally aged samples, artificial aging was performed using the guidelines outlined by TAPPI 544 (formerly ASTM D4714) [5]. Samples were then analysed using a variable angle infrared ATR accessory with set angles of analysis, to give surface and subsurface information. Changes in the paper chemistry, due to factors other than cellulose degradation, will be discussed as a function of depth from the surface.

Acknowledgement
We would like to acknowledge Document Examination Solutions for their assistance in the collection of the Shoalhaven paper samples

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FULL PAPER

ALD coatings to protect metal art objects from atmospheric corrosion

R. WIESINGER[1], L.PAGNIN[1], P. BALOH[2], H. GROTHE[2], AND M. SCHREINER[1]

[1] *Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Schillerplatz 3, Vienna, 1010, Austria*
e-mail.r.wiesinger@akbild.ac.at
[2] *Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165, Vienna,1060, Austria*

Metals such as copper, silver and its alloys have played a key role in the course of civilization. They have had a profound influence on the evolution of human societies and they are central to many technologies. Metals and its alloys have been valued as precious materials since time memorial with shiny brightness and wide use in daily life for jewellery, fine utensils, coinage, and photography. As those metals are exposed to different indoor and outdoor environments the function of the material can be affected or even destroyed by the interaction of the metal surface with the ambient chemicals. Conventional atmospheric parameters that affect metals comprise weathering factors (temperature, moisture, solar radiation, wind velocity, etc.), air pollutants (H_2S, SO_2, CO_2, etc.) and aerosols. The increasing concentration of anthropogenic caused corrosive gases mainly present in urban environment atmospheres is challenging corrosion scientists as well as scientists and conservators dealing with art objects in museums, private collections or archaeological findings [1-4]. As our cultural heritage is inherited from the past generations, it is our responsibility to preserve and protect this cultural property for future generations. Therefore, a fundamental understanding of the chemistry occurring on the surfaces and interfaces is needed in order to enable controlling material degradation in the near future. For this reason, it is of special interest to developing methods and strategies in order to prevent those atmospheric attacks.

In conservation-restoration, nitrocellulose coatings are often used to prevent metals from tarnishing, however, non-uniform coatings and degradation limit their effectiveness over time. A new method for creating uniform and dense coatings e.g. atomic layer deposition (ALD) with aluminium oxide was explored [5]. The main objective was to apply ALD coatings on different metal substrates and explore their effectiveness under ambient aging conditions. Artificial aging was performed under different relative humidity contents (50 – 90 %RH) and concentration of corrosive gases: H_2S, SO_2, NO_x and O_3 (ppb-ppm range). During sample weathering chemical reactions were tracked in-situ and in a time-resolved way by Infrared Reflection Absorption Spectroscopy (IRRAS). Furthermore, Raman spectroscopic imaging, Scanning Kelvin Probe (SKP) and Atomic Force Microscopy (AFM) were applied. The results impressively show that the ALD coating protects the metal surface against most inorganic corrosive gases and decrease the corrosion rates by a factor of 10^{-2}.

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FULL PAPER

Terahertz Spectroscopy Applied to Pigment Identification

A. D. SQUIRES[1], M. KELLY[2], R. A. LEWIS[1]

[1]Institute for Superconducting and Electronic Materials and School of Physics, University of Wollongong, Wollongong, 2522, NSW, Australia asquires@uow.edu.au
[2]Faculty of Arts and Social Sciences and Sydney College of the Arts, University of Sydney, Sydney, 2006, NSW, Australia

Recent years have seen a large development in the use of terahertz (THz) radiation for applications in art analysis and conservation science. Favourable characteristics of THz waves, situated at the far infrared region of the electromagnetic spectrum, allow a large depth penetration into dielectric materials permitting *in situ*, non-destructive and non-invasive analysis of artworks and culturally significant pieces, along with their constituent surface and sub-surface materials [1, 2], including pigments, binders and substrates [3,4].

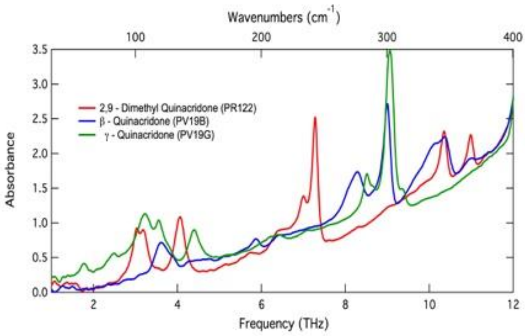

Fig. 1. Terahertz spectra of three quinacridone variants: β phase (PV19B), γ phase (PV19G) and 2,9-dimethyl quinacridone (PR122) [5].

We present THz spectra of a series of contemporary and traditional pigments used in artworks and across industry from 1 – 20 THz via synchrotron radiation. Specifically, we show the spectral properties of quinacridone and phthalocyanine as well as an array of ochre pigments. Quinacridone and phthalocyanine, the most important synthetic pigments in red-violet and blue-green shades respectively are shown to have 'fingerprint' spectra, with associated temperature dependence. THz photons distinguish polymorphs of these pigments (Fig. 1.), not achievable with competing modalities using x-rays. The fundamental origins of the resonances in quinacridone are revealed through solid state density function theory to consist of wagging, rocking and twisting motions of the base quinacridone molecules [5]. Earth-based iron oxide ochre pigments found in many indigenous and culturally significant artefacts also show characteristic, sometimes temperature dependent, absorptions for THz frequencies. Similarly, Hematite, limonite, goethite and magnetite based pigments are clearly resolved in the THz regime. Strong distinction is observed for natural and synthetic counterparts of the same pigment class, with subtle variations in similar pigments from varying geographical origins. Processing techniques, such as heating in 'burnt' varieties is reflected in the THz profile suggesting applications in tracking similar processes occurring naturally. We confirm the utility of THz spectroscopy in understanding artwork pigmentation leading to applications in identifying optically similar materials, fraud detection in reproductions, dating of artworks and sourcing the geographical timeline of culturally significant items.

Acknowledgement
We acknowledge travel funding and experimental support of the Australian Centre for Synchrotron Science, particularly Dom Appadoo and Ruth Plathe.

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FULL PAPER

Reassessing reference materials: surprises encountered when building a spectral library

G.D. SMITH[1], H. KASTENHOLZ[2], V. CHEN[1] AND A. WILSON[2]

[1]*Indianapolis Museum of Art at Newfields, 4000 Michigan Rd., Indianapolis, IN 46208, USA e-mail. gdsmith@discovernewfields.org*
[2]*Butler University, 4600 Sunset Rd., Indianapolis, IN 46208, USA*

Chemical analysis of cultural heritage objects usually requires the comparison of instrumental data collected from the object to that of a known reference compound in a fingerprint matching approach to identification. The accuracy of these analyses relies on the availability of authentic, genuine samples from a wide array of materials including alloys, pigments, dyes, binding media, and synthetic plastics that can be systematically characterized to produce libraries of reference data. Although that statement may seem axiomatic, the appropriateness of a "reference material' in the field of conservation science is in fact problematic. Rarely do the cultural materials being investigated appear in commercial offerings of certified reference materials (CRMs) that have been thoroughly vetted using a range of analytical techniques. Therefore, conservation scientists procure comparison materials from a variety of sources including historic collections of artists' materials, from vendors specializing in traditional artists' materials, and from major chemical suppliers. Occasionally, an historic artists' material is no longer produced, and so it must be synthesized by the scientist using modern materials and methods. The identity of these variously sourced materials is often accepted at face value and analysed using a single technique in the generation of reference library data. If the sample is in fact mislabelled or misrepresented, the resulting data is inaccurate and can impact future conservation science research.

As an example, Fig. 1 shows the Raman spectrum collected from bright green particles observed in the Kremer Pigmente product #40821 sold as *Green Earth from Verona, genuine, pure*. Despite the suggestion from the label that this is an untainted Italian earth pigment, the product was found to be significantly adulterated with the synthetic organic pigment phthalocyanine green [1]. It is currently unknown when the adulteration occurs during the mining, packaging, and material procurement process. It is speculated that these additions are made to maintain colour consistency in commercial pigments or to allow mining of the earth pigments into lesser quality deposits.

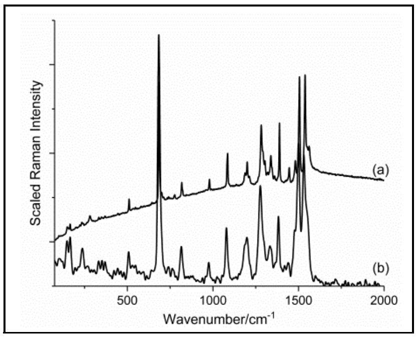

Fig. 1. Raman spectrum of (a) Kremer #40821 *Green Earth from Verona, genuine, pure* compared to (b) Kremer #23000 phthalocyanine green, PG7.

In 2010, the Indianapolis Museum of Art (IMA) opened its conservation science laboratory, and the lab began collecting reference materials to support ongoing technical studies and research and to generate in-house reference data for multiple analytical techniques. A surprising number of those samples proved not to be what was purported. In addition to products offered for conservation use, instances of inaccurate materials were found from major chemical supply houses and industrial vendors. The types of materials observed to be mislabelled or adulterated included dye botanicals, mineral pigments, plastics, and synthetic colorants. This presentation will discuss the issues inherent in reference material selection, the techniques used to verify composition and identity, and the few instances where synthesis of a commercially unavailable reference compound was required. The impact of these case studies on spectral library generation will be explored.

Acknowledgement
Financial support for this work was provided by the Butler Summer Institute, the Frenzel Family Charitable Lead Trust, the Carter Family Foundation, and John and Sarah Lechleiter.

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KEYNOTE PRESENTATION

Binders and pigments used in traditional Aboriginal bark paintings

N. KHANDEKAR[1], G. RAYNER[1], D.P. KIRBY[1] AND K. EREMIN[1],

[1]Straus Center for Conservation and Technical Studies, Harvard Art Museums, Cambridge, USA, narayan_khandekar@harvard.edu

In conjunction with the Harvard Art Museums exhibition *Everywhen: The eternal present in Indigenous art from Australia*, the Straus Center for Conservation and Technical Studies, has conducted a major survey of the pigments and binders used in traditional Aboriginal bark paintings from Arnhem Land, Groote Eylandt, the Kimberley and the Tiwi Islands. Paints were analyzed for: binding media using Fourier transform infrared spectrometry and pyrolysis gas chromatography mass spectrometry; pigments by laser ablation-inductively coupled plasma-mass spectrometry and Neutron Activation Analysis (NAA) to determine if an elemental fingerprint could be identified. Approximately two hundred samples from fifty paintings were analyzed from: Museum Victoria; Ian Potter Museum of Art, University of Melbourne; National Gallery of Australia; Art Gallery of New South Wales; Australian Museum; National Gallery of Victoria; Macleay Museum, University of Sydney; Peabody Museum of Archaeology and Ethnology, Harvard University. The following art centers provided standard pigments and binders: Buku Larrnggay Mulka, Yirrkala, NT; Tiwi Design, Bathurst Island, NT; Warringarri, Kununurra, WA. In addition conversations were had with artists and co-ordinators working at the art centers to determine consistency or variation from the written anthropologist's accounts.

Binders were detected in 77% of the samples analyzed. No proteins, waxes, fats or blood were observed as a binder. The presence of nitrocellulose on Groote Eylandt paintings was connected to records from the 1948 expedition linking the condition of the paintings to an application of Duco to consolidate them. In addition evidence of an insect repellant from the same expedition was also detected. Materials, such as battery black and commercial silver paint were identified and analyzed on paintings from the 1940s and 1920s showing that artists were willing to incorporate new materials into their practice as they became available. Orchid juice was chemically identified as a binder in a painting for the first time and was identified in the oldest bark paintings dating to pre-1878. The concentration of orchid juice in the paint samples can be seen as an indication of the application methods.

The use of a variety of blacks from Groote Eylandt was identified as originating from natural manganese ore, dry cell batteries and charcoal. The differences in elemental fingerprints between ochres of the same location, as well as from painting samples indicates that more studies are required on a local level to determine the source and movement of ochres.

Acknowledgement
Thanks to Tom Lentz, Stephen Gilchrist , Mary Schneider-Enriquez and colleagues from Harvard Art Museums; Lindy Allen, Val Brown, Samantha Hamilton, Melanie Roberts and Dermot Henry from Museums Victoria; Chris MacAuliffe, Jay Miller and Robyn Hovey from the Ian Potter Museum of Art, Melbourne University; Beata Tworek-Matuszkiewicz and Debbie Ward from the National Gallery of Australia; Kerry Head, Paula Dredge and Sarah Bunn from the Art Gallery of NSW; Colin MacGregor, Penny Norton and Rebecca Fisher from the Australian Museum; David Ellis, Alayne Alvis and Jude Philp from the Macleay Museum, Sydney University; Carl Villis, Marika Strohschnieder and Judith Ryan from the National Gallery of Victoria; Christina Hodge, William Fash, David Pilbeam, T. Rose Holdcraft and Scott Fulton from the Peabody Museum of Archaeology and Ethnology, Harvard University; Michaela Schmull and Emily Wood from the Harvard University Herbaria; Steve Anderson and Gordon Pupangamarri from Tiwi Design; Cathy Cummins, Peggy Griffiths, Alan Griffiths and Lachlan Raymond from Warringarri Aboriginal Arts; Will Stubbs, DJ Djuwakan 2 Marika, Barayuwa Munungurr, Kade McDonald, Nyapanyapa Yunupingu and Mulkun Wirrpanda from Buku-Larrnggay Mulka Center. The authors would like to thank His Excellency the Honorable Kim Beazley AC for his support of this. An enormous thanks to the Committee for Australian Studies at Harvard University, especially David Haig, Chris MacAuliffe and Maria Gough, for supporting and funding this research.

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FULL PAPER

Project plastics: how to identify plastics without a lab

S. DE GROOT[1], C. VAN AUBEL[2], O. VAN ROOIJEN[2], H. VAN KEULEN[1]

[1]Cultural Heritage Agency of the Netherlands (RCE), Hobbemastraat 22,1071 ZC, Amsterdam, the Netherlands.
s.de.groot@cultureelerfgoed.nl
[2]Foundation for the Conservation of Contemporary Art (SBMK), Hertogstraat 5, 5211 AN ,'s Hertogenbosch, the Netherlands

Collections of contemporary art and design objects contain numerous artefacts made of plastic. To identify the material composition of these objects specialist knowledge is required, which is often not present in museums without a laboratory. The Plastics Project[1] brings together conservation scientists, conservators and no less than ten major museums and curators in the Netherlands. The projects aim is to develop a do-it-yourself method comprising a digital identification tool and a do-it-yourself kit, by which means administrators and conservators will be enabled to identify a large part of their plastic collections themselves, to monitor them and take appropriate measures for preventive conservation.

The objective of the project is to improve the sustainability, visibility and accessibility of objects made of plastic. A representative part of the collections of the ten museums will be identified and registered in the museum information systems. Participants learn to identify plastics 'on the job' and when needed additional research using Fourier Transform Infrared Spectroscopy (FTIR) will be carried out. By developing preventive measures in collaboration, plastic collections will be maintained in a proper way and knowledge will be secured within the organizations.

During the first phase of the project (April 2017 - April 2018) the digital identification tool for the identification of plastics and the do-it-yourself kit have been developed, this provides a basic means for identification and a digital platform helps collection managers by distributing information on the most common and / or problematic types of plastics. Those examples are illustrated by iconic works to which the plastics have been applied.

During the second phase (April 2018 - April 2019) ten surveys in the collections of the participating museums will be carried out during on the job workshops, in which collection keepers of participating institutions work closely with the four scientists from the Cultural Heritage Agency of the Netherlands (RCE). Results obtained using the digital identification tool are evaluated using portable FTIR equipment.

During the presentation at IRUG13 an overview of the project, the development of the digital identification tool, the development of the do-it-yourself kit and results of the surveys will be presented.

Acknowledgement
The Plastics project is coordinated by the Foundation for Conservation of Contemporary Art (SBMK) and the Netherlands Institute for Conservation, Art and Science (NICAS), a collaboration between the Cultural Heritage Agency of the Netherlands (RCE), Rijksmuseum, the University of Amsterdam and the University of Delft. Partners in the project are: Bonnefantenmuseum, Centraal Museum Utrecht, Gemeentemuseum The Hague, Kröller-Müller Museum, Museum Boijmans Van Beuningen, Schunck*, Stedelijk Museum Amsterdam, Van Abbemuseum, Rabo Art Collection and Collections of the RCE. This project has kindly been supported by financial contributions from the Gieskes-Strijbis Fund and Mondriaan fund.

FULL PAPER

Assessment of chemical ageing of cellulose acetate.

S.L. GATENBY [1]

[1] Museum of Applied Arts and Sciences, 500 Harris Street, Ultimo, 2007 NSW, Australia. sueg@phm.gov.au

Historic collections give researchers the opportunity to analyse aged materials and study their deterioration. Over time, these samples have become a reference collection for these studies. This paper is an example of how museum reference samples were used to assess the chemical ageing of cellulose acetate.

The MAAS Powerhouse Museum has a historic collection of cellulose acetate samples from the 1930's. Cellulose acetate is originally associated with photographic films, but it is the first plastic, along with cellulose nitrate used by artists. Cellulose acetate is now degrading in sculptures by Naum Gabo and paintings on cellulose acetate by Laszlo Moholy-Nagy.

A recent request from the Getty Conservation Institute for access to our 1930's cellulose acetate samples was received. Two types of analysis were proposed. Gas Chromatography Mass Spectrometry (GCMS) to determine % plasticiser and Ion Chromatography (IC) to calculate % acetyl for the cellulose acetate. The types of plasticizers were also identified. The research interest was for data to help with determining deterioration factors for modern artworks as well as the Walt Disney animation cells.

The Getty analysis was undertaken, and results found that 2 cellulose acetate samples were in poor condition; 0% acetyl values, with the complete loss of acetate and were now cellulose only. Also, they had lost significant amount of their plasticisers less than 0.1%. The other samples were ½ de-acetylated and showed that they were actively deteriorating. These analytical methods can quantify the degradation of the cellulose acetate.

MAAS carried out ATR-FTIR analysis of the historic 1930's cellulose acetate samples to determine any correlations with the Getty study. The ATR-FTIR results shows decreasing levels of acetyl group, and complete loss of the acetyl group for the fully deteriorated samples. The spectrum is now cellulose. Identification of the compositional differences between the samples was carried out.

This loss of the plasticiser and acetyl groups cause significant changes to the samples. From a flexible film to a brittle and extremely fragile sample. These 3 identification methods showed that as the cellulose acetate degrades there is a decrease in levels of acetyl group (de-acetylation) with proportional increase in the hydroxyl group and loss of plasticiser.

MAAS study demonstrated that the ATR-FTIR is a value tool for non-invasive identification and assessment of cellulose acetate degradation. The calculation of percentage of plasticiser and acetyl group provided a more detailed assessment of the deterioration, although it was an invasive method it used very small samples sizes. To be able to get a close up picture of the deterioration, it is necessary to undertake this level of analysis to fully understand the chemical ageing of these samples.

Acknowledgement
Joy Mazurek, Assistant Scientist, the Getty Conservation Institute.
Professor Robert Burford, Museum of Applied Arts and Sciences.

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FULL PAPER

Application and advantages of external reflection in the material determination of photographic materials, negatives and film for a fast material testing via FTIR spectroscopy

T. ALLSCHER[1]

[1]Division Material Science and Art Technology, Institute for Conservation and Restoration,
Bayerische Staatsbibliothek, Ludwigstraße 16, 80539 München, Germany, T +49 (0)89 - 28638-2396,
Email: thorsten.allscher@bsb-muenchen.de

For an informed decision on specific preservation requirements, restoration and conservation treatments or storage/exhibition environments a detailed analysis or at least a basic determination of materials is essential. For photographic material, e.g. spot testing is still a common method to determine the emulsion type to distinguish between albumin, collodion or gelatin. Although meaningful, this test is neither non-invasive nor contactless, but alters the object at the site being examined.

A more specific and non-invasive method to analyze the photographic materials is the application of ATR-FTIR spectroscopy. With the release of "The Atlas of Analytical Signatures of Photographic Processes"[1] an extensive reference work on the use ATR-FTIR spectroscopy of the different types of photographs is available. All common types of photographs are analyzed and the interpreted ATR-IR spectra can be used to identify the measured samples.

The application of ATR-FTIR spectroscopy becomes difficult when the photograph has a delicate surface or is glued to an album and the sample does not get enough contact to the surface of the ATR unit for an clear measurement.

In these and other cases, the external reflection mode is a worthy and truly non-invasive and contactless alternative measurement. Various examples show the applicability of external reflection to identify the photographic material although the resulting spectra are not directly comparable to the known and published ATR-FTIR spectra.

Even more powerful is the application of external reflection to identify negative and film material via rapid noninvasive Transflection FTIR spectroscopy with an aluminium foil reflector.

Cellulose nitrate is highly flammable and can be dangerous, producing toxic gases and in extreme cases, exploding in the event of a fire. It is essential to locate and identify this material in the collections to take care of correct storage, copying or disposal of such negative and film material.

Acetylated cellulose plastic negatives and transparencies of all forms (diacetate, acetate butyrate and triacetate, etc.) are unstable and eventually shrink and release acetic acid vapour (known as vinegar syndrome) which can affect neighbouring collections.

It is very important to have a fast and reliable method to determine the materials beyond any doubt. As negatives are coated with gelatin on both sides on the film there is almost no possibility to measure the carrier material with ATR-FTIR spectroscopy.

The application of an aluminium reflector allows the measurement of all layers, the materials show clearly distinguishable spectra, which allow a quick and easy identification of the carrier material of negatives or film (Fig. 1).

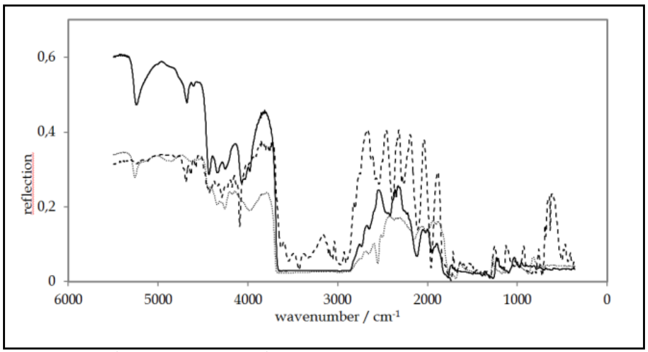

Fig. 1. Transflection spectra of nitrate (dotted line), acetate (solid line) and polyester (dashed line) negative material.

The presentation will introduce the advantages of external reflection in the material determination of photographic materials, negatives and film for a fast, contactless und non-invasive material testing via FTIR spectroscopy.

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FULL PAPER

A spectroscopic investigation of Paraloid blends for use as archaeological adhesives

Z.M. Xu[1], P.S. Thomas[1] and H. Jones-Amin[2] and B. H. Stuart[3]

[1]School of Mathematical and Physical Sciences, University of Technology Sydney, 15 Broadway, Ultimo, 2007, NSW, Australia
[2]Monash Indigenous Studies Centre, Monash University, Clayton, 3800, VIC, Australia
[3]Centre for Forensic Science, University of Technology Sydney, 15 Broadway, Ultimo, 2007, NSW, Australia
email.barbara.stuart@uts.edu.au

Paraloid B72 is an acrylic resin, comprised of an ethyl methacrylate – methyl acrylate copolymer, commonly used by conservators for the repair and conservation of a multitude of objects. The advantageous mechanical properties, stability, transparency and reversibility of this resin has seen it widely adopted. However, the applicability of this adhesive for use in hot climates has been raised in several studies [1,2]. Issues with the properties of Paraloid B72 have been reported with its use on ceramic objects being repaired at the Kaman-Kalehöyük archaeological site in Turkey, where high working temperatures are regularly encountered. As Paraloid B72 has a glass transition temperature (T_g) of 40°C, the adhesive will soften in hot environments and its applicability in archaeological sites located in hot regions is limited. An established method of modifying the T_g of polymers is to blend with another polymer with a suitable T_g. Conservators have made attempts to improve the working properties of Paraloid B72 by blending with other polymers such as Paraloid B48N (a methyl methacrylate-butyl acrylate copolymer) and Butvar B98 (poly(vinyl butyral)) [2].

For the current study, mixtures of Paraloid B72 and Paraloid B48N have been investigated in order to establish if this combination currently used in the field provides a suitable improvement on pure Paraloid B72 as an adhesive. Infrared and Raman spectroscopies have been employed to examine the structural properties of blends produced over a range of concentrations in different solvent systems. Thermal analysis has also been used to determine the miscibility and glass transition temperatures of the blends.

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FULL PAPER

A Case Study: Two Newly Discovered Jackson Pollock Paintings?

T. J TAGUE, JR.[1] AND J. KNOWLES[2]

[1]*Bruker Corporation, 40 Manning Road, Billerica, MA 01821, USA tom.tague@bruker.com*
[2]*MicroVisionLabs Inc., 187 Billerica Road, Chelmsford, MA 01824, USA John@MicroVisionLabs.com*

Jackson Pollock was a complex individual who had a tremendous impact on the art community with his unique style, technique, and vision. His works have attracted the attention of experts in the field of art conservation and authentication for many years. More recently, there have been discoveries of new paintings being possibly attributed to Pollock. In performing an authentication of any art object, it is important to consider provenance first, followed by careful technical analysis. Lastly, a thorough scientific analysis should be performed.

In this investigation, two paintings are reported to have been given as payment to a hotel located in Mill Hall, PA in 1952 or earlier. The custody of the paintings is well documented from this point on. The two paintings were purchased privately in 1991 by the current owners. The previous owner purchased both paintings from the Lockhaven Motel in 1961, while traveling through Mill Hall as a salesman. The Lockhaven motel which was opened in 1961 by Ralph Vogel was razed from the Clintonian Hotel Tavern, which opened in 1946 and purchased by Mr. Vogel in 1952. The paintings are applied to Masonite board that was readily available in the time frame under consideration. The paintings, not being considered of high value at the time, had been trimmed to fit into frames already available to the owner. One of the paintings has a Jackson Pollock signature and the other is absent of any signature. There is paint splatter on the back of both objects and three partial fingerprints on the multicolored painting (Mill Hall 1). On the predominantly black and white painting (Mill Hall 2), it would appear that Pollock experimented with applying paint in the form of letters using his unique form, fig. 1. He used his own name in doing this and the letters of his name are evident under close examination.

Fig. 1. Mill Hall 2 painting with Jackson Pollock lettering evident on bottom half of object.

The scientific analysis of these two paintings was conducted utilizing well established methods. A visual analysis of the objects was performed using light from the UV to the NIR. This allowed for the identification of any potential underlying drawing or painting. An elemental analysis was conducted using x-ray fluorescence (XRF) spectroscopy and the chemical analysis utilizing infrared (IR) and Raman spectroscopy. The resulting spectra were compared to reference spectra collected from pigments of that time. Microscopic sections were removed in order to perform the microscopic IR and Raman microanalysis. A handwriting analysis was conducted by an expert in the field to compare the signature to other signatures previously attributed to Pollock. Lastly, the retained fingerprints were analysed by an expert in Pollock fingerprints. The results of the investigation will be presented.

FULL PAPER

Macro-X-ray fluorescence in combination with micro-Raman spectroscopy in the battle against forged paintings: a powerful synergy

S. SAVERWYNS[1], W. FREMOUT[1] AND A. COUDRAY[1]

[1]Royal Institute for Cultural Heritage (KIK-IRPA), Painting Lab, Jubelpark 1, 1000 Brussels, Belgium, steven.saverwyns@kikirpa.be

Copies or fake works of art have plagued the market for centuries. With prices of works of art on the rise, it can only be predicted that falsifications will keep on flooding the market, as illustrated in the recent past by numerous cases in which works of art are exposed as being fakes. Identifying fake works of art has for long time been the exclusive field of 'the expert', often a specialised art-historian. However, with the rise of technology the expert's opinion has more and more been supported by scientific analyses. Often these analyses can now be the starting point in the authentication study: when material-technical analysis can prove the work to be a copy or a fake, the often hard-to-reach expert is no longer needed.

In this presentation the focus is placed on analytical authentication studies of (modern) paintings. Identification of synthetic organic pigments (SOPs), mainly introduced in the 20th century, is often of key importance. With well-known dates of discovery or commercialisation, identification of SOPs permit to postulate an earliest possible creation date of a painting, which in turn can provide information on its authenticity. Micro-Raman spectroscopy is currently the most adequate technique of identifying SOPs thanks to its high sensitivity and specificity, combined with a non-destructive and even non-invasive character. Analysing a complete painting by micro-Raman spectroscopy, however, can be time-consuming, especially when inorganic pigments are analysed, that can be more easily identified by other means such as X-ray fluorescence (XRF). This last technique used to be also a point analysis technique, but since the introduction a few years ago of macro-XRF (MA-XRF), the complete paint surface can be scanned. As such, element distribution maps are obtained, showing where inorganic pigments are located, often permitting their identification. On the other hand, when the colour observed cannot be explained based on the MA-XRF results, the presence of SOPs is a possibility. MA-XRF hence permits to identify quickly inorganic pigments, and allows to localise SOPs which can in turn be identified by micro-Raman spectroscopy.

The synergy of both techniques will be illustrated through several case studies conducted over the last years. The substantial number of paintings investigated, allows also to summarize which SOPs are (most frequently) encountered in copies and fakes.

FULL PAPER

Portable Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for non-invasive screening and identification of varnishes in painting collections. A pilot study on paintings by Edvard Munch

T. FORD[1], A. RIZZO[2], E. HENDRIKS[3], T. FRØYSAKER[4] AND F. CARUSO[4]

[1]The National Museum of Art, P.O. Box 7014, St.Olavs Plass, 0130, Oslo, Norway. thierry.ford@nasjonalmuseet.no
[2]The Metropolitan Museum of Art, 1000 5th avenue, New York, 10028, NY, USA
[3]University of Amsterdam (UvA), Programme Conservation and Restoration of Cultural Heritage, Johannes Vermeerplein 1, 1071 DV, Amsterdam, Netherlands
[4]University of Oslo (UiO), Institute for Archaeology, Conservation and History (IAKH), Conservation Studies, Postboks 1008 Blindern, 0315 Oslo, Norway

The availability and popularity of portable non-invasive instrumentation for the study of paintings has increased due to a shift away from the micro-invasive techniques [1]. Fourier transform infrared spectroscopy (FTIR) is a successful and established technique used for the characterisation of organic materials in paint films and varnish coatings. In addition, portable FTIR (pFTIR) spectrometers allow for non-invasive and *in situ* analyses. This overcomes the disadvantages associated with micro-sampling from a specific spot, as the pFTIR enables unlimited examination of the painted surface [2]. However, the practical applications and capabilities of pFTIR as a suitable screening method for the chemical characterization of varnish coatings in painting collections require systematic evaluation.

This pilot study involves a selection of paintings taken from the collection of 56 works by Edvard Munch belonging to The National Museum of Art (NMK) in Norway. Between 1909 and 1980, the Museum was embroiled in a varnish controversy due to their application of, first natural and then synthetic, varnish coatings to 48 of the Munch paintings. A series of public debates opposed the Museum's varnishing practice, especially regarding unvarnished works, questioning the authenticity of the artist's paint surfaces [3].

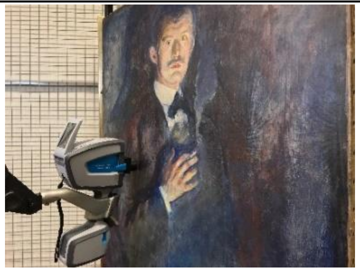

Fig. 1. Detail of pFTIR set up during varnish examination of Munch's Self-Portrait with Cigarette (1895, NG.M.00470).

A selection of varnished and unvarnished Munch paintings was screened using an Agilent 4300 pFTIR spectrometer. Different regions of the painted surfaces were analysed in Diffuse Reflectance (DRIFTS). The examined paintings date from a similar period (1890s) and are documented as having been treated at the Museum with one of the following types of natural or low molecular weight synthetic varnish coatings: dammar, mastic, Matt Tavelferniss (Becker), ketone (polycyclohexanone, BASF) and MS2A (reduced or hydrogenated cyclohexanone-co-methyl-cyclohexanone, Howards of Ilford).

Surface microscopy and multispectral imaging (UV, 320-400 nm; IR, 700-1100 nm) of the varnished surfaces initially assisted the mapping and selection of areas relevant for the portable DRIFTS measurements. Reference spectra from known dry varnish samples were obtained and compared with spectra acquired from a select number of micro-samples, taken from the same spot locations. Further comparisons were also undertaken with DRIFTS spectra from aged mock-up samples of varnish.

Preliminary measurements undertaken in Spring 2018 showed promising results. Further tests, carried out in Summer/Autumn of 2018, will provide an insight into the capabilities, limitations and practical applications of portable DRIFTS for the identification of varnish coatings in paintings. Finally, the study will propose guidelines for employing portable DRIFTS on varnished paintings that can easily be adopted by conservators.

Acknowledgement
The authors wish to acknowledge the NMK for access to the paintings and for funding Thierry Ford's PhD study.

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FULL PAPER

Raman Spectroscopy and Laser Desorption Ionization Mass Spectrometry (LDI-MS) as complementary editors of structures of historical and novel azo-pigments

S.Q. LOMAX[1] AND J. F. LOMAX[2]

[1]*National Gallery of Art, 2000B South Club Drive, Landover MD 20785 USA e-mail.s-lomax@nga.gov*
[2]*Chemistry Department, U.S. Naval Academy, 572 Holloway Rd.., Annapolis, 21402, MD, USA*

Synthetic organic pigments (SOP's) have been used in works of art in various media for over 100 years. During this time, hundreds have been introduced.
Due to a variety of reasons, including cost and insufficient fastness properties, some SOPs have been removed from production. Their identification is very important because their definite chronological information is of use for authenticity issues and their lack of fastness may lead to conservation issues. Because of their limited range of time of commercial availability, samples of these historical pigments are often not available for characterization by modern analytical techniques. A large number of these historical pigments are azo (N=N) containing, including members of the pigment classes: arylide (Hansa) yellow, diarylide yellow and oranges, as well as the red Naphthol AS class.

A number of historical pigments were synthesized using traditional diazotization reactions. These two step reactions involve the formation of a diazonium salt in situ which is then reacted with appropriately functionalized coupling components to generate the pigment. The pigments synthesized include the Naphthol AS pigments PR7, PR10, PR11, PR18 and PR19, the arylide yellows PY49, PY98 and PY203 and the diarylide yellow pigments PY113, PY124, PO14 and PO15.[1] The pigments were characterized by Raman spectroscopy and Laser Desorption Ionization Mass Spectrometry (LDI-MS). In addition, a series of novel diarylide pigments derived a compound variously known as Naphthol AS-G or Diacetylacetotolidide were prepared.

Raman spectroscopy and LDI/MS provide complementary information about the pigment and are the most useful techniques for their characterization. LDI/MS was performed in both positive and negative ion modes; the negative ion spectra in general has less fragmentation and are useful in identifying the molecular ion. A representative Raman spectrum is shown in Figure 1 of PO14, a diarylide orange pigment. The strong aromatic ring vibration is found at 1602 cm^{-1}, 1401 cm^{-1} is due to the symmetric N=N stretch, the peak at 1325 cm^{-1} is also due to the symmetric stretching vibration of the azo group, peaks at 1237 and 1268 cm^{-1} are due to the C-H bending vibration, and the peak at 1123 cm^{-1} is due to the C-N stretch. LDI/MS and Raman spectra of the newly synthesized compounds will be shown.

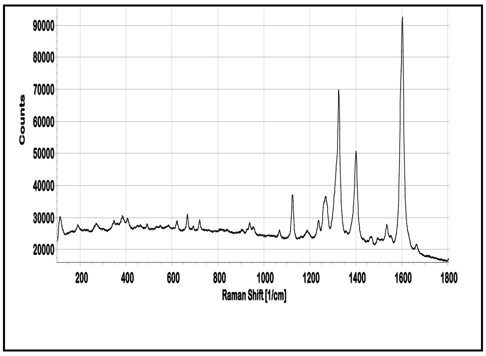

Fig. 1. Raman spectrum of historic pigment PO14

Acknowledgement
We acknowledge work done by undergraduate midshipmen at the United States Naval Academy, including Trevor Graham, Thomas Moore, Carly Knapp and Mary Campbell.

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FULL PAPER

Study of metal soaps protrusions in Georgia O'Keeffe oil paintings by FESEM-EDS and FTIR spectroscopy.

A. S. ORTIZ MIRANDA[1], J. SALVANT[2], M. WALTON[1] AND D. KRONKRIGHT[3]

[1]*Center for Scientific Studies in the Arts, Northwestern University, Evanston, IL, USA e-mail: annette.miranda@northwestern.edu*
[2]*C2RMF, Palais du Louvre, Paris, France*
[3]*Georgia O'Keeffe Museum, Santa Fe, NM, USA*

Protrusions observed in a significant number of oil paintings by Georgia O'Keeffe (1887 – 1986) varying with up to several hundreds of microns are associated to the presence of metal soaps. Metal soaps are compounds containing heavy metals combined with carboxylic acids, which aggregates into protrusions. This deterioration process affects a wide number of oil-based paintings belonging to all periods of art history worldwide. A large number of literature oriented to a better understanding of metal soaps protrusions formation and development can be found. The presence and potential ongoing growth of protrusions on paintings raises significant concerns for their long-term preservation. Characterizing the protrusions, their distribution over the surface of the artworks and monitoring their development has become a conservation priority for O'Keeffe oeuvre.

The study presented here focus on the characterization of protrusions and how this is related with the materials used by the artist. For this purpose, a multi-technique approach including FTIR and FESEM-EDS was performed. The FTIR analysis carried out confirms that the commercial primer is composed of lead white ($PbCO_3$), barium sulphate ($BaSO_4$) and calcium carbonate ($CaCO_3$). Examination of the samples revealed the presence of lead carboxylates in the ground and the paint layer (Mills et al., 2008; Tempest et al., 2010). The regions that are lead-rich correlate with the areas with higher occurrence of surface protrusions. These observations suggest that the specific type of lead white paint formulation employed by O'Keeffe and its proportion play an important role in the development of surface protrusions.

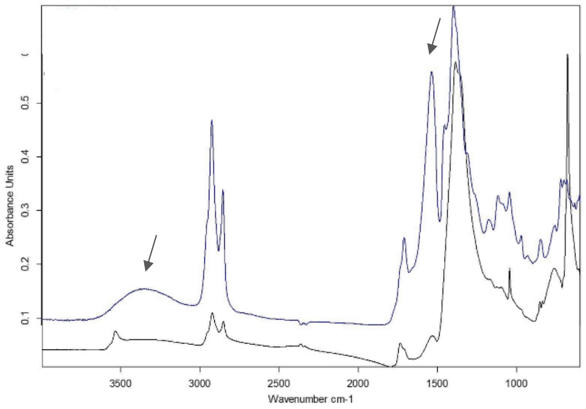

Fig. 1. FTIR spectra of a point in the protrusion (blue) and the immediate paint layer (black), most significant changes ascribed to the presence of metal-carboxylates are indicated by arrows.

Acknowledgement
Research at the NU-ACCESS is supported by generous grants from the Andrew W. Mellon Foundation and the National Endowment for Humanities (NEH).

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FULL PAPER

Investigation into the Behaviour of Hydrogenated Castor Oil in Modern Oil Paints

K. VERNON, N. TSE, C. GRECH

Grimwade Centre for Cultural Materials Conservation, The University of Melbourne, Swanston Street, Carlton, 3053, Victoria, Australia, kimvernon@gmail.com.au

In recent years there have been reports of hydrogenated castor oil (also known as HCO or castor wax) being used as an additive in commercial artists' oil paints by various oil paint manufacturers. Francesca Izzo (2010) noted that hydrogenated castor oil had been used in formulations by several modern oil paint manufacturers as a stabiliser and is 'normally added up to 2% by weight'[1]. The additions of HCO to oil paint formulations is possibly due to its function as rheology modifier to improve handling properties and perhaps the perceived quality of the paint; a stabiliser to reduce separation of pigment and binder in the tube; and as an extender to 'bulk out' the more expensive pigments or to reduce the tinting strength of particular pigments like the modern synthetic organic colours. Gillian Osmond (2013), however, considers the possible destabilising effects of HCO as a paint additive with zinc oxide in oil based paints[2].

Given these concerns, this paper investigates the behaviour of hydrogenated castor oil in oil paint films through materials analysis and discussions with an artists' oil paint manufacturer to assess the influence of HCO. Control and aged films with and without HCO were analysed with FTIR-ATR, GC-MS, colorimetry and gloss measurements to assess their behaviour, polymerisation, gloss, chroma and yellowing in the paint films. The results indicated that the paint films containing HCO were particularly sensitive to accelerated ageing techniques in comparison to the control samples. GC-MS obtained fatty acid data indicated a significant lowering of the palmitic/stearic acid ratio in aged HCO containing paint films. FTIR-ATR identified key differences between the HCO containing paints and control samples at the surface and paint/support interface.

It is hoped that this research can lead to a better understanding of the behaviour of HCO in modern oil colours by gaining insight into its effect on ageing oil paint films.

Acknowledgement
This research is part of a minor thesis project being undertaken at the Grimwade Centre for Cultural Materials Conservation, The University of Melbourne and we wish to acknowledge TRACEEs in the School of Chemistry.

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FULL PAPER

Surface analyses for conservation

D. THICKETT[1], B. PRETZEL[2]

[1]*English Heritage, Rangers House, Chesterfield Walk, London, SE108QX, UK e-mail.david.thickett@english-heritage.org.uk*
[2]*Victoria and Albert Museum, Cromwell St, South Kensington, London, UK*

Several FTIR techniques are surface sensitive. This sensitivity can be utilized to help with a wide range conservation problems, described below.

The Amplif-IR accessory uses an adjustable height gold mirror to bounce the IR beam many times across a surface. This can give extreme sensitivity, with the manufacturers' literature discussing detection limits in the order of 1nm films. Haze and smoke generators are increasingly being introduced into displays or for special events or filming. Concerns about impact on collection have led to commercial analysis trying to detect deposits. These analyses did not detect anything outside of rooms where the generators were used. The analysis relied on solvent extraction of exposed glass slides followed by drying and analysis on sodium chloride plates, but the detection limits where quite high. Dust deposition rate monitoring on glass slides exposed to the haze during filming, indicated a significantly increased deposition rate after re-opening. Gold coated glass slides were exposed to several haze types. Although the mineral oil used has only 3 peaks beyond those from CH stretching, these peaks were observed on several samples. Quantification using increasing dilutions indicated deposited amounts in the order of 10s of nanograms. This confirmation of residues is essential to determine the extent to which such haze spreads throughout a building, the effectiveness of any mitigation, and the risk this will pose to collections.

Renaissance wax coating of steel coupons were observed to increase the rate of corrosion (after a period) in the saline and high RH environment of Dover Secret Wartime Tunnels. The mechanism was obviously of interest. Two methods of analysis were undertaken with a Nicolet Inspect IR microscope running off an Omnic 360 bench. A silicon ATR head gave surface sensitivity of approximately 1.6 microns in the 1643cm-1 ν2 band of water. Direct reflection analysed the whole depth of the wax down to the metal surface. The wax layer thickness could be accurately measured as well with this technique. No bands attributed to water were observed in the ATR spectrum, whilst very strong bands were observed on the direct reflection spectrum. Careful, sequential removal of the wax indicated the water was concentrated in the lower 6-10 microns of the wax layer. Experiments exposing fresh samples to fluctuating RHs indicated that water deliquesced into pores in the wax and a layer in the bottom of the pores that remained for several weeks at low RH.

A series of important daguerreotypes of Darwin are displayed at Downe House. Crystals were observed on the surfaces of the glass in the original packets. These were analysed as sodium formate. The degree of degradation of the glass in different areas was important to understand the deterioration mechanism. Analysis of cross sections of the glasses with SEM-EDX could not detect a gel layer. This was hindered by the quality of the polishing of the glass resin interface. Analysis with Germanium ATR on a FTIR microscope gave strong evidence of glass deterioration. The inner glass surface was always more deteriorated and the degree of deterioration inversely correlated with the distance between the inner glass surface and the daguerreotype or brass matt surface.

Acknowledgement
We acknowledge Marianne Odlyha for kind access to the Amplif-IR equipment.

FULL PAPER

A spectroscopic look at Indian yellow pigment and related compounds

A. SHUGAR[1], R. PLOEGER[1], G.D. SMITH[2] AND V. CHEN[2]

[1]Patricia H. and Richard E. Garman Art Conservation Department, SUNY Buffalo State, 1300 Elmwood Ave, Buffalo, NY, 14222, USA
e-mail: shugaran@buffalostate.edu
[2] Conservation Science Laboratory, Indianapolis Museum of Art at Newfields, 4000 Michigan Road, Indianapolis, IN, 46208, USA

Indian yellow has been a mysterious pigment since it arrived in Europe in the 17th or 18th century [1]. A great amount of curiosity and research has been directed to understanding its origin over the past two centuries – was it earth, plant or animal based [1]? An 1883 written eye-witness account by T.N. Mukharji, an Indian government employee tasked with documenting its origin, appeared in the Journal of the Society of Arts [2]. This account was in response to a formal request from Sir Hooker at the Royal Botanical Gardens, Kew (England) who wanted to understand the origin of the pigment, and who also wanted to facilitate a scientific sample and analysis request from Prof. Graebe (Geneva, Switzerland). T.N. Mukharji described a small group of milkmen who produced the pigment from the urine of cows fed a mango-leave rich diet [2], which corroborated some concurrent thoughts in Europe, though disagreed with others.

Mid and late 19th century research into the pigment was motivated by the unverified reports that it was a urinary sediment. Scientists were interested in its chemical structure and composition, and if and how it related to metabolic pathways; by the late 1870s the chemical structure of the pigment was correctly identified as a glucuronic acid conjugate of euxanthone [1]. Prof Graebe was aware of this work as he references it in his report [3], though in the next 20 years, this connection between biochemical research and artists' pigment was lost. As well, in the early 20th century, the manufacturing of the pigment ceased, as well as all known local written and oral knowledge. It wasn't until the 1980s with the publication of Artists' Pigments, whose first chapter was about Indian yellow, that the general interest of this pigment was revived [4].

T.N. Mukharji ended his 1883 report [2] with a list of production materials and pigment-ball samples sent to Sir Hooker in Kew. These samples were rediscovered in the Economic Botany Collection in Kew in 2016 and characterized alongside known reference materials of Indian yellow. This paper will describe the spectroscopic analysis – Fourier transform infrared spectroscopy and Raman Spectroscopy - of the materials in the context of the theory of an animal origin. Differences between the exterior and interior of the pigment-balls will be described, along with observations of residues on pigment production tools. A series of known Indian yellow reference samples with varying degrees of processing were also investigated. Finally, euxanthone was prepared in the laboratory for comparison purposes, and these studies are the first to report the spectral data for this compound.

Fig. 1. A sample of an unprocessed pigment-ball of Indian yellow (Economic Botany Collection, Kew)

Acknowledgement
We sincerely thank the Economic Botany Collection at the Royal Botanic Gardens at Kew for allowing us to visit and to sample the collection. We would also like to thank Nicholas Walt at L. Cornelissen & Son (London, UK) for visiting with us, sharing his colourman's knowledge, and giving us a sample of Indian yellow. We would also like to thank Narayan Khandekar at the Straus Center for Conservation and Technical Studies (Cambridge, MA, USA) for providing the Forbes collection samples. Finally, we would like to thank the Andrew W. Mellon Foundation for providing funding for travel and research, and The Carter Family Foundation and John and Sarah Lechleiter for support of the IMA at Newfields dye analysis program.

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FULL PAPER

Characterisation of contents from the coffin of the 2500-year-old Egyptian mummy Mer-Neith-it-es

J. R. FRASER[1], C. LORD[1], M. L. WOOD[2], T. M. HARRISON[2] AND E. A. CARTER[2]

[1]Sydney University Museums, Nicholson Collection, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia, james.fraser@sydney.edu.au
[2]Sydney Analytical, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia

In 1858, Sir Charles Nicholson purchased an Egyptian cedar-wood coffin made for the woman Mer-Neith-it-es from Saqqara, Egypt, and donated it to the University of Sydney as a foundation piece for the Nicholson Museum. Although previously thought to be empty [1], the coffin contains the heavily disturbed remains of a mummy, torn apart by tomb robbers looking for amulets and jewels.

The mixed contents include bandages, bones, beads and resin. It is highly unusual for complete but disturbed mummies to survive in museum collections, as museums have historically sought complete mummies for display. Most extant mummies are thus well-preserved specimens within undisturbed bandages. Consequently, scientific investigation of mummies is usually limited to non-invasive and non-destructive techniques. The mixed remains within the Mer-Neith-it-es coffin therefore present a unique opportunity to conduct a comprehensive suite of scientific analyses of a mummified individual.

This paper presents some preliminary results of a collaborative project between the Nicholson Museum and Sydney Analytical. Raman, IR and XRF analyses were undertaken to investigate the various objects excavated from the coffin in 2018.

Fig. 1. Disarticulated contents inside the cedar coffin of the woman Mer-Neith-it-es; 26th Dynasty (664 BC - 525 BC, Saite Period); Saqqara, Lower Egypt (NMR.29.1-2) Nicholson Museum, the University of Sydney.

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FULL PAPER

Identification and Characterisation of Faience beads from the coffin of the 26th dynasty Egyptian mummy Mer-Neith-it-es

M. L. WOOD[1], T. M. HARRISON[1], E. A. CARTER[1], M. WHITFORD[2], C. LORD[3] AND J. R. FRASER[3]

[1]Sydney Analytical, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia, m.wood@sydney.edu.au
[2]Department of Physics and Astronomy, Macquarie University, Balaclava Road, North Ryde, 2109, NSW, Australia
[3]The Nicholson Museum, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia

In 1860, the Nicholson Museum acquired a cedar-wood Egyptian coffin for the lady Mer-Neith-it-es. Dated stylistically to the 26th Dynasty (664-525 BC), the coffin contained the heavily disturbed remains of a mummy that had been torn apart by tomb robbers. These remains were excavated in March 2018, yielding an astonishing assemblage of materials including bones, bandages and resin.

However, the most surprising discovery was over 7,100 beads, found scattered throughout the disarticulated remains. These beads derive from a beaded net, once placed over the body within the coffin, but destroyed by robbers searching for amulets and jewels within the bandages beneath. The beads exhibit an extraordinary range of size, colour, shape and materials, suggesting that the net would have been woven with intricate designs, probably associated with the god Osiris, guardian of the dead. The beads were made from materials including glazed faience, bone or ivory, and variously coloured stone.

Here we present the initial results of a collaborative project between the Nicholson Museum, Sydney Analytical at the University of Sydney and Macquarie University that uses a combination of Raman, IR and XRF spectroscopies for the identification and characterisation of the beads. Understanding the full range of local and imported materials used within a single net will reveal information about the complexity of the Egyptian trade economy in the 26th Dynasty and will help to determine the social status of Mer-Neith-it-es herself.

Fig. 1. Cedar coffin of the woman Mer-Neith-it-es; 26th Dynasty (664 BC - 525 BC, Saite Period); Saqqara, Lower Egypt (NMR.29.1-2) Nicholson Museum, the University of Sydney.

Acknowledgements
The authors would like to acknowledge the support provided by the Core Research Facilities (CRF), at The University of Sydney, for funds provided to purchase the equipment used in this study.

FULL PAPER

Infrared chemical mapping of degradation products in cross-sections from paintings and painted objects

E. J. HENDERSON[1]

[1]*Canadian Conservation Institute, 1030 Innes Rd., Ottawa, Ontario, K1B 4S7, Canada, eric.henderson@canada.ca*

Works of art and cultural heritage objects are continuously subjected to degradation processes that can significantly compromise their integrity, function and aesthetic quality. One of the primary objectives of the Conservation Science Division at the Canadian Conservation Institute (CCI) is to assist heritage institutions and professionals by undertaking detailed chemical and materials analysis of these objects. Documenting their composition is the first step in ensuring their conservation, by providing important information both about their material history as well as their state of preservation.

Paintings and painted objects in particular are quite susceptible to degradation. Paint layers are usually composed of complex mixtures of materials that can participate in chemical degradation processes. The identification of the constituent materials in paint (including binders, pigments, and fillers) and the degradation products within paint layers is of particular importance, as it can further our understanding of the chemical species, interactions, and mechanisms that are involved in these processes, inform treatment plans to address and target specific problems, advise on display and storage in museums, and advance the knowledge of the materials and techniques of the artists who created the works.

This contribution will present the materials analysis of several cross-sections from paintings and painted objects from works in Canadian collections. Recent results on the use of FTIR chemical mapping, undertaken at the Canadian Light Source synchrotron facility, to map the distribution of paint components and metal fatty acid salt (metal soaps) degradation products in cross-sections from several paintings will be presented. In particular, the talk will highlight results on the mapping of zinc soaps in the paintings *Nature morte à la mandolin* (1952-1953) by Jean Dallaire, *Equations in Space* (1936) by Lawren Harris, and *Womenizer* (2004) by Alex Janvier, lead soaps in *L'Annonciation* (1776) by Jean-Antoine Aide-Créquy, and calcium soaps in *Le martyre de Saint-Pierre de Vérone* (mid-nineteenth century) by Théophile Hamel. As well, the mapping of copper and calcium soaps in a cross-section from a ceremonial copper object (T'lakwa) from the Kwakwaka'wakw First Nation will be presented.

Many of the samples were analyzed using different instrumental configurations, including synchrotron reflection-FTIR single point analysis, external reflection-FTIR spectroscopy with a wide field of view FPA detector, and ATR-FTIR spectroscopy with an FPA detector with a narrower field of view. FTIR spectra and mapping results obtained using these different instrumental configurations will be compared, and the strengths and challenges of each technique discussed. The use of spectral transformations for the correction of reflection spectra will be also be highlighted, as well as the choice of spectral integration windows for samples with mixed metal fatty acid salts.

FULL PAPER

Infrared microspectroscopy of cultural heritage materials at the Australian Synchrotron

M. J. Tobin[1], J. Vongsvivut[1] D. E. Martin[1], K. R. Bambery[1], T. T. M. Ho[1], D.R.T. Appadoo[1], R. Plathe[1], L. Puskar[2]

[1]Australian Synchrotron, ANSTO, 800 Blackburn Road, Clayton, VIC 3168, Australia
[2]Helmholtz-Zentrum für Materialien und Energie GmbH, Berlin, 12489 Germany

The Australian Synchrotron operates two infrared beamlines for infrared spectroscopy and microspectroscopy. The Infrared Microspectroscopy (IRM) beamline operates in the mid-IR spectral range for the microanalysis of solid materials, whereas the THz/Far-IR beamline operates the far-IR spectral range for the study of both gases and solids.

The IRM beamline is equipped with a Bruker Hyperion 3000 FTIR microscope, which provides a highly focused infrared beam with a spot size of between 5 and 10 microns. The ability of this system to provide high signal-to-noise FTIR spectra from micron-scale particles has led to many applications at the beamline in the cultural heritage field, with up to 25% of all scheduled experiments during some allocation periods being in the areas of cultural heritage and forensic science. The beamline provides multiple sampling accessories and measurement configurations, including transmission analysis through a micro-compression cell and a heated stage, reflectance and grazing angle analysis of surfaces, and micro ATR analysis of materials that cannot be prepared for transmission.

More recently, the IRM beamline has offered a "macro" ATR accessory, which enables rapid FTIR mapping of materials with minimum sample preparation with a lateral resolution of around 1 micron, with a requirement to only bring the ATR crystal into contact with the sample once.

Studies conducted successfully at the IRM beamline have included the analysis of pigments in a paint multilayer from the exterior of a historic building in Fitzroy, Victoria, in which micron-scale particles of Prussian Blue were identified by micro ATR analysis of embedded and polished paint fragments [1]. Transmission FTIR of microscopic samples of material enabled the analysis of pigments present in ochres used in the aboriginal Australian rock art from Jawoyn Country, Arnhem Land, Australia [2]. This study was completed using complementary Raman and X-ray diffraction analysis, whereby the FTIR spectra of particles of distinctive red, yellow and purple pigments confirmed the presence of goethite, and showed evidence of heating of haematite in the production of the purple pigment. In a study that was conducted to understand better the potential hazards that may exist within the collection of Museums Victoria, three sets of poison-tipped darts, acquired from Malaysia between 1873 and 1971, were analysed for evidence of residual toxins within the tip coatings. Analysis of microscopic particles from the dart tips positively identified cardiac glycoside toxins, as well as other plant derived materials used in the production of the tip coatings [3].

Fig. 1. Malaysian darts and bamboo quiver (X 008904), from which poison was identified.

The far-IR spectral range may offer additional chemical information for cultural materials, in particular for paints and pigments, where compounds containing heavy metals might be expected to have absorption peaks beyond the spectral sensitivity range of our mid-IR microscope detector. For this purpose we have conducted successful preliminary measurements on the IRM beamline using a bolometer detector, extending the spectral range to 250 cm^{-1}, and on the THz/Far-IR beamline where the spectral range extends to around 10 cm^{-1}.

Acknowledgement
We gratefully acknowledge Museums Victoria for the use of the images of Malaysian darts and bamboo quiver shown in Fig. 1.

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FULL PAPER

FTIR and Raman spectroscopy in combination with XRF for the characterization of medieval manuscripts on parchment

M. SCHREINER[1,2], W. VETTER[1], B. FRÜHMANN[1], AND F. CAPPA[1]

[1]*Institute of Science and Technology in Art, Academy of Fine Arts, Schillerplatz 3, Vienna, 1010, Austria*
m.schreiner@akbild.ac.at
[2] *Institute of Chemical Technologies and Analytics, Technische Universität Wien, Getreidemarkt 9, Vienna, 1060, Austria*

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. Simultaneously, the booming development of analytical methods has offered the possibility to use a great number of new micro-analytical techniques with non-sampling and in-situ applicability for the material analysis of written heritage objects [1]. The Centre of Image and Material Analysis in Cultural Heritage (CIMA) in Vienna is the result of such an interdisciplinary co-operation and represents an interuniversity research institution for the investigation of cultural heritage [2]. The presentation gives an overview of this interdisciplinary project, where the material investigations aim to determine the composition of inks, pigments, and binding media used for the text and the illumination, as well as the characterization of the writing support (mainly parchment). These investigations 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 in the reflection mode (rFTIR) 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 characterized and 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.

The manuscripts investigated so far originate from the Medieval Ages and are 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), Bibliotheca Comunale Trento (Italy), National and University Library Ljubljana (Slovenia), National Library Budapest (Hungary), National Library Zagreb (Kroatia) and finally in the Biblioteca Apostolica Vaticana (Vatican).

Within this selection, 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, 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.

In the course of the project, a common database will be implemented which contains the information gained from the imaging, image enhancement as well as chemical and philological investigations. The final objective of the research is to compare the data gained to reveal correlations within data stemming from multiple modalities and, in general, to make new scholarly and scientific findings.

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FULL PAPER

Salvator Mundi: An Investigation of the Materials and Techniques

N. Gutman Rieppi[1], B. A. Price[2], K. Sutherland[3], T. J. Tague, Jr.[4], R. Newman[5], P. Wang[4], and T. Wang[4]

[1]*Art Analysis & Research, LLC, New York, NY 10036, USA nrieppi@artanalysis.com*
[2]*Philadelphia, PA 19101, USA*
[3]*The Art Institute of Chicago, 111 S. Michigan Ave, Chicago, IL 60603, USA*
[4]*Bruker Optics Inc., 40 Manning Road, Billerica, MA 01821, USA*
[5]*Museum of Fine Arts, Boston, MA, 465 Huntington Avenue, Boston, MA 02115, USA*

Before the start of its restoration in 2007 by Diane Dwyer Modestini, the Salvator Mundi was thought to be one of a number of copies of a long-lost Leonardo da Vinci painting, depicting Christ giving a blessing with his right hand while holding a crystal orb in his left. Prior to the restoration, the painting had been purchased at an estate sale for a modest 10,000 USD. After study and restoration, the painting appeared in the landmark exhibition Leonardo da Vinci: Painter at the Court of Milan at the National Gallery, London (2011-2012).[1] It eventually sold for 450M USD in 2017.

Over a two-year period, in the early phases of restoration, we carried out a scientific examination to characterize the painting's materials and techniques. We employed a complement of examination and instrumental methods, including stereomicroscopy, x-radiography, infrared reflectography (IRR), visible and fluorescent light microscopy (VLM and FLM), x-ray fluorescence spectroscopy (XRF), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Raman microspectroscopy, Fourier transform infrared microspectroscopy (MFTIR) with attenuated total reflection (ATR-FTIR), and pyrolysis gas chromatography-mass spectrometry (Py-GCMS). Pigments identified included lead white, vermilion, iron oxide earth, red lake, natural ultramarine, lead tin yellow (Type I), umber, and charcoal, carbon and bone blacks, along with soda lime glass. Walnut oil medium was determined by Py-GCMS.

Sampling was necessarily limited for this important painting. Paint cross-sections of microscopic samples revealed the stratigraphy of the painting: a sizing medium, a white ground, and an off-white imprimitura, followed by a complex sequence of paint layers that had been applied skillfully to achieve sophisticated visual effects. To extrapolate from the cross-sections to an understanding of the artist's approach, schematics were developed that may reasonably represent the various stages of the painting's execution.

Fig. 1. *Salvator Mundi*, c. 1500

This paper will focus on the scientific findings, which proved essential to facilitate an informed comparison of the painting with others by Leonardo and his contemporaries.

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POSTER

Rapid Identification of Cellulose Nitrate Film in Historic Photograph Collections

E. A. CARTER[1], M. L. WOOD[1], T. M. HARRISON[1], J. BRAZIER[2], J. PHILP[2] AND L. RONAI[3]

[1]*Sydney Analytical, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia, elizabeth.carter@sydney.edu.au*
[2]*Sydney University Museums, Nicholson Collection, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia*
[3]*Australian National Maritime Museum, Darling Harbour, Wharf 7, 58 Pirrama Rd, Pyrmont, 2009, NSW, Australia*

Cellulose nitrate film was used by photographers and movie filmmakers from its release in 1887 to 1950. The storage of material with this film base is a challenge for cultural institutions because of its instability and hazardous nature, as nitrate is highly flammable and decomposes with age. The Historic Photograph Collection, part of the Macleay museum holds several thousand still film negatives that have been identified or are suspected to be cellulose nitrate (CN). The Historic Photograph Collection comprises a wide variety of photographic formats dating from the mid-19th to mid-20th centuries. With its portraits, landscape and town views, family albums, images from travels and expeditions, scenes of university life, scientific work and ethnographic photographs, it is a rich historical resource.

In 2016 The CAN Project commenced to address the needs of cellulose nitrate (CN) and cellulose acetate (CA) transparent plastic film supports in the National Maritime Collection. It has been ten years since the Australian National Maritime Museum (ANMM) has evaluated its approach to manage the risks CN and CA pose to other collection items and humans.

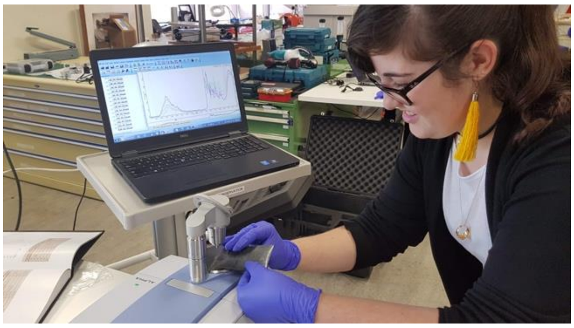

Fig. 1. Preliminary testing of ANMM samples using FTIR/ATR spectroscopy

In regard to both collections of most concern is the identification and management of the cellulose nitrate negatives. While storage at low temperatures has been used to delay degradation and the release of nitric acid, this film poses a risk to staff and to the rest of the collection. Currently the degradation of cellulose acetate is measured using the AD (Acid Detection) strip test which requires 24-48 hours of off-gassing to occur. However, it cannot distinguish between cellulose nitrate and cellulose acetate. Cellulose nitrate can be identified using a number of destructive testing methods that are problematic for collecting institutions. To safely and rapidly identify large numbers of negatives with a non-invasive technique would assist many collections and collecting institutions. Samples from both the Sydney University Museum and ANMM collections, have been investigated using both IR (ATR and Reflectance) and Raman spectroscopy. Preliminary findings indicate that IR Reflectance spectroscopy allows for the rapid identification of CN and CA. The data collected from this project provides an opportunity to contribute to a large collaborative ARC Linkage project to investigate malignant plastics by establishing their identification and studying their deterioration and conservation.

Acknowledgements
The authors would like to acknowledge the support provided by the Core Research Facilities (CRF), at The University of Sydney, for funds provided to purchase the equipment used in this study. This research is supported by the Australian Government through the Australian Research Council's *Linkage Projects* funding scheme (project LP160100160).

POSTER

An Overview of the Use of Raman Microspectroscopy for the Identification of Gemstones in Museum Objects

M. DERRICK[1], AND R. NEWMAN[1]

[1]*Museum of Fine Arts, 465 Huntington Avenue, Boston, MA 02115, USA.*

Raman microspectroscopy is a powerful tool for identification of gemstones. Its speed and non-invasive nature make it ideal for analysis of museum jewelry. The technique can frequently be directly applied to gemstones in their jewelry settings. The Raman fingerprint provides a precise chemical identity for the stones that can be used not only to determine the correct species, but sometimes even to identify a gemstone's original source. Precious stones, (diamond, emerald, ruby, sapphire, pearl, etc) as well as semiprecious stones (alexandrite, chrysolite, turquoise, garnet, topaz, peridot, amber, quartz, coral, etc.) are all easy to identify when compared to reference spectra in the IRUG library. Fake gemstones are often made from zircon, tanzanite, rutile, strontium titanate, glass or plastic.

Once a gemstone's chemical composition and crystalline structure are identified, the next steps for its identification are optical characterization of its color and transparency. If the Raman spectrum identifies the stone as quartz, its color can provide the variety name (citrine, amethyst, smoky quartz). Varieties of chalcedony, which is found in opaque stones such as agate, onyx, jaspar, and opal, can also be specified based on color and other visible features of the stones.

Standard gemological examinations include color and transparency, along with measurement of refractive index, birefringence, pleochroism, and inclusions. Even with care, these standard tests can have difficulty discriminating between red to purple stones such as garnet, amethysts, beryl, natural and synthetic rubies, topaz, and spinel. Raman spectra for these gemstones are distinct.

Garnet encompasses a group of six endmember compounds (almandine, pyrope, spessartine, grossular, andradite, and uvarovite), each of which can be distinguished by Raman. Solid solutions of two (or more) of these endmembers often occur and can be specific to the location of their source. To some extent, the chemical composition of solid solution garnets can be estimated from their Raman spectra.

In the current market, gemstone modifications such as heat treatments, dyes, impregnation, and composite layering are common. Raman microspectroscopy can identify many of these enhancement methods and has the additional advantage of identifying several types of inclusions. For example, rutile can form needle-like inclusion in natural corundum, and thus its presence in a corundum spectrum is indicative of a natural, non-synthetic stone. Emerald, i.e. green beryl, has often been treated with epoxy to minimize the visible appearance of fractures. These organic additives can often be determined using a full-range spectrum (3500-50 cm-1).

POSTER

Problems with obtaining good quality degradation spectra on three dimensional museum items

R.A. GOODALL[1], K. PALMER[1], A. CANNON[1]

[1] *Museums Victoria, 11 Nicholson Street, Melbourne, 3053, Australia, rgoodall@museum.vic.gov.au*

Museums Victoria has been committed to using infrared spectroscopy for the identification of plastic based items in its extensive collections for many years. In 2013 we focused this interest with the commencement of semi-random surveys to identify the polymers used. Collaboration in 2014 with the University of Melbourne lead to a successful McCoy Seed Funding grant to investigate "Cellulose Nitrate in Museum Collections". We have further collaborated with a group of collection institutions and universities in the ARC funded project "A national framework for managing malignant plastics in museum collections". Aiming to develop methods for predicting and increasing the lifespan of malignant plastics in museum collections by studying their identification, deterioration and conservation we have commenced surveying the collection. The expansion of our collection surveys now includes a detailed condition report on each plastic item and the identification of plastic type by infrared spectroscopy while trying to identify any degradation of the materials.

A major part of this survey for Museums Victoria is the identification of plastic types and as the survey progresses the identification of degradation markers in the infrared spectra. Collection items present a unique problem for analysis as it must be achieved without damage to or sampling of the item under examination. Infrared analysis although a useful tool for the identification of polymer type has presented some problems. The preferred sampling technique is ATR which results in a spectrum that can be readily compared with commercial spectral libraries and with spectra from other members of the ARC group. Positioning the items on the ATR crystal usually involves using a corner or in some instances an edge to obtain contact with the diamond crystal. Degradation patterns on the object frequently do not match with accessible testing locations. Some improvement has been gain with the use of a front facing reflectance module but due to the shape of many three dimensional objects it is still proving difficult to access all locations and surfaces.

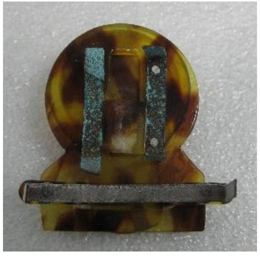
Fig. 1. Cellulose nitrate object with severe corrosion on metal parts.

Case studies of problematic objects will be discussed, for example cellulose nitrate degradation often starts inside the object and travels outwards towards the surface (Shashoua2008) corner surface testing will not pick up early signs of degradation and testing may therefore underestimate the extent of degradation in the object. Even when visible signs of corrosion are present on metal parts of an object, Figure 1, the infrared spectrum obtained on an accessible part of the object has not presented indicator bands of the plastic degradation. The diffusion of plasticisers to the surface of objects, particularly with PVC also make it difficult to use surface techniques such as FTIR-ATR and FTIR-Reflectance to detect the level of degradation. The possible use of handheld spectrometers to access more surfaces in the future is being investigated.

Acknowledgement
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POSTER

Assessing portable Raman spectroscopy for testing ethanol concentration in specimen jars of the natural history collection

T. M. HARRISON[1], E. A. CARTER[1], M. L. WOOD[1], A. GILL[2] AND J. PHILP[2]

[1]Sydney Analytical, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia, elizabeth.carter@sydney.edu.au
[2]Sydney University Museums, Nicholson Collection, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia

Sydney University Museums have an extensive collection of Natural History Specimens. The wet specimens' collection includes fish, mammals, reptiles and marine invertebrates suspended in solution. The predominant suspension is a 75% ethanol: 25% water (v/v) solution. The specimen jars have been closed by a number of methods and over time the evaporation of ethanol changes the concentration of the liquid. This can be potentially dangerous for the longevity of the specimens housed in the solution and should be monitored at regular intervals. In some instances, it is feasible to open the specimen jars and test the solution, however, it would be of great benefit to Museum staff if portable equipment could provide a sufficiently accurate determination of the concentration of ethanol without requiring the opening of the jars.

Here we assess the viability of two Raman spectrometers for determining the percent ethanol in solution in specimen jars belonging to the Sydney University Museums Collection.

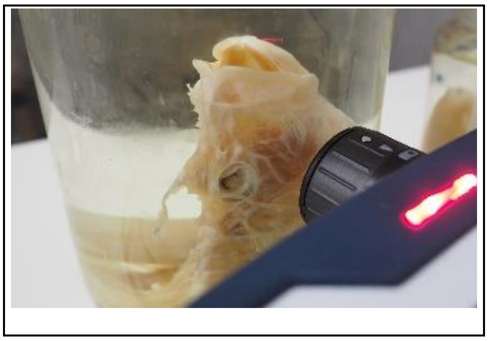

Fig. 1. Portable Raman analysis of wet specimens from the Natural History Collection, Sydney University Museums.

Acknowledgements
The authors would like to acknowledge the support provided by the Core Research Facilities (CRF), at The University of Sydney, for funds provided to purchase the Bruker BRAVO Raman used in this study. The authors would also like to thank Mr Richard Streamer of Pacific Instruments for the loan of the portable Rigaku Raman spectrometer.

POSTER

Combined FTIR and pyrolysis GC/MS for the identification of challenging fibre sub-types

Y. King[1], J. Robertson[1] and J. Hoogewerff[1].

[1]*National Centre for Forensic Studies, University of Canberra, ACT 2617, Australia. Email: Jurian.Hoogewerff@Canberra.edu.au*

The analysis and identification of unknown fabrics and fibers is a common challenge both in forensic science and in cultural heritage conservation. The amount of material under investigation is often limited in forensic science due to transfer and persistence of the fibers on a suspect. In conservation the amount is often limited by accessibility or the desire to limit damage to artefacts. After an initial visual (microscopic) inspection fibers can usually be classified as natural or synthetic and after subsequent FTIR analysis attributed to more narrowly defined compound classes based on the observed functional groups. However, FTIR is not always able to discriminate different sub-types or individual manufacturers of acrylic, nylon, polyester and polyethylene fibers. Improving the identification of these sub-types will help improve the evidential value of fibers, independent of the evidence being incriminating or exculpatory.

In the present study a fiber sample set collected originally by the UK Forensic Science Service was investigated with both FTIR microscopy (μ-FTIR, Nicolet Continiuμm Microscope) using a diamond anvil cell, and pyrolysis gas chromatography mass spectrometry (py-GC/MS, Pyromat Curie-point pyrolyzer with a Perkin Elmer AutoSystem XL Gas Chromatograph and TurboMass Mass Spectrometer). The following fiber types were analyzed by single fibers but in triplicate: Acetate Chromspun®, Courtelle Acrylic, Acrilan® Acrylic, Orlon 42 Acrylic, Modacrylic SEF®, Nylon 6, Nylon 66, Dacron Polyester, Kodel® Polyester, Polyethylene, Polyethylene/butyl rubber blend, Polypropylene Ulstron and the EU standard EC680 polyethylene was used as daily quality control standard in both methods. On the FTIR the fibers were identified by the observed bands and using databases. On the GCMS the retention times and NIST fragmentation pattern database were used for compound identification. One of the main challenges with the py-GC/MS was mounting a single, 2 cm (often recalcitrant), fiber on the thin Curie needle. Needles with slightly different alloy composition were tested to find those with the ideal Curie temperature (in the applied magnetic field) for each fiber type: 510°C for acetate and modacrylics and 610°C for all the other types.

The μ-FTIR was able to distinguish between a number of fiber types but not between the acrylic Courtelle and Orlon 42, between SEF® modacrylic and Acrilan®, and poorly between Dacron and Kodel® polyester. The py-GC/MS results showed similar pyrolysis chromatograms, or pyrograms, for all the acrylics: Courtelle, Orlon 42, SEF® modacrylic and Acrilan® but also distinctive peaks which were identified as different breakdown products. The Dacron and Kodel® polyesters could be distinguished by a prominent vinyl benzoate peak in the Dacron pyrogram absent in Kodel®. Although nylon 6 and nylon 66 could be distinguished by μ-FTIR, the pyrograms showed that the presence of carprolactam or cyclopentanone in the pyrograms could be used for the confirmation of nylon 6 or nylon 66 respectively.

All distinguishable μ-FTIR and py-GC/MS features were combined and tested against a set of eight blind samples including blends with natural fibers. All synthetic fibers studied were correctly identified. Future research will include more fiber types and strategies to identify blends.

POSTER

Vibrational analysis of β-naphthol colorants: a comparative study through IR and Raman spectroscopy

M. PICOLLO[1], E. M. ANGELIN[2], D. BERSANI[3] AND M. J. MELO[2]

[1] "Nello Carrara" Institute of Applied Physics, National Research Council, Via Madonna del Piano 10, Sesto Fiorentino, 50019, Italy
[2] DCR and LAQV-REQUIMTE, Faculty of Sciences and Technology, NOVA University of Lisbon, Campus da Caparica, Caparica, 2829-516, Portugal mjm@fct.unl.pt
[1] Department of Mathematical, Physical and Computer Sciences, University of Parma, Viale G.P. Usberti 7/a, 43100 Parma, Italy

IR and Raman spectroscopy have been extensively used to identify synthetic organic colorants (dyes and pigments) as masstone and powders as well as in works of art. Besides the experimental difficulties in their identification, the vibrational analysis of the individual colorant is challenging owing to the numerous vibrational bands usually observed. Normally within the same class of material, the colorants differ in chemical structure only by the position and nature of substituents on the aromatic rings, making definitive their discrimination difficult.

Although many IR and Raman databases are available for the colorant identification [1,2], few Raman studies have been devoted to the interpretation of vibrational spectra of synthetic organic colorants [3-5]. Actually, many vibrational spectra are poorly interpreted representing a lack of knowledge on this class of synthetic materials' molecular spectroscopic properties.

In this work, a systematic vibrational study of different β-naphthol colorants by IR and Raman spectroscopy is presented. β-naphthols compounds, by the end of the 19th century, were one of the first classes of colorants to be synthetized characterized by 1-arylazo-2-naphthol basic skeleton (Figure 1). Found as colorants for printing inks, plastics, paints, artists' colour, tinctorial applications, the historical impact β-naphthol reds is widely referred in literature [6,7]. The comprehensive understating of their vibrational properties can support the investigation of their degradation mechanism, which are already reported to be found in painting [8] and plastics [9], by using molecular spectroscopic approaches.

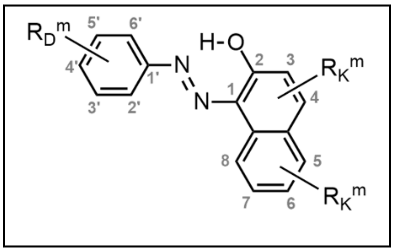

Fig. 1. 1-arylazo-2-naphthol basic skeleton. R_D^m, substituent at the moiety of the azo component; R_K^m, substituent at the moiety of the coupling component; m, from 0 to 3.

Starting from the basic chemical structure of this class of colorants, represented by the dye Solvent Yellow 14 (C.I. 12055), the influence of substituents on the aromatic rings of the phenylazo and 2-naphthol moieties (R_D^m and R_K^m respectively) in the IR and Raman molecular vibrational frequencies have been investigated. In addition, the impact of the laser wavelength on the definition of the Raman spectra have been studied. The correlations between vibrational frequencies and molecular structure will be discussed at the light of the existing literature.

Acknowledgement
This work was supported by Fundação para a Ciência e a Tecnologia, Ministério da Educação e da Ciência, (FCT/MEC), Portugal, through doctoral program CORES_PD/00253/2012 and PB/BD/114412/2016 doctoral grant; Associate Laboratory for Green Chemistry LAQV which is financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265).

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POSTER

Japanese *sugito* in the Philadelphia Museum of Art: investigation of painted decorations and soluble nylon coatings

B. A. PRICE[1], G. A. ARBUCKLE-KEIL, K. DUFFY[1], P. A. OLLEY[1], K. SHULMAN[1], M. DUSTIN[1], W. KAO[1], F. FISCHER[1], K. KINOSHITA[1]

[1]Philadelphia Museum of Art, PO Box 7646, Philadelphia, PA, 19101, USA bprice@philamuseum.org
[2]Rutgers University, 315 Penn Street, Camden, NJ, 08102, USA

Twenty cedar wood sliding doors (*sugito*) are in the East Asian Art Collection of the Philadelphia Museum of Art (PMA). *Sugito* were commissioned from the 16th century through the Edo Period (1615-1868) for architectural spaces, such as castles and estates of military and civilian elite, with panel sizes varying with intended site. The PMA *sugito* are painted masterfully in polychrome with figures, flora and fauna carrying seasonal and symbolic meanings. Comparable *sugito* are in Nagoya and Nijo Castles, Japan.

The PMA *sugito* provided a unique opportunity to study the painted decorations and share information with colleagues in Japan, as these objects are outside the Cultural Properties Designation of Japan. Judicious sampling based on object condition allowed for multiple analytical techniques. Paint constituents were characterized by vibrational spectroscopy (Fourier transform infrared microspectroscopy (MFTIR), Raman microspectroscopy), pyrolysis gas chromatography-mass spectrometry (Py-GCMS), x-ray fluorescence spectroscopy, scanning electron microscopy with energy dispersive spectroscopy and x-ray diffraction (XRD). The *sugito* pigment palette was found to be limited: vermilion/cinnabar (HgS), red lead (Pb_3O_4), lac ($C_{20}H_{14}O_{11}$), azurite [$Cu_3(CO_3)_2(OH)_2$], indigo [$C_{16}H_{10}N_2O_2$], malachite [$Cu_2CO_3(OH)_2$], brochantite [$Cu_4SO_4(OH)_6$], calcite ($CaCO_3$), carbon black [C] and gold (Au). The finding of brochantite pigment is unusual. Minerals containing copper (Cu) and arsenic (As), with or without zinc (Zn), were detected with the malachite. XRD indicated cornwallite [$Cu_5(AsO_4)_2(OH)_4$] and philipsburgite [$(Cu,Zn)_6(AsO_4,PO4)_2(OH)_6\bullet(H_2O)$], which can co-occur with malachite. The Yamato (Ofuku) mine, Yamaguchi Prefecture, was listed in 2011 as the only confirmed locality with philipsburgite in Japan.[1]

Fig. 1. *Sugito*; Courtier on Horseback; Japan, Edo Period, 161.9 cm x 157.4 cm, Acc# 1966-211-11a,b,-12a,b; Fiske Kimball Fund & Marie Kimball Fund

According to PMA conservation records, the *sugito* were coated in the 1960s with soluble nylon to protect and consolidate the decoration. Soluble nylon is derived from highly insoluble nylon 6,6 by partial derivatization to form N-methoxymethyl nylon 6,6, which is soluble in methanol. The derivatized polymer was favoured for its flexibility, clarity and adhesive properties but is no longer used as it becomes insoluble and accumulates particulates.[2] Although the specific manufacturer of the soluble nylon on the *sugito* is unknown, period art conservation literature refers to Calaton CB® (Grade DV55), a product from Imperial Chemical Industries (ICI).[3] Thus, samples of Calaton CB® powder were obtained for comparison to the *sugito* coatings from the Winterthur Museum, Getty Conservation Institute and Art Institute of Chicago. FTIR, Raman, Py-GCMS, and thermal analysis (thermogravimetric analysis coupled with FTIR, differential scanning calorimetry) were applied to Calaton CB® powder(s), its cast films and *sugito* coatings, indicating nylon 6,6 as the major component. Minor differences were observed between IR spectra of the *sugito* coatings and cast films.[4]

Acknowledgement
We are grateful to PMA senior conservators Sally Malenka and Behrooz Salimnejad, and Tim Fawcett, International Centre for Diffraction Data, Newton Square, PA, USA, for their expert contributions to this project.

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POSTER

The IRIS beamline: Applications to Cultural Heritage Materials

L. PUSKAR[1], E. RITTER[2], U. SCHADE[1]

[1] *Helmholtz-Zentrum für Materialien und Energie GmbH, Berlin, 12489, Germany*
[2] *Experimentelle Biophysik, Humboldt-Universität zu Berlin, Berlin, 10115, Germany*

At BESSY II synchrotron the infrared beamline IRIS is involved in a wide range of applications and materials studies including those of cultural heritage materials. The beamline consists of several end stations taking advantage of highly brilliant infrared radiation in the mid- and far-IR regions down to 30 cm^{-1} and lower, when BESSY II operates in the low-α mode producing high power coherent terahertz (THz) radiation [1].

The microspectroscopy station comprising a Nicolet Continuum infrared microscope is coupled to a Nexus 870 FT-IR spectrometer and operates in the mid-IR region. A polarization modulation device allows microspectroscopic studies of the vibrational linear dichroism so that samples with preferred molecular orientations can be investigated. The spatial resolution (5-10 microns) of the microscope allows for mapping of small areas of heterogeneous samples, whereas the high temporal resolution permits dynamic processes such as the response of a sample to mechanical stress or UV exposure to be investigated.

The spectroscopy station uses a Bruker Vertex FTIR spectrometer providing higher flux in the far-IR/THz region. A custom made FIR/MIR microscope with long focal distance is available for transmission and reflection measurements of large and free standing samples. Anisotropy in samples can be investigated by polarised far-IR dichroic spectroscopy.

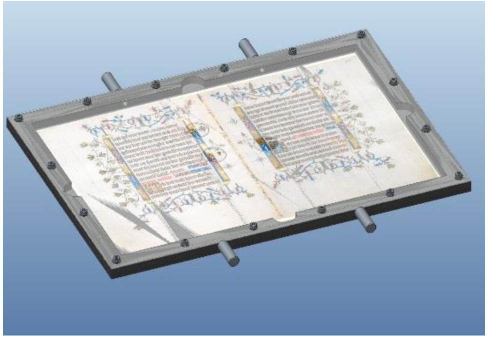

Fig. 1. Schematic of a controlled environmental conditions microscope sample stage holder containing a parchment sample.

Some of the recent applications on the IRIS beamline include the study of an illuminated medieval manuscript on parchment, the prayer book of Mary of Guelders (1415, Netherlands) kept in the “Staatsbibliothek zu Berlin, Stiftung Preußischer Kulturbesitz”. The IRIS microscpectroscopy beamline was utilised to help identify structural and chemical changes related to the possible alterations and fragile parts of the manuscript.

In another study, wooden artefacts dating from the Viking Age from the collection of the Oseberg find have been investigated. Early conservation treatments applied around one hundred years ago, in particular alum salts, resulted in continuing deterioration of the artefacts. Careful identification of the materials present in these objects, their reaction and decomposition products, is necessary for development of suitable preservation strategies [2].

Polychrome decorations of the Alhambra monument (Granada) have been investigated to better understand the alterations and mechanisms of deterioration processes in aid of their conservation. With FTIR microspectroscopy the nature and location of the original pigments and binders and reaction compounds in the paint layers were investigated [3].

Acknowledgement
We acknowledge Rathgen-Forschungslabor-Staatliche Museen zu Berlin; Museum of Cultural History-Department of Conservation, University of Oslo; Department of Physical and Analytical Chemitry, University of Jaén.

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POSTER

An indigo we didn't know: characterization and first identification of 5,5'-dibromoindigo dye in a Japanese yukata

G.D. SMITH[1], V.J. CHEN[1], A. HOLDEN[1], MELINDA KEEFE[2] AND S. LIEB[3]

[1]*Indianapolis Museum of Art at Newfields, 4000 Michigan Rd., Indianapolis, IN 46208, USA e-mail. gdsmith@discovernewfields.org*
[2]*Dow Chemical Company, 1702 Building, Midland, MI 48674, USA*
[3]*Butler University, 4600 Sunset Rd., Indianapolis, IN 46208, USA*

The exploitation of natural sources and later synthetic molecules to generate blue to purple coloration in textiles has a long history in the dyer's craft. Natural indigoids such as indigo, woad, and Tyrian or shellfish purple served this purpose for millennia, but in the late 1800s synthetic analogues, in particular indigotin, quickly replaced natural indigo. Halogenated versions of the dye were also created, and some like 5,5'-dibromoindigo were apparently brought to market [1], but have not been significantly discussed in the literature or found in forensic and technical art history investigations of textiles.

This presentation reports the first identification in a museum context of this unusual synthetic brominated analogue of indigo, discovered on two mid-20th century Japanese *yukata*. Fig.1. shows one example of a shibori dyed summer garment. Full analytical data collected on reference materials using liquid chromatography-mass spectrometry, UV-visible spectroscopy, Raman microspectroscopy, Fourier transform infrared spectroscopy, and X-ray fluorescence spectroscopy were collected to assist with future identifications of this relatively unknown colorant. Density functional theory (DFT) applied to 5,5'-dibromoindigo was used to confirm the experimental Raman spectra and to refute the possibility that the *yukata* dyes could be the now unavailable 4,4'- or 7,7'-dibromoindigo analogues.

Fig. 1. *Informal Summer Kimono*, IMA#2015.112, c. 1950s, cotton, 60 x 50¾ in., Gift of Jeffery Krauss.

Acknowledgement
Financial support for this work was provided by the Frenzel Family Charitable Lead Trust, the Carter Family Foundation, and John and Sarah Lechleiter.

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POSTER

A spectroscopic investigation of sculptural modelling clay materials for conservation purposes

B. H. STUART[1], P.S. THOMAS[2], M. BARRETT[3] AND K. HEAD[3]

[1]Centre for Forensic Science, University of Technology Sydney, 15 Broadway, Ultimo, 2007, NSW, Australia e-mail.barbara.stuart@uts.edu.au
[2]School of Mathematical and Physical Sciences, University of Technology Sydney, 15 Broadway, Ultimo, 2007, NSW, Australia
[3]Conservation Department, Art Gallery of New South Wales, Art Gallery Rd, Sydney, 2000, NSW, Australia

Modelling clays have proved popular for use in sculptures due to their malleability and non-drying attributes. The Art Gallery of New South Wales (AGNSW) holds a number of works comprised of modelling clays. Signs of distortion are evident in some of these works. Modelling materials have been in use since the end of the nineteenth century, but reported information about the long-term stability of such materials in artworks has been limited [1]. In order to establish the best approach to the conservation of items produced using such materials, an investigation has been carried out to determine the exact nature of the materials employed by the artists and to investigate the impact of composition on longevity. Infrared and Raman spectroscopies have been used to characterise the modelling materials. In case studies of works held by the AGNSW produced in recent decades, Plasticine was identified as the material employed by the artists. Infrared spectroscopy enabled the inorganic and organic components to be specifically identified, while Raman spectroscopy was used to identify the pigment composition. A comparison of the spectra obtained for sculptural specimens with new unused commercial Plasticine has enabled a prediction of changes in chemical composition over time, which in turn may be correlated with the physical properties of Plasticine.

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POSTER

Application of ATR/FTIR to case studies in preventive conservation and novel conservation treatments

M.ODLYHA [1], D.THICKETT [2], A.BARTOLETTI [3], A.BRIDAROLLI [3], L. BOZEC [3], M. ANDERS[4], P. MATTEAZZI [5], A. HAWLEY [6], N.TERRILL[7] , E.GONZALEZ-ATEAGA [8], A.LIUVERAS-TENORIO[9], D. CHELAZZI [10], R.GIORGI [10], P. BAGLIONI [10]

[1] Birkbeck,University of London, Malet St., London WC1H 0NL UK, m.odlyha@bk.ac.uk
[2] English Heritage Rangers House Flat, Chesterfield Walk, London, SE10 8QX
[3] UCL Eastman Dental Institute, London UK,
[4] ZFB Zentrum für Bucherhaltung GmbH, Leipzig Germany
[5] MBN Nanomaterialia SpA Venice Area, Italy
[6] Synchrotron Light Source Australia Pty Ltd, Clayton , Vic., Australia
[7] Diamond Light Source,Didcot,UK.,
[8] Instituto del Patrimonio Cultural de Espaňa, Madrid,Spain
[9] Dept. of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 13, I-56124 Pisa, Italy
[10] CSGI,Dept of Chemistry·University of Florence, Florence, Italy

The first case study involves the characterisation of the state of deterioration of polyethylene and polpropylene Stewart boxes used for storage of archaeological iron objects. This was measured by Fourier transform infra-red (FTIR) spectroscopy and differential scanning calorimetry (DSC). The FTIR spectra allowed us to evaluate the crystallinity fraction from two specific peaks (997 and 972 cm^{-1}) and one reference peak (917 cm^{-1}). The measurement of crystalline fraction will be presented together with that measured by DSC. The enthalpy of the melting peak in DSC was compared to published values of 100% crystalline polyethylene and polypropylene to determine the degree of crystallinity. The two methods in some cases showed differences which could be due to difference between surface and bulk measurements. The permeability of both polyethylenes and polypropylenes increases as the number and size of amorphous regimes increases and the degree of crystallinity decreases. This is not what is required for the storage boxes so estimation of crystallinity fraction is an important parameter for characterising the boxes.

The second case study presented here involves novel conservation treatments applied to leather-based objects. In the past few years there has been a growing interest in the application of nanotechnology to the preservation of art objects and recent testing was performed in the framework of the EU funded NANOFORART project (http://www.nanoforat.eu). The overall aim was to assess the impact of novel nanoformulations synthesised for the conservation of a wide range of cultural heritage materials, including collagen-based materials. Methods used to conserve leather objects are always under review and in current practice there has been a movement away from interventive treatment towards a more preventive approach . Recent developments, however, in improved damage assessment techniques for collagen in parchment has provided a set of damage markers from the nano to the macro scale . Different formulations have been developed for the conservation of leather addressing issues related to the cleaning and pH adjustment of leather [1]. Samples tested included : modern vegetable tanned (sumac) leather and historical samples: the cover of a Luther bible (1749 AD) and the cover of a Missale Romanum (Roman Missal, 1725 AD). Both historical samples exhibited surface deposits of dirt, salts, or waxy (or lipid materials) which needed to be removed. Current work has included characterization of state of preservation of a 16th cent historical bookbinding. Damage assessment was made using FTIR and this was supported by other techniques e.g SAXS.

Some mention will be made of current work on other materials where FTIR makes a contribution and includes : evaluation of (1) the treatment of painting canvases using nanocellulose which is part of the NANORESTART project [http://www.nanorestart.eu/] and the doctoral programme (SEAHA) [http://www.seaha-cdt.ac.uk/] and (2) characterization of model varnished wood samples prepared according to traditional recipes used for violin varnishes. Nanomechanical measurements using Atomic Force Microscopy (AFM) showed that samples which were oil-based differed in stiffness from resin-based samples. Complementary synchrotron micro-FTIR revealed that for oil-based samples the degree of penetration was greater than for the resin-based samples.

Acknowledgements
The authors thank the European Commission DG-RTD (5th , 6th and 7th framework) and H2020 and the Engineering and Physical Sciences Research Council (EPSRC,UK) Centre for Doctoral Training Science and Engineering in Arts, Heritage and Archaeology (SEAHA) Associazione Liutaria Italiana ALI , WoodMusICK FPS COST action FP1302, il PRIN 2010-2011: “Sustainability in cultural heritage: from diagnosis to the development of innovative systems for consolidation, cleaning and protection

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POSTER

Characterization and quantification study of lacquer materials by FTIR analysis

S. Wei[1], Q. X.Y. Fu[1] and Y. Li[1]

[1]Institute of Cultural Heritage and History of Science & Technology, Beijing University of Science and Technology, Beijing 100083, China
e-mail.sywei66@hotmail.com

The lacquer crafts in China have a long history that can be traced back to the Neolithic. The best quality lacquer objects are produced through a long manufacturing process in which a large number of lacquer layers, alone or mixed with other materials, are applied. Raw lacquer was always modified with a drying oil to retard the rate of hardening and affected the physical properties of the film.

Lacquer originates as the sap of lac trees and is tapped from the tree, which can be applied to a wooden object with a brush. According to the region of the tree origin there are three types of oriental lacquers - Rhus vernicifera (the phenol derivative is urushiol), Rhus succedanea (the phenol derivative is laccol) and Melanorrhoea usitate (the phenol derivative is thitsiol). These monomers are considered as the most characteristic markers to distinguish particular lacquer. Lacquer film is a cross-linked polymer that polymerised by laccase and it is insoluble in most solvents. Due to this fact, only a few analytical techniques are available for the scientific investigation and determination of the chemical compositions of such materials. Fourier transform infrared spectroscopy [1] and pyrolysis gas chromatography and mass spectrometry Py-GC/MS have been mostly applied [2].

Tung oil is derived from the fruits of the Tung tree, originating in Asia. It was reported to be used in lacquers to improve the process of a film formation. The amount of oil content mixed with lacquer is very important for the quality of lacquer film. In this study, tung oil mixed with Chinese raw lacquer in different portion was investigated by FTIR and Py-GC/MS to see the possibility to characterize and quantify the relative content of tung oil in the lacquer film. The initial FTIR analysis results of the lacquer mixed with different portion of oil are demonstrated in figure 1. From figure 1, it can be seen that the peak (P1) of the vibration of carbonyl group at1740 cm^{-1} increase when the tung oil content increased. The two peaks (P2) of benzene in urushiol of the lacquer at 1592 cm^{-1} and 1620 cm^{-1} could be observed in all the samples. The peak ratio P1/P2 is proportional to the oil content, which may be indicator to semi-quantify the relative content of tung oil in the lacquer film. However, further study is needed considering the influence of ageing.

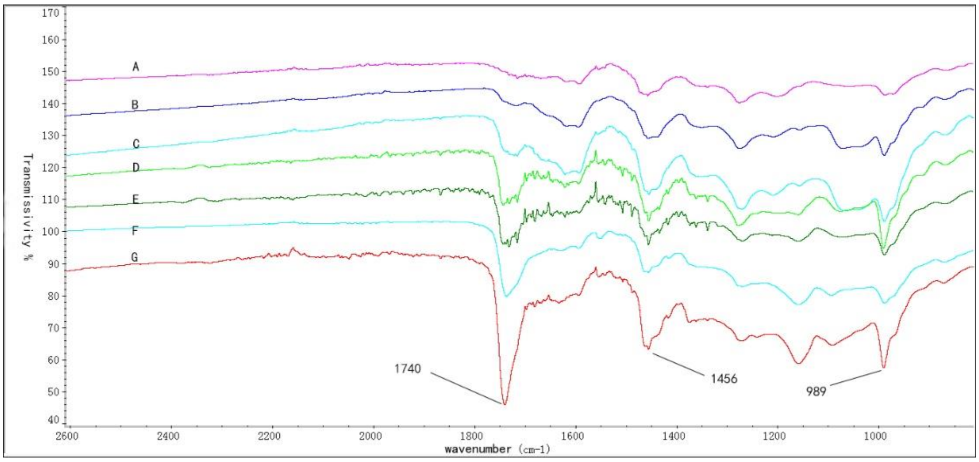

Fig 1. The spectra of the samples of Chinese raw lacquer mixed with different portion of tung oil. A) 0% oil, B) 5% oil, C) 10% oil, D) 20% oil, E) 30% oil, F) 40% oil, G) 50% oil.

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POSTER

Neutron, proton and ion based techniques for heritage materials: a synergistic approach at ANSTO

R. WHITE[1] AND F. SALVEMINI[1]

[1]Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, 2234, New South Wales, Australia
rew@ansto.gov.au

Over recent decades, nuclear methods have been established as an innovative and attractive investigative approach to characterise heritage materials. Providing a powerful and versatile way to look at the structure and dynamics of materials at the atomic level, they extract maximum information from an object without the need for sampling or invasive procedures. ANSTO's facilities offer a wide range of unique techniques for cultural heritage research.

A strategic scientific research project Cultural Heritage has been initiated at the Australian Nuclear Science and Technology Organisation (ANSTO). The project aims to promote the access to the suite of nuclear methods available across the organisation. It also promotes the use of our non-invasive analytical approaches in the fields of cultural-heritage, archaeology, and conservation science. The latest scientific analytical tools, which are available under the operation of ANSTO, including neutron-, synchrotron- and accelerator-based techniques, have been increasingly demanded for a wide range of applications to heritage materials.

In this presentation, current and future perspective on the integrated application of nuclear techniques for heritage materials will be discussed.

Recent studies, in collaboration with the cultural heritage community, include:

- Neutron diffraction and imaging techniques were applied to shed light on the manufacturing procedure developed to produce a particular variety of silver coins, called incuse, minted around 540 BC in the cities of Southern Italy.
- A set of Egyptian mummies were successfully dated and attributed by 14C accelerator mass spectrometry (AMS) analysis on small amounts of the wrapping material.
- The combination of Ion Beam Analysis (IBA), Neutron Activation Analysis (NAA) and X-ray Fluorescence Microscopy (XFM) helped in the characterization and study of provenance of Aboriginal pigments and artefacts.
- Synchrotron IR microscopy and spectroscopy investigated the degradation and conservation of acrylic emulsion paints, and the degradation of cellulose nitrate artefacts in museum collections

POSTER

The potential of IR and Raman spectroscopy to determine pigment and binder concentration in modern paint samples

R. Wiesinger[1], L.Pagnin[1], M. Anghelone[1], L. M. Moretto[2], E. F. Orsega[2], and M. Schreiner[1]

[1] *Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Schillerplatz 3, Vienna, 1010, Austria*
e-mail.r.wiesinger@akbild.ac.at
[2] *Dept. of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, Mestre (Venice), 30172, Italy*

Considering the techniques employed by artists, such as painting style, colour palette and composition of the colors, this knowledge is of high importance not only to attribute works of art to the workshop or artist but also to develop strategies and measures for the conservation and restoration of the art. While much research has been devoted to investigating the composition of an artist's materials from a qualitative point of view in the past, little effort has been made in terms of quantitative analyses [1-3]. The study presented here aimed to identify and quantify relative concentrations of binders and pigments in different paint samples by IR and Raman spectroscopy. The materials under investigation were acrylic (Plextol D498) and alkyd (Alkyd Medium 4) polymeric binders in mixture with different inorganic pigments: artificial ultramarine blue, chromium oxide green and cadmium yellow. The aim of this study was to explore the potential of ATR-FTIR and Raman spectroscopy to quantify the relative concentrations of pigments and binders in paint samples. To perform this quantitative evaluation, reference samples of known concentrations were prepared and analysed by ATR-FTIR and Raman spectroscopies in order to find a fitting quantification method. In a further step, characteristic spectral features that may act as signatures for the composition of pigment and binder had to be defined [4]. To create calibration curves, the integration method for obtaining the spectral band areas ascribed to different pigments and binders had to be evaluated. As a proof of concept, the quantification method was tested by additionally prepared samples and a commercially available paint tube, where we could show that the proposed method can be used to quantify the composition of two-component paint mixtures. The results obtained confirm that the quantitative method developed for IR and Raman spectroscopy is able to efficiently determine different pigment and binder concentrations of paint samples with high accuracy [5].

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POSTER

Identifying the origins of Chocolate-on-White ware, a Bronze Age ware from Jordan

P. DONNELLY[1], L. LEUNG[2] AND M. L. WOOD[3]

[1]Chau Chak Wing Musuem,The University of Sydney, City Road, Camperdown, 2006, NSW, Australia paul.donnelly@sydney.edu.au
[2]Department of Archaeology, The University of Sydney, Sydney, NSW, 2006, Australia
[3]Sydney Analytical, The University of Sydney, City Road, Camperdown, 2006, NSW, Australia

From the end of the Middle Bronze Age, into the first half of the Late Bronze Age (c. 1600-1450 BCE), Chocolate-on-White ware was the most distinctive and stylistically dramatic pottery produced in the southern Levant of the eastern Mediterranean (modern-day Jordan, Palestinian Territories, and Israel). As a fine (non-storage) ware covered in a fine white slip burnished and decorated with red-brown linear patterns, it can be assumed Chocolate-on-White had a privileged position at the table of the society in which it was used. Given this distinction in the material culture of the archaeology of the region, the study of Chocolate-on-White ware has much to offer towards a better understanding of the people, commerce and politics of the Canaanite period.

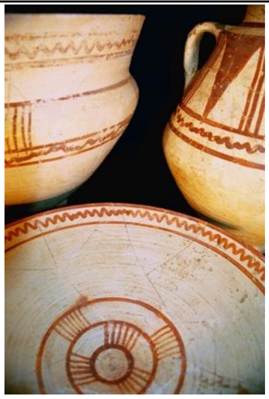

Fig. 1. Chocolate-on-White ware vessels from Tomb 62, Pella, Jordan, c.1550 BCE

To date, elemental analysis (notably NAA) of the fabric has contributed to broadly identifying a normative group (and its subgroups) as distinct to a substantial number of White Slip Burnished Painted (WSBP), White Slip Burnished (WSB), and White Slip Painted (WSP) examples which, though superficially similar to Chocolate-on-White, span a chronologically broader span and thus dilute the ware's true potential as a societal identifier and chronological marker.

The collation of distribution patterns (find-spots) and elemental analysis has been successful in broadly identifying groups to ostensible clay beds with a centre in the north Jordan Valley and possibly the site of Pella, but there is also evidence to suggest another group possibly to the south and centred around the site of Lachish. This, otherwise normative group, has the notable distinction of a bichrome decoration combining the red-brown with a yellow-brown contrast (half-jokingly referred to as Chocolate and Caramel-on-White). Occasionally we also see added black combined with this variant. Identifying the potential geographic division between these variants is the core of this current round of analysis.

The current analysis using FTIR and Raman spectroscopy at the University of Sydney is building upon this earlier research by analysing this surface decoration of both types to explore a more nuanced interpretation of groupings and ultimately determine if the bichrome version of the ware has a bichrome 'cousin' in the south. Should this be determined, new questions arise regarding relationships between the disparate sites of Pella and Lachish that have important implications to our understanding of the socio-political environment of the Bronze-Age Levant.

Acknowledgement
With thanks to the Department of Antiquities of The Royal Hashemite Kingdom of Jordan and The University of Sydney Expedition to Pella.

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