Book of Abstracts

Editor
Peter Vandenabele

Graphical Designer
Debbie Lauwers

Web Designer
Anastasia Rousaki and Philip Brondeel

ISBN
978-94-6197-367-2
Dear Participants of the InArt 2016

On behalf of the international scientific committee and the local organising committee of the InArt 2016 conference, I am pleased to welcome you in Ghent. This mediaeval town will host the 2nd International Conference on Innovation in Art Research and Technology, shortly: InArt. This meeting follows on the successful conference, organised in 2013 in Évora (Portugal) by Antonio Estevao Candeias, Irina Sandu and their teams.

These meetings focus on the interface between humanities and natural sciences and tries to provide a forum for continuous discussion between interdisciplinary research groups in archæometry. The conference aims at merging high level scientific research with a pleasant atmosphere, which tries to encourage open discussion between colleagues.

This book of abstracts comprises the abstracts of oral and poster presentations of the InArt 2016 conference. The abstracts of oral presentations are organised according to the day on which they will be presented during the conference. The abstracts of the posters are listed according to the poster session to which they belong.

We are extremely grateful to the companies and individuals who assisted in this conference. It is thanks to their support that we are able to organise the scientific and social events during this conference. Particularly, we would like to thank our Platinum sponsor, BRS, for their generous support. Also, the financial support of the golden sponsors is greatly appreciated: B&WTEK Inc., Smarttech LTD, Bruker Optics, Hírox Europe, VM Vision international bvba, XG Lab, Fondis Bioritech. Also, the support of the other sponsors is well-received: Chocolaterie Van Hoorbeke, Benelux Scientific. Finally, the support of the faculty of Arts and Philosophy of Ghent University is greatly acknowledged.

As all participants will experience during the conference, for the practical organisation of this event, we are happy for all support we get from technical staff, PhD students and students who invest time and efforts to make this conference a pleasant experience.

We hope that your visit to this conference and your stay in Ghent will inspire you for new projects in this exciting field of research!

Peter Vandenabeele.
Scientific Committee

Prof Dr Peter Vandenabeele
Department of Archaeology, Ghent University, Ghent, Belgium

Prof Dr Danilo Bersani
Department of Physics and Earth Sciences, University of Parma, Parma, Italy

Prof Dr António Candeias
Department of Chemistry, Universidade de Évora, Évora, Portugal

Prof Dr Perla Colombini
Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy

Prof Dr Howell Edwards
Department of Chemistry and Forensic Science, University of Bradford, Bradford, United Kingdom

Dr Terje Grøntoft
Urban Environment and Industry Department, Norwegian Institute for Air Research, Oslo, Norway

Prof Dr Jan Jehlička
Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Prague, Czech Republic

Dr Eleni Kouloumpi
Laboratory of Physicochemical Research, National Gallery - Alexandros Soutzos Museum, Athens, Greece

Prof Dr Maximiliaan Martens
Department of Art, music and theatre sciences, Ghent University, Ghent, Belgium

Prof Dr Luc Moens
Department of Analytical Chemistry, Ghent University, Ghent, Belgium

Prof Dr Manfred Schreiner
Institute of Science and Technology in Art, Academy of Fine Arts, Vienna, Austria

Prof Dr David Strivay
Physics Department, Université de Liège, Liège, Belgium

Prof Dr Geert Van der Snickt
Department of Chemistry, University of Antwerp, Antwerp, Belgium

Dr Dimitri Vandenbergh
Department of Geology and Soil Science, Ghent University, Ghent, Belgium
Organizing Committee

Prof Dr Peter Vandenabeele
Department of Archaeology, Ghent University, Belgium

Prof Dr Luc Moens
Department of Analytical Chemistry, Ghent University, Belgium

Alessia Coccato
Department of Archaeology, Ghent University, Belgium

Mafalda Costa
Department of Archaeology, Ghent University, Belgium

Wendy Dekein
Department of Archaeology, Ghent University, Belgium

Debbie Lauwers
Department of Analytical Chemistry, Ghent University, Belgium

Sylvia Lycke
Department of Analytical Chemistry and Department of Archaeology, Ghent University, Belgium

Possum Pince
Department of Archaeology, Ghent University, Belgium

Ariane Raman
Department of Archaeology, Ghent University, Belgium

Anastasia Rousaki
Department of Analytical Chemistry, Ghent University, Belgium

Prof Dr David Strivay
Physics Department, Université de Liège, Liège, Belgium, Belgium

Prof Dr Geert Van der Snickt
Department of Chemistry, University of Antwerp, Antwerp, Belgium

Jolien Van Pevenage
Department of Analytical Chemistry, Ghent University, Belgium
Keynote Speakers

Prof Dr Antonio Candeias
Department of Chemistry, Universidade de Evora, Evora, Portugal

Prof Dr Mary Kate Donais
Department of Chemistry, Saint Anselm College, Manchester, United States of America

Prof Dr Howell Edwards
Department of Chemistry and Forensic Science, University of Bradford, Bradford, United Kingdom

Dr Terje Grontoft
Urban Environment and Industry Department, Norwegian Institute for Air Research, Oslo, Norway

Prof Dr Jan Jehlicka
Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Prague, Czech Republic

Prof Dr Manfred Schreiner
Institute of Science and Technology in Art, Academy of Fine Arts, Vienna, Austria
CEM Microwave systems for Digestion-Extraction-Process measurement

TSI Precision Measurement Systems: LIBS – RAMAN – NIR

TSHR Element analyzers Total N – S – Cl

Teledyne Isco: Syringe pumps – Flash and Prep Chromatography

Syrris: Flow and Batch Chemistry

Your innovation is our goal

BRS | www.brs.be | 02 334 22 70 | info@brs.be

B&W TEK
Your Spectroscopy Partner

SPECTROMETERS | LASERS | TOTAL SOLUTIONS

i-Raman® Portable Raman Spectrometer Series for Art & Archaeology Applications

- Small size, lightweight fiber-optic probe system for on-site analysis
- Non-destructive measurements of artifacts
- Analysis of pigments, organics, and inorganics
- Laser power adjustable down to 1%

www.bwtek.com | +1-302-709-3929 | marketing@gmail.com
Portable Analytical Instruments

NEW

Macro XRF scanner

“ELIO” XRF spot analysis and portable mapping

XRF and Raman combined

VM ViSion

THE BEST OF BREED IN NDT

VM-Vision is an engineering company specialized in non-destructive testing devices. The recently delivered handheld XRF to the University of Ghent is a valuable tool for many samples of archaeological importance. X-ray fluorescence (XRF) and X-ray diffraction analysis (XRD) is a standard technique widely used and accepted by art historians, archaeologists, curators and conservators as this method enables about the manufacturing process and the condition of an object without "touching" the artifact.

VM ViSion - Molenbergstraat 39 - (B) 9190 Stekene - tel: +32 3 789 36 02- mail: info@vm-vision.eu - website: www.vm-vision.eu
Fondis Bioritech, value added reseller of scientific measurement solutions, offers a complete range of portable X-ray fluorescence and Raman spectrometers.

They have been designed to perform on-site and non-destructive analysis, thanks to their ergonomic design, robustness and ease of use.

- Restoration and authentication of works of art, paintings, statues, ...
- Analysis for exploration and geochemical

Fondis Bioritech
+33 1 34 52 10 30 info@fondis-bioritech.com www.fondis-bioritech.com

Sponsors

The only Raman microscope with permanent wavelength calibration

- High wavenumber accuracy (Sure, Calib)
- High ease of use, compact, flexible
- Concrete rubber and corrosion for a smart removal of fluorescence background
- High performance compact design with Hexfocus®
- Up to four excitation lasers

The SENTERRA is the first dispersive Raman microscope with high user comfort, in contrast to conventional instrumentation no calibration of the wavelength scale is required as the system is permanently calibrated with extremely high accuracy.

As this system further provides high sensitivity and control capabilities, the SENTERRA is the perfect Raman microscope for a very broad range of applications.

Contact us for more details:
www.bruker.com/senterra

Innovation with Integrity
“Two generations of chocolate makers bring you the best in traditional and classic Belgian chocolaterie.”

Cédric Van Hoorebeke
CHOCOLATIER

Jan Breydelstraat 1 – 9000 Gent. Tel:+32 (0)9 224 25 10 – info@chocolatesvanhoorebeke.be – daily open from 10-18h
### Conference Agenda

<table>
<thead>
<tr>
<th>Monday 21 March 2016</th>
<th>Tuesday 22 March 2016</th>
<th>Wednesday 23 March 2016</th>
<th>Thursday 24 March 2016</th>
<th>Friday 25 March 2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 9:00</td>
<td>Registration</td>
<td>9:00 9:30</td>
<td>Opening</td>
<td>9:00 9:40</td>
</tr>
<tr>
<td>9:00 9:30</td>
<td>PL 1</td>
<td>9:00 9:40</td>
<td>OC-A-3.1 OC-B-3.1</td>
<td>9:00 9:40</td>
</tr>
<tr>
<td>9:30 10:10</td>
<td>Coffee break</td>
<td>9:00 10:02</td>
<td>OC-A-3.2 OC-B-3.2</td>
<td>9:00 10:02</td>
</tr>
<tr>
<td>10:10 10:40</td>
<td>OC-A-1.1 OC-B-1.1</td>
<td>10:00 10:50</td>
<td>Coffee break</td>
<td>10:00 10:50</td>
</tr>
<tr>
<td>10:40 11:00</td>
<td>OC-A-1.2 OC-B-1.2</td>
<td>10:00 11:00</td>
<td>OC-A-3.3 OC-B-3.3</td>
<td>10:00 11:00</td>
</tr>
<tr>
<td>11:00 11:20</td>
<td>OC-A-1.3 OC-B-1.3</td>
<td>11:00 11:30</td>
<td>OC-A-3.4 OC-B-3.4</td>
<td>11:00 11:30</td>
</tr>
<tr>
<td>11:20 11:40</td>
<td>OC-A-1.4 OC-B-1.4</td>
<td>11:00 11:50</td>
<td>OC-A-3.5 OC-B-3.5</td>
<td>11:00 11:50</td>
</tr>
<tr>
<td>11:40 12:00</td>
<td>Lunch</td>
<td>11:50 14:00</td>
<td>Lunch</td>
<td>11:50 14:00</td>
</tr>
<tr>
<td>12:00 14:00</td>
<td>PL 2</td>
<td>14:00 14:40</td>
<td>PL 4</td>
<td>14:00 14:40</td>
</tr>
<tr>
<td>14:00 14:40</td>
<td>Sponsor talk 1.1</td>
<td>14:40 15:00</td>
<td>Sponsor talk 2.1</td>
<td>14:40 15:00</td>
</tr>
<tr>
<td>15:00 15:20</td>
<td>Sponsor talk 1.2</td>
<td>15:00 15:20</td>
<td>Sponsor talk 2.2</td>
<td>15:00 15:20</td>
</tr>
<tr>
<td>15:20 15:50</td>
<td>Coffee break</td>
<td>15:20 15:40</td>
<td>Sponsor talk 2.3</td>
<td>15:20 16:00</td>
</tr>
<tr>
<td>15:50 16:10</td>
<td>OC-A-2.1 OC-B-2.1</td>
<td>15:40 16:20</td>
<td>Flash presentations 1</td>
<td>16:00 17:40</td>
</tr>
<tr>
<td>16:10 16:30</td>
<td>OC-A-2.2 OC-B-2.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:30 16:50</td>
<td>OC-A-2.3 OC-B-2.3</td>
<td>16:20 18:00</td>
<td>Poster session 1 + reception</td>
<td>16:00 17:40</td>
</tr>
<tr>
<td>16:00 18:00</td>
<td>Poster session 1 + reception</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17:40</td>
<td>Conference dinner</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Programme

**Monday, March 21, 2016**

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 - 9:00</td>
<td>Registration</td>
</tr>
<tr>
<td>9:00 - 9:30</td>
<td>Opening Ceremony – Conference Room A</td>
</tr>
<tr>
<td>9:30 - 10:10</td>
<td>Plenary lecture – Conference Room A &amp; B</td>
</tr>
<tr>
<td>10:10 - 10:40</td>
<td>Coffee Break</td>
</tr>
<tr>
<td>10:40 - 11:00</td>
<td><strong>Conference Room A</strong></td>
</tr>
<tr>
<td></td>
<td>Ina Reiche</td>
</tr>
<tr>
<td></td>
<td><em>Coupling scanning macro-XRF and confocal micro-XRF to study the three successive versions of the painting L'Homme blessé by G. Courbet</em></td>
</tr>
<tr>
<td>11:00 - 11:20</td>
<td><strong>Conference Room B</strong></td>
</tr>
<tr>
<td></td>
<td>Lucy’t Hart</td>
</tr>
<tr>
<td></td>
<td><em>Monitoring the Impact of the Indoor Air Quality on Metallic Heritage</em></td>
</tr>
<tr>
<td>11:00 - 11:20</td>
<td>Martina Griesser</td>
</tr>
<tr>
<td></td>
<td><em>Application of Neutron-based Analytical Techniques for the Non-destructive Investigation of the Coinage of Antique Bronze Coins</em></td>
</tr>
<tr>
<td>11:20 - 11:40</td>
<td><strong>Conference Room A</strong></td>
</tr>
<tr>
<td></td>
<td>Olivier Schalm</td>
</tr>
<tr>
<td></td>
<td><em>Laminated altered layers in historical glass: density variations of silica nanoparticle random packings as explanation for the observed lamellae</em></td>
</tr>
<tr>
<td>11:40 - 12:00</td>
<td><strong>Conference Room B</strong></td>
</tr>
<tr>
<td></td>
<td>Cátia Salvador</td>
</tr>
<tr>
<td></td>
<td><em>Innovative mitigation strategies to easel paintings safeguard</em></td>
</tr>
<tr>
<td>12:00 - 14:00</td>
<td>Lunch break</td>
</tr>
<tr>
<td>14:00 - 14:40</td>
<td>Terje Grøntoft</td>
</tr>
<tr>
<td></td>
<td><em>Assessment of indoor air quality and the risk of damage to cultural heritage objects using MEMORI® dosimetry</em></td>
</tr>
<tr>
<td>14:40 - 15:00</td>
<td>Sponsor talk – BRS</td>
</tr>
<tr>
<td>15:00 - 15:20</td>
<td>Sponsor talk – Bruker</td>
</tr>
<tr>
<td>15:20 - 15:50</td>
<td>Coffee Break</td>
</tr>
<tr>
<td>15:50 - 16:10</td>
<td><strong>Conference Room A</strong></td>
</tr>
<tr>
<td></td>
<td>Aoife Daly</td>
</tr>
<tr>
<td></td>
<td><em>Non-invasive tree-ring analysis-archaeology &amp; art</em></td>
</tr>
<tr>
<td>16:10 - 16:30</td>
<td><strong>Conference Room B</strong></td>
</tr>
<tr>
<td></td>
<td>Maduka L. Weththimuni</td>
</tr>
<tr>
<td></td>
<td><em>Shellac-based nanocomposites for protection of wood surface</em></td>
</tr>
<tr>
<td>16:10 - 16:30</td>
<td>Marcello Manfredi</td>
</tr>
<tr>
<td></td>
<td><em>Non-invasive Characterization of Colourants by Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT)</em></td>
</tr>
<tr>
<td>16:30 - 16:50</td>
<td><strong>Conference Room A</strong></td>
</tr>
<tr>
<td></td>
<td>Alessia Coccato</td>
</tr>
<tr>
<td></td>
<td><em>Combined historical, physical anthropology, archaeological, and archaeoietrical approaches to understand glass beads from the Kongo Central province, Democratic Republic of Congo (DRC)</em></td>
</tr>
<tr>
<td>16:30 - 16:50</td>
<td><strong>Conference Room B</strong></td>
</tr>
<tr>
<td></td>
<td>Marianne Odlyha</td>
</tr>
<tr>
<td></td>
<td><em>Preservation of cellulose and collagen-based materials using novel nanoparticle-based treatment and non-destructive evaluation techniques</em></td>
</tr>
<tr>
<td>18:00</td>
<td>Welcome reception – Cultuurkapel Sint-Vincent</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------</td>
</tr>
</tbody>
</table>
| 9:00 - 9:40 | Plenary lecture – Conference Room A & B      |                      | Howell G.M. Edwards  
Biodegradation of Art Works and Archaeological Artefacts Studied by Raman Spectroscopy : Space Mission Science Data Applied to Cultural Heritage Preservation |
| 9:40 - 10:00 | Aurélie Mounier                              | Conference Room A    | Pigments & Dyes in a collection of medieval illuminations (14th – 16th century)                |
|            | Conference Room B                            |                      | Alice Gimat  
Paper decay induced by iron gall ink: an investigation of the mechanism using cellobiose |
| 10:00 - 10:20 | Clara Granzotto                              | Conference Room A    | Improved MALDI mass fingerprinting for identification and discrimination of Acacia gums in samples from works of art |
|            | Conference Room B                            |                      | Tânia Rosado  
Stone weathering by microbial activity – The case of Convent of Christ |
| 10:20 - 10:50 | Coffee break                                 |                      |                                                  |
| 10:50 - 11:10 | Federica Pozzi                              | Conference Room A    | Conquering space with matter: an in-depth study of Alberto Burri’s materials and techniques |
|            | Conference Room B                            |                      | Kepa Castro  
Characterising the underwater corrosion system of iron nails coming from a shipwreck |
| 11:10 - 11:30 | Astrid Harth                                | Conference Room A    | Assessing issues of attribution by means of technical research: a disputed Van Dyck reconsidered |
|            | Conference Room B                            |                      | Rafaela Debastiani  
Analysis of pigments from fragments of Roman wall paintings from Germania Superior |
| 11:30 - 11:50 | Armida Sodo                                 | Conference Room A    | Chemical and Spectroscopic investigation of the Raphael’s Cartoon for the School of Athens from Pinacoteca Ambrosiana |
|            | Conference Room B                            |                      | Hilde De Clercq  
Rehabilitation of farms – limits of salt content |
| 11:50 - 14:00 | Lunch break                                 |                      |                                                  |
| 14:00 - 14:40 | Plenary lecture – Conference Room A & B      |                      | Mary-Kate Donais  
The Saint Anselm College Italy Excavations - Research and Training |
| 14:40 - 15:00 | Sponsor talk – B&W Tek                      |                      |                                                  |
| 15:00 - 15:20 | Sponsor talk – Smarttech LTD                |                      |                                                  |
| 15:20 - 15:40 | Sponsor talk – Hirox Europe                 |                      |                                                  |
| 15:40 - 16:20 | Flash presentation 1                        |                      |                                                  |
| 16:20 - 18:00 | Poster session 1 + Reception                |                      |                                                  |

**Tuesday, March 22, 2016**

**Wednesday, March 23, 2016**

Conference Excursion (Lunch and Dinner included)
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Location</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00 - 9:40</td>
<td>Plenary lecture – Conference Room A &amp; B</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Jan Jehlička</strong></td>
<td></td>
<td><em>Comparison of Miniature Raman Spectrometric Devices and Gemtesting Systems for Identification of Gemstones</em></td>
</tr>
<tr>
<td>9:40 - 10:00</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Antonio Hernanz</strong></td>
<td></td>
<td><em>Raman microscopy of hand stencils rock art from Yabrai Mountain, Inner Mongolia Autonomous Region, China</em></td>
</tr>
<tr>
<td></td>
<td><strong>Fauzia Albertin</strong></td>
<td></td>
<td><em>Tomography reads inside ancient books</em></td>
</tr>
<tr>
<td>10:00 - 10:20</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Philippe Colomban</strong></td>
<td></td>
<td><em>On-site identification of Sceaux porcelain and faience using portable Raman instrument</em></td>
</tr>
<tr>
<td></td>
<td><strong>Jan Van den Bulcke</strong></td>
<td></td>
<td><em>Looking inside valuable wooden objects with X-ray CT @ UGCT</em></td>
</tr>
<tr>
<td>10:20 - 10:50</td>
<td>Coffee break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:50 - 11:10</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Claudia Conti</strong></td>
<td></td>
<td><em>Non-destructive subsurface investigation of art materials with Micro-SORS</em></td>
</tr>
<tr>
<td></td>
<td><strong>Adele DeCruz</strong></td>
<td></td>
<td><em>Observations on the use of OCT to examine the varnish layer of paintings</em></td>
</tr>
<tr>
<td>11:10 - 11:30</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Debbie Lauwers</strong></td>
<td></td>
<td><em>A novel concept towards in-situ Raman mappings using a portable Raman spectrometer</em></td>
</tr>
<tr>
<td></td>
<td><strong>Tom Callewaert</strong></td>
<td></td>
<td><em>Segmentation of thin varnish layers in OCT images of works of art</em></td>
</tr>
<tr>
<td>11:30 - 11:50</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Christoph Herm</strong></td>
<td></td>
<td><em>Analysis of Wilhelm Ostwald’s “Colour Organ” with Raman Micro-spectroscopy</em></td>
</tr>
<tr>
<td></td>
<td><strong>Manuel Dierick</strong></td>
<td></td>
<td><em>The use of micro-CT in cultural heritage research</em></td>
</tr>
<tr>
<td>11:50 - 14:00</td>
<td>Lunch break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:00 - 14:40</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Manfred Schreiner</strong></td>
<td></td>
<td><em>Multispectral Imaging and Material Analysis for the Visualization and Documentation of Manuscripts</em></td>
</tr>
<tr>
<td>14:40 - 15:00</td>
<td>Sponsor talk – XG Lab</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15:00 - 15:20</td>
<td>Sponsor talk – Fondis Bioritech</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15:20 - 16:00</td>
<td>Flash presentation 2</td>
<td>Conference Room A</td>
<td></td>
</tr>
<tr>
<td>16:00 - 17:40</td>
<td>Poster session 2 + Reception</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19:30</td>
<td>Conference dinner – Hotel Monasterium PoortAckere</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Conference Room A</td>
<td>Conference Room B</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>9:40 - 10:00</td>
<td><strong>Ilaria Serafini</strong>&lt;br&gt;A multi-analytical approach for characterization of orcein dyes in historical textiles, extracted through a new alkaline extraction protocol</td>
<td><strong>Ferruccio Petrucci</strong>&lt;br&gt;Radiocarbon dating of 20th century works of art</td>
<td></td>
</tr>
<tr>
<td>10:00 - 10:20</td>
<td><strong>Louise Decq</strong>&lt;br&gt;Development of an analytical procedure for the analysis of European lacquer</td>
<td><strong>Reza Sohbati</strong>&lt;br&gt;Optically stimulated luminescence dating of rock surfaces</td>
<td></td>
</tr>
<tr>
<td>10:20 - 10:50</td>
<td>Coffee break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:50 - 11:10</td>
<td><strong>Barbara Łydżba-Kopczyńska</strong>&lt;br&gt;Determination of authenticity of paintings using &quot;attribution markers&quot; and data mining techniques</td>
<td><strong>Pieter-Jan Sabbe</strong>&lt;br&gt;Chemical imaging of heritage metal surfaces with X-ray-excited Optical Microscopy</td>
<td></td>
</tr>
<tr>
<td>11:10 - 11:30</td>
<td><strong>Marina González-Pérez</strong>&lt;br&gt;Optimizing the FISH protocol for analyzing Cultural Heritage microcolonizers: microwave fixation</td>
<td><strong>Marine Cotte</strong>&lt;br&gt;The X-ray and infrared microspectroscopy beamline ID21: applications to 19th-20th C. artistic materials</td>
<td></td>
</tr>
<tr>
<td>11:30 - 11:50</td>
<td><strong>Allesandro Mandelli</strong>&lt;br&gt;Innovative diagnostic models of artefacts: the case study of Michelangelo’s Pietà Rondanini</td>
<td><strong>Xiangjun Wei</strong>&lt;br&gt;The stratified structure of ancient paintings in Forbidden City studied by Synchrotron radiation micro X-ray methods</td>
<td></td>
</tr>
<tr>
<td>11:50</td>
<td>Closing Ceremony</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
List of accepted works
PL: Plenary Lecture
OC: Oral Contribution
P: Poster Presentation
S: Sponsor Presentation/talk

Monday, March 21, 2016

Heritage Conservation and Art Research – a critical perspective
Antonio Candeias
PL-1 37

Assessment of indoor air quality and the risk of damage to cultural heritage objects using MEMORI® dosimetry
Terje Grøntoft, D.Thickett, P. Lankester, S. Hackney, J.H. Townsend, K. Ramsholt and M. Garrido
PL-2 39

Oral Session A1

Coupling scanning macro-XRF and confocal micro-XRF to study the three successive versions of the painting L’Homme blessé by G. Courbet
Ina Reiche, Myriam Eveno, Thomas Calligaro, Laurent Pichon, Katharina Müller, Eric Laval, Erin Mysak, Bruno Mottin
OC-A-1.1 41

Application of Neutron-based Analytical Techniques for the Non-destructive Investigation of the Coinage of Antique Bronze Coins
Martina Griesser, René Traum, Winfried Kockelmann, Klaudia Hradil
OC-A-1.2 42

Laminated altered layers in historical glass: density variations of silica nanoparticle random packings as explanation for the observed lamellae
Olivier Schalm, Willemien Anaf
OC-A-1.3 44

Forensic Art History: The Anders Ädel Pigment Dispute 1839-1841
Ingalill Nyström, Jacob Thomas, Johan Knutsson, Anneli Palmsköld, Kaj Thuresson, Anders Assis
OC-A-1.4 46

Oral Session B1

Monitoring the Impact of the Indoor Air Quality on Metallic Heritage
Lucy ’t Hart, Patrick Storme, Willemien Anaf, Olivier Schalm
OC-B-1.1 48

Acidic degradation patterns of photographic dyes
Evert B. Reijers, Cecilia W.L. Jespers, Maxime A.C. van Wiggen and Leonardus W. Jenneskens
OC-B-1.2 50

Innovative mitigation strategies to easel paintings safeguard
Cátia Salvador, Mara Silva, Tânia Rosado, Rui Bordalo, António Candeias, Ana Teresa Caldeira
OC-B-1.3 52

Influence of Solvents on Cellulose Average Degree of Polymerization
Jan Krejčí, Markéta Škrdlantová, Klára Drábková
OC-B-1.4 54
Sponsor Session 1

Raman Spectroscopy and Automated Fluorescence Removal for Pigment Identification in Art Conservation Applications  
**BRS**

S-1.1  55

Applied IR and Raman Micro-spectroscopy for Art Conservation Research  
**Bruker Optics**

S-1.2  54

Oral Session A2

Non-invasive tree-ring analysis-archaeology & art  
**Aoife Daly, Noëlle Streeton**

OC-A-2.1  57

Non-invasive Characterization of Colourants by Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT)  
**Marcello Manfredi, Elettra Barberis, Maurizio Aceto and Emilio Marengo**

OC-A-2.2  59

Combined historical, physical anthropology, archaeological, and archaeometrical approaches to understand glass beads from Kongo Central province, Democratic Republic of Congo (DRC)  
**Alessia Coccato, Anastasia Rousaki, Mafalda Costa, Bernard Clist, Koen Bostoen, Peter Vandenabeele**

OC-A-2.3  61

Oral Session B2

Shellac-based nanocomposites for protection of wood surface  
**Maduka L. Weththimuni, Doretta Capsoni, Chiara Milanese, Maurizio Licchelli and Marco Malagodi**

OC-B-2.1  63

Innovative application of Advanced nanomaterials designing future treatment technology for Art conservation  
**Tomas Markevičius, Helmut Meyer, Nina Olsson, Kate Seymour, Rocco Furfuri**

OC-B-2.2  65

Preservation of cellulose and collagen-based materials using novel nanoparticle-based treatment and non-destructive evaluation techniques  
**Marianne Odlyha, Laurent Bozec, Angelica Bartoletti, Elena Gonzalez, David Chelazzi, Rodorico Giorgi, Piero Baglioni, Paolo Matteazzi, John Duncan**

OC-B-2.3  67
Tuesday, March 22, 2016

Biodegradation of Art Works and Archaeological Artefacts Studied by Raman Spectroscopy: Space Mission Science Data Applied to Cultural Heritage Preservation
Howell G.M. Edwards

The Saint Anselm College Italy Excavations - Research and Training
Mary-Kate Donais, David George

Oral Session A3

Pigments & Dyes in a collection of medieval illuminations (14th - 16th century)
Aurélie Mounier, Floréal Daniel

Improved MALDI mass fingerprinting for identification and discrimination of Acacia gums in samples from works of art
Clara Granzotto, Ken Sutherland, Julie Arslanoglu

Conquering space with matter: an in-depth study of Alberto Burri's materials and techniques
Frederica Pozzi, Julie Arslanoglu, Federico Carò, Carol Stringari

Assessing issues of attribution by means of technical research: a disputed Van Dyck reconsidered
Astrid Harth, Olivier Schalm, Geert Van der Snickt, Koen Janssens

Chemical and Spectroscopic investigation of the Raphael's Cartoon for the School of Athens from Pinacoteca Ambrosiana
Armida Sodo, Annalaura Casanova Municchia, Marcella Ioele, Maria Antonietta Ricci, Alfonso Pio Russo

Oral Session B3

Paper decay induced by iron gall ink: an investigation of the mechanism using cellobiose
Alice Gimat, Anne-Laurence Dupont, Pascale Massiani and Véronique Rouchon

Stone weathering by microbial activity – The case of Convent of Christ
Tânia Rosado, Mara Silva, Mónica Lança, Carla Nogueira, Rita Santos, José Mirão, António Candeias and Ana Teresa Caldeira

Characterising the underwater corrosion system of iron nails coming from a shipwreck
Kepa Castro, Julene Aramendia, Leticia Gomez-Nubla, Ludovic Bellot-Gurlet, Laura García, Iñaki García-Camino, Manuel Izaguirre, Juan Manuel Madariaga
<table>
<thead>
<tr>
<th>Book of Abstracts</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis of pigments from fragments of Roman wall paintings from Germania Superior</td>
<td>OC-B-3.4 90</td>
</tr>
<tr>
<td>Rafaela Debastiani, Rolf Simon, Stefan Heißler, Andrea Wähning, Markus Meinen, Peter Henrich, Tilo Baumbach and Michael Fiederle</td>
<td></td>
</tr>
<tr>
<td>Rehabilitation of farms – limits of salt content</td>
<td>OC-B-3.5 92</td>
</tr>
<tr>
<td>Hilde De Clercq, S. Godts</td>
<td></td>
</tr>
</tbody>
</table>

### Sponsor Session 2

3D spectroscopic mapping tomography applied to art objects diagnosis | S-2.1 93 |
| B&WTEK | |

The issue of digitization of cultural heritage objects using non-contact structural LED light 3D scanning | S-2.2 95 |
| Smarttech LTD | |

Hirox RH-2000 3D digital microscope | S-2.3 96 |
| Hirox Europe | |

### Poster Session 1

Characterization of compounds present in lake and textile, through ammonia mild extraction technique and micro-sampling with Ag-gel matrix associated with SERS analysis | P-1.1 147 |
| Livia Lombardi, Ilaria Serafini, Claudia Fasolato, Paolo Postorino, Fabio Sciubba, Marcella Guiso, Armandodoriano Bianco | |

A copy of the icon as a non-invasive test technical and technological formation of the original | P-1.2 149 |
| Stępień Danuta, Mariola Pachnia, Cathy Carman | |

Spectroscopic study on accelerated ageing of materials used in contemporary art | P-1.3 150 |
| Alessandro Ciccola, Marcella Guiso, Claudia Fasolato, Fabio Sciubba, Paolo Postorino and Armandodoriano Bianco | |

An XRF study of a Late Bronze Age bronze fibula from Sardinia (Italy) | P-1.4 151 |
| Nick Schiavon, Antonio Brunetti, Anna Depalmas, Claudio Bulla, Alba Canu | |

Imaging and X-ray spectroscopic techniques used in a Portuguese organ pipe | P-1.5 152 |
| Joana Fanico, Agnès Le Gac, Sónia Costa, José Mirão, António Candeias | |

Pigments and dyes for art: a scientific database of ancient, modern and contemporary materials | P-1.6 154 |
| Tiziana Cavalieri, Paola Buscaglia, Marco Nervo, Anna Piccirillo, Marco Pisani, Paolo Triolo, Massimo Zucco | |

Analysis of the Notger Gospel book by PIXE, XRF and Raman spectroscopies | P-1.7 156 |
| David Strivay, François-Philippe Hocquet, Fanny Dombret, Cécile Oger | |

---

*2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium*
<table>
<thead>
<tr>
<th>Contributions</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification of binders in copper portrait miniatures of 17th and 18th centuries by µ-ATR-FTIR and Py-GC-MS</td>
<td>P-1.8</td>
</tr>
<tr>
<td>Dora Teixeira, Alfredina Veiga, Ana Manhita, Catarina Miguel, António Candeias, Paulo Rodrigues, Jorge Ginja Teixeira</td>
<td>157</td>
</tr>
<tr>
<td>Evaluation of Laser Cleaning of Parchment, Wool and Feather with High Performance Liquid Chromatography and Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy</td>
<td>P-1.9</td>
</tr>
<tr>
<td>Stamatis Boyatzis, Eleni Ioakimoglou, Eleni Tziamourani, Efrosini Karantoni, Ekaterini Malea, Stavroula Rapti, Paraskevi Pouli, Athanassia Papanikolaou, Kristallia Melessanaki and Georgios Panagiaris</td>
<td>159</td>
</tr>
<tr>
<td>Multi-analytical study on two daguerreotype case components</td>
<td>P-1.10</td>
</tr>
<tr>
<td>Teresa Ferreira, Evan Maina Maingi, Margarida Nunes, Cátia Relvas, Sónia Costa, Catarina Miguel</td>
<td>161</td>
</tr>
<tr>
<td>Physicochemical characterization of two 19th century daguerreotypes by non-invasive analytical techniques</td>
<td>P-1.11</td>
</tr>
<tr>
<td>Teresa Ferreira, Evan Maina Maingi, Margarida Nunes, Cátia Relvas, Sónia Costa, Catarina Miguel</td>
<td>163</td>
</tr>
<tr>
<td>The use of colour on pottery decoration from late Holocene South American hunter gatherers</td>
<td>P-1.12</td>
</tr>
<tr>
<td>Veronica Aldazabal, Debbie Lauwers, Peter Vandenabeele, Luc Moens, Cristina Vazquez</td>
<td>165</td>
</tr>
<tr>
<td>A new scanner for in-situ digital radiography of paintings</td>
<td>P-1.13</td>
</tr>
<tr>
<td>Anna Impallaria, Federico Evangelisti, Ferruccio Petrucci, Flavia Tisato, Lisa Castelli, Francesco Taccetti</td>
<td>167</td>
</tr>
<tr>
<td>Distinguishable features between a 16th Century Portuguese-Flemish Master and his follower: technical and analytical contributions</td>
<td>P-1.14</td>
</tr>
<tr>
<td>Sara Valadas, José Mirão, Cristina Barrocas Dias, Peter Vandenabeele, António Candeias</td>
<td>169</td>
</tr>
<tr>
<td>Principal component analysis of chromatic parameters measured on atmospheric aged paint dosimeters</td>
<td>P-1.15</td>
</tr>
<tr>
<td>Agustin Herrera, D. Ballabio, R. Todeschini, N. Navas and C. Cardell</td>
<td>171</td>
</tr>
<tr>
<td>Preliminary studies of ultraviolet radiation over time in paint mock-ups</td>
<td>P-1.16</td>
</tr>
<tr>
<td>Agustin Herrera, F. Grisoni, D. Ballabio, R. Todeschini, N. Navas and C. Cardell</td>
<td>173</td>
</tr>
<tr>
<td>Beaming into the Iron Age: Handheld X-ray Fluorescence on Iron Age ceramics from Luristan (Iran)</td>
<td>P-1.17</td>
</tr>
<tr>
<td>Possum Pince, Peter Vandenabeele</td>
<td>175</td>
</tr>
<tr>
<td>Effect of acid rain on the leaching of heavy metals on CorTen steel structures</td>
<td>P-1.18</td>
</tr>
<tr>
<td>Patricia Ruiz, Julene Aramendia, Kepa Castro, Juan Manuel Madariaga</td>
<td>176</td>
</tr>
<tr>
<td>Analytical Characterization of glass tesserae from mosaics of Early Christian basilicas in Albania</td>
<td>P-1.19</td>
</tr>
<tr>
<td>Esmeralda Vataj, Teuta Dilo, Elio Hobdari, Stefan Röhrs, Peter Vandenabeele, Nikolla Civici</td>
<td>178</td>
</tr>
<tr>
<td>Title</td>
<td>Authors</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>--------------------------------------------------------------</td>
</tr>
<tr>
<td>SERS analysis of basic and acid early synthetic dyes on wool</td>
<td>Maria Vega Cañamares, Chiara Deriu, Rocco Mazzeo, Silvia Prati, Santiago Sanchez-Cortes</td>
</tr>
<tr>
<td>Portable XRF vs benchtop EDX devices: Application for elemental</td>
<td>Toufik A. Mostefaoui, L. Idjouadiene, V. Marzo, L. Bonizzoni, M. Gargano, N. Ludwig</td>
</tr>
<tr>
<td>identification in Archeology</td>
<td></td>
</tr>
<tr>
<td>Application of non-destructive technical to study some manuscripts</td>
<td>Lynda Idjouadiene, T. A. Mostefaoui, V. Marzo, N. Ludwig, L. Bonizzoni, M. Gargano</td>
</tr>
<tr>
<td>of Algerian heritage</td>
<td></td>
</tr>
<tr>
<td>Analysis of pigments on a 16th century wood panel painting by portable</td>
<td>E. Stanzania, Danilo Bersani, Pierre Paulo Lottici, Philip Colomban</td>
</tr>
<tr>
<td>and laboratory Raman instruments</td>
<td></td>
</tr>
<tr>
<td>Multi-technical approach for the study of archaeological and artistic</td>
<td>Justine Vernet, Valeria Bongiorno, Giorgia Ghiara, Paolo Piccardo</td>
</tr>
<tr>
<td>bronze objects</td>
<td></td>
</tr>
<tr>
<td>Role of lead as a major alloying element in tin bronzes of</td>
<td>Justine Vernet, Paolo Piccardo</td>
</tr>
<tr>
<td>archaeological and artistic interest</td>
<td></td>
</tr>
<tr>
<td>On the degradation of plastic soldier toys at Oporto Military</td>
<td>Ana Teresa Caldeira, António Pereira, António Candelas, José Mirão, Peter Vandenabeele</td>
</tr>
<tr>
<td>Museum</td>
<td></td>
</tr>
<tr>
<td>The euclidean distance tool as discriminator of very similar Raman</td>
<td>Antonio Ramos de Torres, S. Ruiz-Moreno</td>
</tr>
<tr>
<td>spectra: application to pigment analysis in mixtures</td>
<td></td>
</tr>
<tr>
<td>Elemental and molecular mapping of pigments in painted artworks</td>
<td>Sara Mosca, Roberto Alberti, Tommaso Frizzi, Valentina Capogrosso, Austin Nevin, Gianluca Valentini and Daniela Comelli</td>
</tr>
<tr>
<td>Visualization and quantification of weathering effects and water</td>
<td>Simona Raneri, Germana Barone, Paolo Mazzoleni, Eva Rabot</td>
</tr>
<tr>
<td>uptake processes in natural building stones by using neutron imaging</td>
<td></td>
</tr>
<tr>
<td>Degradation Study of Plastic Materials Used in Contemporary Art by</td>
<td>Elettra Barberis, Marcello Manfredi, Emilio Marengo</td>
</tr>
<tr>
<td>Non-invasive Portable Infrared Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Non-Invasive Material Analysis of Parchment Manuscripts by</td>
<td>Wilfried Vetter, Bernadette Frühmann, Federica Cappa, Manfred Schreiner</td>
</tr>
<tr>
<td>Reflection-FTIR, XRF and Raman- Possibilities and Limitations</td>
<td></td>
</tr>
<tr>
<td>A novel approach for characterisation of polymers used in modern art</td>
<td>Donald Sale, Angelica Bartoletti, Marianne Odlyha and Laurent Bozec</td>
</tr>
<tr>
<td>conservation using Localised Thermal Analysis</td>
<td></td>
</tr>
<tr>
<td>Fast degradation and monitoring of arsenic sulfide pigments with</td>
<td>Marc Vermeulen, Jana Sanyova, Koen Janssens, Karolien De Wael</td>
</tr>
<tr>
<td>Raman spectroscopy-electrochemistry</td>
<td></td>
</tr>
</tbody>
</table>

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
### Thursday, March 24, 2016

**Comparison of Miniature Raman Spectrometric Devices and Gemtesting Systems for Identification of Gemstones**

*Jan Jehlička, Jaroslav Hyršl, Laura Minaříková and Adam Culka*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL-5</td>
<td>99</td>
</tr>
</tbody>
</table>

**Multispectral Imaging and Material Analysis for the Visualization and Documentation of Manuscripts**

*Manfred Schreiner, Heinz Miklas, Claudia Rapp, Robert Sablatnig, Wilfried Vetter, Bernadette Fruehmann, Federica Cappa, Fabian Hollaus*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL-6</td>
<td>100</td>
</tr>
</tbody>
</table>

### Oral Session A5

**Raman microscopy of hand stencils rock art from Yabrai Mountain, Inner Mongolia Autonomous Region, China**

*Antonio Hernanz, Mercedes Iriarte, Nai’ang Wang, Jinlong Chang*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-A-5.1</td>
<td>102</td>
</tr>
</tbody>
</table>

**On-site identification of Sceaux porcelain and faience using portable Raman instrument**

*Philippe Colomban, D. Mancini, C. Dupont-Logié*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-A-5.2</td>
<td>104</td>
</tr>
</tbody>
</table>

**Non-destructive subsurface investigation of art materials with Micro-SORS**

*Claudia Conti, Alessandra Botteon, Chiara Colombo, Marco Realini, Pavel Matousek*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-A-5.3</td>
<td>105</td>
</tr>
</tbody>
</table>

**A novel concept towards in-situ Raman mappings using a portable Raman spectrometer**

*Debbie Lauwers, Philip Brondeel, Peter Vandenabeele, Luc Moens*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-A-5.4</td>
<td>107</td>
</tr>
</tbody>
</table>

**Analysis of Wilhelm Ostwald's "Colour Organ" with Raman Microspectroscopy**

*Christoph Herm, Alexandra Bridarolli*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-A-5.5</td>
<td>109</td>
</tr>
</tbody>
</table>

### Oral Session B5

**Tomography reads inside ancient books**

*Fauzia Albertin, Eva Peccenini, Matteo Bettuzzi, Rosa Brancaccio, Maria Pia Morigi, Franco Casali and Giorgio Margaritondo*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-B-5.1</td>
<td>111</td>
</tr>
</tbody>
</table>

**Looking inside valuable wooden objects with X-ray CT @ UGCT**

*Jan Van den Bulcke, Denis Van Loo, Manuel Dierick, Bert Masschaele, Matthieu Boone, Kristof Haneca, Koen Deforce, Luc Van Hoorebeke, Hans Beeckman, Manu Frederickx, Valerio Lorenzoni and Joris Van Acker*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-B-5.2</td>
<td>113</td>
</tr>
</tbody>
</table>

**Observations on the use of OCT to examine the varnish layer of paintings**

*Adele DeCruz, Derek Nankivil, Joseph A. Izatt*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-B-5.3</td>
<td>115</td>
</tr>
</tbody>
</table>

**Segmentation of thin varnish layers in OCT images of works of art**

*Tom Callewaert, Joris Dik, Jeroen Kalkman*

<table>
<thead>
<tr>
<th>Session No.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-B-5.4</td>
<td>117</td>
</tr>
<tr>
<td>Book of Abstracts</td>
<td>Contributions</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>The use of micro-CT in cultural heritage research</td>
<td>OC-B-5.5 119</td>
</tr>
<tr>
<td><strong>Manuel Dierick, Matthieu Boone, Amelie De Muynck, Thomas De Schryver, Jelle Dhaene, Joris Van Acker, Jan Van den Bulcke, Veerle Cnudde, Denis Van Loo, Bert Masschaele and Luc Van Hoorebeke</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Sponsor Session 3**

XGLab’s new instrumentation for the analysis of cultural heritage

XG Lab

Fondis Bioritech – Niton XRF analyzers

Fondis Bioritech

**Poster Session 2**

Disclosing Van Eyck’s original paint layers on the Ghent Altarpiece by combined MA-XRF scanning and SEM-EDX analysis

**Geert Van Der Snickt, Hélène Dubois, Jana Sanyova, Alexia Coudray, Cecile Glaude, Stijn Legrand and Koen Janssens**

Nanoscale structures of fossil bones and growth processes for burned bones

**Giampaolo Piga, Maria Dolors Baró, Irati Golvano Escobal, Antonio Brunetti, Stefano Enzo, Sebastiano Garroni**

Non-invasive archaeometrical studies by new portable hybrid energy dispersive x-ray diffraction and x-ray fluorescence system

**Ariadna Mendoza Cuevaas, Jorge Fernandez-de-Cossio Dorta-Duque, Federico Bernardini**

A combined approach for the identification of handwritings in paper documents: the case of Antonio Stradivari’s relics

**Giusj Valentina Fichera, Piercarlo Dondi, Maurizio Licchelli, Luca Lombardi, Fausto Cacciatori, Marco D’Agostino and Marco Malagodi**

Evaluation of the Protective Capacity of Coatings on Silver Foil Exposed to H$_2$S, HCl and H$_3$CCOOH as a Model for the Ghent Altarpiece Gilded Frames

**Anastasia Rousaki, Peter Vandenabeele, Jana Sanyova, Hélène Dubois, Luc Moens**

The first look is never the true look - the comparative study of six Portuguese 16th century illuminated Charters based on spectroscopy and chemometrics analysis

**Catarina Miguel, Cristina Barrocas Dias, Teresa Ferreira, António Candeias**

Bright reds...or not so bright - the degradation of vermilion reds on medieval illuminations from Alcobaca, Troyes and the Vatican collections

**Catarina Miguel, Cristina Barrocas Dias, Maria Luísa Carvalho, António Candeias**
<table>
<thead>
<tr>
<th>Book of Abstracts</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monitoring of penetration depth of consolidants applied to carbonate and silicate substrates by Raman and FTIR spectroscopy</td>
<td>P-2.8 214</td>
</tr>
<tr>
<td>Lea Legan, Klara Retko, Tanja Špec, Polonca Ropret, Luka Škrlep, Andreja Ponderak, Andrijana Sever Škapin</td>
<td></td>
</tr>
<tr>
<td>Non-destructive Raman investigations on wall paintings at Sala Vaccarini in Catania (Sicily)</td>
<td>P-2.9 216</td>
</tr>
<tr>
<td>Germana Barone, Danilo Bersani, Alessia Coccato, Debbie Lauwers, Paolo Mazzoleni, Simona Raneri, Peter Vandenabeele, Davide Manzini, Giuseppe Agostino, Nicola Francesco Neri</td>
<td></td>
</tr>
<tr>
<td>Light, Shadows and Surface Characteristics. The Multispectral Portable Light Drome</td>
<td>P-2.10 218</td>
</tr>
<tr>
<td>Lieve Watteeuw, Hendrik Hameeuw, Bruno Vandermeulen, Athena Van der Perre, Vanessa Boschloos, Luc Delvaux, Marina Van Bos, Marc Proesmans, Luc Van Gool</td>
<td></td>
</tr>
<tr>
<td>The case-study of &quot;The daughters of the emperor Ferdinand I&quot; by Jakob seisenegger, in Trento (Italy): Analytical hygro-mechanical results as a support in risk assessment for technical interventions</td>
<td>P-2.11 220</td>
</tr>
<tr>
<td>Paolo Dionisi-Vici, Francesca Raffaelli and Alberto Finozzi</td>
<td></td>
</tr>
<tr>
<td>Development of a translation stage for in situ non-invasive analysis and high resolution imaging</td>
<td>P-2.12 221</td>
</tr>
<tr>
<td>David Strivay, Mathieu Clar, Said Rakka, François-Philippe Hocquet, Catherine Defeyt</td>
<td></td>
</tr>
<tr>
<td>Restoration of a broken statue: reassembling of two stone parts coming from St. John church in Asti</td>
<td>P-2.13 222</td>
</tr>
<tr>
<td>Serena Di Gaetano, Nicola Amapane, Fabrizio Crivello, Anna Piccirillo, Tommaso Poli, Laura Porcu, Maria Concetta Capua</td>
<td></td>
</tr>
<tr>
<td>Talavera de la Reina tiles in Portugal: a study of materials and technology</td>
<td>P-2.14 224</td>
</tr>
<tr>
<td>Teresa Ferreira, Cátia Relvas, Margarida Nunes, Luís C. Alves, António Candeias, José Mirão, Celso Mangucci</td>
<td></td>
</tr>
<tr>
<td>Optimization of Total Reflection X-ray Fluorescence analysis of pigments</td>
<td>P-2.15 225</td>
</tr>
<tr>
<td>Alessia Coccato, Bart Vekemans, Laszlo Vincze, Luc Moens, Peter Vandenabeele</td>
<td></td>
</tr>
<tr>
<td>Uncover the mantle: rediscovering Gregório Lopes palette and technique with a study on the painting &quot;Mater Misericordiae&quot;?</td>
<td>P-2.16 226</td>
</tr>
<tr>
<td>Vanessa Antunes, António Candeias, Maria L. Carvalho, Ana I. Seruya, Maria J.Francisco, Sonia Costa, Alexandra Lauw, Vítor Serrão, Marta Manso</td>
<td></td>
</tr>
<tr>
<td>The importance of analytical techniques and cross-check of data in a painting by Francisco Pinto Pereira</td>
<td>P-2.17 228</td>
</tr>
<tr>
<td>Nidia Silva, Agnès Le Gac, Sónia Costa, José Mirão, António Candeias</td>
<td></td>
</tr>
<tr>
<td>Green colour in the 16th century Portuguese paintings of the Funchal’s Cathedral altarpiece</td>
<td>P-2.18 230</td>
</tr>
<tr>
<td>Sofia Gomes, Sofia Gomes, Mercês Lorena, Peter Vandenabeele, Debbie Lawers, Alessia Coccato, Sara Valadas and António Candeias</td>
<td></td>
</tr>
</tbody>
</table>

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
Pigment and morphological analysis of an oil painting attributed to the young Picasso

*María Conception Chillón, Sergio Ruiz-Moreno*

Characterization of the artificial patinas on a bronze sculpture "Ettore e Andromaca" of the museum Carlo Bilotti - Aranciera di Villa Borghese (Rome)

*Annalaura Casanova Municchia, Giorgio D’Ercoli, Ilma Reho, Maria Antonietta Ricci, Armida Sodo*

Diagnosis of materials and effectiveness of Er:YAG Laser cleaning in a Borrassa's Panel Painting (15th Century)

*Adele De Cruz, Alessia Andreotti, William P. Brown, Mara Camaiti, Maria Perla Colombini*

Go with the flow: A preliminary rheological study to 17th century clear varnish recipes and components

*Vincent Cattersel, Louise Decq, Delphine Steyaert, Charles Indekeu, Emile Van Binnebeke, Wim Fremout and Steven Saverwyns*

Instrumental techniques used to identify proteins binding to wood icons from the XVIII century

*Nicoletta Vornicu, Maria Urma, Mirela-Fernanda Zaltariov, Cristina Bibire*

In situ Raman study of marble capitals in the Alhambra

*Paz Arjonilla Ureña, Ana Domínguez Vidal, María José de la Torre López, Elena Correa Gómez, Ramón Rubio Domene, Mª José Ayora Cañada*

A Software Platform Proposal for the Automated Interpretation of Spectra in Artworks Analysis

*Juanjo Gonzalez-Vidal, Rosanna Pérez-Pueyo, María José Soneira*

Helping art historians. A new insight look at the 16th century fresco “The Good and the Bad Judge”? with technical photography and micro-analytical research

*Milene Gil, C. Araujo, M.L. Carvalho, S. Longelin, C. Souto, L. Dias, J. Frade, I. Ribeiro, J. Mirão and A. Candeias*

Multi-analytical study of the metal ion-anthraquinone complex in red lake pigments

*Sara Bellei, Daniela Comelli, Sara Mosca, Ilaria Bargiglia, Cosimo d’Andrea, Barbara Berrie, and Austin Nevin*

Study of crystal defects in historical semiconductor pigments through time-resolved photo-luminescence spectroscopy

*Alessia Artesani, Daniela Comelli, Austin Nevin, Cosimo D’Andrea, Anna Cesaratto, Sara Bellei, Valentina Capogrosso, Sara Mosca and Gianluca Valentini*

Thermoluminescence Application

*David Price*

Interactions with adhesives and varnishes on a contemporary cardboard mosaic: Codex Vitae by Anna Moro Lin 2008

*Ilina Udrea, Rosanna Chiggiato*
<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyphasic analysis of cultural heritage deleterious filamentous fungi</td>
<td>Margarida Isabel Martins Pires, Tânia Rosado, Maria do Rosário Martins, António Candeias, Ana Teresa Caldeira</td>
<td>P-2.31</td>
<td>254</td>
</tr>
<tr>
<td>&quot;Color is a kind of holy substance for me&quot; : analytical study of the Sam Francis' palette from the 1940's to the 1990's</td>
<td>Catherine Defeyt, Joy Mazurek, Aneta Zebala, Debra Burchett-Lere</td>
<td>P-2.32</td>
<td>256</td>
</tr>
<tr>
<td>Combined XRF and FTIR-ATR investigation on the mummy of Darder Museum (Banyoles-Girona, Spain)</td>
<td>Antonio Brunetti, Giampaolo Piga, Albert Isidro, Maria José Adserías-Garriga, Assumpció Malgosa</td>
<td>P-2.33</td>
<td>258</td>
</tr>
</tbody>
</table>

**Friday, March 25, 2016**

**Oral Session A7**

A multi-analytical approach for characterization of orcein dyes in historical textiles, extracted through a new alkaline extraction protocol

Ilaria Serafini, Livia Lombardi, Fabio Scibba, Claudia Fasolato, Paolo Postorino, Marcella Guiso, Maurizio Bruno, Armandodoriano Bianco

Development of an analytical procedure for the analysis of European lacquer

Louise Decq, Vincent Cattersel, Delphine Steyaert, Michael Schilling, Frederic Lynen, Viviane Leyman, Charles Indekeu, Emile Van Binnebeke, Wim Fremout and Steven Saverwyns

Determination of authenticity of paintings using "attribution markers" and data mining techniques

Barbara Łydżba-Kopezyńska, Janusz Szwabiński

Optimizing the FISH protocol for analyzing Cultural Heritage microcolonizers: microwave fixation

Marina González-Pérez, Ricardo Veira, António Pereira, António Candeias, Ana Teresa Caldeira

Innovative diagnostic models of artefacts: the case study of Michelangelo's Pietà Rondanini

Lucia Toniolo, Cristiana Achille, Gianluca Valentini, Valentina Capogrosso, Francesco Fassi, Sara Goidanich, Davide Gulotta, Alessandro Mandelli, Sara Mosca, Austin Nevin

**Oral Session B7**

Radiocarbon dating of 20th century works of art

Ferruccio Petrucci, Lucia Caforio, Maria Elena Fedi, Pier Andrea Mandò, Eva Peccenini, Virginia Pellicori, Peter Rylands, Paul Schwartzbaum, Francesco Taccetti

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
Optically stimulated luminescence dating of rock surfaces
Reza Sohbati, Andrew Murray, Mayank Jain, Trine Freiesleben, Sahar al Khasawneh

Chemical imaging of heritage metal surfaces with X-ray-excited Optical Microscopy
Pieter-Jan Sabbe, Mark Dowsett, Matt Hand, Mark Jones and Annemie Adriaens

The X-ray and infrared micro-spectroscopy beamline ID21: applications to 19th-20th C. artistic materials

The stratified structure of ancient paintings in Forbidden City studied by Synchrotron radiation micro X-ray methods
Xiangjun Wei, Yong Lei, Lihua Wang, Yuying Huang
Monday, March 21, 2016
Heritage Conservation and Art Research – a critical perspective

A. Candeias 1,2

1 HERCULES Laboratory| Institute for Research and Advanced Studies and Chemistry Department | School of Sciences and Technology, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal
2 Jose de Figueiredo National Conservation Restoration Laboratory, General Directorate for Cultural Heritage, Rua das Janelas Verdes, 1249-017 Lisbon, Portugal

*candeias@uevora.pt

Keywords: heritage conservation; art research; analytical methodologies

Heritage research is one of the fundamental pillars of safeguarding cultural heritage. It must encompass a multidisciplinary approach comprising history, art history, conservation-restoration and material research. Scientific studies, from macro to micro and nano/molecular level, encourage a deeper understanding of cultural heritage in its multiple aspects: as testimony of historical, artistic and social concepts; as objects with a typical structure, materiality, and three-dimensional features; and as surfaces and interfaces with specific features and behaviours when exposed to environmental factors.

Nevertheless, research regarding cultural heritage may be misdirected. Most often, this happens due to a number of contributing factors: the use of heritage artefacts for the sole purpose to show the power and capability of an analytical technique without special value from the standpoint of the history, knowledge or conservation of that piece; the use of narrow analytical regime or tendency to focus on specific research details resulting in incomplete information that can be problematic for further conservation-restoration interventions or historical studies; and excessive sampling of historical artefacts without precise criteria regarding the research objectives or purposes.

The scientific analysis of cultural heritage raises several ethical issues including the idea that the artwork, scrutinized in every physical aspect, may be reduced to a sum of analytical results in the detriment of its aesthetic and social values. There is also a serious concern about the alteration of artworks by the analytical method, especially if sample removal is necessary.

Although in-situ analysis is already a common stage in a multi-analytical methodology, as well as a main goal in cultural heritage research development, micro-sampling is, in most cases, still needed as it presents several advantages such as the possibility to conduct stratigraphic analysis. Micro-sampling does not require to take the object out of the building, which usually involves extreme insurance values and packaging, or to move the analytical instrumentation. Also, more than one analytical method can often be employed with the same sample, providing a much more comprehensive analysis.
Another important concern is the fact that the range of analytical techniques currently available for heritage research is very broad. Since each technique gives its own type of information and has its own suitability, strengths and weaknesses, a previous assessment is essential to avoid a disoriented and useless examination. However, in some cases researchers tend to use a wide range of analytical techniques without any real gain in terms of information.

Furthermore, presently it is common to perform analysis under the framework of conservation restoration interventions and, in several countries, legislation has made this a pre-requisite for approval. However, conservation materials and methodologies tend to be standardized by conservation teams and often analytical results are delivered only at the end of the intervention having no benefit for the rationalization of the methodologies. This is due in many cases to the fact that procurements do not take into consideration the time that is needed for the analysis and for the integration of the analytical data being exclusively focused on the conservation intervention process.

Finally, the preservation of tangible and intangible cultural heritage is a key issue that calls for the development and revitalization of research and for the implementation of integrated strategies, including novel dissemination technologies that will help with its valorisation and promotion. The conceptions and misconceptions that our field is presently dealing with have been the rationale behind this talk.
Assessment of indoor air quality and the risk of damage to cultural heritage objects using MEMORI® dosimetry


1 NILU-Norwegian Institute for Air Research, Department for Urban Environment and Industry, P.O.box 100, NO-2027 Kjeller (Norway). Tel. +4763898923
2 English Heritage, Rangers House, Chesterfield Walk, London SE10 8QX (UK).
3 Tate, Institution, Conservation Department, Tate Britain, Millbank, London SW1P 4RG (UK).
4 The National Archives of Norway, The Preservation and Supervision Department, P.O.Box 4013 Ullevål stadion, N-0806 Oslo (Norway).

* teg@nilu.no, +4763898923/+4763898950

Keywords: MEMORI® dosimeter; microclimate frame; showcase; movable cultural heritage; indoor air quality; air pollution, preventive conservation; organic acids.

Air pollution is one of the environmental influences that degrade cultural heritage objects situated indoors. Other essential influences, such as temperature, relative humidity and light are often well monitored. The presence of air pollutants is less often measured or included in risk assessment. The MEMORI® technology presented was developed as a tool for easy measurement and assessment of the general risk of degradation of heritage objects situated indoors due to indoor exposure to air pollutants [1].

MEMORI® dosimetry was performed in locations belonging to English Heritage (Figure 1) and Tate (both located in London) and the National Archives of Norway in Oslo, to assess air quality. The related damage risk for collection objects and the protection offered by display and storage designs, was assessed. A high level of acidic effect was observed inside a number of showcases, and a high level of oxidizing effect was observed in some room locations. Relatively simple mitigation measures, such as constructing tightly sealed showcases using low emitting materials; installing active carbon absorbing media inside a “microclimate” frame and using cardboard storage boxes for paper, significantly improved air quality. Overall, implementation of such measures is likely to improve the preservation of objects and reduce conservation costs.
Figure 1: MEMORI® results from measurements in English Heritage locations, with colour evaluation for copper alloys and ceramics. “Red” indicates that damage is likely to occur to objects within three years and that damage will require interventive conservation. “Yellow” indicates a situation in between. Three distinctive groups of two measurement results are noted on the upper diagram; the corner case (1a) and an alcove case (1b) in the bronzes room in Ranger’s House; the centre desktop case in the bronzes room in Ranger’s House (2c) and the showcase in the plate and china room in Apsley House (2d); and the plate and china room in Apsley House (3e) and the bronzes room in Ranger’s House (3f).

References:
Coupling scanning macro-XRF and confocal micro-XRF to study the three successive versions of the painting *L'Homme blessé* by G. Courbet

Ina Reiche¹², Myriam Eveno³, Thomas Calligaro³, Laurent Pichon³, Katharina Müller³, Eric Laval³, Erin Mysak³⁴, Bruno Mottin³

¹ Rathgen Research Laboratory – National Museums in Berlin, Germany, Schlossstr. 1a, 14059 Berlin (Germany), +49-30-266427101, i.reiche@smb.spk-berlin.de.
² Laboratoire d’Archéologie Moléculaire et Structurale, UMR 8220 CNRS UPMC, Université Paris 06 - Sorbonne Universités, 4 place Jussieu, 75005 Paris (France).
³ Centre de Recherche et de Restauration des Musées de France, 14 quai François Mitterrand, 75001 Paris (France).

* i.reiche@smb.spk-berlin.de, phone: +49+30-266427101

**Keywords:** Scanning Macro-XRF; confocal micro-XRF; elemental imaging; paints; stratigraphy; hidden paintings; Gustave Courbet

The study of paintings using non-invasive analytical imaging methods allows today in-depth insights onto the chemical composition of its paint layers, changes of composition, overpaints and former restorations. A well-established method revealing the chemistry of paintings is two-dimensional (2D) macro-X-ray fluorescence imaging (MA-XRF). This method gives an averaged image of the chemical composition of all detectable paint layers. Only partial information on the paint layer stratigraphy can be gained by combining information from different examinations and observations including X-ray radiography (XRR) and multispectral imaging methods. However, revealing distinct paint layers, their composition, thickness and succession is crucial to a better understanding of the genesis of the art work, the artist’s process and in general the historical context of the painting. To overcome this lack, new approaches have been developed that allow non-invasive three-dimensional (3D) analyses of the chemical composition of the paint stratigraphy including depth-resolved analyses with confocal XRF set-ups (CXRF) [1]. In this study we present the first combined use of MA-XRF with CXRF applied to a famous painting by Gustave Courbet “*L’Homme blessé*” kept at the Musée d’Orsay in Paris. Large elemental maps of Hg, Cu, As, Fe, Zn, Cr, Ba, Pb and Ca obtained on the painting are discussed in combination with depth profiles on strategic points crossing the three painting compositions. Our study allowed evidencing the order of three successive versions of this painting. It also highlights the importance of crossing complementary imaging methods in order to obtain a complete three-dimensional (3D) vision of the chemistry and stratigraphy of paintings.

**References:**

Application of Neutron-based Analytical Techniques for the Non-destructive Investigation of the Coinage of Antique Bronze Coins

Martina Griesser¹, René Traum², Winfried Kockelmann³ and Klaudia Hradil⁴

¹ Kunsthistorisches Museum Vienna, Conservation Science Department, Burgring 5, A-1010 Vienna (Austria), Tel. +43-1-52524-5701, martina.griesser@khm.at.
² Kunsthistorisches Museum Vienna, Coin Cabinet, Burgring 5, A-1010 Vienna (Austria).
³ Rutherford Appleton Laboratory, ISIS, Harwell Oxford, Didcot, OX11 0QX (United Kingdom).
⁴ Vienna University of Technology, X-Ray Center, Getreidemarkt 9, A-1060 Vienna (Austria).

Keywords: bronze coins; coinage; neutron tomography; neutron diffraction; texture analysis

The Kunsthistorisches Museum Vienna (KHM) holds one of the biggest collections of antique Greek and Roman coins worldwide inside its Coin Cabinet. Within a four years research project funded by the Jubiläumsfonds der Oesterreichischen Nationalbank (project no. 11990) a group of ancient Greek bronze coins was brought into the focus of research, due to the observation of severe corrosion on many of the coins. By applying different analytical techniques to study their alloy compositions and the corrosion phases developing on a set of 1,200 so-called “Greek Imperials” – coins minted during the Roman imperial time (50 to 280 AD) in the Eastern provinces of the Roman Empire – first hints concerning their manufacturing technique could be gained [1, 2].

The permission to produce bronze coins was granted by the Roman Empire to a multitude of cities during all periods of antique coinage, while the minting of coins from precious metals (gold and silver) was reserved for the Imperial mints, mainly the one based in Rome, only. The “Greek Imperials” were manufactured using unique and local symbols, different well-known casting and minting techniques, and most probably also locally available raw materials. Therefore, size, weight, alloy composition and numismatic quality can vary in a wide range. As a consequence of the alterations of the coins’ surfaces due to corrosion during burial and/or storage, it is not always possible from visual inspection or microscopic investigation to definitely conclude on the production technique used, i.e. either cast only or cast and minted.

To gain more information on the manufacturing method different neutron-based analytical techniques were applied to a selected number of objects, mainly “Greek Imperials” as well as some selected Roman coins for comparison. At first, the bulk compositions of the coins were investigated by non-destructive neutron diffraction (ISIS, UK) confirming the use of lead rich bronzes for the Greek coins studied, which are the ones exhibiting whitish corrosion to different degrees. Furthermore, the presence of lead rich inclusions in a copper rich matrix could be detected within the bulk of these

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
objects by applying neutron tomography (Paul Scherrer Institute, Switzerland; in cooperation with the Vienna University of Technology) [1, 2]. In some cases, the appearance of the inclusions – round or flat – can be used to distinguish minted coins from cast ones.

Further studies are now focusing on the investigation of the manufacturing techniques of the “Greek Imperials”. Therefore, a set of replicas was cast using a copper/lead-alloy containing 30 wt% Pb by applying two different antique casting techniques: either a vertical casting set-up in a clam-shelled mould or a horizontal casting in an open mould. To mimic a subsequent minting process, i.e. the compression of the antique coins, a selected number of the replicas was cold forged by hammering; to further increase the thermal influence of the hammering process on their textures some replicas were additionally compressed in the red-hot state.

About 20 antique coins and 15 replicas were analysed by bulk neutron texture analysis (ISIS, UK), which is capable of revealing changes in the microcrystalline structure of the alloys related to the mechanical casting and minting processes in a non-destructive way. Although the data interpretation is still ongoing, first results support the assumption that clear differences in the textures can be seen for cast only in contrast to cast and minted (hammered) coins and replicas. These new results are in single cases also contradicting the classification of the production technique of the “Greek Imperials” as yet based on visible inspection and investigation by optical microscopy only.

The presentation will focus on the discussion of the capabilities and limitations of non-destructive investigations by neutron-based analytical techniques (neutron tomography, neutron diffraction and the study of plastic deformation by texture analysis) to reveal the manufacturing technique of antique bronze coins based on unpublished research results.

References
Laminated altered layers in historical glass: density variations of silica nanoparticle random packings as explanation for the observed lamellae

Olivier Schalm1*, Willemien Anaf2

1 University of Antwerp, Conservation Studies, Blindestraat 9, B-2000, Antwerp, Belgium Tel. +3232137134, Olivier.schalm@uantwerpen.be.
2 University of Antwerp, Department of Chemistry, Universiteitsplein 1, B-2610, Antwerp, Belgium

* Olivier.schalm@uantwerpen.be.

Keywords: glass; degradation; lamellae; random packing; packing density

One of the most striking but unexplained phenomena in the natural degradation of glass is the transformation of an almost colourless, transparent and homogeneous glass into a coloured, opaque and heterogeneous product. In many cases, such heterogeneous products are build up by numerous lamellae with a thickness between 0.1 µm and 10 µm. While the basic mechanism of glass alteration is considered to be known for a long time and the resulting altered layer appears to be well described at the molecular level, the formation of lamellae at the µm-level still needs to be explored in detail. The presence of such lamellae is usually explained by cracks between the lamellae or by lamellae with alternating composition. However, these explanations are not able to describe all the observed properties of transformed glass (e.g., the rather strong attachment of lamellae to one another, a maximum Mn-content in the darker lamellae), phenomena (e.g., advanced diffusion fronts of Mn-rich compounds in the darker lamellae) and experiments performed on transformed glass (e.g., no voids remain inside transformed glass when Mn-rich inclusions are dissolved).

A series of 14-17th century archaeological glass artefacts have been analysed in detail by means of optical microscopy, confocal microscopy, electron microscopy and FTIR microscopy. The samples analysed were exemplary for many historical artefacts. Therefore, the analytical results could be extrapolated to a general model that is shown in Fig. 1. The model connects the complex heterogeneous microscopic structure to the well-known molecular structure of transformed glass. It assumes that transformed glass consists of a random packing of ~25 nm-sized silica particles. The difference between lamellae is the result of a random close packing of nanoparticles with a typical packing density of 0.62-0.64 alternated with random loose packings of identical particles but with a packing density of 0.52-0.55. This model is able to explain numerous properties of transformed glass. Among these properties are the quantities that are responsible for the contrast between lamellae seen in the microscopic techniques used. These quantities are given in the list below and can all be explained by the packing density.
1. The brightness of the lamellae in backscattered electron images is proportional to the packing density due to the variable fraction of solid material in the interaction volume. The difference in packing density between lamellae also results in Si-Kα intensity fluctuations of about 20%.

2. A chemical contrast can be formed when precipitations fill the pores in the lamellae. Since lamellae with lower packing density have the highest porosity, they will contain a higher amount of precipitates. When the precipitates dominate the mean atomic number of the lamellae, the contrast in backscattered electron images can be reversed when compared to the previous item;

3. In dark field observation, the fluctuating packing densities result in changing scattering intensities due to a variable amount of scattering centres per unit volume;

4. In some cases, there is a preferential formation of Mn-rich inclusions in the low packing lamellae resulting in an additional chemical contrast between adjacent lamellae, which can be seen in backscattered electron images. Moreover, in dark field observation the Mn-containing lamellae are black coloured while in bright field observation they appear as the brighter ones.

5. For some polished cross-sectioned samples, there is a difference in surface roughness between subsequent lamellae, resulting in additional contrasts in bright field, dark field and in differential interference observation mode. Most probably, the polishing action removes easier particles from the lamellae with random loose packing resulting in an enhanced surface roughness.

Fig. 1: The internal structure of transformed glass containing lamellae from the macroscopic scale down to the molecular scale. a) Transformed glass containing lamellae at the µm-level that can be visualized with various microscopic techniques; b) The random packing of silica nanoparticles with different packing densities explaining the differences between subsequent lamellae; c) molecular structure of a single nanoparticle consisting of a vitreous silica structure.
Forensic Art History: The Anders Ädel Pigment Dispute 1839-1841

Ingalill Nyström*, Jacob Thomas1, Johan Knutsson2, Anneli Palmsköld1, Kaj Thuresson3, Anders Assis4

1 University of Gothenburg, Department of Conservation, Faculty of Science, Guldhedsqatan 5A, Box 130, 405 30 Gothenburg (Sweden), tel. +46(0)317865701, fax: +46 31 786 47 email address: ingalill.nystrom@conservation.gu.se
2 Linköping University, Carl Malmsten furniture studies, Larsbergsvägen 8, 181 39 Lidingö (Sweden).
3 The Swedish National Heritage Board (RAÄ), Conservation science department, Artillerigatan 33A, Box 1114, 621 22 Visby (Sweden).
4 Ljusdalsbygdens museum, Museivägen 5, 827 33 Ljusdal (Sweden).

* ingalill.nystrom@conservation.gu.se

Keywords: XRF; DSA-ToF-MS; Raman; GC-MS; interdisciplinary; Folk art; pigment; paint.

This multidisciplinary study concerns a 19th century dispute regarding three pieces of painted furniture -a table, a chest and a small casket- decorated by the 19th century painter Anders Ädel (1809-1888) from Söderhamn, Hälsingland, Sweden. Ädel is considered as one of the foremost painters in Hälsingland. His art works - painted furniture and interiors - are displayed in museums, private homes and can also be found in some of the sites of the UNESCO World Heritage Decorated farmhouses of Hälsingland. In 1839 Ädel accused his client, the farmer Erik Olofsson, in court of having paid too little for the objects as he used more pigments than those for which he had been paid; this was after Ädel was first sued by the pigment merchant Forsberg for an unpaid bill [1,2]. Almost 180 years later scientific methods combined with historic source research have been used to understand what pigments and techniques Ädel actually used when painting the furniture. Through this study we demonstrate how multidisciplinary collaboration between natural sciences and humanities can contribute to deeper knowledge and new interpretations of historical materials. The scientific analyses were preceded by historic analyses of the juridical protocols found in archives. Non-invasive analyses using different XRF were conducted directly on the painted furniture in situ, see fig 1. Additionally, samples were taken for supplementary analyses using FT-Raman spectroscopy and DSA-ToF-MS and GC-MS. According to the judicial protocol the defendant, Olofsson, claimed that he had already paid for the artist’s materials i.e. linseed oil, lead white, red lead, cinnabar, Prussian blue, “silverglitt” (lead yellow) and "móngel" (unknown). Ädel then called in a guild painter named Blombergsson who declared that there seemed to be more pigments used in the painted furniture than those mentioned. He also believed that the work should be valued higher. Indeed, our results show that Ädel did use different pigments than those bought. For example, preliminary results show that Prussian blue was not used but rather indigo (according to FT-Raman spectra). Analysis of the green paint shows that Ädel used a mixture of green pigments including one that contains copper and arsenic indicating emerald green. In conclusion, the forensic evidence gathered so far in this study...
suggests that Ådel rather painted with slightly different pigments than those the client Olofsson had purchased for the commission. Apart from this, the judicial protocols give an insight of what pigments Ådel had access to and when combined with the scientific analyses this information can give historic evidence of the artist's materials and painting technique.

Fig 1: µXRF analyses at Ljusdalsbygdens museum, Kaj Thuresson

Acknowledgement:

The presented study is part of a larger interdisciplinary project “A holistic study of Decorated Farmhouses of Hälsingland”, in which methods from natural and historical sciences are applied to the decorative folk arts and crafts in the farmhouses of Hälsingland, UNSCO World Heritage. The project is four years long and funded by the Swedish Research Council. The study is a collaboration between different researchers: conservation scientists, chemists, physicists, conservators, art historians and ethnologists and the project participants besides the authors are:

Yvonne Fors¹,³, chemist, Dep. of Cons, GU/Dep. of Cons. science, RAÄ
Thomas Zack, geologist, Earth Science, University of Gothenburg
Aleksandar Matic, physicist, Applied Physics, Chalmers
Florian Nitze, physicist, Dep. of Chemical and Biological Engineering, Chalmers
Susanne Wilken, physicist, Applied Physics, Chalmers
The project is also collaborating with other experts such as:
Sven Isaksson, Archeologist, Archeological Research lab, University of Stockholm
Lars Nylander, Antiquarian, Hälsinglands museum, Hudiksvall
Mélanie Platzgummer, World heritage coordinator Bollnäs county.
Lena Landström, World heritage coordinator, Gävleborg county administrative board
Photographer: Yngve Söderquist, Ljusdalsbygdens museum, Ljusdal

References:

Monitoring the Impact of the Indoor Air Quality on Metallic Heritage

Lucy ‘t Hart¹, Patrick Storme¹, Willemien Anaf² and Olivier Schalm¹

¹ University of Antwerp, Faculty of Design Sciences, Conservation Department, Blindestraat 9, 2000 Antwerpen, +3232137134, Pieternel.tHart@uantwerpen.be*
² Royal Museum of Fine Arts Brussels, Scientific Research, Museumstraat 9, 1000 Brussel.

Keywords: indoor air quality; preventive conservation; corrosion monitoring systems;

The indoor air quality (IAQ) highly influences the preservation of heritage objects. It is determined by environmental parameters such as temperature, humidity, light, pollutants, etc. However, due to synergetic effects the measurements of individual parameters are not sufficient to determine transformation rates of historical materials. In order to solve this, the BELSPO AIRCHECQ-project [1] is developing an innovative monitoring kit that measures continuously and simultaneously both environmental parameters and material behaviour, enabling the study of the cause-effect relationship.

The present study is part of the AIRCHECQ-project and explores the possibilities of sacrificial metal sensors (Ag, Cu and Pb) to monitor material behaviour. First, we studied how the aggressiveness of ambient air towards metallic objects can be monitored. Three aspects of interest of these metal sensors were investigated by exposing the metals to controlled corrosion conditions.

1. **Visual appearance**: quantifiable parameters such as discolouration and loss of gloss are linked to the esthetical distortion of historical objects, indicating when conservation actions should be applied.
2. **Identification of corrosion products**: due to selective metal sensitivity, metal sensors give an indication of the presence of various airborne pollutant concentrations. Some of these pollutants are below the detection limit of diffusion tubes.
3. **Corrosion rate**: certain metal sensors are also able to continuously measure the corrosion rate (e.g. AirCorr, Purafil et al.). Unfortunately, the relation between the corrosion rate and air aggressiveness of ambient air towards an historical collection is still unclear.

Three different corrosion monitoring systems were compared in two different monitoring campaigns: [1] the library archive of the Royal Academy of Fine Arts, Antwerp and [2] an exhibition room in the Royal Museum of Fine Arts, Brussels. The corrosion rates were determined with voltammetry, the electrical resistance change of a metallic nanowire, or the mass change of a metal coated quartz crystal microbalance. Afterwards, the sensors were analysed by means of optical microscopy, scanning electron microscopy, spectrophotometry and a gloss meter.

*2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium*
Two of the tested sensors were able to determine the silver and copper corrosion rate continuously through an in situ analysis. From these two sensors, the ‘610 Atmospheric Corrosion’-metal sensor [2] was the most reliable continuous system and was therefore implemented in the AIRCHECQ monitoring kit, shown in figure 1. The data streams were used to estimate the behaviour of historic materials. Moreover, such data can be used to visualize the air aggressiveness over time and to adapt mitigation actions accordingly. The kit even acts as an early-warning system by detecting the impact of sudden changes on materials. In this way, we provide heritage caretakers an understanding of the damaging effect of the environment on their collection.

Fig. 1: Schematic overview of a multipurpose data logger monitoring environmental behaviour and material behaviour simultaneously. The 610 Atmospheric Corrosion-sensor, monitoring change in electrical resistance is displayed on the left side.

References:
[1] The AIRCHECQ (Air Identification and Registration for Cultural Heritage: Enhancing Climate Quality) project is a Belgian project funded by BELSPO. More information on www.uantwerpen.be/airchecq

Acidic degradation patterns of photographic dyes

Evert B. Reijers¹*, Cecilia W.L. Jespers¹, Maxime A.C. van Wiggen¹ and Leonardus W. Jenneskens¹

¹ Utrecht University, Organic Chemistry and Catalysis, Universiteitsweg 99, 2584 CG, Utrecht (The Netherlands)

* tel: +31 30 2533120, Email: e.b.reijers@uu.nl

Keywords: photography; degradation; UV-VIS; NMR; GC-MS

Photography has increasingly been used as an integral part of many artworks ever since the advent of commonly accessible photography in the 1950s. While the degradation of photographs as such has been relatively well-described, composite so-called photoworks remain somewhat ill-understood.[1] One example of these photoworks is Russian Diplomacy by Dutch artist Ger van Elk (1941-2014), a large chromogenic photograph partially painted with an acrylic resin and encased in a Plexiglas® protective plate on both sides. On removal of this plate, a clear smell of acetic acid was detected, indicating that a microclimate under the plate had been collecting some offgassing volatiles from the various materials incorporated in the artwork. All black photographic areas of the artwork were strongly discolored towards purple, rendering it unsuitable for exposition and largely destroying the meaning of the work. According to the theory of subtractive colors, a color change towards purple indicates that yellow dye is degrading fastest, leaving cyan and mainly magenta to make up the color.

In order to determine the cause of this undesired and unusually fast discoloration, we first synthesized model compounds for all three photodyes (yellow, magenta and cyan) by adapting literature procedures (Fig. 1).[2-4] We then investigated the behaviour of these dyes in an acidic environment by subjecting them to buffers of varying pH (1-7). While magenta dyes show less than 10 % absorption loss at $\lambda_{max}$ for up to 40 days at pH 4, cyan and particularly yellow dyes show rapid degradation around pH 4. Yellow dye in particular has degraded completely within 18 hours at pH 4, in accordance with the discoloration seen on Russian Diplomacy. Photographic gelatin has its isoelectric point around pH 4.8, and therefore only a relative small amount of additional acid would be required to lower the pH of the photograph sufficiently for this reaction to occur.

We then set out to determine the mechanism behind the increased propensity of yellow dye to degrade compared to the other dyes under these circumstances. The reaction appears to be acid-catalysed, and accordingly it was found that an acid-catalysed Schiff base hydrolysis is the most likely candidate. This would break the dye’s conjugated $\pi$-system into two parts, largely negating its ability to absorb visual light. Hydrolysis products were observed by GC-MS and $^1$H NMR, although not all predicted hydrolysis products were observed directly. The observed pH range also agrees with conventional wisdom that Schiff bases are formed around pH 5; hydrolysis takes place
at (much) lower pH. This mechanism provides a qualitative explanation for the relative instability of yellow dye towards this degradation pathway: one of the products is a triketone that rapidly degrades further into a diketone species; both were observed in GC-MS although attempts to isolate them further have failed thus far. Contrarily, degradation products from cyan and magenta dyes cannot easily degrade further and may even reverse to the original dye. Accordingly, we find that cyan and magenta dyes are partially restored on neutralization of the solvent, while yellow dyes are quenched to a much larger extent.

These results show the importance of tight control on acid and humidity levels even in artworks that appear to be preserved well. Microclimates such as those generated under glass plates can collect offgassing volatiles for many years, and these can have great impact; storage and preventative conservation efforts remain the best way to deal with this type of degradation. In theory, this degradation and therefore the effective destruction of this (and other) artworks could have been prevented by removing the glass, in effect removing the microclimate and improving the ventilation.

![Figure 1. Three model photographic dyes: yellow, cyan and magenta](image)

References


Innovative mitigation strategies to easel paintings safeguard

Cátia Salvador¹, Mara Silva¹, Tânia Rosado¹, Rui Bordalo¹, António Candeias¹,²*, Ana Teresa Caldeira¹,²*

¹ HERCULES Laboratory, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora (Portugal)
² Chemistry Department, Scholl of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora (Portugal)
³ Geosciences Department, Scholl of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora (Portugal)

* atc@uevora.pt, +351 266 740 800

Keywords: biodegradation/biodeterioration; easel paintings; microbial contamination; natural biocides; novel conservative formulations; mitigation approaches

Biodeterioration phenomenon is a relevant issue for preservation/conservation of the Cultural Heritage artworks, whose rehabilitation is imperative. Recently, several studies have been performed in order to identify the main biodeteriogenic agents involved in artworks deterioration¹. Easel paintings constitute relevant cultural heritage assets due to their important historic and cultural value. Unfortunately, these artworks can be affected by microbial contamination due to the presence of several organic materials, namely proteic compounds, used as additives in the different paint layers, as well as, as support materials like wood, paper, fabric or parchment. The microbial proliferation can be responsible for different easel paintings alteration, affecting aesthetically and structurally these artworks. The main damages detected are stains and biofilms formation, chromatic alterations, exfoliations, cracks and detachment of pictoric layers². Thus, it is crucial to characterise the coloniser population and to identify the biodeteriogenic agents, in order to correlate the biodeteriorative capacity with the damages observed. According to this, novel mitigation strategies are being developed, envisaging microbial communities elimination and prevention of further recolonisation, to promote the longevity of the paintings. In this research field, great efforts have been made for the production of new green biocides, which are non-toxic, easy and low cost production, being a good alternative for the hazard commercial biocides.

In this way, Bacillus species are emerging as a promising alternative for built heritage treatment and rehabilitation. They produce a great diversity of secondary metabolites with biological activity, well known to possess antagonistic activities against many fungal pathogens. This unique capacity are due to antifungal lipopeptides production such as surfactin, fengycin and iturin with amphiphilic membrane-activation properties. Attending to the efficiency of the natural biocides produced by our research group³, different mitigation strategies are developed by the incorporation of the novel compounds in materials used in the conservation and restoration process. This methodology aims to outline an innovative approach for new mitigation strategies, constituting a useful tool for safeguard and preservation of cultural heritage.
Four easel paintings of Giorgio Marini (19th century, 80-90’s), with evident chromatic alterations and different alteration states were analysed. This study aims to characterise and identify the microbial communities associated to the degradation of these artworks. On the other hand, mitigation strategies are being developed for in situ application, to promote effective conservation-intervention processes.

The presence of microbial contamination was assessed by scanning electron microscopy (SEM) and cultivation methods. The cultivable microbial population was characterised based on macroscopic and microscopic features. Antifungal activity, using new green biocides and commercial compounds, were performed against the fungal populations present in the Giorgio Marini paintings.

The predominant microbial population present in these paintings are filamentous fungi of the genera *Penicillium*, *Aspergillus*, *Alternaria*, *Cladosporium* and *Mucor*. The main incidence of these fungal communities were found in areas with evident structural and aesthetic damages, which were confirmed by scanning electron microscopic analyses that allow the observation of the fungal hyphae proliferation capacity and extent.

The antifungal assays showed that the bioactive compounds produced by *Bacillus* have high capacity to inhibit fungal growth of the strains isolated from the paintings, revealing higher efficiency than the commercial biocides usually applied.

![Figure 1: Giorgio Marini easel painting with sampling process evidenced (a), which allowed the detection of fungal proliferation by SEM (b) and the identification of *Penicillium* strains between the microbiological communities (c), whose development can be inhibit in the presence of natural biocides (d).](image)

Taking into account the effectiveness of the natural biocides developed, different mitigation strategies are in progress, testing new formulations by the incorporation of these compounds in several materials frequently applied in the easel paintings conservation processes. The combination of these materials intend to plan innovative formulations based on the application of natural biocides in distinct application formulae, constituting novel mitigation solutions for Cultural Heritage safeguard.

**References:**

Influence of Solvents on Cellulose Average Degree of Polymerization

Ing. Jan Krejčí, Ing. Markéta Škrdlantová, Ph.D., Ing. Klára Drábková

1 University of Chemistry and Technology, Prague, Department of Technology of Monument Conservation, Technicka 5, 166 28 Prague (Czech Republic), krejcij@vscht.cz
2 University of Chemistry and Technology, Prague, Department of Technology of Monument Conservation, Technicka 5, 166 28 Prague (Czech Republic).
3 University of Chemistry and Technology, Prague, Department of Technology of Monument Conservation, Technicka 5, 166 28 Prague (Czech Republic).

Keywords: cellulose; solvents; degree of polymerization; degradation; viscometry

This study discusses different methods for determination of damage of cotton textiles. Special attention was focused on determining the degree of polymerization of cellulose. An influence of the selected solvent systems on cellulose average degree of polymerization was studied – 9% solution of LiCl in N,N-dimethylacetamide; ferric-sodium-tartaric acid complex (FeTNa); bis-(ethylenediamine)copper(II) hydroxide (CED); tris-(ethylenediamine)cadmium(II) hydroxide (cadoxene). The stability of selected cellulose solutions was also studied.

References:
Raman Spectroscopy and Automated Fluorescence Removal for Pigment Identification in Art Conservation Applications

Amy J.R. Bauer¹ and Mary Kate Donais²

¹ TSI Incorporated, 500 Cardigan Road, Shoreview, MN 55126, USA 1-651-765-3701, fax 1-651-490-4025, amy.bauer@tsi.com*.
² Saint Anselm College, 100 Saint Anselm Drive #1705, Manchester, NH 03102, USA.

Keywords: Raman spectroscopy, background correction; signal processing; fresco; pigment

Raman spectroscopy is a valuable tool in the arsenal of the art conservationist. Through the acquisition of a vibrational spectrum of the surface of a sample, various types of important information can be gleaned. Of particular interest are chemical composition of colorants (inorganic vs. organic, potential origin of the minerals used in pigments and what weathering or environmental damage has occurred, for example). Additionally, this information helps to establish authenticity and provenance of paint and pigment substances. This presentation will focus on our efforts to develop more effective measurement methods for the challenging pigments that are encountered in older artifacts, especially those with green and blue-green mineral pigments, which have been found in the past to have a forbidding amount of native fluorescence.

The samples that will be of chief interest will be pigment chips from frescoes from the Coriglia excavation site near Orvieto, Italy. Data will be collected at 785 nm and background corrected to remove fluorescence commonly associated with Raman measurements of pigment materials. The resultant spectra will be compared with pigment and mineral databases, as well as mineral pigments purchased from art supply dealers.
Applied IR and Raman Micro-spectroscopy for Art Conservation Research

Hanne. Hoskens¹, Martin Luft², Dr. Matthias Boëse ², Dr.Diego Sali³

¹ Bruker Belgium NV/SA.Kolonelbourgrlaat 122/B5, Evere, Belgium, +32 2 726 76 26, hanne.hoskens@bruker.com
² Bruker Optics, Rudolf-Plank-Strasse 27, 76275 Ettlingen, Germany
³ Bruker Italia S.r.l., Viale V. Lancetti, 43 Italy, 20158 Milano; Italy

Keywords: IR; spectroscopy; Raman; microscopy; FTIR

Non-destructive analytical sampling techniques are required for art historians, museum conservators and scientists who characterize the attribution of historical period and genuineness of an artifact.

FT-IR and Raman spectroscopy are widely used and powerful tools for the identification and characterization of a broad range of materials. Both techniques allow minimal to non-invasive examination of art objects like paintings, sculptures, parchments, tissues, tapestries and others. Chemical compounds that were used to create a certain piece or art are identified via their typical spectral bands. Using this information adequate restoration methods can be selected. Moreover these findings allow investigation of potentially forged art objects by comparing the found chemical compounds with artistic materials that actually were available in the time of origin.

IR and Raman microspectroscopic approaches for the analysis of historic paintings are presented. Examples of the selective microanalysis of single spots on the sample as well as chemical imaging of larger sample areas are shown.

Furthermore a non-invasive and non-destructive approach to perform FT-IR spectroscopic measurements directly in situ in front of the artwork is presented. A selection of applications performed at universities and museums will be shown: gems and stones, mural painting [1], ancient painting by Giotto [2] and modern painting by Mario Schifano [3]. Pictures and spectra will be presented, focusing on technical aspects.

References:
[3] K.Tamà, Studio mediante tecniche spettroscopiche delle opere pittoriche Notte Tempo (In Italia) e Senza Titolo di Mario Schifano, 2010, Tesi di laurea, Università di Parma, Italy
Non-invasive tree-ring analysis – archaeology & art

Aoife Daly¹, Noëlle Streeton²

¹ Centre for Art Technological Studies and Conservation (CATS), Statens Museum for Kunst, Sølvgade 48-50, DK-1307 Copenhagen K (Denmark), Tel. +45 2625 4108, aoife.daly@smk.dk.
² Conservation Studies, Department of Archaeology, Conservation and History (IAKH), University of Oslo, Post box 1019, Blindern, NO-0315 Oslo (Norway), n.l.w.streeton@iakh.uio.no

* aoife.daly@smk.dk

Keywords: non-destructive; provenance; timber trade; dendrochronology; precise dating; painted ecclesiastical art

A technique for non-invasive dendrochronological analysis of oak was developed in the project DendroCT and published in 2012.¹ Wood from the iconic Viking ship burials from the Oslo fjord at Oseberg and Gokstad was CT-scanned, using an industrial CT scanner at the Norwegian Geotechnical Institute. X-ray images of sections through the dry oak objects from these burials were of such clarity that reliable tree-ring measurement was possible. The precise dating and the identification of the provenance of the trees used in these burials is now possible, completely non-invasively.²

New attempts at non-invasive tree-ring analysis have taken a different direction within the research project ‘After the Black Death: Painting and Polychrome Sculpture in Norway, 1350–1550’.³ The project is co-led by Noëlle Streeton and Tine Frøysaker, based in Conservation Studies, University of Oslo (UiO). The source material is a collection of late-medieval objects from Norwegian churches owned by the Museum of Cultural History in Oslo. The majority of these cannot be sampled, and many are too large to fit in the CT-scanner. For these reasons, a combined approach has been adopted, utilizing an imaging technique that has been developed by the first author, Aoife Daly, and where possible followed by CT-scanning. Both techniques are non-invasive and have yielded reliable results.

In this paper we will present preliminary results from a total of 11 objects, which included corpus boxes, painted wing panels, reliefs and polychrome sculptures. These results were derived in the first instance from macro-photographs taken to measure tree-rings on eight of the 11 objects. Images included a ruler for scale and encompassed areas with exposed wood that had either never been painted or where there was significant paint loss. Reliable measurements, even on the longitudinal section of oak planks, have resulted in the dating of the wood used to make these objects. Furthermore, the region of origin of the timber has also been identified in most instances. However, in a number of instances, this imaging technique did not lead to a conclusive result and for those that met the size requirement, CT-scanning was the next step. The wing panels from one altarpiece and two small shrines, along with a selection of sculptures were taken for scanning in August 2015. The aim was both to check results from imaging and to gain new information from objects that were entirely painted. In addition, during
the process of scanning questions were answered about whether metal foils from gilded passages (containing gold, silver, tin, etc.) would interfere with the X-ray and obscure the lower density wood. Clear images of the tree-rings were attained, and these are now ready for analysis.

New and extensive experimentation with this combined technique has allowed us to test the efficacy of imaging and scanning, with the intention of refining the approach for archaeometry.

References:


Polychrome sculptures from Onsøy church (Østfold, Norway), mounted on an upright and placed in the CT-scanner at the Norwegian Geotechnical Institute. The objects are ready for scanning.
Non-invasive Characterization of Colourants by Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT)

Marcello Manfredi$^{1,2}$, Eletra Barberis$^{1,2}$, Maurizio Aceto$^2$ and Emilio Marengo$^2$

1 ISALIT, Spin-off of Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale T. Michel 5, 15121, Alessandria (Italy), Tel. 00390131229332, e-mail address marcello.manfredi@uniupo.it.

2 Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale T. Michel 11, 15121, Alessandria (Italy),

* marcello.manfredi@uniupo.it, 00390131229332

Keywords: Non-invasive analysis; Pigment characterization; DRIFT spectroscopy; Surface analysis; In-situ technique

In recent years, spectroscopic techniques have been widely employed for the analysis and characterization of cultural heritage objects. But these methodologies are not always non-invasive and often require micro sampling, which is sometimes not possible particularly for precious or fragile artworks [1].

In this work we present a portable diffuse reflectance infrared Fourier transform (DRIFT) method for the non-invasive characterization of colourants prepared by painting areas on parchment and using egg white and gum Arabic as binders, according to ancient recipes. DRIFT spectroscopy has been already applied both for the non-invasive analysis of grounds in painting and building heritage materials [2, 3]. The applicability of a diffuse reflectance infrared Fourier transform handled device to perform in situ analysis of colourants will be shown, creating and discussing a spectral database that can be very useful to conservators.

Nearly 70 different colourants, prepared both with egg white and gum Arabic, were analysed with DRIFT spectroscopy. In example, we were able to identify several yellow pigments like orpiment, litharge, lead–tin yellow, lead antimonite and different yellow ochres. We were also able to characterize many red (red ochres, hematite, etc.) and blue (lapis lazuli, azurite, indigo, etc.) colourants.

Chemometric techniques like principal component analysis and classification methods have already been applied to extract systematic information and for the characterization of complex materials in the field of cultural heritage [4]. Here we used classification methods and statistics for classification and identification purposes in order to discriminate the classes of samples.
In conclusion we can affirm that with the portable DRIFT method there is no need to touch the sample surface and the analysis can be done directly in situ, allowing the quick chemical characterization of a large number of areas in a non-invasive manner.

Fig. 1: DRIFT infrared spectrometer during the analysis of a piece of parchment.

References:
Combined historical, physical anthropology, archaeological, and archaeometrical approaches to understand glass beads from Kongo Central province, Democratic Republic of Congo (DRC)

Alessia Coccato1*, Anastasia Rousaki2, Mafalda Costa1,4, Bernard Clist3, Koen Bostoen3, Peter Vandenabeele1

1 Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium. Tel. +32 9 264 4719, email: Alessia.coccato@ugent.be
2 Ghent University, Department of Analytical Chemistry, Krijgslaan 281, S12, B-9000 Ghent, Belgium.
3 Ghent University, KongoKing Research Group, Department of Languages and Cultures, Blandijnberg 2, B-9000 Ghent, Belgium
4 HERCULES Laboratory, University of Évora (Évora, Portugal)

Keywords: beads; glass; Raman spectroscopy; X-ray fluorescence; chemometrics; Western Central Africa; archaeometry

Archaeological excavations have been carried out in Kongo Central province of the DRC since 2012 in the framework of the KongoKing project [1],[2],[3],[4]. The project is devoted to the study of the origin and early history of the Kongo kingdom (before AD 1400) through an interdisciplinary approach (archaeology and historical linguistics).

During the 2012 and 2013 field seasons, a small cemetery of high social status men and women was discovered then completely excavated on the Kindoki hilltop north of the Mbanza Nsundi village ([5],[6]). In addition to the specific structure of all the tombs, denoting time consuming organisation of the local community, specific male high status symbols like swords and sabres were found in 5 of the 11 tombs, while hundreds of glass beads and specific iron anklets were found in the 2 female tombs. The identical way of constructing the tombs, their being very close one to teach other, the fact they are all oriented the same way, suggests the deceased were linked in some way, maybe the same ruling clan of the Nsundi province during the late 17th century to the early 19th century.

The metal beads and bells, the shell beads and the glass beads discovered in 4 of the 11 tombs also suggest a difference between bead types associated to male and female burials. The beads excavated have been analysed by means of handheld X-ray fluorescence and micro Raman spectroscopy, in order to characterize the glass matrix as well as the pigments and opacifiers. This information can help to clarify the manufacture technique and serve as an indicator of the origin of the beads. Moreover, the application of chemometrics on the data obtained from the handheld X-ray fluorescence can highlight similarities in the glass composition.
The combination of Raman spectroscopy with elemental techniques for the study of glass materials is well established, yet it was not often applied to the study of glass trade beads [7].

The qualitative information provided by hXRF can be successfully improved by the observation of the Raman signature of the glass: the bending and stretching modes of the silicate network are affected by the type and amount of stabilizers, flux and network formers (Ca, Mg; Na, K; Pb), so that different types of glass can be recognized on the basis of their spectrum [8].

References:
Shellac-based nanocomposites for protection of wood surface

Maduka. L. Weththimuni1*, Doretta Capsoni1, Chiara Milanese1, Maurizio Licchelli1,2 and Marco Malagodi2,3

1 Università di Pavia, Dipartimento di Chimica, via T. Taramelli 12, 27100 Pavia (Italy), Tel. +390382987333, madukalankani.weththimuni01@universitadipavia.it.
2 Università di Pavia, Laboratorio Arvedi di Diagnostica Non Invasiva, via Bell'Aspa 3, 26100 Cremona (Italy).
3 Università di Pavia, Dipartimento di Musicologia e Beni Culturali, Corso G. Garibaldi 178, 26100 Cremona (Italy).

Keywords: wood protection; shellac; nanoparticles; functionalization; degradation.

Surface coating is the most common method used to protect wood against deterioration and improve and stabilize its distinctive appearance. Shellac is a natural resin of animal origin secreted by lac insects (e.g. Kerria Lacca, Laccifer Lacca). Shellac (SH) has been widely used as a protective material for wooden artefacts (e.g. furniture and musical instruments) due to its excellent properties. Despite the advantages, the use of shellac has significantly declined, because of some limitations such as softness of the coating, photodegradation, and sensitivity to alcoholic solvents and to pH variations [1-2].

The main aim of this study was to improve the shellac properties, by introducing nano-sized particles into the resin matrix. All the properties of the resulting nanocomposites were investigated in order to select the material(s) displaying the best performance. At first, dewaxed natural shellac was modified by simply dispersing different inorganic nanoparticles (NP) into shellac solution. For instance, SiO$_2$ as well as ZrO$_2$ NP were added with the aim of improving hardness of the resulting coating, while ZnO NP were expected to improve its resistance to photodegradation and antifungal performances. Furthermore, surface functionalization of NP was done in order to enhance the compatibility of NP, to prevent NP from aggregation, as well as to render NP chemically reactive. For this purpose, both ZrO$_2$ and ZnO NP were synthesized in the laboratory and then, they were functionalized by an alcoxysilane derivative (3-glycidoxypropyltrimethoxysilane, GPTMS).

Both NP and functionalized NP were characterized using different techniques such as dynamic light scattering (DLS), X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), NMR spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). DLS, XRD and SEM experiments suggest that ZnO particles have a size ranging between 63 and 146 nm and a spherical shape, while ZrO$_2$ nanoparticles are both spherical and hexagonal and their size is in the 93-200 nm range.
Nanocomposites (NP-shellac and functionalized NP-shellac) were characterised by performing different experimental analyses both on modified shellac films and on Maple wood specimens treated by brushing. All the properties of shellac-based materials were investigated by different experimental and instrumental techniques: chromatic variation, contact angle measurements, solubility and alkali resistance tests, moisture adsorption measurements, hardness and adhesion tests, X-ray, FTIR, NMR, SEM-EDS, TGA, DSC, UV and solar ageing tests.

Dispersion of plain NP into shellac solution generally produced turbidity and observations of treated wood surface suggested that NP distribution in the shellac matrix was not completely homogeneous owing to the presence of some aggregated areas. On the contrary, coatings obtained after dispersing functionalized NP display a satisfactory homogeneity. All the shellac-based nanocomposites applied on wood specimens provided good quality coatings whose thickness (about 25 µm) was very close to real applications (see Fig.1). Solubility test showed that GPTMS-capped NP in shellac matrix improved the alcohol resistance to a great extent (> 50%). In general, addition of inorganic NP into organic matrixes causes a decrease of glass transition temperature (Tg) [3]. DSC analyses performed on nanocomposites studied in this work suggest that shellac films containing functionalised NP display almost unchanged Tg values. Hardness measurements performed according to international standards indicate that the presence of SiO\textsubscript{2} NP and ZrO\textsubscript{2} NP (both plain and functionalised) in shellac improves the hardness of the resulting coatings. Addition of ZnO and GPTMS-capped ZnO NP to shellac provide good photo-protection as suggested by the almost unaltered chromatic properties (L\textsuperscript{*}, a\textsuperscript{*} and b\textsuperscript{*} coordinates of the CIELAB space) observed even after long solar lamp irradiation (1000h).

![Fig. 1. SEM-EDS experiment performed on maple specimen treated with silica NP-shellac (cross section): SEM micrograph indicating the coating thickness (left) and EDS spectra measured at different depth (right).](image)

**References:**


Innovative application of advanced nanomaterials
designing future treatment technology for art conservation

Tomas Markevičius, Helmut Meyer, Nina Olsson, Kate Seymour, Rocco Furferi
IMAT project under the European Commission under the Seventh Framework Program (FP7) for research (ENV-NMP.2011.2.2-5) coordinated by the University of Florence, Florence, Italy

Keywords: nanotubes, nanotechnology, nanomaterials, conservation, paintings, artworks, warming

For those charged with the strategic development of best practices in conservation approaches, it goes without saying that the creation of new conservation materials and sophisticated instrumentation is of fundamental importance, especially in the field of conservation of modern and contemporary art, where the need for non-conventional approaches in treatment choices, cutting-edge scientific research, methodological compromises, ethical dilemmas and constant innovative thinking are paramount. In advanced material science and cutting edge technologies, nano-scale materials are having an ever increasing impact on all spheres of human life and also provide valuable potential for the conservation of modern art. They offer possibilities to invent innovative new conservation materials and technologies with qualities that are unobtainable with the traditional materials.

The paper presents the results of the first successful application of astounding one-atom-thick nanomaterials in art conservation - carbon nanotubes and silver nanoparticles - obtained during the IMAT Research Project under the Seventh Framework Program (FP7) for research (ENV-NMP.2011.2.2-5) coordinated by the University of Florence. The IMAT project explored the application of carbon nanotubes and silver nanoparticles while inventing a series of innovative, mobile, state-of-the-art precision instruments for accurate and selective mild heat transfer. Conservators apply
heat transfer for diverse treatments, but conventional tools cannot provide the required control through accuracy and uniformity of heat transfer, are unable to target locally, lack versatility and mobility and often carry risk or even cause damages. Thermoconductive nanomaterials could change this situation radically.

**IMAT heating mat and temperature control console with IMAT wireless sensor and IMAT workshop at Villa La Quete, University of Florence, Florence, Italy, Nov 2014**

The mobile IMAT mild heat transfer system, based on carbon-nanotubes and silver nanoparticles, gives superior performance, unsurpassed heating accuracy at low temperature ranges and lower impact. The IMAT project met the need for a flexible, breathable, and transparent contact heater for the use in numerous conservation treatments, including consolidation / flattening of cupped / delaminating paint films, flattening planar distortions of textile or paper support, activating adhesives used for consolidation or attachment of auxiliary support, activating solvent gels or enzymes in cleaning of surfaces, disinfecting textiles and other applications, wherever the safe, selective and accurate heating has to be applied.

The paper explores the working principles of mobile IMAT warming system based on innovative electrically conductive *smart* textiles with electrically and thermally conductive nanomaterials, which employs an ultra low voltage electricity to provide a combination of uniform and accurate radiant and conductive warming. The new technology is illustrated with selected treatments by conservators in Italy, the Netherlands and USA where the new CNT heating mats were successfully experimented and used in actual treatments. The paper discusses how this new application of nanotechnology could increase the safety and efficiency of diverse conservation treatments filling a critical gap in the conservator’s toolbox for an instrument that provides accuracy, selectivity and portability when the application of heat is required, emphasizing the need for continuous innovation and integration of contemporary science and cutting edge treatment technologies, fundamental for the advancement of art conservation.
Preservation of cellulose and collagen-based materials using novel nanoparticle-based treatment and non-destructive evaluation techniques

Marianne Odlyha* 1, Laurent Bozec 2, Angelica Bartoletti 2, Elena Gonzalez 3, David Chelazzi 4, Rodorico Giorgi 4, Piero Baglioni 4, Paolo Matteazzi 5, John Duncan 6

1 Birkbeck, University of London, Dept of Biological Sciences, Malet St London WC1E 7HX
2 University College London, Eastman Dental Institute, 256, Gray’s Inn Rd, WC1X 8LD UK
3 Institute for Cultural Patrimonie (IPCE) Calle Pintor El Greco 4 Ciudad Univeristaria 28040 Madrid, Spain
4 University of Florence Centre for Colloid and Surface Science (CSGI), Via della Lastruccia 3 Florence, Italy
5 MBN Nanomaterialia S.p.A Via G. Bortolan, 42 31050 Vascon di Carbonera (TV), Italy.
6 Lacerta Technology 80 Hathern Rd, Shepshed, Loughborough, Leicestershire LE12 9GX, U.K

*m.odlyha@bbk.ac.uk

Keywords: nanoparticles; cellulose; collagen; atomic force microscopy, dielectric analysis

The preservation of cellulose- and in particular collagen-based based cultural heritage objects (parchment and leather) have posed a challenge for conservators. Both paper and parchment in the form of archival material bear the testimony of recorded cultural history and this necessitates their preservation. Vegetable tanned leather is used in historical bookbindings and is essential for the preservation of thousands of precious volumes in historical libraries. In the case of paper manuscripts the use of nanodispersions in organic solvents has been shown to be successful and they have been applied to historically important manuscripts dating from the 14th to 20th centuries [1-2]. It was demonstrated that the nanoparticles penetrate within the cellulose fibres of the paper and neutralize the inherent acidity. The recent work in the EU-funded NANOFOART project FP7 No. 282816 (Nano-materials for the conservation and preservation of movable and immovable artworks project, http://www.nanoforart.eu) has provided further formulations of nanoparticle dispersions of calcium hydroxide in selected solvents e.g ethanol and propanol, and historical samples with differing levels of degradation were treated. For collagen-based materials this is the first time that this approach has been used and calcium carbonate and calcium lactate nanoparticles in addition to calcium hydroxide nanoparticles were applied. The nanodispersions were provided by CSGI and were fully characterized in terms of size and morphology at the UCL Eastman Dental Institute. The effect of the conservation treatment on paper was shown to improve its thermal stability and to increase the value of pH. The different papers also showed differences in response to the treatment used and indication that possibly some crosslinking is occurring with the calcium hydroxide nanoparticles which does not occur with the traditional calcium bicarbonate treatment. Techniques included thermal and X-ray surface analytical techniques. In the case of collagen-based
artefacts, such as parchment and leather, particular care was taken to evaluate, in the first case, the effect of solvents used in these dispersions. Atomic force microscopy (AFM) and localised thermal analysis (LTA) were used to evaluate the state of the collagen in parchment and leather [3-4].

The effect of controlled programmed increase in RH on the dielectric properties of collagen-based artefacts was also recorded before and after conservation treatment. In parchment and leather collagen I is the main component. On ageing changes occur which may give rise to excessive proportions of acids that promote hydrolysis of collagen. The lowering of pH leads to swelling of the fibrils with gradual gelatinisation and loss of the triple helix structure. Adjustment of pH poses a challenge to conservators due to the sensitivity of parchment to aqueous-based treatment particularly if there are already gelatinised areas present. For parchment samples treated with calcium hydroxide and calcium carbonate nanoparticles dispersed in cyclohexane it was found that the conductivity values were higher for the calcium carbonate treated sample. The increase is due to the additional presence of calcium carbonate which caused an increase in the relative permittivity of the sample. Furthermore XPS data showed that surface N/C ratios were lowered in the calcium carbonate treated sample compared to the calcium hydroxide sample indicating that the N-containing groups in the sample (amino acid residues) were protected by the surface coating enriched with calcium carbonate. In the case of vegetable tanned (sumac) leather samples nanoparticles of calcium lactate in isopropanol were used [5]. Leather differs from parchment as it includes additional treatment using tanning agents which poses a further challenge for the conservator as the pH must not exceed pH = 6 as this could cause detannage. Here as for the parchment sample an increase in conductivity in the treated sample was observed and once again XPS showed low N/C ratios in the treated sample indicating once more that surface coverage occurred protecting the N-containing groups. In both cases, parchment and leather, no damage to the collagen structure occurred as observed from spectroscopic and mechanical methods used for damage assessment of collagen [6]. Where damage did occur in accelerated heat aged samples of parchment and leather and where the collagen triple helix structure was affected then a lowering of conductivity was observed with lowering of shrinkage temperature and change in mechanical properties. Nano-particle-treated samples, however, resisted aging compared to the untreated ones. So controlled environment dielectric analysis through monitoring the response to uptake of moisture and behaviour at elevated values of RH (80%) provided a sensitive non-invasive method for detecting the effect of nanoparticle treatment on collagen-based materials.

References
Tuesday, March 22, 2016

Howell Gwynne Mort Edwards

1 Division of Chemical & Forensic Sciences, Faculty of Life Sciences, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK.
Email: h.g.m.edwards@bradford.ac.uk, Tel: 00-44-1274-233770

Keywords: Biodegradation; Raman spectral signatures; Bioarchaeology; Frescoes; Mummies; Ivories; Cyanobacterial colonisation.

The identification of biological colonisation in archaeological artefacts and ancient art works represents major problems for the preservation of materials and objects of cultural heritage with the realisation that the deleterious effects of this colonisation can be ongoing even when the artworks have been apparently suitably prepared for storage or exhibition. The conservation strategies and curation of biodegraded objects from archaeological sites are especially difficult to envisage when the incipient damage is apparently dormant and has yet to be made evident. Artefacts composed of biological materials are particularly susceptible to biological degradation especially by extremophilic organisms which have developed sophisticated chemical protection strategies for survival in extreme environments. The application of analytical Raman spectroscopic techniques to the characterisation of the chemical composition of mineral and synthetic paint pigments, ceramics, resins, dyes, textiles and human skeletal remains is also now finding much interest in cultural heritage science. During these studies it has become apparent that the spectral signatures of the biological colonisations that are responsible for the serious biodeterioration or biodegradation of archaeological artefacts and art works are comparable with those which are found in terrestrial extreme environments and geological niches now being studied with remote robotic Raman spectroscopic instrumentation destined for adoption on planetary surface and subsurface exploration rover vehicles for the detection of extinct or extant life.

The miniaturisation of Raman spectrometers for the detection of life signatures on planets and their satellites in our Solar System is exemplified by the forthcoming ESA ExoMars mission to the planet Mars in 2018 which will specifically search for extant or extinct life in the Martian subsurface geological record through a powerful suite of instrumentation that includes a Raman laser spectrometer for the first time. A database of key Raman spectral signatures of species such as carotenoids, chlorophyll, scytonemin and other key protective biochemicals produced by terrestrial cyanobacterial and lichen extremophiles which exist in geological niches in stressed hot and cold terrestrial environments, such as the Atacama Desert and the Dry Valleys in Antarctica, has been compiled to identify the presence of biological colonisation in suitable rock matrices. The adaptation of the mineralogy and the host geological matrices by the cyanobacterial colonies and their production of protective biochemicals.
is a vital requirement for the survival strategy for biological growth and evolution. This is also analogous to the biological colonisation of archaeological relics excavated from a depositional environment and on art works exposed to polluted environments; a readily available spectral database can hence be assimilated for the identification and characterisation of areas of biological degradation in ancient artefacts which may be used to alert conservators to the urgent need for restorative and preservative strategies to prevent further ongoing specimen deterioration subsequent to superficial cleaning procedures being undertaken.

The potential afforded by the reduction in size and increased portability of Raman spectrometers appeals to archaeologists and conservation scientists for the in situ analytical measurements that can be performed on objects without the need for destructive sampling, often in inaccessible locations, and an awareness that the Raman spectral information can reveal the presence of unsuspected biological agents that could cause the ongoing deterioration of a cultural object need to be recognised. Also, the unsightly growths of cyanobacteria and lichen communities on exposed works of art such as wall paintings, statues and frescoes can be very deleterious and damaging to their artistic appreciation; in this context, the ability of biological colonies to inhabit mineral pigments which are often very hazardous and highly toxic to humans, such as the oxides and sulfides of lead, copper, mercury, antimony and arsenic, provides an example of extremophilic behaviour which equally matches the strategies they have adopted to overcome extremes of temperature, pH, radiation insolation and barometric pressure elsewhere terrestrially.

Hence, in this presentation we shall explore some examples of the occurrence of biological colonisation of art works and artefacts in which Raman spectroscopy has provided novel information about the onset of degenerative processes which are often apparent spectroscopically before they are observed visually; this affords the establishment of analytical Raman spectroscopy as an early warning monitor of biological degradation in an art work or artefact which may therefore require urgent and additional conservation treatment to prevent further damage occurring and which will lend support to the apparently unrelated scientific engagement between Raman spectroscopists working on space missions and in the field of cultural heritage preservation. The following case-studies will be used as an illustration:

- Lichen degradation of wall-paintings;
- Biological colonisation of badly damaged frescoes undergoing restoration;
- Biodegradation of human mummies from Egyptian Dynastic burials preserved in museum collections;
- Biomineral degradation of human skeletal remains;
- Biological spectral signatures in archaeological excavations of human skeletal and mammoth ivory remains.

Space mission derived data for key biological signatures for the identification of similar signatures from biodegraded artefacts from archaeological excavations will inform future Raman spectroscopic applications to archaeological and cultural heritage site work and to the identification of biological and associated mineralogical materials which could inform future conservation protocols and restorative approaches for the protection of our art work and cultural heritage.
The Saint Anselm College Italy Excavations – Research and Training

Mary Kate Donais¹, David George²

¹ Saint Anselm College, Department of Chemistry, 100 Saint Anselm Drive, 03012, Manchester, New Hampshire (USA), 603-641-7218, mdonais@anselm.edu
² Saint Anselm College, Department of Classics, 100 Saint Anselm Drive, 03102, Manchester, New Hampshire (USA).

Keywords: field archaeology; excavation program; Roman; Etruscan; training; portable spectroscopy, handheld instrumentation

Saint Anselm College, a small liberal arts college in the northeast United States, has been excavating in the Orvieto region of Italy since 2006. The program has evolved over the years in a number of ways including: 1) the pool of participants; 2) the sites explored; and 3) the research design/approach. These three points will be discussed as they relate to the program today and how some of the more important changes came about.

The sites excavated and/or studied include

- Coriglia – an Etrusco-Romano site that begins in 1000 BCE and was used until the 14th century CE
- the Monterubiaglio Roman tower – a Roman building turned into a castle in 8th century CE
- Cavità 254 – many questions remain concerning the origin, purpose, and history of this site
- Sant’Ansano – a late antique building turned into a proto-Christian church and used into the 18th century CE
- Crocifisso Del Tufo – an Etruscan necropolis from the 6th century BCE
- Castel Georgio – an Etruscan necropolis from the 4th century BCE

The program is currently operated as both an abroad educational experience for Saint Anselm College students as well as a field school for students from other academic programs. No specific training, prerequisites, or areas of study are required prior to participation. The program’s success is demonstrated by the many students that return across multiple seasons.

Regarding our research design and approach, chemical characterization of excavation materials was started in 2007 (the program’s second year) as laboratory-based work and has evolved since then to also include portable instrumentation at the sites. Data collection protocols and data processing/analysis approaches also have been refined with each season. Research examples will be presented and discussed to illustrate the essential role portable instrumentation now plays within our research design.
Pigments & Dyes in a collection of medieval illuminations (14th – 16th century)

Aurélie Mounier*, Floréal Daniel

1 Institut de Recherche sur les Archéomatériaux (UMR 5060 CNRS – Université Bordeaux Montaigne), Centre de Recherche en Physique Appliquée à l'Archéologie, Maison de l'archéologie, 33607 PESSAC Cedex, France.

* 05-57-12-45-51 / mounieraurelie33@yahoo.fr

Keywords: Hyperspectral imaging; Raman spectroscopy; X-Ray Fluorescence; FORS-NIR; non-invasive methods; pigments; dyes; miniatures.

The Marcadé Collection, part of the treasury of the Bordeaux Cathedral, was constituted at the beginning of the 20th century by the canon Marcadé. It count 42 illuminations (fig.1a) dated from the 14th to the 16th century and coming from five provenances (France, Italy, Germany, Netherlands, Spain). This collection was newly restored and exposed in the cathedral. For a better knowledge of these manuscripts paintings, the pigments and dyes have been analyzed in some of the illuminations. Thirteen illuminations were chosen in order to represent the diversity of the collection (provenances and dating). For the study of these fragile objects, our methodology was adapted (fig.1b). The aim of this study is to compare painting materials in the illuminations of the five provenances and dating used and to discuss the potentialities of the analytical techniques [1].

Hyperspectral imaging (HSI) has the advantage to be a rapid, mobile and to give reflectance spectra on the entire image, for each pixel. The datacube obtained was treated to visualize RGB, greyscale and infrared false colour images which give a first idea of materials used by comparing with images of reference pigments. The software allows us to map the pigments identified by comparison with reflectance spectra of our reference database pigments prepared with medieval techniques. For the mapping, a Spectral Angle Mapper (SAM) classification is applied to facilitate the matching between reference spectra and the unknown spectra of the illuminations.

Some difficulties of interpretation of reflectance spectra appear for organic dyes and pigments where the reflectance spectra present few inflection points (some white, black or yellow pigments). When doubts subsist or when we have to confirm the identification, point techniques such as Raman and X-ray spectroscopy (XRF) were used. Fiber Optic Reflectance Spectroscopy in the Near Infrared range (FORS-NIR) was used especially for green copper pigments. Indeed, copper green pigments present difficulties of identification with Raman because of the fluorescence and XRF analysis just identify copper element. The NIR has to be proven a good option to distinguish varieties of verdigris (vert au sel / salts green...), resinate or malachite.
Analyses have defined for each illumination the chromatic palette. The range is more limited and the color processing is done in flat areas for Italian illuminated manuscripts, the oldest of the collection. Additionally, the most expensive blue pigment, lapis lazuli, has only been identified thereon [2]. From the illuminations of the 15th century, the palette is enriched and the use of organic pigments more systematic (indigo, stil-de-grain). The palette is very rich in the paintings of the 16th century with the use of organic dyes in many highlights and details. New yellow pigments, red-orange and purple complement the basic pallet (azurite, red lead, cinnabar, lead white, lead-tin yellow...) with the use of dyes (buckthorn, bucktooth, brazilwood, cochineal...). As concerns the gilding, gold leaf is found in the oldest illuminated manuscripts of the collection, shell gold being used in most recent times. An exception for German illuminations where gold foil laid on a sheet of tin has been used, technical zwischgold named and widely used for gildings in medieval wall paintings [3].

The combination of non-invasive techniques has identified most of the materials and gives a good overview of pigments and dyes used, in particular thanks to the mapping of HSI. The choice of techniques responds well to the fragility and preciousness of works and helped to quickly acquire spectra needed to identify the materials. Some doubts remain especially for the precise identification of dyes even if attribution hypotheses have been advanced by comparing the spectra obtained with the pigments from our reference database.

References:
Improved MALDI mass fingerprinting for identification and discrimination of Acacia gums in samples from works of art

Clara Granzotto¹, Ken Sutherland², Julie Arslanoglu³

¹ Northwestern University / Art Institute of Chicago Center for Scientific Studies in the Arts (NU-ACCESS), 2145 Sheridan Road, Evanston, IL 60208 (USA).
² The Art Institute of Chicago, Conservation Department, 111 South Michigan Ave, Chicago, IL 60603 (USA).
³ The Metropolitan Museum of Art, Scientific Research Department, 1000 5th Ave, New York, NY 10028 (USA).

* clara.granzotto@metmuseum.org, (+1) 212-396-5509

Keywords: plant gums; MALDI-MS; enzymatic digestion; gum arabic; organic binders

This paper reports substantial improvements in a method for characterizing plant gums in cultural heritage materials using matrix assisted laser desorption ionization mass spectrometry (MALDI-MS). Analysis of reference materials demonstrated the potential of this new technique to discriminate gums obtained from different Acacia species. An optimized experimental approach with enhanced detection limits was successfully applied to the analysis of microscopic samples from a painting by Georges Braque (1882-1963), in which two species of Acacia gum were detected.

In the cultural heritage field, characterization of plant gums is usually based on the monosaccharide composition, as determined by gas chromatography mass spectrometry (GC-MS) after complete acid hydrolysis, or with use of pyrolysis techniques. However, the data can be difficult to interpret due to chemical similarity of the monomers and the presence of multiple isomers and derivatives. Recently a new strategy for plant gum identification was developed involving partial enzymatic digestion followed by analysis of the released oligosaccharides by MALDI-MS. Due to significant differences in their polysaccharide structure, gum arabic, tragacanth, locust bean and cherry gums could be discriminated according to their unique MS fingerprint.

A limitation of the initial analytical protocol was that c. 1 mg of plant gum was required to generate MS fingerprints. This is well in excess of the amount of sample typically obtained from a museum artefact, which may be in the order of tens of micrograms, and is often complex (i.e. consisting of multiple organic/inorganic materials, in addition to the suspected polysaccharide). In this work several approaches were pursued in order to decrease the amount of sample necessary to generate a reproducible and characteristic MS profile. A variety of filter devices were tested and not found to be effective; however, a significant improvement was obtained by scaling down the amounts of enzyme and buffer and modifying the digestion timing. Results showed a remarkable improvement in detection limits, with characteristic spectra generated from as little as 0.1 µg gum.
Attention was then focused on the study of the most widespread gum encountered in museum artefacts: gum arabic. Among the almost 900 species of Acacia, this gum is predominantly obtained from two Acacia species: *A. senegal* and *A. seyal*. 24 samples of gums from different Acacia species and geographic areas were obtained from the Economic Botany collections of the Field Museum of Natural History (Chicago, IL). While no significant differences were observed in the MS profile due to the geographical provenance, very diverse results were obtained for gums from *A. seyal* and *A. senegal*, reflecting differences in their chemical structure and composition [5]. Furthermore, other Acacia species (e.g. *A. ferruginea, A. microbotrya, A. dealbata, A. penninervis*) showed some specific oligosaccharides, indicating that they too could be distinguished from both *A. seyal* and *senegal*.

Finally the improved analytical strategy was validated by application to samples from a late painting by Georges Braque, *Ajax* (1949/54, Art Institute of Chicago, 1997.447). Previous analysis by pyrolysis GC-MS with tetramethylammonium hydroxide reagent showed the presence of drying oil and diterpene resin, with evidence for Acacia gum in some samples, although the data were ambiguous due to the low levels of carbohydrate derivatives detected [6]. Despite the complexity and small sample size (a few tens of micrograms at most), MALDI analysis showed the presence of gum arabic from *A. senegal* in one sample, and of a gum from a different Acacia species (probably *A. seyal*) in a second sample. The finding of Acacia gum in addition to oil supports visual observations suggesting that Braque used mixed media for this painting. This promising result reveals that ageing and the presence of other media and pigments do not appear to interfere significantly with the enzymatic digestion and analysis, thus demonstrating the robustness of the method and the feasibility of applying the strategy to samples of significant complexity and age, such as those from works of art and archaeological artefacts. The ability to discriminate gums of different Acacia species is potentially valuable to study questions of provenance in the use of these materials by artists and paint manufacturers.

**Acknowledgement:** NU-ACCESS is funded through a grant from the Andrew W. Mellon Foundation. Supplemental support is provided by the Materials Research Center, the Office of the Vice President for Research, the McCormick School of Engineering and Applied Science and the Department of Materials Science and Engineering at Northwestern University

**References:**


Conquering space with matter: an in-depth study of Alberto Burri’s materials and techniques

Federica Pozzi1*, Julie Arslanoglu2, Federico Carò2, Carol Stringari1

1 Solomon R. Guggenheim Museum, Department of Conservation, 1071 Fifth avenue, New York, NY 10128, United States.
2 Metropolitan Museum of Art, Department of Scientific Research, 1000 Fifth avenue, New York, NY 10028, United States.

* Corresponding author. Phone: +1(212)423-3782 / Email: fpozzi@guggenheim.org

Keywords: Alberto Burri; modern art; painting; materials and techniques; scientific analysis; non-invasive techniques; micro-invasive techniques.

Alberto Burri (1915-1995) was a pioneering Italian painter and sculptor. Born in Città di Castello, a small town in the region of Umbria, he earned a medical degree from the University of Perugia. While serving in the Ethiopian campaign and in World War II, first as a frontline soldier and then as a physician, he was captured and sent to a prisoner-of-war camp in Hereford, Texas. It was there that Burri disavowed the medical profession and began to paint. He held a pivotal position in the modern post-war era, exhibiting in Rome and New York in the early 1950s [1]. He worked in series that were titled according to materials and process used, manipulating matter by burning, slashing, tearing and sewing. Burri systematically incorporated unconventional materials, such as household linens and items of clothing, burlap sacks, tar, and newly manufactured industrial products (plastic sheeting, wood veneer, cold-rolled steel) into his creations.

The present contribution describes an in-depth scientific investigation of a selection of 14 paintings by Burri, each belonging to one of his series: Sacchi (sacks), Bianchi (whites), Catrami (tars), Muffe (molds), Gobbi (hunchbacks), Legni (woods), Combustioni plastiche (plastic combustions), Ferri (irons), Cretti (monochromatic fields of induced craquelure), and Cellotex (compositions on flayed fiberboard). Compared to previous works on Burri [2,3], elemental information obtained non-invasively via X-ray fluorescence (XRF) spectroscopy was here combined with detailed characterization of the organic and inorganic pigments, fillers, extenders, and binding media by means of micro-invasive techniques, including pyrolysis - gas chromatography / mass spectrometry (py-GC/MS), Fourier-transform infrared (FTIR) and Raman spectroscopies, and scanning electron microscopy / energy dispersive X-ray spectrometry (SEM/EDS).

Results delivered by this technical study have provided a deeper understanding of the multifaceted nature of Burri’s working practice and elucidated his liberal experimentation with materials. Through the joint use of traditional pigments and binders along with industrial products newly introduced to the market, the artist encapsulated space into highly dramatic compositions at the boundaries between painting and relief sculpture.
Back-scattered electron image of a sample removed from Burri’s *Muffa T* (Godwin-Ternbach Museum, Queens, New York, accession number X.2012.858, 1952). SEM/EDS analysis revealed that the mold-like accretions that permeate the surface of the painting were primarily built up using composite conglomerations of pumice stone, calcite, feldspar and other silicate minerals, mixed in with an abundance of brass flakes.

References:


Assessing issues of attribution by means of technical research: a disputed Van Dyck reconsidered

Astrid Harth1*, Olivier Schalm2, Geert Van der Snickt3, Koen Janssens3

1 Ghent University/Research Foundation - Flanders, Department of Art, Music and Theatre Sciences, Sint-Pietersnieuwstraat 41 B4, 9000 Ghent (Belgium), Tel. +32 477.29.17.69, astrid.harth@ugent.be.*
2 University of Antwerp, Conservation Studies, Blindestraat 9, 2000 Antwerp (Belgium).
3 University of Antwerp, Department of Chemistry, AXES group, Groenenborgerlaan 171, 2000 Antwerp (Belgium).

Keywords: Issues of attribution; painting; imaging and analytical techniques

Over the past decades, technical study of artworks proved valuable for addressing issues of attribution.[1] By revealing new information about painting materials and techniques, advanced imaging tools and chemical analyses (e.g. Infrared reflectography, Macroscopic X-ray fluorescence and XRF analysis) challenge and broaden the current interpretative value of technical investigations of artworks.[2-3] However, despite the recurring introduction of improved diagnostic techniques for the study of paintings and the increasing knowledge of painters’ modus operandi, ‘advances in the methodology of attribution have seemed to progress at a snail’s pace’[4]. Hence, the main problem in this research field is how to transform technical data into meaningful information favoring or opposing a specific attribution. This issue can be solved by identifying distinctive materials and techniques as markers in a set of reference artworks for a specific master, workshop, school or period.[5]

In this study we assess how an object-based methodology can assist in addressing attribution problems. The method was applied on a case study, i.e. the painting Saint Jerome attributed to Anthony van Dyck[6] of the Antwerp Museum Maagdenhuis, which presented useful evidence on the issue of markers. For the painting Saint Jerome, in-depth art historical and archival research did not result in a clear attribution to Van Dyck. Limited information on the painting’s origin and history could be retraced as the earliest written document on the picture’s provenance dates from 1841. Therefore, Van Dyck’s working procedures were studied by systematically gathering available compositional data derived from a set of 37 reference paintings.[7-16] Additionally, the Antwerp painting’s origin, history, iconographic program, formal features, current condition, physical and technical aspects were examined. Hence, the obtained compositional data of the painting could be studied within a broader art historical and technical context to determine whether the identified painting materials and techniques could be used as markers. This holistic approach thus allowed us to simultaneously assess art historical and technical data in order to systematically refine our observations and conclusions. As such, the selected markers could be determined for the painting under study, allowing a comparison with the working procedures of Van Dyck. In what follows, we elaborate on the results of the proposed object-based methodology applied to the specific case.

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
Based on the identified working procedures of Van Dyck, the layer build-up, chemical composition and microstructure of the painting were determined by chemical analysis and imaging techniques (e.g. IRR, XRR, Portable XRF, FE-SEM-EDX and MA-XRF scanning). From this working procedure, a set of 4 markers could be identified opposing the painting’s current attribution to Van Dyck. First, the identified type of support of the painting *Saint Jerome*, which is plain-weave canvas with a low density, deviates from Van Dyck’s choice of canvas supports. More specifically, he preferred plain and tabby-weave canvas with a high density. Second, the picture is painted on top of a red chalk-based ground with a grey priming. This canvas preparation type differs from Van Dyck’s usage of white and pale colored chalk-based grounds with various types of primings. Third, the identified blue pigment employed in the painting *Saint Jerome* for the depiction of the blue drapery is smalt. Van Dyck, however, favored the usage of the organic pigment indigo to construct blue draperies. Fourth, the identified complex method of paint application to depict the flesh tones in the painting *Saint Jerome* substantially diverges from Van Dyck’s art practice, who models the human flesh in a single layer. In conclusion, the materials and techniques used in the picture *Saint Jerome* clearly deviate from Van Dyck’s working process. These findings thus led us to the conclusion that the painting is not by Anthony van Dyck.

References:
Chemical and Spectroscopic investigation of the Raphael's Cartoon for the School of Athens from Pinacoteca Ambrosiana

Armida Sodo1*, Annalaura Casanova Municchia1, Marcella Ioele2, Maria Antonietta Ricci1, Alfonso Pio Russo1

1 Università Roma Tre, Dipartimento di Scienze, Via della Vasca Navale 84, 00146 Rome (Italy).
2 Istituto Superiore per la Conservazione e il Restauro, Laboratorio di Chimica, via di San Michele 23, 00153, Rome, (Italy).

* sodo@fis.uniroma3.it, +39 06 5733 7238

Keywords: Preparatory cartoon; “School of Athens”; paper; Raman spectroscopy; chemical analyses

Several preparatory drawings of the famous fresco by Raffaello Sanzio “School of Athens” (Vatican Museum) have been preserved. Among these, the cartoon shown in Fig.1 (A), and stored at the Pinacoteca Ambrosiana (Milano, Italy), is the most important and closely corresponding to the Vatican fresco. This is the first large-size cartoon, the only full-scale Renaissance one preserved, and a unique insight into one of Raffaello’s most famous works [1].

This cartoon dates back to about 1510 and is a full-scale (8 x 3 m²) reproduction of the fresco, made of 210 sheets of paper linked together and glued to a canvas support. It has been used by Raffaello to report on the fresco wall the key outlines of the project, as demonstrated by the visible pin-prick holes, and to define details of lighting and shading.

The drawing shows past great philosophers, scientists, mathematicians, astronomers and architects (often represented with the aspect of famous Raphael contemporary artists), surrounding the two central figures of Plato and Aristotele. The upper part of the fresco drawing (architectural structures) is missing. Also missing with respect to the fresco is the figure of Heraclitus (with the aspect of Michelangelo Buonarroti).

Due to its historical and artistic relevance, this masterpiece had a troubled story [1, 2]: in particular, in 1796 it was disassembled and transported by Napoleon to France where in 1797 it underwent a significant restoration intervention before being exposed at the Louvre Museum.

In order to characterize the cartoon and the drawing and to investigate its conservation state, several scientific analyses have been performed, both in situ and on
laboratory samples. This multi-analytical approach has allowed to identify most of the materials used in the original drawing and in the restored areas, and to draw a map of previous restoration works. Here we report the main results obtained by Raman and FT-IR spectroscopy, Scanning Electron Microscopy equipped with X-ray micro-analysis (SEM-EDS), pH measurements and micro-chemical tests. pH measurements proved the absence of an acidic decay of the paper. The original paper from linen and hemp fibres is well-preserved, filled with calcium carbonate, and received a light sizing with protein glue, now almost completely transformed into oxalates. 1797 French intervention paper is of lower quality and has been covered with a patina of lead white in Arabic gum, probably to accord the colour to the tone of the original. Both papers are stuck to a support paper with flour glue (containing starch and gluten) and glued with the same adhesive to a canvas lining. Indeed, in-situ Raman spectroscopy has clearly shown that the original drawing was done by a lead white and carbon black ink (spectrum I in Fig.1 B), while the restored areas have been drawn by using graphite (spectrum II in Fig.1 B).

Fig.1. A): Raphael's Cartoon for the School of Athens. Pinacoteca Ambrosiana, Milan. B): In situ Raman spectra of two different drawing area, denominated I and II in the figure.

Acknowledgements:

We would like to thank Mons. Buzzi and all the staff of the Pinacoteca Ambrosiana for giving us the opportunity to study this wonderful artefact and Renishaw S.p.a. and in particular Dr. Riccardo Tagliapietra for technical and scientific assistance.

References:

Paper decay induced by iron gall ink: an investigation of the mechanism using cellobiose

Alice Gimat¹²*, Anne-Laurence Dupont¹, Pascale Massiani² and Véronique Rouchon¹

¹ Sorbonne Universités, Centre de Recherche sur la Conservation (CRC), MCC-MNHN-CNRS URS3224, 36 rue Geoffroy-Saint-Hilaire, 75005 Paris (France).
² Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7197, Laboratoire de Réactivité de Surface, 3 rue Galilée, 94200 Ivry sur Seine (France).
* Corresponding author: Tel. +33140795310, alice.gimat@orange.fr.

Keywords: cellulose; degradation; iron; cellobiose; oxidation; hydrolysis

Iron gall ink corrosion is a challenging issue for written cultural heritage conservation. Yet, the chemical mechanisms underlying the degradation still remain, in its details, poorly understood. In an acidic environment, acid catalysed hydrolysis is the main degradation pathway of cellulose, but in the presence of iron, it can be combined with iron-catalysed oxidation via Fenton reactions which most probably predominate in mild alkaline conditions [1]. These considerations rely on the following facts: (i) hydroxyl radicals have been experimentally evidenced in mild alkaline conditions [2] but not in acidic conditions, and (ii) paper degradation significantly increases at low pH [3]. However, a recent study using papers impregnated with acidic iron gall inks showed that oxygen was essential for the cellulose chains scissions [4], questioning the role of oxygen for cellulose depolymerisation in acidic conditions. Based on these findings, the present work aims at getting a deeper insight into the chemical mechanisms involved in Fe(II)/Fe(III) induced cellulose degradation.

In the light of the impact of oxygen on the degradation, we investigated the presence of reactive oxygen species in model "inked Whatman paper" samples using Electron Spin Resonance Spectroscopy. We found that the iron in solution leached out of the paper was the source of an ESR-signal that varied with the Fe(II) concentration in the medium, which indicated that reactive oxygen species were present.

We then simplified the system under study and used cellobiose, the structural repeating unit of cellulose, to model the iron-catalysed degradation. Cellobiose is a disaccharide composed of two glucose molecules linked by a β(1→4) bond. In acidic conditions cellobiose hydrolyses into two glucose units that can be easily identified and quantified. These molecules are soluble in water, which allows the use of different analytical tools to follow bond breaking and identify the degradation products. Aqueous solutions containing cellobiose and Fe(II)/Fe(III) sulphate were prepared in different conditions of pH and atmosphere (under argon or oxygen). The evolution of cellobiose and glucose concentrations versus time was monitored using capillary electrophoresis with PDA detection. Simultaneously the evolution of Fe(II) and Fe(III) concentrations was followed using UV-Vis spectrophometry. The results indicated that the protons produced in solution during the formation of iron oxide hydroxide were a key parameter that can explain the glycosidic bond cleavage.
Acknowledgement:
This work is supported by French state funds through the "Investissements d'Avenir" program (ANR-11-IDEX-0004-02), more specifically within the Cluster of Excellence (LABEX) MATISSE.

References:
Stone weathering by microbial activity – The case of Convent of Christ

Tânia Rosado¹, Mara Silva¹², Mónica Lança², Carla Nogueira², Rita Santos², José Mirão³, António Candeias¹² and Ana Teresa Caldeira¹*

¹ HERCULES Laboratory, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora (Portugal)
² Chemistry Department, Scholl of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora (Portugal)
³ Geosciences Department, Scholl of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora (Portugal)

*atc@uevora.pt, +351 266 740 800

Keywords: biodegradation/biodeterioration; microbial communities; stones alteration; fungal inhibition; biocides treatment

The usage of stone in artworks goes back to our ancestors due to the inherent characteristics of this material, particularly their highl resistant, durability and versatility. Unfortunately, stone materials are subjected to negative natural and anthropogenic factors that modify the appearance of the surfaces and their integrity. Weathering processes lead to changes in rock surfaces exposed to open air being the result of different chemical, physical and biological agents, which promotes the production of bio-minerals and/or erosion mechanisms. The contribution of microorganisms has been almost neglected, however algae, cyanobacteria, lichens, fungi and bacteria have been revealed potentially harmful for stone artworks. Cyanobacteria and algae are pioneer organisms, which colonise habitats potentially unavailable for living organisms and transform them, allowing the colonisation of the other groups of microorganisms. Their development adversely alters the aesthetic aspect and structural integrity, affecting the historic and cultural value of the monuments. In this way, the investigation of the microbial population dynamics present in rock artworks and the interpretation of their role in the biodeterioration/biodegradation is crucial for the safeguard of Cultural Heritage.

The Convent of Christ in Tomar, Portugal, (Fig. 1) classified as UNESCO World Heritage, is an emblematic monument with a wide diversity of sculpted stone, particularly in the Cloisters and in the Manueline window. These present evident structural and aesthetic damages like coloured stains, biofilm formation and structural degradation, strongly suggesting the presence of biological contamination. The main goal of this work was to perform a comprehensive multidisciplinary approach to understand the biological colonisation and biodegradation of architectural stone materials, trying to find solutions to eliminate them and avoid recolonisation, in order to preserve this historical monument.

The first step included the sampling process, using non- and micro-invasive methods, under semi-aseptic conditions. After that, the microbiological characterisation was performed, involving 1) scanning electronic microscopy analysis, to assess biological contamination presence, 2) culture-dependent methods to characterise the
cultivable microbiological population available in the Convent, 3) molecular approaches based on Next Generation Sequencing (NGS) to fully identify the microbiota. Mitigation strategies were also accomplished by the application of natural and commercial biocides against the microbial population.

The cultivable biodiversity identified in this historic monument were cyanobacteria, bacteria, yeast and filamentous fungi. However, the fungal population were the predominant constituents of the community, being detected fungi of the genera *Penicillium*, *Aspergillus*, *Trichothecium*, but also unclassified strains. The presence of bacteria, cyanobacteria and yeasts seems to be related with orange/pink spots detected in the Manuine Window, Primitive Cloister and Santa Barbara Cloister. Different *Penicillium* strains appear to be the main responsible for green/whitish colouration in the 1st floor of the Main Cloister, forming a thick biofilm that covers all the stone surface. Thus, it is possible to correlate highest levels of contamination with high degradation signals present on the Convent, which evidence the negative effect of the microbiological proliferation. According to this indication, the elimination of these agents is crucial to the safeguard of this monument. To try to solve the biodegradation problem, simulation assays using several commercial and natural biocides were performed on local stone slabs. Highly satisfactory fungal inhibition results were obtained for the natural biocides evidencing their great efficacy.

This work showed that the application of complementary methodologies is an efficient strategy to identify and characterise the microbiological population, and to understand their effect in the stones decay in order to be outlined an effective plan of conservation and intervention process that include mitigation treatment, to avoid the destruction of this cultural asset a promote their preservation and safeguard.

Figure 1. Convent of Christ in Tomar (Portugal) and detail of the Manuine window.

The authors gratefully acknowledge the Fundação para a Ciência e Tecnologia and COMPETE / European Union for financial support (through project UID/Multi/04449/2013).

References:
Characterising the underwater corrosion system of iron nails coming from a shipwreck

Julene Aramendia\textsuperscript{1,2}, Leticia Gomez-Nubla\textsuperscript{2}, Ludovic Bellot-Gurlet\textsuperscript{1}, Kepa Castro\textsuperscript{2}, Laura García\textsuperscript{3}, Iñaki García-Camino\textsuperscript{3}, Manuel Izaguirre\textsuperscript{4}, Juan Manuel Madariaga\textsuperscript{2}

\textsuperscript{1} Sorbonne Universités, UPMC Université Paris 6, MONARIS "de la Molécule aux Nanoobjets : Réactivité, Interactions et Spectroscopies", UMR 8233, UPMC-CNRS, 75252 Paris Cedex 05, France, julene.aramendia@ehu.eus
\textsuperscript{2} Department of Analytical Chemistry, University of the Basque Country UPV/EHU, P.O.Box 644, E-48080 Bilbao, Spain.
\textsuperscript{3} Arkeologi Museoa/ Museo de Arqueología de Bizkaia. Calzadas de Mallona, 2, 48006 Bilbao, Spain.
\textsuperscript{4} Sociedad de Investigación Submarina INSUB. Palacio de Okendo. C/Zemoria s/n Donostia 20013, 3223, Spain.

* julene.aramendia@ehu.eus, Department of Analytical Chemistry, University of the Basque Country UPV/EHU, P.O.Box 644, E-48080 Bilbao, Spain, Phone: +34 946018297, Fax: +34 946013500

Keywords: Iron; archaeology; underwater corrosion; Raman spectroscopy; SEM-EDS; sulfates; microbiologically induced corrosion

Archaeological materials are very precious materials for the understanding of the past societies. However, the conditions to which they are subjected make difficult the preservation and conservation works. Moreover, in the case of waterlogged archaeological sites, the physic-chemical changes that the pieces suffer when they are extracted from the sediment are huge and pretty much different to those that occur in soil-burials. This fact is due to differences in factors such as oxygen, temperature, salinity and the surrounding biota. Therefore, the degradation patterns are different and the conservation and preservation measures should be different too. However, these underwater degradation mechanisms are not so well defined yet, unlike what occurs, for example, with soil-burials. Taking this fact into account, it results really interesting to define the kind of processes that are taking place in these kind of environments.

For this work some iron nails from a shipwreck were selected in order to ascertain what kind of degradation pathways were occurring. The Urbieta shipwreck is the most ancient vessel recovered until the moment in the Cantabric Sea. The pinnace, dated from the XV century, was used at the beginning for coastal fishing and during the last years it was used for the transporting of mineral, such as iron, between different points of the Basque Country (Northern Spain). It is thought, due to the structure, that it was influenced by the naval construction developed in the Scandinavian Peninsula. Urbieta shipwreck was discovered in 1998 during some works performed for the dragging of the Gernika estuary.

The shipwreck was made in wood, with the particularity that the wooden structure was assembled and fixed with iron nails. Regarding the conservation state, it can be said that only the part that was buried in the sediment was conserved, whereas...
the rest of the ship disappeared completely. In 1998, when it was extracted from the archaeological emplacement, the remaining structure was transported to a warehouse where the wood, together with the iron accessories, were subjected to a desalination process and then treated with polyethylene glycol 4000 (PEG) bath. Some of the nails were also independently treated with tannic acid to stabilize the corrosion layers.

For the characterization of the iron nails Raman spectroscopy and SEM-EDS were employed. In order to go further in the analysis of the corrosion and its stratigraphy, some cross sections were also prepared. SEM-EDS analyses were performed with a JEOL JSM-5510LV system for the elemental characterization of the samples. In addition, molecular characterization was carried out by means of a Horiba Jobin Yvon Raman spectrometer using a 532 nm laser.

The results showed that the nails were affected by a possible microbiologically induced corrosion process [1]. Concretely, sulfate reducing bacteria seemed to be transforming the samples, since compounds such as different oxidation states of pyrite (FeS₂) and marcasite (FeS₂) were detected. The precursor of these compounds could be the detected rozenite (FeSO₄·7H₂O). In addition, siderite carbonate was also detected in the analyzed nails. On the other hand, by SEM-EDS it was observed that a high concentration of zinc was present in all the nails. By means of Raman spectroscopy it was observed that this Zn was really reactive and different zinc hydroxides and sulfates were detected. Besides, cross section preparations were analyzed by SEM-EDS in order to see if the Zn were belonging to the metal or not and it was noticed that the Zn was only present in the surface of the nails, therefore related to a pollution from the environment.

Figure 1. Raman spectra of different compounds found in the corroded shipwreck nails.

Acknowledgements: The research leading to these results has received funding from the European Union’s Seventh Framework Programme (FP7/2007-2013 - MSCA-COFUND) under grant agreement n°245743 - Post-doctoral programme Braudel-IFER-FMSH in association with the LabEx MiChem (ANR-11-IDEX-0004-02) and in collaboration with MONARIS UMR 8233 laboratory. This work has been financially supported by the project DISILICA-1930 (Ref: BIA2014-59124-P) from the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER)

References:
Analysis of pigments from fragments of Roman wall paintings from Germania Superior

Rafaela Debastiani¹, Rolf Simon¹, Stefan Heißler², Andrea Wähning³, Markus Meinen⁴, Peter Henrich⁴, Tilo Baumbach¹ and Michael Fiederle¹

1 Karlsruhe Institute of Technology, IPS – ANKA, Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafe (Germany), (+49) 0721 60826108, rafaela.debastiani@partner.kit.edu.
2 Karlsruhe Institute of Technology, IFG, Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafe (Germany).
3 Badisches Landesmuseum Karlsruhe, Schlossbezirk 10, 76131 Karlsruhe (Germany).
4 Generaldirektion Kulturelles Erbe, Niederberger Höhe 1, 56077, Koblenz (Germany).

* rafaela.debastiani@partner.kit.edu, (+49) 0721 60826108

Keywords: Roman mural paintings; pigments; SR-MA-XRF; ANKA

Antique mural paintings from the Roman province Germania Superior were the focus of this study. At the KIT facilities ANKA and IFG synchrotron-based scanning macro X-ray fluorescence spectroscopy (SR-MA-XRF) and IR spectroscopy were employed on the paint layer of selected fragments in order to unveil the composition and origin of the pigments and to elucidate techniques and skill of the painters. These conditions may give hint to the function of the building and to the prestige of its owners. The study was executed on fragments sampled from different sites predominantly in the vicinity of a 440 km segment of the Rhine river valley, Mendig*, Mülheim-Kärlich [1], Koblenz_Remstecken, Weißenthurm, Ladenburg (Lopodunum), Wössingen [2], Augst (Augusta Raurica), and one site from the Neckar river valley, Rottenburg (Sumelocenna).

Infrared spectroscopy identified mainly water, calcium carbonate and gypsum in the plaster of the fragments. Pigment metals were detected in the XRF experiments. Green, yellow and red pigments used in the investigated sites are predominantly earth pigments, based on iron compounds: green earth, yellow and red ochre (Figure 1a). In fragments of a painting once situated in the apsis of a Frigidarium (cold bath) of a luxurious villa rustica [1] we analyzed the presence of lead in the red pigment area, suggesting the use of red lead as red pigment, besides two different yellows (yellow ochre and yellow organic dye + chalk) and a copper based blue pigment, presumably azurite (Figure 1b). Besides the main elements, impurities are detectable by XRF, and their evaluation can help to identify the origin of the pigments.
The names of the Roman towns (civitates) are given where appropriate; the other sites specify locations of countryside villas (villae rusticae).

References:
Rehabilitation of farms – limits of salt content

H. De Clercq¹ and S. Godts¹

¹ Royal Institute for Cultural Heritage (KIK-IRPA), Brussels (Belgium)

* hilde.declercq@kikirpa.be

The rehabilitation of historic buildings is a practice that aims to turn a historic property into a state of private or commercial use, while preserving its historic, architectural and cultural value and respecting items of authenticity, compatibility and sustainability. What once started as a modest use of a local fired brick and a mortar, is today the subject of ambiguous rehabilitation campaigns according to rules of comfort and hygiene of the 21st century.

A proper pre-investigation concerning the diagnosis of damage phenomena and the risk assessment of restoration interventions is a crucial condition for the success of a restoration campaign. The question of “How to optimally preserve a monument within its current conditions” is replaced by “How can a monument optimally perform in the conditions suited to the assigned rehabilitation project”.

Today historic farms and their surroundings after being abandoned for several decades are the subject of different types of private or commercial rehabilitation projects. An example of such a project is a farm ‘Hof De Pleyne’ in Loppem (West-Flanders). The project planned to integrate the former barns as kitchen of a global ambitious restaurant design. This paper deals with the limits of salt content with respect to the desired rehabilitation facilities, while respecting safety regulations.
3D spectroscopic mapping tomography applied to art objects diagnosis

Georgios Karagiannis, “ORMYLIA” Foundation, Diagnostic Centre

In this work, acoustic microscopy, infrared reflectance spectroscopy and imaging, Raman and microRaman spectroscopy is used in order to study the stratigraphic structure of a painted art object. The tomographic images in a region of interest (ROI) of the art object is acquired using acoustic microscopy and the distribution of the materials in the ROI is acquired using infrared reflectance and raman spectroscopy. Using the acquired spectra from both the spectroscopies (Infrared and Raman) the 3D segmentation – clustering of the spectra dataset acquired from the ROI of the painted art object in order to display in high resolution the distribution of the materials in the stratigraphy. The clusters are consisted of spectra that have similar characteristics (for both the modalities Infrared and Raman) and thus are indicating the existence of similar materials; hence, similar chemical composition. The spatial distribution of such clusters can be illustrated in pseudocolor images, in which each pixel of image is colored according to its cluster membership. Such mapping images convey information about the spatial distribution of the chemical substances in an object.

An ALPHA (Bruker) infrared spectroscope with special adapted reflectance illumination area and a micro exRaman (BWTEK) where used in order to acquire the array of spectra and a custom acoustic microscope for the acquisition of the tomographic data (Figure 1). The spectral area in the infrared area of the spectrum covered by ALPHA is from 7500-375cm-1. The Raman laser source that is used has excitation in 1064, i.e., near infrared (NIR). Both the wavelengths that are used form both the spectroscopic modalities ensure the penetration of the radiation in deeper layers. Furthermore, the optical microscopy camera, where the Raman probe is plugged in, is attached to a computerized numerical control (CNC) system which is driven by a software that is specially developed for the scanning of the object with the probes of all the modalities (Acoustic Microscopy, Infrared reflectance spectroscopy and Raman spectroscopy) (Figure 1 and Figure 2). Thus, the mapping images that are produced by clustering the acquired spectra (specifying specific bands of Raman shifts and wavelength bands of infrared spectra) can provide stratigraphic information in the

Figure 1: Infrared ALPHA (a), Raman (b) System and the acoustic microscopy transducer(b) mounted on the XYZ moving stages (CNC) system.

Figure 2: Acquisition using the Raman System: (a) Hardware part, Raman spectrometer, probe and the micro-camera mounted on the XYZ moving stages (CNC) system. (b) Software part, the control of CNC and Raman device for the acquisition of spectra in the specified ROI.
mapping images, i.e. images that convey information of the distribution of substances from deeper, as well. To cluster the spectra, unsupervised machine learning algorithms are applied, e.g., hierarchical clustering. The clustering images derived by the Raman and infrared modalities are registered on the tomographic images providing to the user a high fidelity information of the distribution of the materials in the 3D structure. The whole dataset is supported by the infrared reflectoscopy images acquired from the icon using the well-known infrared reflectoscopy imaging technique providing the user pictorial information on the existing beneath icon. This software except for the conventional CNC operation allows the user to parametrize the spectrometer and check each and every measurement to ensure proper acquisition. This facility is important in painting investigation because some materials are vulnerable to such specific parametrization that other materials demand.

The technique is tested on a portable experimental overpainted icon of a known stratigraphy. It could be referred also as a phantom painting (Figure 3). The two byzantine paintings that consist of the experimental icon, the one of the top of the other, and the region of interest (ROI) where the spectra acquired are illustrated in Figure 2. Finally, the results of the investigation, i.e. the stratigraphic mapping imaging of the ROI, are illustrated in revealing features from the under icon. Specifically, the under icon, i.e., the wavy hair of “Saint James”, can be separated from upper icon, i.e., the halo of Mother of God in the “Descent of the Cross” (Figure 4). The clustering images derived by the Raman and infrared modalities registered on the tomographic images and the infrared reflectoscopy images are provided in Figure 5 and Figure 6.

![Figure 3: The icon contains two pictures, one of top of the other. The scene of the "Descent from the Cross" was painted over the icon of (c) "Saint James", which was vertically half covered with an intermediate preparation layer and (b) is the superposition of the picture in (a) and the picture in (c).](image1)

![Figure 4: Clusters of the spectra in the ROI for three Raman shift bands. These bands in wavenumbers are (a) 0 – 2500 cm⁻¹, (b) 600 – 1000 cm⁻¹ and (c) 1400 – 1800 cm⁻¹.](image2)

![Figure 5: The raman and infrared clustering images registered on the infrared reflectoscopy images](image3)

![Figure 6: The raman and infrared clustering images registered on the tomographic images and the infrared reflectoscopy images](image4)

**Acknowledgement**: This work was partially supported by the scan4reco funded H2020 project.

The issue of digitization of cultural heritage objects using non-contact structural LED light 3D scanning

Marcin Dębek

1 Smarttech 3D, Raclawicka 30 street, 05-092 Lomianki (Poland), Tel. +48 22 751 19 16, md@smarttech3d.com.

Keywords: 3D scanning; 3D digitization; visualization; virtual research

The presentation aims to introduce the possibility of using modern measuring technology in archiving and documentation of historic relics. Will be presented the main method of making three-dimensional digitization, the current devices on the market and wide possibilities of using this technology in maintenance, archiving and research.

3D scanning methods will be shown on examples with discussed opportunities of this technology. Furthermore we will underline differences between 3D digitization and 3D visualisation. The audience will have the opportunity to explore the capabilities of the software – how to quickly get information about volume, surface of the area, make crosssection and do a virtual reconstruction.

On the certain examples will be shown process of creating full documentation of scanned objects, different aspects of scanning sculptures, architectural elements and relocating relics in order to support the reconstruction.

References:
HIROX RH-2000 3D DIGITAL MICROSCOPE

Emilien Leonhardt, Hirox Europe – Jyfel
300 RN 6, Le Bois des Côtes, Bât. A, F-69760 Limonest (France)
Tel. +33 (0)4 26 250 340, info@hirox-europe.com

Keywords: Microscopy; Non-destructive; High resolution; 2D & 3D measurements; 3D modelling; Multiple lighting; Modular configuration

Discover the ideal non-destructive inspection & measurement tool for Cultural Heritage and Art Restoration: the new Hirox RH-2000 3D Digital Microscope!

Our 35 years of experience with museums allowed us to develop the perfect tool for Cultural Heritage applications: Paintings, Metal Artifacts, Textile, Archeology, Wood, Statues, Jewelry and many more!

This portable system allows fast macro inspection up to highest resolution micro details, high resolution image and video documentation, easy measurement from simple distance or area up to high accuracy 3D profiling (incl. height and volume): all this in one system! You will be amazed by its unique flexibility!

Hirox high quality optical, mechanical, and lighting design give this new 3D Digital Video Microscope System the highest optical inspection power (0.1x up to 10,000x) with large depth of field and working distance, along with a variety of options and adapters, including the patented Hirox 3D rotary head adapter.


Hirox is used in the following museums and universities for cultural heritage:

- Musée du Louvre - Paris
- Kunst Historisches Museum - Vienna
- Rijksmuseum - Amsterdam
- Hermitage - St Petersburg
- TATE - London
- Cyprus Institute - Cyprus
- KIK IRPA - Brussels
- University of Ghent (Van Eyck)
- University of Roma (conservation)
- Vatican Museum
- TEFAF - Maastricht
- Institut Català de Paleoeologia Humana i Evolució Social (IPHES) - Tarragona
- Van Gogh Museum – Amsterdam
- Bavarian Federal Library – Munich
- Bibliothèque Nationale de France - Paris
- German Archaeological Institute (DAI) – Berlin
Comparison of Miniature Raman Spectrometric Devices and Gemtesting Systems for Identification of Gemstones

Jan Jehlička*, Jaroslav Hyršl, Laura Minaříková and Adam Culka

Charles University in Prague, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 12843 Prague (Czech republic), Tel. +420221951503, jehlicka@natur.cuni.cz (corresponding author).

Keywords: portable Raman spectrometers; gemtesting Raman systems; gemmology; precious stones; comparative study.

Portable Raman spectrometers seems to be valuable instruments for mineralogists and geologists. More recently excellent possibilities of using those tools in gemology have been shown [1, 2]. Here, for the first time, the evaluation of two miniature Raman devices and one non-portable gemtesting Raman system for a non-destructive and fast unambiguous identification and characterization of cut gemstones is reported. Comparison of practical aspects of the use of those instruments is given studying a series of traditional and less traditional gemstones. The experience obtained with different excitation wavelengths is reported as well as a discussion of the limits of recording diagnostic Raman bands of gemstones mainly of the groups of oxides, silicates and phosphates. The focus of this study is the evaluation of practical aspects of the use of miniature portable Raman devices and a non-portable gemtesting Raman system (Gemplab Research and Technology, Canadian Institute of Gemmology). The latter instrument allows recording photoluminescence spectra. Excellent results (S/N ratio, position of Raman features) were obtained using the Inspector Raman (DeltaNu) handheld system equipped with 732 nm diode. The Rigaku pistol-like instrument with 532 nm diode showed good potential for unambiguous diamond identification however problematic features occur frequently in the spectra including strong artifacts. Important and useful information for provenancing - the position of bands of OH stretching modes of gemstones (~3600 cm⁻¹, i.e. emeralds, [3]) cannot be obtained using common handheld Raman spectrometers due to limited wavelength range of spectra accessible. The gemtesting Raman system used in this study permits to record acceptable Raman spectra of gemstones. Under optimized conditions this allows to discriminate these minerals. The additional advantage consisting in the possibility to obtain photoluminescence spectra using this system is highlighted.

References:
Multispectral Imaging and Material Analysis for the Visualization and Documentation of Manuscripts

Manfred Schreiner¹, Heinz Miklas², Claudia Rapp³, Robert Sablatnig⁴, Wilfried Vetter¹, Bernadette Fruehmann¹, Federica Cappa¹, Fabian Hollaus⁴

¹ Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Schillerplatz 3, 1010 Vienna, Austria
² Institute of Slavic Studies, University of Vienna, Spitalgasse 2, Hof 3, 1090 Vienna, Austria
³ Institute of Byzantine and Modern Greek Studies, University of Vienna, Postgasse 7, 1010 Vienna, Austria
⁴ Computer Vision Lab, Vienna University of Technology, Favoritenstrasse 9-11, 1040 Vienna, Austria

Email: m.schreiner@akbild.ac.at  tel.no. +43 1 58816 8600, fax: +43 1 58816 8699

Keywords: MultiSpectral Imaging (MSI); visualization, manuscripts; palimpsest; non-invasive analysis; XRF; FTIR; Raman spectroscopy

This presentation will report on the interdisciplinary cooperation within the framework of the HRSM-project [1]. Specialized in research in the fields of imaging, image enhancement and analysis as well as the non-invasive chemical analysis of materials used for the production of historical objects, the new Centre of Image and Material Analysis in Cultural Heritage CIMA represents a unique facility with an interdisciplinary approach to the investigation of cultural heritage. The Centre founded in early 2014 brings together the expertise of three disciplines from three universities: Philology (University of Vienna), Computer Science (Vienna University of Technology) and Chemistry (Vienna Academy of Fine Arts). The main idea behind the foundation of CIMA was to extend and strengthen co-operations by establishing a central laboratory that offers its services to universities, libraries, museums, exhibitions etc.

Using modern computer technologies for MultiSpectral Imaging (MSI) and document analysis the manuscripts are examined with a portable MSI acquisition system containing two different cameras: a Hamamatsu C9300-124 Near Infrared (NIR) greyscale camera and a Nikon D4 SLR camera, which is used for white light and UV fluorescence images. The lighting is provided by two LED panels which enable imaging in 11 narrowband spectral ranges. The imaging in narrow spectral ranges leads to a contrast enhancement of the degraded characters – compared to white light illumination. E.g., faded out script is usually most visible in UV fluorescence images. This can be attributed to the circumstance that the parchment is fluorescent under UV light, whereas e.g. iron-gall ink is attenuating the UV light. Hence, the contrast between the characters and the remaining background regions is increased under UV illumination, compared to white light.

Thus, in order to further increase the contrast of the degraded characters several enhancement techniques are applied: Principal Component Analysis (PCA), Independent Component Analysis (ICA) and Linear Discriminant Analysis (LDA). Such dimension reduction techniques are used to lower the third dimension of the multi-spectral scan in order to extract the relevant information, which is in our case the
handwriting. Thus, for manuscripts containing a single writing, the MSI scans are reduced to just one image emphasizing the ancient text. For palimpsests, the third dimension of the MS scan is reduced to two images emphasizing the two different layers of texts.

Figure (from left to right): White light image, UV fluorescence image, results of PCA, ICA and LDA.

The material investigations aim at the determination of the inks and pigments used for writing and illuminating, in contrast to the support (presently parchment) of the manuscripts. For the CIMA investigations a transportable XRF analyzer developed and assembled at the Academy of Fine Arts Vienna is available. The system is based on energy dispersive XRF using an Oxford XTF5011 50W-Rhodium X-ray tube, a Röntec XFlash 1000 silicon drift-chamber detector and two lasers for positioning. Additionally, a novel external reflection-FTIR unit of Bruker Optics, Germany, could be applied to various manuscripts. The reflection module, which can be mounted to the portable Bruker ALPHA FTIR spectrometer focuses the IR beam via mirrors to the object. The analysed area is in the range of approximately 5 mm in diameter. The reflected radiation (4000 – 450 cm\(^{-1}\)) is focused again by mirrors to the DTGS-detector and has to be mathematically treated by Kramers-Kronig-Transformation (KKT) in order to achieve a so-called absorption index spectrum, which can be compared with an IR spectrum obtained in the transmission mode [6]. Finally, the compound specific FTIR results are accomplished by Raman investigations made possible by the acquisition through the HRSM-project of a portable spectrometer (type ENW.450.10020 of Soliton, Germany).

Until now, CIMA has applied its methodology and technical expertise to badly preserved or rewritten manuscripts (palimpsests) from the 8\(^{th}\) to the 14\(^{th}\) centuries (mainly in Slavic, Greek and Latin). The material investigations aim at the identification of the inks and pigments used for writing and illuminating in contrast to the supporting material (presently the focus is on parchment). MSI is used to increase the legibility of degraded writings and the document analysis techniques developed involve Optical Character Recognition (OCR), writer identification and layout analysis.

In the course of the project, a common database will be created which contains the information gained from the imaging, image enhancement, chemical and philological investigations. The final objective of CIMA’s is to compare the data generated in the course of its research, to reveal correlations stemming from multiple modalities (writing material and its preparation, inks and pigments, reflectivity etc.) in order to advance the research agenda at the intersection of science and the humanities.

Raman microscopy of hand stencils rock art from Yabrai Mountain, Inner Mongolia Autonomous Region, China

Antonio Hernanz¹, Mercedes Iriarte¹, Nai’ang Wang², Jinlong Chang²

¹ Universidad Nacional de Educación a Distancia (UNED), Departamento de Ciencias y Técnicas Fisicoquímicas, Paseo Senda del Rey, 9, E-28040 Madrid (Spain), Tel. no. (+34) 91 3987377, ahernanz@ccia.uned.es.
² Lanzhou University, College of Earth and Environmental Sciences, Center for Hydrologic Cycle and Water Resources in Arid Region, Lanzhou University, 730000 Lanzhou, (China).

* Corresponding author: Antonio Hernanz, ahernanz@ccia.uned.es, phone (+34) 91 3987377, fax (+34) 91 3986697

Keywords: Raman microscopy; pigments; rock paintings; prehistoric paintings; rock art conservation.

The Alxa Right Banner is an area in the Western Inner Mongolia Autonomous Region of China. Most part of it is a desert. Many rock art sites with carvings have been found in this area. Two of them, the Taorengaole and Elesenhutele rock shelters are in the hinterland of the Yabrai Mountain and contain coloured hand stencils that have been sampled to identify the pictorial materials used by Raman microscopy. The pictographs of Taorengaole were discovered on 2009 and those of Elesenhutele on 1998. They are painted in dark red and dark grey colours. They could be associated to Middle or Later Neolithic cultures and the probable origins of the HuaXia Nation.

Minerals α-quartz, microcline, albite and anatase have been detected in the granitic rocks supporting the paintings. Crusts with gypsum, bassanite, anhydrite, whewellite and weddellite cover the rocky surface of the painting panels. Studies of paintings on the walls of rock shelters reveal that the presence of gypsum crusts is a common finding.¹,⁴ Bassanite and anhydrite could be the result of dehydration processes of gypsum in desert areas. The existence of gypsum layers on the rock surface could provoke a deteriorative effect on the paintings of the rock shelters resulting in granite flaking and spallation.⁴ Calcium oxalates, whewellite and weddellite, could have been produced by colonies of lichens that lived on the rock surface.⁵ The microstratigraphic distribution of the oxalate layers can be useful to achieve the radiocarbon dating of the paintings.⁵,⁷ Desert dust deposition could have been the origin of calcite and dolomite micro-particles observed on the surface of the granitic rocks. Haematite is the pigment used in the red hand stencils and graphite has been used in the dark grey ones. No graphite deposits or mines are the region. Laser power to record the Raman spectra was reduced in order to avoid "graphitisation" of organic materials. To our knowledge this is the first time that graphite appears as black pigment in rock art, an interesting novelty.
Figure 1. (A) Geographic location of the Taorengaole and Elesenhutele sites. (B) Image of one hand stencil from the Taorengaole site. (C) Raman spectrum of a specimen of red paint from a hand stencil of Taorengaole site. Labels: a, anhydrite; h, haematite; w, whewellite. (D) Raman spectrum of a specimen of dark gray paint from a hand stencil of Elesenhutele site. The Raman band of pure graphite is shown.

References
On-site identification of Sceaux porcelain and faience using portable Raman instrument

D. Mancini\textsuperscript{1,2}, C. Dupont-Logié\textsuperscript{3}, Ph. Colomban\textsuperscript{1,2}\textsuperscript{*}

\textsuperscript{1} Sorbonne Universités, UPMC Univ Paris 06, UMR 8233, MONARIS, 75005, Paris, France
\textsuperscript{2} CNRS-IP2CT, UMR 8233, MONARIS, 75005, Paris, France
\textsuperscript{3} Département du Patrimoine et des Collections de la Cité de la Céramique, 92310 Sèvres, France

\textsuperscript{*} philippe.colomban@upmc.fr

A selection of 25 objects from the Département du Patrimoine et des Collections de la Cité de la Céramique, Sèvres, France, attributed to 18th century Sceaux Factory production, have been analyzed with a portable 532nm Raman spectrometer in museum reserves. Sceaux Factory production is poor documented and it was reported that different technologies were used to produce soft-paste and hard-paste porcelains as well as fine faïences. The identification of the crystalline phases of the body and pigments allows differentiating the different technologies. Comparison is made with porcelains and faïences produced by other Factories in Paris area (Chantilly, Saint-Cloud, Mennecy, Vincennes/Sèvres, etc.).

References
Non-destructive subsurface investigation of art materials with Micro-SORS

Claudia Conti¹*, Alessandra Botteon¹, Chiara Colombo¹, Marco Realini¹ and Pavel Matousek²

1 Institute for the Conservation and Valorization of Cultural Heritage (ICVBC), National Research Council, Via Cozzi 53, 20125, Milano, Italy, tel. +39 (0)2 66173337; email: c.conti@icvbc.cnr.it

2 Central Laser Facility, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Harwell Oxford, OX11 0QX, United Kingdom

Keywords: micro-SORS; subsurface; painted layers; non-destructive; Raman spectroscopy.

Micro-SORS is a recently developed method providing a new analytical capability for investigating non-destructively the chemical composition of subsurface, micrometer-scale-thick diffusely scattering layers at depths beyond the reach of conventional confocal Raman microscopy. The technique combines conventional Spatially Offset Raman Spectroscopy [1] with microscopy concepts and represents a new imaging modality in Raman microscopy. The concept is demonstrated by recovering the pure Raman spectra of sublayers that are obscured by the surface layer(s) [2].

Micro-SORS has been successfully used for the non-destructive characterisation of stratified polymer systems, analysis of layered biological samples and forensic analysis [3]. One of the most topical application concerns the investigation of multi-stratified painted layers and the detection of conservation or decay products below the surface in Cultural Heritage, required to avoid destructive cross sectional analysis [4].

The presentation will outline the concept, exemplify the technique performance on objects of art including our latest results on the prediction of thickness of painted layers in multi-stratified systems.

References:

Figure 1: micro-SORS measurement carried out on a terracotta painted sculpture originating from Varese Sacred Mount in Italy; left) fragment image (the white square indicates the area analysed with micro-SORS); right) micro-SORS defocused spectra, shown for different distances from the imaged plane indicated next to each spectrum (0 = ‘imaged’ position), and reference spectra of the detected red pigments, cinnabar and red lead.
A novel concept towards in-situ Raman mappings using a portable Raman spectrometer.

Debbie Lauwers¹, Philip Brondeel¹, Peter Vandenabeele², Luc Moens¹

¹ Ghent University, Faculty of Sciences, Department of Analytical Chemistry, Raman Spectroscopy Research Group, Krijgslaan 281, S12, B-9000 Ghent (Belgium), tel. +32 (0)9 264 48 45, email: Debbie.Lauwers@Ugent.be
² Department of Archaeology, Archaeometry research group, Ghent University, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium; Tel: +32 (0)9 264 47 17, +32 (0)9 331 01 66; Email: Peter.Vandenabeele@Ugent.be

* Debbie.Lauwers@UGent.be

Keywords: Mobile Raman spectroscopy; mapping system

Mobile Raman instrumentation is often used for in-situ characterisation and identification of inorganic and organic materials in art and archaeometry [1]. A large amount of publications can be found on on-site, molecular examination of mediaeval wall paintings, museum objects, geo-biological samples, etc.[2]–[5]. In all these cases point measurements were performed but wouldn’t it be interesting to relate chemical (molecular) information with spatial distribution?

Until now, Raman mappings are only performed in laboratory experiments: by using an XY stage the investigated object is moved step by step under the microscope attached to the spectrometer [6]–[8]. The main limitation of this approach is the restriction of the sample size: the object has to fit under the microscope and should be sufficiently flat, even if an autofocus system is present [6]. In this project, we want to implement this approach outside the laboratory and use it in the field.

For the development of an in-situ Raman mapping system, the portable Raman spectrometer, EZRAMAN-I-DUAL Raman system (Enwave Optonics ®), of our research group is adjusted. The fiber-optic-based device is equipped with two type of lasers, a red diode laser (785 nm) and a green Nd:YAG laser (532 nm) and has three interchangeable lenses: a standard lens (STD), a long working distance lens (LWD) and a high numerical aperture lens (HiNA). The Raman spectrometer also consist of an adjustable power controller for each laser and a CCD detection system. Further specifications can be found in D. Lauwers et al. (2013) [9].

As mentioned above, the portable instrumentation is equipped with fiber-optic probeheads. This creates the possibility to move the probeheads instead of the object, so large and/or non-transportable objects also can be analysed. To make this operation feasible, a stable motorized stage is developed (Figure 1a), including programming suitable software to control the whole system.

Not only the set-up of the instrumentation is of great importance, data quality and data treatment are important aspects. Porcelain cards are analysed to test whether...
good spectra can be obtained with (very) short measuring times. A first result can be found in Figure 1b.

![Image of in-situ set-up](image1.png)

**Figure 1a.** In-situ set-up, developed in-house. **b.** Preliminary result of the data-treatment of a mapped area.

**Conclusion**

Although the development is a challenging task, the first steps towards an in-situ Raman mapping system are very promising. Additional tests on art applications will help the further development.

**Acknowledgments**

The authors thank Ghent University for its financial support through the concerted research actions (GOA) program.

**References**

Analysis of Wilhelm Ostwald’s „Colour Organ“ with Raman Microspectroscopy

Alexandra Bridarolli, Christoph Herm

1 University College London, UCL Eastman Dental Institute, Division of Biomaterials and Tissue Engineering, 256 Gray’s Inn Road, London WC1X 8LD (UK)
2 Dresden Academy of Fine Arts, Laboratory for Archaeometry, Guentzstrasse 34, D-01307 Dresden (Germany), (corresponding author); Tel. +49 351 4402 2105, herm@hfbk-dresden.de.

Keywords: Wilhelm Ostwald; colour system; synthetic dye; Raman spectroscopy; thin layer chromatography

Introduction

The chemist and Nobel Prize winner Wilhelm Ostwald (1853 – 1932) has developed a specific colour system from the year 1914 on. A great deal of Ostwald’s heritage is still being kept at his former house „Energy Estate“ at Grossbothen near Leipzig, Germany. The so-called „Scientific Colour Organ“, produced in 1925, consists of a number of coloured powders. The twenty-four powders under this investigation form the first color circle and are designated „pa“. Theoretically these materials resemble pure pigments without any content of black or white. Additionally, some specimens of a ring “ea” were analyzed, theoretically representing mixtures of hues from the “pa” ring with white pigment. Although the theoretical background of the colour system is well understood, only little is known about the chemical composition of the material representing it. A few details were published by Ostwald himself [1], but no analysis has been undertaken so far. Knowledge of the composition of the powders is not only important to understand how the colour system was realized, but is also essential to estimate their light fastness.

Methods and Experimental

Each sample was measured in two or three different areas using dispersive Raman spectroscopy attached to a microscope (Horiba – Jobin Yvon XPlORA, 785 and 532 nm). The samples were measured directly as well as using alternative techniques such as potassium bromide pellets for sensible samples or photo-bleaching against fluorescence phenomena. Samples from the “ea” ring were additionally measured with a dispersive NIR-FT-Raman spectrometer (1064nm). In view of the limits of the Raman spectroscopy thin layer chromatography (TLC) was carried out on silica plates. Different eluents were developed for different classes of dyes, consisting of dichloromethane / methanol or ethanol / water or pyridine / methylbenzene / n-hexane, resp. [2,3] Subsequently, Raman spectroscopy was directly applied to the stains on the chromatographic plates.
Results and discussion

Preliminary light microscopic investigation showed that all “pa” powders except one (“13pa”) were composed of at least two different types of particles. By Raman spectroscopy, barium sulphate was identified in all samples with the one exception, indicating lithopone, a mixture of BaSO₄ and zinc sulphide. This pigment has been found in a pure white sample from the Oswald Colour Organ as well. The Raman spectra furthermore indicated that the colour circle was produced by the combination of six different synthetic organic dyes and pigments to create binary or ternary mixtures together with additional lithopone. The synthetic organic pigments are: PY3 (monoazo); PO5 (β-naphtol); PR81:1 or PR169 (phenylxanthene); PV2 (phenylxanthene); and two unknown triarylcarbonium dyes. For all dispersive Raman spectra obtained from the “ea” samples a strong fluorescent background hindered the identification of the sample composition. Only by FT-NIR-Raman spectroscopy the white pigment content could be identified, which is lithopone.

The application of thin layer chromatography revealed additional components for five of the hues that, however, already were proven for other hues. To confirm this assumption, these spots were measured with Raman spectroscopy directly on their substrate. However, no significant Raman spectra from the spots corresponding to the two unknown triarylcarbonium pigments could be measured. The particular difficulties in identifying triarylcarbonium pigments through Raman spectroscopy have been already mentioned in the literature [3].

Conclusions

Although two triarylcarbonium pigments could not be clearly identified, the use of Raman spectroscopy for the study of the colour ring “pa” from the “Colour Organ” by Wilhelm Ostwald has lead to consistent results. Six different synthetic organic pigments have been used together with two synthetic inorganic pigments. Obviously Oswald has switched to more light stable synthetic organic pigments for his “Colour Organ” from 1925, because different synthetic dyes are mentioned for production of coloured samples in his book from 1923 [1]. The efficiency, workability and applicability of thin layer chromatography as a complementary technique for identification of organic pigments is shown in the investigation.

References

**Tomography reads inside ancient books**

Fauzia Albertin¹, Eva Peccenini²,³,⁴, Matteo Bettuzzi²,³,⁴, Rosa Brancaccio²,³,⁴, Maria Pia Morigi²,³,⁴, Franco Casali²,³ and Giorgio Margaritondo¹

¹ Faculté des sciences de base, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.
² Centro Fermi, 00184 Roma, Italy.
³ Dipartimento di Fisica e Astronomia, Università di Bologna, 40126 Bologna, Italy.
⁴ INFN Sezione di Bologna, 40126 Bologna, Italy.

* Corresponding author’s email address: fauzia.albertin@epfl.ch, phone: +41-21-6934304

**Keywords:** manuscripts; x-ray; tomography; digitization; ancient inks; iron gall.

We successfully tested the x-ray tomography “virtual reading” technique on closed ancient specimens, including a 200-page handwritten physics book from 1790. Tomographic reconstructions of projection radiograph sets enabled us to identify characters and words from individual pages. These results constitute an important step towards our final objective of non-invasively reading ancient manuscripts of the Venice Archivio di Stato.

Figure 1 shows two examples of the results. The top-left picture is a 3-dimensional tomographically reconstructed side view of a folded 1679 administrative manuscript. The tomography clearly reveals the x-ray-absorbing ink on the individual pages. The middle-left picture shows writing extracted from a single sheet: the words “Giugno 1679” (June 1679) are readily recognizable.

The bottom-left picture is a tomographic side view of the handwritten physics book with a large number of pages. The picture on the right-hand side shows one example of page reconstruction revealing an extended text.

To control the possible x-ray damage, we conducted these first tests with very limited x-ray intensity and long image acquisition times. Taking a 900-radiograph projection set required 1 hour for the smaller object and several hours for the book. The long times notwithstanding, we found no evidence whatsoever of radiation damage.

We can thus predict that, after optimization, the data taking will be drastically shorter without introducing damage. Moreover, with x-rays we do not need to open up the specimens, further reducing the risks for fragile items.

Note that we obtained the present results with a conventional x-ray source rather than with a centralized synchrotron facility. The corresponding equipment can be easily moved for in situ analysis of ancient collections.
This is quite important, since our research on virtual reading by x-ray tomography is within the strategic project “Venice Time Machine” -- which includes the analysis of the huge manuscript collection of the Archivio di Stato. Moving such specimens to a centralized facility would be logistically unfeasible and unacceptably risky.

The results, and in particular the top-left picture in Fig. 1, graphically illustrate the technical foundations of our technique. One can see indeed the strong x-ray absorption by the inks. This would not occur for modern organic-based inks or for other carbon-based pigments. Fortunately, the inks used in Europe over a millennium were variations of the “iron gall” recipe: such inks contain a large iron concentration that explains the strong x-ray absorption. Our own tests [1] revealed this feature for a variety of manuscripts of different ages. Furthermore, strong x-ray absorption was also present for red inks, due to mercury.

The general background for the present tests was provided by previous experiments by other authors and by ourselves [1] - demonstrating the feasibility of the approach. With the present tests, we enter a new phase in which we can analyze large specimens with many pages. The success of this work is therefore crucial for the future applications of the technique - not only to the Archivio di Stato but to many other ancient collections of high historical value, paving the way to their practical use and to the digital preservation of their content.

References:

Fig. 1 – X-ray tomography reconstructions from two different specimens: a folded 1679 manuscript (left, top and middle) and from a handwritten 1790 physics book (bottom left and right). Without opening the specimens, we could detect characters and words. Note the x-ray-absorbing ink in the top-left side view.
Looking inside valuable wooden objects with
X-ray CT @ UGCT

Jan Van den Bulcke1*, Denis Van Loo2, Manuel Dierick3, Bert Masschaele2, Matthieu Boone3, Kristof Haneca4, Koen Deforce4, Luc Van Hoorebeke3, Hans Beeckman5, Manu Frederickx6,7, Valerio Lorenzoni8 and Joris Van Acker1

1 UGCT – Laboratory of Wood Technology, Department of Forest and Water Management, Ghent University, Coupure Links 653, 9000 Gent (Belgium), Tel. +32 9 264 61 25, Jan.VandenBulcke@UGent.be.
2 XRE, X-Ray Engineering bvba, De Pintelaan 111, 9000 Gent (Belgium).
3 UGCT – Department of Physics and Astronomy, Ghent University, Proeftuinstraat 86, 9000 Gent (Belgium).
4 Flanders Heritage Agency, Koning Albert II-laan 19, bus 5, 1210 Brussel (Belgium).
5 Royal Museum for Central Africa, Wood Biology Service, Leuvensesteenweg 13, 3080 Tervuren (Belgium).
6 Department of Design, School of Arts, University College Ghent, Jozef Kluyskensstraat 2, 9000 Gent (Belgium).
7 Object Conservation Department, Metropolitan Museum of Art, 1000 Fifth Ave, New York 10028 (United States).
8 Institute for Psychoacoustics and Electronic Music, Department of Musicology, Sint-Pietersnieuwestraat 41 Blok 2, 9000 Gent (Belgium).

* Jan.VandenBulcke@UGent.be, +32 9 264 61 25

Keywords: X-ray CT; wood; wood identification; structural quantification; tree ring analysis; musical instruments; sculptures; multiscale scanning

X-ray Computed Tomography has become a well-established technique during the last decades. This non-destructive method is indispensable for many research fields, thus its use in art research is therefore obvious. At UGCT (www.ugct.ugent.be), the Ghent University Center for X-ray Tomography, a series of scanners has been developed to meet the need of scanning different types of objects, which can have very different chemical composition and different dimensions. Furthermore, in some cases experiments with connection to peripheral equipment are of interest or even the requirement to have a static sample and a rotating scanner. The different scanners at UGCT as such allow to address many different research questions. For valuable wooden objects, the technique can offer opportunities ranging from visual assessment to quantification of features of interest. Investigation of wooden objects is challenging, given the hierarchical nature of wood at one hand and the diversity of the objects at the other hand. We will show several examples using the HECTOR and Nanowood scanner, for the investigation of wooden musical instruments [1], valuable ethnological sculptures, wood identification of small pieces of wood from an archaeological excavation [2], etc.

Nanowood [3] is a multi-resolution X-ray CT scanner specifically designed to obtain scans of samples with a maximum diameter of 37 cm at a resolution of approximately 0.2mm down to a resolution of approximately 400 nm for objects that

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium

113
have about the size of a splinter. Nanowood is specifically designed for wood research sensu lato. HECTOR is a High Energy CT scanner Optimized for Research [4], built in collaboration with the UGCT spin-off company XRE (www.xre.be), with a maximum resolution of 3 µm. Objects with a maximum diameter of 85 cm and a maximum weight of 80 kg can be scanned. Both systems have a generic in-house developed CT scanner control software platform [5] that allows full control of the scanner hardware. Reconstruction of the scans is performed with the Octopus Reconstruction software package [6], licensed via InsideMatters.

Figure 1 illustrates a series of scans of different objects, showing the wide range of information that can be gathered using both systems.

![Figure 1](image_url)

Figure 1. 3D rendering of the central part of a cello (1), cross-section through a violin (2), 3D rendering of an ethnographic sculpture of the DR Congo (3) and cross-section through corrosion-preserved hardwood scanned at submicron level (4). Approximate dimensions indicated by scale bar.

References:
Observations on the use of OCT to examine the varnish layer of paintings

Derek Nankivil¹, Joseph A. Izatt¹ and Adele DeCruz*²

¹ Duke University, Dept. of Biomedical Engineering, Durham, NC, USA 27708
² Duke University, Depts. of Chemistry & Biology, Durham, NC USA 27708
adecruz@duke.edu, 001 919 613 5024

Keywords: OCT; varnish; paintings; Er:YAG laser; conservation.

To restore the original intent of the artist, art conservation is moving towards an increased use of laser ablation to remove varnish layers, which have become encrusted with contaminants or have been otherwise altered over the years. It should be possible to guide the restoration process with imaging modalities that provide information about the varnish layer. In paintings where the encrustation has not rendered the varnish completely opaque, Optical Coherence Tomography (OCT) has the potential to provide details about the structure and thickness of the varnish layer in a non-invasive manner.

In this study, OCT was used to visualize and quantify the varnish layer of paintings and to verify the success of efforts by conservators to remove the varnish layer using laser ablation. A free-running Er:YAG (MonaLaser, Orlando, Florida) laser with a central wavelength of 2.94 μm, a repetition rate of 15 kHz and an optical power of 1 mW was used to remove the varnish. A spectral domain OCT system with a Michelson topology was constructed using a broadband superluminescent diode (SLD-371, Superlum, Carrigtwohill, Ireland) with a central wavelength of 840 nm and a 50 nm bandwidth and a line scan CMOS sensor (AViiVA, e2v Inc., Milpitas CA) with a 20 kHz line rate. The sample arm design utilized a 4f relay between the first and second galvanometer and a telecentric beam delivery system to minimize optical distortions. The OCT system provided an 8.5 μm axial and 7.5 μm lateral resolution, a sensitivity of 105 dB, an imaging range of 0.8 mm (6dB fall off) and a field of view of 5 x 5 mm.

Samples, including pigment, varnish and substrate, approximately 1 mm² in size, were removed from an oil painting on panel (San Giorgio Maggiore) by Martin Rico (1833-1908) and imaged using Environmental Scanning Electron Microscopy (ESEM). Varnish thickness obtained from OCT was validated by similar measurements obtained from ESEM. In addition, other paintings, including a late 18th century landscape, signed Thomas Gainsborough, were imaged with OCT to compare neighboring regions before and after laser treatment and to examine the layering of the artist’s signature in an effort to determine its authenticity.

Varnish layer thickness was 10.8 ± 3.8 μm and 12.7 ± 0.7 μm measured by OCT and ESEM respectively. Complete varnish layer removal was observed in several regions of paintings after laser treatment with occasional residual varnish in regions of
significant surface topological variation. Additionally, the presence of over-paint and differences in penetration depth were observed in the OCT cross-sections.

We believe that this is the first demonstration of the application of OCT to show that the varnish is removed by Er:YAG laser treatment. In conclusion, we demonstrate that OCT may provide a non-invasive technique that provides measures of the varnish layer and verification of its removal after laser ablation-based conservation efforts.
Segmentation of thin varnish layers in OCT images of works of art

Tom Callewaert1,2,*, Joris Dik2, Jeroen Kalkman1

1 Delft University of Technology, Department of Imaging Physics, Lorentzweg 1, 2628 CJ, Delft, The Netherlands.
2 Delft University of Technology, Laboratory of Materials Science, Mekelweg 2, 2628 CD, Delft, The Netherlands.

* t.w.j.callewaert@tudelft.nl

Keywords: Image processing; Image analysis; Optical coherence tomography; Signal processing

In this work we present a method to segment images which were obtained by optical coherence tomography (OCT). Existing algorithms focus on the segmentation of retinal layers. Unfortunately, there is a total lack of such image processing tools, with respect to images obtained from material property studies. We use graph cut theory in order to obtain the initial segmentation and subsequently implement fuzzy set theory to refine the intermediary results. By means of this approach we are able to analyse the layered structure of a range of artworks. We established that the algorithm is able to semi-automatically segment an arbitrary number of varnish layers, and successfully deals with discontinuities in the structures. Our work shows the value of segmented OCT images for the preservation, conservation, and restauration of works of art.

During the last few years, different reports have indicated the value of Optical Coherence Tomography (OCT) for material science research [1]. For the field of materials science in art and archaeology, OCT is especially promising, due to its non-invasive nature and high axial/lateral resolution. Both properties make it an ideal supplementation to current imaging technologies. Our OCT imaging system (customized Ganymedes, Thorlabs GmbH) has an axial (depth) resolution of 3.0 µm and a lateral resolution of 4 µm in air. Sample properties such as stratigraphy, layer thickness, attenuation coefficient and refractive index are accessible from the OCT signal.

In this study we investigate OCT images of varnish layers, these images include information about layer thickness and distribution. Precise and automatic segmentation of images obtained by OCT is therefore crucial to obtain information of stratigraphy over large areas. Manual segmentation of the image data is subjective and time consuming. We apply graph cut theory on the obtained OCT images, Graph cut theory is more flexible compared to previous work and is applicable to different layer-substrate structures, while retaining the same mathematical framework. Initial segmentation of the image is based on graph based cut segmentation theory [2]. We then furthermore refine the segmentation results by defining a fuzzy inference system [3]
The most important concepts for graph theory are: vertices (commonly referred to as edges) and nodes. In our case the pixels composing the image are the nodes and the different layer boundaries are the edges. We assign weights to intensity transitions along the axial axis. By connecting the appropriate weights, we obtain a segmented image. The method is compatible with different numbers of layers on a substrate. The substrate may also vary as far as the algorithm is concerned. This versatility is rather rare and allows for analysis of different datasets. We analysed data originating from OCT images of different works of art; canvas paintings, cardboard paintings, varnished wood, photographic paper and lithographic prints among others. All samples gave good segmentation results, as long as the varnish is sufficiently transparent. Eventually we obtain the final segmented image.

Figure 10 provides an overview of the different steps of the graph cut segmentation algorithm, for a varnish covered wood sample. The initial B-Scan (Figure 1a) is loaded and the boundaries of the varnish and substrate are determined (Figure 1b). The search for additional layers is restricted between the previous regions and further layers are determined (Figure 1c), finally we obtain the segmented image (Figure 1d), showing the individual varnish layers. The process of estimating the condition of a varnish layer (during restauration as well) is simplified, without damaging the work of art.

Figure 2: (a) Measured B-Scan. (b) Determination of the outer boundaries of the varnish layers. (c) Additional segmentation of remaining varnish boundaries. (d) Segmented Image with layer dimensions as small as 10 µm

References:
The use of micro-CT in cultural heritage research

Manuel Dierick¹, Matthieu Boone¹, Amelie De Muynck¹, Thomas De Schryver¹, Jelle Dhaene¹, Joris Van Acker², Jan Van den Bulcke², Veerle Cnudde³, Denis Van Loo⁴, Bert Masschaele⁴ and Luc Van Hoorebeke¹

¹ UGCT – Department of Physics and Astronomy, Proeftuinstraat 86, 9000 Gent (Belgium), Tel. +32/92646611, manuel.dierick@UGent.be.
² UGCT – Laboratory of Wood Technology, Department of Forest and Water Management, Ghent University, Coupure Links 653, 9000 Gent (Belgium).
³ UGCT – PProGRes, Dept. of Geology and Soil Science, Ghent University, Krijgslaan 281 (S8), 9000 Gent (Belgium).
⁴ XRE, X-Ray Engineering bvba, De Pintelaan 111, 9000 Gent (Belgium).

* manuel.dierick@UGent.be, +32 9 264 66 11

Keywords: tomography; X-ray; 3D imaging; microscopy, non-destructive; radiography

X-ray tomography is a 3D imaging technique which uses penetrating X-rays to visualize the internal shape and structure of objects. Although it is best known for its use in medical imaging, it is increasingly used in both academic research and industry. Applications include material research, quality control, metrology etc. Desktop scanners have found their way into the lab environment, and spatial resolution has steadily improved to the micrometer (micro-CT) or even sub-micrometer (nano-CT) range. The non-destructive nature of CT is a strong asset, particularly in cultural heritage research where, for obvious reasons, the sample needs to remain intact. Applications in cultural heritage include investigation of large macroscopic objects such as musical instruments [1], statues, pottery, etc. but also microscopic investigation of for example the pore structure of ceramics or fungal decay in wood.

This presentation gives an overview of the possibilities and caveats of micro-CT in the field of cultural heritage. More specifically the scanner facilities of UGCT, the Centre for X-ray Tomography of the Ghent University (www.ugct.ugent.be) will be described. This user facility offers researchers access to state-of-the-art micro- and nano-CT scanning infrastructure and expertise. Four scanners are currently operational, offering a wide range of possibilities in terms of sample size, scanning speed, spatial resolution etc. These scanners are designed and built by the Radiation Physics group within UGCT, and specifically optimized for scientific research. HECTOR is a high energy micro-CT scanner [2], built in collaboration with the UGCT spin-off company XRE (www.xre.be). Its relatively high X-ray energy of 240kV allows scans of big and dense objects up to 80cm diameter, but it also reaches resolutions down to 3µm in small objects. MEDUSA pushes the resolution to below 1 µm and is therefore used mainly for microscopic studies of samples in the millimetre range. NANOWOOD [3] was designed specifically for wood research with a wide resolution range down to 400nm. Finally the EMCT [3] is a gantry scanner where, contrary to the other systems, the sample remains stationary during the scan, but the tube and detector assembly rotates
around the sample instead. This allows the study of dynamic phenomena such as the uptake of water in building materials.

Tomography data can be used in different ways beyond mere visualisation of internal structures. The grey levels can provide accurate information about mass density or material composition. Year ring patterns in wood can be used for precise dating. Morphological analysis can generate distributions of shape parameters such as pore size or orientation [4]. Finally some case studies will be discussed that illustrate the added value of micro-CT to the field of cultural heritage. These include archaeological finds such as a Roman lock mechanism found in Oudenburg (Belgium), a study of wooden musical instruments [1], and some bronze statues. Figure 1 illustrates the internal structure of an ancient Roman lock mechanism (Image courtesy Sofie Vanhoutte, Flanders Heritage Agency).

![Figure 1](image.png)

Figure 1. The internal mechanism of a heavily corroded ancient Roman lock revealed by virtual sectioning through CT image data. (© Sofie Vanhoutte, Flanders Heritage Agency)

References:
XGLab’s new instrumentation for the analysis of cultural heritage

Tommaso Frizzi\textsuperscript{1}, Roberto Alberti\textsuperscript{1}, Luca Bombelli\textsuperscript{1}, Michele Gironda\textsuperscript{1}

\textsuperscript{1} XGLab SRL, Via F. d’Ovidio 3, I-20131 Milano (Italy), Tel. +39 0249660460, info@xglab.it.

Keywords: portable; Raman; XRF; scanner; mapping;

XGLab has been developing portable instrumentation for the analysis of materials since 2009. Starting from its first pXRF “ELIO”, XGLab designed a new set of portable devices to expand its analytical capabilities. We’ll present the full portfolio of XGLab’s products dedicated to the cultural heritage and objects analysis in general.

ELIO is an X-Ray Fluorescence spectrometer capable of in-situ, fast, non-destructive and non-invasive analyses on metals, jewels, ceramic objects, seals, glass objects, paintings, frescos, marbles, printed materials such as documents and books, parchments and manuscripts, material research and elemental analysis in general [1]. Thanks to its small spot-size (1mm), the integrated video camera, the high rate X-ray tube and detector capabilities, the easy-to-use software, the small dimensions, ELIO represents the must-to-have XRF analyzer for people working in the cultural heritage field.

XGLab recently developed a mapping option to transform ELIO in a powerful portable XRF mapping system. The measurement head is driven by two motorized stages to perform a scan of up to 10cm x 10cm areas, storing all the spectral information and all the photos, allowing for easy superposition of the XRF and optical images.

A novel portable analytical tool, “XRaman”, implementing contemporary two diagnostic techniques, will be also presented. XRaMan is a portable spectrometer designed to perform in-situ, fast and non-destructive combined elemental and molecular...
analyses, by the complementary EDXRF and Raman techniques. XRF and Raman components are highly integrated into the compact detection head and the perfect coincidence of the analysis area is always under the control of the operator thanks to several other monitoring systems (pointing lasers, microscope camera, external camera). The system works in a complete non-contact mode with an optimal focus distance of about 1cm from the sample.

Figure 3 On the left: the XRaman device. In the center: Costa Rican Crocodile Effigy Pendant TL.2009.20.273 from Walters Art Museum, Baltimore, USA. On the right: XRF and Raman analyses in 2016 using the portable XGLab’s XRaman system; the results confirmed the major mineral constituent as jadeite, with albite also detected.

Figure 4 Comparison between the Raman spectrum obtained by Xraman from the sample and reference Raman spectra

The last R&D effort from XGLab laboratories is a fast macro-XRF scanner. It allows for up to 60cm x 40cm area scanning. As an example, the map in Figure 3 is 12cm x 7.5cm and it has been acquired in 30 minutes with a resolution of 0.5mm. The X-ray excitation is collimated from 0.5mm to 2mm (software-selectable) and no x-ray lenses are used, which results in good efficiency even for light elements. The XRF scanner can turn into a portable spot-XRF device by detaching the measurement head from the supporting frame.

Figure 5 On the left: new XGLab’s macro XRF scanner. On the right: picture (top) and correspondent XRF map (bottom) realized in 30 minutes (0.5mm spatial resolution, 12 cm x 7.5 cm)

References:
Fondis Bioritech – Niton XRF analyzers

Rémy Blot

Fondis Bioritech, 26 Avenue René Duguay Trouin, Entrée D, Voisins-le-Bretonneux, 78960 (France), +33(0)1 34 52 10 30, info@fondisbioritech.com

Keywords: Niton analyzers; Handheld XRF analyzers; nondestructive testing solutions; elemental analysis.

Fondis Bioritech, value added reseller of scientific measurement solutions, offers a complete range of portable X-ray fluorescence spectrometers. They have been designed to perform on-site and non-destructive analysis, thanks to their ergonomic design, robustness and ease of use.

Thermo Scientific Niton analyzers are the ideal tools for archaeometry. Niton analyzers provide you a lab-quality analysis in the palm of your hand. Indeed, you have the ability to obtain quantitative elemental data in the field, in real time. Niton analyzers are accurate and robust instruments for art conservation and archaeometric analysis. They have the ability to identify and quantify any element from Mg through U in any sample.

It’s easy to analyze clays and ceramics, soils, lithic materials, textiles, alloys, paintings, pigments, glazes, construction materials, clothing, bones, teeth, precious metals with Niton analyzers.

For instance, the analyzers help you to establish provenance. It identifies components of pigments and other materials in paintings and glazes to assist in the preservation and restoration of artifacts. Paintings can be examined safely without even removing them from the frame.

Niton analyzers are also useful to help to authenticate a variety of art and artifacts. Use elemental composition data to identify how objects have been preserved in the past, and how to better conserve them for the future.

Niton analyzers are the right tools for archaeometry.
A multi-analytical approach for characterization of orcein dyes in historical textiles, extracted through a new alkaline extraction protocol

Ilaria Serafini¹², Livia Lombardi¹², Fabio Sciubba¹, Claudia Fasolato³, Paolo Postorino³, Marcella Guiso¹, Maurizio Bruno⁴, Armandadoriano Bianco¹

¹ Dipartimento di Chimica (ilaria.serafini@uniroma1.it, +39 0649913622),
² Dipartimento di Scienze della Terra,
³ Dipartimento di Fisica, Università di Roma “La Sapienza”, Piazzale Aldo Moro 5, 00185 Roma (Italy),
⁴ Università degli studi di Palermo, Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche, Piazza Marina 61, 90133 Palermo (Italy)

* ilaria.serafini@uniroma1.it, +39 0649913622

Keywords: orcein dyes; mild extraction; textiles; SERS; ESI-MS; NMR.

Since the arising of the art of dyeing, dyers drew their attention to improve the ways of colouring with dyes extracted from locally available sources. Lichens have been also employed, the most famous example being orchil: this name indicates any of several lichens, chiefly of the genus Roccella, from which a purple dye is obtained. In history, the largest employment of this material coincided with the maximum request of shellfish; its use is often attested to substitute the more precious Tyrian purple [1]. In fact, obtaining a purple colour from lichens requires less quantity of raw materials compared to mollusk, requested for the dyeing bath.

However, to prepare the dye bath, the lichens requires a chemical pretreatment. In fact, the lichen does not contain any phenoazone compounds, the real chromophores, but some precursors, such as the orsellinic or lecanoric acid. These latter have to be hydrolyzed in a strong alkaline environment and decarboxylated to orcinol. Finally, oxygen and ammonia lead to phenoazone structures [2,3], resulting in a mixture of α-, β-, γ- amino or hydroxy- orcein and β-, γ- amino orceimine, which has been used until the born of its synthetic substitute, the mauveine [2].

In the last years, researchers have faced a dramatic challenge, concerning this dye: orcein, in fact, is not easily recognizable, due to its low photo-stability. For this reason, even if its use is well known, only few papers report the identification of this dye in historical manufacture [4]. The research is moving to improve non-invasive analyses, carried out directly on artworks, such as Raman spectroscopy, UV-Vis fluorimetry, etc. [1, 4-6]. On the other hand, the micro-invasive analytical approaches are focused on the optimization of both LC-MS and MALDI-ToF protocols [4, 5, 7].

In this paper, we present a multi-analytical approach for the characterization of orcein dyes. First of all, to evaluate the applicability of this protocol and collected
reference data, we prepared dyed yarns in our laboratory, following the ancient recipes [8].

Then, SERS experiments were performed directly on fibers [6] and a new extraction protocol, based on the use of ammonia and EDTA, has been applied on the dyed yarns [9]. This methodology has been developed for anthraquinone dyes, where the main aim was the preservation of glycosylated compounds, which can be lost with acidic conditions, typical of usual extraction protocols. However, in order to evaluate the efficiency of this new extraction method also on this class of dyes, it has been used instead of the common extraction in formic acid. The extracts, from laboratory dyed yarns, have been analyzed through $^1$H-NMR, HPLC-DAD, ESI-MS and HPTLC-SERS.

Collected these reference data, the protocol has been applied on historical samples from a mauve silk dress (late XIX century), belonged to a Sicilian noblewoman, provided by University of Palermo. To evaluate the synthetic or natural origin of purple dye, firstly we performed SERS on fiber analysis, which has revealed that the dress was obtained using mauveine textiles for some details and orcein for others. To confirm these identifications and deepen the study of these historical samples, the new mild extraction protocol and the multi analytical approach were applied.

We present in this communication the results of our approach, for the study of organic dyes in cultural heritage artworks, based on the comparison between data obtained from the real samples and those coming from standards.

References:
Development of an analytical procedure for the analysis of European lacquer

Louise Decq¹⁵, Vincent Cattersel², Delphine Steyaert³, Michael Schilling⁴, Frederic Lynen⁵, Viviane Leyman⁶, Charles Indekeu², Emilie Van Binnebeke³, Wim Fremout¹ and Steven Saverwyns¹

¹ Royal Institute for Cultural Heritage (KIK-IRPA), Department Laboratories, Jubelpark 1, 1000 Brussels (Belgium), Tel.+32-2-7396711, louise.decq@kikirpa.be / steven.saverwyns@kikirpa.be (corresponding authors).
² University of Antwerp, Conservation Studies – Heritage & Sustainability, Blindestraat 9, 2000 Antwerp (Belgium).
³ Royal Museums of Art and History (RMAH), Jubelpark 10, 1000 Brussels (Belgium).
⁴ Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles, CA 90049-1684 (USA).
⁵ Ghent University, Department of Organic Chemistry, Krijgslaan 281, 9000 Ghent (Belgium).
⁶ Botanic Garden Meise, Nieuwelaan 38, 1860 Meise (Belgium).

Keywords: European lacquer; THM-Py-GC/MS; quality control; semi-automatic data treatment; AMDIS

Starting from the 17th century, European craftsmen produced high-glossy luxury items, inspired by the success of imported oriental lacquer, but using natural resins as alternative raw materials. The interdisciplinary project European Lacquer in Context (ELinC) aims to discover the history, chemistry and technology of these fascinating objects. Main partners in this project are The Royal Institute for Cultural Heritage (KIK-IRPA, Brussels) for the chemical study, University of Antwerp (UA, Antwerp) for physical and technological aspects, the Royal Museums of Art and History (RMAH, Brussels) for the art historical study and for granting access to the lacquered objects from their collection, and the Getty Conservation Institute (GCI, Los Angeles) for the exchange of information, following their expertise in the analysis of mainly Asian lacquer. The research project incorporates, amongst others, the study of ancient recipes, ingredients, mock-up samples, artificially aged samples and lacquered objects, and tries to get a view on lacquer production in our regions.

For the reproduction of lacquers following historical recipes, a large amount of natural resins and other ingredients were purchased. To assess the purity and labeling of these commercially available natural resins, they were compared with trusted reference samples from botanical and historical collections, using pyrolysis-gas chromatography/mass spectrometry with thermally-assisted hydrolysis and methylation (THM-Py-GC/MS). The results showed that a significant portion of the commercial resins were impure or incorrectly labeled.

For both the analysis of the pure basic materials as for the subsequent analysis of historical lacquered items, the THM-Py-GC/MS technique was optimized for gathering of maximal information on the compounds present, using only very small samples. Pyrolysis temperature programs are compared for five natural resins, all important ingredients for European lacquer.
As European lacquers are complex mixtures of natural resins, a semi-automatic procedure was developed in close collaboration with the GCI in order to facilitate and improve the interpretation of the THM-Py-GC/MS chromatograms. The AMDIS software (Automated Mass spectral Deconvolution and Identification System) in combination with a specific 'RAdICAL' lacquer target library has been enlarged and used for this purpose. The target library plays a key role in the identification procedure, and is composed of markers, characteristic for specific resins and other ingredients. As the composition of resins can change drastically upon aging, not only fresh resins were used to compile the data, but also artificially aged ones. The AMDIS software, in combination with a data interpretation worksheet created by the GCI, proved to be very powerful for the quick and reliable identification of European lacquers.

This presentation will discuss the results of the quality control of natural resins, the optimization of THM-Py-GC/MS for European lacquer analysis and the semi-automatic data treatment using AMDIS. The methodology will be illustrated with the analysis of artificially aged resin samples and samples from historical lacquer.
Determination of authenticity of paintings using “attribution markers” and data mining techniques

Barbara Łydżba-Kopczyńska¹,², Janusz Szwabiński³,

¹ University of Wrocław, Faculty of Chemistry, Cultural Heritage Research Laboratory, F. Joliot-Curie 14, 50-383 Wrocław (Poland), tel. +48713757379, barbara.lydzba@chem.uni.wroc.pl
² National Museum in Kraków, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14, 31-109 Kraków (Poland).
³ University of Wrocław, Institute of Theoretical Physics, M. Bochnia 9, 50-204 Wrocław (Poland).

* barbara.lydzba@chem.uni.wroc.pl, tel. +48 71 3757379

Keywords: authentication; painting analysis; machine learning; data mining

Detection of forgery in paintings can be an extremely challenging task. Usually, an art expert has to analyze many different types of evidence before reaching a conclusion on the authenticity of a given painting. It may include: (1) technical analyses of the pigments and other materials used and methods of their preparation, (2) studies of the process of painting's creation observed for instance through X-ray and infrared imaging, (3) analysis of visual aspects and the style of the work, as well as (4) tracing of all documents that may be related to the painting (e.g. artist's correspondence, confirmations of ownership). As a consequence, the expert may be overwhelmed with a huge amount of formless data from different sources, which have to be combined to yield a result.

In Ref. [1] a list of authenticity/attribution markers has been proposed as an attempt to simplify and speed up the process of data analysis and decision making by an art expert. In this talk we will go one step further and use machine learning techniques (in particular decision trees) to build a prototype of a scoring system, which will automatically classify the paintings according to the list of attribution markers and in this way support the decision making process. Machine learning explores the construction and study of algorithms that can learn from data and make predictions on it. Decision trees are an example of such an algorithm often used in data analysis for classification purposes. A decision tree is a flowchart-like structure in which each internal node stands for a test on an attribute (e.g. historical pigments), each branch represents the outcome of the test (e.g. »yes« or »no«) and each leaf node represents a decision taken after testing all attributes (e.g. »original« or »fake«). The paths from root of the tree to the leaf nodes correspond to classification rules. The resulting classification tree may be used as an input for decision making. Similar scoring systems are already used with success in banking, business intelligence and fraud detection.

The system will be tested on selected artwork by Gianfrancesco Penni, Jacopo Tintoretto, Michael Leopold Willmann Jeremias J. Knechtel and Artur Grottger and selected artworks from the collection of National Museum in Krakow.


²nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
Optimizing the FISH protocol for analyzing Cultural Heritage microcolonizers: microwave fixation

M. González-Pérez 1, Ricardo Veira2, António Pereira1,2 António Candeias1,2, Ana Teresa Caldeira1,2*

1 Évora University, HERCULES Laboratory, Largo Marquês de Marialva 8, 7000-809, Évora (Portugal), +351 266 740 800, atc@uevora.pt
2 Évora University, Chemistry Department, School of Sciences and Technology, Rua Romão Ramalho 59 7000–671, Évora (Portugal)

* atc@uevora.pt, +351 266 740 800

Keywords: Fluorescence In Situ Hybridization; RNA-FISH; Biodeterioration; Biodegradation; Cultural Heritage Microbiology; Phylogenetic staining;

Microbial communities are key players in the decay of Cultural Heritage (CH) assets.[1] However, until recently, their crucial action in this process has been underestimated and the majority of their components have remained unknown.[2] Despite substantial progress in the last decades, more advances are needed to facilitate the characterization of these microorganisms and understanding of their role in the deterioration process.[1,2] The development and adaptation of biotechnological tools to investigate this process will contribute to simplify the intricate endeavor of identifying the concrete needs for prevention, control and mitigation of microbial colonization.[1,2] These tools should: i) be versatile for its application according to the sampling possibilities of CH materials (ex situ or in situ, micro-invasively or non-invasively); and ii) provide information about the extension, depth, identity and viability of the colonizing microorganisms. Fluorescence In Situ Hybridization targeting ribonucleic acid molecules (RNA-FISH), has been shown to be a potent technique that, in addition to meet all these requirements, is simple, rapid, low-cost and even accessible for non-specialist.[3,4] Nevertheless, its use in CH field has not been widely exploited. Thus, our research efforts are focused on adapting and optimizing RNA-FISH procedures for analyzing the microbial colonizers of CH objects.

Previous research of our group has resulted in the development of a FISH protocol that has been successfully applied for ex situ analysis of fungi and bacteria, and in situ analysis of fungi thriving in mortars.[5,6,7] However, more efforts are needed in order to shorten the protocol and enhance the signals obtained. Using microwave irradiation for fixation could be an alternative to improve the protocol since i) cell fixation has a remarkable influence on the quality of FISH results;[4] ii) fixation with microwaves has been proven to be a suitable procedure for microbial cells and immunocytochemical samples preserving their morphology;[8] iii) microwave pre-treatment enhances the effectiveness FISH results in immunohistochemistry analysis[8] and of staining of fungal conidia with fluorescent dyes.[9] Thus, the aim of this work was to investigate the possibility of optimizing the protocol previously developed by us, that involved
fixation of the cells using chemical fixatives taking 40 to 90 min, using microwave-assisted fixation.

In this way, the efficiencies of the FISH protocol using various fixation procedures were compared in terms of the fluorescent intensity per cell and of the percentage of cells that became fluorescent after hybridization. The fixation procedures were: i) absolute ethanol for 60 min (EtOH), as in the original protocol; ii) microwaves for 30 s (MW); iii) absolute ethanol for 60 min and microwaves for 30 s (EtOH+MW); iii) absolute ethanol for 60 min and, after that, simultaneous treatment of microwaves and ethanol for 30 s (EtOH+MW/EtOH); iv) simultaneous treatment of microwaves and ethanol for 30 s (MW/EtOH). *Saccharomyces cerevisiae* CCM1 396 cells in exponential phase were used, as it has also been done for developing the original FISH protocol. For hybridization, 10^6 fixed cells were incubated in hybridization buffer containing EUK516-Cy3 probe. Each fixation procedure was tested carrying out triplicates which were each analyzed three times by flow cytometry.

Stained cells with high fluorescent intensities were obtained by using each of the fixation procedures tested. Although, the average fluorescent intensities obtained have found to decrease in the order: MW > EtOH > MW/EtOH> EtOH+MW> EtOH+MW/EtOH. However, in terms of yield of stained cells, the trend observed was the following: EtOH+MW/EtOH > EtOH+MW > EtOH > MW; MW/EtOH. Whereas independently of the fixative employed, high yields of fluorescent cells were obtained (30 to 60%), great variations are observed by using the different fixation procedures. It is noteworthy that with the fixation method that yields lowest percentage of stained cells, MW, the highest fluorescence intensities has been observed. The opposite is true for EtOH+MW/EtOH fixation. Thus, in view of the results obtained with *S. cerevisiae*, it can be concluded that microwave fixation enhances the FISH signals, reducing the fixation time from 40-90 min to 30 s and avoiding the addition of chemicals which would alter the macromolecules in the cells and the distribution of the microorganisms for *in situ* analysis. Whereas more research is required, these promising findings point out the possibility of applying microwave fixation to enhance the protocol for analyzing microorganisms colonizing CH and encourage the development of a practical kit for *in situ* analysis at point-of-care.

This work has been supported by FCT through SFRH/BPD/100754/2014 fellowship and by FEDER funds through INALENTEJO program, IMAGOS/APOLLO project (ALENT-07-0224-FEDER-001760).

References:
Innovative diagnostic models of artefacts: the case study of Michelangelo’s Pietà Rondanini

Cristiana Achille1, Lucia Toniolo2*, Gianluca Valentini3, Valentina Capogrosso3, Francesco Fassi1, Sara Goidanich2, Davide Gulotta2, Alessandro Mandelli1, Sara Mosca3, Austin Nevin4

1 Politecnico di Milano, Department ABC, Piazza Leonardo da Vinci 32, 20133 Milan (Italy).
2 Politecnico di Milano, Department CMIC, Piazza Leonardo da Vinci 32, 20133 Milan (Italy). +390223993042, lucia.toniolo@polimi.it (*corresponding author)
3 Politecnico di Milano, Department FIS, Piazza Leonardo da Vinci 32, 20133 Milan (Italy).
4 CNR-IFN, Piazza Leonardo da Vinci 32, 20133 Milan (Italy).

Keywords: reflectance spectrophotometry; colour measurements; multispectral imaging; real based model; photogrammetry; web sharing.

In order to make an exhaustive survey of the Michelangelo’s sculpture before its displacement in the new exposition room - the restored “ex Ospedale degli Spagnoli” - at Castello Sforzesco in Milan, a complete relief of the Pietà Rondanini was carried out to test and define innovative techniques of multi-digitalizing for the documentation and enhancement of Cultural Heritage. The goal of the survey is the creation of three-dimensional models of the Pietà in scale 1:1 aimed at geo-referencing the diagnostic and at monitoring the activities and results.

The sculpture surface was monitored since 2002, before and after the cleaning operations carried out by Dr. S. Vedovello (CBC Coop., Rome, Italy) in 2003-04 [1]; the evolution of the colour parameters over time was studied together with the state of conservation of the marble substrate in the years 2004-2015. Specific pilot areas were selected to monitor the different soiling phenomena, according to the finishing and orientation of the marble surface, by means of VIS spectrophotometry and digital microscopy. Multispectral Imaging of some of the pilot areas was carried out to assess the conservation state of the most critical parts affected by formation of patina and colour alteration. Some patinas were also monitored by Raman portable spectroscopy.

The 3D models were generated from the data of photogrammetric survey (images) and data acquired by structured light scanner1 (range image). In a previous phase, some survey tests were performed both with photogrammetric approach and with a structured light scanner [2]. The objects of the survey tests were hand-made artifacts of different dimensions: from smaller ones, such as single body parts of statues, to whole sculptures. The aim was the definition of digitalization models, survey parameters, sensors, acquisition geometries and calibrations considering the characteristics of the objects and the surrounding environments. In fact, the results are mostly influenced by the texture of the artifacts, the dimension, the lighting conditions and the available time. The outcomes of the tests give some precise indications regarding the strategies to adopt in order to obtain digital models at 1:1 rendering scale. The

1The instruments are produced by Open Technologies, Rezzato Brescia, Italy
obtained results suggested how to proceed to survey the whole statue applying the consolidated pipeline and the same working method in order to produce a high-detailed, accurate and complex 3D model of Pietà Rondanini. The models achieved through photogrammetric and scanner approaches were compared in order to validate the workflow and the results. The alignment of the models was possible thanks to some well-distributed targets on the surface of the sculpture. The scale of the photogrammetric model was acquired putting into the scene three different calibrated bars with a precision of hundredth of a millimeter. The circle, non-coded targets were automatically recognized both by the software of the scanner and by the photogrammetric one. The coordinates of the centers were sampled autonomously from the range-images model that was used as reference.

The obtained 1:1 scale model, integrated by the diagnostic and monitoring data, can be considered an effective and user-friendly tool for the activities of the different professionals involved in conservation and valorization: art historians, conservators and experts. Consultation via web (http://pietarondanini.-bim3dsurvey.it) certainly contributes to spread the information and simplify the access to a complex of data which generally cannot be easily consulted by the scientific and public community.

Acknowledgements The Authors wish to thank the Project “Smart Culture” financed by Regione Lombardia, Italy, within the framework of the FESR-POR Competitività 2007-13.

References

Workflow for the implementation of the diagnostic model of the Pietà Rondanini
Radiocarbon dating of 20th century works of art

Ferruccio Petrucci1,2,3,*
Lucia Caforio1,4
Maria Elena Fedi1,4
Pier Andrea Mandò1,5
Eva Peccenini6
Virginia Pellicori1
Peter Rylands7
Paul Schwartzbaum8
Francesco Taccetti4

1 University of Ferrara, Department of Physics and Earth Science, Via Saragat 1, 44122 Ferrara (Italy)
2 NFN - Sezione di Ferrara, Via Saragat 1, 44122 Ferrara (Italy)
3 TekneHub Ferrara, via Saragat 13, 44122 Ferrara (Italy)
4 INFN, Sezione di Firenze, Via G. Sansone 1, 50019 Sesto Fiorentino FI (Italy)
5 Dipartimento di Fisica e Astronomia, Università di Firenze, Via G. Sansone, 1, 50019 Sesto Fiorentino FI, (Italy)
6 Dipartimento di Fisica Università and INFN, Viale Berti Pichat 6/2 40127 Bologna (Italy) and Centro Fermi, Piazza del Viminale, 00184 Roma (Italy)
7 Peggy Guggenheim Collection, Dorsoduro, 701-704, 30123 Venezia (Italy)
8 Solomon R. Guggenheim Foundation, 1071 5th Ave, New York, NY 10128, (USA)

* petrucci@fe.infn.it, +39 0532 974264, fax +39 0532 974343

Keywords: Radiocarbon dating; modern art; canvas; paper; Fernand Léger.

Recalling the principle of the radiocarbon method, the accurate determination of the radioactive isotope $^{14}C$ in an organic sample is the basis for its dating. Any animal or plant maintains, during its life, a $^{14}C$ concentration in equilibrium with that of the biosphere and since its death this concentration decays with the half life of the isotope. The comparison of the measured $^{14}C$ content of the sample and the atmosphere concentration gives the input for the age determination.

In the most recent times the atmospheric tests of nuclear weapons caused a sudden increase of the radiocarbon concentration in atmosphere since 1955, reaching its maximum value in 1963-1965. Stopped the nuclear tests in atmosphere, the $^{14}C$ concentration started to decrease. This behaviour of the radiocarbon concentration is called “Bomb Peak” and it has successfully been used as a tool for dating recent finds, in forensic sciences and biology. In the art field the possibility of dating canvas and paper, widely used as support for paintings, may be an invaluable tool in modern art studies.

The scientific study of a painting attributed to F.Léger, whose origin was questioned by some art historians, was asked by the Peggy Guggenheim Collection (PGC) in Venice and led to the radiocarbon dating of the canvas. The response of the radiocarbon measurement, performed by AMS at the LABeC laboratory in Florence, was conclusive: the high level of detected radioactivity was inconsistent with the life of the artist himself, who died in 1955. The cotton of the canvas, indeed, was alive not before 1959. For the first time the falsity of a painting has been demonstrated, dating a fragment of canvas taken from the backside of the work [1].

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
A first systematic test on canvases taken from dated paintings of the second half of 20th century (Tab.1) was performed at the LABeC. The results were fully compatible with the dates marked on the work itself. The accuracy of 2-3 years, at 67% confidence level, may be useful both for studies on the artist chronology and for authentication purposes. Fragments may be taken from not-painted parts of the artwork and the sensitivity of the AMS method allows small samples at the level of milligrams.

Particular care has to be devoted to the possible contamination of natural fibers by synthetic additives and fibers, poor in radiocarbon content and so liable to distort the dating. Tests on fine paper for artists have been done as well, with good results. In this case too, a possible different preparation of samples may be needed, to prevent contamination by low radiocarbon sources.

<table>
<thead>
<tr>
<th>Canvas sample code</th>
<th>Year on painting</th>
<th>14C conc. (pMC)</th>
<th>Calibrated age(*) (AD)</th>
<th>Paper sample code</th>
<th>Printing year</th>
<th>14C conc. (pMC)</th>
<th>Calibrated age(*) (AD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Can1962</td>
<td>1962</td>
<td>109.19 ± 0.76</td>
<td>1956-1957</td>
<td>Carma60</td>
<td>1960</td>
<td>102.80 ± 0.63</td>
<td>1954-1956</td>
</tr>
<tr>
<td>Can1965</td>
<td>1965</td>
<td>167.55 ± 2.18</td>
<td>1965-1966</td>
<td>Abe61</td>
<td>1961</td>
<td>111.75 ± 0.79</td>
<td>1957-1958</td>
</tr>
<tr>
<td>Can1966B</td>
<td>1966</td>
<td>109.09 ± 0.38</td>
<td>1956-1957</td>
<td>Far63</td>
<td>1963</td>
<td>111.45 ± 0.68</td>
<td>1957</td>
</tr>
<tr>
<td>Can1966N</td>
<td>1966</td>
<td>171.1 ± 1.09</td>
<td>1965-1966</td>
<td>Seve65</td>
<td>1965</td>
<td>117.41 ± 0.82</td>
<td>1958-1959</td>
</tr>
<tr>
<td>Can1971A</td>
<td>1971</td>
<td>172.98 ± 0.55</td>
<td>1965-1966</td>
<td>Cobra68</td>
<td>1968</td>
<td>147.66 ± 0.80</td>
<td>1962-1963</td>
</tr>
<tr>
<td>Can1971C</td>
<td>1971</td>
<td>121.83 ± 0.80</td>
<td>1959-1962</td>
<td>Mac70</td>
<td>1970</td>
<td>101.60 ± 0.59</td>
<td>1953-1956</td>
</tr>
<tr>
<td>Can1980</td>
<td>1980</td>
<td>112.76 ± 0.64</td>
<td>1957-1958</td>
<td>Moore71</td>
<td>1971</td>
<td>137.29 ± 0.98</td>
<td>1962</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Candi76</td>
<td>1976</td>
<td>131.69 ± 0.36</td>
<td>1962</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Papa80</td>
<td>1980</td>
<td>132.01 ± 0.63</td>
<td>1961-1962</td>
</tr>
</tbody>
</table>

Data of canvas samples of the bomb peak period: the year on painting, the measured radiocarbon concentrations and the corresponding calibrated age are reported.

Data of cardboard samples of the bomb peak period: the printing year, the measured radiocarbon concentration and the corresponding calibrated age are reported.

(*) Calibrated time intervals are quoted at 68% level of probability.

<table>
<thead>
<tr>
<th>References:</th>
</tr>
</thead>
</table>
Optically stimulated luminescence dating of rock surfaces

Reza Sohbati1*, Andrew Murray2, Mayank Jain1, Trine Freiesleben2, Sahar al Khasawneh2,3

1 Center for Nuclear Technologies, Technical University of Denmark, DTU Risø Campus, Roskilde 4000, Denmark
2 Nordic Laboratory for Luminescence Dating, Department of Geoscience, Aarhus University, DTU Risø Campus, Roskilde 4000, Denmark
3 Institute für Vorderasiatische Archäologie, Freieuniversität, Berlin, Germany

*Corresponding author: resih@dtu.dk

Keywords: Optically stimulated luminescence; rock-surface dating; quartz; feldspar; archaeology

Optically stimulated luminescence (OSL) dating is a well-established method of absolute chronology that has been successfully applied to a wide range of fine-grained sediments to provide depositional ages from a few years to several tens of thousands and even several hundred thousand years. In recent years, the direct application of OSL dating to rock surfaces has attracted considerable interest. In archaeology, there are many examples of rock surfaces, rock art, and stone structures whose chronology is of great importance to understanding the way in which people have used the landscape. We have recently developed a new technique of optically stimulated luminescence (OSL) dating that is directly applicable to rock surfaces. Here, we demonstrate the application of this new technique to rock samples from four different archaeological sites of different ages around the world: 1) a Rodedian prehistoric shrine from Israel, 2) a Barrier Canyon Style rock art from Utah, USA, 3) a whetstone from an Iron Age village in Denmark and 4) a desert kite in Jordan. The advantage of the new OSL rock surface dating technique to that of the conventional OSL sediment burial dating is that rocks can retain a record of their depositional history in their OSL-depth profiles. This allows us to recover multiple burial/exposure events in the history of our samples and, in two cases, estimate the duration of these events using known-age profiles.
Chemical imaging of heritage metal surfaces with X-ray-excited optical microscopy.

Pieter-Jan Sabbe\textsuperscript{1}, Mark Dowsett\textsuperscript{2}, Matt Hand\textsuperscript{2}, Mark Jones\textsuperscript{3} and Annemie Adriaens\textsuperscript{1}

\textsuperscript{1} Ghent University, Department of Analytical Chemistry, Krijgslaan 281 S12, 9000 Ghent (Belgium), Tel.: +3292644828, pieterjan.sabbe@ugent.be

\textsuperscript{2} University of Warwick, Department of Physics, Gibbert Hill Rd. Coventry CV4 7AL (United Kingdom)

\textsuperscript{3} The Mary Rose museum, Main Rd. Portsmouth PO1 3PY (United Kingdom)

* pieterjan.sabbe@ugent.be, Tel. +3292644828

Keywords: Patina Mapping; X-Ray-Excited Optical Microscopy (XEOM), XEOL-XANES, Metal Corrosion, The Mary Rose

Heritage tourism represents a significant source of income for the European Union [1]. The metallic heritage is vital to this, but corrodes and degrades over time unless it is conserved and protected. Such measures need to be informed by a detailed knowledge of the chemistry of conserved and unconserved surfaces. This requires specific techniques and instrumentation which should be preferably non-destructive and non-invasive. Traditional radiation-based mapping systems (XRF, XAS) require a scanning microprobe to build up a chemical map with micrometer resolution. Notwithstanding the efficiency of these techniques, it was shown that the power density of the microprobe beam needed for image acquisition of a large area on a reasonable time-scale is high enough to damage the patina of the artifact and modify its surface chemistry [2].

XEOM\textsuperscript{1} (Fig. 1A), a novel X-ray excited optical microscopy system, is presented as an alternative tool for non-destructive chemical imaging of heritage metal surfaces in air and controlled atmosphere. In contrast to scanning a sample with an X-ray microprobe, imaging is done by simultaneously illuminating a few square millimeters of the sample with a large monochromated X-ray beam. This way, the power density of the X-ray beam can be kept about 4 orders of magnitude lower than a micro-sized X-ray beam, thus conserving the patina and its surface chemistry.

XEOM exploits the effect in which X-ray absorption results in the emission of electromagnetic radiation in the visible and near-visible bands, a phenomenon known as X-ray-excited optical luminescence (XEOL). Where the intensity of XEOL is modulated by the photoelectron escape probability as modified through scattering with neighboring atoms, it can also carry information on X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS)[3]. The resulting spectroscopy: XEOL-XAS allows, similarly to conventional XAS, one to obtain information regarding the chemical state and short-range atomic order from both crystalline and amorphous materials. Moreover, due to the shallow escape depth of the optical photons in non-transparent materials, the collected data is representative of the surface top 200 nm of the sample under investigation. Hence XEOL-XANES is well suited for heritage metal corrosion analysis and yields information complementary to X-ray diffraction, and conventional XAS, but with higher surface specificity.
XEOM 1 typically captures a series of images with a CCD-camera at various points across the absorption edge of the targeted element. XEOL-XANES spectra holding the desired information can subsequently be extracted out of the entire image or a user-defined regions of interest (RoI) in the image ‘stack’ by our custom imaging software (esaProject 2015). During a final stage, features characteristic for certain aspects of the surface chemistry such as edge-shift (oxidation state) and edge-height (elemental concentration) can be extracted out of the yielded XEOL-XANES spectra and processed into a color-coded chemical maps (Fig.1B).

The ground work for the imaging of copper and copper corrosion products typically observed on copper and bronze heritage artifacts (cuprite Cu2O, nantokite CuCl, atacamite/paratacamite Cu2Cl(OH)3) was established during a preliminary study by imaging copper assessment samples exhibiting well-defined areas of varying patination [4,5]. Along with copper, initial studies were performed on other heritage metal corrosion products such as those on tin, silver and lead. These prove to yield informative XEOL spectra, and are thus suitable for further study with XEOM 1. A preliminary study has commenced on 11 artefacts recovered from the wreck of King Henry VIII’s flagship the Mary Rose after being immersed in the Solent for 437 years. An oxidation state map of the surface of a brass chain mail link could be extracted revealing the presence of cuprite (Cu2O) and tenorite (CuO)[6]. (Fig.1C)

![Fig.1 A) Cross section of XEOM 1 microscope B) oxidation state map of copper/cuprite test sample C) Surface map of bronze chain mail link retrieved of King Henry VII’s flagship : ‘The Mary Rose’](image)

References
The X-ray and infrared micro-spectroscopy beamline ID21: applications to 19th-20th C. artistic materials

Marine Cotte1,2*, Emeline Pouyet1,7, Murielle Salomé1, Wout De Nolf1, H. Castillo-Michel1, D. Bugnazet1, Camille Rivard1, B. Hesse1, Letizia Monico3,4, Koen Janssens4, Louisiane Verger5,6, Laurent Cormier5, Olivier Dargaud6, Jennifer Mass8, Juliette Langlois9, Nathalie Balcar9

1 European Synchrotron Radiation Facility, 71 avenue des martyrs 38000 Grenoble, (France), +33476882127, cotte@esrf.fr
2 Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d’archéologie moléculaire et structurale (LAMS), 4 place Jussieu 75005 Paris (France).
3 CNR-ISTM and SMAArt Centre, c/o Department of Chemistry, Biology and Biotechnologies, University of Perugia, via Elce di Sotto 8, 06123 Perugia (Italy).
4 University of Antwerp, Department of Chemistry, AXES Research group, Groenenborgerlaan 171, B-2020 Antwerp (Belgium).
5 Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Universités, UPMC Univ Paris 06, CNRS UMR 7590, Museum National d’Histoire Naturelle, IRD UMR 206, 4 place Jussieu, 75005 Paris (France)
6 Cité de la Céramique - Sèvres et Limoges, 2 place de la Manufacture, 92310 Sèvres (France)
7 ARC-Nucléart - CEA/Grenoble, 17 rue des Martyrs, 38054 GRENOBLE Cedex 9, (France).
8 Scientific Research and Analysis Laboratory, Conservation Department, Winterthur Museum, Winterthur, DE 19735 (USA).
9 Centre de Recherche et de Restauration des Musées de France (C2RMF), Palais du Louvre, Quai François Mitterrand 14, 75001 Paris (France).

Keywords: synchrotron; µXRF; µXANES; µFTIR, µXRD

Over the last 10 years, the ID21 beamline at the European Synchrotron Radiation Facility has welcomed many experiments focusing on the study of ancient and artistic materials. Projects from this community represent about 25% of the beamtime. This high interest can be explained by the very good agreement between the technical requirements associated with the study of artistic materials (complexity and heterogeneity at the micron scale) and the instrumental capabilities offered at the beamline. The beamline hosts four complementary end-stations:

1- a scanning X-ray microscope operates in the tender X-ray domain (2-9keV), under vacuum (and in cryo conditions, if needed). It offers 2D micro X-ray fluorescence (µXRF) for elemental mapping, and micro X-ray absorption near-edge structure (µXANES) spectroscopy for local speciation analysis. Beam can be focused down to ~0.3µm(ver.)x0.7µm(hor.). The energy range gives access to the K-edge of elements from P to Cu. In particular, it covers the 3d transition metals, which have fundamental roles in the color of many artistic materials (pigments, glasses, ceramics) and can be found in metallic alloys as well. Moreover, it covers the 2-3keV range, i.e. the K-edge of P, Cl, and more particularly S, involved in degradation phenomena affecting various pigments (e.g. in various metallic sulphide pigments, such as HgS (red), CdS (yellow),
As$_2$S$_3$ (yellow), and in lapis lazuli (blue). The chemical modification of these compounds (for sulphides pigments, quite often through an oxidation into sulphates, or substitution by other environmental anions such as chlorides or oxalates; photo-reduction in the case of lead chromates) ends into a dramatic modification of the colour. μXANES analyses of both well-preserved and altered pigments from historical and artificially aged paintings aim at identifying i) the original pigments’ composition and potentially the manufacturing recipes and ii) the environmental parameters (light, pollutants, humidity, temperature, etc.) which can influence these degradation processes.

2- a full-field XANES instrument, also operating under vacuum, and in the same energy range, offers a similar spectroscopic characterization, but in imaging mode. Providing that absorption can be measured in transmission, full 2D speciation maps can be obtained, with micrometric resolution (Pixel size ranging from 0.3 μm to 1.4 μm), over millimetric field of view.

3- a second scanning X-ray microscope operates in air, at fixed energy (8.5keV), in both pink ($\Delta E/E=10^{-2}$) and monochromatic ($\Delta E/E=10^{-4}$) modes and offers a combined micro X-ray diffraction / μXRF 2D mapping capabilities. The beam can be focused down to ~0.7μm(vert.)x1.7μm(hor.). This end-station offers more precise identification of crystallized phases.

4. Finally, a scanning Fourier Transform Infrared (FTIR) microscope provides molecular identification and 2D mapping, with a beam size of 5-10μm. This instrument is particularly useful to study organic materials.

Here, we will illustrate the multi-capabilities offered by ID21 for Cultural Heritage through different recent studies combining the capabilities of one or several instruments listed above. Recent instrumental developments and new strategies for sample preparation will be presented as well [1]. In particular, we will focus on the study of artistic materials introduced in the 19$^{th}$ and 20$^{th}$ century: chromium spinels used in porcelains from Manufacture of Sèvres [2]; employ and degradation of lead chromates in Impressionist/Post-Impressionist paintings, in particular those by Van Gogh [3]; degradation of cadmium yellow pigments in Matisse’s paintings [4] and use and degradation of modelling materials in sculptures by Auguste Rodin [5].

References:
The stratified structure of ancient paintings in Forbidden City studied by Synchrotron radiation micro X-ray methods

Xiangjun Wei¹, Yong Lei², Lihua Wang¹, Yuying Huang¹

¹ Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 239 Zhang Heng Road, Pudong New District, 201204 Shanghai (China), Tel.86-21-33933212, weixj@sinap.ac.cn
² The Palace Museum, 4 Jingshan Qianjie,100009 Beijing (China)

* weixj@sinap.ac.cn, phone 86-21-33933212/fax 86-21-33933212

Keywords: Doucai; Wallpaper; micro XRF; Confocal micro X-ray

Painting structures of different ancient samples were studied by synchrotron radiation confocal micro-X-ray and linear scanning micro-XRF separately. Two samples are from Qianlong Garden in Forbidden City, including the Doucai porcelain in Yanqu Lou (Building of Extended Delight) and the wallpaper in Yang He Jing She. Confocal micro-X-ray method, with the depth resolution about 30–60 micrometer, is proved to be a nondestructive tools for directly 3D elemental analysis. Linear scanning micro-XRF also can provide stratified information of the painting layers through the analysis of elemental distribution features along the scanning direction. If the thickness of each painting layer is about several tens of micrometers to hundreds of micrometers, confocal micro-X-ray is more suitable for probing its stratified structure. And if each painting layer is thinner than several tens of micrometers, linear scanning micro-XRF is more effective. Furthermore, confocal micro-XAFS could be easily realized at synchrotron radiation facility just by energy scanning near the absorption edge of an element, thus their chemical information will be obtained. Taking advantage of confocal micro-X-ray and linear scanning micro-XRF, a lot of paintings can be analyzed effectively.
Poster session 1
Characterization of compounds present in lake and textile, through ammonia mild extraction technique and micro-sampling with Ag-gel matrix associated with SERS analysis

Livia Lombardi1,2, Ilaria Serafini 1,2, Claudia Fasolato 3, Paolo Postorino 3, Fabio Sciubba1, Marcella Guiso 1, Armandodoriano Bianco 1

Università di Roma “La Sapienza”, Dipartimento di Chimica1 (06/49913622, livia.lombardi@uniroma1.it), Dipartimento di Scienze della Terra2, Dipartimento di Fisica3, Piazzale A. Moro 5, 00185, Rome (Italy).

* livia.lombardi@uniroma1.it, 06/49913622

Keywords: natural dyes; lakes; textiles; mild extraction technique; SERS; micro-sampling; SERS active substrate; HPTLC-SERS

Until the introduction of synthetic dyes in the XIX century, artworks were realized using lakes and textiles prepared from natural raw materials. The precipitation of lake pigments and the dyeing process generally occurs due to the formation of a complex with different cations. The complexes thus obtained are particularly stable and insoluble in water or common organic solvents. So, to perform the analysis, it is necessary to break the complex and then extract the compounds.

The method most commonly used until now had been a mixture of organic solvent with strong acid as HCl or H2SO4[1]. This method ensured high yield of extraction producing, however, hydrolysis of glycosidic compounds in the sample and allowing only the identification of the main aglycones. Our new extraction method[2], based on the use of ammonia in association with sodium EDTA, was developed to preserve the glycosidic compounds present and then get closer to the real molecule pattern involved in lake precipitation and dyeing process. This is very important to understand the chemical nature of the compounds and then adequately respond, for example, to questions regarding the proper storage conditions, the dating or the provenance of an artwork.

In order to indentify the compounds presents in the ammonia extract of lakes and textiles, in the first step of the research, samples of lakes and wool dyed with different type of natural dyes (such as different species of Rubiaceae, Reseda luteola, American cochineal, Armenian cochineal) were prepared, following the recipes contained in ancient and medieval treatises [3,4]. Then, chromatographic separation of ammonia extracts were performed and the fractions obtained were analyzed using NMR, ESI-MS, to identify the isolated compounds, and HPTLC-SERS (Surface Enhanced Raman Spectroscopy) was performed.
The choice to perform this particular type of investigation is related to the fact that in real cases it is very important to apply techniques that allow a rapid, minimally invasive and highly sensitive identification of natural organic dyes and micro-invasive SERS techniques present these characteristics.

In particular, attention has focused on the use of solid matrices and, among those subject of the most recent publications, was particularly interesting the Ag-Agar matrix \(^5\), for the extraction of dyes from textiles and their subsequent identification by SERS. Basing on the experience gained and the problems found in the use of the Ag-agar matrix we developed a new analytical protocol \(^6\), applying for the first time an Ag-gel matrix to painted surface. We introduced a new type of gel which, due to its transparency, the lower gelling temperature and the greater rigidity is better compared to the Agar and, in addition, a specific KIT \(^6\) was designed, which contains devices especially designed and everything necessary for the execution of the protocol and aimed to make it simple, rapid and reproducible.

The results of micro-sampling tests allow us to affirm that the average size of the micro-samples taken from painted surface with the technique developed are much lower than a millimeter (~20 μm). Moreover, from the video-colorimetric investigations conducted, it is clear that there is no visible change in the optical properties after the micro-sampling.

To interpret the SERS spectra of micro-samples of lake and textile extract on our Ag-gel matrix, we use as reference the spectra obtained from fraction analysed by HPTLC-SERS. Comparing the SERS reference spectra of the isolated compounds and SERS spectra obtained from micro-samples, withdrawn using the Ag-gel matrix, we identified useful signals to discriminate the presence or absence of glycosylated compounds or particular molecules \(^7\). This allows to speculate about the process of preparation or the provenance of lakes or textiles.

References
\(^3\) M. P. Merrifield, *Original Treatises, Dating from the XIIth to the XVIIIth Centuries, on the Arts of Painting*, John Murray, London, 1849.
\(^6\) L. Lombardi, M. Guiso, A. Bianco, Protocol and Kit for the micro-invasive sampling from manufs, 2015, patent n° 102015000042409
A copy of the icon as a non-invasive test technical and technological formation of the original

Prof. Danuta Stępień, Mariola Pachnia MA, Cathy Carman

1 Academy of Fine Art in Warsaw, Conservation and Restoration of Fine Art, ul. Krakowskie Przedmieście 5, 00-068 Warszawa (Poland), tel.: 0048 799158513 (Mariola Pachnia), e-mail address: pachniam@wp.pl (Mariola Pachnia).

Keywords: icon; copy; technological process; religious art

We would like to present a technological process of Yolk tempera as a technique in painting icons, according to old messages and works of selected artists by Danuta Stępień and Mariola Pachnia; Academy of Fine Arts in Warsaw. Department of Conservation and Restoration of Works of Art.

By using this traditional technique of Yolk tempera some copies were made under the guidance of prof. Danuta Stępień in order to preserve this technique and the old recipes which were implemented.

References:
Spectroscopic study on accelerated ageing of materials used in contemporary art

Alessandro Ciccola1, Marcella Guiso1, Claudia Fasolato2, Fabio Sciubba1, Paolo Postorino2 and Armandodoriano Bianco1

1 Dipartimento di Chimica
2 Dipartimento di Fisica
Università di Roma “La Sapienza”, piazzale Aldo Moro 5, 00185, Roma (Italy)

* alessandro.ciccola@uniroma1.it, +39 06 4991 3229

Keywords: contemporary art; synthetic pigments; accelerated ageing; UV–Vis spectroscopy; NMR.

Pictorial films in contemporary art represent a challenge for conservation, from many points of view. First of all, contemporary artists often use fairly new materials (from XIX and XX centuries) that derive from industrial productions and whose stability is not ensured. Furthermore, in artworks, pigments and binders are combined with other materials that do not belong to traditional chemical classes used in the artistic field. In addition, especially with regards to street art, the artworks can be exposed in untypical conditions and subjected to aggressive environmental agents.

The aim of this study, part of a PhD project, is the characterization of pictorial films in synthetic organic pigments and acrylic binder, typical of 20th century, in terms of stability and degradation products through accelerated ageing. For this reason, different accelerated ageing processes are used to consider influence of multiple factors – UV radiation, solar light, thermic stress- in monitoring of temperature and Relative Humidity.

The characterization of ageing is based on several spectroscopic techniques. Colorimetry and reflectance spectroscopy are used to monitor chromatic variations that can be indicative of chemical or structural changes in pictorial films, while UV-visible molecular spectroscopy can result useful to explain chromophores variations. Structural determinations of degradation products are based on 1D- and 2D-NMR techniques[1,2], that can even provide interesting information about pigment-binder interaction as accelerated ageing is proceeding. Other techniques commonly used in cultural heritage diagnostics – such as FTIR and Raman spectroscopies[3,4]- are used to confirm hypotheses on degradation processes.

References:
An XRF study of a Late Bronze Age bronze fibula from Sardinia (Italy)

Antonio Brunetti1, Anna Depalmas2, Claudio Bulla2, Alba Canu3, Nick Schiavon4*,

1 Dipartimento Polcoming, Università di Sassari, Italia.
2 Dipartimento di Storia, Scienze dell’uomo e della Formazione, Università di Sassari, Italia.
3 Centro di Restauro della Soprintendenza per i Beni Archeologici, Sassari, Cagliari, Italy
4 Hercules Laboratory for the Study and Conservation of Cultural Heritage, University of Évora – Portugal.

* schiavon@uevora.pt, ++351 939007452

Keywords: XRF; Montecarlo Simulation; Late Bronze Age;

An unique fibula of late bronze age has been recently discovered at the famous Nuragic sanctuary archaeological site of Abini-Teti, near the town of Nuoro in the island of Sardinia, Italy. From a manufacturing point of view, the artifact shows affinities with objects typically being produced in the same period in Northern regions of Italy: its origin has therefore not been determined so far with certainty. It could represent an imported object or a rare example of local production of this typology of artifact. In order to obtain this information, in this study Non Destructive (ND) XRF measurements combined with Monte Carlo simulation study have been performed. Analyses were carried out in two phases before and after restoration in order to help the work of restorers and at the same time confirm previous studies [1-3 testing the performance of the combined analytical approach XRF/Monte Carlo simulations as an useful tool in the ND examination of patina-covered bronze precious archaeological specimens. The results obtained are reported and discussed.

References:
Imaging and X-ray spectroscopic techniques used in a Portuguese organ pipe

Joana Fanico¹*, Agnès Le Gac¹², Sónia Costa³, José Mirão³, António Candeias³

¹ Departamento de Conservação e Restauro (DCR), Faculdade de Ciências e Tecnologia (FCT), Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
² Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação (LIBPhys), FCT, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
³ Laboratório Hércules, Centro de Química de Évora, Universidade de Évora, 7000-809 Évora, Portugal

* email of corresponding author: j.fanico@campus.fct.unl.pt, phone: +351 915058699

Keywords: Organ Pipe; Digital Photography; Portable Digital Radiography; Optical Microscopy; SEM imaging; SEM-EDS; µ-XRD.

Located in the Mosteiro de São Martinho in Tibães, Portugal (the mother house for the Benedictine community of Portugal and Brasil), the large Portuguese organ pipe by the organ maker D. Francisco Solha, dated 1785, is assumed as one of the most prestigious instrument of this period, with its characteristic horizontal trumpets [1]. From an aesthetic point of view, the organ pipes finishes studied in Portugal are quite scarce. This one reflects especially well the spirit of the Rococo style through the richness of the polychrome coating and gilding, based on the very particular techniques of decoration with marble-like effects.

Regarding its architectural structure, this large organ pipe is composed of three main elements: a highly decorative case with ornate carvings, the balustrade and the basin which is supported by three caricatural satyrs atlantis, On the top of the façade are sighted sculptures of the three virtues - hope, faith and charity. The whole architectural design by the Benedictine monk Frei José António Vilaça was materialized by the masters carvers Luis de Sousa Neves and João Bernardo da Silva [1, 2].

This is an exceptional artwork and a musical instrument that is well documented in account books and contracts. These occasionally refer to the materials used to decorate the organ pipe, their prices, quality, quantity and provenance for a specific work, and also for some decoration within the church [3]. As far as the polychrome coating and gilding implementation is concerned, these sources are very helpful in a research aiming at confirming the materials used and the construction techniques employed.

This study focus mainly on imaging techniques. Besides fundamental visual records first obtained in situ by digital photography (DP) under visible and ultraviolet illumination, portable X-ray Radiography (XRR) was carried out in an attempt to put in evidence specific aspects of the organ pipe inner structure, assembly and polychrome coating implementation [4] (Fig. 1). On the basis of a very selective micro-sampling
performed on the three different parts of the organ pipe, Optical Microscopy (OM) equipped with several filters, including ultraviolet light, was used on samples cross-sections to assess the layer build up. Every ground and pictorial layer was also observed by SEM imaging (SE and BSE modes) for the layer structure morphological aspects.

Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) analysis was carried out for elemental composition and mapping of the inorganic compounds. Micro X-ray diffraction (μ-DRX) was used to identify several crystalline phases within the compounds and complement the previous results, as this was successfully applied to another type of instrument like harpsichords [5]

The overall data gathered in this study was of major importance to broaden our understanding of the nature of the materials used in the Tibães organ pipe finishes, their morphology and technological processes. The results obtained by the aforementioned imaging and X-ray spectroscopic techniques will be discussed in the poster.

References
Pigments and dyes for art: a scientific database of ancient, modern and contemporary materials

Tiziana Cavaleri¹, Paola Buscaglia², Marco Nervo¹, Anna Piccirillo¹, Marco Pisani³, Paolo Triolo⁴, Massimo Zucco³

¹ Fondazione Centro Conservazione e Restauro (CCR) La Venaria Reale, Laboratori Scientifici, via XX Settembre 18, 10078 Venaria Reale, Torino (Italy), Tel. +39 011 4993031, tiziana.cavaleri@centrorestaurovenaria.it
² Fondazione Centro Conservazione e Restauro (CCR) La Venaria Reale, Laboratori di Restauro, via XX Settembre 18, 10078 Venaria Reale, Torino (Italy).
³ Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, 10135 Torino (Italy).
⁴ Consultant at Fondazione Centro Conservazione e Restauro (CCR) La Venaria Reale, Laboratori Scientifici, via XX Settembre 18, 10078 Venaria Reale, Torino (Italy).

* tiziana.cavaleri@centrorestaurovenaria.it, +39 011 499 3031

Keywords: pigment and dyes identification; art; scientific database; noninvasive techniques.

In the Italian context of art and restoration, Centro Conservazione e Restauro (CCR) “La Venaria Reale” is a relatively young institution, where different competences live side by side and cooperate to study, restore and value works of art. Covering different sectors, we have to face materials of various typologies and in extremely different conservation conditions, from Egyptian archeological textiles [1] to the contemporary paintings of still alive artists [2]. That is a challenging work which cannot disregard a scientific study of the artistic materials, of their chemical structure and their physical properties, of their interactions and the degradation phenomena.

In order to acquire useful data for revealing the artwork’s technique, we usually refer to a database or we pass through the study of an ad hoc prepared sample that could simulate the real situation, the artwork’s technique or its condition. Here we present a bigger project in which we tried to prepare reference samples that might help us in future studies of polychrome paintings: that is a database of pictorial sample layers made of around 300 pigments and/or dyes used from the Antiquity to the Modern and Contemporary Art. The palette realization involved the competence of a restorer; then, the CCR scientific laboratories carried out different analyses for creating the database. Moreover, the INRIM researcher group acquired for each palette the hyperspectral cube by means of their innovative prototype based on a Fabry-Perot interferometer [3]: that collaboration was the means for creating the first wide database on pictorial materials for this new instrument too.

All pigments and dyes we used were powders produced by Kremer Pigmente GmbH & Co. KG. Starting from the technical schedules, we carried out analyses on few grains of powder by means of FT-IR spectroscopy in ATR modality, revealing for instance the presence of barium sulfate in many pigments; with the same technique, we analyzed the two binders. We realized the palette on wooden supports prepared evenly with a layer of stucco (gypsum and animal glue); over the stucco, we made three
different kinds of graphic signs for simulating the underdrawing (in ocher, charcoal and ink) and then we realized the painting layers. Finally, we used two kinds of varnish (natural and synthetic resins) as finishing layer, leaving for each sample one small area unprotected. As mentioned, we believed appropriate to use two types of binder (oil and tempera) for each pigment, in order to evaluate their influence in the imaging and scientific analyses, the same as we did with the varnishes.

On the so-prepared pigment palette, we carried out imaging techniques following the British Museum’s recommendations [4] about survey methods, post-production and diagnostic applicability. In particular, after taking photographs in diffused visible light, we acquired the reflectography in two near-infrared bands (780 nm - 950 nm and 950 nm – 1150 nm), that are useful, for instance, in revealing the underdrawing. We acquired the ultraviolet fluorescence, for gathering the specific response of pigments and their influence to the protective layer UV fluorescence; we picked up UV reflectography (300 nm – 380 nm), useful for studying binders and pigments, and we acquired the visible infrared induced luminescence (VIL), an incisive technique in the identification of some pigments such as Egyptian blue [5]. From those techniques, we elaborated also false colors images, and in particular useful for revealing metameric pigments, testing in particular the UV fluorescence false color image in the standard mode and in the UVC-green channel mode. We also carried out digital radiographies used to characterize the pigments behavior with respect to the energy of X-rays [6]. We finally analyzed any sample in fiber optics reflectance spectroscopy (FORS), comparing spectra to the ones obtained by the hyperspectral camera [7], and in X-ray fluorescence (XRF). One month after the binders dried, we analyses any sample by means of FT-IR spectroscopy equipped with a microscope in micro-ATR modality in order to highlight the possible formation of interaction products, finding for instance metal carboxylates.

References:
Analysis of the Notger Gospel book by PIXE, XRF and Raman spectroscopies

François-Philippe Hocquet\textsuperscript{1,2}, Fanny Dombret\textsuperscript{2}, Cécile Oger\textsuperscript{2,3} and David Strivay\textsuperscript{1,2}

\textsuperscript{1} Université de Liège, Spectroscopie Atomique et Nucléaire, Archéométrie, Sart Tilman B15, 4000 Liège (Belgium), Tel. +3243663695 (corresponding author), dstrivay@ulg.ac.be (corresponding author).
\textsuperscript{2} Université de Liège, Centre Européen d’Archéométrie, Sart Tilman B15, 4000 Liège (Belgium).
\textsuperscript{3} Université de Liège, CARE Bibliothèque, Place du XX-Août, 4000 Liège (Belgium).

\* dstrivay@ulg.ac.be, +3243663695/+3243662884

**Keywords:** Gospel book, PIXE, XRF, enamel, brass

Notger Gospel book is a parchment manuscript from the 10th century with a sumptuous binding, an ivory plate, enamels and gilt brass (10th, 13th. and 16\textsuperscript{th} centuries). Notger (940 - 1008) was a Benedictine monk that became bishop in 972 and then first prince-bishop (980–1008) of the Prince-Bishopric of Liège (now in Belgium). The binding of the Gospels consists of a central plate ivory (10th c.) apparently representing Notger kneeling before a shrine-shaped chapel and behind him a seat. The bishop holds a book with both hands. This treasure is now kept at the Curtius Museum in Liège.

A complete analysis of its binding has been performed by PIXE, XRF and Raman analysis with particular attention on the enamels and the brass. Results will be presented and discussed in relation with similar objects from Mosan Art.
Identification of binders in copper portrait miniatures of 17th and 18th centuries by µ-ATR-FTIR and Py-GC-MS

Dora Martins Teixeira¹²*, Alfredina Veiga¹, Ana Manhita¹, Catarina Miguel¹, António Candeias¹², Paulo Rodrigues³, Jorge Ginja Teixeira¹²

¹ HERCULES Lab., Évora University, Palácio do Vimioso, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal.
² Chemistry Department of Science and Technology School, Évora University, Colégio Luís António Verney, R. Romão Ramalho, 59, 7000-671 Évora, Portugal.
³ History Department of Social Sciences School, Évora University, Colégio do Espírito Santo, Largo dos Colegiados 2, 7000-803 & Centre for Art History and Artistic Research (CHAIA), Évora University, Palácio do Vimioso, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal.

* Phone: +351266745311, Fax: +351266745303, E-mail: dmt@uevora.pt

Keywords: portrait miniature; copper support; µ-ATR-FTIR; Py-GC-MS; binders; drying oils.

Four miniature paintings on copper support from Évora Museum (Portugal) were studied in order to identify the kind of binder used. The miniatures studied are part of the collection that belonged mainly to the Portuguese Royal Family (Casa de Bragança). Until now, the information that can be obtained in the literature about the binding media used in paintings on copper support during the period from XVI to the XVIII centuries is very scarce, but analysis carried out so far suggest that linseed oil was used. According to the literature, the materials used in the preparatory and chromatic layers were usually pigments ground in linseed oil [1-3].

Fourier transform infrared spectroscopy (µ-ATR-FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) were used as complementary techniques to investigate the organic binder used in these paintings. The first step of this work was an exhaustive preliminary study using µ-ATR-FTIR in order to obtain as much information as possible, performed non destructively on the surface of the painting. Then, to confirm and complement the µ-ATR-FTIR results, a limited number of micro-samples were collected from the paintings and analyzed by Py-GC-MS.

The results obtained indicate that the studied portraits were painted using a siccative oil. The infrared data suggested the oil nature of the binder, since the IR spectra showed the characteristic bands attributed to the free fatty or dicarboxylic acids resulting from the aging of the drying oil. The Py-GC-MS analysis of the micro-samples collected from the paintings, after derivatization with tetramethylammonium hydroxide (TMAH), confirmed the use of a drying oil as binder, since it were detected in all chromatograms the presence of the characteristic methylated monocarboxylic and dicarboxylic acids, and the absence of protein biomarkers. The ratio of the quantities of azelaic (A) and palmitic (P) acids has been described as a parameter to distinguish
between drying oils, egg and egg oil mixture (tempera grassa). The ratio palmitic acid (P)/stearic acid (S) can be used to distinguish between drying oils, since these two fatty acids are less subject to chemical reactions during ageing. The sum of the amounts of dicarboxylic acids (ΣD) over the total fatty acid content is another parameter that can be used to identify the type of lipid binder, since if ΣD is superior to 30% of the total fatty acid content, a drying oil is the only lipid binder present [3-6]. Typical values of A/P and ΣD for drying oils were obtained for all samples. For three of the paintings, the P/S ratios obtained correspond to typical P/S values for linseed oil, as predicted by the historical references. However, the sample collected from one of the portraits showed a P/S ratio characteristic of walnut oil, leading us to the conclusion that this binder was used as siccative oil in this painting. More studies are being performed with other portraits of the collection, in order to determine the presence of other siccative oils or proteinaceous binders in these paintings.

References:
Evaluation of Laser Cleaning of Parchment, Wool and Feather with High Performance Liquid Chromatography and Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy

Stamatis C. Boyatzis\textsuperscript{1}, Eleni Ioakimoglou\textsuperscript{1}, Eleni Tziamourani\textsuperscript{1}, Efrosini Karantoni\textsuperscript{1}, Ekaterini Malea\textsuperscript{1}, Stavroula Rapti\textsuperscript{1}, Paraskevi Pouli\textsuperscript{2}, Athanassia Papanikolaou\textsuperscript{2}, Kristallia Melessanaki\textsuperscript{2} and Georgios Panagiaris\textsuperscript{1}

\textsuperscript{1} Technological Educational Institute of Athens (TEI-A), Department of Conservation of Antiquities and Works of Art, Aghiou Spyridonos, 12243 Egaleo (Greece), Tel. +302105385464

\textsuperscript{2} Institute of Electronic Structure and Laser, Foundation for Research and Technology - Hellas, 711 10 Heraklion, (Greece).

* sbayatzis@teiath.gr, +302105385464/+302105385406

Keywords: laser cleaning; parchment; wool; collagen; keratin; aminoacid; HPLC; FTIR

Objectives of Research. This study was designed to investigate the effectiveness of laser cleaning, which, through the past 20 years has been evolved into a unique conservation tool, along with assessing the final condition in specimens of parchment, wool textile as well as duck and flamingo feather on the molecular level. To this end, aminoacid analysis of protein materials with high performance liquid chromatography (HPLC), as well as ATR-FTIR spectroscopy of selected surface spots in each specimen were employed.

Specimen preparation: Square (approx. 4×4 cm) wool specimens were stained in contact with wet iron wool and its corrosion product. Rectangular (approx. 3×9 cm) parchment specimens were iron-stained by (a) applying aqueous suspension of the iron wool-generated corrosion product and (b) sprinkling the dried corrosion product powder on the specimens. Finally, duck and flamingo feathers were soiled with museum dust. For comparison reasons, in parchment specimens, approximately half of their areas has been kept unstained, while for textile and feather, similar specimens were selected and were kept unsoiled, and were accordingly considered for identical trials.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Selected stained/soiled specimens: (a) parchment; (b) wool textile; (c) duck feather. Laser-irradiated areas are outlined.}
\end{figure}

2\textsuperscript{nd} International Conference on Innovation in Art Research and Technology, 21–25 March 2016, Ghent, Belgium
**Laser cleaning conditions:** A Q-Switched (QS) Nd:YAG nanosecond laser and a fibre-coupled short free running (SFR) microsecond laser were employed for the cleaning trials. In both systems, the fundamental wavelength lies in the infrared region (1064 nm). In addition, the QS laser provides the opportunity of using the second harmonic and the third harmonic wavelengths which correspond to visible radiation (532 nm) and UV radiation (355 nm), respectively. In each specimen, both stained/soiled and unstained/unsoiled areas were laser-irradiated with identical conditions for comparison reasons (see Figure 1).

**Analysis Results.** In all cases, analysis of laser-irradiated and non-irradiated stained/soiled areas was carried in comparison to unstained/unsoiled areas.

**Reverse Phase High Performance Liquid Chromatography results:** Amino acid analysis using derivatisation with 9-fluorenylmethyl chloroformate and reverse phase HPLC-FLUO was done aiming at investigating possible characteristic alterations in amino acid composition of parchment and wool proteins as well at the detection of breakdown products as possible oxidation markers. Throughout the studied samples, no significant changes in amino acid composition of both keratin and collagen were observed between the reference and irradiated specimens; only a very small decrease of tyrosine amounts were detected in laser-irradiated wool areas. In addition, no typical oxidation markers of collagen or keratin were detected in irradiated areas, with the exception of cysteic acid; this however, was also found at comparable levels in non-irradiated areas. The results suggest that practically no damage in the primary structure of both proteins was induced by laser cleaning trials in the studied spots.

**FTIR Results:** In ATR-FTIR spectra the staining on parchment and wool textile samples was evident by identifying iron hydroxy-oxide (α-FeOOH) in all stained areas. Residual quantities of this were found in some laser–cleaned areas suggesting incomplete removal of stains; in a number of cases, however, cleaning was found almost complete. In the case of feather, soiling with museum dust was confirmed, by identifying calcite and silicates in all soiled areas. Small, residual amounts of these were also found in all laser-cleaned spots, also suggesting incomplete soiling removal through the laser-cleaning process. The base material in all cases was clearly investigated providing excellent quality spectra of collagenous material (parchment) and α-keratin (wool). In laser-irradiated areas with mild laser conditions, no changes on both materials could be detected. However, in the cases of more severe laser conditions (higher fluence and pulse number) small-scale changes in the protein secondary structure were reproducibly found in various sampling spots, suggesting moderate loosening of the three-dimensional protein architecture.

**References:**


Multi-analytical study on two daguerreotype case components

Evan Maina Maingi¹, Margarida Nunes¹, Cátia Relvas¹, Sónia Costa¹, Catarina Miguel¹, Teresa Ferreira¹,²*

¹ HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7000-554 Évora, Portugal
² Chemistry Department at the Science and Technology School, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

*tasf@uevora.pt, +351 266 740 800

Keywords: daguerreotype; case component; multi-analytical characterization

Daguerreotypes were always enclosed in hinged miniature cases with a glass cover protecting the fragile surface. Casing of daguerreotypes was a traditional way in which the portraits were stored and displayed during the 18th and 19th centuries. Typically, components of a daguerreotype case include the daguerreotype itself, a brass mat (sometimes stamped with decorative motifs) and a protective glass cover. All these components (daguerreotype, brass mat and glass cover) were held together with a paper tape with some sort of adhesive, the latter often covered with a decorated brass foil referred to as a ‘preserver’ [1]. According to Clark (2013), an image with a preserver dates after 1847. The materials were then placed in small cases made of leather, wood, papier mache or molded plastic. Thermoplastic or Union case are known to be dated after 1856 [2]. The resultant case was hinged with clasps and padded inside with some soft cloth. The daguerreotype case meant to protect the image surface, actually creates an environment that facilitates deterioration of the image. There are problems emanating from corrosion of the glass cover. The use of a protective cover glass bound to the frame using a sealing paper tape creates a conducive environment for glass corrosion on the inside of the cover glass compromising the general conservation status of the whole photographic package. The composition and manufacturing procedures of the sealing paper tapes make them particularly vulnerable to damage as well as reactive to environmental contaminants and solvents used in conservation treatments. The brass mat, usually an alloy of copper and zinc, has on the other hand been known to promote deterioration. Interaction of brass mat with other components of the package such as the glass cover give rise to corrosion products; usually promoted by degradation of brass mat constituent elements i.e. copper and zinc [3].

In this work, multi-analytical instrumental techniques were applied to study the morphology and degradation status of the various components of two daguerreotype cases. The techniques used included technical photography, optical microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and micro-Fourier transform infrared spectroscopy (µ-FTIR). The inside surface of the protective glass cover (Dag 2) showed, under optical microscope, some degree of corrosion which appeared in form of surface clouding, conspicuous rounded spots, scratches, whitish blister-like deposits on the surface among other pathologies. SEM-EDS indicated the blisters to be largely composed of sulfates as a result of contamination from residual sodium thiosulfate. Localized corrosion debris composed of copper, zinc and chlorine were identified on the glass surface especially on those areas in contact with the brass mat. SEM-EDS also indicated the protective glass cover to have been formed from soda-lime, mainly composed of silicon dioxide, sodium and...
calcium oxides among other compounds. SEM-EDS analyses showed the fibers of the
sealing paper tape (Dag 2) to be intact and in comparatively good conservation status.
Calcium sulfates and aluminium silicates used as filler materials were also identified.
Hydrated aluminium silicate (Al₂O₃·SiO₂·2H₂O) fillers, referred to as kaolin fillers,
were very common in most grades of 19th century papers [4, 5]. The uneven
accumulation of these aggregates, as observed in SEM, showed a poor distribution of
the filler materials during the paper manufacturing. SEM-EDS and µ-FTIR analyses of
the brass mats surfaces (both Dags) revealed a layer composed of a mixture of a natural
resin and a fatty acid; this layer was part of the adhesive applied on the brass mat surface
to attach it to the daguerreotype plate. µ-FTIR analyses also indicated the use of Arabic
gum as the adhesive on the sealing paper tapes from both daguerreotypes.

References
Physicochemical characterization of two 19th century daguerreotypes by non-invasive analytical techniques

Evan Maina Maingi¹, Margarida Nunes¹, Cátia Relvas¹, Sónia Costa¹, Catarina Miguel¹, Teresa Ferreira¹, ²*

¹ HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7000-554 Évora, Portugal
² Chemistry Department at the Science and Technology School, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

* tasf@uevora.pt, +351 266 740 800

Keywords: daguerreotype; non-invasive techniques; technical photography; SEM-EDS; micro-Raman; micro-FT-IR; micro-XRD

The characterization of the conservation status of photographic materials is usually assessed through visual analysis or optical microscopy. However, many of these materials cannot be completely characterized by a simple visual-optical evaluation and need more non-invasive multi-analytical techniques [1]. Most importantly, these techniques need to be safe, non-contact and non-destructive and well suited for in situ analysis of cultural heritage objects and especially for the extremely vulnerable daguerreotype photographs.

Daguerreotypes were the first successful photographic images presented to the world in Paris in 1839 by Louis Daguerre. The invention of the daguerreotype process during the mid 19th century heralded the beginning of permanent and practical form of photography. This first form of photography was an instant success, and for over 15 years it was the dominant photographic process. Although millions of daguerreotypes were made between 1839 and 1860, the extreme vulnerability of the image recorded directly on a polished silver plate led to the loss of many of them in a few short years. Those that survived generally suffer from several corrosion phenomena, usually manifested by highly coloured surface tarnish and obscuring corrosion products on their surface. Worst still the plates remain highly vulnerable [2]. The most common form of deterioration found on daguerreotypes is a surface tarnish exhibiting interference colors. Previous analyses have identified this typical tarnish as consisting of silver sulfide, commonly referred to as ‘silver mirroring’. Degradation in terms of formation of a hazy, spread out white surface layer and white spots obstructing the images has also been previously reported and has been explained as those of silver chloride [3]. The daguerreotype enclosure meant to protect the image surface actually creates an environment that facilitates deterioration of the image. Silver-mercury amalgam particles, responsible for the image, tend to react particularly with atmospheric sulfur or chlorine leading to surface tarnishing. Various methods were applied in an attempt to remove the tarnish from daguerreotypes. However, many of these methods are now known to etch the plate, remove the image particles, and more so, the chemical residues cause further deterioration [4].
In this work, examples of the application of *in situ*, non-invasive and non-destructive multi-analytical instrumental techniques used to study the morphology and degradation status of two daguerreotypes are presented. This was in order to cross-check information about the production processes and the degradation status of the studied items with previous information from conservators.

The analytical techniques used for the morphological and chemical characterization included technical photography, optical microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), micro X-ray diffraction (μXRD), micro-Fourier transform infrared spectroscopy (μ-FTIR) and micro-Raman spectroscopy. SEM analyses revealed differences in density of particles forming the image, with highlight areas having much higher number of particles, with spherical shape, while shadow areas presented much smaller number of particles with more elongated shapes among others. SEM-EDS analyses found these image forming particles to be an amalgam of silver and mercury. EDS analyses revealed that both daguerreotypes were gilded and gold covered the plates’ entire surface as a thin layer. In fact, SEM images of the peeling of this layer were obtained during this work. Gold was also used to enhance jewelry. Mercury was only detected on the image forming particles in an amalgam with silver. Cuprite corrosion product was identified by μ-XRD on the backside of the two copper plates. Raman spectroscopy identified silver sulfide as the main cause of surface tarnish, while micro-FTIR revealed isolated cases of oxalates and carbonates. FTIR analysis also indicated one of the daguerreotypes to have been varnished with a natural resin.

References:
The use of colour on pottery decoration from late Holocene South American hunter gatherers

Veronica Aldazabal¹, Debbie Lauwers², Peter Vandenabeele³, Luc Moens², Cristina Vazquez⁴

¹ IMIHIHIU-CONICET, Saavedra 15-5º, C1083ACA- Ciudad autónoma de Buenos Aires, Argentina, varalda2@gmail.com. +54 011- 49538548.
² Ghent University, Department of Analytical Chemistry, Krijgslaan 281, S12, B-9000 Ghent, Belgium.
³ Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium.

Keywords: Raman spectroscopy; pottery analysis; pigments.

In this work, two groups of pottery, collected in Buenos Aires, are considered. A first set are fragments of decorated pottery (D1 to D4-C32) of hunter-gatherer and fishermen societies from different camp settlements. These locations date from the late Holocene (1000 to 600 years AP) where many activities, such as the manufacture of pottery, were carried out. The second group contains samples of indigenous tradition pottery which date from XVIII and XIX centuries, based on archaeological/historical context. They show similar pattern of pottery manufacturing and decoration (B42 B40 B41) as for group 1. There is a discussion relating to whether all the shards were made by Indians in the city, following their tradition or trade. In the latter case, the aim is to test the hypothesis comparing the two group of samples.

The study focuses on the investigation of the raw materials (pigments) used for the decoration in both groups. We aim to identify the pigment composition; knowing how the pigment was applied (alone, in a mixture of clay, other) and determine if the used pigments are similar. This approach is an uncharted territory in the field of pottery production from the area under study. Next to this, similarities or differences between the ceramic assemblages are examined.

The Raman results suggest a similar production between the two groups. The red pigment used for the decoration is basically haematite (α-Fe₂O₃). This mineral has two characteristic Raman modes: A1g mode (226 cm⁻¹) and Eg mode (245, 293, 411, 610 cm⁻¹). In some cases, broadening of these bands appears and can be related to different things: dehydration of goethite, weathering processes, biodegradation, etc. [Faria, 2007]. The weak band at 144 cm⁻¹ is attributed to anatase (TiO₂) which could be present as an ancillary component of silicates [Striova, 2006].
The identification of this mineral haematite, which is detected on one or both sides of the vessels, suggest that the pottery has been traded. The raw material was not available on the market in Buenos Aires. On the contrary, the composition studies of ceramic pastes by neutron activation analysis (Aldazabal et al 2014) suggest local manufacturing, facilitated by a widely availability of the clays.

References:
A new scanner for *in-situ* digital radiography of paintings

Anna Impallaria¹,²,³, Federico Evangelisti¹, Ferruccio Petrucci¹,²,³, Flavia Tisato¹,³, Lisa Castelli⁴, Francesco Taccetti⁴

¹ University of Ferrara, Department of Physics and Earth Science, Via Saragat 1, 44122 Ferrara (Italy), tel +39 0532 974211, e-mail:dipartimento-fst@pec.unife.it
² INFN - Sezione di Ferrara, Via Saragat 1, 44122 Ferrara (Italy)
³ TekneHub Ferrara, via Saragat 13, 44122 Ferrara (Italy)
⁴ INFN, Sezione di Firenze, Via G. Sansone 1, 50019 Sesto Fiorentino (Italy)

* impallaria@fe.infn.it, +39 0532 974338

**Keywords:** digital radiography; scanning system; *in situ* analysis; image diagnostics

X-ray radiography is one of the most widely used imaging techniques in the field of Cultural Heritage, both for conservation and investigation purposes. [1] Performing radiographies in museums, thus avoiding movements of works of art, has been recently made easy by digital acquisition of images, but when the *whole scan* of a large painting is required, technical solutions for a portable device are still not at hand. [2][3] The inherent weight of the X-ray tube, including protection shields, and of the high voltage generator makes the design of a “portable” device very difficult. In this project the solution of the puzzle was separating devices devoted to different tasks, in order to maintain each item under 50 kg weight, thus being transportable with minimum effort.

The proper RX scanner is composed of two independent frames (Fig.1) in aluminum, carrying and moving the X-ray tube and the digital detector. For both units, a couple of DC servomotors (G5© by Omron Electronics Ltd, UK) are driving the movements on X and Y axis. A third frame is added, to support the painting. The distance between the two units is usually set at 1 m and the work of art is located as close as possible to the detector, to minimize magnification and penumbra effects. Both units may be moved or installed on a scaffold, to scan wider paintings.

Leveling of the frames and alignment of X-ray beam with detector is performed by setting the leveling feet, collimating the beam with a small pinhole. Once aligned the units, the scan is automatically performed by remote control of motion, on horizontal and vertical axis, by dedicated software (NS-Runtime© rel.1.2 by Omron Co.). X-ray tube and detector move simultaneously and stop at the foreseen position for image acquisition. X-ray shot and digital acquisition follow, then the following position is reached. The scan is tailored to each painting, and the digital images are automatically stitched at the end of the scan. For instance, a painting of size 1 x 1 m² requires 144 shots and about 3-hour scan. The stitching is a matter of few minutes.
The X-ray tube is a Varian M-143T with tungsten anode, maximum anode voltage 49 kV, air cooled. The detector is a Teledyne DALSA (Canada) RadEye200, a two dimensional CMOS photodiode array combined with a Gd$_2$O$_2$S scintillator screen. It is composed of 1024 x 1000 pixel, of side length 96 µm. Depth of digitization is 12 bit/pixel. The scanning system has been designed, realized and tested. It has proved to recover each position in the scan within one pixel width and to be stable during all acquisitions.

Figure 6: Design of the scanner for digital radiography. The detector is hidden by the painting and is aligned with the X-ray tube, mounted on the frame to the right.

The authors gratefully acknowledge the contribution of Luca Landi and Stefano Squerzanti, of the Mechanics Service of the Dept. of Physics and Earth Sciences and INFN – Ferrara, for the invaluable help in the construction of the device.

This project has been supported by INFN National Network on Cultural Heritage (CHNet) and by the 5th Scientific Commission of INFN.

References:
Distinguishable features between a 16th Century Portuguese-Flemish Master and his follower: technical and analytical contributions

Sara Valadas¹, José Mirão¹, Cristina Dias¹, Peter Vandenabeele², António Candeias¹,³*

¹ HERCULES Laboratory, Institute for Advanced Studies and Research, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora (Portugal)
² Laboratory of Analytical Chemistry, Ghent University, Proeftuinstraat 86, B-9000 Ghent (Belgium)
³ Jose de Figueiredo Lab., General Directorate of Cultural Heritage, Rua das Janelas Verdes 37, 1300-001 Lisbon (Portugal)

* candeias@uevora.pt

Keywords: 16th century Portuguese-Flemish easel paintings; surface exams; underdrawing; micro-analysis.

This investigation is focused on the contributions of surface exams and micro-analytical research in the study of twenty one paintings attributed to Frei Carlos workshop, one of the most important Portuguese-Flemish painters, active during the first half of the sixteenth Century.

"Portuguese-Flemish Painting" is a common expression used in the history of Portuguese painting of the first third of the sixteenth century and in its most basic meaning designates the work of Flemish masters who settled in Portugal during the reign of King Manuel (1495-1521) contributing decisively to the process of renewal of Portuguese painting at the time [1].

The integrated approach combines historical research on documental sources with surface examination and material characterization of the paintings by using state-of-art analytical techniques. Microanalysis was carried out by optical microscopy, micro-Fourier-transform infrared-spectroscopy, micro-Raman spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry, micro-X-ray diffraction analysis (XRD), high performance liquid chromatography (HPLC) and Pyrolysis gas chromatography mass spectrometry (Py-GCMS).

This complementary surface and analytical research was applied in the technical and material characterization of grounds, underdrawings, primings, paint layers and its multi-layered build-up, providing access to the painter’s materials used in the technical execution of the paintings and details of the technique of artistic production. This study also intends to expose some usual details of the artist’s technique which are possibly related to the Master’s Flemish influence [2].
More significant findings are related to identification of iron gall-ink and/or carbon in the underdrawings by combining elemental and molecular analytical techniques (µ-FTIR, SEM-EDS and µ-Raman) and relating it with surface analysis by standard light photography, infrared reflectography and infrared photography. These data seem to answer long-standing questions raised in the field of Art History related to the heterogeneity of this Master’s work transmitted by the analysis of underdrawing. Regarding the Master’s palette, lead white, lead tin yellow, vermilion, ochres, carbon black, azurite, ultramarine blue, verdigris, red and yellow lakes were found together with an unusual green pigment, namely brochantite [3].

The knowledge of some particularities of the Master’s technique also allowed a new comparison with two paintings that had been attributed with some reserves to this Portuguese-Flemish workshop. More recently, as a result of a collaborative study, [4] an extensive infrared reflectography campaign was made, giving new data concerning underdrawings technical execution and contributing to differentiate, in these two paintings, another “hand”, attributed to a follower of Frei Carlos [5].

Complementary analytical research also added a new and deep insight into Frei Carlos workshop and his follower, evidencing the materials used, their models and sources of artistic inspiration, execution techniques and pictorial construction procedures that could specifically relate or distinguish between them.

Acknowledgments

The authors wish to acknowledge the Fundação para a Ciência e Tecnologia for financial support (PhD grant SFRH / BD / 66068 / 2009 and project ONFINARTS PTDC/EAT-HAT/115692/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund. The research team also wishes to thank the scientific support of the HERCULES Lab and José de Figueiredo Lab and all collaborations with Évora Museum and National Ancient Art Museum.

References:
Principal component analysis of chromatic parameters measured on atmospheric aged paint dosimeters

A Herrera¹, D. Ballabio ², R. Todeschini², N. Navas³ and C. Cardell¹

1 Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain, Tel. 0034958242725, jaherrera@ugr.es.
2 Dept. of Earth and Environmental Sciences University of Milano-Bicocca, P.za della Scienza 1, 20126 Milano, Italy.
3 Dept. Analytical Chemistry, and Biomedical Research Institute of Granada (IBIG), University of Granada, Faculty of Science, Campus Fuentenueva s/n, 18071 Granada, Spain

Keywords: paint dosimeter; natural aging test; portable spectrophotometer; PCA;

Decay of outdoor paint artworks due to polluted urban atmospheres is an outstanding problem with paramount cultural and economic consequences that is attracting the attention of researchers in the last decades [1][2]. In this context, evaluation of the effects of urban atmospheric aerosols on the pigment-binder interactions of such paintings is a crucial issue that requires an in-depth investigation. The present work is part of two Spanish research projects devoted to analyze pigment-binder interactions in polychromes and paint dosimeters exposed to open and semi-open monuments in the city of Granada (Spain).

The paint dosimeters were prepared according to standards similar to those used by medieval artists. On glass slides were spread either egg yolk or rabbit glue binders, as well as paint binary mixtures composed of pure lapis lazuli, malachite, smalt and azurite (different crystal sizes for these two last) mixed with one of the above mentioned binders [3]. Sets of paint dosimeters were exposed in eight strategic open-air monuments and removed after 18 months to characterize their natural ageing using an array of different analytical techniques. We present here the results of the color measurement campaign preformed “in situ” using a portable spectrophotometer. Chromatic measurements of the paint dosimeters were done at the start of the natural ageing test and periodically. The obtained data were expressed in the CIE L*a*b* and CIE L*H*C* color systems. Later on a multivariate analysis of the variation of the chromatic parameters (L*, a*, b*, H*, C* and ΔE*) over time was carried out using Principal Component Analysis (PCA) [4]. The PCs were calculated on the autoscaled data (mean-centering and unit variance) in order to make comparable differences in variable units [5].

Results suggested that there is a relationship between the first principal component (PC1) and the color measurement over time. On the other hand, the type of binder is discriminating using scores on PC2. This is interesting considering that for instance the malachite-egg yolk dosimeter cannot be distinguished by naked eye from the malachite-rabbit glue dosimeter. In the loading plot it was found that all chromatic parameters...
have a high influence on PC1 with the exception of luminosity (L*), which is for its part the most influential on PC2. Consequently, luminosity is the most important factor to discriminate the type of binder. When dealing with egg yolk binder, b* (+b* yellow to -b* blue) is one of the key parameter related to color change over time, since it has positive loadings on PC1 and PC2, as well as egg yolk-based samples measured at the highest exposure times. Thus, egg yolk-based samples which colors were measured at the start of the natural ageing test are characterized by low b* values which increases with time of exposure to the atmospheric conditions; this means that dosimeters containing egg yolk become yellower over time. Likewise, the samples comprising rabbit glue binder were characterized by low b* values at the lowest measurement times. However here the chromatic parameters a* (a* red to -a* green) and ∆E (total chromatic difference) are the decisive factors affecting the color changes over time. Results show that color variation is higher for rabbit blue-based samples which in addition turn more reddish with increasing exposure times.

**Acknowledgements:**

Andalussian Research Groups RNM-179, FQM-118, Milano Chemometrics and QSAR Research Group. Spanish Research Projects AERIMPACT (CGL2012-30729) and EXPOAIR (P12-FQM-1889) for financial support.

**References**


Preliminary studies of ultraviolet radiation over time in paint mock-ups.

A.Herrera¹, F.Grisoni ², D. Ballabio ², R. Todeschini², N. Navas ³ and C. Cardell¹

¹ Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain, Tel. 0034958242725, jaherrera@ugr.es
² Dept. of Earth and Environmental Sciences University of Milano-Bicocca, P.za della Scienza 1, 20126 Milano, Italy.
³ Dept. Analytical Chemistry, and Biomedical Research Institute of Granada (IBIG), University of Granada, Faculty of Science, Campus Fuentenueva s/n, 18071 Granada, Spain.

Keywords: paint mock-ups, UV artificial ageing test; MALDI-TOF-MS; micro-Raman spectroscopy; portable spectrophotometer; similarity index.

Degradation and darkening of outdoor paintings exposed to polluted and coastal urban atmosphere is acquiring significance due to new atmospheric contaminants and the effects of climate change. This problem is enhanced by heavy traffic in hot seaside Mediterranean cities. On the other hand, organic materials used in art generally deserve special attention in the conservation of paintings due to their tendency to undergo severe degradation, transformation and oxidation processes with respect to the inorganic constituents. Therefore a major problem with organic binders used in objects of Cultural Heritage is their short lifetime due to their susceptibility to various degrading processes. Particularly, in art paintings, discoloration, cracking and chemical weathering are the results of physicochemical processes that usually originate from oxygen and exposure to UV light [1]. Nevertheless, in the particular case of protein-based binders, it is said that their stability in various atmospheric conditions is exceptional as compared with the yellowing and brittleness of aged oils and resins [2]. This may be the reason why the ageing process of oils and resins has been widely discussed [3][4][5], while the ageing of proteins used in painting has scarcely been studied [2][6].

The aim of this paper is to present the preliminary results of the effects of UV radiation in paint mock-ups over time. Paint mock-ups were prepared according to medieval artists processes using 10 pigments (lapis lazuli, azurite, smalt, malachite, hematite, cinnabar, minium, calcite, gypsum and white lead) mixed with egg yolk binder. The mixtures were spread on glass slides. As well mock-ups only comprising egg yolk binder were prepared. The applied analytical techniques were MALDI-TOF-MS, micro-Raman spectroscopy (MRS) and portable spectrophotometer [6][7].

First a specific MALDI-TOF-MS strategy was designed to analyze these particular samples based on previous studies. [7]. Later on data were processed and compared with those included in international lipid databases. In such a way, qualitative information was obtained from m/z spectrum. Using Mathlab programming, his data of m/z spectrum were converted to binary data with the same parameters dimensions. Thus we could calculate distance vectors using similarity index (Jacque-Tanimoto method)
between the blank samples and the UV aged samples [8]. These data have revealed markers and differences between all the paint samples groups.

Color measurements were also carried out on the blank and the UV aged samples, in order to evaluate potential color variations among different paint mock-ups due to UV radiation. On the other hand the paint samples were analyzed by MRS with the purpose to discern if the registered variations were produced by organic and inorganic materials, or both.

Acknowledgements:

Andalussian Research Groups RNM-179, FQM-118, Milano Chemometrics and QSAR Research Group. Spanish Research Projects AERIMPACT (CGL2012-30729), and EXPOAIR (P12-FQM-1889) for financial support.

References
Beaming into the Iron Age: 
Handheld X-ray Fluorescence on Iron Age ceramics from Luristan (Iran)

Possum Pincé¹, Peter Vandenabeele

¹ Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 33-35, 9000 Ghent (Belgium), +32 (0)9 331 01 63, Possum.Pince@UGent.be.

Keywords: handheld X-ray Fluorescence; Luristan (Iran); ceramics; Iron Age

This paper presents the results of the archaeometric analysis on Iron Age (1450-500 BCE) ceramics from Luristan (Iran). These ceramics belong to different sites and are classified into several stylistic groups. The applied analytical method is handheld X-ray Fluorescence (hXRF), which is a non-destructive technique to study the elemental fingerprint of ceramics. The aim is to identify distinctive compositional groups in the Luristan ceramics. Based on these hXRF results, the dataset will be enlarged and other techniques such as Micro X-ray Fluorescence (µXRF) and thin section petrography will be applied to elucidate the factors influencing these compositional groups such as provenance and manufacturing methods. The combination of these analytical and petrographic techniques will contribute to our knowledge of the primary materials, the technological processes and the social and economic identity of the studied ceramics.

This study is part of a larger investigation on the chemical and mineralogical characterization of the ceramics from the Vanden Berghe collection present at the Royal Museums of Arts and History (Brussels, Belgium).
Effect of acid rain on the leaching of heavy metals on CorTen steel structures

Patricia Ruiz¹, Julene Aramendia¹, Kepa Castro¹, Juan Manuel Madariaga¹

¹Department of Analytical Chemistry, University of the Basque Country UPV/EHU, P.O.Box 644, E-48080 Bilbao, Spain. pruiz015@ikasle.ehu.eus

Keywords: weathering steel; protective layer; metal leaching; corrosion; synthetic acid rain

CorTen steel is a type of weathering steel which has a special resistance against the atmospheric corrosion through the formation of a protective layer. This layer is formed, among others, due to the reaction of some alloy elements present in the steel with reactive species, such as sulphur and nitrogen oxides, which are present in the environment. For that reason, it is a widely used material in outdoor structures (facades, bridges) and it is in vogue among modern sculptors because this material changes its texture and colour with the pass of time. However, depending on the location, some problems could appear in the development of the protective layer. For instance, even if the acid gases collaborate in the formation of the rust layer, when they appear in high concentration they can be counter-productive in the well development of the protective layer. In fact, acid rain can accelerate the corrosion process causing the leaching of some steel alloy metals. In consequence, the corrosion can be the responsible of the destruction of the structure, and moreover, the responsible of several negative environmental impacts due to the toxicity of those leached metals. [¹, ²]

Taking into account the importance of the acid rain effects into weathering steel, the aim of the present work was to study what kind of metallic salts were formed in the protective layer due to the effect of the acid rain. Moreover, it was also an aim to quantify how much metal is leached from due to the reaction of the material with the acid rain.

In order to accomplish the mentioned objectives, a simulation of acid rain effect was made immersing steel pieces in synthetic acid rain water during, at least, two weeks. The weathering steel pieces were obtained from the casting that was used for a sculpture made by the Spanish sculptor Eduardo Chillida. This sculpture is exhibited outdoors in Bilbao city (Northern Spain), which is subjected to a corrosive atmosphere due to the high humidity and the presence of acid gases. This sculpture is suffering a detaching process due to the action of the pollution. Therefore, the attainment of this study will help in the comprehension of the conservation problems of the mentioned sculpture without the necessity of performing any sampling procedure.

After the immersion of the steel pieces, they were analyzed by means of Raman spectroscopy, ICP-MS and XRF. For the molecular characterization of the protective layer an InnoRam B&W TEK (MicroBeam) Raman spectrometer was employed using a 780 nm laser. In order to quantify the amount of metals that were leached ICP-MS
NexION 300 (Perkin Elmer) was used. Finally, to support these results, the stained present in the marble slab where the piece of steel was placed for the experiments was analysed with an X-MET5100 handheld gun (Oxford Instruments).

Raman results showed that the main components of protective layer were iron oxides such as lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and magnetite (Fe₃O₄). These results were expected because iron is the major metal in the initial composition of the steel. More specifically, lepidocrocite appeared in most of the spectra because it is the first step in the development of the protective layer. Apart from the typical iron oxides, some amorphous phases such as maghemite were also identified. Besides, a high presence of gypsum (CaSO₄·2H₂O) was found. Finally, through Raman spectroscopy, some other sulphates were detected (iron sulphates among others). On the other hand, by ICP-MS the water where the pieces were immersed was analysed. According to the results, it could be seen that iron was leached in higher amount comparing with the other metals of the steel alloy. Besides, together with iron, it was found that manganese and zinc were leaching in high concentration.

Finally, with the XRF analysis performed over the marble slab, it could be confirmed that iron and manganese were deposited on the surface in high extent. This fact means that, after the leaching of the metals, they precipitate again. The obtained concentrations were scaled and related to the dimensions of the analysed pieces of steel, confirming that the amount of metals leached was important and it should be taken into account to know the environmental effects that larger structures could cause.

Acknowledgments:

This work has been financially supported by the project DISILICA-1930 (Ref: BIA2014-59124-P) from the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

References:
Analytical Characterization of glass tesserae from mosaics of Early Christian basilicas in Albania

Esmeralda Vataj¹, Teuta Dilo², Elio Hobdari³, Stefan Röhrs⁴, Peter Vandenabeele⁵, Nikolla Civici¹∗

¹ Institute of Applied Nuclear Physics, University of Tirana, Albania
² Department of Physics, Faculty of Natural Science, University of Tirana, Albania
³ Institute of Archaeology, Centre of Albanian Studies, Tirana, Albania
⁴ Staatliche Museen zu Berlin - Prussian Cultural Heritage, Rathgen Research Laboratory
⁵ Department of Archaeology, Ghent University, Belgium

During the last years there has been an increasing interest from both archaeologists and scientists for the study of glass archaeological finds in Albania. The present study constitutes the first attempt to study the glass mosaic tesserae of different colours recovered from the archeological excavation of the mosaics at the Early Christian basilicas in Bylis, Lin and Elbasan, belonging to V-VI century AD. The main objective of the study is the characterization of the type of materials, glass matrix and coloring and opacifying agents, used for their production.

A multi analytical approach, which includes optical microscopy, scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS), micro X-ray fluorescence and Raman spectroscopy, is used during the investigation of around 70 tesserae of different colours collected from the three sites.

All the tesserae are opaque and have heterogeneous surfaces with several bubbles and crystalline inclusions. Most of the glass tesserae have the characteristic soda-lime-silica composition and low concentrations of potash and magnesia indicate Natron as soda source, which is typical for the Roman glass. Compounds of Mn, Fe, Cu, Co, Pb and Sn were used as colorants in the tesserae of different colours. Mineral inclusions are mostly composed of undissolved raw materials i.e silicon, calcium and tin rich particles. It is interesting to notice that SnO₂ has been used as opacifier in all the tesserae. Thin Au foils placed between two transparent glasses were identified in the gold coloured tesserae.
SERS analysis of basic and acid early synthetic dyes on wool

Maria Vega Cañamares¹, Chiara Deriu¹², Rocco Mazzeo²³, Silvia Prati²³ and Santiago Sanchez-Cortes¹

¹ Instituto de Estructura de la Materia (IEM-CSIC), Serrano 121, 28006 Madrid (Spain), Tel. +34915616800, mvca@iem.cfmac.csic.es.
² University of Bologna, Microchemistry and Microscopy Art Diagnostic Laboratory M2ADL, Ravenna Campus, Guaccimanni 42, 48121, Ravenna (Italy).
³ University of Bologna, Department of Chemistry “G. Ciamician”, Selmi 2, 40126, Bologna (Italy).

* Corresponding author’s email address, phone/fax

Keywords: SERS; wool; cationic dyes; anionic dyes; pH

In ancient times, the available molecules for dyeing processes were of natural origin, most of which were incapable of fixing directly to the substrate [1]. For this reason fibres were mordanted, usually by means of metallic salts able to form complexes with the natural dyes, and act as a 'bridge' between the fibre and the colorant [2]. On the contrary, the vast majority of textile dyes used nowadays possess substrate-specificity, that is, the ability to dye a given fibre class without the use of mordants [2]. What makes it possible for such dyes to directly fix to a substrate is the presence of functional groups able to interact with the constituting chemical units of a textile. In the case of wool its amphoteric character allows the efficient use of both anionic (Acid) and cationic (Basic) dyes. The acidic groups confer the molecule water-solubility and negative charge, the latter being the major driving factor of the dying mechanism [2]. Acid dyes are applied to the fibres in acidic conditions. In such environments, the protein components of wool acquire a positive charge, due to the protonation of the basic side-chain moieties and to the neutralization of the acid functions [2, 3]. As far as basic dyes are concerned, the way in which they are applied to wool resembles the one just seen for acid dyes. Accordingly, their mechanism of fixation to the fibre is propelled by electrostatic interactions between the dye cation and the negatively charged moieties within the protein [2, 3].

Synthetic dyes meant technological simplifications to the home and industrial textile production. Thus, their use was rather widespread. However, a lack of comprehensive scientific and conservation literature on these molecules could be linked to the fact that the attention on the characterization of contemporary works of art has been made just relatively recently [4].

The analysis of dyes in cultural heritage samples is a well-known challenging task, due to their inherent high tinting strength and consequent low concentration in the carrying matrix [5]. This fact severely limits the number of analytical techniques that can be efficiently and micro-destructively employed for their detection and
unambiguous identification. The introduction of Surface-Enhanced Raman Spectroscopy (SERS) [6] to the field of conservation science has made the study of such materials possible and more straightforward, both as free molecules [7] and as dyed fibres [8]. This is possible due to the SERS ability to yield good signal-to-noise ratio spectra from minute amounts of sample, as well as to the quenching of the fluorescence emission. Such advantages have been exploited for the elaboration of a quick and pre-treatment-less methodology based on SERS, for the analysis of three early synthetic dyes (Acid Orange 7, CI 15510; Basic Violet 14, CI 42510; and Basic Violet 3, CI 42555) in minute wool yarns fragments (figure 1).

A small amount of dyed wool fibre was placed inside a glass tube along with a triply washed modification of the standard Lee-Meisel silver colloid [9] and KNO₃ 0.5M as aggregating agent. Such dispersion was analysed in a macro Raman arrangement. A further modification of colloid by adjusting the pH value to 4 with diluted HNO₃ was established as the SERS substrate for the analysis of anionic dyes on wool. This methodology was satisfactorily applied to the detection of AO7, a very difficult SERS probe due to its anionic character and to the presence of Cl⁻ ions deriving from its synthesis, which are known to negatively affect SERS experiments.

![Figure 1. SERS spectra of dyed wool fibres.](image)

References:
Portable XRF vs benchtop EDX devices: Application for field elemental identification.

T. A. Mostefaoui\textsuperscript{1}, L. Idjouadiene\textsuperscript{1}, V. Marzo\textsuperscript{2}, L. Bonizzoni\textsuperscript{2}, M. Gargano\textsuperscript{2}, N. Ludwig\textsuperscript{2}

\textsuperscript{1} Equipe LuMaNo, Laboratoire de Physico-Chimie des Matériaux et Catalyse, Université A. Mira, 06000, Béjaia (Algeria), +213 55 22 762 77, toufik.amayas@gmail.com (corresponding author).
\textsuperscript{2} Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, 20133 Milano, (Italia).

Keywords: pXRF ; EDX ; elemental analysis ; characterization ; comparative study; Archaeometry

In the cultural heritage field, it is often impossible to move the objects under investigation to the laboratory for analysis; moreover, sometimes they are even too large to be put inside commercial spectrometers. In these cases, practical solutions should be found for their precise characterization, as the identification of their constituent materials provides valuable and critical information in multiple related areas. Such artefacts are also unique and no sample can be taken; consequently, non-destructive methods are required. For these reason, portable tools are the best choice, allowing in field analyses of any shape and dimension materials. In this paper, we undertook a comparative study between two techniques, namely the SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy) and portable XRF (X-ray fluorescence). We analysed pottery sherds, antique coins and manuscripts with the two techniques and we concluded that, in the considered case study, portable instrument can be a good solution for in field work and gives comparable results than a more sophisticated laboratory instrument. For this work, we have used an Assing Lithos 3000 as portable EDXRF spectrometer and an FEI Quanta 200 SEM as benchtop EDX device.
Application of non-destructive technical to study some manuscripts of Algerian heritage

L. Idjouadiene¹*, T. A. Mostefaoui¹, V. Marzo², N. Ludwig², L. Bonizzoni², M. Gargano²,

¹ Equipe LuMaNo, Laboratoire de Physico-Chimie des Matériaux et Catalyse, Université A. Mira, Béjaia (Algeria), lynda.idjouadiene@univ-bejaia.dz
² Dipartimento di Fisica, Università degli Studi di Milan, via Celoria 16, 20133 Milano (Italia)

Keywords: manuscripts; pigments; non-destructive technical; XRF; FORS; ATR; archeometry

Knowledge of heritage objects is an important branch of art history. The analytical approach of these objects renews their study. Indeed, the identification of their constituent materials provides valuable and critical information in multiple related areas. The preservation of this wealth has to tackle inter alia the identification, localization, classification and restoration of these heritage objects. Historical pieces are unique and have often crossed centuries, or even millennia, making them extremely fragile. Handling them should be done with great skill. Any analysis should be non-destructive and ensure that no irreparable damage will be done for them. Thanks to scientific and technological advances this became possible, and a branch of physical chemistry has developed and has emerged: the Archaeometry. The archaeometry through these technical analyses can answer long unanswered questions. Unfortunately, our country (Algeria) is experiencing a marked delay in the introduction of these new techniques for the study and the preservation of our archaeological heritage. In this paper, we present a study of some manuscripts of Algerian heritage. We used XRF spectroscopy, FORS and ATR to characterize these manuscripts to study and discuss the materials (inks and pigments) that were used.
Analysis of pigments on a 16\textsuperscript{th} century wood panel painting by portable and laboratory Raman instruments

E. Stanzania\textsuperscript{1,2,3}, D. Bersani\textsuperscript{1}, P. P. Lottici\textsuperscript{1}, Ph. Colomban\textsuperscript{2,3*}

\textsuperscript{1} Università di Parma, Dipartimento di Fisica e Scienze della Terra, 43124 Parma, Italia
\textsuperscript{2} Sorbonne Universités, UPMC Univ Paris 06, UMR 8233, MONARIS, 75005, Paris, France
\textsuperscript{3} CNRS-IP2CT, UMR 8233, MONARIS, 75005, Paris, France

* philippe.colomban@upmc.fr

This study aims to analyse a wooden panel painting, dated to the early sixteenth century, mainly by Raman and infrared spectroscopies. Raman spectra were recorded using portable Raman instruments with laser excitation lines at 532 and 785 nm and fixed Raman instruments at 532, 633, 785 and 1064 nm. Infrared analyses were made in Attenuated Total Reflection (ATR-FTIR) mode. Using the portable instrument, the Raman spectra evidence only white lead, calcite and vermilion. Raman spectra recorded by fixed-instrument enabled the identification of the artist’s palette: i) white lead, calcite, gypsum and cerussite for white colour; ii) vermilion, red lead, litharge, haematite for red; iii) azurite, indigo and lapis lazuli for blue. IR spectra gave information on organic binding media. XRF analysis on a brown pigment suggested a mixture of a red pigment (such as haematite and/or minium) and a green one as malachite. GC-MS analysis allowed identifying terpenic resin in the composition of the outer protective layer.
Multi-technical approach for the study of archaeological and artistic bronze objects

Justine Vernet¹, Valeria Bongiorno², Giorgia Ghiara¹³, Paolo Piccardo¹²³

¹ Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale (DCCI), via Dodecaneso 31, 16146 Genoa, ITALY. Tel.+390103536145, justine.vernet@yahoo.fr.
² Consiglio Nazionale delle Ricerche (CNR), Istituto per l’Energetica e le Interfasi (IENI), Via De Marini 6, 16149 Genoa, ITALY
³ Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, (INSTM), via G. Giusti 9, 50121 Florence, ITALY.

*justine.vernet@yahoo.fr, +39 010 353 6145

Keywords: tin bronze alloy; corrosion; artistic patinas; XRF; Raman

In the field of cultural heritage, it is no more to demonstrate that a complete investigation of artefacts and artworks requires over all a strong multidisciplinary approach, in order to increase the knowledges of the object, as well as the understanding of the intangible culture within which it was created. Particularly for metallic productions, the science of materials may bring precious information concerning alloy choices, casting techniques, thermomechanical manufacturing treatments or finishing steps, in the way to determine to what extent this production follow aesthetic, economic or technical purposes. A full study of a metallic artefacts includes then the characterization of the constitutive components of the bulk, as well as the superficial patinas (natural or artistic), but also the description of the processes involved for its production, and the alteration mechanisms to which it is exposed (corrosion process).

The current work presents a multi-technical study of artistic and archaeological bronze objects, investigating their various life steps: main manufacturing process, finishing treatments and long-term alteration. This study aims hence to show how many different perspectives can be extracted from the same material present in various contexts described below.

- Influence of alloying elements in the Cu-Sn matrix

Lead is a historic alloying element in the composition of bronzes and is known to increase the machinability and the castability of the alloy, particularly in the statuary field [1-2]. However, due to the lack of effective scientific research on the effect of such addition on the castability of the alloy [2-3], those parameters remain under empirical appreciation of the founder and limit the understanding of ancient bronze objects, as well as the manufacturing technique used by contemporary artists. Moreover, the insolubility of lead in a Cu-Sn alloy, leading to the formation of nodules in the principal matrix, implicate several issues for the representative characterization of the alloy trough non-destructive and non-invasive analysis, in particular in the case of the monumental statuary.
- Study of artistic patinas in situ and on reproductions

The ‘artistic’ patina is a coating applied by an artist, a specialist or a foundry man on a metal surface in order to produce color effects, homogenize the treated area and hide, if necessary, manufacturing defects [4-5]. The ‘artistic’ patination is a process based on the cold or hot application of inorganic (e.g. iron or copper based salts) and/or organic compounds [8]. The latter are frequently called ‘varnishes’ or ‘lacquers’, in the art-historical literature [6-7]. The ‘artistic’ coating can also be considered as a barrier against corrosion since it represents the real artwork surface and, as a matter of fact, the first part reacting with the agents of degradation. Its protective behaviour depends on its morphology (e.g. thickness, porosity, adhesion to the metallic substrate) and chemical composition, the metallic substrate peculiarities, the characteristics of the exposure environments (e.g. T, RH, presence of pollutants).

- Study of the corrosion processes

Corrosion is a natural process affecting every metallic artefact which tend to reach a stable state. The consequence of this process is the formation of different oxidation layers which are commonly called natural patinas [9]. Copper-based artefacts exhibit many types of patina layers – differing in morphology, chemistry and color – generally depending on the corrosive environments, exposition periods, chemical, physical and biological parameters influencing the phenomenon [10].

Recently archaeological objects have been extensively studied under the scientific point of view [9–10]. It is well known that on copper based alloys exposed to burial conditions stabilizations mechanisms leading to a steady state influence the patina composition of the object itself. Usually a full stability is reached in a relatively long period of time due to slower kinetics.

The present study was carried out using non-destructive analytical techniques as portative X-Ray fluorescence (XRF), Scanning Electron Microscopy coupled with an Energy Dispersive X-Ray Spectrometer (SEM-EDXS) and microRaman Spectroscopy (μRS) in order to explore the previous points of the alloy-patina-environment system.

References

Role of lead as a major alloying element in tin bronzes of archaeological and artistic interest

Justine Vernet¹ and Paolo Piccardo¹,²,³

¹ Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale (DCCI), via Dodecaneso 31, 16146 Genoa, ITALY. Tel. +39 010 353 6145, justine.vernet@yahoo.fr
² Consiglio Nazionale delle Ricerche (CNR), Istituto per l’Energetica e le Interfasi (IENI), Via De Marini 6, 16149 Genoa, ITALY
³ Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via G. Giusti 9, 50121 Florence, ITALY.

* justine.vernet@yahoo.fr, +39 010 353 6145

Keywords: leaded tin bronzes; castability; lead segregation; cooling rate; thermal dilatometric analysis; DTA

Bronze is a key material in the humankind technologic development and may be seen as a mirror of past civilisations and societies it has been through. Even with the large development of ferrous alloys during the 19th century, bronze keeps creating a strong fascination and its alloys are still widely used for special applications where all of their specific characteristics are required, especially for the great statuary.

The choice of an alloy composition for the production of objects mainly depends on the ease of the material to be manufactured and its compatibility with the future applications. Lead is a historic alloying element added to the composition of tin bronzes and it is recognized to increase the machinability and the castability of the alloy, particularly in the statuary field. However, due to the lack of effective scientific research on the effect of such addition on the castability of the alloy, those parameters remain under empirical appreciation of the founder and limit the understanding of ancient bronze objects, as well as the manufacturing technique used by contemporary artists. Moreover, the insolubility of lead in a Cu-Sn matrix leads to the formation of nodules in the principal matrix and implicates several issues for the representative characterization of the alloy through non-destructive and non-invasive analysis, in particular in the case of the monumental statuary. Finally, no study have yet investigate the influence of cooling rate on the Cu-Pb-Sn microstructure alloys.

The present study was carried on experimental ingots of leaded tin bronzes (Cu/Sn 90/10 by weight, and Pb from 1 to 10% wt.), casted in a first time in a cast-iron ingot mould for a higher cooling rate, in order to observe the size and the repartition of lead nodules in the ingot with the increasing of the element content.

A classical metallographic protocol has been established to characterize the ingot:
1) a macroscopic observation (Stereoscope) of the surface to establish a first visual link between lead content and casting quality

2) a macroscopic observation (Stereoscope) of etched transversal sections to identify the size of grains in different points along the median line of the ingot;

3) a microscopic observation (LOM-BF) of etched cross-sections to determine the lead nodules repartition;

4) a compositional analysis (SEM-EDXS) in order to design the concentration map of lead in the tin matrix.

Thermal dilatometric analysis have been carried out in order to estimate how the presence of lead is affecting the dimensional changes during cooling of an ingot. Metallographic characterization of cross sections in fixed positions of the ingot allowed to describe the solidification mechanisms according to the position on the mould. Differential Thermal Analysis at various cooling rate is used to draw the out of equilibrium diagrams for the CuSn10 (wt.%) alloy in order to set up a technique for further exploitation.

First results show that no direct relation can be drawn between increase of lead content and fluidity from the observation of cast defects (shrinkage, sprue exits, and porosity) from the macroscopic observations. However, a first tendency appears: as lead content increases, the texture of the alloy seems to become pastier and mould detail are better reproduced on the final ingot surface. In the first instance, it seems that the addition of lead in the bronze alloy bring a better filling of the mould, not by increasing the fluidity, but by better reproducing the superficial features of the mould. The dilatometric investigations are meant to understand if while cooling to room temperature the shrinkage of the alloy (CuSn10 wt.%) is affected by the presence of lead.

References:
On the degradation of plastic soldier toys at Oporto Military Museum

A. Pereira¹, A. Candeias¹², J. Mirão¹, P. Vandenabeele³, A.T. Caldeira¹*  

¹ HERCULES Laboratory, School of Science and Technology of Évora University, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal  
² José de Figueiredo National Conservation Restoration Laboratory, General Directorate for Cultural Heritage, Rua das Janelas Verdes, 1249-017 Lisbon, Portugal  
³ Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35, S-12, B-9000 Ghent, Belgium  

*atc@uevora.pt, +351 266 740 800  

Keywords: plastics, polymers and additives, NMR, reflectance FTIR  

Today, plastics, a mixture of polymers of high molecular weight and other substances added to improve their mechanical properties, are widely present in numerous modern art museum collections worldwide. Unfortunately, many man-made mouldable polymeric materials are relatively short-living compared to other materials found in historical collections, such as wood, stone, bone, paper and parchment. Whereas the ageing and degradation of a plastic artefact in non-museum circumstances can be tackled through replacement, degradation in a heritage context takes with it the importance of originality and cultural significance.

The visual changes in an artefact, such as deformation, shrinkage, the appearance of cracks and changes in colour and gloss, are usually only present in an object in an advanced stage of degradation. Once initiated, plastic degradation cannot be prevented, reversed or stopped, but sometimes it may be slowed down. This is achieved by ‘preventive or inhibitive conservation’ whereby contributing factors such as light, heat, humidity, oxygen and acids, are removed, or their level reduced from the vicinity of the objects.

The identification of materials in museum collections is of utmost importance for the conservators because it will improve the knowledge of the conservation conditions of the objects, especially when they have suffered degradation.

This research was prompted by an urgent call from the Oporto Military Museum regarding an accelerated severe degradation process of a set of soldier toys dating back to the middle of the 20th century, and presents a quick and non-destructive methodology, for the identification of polymers and their additives, on plastic artefacts in museums. NMR (Nuclear Magnetic Resonance) analyses of surface leachates together with reflectance FTIR (Fourier Transform Infrared Spectroscopy) and micro-XRD (X-ray diffraction) analyses of the objects surface allowed the full characterization of the structure of these materials and correct identification of each one. The NMR technique identified unequivocally a great number of additives, exceeding the Py-GC-MS destructive methodology in number and efficiency. Crystalline exudates were

²nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
confirmed by micro-XRD. Additionally, the reflectance FTIR provided exactly the same information of the destructive micro-FTIR about the polymer structure and confirmed the presence of some additives.

The soldier toys were correctly identified with this new methodology, as being made of plastics derived from cellulose acetate, with high amounts of the additive triphenyl phosphate.
The Euclidean distance tool as discriminator of very similar Raman spectra: application to pigment analysis in mixtures

A.R. de Torres and S. Ruiz-Moreno

Polytechnic University of Catalonia, Signal Theory and Communications Department, C/ Jordi Girona 1-3, 08034 Barcelona (Spain), Tel. +34 934016443, antonio.ramos@tsc.upc.edu, sruiz@tsc.upc.edu

Keywords: Raman spectroscopy; Pigments; Euclidean distance; Spectral discrimination.

In many experimental situations it is difficult to identify a pigment from its obtained Raman spectrum. A usual cause is the fluorescence due to the binders and varnishes, which could in many cases mask, partially or totally, any of the secondary bands of the spectrum. In addition, it may occur that two different pigments have located its respective fundamental band (perhaps the only recognizable) in a very close spectral position (differences about 1 or 2 cm$^{-1}$, for example). And, on the other hand, also one could face up a situation in which these pigments are mixed in a very fluorescence oil medium.

The main idea of the present work is to use the concept of Euclidean distance in order to discriminate in a mixture of pigments the fundamental band of each one when the experimental circumstances are difficult as exposed above. In the figure, as an example, the experimental case of a mixture composed of ultramarine blue and red lead is presented. The three spectra corresponding to the individual pigments and the spectrum of the experimental mixture are shown (see legend). By means of the Euclidean distance between the spectrum of the mixture and the individual spectra, calculated in the spectral region of interest (500 to 600 cm$^{-1}$), the fundamental bands of these pigments, located at 546 and 547 cm$^{-1}$ (blue and red, respectively), have been determined. In this communication, many experimental aspects and problems affecting to the spectral quality, as fluorescence shot noise and spectral resolution of monochromator among others, are investigated.
Elemental and molecular mapping of pigments in painted artworks

Sara Mosca¹, Roberto Alberti², Tommaso Frizzi², Valentina Capogrosso¹, Austin Nevin³, Gianluca Valentini¹ and Daniela Comelli¹

¹ Politecnico di Milano, Physics Department, Piazza Leonardo da Vinci, 32, Milano, Italy. Tel. +39 02 23996589, sara.mosca@polimi.it.
² XGLab Srl, Via Francesco D'Ovidio 3, 20131 Milano (Italy)
³ IFN-CNR, Piazza Leonardo da Vinci, 32, Milano, Italy.

* Sara Mosca, Email: sara.mosca@polimi.it, Fax: +39 02 23996126, Phone: +39 02 23996589

Keywords: X-ray fluorescence (XRF) mapping; Raman mapping; visible multispectral imaging; In-situ non-invasive analysis; Multivariate analysis.

We propose a completely non-invasive approach based on the combination of three highly-complementary imaging techniques, X-Ray Fluorescence (XRF) mapping, Raman mapping and visible multispectral imaging, for the identification and mapping of pigments in surface and hidden layers of a painting.

In our approach, macro-XRF mapping is performed through a new portable scanning device developed by XGLab SRL. The compact XRF head is driven by two light linear motors. The excitation, which is not guided by any X-ray optics, allows the acquisition of the fluorescence spectrum emitted with a good sensitivity also to lighter elements. The maximum scan-area depends on the tripod and motor arrangements, with typical values of 10 cm². Thanks to the high degree of penetration of the X-ray based technique, the XRF device allows the mapping of the spatial and sub-layer distribution of elements: taking advantage of the different absorption coefficient of the characteristic X-ray emission lines of a specific element [1-2], it is possible to differentiate X-ray emissions from different layers of a painted artwork. The attribution of a specific element to a certain layer of a painting is particularly effective when applied with a mapping or imaging device, since the provided spatial information is essential for detecting the morphology of hidden painted layers. The remote Raman spectrometer is a custom-made transportable system based on a 785 nm diode laser, a pair of galvanometric mirrors and a custom optical system. The device can easily map a surface of 9 cm² in diameter at a working distance of 30 cm [3]. Thanks to the larger spot size (0.5 mm) respect to the one achieved with the conventional Raman micro-probe, the surface receives a lower irradiance, reducing the risk of possible thermal damage, an issue of particular relevance for the analysis of fragile and thin painted artworks.

The visible multispectral imaging camera is based on a low-noise monochrome camera equipped with a liquid-crystal tuneable filter working in the spectral range between 400 and 720 nm.
The imaging technique, combined with novel methods of cluster analysis of multivariate spectral data, makes it possible to map areas of paintings with similar spectral features and color properties, which correlate with the presence of the same pigment or mixture of pigments. The two complementary mapping techniques (XRF and Raman), both in a macro scale, allow the acquisition of elemental and molecular data providing pigment identification with a high degree of confidence. Moreover, the integration of data from XRF and Raman spectroscopies is of great value also for the correct attribution of a pigment to a superficial or to a hidden layer since the two techniques are sensitive to different painted layers.

Examples of applications on model paintings (figure 1) and in situ case studies will be discussed. Advantages of this image-based multi-analytical approach will be discussed, thus informing future analysis on other heterogeneous works of art.

Figure 1. (a) Cluster analysis of a model painting on the basis of its visible multispectral dataset. The black square points out the areas analysed with the remote Raman mapping device. (b)-(c) Raman maps: spatial distribution of white lead (b) and cinnabar (c). Raman spectra of white lead (d) and cinnabar (e) related to the spatial distribution shown above.

References:
Visualization and quantification of weathering effects and water uptake processes in natural building stones by using neutron imaging

Germana Barone1, Paolo Mazzoleni1, Simona Raneri1*, Eva Rabot2

1 University of Catania, Biological, Geological and Environmental Science Department, Corso Italia, 57, 95129, Catania (Italy), +39 095 7195786, sraneri@unict.it.
2 Laboratoire Léon Brillouin (CNRS/CEA), CEA Saclay, 91191, Gif-sur-Yvette, Cedex (France)

* sraneri@unict.it, +39 095 7195786

Keywords: building stones; neutron radiography; Cultural Heritages; calcarenites; water capillary uptake; weathering; salt crystallization; imaging techniques.

Calcarenites are the most widely used natural building stones in Sicily. They are frequently subjected to very intense degradation due to salt growth [1, 2]. This process is often responsible for strong modifications of their pore network [3] and has a great influence in the mechanical properties and the durability of materials [4]. In addition, as water transport has a key role in the degradation processes, the quantification and visualization of fluid flow into the pore network of degraded stones represent useful tools in understanding the weathering process.

Classical approaches are usually performed by applying laboratory test routines for the determination of water absorption parameters. However, they cannot provide a description of the local distribution of water inside the stone. In this framework, neutron imaging has been demonstrated as a powerful technique for the visualization and quantification of the water distribution in partially saturated porous media [5]. Moreover, the possibility to perform dynamic measurements allowed monitoring the water uptake as function of time and to explore the complex processes involved in fluid transport [6-8].

In this study neutron radiography has been used with the aim of: a) monitoring and visualizing the fluid flow patterns inside porous structure of a local calcarenite widely used as building and replace stone in several Cultural Heritages, namely Sabucina Stone; b) quantifying the water distribution as function of time, in order to understand the effects of weathering on the behavior of the stone against water. In detail, samples of un-weathered and artificially weathered[9] Sabucina Stone have been scanned with neutron imaging technique at the IMAGINE beam line located at the Laboratoire Léon Brillouin (CEA/CNRS) in Saclay (France). Capillary water uptake has been monitored over time in samples subjected to different salt crystallization cycles.

Beside the qualitative data acquired from the raw neutron images (Figure 1(a)), quantitative results have been obtained thanks to the image processing of the radiographs (Figure 1(b)) [10]. First of all, the evolution of the wetting front position over time has been observed and the penetration coefficient has been determined. The results demonstrated that changes in the hydric properties of the stone occurred with the intensification of the degradation process. Even if a good agreement with standard
capillary absorption test has been obtained [11], the non-perfect linearity of capillary uptake process has been evaluated, due to the evidence of preferential flow paths. Therefore, neutron images have been processed in order to obtain quantitative water distributions as function of time. The contour plot of the water content value highlighted that degraded stones absorbed greater volumes of water than the un-weathered ones, due to the strong modification of their pore structure. Moreover, in weathered samples the quicker and deeper vertical spreading of the water was associated with an intense horizontal migration through pores enlarged by the degradation mechanisms. Finally, side effects, probably due to the more intense action of the degradation process close to the sample surface, were evidenced, determining different capillary absorption properties for the inner and surface regions. In conclusion, neutron radiography has allowed a better understanding of the deterioration mechanisms affecting physical properties of building stones, supplying relevant data for planning powerfully actions to improve their durability.

Figure 7. (a) Neutron radiographies and (b) water content distribution (WC%) as function of time and degradation degree in samples representative of un-weathered and weathered Sabucina stones

References:
Degradation Study of Plastic Materials Used in Contemporary Art by Non-invasive Portable Infrared Spectroscopy

Elettra Barberis\textsuperscript{1,2}, Marcello Manfredi\textsuperscript{1,2} and Emilio Marengo\textsuperscript{2}

\textsuperscript{1} ISALIT, Spin-off of Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale T. Michel 5, 15121, Alessandria (Italy), Tel. 00390131229332, e-mail address elettra.barberis@alice.it.
\textsuperscript{2} Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale T. Michel 11, 15121, Alessandria (Italy).

Keywords: Plastic degradation; Contemporary art materials; ATR spectroscopy; Surface analysis; Portable analysis

Today, artworks partially or completely made of plastic materials can be found in almost all international museums or collections. The deterioration of these objects is now becoming evident [1], mainly because these synthetic materials are not designed for a long life, and the characterization of their state of conservation may help curators and conservators.

ATR (Attenuated Total Reflectance) infrared spectroscopy, a well-established technique, is widely used for the analysis of cultural heritage materials and recently has been employed for the characterization of plastics used in contemporary art [2]. With the development of portable devices, the non-invasive analyses of artwork materials grew up: in this research we studied the degradation of plastic materials used in contemporary art by using a portable infrared spectrometer. Through the use of the non-invasive ATR device, we monitored the degradation of several plastics that were artificially aged in solar box, creating an infrared library of the conservation state of plastics. The database can be then used to understand how much degraded is a real artworks, helping in this way the work of conservators.

Several types of plastics, which include polypropylene (PP), polycarbonate (PC), polyurethane (PU), polyamide (PA) and some blends, were characterized with a portable ATR spectrometer by simply touching the plastic surface with the ATR crystal: in this way no sampling is needed keeping the method non-invasive. The samples were then degraded simulating about 200 years of museum light exposure. The ageing was monitored by ATR acquiring infrared spectra of the samples over the time.

In this research we investigated the applicability of a portable ATR for the non-invasive characterization and degradation monitoring of plastics used in contemporary art. This method can be very useful for taking care of artworks because is non-invasive and the analysis can be done directly in situ.

References:
Non-Invasive Material Analysis of Parchment Manuscripts by Reflection-FTIR, XRF and Raman – Possibilities and Limitations

Wilfried Vetter, Bernadette Frühmann, Federica Cappa and Manfred Schreiner

Academy of Fine Arts Vienna, Institute of Science and Technology in Art (ISTA), Schillerplatz 3, 1010 Vienna, Tel. +431588168614, w.vetter@akbild.ac.at

Keywords: non-invasive; manuscripts; parchment; reflection-FTIR, Raman, XRF; material analysis; mobile instrumentation;

Parchment manuscripts are an important part of the world’s cultural heritage and numerous objects were kept in libraries, museums and collections. Many of these are objects of research for several disciplines, for example philology, art history, archaeology etc. Moreover, conservators and restorers are concerned with manuscripts, as many show remarkable signs of wear and degradation. Although the scientific research questions or questions concerning strategies for action may vary for the disciplines mentioned, material analysis offers the potential to contribute to all in many ways. For example, the knowledge about the materials used for an object is important for the selection of adequate conservation/restoration strategies, whereas the characterisation of inks could be useful for an attribution of a text to a particular writer, which is a frequent question for philologists. For these reasons, the objective of our investigation was a comprehensive characterisation of the materials in the manuscripts studied with regard to the parchment support, inks and pigments as well as possible degradation products.

We used non-invasive reflection-FTIR (rFTIR) and XRF for the analysis of 18 codices and 12 fragments of various origin (Glagolitic, Greek, Cyrillic, Latin, Middle High German and Georgian) of the 6th to the 16th century. Additionally, a recently purchased Raman spectrometer was used to analyse five codices. The mobile instrumentation allowed on-site analyses in several libraries, where the objects were in a horizontal position during analysis. The diameter of the analysed area was 3 mm in case of rFTIR, 1 mm for XRF and < 1 mm for Raman.

From the rFTIR results obtained, we were able to differentiate parchment supports with various surface treatments, in particular chalk, which was used to whiten the surface, silicates, most probably deriving from polishing with pumice, calcium soaps from unclear origin and parchments without, or at least without remains of a surface treatment. On several parchments, evidence was found for oxidative degradation. An increased iron and/or copper content was frequently detected using XRF in black and brownish inks, which might be an indication for the use of iron gall ink. However, these results could not be proofed using rFTIR. In contrast, it was possible to identify iron gall ink with Raman spectroscopy. Calcium oxalate was detected frequently in areas with black and brown inks by rFTIR, which is most probably a degradation product of ink components due to microbial activity (mould...
fungi). The pigments identified in illuminations and initials include vermillion, minium, red iron oxide, orpiment, lapis lazuli, azurite, atacamite, green earth, umber and lead white. Concerning the green colorants, a clear identification by rFTIR was not possible in several cases, although copper was detected by XRF. Moreover, no evidence was found for the use of organic colorants, e.g. indigo. A protein binding medium was identified in combination with vermillion and orpiment by rFTIR in several cases, whereas the binder of other pigments could not be determined. XRF revealed further that gold and silver alloys were applied for illuminations. Moreover, rFTIR allowed to identify a gypsum layer as support for leaf gold and thus provided insight into the manufacturing technique of such decorative elements. Last but not least, a thin (invisible) layer of beeswax was detected on some folios in a religious manuscript, which may derive from reading in candle light.

We can conclude from the results of our studies that the use of complementary rFTIR, XRF and Raman enabled the non-invasive characterisation of several writing and painting materials in illuminated manuscripts. It was also possible to gain information about the production and use of the manuscripts and furthermore to identify degradation products.
A novel approach for characterisation of polymers in modern art conservation using Localised Thermal Analysis (LTA)

Donald Sale1, Angelica Bartoletti2, Marianne Odlyha3 and Laurent Bozec2

1 Art and Conservation Research, 78 Plimsoll Road, London, N4 2EE, +44(0)7960699936, donssale@gmail.com
2 University College London, Biomaterials and Tissue Engineering Department - Eastman Dental Institute, 256 Gray’s Inn Rd., WC1X 8LD UK
3 Birkbeck, University of London, Dept of Biological Sciences, Malet St London WC1E 7HX.

* donssale@gmail.com, angelica.bartoletti.12@ucl.ac.uk

Keywords: Localised Thermal Analysis; polymer; glass transition temperature

The conservation of modern art objects made of transparent thermoplastic materials presents a challenge to conservators. This is due to the differing sensitivities of the polymers present in the artworks, significant aesthetic constraints, and the ageing character of the polymers used as conservation adhesives and varnishes. The conservation resin mixture 1:1 Paraloid B-67 (PiBMA) / Paraloid F-10 (PnBMA) has many properties to recommend its use as a conservation adhesive, in media, and as a varnish for transparent PMMA architectural models, art and design. The polymers have a long history of study, and use in the past as a conservation varnish for paintings. The isomers have different molecular structures and glass transition temperatures (Tg), and combining them improves their working properties and bond strength. This BMA mixture has a good appearance due to the similar refractive indices to PMMA, its consistent surface wetting and saturation, and its resistance to yellowing, even when exposed to extreme environmental conditions. Importantly, the BMA mixture in specified aliphatic hydrocarbon solvents, has been proven to be safe to use without causing damage or stress-crazing to solvent sensitive PMMA following ASTM standard assessment procedures.

The aim of this study was to determine the glass transition temperature (Tg) of the BMA mixture and to investigate the impact of environmental conditions on the BMA mixture in order to evaluate its suitability and application for the conservation of contemporary art. To predict aging behaviour, samples of the BMA mixture were exposed to a range of artificial environmental conditions, and the samples were assessed and stored in the dark for future study. In this study a set of samples was prepared in collaboration with the Tate Conservation Dept. and their characterisation was performed in collaboration with the Getty Conservation Institute. The control samples were stored in dark ambient conditions, and were compared to those exposed to intense heat, museum light, and combinations of each. A set of samples was exposed to an equivalent dose of light in a museum window to investigate the impact of the spectral distribution of filtered sunlight, and daily cycles of different levels of light, heat and relative humidity. After 20 years of dark aging the samples were analysed using Fourier Transform Infrared (FTIR) Spectroscopy, Thermo Gravimetric Analysis (TGA), Pyrolysis Gas Chromatography.
Mass-Spectrometry (Py GC-MS), and Dynamic Load Thermal Mechanical Analysis (DL TMA). Moreover, Localised Thermal Analysis (LTA) has been used for the first time to characterise the thermo-mechanical properties at the nanoscale of these materials used in cultural heritage conservation. Measurements were performed with a Bruker thermal analysis accessory (VITA) used in conjunction with a Veeco diCaliber AFM. A VITA-HE-NANOTA-200A probe was used and calibrated for temperature by melting samples of known melting temperature (PLC, PE, PET). All the measurements were repeated at different locations (N=40) on the samples by applying to the probe a linear temperature ramp of 10°C/s from room temperature to 100°C. The application of this technique requires minimum sample preparation and can also be used directly on the sample.

In a previous unpublished study, $T_g$ measurements from the bulk sample were made by DL TMA analysis. The $T_g$ values of the aged BMA mixture were found to increase more in samples exposed to multiple environmental conditions involving partial doses of high heat (50%) combined with a partial dose of light (25%), or a full dose of light in a museum window (100%) with cycles of changing levels of filtered sunlight, temperature and humidity. With DL TMA the $T_g$ increased less in samples exposed to a continuous full dose of only heat (100%) or artificial museum light (100%). The changes in $T_g$ resulting from the aging conditions, are in agreement with research performed by other workers in relation to studies of varnishes for easel paintings conservation.

The clear advantage of using Localised Thermal Analysis is to obtain information on the changes occurring in the first few nanometres of the sample’s surface. Natural aging can cause localised regions with different degrees of crosslinking which can contribute eventually to differences in the appearance of objects. The application of the LTA technique allows mapping of the evolution of surface changes and contributes to a better understanding of the degradation initiated at the nano level.
Fast degradation and monitoring of arsenic sulfide pigments with Raman spectroscopy-electrochemistry

Marc Vermeulen1*, Jana Sanyova1, Koen Janssens2 and Karolien De Wael2

1 Laboratory of polychrome artifacts, Royal Institute for Cultural Heritage, Parc du Cinquantenaire 1, B-1000 Brussels (Belgium), tel. +32 2 7396848, email: marc.vermeulen@kikirpa.be
2 AXES Research Group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp (Belgium).

Keywords: Arsenic sulfides; Raman spectroscopy; electrochemistry; degradation

Since antiquity, semi-conductors such as vermilion (HgS), cadmium yellow and red (CdS and CdS,Se), titanium white (TiO2) or arsenic sulfides (As2S3/As4S4) appear to have been widely used by artists as pigments. Even though they are all semi-conductors, they present different behaviors toward light, some being more stable than others. It has recently been established that (in)stability of the pigments can be rapidly characterized by measuring their thermodynamic oxidation and reduction potential [1, 2]. This method does not require lengthy exposure of the pigments to (chemical or physical) degrading agents.

The arsenic sulfide pigments group (the yellow orpiment, As2S3 and red realgar, As4S4) appears to be part of the non-stable pigments, quickly degrading to arsenic oxide and arsenates upon light exposure [3, 4]. As the different forms of arsenic sulfides are excellent Raman scatters [5], their photo-oxidation can easily be monitored with the aid of Raman spectroscopy. Additionally, changes in photo-activity can be recorded via electrochemistry, and such measurements may be indicative of changes in the pigment structure. The Raman spectral data may help to better identify the chemical (redox) transformations that give rise to the photocurrent. The combination of an electrochemical setup and Raman spectroscopy appears then to be powerful combination to understand the rather complex photo-oxidation of arsenic sulfide pigments. Experiments conducted on natural commercially available pigments show that a short exposure to a green laser for a given period of time induces a degradation phase that is also recorded on naturally aged/degraded samples from an Egyptian canopic jar or an 18th-century French chinoiserie. A decrease in photo-current is also monitored which is most likely due to the transformation of arsenic sulfide into its oxidized form(s). This communication will present the results obtained for the fast laser-induced degradation of arsenic sulfide monitored with the tandem Raman spectroscopy-electrochemistry and compare the results with the naturally aged historical samples.

Acknowledgements
This work has been financially supported by the Belgian Science Policy Office (BELSPO) through the research program Science for a Sustainable Development – SDD, “Long-term role and fate of metal-sulfides in painted works of art – S2ART” (SD/RI/04A).

References
Poster session 2
Disclosing Van Eyck’s original paint layers on the Ghent Altarpiece by combined MA-XRF scanning and SEM-EDX analysis

Geert Van der Snickt¹, Hélène Dubois², Jana Sanyova², Alexia Coudray², Cecile Glaude², Stijn Legrand¹ and Koen Janssens¹

¹ University of Antwerp, Department of Chemistry, AXES research group, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
² KIK-IRPA, Jubelpark 1, 1000 Brussels, Belgium

In 2012, the first phase of a long-awaited comprehensive conservation campaign on Van Eyck’s Ghent Altar Piece was initiated. This first phase focuses on the verso side of the panels and will run until 2018. Prior to and during the actual treatment, the panels of this renown polyptych were subject to extensive research. Although conservation text-books invariably stress its importance, the added value of an integrated, interdisciplinary study is not always crystal clear to decision makers and therefore often not comprehensively pursued. In this case, the combined efforts of numerous scientist and scholars have a straightforward and far-reaching impact on the conservation strategy.

In this poster we present the insights obtained by combining Macro X-Ray Fluorescence (MA-XRF) scanning and measurements performed by means of a Scanning Electron Microscope equipped with an Energy Dispersive X-ray spectrometer (SEM-EDX) on cross-sectioned samples. Combination of the first, non-invasive chemical imaging technique with the spot analyses of the latter provided unambiguous proof of a daring hypothesis that was formulated by the team of conservators, early in the treatment process. By presenting compositional information from the entire paint surface in a visual manner, the MA-XRF images visualised how the composition was largely overpainted during a previous intervention, to an extent that had never been suspected. Moreover, the ensuing elemental distribution maps allowed assessing the condition and superior quality of the overpainted scenes.

Although the surface painting closely follows the forms and volumes of Van Eyck’s hidden original layers, the scans reveal a comparatively more contrasty composition with a more elaborated gradation of tones and additional highlights. The elemental maps provided an additional clue by revealing distinct lacunae in areas where the painting presents a pristine surface. Visualisation of these sparse defects indicated that the overpainted scenes were in a relatively good condition, a finding that strongly sustained the pending choice for uncovering the original paint. SEM-EDX on paint cross-sections appeared indispensable for obtaining more precise information on the layer build-up. Apart from supplementary detection of elements with low atomic number for which MA-XRF is insensitive, SEM-EDX allowed situating the detected MA-XRF signals within the paint stratigraphy, thus permitting a more accurate interpretation of the distribution maps.
Nanoscale structures of fossil bones and growth processes for burned bones

Giampaolo Piga1*, Maria Dolors Baró2, Irati Golvan Escobal2, Antonio Brunetti1, Stefano Enzo3, Sebastiano Garroni3

1 Department of Political Science, Communication, Engineering and Information Technologies, University of Sassari. Viale Mancini 5, I–07100 Sassari (Italy).
2 Departament de Física, Universitat Autònoma de Barcelona (UAB), E-01893 Bellaterra (Spain).
3 Department of Chemistry and Pharmacy, University of Sassari. Via Vienna 2, I–07100 Sassari (Italy).

* corresponding author: Dr. Giampaolo Piga, giapiga@uniss.it, +393407840935

Keywords: burned bones; fossil bones; X-ray fluorescence; TEM imaging; X-ray Diffraction (XRD).

Bones and teeth are often the only direct remains of animals and humans and hence represent valuable archives for a number of disciplines such as: Biomedicine, Archaeology, Forensic Sciences, Anthropology and Paleontology.

A number of different factors can alter this mineral composition. One of the more significant changes to the microstructure of bone (i.e. to its spatial extension) occurs when this material is heated. Heated bone is one of the most challenging osteological materials to study, since the process of heating produces a range of complicated changes within the material already complex by itself.

Severe changes involving the structure and chemical composition of bones may also occur during the fossilization process. In this study we present a combined investigation by X-ray fluorescence (XRF), TEM imaging and powder X-ray Diffraction (XRD), supplemented with the Rietveld analysis, conducted on recent, burned and fossil bone specimens from present time and back to Middle Triassic age to (around 245 Ma) assess the nanoscale structures to which bioapatite mineral may be subjected.

References
Non invasive archaeometrical studies by new portable hybrid energy dispersive x-ray diffraction and x-ray fluorescence system

Ariadna Mendoza Cuevas¹,², Jorge Fernandez-de-Cossio Dorta-Duque³, Federico Bernardini¹

¹ International Center for Theoretical Physics, Strada Costiera 11, Trieste 34 151 (Italy) 39 040 2240 11, ari.mendoz0@gmail.com
² Havana Historian’s Office, Archaeometry Laboratory., San Ignacio y Obispo Habana Vieja, Habana 10 100 (Cuba)
³ Center for Genetic Engineering and Biotechnology, Bioinformatics Department, Ave. 31 e/ 158 y 190 Playa, Havana 11 300, Habana (Cuba)

* ari.mendoz0@gmail.com, 39 040 2240 11

Keywords: X-ray fluorescence; X-ray Diffraction; Non-invasive

A portable X-ray diffraction (XRD) and X-ray fluorescence (XRF) system, based on energy dispersive detection (ED XRD-XRF) in reflection mode, has been developed for the non-invasive analysis of artworks and archeological artifacts [1]. This analytical system is an open-work platform based on a low-power miniaturized X-ray tube (Ag or Pd anode) and a single Si-drift detector. ED XRD-XRF apparatus can be improved by multiple angle scanning implementing a hybrid system that take advantage of shorter acquisition time and higher energy penetration in EDXRD, and of higher inter-planar distance resolution in ADXRD. Methods for data processing at low energy range use 3D (intensity, energy and angle) data showing Iso-d curves, a hybrid diffractogram and corrections of line shifts due to different positioning of the irradiated spot on the cultural heritage object [2].

Some Archaeometrical studies that require combined non-invasive XRF-XRD analysis demonstrate the analytical performance of described portable system. XRF-XRD characterization of ancient pigments in paintings and identification of jadeite-jade in ‘green stone’ archaeological artifacts are discussed.

References:
A combined approach for the identification of handwritings in paper documents: the case of Antonio Stradivari’s relics

Giusj Valentina Fichera¹, Piercarlo Dondi¹, Maurizio Licchelli¹², Luca Lombardi³, Fausto Cacciatori⁴, Marco D’Agostino⁵ and Marco Malagodi¹⁵

¹ University of Pavia, Arvedi Laboratory of Non-Invasive Diagnostics, Via Bell’Aspa 3, 26100 Cremona (Italy), Tel. +39 0372 567770, e-mail giusj.fichera@unipv.it.
² University of Pavia, Department of Chemistry, Via Taramelli 12, 27100, Pavia (Italy).
³ University of Pavia, Department of Electrical, Computer and Biomedical Engineering, Via Ferrata 5, 27100 Pavia (Italy).
⁴ Fondazione Museo del Violino Antonio Stradivari, Piazza Marconi 5, 26100 Cremona, (Italy).
⁵ University of Pavia, Dipartimento di Musicologia e Beni Culturali, Corso Garibaldi 178, 26100 Cremona (Italy).

Keywords: inks; handwritings; writer identification; XRF; metal impurities; image analysis; Stradivari

The present contribution concerns the study of the Antonio Stradivari’s handwritings held in the Museo del Violino in Cremona. A considerable number of those relics consists of paper models, which contain indications and technical notes of the great luthier. After Stradivari death (first half of the 18th century), over the centuries, the collection underwent several cataloguing carried out by different owners. New annotations and handwritings added to the original relics, often imitating the Stradivari handwriting, represent a limit in the identification of the original documents for the curators. Attributions have been made until now just on the basis of the paleographic examination [1]. However this kind of study takes a lot of time to be performed and also requires a deep knowledge of the main features of Stradivari’s handwriting.

In this work we propose a new approach to solve the problem by the simultaneous use of image elaboration and of X-Ray Fluorescence (XRF) spectroscopy analysis (Fig. 1): the former provides a fast and automatic screening of the documents; the latter analyzes the elemental composition of the inks [2]. The handwriting recognition and identification is a well known task in image analysis [3], but it was rarely used in the field of historical documents. In the current case, palaeographic studies have identified some characteristic letters in Stradivari’s handwriting [1]. Starting from this sample set, we chose some of the most frequent letters as a target for our recognition algorithm, based on a variation of a classic template matching. The procedure segments the writings, normalizes the data, with respect to scale and rotation, and selects the regions with a higher similarity. Even if this method is very fast and can provide a rapid classification of paper relics, it can produce false positive detections in case of imitators of the original Stradivari’s handwriting or false negative in case of discoloured or damaged writings. In these situations XRF spectroscopy can be very helpful. Determination of transition metals and of their concentration ratios is a common method to characterize historical inks, in particular the iron-gall ones. It is well known that historical metal-gall inks often contain traces of metal ions other than iron, which could be important parameters to assess the inks composition [4]. Specifically, the ratios
between iron and other metals (such as Fe/Cu, Fe/Zn and Fe/Ni) could be used as “fingerprint information” to identify a specific handwriting and distinguish it from others. In this work several handwritings have been analysed by XRF spectroscopy using as references different inks belonging to handwritings certainly attributed to Stradivari. Obtained results have been clustered in different groups in function of their elemental composition.

The proposed approach provided good results compared to all the relics set analysed: it showed that more than 60% of the relics could be attributed to Antonio Stradivari.

Fig.1 - Example on relic MS234: original document (bottom left), letters detection (top) and one of the most representative spectra obtained by XRF analysis of ink (bottom right).

Acknowledgements: We would like to thank the “Fondazione Antonio Stradivari Museo del Violino” of Cremona for the collaboration and availability to improve this research. We are grateful to the “Fondazione Cariplo” for the financing of the research activities.

References:
Evaluation of the Protective Capacity of Coatings on Silver Foil Exposed to H₂S, HCl and H₃CCOOH as a Model for the Ghent Altarpiece Gilded Frames

Anastasia Rousaki¹*, Peter Vandenaeele², Jana Sanyova³, Hélène Dubois³,4 Luc Moens¹

¹ Ghent University, Department of Analytical Chemistry, Krijgslaan 281, S12, B-9000 Ghent, Belgium.
² Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium.
³ Royal Institute for Cultural Heritage-KIK/IRPA, Polychrome Artefacts Laboratory, 1, Parc du Cinquantenaire, 1000 Brussels.
⁴ Ghent University, Department of Arts, Sint-Pietersnieuwstraat 41, B-9000 Ghent, Belgium.

* Anastasia.Rousaki@UGent.be, Raman@UGent.be

**Keywords:** silver; corrosion; Raman spectroscopy; Ghent Altarpiece; tarnishing; varnish; hydrogen sulphide

Protecting the silver gilding foil from the original frames of Ghent Altarpiece, is a major conservation issue for the preservation of this magnificent polyptych. During the present conservation campaign, conducted by the Royal Institute for Cultural Heritage (KIK-IRPA), the silver gilding is cleaned from additional overpainting in order to recover the original polychromy. The coloured glazes originally coating the silver foil are still present but both are degraded and abraded. The scientific question, relating to the exposure of the polychromy to the air, is which varnish coating could best protect the silver foil from atmospheric pollutants and corrosion. However, the selection of the varnish is not only determined by its protective capacity, but also by its stability, its appearance, the requirement for reversibility, etc.

In the concept of this particular project, an extended literature research has been performed on silver corrosion. Hydrogen sulfide (H₂S), carbonyl sulphide (COS), ozone (O₃), particulate chlorine and hydrogen chloride (HCl) all influence silver corrosion rate¹,². Some other pollutants that could be present in indoor environments are acetic (H₃CCOOH) and formic (HCOOH) acid, sulphur dioxide (SO₂), nitrogen dioxide (NO₂), formaldehyde (CH₂O), ammonia (NH₃) etc. Though there is literature on experimental silver corrosion, mostly concerning outdoor environments and/or uncoated silver, the corrosion of coated silver for indoor purposes is less studied and concerns massive silver objects rather than silver foil²,³,⁴. The aim of the current research is to investigate the protective capacity of five different varnishes on silver foil. Their selection was based on conservation practice and literature. The results of this work will be taken into account when selecting the protective coating for the frames of Ghent Altarpiece.

Glass slides were brushed with one stroke of varnish under investigation. Silver foil was adhered on top. The samples were left to air-dry for one day and the same varnish was applied on top of the foil. The protective capacity of the varnishes was tested in three different
environments (hydrogen sulphide (H₂S), acetic acid (H₃COOH) and hydrochloric acid (HCl)) in laboratory desiccators, in darkness. After exposure, the samples were left to air-dry for one week and subsequently analysed, to track the corrosion products.

Figure 1: Pictures of the custom-made sample holder and the desiccator containing acetic acid environment.

Acknowledgements

The authors thank Ghent University for its financial support through the concerted research actions (GOA) programme.

References:

The first look is never the true look – the comparative study of six Portuguese 16th century illuminated Charters based on spectroscopy and chemometrics analysis

Catarina Miguel\textsuperscript{1*}, Cristina Dias\textsuperscript{1,2}, Teresa Ferreira\textsuperscript{1,2} and António Candeias\textsuperscript{1,2}

\textsuperscript{1} Laboratório HERCULES - Universidade de Évora. Largo Marquês de Marialva, 8, 7000-809 Évora (Portugal).
\textsuperscript{2} Departamento de Química, Escola de Ciência e Tecnologia, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671 Évora (Portugal).

* cpm@uevora.pt

Keywords: Charters; illuminations; spectroscopy; chemometrics

During the 16\textsuperscript{th} century the Portuguese King D. Manuel I (1469-1521) undertook the reform of the Charters of the Cities and Villages of the Kingdom. Although the productions of the texts were of the competence of the authorities of the kingdom, the local authorities should financially support the production of the Charters and of its illuminations. In this sense, a comparative study of the materials and paintings techniques of these illuminated manuscripts strongly reflects the cultural, political and financial capabilities of each City and Village at the time of its production.

The comparative study based on spectroscopic analysis of the materials used to produce six manueline Charters (the Charters of Alcochete, Terena, Alandroal, Marvão, Lousã and Évora) highlighted interesting differences between them, namely the use of different pigments and colourants (such as the presence of different green and yellow pigments and the use of indigo restricted to the Charter of Évora) and of different paints formulations. The results obtained by \textsuperscript{\textdagger}FTIR, \textsuperscript{\textdagger}Raman, XRF and SEM-EDS where analyzed following a chemometric approach, reflecting interesting fingerprints for its productions. Py-GC-MS corroborated these new findings. Besides the production of the illuminated paints, the analysis of the inks and of the writing over-layers enabled to establish the modus operandi for producing the manueline Charters. With these new and revealing findings it was changed the Art Historian perspective for the production of the Portuguese manueline Charters during the Renaissance period.
Figure 1. The comparative study of six Portuguese 16th century illuminated Charters based on spectroscopy and chemometric analysis: a) The charter of Évora (1501), b) μ-Raman analysis of the Charter of Terena (1514) and c) XRF analysis of the Charter of Alcochete (1515).

References:
**Bright reds... or not so bright – the degradation of vermilion reds on medieval illuminations from Alcobaça, Troyes and the Vatican collections**

**Catarina Miguel**1*, Cristina Dias1,2, Maria Luísa Carvalho3,4 and António Candeias1,2

1 Laboratório HERCULES - Universidade de Évora. Largo Marquês de Marialva, 8, 7000-809 Évora (Portugal).
2 Departamento de Química, Escola de Ciência e Tecnologia, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671 Évora (Portugal).
3 Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica (Portugal).
4 LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal.

*cpm@uevora.pt

**Keywords:** Vermilion; illuminations; spectroscopy; degradation

Medieval illuminated books are among the most important testimonies of medieval culture and knowledge. During the medieval period, the Cistercian order placed an important role on the development of the cultural, political and the knowledge of Europe. In Portugal, the first Cistercian monastery was funded in Alcobaça (in 1153) and was affiliated with the Mother-abbey of Clairvaux. Despite the instructions of Saint Bernard rule for the use of monochromism on the production of illuminated manuscripts, Alcobaça presents illuminations with a considerable range of colours. On the other hand, on the manuscripts from Clairvaux, nowadays belonging to the Bibliothèque du Grand Troyes collection, only the red or blue colours were used. Enforcement of the Saint Bernardo rule was also found in the Cistercian manuscripts preserved at the Biblioteca Apostolica Vaticana.

The study of a set of 11th-13th century manuscripts from Alcobaça, Troyes and the Vatican collections evidenced the presence of a dark-purple-iridescent degradation on some of the vermilion-based paints; while others (sometimes in the same manuscripts or even in the same folium) do not present evidences of degradation. The materials (pigments, binders and extenders) and the degradation products of the red paints present in a selection of manuscripts from these three collections were characterized by portable-Raman, portable-FTIR, XRF, FORS, SEM-EDS and □-XRD analysis, with the aim of characterizing the degradation mechanisms that are occurring in these vermilion-based paints. Historical accurate reconstructions based on the obtained results and on medieval treatises were produced and accelerated aged for supporting the study of the degradation mechanisms. By completely understanding all these parameters, we aim to propose long-term effective restoration and preservation procedures, to ensure its visual and meaning readability for the next generations.
Figure 1. Details of red paint degradations found in an illumination from Alcobaça 420, f.73 (Legendarium, 12th-13th century). Photos © BNP.

References:
**Monitoring of penetration depth of consolidants applied to carbonate and silicate substrates by Raman and FTIR spectroscopy**

*Lea Legan*\(^1\)*, Klara Retko\(^1,2\), Tanja Špec\(^1\), Polonca Ropret\(^1,3\), Luka Škrlep\(^1\), Andreja Pondelak\(^4\), Andrijana Sever Škapin\(^4\)

\(^1\) Research Institute, Conservation Centre, Institute for the Protection of Cultural Heritage of Slovenia, Poljanska 40, SI-1000 Ljubljana (Slovenia), 0038612343170, lea.legan@zvkds.si
\(^2\) University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, SI-1000 Ljubljana (Slovenia)
\(^3\) Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Rd., Suitland, MD, 20746 (USA)
\(^4\) Slovenian National Building and Civil Engineering Institute, Dimičeva 12, SI-1000 Ljubljana (Slovenia)

* Corresponding author: lea.legan@zvkds.si

**Keywords:** penetration depth; carbonate-forming consolidant; silicate-forming consolidant; micro-Raman spectroscopy; FTIR spectroscopy

Conservation of immovable cultural heritage assets often comprises an application of consolidants and protective coatings. The selection of appropriate consolidant should be carefully made and it should be based on previously performed analyses, which reveal the intrinsic substrates’ properties, as well as chemical and/or physical properties of the consolidating material itself. The appropriate penetration depth is one of the criteria to consider the consolidation process as successful, otherwise, there is a risk of further degradation of priceless cultural heritage objects\(^1,2,3\).

This work aimed to research the penetration depth of newly developed consolidants under the framework of HEROMAT FP7 project. It was performed on two different carbonate and silicate model substrates, *i.e.* render and stone, respectively, which mimic the composition and structure of building materials at baroque Dornava Manor in Slovenia. The surface of the render model substrate was treated with three different carbonate forming consolidating products (namely CFW, CF1 and CF2), while the TEOS-based consolidant CF4 was applied on the surface of the silicate stone substrate. Furthermore, the penetration depth of consolidants was investigated also in relation to different application techniques (brush, airless spray, roller, cellulose pulp), which are usually employed in restoration treatments or refurbishment of buildings. This allowed the study of the effectiveness of most common application methods. Micro-Raman and micro-Fourier transform infrared spectroscopy (FTIR) spectroscopy were determined as promising methods for monitoring of penetration depth of carbonate and silicate forming consolidants applied to carbonate and silicate substrates, respectively. For the investigation of the penetration depth of carbonate-forming consolidants, the indicator sodium nitroprusside (5% water solution) was applied over the area of the penetration...
depth profile of render substrate. The subsequent Raman analysis allowed a more precise assessment of the occurrence of the consolidant within the carbonate substrate. It was demonstrated that the penetration depth can be controlled by the selection of the appropriate application method. In the case of application of consolidant in the cellulose pulp, the time of application plays a crucial role. The method of application can therefore be adjusted according to the damage of the object, i.e. to consolidate only the surface or also the bulk.

Acknowledgements:

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°282992; project acronym: HEROMAT; project title: PROTECTION OF CULTURAL HERITAGE OBJECTS WITH MULTIFUNCTIONAL ADVANCED MATERIALS; coordinator: Faculty of Technology, University of Novi Sad, NoviSad, Serbia; research area: ENV-NMP.2011.3.2.1-1 Development of advanced compatible materials and techniques and their application for the protection, conservation and restoration of cultural heritage assets; type of funding scheme: SME targeted Collaborative Project; web address: http://www.heromat.com/

References:
Non-destructive Raman investigations on wall paintings at Sala Vaccarini in Catania (Sicily)

Germana Barone1*, Danilo Bersani2, Alessia Coccato3, Debbie Lauwers4, Paolo Mazzoleni1, Simona Raneri4, Peter Vandenabeele3, Davide Manzini5, Giuseppe Agostino6, Nicola Francesco Neri6

1 University of Catania, Department of Biological, Geological and Environment Sciences, Corso Italia, 57, 95129, Catania (Italy), gbarone@unict.it, +39 095 7195742
2 University of Parma, Physics and Earth Science Department, Parco Area delle Scienze, 7/a, 43124, Parma (Italy)
3 Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35, B-9000, Ghent (Belgium)
4 Ghent University, Department of Analytical chemistry, Krijgslaan 281, B-9000, Ghent (Belgium)
5 Madatec S.r.l., Via Montegrappa, 18, 20060, Pessano con Bornago, Milano, Italy
6 Superintendence of Cultural Heritage of Catania, Via Luigi Sturzo, 62, 95100, Catania (Italy)

* gbarone@unict.it, +39 095 7195742

Keywords: pigments; Raman spectroscopy; portable equipment; restoration works; Sala Vaccarini Catania

In the framework of the restoration works carried out under the supervision of Superintendence of Catania at the Libraries “Civica and A. Ursino Recupero”, part of the 16th century monumental complex of Benedictine Monastery (Catania, Sicily), an archaeometrical investigation of the Sala Vaccarini wall paintings has been carried out.

Sala Vaccarini is one of the historical Libraries of the Benedictine Monastery and preserves unique manuscripts collected by the monk Niccolò Riccioli e Paternò (1695-1783), who financed the realization of the Monastery Libraries. It was built by the architect Giovanni Battista Vaccarini in 1773, during the reconstruction works performed after the 1693 earthquake that partially destroyed the city of Catania. The well-known Sicilian painter Giovan Battista Piparo (1730-1754), who realized splendid medallions representing the Virtues, the Arts (Figure 1 (a)) and the Sciences, decorated the vaults of the library.

In view of the exceptional value of these wall paintings, a campaign of in situ measurements has been performed in order to investigate aspects as pigmenting agents, preparation layers and deterioration processes. In detail, spectroscopic analyses by using portable Raman equipment have been performed, considering the effectiveness of the method in characterizing pigments in non-destructive and non-invasive way [1-5] and the availability of a large number of databases for the identification of ancient and modern pigments [6-9]. Raman spectra were collected by a portable EZRAMAN-I-DUAL Raman system (Enwave Optronics, Irvine CA, USA) equipped with a near-infrared diode laser (785 nm) and a green Nd:YAG laser (532 nm), and a BWTek instrument equipped with 1064 nm line. Finally, additionally measurements have been
carried out on small fragments sampled from the vaults by using the laboratory micro-Raman apparatus Jasco NRS-3100, equipped with laser excitation sources at 785 nm and 532 nm.

The obtained results (Figure 1(b)) allow us to achieve a complete characterization of the pigments used in the paintings of the vaults, supplying fundamental information to the restorers, useful for planning appropriate conservation and preservation actions. Moreover, the campaign offered the possibility to compare the efficiency of different laser lines in both portable and laboratory Raman spectrometers.

![Figure 1](image)

**Figure 1.** (a) An exquisite example of the wall paintings analysed at Sala Vaccarini (Catania) and (b) Raman spectra collected by 1064 nm line on red and black pigments, as examples.

**References:**
Light, Shadows and Surface Characteristics.
The Multispectral Portable Light Dome

Lieve Watteeuw 1*, Hendrik Hameeuw 1,3, Bruno Vandermeulen 1, Athena Van der Perre 1,3, Vanessa Boschloos 3, Luc Delvaux 3, Marina Van Bos 4, Marc Proesmans 2, Luc Van Gool 2

1 KU Leuven, Faculty of Arts, Blijde Inkomststraat 21, 3000 Leuven (Belgium), 2 KU Leuven, VISICS, ESAT/PSI, Arenberg 10, 3001 Leuven (Belgium). 3 Royal Museums of Art and History (RMAH), Antiquity department, Jubelpark 10, 1000 Brussels (Belgium). 4 Royal Institute for Cultural Heritage, Jubelpark 1, Brussels (Belgium).

* Lieve Watteeuw, tel.: 0032 486834285, lieve.watteeuw@arts.kuleuven.be

Keywords: multispectral imaging; photometric stereo; conservation; (mobile) documentation; non-invasive techniques; art-technical studies

The interplay of changing light directions and shades play a central role for an examiner to explore and understand the material characteristics of a surface. A researcher or restorer/conservator is in the first place trained to apply this with the naked eye using white (VIS) light. Since several decades multispectral imaging (UV, IR and near-IR) has proven its value for the field of cultural heritage studies, especially as one of its main advantages lies in the non-invasive / non-destructive character of this approach. In art technical research, conservation science and archaeology, applying these different spectra enables a precise examination and identification of colours and pigments, the visualisation of underlying features, and the identification of varying materials or surface conditions. A shortcoming of these approaches, however, is the absence of geometrical information on the surface in these datasets and the user-friendliness of their acquisition and viewer systems.

Within the framework of the research projects RICH (University of Leuven) and EES (Royal Museums of Art and History, Brussels), a multispectral, multi-directional, portable and dome-shaped acquisition system has been developed in collaboration with the ESAT-VISICS research group of the University of Leuven. This Multispectral Portable Light Dome (PLD) consists of a hemispherical structure, with an overhead camera and LEDs emitting in five different parts of the electromagnetic spectrum, ranging from ultraviolet over visible to infrared light, regularly covering the dome’s inside surface. With the associated software solution, virtual relighting and enhancements can be applied in a real-time, interactive manner. The dome extracts genuine 3D and shading information based on the principles of photometric stereo. This innovative approach allows for instantaneous alternations between the computations in the IR, R, G, B and UV light spectra. All visualization modes are based on a single recording procedure, taking only a few minutes. They enable the detection of object surfaces even when difficult to access, the generation of
2D+ models, and the life-like or visually enhanced interaction with the recorded artefact. This leads to a user-friendly and cost-effective methodology, applicable to a wide variety of heritage objects.

The MS system has been used by the RICH and EES projects for the research on medieval manuscript illuminations and fragile Egyptian objects. Imaging the characteristics of the undulating parchment, the pictorial layers, the laid gold, the faded inscriptions and the tactile characteristics of the art and physical objects reveals to scholars and conservators the ‘hand’, the techniques and the materials of the original artists and artefacts. Preliminary results have shown this system can 1) document and measure the 3D surface structure of the objects, 2) the sequence of the writing, 3) the underdrawing, 4) the preparation of gilded layers, 5) the brushstrokes applying the different mineral and organic materials, 6) the finishing of the pictorial touch with glazes and pen work, 7) re-visualize faded pigments and inscriptions, 8) examine the MS results in combination with the actual relief characteristics and properties of the physical object. Besides supporting questions of attribution, changes and decay of the material characteristics can be monitored, supporting decision-making in the conservation protocol.

The case-study of “The daughters of the Emperor Ferdinand I” by Jakob Seisenegger, in Trento (Italy): analytical hygro-mechanical results as a support in risk assessment for technical interventions

Paolo Dionisi-Vici 1, Francesca Raffaelli 2 and Alberto Finozzi 3

1 IVALSA-CNR, Via Biasi 75, 38010 San Michele all’Adige (TN), Italy, +393296116816, paolo.dionisivici@gmail.com
2 Soprintendenza per i Beni Storico Artistici della Provincia Autonoma, Via S. Marco 27, Trento, Italy
3 Free-lance conservator, Via Giuseppe Mazzini 43, Schio (VI), Italy

Keywords: Long-term monitoring; hygro-mechanical response; EMC; stiffening elements.

In this paper we describe a long-term monitoring experience on a Panel Painting, carried out using a whole set of analytical tools before the scheduled conservation intervention.

The object under analysis is a painting of the XVI century, “The daughters of the Emperor Ferdinand I” by Jakob Seisenegger, painted around 1543 and preserved in the storerooms of the Superintendency of the Trento Province and of pertinence of the Buonconsiglio Castle.

The wooden support is built in a particular way: many narrow planks of pear wood were used, and some degradation evidences are visible, caused by the previous storing conditions and by old strong conservation interventions, when the present battened cross-beams structure was applied.

The panel painting has been monitored for some years both from the physical and mechanical point of view in its storeroom, climatically uncontrolled for most of the time, using:

- displacement transducers, put in different positions, relevant from the structural point of view;
- micro-climatic monitoring (Temperature and Relative Humidity);
- mass variation monitoring with an innovative differential scale able to measure the variation with an otherwise impossible resolution.

In the last year a specific test has been devised and performed in a tightly controlled environment, with predetermined cycles simulating a weekly fluctuation.

The results of the monitoring have been used to provide the experimental tendencies of the painting as a support to define the mechanical parameters for the design of the stiffness of the new crosspieces that will be applied to the panel and for the definition of the acceptable fluctuations of the microclimate of the exhibiting site.

This research has been performed in collaboration with the Department of Culture of the Autonomous Province of Trento.
Development of a translation stage for in situ non-invasive analysis and high resolution imaging

David Strivay\textsuperscript{1,2}, Mathieu Clar\textsuperscript{1}, Said Rakka\textsuperscript{1,2}, François-Philippe Hocquet\textsuperscript{1,2} and Catherine Defeyt\textsuperscript{1,2}

1 Université de Liège, Spectroscopie Atomique et Nucléaire, Archéométrie, Sart Tilman B15, 4000 Liège (Belgium), Tel. +3243663695 (corresponding author), dstrivay@ulg.ac.be (corresponding author).
2 Université de Liège, Centre Européen d’Archéométrie, Sart Tilman B15, 4000 Liège (Belgium).

* dstrivay@ulg.ac.be, +3243663695/+3243662884

Keywords: translation stage, technical development, XRF, high-resolution imaging, automatic acquisition

Non-invasive imaging techniques and analytical instrumentation for cultural heritage object studies have undergone a tremendous development over the last years. Many new miniature and/or handheld systems have been developed and optimized. Nonetheless, these instruments are usually used with a tripod or a manual position system. This is very time consuming when performing point analysis or 2D scanning of a surface.

The Centre Européen d’Archéométrie (CEA) has build a translation system made of pluggable rails of 1 m long with a maximum length and height of 3 m. Three motors embedded in the system allow the platform to be moved along these axis, toward and backward from the sample. The rails hold a displacement system, providing a continuous movement. Any position can be reached with a reproducibility of 0.1 mm. The displacements are controlled by an Ethernet connection through a laptop computer running a multiplatform homemade software written in JAVA. This software allows a complete control over the positioning using a simple, unique, and concise interface. Automatic scanning can be performed over a large surface of 3 meters on 3 meters. The Ethernet wires provide also the power for the different motors and, if necessary the detection head.

The platform has been originally designed for a XRF detection head (with its full power alimentation) but now can accommodate many different systems like IR reflectography, digital camera, hyperspectral camera, Raman probes, etc. The positioning system can be modified to combine the acquisition software of the imaging or analytical techniques and the positioning software.
Restoration of a broken statue: reassembling of two stone parts coming from St. John church in Asti

Serena Di Gaetano¹, Nicola Amapane², Fabrizio Crivello³, Anna Piccirillo⁴, Tommaso Poli⁵, Laura Porcu⁶, Maria Concetta Capua⁷

¹ Musei Vaticani, Laboratory of Restoration of Marble and Casts, vialle Vaticano 00165, Roma (Città del Vaticano), tel. 346-3030411, mail adress serenadigaetano6@gmail.com
² Università degli Studi di Torino, Department of Physics, via Giuria 1, 10125, Torino (Italy).
³ Università degli Studi di Torino, Department of Historical Studies, Palazzo Nuovo, via S. Ottavio 20, 10124, Torino, (Italy).
⁴ Centro Conservazione e Restauro, LaboS, via XX Settembre 18, 10078, Venaria Reale, (Italy)
⁵ Università degli Studi di Torino, Department of Chemistry, via Giuria 7, 10127, Torino, (Italy).
⁶ KIK-IRPA, Parc du Cinquantenaire 1, B-1000, Bruxelles, (Belgium).
⁷ Università degli Studi di Torino, SUSCOR, via XX Settembre 18, 10078, Venaria Reale, (Italy).

Keywords: 3d laser scanning; 3d printing; non-invasive recomposition; medieval statue; consolidating experimentation; calcarenite stone;

This study focuses on the restoration of two stone elements coming from a polychrome statue found in two different digs around the Episcopal Complex in Asti. They represent a chest dressed in classical clothes with a not identified attribute on the left hand, and carved bottom clothes. The different state of conservation of the two parts posed some difficulties in understanding their original forms and volumes, so that they were never considered as part of the same artefact. After an accurate study of the execution technique, the constituent material, and of the state of conservation, it has been possible to recognize the two pieces as being the upper and the lower part of the same statue, which experienced a different conservation history.

The restoration proposal, beyond the study of the two objects and of their main degradation phenomena, aimed at the recomposition of the two fragments. The study started with a multidisciplinary diagnostic plan to analyze the few traces of polychrome, the original stone, and the composition of the external brown patina. The chemical analysis confirmed the linking between the two elements. An innovative method of recomposition of the two stone parts has been adopted, consisting in the realization of a rigid counterform with the help of 3D laser scanning and 3D printing technology. The ability of the printed supports in ABS (five in total) to follow the surface of the two faces of breakage has made it possible to avoid the use of adhesive or metal pins, exploiting the weight of the upper part to stabilize the junction (fig.1). This allowed the artefact to be recomposed without any damage, and with a totally non-invasive and completely reversible intervention.
A specific experimentation has been carried out in order to define the most suitable treatment for the light superficial consolidation. Aesthetical issues and the respect of the materials has been the main focus of this experimentation, considering the minimal powdering of the surface.

Figure 1: Recomposition of the statue with ABS supports. They reproduce the exact morphology of the two faces of breakage, restoring the original static structure.

An important art historical research has accompanied the study of the statue from the beginning, and suggested a possible iconographic reading of the subject and the classification of the work in the context of Gothic sculpture in Piedmont.
Talavera de la Reina tiles in Portugal: a study of materials and technology

Teresa Ferreira1,2*, Cátia Relvas1, Margarida Nunes1, Luís C. Alves3, António Candeias1,2, José Mirão1,4, Celso Mangucci1

1 HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7000-554 Évora, Portugal.
2 Chemistry Department at the Science and Technology School, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal.
3 C2TN-IST/UL, Centro de Ciências e Tecnologia Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela, Portugal.
4 Geosciences Department at the Science and Technology School, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal.

* tasf@uevora.pt, +351 266 740 800

Keywords: Talavera de la Reina; Majolica; tiles; VP-SEM-EDS; µ-XRD; µ-Raman; PIXE; LA-ICP-MS.

Decorative tiles are an important part of Portugal architectural heritage, as they have widely been used since the 15th century [1]. In the 16th century Seville was a ceramic production centre full of technological innovation and enriched by the hand of the Italian masters, being Francisco Niculoso one of the most famous. Majolica made possible the use of new colour pigments and allowed a variety of figurative and historical themes. Majolica production, with an extended variety of polychromies coexisted with the Hispano-Moresque tradition on the arista tiles and the ceramic production with metallic reflections. During the 16th century, Talavera de la Reina gained importance due to the knowledge of the Flemish artists. Altar frontals and pattern tiles will be the most typical production from this ceramic centre, with documented exports to Portugal [2].

The aim of this work was to study and compare an altar frontal and a pattern panel attributed to Talavera de la Reina production centre and a set of decorative tiles whose origin in Talavera is documented. The altar frontal and the pattern panel dated from the first quarter of the 17th century and nowadays belong to the Museum of Évora and the Town hall of the city of Évora (at Remédios Monastery). The set of decorative tiles, still in situ, was an order for the Ducal Palace in Vila Viçosa (near Évora) and it is attributed to the workshop of Fernando de Loaysa. The chemical and mineralogical study of the ceramic body and the evaluation of the glaze-ceramic interface and the glaze composition were carried out on small fragments obtained from the three groups of tiles under study and intended to deepen the knowledge on Talavera production materials and technology. The ceramic body composition and the interface and glaze morphology were analysed by variable pressure scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (VP-SEM-EDS). Micro-X-ray diffraction (µ-XRD) and micro-Raman spectroscopy were also used for the evaluation of the ceramic body and the interface composition. Major constituents of the glaze were obtained by particle-induced X-ray emission (PIXE) while trace elements analysis was carried out by laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS).

References:
Optimization of Total Reflection X-ray Fluorescence analysis of pigments

Alessia Coccato¹, Bart Vekemans², Laszlo Vincze², Luc Moens² and Peter Vandenabeele¹

¹ Ghent University, Department of Archaeology, Sint-Pietersnieuwstraat 35, B-9000, Ghent (Belgium)
² Ghent University, Department of Analytical chemistry, Krijgslaan 281, B-9000, Ghent (Belgium)

* Raman@ugent.be

Keywords: TXRF; archaeometry; quantification; pigments

Total reflection X-ray fluorescence (TXRF) analysis is a sensitive multielemental technique, appreciated in many fields of research (such as environmental studies, biology, industry, archaeology [1]) for a variety of reasons. TXRF requires little sample (≤μg), limited sample preparation, and allows for quantification [1], [2]. The only condition is that the prepared sample for the analysis is (or can be considered) a thin film. This applies to evaporated droplets (10μL of dissolved samples) and to powders whose particles are in the range of tens of micrometers [2].

The investigation of real paint samples is a complex issue from many points of view. Most of the time, in fact, pigments were mixed to obtain the desired shade. This affects the representativity of sampling [4]. Elemental ratios can however be used to determine mixing ratios of pigments [5], [6].

A Mo-W double anode TXRF instrument (TX2000 by G.N.R., Italy) was characterized in order to evaluate its performances in relation to cultural heritage materials analysis (i.e. pigments). Multielement standard solutions were used to quantify the lower limits of detection (LLD) and relative sensitivities (Ri,IS). These parameters are necessary for evaluating the sensitivity of the technique and to assess the cleanliness of quartz supports (i.e. contaminants present below detection limit). Moreover, standardless relative quantification can be achieved thanks to the calculated sensitivity parameters [2]. Different sources of uncertainty contribute to the accuracy of the analysis, and have to be taken into account. These are mainly related to the sample preparation and to the instrumental repeatability [3].

References:
Uncover the mantle: rediscovering Gregório Lopes palette and technique with a study on the painting “Mater Misericordiae”

Vanessa Antunes1,2, António Candeias3,4, Maria L. Carvalho2, Ana I. Seruya2, Maria J. Francisco5, Sonia Costa4, Alexandra Lauw6, Vitor Serrão1, Marta Manso2,7* 

1 ARTIS-Instituto História da Arte da Faculdade de Letras da Universidade de Lisboa (ARTIS-FLUL), Alameda da Universidade, 1600-214 Lisboa, Portugal
2 LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal
3 Laboratório José de Figueiredo / Direcção-Geral do Património Cultural (LJF-DGPC), Rua das Janelas Verdes 37, 1249-018 Lisboa, Portugal
4 Laboratório HERCULES, Escola de Ciências e Tecnologia, Universidade de Évora, Largo Marquês de Universidade de Évora, Largo Marquês de Marialva 8, 7000-676 Évora, Portugal
5 Setubal Museum, R. Acácio Barradas 2, 2900-197 ,Setúbal, Portugal
6 Centro de Estudos Florestais, Instituto Superior de Agronomia, Tapada da Ajuda, 1349-017 Lisboa, Portugal

* Corresponding author’s email marta974@gmail.com

Keywords: ground layer; gypsum; anhydrite; Portuguese painting; EDXRF; µ-XRD; SEM-EDS; µ-Raman; IRR; dendrochronology.

Abstract

Gregorio Lopes (c. 1490-1550) was one of the most prominent painters of the Renaissance and Mannerism in Portugal. The painting “Mater Misericordiae” from Sesimbra Holy House of Mercy, made circa 1535 is one of the most significant works of the artist, and his only painting on this theme. The recent restoration of the painting provided the possibility to study materially the painting for the first time, with a multianalytical methodology incorporating micro-X-ray Diffraction (µ-XRD), Energy Dispersive X-ray Fluorescence spectroscopy (EDXRF), scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS), micro-Raman spectroscopy (µ-Raman). The analytical study was complemented by Infrared reflectography (IRR), allowing the study of the underdrawing technique and also by a dendrochronological approach to confirm the date of the wooden panel. The results of this study were compared with previous ones on the painter’s workshop and significant differences and similitudes were found in the materials and techniques used.

Introduction

Gregório Lopes was Royal painter to the Kings Manuel I and John III. The artist was nominated Knight of the Order of Santiago in 1524. Recognized by its
individualized style, differing from the common collectivist tendency of the time\(^1\), the artist is one of the Portuguese painters with more assigned work and was the introducer of Antwerp Mannerism in Portugal. His partnership work is also well known, having performed artistic contracts with other painters (Gaspar Vaz, Garcia Fernandes, and Cristóvão de Figueiredo, known as the “Ferreirim masters in 1533-34, for the execution of the Ferreirim Monastery altarpieces in Lamego. During his life, he also worked from north to south of Portugal, having paintings in Lisbon, Coimbra and Évora.

The importance of Gregório Lopes in the Portuguese painting panorama lead to a publication, in 1999, by Instituto Português de Conservação e Restauro\(^2\), bringing to light the research on his painting materials and the characterization of the workshop palette. The colours of the workshop palette characterized were: for white, lead white; for brown, ochre; for green, Malachite, copper resinate and verdigris; for red, red ochre, vermillion and possibly dye madder and Kermes; for yellow, tin and lead yellow and ochre; finally, for blue, azurite, and for black, animal charcoal\(^3\).

The analytical results of the painting “Mater Misericordiae” confirmed the presence of the pigments previously identified in the characterization of the artist palette with the exception of animal charcoal. In this painting, vegetable charcoal was used instead, both in the underdrawings and in the mixture with different colours to obtain the shadow areas of the painting, being animal charcoal absent.

Azurite grains of irregular shape and oversized dimension, a particular characteristic of this painting workshop\(^3\), were also found in the blue colour of the sky and in the Virgin’s mantle, as well as in other blue layers in the painting.

The ground layer of the painting is also of calcium sulphate, more specifically of “gesso grosso” (coarse gypsum, having more anhydrite than gypsum), according to the other paintings of the workshop studied and also to the ground layers used by the Lisbon workshop painters\(^3-5\).

References


The importance of analytical techniques and cross-check of data in a painting by Francisco Pinto Pereira

Nídia Silva¹, Agnès Le Gac¹², Sónia Costa³, José Mirão³ António Candeias³

¹ Departamento de Conservação e Restauro (DCR), Faculdade de Ciências e Tecnologia (FCT), Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
² Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação (LIBPhys), FCT, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
³ Laboratório Hércules, Centro de Química de Évora, Universidade de Évora, 7000-809 Évora, Portugal

*e-mail of corresponding author: nc.silva@campus.fct.unl.pt, phone: +351 912095704

Keywords: Francisco Pinto Pereira; painting; Digital Photography; Portable Digital Radiography; Optical Microscopy; SEM imaging; SEM-EDS; μ-XRD.

This work aims at pioneering the study of colors and techniques used by the Portuguese Master Francisco Pinto Pereira for the composition of his paintings. The painter was a contemporary of King John V (first half of the eighteenth century), in a reign that was marked, in Portugal, by brightness, luxury, the wealth of costumes and jewelry, always following the French trend. The luxury also stretched in the order of works of art and music [1][2].

The main focus of this study consists in a painting (oil on canvas) which was commissioned to the painter by the monarch, for one of the side chapels of the royal basilica of Mafra and is dated 1730. The canvas is semi-circular, it has 153,5 cm of width and 309 cm of length and it is supported in a wooden stretcher with 6.5 cm of thickness. It is a representation of two Saints accompanied by cherubs and angels and it is currently not possible to distinguish the saints due to the darkening of the surface layer. The back of the canvas is covered with a dark red layer (unknown to date).

Digital Photography was used in situ under normal and ultraviolet light. Micro-sampling was carried out and examined by means of optical microscopy (equipped with different filters) and SEM-EDS. These techniques are complementary since one cross-checked, the data can be confirmed that would otherwise be unclear.

SEM-EDS for example, is a great addition to optical microscopy because although it does not provide a color image, it has a higher resolution and depth of field, achieving an image with higher definition [3]. It thus provides accurate information on which elements are present within the samples, the layer build up. the layers thickness and their topography [3] [4].

In the ground layer of all samples, the presence of elements associated with earth pigments, such as iron, silicon, manganese, aluminum, calcium, sodium and potassium, was verified. In that way it was possible to relate this information with the dark
orange/brown color observed by optical microscopy (figure1). It is possible to confirm that is the same ground layer in all samples and it was presumably applied in a very even way.

The paint layers show different aspect and elements between the samples, related with different colors used by the artist. In the background regions it is possible to conclude that a dark color mainly composed by iron, lead, carbon, calcium and phosphor was applied. In the areas related with carnation (figure 1) tin, antimony, mercury, sulfur, barium and lead were mainly detected. The tin and the antimony are related with the yellow particles as it can be seen in optical microscopy and the mercury is associated to the red particles. The elements present in the paint layers from the background are presumably associated to a mixture of carbon black and white lead. On the other hand the elements that compose the carnation areas are probably related to a mixture of lead-tin-antimony yellow, vermilion and barium white.

Figure 1 – Sample in a carnation area: a) Optical microscopy in interferential contrast lighting (F3); Scale 3 (20X objective); sensitivity 30; b) Optical microscopy in Ultraviolet lighting (F5); Scale 3 (20X objective); sensitivity 75; c) SEM image with 20 KeV; 11.8mm; x 300; 40Pa; Backscattering electron.

For a better understanding and conclusion of the colors and techniques used by Francisco Pinto Pereira, further scientific analysis with complementary techniques, such as portable digital radiography, X- ray diffraction, micro FT-IR microscopy, X-ray fluorescence and also gas chromatography associated with mass spectroscopy, will be carried out.

References

Green colour in the 16th century Portuguese paintings of the Funchal’s Cathedral altarpiece

Sofia Gomes¹, Mercês Lorena¹, Peter Vandenabeele², Debbie Lawers³, Alessia Coccato², Sara Valadas⁴ and António Candeias¹,4*

¹ José de Figueiredo Lab., General Directorate for Cultural Heritage, Rua das Janelas Verdes 37, 1300-001 Lisbon, Portugal
² Department of Archaeology, Ghent University, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium
³ Évora University, HERCULES Laboratory, School of Sciences and Technology, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal
⁴ Department of Analytical Chemistry, Ghent University, Krijgslaan 281, B-9000 Ghent, Belgium

* candeias@uevora.pt

Keywords: Green pigments; easel painting; execution technique.

Scientific analysis of paintings together with the reading of treatises and other documents bring important information regarding paintings materials and techniques. This study outlines the construction technique of the green color in the paintings of the main chapel’s altarpiece of Funchal’s Cathedral. Several questions arose during the conservation and restoration intervention of these 16th-century paintings. In fact and due to the previous interventions on the altarpiece, this color was considered to be an overpaint layer during the intervention. The study addressed specific questions: How is the color buildup of the green areas? What are the pigments used? How were the pigments applied?

The artist selection of the pigments available at the time and its use in the painting together with the pigment mixture in the paint layer and the number and thickness of these layers are relevant in the artwork characterization. Moreover, its identification and use may have an important meaning regarding the artist or the period of the paintings [1].

For this study were considered the green areas from the figures’ drapery of seven of the twelve paintings in order to find differences and similarities between the structure and the composition of the painting layers. Different green copper pigments were identified in the green layers mixed with azurite, lead white, lead tin yellow type I and carbon black to obtain specific hues and shades.

Further investigation through scientific examination of cross sections showed how the painting layers were applied and what pigments were used. Most of the microsamples follow the same structure: a ground layer, a light yellow or white under-painting and a top green layer.
The sources suggest that after the oil-based paints had become common; this light under-layer was used in order to achieve maximum luminosity [2]. Remaining partly visible beneath a green layer, this under-painting layer can be employed as an under-modelling layer, which is achieved with lead white or lead tin yellow type I for the highlights and with carbon black used to create shadows in the folds [3, 4]. In Filipe Nunes’ treatise on painting (Arte da Pintura, Symmetria, e Perspectiva) from 1615, he describes how to do the undermodelling by using white and black pigments covered by a green transparent layer of verdigris [5]. With this color structure a strong contrast between light and shadow was produced and the cloth’s folds were enhanced.

Furthermore, a different structure of painting layers was detected: a ground layer followed by a single layer of green mixed with lead tin yellow type I and carbon black to obtain a light or dark green hue. This technical solution is due to the fact that at that time it was difficult to find a green pigment which offered a really intense hue as well as stability. To increase greens’ intensity many painters used mixtures of blue and yellow or a little of yellow or white was sometimes added [2].

References:
[1] A. J. Cruz. A matéria de que é feita a cor, Os pigmentos utilizados em pintura e a sua identificação e caracterização.
Pigment and morphological analysis of an oil painting attributed to the young Picasso

M. C. Chillón, S. Ruiz-Moreno

Polytechnic University of Catalonia, Signal Theory and Communications Department, C/ Jordi Girona 1-3, 08034 Barcelona (Spain), Tel. +34934016443, +34934054608, mcchillon@actioarteyciencia.com, sruiz@tsc.upc.edu

**Keywords:** Global research; Pigment Raman analysis; Comparative images analysis

In this work, an oil painting on canvas (“La niña”, 115 cm. x 85 cm.) that Manuel Blasco Alarcón attributed in 1981 to the youth period of P. R. Picasso \(^{(1)}\), has been investigated.

A first analysis of the artwork with Raman spectroscopy revealed the abundant presence of, among others, phthalocyanines (blue and green), titanium white (anatase) and the organic pigment PR112 (azo). Obviously, the use of these pigments was not possible in the last decade of the XIX\(^{th}\) century. By means of an exhaustive observation with a binocular, it was deduced that the artwork was retouched in a great part of its surface. After a complete cleaning process, today the painting can be observed as in its original state (see figure). Then, by means of a new and complete pigment analysis, a usual and typical palette corresponding to the late of XIX\(^{th}\) century was identified (attached in the figure). This result and the obtained ones by a morphological comparison between the young Picasso and the face of “La niña”, supports, in an objective way, the starting authorship hypothesis.


<table>
<thead>
<tr>
<th>Identified pigments (before cleaning)</th>
<th>Original palette (after cleaning)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phthalocyanine green</td>
<td>White lead</td>
</tr>
<tr>
<td>Phthalocyanine blue</td>
<td>Vermilion</td>
</tr>
<tr>
<td>Titanium white (anatase)</td>
<td>Red lead</td>
</tr>
<tr>
<td>PR 112</td>
<td>Chrome yellow</td>
</tr>
<tr>
<td></td>
<td>Cobalt blue</td>
</tr>
<tr>
<td></td>
<td>Prussian blue</td>
</tr>
<tr>
<td></td>
<td>Ultramarine blue</td>
</tr>
<tr>
<td></td>
<td>Charcoal black</td>
</tr>
</tbody>
</table>

Before (left) and after (right) the cleaning process

Overlapping of both faces: “La Niña” and Picasso
Characterization of the artificial patinas on a bronze sculpture “Ettore e Andromaca” of the museum Carlo Bilotti - Aranciera di Villa Borghese (Rome).

Annalaura Casanova Municchia1*, Giorgio D’Ercoli2, Ilma Reho3
Maria Antonietta Ricci1, Armida Sodo1

1 Università Roma Tre, Dipartimento di Scienze, Via della Vasca Navale 84, 00146 Rome (Italy).
2 Istituto Superiore per la Conservazione ed il Restauro (ISCR), Via di S. Michele, 23, 00153 Rome (Italy)
3 Museo Carlo Bilotti Aranciera di Villa Borghese, Sovrintendenza Capitolina ai BB.CC. Viale Fiorello La Guardia, 6, 00197 Rome (Italy).

* E-mail: acasanovamunicchia@uniroma3.it. Tel: +39 06/57336374.

Keywords: artificial patina; bronze; nitrate patina; Raman spectroscopy

“Ettore e Andromaca” is a monumental bronze sculpture (Fig. 1a) after a plaster model made by de Chirico in 1966, commissioned by the art collector Carlo Bilotti to the Foundation Giorgio and Isa de Chirico. The sculpture is exposed in the area in front of the “Aranciera” of Villa Borghese (Roma), present location of the contemporary art museum named after Carlo Bilotti. As other contemporary bronzes, “Ettore ed Andromaca” shows a brown and a green patina on its surface. Such artificial patinas were applied by the artists on the surface of their bronze sculptures for aesthetic aims, using several different recipes [1]. The most common were green patinas, based on copper nitrate, and brown patinas, based on ferric nitrate [2, 3].

In the recent literature, several multidisciplinary approaches have been used in order to identify both the corrosion products and the artificial patina on bronze surfaces [2, 3, 4, 5, 6]. The aim of the present study is to identify the composition of the artificial patinas covering “Ettore e Andromaca”, by Scanning Electron Microscopy (SEM) equipped with X-ray micro-analysis (EDS), X-ray diffraction analysis (XRD) and Raman spectroscopy. At the same time, these techniques can point out the nature of the corrosion products, due to its outdoor exposition.

To this aim, we have scraped off from the bronze statue differently colored samples (located both in the green and the brown area). Our results have shown that the brown patina mainly consists of copper oxides (Cuprite, Cu$_2$O), (Tenorite, CuO) and copper nitrate (Gerhardtite, Cu$_2$(OH)$_3$NO$_3$), whereas the green patina, as shown by Raman spectrum in Fig 1b, consists of copper sulfate (Brochantite, Cu$_4$SO$_4$(OH)$_6$) and copper nitrate (Gerhardtite). In all samples we have also detected the amorphous carbon spectral fingerprints, likely due to the external pollution contamination.

This study gives an interesting contribution to a better understanding of artificial patinas composition and their behavior when exposed to natural atmospheric conditions.
Fig. 1 A) The bronze sculpture “Ettore e Andromaca”; B) Raman Spectrum of the green sample. Label B marks Brochantite, N of copper nitrate, C of amorphous carbon.

References:
Diagnosis of materials and effectiveness of Er:YAG Laser cleaning in a Borrassa’s Panel Painting (15th Century)

Adele DeCruz¹, Alessia Andreotti², William P. Brown³, Mara Camaiti⁴, Maria Perla Colombini¹,⁵

¹ Duke University, Department of Biology/Chemistry, Box 90338, Durham, NC 27708, Telephone number: (919) 613-5024, email Address: a.decruz@duke.edu.
² Department of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 13, 56127, Pisa, Italy.
³ North Carolina Museum of Art, 4630 Mail Service Center, Raleigh, NC 27699-4630.
⁴ National Research Council of Italy, Institute of Geosciences and Earth Resources, Via la Pira, 4, 50121 Florence, Italy.
⁵ Institute of Conservation and Valorization of Cultural Heritage (ICVBC-CNR), via Madonna del Piano 10, Sesto Fiorentino, Italy.

Keywords: Er:YAG laser cleaning; material identification; GC-MS; FT-IR; SEM-EDX

A 15th Century panel painting by Lluís Borrassà (1360-1425) Christ before Pilot was the object of a restoration at the North Carolina Museum of Art. A multi-analytical approach based on Fourier transform infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM-EDX) and Gas Chromatography-Mass Spectrometry (GC/MS) also coupled with a pyrolizer (PY/GC-MS) was used to investigate the origin of the darkened coating obscuring the work of art in order to find a proper cleaning procedure. The results evidenced the presence of different restoration materials that constituted the superficial patina, which was difficult to remove by conventional solvent cleaning methods. The Erbium: YAG laser operating at 2.94 µm was tested as an innovative alternative method to the traditional solvent mixture and gels. Because of the presence of multi layers of over-painting and restoration materials the Er:YAG laser also proved beneficial as a non-destructive and selective sampling tool. The organic material was collected by positioning a microscope glass coverslip (15x15 mm) on the painting surface, followed with laser ablation that removed the material, which condensed on the glass that was then submitted for the FT-IR and GC-MS analysis. Different old and more recent restoration material such as animal glue, a pine resin resin, a plant oil and a synthetic paraffine have been identified (see Figure below). The acquired new knowledge of the characterised materials and optimisation of the cleaning methods, guided the conservators to choose the best restoration conditions and perform a safe and successful cleaning of the painting especially the blue pigment, which was covered with intractable restoration material. The Er:YAG was an efficient and safe method to remove these materials.
Figure. Extract ion chromatograms of specific class of compounds for the lipid fraction of the sample collected from the blue Christ robe; a) lipids pattern: 1: lauric acid; 2: suberic acid; 3: azelaic acid; 4: myristic acid; 5: sebacic acid; 6: palmitic acid; 7: oleic acid; 8: stearic acid; *: aromatic compounds differently substituted b) plant sterols pattern (#); c) characteristic compounds of pine resin: didehydroabietic, dehydroabietic and 7-oxo-didehydroabietic acid) hydrocarbons of a synthetic paraffin
Go with the flow: A preliminary rheological study to 17th century clear varnish recipes and components

Vincent Cattersel¹, Louise Decq² 4, Delphine Steyaert³, Charles Indekeu¹, Emile Van Binnebeke³, Wim Fremout² and Steven Saverwyns²

¹ University of Antwerp, Conservation Studies – Heritage and Sustainability, Blindestraat 9, B-2000 Antwerp (Belgium), +32-3-2137134, vincent.cattersel@uantwerpen.be (corresponding author).
² Royal Institute for Cultural Heritage (KIK-IRPA), Department Laboratories, Jubelpark 1, B-1000 Brussels (Belgium)
³ Royal Museums of Art and History (RMAH), Jubelpark 10, B-1000 Brussels (Belgium)
⁴ Ghent University, Department of Organic Chemistry, Krijgslaan 281, B-9000 Ghent (Belgium).

Keywords: Rheology; varnish; lacquer; historical art-technology

Seventeenth and Eighteenth century European varnish and lacquer recipes are intricate mixtures of raw components such as oils, balsams, gums and resins. Many contemporary treatises describe the solid raw components and the dried varnish film using sensory based adjectives. For these observable characteristics of solids, the author(s) had an elaborate vocabulary at their disposal, allowing them to assess the component’s or varnish’s quality by describing shape, color, gloss, clarity, fracture, and sense of smell. However, the lingo for describing the characteristics of a liquid or the liquid phase of the varnish refers mostly to their ‘viscosity’. The limited terminology to describe liquids, and the subjective nature of whether a product is considered viscous or not, indicates that properties of a liquid were more difficult to express. At least some empirical knowledge must have been at hand since painters were able to control their paint’s flow properties to create impastos.

To date, few studies have investigated the rheological properties of historical paint and varnish recipes and their natural raw components. Previous studies mainly focused on common paint and varnish media such as linseed oil, oil of turpentine and mastic.¹ ² Others have attempted to characterize the wet paint’s flow dynamics using the dried paint texture and topography of a particular artwork.³ ⁴ To our knowledge, no study has focused on the possibility that historical varnish formulations may have been related to the artist’s attempt to ameliorate flow and application properties, and by doing so aiming to increase the workshop’s manufacturing yield and the final product’s quality. Consequently, the rheology of historical varnishes and the components’ influence on the varnish’s flow in 17th and 18th century varnish formulations remain largely unexplored. The aim of this study is to describe a selection of components’ rheological characteristics and their relations in varnish formulation technology by reconstructing an historical alcohol-based recipe. Thus, trying to gain insight on whether (empirical) knowledge about flow and application behavior might have influenced the design of varnish formulations during the late 17th and early 18th century.
As part of the ‘European Lacquer in Context’ project, the original materials of a late 17th century transparent white lacquered cabinet from a private collection was studied.[5-6-7] The original lacquer layer was analyzed for its components by means of py-GC/MS. The py-GC/MS results allowed for reverse engineering and the identification of several historical recipes which may have been used on this object. Three recipe candidates were selected and recreated using the original recipe’s instructions. Conversion of the region and time-dependent Imperial units to today’s metric units was done using reference works.[8-9-10]

A Merlin VR Rotational Rheometer (Rheosys) equipped with a cone and plate geometry (30mm, 2°, gap set 70µm) was used to obtain rheograms. All measurements are performed at 25°C (± 0.01) using an integrated Peltier Temperature control system. A solvent trap is used to prevent solvent loss and drying of the sample during time of measurement. Rheological measurements are performed on both components and at different stages of the reconstruction process. Tests are conducted in order to classify the liquids or mixtures as (non-)Newtonian and to observe time and/or shear dependent behavior. Leveling properties at different stages of the production process and the final mixtures are assessed by applying the mixtures on a float glass substrate by brush. The leveling of the dried film is examined by 3D acquisition of the layer’s topography with an Olympus DSX510 digital microscope.

The results show significant flow and application characteristics which are related to the addition of the raw components in the varnish’s mixture. Less stable components were added to enhance the rheology in such manner that it was beneficial for the application and leveling of the lacquer film.

References
[7] This study is conducted under the European Lacquer in Context project (ELinC), a four year interdisciplinary study funded by BELSPO, Brain-be. This project is a collaboration between the Royal Institute for Cultural Heritage, the University of Antwerp, the Royal Museums of Art and History, and the Getty Conservation Institute (Los Angeles, US). The University of Antwerp's work packages consist of a technological and physical study of European lacquer and varnish recipes from the 16th century to the 19th century.
Instrumental techniques used to identify proteins binding to wood icons from the XVIII century

Nicoleta Vornicu¹, Maria Urma², Mirela-Fernanda Zaltariov³, Cristina Bibire¹

¹ Metropolitan Research Center T.A.B.O.R, Iasi, Romania
² George Enescu University of Arts, Iasi, Romania
³ Petru Poni Institute of Macromolecular Chemistry, Iaşi

Identifying the binder composition used in making icon painting in the XVIII century bring the an important contribution to the authenticity of the painting materials and techniques of manufacturing.

The paper shows the use of complementary techniques of investigation (OM, SEM EDAX, FT-IR, micro-Raman) to identify binding proteins and establishing art of making wooden icon painting "St. Peter and Paul" that belongs iconostasis monastery Dragomirna, Suceava, Romania.

These methods are rapid and reproducible in case the icons the painted on wood. We collected more samples from different areas of icon to have more complete information and to avoid confusion that can occur in areas repainted. The results showed the effectiveness of integrated protocol used, highlighting the potential for its use in the investigation and conservation of paintings on wood.
In situ Raman study of marble capitals in the Alhambra

Paz Arjonilla Ureña 1*, Ana Vidal Domínguez1, María José de la Torre López 2, Elena Correa Gómez3, Ramón Rubio Domene3, Mª José Ayora Cañada1.

1 Universidad de Jaén, Department of Physical and Analytical Chemistry, Campus Las Lagunillas E-23071, Jaén (Spain), Tlf: 953213627, E-mail: mpurena@ujaen.es
2 Department of Geology, Universidad de Jaén, EPS-Linares, Alfonso X El Sabio 28, Universidad de Jaén, E-23700 Linares (Spain).
3 Conservation Department, Council of The Alhambra and Generalife, Granada, Spain.

Keywords: pigments; Alhambra; Raman spectroscopy; non-invasive; on-site; marble; lapislazuli; cinnabar.

The marble capitals of three different sites, the Mexuar, the Hall of the Abencerrages and the Court of the Myrtles, in the Alhambra complex (Granada, Spain) have been investigated by means of Raman micro-spectroscopy. The decoration of the capitals exhibits mainly blue, red, black and gilding motifs with different state of conservation. In addition of preserving the artwork with a non-invasive study, the on-site investigation gives a more representative knowledge of the art objects because the measurements are not limited to the amount of samples that can be taken (few and small).

The equipment used was an innoRam (B&W TEK), with a laser of 785 nm and a back thinned two dimensional CCD detector thermoelectrically cooled at -20ºC covering a spectral range of 65–3000 Åcm⁻¹. The Raman fiber optic microprobe was attached to a videomicroscope with integrated camera and LED illuminator because we needed working with precision spot sampling as in some cases the pigments were very degraded so we had a very small size of sample. To analyse the different painted areas, the videomicroscope was mounted on a tripod motorised in the X–Y–Z axes with remote control. This allowed the adjustment of the position and the focusing of the laser beam on the surface of the artwork. The extensive tripod and the arm where the videomicroscope with the probe head is located help to reach the capitals of the columns (at about 3 meters height).

The data obtained from the Raman spectrum were of good quality despite of the adverse conditions out of the laboratory, for example, the flash of the camera of the tourists, the wind, the dust, the vibrations of the tripod because of the height and the sunlight in open courts. The information gathered has given us knowledge of what pigments were used in the past to decorate these halls of the Alhambra. In the Mexuar, some pigments were found applied directly on the stone, marble. Over this pictorial layer, other pigments and gildings were applied above a preparation gypsum layer with a red bole. This suggests that pigments applied directly on the marble are from the Nasrid period whereas the redecoration which seems to hide the originals was made during the Christian occupation and posterior restorations. This second layer appears
very degraded which allow to appreciate the original one. The original pigments were identified as natural lapislazuli, carbon black and cinnabar. In the other hand, the blue pigment above the gypsum layer seems to be azurite. The red colour of the red bole is due to the presence of iron oxide in the clay. In the Court of the Myrtles we have found natural lapislazuli and carbon black directly applied on the stone. In the Hall of the Abencerrages the pigments seems to have been applied directly on the marble without a preparation layer but it is necessary to do a more deep investigation to confirm it. Cinnabar and its degradation product, calomel, were found in the red decorations. We have also seen gilding, carbon black and blue areas very well conserved of lapislazuli [1].

In conclusion, the portable Raman micro-spectroscopy has allowed a completely non-invasive study of both the pigments which are decorating the capitals of the some columns in the Alhambra and some of their degradation materials. Especially interesting was the identification of completely different materials in the original Nasrid art in comparison with the Christian redecoration.

![Figure 8. Raman micro-spectrometer equipment working in the Hall Mexuar.](image)

**Acknowledgements.**

This work was financed by the research project BIA2013-41686-R from the Spanish Ministry of Economy and competitiveness and FEDER funds

**References:**

A Software Platform Proposal for the Automated Interpretation of Spectra in Artworks Analysis

Juanjo González-Vidal\textsuperscript{1,2}, Rosanna Pérez-Pueyo\textsuperscript{1}, María José Soneira\textsuperscript{1}

\textsuperscript{1} Universitat Politècnica de Catalunya, Signal Theory and Communications Department, Sor Eulàlia d'Anzizu s/n, D5-101, Campus Nord, 08034, Barcelona (Spain), Tel. +34 93 401 6442, email: juanjo.glezvidal@tsc.upc.edu

\textsuperscript{2} DAPCOM Data Services, European Space Agency Business Incubation Centre, Esteve Terrades 1, 08860, Castelldefels, Barcelona (Spain), Tel: +34 93 4 137 578

Keywords: spectroscopy; automated interpretation; data handling; data processing; software platform; software development

The application of spectroscopic techniques is crucial for conservators and art historians who require knowledge of materials used in works of art (pigments, dyes, binders, additives, ...) in particular instances. In this sense, the knowledge of pigments which were in use on the ancient artists’ palettes is fundamental to preserve the art works. In addition, this knowledge is important to determine correct conservation approaches, to study degradation processes or authenticity-related issues. For instance, the proper interpretation of molecular signatures from vibrational spectroscopies gives valuable information about the materials used by the artists. In this regard, the spectral identification is one of the essential interpretations to be performed, which is generally carried out by visual comparison between the unknown spectra with an appropriate database of reference spectra. This identification approach while being simple and intuitive may turn out a complex task which usually requires an experienced analyst and inevitably introduces an element of subjectivity linked to the intervention of the investigator. Besides, these analyses can be limited due to interferences from other phenomena like noises or admixtures. This task is further complicated when the spectra are to be interpreted by a software system. Of course, the noise impact must be reduced to have an effective identification and a robust strategy for processing multi-component spectra needs to be implemented. Clearly, an automated methodology for a reliable spectral interpretation is of practical interest.

Nowadays, the multi-disciplinary scientific community devoted to the analysis and preservation of cultural heritage is immersed in the need of handling and interpreting an overwhelming amount of data. Indeed, data volumes cultural heritage experts deal with exponentially rises on account of the availability of a wide range of spectroscopic techniques. A clear example can be seen in the multi-analytical approaches taken to analyze the constituent pigmentation in art works\textsuperscript{1,2}. Measurements through several spectroscopic techniques performed on a single point in the art object under analysis provide a noteworthy volume of data. Another example related to these complex data handling processes is image data which in the form of spectra dominate data storage volumes in spectral imaging\textsuperscript{3}. As it can be seen from these examples, a significant volume of spectral data is generated, which needs to be stored and properly processed in order to be appropriately analyzed and interpreted. Therefore, the scientific
community working in the cultural heritage field may increasingly need to consume data processing software products and services.

Consequently, this work introduces a software platform developed for the advanced interpretation and handling of data coming from spectroscopic techniques applied to the analysis of art works. With this, the community may benefit from the usage of an intuitive, user-friendly and easy-to-use open-source platform, which integrates art historical information and spectroscopic data from art materials in a common manner. The main aim of the platform is to establish a software framework focused on the automated spectral analysis which may be extended with contributions from the different cultural heritage research groups according to the software development standards. Therefore, the most ambitious objective of this work is to setup a useful spectral data processing platform for art works analysis. In this way, it claims to standardize the way of interpreting the spectroscopic data measured from art materials, providing insight from the spectral measurements in an objective way in order to help in the decision-making process. The robust, reliable and consistent results obtained so far on Raman spectra (the authors’ field of work) demonstrate the competitiveness of the data processing solutions currently implemented.

References:
Helping art historians. A new insight look at the 16th century fresco “The Good and the Bad Judge” with technical photography and micro-analytical research

M.Gil1,*, C.Araujo2, M.L.Carvalho3, S.Longelin3, C. Souto1, L.Dias1, J.Frade4, I.Ribeiro4, J.Mirão1,5 and A. Candeias1,5,6

1 HERCULES Laboratory, Évora University, Largo Marquês de Marialva 8, 7000-671 Évora, Portugal.
2 Department of History, University of Évora, Colégio do Espírito Santo, 7000 Évora, Portugal
3 Évora, Atomic Physics Centre, Lisbon University, Av. Prof. Gama Pinto 2, 1649-003, Lisbon, Portugal
4 José de Figueiredo Conservation and Restoration Laboratory, General Directorate for Cultural Heritage, Rua das Janelas Verdes 37, 1300-001 Lisbon, Portugal
5 Evora Geophysics Centre and Geosciences Department, Évora University, Rua Romão Ramalho 59, 7000-671 Évora, Portugal
6 Evora Chemistry Department, Evora University, Rua Romão Ramalho 59, 7000-671

*Email:milenegil@gmail.com

This paper describes a study carried out on the emblematic mural painting so-called “Fresco of the Good and Bad Judge” located at the medieval village of Monsaraz (southern Portugal). This painting, with two distinct narratives, is thematically unique in Portugal and rare in the context of European Renaissance art. Scientific research was undertaken to help art historians to clarify doubts about the chronology of the two painted scenes through a technical study and a material characterization.

Fig. Details of technical features of the figures from the two scenes in Vis frontal and tacking light (Ar and Dr).
In situ technical photography (TP) in Vis, RAK and IR was complemented with elemental and chemical analyses by optical and scanning electron microscopy (OM and SEM-EDS), μ-Raman spectroscopy and Fourier transform infrared micro spectroscopy (μ-FT-IR). TP shows several analogies between the two scenes in terms of plaster work and pictorial techniques strongly suggesting one single painting campaign. The mortars of both scenes are made of lime with different ratios of calcium (Ca) and magnesium (Mg) mixed with siliceous and granitic aggregates. An intonachino made with a more calcitic lime is visible in all carnations. The pigments identified in both scenes were cinnabar (HgS), red and yellow ochres (Fe₂O₃ and FeO(OH) as chromophores), carbon black (C) and azurite (2CuCO₃.Cu(OH)₂).

Acknowledgement

The authors acknowledge Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1, co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM’ART PTDC/CPC-EAT/4769/2012, financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP). The authors also would like to acknowledge the City Hall of Reguengos de Monsaraz and Direção Regional de Cultural do Alentejo for allowing this study.
Multi-analytical study of the metal ion-anthraquinone complex in red lake pigments

Sara Bellei¹,² *, Daniela Comelli², Sara Mosca², Ilaria Bargigia³, Cosimo d’Andrea³, Barbara Berrie⁴, and Austin Nevin¹

Keywords: red lake pigments; anthraquinone; metal-dye complex, time-resolved photoluminescence (TRPL); SEM-EDX; FT-IR

Coordination of metal-dye complexes in anthraquinone-based lake pigments was studied using a complementary approach based on laboratory photoluminescence (PL) analysis, Scanning Electron Microscopy with Energy-Dispersive X-Ray Spectroscopy (SEM-EDX), and Fourier Transform Infrared Spectroscopy (FT-IR) to examine the environment of different metal ions.

Samples under investigation consisted of madder (which contains anthraquinones purpurin and alizarin) and cochineal (carminic acid) dyes precipitated with different metals which included Al, Al-Ca, Cu, Fe, and Sn. Samples comprised of commercially available lake pigments and accurate reconstructions of historical recipes[1]. Pigments prepared were applied as watercolours onto paper substrates with different pH ranging from slightly acidic, to alkaline.

Lake pigments are extremely difficult to characterize due to the complexity of their chemical composition, which depends on both the dyestuff used and the dying process which involves the complexation with a metal ion-containing mordant. Analytical procedures, based on Surface Enhanced Raman Scattering Spectroscopy (SERS) or on separation techniques, such as High Performance Liquid Chromatography (HPLC) provide outstanding results in the identification and characterization of the dye materials and molecules[2]. Nevertheless, these established techniques do not allow the characterization of the dye-mordant complexes as a whole, which are destroyed during sample preparation, and little is known about the dye-metal ion complex which are generally amorphous, hence cannot be characterized using X-ray diffraction. Non-destructive UV- or visible-induced photoluminescence (PL) spectroscopy is often used for detecting traces of lake pigments, due to its high-sensitivity, even though the PL broad emission spectra of lake pigments are generally not specific enough for their precise identification[3]. Time Resolved Photoluminescence (TRPL) spectroscopy has
been established as an efficient tool for differentiating materials, mapping distributions, and detecting chemical changes in a wide range of cultural heritage materials[4]. In lake pigments, the decay kinetics of PL emission are influenced by both the dye molecule and the ion mordant; therefore, the study of dynamic processes through TRPL spectroscopy can provide valuable information for studying the chemical interaction between the dye and the mordant in a non-destructive way.

SEM-EDX and IR analysis were used as preliminary techniques for the examination of the pigments during their manufacturing process. The characterization of the morphology of pigment particles, as well as of the other products formed during the precipitation reactions allowed to understand how the different metal substrates contribute to the chemical and physical properties of the lake pigment. FT-IR analysis allowed to gain structural information on bonding between the organic molecule and the metal ions. Two different PL spectroscopy devices for resolving decay kinetics from ps to ms were employed: a portable nanosecond time-gated spectrometer with luminescence excitation provided by a Q-switching Nd:YAG laser and a more complex laboratory set-up, based on a fs tunable laser source and a fast streak camera detector. Future aims will focus on the integration of PL spectroscopy with complementary analytical techniques and on the establishment of a standardize protocol for the study of this material, both as a pigment and in works of art. Insights into the material composition and optical properties obtained will help in the establishment of a standardized protocol for future analysis of these materials, both as bulk pigments and in works of art.

References:
Study of crystal defects in historical semiconductor pigments through time-resolved photo-luminescence spectroscopy

Alessia Artesani¹, Daniela Comelli¹, Austin Nevin², Cosimo D’Andrea³, Anna Cesaratto⁴, Sara Bellei², Valentina Capogrosso¹, Sara Mosca¹ and Gianluca Valentini¹

¹ Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano (Italy). Tel. +39 02 23996165, daniela.comelli@polimi.it.
³ Center for Nano-Science and Technology @POLIMI, Istituto Italiano di Tecnologia, via G. Pascoli 70/3, I-20133 Milano (Italy).
⁴ Department of Scientific Research, The Metropolitan Museum of Art, New York NY (USA).

* alessia.artesani@polimi.it, +39-0223996162

Keywords: Photo-luminescence; modern semiconductor pigments; trap state levels; crystal defects.

We propose a photo-physics study of Zn- and Cd-based semiconductor pigments to probe the presence of intrinsic crystal defects and impurities in historical pigment samples.

While the photo-physical properties of CdS, CdSe and ZnO nanostructures have been widely explored, only few papers have dealt with bulk materials, as those present in artist pigments [1,2]. Indeed, a better understanding of crystal defects in such semiconductor pigments widely used by important modern painters is essential for elucidating degradation pathways [3] or for a better understanding of pigment synthesis processes. A previous study of the kinetic photo-luminescence (PL) emission properties of commercially available Cd-based pigments has stated that spectral and lifetime properties depend on excitation irradiance with carrier recombination phenomena being highly influenced by electron trapping in deep trap states [2]. Here, the same approach is proposed for the study of valuable historical semiconductor pigments representative of the artist materials available at the turn of the 20th C..

Ten historical samples of yellow and orange Cadmium pigments (available in powder form) produced at the end of the 19th C. by different suppliers and ten historical samples of Zinc White from a collection of Lefranc-Bourgeois Raffaelli pastels have been analyzed. As a comparison, results of analysis of commercial Cadmium Yellow, Cadmium orange and Zinc White pigments (Kremer pigmente GmbH) are reported.
Bulk XRF and Raman analysis of samples have provided a preliminary characterization of samples in terms of pigment and binder (when present) composition. Time-resolved photo-luminescence (PL) spectroscopy has allowed the characterization of the main radiative decay pathways of semiconductor pigments: the rapid (picosecond) band-edge (BE) emission and the microsecond deep trap-state (TS) emissions. The features of BE emission are clearly linked to pigment chemical composition and crystal structure, while TS emissions are unspecific and highly heterogeneous amongst samples (Figure 1), pointing out that a variety of crystal defects are present in historical samples, likely introduced during pigment synthesis or following degradation phenomena. Results from ongoing studies using complementary spectroscopic techniques will be presented and will allow the correlation of results of PL spectroscopy analysis with the presence of specific crystal defects: electron paramagnetic resonance (EPR) analysis is aimed at assessing the presence of specific impurities and defects, responsible for the trap state emission properties of the pigment; X-ray photoelectron spectroscopy (XPS) has been used for investigating the presence of oxygen vacancies and interstitial oxygen defects in ZnO samples. Femtosecond pump-probe spectroscopy will be finally evaluated for studying the dynamics of carrier trapping to the intrinsic defects.

Figure 1. Results of PL spectroscopy analysis of historical Cadmium pigments, revealing a great heterogeneity amongst samples in terms of both BE and TS emissions: PL spectra following Q-switched pulsed (left panel) and CW (right panel) excitation.

References:
Thermoluminescence Application

David M. Price

School of Earth & Environmental Sciences, GeoQuest Research Centre, University of Wollongong, Northfields Av., Wollongong, NSW 2526, Australia +61 2 42213632

email: dprice@uow.edu.au , phone: +61 2 4221 3632

Keywords: Thermoluminescence; chronology; archaeology; geomorphology

Thermoluminescence (TL) is a trapped electron method of age determination dependant upon the creation of trapped electrons at lattice imperfections within crystalline materials such as quartz. Quartz in particular has the ability to stably store such energy over very long periods of time. The rate of acquisition of this trapped energy is in turn dependant upon the presence of trace amounts of long-lived isotopes of uranium, thorium and potassium and to a much lesser extent rubidium and cosmic radiation. Upon heating this stored energy is released and emitted in the form of light i.e. thermoluminescence. The amount of light emitted therefore provides a measure of the time of storage and the radiation flux providing the energy to raise these trapped electron up to their electron trap energy levels [1]. This ability therefore may be employed in the determination of time since the latest heating or solar exposure of a ceramic ware or a sedimentary deposit. This presentation provides examples of these many applications.

Example 1. Pottery authentication and absolute age determination

It looks like a Tang Dynasty camel but is it genuine or a copy crest ed to mislead the unwary. Thermoluminescence may be employed to distinguish between the two using only a minimum of sample taken from the underside of the art object.

Given the availability of rather more sample material and a knowledge of its environment i.e. burial or storage environment for example, TL may be used to determine the absolute age of an artefact.

Example 2. Bronze Artefacts – casting core material

These are essentially fired clay/sand and given their accessibility may be employed in the authenticity of bronze artefacts in the same manner as pottery.
Example 3. Archaeological Applications – hearths, heating stones, metallic slags

Thermoluminescence is frequently employed in the age determination of baked fire hearths such as those excavated at Lake Mungo in Western NSW [2] and fired aboriginal heating stones. Heated sand associated with metal slags and kiln bricks [3] may also be dated using this method giving valuable information regarding the time of metal or pottery production.

Example 4. Pottery, sherds, bricks etc

Accurate age determination of excavated pottery, sherds, tile [4] or brick fragments [3] requires a knowledge of the environmental burial conditions as the radiation flux emanating from the burial soil/sand must be taken into consideration as must the burial depth and moisture content of the site.

Example 5. Sedimentary dating; aeolian and fluvial

Australia has proved well suited to the application of luminescence in the age determination of sediments of both Aeolian [5] and water borne [6] sediments. This success may be attributed to long sediment distances, low energy water transport conditions over long time periods and of course high solar exposure thus efficient resetting of previously acquired TL energy i.e. trapped electrons.

Example 6. Differences in sedimentary source – quartz grains of different origin

As previously mentioned TL is a trapped electron method of age determination. Electrons are trapped at crystalline lattice defects which may be created at the time of the growth of the crystal. Quartz grains therefore contain different impurities and at different concentrations which, when heated, give rise to characteristic to TL spectra. This fingerprinting property may be utilised to demonstrate the possibility of units within a sedimentary sequence being derived from more than one source, thus suggestive of a change in sediment supply [7].

References
Interactions with adhesives and varnishes on a contemporary cardboard mosaic: Codex Vitae by Anna Moro Lin 2008

Ilina Udrea¹, Rosanna Chiggiato²

¹ Expert Diagnostic Applied to Cultural Heritage, ITOG -Institute of Graphic and Visual Arts - via Pietro Sola 29, 31059, Zero Branco (TV) IT, ilinaudrea@gmail.com or info@itog-ve.org, 00393477842510

² Adjunct Professor Technology for Conservation and Restoration: Methodologies for Paper Conservation Cà Foscari University Via Torino 155/b 30170 Venezia, Italy, ITOG -Institute of Graphic and Visual Arts - via Pietro Sola 29, 31059, Zero Branco (TV) IT, rochiggiato@gmail.com or info@itog-ve.org

Keywords: contemporary art; cellulose; degradation; colorimetry; SEM - EDS; pH; ATR - FTIR; GC - MS.

Codex Vitae is a contemporary mosaic opera that belongs to the Venetian artist Anna Moro Lin, who chose herself as a translator of the masterpiece into contemporary language. Codex Vitae is a very ancient iconographic theme: the Tree of Life. The contemporary masterpiece has 1531 tiles of different sizes, showing several heterogeneous complex and unstable polymeric materials, ranging from cardboard to newsprint paper treated with colors, paints and various synthetic adhesives. Despite its young age the intrinsic nature of the materials resulted in a degradation of its components.

This degradation is most developed on the material that acts as support: the cardboard. The chemical composition of materials and degradation phenomena undergone by the masterpiece are presented here. The object has been observed with diagnostic analyses such as photographic investigations (photography, digital microscope and an optical microscope), the analysis of physical (SEM-EDS, colorimetry), chemical analysis (pH, spot test) and chemical instrumental analysis ATR-FTIR, GC-MS.

The diagnostic analysis has identified the components of cellulose fibers as fibers composed essentially by wood pulp with addition of fillers and sizing. The synergistic interaction of the two main phenomena of degradation (oxidation and hydrolysis - acid and basic-) resulted in an increased acidity character of cellulose fibers, and consequently, a higher sensitivity to possible degradation.

What has been acquired from this study will support a possible future preservation intervention.
The figure shows the partial results obtained from the following diagnostic analysis: 1/4 - photographic observations; 5 - digital microscopic; 6/7 SEM-EDS; 8 - colorimetry; 9 - comparison of the spectra belonging to sample of the work of art's with a shade reference corresponding to wood pulp; 10 - pH; 11 - GC-MS; 12/15 - ATR-FTIR.
Polyphasic analysis of cultural heritage deleterious filamentous fungi

Margarida Isabel Martins Pires¹, Tânia Rosado², Maria do Rosário Martins¹,²,³, António Candeias¹,² and Ana Teresa Caldeira¹,²

¹ Chemistry Department, Scholl of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora (Portugal). Tel. Telephone number (corresponding author), e-mail address (corresponding author).
² HERCULES Laboratory, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora (Portugal).
³ Institute of Mediterranean Agricultural and Environmental Sciences (ICAAM), Évora University, Núcleo da Mitra, Apartado 94, 7006-554 Évora (Portugal).

* atc@uevora.pt, +351 266 740 800

Keywords: Biodeterioration; fungi; Cultural Heritage; Polyphasic Approach

Objects and architectural monuments belonging to our Cultural Heritage are exposed to several degradation agents, such as environmental pollutants (inorganic and organic), climatic factors (temperature, humidity, sun exposure, rain and other precipitation), chemical treatments (biocides, surfactants and hydrophobic compounds) and microorganisms. In recent years, the importance of microorganism growth on artwork materials, like mural paintings, paper, ivory, wood, stone and others, has been take into account on the alterations that affect artworks integrity [1, 2].

Biodeterioration can be responsible by the aesthetical and/or structural damages on Cultural assets, due to pigments production, biofilms formation, and physical and chemical alterations of the constituents. Among all the microbial organisms that colonise artworks, fungi, bacteria, cyanobacteria and lichens are the most harmful. These specific microbial communities will grow depending on the environmental conditions and the capacity of the substratum to provide different ecological niches [2, 3].

Fungal biodeterioration is one of the most important decay mechanisms acting in the progressive loss of our Cultural assets. The main aggressions promoted by these microorganisms include: degradation of organic and mineral substances to obtain nutrients and extract energy; production of molecules, such as acids or complexing agents; and excretion of metabolic products, which can cause aesthetically undesirable effects. Therefore, a more complete knowledge of biodeterioration phenomena and microbial diversity is needed since it may provide useful information and, consequently, recommendations for greatest restoration/preservation processes [4, 5].

Traditionally, the methodology used for the identification of microorganisms from different types of materials of Cultural Heritage was based on the application of cultivation methods. However, nowadays it is generally accepted that these techniques recover only a very small percentage of the total microorganisms present in environmental samples [6].

So, in this work, a polyphasic approach has been applied in order to characterise the microbial colonization and to fulfil the drawbacks of microbial communities’
identification. For this study, 48 fungi from the HERCULES Laboratory collection, isolated from different artwork materials were analysed. This methodology allies data obtained from several techniques - macro- and micromorphological characterisation of culture-dependent microorganisms, and molecular and spectral methods – in order to acquire a larger amount, and above all, trustworthy information.

Regarding the macro- and micromorphological characterisation, three different culture media were used and, in this phase, it was possible to detect differences between fungi that previously looked the same, and even identify some of them.

Spectroscopic analyses by μ-FTIR and μ-Raman, gradually became established techniques for the non-destructive identification and study of ancient materials, providing a specific snapshot of the total molecular composition and allowing an accurate identification and characterisation of the microorganisms. Also, in FTIR, which apparently presented best results in comparison with Raman spectroscopy, two major characteristic bands, 1030 and 1650 cm\(^{-1}\), representing carbohydrates or polysaccharide-like substances and amide I (proteins), respectively, were found in all fungi tested, which seem to be good biomarkers for fungal contamination. The SEM-EDS microanalysis allowed the observation and surface characterization of inorganic and organic materials at a higher resolution and depth of field than conventional optical microscopy. This methodology can also determine elemental composition of the support material, attacked areas, abiotic deposits and biofilms, and the presence, morphology and distribution of microorganisms within biofilms. This analysis helped to corroborate, or deny, previously proposed identifications [7].

The molecular analyses involved qPCR – which quantifies, in a reproducible and accurate way, microorganisms’ concentrations in real samples -, M13-PCR and β-tubulin-PCR fingerprinting and ITS-PCR sequencing for upcoming phylogenetic tree analysis. PCR amplifying techniques are advantageous for the analysis of the very small samples typically collected in cultural property objects and constructions [7].

This assembly of methodologies have allowed facing the multiple limitations of traditional culture methodologies, enabling the characterisation of uncultivable population. While it is possible to observe differences between several microorganisms, the molecular and spectral methodologies generate a specific fingerprint associated with each microbiological isolate, which act as biomarkers, providing useful information that can be used to discriminate them, and may be useful to \textit{in situ} or \textit{ex situ} analysis of microbiological contamination of artworks.

References:
“Color is a kind of holy substance for me” [1]: analytical study of the Sam Francis’ palette from the 1940’s to the 1990’s

Catherine Defeyt1,2, Joy Mazurek2, Aneta Zebala3 and Debra Burchett-Lere4

1 University of Liège, Centre Européen d’Archéométrie, Allée du 6 Août 10, 4000 Liège, (Belgium). Tel. +32 43663639, Catherine.defeyt@ulg.ac.be.
2 Getty Conservation Institute, Science, Getty Center Drive 1200, CA90049 Los Angeles (USA).
3 Aneta Zebala Paintings Conservation, Head Conservator, 22nd Street 2237, CA90405 Santa Monica (USA).
4 The Sam Francis Foundation, Foundation Director, North Central Avenue, 1146, CA91202 Glendale (USA).

Keywords: Sam Francis palette; SOPs, Raman spectroscopy, retouching pigments

The Sam Francis’s colors, literally described as vivid, saturated, pure, vibrant intense and rich, largely contribute to the unique character of his work [2]. This idiosyncrasy explains the interest in conducting an extended study on the Francis’ painting materials through analytical techniques. On the other hand, many Francis’ paintings display colored surfaces that exhibit bronzing, fluorescent or opalescent effects. As a consequence, retouching paint losses from Sam Francis works may become a challenging task for the involved conservators, the degree of the color matching required in the imitative technique being particularly difficult to attain, in the presence of such surfaces. Furthermore, the attained degree of the color match has to be conserved in all conditions of illumination and observation. The use of pigments chemically similar to the original ones is often necessary for matching highly chromatic pigments [3-4]. Though, many modern synthetic organic pigments (SOPs) possess high color strength. That is why the characterization of the Francis palette would provide helpful information to the conservators, which have to deal with this type of issue.

The upcoming Getty publication Sam Francis: The Artist’s Materials, planned for 2016, offered the opportunity for in-depth analyses of hundreds paint samples. Almost three hundreds of paint fragments supplied by the Sam Francis Foundation have been investigated at the GCI laboratory, by using three complementary analytical techniques, Py-GC-MS, Raman and FTIR spectroscopies. The Raman spectroscopy is one of the most efficient techniques for identifying SOPs in paint systems, while the Py-GC-MS and FTIR methods provide essential information concerning the binding media. The analyzed paint fragments were sampled from twenty-nine canvases and works on paper, made between 1946 and 1992.

Although, primary established in Southern California, Sam Francis spent numerous long journeys in different places around the world, including Paris, Bern, Mexico City, New York and Tokyo. However, the material study has outlined the
uninterrupted use of certain classes of SOPs in specific colors. For example, copper phthalocyanine (CuPc) pigments were systematically detected in the blue and green samples, while azo pigments have been identified in most of the yellow areas sampled from post 1940s works. Regardless of the support and the paint technique, the Francis’ blues primary contain Ultramarine and/or CuPc blue pigments. And, it has been shown that the bronzing blue surfaces noticed for some of the investigated artworks correspond to PB15-based paint films.

The present study has also underlined the recurrent use of perinone orange and dioxazine violet in fluorescent orange and purple area. Despite the early introduction of SOPs, on the Francis’ palette, the works dating from the 1940’s remained mainly composed of traditional inorganic pigments, for instance lead white and red, chrome yellow, viridian and iron oxides. Interestingly, various binding media, i.e. Shellac gum, modified and unmodified oils, PVA, alkyd resins and acrylic copolymers have been identified. Actually, the investigated samples have pointed out the frequent combination of more than three types of binders on a same painting. Through the identification of the various SOPs used by Francis over fifty years, this research provide helpful information for selecting the most appropriate retouching pigments.

References:
Combined XRF and FTIR-ATR investigation on the mummy of Darder Museum (Banyoles-Girona, Spain)

Giampaolo Piga¹, Antonio Brunetti*, Albert Isidro²,³, Maria José Adserias-Garriga⁴, Assumpció Malgosa²

¹ Department of Political Science, Communication, Engineering and Information Technologies, University of Sassari. Viale Mancini 5, I–07100 Sassari (Italy).
² GROB (Grup de Recerca en Osteobiografia), Unitat d’Antropologia Biológica, Dept. BABVE, Facultat de Biociències, Universitat Autònoma de Barcelona, Spain.
³ Hospital Universitari Sagrat Cor de Barcelona (Barcelona, Spain).
⁴ Faculty of Dentistry. University of Barcelona (Spain)

* corresponding author: Prof. Antonio Brunetti, brunetti@uniss.it, +393204329024

Keywords: X-ray fluorescence (XRF), Fourier Transform Infrared spectroscopy attenuated total reflectance (FTIR-ATR), mummy embalming process.

X-ray fluorescence spectrometry (XRF) is a technique that has been recently employed in both archaeological and forensic contexts. In archaeology it is useful to study elemental concentrations in bones and to evaluate diagenesis or fossilization processes even though this technique is barely used for this scope. XRF analyses are thus recommended to study chemical composition of human bones of different age and conditions. It can be applied even in the case of bodies with a precise archaeological and burying context, especially in cases of important historical characters because known information allows to verify the hypothesis, and in cases of precious samples such as mummies of different cultures. This is the specific case that we are going to present hereafter.

The main aim of this work is to present a multi elemental analysis carried out with a portable energy–dispersive XRF instrument and with a laboratory XRF spectrometer, supplemented with µ-X-Ray Fluorescence maps and Fourier Transform Infrared spectroscopy attenuated total reflectance (FTIR-ATR), on bone fragments and various textile specimens belonging to the mummy exhibited at the Darder museum (Banyoles-Girona, Spain) in order to evaluate the bone elemental composition and to reconstruct the embalming process.

The XRF investigation showed the presence of several chemical elements. The appreciable concentration of metals, transitional elements and elements normally unexpected in the bone composition can be related to the processes of body mumification. The FTIR-ATR has revealed the presence of waxes as filler material.

Reference
<table>
<thead>
<tr>
<th>Book of Abstracts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Index</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A</th>
<th>Boyatzis, Stamatis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aceto, Maurizio</td>
<td>159</td>
</tr>
<tr>
<td>Achille, Cristina</td>
<td></td>
</tr>
<tr>
<td>Adriani, Annemie</td>
<td></td>
</tr>
<tr>
<td>Adserias-Garriga, Maria José</td>
<td></td>
</tr>
<tr>
<td>Agostino, Giuseppe</td>
<td></td>
</tr>
<tr>
<td>Albertin, Roberto</td>
<td></td>
</tr>
<tr>
<td>Albertin, Fauzia</td>
<td></td>
</tr>
<tr>
<td>Aldazarbal, Veronica</td>
<td></td>
</tr>
<tr>
<td>Alves, Luis C.</td>
<td></td>
</tr>
<tr>
<td>Amapane, Nicola</td>
<td></td>
</tr>
<tr>
<td>Anaf, Willemien</td>
<td></td>
</tr>
<tr>
<td>Andreotti, Alessia</td>
<td></td>
</tr>
<tr>
<td>Antunes, Vanessa</td>
<td></td>
</tr>
<tr>
<td>Aramendia, Julene</td>
<td></td>
</tr>
<tr>
<td>Aronjilla Ureña, Paz</td>
<td></td>
</tr>
<tr>
<td>Arslanoglu, Julie</td>
<td></td>
</tr>
<tr>
<td>Artesani, Alessia</td>
<td></td>
</tr>
<tr>
<td>Assis, Anders</td>
<td></td>
</tr>
<tr>
<td>Ayora Cañada, José M.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Capogrosso, Valentina</td>
</tr>
<tr>
<td>Baglioni, Piero</td>
<td>134,191,248</td>
</tr>
<tr>
<td>Balcar, Nathalie</td>
<td></td>
</tr>
<tr>
<td>Ballabio, D.</td>
<td>171,173</td>
</tr>
<tr>
<td>Barberis, Elettra</td>
<td>59,195</td>
</tr>
<tr>
<td>Bargigia, Ilaria</td>
<td>246</td>
</tr>
<tr>
<td>Baró, Maria Dolors</td>
<td>204</td>
</tr>
<tr>
<td>Barone, Germana</td>
<td>193,216</td>
</tr>
<tr>
<td>Bartoletti, Angelica</td>
<td>67,198</td>
</tr>
<tr>
<td>Baumbach, Tilo</td>
<td>90</td>
</tr>
<tr>
<td>Beeckman, Hans</td>
<td>113</td>
</tr>
<tr>
<td>Bellei, Sara</td>
<td>246,248</td>
</tr>
<tr>
<td>Bellot-Gurlet, Ludovic</td>
<td>88</td>
</tr>
<tr>
<td>Bernardini, Frederico</td>
<td>205</td>
</tr>
<tr>
<td>Berrie, Barbara</td>
<td>46</td>
</tr>
<tr>
<td>Bersani, Daniolo</td>
<td>183,216</td>
</tr>
<tr>
<td>Bettuzzi, Matteo</td>
<td>111</td>
</tr>
<tr>
<td>Bianco, Armandodoriano</td>
<td>127,147</td>
</tr>
<tr>
<td>Bibire, Cristina</td>
<td>239</td>
</tr>
<tr>
<td>Bongiorno, Valeria</td>
<td>184</td>
</tr>
<tr>
<td>Boone, Matthieu</td>
<td>113,119</td>
</tr>
<tr>
<td>Bordalo, Rui</td>
<td>52</td>
</tr>
<tr>
<td>Boschloos, Vanessa</td>
<td>220</td>
</tr>
<tr>
<td>Bostoen, Koen</td>
<td>61</td>
</tr>
<tr>
<td>Botteon, Alessandra</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Canali, Franco</td>
</tr>
<tr>
<td>Cacciatori, Fausto</td>
<td>206</td>
</tr>
<tr>
<td>Caforio, Lucia</td>
<td>136</td>
</tr>
<tr>
<td>Caldeira, Ana Teresa</td>
<td>52,132,86,188</td>
</tr>
<tr>
<td>Callewaert, Tom</td>
<td>117</td>
</tr>
<tr>
<td>Calligaro, Thomas</td>
<td>41</td>
</tr>
<tr>
<td>Camaiti, Mara</td>
<td>235</td>
</tr>
<tr>
<td>Cañamases, Maria Vega</td>
<td>179</td>
</tr>
<tr>
<td>Candeias, Antonio</td>
<td>37,52,86,132,</td>
</tr>
<tr>
<td></td>
<td>152,157,169,</td>
</tr>
<tr>
<td></td>
<td>188,210,212,</td>
</tr>
<tr>
<td></td>
<td>224,226,228,</td>
</tr>
<tr>
<td></td>
<td>230,244,254</td>
</tr>
<tr>
<td>Canu, Alba</td>
<td>151</td>
</tr>
<tr>
<td>Capogrosso, Valentina</td>
<td></td>
</tr>
<tr>
<td>Cappa, Frederica</td>
<td>100,196</td>
</tr>
<tr>
<td>Capsoni, Doretta</td>
<td>63</td>
</tr>
<tr>
<td>Cardell, C.</td>
<td>171,173</td>
</tr>
<tr>
<td>Carman, Cathy</td>
<td>149</td>
</tr>
<tr>
<td>Carù, Federico</td>
<td>78</td>
</tr>
<tr>
<td>Carvalho, Maria Luísa</td>
<td>212,226</td>
</tr>
<tr>
<td>Casali, Franco</td>
<td>111</td>
</tr>
<tr>
<td>Castelli, Lisa</td>
<td>167</td>
</tr>
<tr>
<td>Castro, Kepa</td>
<td>88,176</td>
</tr>
<tr>
<td>Cattersel, Vincent</td>
<td>129,237</td>
</tr>
<tr>
<td>Cavalieri, Tiziana</td>
<td>154</td>
</tr>
<tr>
<td>Cesareatto, Anna</td>
<td>248</td>
</tr>
<tr>
<td>Chang, Jinhong</td>
<td>102</td>
</tr>
<tr>
<td>Chelazzi, David</td>
<td>67</td>
</tr>
<tr>
<td>Chiggio, Rosanna</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2nd International Conference on Innovation in Art Research and Technology, 21–25 March 2016, Ghent, Belgium

261
<table>
<thead>
<tr>
<th>Book of Abstracts</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chillón, María Concepción</td>
<td>232</td>
</tr>
<tr>
<td>Ciccola, Alessandro</td>
<td>150</td>
</tr>
<tr>
<td>Civici, Niko</td>
<td>178</td>
</tr>
<tr>
<td>Clar, Mathieu</td>
<td>221</td>
</tr>
<tr>
<td>Clist, Bernard</td>
<td>61</td>
</tr>
<tr>
<td>Cnudde, Veerle</td>
<td>119</td>
</tr>
<tr>
<td>Coccato, Alessia</td>
<td>61, 216, 225, 230</td>
</tr>
<tr>
<td>Colombini, Maria Perla</td>
<td>235</td>
</tr>
<tr>
<td>Colombro, Chiara</td>
<td>105</td>
</tr>
<tr>
<td>Colomban, Philippe</td>
<td>104, 183</td>
</tr>
<tr>
<td>Concetta Capua, Maria</td>
<td>222</td>
</tr>
<tr>
<td>Conti, Claudia</td>
<td>105</td>
</tr>
<tr>
<td>Comelli, Daniela</td>
<td>191, 246, 248</td>
</tr>
<tr>
<td>Cormier, Laurent</td>
<td>141</td>
</tr>
<tr>
<td>Costa, Sónia</td>
<td>152, 161, 163, 226, 228</td>
</tr>
<tr>
<td>Costa, Mafalda</td>
<td>61</td>
</tr>
<tr>
<td>Cotte, Marine</td>
<td>141</td>
</tr>
<tr>
<td>Coudray, Alexia</td>
<td>203</td>
</tr>
<tr>
<td>Crivello, Fabrizio</td>
<td>222</td>
</tr>
<tr>
<td>Cuevas, Ariadna Mendoza</td>
<td>205</td>
</tr>
<tr>
<td>Culka, Adam</td>
<td>99</td>
</tr>
<tr>
<td>Dias, L.</td>
<td>244</td>
</tr>
<tr>
<td>Dierick, Manuel</td>
<td>113, 119</td>
</tr>
<tr>
<td>Di Gaetano, Serena</td>
<td>222</td>
</tr>
<tr>
<td>Dik, Joris</td>
<td>117</td>
</tr>
<tr>
<td>Dilo, Teuta</td>
<td>178</td>
</tr>
<tr>
<td>Domene, Ramón Rubio</td>
<td>240</td>
</tr>
<tr>
<td>Donais, Mary-Kate</td>
<td>73</td>
</tr>
<tr>
<td>Dionisi-Vici, Paolo</td>
<td>220</td>
</tr>
<tr>
<td>Dombret, Fanny</td>
<td>156</td>
</tr>
<tr>
<td>Domínguez Vidal, Ana</td>
<td>240</td>
</tr>
<tr>
<td>Dondi, Piercarlo</td>
<td>206</td>
</tr>
<tr>
<td>Dowsett, Mark</td>
<td>139</td>
</tr>
<tr>
<td>Drábková, Klára</td>
<td>54</td>
</tr>
<tr>
<td>Dubois, Hélène</td>
<td>203, 208</td>
</tr>
<tr>
<td>Duncan, John</td>
<td>67</td>
</tr>
<tr>
<td>Dupont, Anne-Laurence</td>
<td>84</td>
</tr>
<tr>
<td>Dupont-Logié, C.</td>
<td>104</td>
</tr>
<tr>
<td>Edwards, Howell</td>
<td>71</td>
</tr>
<tr>
<td>Enzo, Stefano</td>
<td>204</td>
</tr>
<tr>
<td>Escobal, Irati Golvan</td>
<td>204</td>
</tr>
<tr>
<td>Evangelisti, Federico</td>
<td>167</td>
</tr>
<tr>
<td>Eveno, Myriam</td>
<td>41</td>
</tr>
<tr>
<td>D’Agostino, Marco</td>
<td>206</td>
</tr>
<tr>
<td>d’Andrea, Cosimo</td>
<td>246, 248</td>
</tr>
<tr>
<td>Daly, Aoife</td>
<td>57</td>
</tr>
<tr>
<td>Daniel, Floréal</td>
<td>74</td>
</tr>
<tr>
<td>Danuta, Stępień</td>
<td>149</td>
</tr>
<tr>
<td>Dargaud, Olivier</td>
<td>141</td>
</tr>
<tr>
<td>Decq, Louise</td>
<td>129, 237</td>
</tr>
<tr>
<td>De Clercq, Hilde</td>
<td>92</td>
</tr>
<tr>
<td>DeCruz, Adele</td>
<td>115, 235</td>
</tr>
<tr>
<td>Debastiani, Rafaela</td>
<td>90</td>
</tr>
<tr>
<td>Defeyt, Catherine</td>
<td>221, 256</td>
</tr>
<tr>
<td>Deforce, Koen</td>
<td>113</td>
</tr>
<tr>
<td>de la Torre Lopez, María José</td>
<td>240</td>
</tr>
<tr>
<td>Delvaux, Luc</td>
<td>218</td>
</tr>
<tr>
<td>De Muynck, Amelie</td>
<td>119</td>
</tr>
<tr>
<td>De Nolf, Wout</td>
<td>141</td>
</tr>
<tr>
<td>Depalmas, Anna</td>
<td>151</td>
</tr>
<tr>
<td>D’Ercoli, Giorgio</td>
<td>233</td>
</tr>
<tr>
<td>Deriu, Chiara</td>
<td>179</td>
</tr>
<tr>
<td>De Schryver, Thomas</td>
<td>119</td>
</tr>
<tr>
<td>De Waele, Karolien</td>
<td>200</td>
</tr>
<tr>
<td>Dhaene, Jelle</td>
<td>119</td>
</tr>
<tr>
<td>Dias, Cristina Barrocas</td>
<td>169, 210</td>
</tr>
<tr>
<td>Fondis Bioritech</td>
<td>123</td>
</tr>
<tr>
<td>Frade, J.</td>
<td>244</td>
</tr>
<tr>
<td>Francisco, Maria J.</td>
<td>226</td>
</tr>
<tr>
<td>Frederickx, Manu</td>
<td>113</td>
</tr>
<tr>
<td>Freiesleben, Trine</td>
<td>138</td>
</tr>
<tr>
<td>Fremout, Wim</td>
<td>129, 237</td>
</tr>
<tr>
<td>Frizzi, Tommaso</td>
<td>191</td>
</tr>
<tr>
<td>Fruhmann, Bernadette</td>
<td>100, 196</td>
</tr>
<tr>
<td>Furferi, Rocco</td>
<td>65</td>
</tr>
<tr>
<td>Name</td>
<td>Page(s)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Garcia, Laura</td>
<td>88</td>
</tr>
<tr>
<td>García-Camino, Iñaki</td>
<td>88</td>
</tr>
<tr>
<td>Gargano, M.</td>
<td>181,182</td>
</tr>
<tr>
<td>Garrido, M.</td>
<td>39</td>
</tr>
<tr>
<td>Garonni, Sebastiano</td>
<td>204</td>
</tr>
<tr>
<td>George, David</td>
<td>73</td>
</tr>
<tr>
<td>Ghiara, Giorgia</td>
<td>184</td>
</tr>
<tr>
<td>Gil, Milene</td>
<td>244</td>
</tr>
<tr>
<td>Gimat, Alice</td>
<td>84</td>
</tr>
<tr>
<td>Giorgi, Roderico</td>
<td>67</td>
</tr>
<tr>
<td>Glaude, Cecile</td>
<td>203</td>
</tr>
<tr>
<td>Godts, S.</td>
<td>92</td>
</tr>
<tr>
<td>Goidanich, Sara</td>
<td>134</td>
</tr>
<tr>
<td>Gomes, Sofia</td>
<td>230</td>
</tr>
<tr>
<td>Gómez, Elena Correa</td>
<td>240</td>
</tr>
<tr>
<td>Gomez-Nubla, Leticia</td>
<td>88</td>
</tr>
<tr>
<td>Gonzalez, Elena</td>
<td>67</td>
</tr>
<tr>
<td>González-Pérez, Marina</td>
<td>132</td>
</tr>
<tr>
<td>Gonzalez-Vidal, Juanjo</td>
<td>242</td>
</tr>
<tr>
<td>Granzotto, Clara</td>
<td>76</td>
</tr>
<tr>
<td>Grießer, Martina</td>
<td>42</td>
</tr>
<tr>
<td>Grisoni, F.</td>
<td>173</td>
</tr>
<tr>
<td>Grøntoft, Terje</td>
<td>39</td>
</tr>
<tr>
<td>Guiso, Marcella</td>
<td>127,147</td>
</tr>
<tr>
<td>Gulotta, Davide</td>
<td>134</td>
</tr>
<tr>
<td>Idjouadiene, Lynda</td>
<td>181,182</td>
</tr>
<tr>
<td>Impallaria, Anna</td>
<td>167</td>
</tr>
<tr>
<td>Indekeu, Charles</td>
<td>129,237</td>
</tr>
<tr>
<td>Ioakimoglou, Eleni</td>
<td>159</td>
</tr>
<tr>
<td>Ioele, Marcella</td>
<td>82</td>
</tr>
<tr>
<td>Izaguirre, Manuel</td>
<td>88</td>
</tr>
<tr>
<td>Izatt, Joseph A.</td>
<td>115</td>
</tr>
<tr>
<td>Isidro, Albert</td>
<td>258</td>
</tr>
<tr>
<td>Jain, Mayank</td>
<td>138</td>
</tr>
<tr>
<td>Janssens, Koen</td>
<td>80,141,200</td>
</tr>
<tr>
<td>Jehlička, Jan</td>
<td>99</td>
</tr>
<tr>
<td>Jenneskens, Leonardus W.</td>
<td>50</td>
</tr>
<tr>
<td>Jesper, Cecilia W.L.</td>
<td>50</td>
</tr>
<tr>
<td>Jones, Mark</td>
<td>139</td>
</tr>
<tr>
<td>Kalkman, Jeroen</td>
<td>117</td>
</tr>
<tr>
<td>Karantoni, Eleni Efrosini</td>
<td>159</td>
</tr>
<tr>
<td>Khasawneh, Sahar al</td>
<td>138</td>
</tr>
<tr>
<td>Kockelmann, Winfried</td>
<td>42</td>
</tr>
<tr>
<td>Knutsson, Johan</td>
<td>46</td>
</tr>
<tr>
<td>Krejčí, Jan</td>
<td>54</td>
</tr>
<tr>
<td>Lança, Mónica</td>
<td>86</td>
</tr>
<tr>
<td>Langlois, Juliette</td>
<td>141</td>
</tr>
<tr>
<td>Lankester, P.</td>
<td>39</td>
</tr>
<tr>
<td>Lauw, Alexandra</td>
<td>226</td>
</tr>
<tr>
<td>Lauwers, Debbie</td>
<td>107,165,216,230</td>
</tr>
<tr>
<td>Laval, Eric</td>
<td>41</td>
</tr>
<tr>
<td>Le Gac, Agnès</td>
<td>152,228</td>
</tr>
<tr>
<td>Legan, Lea</td>
<td>214</td>
</tr>
<tr>
<td>Legrand, Stijn</td>
<td>203</td>
</tr>
<tr>
<td>Lei, Yong</td>
<td>143</td>
</tr>
<tr>
<td>Leyman, Viviane</td>
<td>129</td>
</tr>
<tr>
<td>Licchelli, Maurizio</td>
<td>63,206</td>
</tr>
<tr>
<td>Lombardi, Livia</td>
<td>127,147,206</td>
</tr>
<tr>
<td>Longelin, S.</td>
<td>244</td>
</tr>
<tr>
<td>Lorena, Mercès</td>
<td>230</td>
</tr>
<tr>
<td>Lorenzoni, Valerio</td>
<td>113</td>
</tr>
<tr>
<td>Lotticci, Pierre Paulo</td>
<td>183</td>
</tr>
<tr>
<td>Ludwig, N.</td>
<td>181,182</td>
</tr>
<tr>
<td>Łydżba-Kopczyńska, Barbara</td>
<td>131</td>
</tr>
</tbody>
</table>

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lynen, Frederic</td>
<td>129</td>
</tr>
<tr>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Madariaga, Juan Manuel</td>
<td>88,176</td>
</tr>
<tr>
<td>Maingi, Evan Maina</td>
<td>161,163</td>
</tr>
<tr>
<td>Malagodi, Marco</td>
<td>63,206</td>
</tr>
<tr>
<td>Malea, Ekaterini</td>
<td>159</td>
</tr>
<tr>
<td>Malgosa, Assumpció</td>
<td>258</td>
</tr>
<tr>
<td>Mancini, D.</td>
<td>104</td>
</tr>
<tr>
<td>Mandelli, Alessandro</td>
<td>134</td>
</tr>
<tr>
<td>Mandò, Pier Andrea</td>
<td>136</td>
</tr>
<tr>
<td>Manfredi, Marcello</td>
<td>59,195</td>
</tr>
<tr>
<td>Mangucci, Celso</td>
<td>224</td>
</tr>
<tr>
<td>Manhita, Ana</td>
<td>157</td>
</tr>
<tr>
<td>Manso, Marta</td>
<td>226</td>
</tr>
<tr>
<td>Manzini, Davide</td>
<td>216</td>
</tr>
<tr>
<td>Marengo, Emilio</td>
<td>59,195</td>
</tr>
<tr>
<td>Margaritondo, Giorgio</td>
<td>111</td>
</tr>
<tr>
<td>Markevičius, Tomas</td>
<td>65</td>
</tr>
<tr>
<td>Martins, Maria do Rosário</td>
<td>254</td>
</tr>
<tr>
<td>Marzo, V.</td>
<td>181,182</td>
</tr>
<tr>
<td>Mass, Jennifer</td>
<td>141</td>
</tr>
<tr>
<td>Masschaele, Bert</td>
<td>113,119</td>
</tr>
<tr>
<td>Massiani, Pascale</td>
<td>84</td>
</tr>
<tr>
<td>Matousek, Pavel</td>
<td>105</td>
</tr>
<tr>
<td>Matteazzi, Paolo</td>
<td>67</td>
</tr>
<tr>
<td>Mazurek, Joy</td>
<td>256</td>
</tr>
<tr>
<td>Mazzeo, Rocco</td>
<td>179</td>
</tr>
<tr>
<td>Mazzoleni, Paolo</td>
<td>193,216</td>
</tr>
<tr>
<td>Meinen, Markus</td>
<td>90</td>
</tr>
<tr>
<td>Melessanaki, Kristallia</td>
<td>159</td>
</tr>
<tr>
<td>Meyer, Helmut</td>
<td>65</td>
</tr>
<tr>
<td>Miguel, Catarina</td>
<td>157,161,163, 210,212</td>
</tr>
<tr>
<td>Miklas, Heinz</td>
<td>100</td>
</tr>
<tr>
<td>Milanese, Chiara</td>
<td>63</td>
</tr>
<tr>
<td>Mináňková, Laura</td>
<td>99</td>
</tr>
<tr>
<td>Mirão, José</td>
<td>86,152,169, 188,224,228, 244</td>
</tr>
<tr>
<td>Moens, Luc</td>
<td>107,165,208, 225</td>
</tr>
<tr>
<td>Monico, Letizia</td>
<td>141</td>
</tr>
<tr>
<td>Morigi, Maria Pia</td>
<td>111</td>
</tr>
<tr>
<td>Mosca, Sara</td>
<td>134,191,246, 248</td>
</tr>
<tr>
<td>Mostefaoui, Toufik A.</td>
<td>181,182</td>
</tr>
<tr>
<td>Mottin, Bruno</td>
<td>41</td>
</tr>
<tr>
<td>Mounier, Aurélie</td>
<td>74</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Müller, Katharina</td>
<td>41</td>
</tr>
<tr>
<td>Municchia, Annalaura</td>
<td>82,233</td>
</tr>
<tr>
<td>Casanova</td>
<td></td>
</tr>
<tr>
<td>Murray, Andrew</td>
<td>138</td>
</tr>
<tr>
<td>Mysak, Erin</td>
<td>41</td>
</tr>
<tr>
<td>N</td>
<td></td>
</tr>
<tr>
<td>Nankivil, Derek</td>
<td>115</td>
</tr>
<tr>
<td>Navas, N.</td>
<td>171,173</td>
</tr>
<tr>
<td>Neri, Nicola Francesco</td>
<td>216</td>
</tr>
<tr>
<td>Nervo, Marco</td>
<td>154</td>
</tr>
<tr>
<td>Nevin, Austin</td>
<td>134,191,246, 248</td>
</tr>
<tr>
<td>Nogueira, Carla</td>
<td>86</td>
</tr>
<tr>
<td>Nunes, Margarida</td>
<td>161,163,224</td>
</tr>
<tr>
<td>Nyström, Ingulill</td>
<td>46</td>
</tr>
<tr>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Odlyha, Marianne</td>
<td>67,198</td>
</tr>
<tr>
<td>Oger, Cécile</td>
<td>156</td>
</tr>
<tr>
<td>Olsson, Nina</td>
<td>65</td>
</tr>
<tr>
<td>P</td>
<td></td>
</tr>
<tr>
<td>Pachnia, Mariola</td>
<td>149</td>
</tr>
<tr>
<td>Palmsköld, Anneli</td>
<td>46</td>
</tr>
<tr>
<td>Panagiaris, Georgios</td>
<td>159</td>
</tr>
<tr>
<td>Papanikolaou, Athanassia</td>
<td>159</td>
</tr>
<tr>
<td>Peccenini, Eva</td>
<td>111,136</td>
</tr>
<tr>
<td>Pellicori, Virginia</td>
<td>136</td>
</tr>
<tr>
<td>Pérez-Pueyo, Rosanna</td>
<td>242</td>
</tr>
<tr>
<td>Pereira, António</td>
<td>132,188</td>
</tr>
<tr>
<td>Petrucci, Ferruccio</td>
<td>136,167</td>
</tr>
<tr>
<td>Pichon, Laurent</td>
<td>41</td>
</tr>
<tr>
<td>Piccardo, Paolo</td>
<td>184,186</td>
</tr>
<tr>
<td>Piccirillo, Anna</td>
<td>154,222</td>
</tr>
<tr>
<td>Piga, Giampaolo</td>
<td>204,258</td>
</tr>
<tr>
<td>Pince, Possum</td>
<td>175</td>
</tr>
<tr>
<td>Pires, Margarida Isabel</td>
<td>254</td>
</tr>
<tr>
<td>Martins</td>
<td></td>
</tr>
<tr>
<td>Pisani, Marco</td>
<td>154</td>
</tr>
<tr>
<td>Poli, Tommaso</td>
<td>222</td>
</tr>
<tr>
<td>Pondelak, Andreja</td>
<td>214</td>
</tr>
<tr>
<td>Porcu, Laura</td>
<td>222</td>
</tr>
<tr>
<td>Postorino, Paolo</td>
<td>127,147</td>
</tr>
<tr>
<td>Pouyet, Emeline</td>
<td>141</td>
</tr>
<tr>
<td>Pouli, Paraskevi</td>
<td>159</td>
</tr>
<tr>
<td>Pozzi, Federica</td>
<td>78</td>
</tr>
<tr>
<td>Prati, Silvia</td>
<td>179</td>
</tr>
</tbody>
</table>

2nd International Conference on Innovation in Art Research and Technology, 21-25 March 2016, Ghent, Belgium
<table>
<thead>
<tr>
<th>Name</th>
<th>Page Number(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price, David</td>
<td>250</td>
</tr>
<tr>
<td>Proesmans, Marc</td>
<td>218</td>
</tr>
<tr>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Rabot, Eva</td>
<td>193</td>
</tr>
<tr>
<td>Raffaelli, Francesca</td>
<td>220</td>
</tr>
<tr>
<td>Rakkaa, Said</td>
<td>221</td>
</tr>
<tr>
<td>Ramos de Torres, Antonio</td>
<td>190</td>
</tr>
<tr>
<td>Ramsholt, K.</td>
<td>39</td>
</tr>
<tr>
<td>Raneri, Simona</td>
<td>193, 216</td>
</tr>
<tr>
<td>Rapp, Claudia</td>
<td>100</td>
</tr>
<tr>
<td>Rapti, Stavroula</td>
<td>159</td>
</tr>
<tr>
<td>Realini, Marco</td>
<td>105</td>
</tr>
<tr>
<td>Reho, Ilma</td>
<td>233</td>
</tr>
<tr>
<td>Reiche, Ina</td>
<td>41</td>
</tr>
<tr>
<td>Reijers, Evert Bastiaan</td>
<td>50</td>
</tr>
<tr>
<td>Retko, Klara</td>
<td>214</td>
</tr>
<tr>
<td>Ribeiro, I.</td>
<td>244</td>
</tr>
<tr>
<td>Ricci, Maria Antonietta</td>
<td>82, 233</td>
</tr>
<tr>
<td>Relvas, Cátia</td>
<td>161, 163</td>
</tr>
<tr>
<td>Rivard, Camille</td>
<td>141</td>
</tr>
<tr>
<td>Rodrigues, Paulo</td>
<td>157</td>
</tr>
<tr>
<td>Röhrs, Stefan</td>
<td>178</td>
</tr>
<tr>
<td>Ropret, Polonca</td>
<td>214</td>
</tr>
<tr>
<td>Rosado, Tânia</td>
<td>52, 86, 254</td>
</tr>
<tr>
<td>Roucho, Véronique</td>
<td>84</td>
</tr>
<tr>
<td>Rousaki, Anastasia</td>
<td>61, 208</td>
</tr>
<tr>
<td>Ruiz, Patricia</td>
<td>176</td>
</tr>
<tr>
<td>Ruiz-Moreno, Sergio</td>
<td>190, 232</td>
</tr>
<tr>
<td>Russo, Alfonso Pio</td>
<td>82</td>
</tr>
<tr>
<td>Rylands, Peter</td>
<td>136</td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Sabbe, Pieter-Jan</td>
<td>139</td>
</tr>
<tr>
<td>Sablatnig, Robert</td>
<td>100</td>
</tr>
<tr>
<td>Sale, Donald</td>
<td>198</td>
</tr>
<tr>
<td>Salomé, Murielle</td>
<td>141</td>
</tr>
<tr>
<td>Salvador, Cátia</td>
<td>52</td>
</tr>
<tr>
<td>Sanchez-Cortes, Santiago</td>
<td>179</td>
</tr>
<tr>
<td>Santos, Rita</td>
<td>86</td>
</tr>
<tr>
<td>Sanyova, Jana</td>
<td>200, 203, 208</td>
</tr>
<tr>
<td>Saverywns, Steven</td>
<td>129, 237</td>
</tr>
<tr>
<td>Schalm, Olivier</td>
<td>44, 48, 80</td>
</tr>
<tr>
<td>Schiavon, Nicola</td>
<td>151</td>
</tr>
<tr>
<td>Schilling, Michael</td>
<td>129</td>
</tr>
<tr>
<td>Schreiner, Manfred</td>
<td>100, 196</td>
</tr>
<tr>
<td>Schwartzbaum, Paul</td>
<td>136</td>
</tr>
<tr>
<td>Scibua, Fabio</td>
<td>127, 147</td>
</tr>
<tr>
<td>Serafini, Ilaria</td>
<td>127, 147</td>
</tr>
<tr>
<td>Serrão, Vitor</td>
<td>226</td>
</tr>
<tr>
<td>Seruya, Ana I.</td>
<td>226</td>
</tr>
<tr>
<td>Seymour, Kate</td>
<td>65</td>
</tr>
<tr>
<td>Silva, Mara</td>
<td>52, 86</td>
</tr>
<tr>
<td>Silva, Nidia</td>
<td>228</td>
</tr>
<tr>
<td>Simon, Rolf</td>
<td>90</td>
</tr>
<tr>
<td>Škabin, Andrijana Sever</td>
<td>214</td>
</tr>
<tr>
<td>Škdiantová, Markéta</td>
<td>54</td>
</tr>
<tr>
<td>Škrlep, Luka</td>
<td>214</td>
</tr>
<tr>
<td>Smarttech LTD</td>
<td>95</td>
</tr>
<tr>
<td>Sodo, Armida</td>
<td>82, 233</td>
</tr>
<tr>
<td>Solhbiati, Reza</td>
<td>138</td>
</tr>
<tr>
<td>Soneira, María José</td>
<td>242</td>
</tr>
<tr>
<td>Souto, C.</td>
<td>244</td>
</tr>
<tr>
<td>Špec, Tanja</td>
<td>214</td>
</tr>
<tr>
<td>Stanzania, E.</td>
<td>183</td>
</tr>
<tr>
<td>Steyaert, Delphine</td>
<td>129, 237</td>
</tr>
<tr>
<td>Storme, Patrick</td>
<td>48</td>
</tr>
<tr>
<td>Streeton, Noëlle</td>
<td>57</td>
</tr>
<tr>
<td>Stringari, Carol</td>
<td>78</td>
</tr>
<tr>
<td>Strivay, David</td>
<td>156, 221</td>
</tr>
<tr>
<td>Sutherland, Ken</td>
<td>76</td>
</tr>
<tr>
<td>Szwabíński, Janusz</td>
<td>131</td>
</tr>
<tr>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Taccetti, Francesco</td>
<td>136, 167</td>
</tr>
<tr>
<td>Teixeira, Dora</td>
<td>157</td>
</tr>
<tr>
<td>Teixeira, Jorge Ginja</td>
<td>157</td>
</tr>
<tr>
<td>Thickett, D.</td>
<td>39</td>
</tr>
<tr>
<td>Thomas, Jacob</td>
<td>46</td>
</tr>
<tr>
<td>Thuresson, Kaj</td>
<td>46</td>
</tr>
<tr>
<td>Tisato, Flavia</td>
<td>167</td>
</tr>
<tr>
<td>Todeschini, R.</td>
<td>171, 173</td>
</tr>
<tr>
<td>Toniolo, Lucia</td>
<td>134</td>
</tr>
<tr>
<td>Townsend, J.H.</td>
<td>39</td>
</tr>
<tr>
<td>Traum, René</td>
<td>42</td>
</tr>
<tr>
<td>Triolo, Paolo</td>
<td>154</td>
</tr>
<tr>
<td>Tziamourani, Eleni</td>
<td>159</td>
</tr>
<tr>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Udrea, Iliina</td>
<td>252</td>
</tr>
<tr>
<td>Urma, Maria</td>
<td>239</td>
</tr>
<tr>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Pages</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Valadas, Sara</td>
<td>169,230</td>
</tr>
<tr>
<td>Valentini, Gianluca</td>
<td>134,191,248</td>
</tr>
<tr>
<td>Van Acker, Joris</td>
<td>113,119</td>
</tr>
<tr>
<td>Van Binnebeke, Emile</td>
<td>129,237</td>
</tr>
<tr>
<td>Van Bos, Marina</td>
<td>218</td>
</tr>
<tr>
<td>Vandebaelee, Peter</td>
<td>61,107,165, 169,175,178, 188,208,216, 225,230</td>
</tr>
<tr>
<td>Van den Bulcke, Jan</td>
<td>113,119</td>
</tr>
<tr>
<td>Vandermeulen, Bruno</td>
<td>218</td>
</tr>
<tr>
<td>Van der Perre, Athena</td>
<td>218</td>
</tr>
<tr>
<td>Van Der Snickt, Geert</td>
<td>80,203</td>
</tr>
<tr>
<td>Van Gool, Luc</td>
<td>218</td>
</tr>
<tr>
<td>Van Hoorebeke, Luc</td>
<td>113,119</td>
</tr>
<tr>
<td>Van Loo, Denis</td>
<td>113,119</td>
</tr>
<tr>
<td>van Wiggen, Maxime A.C.</td>
<td>50</td>
</tr>
<tr>
<td>Vataj, Esmeralda</td>
<td>178</td>
</tr>
<tr>
<td>Vazquez, Cristina</td>
<td>165</td>
</tr>
<tr>
<td>Veiga, Alfredina</td>
<td>157</td>
</tr>
<tr>
<td>Veira, Ricardo</td>
<td>132</td>
</tr>
<tr>
<td>Vekemans, Bart</td>
<td>225</td>
</tr>
<tr>
<td>Verger, Louisiane</td>
<td>141</td>
</tr>
<tr>
<td>Vermeulen, Marc</td>
<td>200</td>
</tr>
<tr>
<td>Vernet, Justine</td>
<td>184,186</td>
</tr>
</tbody>
</table>